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POLYSULFURATED AROMATIC COMPOUNDS:
PREPARATION AND PHOTOPHYSICAL PROPERTIES

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Esame finale anno 2013

"Now I guess I'll have to tell'em
That I got no cerebellum
Gonna get my Ph.D.
I'm a teenage lobotomy"

— The Ramones, 1977

Contents

Preface

The purpose of this thesis is to describe most of the research that I have accomplished during the months (21, in total) I spent as an apprentice in photophysics at the University of Bologna under the supervision of Prof. Paola Ceroni and at the Aix-Marseille University/CINaM (15 months in total) under the supervision of Prof. Marc Gingras, where I managed to discover only a small part of the discipline of organic chemistry.

In the beginning of this thesis (chapters 1 and 2) I will take a survey on the basic principles of supramolecular chemistry and photochemistry; in chapter 3 I will present briefly the main techniques that I used and learnt in the two main disciplines of my research: instrumental analysis in photophysics and synthetic methods based on sulfur chemistry. In chapter 4 a brief historical background and potential applications of persulfurated compounds are described.

Then, the subsequent chapters are divided by the class of compounds studied: first, in chapter 5, I will illustrate the synthesis, photophysical properties of sulfur-based molecular asterisks, describing later their applications. In the same way, in chapter 6 and 7, synthesis and properties of two compounds based on an aromatic core with appended terpyridyl units are shown; the properties of terpyridyl-based dendrons (model compounds) are presented as well. Finally, in chapter 8 I propose some future works based on similar compounds.

List of abbreviations

AFM: atomic force microscopy

AIE: aggregation induced emission

CT: charge transfer

DCM: dichloromethane

DCTB: *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile

DMF: *N,N*-dimethylformamide

DMI: 1,3-dimethyl-2-imidazolidinone

DMSO: dimethylsulfoxide

EA: elemental analysis

ESI–MS: electron spray ionization mass spectrometry

eT: electron transfer

ET: energy transfer

HMPA: hexamethylphosphoramide

HPLC: high-performance liquid chromatography

HR-MS: high resolution mass spectrometry

ICT: intramolecular charge transfer

ILCT: intraligand charge transfer

LC: ligand centered

LR-MS: low resolution mass spectrometry

MALDI-MS: matrix assisted laser desorption ionization mass spectrometry

MeCN: acetonitrile

MeOH: methanol

MOF: metal organic framework

NIR: near infrared

NMR: nuclear magnetic resonance

NP: nanoparticle

OLED: organic light emitting diode

PDI: polydispersity index

PEG: polyethileneglycole

PEGME: polyethileneglycole methylether

PET: photo induced energy transfer

phen: 1,10-phenanthroline

PMMA: poly(methyl methacrylate)

RIR: restriction of molecular rotations

RT: room temperature

t-butOK: potassium tert-butyloxide

terpy: 2,6-bis(2-pyridyl)pyridine

THF: tetrahydrofuran

TLC: thin layer chromatography

XRD: x-rays diffraction

Chapter 1

Introduction

1.1 Supramolecular chemistry

« Chemistry is the science of matter and of its transformations, and life is its highest expression. It provides structures endowed with properties and develops processes for the synthesis of structures. It plays a primordial role in out understanding of material phenomena, in our capability to act upon them, to modify them, to control them and to invent new expressions of them. Chemistry is also a science of transfers, a communication centre and a relay between the simple and the complex, between the laws of physics and the rules of life, between the basic and the applied. If it is thus defined in its interdisciplinary relationships, it is also defined in itself, by its object and its method. [...]

Supramolecular chemistry is a highly interdisciplinary field of science covering the chemical, physical, and biologic features of the chemical species of greater complexity than molecules themselves, that are held together and organized by means of intermolecular (or non-covalent) binding interactions. [...]

Its roots extend into organic chemistry and the synthetic procedures for molecular construction, into coordination chemistry and metal ion-ligand

complexes, into physical chemistry and the experimental and theoretical studies of interactions, into biochemistry and the biological processes that all start with substrate binding and recognition, into materials science and the mechanical properties of solids. [...]
Drawing on the physics of organized condensed matter and expanding over the biology of large molecular assemblies, supramolecular chemistry expands into a *supramolecular science.* »[1]

The basic concepts in supramolecular chemistry[2] are based on the fact that different molecules, having proper shape and characteristics, could work together by means of intermolecular interactions – van der Waals interactions, hydrogen bonding, charge transfer interactions, π-π stacking or electrostatic forces – to give discrete species, in analogy to atoms held together in molecules.[3,4] These concepts have been clarified and developed following the Nobel prize award to Charles J. Pedersen, Jean-Marie Lehn and Donald J. Cram in 1987.
Polynuclear complexes and dendrimers can also be considered as super-molecules, since these systems are able to perform functions that isolated molecular components are not able to perform singularly.[5,6]
We can state therefore that in a *supermolecule* properties are arising from cooperation of components and they come not simply from the sum of their contributions.
With supramolecular chemistry development, scientists started to syn-thesize more complicate architectures in which each molecular component was designed to perform a specific function;[7] nowadays, thanks to the

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[1] Excerpt from J. M. Lehn, *"Supramolecular chemistry: concepts and perspectives"*, Wiley-VCH, Weinheim, **1995**.

[2] Lehn J.-M., *Science*, **1985**, *227*, 849.

[3] Lehn J.-M., *Science*, **1993**, *260*, 1762.

[4] Philp D., Stoddart J. F., *Angew. Chem. Int. Ed.*, **1996**, *35*, 1154.

[5] Gust D., Moore T. A., Moore A. L., Makings L. R., Seely G. R., Ma X., Trier T. T., Gao F., *J. Am. Chem. Soc.*, **1988**, *110*, 7567.

[6] Balzani V., Juris A., Venturi M., *Chem. Rev.*, **1996**, *96*, 759.

[7] Vögtle F., *"Supramolecular chemistry"*, Wiley-VCH, New York, USA, **1991**.

great evolution in synthetic methods, chemists can design and actually build up fine-tuned multicomponent systems at molecular level, making supramolecular chemistry a fundamental support to obtain new intelligent materials towards miniaturization technologies.[8,9]

1.2 Where scale matters: from small to nano

"A biological system can be exceedingly small. Many of the cells are very tiny, but they are very active; they manufacture various substances; they walk around; they wiggle; and they do all kinds of marvelous things – all on a very small scale. Also, they store information. Consider the possibility that we too can make a thing very small which does what we want – that we can manufacture an object that maneuvers at that level." [10]

When Richard Feynman (at the time not yet a Nobel Laureate) gave his visionary talk at the annual meeting of the American Physical Society he presented in basic principles the matter of huge efforts in the future 60 years of scientific researches. Extrapolating from known physical laws, Feynman envisioned a technology using the ultimate toolbox of nature, building nano objects atom by atom or molecule by molecule. Since the 1980s, many inventions and discoveries in the fabrication of nano objects have become a testament to his vision.

Nanotechnology literally relates to any technology performed on a nanoscale that has applications in the real world.[11] It encompasses the production and application of physical, chemical and biological systems at

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[8] Lehn J.-M., *Science*, **2002**, *295*, 2400.

[9] Lehn J.-M., *Chem. Soc. Rev.*, **2007**, *36*, 151.

[10] From the talk *"There's plenty of room at the bottom"*, delivered by Richard P. Feynman at the annual meeting of the American Physical Society at the California Institute of Technology, Pasadena, CA, on December 29, 1959.

[11] Drexler K. E., *Enginges of creation: the coming era of nanotechnology*, Anchor press, New York, USA, **1986**

scales ranging from individual atoms or molecules to submicron dimensions, as well as the integration of the resulting nanostructures into larger systems. Nanotechnology is likely to have a deep impact on our economy and society in the next years, comparable to that of semiconductor technology in the second half of the 20th century for electronics, as well as information technology or cellular and molecular biology. It is widely felt that nanotechnology will be the next industrial revolution.[12]

Molecules are convenient building blocks to build nanoscale devices and machines[13] since they are stable and useful species which Nature itself uses to construct powerful nanodevices that sustain life.
Generally, to realize nano-objects, we can distinguish between two main approaches: the *top-down* approach refers to common technologies that account to externally controlled processes from larger entities. This is a quite common methodology[14] in many applied fields of technology, even if the physical limit of capability is approaching (figure 1.1).

Figure 1.1: microfabrication at subdiffraction-limit resolution. A titanium sapphire laser operating in mode-lock at 76 MHz and 780 nm with a 150-femtosecond pulse width was used as an exposure source.

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[12] Bhushan B., *"Springer handbook of Nanotechnology"*, Springer-Verlag, Berlin-Heidelberg, **2004**.

[13] Balzani V., Credi A., Venturi M., *Chem. Eur. J.*, **2002**, *8*, 5524.

[14] Kawata S., Sun H. B., Tanaka T., Takada K., *Nature*, **2001**, *412*, 697.

On the other hand, in the *bottom-up* approach, the use of smaller components (molecules) to build more complicated nano-devices is conceived: molecular subunits can assemble together chemically to obtain smart materials, opening a virtually incalculable number of applications. In addition, this approach could contribute radically to the interpretation of natural phenomena, in which complicated devices and machines are involved.

These evaluations had an increasing interest in recent years, when new interesting and powerful techniques have been developed: nowadays, it has become frequent the use of special spectroscopical and microscopy methods, able to see discrete moieties at the nano-scale level.[15,16,17,18]

Nanoscale "objects" can exhibit characteristic structures, showing peculiar properties and performing specific operations.[19,20] The artificial molecular devices and machines belong to this class of systems, even when they are inspired to natural phenomena: for example we can cite the light-driven hybrid systems for producing ATP, pumping calcium ions,[21,22] and the DNA walking device.[23] All of the natural molecular devices and machines, from the light-harvesting antennae of the photosynthetic systems to rotary motors inside our cells (figure 1.2), also can be considered part of this category.[24]

[15] Moerner W. E., Orrit M., *Science*, **1999**, *283*, 1670.

[16] Zander C., Enderlein J., Keller R. A., *"Single molecule detection in solution: methods and applications"*, Wiley-VCH Verlag GmbH & Co., **2002**.

[17] Crommie M. F., *Science*, **2005**, *309*, 1509.

[18] Manoharan H. C., Lutz C. P., Eigler D. M., *Nature*, **2000**, *403*, 512.

[19] Balzani V., *Small*, **2005**, *1*, 278.

[20] Whitesides G. M., *Small*, **2005**, *1*, 172.

[21] Steinberg-Yfrach G., Rigaud J.-L., Durantini E. N., Moore A. L., Gust S., Moore T. A., *Nature*, **1998**, *392*, 479.

[22] Bennett I. M., Vanegas Farfano H. M., Bogani F., Primak A., Liddell P. A., Otero L., Sereno L., Silber J. J., Moore A. L., Moore T. A., Gust S., *Nature*, **2002**, *420*, 398.

[23] Sherman W. B., Seeman N. C., *Nano Lett.*, **2004**, *4*, 1203.

[24] Goodsell D. S., *"Bionanotechnology: lessons from Nature"*, Wiley-Liss Inc., Hoboken, NJ, USA, **2004**.

Figure 1.2: performing energy transformation, ATPase is a powerful rotary motor and generator. The total height has been measured around 12-14 nm.

1.2.1 Discovering organic nanomaterials

One of the most interesting aspects of nano-objects is that their properties often differ significantly from those of the corresponding bulk materials, for example the optical and electronic properties of inorganic semiconductor nanoparticles are known to depend upon the particle size.[25]

As stated above, technical developments have stimulated chemists to study ways to efficiently synthesize a wide range of materials (like conjugated polymers, polycyclic aromatic hydrocarbons, dyes, dendrimers and bioma-

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[25] Descalzo A. B., Martínez-Máñez R., Sancenón F., Hoffmann K., Rurack K., *Angew. Chem. Int. Ed.*, **2006**, *45*, 5924.

terials) which can self-assemble to form functional nanostructures.[26] For example, conjugated polymers have had more and more attention recently as organic semiconductors for use in devices such as light-emitting diodes (LEDs)[27] and solar cells among the others.[28]

Dendrimers, have already served as functional molecules in nanotechnology and nanoscience,[29] mainly as light-harvesting materials.[30] Most types of dendrimers exhibit flexible branches which are easily deformed and can even bend towards the center of the molecule. As a result an empty space between groups in the interior could be formed by design, showing in addition the possibility of manipulation to produce high selectivity for guest molecules. This specificity in host-guest interactions could then be used for sensing, for example, by selective incorporation of molecules, or to create a nano-reactor in which reactions can occur selectively.

In summary, the optical, electronic, and phase-forming properties of a multitude of molecules such polycyclic aromatic hydrocarbons, dyes, dendrimers and combinations of these structural elements can be nowadays manipulated quite easily by synthetic means. This knowledge not only allows the design of improved nanomaterials but also provides useful information about the behavior of the extremely sophisticated light-harvesting and other systems found in living organisms. It is worth mentioning that there is still considerable possibility for improvements in bulk organic electronic devices through investigation of the behavior of their component materials at the nanoscale, in order to optimize them.[31]

[26] Grimsdale A. C., Müllen K., *Angew. Chem. Int. Ed.*, **2005**, *44*, 5592.

[27] Kraft A., Grimsdale A. C., Holmes A. B., *Angew. Chem. Int. Ed.*, **1998**, *37*, 402.

[28] Brabec C. J., Sariciftci N. S., Hummelen J. C., *Adv. Funct. Mater.*, **2001**, *11*, 15.

[29] Fréchet J. M. J., *Macromol. Symp.*, **2003**, *201*, 11.

[30] Adronov A., Fréchet J. M. J., *Chem. Commun.*, **2000**, 1701.

[31] Joachim C., *Nature Mater.*, **2005**, *4*, 107.

Chapter 2

Fundamental principles in photochemistry

Photochemistry is a science focused on the description of physical and chemical process, induced by the absorption of photons. It is a very broad discipline, embracing an extensive range of energetic, structural and dynamic processes.[32]

Relatively new but very interesting applications of photochemistry are in the field of molecular devices. For instance, the possibility of using light energy as input to induce molecular movements is very important because it offers the possibility to make molecular machine work without accumulation of waste products.

Other advantages of using photochemical energy input are: (i) light can be switched on and off very easily and rapidly (ii) lasers provide the opportunity of working in a very small space and very short time domains (iii) photons, besides supplying the energy needed to make the machine work, can also be useful to "read" the state of the system and thus to control and monitor the operations of the machine.

Molecules can be functionalized, in their different topological regions, with luminescent moieties: photoactive units can also be non-covalently hosted

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[32] Ciamician G., *Science*, **1912**, *36*, 385.

in the cavities or associated on the dendrimer surface. Coupling lumin-
escence with dendrimer-like compounds is of particular interest since: (i)
luminescence signals offer a handle to better understand the dendritic
structure and superstructure; moreover, it is possible to monitor the in-
teractions of the macromolecule with other chemical species and with the
environment. (ii) Cooperation among the photoactive components can
allow the dendrimer to perform useful functions such as light harvesting
and signal amplification for sensing purposes.

2.1   Supramolecular photochemistry

While further investigations on the excited state properties of simple mo-
lecules are certainly required to reach a complete understanding of the
photochemical processes, there is an emerging necessity to study the pho-
tochemical behavior of supramolecular species in order to extend our know-
ledge of basic phenomena, make progress towards the understanding of
complex photobiological processes via examination of simpler models, and
find systems that might be useful for practical applications.[33]
The study of new distinctive photochemical, photophysical and electro-
chemical properties of the supermolecule constitutes the main target of
supramolecular photochemistry.
In a supermolecule most of the intrinsic properties of each units are expec-
ted to be maintained with relative minor changes that can be attributed
to the mutual perturbations between the units contained in system. For
this reason the investigation of the photophysical, photochemical and
electrochemical properties of model compounds is absolutely necessary to
understand the properties of supramolecular systems. These properties,
however, are usually not the simple superposition of those of the component
units. In fact, it is possible that processes involving two or more components
take place in a supermolecule, such as (i) intercomponent energy or electron

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[33] Balzani V., Moggi L., Scandola F., *Supramolecular Photochemistry*, NATO ASI Series,
D. Reidel, Dordrecht, **1987**.

transfer and/or (ii) cooperative effects (for example complexation of guest molecules or modification of the physical or chemical properties of the units).

2.2 General aspects

A historical and very useful diagram used in photochemistry to describe the deactivation process of the electronic excited states is the Jablonski diagram (figure 2.1).

Figure 2.1: a basic Jablonski diagram for a generic molecule: S_n are the singlet states, T_n the triplet states, k_{isc} the intersystem crossing rate constant, k_{ic} the internal convertion rate constant, k_{fl} the fluorescence rate constant and k_{ph} the phosphorescence rate constant.

As reported in the diagram, in most cases the ground state of organic molecules is a singlet state (S_0), and the excited states are either singlets (S_1, S_2, etc) or triplets (T_1, T_2, etc). In principle, transitions between states having the same spin value are allowed, whereas those between states

of different spin are forbidden. Therefore, the electronic absorption bands observed in the UV-visible spectrum of molecules usually correspond to $S_0 \rightarrow S_n$ transitions.

Excited states are unstable species which undergo fast deactivation by intrinsic processes (first order kinetics). When a molecule is excited to upper singlet excited states, it usually undergoes a fast and 100% efficient radiationless deactivation (internal conversion, ic) to the lowest excited singlet state, S_1. Such an excited state undergoes deactivation via three competing processes: nonradiative decay to the ground state (internal conversion, rate constant k_{ic}); radiative decay to the ground state (fluorescence, k_{fl}); conversion to the lowest triplet state T_1 (intersystem crossing, k_{isc}). In its turn, T_1 can undergo deactivation via non–radiative (intersystem crossing, k'_{isc}) or radiative (phosphorescence, k_{ph}) decay to the ground state S_0. When the molecule contains heavy atoms, the formally forbidden intersystem crossing and phosphorescence processes become faster.

The kinetic constants of the deactivation processes usually cannot be measured directly. What can be easily measured is the lifetime (τ) of an excited state, i.e. the time needed to reduce the excited state concentration by the factor $1/e$, which is given by the reciprocal of the summation of the first order deactivation rate constants:

$$\tau(S_\mathbf{1}) = \frac{1}{k_{ic} + k_{fl} + k_{isc}} \tag{2.1}$$

$$\tau(T_1) = \frac{1}{k'_{isc} + k_{ph}} \tag{2.2}$$

The orders of magnitude of $\tau(S_1)$ and $\tau(T_1)$ are approximately 10^{-9}–10^{-7} s and 10^{-3}–10^0 s, respectively.

Another quantity that can be measured is the quantum yield of fluorescence (ratio between the number of photons emitted by S_1 and the number of absorbed photons) and phosphorescence (ratio between the number of photons emitted by T_1 and the number of absorbed photons). These quantities, that can obviously range between 0 and 1, are given by the

following expressions:

$$\Phi_{fl} = \frac{k_{fl}}{k_{ic} + k_{fl} + k_{isc}} \tag{2.3}$$

$$\Phi_{ph} = \frac{k_{ph}\, k_{isc}}{(k'_{isc} + k_{ph})(k_{ic} + k_{fl} + k_{isc})} \tag{2.4}$$

Deactivation of an excited state in fluid solution can occur not only by the above mentioned intrinsic (first order) decay channels, but also by interaction with other species (called "quenchers") following second order kinetics. The two most important types of interactions are those leading to energy (eq. 2.6) or electron (eqs. 2.7 and 2.8, respectively) transfer (*A and *B stand for excited molecules).

$$\text{A} + \text{h}\nu \rightarrow {}^*\text{A} \tag{2.5}$$

$$^*\text{A} + \text{B} \rightarrow \text{A} + {}^*\text{B} \tag{2.6}$$

$$^*\text{A} + \text{B} \rightarrow \text{A}^+ + \text{B}^- \tag{2.7}$$

$$^*\text{A} + \text{B} \rightarrow \text{A}^- + \text{B}^+ \tag{2.8}$$

In both cases, the luminescence of the species A is quenched, and in the case of energy transfer the luminescence of species A can be replaced by the luminescence of species B (i.e., a sensitization process).

2.3 Energy and electron transfer

Energy and electron transfer processes can occur not only between distinct molecules in an encounter, but also between nearby molecular components in a supramolecular (multicomponent) species.

For example, in a system consisting of A and B component units, excitation of A (eq. 2.9) may be followed by energy (eq. 2.10) or electron (eqs. 2.11 and 2.12) transfer to B:

$$A \cdots B + h\nu \rightarrow {}^*A \cdots B \qquad (2.9)$$

$$^*A \cdots B \rightarrow A \cdots {}^*B \qquad (2.10)$$

$$^*A \cdots B \rightarrow A^+ \cdots B^- \qquad (2.11)$$

$$^*A \cdots B \rightarrow A^- \cdots B^+ \qquad (2.12)$$

Energy and electron transfer processes between components of a supramolecular species take place following first order kinetics. They must compete, of course, with the intrinsic excited state decay.

Energy transfer requires electronic interactions and therefore its rate decreases with increasing distance, r. Depending on the electronic interaction mechanism, the distance dependence may follow a $1/r^6$ (resonance, also called Förster-type, mechanism) or e^{-r} (exchange, also called Dexter-type, mechanism).[34] In both cases, energy transfer is favoured when the emission spectrum of the donor overlaps the absorption spectrum of the acceptor.

Quenching of an excited state by electron transfer needs electronic interaction between the two partners and obeys the same rules as electron transfer between ground state molecules (Marcus equation and related

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[34] (a) Balzani V., Scandola F., *Supramolecular Photochemistry*, Chichester, UK:Horwood, **1991**. (b) Turro N. J., *Modern Molecular Photochemistry*, Benjamin, **1978**. (c) Gilbert A., Baggott J., *Essentials of Molecular Photochemistry*, Backwell, Oxford, **1991**. (d) Lakowicz J. R., *Principles of Fluorescence Spectroscopy*, Plenum, New York, **1999**.

Figure 2.2: schematic representation of the difference between a supramolecular system and a large molecule based on the effects of photonic or electronic stimuli (from *"Molecular devices and machines"* by V. Balzani, A. Credi and M. Venturi, 2$^{\text{nd}}$ edition, **2008**, Wiley–VCH, Weinheim).

quantum mechanical elaborations), taking into account that the excited state energy can be used, to a first approximation, as an extra free energy contribution for the occurrence of both oxidation and reduction processes.

2.4   Excimers and exciplexes

In most cases, quenching of an excited state (for example, by energy transfer) takes place by a weak electronic interaction. When the excited state and the quencher undergo a relatively strong electronic interaction, new chemical species, which are called excimers (from *exci*ted di*mers*) or exciplexes (from *exci*ted com*plexes*), depending on whether the two interacting units have the same or different chemical nature.

It is important to notice that excimer and exciplex formation is a reversible process and that both excimers and exciplexes sometimes (but not necessarily) can give luminescence. Compared with the "monomer" emission, the emission of an excimer or exciplex is always displaced to lower energy

(longer wavelengths) and usually corresponds to a broad and rather weak band.

Excimers are usually obtained when an excited state of an aromatic molecule interacts with the ground state of a molecule of the same type. For example, between excited and ground state of pyrene units. Exciplexes are obtained when an electron donor (acceptor) excited state interacts with an electron acceptor (donor) ground state molecule. For example, between excited states of aromatic molecules (electron acceptors) and amines (electron donors, see figure 2.3).

Figure 2.3: fluorescence spectra of anthracene in the presence of diethylaniline at various concentrations in toluene (from *"Fast reactions and processes in chemical kinetics"*, A. Weller, John Wiley & Sons, New York, **1967**).

In dendrimers containing a variety of components both exciplex and excimer formation can take place. In such a case, as many as three different types of luminescence can be observed, namely "monomer'' emission, exciplex emission and excimer emission.

It may also happen that in a supramolecular structure like a dendrimer there is a non negligible electronic interaction between adjacent chromophoric units already in the ground state. In such a case, the absorption spectrum of the species may substantially differ from the sum of the absorption

spectra of the component units. When the units have the same chemical nature, the interaction leads to formation of dimers. When the two units are different, the interaction has usually a charge-transfer nature, with formation of charge-transfer complexes. Excitation of such dimers leads to an excited state that is substantially the same as the corresponding excimers, and excitation of the charge-transfer ground state complexes leads to an excited state that is substantially the same as that of the corresponding exciplexes.

2.5 Photochemistry and dendrimers

Dendrimers are tree-like macromolecules with a high degree of order displaying the capability to contain selected chemical species in predetermined sites of their structure.

Dendrimers are drawing the interest of chemists because of their uncommon properties and their potential applications, covering a wide range of fields. It is possible to design and synthesize dendrimers containing a variety of groups in order to get suitable materials and explore their applications.[35,36] Moreover, it is interesting to couple luminescence with dendritic structures, since it represents a tool to detect interactions of dendrimers with other chemical species and it allows to perform "intelligent" functions such as the light harvesting and signal amplification.[37,38] In addition, due to their mutual distance, functional groups in the dendrimer architecture or in proximity of it can easily undergo energy or electron transfer processes.

In the last years, dendrimers have received increasing attentions due to their

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[35] For some reviews, see: a) Chase P. A., Gebbink R. J. M. K., van Koten G., *J. Organomet. Chem.*, **2004**, *689*, 4016. b) Ong W., Gómez-Kaifer M., Kaifer A. E., *Chem. Commun.*, **2004**, *0*, 1677.

[36] See also: a) Ballauff M., Likos C. N., *Angew. Chem. Int. Ed.*, **2004**, *43*, 2998. b) Caminade A. M., Majoral J. P., *Acc. Chem. Res.*, **2004**, *37*, 341.

[37] Scholes G. D., Fleming G. R., Olaya-Castro A., van Grondelle R., *Nature Chem.*, **2011**, *3*, 763.

[38] Balzani V., Ceroni P., Gestermann S., Kauffmann C., Gorka M., Vögtle F., *Chem. Commun.*, **2000**, 853.

use as molecular antennae, in particular for photochemical conversion of solar energy.[39,40] We can define a molecular antenna as a multi-component architecture in which multiple chromophores can absorb light and channel it to a central unit,[41,42] working as an acceptor, similarly to what is occurring in natural photosynthetic processes.[43,44] It is evident that it is necessary to choose properly both donors and acceptors for this purposes, since the efficiency of the molecular antenna is affected by other deactivation processes (i.e. electron transfer, exciplex and excimer formations).

