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MODELLING THE STRUCTURE-PROPERTY RELATIONSHIPS IN REDOX
ACTIVE Π -CONJUGATED MATERIALS

Presentata da: Shuailong Wang

Coordinatore Dottorato

Cristina Puzzarini

Supervisore

Daniele Fazzi

Co-supervisore

Fabrizia Negri

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Abstract

Electrochemical Energy Storage (EES) devices, including batteries and supercapacitors, rely heavily on electrode materials, which determine their efficiency and durability. Organic functional materials have emerged as promising electrodes due to their low cost, sustainable production, and favorable mechanical and thermal properties. This work focuses on three classes of such materials: para-graphdiyne (*p*-CNGDY), conjugated redox polymers (OCRPs), and hexaazatriphenylene-hexacarboxylic acid (HATCOOH) and its derivatives (HATCOOM (M=Na/K)), as summarized below.

The first project investigates graphdiyne (GDY) and its derivatives. We studied three GDY derivatives by varying number and positions of the cyano groups. Using DFT calculations, we analyzed how these factors (position and number) influence the bulk structure, packing, and layer arrangement. Results show that the cyano group arrangement significantly affects interlayer distance, electronic band structure, and lithium adsorption capacity, clarifying the redox mechanism connecting the functional groups and the material properties.

The second project examines organic conjugated redox polymers, specifically polyquinoxalines (PQL) and SBBL. Utilizing DFT and broken-symmetry DFT, we identified a poly-radicaloid character in their electronic structures across multiple redox states. Standard DFT incorrectly estimated reorganization energies, whereas BS-DFT provided physically meaningful trends. Interaction sites between polymer segments and cations were identified using DFT and force-field analyses, thus revealing optimal adsorption locations and illustrating the interaction mechanism.

The third project focuses on hexaazatriphenylene-hexacarboxylic acid (HATCOOH) and its derivatives, HATCOOM (M=Na/K). Based on experimentally X-ray structures, we applied DFT at the ω B97X-D level to study electrochemical properties and alkali-metal adsorption sites to HATCOOH. To explore the intercalation properties of metal ions into the crystalline structures, we modeled the interaction of Na and K cations with respect to the molecular substrate. We incorporated Na and K into HATCOOH upon proper deprotonation. Future work will extend these studies to larger clusters, probing Na/K diffusion pathways and the electrochemical performance of HATCOOM (M=Na/K) anodes for Na/K ion batteries.

Overall, this work provides a bottom-up understanding of structure-property relationships in organic conjugated redox materials, correlating electrochemical states and the interaction between metal-cations and the organic substrate with the physical-chemical operating mechanisms of EES devices.

Chapter 1: Introduction

Electrochemical Energy Storage (EES) systems have emerged in recent decades and play a pivotal role in our daily life and technology. Their relevance in our society and the quest for a better understanding of their fundamental properties are essential for improving their efficiency and designing better materials for future EES applications. The cores of EES devices are the electrodes (i.e., cathode and anode) and the electrolyte. For electrodes, inorganic materials are the main systems under investigation because of their high electronic conductivity [1], high capacity [2], high energy density [3], and durability [4]. For instance, LiFeSO_4F confers a practical capacity of circa 130 to 140 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$, as investigated by Tarascon et al. in experiments [5]. Besides, SiC_3 and SiC_7 monolayers, as lithium-ion battery anodes, exhibit high capacities of 627.09 and 955.84 $\text{mA} \cdot \text{h} \cdot \text{g}^{-1}$ in theoretical calculations [6]. However, drawbacks of inorganic materials, including high costs, toxicity [7], and environmental impact [8], shift attention to other more sustainable solutions, such as organic materials. The latter can be synthesized and produced with sustainable methods (e.g., green chemistry) and at low cost. However, the durability and charge conductivity of organic materials are very low; for example, triquinoxalylene (TQA) organic electrodes exhibited poor cycling stability, with a capacity retention ranging from 81% to 35% for alkali metal batteries [9], and the intrinsic conductivity of pyrene-4,5,9,10-tetraone is poor, leading to low rate performance, with a capacity drop of over 50% at rates exceeding 1C [10], thus impacting their efficiency. Fundamental studies underlying the electrochemical and physicochemical properties of redox-active organic functional materials are still lacking, thus preventing their optimization and application as electrodes in EES devices.