As a core unit, many molecules can be chosen: polycyclic aromatic hydrocarbons (pyrene, perylene, etc.), porphyrins, metal complexes, etc. Among the others, fullerenes show many interesting electronic and photophysical properties which make them appropriate candidates for the synthesis of functional dendrimers;[45] such a molecule can act therefore as a terminal energy receptor in dendrimer based light-harvesting systems.[46]

[39] Balzani V., Ceroni P., Maestri M., Vicinelli V., *Curr. Opin. Chem. Biol.*, **2003**, *7*, 657.

[40] Puntoriero F., Nastasi F., Cavazzini M., Quici S., Campagna S., *Coord. Chem. Rev.*, **2007**, *251*, 536.

[41] Shortreed M. R., Swallen S. F., Shi Z.-Y., Tan W., Xu Z., Devadoss C., Moore J. S., Kopelman R., *J. Phys. Chem. B*, **1997**, *101*, 6318.

[42] Andrews D. L., Bradshaw D. S., Jenkins R. D., Rodríguez J., *Dalton Trans.*, **2009**, 10006.

[43] McConnell I., Li G., Brudvig G. W., *Chem. Biol.*, **2010**, *17*, 434.

[44] Liu Z., Yan H., Wang K., Kuang T., Zhang J., Gui L., An X., Chang W., *Nature*, **2004**, *428*, 287.

[45] Eckert J.-F., Nicoud J.-F., Nierengarten J.-F., Liu S.-G., Echegoyen L., Barigelletti F., Armaroli N., Ouali L., Krasnikov V., Hadziioannou G., *J. Am. Chem. Soc.*, **2000**, *122*, 7467.

[46] Nierengarten J.-F., Armaroli N., Accorsi G., Rio Y., Eckert J.-F., *Chem. Eur. J.*, **2003**, *9*, 36.

Chapter 3

Characterization techniques and methods

3.1 Materials

The investigated compounds have been synthesized in the laboratories of Aix-Marseille Université and CINaM (Centre Interdisciplinaire de Nanoscience à Marseille), under the supervision of prof. Marc Gingras. Details are described in the following chapters.

3.2 Standard characterization techniques

To afford purified compounds standards characterization techniques have been employed: ^{1}H and ^{13}C NMR, mass spectrometry, HPLC, TLC and X-rays diffraction are the most important.

All reagents, catalysts and compounds were purchased from Sigma Aldrich, Alfa Aesar and TCI and used directly, unless specifically mentioned. Solvents were purchased from Sigma Aldrich, Acros Organics or Carlo Erba at the reagent grade with a low water content (sometimes extra dry), and stored over freshly activated 3Å molecular sieves (activated during 5-18 hours at 250°C).

In case of air and moisture sensitive reactions, experiments were run drying all glassware in an oven at 150°C, and cooled down under an argon atmosphere in a drier or in argon pressure.

3.2.1   NMR analysis

^{1}H and ^{13}C NMR were recorded on a Bruker Avance 250 spectrometer equipped with automatic sample loading. Chemical shifts are provided in ppm relative to TMS (δ=0 ppm) or CHCl$_3$ (δ=7.26 ppm for ^{1}H NMR and δ=77.0 ppm for ^{13}C NMR) or to DMSO-d$_6$ (δ=2.50 ppm for ^{1}H NMR and [1]H=39.5 ppm for ^{13}C NMR), according to literature.[47] NMR measurements were performed at 22±2°C. The resonance multiplicity in the ^{1}H and ^{13}C NMR spectra is described as: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *m* (multiplet) and *br* (broad).

3.2.2   Mass spectrometry analysis

High resolution mass spectrometry (HRMS) and low resolution MS analyses were performed at the Spectropôle de Marseille, France.[48]
Electrospray ESI-TOF analyses were achieved on a Q-STAR Elite instrument with an ESI source in a positive mode.
MALDI-TOF analyses were performed on an Autoflex MALDI-TOF Bruker spectrometer.
Otherwise, electron ionization MS analysis were completed on a Shimadzu GC-MS QP2010 SE instrument at 70 eV (direct injection of samples).

3.2.3   Fourier transform infrared spectroscopy

Infrared absorption spectra were recorded on a Perkin Elmer Spectrum 100 instrument, with a Universal ATR accessory (*attenuated total reflectance*

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[47] Gottlieb H. E., Kotlyar V., Nudelman A., *J. Org. Chem.*, **1997**, *62*, 7512.

[48] Dr. Valérie Monnier is acknowledged for completing mass spectrometry analysis and interpretations. We would like to thank Dr. Christophe Chendo of Spéctropole, Marseille, for elemental analysis.

mode, contact crystal: diamond). Solid samples are directly charged at the diamond interface; liquid samples are deposited with the solvent, letting this one to evaporate.

3.2.4   Melting points and X-ray diffraction

Melting points were recorded on a IA9200 apparatus purchased from Thermo Fischer Scientific, and are uncorrected. X-ray diffraction were recorded on Bruker Nonius diffractometer equipped with a FR590 generator ($2K_w$, $l = K_a$ (Mo)) and a Kappa CCD goniometer.

3.2.5   Chromatographic methods

Flash chromatography[49] was performed over silica gel 60, Merck type 230-400 mesh (40-63 µm).
HPLC analytical studies were performed on reverse phase analytical columns (250 x 4.6 cm) on Chromatorex C18A SMB100-10 and Chromatorex C18HE SMB100-5 mounted on a Waters system (Waters, Saint Quentin-en-Yvelines, France) equipped with a Waters 600 pump with a binary gradient unit, a 7125 Rheodyne valve with a 20 µl sample loop, an on-line degassing system, a Waters 2487 UV-vis detector and a Borwin software.

3.3   Basic photophysical techniques

3.3.1   Electronic absorption spectra

All the absorption spectra in the 190–1100 nm range were recorded at room temperature on solutions contained in quartz cuvettes (optical pathlength 1 cm and 5 cm, Hellma® by using a Perkin Elmer λ40 spectrophotometer (figure 3.1). The precision on the wavelength values was ±2 nm. Molar absorption coefficient values were determined using the Lambert–Beer law; the experimental error, mostly due to weighting error, can be estimated to be around ±5%.

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[49] Clark Still W., Kahn M., Mitra A., *J. Org. Chem.*, **1978**, *43*, 2923.

Figure 3.1: schematic experimental set-up for a standard double-beam spectrophotometer.

3.3.2   Luminescence spectra

Fluorescence and phosphorescence emission and excitation spectra in the 250–900 nm range were recorded with Perkin Elmer LS 50 spectrofluorometers equipped with Hamamatsu R928 photomultiplier (schematic representation in figure 3.2).

Room temperature spectra were recorded in the same spectrofluorometric suprasil quartz cuvettes described for the electronic absorption spectra. In order to have comparable luminescence intensity measurements some correction had to be applied to the experimental data. These corrections were introduced to take into account instrumental geometrical effects and the distribution of the exciting light among the species effectively present in the solution.[50,51]

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[50] Credi A., Prodi L., *EPA Newsletter* **1996**, *58*, 50.
[51] Credi A., Prodi L., *Spectrochimica Acta A* **1998**, *54*, 159.

Figure 3.2: schematic representation of a standard spectrofluorometer. The instrument depicted is equipped with monochromators to select both the excitation and emission wavelengths.

Spectra in frozen matrix at 77 K were taken using quartz (or glass) tubes with an internal diameter of about 2 mm and a 20 cm length immersed in liquid nitrogen. A transparent dewar (glass or quartz) with a cylindrical terminal part with a 1 cm external diameter was employed. Such a device easily fits into the sample holder of the spectrofluorometers above indicated. Luminescence spectra recorded in the 650-900 nm region were corrected for the non-linear response of the photomultiplier towards photons of different wavelength making reference to a previously experimentally determined calibration curve obtained. The precision on the wavelength values was ±2 nm.

Luminescence spectra in the near infrared (NIR) region were recorded by a home-made apparatus based on an Edinburgh CD900 spectrofluorimeter, which uses a xenon lamp as the excitation source and a liquid nitrogen cooled hyperpure germanium crystal as a detector.

3.3.3 Luminescence quantum yield

Luminescence quantum yields have been determined on solution samples at room temperature referring to the relative method optimized by Demas and Crosby.[52] The quantum yield is expressed as:

$$\Phi_S = \Phi_R \Big(\frac{A_S}{A_R}\Big)\Big(\frac{n_S}{n_R}\Big)^2 \tag{3.1}$$

where Φ, A and n indicate the luminescence quantum yield, the area subtended by the emission band (in the intensity versus frequency spectrum) and the refractive index of the solvent used for the preparation of the solution, respectively; the subscripts S and R stand for sample and reference, respectively. A_S and A_R must be relative to the same instrumental conditions and to the same solution absorption at the excitation wavelength.

Different standards were selected depending on the spectral region of interests: naphthalene in degassed cyclohexane (Φ=0.23), fluorescein in aqueous sodium hydroxide 0.01 M (Φ=0.90) or quinine sulphate in 0.5 M H_2SO_4 aqueous solution (Φ=0.55). The experimental error was $\pm 15\%$.[53]

3.3.4 Luminescence lifetime measurements

Excited state lifetimes in the range 0.5 ns–10 µs were measured with an Edinburgh Instrument time correlated single-photon counting technique. A schematic view of this instrument is reported in figure 3.3. The excitation impulse is obtained by a gas discharge lamp (model nF900, filled with

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[52] Demas J. N., Crosby G. A., *J. Phys. Chem.*, **1971**, *76*, 1071.

[53] For further specifications on experimental luminescence measurements: Montalti M., Credi A., Prodi L., Gandolfi M. T., *Handbook of Photochemistry*, ed. Taylor & Francis, London, 3rd edn., **2006**.

nitrogen or deuterium, depending on excitation requirements) delivering pulses of 0.5 ns width at a frequency comprised between 1 and 100 kHz or by a pulsed diode laser (280 nm or 406 nm, Picoquant). A photomultiplier tube (Hamamatsu R928P) cooled at -20°C and suitably amplified is used as stop detector.

Lifetimes in the range between 10 µs and 5 s were measured with the same Perkin Elmer LS 50 spectrofluorometer employed for the luminescence spectra acquisition. In this case the excitation pulse is generated by a Xe lamp (5-50 Hz) and the emission decay directly recorded. The experimental error on the lifetime measurements is ±10%.

Figure 3.3: experimental set-up of the single photon counting. TAC is the time-to-amplitude converter; M are the two monochromators for emission and excitation; S is the sample.

3.3.5 Titration experiments

Titration experiments have been performed directly in the spectrofluorometric cuvettes previously described. A given amount (normally 2.5–3

ml) of a solution of the investigated compound was introduced in the cell with conventional pipettes and increasing amounts of a solution of the ion under examination added. Small volumes (of the order of 1–20 µl) were added in order to minimize the dilution effect which anyway was taken into account during data elaboration. Ligand concentrations were typically in the 10^{-5}–10^{-6} M range, while metal or H^+ solutions, before dilution, were between 10^{-3}–10^{-4} M. During the titration, usually both absorption and luminescence spectra were recorded. When possible, the fluorophores were excited at wavelength where absorption changes during the titration were small in order to simplify the luminescence spectra corrections. For the additions Hamilton microlitre syringes were used.

3.4   Dynamic Light Scattering

Advances in laser techniques in the past decades have made possible the improvement in measuring very small frequency shifts in the light scattered by the commonly called *Rayleigh scattering*, coming from dispersions of gases, liquids and solids.

Dynamic Light Scattering (DLS) based methods are nowadays largely used in many research fields, covering disciplines in the fields of physics, chemistry and biology: liquid crystals, colloids, biomolecules (viruses, proteins, etc.), microorganisms and many others. These techniques allow the determination of particle size distribution as well as better interpretations of interactions among quantities of macromolecules and particulates in solution.

In a light-scattering experiment, light from a laser passes through a polarizer to define the polarization of the incident beam, which then impinges on the scattering medium.

The spectral characteristics of the scattered light depend on the time scales characterizing the motions of the scatterers. The quantities measured in light-scattering experiments are the time-correlation function of either

Figure 3.4: schematic diagram of a conventional, 90° dynamic light scattering instrument.

the scattered field or the scattered intensity (or their spectral densities). Consequently, time-correlation functions and their spectral densities are central to an understanding of light scattering.[54]

Considering particles with diameters in the same order of magnitude of the incident wavelength (i.e. *nanoparticles*, particles with an aerodynamic diameter lower than 100 nm), it is more frequent to refer to the *Mie scattering*, which takes account of the polarizability α. In this case the intensity I of the scattering is defined as follows:

$$I = I_0 \frac{8\pi^4 \alpha^2}{\lambda^4 r^2}(1 + cos^2\theta) \tag{3.2}$$

where I_0 and λ are the intensity and wavelength of incident light respectively, r the distance from the scatterer and θ the angle between incident and scattered light.

The motion of massive molecules in solvents consisting of small molecules or particles is described by Brownian motion theory. In this treatise it

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[54] Berne B. J., Pecora R., *Dynamic light scattering with applications to chemistry, biology, and physics*, John Wiley & Sons, New York - USA, **1976**.

is assumed that the force on a Brownian particle, $M(d\mathbf{V}/dt)$, consists of a systematic frictional component, $\zeta\mathbf{V}$, and a random or fluctuating component, $\mathbf{F}(t)$. The equation of motion for the Brownian particle is consequently:

$$M\frac{d\mathbf{V}}{dt} = -\zeta\mathbf{V} + \mathbf{F}(t) \qquad (3.3)$$

where M is the mass of the particle and ζ is called the friction constant. This equation represents the *Langevin equation*. Hydrodynamic studies of the uniform motion of fluids along large spherical bodies show that the friction coefficient is related to the shear viscosity of the solvent η and to the radius of the sphere a by the Stokes formula $\zeta = 6\pi\eta a$. The random force $\mathbf{F}(t)$ arises from occasional fluctuations in which the particle actually experiences collisions that accelerate and decelerate it beyond the systematic frictional force. It is important to specify that the random force is not a prescribed function of the time, but a random function of the time. The Langevin equation is consequently a *stochastic* differential equation, since the $\mathbf{F}(t)$ depends on a Maxwell distribution of particles initial velocities.

Thus, the DLS technique allows to measure fluctuations in scattering intensity from particles in motion, determining their velocity in the media. Smaller particles move faster than larger particles, showing faster variations in scattering intensity.

The autocorrelation function shows the coherence of the signal of scattering intensity with itself: in case of large particles the function assumes constant values for larger times (as a consequence of smaller mobility) and vice versa.

In addition, relation between the diffusion coefficient D and the hydrodynamic radius r_h is defined by the Stokes-Einstein relation:

$$D = \frac{k_B T}{6\pi\eta r_h} \qquad (3.4)$$

where k_B is the Boltzmann's constant, T the temperature and η the viscosity of the solvent or medium. The hydrodynamic radius, determined by means of equation 3.4, corresponds to the radius of a sphere which would

undergo the same brownian motions (i.e. velocity) in the medium. In addition, it is important to state that the scattering intensity is proportional to r_h^6: therefore, smaller nanoparticles tend to scatter less than bigger ones.

From our experimental point of view, the determination of organic nanoparticles size distributions was achieved with a Malvern Nano ZS Dynamic Light Scattering instrument with a 633 nm laser diode.[55] Analyses are usually performed in quartz cuvette, equilibrating temperature automatically at 298 K; average diameter and PDI are obtained in most cases after 4 consecutive measurements of 10-15 runs each, in order to get statistical distributions of the two main parameters.

3.5 Microscopy techniques: AFM

Since 1989, the atomic force microscope (AFM) has emerged as a useful tool for studying surface interactions by means of force-distance curves. A great deal of work has been performed on both its theoretical and experimental aspects.[56] The heart of the AFM is a cantilever with a microfabricated tip that deflects when interacting with the sample surface. That can be scanned by means of a piezoactuator, while the cantilever deflection may be measured in different ways in order to reproduce the sample topography.[57] A general schematization is provided in figure 3.5.

There are two principal modes of acquisition of force-distance curves. In the first mode, called the *contact* mode, the sample is displaced along the Z axis in discrete steps and the variations in cantilever deflection are collected; in the second mode, called the *non-contact* mode, the cantilever is allowed to vibrate by an external piezoelectric transducer while the sample is approached and withdrawn, and the amplitude or the resonance

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[55] For details on the instrument, visit this page on Malvern website.
[56] Binnig G., Quate C. F., Gerber Ch., *Phys. Rev. Lett.*, **1986**, *56*, 930.
[57] Cappella B., Dietler D., *Surface Science Reports*, **1999**, *34*, 1-104.

Figure 3.5: left: schematic representation of the tip-sample system in a AFM microscopy. D is the actual tip-sample distance, whereas Z is the distance between the sample and the cantilever rest position. These two distances differ because of the cantilever deflection δ_C, and because of the sample deformation δ_S. Right: scanning electronic microscopy (SEM) image of a cantilever used for an AFM microscope.

frequency of the cantilever oscillations are collected as a function of tip-sample distance.

AFM images show important information about surface properties with high clarity: in addition, AFM can explore any sufficiently rigid surface either in air or with the sample immersed in a liquid. Recently developed instruments can allow temperature control of the sample, can be equipped with closed chamber for environmental control and can be mounted on an inverted microscope for simultaneous imaging through advanced optical techniques.

The field of view can vary from *ca.* 100 µm to the atomic and molecular scale.[58,59] Compared with scanning electron microscope (SEM), AFM provides a better topographic contrast, in addition to direct measurements

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[58] Sugimoto Y., Pou P., Masayuki A., Jelinek P., Pérez R., Morita S., Custance Ó., *Nature*, **2007**, *446*, 64.

[59] Gross L., Mohn F., Moll N., Liljeroth P., Meyer G., *Science*, **2009**, *325*, 1110.

of surfaces providing quantitative height evaluation.[60,61]

AFM allows of course examination of the morphology of distribution of inorganic and organic particles on surfaces as well as evaluation of the thickness and other topographical features.[62,63]

Concerning our experiments, microscopy images are achieved through a Bruker Multimode 8 AFM nanoscope in tapping mode or *PeakForce* non-contact mode.[64]

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[60] Haugstad G., *Atomic Force Microscopy: understanding basic modes and advanced applications*, John Wiley & Sons, Hoboken, NJ, USA, **2012**.

[61] Braga P. C., Ricci D., *Atomic force microscopy: biomedical methods and applications*, Humana Press Inc, Totowa, NJ, USA, **2004**.

[62] Caruso F., Möhwald H., *Langmuir*, **1999**, *15*, 8276.

[63] Rao A., Schönenberger M., Gnecco E., Glatzel Th., Meyer E., Brändlin D., Scandella L., *JPCS*, **2007**, *61*, 971.

[64] For further details on the instrument, visit this page on Bruker website.

Chapter 4

Polysulfurated compounds: synthesis and applications

4.1 Historical background

Despite relatively easy synthetic procedures for preparing many polysulfurated or persulfurated aromatic compounds, for some of them (especially the persulfurated ones) their chemistry, properties and applications are still quite unexplored, compared to other fields. Aromatic C–S bond formation represents an important topic in many disciplines, particularly in agrochemistry, in pharmaceutical sciences and in materials science. Only recently, several studies were performed in order to obtain modern classes of persulfurated or polysulfurated molecules, which have particular applications in materials chemistry, as well as in supramolecular chemistry, while taking advantage of sulfur chemistry and the modulation of the chemical, physicochemical and photochemical properties.[65]

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[65] Gingras M., Raimundo J. M., Chabre Y. M., *Angew. Chem. Int. Ed.*, **2006**, *45*, 1686.

4.2 Synthetic approaches

Historically, aromatic C–S bond chemistry has always been important and challenging. Many synthetic methods have been proposed to introduce sulfur into aromatic compounds. As for persulfurated aromatic compounds, they have been first a real curiosity, but they also enlightened the importance of C–S bonds in organic chemistry. It is also challenging aromaticity, metal complexation via multiple sulfur atoms and it provokes a fundamental change of the electronic structure and orbitals energy of a compound.

The attempt of a persulfuration of a benzene ring started in 1956,[66] from the work of Rocklin *et al.*, with some studies on the nucleophilic polysubstitution of hexachlorobenzene by thiolates. However the first persulfuration of the hexachlorobenzene molecule was reported in 1959,[67] by using the phenylthiocuprate, and hexacholobenzene near 200°C. Several following works showed that in similar conditions products are achievable by reactions in polar aprotic solvents, typically DMF, HMPA or DMI, in shorter times.[68,69,70,71]

Figure 4.1: first reported synthesis of the hexakis(phenylthio)benzene (see text for references).

[66] Rocklin A. L., *J. Org. Chem.*, **1956**, *21*, 1478.

[67] Adams R., Ferretti A., *J. Am. Chem. Soc.*, **1959**, *81*, 4927.

[68] Beck J. R., Yanher J. A., *J. Org. Chem.*, **1978**, *43*, 2048.

[69] Peach M. E., Rayner E. S., *J. Fluorine Chem.*, **1979**, *13*, 447.

[70] Testaferri L., Tingoli E. S., *J. Org. Chem.*, **1980**, *45*, 4376.

[71] MacNicol D. D., Mallinson P. R., Murphy A., Sym G. J., *Tetrahedron letters*, **1982**, *23*, 4131.

4.2.1   Main methodologies

Two main synthetic routes are attainable to get persulfurated compounds:
the first exploits a aromatic nucleophilic substitution on perhalogeneted
aromatics by means of thiolates salts (see figure 4.2).

Figure 4.2: general synthetic route to achieve persulfurated compounds through
an aromatic nucleophilic substitution.

   This way represents a convenient procedure to realize a reasonably wide
collection of chemical compounds, using cheap primary materials.[72] In
most cases the base is NaH or Cs_2CO_3 or even K_2CO_3, with consequences
on the reaction's kinetics and on the solubility of the reaction environment.
An alternative at this approach is represented by a 3-steps method that
involves a reduction of the intermediate hexakis(iso-propylthio)benzene
(or hexakis(phenylthio)benzene) by means of metallic Na, followed by the
alkylation of the persulfurated aromatic center (figure 4.3). This strategy
is preferable as the thiolates, when involved in aromatic substitutions, are
generally weak nucleophiles; nevertheless, the first way of reaction is widely
used due to the more extreme conditions needed in the second case.
Many polyhalogenated substrates have been employed (see figure 4.4) and
most of them have already been used to achieve persulfurated products.

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[72] Maiolo F., Testaferri L., Tiecco M., Tingoli M., *J. Org. Chem.*, **1981**, *46*, 3070.

Figure 4.3: general synthetic route to achieve persulfurated compounds through the reduction–alkylation approach.

4.3 General properties

Polysulfurated compounds can display several properties duo to the presence of aromaticity of the ring with sp^2-hybridized carbon atoms and to the electronic contribution from numerous divalent sulfur ligands, which also affect stabilization of negative or positive charges. These factors can by consequence have an influence on redox potentials, UV/Vis absorption, conductivity, non-linear optical properties, etc. They are indeed good electron acceptors in spite of a rich electronic density; their intense color and absorbance in the visible spectrum, their luminescence are intriguing for applications as chromophores in molecular systems; their exothermicity and reactivity in the persulfuration of perhalogenated aromatic compounds are also quite interesting.

In section 4.4 some application as nanodevices, organic conductors and ligands for chemical biology are briefly revised.

Figure 4.4: library of perhalogenated molecules used as precursors for sulfur substitutions; -X corresponds to -Cl or -F.

4.4 Applications

4.4.1 Organic materials

Since the field of organic conductors started his development[73] many studies have been carried out on novel organic architectures in order to obtain highly conducting materials; a great portion of them are based on tetrathi-afulvalene (TTF) and derivatives, including polysulfurated molecules and polymers.[74,75]

An example is represented by the molecule in figure 4.5, showing extended charge donors with multiple redox centers arranged regularly in space, following a 2D pattern.[76] In addition, sulfurated compounds featuring

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[73] Ferraris J., Cowan D. O., Walatka V., Perlstein J. H., *J. Am. Chem. Soc.*, **1973**, *95*, 948.

[74] Segura J. L., Martín N., *Angew. Chem. Int. Ed.*, **2001**, *40*, 1372.

[75] Frère P., Skabara P. J., *Chem. Soc. Rev.*, **2005**, *34*, 69.

[76] Wegner R., Beye N., Fanghänel E., Scherer U., Wirschem R., Müllen K., *Synth. Met.*, **1993**, *53*, 353.

covalently linked donor-acceptor units have been proposed (figure 4.6).[77] Although the use of TTF-based architectures did not succeed to afford materials with striking high conductibilities (i.e. higher than 10^{-2} S cm^{-1}), a large variety of sulfurated compounds as molecular conductors has been prepared: many materials showed a semiconducting behavior, while it would be important to solve problems like material aging and oxidation. Recently, charge transport and luminescence properties have been explored in a class of polysulfurated copolymers (figure 4.7): they display a strong fluorescence turn-on in consequence of the exposure to oxidants in solution, due to the chemical conversion of thioethers in sulfides or sulfones.[78]

Concerning the use of similar materials for organic electronic devices it is reported the use of linear benzene-fused bis(tetrathiafulvalene) compounds: a solution processed organic field-effect transistor based on one of these molecules shows high charge mobility (*ca.* 0.02 cm^2 V^{-1} s^{-1}).[79]

More over, coronene-based molecules (similar to the one in figure 4.8) are found to exhibit a three-dimensional aromatic system, displaying tunability of electronic properties once deposited on Au(111) surfaces: it was demonstrated that modifications of the peripheral aryl-groups allow to affect the self-assembly and the charge transport properties of the coronene

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[77] Lahlil K., Moradpour A., Bowlas C., Menou F., Cassoux F., Bonvoisin J., Launay J. P., Dive G., Dehareng D., *J. Am. Chem. Soc.*, **1995**, *117*, 9995.

[78] Dane E. L., King S. B., Swager T. M., *J. Am. Chem. Soc.*, **2010**, *132*, 7758.

[79] Gao X., Wu W., Liu Y., Qiu W., Sun X., Yu G., Zhu D., *Chem. Commun.*, **2006**, *0*, 2750.

Figure 4.5: TTF units are connected together in oligomers in order to get space-extended molecular electron donors (see references in the text).

Figure 4.6: a molecular D-A-D (donor-acceptor-donor) triad builded on persulfurated arenes with a quinone central unit (see references in the text).

Figure 4.7: a diethynil-tetrasulfurated benzene represents a monomer for a subsequent copolymerisation: the obtained material displays both redox and luminescence properties (see references in the text).

derivatives.[80,81]

4.4.2 In nanosciences

Several works have been documented concerning the application of persulfurated molecules as nanoparticles stabilizers, exploiting non-covalent interactions.

As an example, a star-shaped molecule based on a coronene core (figure 4.8) has shown peculiar behavior in the presence of Au^+ in solution. In that case gold nanoparticles with narrow size distribution can be achieved

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[80] Kowalzik P., Atodiresei N., Gingras M., Caciuc V., Schnaebele N., Raimundo J.-M., Blügel S., Waser R., Karthäuser S., *Phys. Chem. Chem. Phys.*, **2012**, *14*, 1635.

[81] Kowalzik P., Rathgeber S., Karthäuser S., Waser R., Schnaebele N., Raimundo J.-M., Gingras M., *New J. Chem.*, **2012**, *36*, 477.

by disproportionation of Au$^+$ ions: the molecular asterisk enhances probability of encounter between metal ions, protecting the resulting small nanoparticles from detrimental aggregation.[82] Nanoparticles are formed conveniently in another reported case using Au$^+$ as stabilizer and a class of polysulfurated dendrimers based on 1,3,5-trisubstituted benzene as ligands. It turns out that both size control and the stability of the nanoparticles are influenced by the type of the ligand–NP interaction.[83]

Figure 4.8: a molecular asterisk based on persulfurated coronene displays affinity towards Au$^+$ ions giving rise to nanoparticles.

4.4.3 In chemical biology

Considering potential bio-inspired interactions, the assembly of multiple carbohydrate-protein complexes is achieved through polyvalency, joining the high selectivity necessary for biological function.[84,85]

A class of polysulfurated and glycosylated star-shaped asterisks can work both as probe and ligand towards Concanavalin A, a well known car-

[82] Bergamini G., Ceroni P., Balzani V., Gingras M., Raimundo J.-M., Morandi V., Merli P. G., *Chem. Commun.*, **2007**, *0*, 4167.

[83] Hermes J. P., Sander F., Peterle T., Urbani R., Pfohl T., Thompson D., Mayor M., *Chem. Eur. J.*, **2011**, *17*, 13473.

[84] Kiessling L. L., Getswicki J. E., *Angew. Chem. Int. Ed.*, **2006**, *45*, 2348.

[85] Mammen M., Choi S.-K., Whitesides G. M., *Angew. Chem. Int. Ed.*, **1998**, *37*, 2754.

bohydrate-binding protein.[86] In particular, these asterisks (figure 4.9) have among the highest inhibition potencies of Concanavaline A-induced hemagglutination, taking advantage of a powerful cross-linking ability which highly affects the inhibition of the protein.[87]

Figure 4.9: a persulfurated benzene core (evidenced in blue) is decorated with α-glucose branches to get an high selectivity ligand towards Concavalin A (see references in the text).

Persulfurated benzene derivatives have been conceived also for bioinorganic and biomimetic systems.[88]
In 1987, Holm and co-workers reported the synthesis of analogues of iron-sulfur protein clusters, which are involved in many biological electron-transfer sites (for examples, ferredoxins and rubredoxins).[89] Due to the up

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[86] Hardman K. D., Ainsworth C. F., *Biochemistry*, **1972**, *11*, 4910.

[87] Sleiman M., Varrot A., Raimundo J.-M., Gingras M., Goekjian P. G., *Chem. Commun.*, **2008**, *0*, 6507.

[88] Evans D. J., Garcia G, Leigh G. J., Newton M. S., Santana M. D., *J. Chem. Soc., Dalton Trans.*, **1992**, *0*, 3229.

[89] Stack T. D. P., Holm R. H., Newton M. S., Santana M. D., *J. Am. Chem. Soc.*,

and down orientation of sulfurated arms surrounding the benzene core, the molecule is showing to bundle an iron cluster in a tripodlike arrangement. The up and down alternating scheme (*ababab*) of the substituents in persubstituted benzene derivatives was exploited in solution.

Other works refer to more complicated double cubane-like clusters, which were characterized by ESR and electrochemical studies,[90,91] as well as Mössbauer measurements.[92]

Biomimetic systems associated to sulfite reductase, nitrogenase and biotin synthase have been reported, too.[93]

4.4.4　In supramolecular chemistry

Several investigations on poly- and persulfurated compounds have been performed in the field of supramolecular chemistry, joining the intriguing properties given by the presence of sulfur atoms, which can affect electronic properties and coordination capabilities.

Since the first discoveries of interactions between macrocycles and metal salts,[94] many groups oriented the research towards exploration of new cyclic ligands, whose architecture is often related to the presence of a templating metal ion. This is the case of a *"Golden wheel"* (figure 4.10) which is made up starting from $(Ph_3P)AuCl$ in DCM and shows an interesting structure with Au^+ ions coordinated to sulfur atoms.[95] In the presence of metal ions such as Ag^+, another small asterisk (hexakis(phenylthio)benzene, figure 4.1) gives rise to a 3D network in consequence of its coordination. In addition, changing the counterion affect the network development: for

1987, *109*, 2546.

[90] Stack T. D. P., Carney M. J., Holm R. H., *J. Am. Chem. Soc.*, **1989**, *111*, 1670.

[91] Huang J., Mukerjee S., Segal B. M., Akashi H., Zhou J., Holm R. H., *J. Am. Chem. Soc.*, **1997**, *119*, 8662.

[92] Weigel J. A., Holm R. H., Surerus K. K., Münck E., *J. Am. Chem. Soc.*, **1989**, *111*, 9246.

[93] Cai L., Weigel J. A., Holm R. H., *J. Am. Chem. Soc.*, **1993**, *115*, 9289.

[94] Pedersen C. J., *J. Am. Chem. Soc.*, **1967**, *89*, 7017.

[95] Yip H. K., Schier A., Riede J., Schmidbaur H., *J. Chem. Soc., Dalton Trans.*, **1994**, *0*, 2333.

Figure 4.10: through non-covalent interactions it is possible to achieve a "Golden wheel", showing a nearly planar structure on the central unit with 6 Au atoms coordinating the 6 sulfur atoms (right, particular of XRD structure, with Au atoms evidenced in gold).

example, nitrate can change the supramolecular topology generating a linear coordination polymer.[96]

Many other works took into account several potentialities of polysulfurated compounds, taking advantage of molecular conformations and electronic properties to explore several systems as cryptands,[97] or redox sensors[98] among the others.

In addition, molecular asterisks were employed in polymeric membranes for applications in ion-selective electrodes, studying selectivity for various metal ions as Ag^+, Cu^{2+}, Pb^{2+}, Ca^{2+}, Na^+, K^+, Cs^+, Hg^{2+}.[99] Second-generation coronene asterisks had the highest selectivity for Ag^+ ions, despite the high affinity towards sulfur atoms of Hg^{2+}, Cu^{2+}, and Pb^{2+}.

In other works, a X-ray crystallographic analysis is presented, showing that the coordination of AgI with octakis(cyclohexanylthio)naphthalene

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[96] Suenaga Y., Kuroda-Sowa T., Maekawa M., Munakata H., *J. Chem. Soc., Dalton Trans*, **2000**, *0*, 3620.

[97] Stack T. D. P., Weigel J. A., Holm R. H., *Inorg. Chem.*, **1990**, *29*, 3745.

[98] Cai L., Holm R. H., *J. Am. Chem. Soc.*, **1994**, *116*, 7177.

[99] Johnson D. R., Pinchart A., Badr I. H. A., Gingras M., Bachas L. G., *Electroanalysis*, **2002**, *14*, 1419.

is able to develop in a 2D sheet structure with cavities.[100] Ag^+ ions are coordinated to two adjacent sulfur ligands on the naphthalene core and two oxygenated ligands from a counteranion in a tetrahedral arrangement. Other organometallic complexes described were those incorporating Ni^{2+}, Zn^{2+}, and Ti^{4+} cations. Polymeric Ni^{2+} complexes originally prepared from benzenehexathiolate and then from indacene derivatives were synthesized in an attempt to discover new mono-, di-, and polydithiolene organic conductors.[101]

Selective formation of 1,3-dithiole-2-thiones from sodium benzenehexathiolate followed by basic hydrolysis of the thionocarbonate group and addition of a titanocene salt provided mononuclear titanocene complexes based on benzenehexathiolate derivatives.[102]

4.4.5 Photochemistry and optics

Polysulfurated compounds have been conceived as suitable materials in optics, too: many investigations demonstrated that sulfur-containing compounds show higher refractive index in respect of those which do not contains sulfur; in addition, some organic polymer is able to change its refractive index with the temperature.[103] Other polysulfurated compounds can find application as electrophotographic materials[104] or in liquid crystals applications as mesogenic phases.[105]

In the following chapters we will explore the potentialities of basic molecular asterisks with aromatic peripheral units as AIE-active materials and coordination capabilities of polysulfurated core ligands towards transition metal ions.

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[100] Suenaga Y., Konaka H., Kitamura K., Kuroda-Sowa T., Maekawa M., Munakata M., *Inorg. Chem. Acta*, **2003**, *351*, 379.

[101] Fanghänel E., Bierwisch J., Richter A. M., Beye N., *Synth. Met.*, **1992**, *47*, 87.

[102] Fanghänel E., Bierwisch J., Ullrich A., Herrmann A., *Chem. Ber.*, **1995**, *128*, 1047.

[103] Gostevskaya V. I., Gavrilova G. M., Afonin A. V., Amosova S. V., *Russ. J. Org. Chem.*, **2001**, *37*, 388.

[104] Takahiro F., Masatoshi T., Hirotoshi K., Atsuo O., *Chem. Abstr.*, **2003**, *139*, 261164.

[105] Praefcke K., Kohne B., Poetsch E., Herz C. P. [Patent: DE 3430482].

Chapter 5

Polysulfurated molecular asterisks

A novel series of molecular asterisks has been developed: the 5 new compounds of the series are fully characterized with the usual techniques (MS, NMR, IR, elemental analysis). Concerning these molecules, in this chapter the synthetic approach, the photophysical characterization and some application will be discussed.

In order to better understand the luminescence properties of different persulfurated asterisks, a library of molecules has been designed by changing the peripheral aromatic unit around the benzene core. The aim of this part of the project is to determine the different behavior in the presence of several different bulky groups in the *ortho* positions of the outermost phenyl units: as a consequence, those ones can affect the intramolecular rotations and excited state decay rates.

5.1 Synthesis

As already mentioned in chapter 4, the synthetic approach that was used to build the new asterisks in figure 5.2 involved exclusively a single step aromatic nucleophilic substitution (see figure 5.1), in which a thiolate

works as a suitable nucleophile on polyhalogenated benzenes. To obtain the compounds, a series of aromatic thiols with different alkylic or alkyloxy functions has been chosen as starting materials. Among them, three have a single function on the position 2 (the -SH function identifies the position 1), while one has two methyl groups in position 2 and 6. Theoretically, without considering kinetic effects, all of those thiols should work with comparable reactivity in the presence of the same type of substrate, in these case hexachlorobenzene of hexafluorobenzene.

Figure 5.1: reaction scheme for molecular asterisks. In our cases R' and R'' can be –H, –CH$_3$, –OCH$_3$ or –CH(CH$_3$)$_2$. When reaction is brought to RT the number of substituents on the aromatic center is easier to control and tetrasubstituted asterisks can be afforded and isolated in satisfactory amounts.

Two prototype compounds have already been prepared precedently: **A6** and **A6-Mep**. The procedure to prepare them helped to the synthetic approach and to better isolate the final products.

Concerning the purification, final compounds are achieved after a simple trituration in solvents (ethanol or toluene), recrystallisation or column chromatography in relation to the solubility and to the amount of impurities in the crude products. Generally, asterisks of the **A6** family show a better solubility in usual solvents than the two tetrasubstituted ones; in addition **A4-OMe** has been isolated by chance trying the reaction to afford **A6-OMe** at RT.

The case of **A4-Me$_2$** deserves a separate mention, as the analogue persubstituted compound has not been isolated. In fact, the kinetic barrier to attach one or two more 2,6-dimethylthiophenyl units on the core seems

Figure 5.2: family of novel polysulfurated molecular asterisks that have been synthesized. Three of them (identified by '**A6**') have a persulfurated core, while the other two ones ('**A4**') are tetra-substituted.

to be too high in these reaction conditions: the two $-CH_3$ groups on the thiol and on the potentially reacting asterisk provide a steric hindrance and nucleophilic attack is prevented. Even after 10 weeks of reaction (solvent is refilled sporadically) the most abundant product in the reaction mixture is **A4-Me$_2$**, which is isolated by crystallization in toluene.

The mechanism involved during the substitution on perhalogenated substrate is not well known yet; nevertheless, one can theorize on the possible reaction path on the basis of the easiest derivatives (i.e. the benzene core partially substituted) which can be isolated, so a generally known reactivity and regioselectivity is accepted. In most of the cases, the di-, tetra and hexasubstituted benzene are easily affordable, while the other intermediates show up in traces only. The reaction occurring seems to move preferably to the formation of *para*-substituted by-products; it

Figure 5.3: the asterisks **A6** and **A6-Mep** were already synthesized and characterized.

has been proposed a classic interpretation (figure 5.4) that involves the formation of a Meisenheimer complex, which could be stabilized by the presence of sulfur atoms around the aromatic ring and in α position in respect of a thioether substituent.

Figure 5.4: proposed mechanism for the nucleophilic aromatic substitutions by a generic aromatic thiol on the hexachlorobenzene in a polar aprotic solvent.

5.1.1 Details

Hexakis(2-methylthiophenyl)-benzene (A6-Me). An oven-dried double-neck flask fitted with a septum was charged with hexachlorobenzene (267.7 mg; 0.94 mmol, 1 eqv) and 1,3-dimethyl-2-imidazolidinone (6 ml) as a solvent. After *o*-thiocresol (1.054 g, 8.49 mmol, 9 eqv) was added via

syringe, NaH (95%, 237 mg, 9.87 mmol, 10.5 eqv) was carefully poured in the reaction at 5-8° C by means of a Gooch tube. A vigorous bubbling developed and the mixture was heated at 60° C for 96 hrs, taking a bright yellow colour. The yellow solid was precipitated in aqueous 2 M NaOH (60 ml), isolated by filtration and then triturated in 15 ml of ethanol/H_2O 80:20 mixture. As impurities remain in the product, the solid was further purified by column chromatography (petroleum ether:toluene 70:30) to give **A6-Me** (483.6 mg, 0.60 mmol, 63%). The product is then crystallized in toluene affording yellow crystals; mp: 193-195° C.

^{1}H NMR (250 MHz, $CDCl_3$): δ=2.20 [s, 18H], 6.66 [dd, J=7.2 Hz, 1.5 Hz, 6H], 6.89-7.06 [m, J=7.5 Hz, 18H].

^{13}C NMR (63 MHz, $CDCl_3$): δ=20.3 [CH_3], 126.0, 126.2, 128.1, 130.2, 136.4, 137.1, 148.2.

Low resolution MS: MALDI (DCTB matrix), calcd. 810.2 Da, founded m/z 810.2 [M]$^+$.

EA: calcd (%) for $C_{48}H_{42}S_6$: C 71.07, H 5.22, S 23.72; found: C 69.75, H 5.18, S 23.28.

Crystallographic data: available.

Hexakis(2-isopropylthiophenyl)-benzene (A6-iPr). In a round bottom flask hexachlorobenzene (18.7 mg; 0.07 mmol, 1 eqv) and Cs_2CO_3 (218.1 mg, 0.67 mmol, 10 eqv) were placed and dried by means of a vacuum pump. Then, in anhydrous and inert conditions (argon atmosphere), DMI (0.6 ml) was poured in as a solvent; 2-isopropylbenzenethiol (0.1 ml, 0.59 mmol, 9 eqv) was added via syringe and the mixture stirred at 100° C for 96 hrs. After being cooled to RT, the mixture was poured in 2 M NaOH (6 ml), extracted three times with toluene (15 ml) and dried on $MgSO_4$. The obtained gel is then triturated in ethanol-water mixture (9:1, 5 ml) and filtered, obtaining a yellow solid. As impurities remain in the products, purification is achieved by column chromatography (petroleum ether:toluene 8:2), giving **A6-iPr** (52.6 mg, 0.053 mmol, 81%), then crystallized in toluene; mp: 215-217° C.

^{1}H NMR (250 MHz, CDCl3): δ=1.09 [ds, 36H], 3.35 [sep, J=3.3 Hz, 6H], 6.56 [dd, J=7.9 Hz, 1.0 Hz, 6H], 6.93 [dt, J=7.5 Hz, 1.6 Hz, 6H], 7.05-7.18 [m, J=7.8 Hz, 1.0 Hz, 12H].

^{13}C NMR (63 MHz, CDCl3): δ= 23.2 [CH$_3$], 30.4 [CH], 125.4, 126.0, 126.3, 128.7, 137.1, 146.7, 150.0.

Low resolution MS: MALDI (DCTB matrix), calcd. 978.35 Da, founded m/z 978.3 [M]$^+$. Analysis completed by Spectropole, Marseilles.

AE: calcd (%) for C$_{60}$H$_{66}$S$_6$: C 73.57, H 6.79, S 19.64; found: C 73.74, H 6.94, S 19.81.

Crystallographic data: available.

Hexakis(2-methoxylthiophenyl)-benzene (A6-OMe). An oven-dried double-neck flask fitted with a septum was charged with hexachlorobenzene (127.8 mg; 0.45 mmol, 1 eqv) and 1,3-dimethyl-2-imidazolidinone (3 ml) as a solvent. After 2-methoxythiophenol (570 mg, 4.07 mmol, 9 eqv) was added via syringe, NaH (60% in oil dispersion, 230 mg, 5.75 mmol, 12 eqv) was carefully poured in the reaction at 5-8° C by means of a Gooch tube. A vigorous bubbling developed and the mixture was heated at 80° C for 50 hrs. During this time a bright yellow colour developed. The mixture is then poured in aqueous NaOH (2 M), obtaining a yellow-green solid, separated on fritted glass and washed several times with H$_2$O. This one is then triturated in an ethanol-water mixture (1:1) and filtered; hence, triturated another time in hot toluene to remove oil traces and filtered on fritted glass, to give 265.8 mg (0.29 mmol, 65%) of yellow product; mp: 250-252° C.

^{1}H NMR (250 MHz, DMSO-d$_6$): δ=3.72 [s, 18H], 6.55 [d, 6H, J=6.6], 6.82 [t, 6H, J=6.8], 6.92 [d, 6H, J=7.6], 7.10 [t, 6H, J=7.1].

Low resolution MS: EI, m/z (rel. %): 763 (32) [M-SPhOMe], 906 (100) [M-H], 907 (58) [M], 908 (43) [M+1]$^+$, 909 (19) [M+2]$^+$.

1,4-dichloro-2,3,5,6-tetrakis(2-methyloxythiophenyl)benzene (A4-OMe). A oven-dried double-neck flask fitted with a septum was

charged with hexachlorobenzene (67.6 mg, 0.24 mmol, 1 eqv) and 1,3-dimethyl-2-imidazolidinone (2 ml) as a solvent. After 2-methoxythiophenol (0.25 ml, 2.05 mmol, 8.7 eqv) was added via syringe, NaH (95%, 56.7 mg, 2.30 mmol, 10 eqv) was carefully poured in the reaction at 5-8° C by means of a Gooch tube. A vigorous bubbling developed and the mixture was stirred at RT for 5 days. The mixture is then poured in aqueous NaOH (2 M), obtaining a yellow solid, separated on fritted glass washed several times with H_2O. At this point the product is first triturated in ethanol (8 ml, 2 h, RT) then in toluene (6 ml, 2 h, 50° C); the compound is then purified with column chromatography (solid deposition, DCM:hexanes 70:30) and crystallised in toluene (slow evaporation) to afford 30.9 mg of yellow solid (18 %); mp: 263-265° C.

^{1}H NMR (250 MHz, $CDCl_3$): δ=3.80 [s, 12H], 6.72-6.79 [m, 12H], 7.05-7.12 [m, 4H].

Low resolution MS: EI, m/z (rel. %): 350 (32), 420 (30), 698 (100) [M]$^+$, 699 (39) [M+1]$^+$, 700 (87) [M+2]$^+$, 701 (33) [M+3]$^+$.

Crystallographic data: available.

1,4-dichloro-2,3,5,6-tetrakis(2,6-dimethylthiophenyl)benzene (A4-Me$_2$). In a round bottom flask hexachlorobenzene (47.7 mg; 0.17 mmol, 1 eqv) and Cs_2CO_3 (549.0 mg, 1.68 mmol, 10 eqv) were placed and dried by means of a vacuum pump. Then, in anhydrous and inert conditions (argon atmosphere), DMI (1.5 ml) was poured in as a solvent; 2,6-dimethylthiophenol (0.2 ml, 1.50 mmol, 9 eqv) was added via syringe and the mixture stirred at 80° C for 10 weeks. During this time the suspension takes a white colour. After being cooled to RT, the mixture was poured in 2 M NaOH (15 ml) and a white solid was obtained, filtered and washed several times with H_2O. The crude mixture is crystallised from slow evaporation of hot toluene, giving 70 mg of transparent crystals. These ones are furthermore triturated in ethanol and recrystallised with the same method, giving 61 mg (Y=53%) of white-yellow crystals; mp: 299-302° C.

Low resolution MS: EI, m/z (rel. %), calculated for $C_{38}H_{36}Cl_2S_4$: 690.11,

founded 416 (27) [M-(Me$_2$PhS)$_2$], 690 (100) [M]$^+$, 691 (44) [M+1], 692 (88) [M+2]$^+$, 693 (35) [M+3]$^+$.

Crystallographic data: available.

5.2 XRD analysis

In order to get more information on the configurations and crystallinity of these molecules several attempts to get the X-rays structures have been completed. In general, asterisks with aromatic peripheral units show a preference in the orientation of the phenyl rings: in one of the first studies the hexakis(phenylthio)benzene (**A6**, figure 5.5) displays a regular alternate *ababab* up-down orientation.[106] This is the usual and most recurrent configuration, although some exceptions exist: when substituent is β-naphtyl or 2-methylphenyl the conformation is *aabbab*.[107,108] In most

Figure 5.5: XRD structure of **A6** (right). Hydrogen atoms and solvent crystallization molecules are omitted for clarity, while the sulfur atoms are evidenced in yellow; the outer phenyl rings appear alternate up and down in respect of the persubstituted benzene central ring (*ababab* arrangement).

cases however, the six sulfur atoms around the phenyl ring are more or less in the same plane of the benzene ring and small distortions of the aromatic center are occurring, as expected.

[106] MacNicol D. D., Wilson D. R., *J. Chem. Soc., Chem. Commun.*, **1976**, 494.

[107] Testaferri L., Tingoli M., Tiecco M., *J. Org. Chem.*, **1980**, *45*, 4376.

[108] Haas A., Krächter H.-U., *Chem. Ber.*, **1988**, *121*, 1833.

Concerning the molecules in figure 5.2, we succeeded to determine the exact crystal structure with good accuracy for most of the asterisks simply getting single crystals after a classical recrystallisation in hot toluene (in the case of **A4-Me₂** recrystallisation is the chosen method to get a more convenient purification).[109] Considering both the smaller asterisks (tetrasubstituted, **A4-Me₂** and **A4-OMe**), we can observe the same scheme of orientation of the external units: more specifically, the external aromatic rings pop up symmetrically in respect of the chlorine atoms, placing themselves one up and one down avoiding sterical hindrance (figure 5.6 and 5.7).

Figure 5.6: XRD structure of **A4-Me₂** (right). Hydrogen atoms are omitted for clarity, while the sulfur atoms are evidenced in yellow and the chlorine atoms in green.

However, some differences in the two structures are evident. In the **A4-OMe** asterisk two external units do not undergo any twist around the C-S bond, while the adjacent ones are forced to a torsion angle of circa 25°. On the other hand, in **A4-Me₂** every couple of peripheral units displays a torsion angle equal to 53° in one case and to -58° in the other, probably due to the larger hindrance of the methyl groups; both structures give rise to a triclinic cell in the lattice.

The case of **A6-Me** and **A6-iPr** is slightly different. For both compounds, the structure that has been determined consists of two conformers

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[109] All single crystal X-rays analysis were kindly performed by Dr. Michel Giorgi, Spectropole, Marseilles.

A4-OMe

Figure 5.7: XRD structure of **A4-OMe** (right). Hydrogen atoms are omitted for clarity, while the sulfur atoms are evidenced in yellow, chlorine atoms in green and oxygen atoms in red.

together in the same unit cell: while in the case of **A6-iPr** actually the two conformers have the same configuration and symmetry only changes (figure 5.8), in the case of **A6-Me** we have evidence of two different conformers with different configurations of the outer units (figure 5.9).

Figure 5.8: XRD structure of **A6-iPr**. The two conformers are evidenced with different colors.

In particular, **A6-iPr** exhibits an unusual *aabaab* orientation, with central benzene plains distorted in both conformers by circa 10° due to the 2 down-oriented subunits.

On the other hand **A6-Me** shows different geometries for the two conformers: in the *aaabbb* orientation the sulfur atoms are considerably out of the benzene plane, with a major torsion of circa 17°. In the *aabbab* configuration the benzene plane is more distorted (more than 10°) allowing

the peripheral units to lay in a more disordered fashion. The calculated structure for this asterisk corresponds with the one already published in 1988 by Stack and Holm.[110]

Figure 5.9: XRD structure of **A6-Me**. Hydrogen atoms are omitted for clarity; the conformer with *aabbab* configuration is evidenced in green, while the one in *aaabbb* in blue.

As stated above, however, the general crystallization of aromatic persubstituted benzenes display a pattern *ababab*. Considering a similar compound, the hexakis(2-methylphenylthio)benzene, it was find out that in the solid state the orientation is *aaabbb*, similarly to the case of our **A6-Me**. According to several NMR studies, it is quite probable that a low difference in the free energy associated to the different conformers in solution is occurring, estimated in 3–4 kJ mol^{-1}.[111,112] This assumption helps us to consider the dynamical equilibria between the different conformers, where the sulfur atoms can freely rotate the external units up and down in respect of the central ring.