Recently emerging organic conjugated systems, which show enhanced solubility [11], efficient electronic transfer kinetics [12], and stiff molecular backbones [13], are flourishing. Yet, little is known about the underlying mechanisms and how electrochemical properties are affected.

During the charging/discharging process, charged states, referred as polarons, are created in the organic materials. Polarons, which are self-trapped charges bound to a displaced nuclear potential, play a crucial role in affecting the electronic properties of redox states, thereby influencing electrochemical functions. [14].

A polaron is a quasiparticle defined as a polarized electron. It is an electronic charge (i.e., a negative electron or a positive hole) added to the system that has been trapped within a potential well formed by the polarizable environment due to the coupling between the charge and the nuclei [15, 16]. Such interaction is also called electron-phonon coupling. Depending on the strength of the electron-phonon coupling, which results in different

spatial polaron delocalizations, a polaron can be defined as a large or small polaron. A large polaron is one in which the polarization cloud expands over many units (e.g., atoms, molecules, polymer units, etc.) and is characterized by weak interactions between electrons and phonons, which cannot tightly confine the charge carrier to a small area. On the contrary, a small polaron is characterized by strong electron-phonon interaction, resulting in a polarization cloud confined within a small area ^[17]. Figure 1.1 reports a sketch comparing a large and a small polaron.

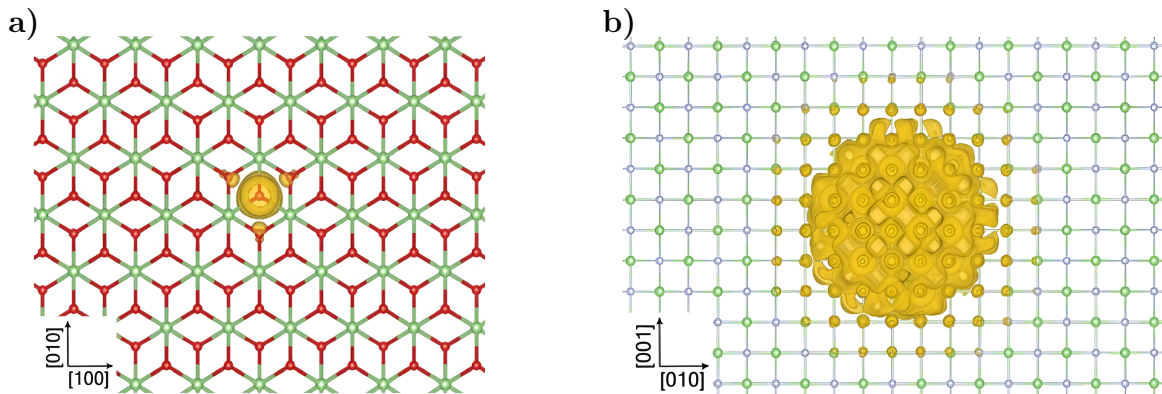


Figure 1.1: a) Small polaron and b) large polaron illustration ^[17].

Over the years, the concept of the polaron has become a fundamental one in condensed matter and solid-state physics, allowing the description of transport properties (e.g., electrical conductivity, spin transport, heat diffusion, etc.) as well as magnetic effects. Therefore, the concept of polarons has broadened, becoming ubiquitous in physics and chemistry, which has provoked the interest of researchers to investigate them in both experiments and theoretical chemistry. Herein, with the development of chemistry, polarons are widening and evolving, thus being classified into bipolarons, magnetic polarons, Jahn–Teller/ferroelectric polarons, 2D polarons ^[18], molecular polarons ^[19], and Zener polarons ^[17]. Besides, polarons have been researched in extensive fields, such as superconductivity ^[20, 21], organic semiconductors ^[22], conducting polymers ^[23], and two-dimensional (2D) materials ^[24].