An analysis on the dependence of the luminesce of another asterisk, **A6-Mep**, in respect of the temperature is provided at section 5.6: we can rationalize the emission behavior as a consequence of the orientation of the different branches of the molecule by increasing or decreasing the tem-

[110] Stack T. D. P., Holm R. H., *J. Am. Chem. Soc.*, **1988**, *110*, 2484.

[111] Clark P. D., Mesher S. T. E., Primak A., Yao H., *Catal. Lett.*, **1997**, *48*, 79.

[112] Wudl F., Nalewajek D., Rotella F. J., Gebert E., *J. Am. Chem. Soc.*, **1981**, *103*, 5885.

perature of the medium. In figure 5.10 we can observe that in the case of **A6-Mep** the *ababab* orientation is restored.

Figure 5.10: XRD structure of **A6-Mep**. Hydrogen atoms are omitted for clarity, sulfur atom are evidenced in yellow.

5.3 Photophysical characterization

All compounds in figure 5.2 have been characterized in DCM by means of a classic spectrophotometric analysis. Materials are solubilized in the solvent by determining precisely the concentration: the molar absorptivity is determined by the Lambert-Beer law as a ratio between the measured absorption and the concentration.

Absorption spectra show a comparable behavior for all asterisks of the same number of substituents, with a main band with a maximum around 320 nm for all the **A6**- series, joining the baseline only at circa 450 nm. In the same way, the molar absorptivity is similar, between 18000 and 20000 M^{-1} cm^{-1}. For this reasons both the solid phase and the solutions of all materials appear in a light yellow color. Data are collected in table 5.1 and shown in figure 5.11.

We can also compare the properties of the **A4**- family with those of persubstituted molecules: in particular the **A4-Me₂** molecule displays

Compound	Absorption in DCM	
	λ (nm)	ε $(\mathrm{M}^{-1}\,\mathrm{cm}^{-1})$
A6	332	18900
A6-Me	332	18900
A6-Mep	326	19200
A6-OMe	332	18400
A6-iPr	332	21500
A4-Me$_2$	314	–

Table 5.1: Absorption data in DCM for asterisks.

a blue-shifted sharper absorption in respect of the **A6**- series. Since no accurate determination of molar absorptivity has been completed due to the low solubility of the compound in DCM, the absorption spectrum is reported in absorbance units. In addition, no absorption information is coming from **A4-OMe** because of the lack of good quantity of material and to the low solubility of the compound.

Concerning the emission, the asterisks exhibit an unusual behavior. In fact, in solution the molecules do not show any appreciable emission in any experimental condition (aerated, argon-purged or completely degassed solutions) or with any instrumental setup (fluorescence or phosphorescence). On the other hand, most of the compounds of this family show a very intense emission in the solid state at RT or in rigid media at 77 K. One explanation of this phenomenon involves usually the inhibition of intramolecular motions, by means of which the non-radiative deactivation usually takes place. Concepts are better elucidated in section 5.4.
As the absorption spectra do not display dramatic differences within the same family of compounds, we can expect that this point do not give important fallouts in terms of luminescence spectra. In fact, all the solids

Figure 5.11: UV-vis molar absorptivity spectra of **A6-Me** (blue line), **A6-iPr** (brown line), **A6-OMe** (red line) and absorption spectrum of **A4-Me₂** (purple line) in DCM at 298 K. In each plot, the spectrum of **A6** (black line) is reported for comparison purpose. The absorbance spectrum of **A4-Me₂** is reported in arbitrary units since no precise determination of ε has been completed.

from the **A6** family do not show a real difference concerning the excited state properties (table 5.2 and figure 5.12): all the emission in solid phase for compounds with aliphatic units on the external substituents show an emission maximum from 515 to 526 nm, with a broad unstructured band which broadens over the 650 nm, displaying a bright green phosphorescence. Hence, there is a faint red-shift in respect of the emission of the model compound **A6**. On the contrary **A6-OMe** gives a blue-shifted

	Emission in solid phase		
Compound	$\boldsymbol{\lambda}_{max}$ (nm)	$\boldsymbol{\tau}$ (µs)	$\boldsymbol{\Phi}_{em}$
A6	515	12.1	–
A6-Me	522	15.8	–
A6-Mep	519	3.0	0.8
A6-OMe	487	6.8	–
A6-iPr	526	5.3	–
A4-OMe	489	6.7	–
A4-Me$_2$	505	9.7	–

Table 5.2: Emission data in solid phase for asterisks.

phosphorescence, with a maximum at around 490 nm, probably due to the presence of the oxygen atoms which can perturb the conjugation over the molecule. Tetrasubstituted asterisks show on the other hand a light blue-shifted emission in solid phase, larger in the case of **A4-OMe**; so, there is a coherence between blue-shift in absorption spectra and emission spectra.

Excited state lifetimes (determined with TCSPC measurements) give full evidence of a triplet emission, with decay times around 10 µs for all molecules. In this case there is no clear evidence of a dependence between the type of substituents and the emission lifetime: in general, a bulkier

Figure 5.12: left: emission spectra from the solid phase of **A6-Me** (blue line), **A6-Mep** (green line), **A6-iPr** (brown line) and **A6-OMe** (red line); right: emission spectra from the solid phase of **A4-Me$_2$** (purple line) and **A4-OMe** (green line). In both families of plots the emission spectrum of **A6** is reported for comparison. λ_{ex}=330 nm, T=298 K.

group seems to not affect radically the rates of the radiative decays.

Since the molecules do not emit in solution, quantum yield has been determined only on the solid phase of **A6-Mep** by means of an integrating sphere measurement ([Eu(phen)$_3$]$^{3+}$ used as a quantum yield reference).[113] The only precise determination of quantum yield for the emission of the solid gives us evidence that this kind of molecules deserves attention as suitable materials for electronics: organic luminescent materials are attracting more and more interest in these recent years for the potential application in optoelectronic devices as the OLEDs (organic light emitting diodes, see section 5.7).

Characterization at low temperatures (typically at 77 K in liquid nitrogen) has been performed to explore the properties of these molecules in rigid environment. In a classic experiment, a solution of the compound is prepared in a DCM:MeOH 1:1 v/v mixture (absorbance is kept normally below 0.6) and put into liquid nitrogen through a quartz tube.

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[113] Quantum yield measurements have been completed by Dr. Gianluca Accorsi (CNR-ISOF, Bologna) and coworkers by means of an integrating sphere apparatus.

Once again, in this condition excited states are only slightly affected and emission spectra are very similar to the ones recorded in the solid phase (see table 5.3 and figure 5.13).

	Emission at 77 K	
Compound	$\boldsymbol{\lambda}_{max}$ (nm)	$\boldsymbol{\tau}$ (ms)
A6	510	–
A6-Me	509	6.2
A6-Mep	509	4.3
A6-OMe	505	4.0
A6-iPr	512	8.9
A4-Me$_2$	488	16.2

Table 5.3: Emission data at 77 K for asterisks.

Figure 5.13: emission spectra taken on 1:1 DCM:MeOH rigid matrix of **A6-Me** (blue line), **A6-iPr** (green line), **A6-OMe** (red line) and **A4-Me$_2$** (dark green line) at 77 K. λ_{ex}=330 nm.

However, all the molecules examined show a rigid matrix enhancing of the luminescence; in addition the quantum yield of **A6-Mep** has been estimated in 0.8 at low temperature, using dansyl amide as a standard, by

means of a cryostat.

The nature of the emissive transition has been investigated with calculation methods and it was revealed to originate from a CT emissive state — the electron poor central persubstituted unit can work as an electron acceptor from the external phenyl rings.

As a comparison, the model compound **B6-iPr** (figure 5.14), which has not aromatic peripheral units, has been studied under similar conditions:[114] it was found out that this molecule does not show any emission at all, even by changing the medium at low temperature or in the solid phase; by the way, the absorption spectra of **B6-iPr** in DCM shows a blue-shifted main band, with a descending trend before 450 nm.

Therefore, the presence of the tolyl substituents has not only an effect on the energy of the lowest spin allowed electronic transition ($S_0 \rightarrow S_1$), as evidenced by the absorption spectra, but also on the rate constants of the deactivation processes of the lowest triplet excited state (T_1).

B6-iPr

Figure 5.14: as a comparison to **A6-Mep**, the absorption and emission properties of 1,2,3,4,5,6-hexakis(isopropylthio)benzene (**B6-iPr**) have been studied.

5.4   The AIE effect

Investigations in solution contributed fundamentally to understanding luminescence processes; in most cases the properties describing these phe-

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[114] The compound was already synthesized and kindly delivered by prof. Gingras group and used as received.

nomena nevertheless are not the same in concentrated solutions. Indeed, it is quite common to find that many organic luminophores show very different light-emitting behaviours: luminescence is weakened or totally quenched in most of the cases (this phenomenon is usually referred as "concentration quenching").

An example is provided by most of aromatic hydrocarbons such as DDPD (*N*,*N*-dicyclohexyl-1,7-dibromo-3,4,9,10-perylenetetracarboxylic diimide): this molecule is soluble in THF, where it shows a strong luminescence. The emission starts weakening once water is added to the solution: because of the immiscibility of the molecule with water, it gives rise to the formation of aggregates and the emission is quenched as a result.

This kind of quenching is common to most of aromatic hydrocarbons and their derivatives,[115] because of the piling-up of molecules forming an aggregate. For these reasons, materials which present this kind of features are normally considered as unavailing for applications in materials chemistry or better in real-world applications.

The AIE (Aggregation Induced Emission) is precisely the opposite phenomenon: useful properties, such as luminescence, are coming from aggregates or, in general, from 'high concentration' conditions.

Taking into account these points, one can start to imagine and design several new AIE luminogens, in order to modulate their properties as a function of their physical state or morphology. In these recent years many research group have completed several studies on this kind of materials, covering possible applications in many different fields; the topic is one of the most lively in nowadays research and it has had increasing attention after its rapid advance.[116]

More in general, materials whose photophysical properties are dependent on changes in physical molecular packing modes — namely *mechanofluorochromic materials* — have a relationship with AIE-active materials.[117]

[115] Birks J. B., *"Photophysics of organic molecules"*, Wiley, London, **1970**.

[116] Hong Y., Lam J. W. Y., Tang B. Z., *Chem. Soc. Rev.*, **2011**, *40*, 5361.

[117] Chi Z., Zhang X., Xu B., Zhou X., Ma C., Zhang Y., Liu S., Xu J., *Chem. Soc.*

One of the most accepted interpretation of the AIE effect refers to the RIR (Restriction of Intramolecular Rotations) as an explication for the increased emission in the solid or aggregate phase. As an example, we can cite the case of HPS (hexaphenylsilole): this molecule is non-planar and it shows six peripheral aromatic units, which can undergo rotations around a C–C bond and against the silacyclopentadiene: in solution these rotations may eliminate the excited state in a non-radiative way, thus representing the easiest way of deactivation. In the aggregate form, however, because of the non-planarity of the molecule, the π-π stacking cannot occur and luminescence is recorded only from the solid phase or in a colloidal dispersion of aggregates.[118]

Several mechanisms besides the RIR have been proposed to provide better interpretation to the AIE process, including the formation of J-aggregates,[119] excimer formation,[120] intramolecular planarization[121] and twisting intramolecular charge transfer.[122]

However, the RIR related processes have been extensively studied: quite recently, studying the luminescence properties of two molecules — the **DCPP** and **DCDPP** pyrazine derivatives, figure 5.15 — it was find out that upon lowering the temperature of solutions the radiative decay rates for both compounds vary appreciably. In particular, because of the presence of two free-rotating phenyl rings in the **DCDPP** molecule, the luminescence quantum yield increases by 72 times at 20 K (in respect at RT), while there is no significant difference in the photophysical properties of the **DCPP**.

Rev., **2012**, *41*, 3878.

[118] Hong Y., Lam J. W. Y., Tang B. Z., *Chem. Comm.*, **2009**, 4332.

[119] An B.-K., Kwon S.-K., Jung S.-D., Park S.-Y., *J. Am. Chem. Soc.*, **2002**, *124*, 14410.

[120] Liu Y., Tao X., Wang F., Shi J., Sun J., Yu W., Ren Y., Zou D., Jiang M., *J. Phys. Chem. C*, **2007**, *111*, 6544.

[121] Sonoda Y., Tsuzuki S., Goto M., Tohnai N., Yoshida M., *J. Phys. Chem. A*, **2010**, *114*, 172.

[122] Hu R., Lager E., Aguilar-Aguilar A., Liu J., Lam J. W. Y., Sung H. H. Y., Williams I. D., Zhong Y., Wong K. S., Pea-Cabrera E., *J. Phys. Chem. C*, **2009**, *113*, 15845.

Figure 5.15: Two pyridine derivatives which can show the importance of the restriction of molecular rotations in the AIE effect interpretation (see text for references).

The rotations of the phenyl rings, are easily inhibited at low temperatures, effectively blocking the non-radiative decay pathways.[123]

5.4.1 Some applications

As already mentioned, an extended library of AIE-active molecules have been collected, so far. A large part of it is built upon two main motives: the tetraphenylethylene unit, which could represent the category of hydrocarbons, and the hexaphenylsilole, based on a silicon heterocycle. The derivatives based on these molecules can work in a vast range of application: as fluorescence sensors, bio-probes, electroluminescence devices and as materials suitable for optoelectronics. These topics are well gathered in the recent (2011) review by Tang *et al*, mentioned above in the text.

Among the others, it is useful to report the case of an OFF-ON sensor based on the tetraphenylethylene moiety (shortened with **TPE-CE4**, figure 5.16). The molecule can work as a off-on fluorimetric potassium sensor: it takes advantage of the selective coordination of K^+ by means of the crown ether (with a well known 1:2 ratio) to generate a rigid architecture which shows an enhancing effect in luminescence intensity as a consequence of the recognition process. Moreover, the molecule displays an high selectivity

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[123] Deng C., Niu Y., Peng Q., Qin A., Shuai Z., Tang B. Z., *J. Chem. Phys.*, **2011**, *135*, 014304.

TPE-CE4

Figure 5.16: combining an AIE-active motif (tetraphenylethylene) and supramolecular recognition (K^+ ions) in a single molecule (see text for references).

among many cations.[124]

Another example which can well illustrate the potential of AIE-based applications is represented by a two-faced molecule, in which two terpyridine moieties can act as typical coordination centers for transition metal ions such as Fe^{II} and Zn^{II} (**TPE-Tpy**, figure 5.17): in this case also, the molecule itself is practically non-luminescent in the solution state, while it becomes emissive in presence of a non-solvent as water. The DLS analysis reveals also the formation of nanoparticles in polar solvent mixtures, indicating that the molecules goes towards the formation of luminescent aggregates. The addition of Zn^{II} ions in an aqueous (1% v/v THF) colloid containing **TPE-Tpy** can reduce the emission intensity and gradually gives rise to a new red-shifted luminescence maximum; this configuration is preserved in organic solvents. One explanation involves the increased conjugation of the system once the Zn^{II} are coordinated, working as a 'bridge' between two adjacent **TPE-Tpy** molecules or aggregate.[125]

To consider this last case is useful as it could represent a valid prototype for

[124] Wang X., Hu J., Liu T., Zhang G., Liu S., *J. Mater. Chem.*, **2012**, *22*, 8622.

[125] Hong Y., Chen S., Leung C. W. T., Lam J. W. Y., Liu J., Tseng N.-W., Kwok R. T. K., Yu Y., Wang Z., Tang B. Z., *ACS Appl. Mater. Interfaces*, **2011**, *3*, 3411.

TPE-Tpy

Figure 5.17: due to the presence of terpyridile moieties, a suitable AIE-active ligand can work as a suitable sensor for Zn^{II} ions in aqueous solutions.

the design of metal sensors based on AIE active moieties; in the following chapters we will deal again with this type of systems.

Even more recently, it was demonstrated that the tetraphenylethylene moiety can become luminescent when the phenyl units are blocked by incorporation of the fluorophore in a rigid MOF (Metal Organic Framework).[126]

In addition, referring to intramolecular motions, the internal torsional barrier could be modulated with the insertion of convenient functional groups at the periphery of the AIE-active unit (see figure 5.18): the outermost carboxylic units work as anchoring groups for metals, being a basis for many reported MOFs.

In this kind of structures based upon tetraphenylethylene derivatives it was revealed that ligand could be locked in high-energy conformations, in accordance with topological design.[127]

However, despite numerous studies, the mechanism of fluorescence quenching in AIE active materials have not been elucidated yet: latterly, the role of low-frequency vibrational dynamics in prototypical molecules as the tetraphenylehtylene has been considered a main focus.[128]

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[126] Shustova N.B., McCarthy B.D., Dincă M., *J. Am. Chem. Soc*, **2011**, *133*, 20126.

[127] Shustova N.B., Cozzolino A.F., Dincă M., *J. Am. Chem. Soc*, **2012**, *134*, 19596.

[128] Shustova N.B., Ong T.C., Cozzolino A.F., Michaelis V. K., Griffin R. G., Dincă M., *J. Am. Chem. Soc.*, **2012**, *134*, 15061.

TPEP-H$_8$

Figure 5.18: a tetraphenylethylene derivative employed in a MOF structure to obtain 'locked' conformations and enhanced luminescence as a consequence (see text for references).

5.5 An AIE effect from nanoparticles

Taking advantage of the intriguing photophysical properties of the family of persulfurated asterisks we decided to explore the potentials of these molecules as suitable materials for nanoparticle-based systems.[129]

In particular **A6-Mep** (figure 5.20), which shows six identical *p*-tolyl peripheral units and represents an isomer in respect of **A6-Me**, is used to prepare kinetically stable colloids in water exhibiting interesting photophysical properties.[130] As a method for the precipitation we experienced a simple reprecipitation method that involves the mix of two solvent — the first is a good solvent for the molecule, whilst the second is a non-solvent. The phenomenon is described as the *'Ouzo effect'*: one can create a dispersion of small droplets in a surrounding liquid phase, normally without using surfactants, dispersing agents or mechanical agitation.

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[129] The following sections take account of this work: Bergamini G., Fermi A., Botta C., Giovanella U., Di Motta S., Negri F., Peresutti R., Gingras M., Ceroni P., *J. Mat. Chem. C*, **2013**, *in press*.

[130] The compound has been sythetized and kindly delivered by Dr. Romain Peresutti, formerly part of prof. Gingras' group at CINaM, Marseilles, and used as received.

As a model, we can consider a ternary liquid system: when water is added to a solution made of a co-solvent and a solute, this could rapidly come out from the equilibrium and form a dispersion of nanoparticles. This event is better described by a three-component phase diagram, in figure 5.19: the formation of stable nanoparticles by a reprecipitation is achieved when solutions are rapidly brought from a one-phase region (i.e. a situation where one of the two main components predominate in weight in respect of the other) to a metastable region, by means of the addition of a non-solvent. Thus, in this condition, Gibbs free energy is not minimized, while nuclei can form spontaneously from small fluctuations of concentration of the solute.[131,132]

Figure 5.19: a three-component phase diagram which illustrates the miscibility-limit curve (*binodal*) and the stability-limit curve (*spinodal*) as a function of weight fraction of the solute and his solvent; the concentration of the third component is found by difference. The black area corresponds to concentrations in which the formation of nanoparticles is relatively stable.

During the past years this phenomenon has been exploited to study many

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[131] Vitale S.A., Katz J.L., *Langmuir*, **2003**, *19*, 4105.
[132] Ganachaud F., Katz J.L., *ChemPhysChem*, **2005**, *6*, 209.

nanoparticle-based systems,[133] while several strategies have been developed for constructing many organic nanostructures with different morphologies, crystallinities and properties (in optoelectronics,[134] luminescent materials,[135] etc.). Also, the physicochemical properties of these systems have been elucidated, such as thermodynamical aspects[136] and relaxation in photophysical processes.[137]

With this premise, we found a satisfactory procedure to prepare relatively

A6-Mep

Figure 5.20: the persulfurated molecular asterisk **A6-Mep** is used to obtain phosphorescent nanoparticles in H_2O.

stable nanoparticles from **A6-Mep**: in a typical experiment, a 0.18 mM solution of **A6-Mep** in THF is added (1.1 ml) under sonication to an aqueous solution (4.5 ml) containing poly(ethylene glycol)-methyl ether (PEGME, 10% w/w) as a stabilizer. A suspension is obtained – once the nanoparticles are developed the solution shows opacity – and readily diluted 1/20 in H_2O, showing an emission spectrum similar to the one reported for the solid **A6-Mep** (see figure 5.22). From dynamic light scattering (DLS) measurements the average diameter of the nanocrystals was estimated to

[133] Kasai H., Kamatani H., Okada S., Oikawa H., Matsuda H., Nakanishi H., *Jpn. J. Appl. Phys.*, **1996**, *35*, L221.

[134] Zhao Y. S., Fu H., Peng A., Ma Y., Xiao D., Yao J., *Adv. Mater.*, **2008**, *20*, 2859.

[135] An B. K., Kwon S. K., Park S. Y., *Angew. Chem. Int. Ed.*, **2007**, *46*, 1978.

[136] Jiang Q., Shi H. X., Zhao M., *J. Chem. Phys.*, **1999**, *111*, 2176.

[137] Chang C.-W., Bhongale C. J., Lee C. S., Huang W. K., Hsu C. S., *J. Chem. Phys. C*, **2012**, *116*, 15146.

100 nm with a very low polydispersity (PDI = 0.069, see figure 5.23). The suspension was stable and no significant change of the emission intensity was observed for ca. 4 hours. On the other hand, without PEGME, no stable suspension was obtained in water.

Figure 5.21: the persulfurated molecular asterisk **A6-Mep** showing phosphorescence from the solid phase, upon excitation in the UV region.

It is worth mentioning that with the presence of a polymer such as PEG (or more precisely PEGMe, in this case) the precipitation of solid **A6-Mep** is prevented, and kinetical mechanisms that move molecules to the formation of a stable colloid are involved. At the end of the experiment DLS analysis are carried out to evaluate the dimensions of the particles, while an approximation that takes account of the presence of multiple component in the colloidal suspension is needed. In fact, as stated above, during the preparation **A6-Mep** is in contact with two solvent, THF and water, in addition to a large presence of polymer. After the second step (i.e. the dilution in water), however, two components are considered as non influencing the DLS measurement: we can approximate under the 5% the total amount in mass coming from the residual THF and the polymer, condition that arguably does not affect so much the refractive index and the viscosity of the colloid. In any case, the solvent are not filtered before the preparation and the size distribution does not show any presence of impurity at larger hydrodynamic radii, as the only DLS signal is coming from **A6-Mep** nanoparticles.

A possible application that we considered is to employ this kind of materials

for photonics glasses or crystals: nevertheless, we did not found appropriate conditions to do that, since one of the more important property of these systems is the extremely low polydispersity (less than 2%) which is a basic requirement to build them.[138] In addition, to achieve photonic glasses or crystals the basic materials should have particular mechanical properties: for these reasons, in many occasions, such materials are coming from specific polymers as PMMA [poly(methylmetacrilate)] or PS (polystirene).

Figure 5.22: absorption (blue line) and phosphorescence spectra (red line, solid) for a suspension of NPs prepared from the persulfurated molecular asterisk **A6-Mep** by means of a reprecipitation method. The dashed red line refers to the phosphorescence recorded for the solid phase.

Concerning the photophysical properties, the NPs have been fully cha-racteri-zed as well: in general, they exhibit similar properties in respect of the solid phase, as already mentioned.

More specifically, absorption spectrum show the same characters of the molecule in solution, but a long tail is clearly visible until 700 nm, due to the Mie effect of light scattering from the particles. The phosphorescence spectrum taken on an aerated solution (instrumental conditions: λ_{ex}=300 nm, delay time=0.05 ms, gate time=1 ms) has a small red-shifted maxi-mum in respect of the solid phase emission, with a sensible broadening

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[138] García P. D., Sapienza R., López C., *Adv. Mater.*, **2010**, *22*, 12.

possibly due to the increased conjugation of the aromatic system within
the nanoparticle. On this point, one can speculate on which species of
luminophores in the particle and in which configuration they are, once
they display luminescence. Further investigations are needed for evaluate
these aspects. The emission's lifetime is recorded as mentioned on an
aerated solution, as the deaeration process (especially the pump-freeze-
thaw procedure) risks to change the morphology of the nanoparticles.
Photophysical data coming from the phosphorescence are collected in table
5.4.

A6-Mep	λ_{max} (nm)	τ_{ph} (μs)	Φ
solid	513	3.0	0.8
NPs	550	5.0	–

Table 5.4: comparison between the phosphorescence data from the solid phase
and nanoparticles from **A6-Mep**.

Figure 5.23: size distribution for a suspension of NPs prepared from the per-
sulfurated molecular asterisk **A6-Mep** by means of a reprecipitation method.
The green line refers to the cumulative frequency distribution of the size of the
nanoparticles.

5.6   Low temperature behavior of A6-Mep

The molecular asterisk **A6-Mep** displays emission only under experimental conditions where the dynamic conformational mobility of the tolylthio groups and rotation around the C-S bonds are restricted either by freezing the solvent or in the powder form. Hence, under these conditions, radiative processes are faster than non-radiative ones.

So, following the luminescence behavior in dependence of the temperature represents another intriguing aspect to better understand the properties of these materials and again, **A6-Mep** could be chosen as a prototype material.

In this regard, the OFF-ON luminescence of the molecule is rationalized with an investigation between 300 and 80 K, in a solvent mixture of DCM:CHCl$_3$ 1:1 – chosen for his good transparence as a glass at low temperatures.

In general, considering the temperature, the emission behavior can be divided in three regions. In the first, from 300 to 165 K, no emission coming from **A6-Mep** is observed; in the second, from 150 to 120 K, a weak emission band with maximum at 555 nm is recorded; in the third, from 110 to 80 K, a strong emission is present with the maximum at 515 nm, recalling the one from the solid phase. The first emission intensity change in the range 165-150 K can be attributed to the glass transition of the solvent.[139]

The OFF-ON luminescence of **A6-Mep** in solution upon decreasing temperature is quite peculiar compared to the usual behavior of phosphorescent organic molecules. For examples, benzophenone derivatives show a phosphorescence band in a rigid matrix at 77 K with a lifetime in the millisecond timescale, but they are phosphorescent also in deoxygenated fluid solution.[140]

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[139] DCM: T$_f$=176 K; MeOH: T$_f$=175-176 K
[140] Wrighton M., Morse D. L., *J. Am. Chem. Soc.*, **1974**, *96*, 998.