Specifically, polarons significantly impact the conductivity properties of EES materials. Here, we focus on polarons in the computational chemistry research area, where polarons play an essential role in conductivity, such as polaron hopping derived from Marcus theory ^[25], charge transfer investigated based on multiscale modeling, Kinetic Monte Carlo ^[26, 27], and formation & excitation energies from wavefunction-based methods ^[28].

In computational chemistry, polarons consist of small polarons and large polarons. Small polarons typically migrate via phonon-assisted hopping, and their mobility changes with varying temperature. In contrast, large polarons tend to exhibit coherent motion similar to free charge carriers, and their mobility decreases with increasing temperature ^[17].

Additionally, the bipolaron (a state in which two polarons are bound together) can be formed, and its binding mechanism is related to the exchange of virtual phonons in real space. Polarons and bipolarons have strong impacts on physical and chemical properties, such as transport and conductivity. For instance, bipolarons can form bands that determine transport behavior in conducting polymers [29].

Here, we clearly distinguish between polarons and bipolarons: a polaron refers to a single-charged state (e.g., radical cation/anion), whereas a two-charged state is termed a bipolaron. For more than two charges, the term "multi-charged" states is employed.

A deep investigation of polaron deformation, especially in EES, reveals that the charge carrier localizes on a certain site. This process is closely related to the reorganization energy in electron-transfer theory [22] (details shown in the following part), which depends on electron and hole transfer. In our work, we utilize the reorganization energy to provide a molecular-level evaluation of electron and hole transfer for the OCRPs polaron and bipolaron.

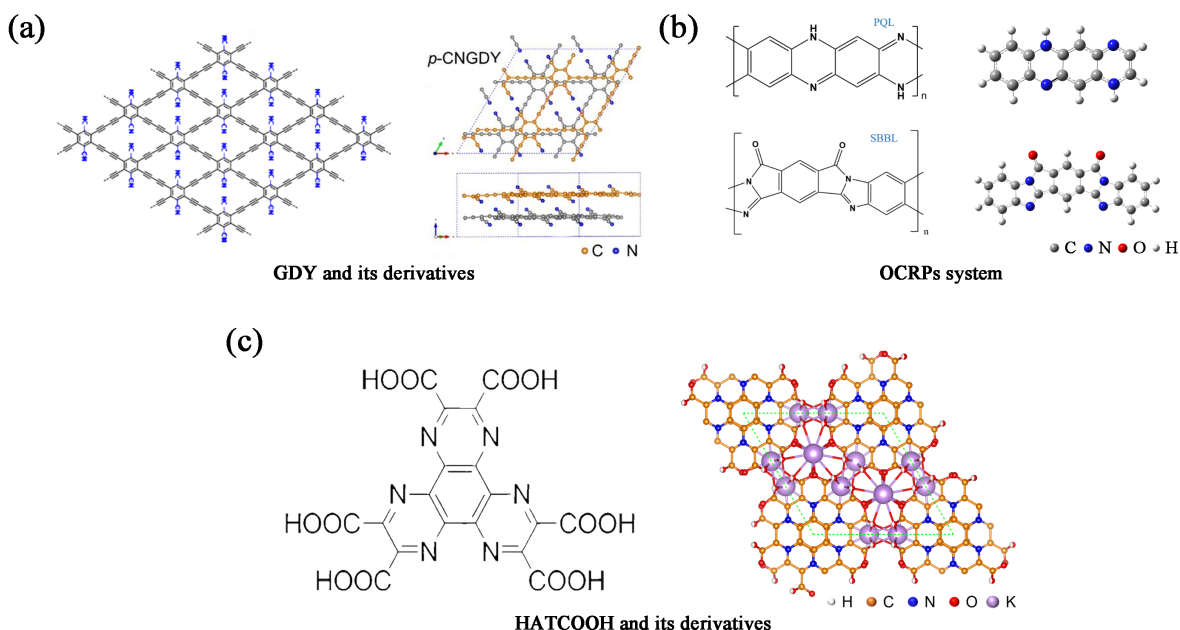


Figure 1.2: (a) GDY and its derivatives (b) OCRPs system (c) HATCOOH and its derivatives

In this work, we investigate via quantum-chemical calculations the structural, electronic, vibrational, and optical properties of three classes of redox compounds, whose chemical and molecular structures are shown in Figure 1.2, aiming to understand the fundamental functional properties in order to draw design rules for future electrode materials by using Gaussian [30], ORCA [31], xTB [32], and other tools.