As reported in figure 5.24, at ca. 115 K an abrupt increase in the emission intensity (more than 30 times) is accompanied by a blue-shift of the emission maximum from 555 to 515 nm. The blue-shift of the emission maximum upon decreasing the temperature points toward a charge transfer (CT) character of the radiative transition. It is usually referred as *rigidochromic effect*, often observed for metal complexes with CT band.[141] Under these conditions, the solvent medium behaves as a rigid cage and intramolecular rotations are inhibited. In our case, the same restriction of rotation can occur in the solid state as a powder due to molecular packing and, to a less extent, in a quite rigid polymeric blend like PMMA.

Figure 5.24: changes in the emission intensities of **A6-Mep** (solid circles) and emission band maximum (solid squares) upon decreasing the temperature from 160 to 85 K. The process is reversible, as demonstrated by the emission intensity changes recorded upon increasing the temperature (red circles). λ_{ex}=325 nm.

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[141] (a) Barigelletti F., Belser P., Von Zelewski A, Juris A., Balzani V., *J. Phys. Chem.*, **1985**, *89*, 3680. (b) Barigelletti F., Juris A., Balzani V., Belser P., Von Zelewski A., *J. Phys. Chem.*, **1987**, *91*, 1095.

5.7   Application of A6-Mep in OLEDs

In order to take advantage of the phosphorescence properties of compound
A6-Mep, we prepared simple solution processable organic LEDs[142] by mix-
ing compound **A6-Mep** in polyvinylcarbazole (PVK), a polymer used very
often in organic light emitting diodes because of its good hole transporting
properties and its high triplet energy level,[143] and 2-(4-biphenylyl)-5-(4-
tert-butylphenyl)-1,3,4-oxadiazole (PBD), often used to improve charge
balance in devices based on PVK.[144]

Devices with the structure ITO/PEDOT/PVK:PBD:**A6-Mep**/Ba/Al dis-
play electroluminescence (EL) spectra peaked at 485 nm, corresponding
to the photoluminescence (PL) spectrum of the blend, forward external
quantum efficiency and luminous efficiency of 0.1% and 0.5 cd/A at 11V
respectively for PVK:PBD:**A6-Mep** at a relative mass concentration of
65:30:5. Interestingly, the EL spectrum recorded at the turn on voltage
(5V) of the devices shows a maximum at *ca.* 535 nm, shifting to 485 nm at
about 6-7 V. This weak emission could be associated to molecules dispersed
in the polymer matrix, while the main blue-shifted emission to microcrystals
having higher phosphorescence quantum efficiency at RT (figure 5.25).

The capabilities of the device are not outstanding since the LED archi-
tecture has not been optimized and the photoluminescence quantum yield
measured in the same blend is much lower (*ca.* 2%) than that measured for
A6-Mep in solid phase (80%). This is probably related to the low rigidity
of the environment and plausible competitive deactivation processes of the
emitting excited states in the blend.

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[142] Fabrication and characterization of **A6-Mep**-based OLEDs were performed by dr.
Chiara Botta and dr. Umberto Giovanella, CNR-ISMAC, Milan.

[143] Remmers M., Neher D., Gruner J., Friend R. H., Gelinck G. H., Barman J. M.,
Quattrocchi C., Dos Santos D. A., Bredas J.-L., *Macromolecules*, **1996**, *29*, 7432.

[144] Giovanella U., Botta C., Papagni A., Tubino R., Miozzo L., *Appl. Phys. Lett.*, **2005**,
87, 171910.

Figure 5.25: Normalized EL spectra of ITO/PEDOT/PVK:PBD:**A6-Mep**/Ba/Al device at different bias voltages.

5.7.1 Details

For LEDs compound **A6-Mep**, the polymer PVK and PBD were dissolved in tetrachloroethane at concentrations of 15 mg/ml. Indium tin oxide (ITO; 15 Ω per square) were used as substrates and cleaned by sonication in distilled water, acetone, and isopropanol. After treatment with nitrogen plasma, 50 nm of poly-(3,4- ethylenedioxythiophene)-poly(styrenesulfonic acid) (PEDOT:PSS) (Clevios P VP AI 4083, H.C. Starck) was spin-coated onto the ITO substrate, and then dried under nitrogen atmosphere at 100°C for 15 minutes.

A thin film (80-100 nm) of material was then spin-coated. A thin layer of Barium (5 nm) and subsequently 100 nm layers of Aluminium were deposited on the top by vacuum (10^{-7} mbar) thermoevaporation. All device preparation steps and characterization were performed inside a drybox system. Current-voltage (I-V) characteristics were recorded with a Keithley 2602 sourcemeter. Luminance of the device was measured with a calibrated photodiode. External quantum efficiency (EQE) in the forward direction was derived, by supposing a lambertian source behavior, according to the

method reported elsewhere.[145]

5.8   Computational studies on A6-Mep

Owing to the flexible degrees of freedom of the peripheral substituents,
the hexathio-benzene compounds are expected to exist in different con-
formations.[146]   For this reason, we explored a number of conformers of
A6-Mep featuring multiple orientations of the tolyl groups with respect
to the benzene core. A schematic representation of the lowest energy
conformers of **A6-Mep** are shown in figure 5.26 and compared to those
of 1,2,3,4,5,6-hexakis(methylthio)benzene, considering molecular surface
representations of their computed ground state equilibrium structures.

Figure 5.26: graphical representation, via molecular surface, of the lowest energy
conformers of **A6-Mep**, optimized at CAM-45 B3LYP/3-21G* level of theory.

Conformers of **A6-Mep** show evidence for the formation of a number
of CH-π interactions between adjacent tolyl groups. The computed lowest

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[145] Giovanella U., Betti P., Botta C., Destri S., Moreau J., Pasini M., Porzio W.,
Vercelli B., Bolognesi A., *Chem. Mater.*, **2011**, *23*, 810.

[146] Calculations and subsequent interpretations were completed in collaboration with
Dr. Simone Di Motta and Prof. Fabrizia Negri, Department of Chemistry, University
of Bologna.

energy structure is conformer B, featuring two CH-π interactions each involving two adjacent benzene rings sitting on the same side with respect to the plane of the benzene core.

The ground-state energy of the four conformers A, B, C and D are found within about 2 kcal/mol (CAM-B3LYP/3-21G*) or about 4 kcal/mol (CAM-B3LYP/6-31G*). Interestingly, the energy order of the A and B conformers is reversed for the methylated not displaying CH-π interactions in agreement with the results reported in the literature.[147] In this regard, we mention that the CAM-B3LYP functional provides energetic results comparable to more sophisticated MP2 calculations.[148]

5.8.1 Role of CH-π interactions: acting on excited states energy

Because of the large dimension of the compounds, we restricted the investigation of the potential energy surface of the lowest triplet to the UCAM-B3LYP level of theory. We validated the chosen level of theory (UCAM-B3LYP) on benzene by comparing the results with those of TD-CAM-B3LYP geometry optimization.

Two triplet structures were found for the A and B conformers of the methylated asterisk: these correspond to two triplet states of different nature. While the highest energy T2 state and less distorted structure is dominated by a charge transfer (CT) character, the lowest energy T1 state, displays a distorted structure and is dominated by the benzenic (BE) character, although the benzene-like orbitals extend also to the sulfur atoms. Unlike benzene, indeed, the triplet BE structure is notably distorted and its energy is remarkably lower than that of the CT structure. At the same time, the distorted BE structure is associated with a remarkable increase of the ground state energy which results in an inversion of the triplet and singlet states as shown schematically in figure 5.27.

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[147] Fleurat-Lessard P., Volatron F., *Chem. Phys. Lett.*, **2009**, *477*, 32.

[148] Mohan N., Vijayalakshmi K. P., Koga N., Cherumuttathu H. S., *J. Comput. Chem.*, **2010**, *31*, 2874.

Figure 5.27: Schematic sketch of the lowest triplet states T2 and T1 (red,blue, respectively) and ground state (black) potential energy curves of methylated benzene asterisk, showing the singlet-triplet crossing. In contrast, the lowest triplet state T1 (green) does not cross the singlet state for most conformers of **A6-Mep**, according to DFT calculations.

Based on these features of the potential energy surfaces of the methylated asterisk, it can be concluded that fast non-radiative deactivation of the triplet state is likely to occur for every isomer of this molecule, because the S0-T1 state crossing can be easily reached.

For the conformers of **A6-Mep** the situation turned out to be more complex and influenced by the presence of CH-π interactions. For conformers B, C and D, featuring more efficient CH-π interactions, the triplet state pattern is remarkably different. The triplet state structures determined by geometry optimization are all above the ground state and luminescence may be expected in this case. In particular, for conformer B, we identified two triplet states, similarly to the case of the hexakis(methylthio)benzene. The less stable structure (T2 state) is dominated by a CT character, while the more distorted and more stable structure (T1 state) retains a con-

tribution from the BE excitation. It is worth noting that the computed TD-CAM-B3LYP $T_2 \rightarrow S_0$ energy of B, C and D conformers at the CT triplet optimized geometries are compatible with the observed luminescence.

Interestingly, the BE triplet state T1 is still well above the ground state and therefore non-radiative deactivation to the ground state should be slowed down in this case possibly also due to an increased barrier between the two triplet states. The only conformer of **A6-Mep** not satisfying the above general pattern is conformer A, characterized by the weakest CH-π interactions because of the large distance between the CH bonds and the aromatic rings. In this case the lowest triplet state 60 potential energy surfaces resemble somewhat to that of M2 since of the two optimized triplet structures, displaying less marked energy difference, the most stable corresponds to an inversion between T1 and S0. Therefore, it can be expected that also in this case a fast non-radiative deactivation of the lowest triplet state can take place.

Interconversion from conformers B (the most dominant form at equilibrium), C or D to A (the only conformer displaying the S0-T1 crossing), is expected to result in fast non-radiative deactivation and can explain the absence of luminescence of 1 in 70 solution at 298 K. In contrast, conformer interconversion is expected to be restricted in a rigid matrix at 77 K and as a powder at room temperature. Since conformer interconversion occurs upon torsion around one or more S-C bonds, we estimated the barrier height for this process by performing a ground state potential energy scan upon rotation of one tolylthio group as shown in figure 5.28.

Since the C-S bond lengths in the triplet state are either similar or shorter than those of the ground state, the computed ground state barrier (ca. 6.5 kcal/mol) can be taken as a lower limit for the triplet state and used for the discussion of conformer interconversion in the triplet state during the triplet state lifetime. On the other hand, from the experimental triplet lifetime in rigid matrix at 77 K or in powder at 298 K we can extract

Figure 5.28: CAM-B3LYP/3-21G* ground state potential energy scan starting from the A conformer of **A6-Mep** and rotating the purple tolylthio group as shown in the figure.

the limiting barrier height Ea that can be overcome via k=1/τ= KBT/h exp(-Ea/KBT) and compare it with the computed barrier in the gas phase. The limiting barrier results to be ca. 3.5 kcal at 77 K and ca. 9.9 kcal/mol as a powder at 298 K. Clearly, in frozen solution, the substituent rotation and equilibration of conformers during triplet state lifetime cannot occur. Similar considerations hold for the powder state since the barrier for tolylthio group rotation will be much larger than that computed in the gas phase. In summary, the pattern of CH-π interactions, active in **A6-Mep** and inactive in hexakis(methylthio)benzene and similarly in **B6-iPr**, reshapes the lowest triplet states of most conformers of **A6-Mep**, and by making inaccessible the S0-T1 state crossing drives different luminescence properties.

While more sophisticated computational investigations would be required to draw more quantitative conclusions, we believe that the qualitative picture emerging from this study provides a reasonable explanation for the observed luminescence properties of dendrimers **A6-Mep** and **B6-iPr**.

5.9   Perspectives

As stated above, the family of molecules that we have developed discloses
more or less the same photophysical properties, showing a *rigidochromic
effect* in most cases which get to a radiative deactivation of the triplet
excited state.

As a perspective, it is nevertheless desirable to design a series of molecules in
which these properties could come out in solution, exploiting the intriguing
characteristics of the persulfurated benzenes. Will it be possible to find
out a persulfurated asterisk hindered and rigid enough to prevent the
non-radiative deactivation of excited states?

In addition, we can directly take advantage of the hexasubstituted benzene
structure to develop a series of compound which could join the fascinating
properties of a phosphorescent unit and a ligand-like behavior: that is the
way we found out with the polysulfurated compounds presented in the
following chapters.

Chapter 6

A terpyridine-based asterisk

After the vast analysis of luminescence properties of the basic asterisks we can now illustrate the behavior of an implemented persulfurated-cored molecule (**A6-Tpy**) that contains suitable external units to perform metal coordination. At first, to get this compound it is necessary to choose a proper moiety: the 2,6-bis(2-pyridyl)pyridine (terpyridine or *terpy*) is a well known ligand for many metal ions and many studies over the years demonstrated its quality in supramolecular recognition systems. In addition, terpy-based complexes show in solution very high complexation constant towards most of the transition metals.[149,150]

The total number of works in the last 30 years concerning terpyridines has had a rapid increase, with a trend that is predicted to continue, since these molecule represents a crucial structural component in metal-based supramolecular architectures.[151,152,153] Free terpyridines derivatives and terpyridine-based complexes can found interest in many fields of chemistry,[154] for example in photochemistry for application as luminescent

[149] Morgan G., Burstall F. H., *J. Chem. Soc.*, **1937**, 1649.

[150] Behrens H., Anders V., *Z. Naturf.*, **1964**, *19b*, 767.

[151] Schubert U. L., Hofmeier H., Newkome G. R., *''Modern terpyridine chemistry''*, Wiley-VCH, Weinheim, **2006**.

[152] Cargill Thompson A. M. W., *Coord. Chem. Rev.*, **1997**, *160*, 1.

[153] Constable E. C., *Chem. Soc. Rev.*, **2007**, *36*, 246.

[154] Wild A., Winter A., Schlütter F., Schubert U. S., *Chem. Soc. Rev.*, **2011**, *40*, 1459.

devices[155], as photosensitizers,[156,157] or in metal-based dendrimers.[158]

From a synthetic point of view, the **A6-Tpy** asterisk (figure 6.1) is achievable with a 3-step route, after a substitution of a hexachlorobenzene by a suitable tolyl-terpyridyl-thiol, similarly to the basic synthesis of asterisks reported in figure 5.1.

We will illustrate in this chapter at first the synthetic procedure to get the peripheral unit and its photophysical characterization; then we will illustrate the synthesis of the entire **A6-Tpy** asterisk with its photophysical properties and coordination capabilities.

A6-Tpy

Figure 6.1: a molecular asterisk with 6 terpyridine moieties appended, **A6-Tpy**.

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[155] Harriman A., Ziessel R., *Coord. Chem. Rev.*, **1998**, *171*, 331.

[156] O'Regan B., Grätzel M., *Nature*, **1991**, *353*, 737.

[157] Sauvage J. P., Chambron J. C., Guillerez S., Coudret C., Balzani V., Barigelletti F., De Cola L., Flamigni L., Guillerez S., *Chem. Rev.*, **1994**, *94*, 993.

[158] Newkome G. R., He E., Moorefield C. N., *Chem. Rev.*, **1999**, *99*, 1689.

6.1 Synthesis of the terpy-based ligand

The tolyl-terpyridine acts as the proper subunit to build the external periphery of the **A6-Tpy** asterisk; the synthetic path to achieve this class of molecules has already made clear in many works.[159,160] Essentially, it represents a variation to the route proposed by Kröhnke,[161] in which 2 equivalents of 2-acetylpyridine can act as nucleophiles in basic media: the generated enolate can attack stepwise an electrophile such as a substituted aromatic aldehyde with a typical Michael addition and afford a dipyridyl-1,5-diketone. This intermediate can undergo oxydation, while the consequent ring closure brings to the symmetric terpyridine skeleton. In figure 6.2 the general synthetic scheme is reported.

Figure 6.2: generic scheme for the synthesis of 4'-arylterpyridines: the key intermediate passes through the formation of a dipyridyl-dione.

In our case the desired **Tpy-SMe** ligand (figure 6.3) is afforded (also at gram scale) with an optimized and modified protocol,[162] involving 2-acetylpyridine and 4-(methylthio)benzaldehyde in a one-pot reaction: we

[159] Potts K. T., *Bull. Soc. Chim. Belg.*, **1990**, *99*, 741.

[160] Fallahpour R.-A., *Synthesis*, **2003**, *2*, 155.

[161] Kröhnke F., *Synthesis*, **1976**, *1*, 1.

[162] Tuccitto N., Torrisi V., Cavazzini M., Morotti T., Puntoriero F., Quici S., Campagna S., Licciardello A., *ChemPhysChem*, **2007**, *8*, 227.

Tpy-SMe

Figure 6.3: the **Tpy-SMe** ligand represents a proper synthetic intermediate in the synthesis of **A6-Tpy**.

can obtain the final product at good purity level after repeated crystalliza-tions with a yield of 45%.

Tpy-SMe is a pale yellow, needle-like crystalline solid, very well soluble in DCM and CHCl$_3$. The product is characterized by standard ^{1}H and ^{13}C NMR and LR-MS, giving evidence of the correct molecular structure. As a corroboration a reversed-phase HPLC analysis has been completed, giving the chromatogram in figure 6.4.[163]

Figure 6.4: reversed-phase HPLC chromatogram on a sample of the isolated **Tpy-SMe**.

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[163] Analysis have been kindly performed by Dr. Guy Félix at CINaM, Marseilles. Conditions: Chromatorex C18 column, 15 cm, mobile phase CH$_3$CN/H$_2$O 80/20, UV detection 254 nm.

Although several studies employed this molecule, especially in surfaces' functionalisation,[164,165] not many metal complexes of **Tpy-SMe** have been isolated or characterized. Quite recently, a Ru^{II} complex has been prepared and structurally described; the structure of $[Ru(\textbf{Tpy-SMe})_2]^{2+}$ is ordinary, with central distances and orientation similar to the $[Ru(terpy)_2]^{2+}$ complex.[166]

6.1.1   Details

Reaction has been run in dry THF (thermally activated molecular sieves, 3Å) and reagents are used as received from Sigma-Aldrich, Alfa Aesar or TCI.

4'-[4-(methylthio)phenyl]-2,2';6',2''-terpyridine (Tpy-SMe). Acetylpyridine (7.67 g, 63.3 mmol, 2.1 eqv) was added dropwise into a suspension of tbutOK (11.19 g, 99.7 mmol, 3.3 eqv) in 150 ml of anhydrous THF. After 2 hrs under stirring at room temperature, 4-(methylthio)benzhaldehyde (4.58 g, 30.1 mmol, 1 eqv) is added dropwise in 5 minutes. The ruby red mixture obtained was stirred for the weekend; after this time a suspension of ammonium acetate (75.98 g, 990 mmol, 33 eqv) in 540 ml of ethanol was added, heating at reflux for 4.5 hrs. During this time a yellow-orange color developed; after cooling at room temperature, the solvent was dried to 1/3 of the starting volume to obtain pale yellow crystals, which were filtered on fritted glass and recrystallized twice in ethanol to afford 4.85 g of **Tpy-SMe** (13.7 mmol, 45%); mp: 173-175° C.

^{1}H NMR (250 MHz, CDCl$_3$): δ= 2.55 [s, 3H; SCH$_3$], 7.35 [bdd, J (H,H)= 7.3 Hz, 4.9 Hz, 2H; tpySCH$_3$ (5,5^{II})], 7.38 [d, J (H,H)= 8.5 Hz, 2H; Ph(3,5)], 7.86 [d, J (H,H)= 8.7 Hz, 2H; Ph(2,6)], 7.88 [ddd, J (H,H)=7.9 Hz, 1.7 Hz, 2H; tpySCH$_3$(4,4^{II})], 8.67 [d, J (H,H)= 8.0 Hz, 2H; tpySCH$_3$ (3,3^{II})], 8.73

[164] Auditore A., Tuccitto N., Marzanni G., Quici S., Puntoriero F., Campagna S., Licciardello A., *Chem. Comm.*, **2003**, *0*, 2494.

[165] Kosbar L., Srinivasan C., Afzali A., Graham T., Copel M., Krusin-Elbaum L., *Langmuir*, **2006**, *22*, 7631.

[166] Constable E. C., Housecroft C. E.., Medlycott E., Neuburger M., Reinders F., Reymann S., Schaffner S., *Inorg. Chem. Comm.*, **2008**, *11*, 518.

[s, 2H; tpySCH$_3$ ($3^I,5^I$)], 8.74 [bd, J (H,H)= 5.0 Hz, 2H; tpySCH$_3$ ($6,6^{II}$)].
^{13}C NMR (63 MHz, CDCl$_3$): δ= 15.5 [CH$_3$], 118.3 [CH; tpySCH$_3$ ($3^I,5^I$)],
121.3 [CH; tpySCH$_3$ ($3,3^{II}$)], 123.8 [CH; tpySCH$_3$ ($5,5^{II}$)], 126.5 [CH;
Ph(3,5)], 127.6 [CH; Ph(2,6), tpy ($5,5^{II}$)], 134.9 (C), 136.8 [CH; tpySCH$_3$
($4,4^{II}$)], 140.0 (C), 149.1 [CH; tpySCH$_3$ ($6,6^{II}$)], 149.5 (C), 155.9 (C), 156.2
(C).

Low resolution MS: ESI (positive, ammonium acetate), C$_{22}$H$_{17}$N$_3$S, [M+H]+,
m/z 356.2 (calcd. 355.4), figure 6.5.

Figure 6.5: LR-MS spectrum of **A6-Tpy** in ESI mode. The product is detected
at 356.2 Da.

6.2   Terpy-based ligands: photophysics

Photophysical characterization has been completed for the pure **Tpy-SMe**,
carrying out analysis in DCM and THF. In both solvents the compound
shows a good stability and no decomposition is evidenced even after several
hours of UV sources exposure.

The absorption spectrum shows a main broad band with a maximum around
300 nm; as it occurs in several similar *p*-substituted 4'-arylterpyrdines,
the lowest energy absorption band rises from the combination of a typical
π_{tpy}-π^*_{tpy} transition and a intramolecular charge transfer (ICT) between the
phenyl-centered MO (π_{ph}) and the former π^*_{tpy}. In fact, it was demonstrated
that the π_{ph} molecular orbital can rise in energy to work as a HOMO in

presence of particular *p*-substituents on the phenyl ring. On the other hand, energy levels of π_{ph} and π^*_{tpy} do not undergo significant changes.[167] In addition, in the case of **Tpy-SMe**, no notable variations in absorption are coming by changing to THF as a solvent.

Figure 6.6: absorption (blue line) and emission (red line, solid) of **Tpy-SMe** in DCM at 298 K. Emission of the solid phase is reported for comparison (dashed red line). λ_{ex}=295 nm.

Emission spectrum shows an unstructured band with a maximum centered around 390 nm, with a τ_{em} related to the deactivation of a singlet excited state; quantum yield has been determined around 0.3 in DCM solutions, while the value is larger in THF (see table 6.1). Emission spectrum has been recorded from the solid phase, too: emission maximum is red-shifted, probably in consequence of intermolecular coupling of electronic transition dipole moments (figure 6.6).

In order to get a comparison, the compound **Tpy-tol** (figure 6.7) has been characterized in DCM;[168] data are collected also in table 6.1.

It is evidenced that the presence of the -SCH$_3$ shifts the emission maximum of circa 50 nm to the red, setting a violet emission for **Tpy-SMe**, while

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[167] Mutai T., Cheon J. D., Arita S., Araki K., *J. Chem. Soc., Perkin Trans. 2*, **2001**, 1045.

[168] Dr. Jennifer K. Molloy and Dr. Maria Elena Gallina are acknowledged for absorption and emission experiments on **Tpy-tol**.

absorption spectra do not show peculiar differences in terms of molar extinction coefficient. This is coherent with the observed emission properties of similar compounds with -NH$_2$ and -NMe$_2$ substituents, with large color shifts in respect of **Tpy-tol**.

Figure 6.7: formula of the **Tpy-tol** compound (left) and comparison between its absorption and emission spectra (blue lines) and those of **Tpy-SMe** (red lines).

Solvent	Absorption		Emission		
	λ (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	τ (ns)	Φ
Tpy-SMe (DCM)	299	33700	386	1.4	0.33
Tpy-SMe (THF)	297	36900	388	1.4	0.52
Tpy-tol (DCM)	297	35600	340	1.7	0.14

Table 6.1: photophysical data related to **Tpy-SMe** and **Tpy-tol** in DCM and THF deaerated solutions.

6.2.1   Terpy ligands *vs.* metals

Coordination chemistry of terpyridine and derivatives *versus* transition metal ions has already been studied in many works over the years, both

from the thermodynamical and kinetics point of view.[169,170] Nevertheless, specific analysis on the interaction of Fe^{II} and Zn^{II} *vs.* **Tpy-SMe** has never been completed yet.

In principle, concerning the free terpyridine ligand, complexes take advantage of a greater chelate effect in respect of the pyridine and 2,2'-bipyridine; in addition, iron(II) complexes bear higher equilibrium constant and lower kinetic lability relatively to the zinc analogues. In the case of Fe^{II} the global[171] thermodynamic constant involved in the formation of $[Fe(terpy)_2]^{2+}$, log β, are very high as expected. This is the case as well for Ni^{II} and Co^{II}, where log β are around 20. On the other hand, zinc ion represents a weaker binding agent (log $\beta \approx 11.9$, unpublished results[172]) although the coordination geometry is a distorted octahedron, common scheme for all the $[M(terpy)_2]^{2+}$ complexes.

By means of a titration in DCM between **Tpy-SMe** and Zn^{II} (standard additions of the metal as the triflate salt, dissolved in MeCN) we can determine the ligand:metal coordination ratio following variations in absorption spectra. In figure 6.8 a new absorption band appears with a maximum at *ca.* 375 nm: in the presence of Zn^{II} complex we can indeed observe a high red-shift in the lowest energy electronic transition and the appearance of a sharp band at lower wavelengths corresponding to the ligand centered (LC) π_{tpy}-π^*_{tpy} transition. Hence, the positive charge on the metal ion seems to affect notably the absorption spectrum of the complex.[173]

Further differences appear analyzing the emission, of course: fluorescence coming from the free ligand is remarkably shifted of *ca.* 100 nm, giving rise

[169] Holyer R. H., Hubbard C. D., Kettle S. F. A., Wilkins R. G., *Inorg. Chem.*, **1966**, *5*, 622.

[170] Kim K. Y., Nancollas G. H, *J. Phys. Chem.*, **1977**, *81*, 948.

[171] In the generic equilibria M + L ⇌ ML and ML + L ⇌ ML$_2$ between a metal ion M and a ligand L, the stepwise equilibrium constants are K_1 and K_2, respectively. We can define the *global* constant β_{1-2} as $\beta_{1-2} = K_1 K_2$

[172] Andres P. R., PhD thesis, Eindhoven University of Technology (Eindhoven), **2004**.

[173] Goodall W., Gareth-Williams J. A., *Chem. Commun.*, **2001**, *11*, 2514.

to a broadened new blue-green emission with a maximum around 500 nm (figure 6.9). Since the first one is completely quenched after the addition of 0.5 eqv of Zn^{II}, we can state again that the coordination ratio is still 2:1. On the other hand, emission coming from the complex does not show any plateau at the maximum, probably in consequence of the collateral equilibrium of formation of the 1:1 complex; it is therefore quite difficult to determine precisely the quantum yield of the complex, estimated around 0.14 in DCM.

Figure 6.8: left: changes in absorption spectra upon titration of a **Tpy-SMe** solution in DCM with a MeCN solution of $Zn(CF_3SO_3)_2$ at 298 K; blue line: original solution of **Tpy-SMe**; red line: end of the titration (ca. 1.1 eqv. $Zn(CF_3SO_3)_2$). Right: absorption profile at 299 nm.

Coordination of Fe^{II} has been taken into account, too: spectral changes in absorption (figure 6.10) show the rising of a typical MLCT band centered at 575 nm as the lowest energy transition of the complex, bearing to a purple colored solution.[174] In respect to the case of the coordination of Zn^{II}, Fe^{II} shows a better kinetic stability, with a clear plateau coming after the addition of 0.5 eqv of metal ion. In this case the MLCT state is not emissive and emission results completely quenched both for the free ligand and the complex.

Due to the presence of the lone pair on nitrogen atoms, terpyridine derivatives can also act as bases of course: absorption and emission titration

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[174] Constable E. C., Ward M. D., Corr S., *Inorg. Chim. Acta*, **1988**, *141*, 201.

Figure 6.9: left: changes in emission spectra upon titration of a **Tpy-SMe** solution in DCM with a MeCN solution of $Zn(CF_3SO_3)_2$ at 298 K; blue line: original solution of **Tpy-SMe**; red line: end of the titration; λ_{ex}=326 nm. Right: emission profiles at 390 nm (blue dots) and 495 nm (red dots).

have been taken upon the addition of CF_3SO_3H. Spectral changes in absorption (figure 6.11) show the presence of two families of isosbestic points, giving indication of the presence of multiple protonation equilibria.[175] Interestingly, both the first and the second protonation are evidenced, with the clear formation of **Tpy-SMe**H_2^{2+} after the addition of 2 eqv of H^+.

Spectral changes in emission (figure 6.12) give useful information, too: at first we can observe the quenching of the original emission of **Tpy-SMe**, which drops down completely after the addition of 1 eqv of H^+; the monoprotonated species shows a weaker emission, with a maximum around 510 nm. This one is once again quenched by the addition of the second equivalent of H^+, with the formation of the diprotonated species which emits very weakly with a broad fluorescence centered at 580 nm.

For comparison purposes, the coordination of Zn^{II} has been analyzed in THF, too: spectral changes (see figure 6.13) do not show significant differences in respect of the case of DCM and coordination ratio is still determined as 2:1. Absorption spectra of the complex show once again a main transition sensibly red-shifted from the original absorption of **Tpy-**

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[175] Albano G., Balzani V., Constable E. C., Maestri M., Smith D. R., *Inorg. Chim. Acta*, **1998**, *277*, 225.

Figure 6.10: left: changes in absorption spectra upon titration of a **Tpy-SMe** solution in DCM with a MeCN solution of Fe(CF$_3$SO$_3$)$_2$ at 298 K; blue line: original solution of **Tpy-SMe**; red line: end of the titration. Right: absorption profiles at 298 nm (blue dots) and 576 nm (red dots).

SMe and a LC transition around 280 nm, coherent with the already mentioned terpyridine-based complexes.

In table 6.2 absorption and emission data taken from THF solution are gathered. In general, we can state that Zn^{II} complex with **Tpy-SMe** displays red-shifted spectra both in absorption and fluorescence, while the emission quantum yield is lowered of a factor 2 *circa* compared to the free ligand in the same solvent.

Compound	Absorption		Emission		
	λ (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	τ (ns)	Φ
Tpy-SMe	297	35600	388	1.4	0.52
[Zn(Tpy-SMe)$_2$]$^{2+}$	346	26600	498	1.1 - 3.4	0.25

Table 6.2: photophysical data comparison between **Tpy-SMe** and [Zn(**Tpy-SMe**)$_2$]$^{2+}$ in THF deaerated solutions.

Figure 6.11: left: changes in absorption spectra upon titration of a **Tpy-SMe** solution in DCM with a MeCN solution of CF_3SO_3H at 298 K; blue line: original solution of **Tpy-SMe**; red line: end of the titration. Right: absorption profiles at 410 nm (blue dots) and 295 nm (red dots).

6.3 Smaller ligands: attempts

In order to investigate different properties and to explore a new class of dendrimers based on polysulfurated cores, a series of dendrons have been designed, considering the terpyridine motif as the essential unit. At first, **Tpy-SMe** was chosen to get a phenyl unit between the terpy moiety and the sulfurated core: however, it would be intriguing to synthesize dendrons which do not exhibit the intermediate aromatic unit such as **atpy-SMe** and, of course, the second generation dendron **Tpy2-SMe**, starting from **Tpy-SMe** itself (see figure 6.14 and section 6.4).

The synthetic approach to achieve **aTpy-SMe** is already known and reactions are quite different to the already explored in figure 6.2.[176,177] The ideal route is a 2-step procedure which passes through the isolation of a dithioacetal, since the one-pot synthesis was attempted but did not give any significant result.[178] The reaction scheme is reported in figure 6.15 and 6.16.

[176] Potts K. T., Usifer D. A., Guadalupe A., Abruna H. D., *J. Am. Chem. Soc.*, **1987**, *109*, 3961.

[177] Potts K. T., Cipullo M. J., Ralli P., Theodoridis G., *J. Org. Chem.*, **1982**, *47*, 3027.

[178] Potts K. T., Ralli P. A., Theodoridis G., Winslow P., *Org. Synth.*, **1990**, *7*, 476.

Figure 6.12: left: changes in emission spectra upon titration of a **Tpy-SMe** solution in DCM with a MeCN solution of CF_3SO_3H at 298 K; blue line: original solution of **Tpy-SMe**; red line: end of the titration. Right: emission profiles at 382 nm (blue dots) and 510 nm (red dots).

Similarly to the reaction to provide **Tpy-SMe**, 2-acetylpyridine can act as nucleophile in basic conditions and attack carbon disulfide; in the presence of iodomethane we can form quite easily the **Py-SMe2** intermediate.

The molecule can react as an electrophile with another equivalent of 2-acetylpyridine, building the terpyridine skeleton with the sulfide unit appended (figure 6.16). The reaction can work quite easily on multigram scale to get **aTpy-SMe** (see section 6.3.1 for details).

However, the corresponding thiol, **aTpy-SH**, has not been achieved with the usual condition: ^{1}H NMR gives evidence of the occurrence of the reaction, but no purification was completed with good results. It seems that the oxidation of the *in situ* generated thiolate is extremely rapid and easy, so a relative good quantity of disulphur is afforded. Many degassing methods were tried during the reaction and the following work-up (Argon purging, pump/freeze/thaw cycles, etc.) but no significant improvement was noticed in terms of purity of the product at the end of the reaction (see figure 6.17).

In general, access to thioether derivatives should be analogous to the

Figure 6.13: left: changes in emission spectra upon titration of a **Terpy-SMe** solution in THF with a MeCN solution of $Zn(CF_3SO_3)_2$ at 298 K; blue line: original solution of **Terpy-SMe**; red line: end of the titration. Right: absorption profiles at 348 nm (blue dots) and 299 nm (red dots).

ether analogues[179] and rely either upon the reaction of an alkanethiol with a 4'-halo-2,2':6',2''-terpyridine or of a haloalkane with 2,2':6',2''-terpyridine-4'(1'H)-thione (tautomeric form of **aTpy-SH**). This last procedure has been quite recently reported[180] but the key intermediate is quite laborious to isolate. Of course, such derivatives could found once again application in the formation of metal complexes (with Fe^{II} and Co^{II}, for example).[181]

6.3.1 Details

3,3-Bis(methylthio)-1-(2-pyridinyl)-2-propen-1-one (py-SMe2). An o-ven-dried round-bottom flask was charged with dried tbutOK (6.50 g, 58 mmol, 2.15 eqv) and anhydrous THF (200 ml) under argon atmosphere; the mixture is stirred at RT, then 2-acetylpyridine was added dropwise (3 ml, 26.8 mmol, 1 eqv), while the suspension takes a bright yellow colour. After 5 minutes, CS_2 (1.7 ml, 28.1 mmol, 1.05 eqv) is also added dropwise

[179] Andres P. R., Hofmeier H., Lohmeijer B. G. G., Schubert U. S., *Synthesis*, **2003**, *18*, 2865.

[180] Schubert U. S., Eschbaumer C., Hien O., Andres P. R., *Tetrahedron Lett.*, **2001**, *42*, 4705.

[181] Andres P. R., Schubert U. S., *Synthesis*, **2004**, *8*, 1229.

Figure 6.14: aTpy-SMe and **Tpy2-SMe** represent two interesting terpy-based dendrons.

Figure 6.15: synthesis of the **py-SMe2** intermediate.

over a period of 5-10 minutes. To the resulting orange mixture CH_3I (3.3 ml, 53 mmol, 2 eqv) was added over 10 minutes; the mixture is stirred at RT for 15 h, while the suspension takes a yellow/ brown colour. After this time, the reaction is quenched in ice-water suspension (600 ml) and allowed to stand for 4-5 h. The resulting yellow solid is filtered and air-dried; the crude product is recrystallized from ethanol, giving 2.90 g (48%) of yellow crystals. Mp: 110-113°C.

^{1}H NMR (250 MHz, $CDCl_3$): δ= 2.55 [s, 3 H], 2.63 [s, 3 H], 7.38 [d of d of d, 1 H, J = 1.3, 6.0, 7.5], 7.64 [s, 1 H], 7.81 [d of t, 1 H, J = 7.8, 1.7], 8.16 [d of t, 1 H, J = 1.1, 7.9], 8.62 [d of m, 1 H J= 7.3].

^{13}C NMR (63 MHz, $CDCl_3$): δ = 15.0, 17.4, 108.9, 122.6, 125.8, 136.9, 148.4, 155.0, 167.6, 184.3.

4'-(Methylthio)-2,2':6',2''-terpyridine (aTpy-SMe). A two-necked oven-dried round-bottom flask was charged with dried tbutOK (5.56 g,

Figure 6.16: synthetic procedure to achieve **aTpy-SMe** from the dithioacetal intermediate (details in the text).

Figure 6.17: synthetic methodology to achieve **aTpy-SH** starting from the **aTpy-SMe** sulfide.

50 mmol, 2.2 eqv), 3,3-bis(methylthio)-1-(2-pyridinyl)-2-propen-1-one (**py-SMe2**, 4.94 g, 22 mmol, 1 eqv) and anhydrous THF (120 ml) in argon atmosphere. Then 2-acetylpyridine was added dropwise (2.7 ml, 24.1 mmol, 1.1 eqv), while the suspension takes a dark red colour; the mixture is stirred for 15 h at RT. After this time, ammonium acetate (21.5 g, 0.24 mol, 11 eqv) is added with 60 ml of glacial acetic acid, heating at 75° C and evaporating residual THF to 1/4 of initial volume (circa 4 h). The resulting black mixture is allowed to chill at RT, quenched with 800 ml of ice/water and allowed to stand at 5° C for 2.5 days. Dark grey crystals are separated on fritted glass; the product is purified by repetitive water precipitations from hot ethanol to give 2.80 g (46%) of gray crystals. Mp: 119-120° C.
^{1}H NMR (250 MHz, CDCl$_3$): δ= 2.66 [s, 3 H], 7.33 [d of d of d, 2 H, J = 1.2, 4.8, 8.5], 7.80 [d of t, 2H, J = 1.8, 7.6], 8.33 [s, 2 H], 8.60–8.71 [m, 4 H].
^{13}C NMR (63 MHz, CDCl$_3$): δ= 13.9, 116.9, 121.3, 123.8, 136.7, 149.0, 152.4, 154.8, 155.9.

6.4   Second generation ligands: attempts

To achieve the second generation dendron **Tpy2-SMe** the first step is represented by the formation of the thiol **Tpy-SH** starting from **Tpy-SMe**, as reported in the scheme in figure 6.18. Following a quite know

Figure 6.18: synthesis of the **Tpy-SH** thiol starting from the corresponding methyl sulfide (references and detail in the text).

strategy,[182] many conditions for the synthesis of the deprotected **Tpy-SH** thiol have been performed: among them, the preferable is described in table 6.3 (tbutSH 5 eqv, DMF, 160° C), also at gram scale, with yields from 80 to 93%.

The thiol **Tpy-SH** has been characterized with ^{1}H and ^{13}C NMR spectroscopy and with FT-IR spectroscopy (-SH function gives often a weak absorption, while the one for –SCH$_3$ is never evident and has no practical significance).

The most evident problems with the reaction to afford **Tpy-SH** were the choice of a suitable base to generate the thiolate *in situ* and its purification. Bases like NaH in oil dispersion are unsuitable, since the thiol is not easily purifiable by means of chromatography (as most of the terpy-based compounds) nor a recrystallization in a proper solvent, due to the probable generation of the corresponding disulfur with dioxygen at high temperatures.

The same product is achievable after optimization of the reaction in ex-

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[182] Pinchart A., Dallaire C., Van Bierbeek A., Gingras M., *Tetrahedron Lett.*, **1999**, *40*, 5479.

cellent yields (see table 6.3) also on multi gram scale: 1.5 eqv of tbuSH
and 2 eqv of *t*butOK in DMF at 160° C for 6 hours gives 2 with 90% yield.
The product is a pale yellow solid, no longer sensible to oxygen in the solid
phase and therefore easily to handle during reactions; nevertheless, it is a
strong requirement to carry out reactions in inert atmosphere (i.e. argon
purged flasks) to avoid oxidation in solution phase.

Substrate	Reagents	Conditions	Yield
Tpy-SMe	• *t*butSH (5 eqv), NaH (7 eqv)	DMF, 160°C, 15 h	–
	• *t*butSH (5 eqv), *t*butOK (7.5 eqv)	DMF, 160°C, 15 h	93%
	• *t*butSH (5 eqv), *t*butOK (7 eqv)	DMF, 160°C, 18 h	87%
	• *t*butSH (2.5 eqv), *t*butOK (3 eqv)	DMF, 160°C, 18 h	80%
	• *t*butSH (1.5 eqv), *t*butOK (2 eqv)	DMF, 160°C, 6 h	90%

Table 6.3: attempts for the reaction to afford **Tpy-SH** (see figure 6.18).

The reaction to afford **Tpy2-SMe** has been therefore tested, following
scheme in figure 6.19 and referring to a already known procedure.[183]
Unfortunately, all the attempts to achieve **Tpy2-SMe** were unsuccessful
as the product was not isolated in good quantities. Also, an alternative
route testing different electrophilicity using **thb** (trihalogenobenzenes) was
tried, giving more or less the same results. Attempts using both **dhb** and
thb are resumed in table 6.4.

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[183] Pinchart A., Dallaire C., Gingras M., *Tetrahedron Lett.*, **1998**, *39*, 543.

Figure 6.19: synthetic procedure to afford the second generation dendron **Tpy2-SMe** from the **Tpy-SH** thiol. Similarly, trihalogenobenzenes (**thb**) have been chosen as an alternative to **dhb**.

Reactions are usually monitored by TLC of by LR-MS (direct injection of samples): we have no evidence of the formation of the disubstituted product by using **thb**, while using **dhb** the major by-product corresponds to **Tpy-SMe** itself, due to the back transthioetherification with the substrate. In addition, there is evidence that substitution is quite slow and not encouraged since times of reaction appear to be long and in some cases we can observe the monosubstitution on the **thb** substrate.

In summary, we can state that this kind of reaction can not take place in the usual conditions: sometimes for similar reactions the use of a metal catalyst as Pd^0 or Cu^I is recommended to ensure good yields.[184,185] Possibly, the presence of the chelating tepyridine units may cause the complexation of the catalyst, inhibiting its capabilities.

6.4.1   Details

4'-[4-(mercapto)phenyl]-2,2';6',2''-terpyridine (Tpy-SH). An oven-dried round-bottom flask fitted with a reflux-condenser was charged with

[184] Xu H. J., Zhao X. Y., Deng J., Fu Y., Feng Y. S., *Tetrahedron Lett.*, **2009**, *50*, 434.

[185] Migita T., Asami Y., Shiobara J., Kato Y., Kosugi M., *Bull. Chem. Soc. Jpn.*, **1980**, *53*, 1385.

Reaction	Reagents	Conditions	Product
Tpy-SMe + **dhb**	• **Tpy-SMe** (2.05 eqv), **X**=Br	DMF, 130°C, 16 h	*a*
	• **Tpy-SMe** (2.05 eqv), **X**=Br	DMF, 90→115°C, 4 d	*b*
	• **Tpy-SMe** (2.05 eqv), **X**=F	DMF, 100→120°C, 4 d	*b*
	• **Tpy-SMe** (2.05 eqv), **X**=F	DMF, 90→130°C, 7 d	*b*
Tpy-SMe + **thb**	• **Tpy-SMe** (2.0 eqv), **X**=Br	DMF, 100°C, 16 h	*c*
	• **Tpy-SMe** (2.0 eqv), **X**=Br	DMF, 100→150°C, 7 d	*c*
	• **Tpy-SMe** (2.1 eqv), **X**=Br	DMF, 100→140°C, 42 h	*d*
	• **Tpy-SMe** (2.05 eqv), **X**=Br	[Pd(P-Ph$_3$)$_4$] 5%, DMSO, 100°C, 6 d	*c*
	• **Tpy-SMe** (2.05 eqv), **X**=Br	DMI, 200°C, 42 h	*c*
	• **Tpy-SMe** (2.1 eqv), **X**=F	DMF, 50°C, 56 h	*e*
	• **Tpy-SMe** (2.05 eqv), **X**=F	DMF, RT, 20 h	*e*

Table 6.4: attempts for the reaction to afford **Tpy2-SMe** (see figure 6.19). Labels: *a*, formation of **Terpy-SMe**; *b*, **dhb** is not consumed during the reaction; *c*, mix of unidentified products; *d*, monosubstituted product; *e*, formation of the corresponding disulfur.

Tpy-SMe (500.2 mg, 1.41 mmol, 1 eqv) and *t*butOK (1109.5 mg, 9.89 mmol, 7 eqv); anhydrous DMF (10 ml) was added under an Ar flux through septum and the yellow mixture was stirred until complete dissolution. After

this time *t*but-SH (640 mg, 7.10 mmol, 5 eqv) was poured in through septum and the mixture heated at 160° C for 18 hrs, keeping argon fluxing during the reaction. After cooling at 5-8° C (ice bath), the red mixture was poured in a quasi-saturated ammonium chloride aqueous solution (100 ml) and a pale yellow solid precipitated. This one is filtered on fritted glass and washed 3 times with distilled water to give 2 (420.1 mg, 1.23 mmol, 87%) in a pale yellow powder; mp: 169-171° C.

^{1}H NMR (250 MHz, CDCl$_3$): δ=3.57 [s, ^{1}H; SH], 7.23 [ddd, J(H,H)= 6.0 Hz, 4.9 Hz, 1.1 Hz 2H; tpySH(5,5^{II})], 7.38 [d, J (H,H)= 8.4 Hz, 2H; Ph(3,5)], 7.77 [d, J (H,H)= 8.3 Hz, 2H; Ph(2,6)], 7.86 [dt, J (H,H)= 7.8 Hz, 1.7 Hz, 2H; tpySH (4,4^{II})], 8.65 [d, J(H,H)= 8.0 Hz, 2H; tpySH(3,3^{II})], 8.58 [s, 2H; tpySH(3^I,5^I)], 8.71 [bd, J (H,H)= 4.6 Hz, 2H; tpySH(6,6^{II})].

^{13}C NMR (63 MHz, CDCl$_3$): δ=118.4 [CH; tpySH(3^I,5^I)], 121.3 [CH; tpySH(3,3^{II})], 123.8 [CH; tpySH(5,5^{II})], 127.9 [CH; Ph(2,6)], 129.5 [CH; Ph(3,5)], 132.5 (C), 135.7 (C), 136.8 [CH; tpySCH$_3$(4,4^{II})], 149.1 [CH; tpySCH$_3$(6,6^{II})], 149.2 (C), 156.0 (C), 156.2 (C).

IR: -SH (2552.3 cm^{-1}, stretching, weak).

Low resolution MS: EI, m/z (rel. %): 308 (50.9%) [M-SH], 340 (20.6%) [M-H], 341 (100%) [M], 342 (26.6%) [M+H]+, 343 (7.7%) [M+2H]$^{2+}$.

6.5   Synthesis of terpy-based molecular asterisk

Once isolated **Tpy-SH** we can think to perform substitution on aromatic substrate as hexachlorobenzene to build up finally **A6-Tpy**, as shown in figure 6.20. As it happened for smaller asterisks in section 5.1, the thiol can act as a nucleophile on a perhalogenated substrate: the reaction can work in the same conditions (9 eqvs of **Tpy-SH** and cesium carbonate as a base) quite easily also using **Tpy-SH**, affording a yellow solid soluble in DCM, CHCl$_3$ and THF. NMR analysis, LR-MS and elemental analysis give confirmation of the isolation of the right product. However, we did not succeed to provide single crystals of the material, as in many solvent the solid precipitates as a powder after attempts to crystalize it.

Figure 6.20: synthetic methodology to afford **A6-Tpy**.

6.5.1 Details

1,2,3,4,5,6-hexakis((4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)thio)benzene (A6-Tpy). In a round bottom flask hexachlorobenzene (41.3 mg, 0.14 mmol, 1 eqv), 4'-[4-(mercapto)phenyl]-2,2';6',2''-terpyridine (**Tpy-SH**) (436.9 mg, 1.28 mmol, 9 eqv) and Cs_2CO_3 (588.2 mg, 1.80 mmol, 12 eqv) were placed and dried by means of a vacuum pump. Then, in anhydrous and inert conditions (argon atmosphere), DMI (5 ml) was poured in as a solvent; the mixture is stirred at 60° C for 4.5 days. After being cooled to RT, the suspension was poured in 1 M NaOH (20 ml). A bright yellow solid precipitated, which is separated by filtration and washed several times with H_2O. The solid is triturated in ethanol to afford 298 mg of product (95%). Mp: 394-397°C.

^{1}H NMR (250 MHz, $CDCl_3$): δ= 7.11 [d of d of d, 12H, J = 1.1, 4.8, 7.4], 7.19 [d, 12H, J = 8.4], 7.69 [dt, 12H, J = 1.8, 7.8], 7.73 [d, 12H, J = 8.4], 8.35 [d, 12H, J = 7.9], 8.45-8.48 [m, 12H], 8.48 [s, 12H].

^{13}C NMR (63 MHz, $CDCl_3$): δ = 118.3, 120.9, 123.3, 128.0, 128.8, 136.3, 136.6, 138.2, 148.1, 148.7, 148.9, 155.3, 155.8.

EA: calcd (%) for $C_{132}H_{84}N_{18}S_6$: C 74.97, H 4.00, N 11.92, S 9.10; found: C 73.15, H 4.03, N 11.60, S 8.97.

Low resolution MS: MALDI (DCTB matrix): calcd. 2113.5 Da, founded m/z 2136.6 [M-Na]$^+$ (figure 6.21).

Figure 6.21: MS of **A6-Tpy**, the sodium adduct is evidenced as the only species in the product of the reaction.

6.6   Photophysical characterization of A6-Tpy

In general, the free **A6-Tpy** ligand shows property similar to those of the smaller asterisks resumed in section 5.3: hence, the asterisk does not emit with appreciable intensities in solution phase (in THF the quantum yield is lower than 0.1%) but displays a interesting phosphorescence in solid phase (figure 6.22).

Figure 6.22: left: comparison between absorption spectra of **A6-Tpy** (solid line) and **Tpy-SMe** (short dashed line) in DCM at 298 K; the long dashed line represents the spectra of **Tpy-SMe** multiplied by 6. Right: emission spectra of the solid phase of **A6-Tpy** (red line) and **A6** (green line) at 298 K.

Absorption spectrum, as expected, exhibits the features of the two components of the molecule: the long tail from 350 to 450 nm is coherent with other absorption spectra of the smaller persulfurated asterisks, imputable once again to a CT transition (see figure 5.11), while at lower wavelengths the absorption of the π_{tpy}-π^*_{tpy} for the 6 terpyridine moieties is evidenced (figure 6.22, left).

However, we can consider as negligible the luminescence in solution in

Figure 6.23: emission spectra on a deaerated **A6-Tpy** solution in THF (blue, solid) at 298 K. Dashed blue line corresponds to the same solution irradiated at 340 nm for several minutes. Excitation spectra, red line (λ_{em}=385 nm) and green line (λ_{em}=470 nm).

any solvent (table 6.5): in figure 6.23 the emission of a deaerated solution is reported, showing not only the low intensities bus also a moderate photosensitivity to UV sources for the molecule in THF. Nevertheless, in this solvent the molecule is fully characterized with photophysical methods provided the preparation of fresh solutions for each experiment. On the other hand, the molecule in DCM shows a higher instability.

Considering excitation spectra, emission seems to come primarily from the terpyridyl moieties, even if the presence of a second emission with a maximum beyond 490 nm is evidenced.