• Graphdiyne

Two-dimensional (2D) materials, such as 2D carbon-based systems, have recently

been the subject of intense studies, thanks to their optoelectronic properties and promising electronic performance. 2D carbon-based materials such as graphdiyne (GDY) represent an optimal platform for tuning the optoelectronic properties via precise chemical functionalization [33, 34]. Given the versatility of GDY, researchers have focused on enhancing its electrochemical properties, such as conductivity and mechanical strength, by doping with various elements. Among them, nitrogen doping is currently one of the most studied heteroatom doping methods adopted to enhance the properties of carbon nanotubes, graphene, and graphdiyne [35]. Here, based on the nitrogen doping method, we investigated experimentally synthesized GDY derivatives, namely CN-GDY, *m*-CNGDY, and *p*-CNGDY, by varying the amount and position of cyano groups. We investigated their electronic properties to evaluate their battery performance. Given the remarkable effectiveness of GDYs in operation, the theoretical computational results detail the underlying mechanism and provide guidance for the synthesis of emerging tunable materials.

- **OCRPs system (PQL and SBBL)**

In this contribution, we investigate via quantum-chemical calculations the structural and electronic properties of a special class of OCRPs, namely ladder polymers [36]. Among ladder OCRPs, we considered polyquinoxalines (PQL) and SBBL, the latter being a simplified derivative of benzobisimidazobenzophenanthroline (BBL), a well-known polymer with high charge, thermal, and ion mobility [37, 38]. By combining density functional theory (DFT), broken-symmetry DFT (BS-DFT), and fragment orbital density analysis (FOD), we revealed the poly-radicaloid character of the electronic structure of neutral and multi-redox states [39]. To validate the reliability of the conclusions, various functionals were utilized for comparison in electronic property calculations, thereby better reflecting the impact of functional choice.

Referring to realistic scenarios involving cations migrating within the electrode, the interaction mechanisms between the conjugated redox centers and multiple metal cations beyond lithium (e.g., Na^+ and K^+) are deeply investigated, thus comprehensively elucidating the ion insertion/deinsertion processes occurring during electrochemical events.

Our study aims to provide an appropriate electronic structure description based on functional performance and to clarify the mechanism between cations and the electrode under realistic conditions.

- **HATCOOH and its derivatives**

HATCOOH is a promising material due to its high capacity and long cycle life,

as concluded from experimental studies. However, few computational studies have been devoted to exploring its electrochemical properties and the interaction behaviors between alkali metal cations and this electrode material when used as a battery anode. In this project, we utilized the ω B97X-D functional to explore electrochemical properties and simulated the case in which injected potassium interacts with the HATCOOH molecule to illustrate the interaction mechanism. Based on the above procedures, we identified the favorable adsorption site from the electrostatic potential and deeply described the interaction mechanism using energy decomposition analysis (referring to electrostatic energy, repulsion energy, and dispersion energy). Further work will focus on simulating the electrode charge/discharge processes, aiming to elucidate the mechanism of alkali metal interaction with the electrode substrate for potassium-ion batteries.

Chapter 2: Aims of the research

In this thesis, we investigate the electrochemical properties by exploring via a bottom-up approach the molecular and electronic structure of both neutral (ground) and charged (polaronic) states. Properties such as the radical character and the intramolecular reorganization energy have been evaluated via DFT calculations. Finally, intermolecular interactions between the organic conjugated systems and the metal-cations proper of EES devices (Li, Na, K) have been characterised via both DFT and FF based energy decomposition analyses. The goals can be divided into: 1) Electronic Mechanisms and 2) Interaction mechanisms.

2.1 Electronic mechanism

- **GDY and GDY derivatives**

Here, the electronic properties of organic redox materials are investigated via quantum-chemical calculations, providing a theoretical description of these systems. GDY and its derivatives, namely CN-GDY, *m*-CNGDY, and *p*-CNGDY, as mentioned in the introduction, exhibit different electronic structures resulting from the number and position of cyano groups, and thus feature distinct optoelectronic properties (e.g., band gap) and structural properties (e.g., layer stacking and packing), which are discussed in Chapter 4. We aim to describe the electrochemical properties of GDYs and their layer stacking arrangements, thereby offering theoretical insights and guidance for experimental synthesis.

- **OCRPs**

For the OCRP systems PQL and SBBL, by combining density functional theory (DFT), broken-symmetry DFT (BS-DFT), and fragment orbital density (FOD) analysis, we revealed the polyradicaloid character of the electronic structure in both neutral and multi-redox states. We found that negative (electron) and positive (hole) charges, here defined as polarons, relax into localized states along the polymer chain, thus exhibiting distinct structural relaxations and electron-phonon coupling properties. Multi-charged species revealed complex electronic structures, characterized by quasi-degenerate multiconfigurational states with various spin multiplicities (e.g., doublet, triplet, quartet, quintet, etc.). Finally, various exchange-correlation (XC) DFT functionals were tested to compare their predictions of electronic properties and to benchmark the study. Specific results and discussions are presented in Chapter 5.

- **HATCOOH and its derivatives**

For the HATCOOH molecule, the electrostatic potential (ESP) was used to visualize the electron distribution and identify the optimal adsorption sites, as discussed in Chapter 6. Further analyses will be performed to provide a deeper understanding of the properties of larger HATCOOH clusters, such as thermal stability and conductivity.

2.2 Interaction mechanism between cations and conjugated systems

The interactions between cations and the substrate strongly affects the variation of the electronic structure, structural properties (such as structural stability), and cation migration rate, thereby influencing the corresponding electrode performance, including cycle life, charge rate, capacity, and so on. In this contribution, we simulated the battery charging/discharging model in which alkali metal cations migrate inside electrode materials and interact with anode materials (GDY and its derivatives, OCRPs system, HATCOOH and its derivatives), as illustrated in Figure 2.1, aiming to comprehensively exhibit the interacting behavior between alkali metal cations and the anode substrate in operating systems.