Compound	Absorption		Emission		
	λ (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	τ	Φ
A6-Tpy (THF)	283	178200	372-482	1 ns	<0.001
A6-Mep (DCM)	326	19200	–	–	–
A6-Tpy (sol.)	–	–	550	1.7-11.6 µs	–
A6-Mep (sol.)	–	–	513	3.0 µs	0.8

Table 6.5: photophysical data comparison between **A6-Tpy** and the **A6-Mep** smaller asterisk, in solution (THF or DCM) and in solid phase.

In consequence of the presence of terpyridine moieties, it will be quite intriguing to investigate the behavior of **A6-Tpy** in solution in presence of the same metal ions considered for **Tpy-SMe**: could we rationalize the development of supramolecular systems involving **A6-Tpy**?

6.7   A6-Tpy: coordination properties *vs.* Fe^{II}

As expected, **A6-Tpy** displays interesting coordination properties towards metal ions as Fe^{II} and Zn^{II}.

The case of the coordination of Fe^{II} represents a classic example of chromogenic sensing (see figure 6.24): similarly to the case of the Fe^{II} complex with **Tpy-SMe**, coordination is accompanied by the typical rising of an MLCT band upon titration of the ligand, while the ligand centered transitions are red-shifted as usual. It is interesting to follow the changes in absorption: the coordination scheme results to be 1:3, because of the presence of 6 terpyridine units which can perform a 1:2 scheme to the Fe^{II} ion. As a result of the coordination, emission is not turned on of course – neither in solid phase – since the new MLCT coming from the complex is not emissive.

At this point, we can speculate on the real coordination scheme: probably,

Figure 6.24: left: changes in absorption spectra upon titration of a **A6-Tpy** solution in THF with a MeCN solution of $Fe(CF_3SO_3)_2$ at 298 K; blue line: original solution of **A6-Tpy**; red line: end of the titration. Right: absorption profiles at 575 nm (blue dots) and 299 nm (red dots).

the [Fe(**Tpy-SMe**)$_2$] units can work as bridges among the different **A6-Tpy**, anchoring the asterisk core. In addition, because of the intrinsic flexibility of the C-S-C bonds, the coordination could bring to a 3D pattern in the space giving rise to an extended supramolecular entity. A model is schematized in figure 6.25. It is probable that this coordination scheme is common to most of the metal ions able to establish strong equilibria towards **A6-Tpy**.

Cumulative thermodynamical association constant has been evaluated larger than 19 by means of Specfit, while it would be of interest a more precise analysis of this aspect making use of calorimetric methods.[186] Anyway, the value is comparable with that determined for free terpyridine in water.

Coordination of Fe^{II} represents therefore a prototypal situation in which **A6-Tpy** could act as the point of start to build supramolecular architectures.

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[186] Gampp H., Maeder M., Mayer C. J., Zuberbühler A., *Talanta*, **1985**, *32*, 257.

Figure 6.25: schematic 2D representation of the coordination pattern after the addition of 3 eqvs of M^{II} to **A6-Tpy**. Terpy units are evidenced in blue.

6.8   A6-Tpy: an AIE effect from Zn^{II} coordination

Coordination of Zn^{II} represents a peculiar case: by means of a classic UV-vis spectrophotometric titration we can determine once again the stoichiometry of the forming complex (figure 6.26). Like in the case of Fe^{II}, also for Zn^{II} the ratio is determined as 1:3. Possibly, the coordination pattern is ascribable to the scheme in figure 6.25 and the cumulative log β is around 20 coherently with the case of Fe^{II}. This is quite in contrast with the free terpyridine which gives indication of less stable complexes in presence of Zn^{II}; complex formation is therefore more favorable for terpy moieties within **A6-Tpy**.

Absorption spectra display a sensible red-shift in respect to the free ligand, changing the solution color to a darker yellow. On the contrary, we can

distinguish the usual LC band around 290 nm, corresponding to the π_{tpy}-π^*_{tpy} transitions of the terpyrdine units.

Figure 6.26: left: changes in absorption spectra upon titration of a **A6-Tpy** solution in THF with a MeCN solution of $Zn(CF_3SO_3)_2$ at 298 K; blue line: original solution of **A6-Tpy**; red line: end of the titration. Right: absorption profiles at 380 nm (blue dots) and 299 nm (red dots).

Luminescence properties of the $[Zn_3(\mathbf{A6\text{-}Tpy})]$ complex are interesting: after the addition of the usual 3 eqvs of Zn^{II} a solution of the complex in THF shows an intense emission. In figure 6.27 excitation and emission spectra are reported: on a aerated solution – in fluorescence mode – we can record a broad emission with a maximum at 515 nm, in the region of the standard emission of **A6-Tpy** in solid phase. The same solution, in the same instrumental conditions, gives a more intense emission once is deaerated (argon flux, 20 minutes, light green in figure 6.27). In phosphorescence mode the resulting emission is centered at 580 nm (red line).

The excitation shows (dark green line) the same structure of the absorption at the end of the titration, even with different heights for each band, suggesting a possible partial energy transfer from the $[Zn\text{-}(terpy)_2]$ complex to the aromatic core.

Thus, the rigidity lent to the entire architecture by the Zn^{II} coordination could turns on the emission of the luminophore **A6-Tpy**. In addition, following the absorption and emission during a titration on a deaerated

Figure 6.27: emission and excitation spectra of solutions of **A6-Tpy** in aerated and deaerated THF, after the complexation of 3 eqv of Zn^{II} recorded with different instrumental setups. Further details in the text.

solution (3 cycles of pump-freeze-thaw each add) we can estimate better the coordination process and the phosphorescence enhancement, as showed in figure 6.29. As already reported above, the absorption spectra (figure 6.28) do not show dramatic changes after the addition of 3 eqv of Zn^{II}.

Differently, the emission profile do not show a clear equilibrium saturation, as the phosphorescence is increasing beyond the addition of 5 eqv of zinc. This could be due to several aspects, like the unreproducibility of the deaeration procedure (for example: part of the solvent can evaporate during the titration, different amounts of oxygen can remain in solution on different samples, etc.).

The same experiment was repeated monitoring the zero-delay phosphorescence during a titration with Zn^{II} on a air equilibrated solution of **A6-Tpy** (figure 6.30): at the beginning, a low intensity emission is recorded, with maxima in the near UV and around 530 nm, as expected. Upon addition of zinc the main emission is turned on and it is not increasing after the third equivalent; moreover, the emission around 380 nm is completely quenched once the equilibrium is reached.

In summary: from solutions of **A6-Tpy** in THF, the emission is oc-

Figure 6.28: left: changes in absorption spectra upon titration of a **A6-Tpy** solution in THF with a MeCN solution of Zn(CF$_3$SO$_3$)$_2$ at 298 K; blue line: original solution of **A6-Tpy**; red line: end of the titration Right: absorption profiles at 378 (blue dots) and 302 nm (red dots).

Figure 6.29: left: phosphorescence spectra taken upon titration of a **A6-Tpy** solution in THF with a MeCN deareated solution of Zn(CF$_3$SO$_3$)$_2$ at 298 K; blue line: original solution of **A6-Tpy**; red line: end of the titration. Right: emission profile at 570 nm. Instrumental parameters: λ_{ex}=327 nm, delay time=70 µs, emission and excitation slits: 10 nm.

curring upon the addition of Zn^{II} as a phosphorescence (figure 6.31). In addition, luminescence coming from the simple [Zn(**Tpy-SMe**)$_2$]$^{2+}$ units results quenched, while the phosphorescence seems to come from the aromatic core, probably due to the restriction of intramolecular rotations

Figure 6.30: left: zero-delay phosphorescence spectra taken upon titration of a **A6-Tpy** air equilibrated solution in THF with a MeCN solution of $Zn(CF_3SO_3)_2$ at 298 K, λ_{ex}=327 nm; blue line: original solution of **A6-Tpy**; red line: end of the titration. Right: emission profiles at 554 nm (blue dots) and 384 nm (red dots).

and larger rigidity. The presence of multiple species (i.e. metalorganic oligomers of different size) involved in the equilibrium is not excluded.

Figure 6.31: schematic representation of the turned-on phosphorescence behavior after the addition of 3 eqvs of Zn^{II} to **A6-Tpy**. Terpy units are evidenced in blue.

Compound	Absorption		Emission		
	$\boldsymbol{\lambda}$ (nm)	$\boldsymbol{\varepsilon}$ (M^{-1} cm^{-1})	$\boldsymbol{\lambda_{max}}$ (nm)	$\boldsymbol{\tau}$	$\boldsymbol{\Phi}$
Tpy-SMe	297	36900	388	1.4 ns	0.52
[Zn(Tpy-SMe)$_2$]$^{2+}$	346	26600	490	1.1-3.4 ns	0.21
A6-Tpy	283	178200	372-482	1 ns	0.001
[Zn$_3$(A6-Tpy)]	289	154000	525	–	0.016
[Zn$_3$(A6-Tpy)] deg.	289	154000	590	2.1-11.3 µs	0.05
[Zn$_3$(A6-Tpy)] sol.	–	–	575	1.7-9.2 µs	–

Table 6.6: photophysical data comparison between the different species involved in **A6-Tpy** complexation with Zn^{II}, in THF or solid phase at 298 K.

6.9   Formation of nanoaggregates

After the coordination of Zn^{II} it is not evident to establish which species are actually the one who generate emission, nor to clarify which is the correct conformations of the molecule in a possible extended entity.[187]
DLS analysis have been completed upon addition of Zn^{II} ions in THF solutions: while intensities of DLS signal can identify a growth of some nano-sized species, the correlograms do not show evidence of well polydispersed species. Even if in figure 6.33 thin distribution are shown, the quality report gives indications of a bad dispersed material and no conclusion could be rationalized.
Further investigations, especially by means of AFM microscopy, remain quite interesting to complete with the aim to attribute the exact nature of the emissive species in the complexes or in the aggregates.

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[187] XRD analysis on powders of [Fe$_3$(**A6-Tpy**)] and [Zn$_3$(**A6-Tpy**)] by Dr. Massimo Gazzano, CNR-ISOF, Bologna, gave confirmation of the presence of an amorphous material. No information on crystalline structure could be provided by the analysis of solid materials.

Figure 6.32: DLS intensities signals upon progressive addition of Zn^{II} to **A6-Tpy** in a THF solution at 293 K. In sequence: red, green, blue and black line (1 eqv per each measurement).

Figure 6.33: DLS intensities distribution by particle size and cumulative frequency (green line) of particles size upon progressive addition of Zn^{II} to **A6-Tpy** in a THF solution at 293 K.

6.10   Overview and perspectives

As we stated in last sections, the persulfurated asterisk **A6-Tpy** acts like a good linking agent, in which the aromatic core represents a good phosphor after the Zn^{II} coordination.

The hexasubstituted asterisk could constitute the member of a new class of designed molecules in which the metal coordination or, more in general, proper supramolecular interactions lead to an emission turn-on. One can design suitable combination of AIE-active and connecting agents, in order to better explore the potential of the AIE emission.

In addition, changing the number of substituents, polysulfurated benzenes

with 4 terpyridine moieties appended could be representative of a new class
of asterisk based on an AIE-active system.

Chapter 7

A pyrene based antenna system

Pyrene and its derivatives have interesting photophysical and electrochemical properties, and, for this reason, they have been widely used in the fields of organic light-emitting devices,[188] field-effect transistors,[189] liquid crystals,[190] biological markers,[191] and ion sensors.[192]

Quite recently, dendrimers based on a tetrasulfurated pyrene platform (**Py-Ph**, in figure 7.1, and derivatives) with aromatic sulfurated peripheral units have been studied and developed.[193]

They exhibit remarkable photophysical and redox properties. In particular, they show a high branch-localized absorption band in the UV region, a core-localized absorption band in the visible region. A strong core-localized

[188] Sagara Y., Mutai T., Yoshikawa I., Araki K., *J. Am. Chem. Soc.*, **2007**, *129*, 1520.

[189] Zhang H., Wang Y., Shao K., Chen S., Qiu W., Sun X., Qi T., Ma Y., Yu G., Su Z., Zhu D., *Chem. Commun.*, **2006**, 755.

[190] Sienkowska M. J., Hirosato M., Kaszynski P., Shimizu Y., *J. Mat. Chem.*, **2007**, *17*, 1392.

[191] Martí A. A., Jockusch S., Stevens N., Jingyue J., Turro N. J., *Acc. Chem. Res.*, **2007**, *40*, 402.

[192] Figueiera-Duarte T. M., Müllen K., *Chem. Rev.*, **2011**, *111*, 7260.

[193] Gingras M., Placide V., Raimundo J.-M., Bergamini G., Ceroni P., Balzani V., *Chem. Eur. J.*, **2008**, *14*, 10357.

fluorescence band is observed even in the presence of oxygen, indicating that the presence of sulfur atoms affects dramatically the excited state properties of the pyrene core. A strong fluorescence is also evidenced in rigid matrix at 77 K, and in the solid state at RT.

This class of dendrimers undergo two successive one-electron reversible electrochemical oxidation processes in DCM solution. The first one-electron oxidation process can be realized using $[AuCl_4]^-$ or Fe^{III} as oxidant agents, leading to the formation of a blue radical cation. In summary, the photophysical and redox properties can be tuned by the length of their branches.

With this premise, the realization of an antenna system based on **Py-Ph** (figure 7.1) could be of real interest to explore the acceptor ability of the pyrene core in energy transfer processes. For this purpose, terpyridine peripheral units can drive the coordination of metal ions and communicate properly with the molecule core: we therefore synthesized **Py-Tpy** with this aim.

Py-Ph

Py-Tpy

Figure 7.1: model compound **Py-Ph** and the recently synthesized **Py-Tpy**.

7.1   Synthesis of Py-Tpy

Similarly to the synthesis of **A6-Tpy**, reported in figure 6.20, the procedure
to get **Py-Tpy** involves a nucleophilic substitution on a tetrabrominated
pyrene,[194] in the conditions already elucidated for other polysulfurated
compounds (figure 5.1). Reaction occurs between the usual partners, even

Figure 7.2: optimized synthetic methodology to achieve **Py-Tpy**.

if running time is maintained longer (more than 6 days) than the case of
A6-Tpy because of the lower reactivity of tetrabromopyrene and to be
sure to complete substitution on the substrate: there is no easy method to
monitor reaction's progression since reactants and product are extremely
insoluble in usual solvents and precursors are air sensitive.

However, the main complication in the synthesis comes from the purification
procedure: for the same reasons, residual quantities of unreacted or partially
substituted tetrabromopyrene could be revealed. Thus, to afford the pure
product several successive triturations in solvents are needed depending on
the kind and the amount of impurity to be eliminated.

Pure product is characterized only by MALDI-MS analysis (figure 7.3) and
by ^{1}H NMR, since in the case of ^{13}C NMR no reliable signal is recorded due

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[194] A good quantity of 1,3,6,8-tetrabromopyrene has been kindly provided by Dr. Virginie
Placide and used as received without further purifications.

to the scarce solubility in deuterated chloroform. However, two distinct peaks coming from the pyrene unit are evidenced in the ^{1}H NMR spectrum recorded in $CDCl_3$; they could genuinely correspond to the two protons in position 2-7 (8.02 ppm, singlet, 2H) and 4,5-9,10 (8.70 ppm, singlet, 4H). Signals are compatible with the ones found out for **Py-Ph** (8.60 ppm, 4H; 7.87 ppm, 2H).

7.1.1   Details

1,3,6,8-tetrakis((4-([2,2':6',2''-terpyridin]-4'-yl)phenyl)thio)pyrene (Py-Tpy). In a round bottom flask 1,3,6,8-tetrabromopyrene (181.4 mg, 0.35 mmol, 1eqv), 4'-[4-(mercapto)phenyl]-2,2';6',2''-terpyridine (**Tpy-SH**) (507.0 mg, 1.48 mmol, 4.3 eqv) and Cs_2CO_3 (590.1 mg, 1.81 mmol, 5.2 eqv) were placed and dried by means of a vacuum pump. Then, in anhydrous and inert conditions (argon atmosphere), DMI (3 ml) was poured in as a solvent; the mixture is stirred at 60° C for 6.5 days. After being cooled to RT, the mixture was poured in 2 M NaOH (30 ml). A bright yellow solid precipitated, which is separated by filtration and washed several times with H_2O.

The crude product is poorly soluble in almost all organic solvents; a first trituration in ethanol (RT, 18 h) is followed by a second in hot toluene (100° C, 24 h). The product is collected on a fritted glass and dried in vacuo for several days to give 413 mg (76%) of yellow powder; mp: 335-336° C.

^{1}H NMR (250 MHz, $CDCl_3$): δ=8.70 [s, 4H; pyr-4H], 8.52 [s, 8H; tpy($3^I,5^I$)], 8.02 [s, 4H; py-4H].

Low resolution MS: MALDI (DCTB matrix), calcd. 1558.4 Da, founded m/z 1558.3 [M]$^+$, 1581.3 [M+Na]$^+$ (figure 7.3).

EA: calcd (%) for $C_{100}H_{62}N_{12}S_4$: C 77.00, H 4.01, N 10.78, S 8.22; found: C 73.61, H 3.88, N 9.93, S 7.30.

Figure 7.3: MS-MALDI spectrum of the purified **Py-Tpy**: two peaks are detected in correspondence of the free molecule and its sodium adduct ([**Py-Tpy**-Na]$^+$).

7.2   Changing peripheral units: attempts

In section 6.3 we illustrated the attempts to get a proper terpy-based thiol, **Tpy-SH**. A test reaction using the crude product of one these reactions was carried out on tetrabromopyrene to proof the availability of a different polysulfurated pyrene with terpy-based peripheral units.

Reaction scheme is reported in figure 7.4: the crude **aTpy-SH** was poured in a flask with tetrabromopyrene and cesium carbonate, performing reaction in DMI at 60°C. After 5 days, the resulting suspension is precipitated in water and isolated as a pale yellow solid.

From a MS-MALDI analysis (figure 7.5) we have evidence of the complete substitution of tetrabromopyrene by **aTpy-SH**, giving a clear isotopic distribution around 1277 Da, corresponding to the adduct [**aPy-Tpy**-Na]$^+$. Unfortunately, we did not succeed to isolate a good amount of **aPy-Tpy** in order to complete the photophysical characterization.

   Reaction is therefore occurring effectively from the *in situ* generated thiolate, as recently reported during the preparation of a Fréchet-type dendron.[195] **ATpy-SH** can be represented in two tautomeric forms: in

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[195] Constable E. C., Hermann B. A., Housecroft C. E., Neuburger M., Schaffner S., Scherer L. J., *New. J. Chem.*, **2005**, *29*, 1475.

Figure 7.4: potential synthetic procedure to afford **aPy-Tpy**.

both the solid state and in solution the thione tautomer is dominant, while it is always possible to generate the thiolate by means of a relatively strong base.

Figure 7.5: MALDI-MS of the mixture of reaction in figure 7.4, exploring the potential synthesis of **aPy-Tpy**.

7.3 Photophysical characterization of Py-Tpy

The purified **Py-Tpy** is a bright yellow solid in powder, which gives a greenish luminescence in the solid phase. The compound is poorly soluble in almost all organic solvents, but enough soluble in $CHCl_3$ for photophysical characterization. Unfortunately, no electrochemical measurement has been performed because of the scarce solubility in organic solvents. In addition, solubility is acceptable in hot DMF, DMSO, toluene and pyridine. It is preferable to avoid as much as possible the use of ultrasounds to solubilize the compound since it seems to degrade with extended sonication; on the other hand the molecule does not display any photosensitivity to UV sources, contrary to the case of **A6-Tpy**.

Figure 7.6: photophysical data of **Py-Tpy**: absorption (green) and emission spectra (blue, λ_{ex}=285 nm) of **Py-Tpy** in a $CHCl_3$ solution at 298 K. The red dashed line refers to the excitation spectrum (λ_{em}=485 nm), while the blue dashed line to the emission on a DMF filtered solution.

Photophysical data are gathered in table 7.1 while spectra are shown in figure 7.6. As expected, the absorption spectrum in $CHCl_3$ presents both the typical features of a tetra-thiosubstitued pyrene and the terpyridyl units on the periphery. Both units show comparable values concerning the molar absorption coefficient ε (*ca.* 40000 $M^{-1}cm^{-1}$ for the pyrene core,

like **Py-Ph** and *ca.* 35000 for each terpy unit, see data for **Tpy-SMe** in table 6.6 and figure 7.7) in respect to the already characterized compounds.

Figure 7.7: comparison between data of **Py-Tpy** and **Tpy-SMe**: absorption (blue) and emission spectra (green, λ_{ex}=285 nm) of **Py-Tpy** in a CHCl$_3$ solution at 298 K; absorption (red solid line, dashed line is multiplied by 4) and emission spectra (orange, λ_{ex}=323 nm) of **Tpy-SMe** in a CHCl$_3$ solution at 298 K.

In DMF, it is necessary to dilute the heated up dispersion in order to reach a decent solubility. By the way, the value of molar absorption coefficient determined in DMF is only an estimation, due to solubility problems.

The emission band shows a maximum at 458 nm, similarly to the investigated compounds of the series; no emission seems to come from the terpyridine moieties (whose emission is rising at 385 nm). From the excitation spectrum we have evidence of a intramolecular *energy transfer* from the tolyl-terpyridile units to the pyrene core with unitary efficiency. There is no evidence of any emission coming from the outermost units.

Emission quantum yield has been estimated to be 52% (quinine sulfate in H$_2$SO$_4$ 0.5 M is used as a standard) and the fluorescence lifetime 1.3 ns (exponential decay fitting is not so good neither with a biexponential curve, $\chi^2 \geq 1.222$). By the way, similarly to the example of **Py-Ph**, we can state

that the emission lifetime is not affected by the presence of dioxygen in solution after degassing a solution with an argon flux for 15-20 min.

Figure 7.8: a comparison between emission spectra of **Py-Tpy** in different phases at 298 K. Blue lines refer to solutions (CHCl$_3$ solid line, DMF dashed line), while the red line refers to the spectrum of the solid phase.

In addition, like the older pyrene-based compounds, the solid phase shows an emission, too (figure 7.8). The maximum is recorded at 500 nm, with a sensible broadening towards the green-yellow region of the visible spectrum (maybe as an effect of the reabsorption in packing molecules in the solid phase).

7.4 Coordination properties of Py-Tpy: Fe^{II}

Similarly to the examples of **Tpy-SMe** and **A6-Tpy**, also for **Py-Tpy** the interaction with metal cations as Fe^{II} and Zn^{II} has been studied in solution with a standard spectrophotometric titration *versus* the triflate salts of the two metals.

Starting from the case of Fe^{II}, we can observe once again the formation

Compound	Absorption		Emission		
	λ (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	τ (ns)	Φ
Py-Tpy (CHCl$_3$)	282	133800	459	1.3	0.52
Py-Ph (DCM)	435	39000	457	1.3	0.33
Py-Tpy (sol.)	–	–	500	1.3 - 8.9	–

Table 7.1: photophysical data comparison between **Py-Tpy** in different phases and **Py-ph** in DCM air equilibrated solutions.

Figure 7.9: left: changing in absorption spectra taken upon titration of a **Py-Tpy** solution in CHCl$_3$ with a MeCN solution of Fe(CF$_3$SO$_3$)$_2$ at 298 K; blue line: original solution of **Py-Tpy**; red line: end of the titration. Right: absorption profiles at 444 nm (blue) and 577 nm (red).

of a complex between the terpyridine units and the metal cations, with a rising MLCT band centered as usual around 585 nm (figure 7.9); thus, the coordination activity makes the molecule act as a chemosensor. Isosbestic points are recorded around 308 nm, for the complexed terpyridine unit, and in the pyrene region (410 and 453 nm) accompanied by a gradually loss of its vibrational substructure. Absorption profiles on two wavelengths clearly show the 1:2 coordination between the ligand and metal ions: there is no evidence of precipitation during the titration. We can state therefore that the outermost branches of the molecule are not flexible enough (due to the

limited rotations around the C-S-C bonds) to build up an intramolecular complex and a supramolecular network is coming up.

No emission is observed during the addition of Fe^{II} so far, but it is presumably completely quenched by the presence of the non-emissive MLCT transition.

7.5 Coordination of Zn^{II}

In absorption, the behavior is quite similar to Fe^{II} for coordination: once again, the complexation equilibrium seems to be 2:1, even with an intrinsic lower thermodynamic stability of the zinc complex (figure 7.10). No MLCT is rising in this case, as expected, while the evolution of isosbestic points is quite similar to the previous case using Fe^{II}. Also in this case, precipitation is not occurring.

Figure 7.10: left: changing in absorption spectra taken upon titration of a **Py-Tpy** solution in CHCl$_3$ with a MeCN solution of Zn(CF$_3$SO$_3$)$_2$ at 298 K; blue line: original solution of **A6-Tpy**; red line: end of the titration. Right: absorption profiles at 347 nm (blue) and 444 nm (red).

In emission, complexation is associated to a complete quenching of the free **Py-Tpy** emission in correspondence of the addition of the two equivalents of Zn^{II}, with the rising of a low intensity ($\Phi \simeq 0.01$) emission at 544 nm (see table 7.2 and figure 7.11). This emission has comparable energy with the one coming from the [Zn(**Tpy-SMe**)$_2$]$^{2+}$ complex but

lower quantum efficiency, indicating that this emission could be quenched by electron transfer.

Figure 7.11: left: emission spectra of **Py-Tpy** in CHCl$_3$ taken upon the addition of Zn^{II}; the red emission at the end of the titration is magnified by a 25 factor (λ_{ex}=320 nm). Right: emission profile at 459 nm.

Compound	Absorption		Emission		
	λ (nm)	ε (M^{-1} cm^{-1})	λ_{max} (nm)	τ (ns)	Φ
Py-Tpy (CHCl$_3$)	282	133800	459	1.4	0.52
[Zn$_2$(Py-Tpy)]	–	–	544	1.4 - 6.8	0.01

Table 7.2: photophysical data comparison between **Py-Tpy** and the zinc complex upon addition of the triflate salt in CHCl$_3$ at 298 K.

However, from excitation spectra analysis (figure 7.11, right) we have evidence that the new weak emission rising after the zinc complexation is associated to the **Py-Tpy** moiety: the absorption spectrum structure is totally matching the excitation spectra, showing that the pyrene core is involved in an energy transfer process (figure 7.12).