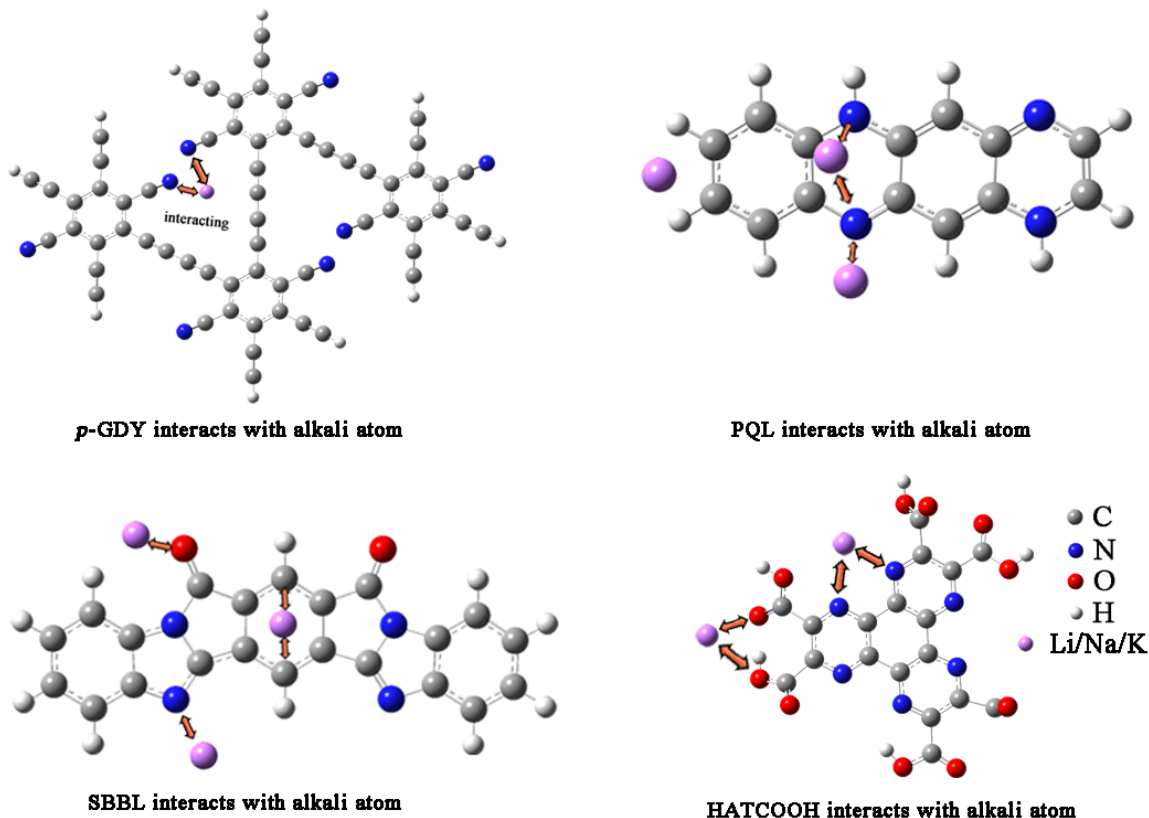


Figure 2.1: Four points method for the calculation of the reorganization energy.

- **GDY and GDY derivatives**

For graphdiyne systems, the favorable adsorption sites are predicted and characterized by computing the adsorption energy, as detailed in Chapter 4. Based on the ranked adsorption sites, lithium ions were sequentially adsorbed onto the substrate, resulting in varying substrate capacities. Herein, the configurations (GDY, CN-GDY, *m*-CNGDY, and *p*-CNGDY) with the maximum lithium uptake were investigated to evaluate their capacities using the theoretical capacity equation. The inserted lithium significantly impacts the structural configuration, slightly distorting the cyano groups and breaking carbon-carbon bonds. Additionally, stacking behavior plays a vital role in structural stability. We investigated the stacking behavior by sliding the upper layer in different directions while constraining the bottom layer, thereby theoretically identifying the most stable configuration.

- **OCRPs system**

For the OCRPs, alkali cations were adsorbed onto the substrates (PQL tetramer and SBBL tetramer) to simulate battery operating conditions. The resulting configurations were analyzed using energy decomposition analysis (EDA) and Mulliken population analysis to elucidate the interaction mechanism between the cations and

the substrate, as shown in Chapter 5.

- **HATCOOH and its derivatives**

For the HATCOOH system, we investigated the interaction between alkali cations (Na^+ and K^+) and the HATCOOH molecule under deprotonation conditions, as relevant to sodium-ion and potassium-ion batteries. In addition to alkali cations, solvents and interaction mechanism between cations and anode materials play a crucial role in structural formation, leading to markedly different configurations. Consequently, the capacity, structural properties, and cycle life of these configurations differ significantly. This project is currently ongoing and details are discussed in Chapter 6.

Chapter 3: Computational Methodology

3.1 Methodology

In this contribution, we combined the Hartree – Fock (HF) method with density functional theory (DFT) to investigate the electrochemical properties. Regarding DFT, we employed standard DFT, unrestricted DFT (UDFT), and broken-symmetry DFT (BS-DFT) to probe the radical/diradical character of the systems, using the functionals: ω B97X-D, B3LYP, and M06-2X. The fractional occupation number weighted density (FOD), computed with ORCA, was used to assess electron correlation within the system. Reorganization energy (λ), a fundamental parameter in charge transfer theory, was adopted to quantify the activation barrier and thereby evaluate the electron transfer rate. For realistic models, energy decomposition analysis (EDA) provides detailed insights into the interactions between alkali metal cations and the substrate, as well as between two isolated fragments.