In addition, we have performed a qualitative titration studying the behavior of the complex upon addition of *cyclam* (1,4,8,11-tetraazacyclotetradecane). The *cyclam* shows a high affinity to the zinc ion and a competitive com-

plexation equilibrium can occur against the **Py-Tpy** ligand. Absorption spectra show a partial decomplexation by means of the macrocycle, while the emission is partially restored, too.

Figure 7.12: comparison between excitation spectrum (λ_{em}=540 nm, red line), the absorption spectrum taken at the end of a titration (green line) and the rising emission (blue).

Hence, we can state that after the coordination with zinc ions new discrete emissive species are growing, with the effect to quench the original emission of the free ligand and to turn-on a new fluorescence, influenced by the mutual orientation of fluorophores in the rising 3D supramolecular oligomer.
In order to achieve more information about the final complex, DLS analysis was carried out upon addition of zinc triflate in CHCl$_3$: during additions it is clear that nanoparticles are growing quite regularly, displaying hydrodynamic radii increasing in the average value (see picture 7.13).

It is important to evidence that dimensions grow steadily until the addition of the second equivalent of Zn^{II}, when particle dimensions stabilize around a distribution in diameter of *ca.* 60 nm, with a very low PDI of 0.066 (figure 7.14) and correlation data that confirm the presence of only one thin distribution of discrete particles. In the original **Py-Tpy** solution no significant DLS signal is recorded.

Figure 7.13: DLS analysis showing formation of nanoparticles during addition of Zn^{II} to a solution of **Py-Tpy** in $CHCl_3$. In progression: red, green, blue, black and pink lines.

Figure 7.14: DLS analysis of nanoparticles coming after the addition of two equivalents of Zn^{II}. Left: distribution histogram of particles and cumulative distribution frequency (green line); right: raw correlation data collected during the DLS experiment (average of 4 measurements of 4 runs each, 298 K).

In addition, nanoparticles do not seem sensible to the presence of a large excess of Zn^{II} in solution. After the addition of circa 250 eqvs of metal ion calculated dimensions do not vary significantly (around 75 nm), while polydispersity increases to 0.216. In any case there is no proof of complete decomplexation, confirmed by the absence of the free ligand emission at 460 nm and no destructive equilibria are taking place.

Information coming from DLS are confirmed by a morphological analysis by means of AFM microscopy[196] which shows a distribution of particles of

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[196] An AFM scanning has been completed on a sample prepared by standard drop-casting on glass, starting from a $CHCl_3$ solution of **Py-Tpy**, which 2.5 eqv of Zn^{II} are added

different shapes, whose average dimensions are determined around 60-70 nm (see figure 7.15).

Figure 7.15: AFM image of a dispersion on glass plate of nanoparticles obtained after coordination of **Py-Tpy** by Zn^{II}; from a topographic analysis particles are 20-30 nm high and 60-70 nm in diameter. Scan is made on a 5.6x5.6 μm area.

7.6 An antenna system with Nd^{III}

Due to the presence of proper coordinating peripheral units, **Py-Tpy** can work with lanthanide ions, whose features bring them commonly to display very low absorption coefficients in visible and UV spectral region.[197] In general, this disadvantage may be overcome by using complexes in which light absorption is performed in ligand-centered or charge-transfer bands. Ligand-sensitized complexes are of great importance because of their peculiar photophysical properties (microsecond to millisecond lifetimes, narrow emission bands, and large Stokes shifts), making them work properly as

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to. Scanning has been performed in *Peakforce* tapping mode (14 KHz) on a Bruker Multimode 8.

[197] Leonard J. P., Nolan C. B., Stromeo F., Gunnlaugsson T., *Top Curr. Chem.*, **2007**, *281*, 1.

labels in luminescence-based bioassays.[198] The time-extended emission of lanthanide(III) cations can be temporally resolved from scattered light and background fluorescence to largely improve experimental sensitivity.[199,200] Lanthanides, with their well-defined energy levels can represent an excellent basis to study different Ln(III)-specific energy transfer processes in many chemical systems.[201]

With this premise, dendrimers can properly play the role of ligands, light-harvesting antennae to collect excitation light and funnel it to a single chromophore (possibly based on lanthanide ions), and nanoscopic containers capable of encapsulating and shielding lanthanide ions.[202,203]

It is significant however to study the interaction of the free **Tpy-SMe** ligand to have a comparison by means of which analyse correctly the coordination properties and the photophysical properties of **Py-Tpy**.

7.6.1   Tpy-SMe as a ligand for Nd[III]

Through a spectrophotometric titration it is possible to determine the coordination scheme of Nd[III] in respect of **Tpy-SMe**. Analysis is carried out in CHCl$_3$ due to the fact that lanthanide ions are generally extremely sensible to water and tend to coordinate oxygen atoms, changing of course photophysical properties and coordination capabilities.[204] In addition, **Py-Tpy** is completely insoluble in water.

Changes in absorption spectra (figure 7.16) show similar trends in

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[198] Bünzli J.-C. G., Piguet C., *Chem. Soc. Rev.*, **2005**, *34*, 1048.

[199] Sabbatini N., Guardigli M., Lehn J.-M., *Coord. Chem. Rev.*, **1993**, *123*, 201.

[200] Moore E. G., Samuel A. P. S., Raymond K. N., *Acc. Chem. Res.*, **2009**, *42*, 542.

[201] Lis S., Elbanowski M., Mąkowska B., Hnatejko Z., *J. Photochem. Photobiol. A: Chem.*, **2002**, *150*, 233.

[202] Vögtle F., Richardt G., Werner N., *"Dendrimer chemistry"*, Wiley-VCH, New York, **2009**.

[203] Giansante C., Ceroni P., Balzani V., Vögtle F., *Angew. Chem. Int. Ed.*, **2008**, *47*, 5422.

[204] Parker D., Dickins R. S., Puschmann H., Crossland C., Howard J. A. K., *Chem. Rev.*, **2002**, *102*, 1977.

Figure 7.16: left: changing in absorption spectra taken upon titration of a **Tpy-SMe** solution in CHCl$_3$ with a MeCN solution of Nd(CF$_3$SO$_3$)$_2$ at 298 K; blue line: original solution of **Tpy-SMe**; red line: end of the titration. Right: absorption profiles at 350 nm (blue) and 299 nm (red).

respect of the titration with Zn^{II}: the lowest energy transition is red-shifted in presence of the ion, while the usual LC transition still rises around 290 nm. On the other hand, following changes in absorption, we can exclude a 2:1 coordination ratio since changes in absorption evidence a plateau after the addition of 1 eqv of Nd^{III}.

Variations in emission (figure 7.17) are validating these assumptions, since the original fluorescence of **Tpy-SMe** is almost completely quenched in the presence of 1 eqv of Nd^{III}; however, we did not record the NIR emission of the complex in this solvent, nor its quantum efficiency.

In summary, we can state that in CHCl$_3$ the terpyridine-based sulfide **Tpy-SMe** represents a 1:1 ligand towards the Nd^{III}.

7.6.2 Py-Tpy *vs.* Nd^{III}

Complexation of Nd^{III} ions has been evaluated. From a spectrophotometric titration (figure 7.18) we can state once again the usual 1:2 coordination, differently to the case of free **Tpy-SMe**, even if probably there is a competitive decomplexation after the addition of more than 2 eqvs of neodymium triflate.

From the emission spectrum it is clear the presence of a typical NIR

Figure 7.17: left: changing in emission spectra taken upon titration of a **Tpy-SMe** solution in CHCl$_3$ with a MeCN solution of Nd(CF$_3$SO$_3$)$_2$ at 298 K; blue line: original solution of **Tpy-SMe**; red line: end of the titration (λ_{ex}=325 nm). Right: emission profiles at 380 nm (blue).

Figure 7.18: left: changing in absorption spectra taken upon titration of a **Py-Tpy** solution in CHCl$_3$ with a MeCN solution of Nd(CF$_3$SO$_3$)$_2$ at 298 K; blue line: original solution of **Py-Tpy**; red line: end of the titration. Right: absorption profiles at 352 nm (blue) and 283 nm (red).

flurorescence of the [Nd(terpy)$_2$] moiety, with a main peak recorded at λ_{max} 1064 nm; in addition, from a comparison between absorption and excitation spectrum (figure 7.19) it seems clear that the pyrene core – whose luminescence is completely quenched once the 1:2 equilibrium is reached – is contributing to the [Nd(terpy)$_2$] emission, too. This could represent a partial *energy transfer* from the pyrene moiety to the complex (Φ_{em} related

to the NIR emission is estimated as 0.17% after comparison with a NIR quantum yield standard, tris(1,1,1,5,5,-hexafluoroacetylacetonato)Nd^{III} in THF-d_8).[205] The quantum efficiency is normally defined as follows, considering the energy transfer process involved:

$$\Phi_{em} = \eta_{et}\,\eta_{Nd} \tag{7.1}$$

where η_{et} is the energy-transfer efficiency and η_{Nd} the intrinsic Nd^{III} moiety emission efficiency.

Figure 7.19: photophysical data of a **Py-Tpy** solution in CHCl$_3$ with 2.5 eqv of Nd(CF$_3$SO$_3$)$_2$ at 298 K. Absorption (green) and excitation spectra (red, λ_{ex}=1064 nm); emission spectrum in the NIR is represented by the blue line.

In figure 7.20 a schematic sketch of the probable supramolecular arrangement after addition of Nd^{III} in CHCl$_3$ solution is represented. We can imagine that in presence of neodymium ions an energy transfer is taking place: exciting the pyrene moiety in correspondence of its S$_1$ transition, around 410 nm, emission is recorded in the NIR spectrum. We can be sure of the selective excitation of the pyrene moiety since each [Nd(terpy)$_2$] unit is not absorbing in the visible region (see figure 7.16). In addition, taking into account information from AFM microscopy, we can not distinguish

[205] Iwamuro M., Wada Y., Kitamura T., Nakashima N., Yanagida S., *Phys. Chem. Chem. Phys.*, **2000**, *2*, 2291.

a precise morphology of the aggregates, which can give rise to capsules, spheres or elongated particles as well in reason of the free rotating sulfur bridges.

It is significative that Nd[III] sensitization is achievable also by means of encapsulation in branched architectures such as dendrimers: they can collect excitation light and encapsulate chemical species in predetermined sites bearing them to stay electronically in contact and performing energy transfer.[206,207,208]

Figure 7.20: schematic 2D representation of the extended network made up of **Py-Tpy** and Nd[III]. An energy transfer takes place from the pyrene moiety to the [Nd(terpy)$_2$] unit, giving rise to a NIR emission. Terpy units are evidenced in blue for clarity.

[206] Kawa M., Fréchet J. M. J., *Chem. Mater.*, **1998**, *10*, 286.

[207] Vicinelli V., Ceroni P., Maestri M., Balzani V., Gorka M., Vögtle F., *J. Am. Chem. Soc.*, **2002**, *124*, 6461.

[208] Cross J. P., Lauz M., Badger P. D., Pétoud S., *J. Am. Chem. Soc.*, **2004**, *126*, 16278.

Chapter 8

Perspectives

As it was elucidated in the previous chapters, many interesting phenomena were described concerning the recently synthesized polysulfurated compounds. Smaller asterisks show in fact an AIE activity in solid phase and rigid media, while for one of them the application as useful phosphor to obtain an OLED device has been demonstrated; the enhancing phosphorescence emission of the hexasubstituted gives useful information about the coordination capabilities of the ligand; by the tetrasulfurated pyrene molecule, complexation towards transition metal ions can occur too, evidencing an energy transfer process in the presence of NIR emitters as Nd(III) ions.

Nevertheless further investigations are needed for all compounds, having an outlook to the future applications.

8.1   Smaller asterisks

Starting from 2-alkyl substituted benzenethiols we have obtained a small collection of asterisks, exploiting the reaction already described in figure 4.2; on the other hand, we did not succeed to isolate asterisk **A6-Me2** (figure 8.1) due probably to the increased kinetic barrier in presence of 2,6-dimethylbenzenethiol. It would be useful to synthesize this molecule,

considering the relation to the analogue persulfurated asterisks and the properties of the parent molecule based on hexaphenylsilole.[209] In that case, molecules are cleverly afforded in two step, completing the functionalization at first, followed by a cyclization with the central ring closure.

A6-Me2

Figure 8.1: asterisk **A6-Me2** has not been isolated yet; the presence of -CH$_3$ units in the *ortho* position may affect the mutual orientation of the external phenyl rings, as well as the photophysical behavior of the molecule in solution.

It is probable that in the presence of so many hindered peripheral functions luminescence may be turned on in solution, eventually representing a full organic triplet emitter. We can envisage, among other possibilities, to build up by means of successive polymerization an hyperbranched architectures[210] (figure 8.2) based on persulfurated benzene molecules: oligomers and polymer in solution could display interesting photophysical properties too, in consequence of the presence of several **A6** units (figure 5.3) connected together by sulfur bridges, increasing the conjugation of the aromatic skeleton.

Even if the synthetic approach to access to these molecular networks will

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[209] Li Z., Dong Y., Mi B., Tang Y., Häussler M., Tong H., Dong Y., Lam J. W. Y., Ren Y., Sung H. H. Y., Wong K. S., Gao P., Williams I. D., Kwok H. S., Tang B. Z., *J. Phys. Chem. B*, **2005**, *109*, 10061.

[210] Wang J., Mei J., Zhao E., Song Z., Qin A., Sun J. Z., Tang B. Z., *Macromolecules*, **2012**, *45*, 7692.

not be not trivial (deactivation of substrates in consequence of the increasing conjugation, collateral polymerizations between the monomers, etc.) we can envisage a possible application of these systems as interesting materials for optoelectronic devices, following the route traced by the simpler **A6-Mep**.

Figure 8.2: some 2D or 3D oligomeric and polymeric architectures based on **A6** (evidenced in blue) are affordable to get new full-organic phosphorescent materials.

Moreover, several further investigations are required at low temperatures on the other members of the **A6-** family: does it exist a real dependence on the type of bulky substituent and the kinetic barrier at low temperatures? finally, is it possible to rationalize the phosphorescence turn-on conditions in function of the peripheral units?

Getting inspired by the formation of phosphorescent nanoparticles starting from **A6-Mep** (see section 5.5) and in order to explore new applications as nano-materials, additional studies on the construction of photonics crystals or glasses could be completed: our asterisks could have the role of dopant agent in polymer nanoparticles able to organize themselves both in regular or irregular structures (figure 8.3). A luminescent material could be obtained (molecules would be immersed in a semi-rigid medium) with

optical properties due to their microstructure's morphology.[211,212]

Figure 8.3: ordered and disordered packing of nanoparticles doped with organic chromophores (as **A6-Mep**) could be achieved by using high transparency polymers as a shell material.

8.2   Functionalized asterisks

Concerning the **A6-Tpy** ligand, we succeed to fully characterize it as a free ligand and in the presence of several transition metal ion, evidencing an interesting behavior after the interaction with Zn^{II}. We still have to give confirmation that **A6-Tpy** works as a luminescent sensor towards metal ions: with this purpose, several analysis are required to proof that luminescence is not affected by other ions such as Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and other alkaline ions of biochemical interest.

In addition, we still have not precise information about the thermodynamical events that play an important role in coordination events: calorimetric analysis of equilibrium phenomena represents a useful method to define the kind of species forming during complexations and to better under-

[211] Jiang P., Bertone J. F., Hwang K. S., Colvin V. J., *Chem. Mater.*, **1999**, *11*, 2132.
[212] Emoto A., Fukuda T., *Appl. Phys. Lett.*, **2012**, *100*, 131901.

stand the physical driving forces which lead to new complex in solution.[213]
Concerning the complexes, FTICR-MS analysis (Fourier Transform Ion
Cyclotron Resonance Mass Spectrometry) is in progress in collaboration
with Prof. Schalley and co-workers (Freie Universität Berlin, Germany)
to achieve more information about the real configuration and the degree
of polymerization in the iron(II) and zinc(II) complexes with **A6-Tpy**.
Apparently, it is not simple to establish correctly the precise structure that
are occurring in solution, since the complexed species build even at low
concentrations too big arrays to analyze them; moreover, the binding seems
to be too strong to obtain [Fe(**A6-Tpy**)] fragments, so that only unbound
A6-Tpy molecules are observed as the protonated species.

However, also from DLS analysis we can theorize that some tridimen-
sional nano-aggregates are growing upon the interaction with coordinating
ions, due to the several orientations forced by the C-S-C bonds: this
hypothesis could exclude the potential employment of the molecule in a
two-dimensional mono-layered organometallic polymer.[214,215] In any case,
AFM analysis on the aggregates, both coming from complexation of Zn[II]
and Fe[II], will be useful to establish their morphology.

As solid phase complexes precipitate as amorphous powders, several at-
tempts to achieve XRD-diffraction crystals have also to be obtained together
with structural information.

From the synthetic point of view, we can think to develop the family
with some new component: reaction to obtain terpyridyl tetrasubstitued
benzenes were already attempted to give products like **A4-Tpy** in figure
8.4, even if further purifications are needed. Reaction is carried out in the

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[213] Schalley C. A., Schmidtchen F. P., "Isothermal Titration calorimetry in supramolecu-
lar chemistry" in *"Analytical methods in supramolecular chemistry, 2nd Edition"*,
Wiley-VCH, **2012**.

[214] Bauer T., Zheng Z., Renn A., Enning R., Stemmer A., Sakamoto J., Schlüter D.,
Angew. Chem. Int. Ed., **2011**, *50*, 7879.

[215] Kissel P., van Heijst J., Enning R., Stemmer A., Schlüter D., Sakamoto J., *Org.
Lett.*, **2010**, *12*, 2778.

usual conditions, playing simply on the stoichiometry between **Tpy-SH**
(4.1 eqvs) and perhalogenobenzene.

A4-Tpy

Figure 8.4: new tetrasubstituted asterisk decorated with terpyridyl units, **A4-Tpy**, have been prepared but not purified; they could represent new interesting molecules to clarify some coordination pattern. -X can be -Cl or -F.

As stated for the other ligands, it could be intriguing to explore the potential coordination capabilities of these compounds, giving rise to extended arrays both with **A6-Tpy** and **Py-Tpy**, which could give rise to luminescent moieties (schematic in figure 8.5).

8.3 Pyrene-core molecules

As **Py-Tpy** shows complexation capabilities similar to the case of **A6-Tpy**, thermodynamic analysis of complexation equilibria can provide useful information.

Concerning the complexes, the formation of nanoparticles has been confirmed by DLS analysis and AFM microscopy: it would be intriguing to better determine how and with which conformation these nanoparticles can grow in solution. In addition, as recently reported, similar compounds

Figure 8.5: showing the same coordination ratio towards metal ions, **A6-Tpy** and **Py-Tpy** could organize themselves in extended networks.

and aggregates are found to be highly stable porous materials:[216],[217] do clusters of **Py-Tpy** complexes show the same effect in trapping natural gases? is there any effect on luminescence?

Concerning photphysical characterization, it will be fascinating to elucidate which is the real photophysical nature of the energy transfer process from the pyrene moieties to the [Nd(terpy)$_2$] unit: when donor and acceptor are taken in proximity as in such cases, the transfer mechanism could be both "through bond" (i.e. a Dexter ET) or "through space" (Förster mechanism), with an intermolecular process. On the other hand, it is desirable to better analyze the redox properties of the molecule, even if solubility problems might represent a drawback to electrochemical analysis.

[216] Yuan Y., Sun F., Ren H., Jing X., Wang W., Ma H., Zhao H., Zhu G., *J. Mater. Chem.*, **2011**, *21*, 13498.

[217] Yana Z., Ma H., Ren H., Yuan R., Zou X., Sun F., Zhu G., *Micropor. Mesopor. Mat.*, **2013**, *in press*.

Figure 8.6: the nature of the energy transfer process to the terpyridyl units (evidenced in blue) after complexation of **Py-Tpy** is still to explore.

Appendix

Summary in English

The aim of this thesis was the synthesis and photophysical characterization of some new polysulfurated aromatic compounds: this class of molecules can offer intriguing properties, potentially useful for the construction of new materials for optoelectronic devices.

Two main families of compounds have been synthesized: the first is represented by a series of small molecular asterisks, with peripheral aromatic units, showing luminescence in solid phase or in highly rigid conditions. All compounds with peripheral substituents display an AIE behavior (Aggregation Induced Emission) with radiative deactivation of the triplet states.

Taking inspiration from these smaller asterisks, a larger molecule with the same geometry has been designed, decorated with terpyridyl moieties as the outermost units: this compound shows great affinity for the coordination of several transition metal ions, changing luminescence properties after the interaction with zinc ions.

With the same intentions, a tetrasulfurated pyrene-core molecule with terpyridyl external units has been synthesized and isolated: this ligand exhibits good coordination capabilities towards transition metal ions, giving rise to luminescent nanoaggregates upon addition of zinc(II), characterized

by DLS and AFM microscopy. In addition a NIR emission is recorded after coordination of neodymium(III), showing evidence of an intramolecular energy transfer process.

Summary in French

Durant mon Doctorat de Sciences Chimiques, effectué en co-tutelle entre l'Université de Bologne et l'Université de Aix-Marseille, j'ai pris en charge la synthèse et la caractérisation d'une série de composés aromatiques soufrés qui bénéficient de propriétés photophysiques intéressantes.

Pour chacune des molécules réalisées, des études approfondies ont été effectuées en utilisant des technique d'analyse traditionnelles à la synthèse organique et inorganique d'une part, et spécifique au domaine de la caractérisation photophysique en solution ou à l'état solide d'autre part. En effet, durant le processus de synthèse, les molécules cibles ainsi que les composés intermédiaires ont été caractérisés en utilisant des méthodes chromatographiques (LC, HPLC), spectroscopiques (RMN et infra-rouge) ainsi qu'en utilisant diverses spectrométrie de masse (MALDI, ESI, IE). En parallèle, les propriétés photophysiques de chaque composé ont été évaluées par spectroscopie d'absorption UV-vis et d'émission de fluorescence et de phosphorescence.

Ce travail de thèse a été essentiellement concentré sur deux classes de composés : la première s'apparente à des astérisques moléculaires contenant un coeur benzénique persoufré, fonctionnalisé avec des unités périphériques aromatiques. Dans chaque cas, des groupes stériquement encombrants ont été greffés sur les unités aromatiques situées à la périphérie des molécules. Une telle ingénierie moléculaire, offre à chaque molécule de la série la capacité de fonctionner comme luminophore AIE (Emission Induite par l'Agrégation) à l'état solide ou dans des milieux à haute rigidité, par conséquent cet effet a été minutieusement étudié, et dans chaque cas une émission de phosphorescence, provoquée par ce phénomène d'agrégation, a été détéctée. La deuxième famille de molécule est basée sur la même géométrie en astérisque. Cependant, chaque ligand de cette série utilise des unités terpyridyles comme unité périphérique, capables d'interagir avec des métaux de transition comme le fer(III) et le zinc. Le comportement

de chaque molécule a donc été étudié en présence de Fe(III) et de Zn(II) et dans chaque cas la formation stable et quasi-sélective d'architectures polymétalliques a été détectée. Les études physico-chimiques des structures issues de la complexation du zinc, ont démontré que leur propriétés photophysiques pouvaient être modulées en fonction de la rigidité du système.

Enfin, la dernière partie de mon travail de thèse a été concentrée sur la synthèse et l'étude d'un troisième type de systèmes qui a été obtenu par le remplacement du coeur benzénique des astérisques par une fonction pyrene polysoufrée, en conservant les mêmes unités périphériques. Chacun de ces composés a montré, non-seulement, des propriétés photophysiques intéressantes mais aussi des capacités de coordinations remarquables envers les ions métalliques, tels que le Fe(III), Zn(II) et le Nd(III). Par exemple, en présence de Zn(II) la molécule est capable de s'auto-organiser en réseaux étendus et la luminescence de cette architecture est issue d'un processus de transfert d'énergie depuis l'unité centrale de type pyrene. Le même effet a été observé dans le cas des architectures issue de la coordination du Nd(III) ce qui a permis la génération d'émission dans le domaine du proche infra-rouge.

Summary in Italian

Durante il corso di Dottorato in Scienze Chimiche, trascorso in parte all'Università di Bologna e in parte alla Aix-Marseille Université e CINaM, Marsiglia (Francia), sono stati sintetizzati e caratterizzati principalmente composti aromatici polisulfurati, i quali presentano interessanti proprietà fotofisiche.

Per tutte le molecole realizzate si sono approfondite le competenze sia nell'analisi fotofisica sia in quella puramente sintetica: le tecniche analitiche di base come spettroscopia NMR, spettrometria di massa e cromatografia sono state utilizzate durante il processo sintetico, mentre tecniche di spettroscopia di assorbimento UV-vis e di fluorescenza sono alla base della caratterizzazione fotofisica di specie in soluzione.

Entrando nello specifico, sono state realizzate due classi di composti: della prima fanno parte una famiglia di asterischi molecolari a *core* benzenico persulforato. Queste molecole sono accomunate dalla presenza di gruppi stericamente ingombranti sulle unità aromatiche esterne: è stato interessante studiare il comportamento di tali composti in qualità di luminofori AIE (Aggregation Induced Emission) allo stato solido o in condizioni di alta rigidità del mezzo in cui sono immersi. In queste condizioni le molecole dimostrano di emettere emissione di fosforescenza.

Prendendo ispirazione da questi asterischi di minori dimensioni, si è realizzata una struttura basata sulla stessa geometria, ma che presenta leganti terpiridinici esterni. Questo composto mostra di conseguenza grande affinità per la coordinazione di ioni metallici come ferro e zinco; inoltre, con quest'ultimo, le proprietà fotofisiche del composto cambiano sensibilmente in conseguenza dell'aumento della rigidità del sistema.

Per ultima, una molecola a nucleo pirene tetrasulfurato e unità periferiche terpiridile, ha mostrato interessanti proprietà emissive e di coordinazione

nei confronti di ferro, zinco e neodimio. In particolare, in presenza di zinco, la molecola dimostra di organizzarsi in *network* estesi, la cui luminescenza è conseguenza di un trasferimento di energia dall'unità centrale pirene; questo processo può avvenire anche attraverso la coordinazione di neodimio, in conseguenza della quale si può generare un'emissione nello spettro infrarosso.

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LATEX