3.1.1 Hartree-Fock method

In computational physics and chemistry, the Hartree-Fock (HF) method is an approximate approach for determining the wavefunction and energy of a quantum many-body system in a stationary state. It dates back to the late 1920s and was developed following the discovery of the Schrödinger equation in 1926 [40].

Given the extreme complexity of atomic systems (comprising nuclei and electrons), the method introduces five major approximations to treat the many-body problem:

1. **Born-Oppenheimer approximation:** The full molecular wavefunction is a function of both electronic and nuclear coordinates. This approximation assumes that nuclei are fixed due to their much larger mass compared to electrons [41].
2. **Non-relativistic treatment:** Relativistic effects are neglected.
3. **Finite basis set expansion:** The variational wavefunction is expressed as a linear combination of a finite number of basis functions, which are typically chosen to be orthogonal. The basis set is assumed to be approximately complete.
4. **Single Slater determinant:** Each electronic state is represented by a single Slater determinant, an antisymmetrized product of one-electron wavefunctions (i.e., orbitals).
5. **Mean-field approximation:** Electron-electron interactions are treated in an average (mean-field) manner. Effects arising from deviations from this assumption are

neglected. These neglected effects are collectively referred to as *electron correlation*. However, the term "electron correlation" strictly encompasses both Coulomb correlation and Fermi correlation. The latter arises from electron exchange and is fully accounted for in the Hartree-Fock method. Thus, in this terminology, HF neglects only the *Coulomb correlation*. This neglect is a significant limitation, as it explains Hartree-Fock's inability to describe London dispersion forces.

Based on the above assumptions, the following equations are obtained:
Hamiltonian operator of the system:

$$H_{\text{total}} = T_n + H_e + H_{\text{mp}} = T_n + (T_e + V_{ne} + V_{ee} + V_{nn}) + H_{\text{mp}} \quad (3-1)$$

In this expression, T_n denotes the kinetic energy of the nuclei, H_e is the electronic Hamiltonian operator that accounts for the kinetic energy of the electrons and their mutual interactions, and H_{mp} describes many-particle coupling effects in the system, including Coulomb and repulsive contributions.

The electronic part H_e is expanded as follows: T_e represents the kinetic energy of the electrons, while V_{ne} , V_{ee} , and V_{nn} denote the electron-nucleus attraction, electron-electron repulsion, and nucleus-nucleus repulsion energies, respectively.

The Hartree-Fock eigenvalue equation is then given by:

$$\hat{H}_{\text{total}}\phi_i = E\phi_i \quad (3-2)$$

This framework enables a reasonably accurate description of molecular properties, including energy, optical response, and electronic structure.

However, within the Hartree-Fock method, the electron-electron interaction term V_{ee} neglects the instantaneous correlation between electrons. As a result, the Coulomb term only describes long-range electrostatic interactions and fails to capture the dynamic correlation (i.e., the tendency of electrons to avoid each other). Furthermore, the exchange term in V_{ee} accounts only for the non-classical correlation between electrons of the same spin (arising from the Pauli exclusion principle) and cannot describe Coulomb correlation between electrons with opposite spins ^[43]. For a more accurate description of the system, we turn to density functional theory, as discussed in the following section.

3.1.2 Density Functional Theory (DFT)

3.1.2.1 Hohenberg-Kohn theory

All physical properties of a ground-state many-electron system are uniquely determined by the electron density, which serves as the fundamental variable. This realization is achieved by applying the variational principle to minimize the energy functional of the electron density, thereby yielding the ground state of the system [44]. The theory is formulated for the non-uniform electron gas and comprises two fundamental theorems:

- (i) For a spin-unpolarized electron system, the external potential (i.e., the potential excluding electron-electron interactions) is uniquely determined, up to an additive constant, by the ground-state electron density.
- (ii) For a given external potential, the ground-state energy of the system corresponds to the global minimum of the energy functional [44].

Thus, the total energy functional of the system can be expressed as:

$$E[\rho] = \int V_{\text{ext}}(\mathbf{r})\rho(\mathbf{r}) d\mathbf{r} + T[\rho] + \frac{e^2}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' + E_{\text{xc}}[\rho], \quad (3-3)$$

where the terms on the right-hand side represent, in order: the electron-external field interaction energy, the kinetic energy of the non-interacting reference system, the classical Coulomb (Hartree) energy, and the exchange-correlation energy functional.

However, the exact form of the exchange - correlation functional $E_{\text{xc}}[\rho]$ remains unknown, necessitating approximations for practical applications.

3.1.2.2 Kohn-Sham equation

The Kohn-Sham method replaces an interacting many-body system—governed by a complex many-body Hamiltonian—with a fictitious non-interacting system that is easier to solve. Since there is no unique way to construct such a simpler system, Kohn and Sham introduced a specific ansatz: they assumed that the ground-state electron density of the original interacting system is identical to that of a carefully chosen non-interacting reference system [45].

The single-particle Schrödinger-like equations for this non-interacting system are exactly solvable, and all the many-body effects that are difficult to treat explicitly are encapsulated in the exchange-correlation functional. By solving these Kohn-Sham equations, one obtains the ground-state electron density and total energy of the original interacting system. The accuracy of the results is thus limited solely by the approximation employed for the exchange-correlation functional.

The Kohn-Sham energy functional is derived from the Hohenberg-Kohn theorems

and is expressed as:

$$E_{\text{KS}}[n] = T_s[n] + \int v_{\text{ext}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{\text{Hartree}}[n] + E_{\text{II}} + E_{\text{xc}}[n]. \quad (3-4)$$

Here, $v_{\text{ext}}(\mathbf{r})$ denotes the external potential arising from the nuclei and any applied external fields, and E_{II} represents the classical nucleus-nucleus repulsion energy. The sum of the Hartree term $E_{\text{Hartree}}[n]$ and the exchange-correlation term $E_{\text{xc}}[n]$ accounts for all electron-electron interactions beyond the mean-field level. By applying the Hohenberg-Kohn framework to the non-interacting reference system, the kinetic energy $T_s[n]$ is obtained as an explicit functional of the density.

Consequently, all exchange and correlation effects are contained exclusively in the exchange-correlation energy $E_{\text{xc}}[n]$. By comparing the total energy expressions of the Hohenberg-Kohn and Kohn-Sham formalisms, the exchange-correlation energy can be formally defined as ^[45]:

$$E_{\text{xc}}[n] = \langle \hat{T} \rangle - T_s[n] + \langle \hat{V}_{\text{ee}} \rangle - E_{\text{Hartree}}[n], \quad (3-5)$$

where $\langle \hat{T} \rangle$ and $\langle \hat{V}_{\text{ee}} \rangle$ are the exact kinetic and electron-electron interaction energies of the true interacting system, respectively.

Here, $[n]$ indicates that the quantity is a functional of the electron density $n(\mathbf{r})$. As evident from the equation above, $E_{\text{xc}}[n]$ must be a density functional because all terms on the right-hand side are functionals of $n(\mathbf{r})$. Physically, $E_{\text{xc}}[n]$ represents the difference between the true many-body kinetic and electron-electron interaction energies and those of the non-interacting Kohn-Sham reference system.

3.1.2.3 Broken symmetry DFT (BS-DFT)

Open-shell character is a very important property to describe and take into account, for both neutral and charged molecular systems showing radicaloid character (e.g., diradicals). However, standard DFT encounters fundamental difficulties in characterizing this issue, since DFT typically employs a single Slater determinant to describe the electronic wavefunction [46]. In our work, we introduced a methodology, namely broken-symmetry density functional theory (BS-DFT), to accurately describe the electrochemical properties of the molecular system.

Using restricted DFT methods directly can yield completely erroneous results, while unrestricted methods (UDFT) allow for different spatial orbitals for α and β electrons but still fail to directly obtain pure spin states, resulting in calculated energies that lack clear physical significance [47].

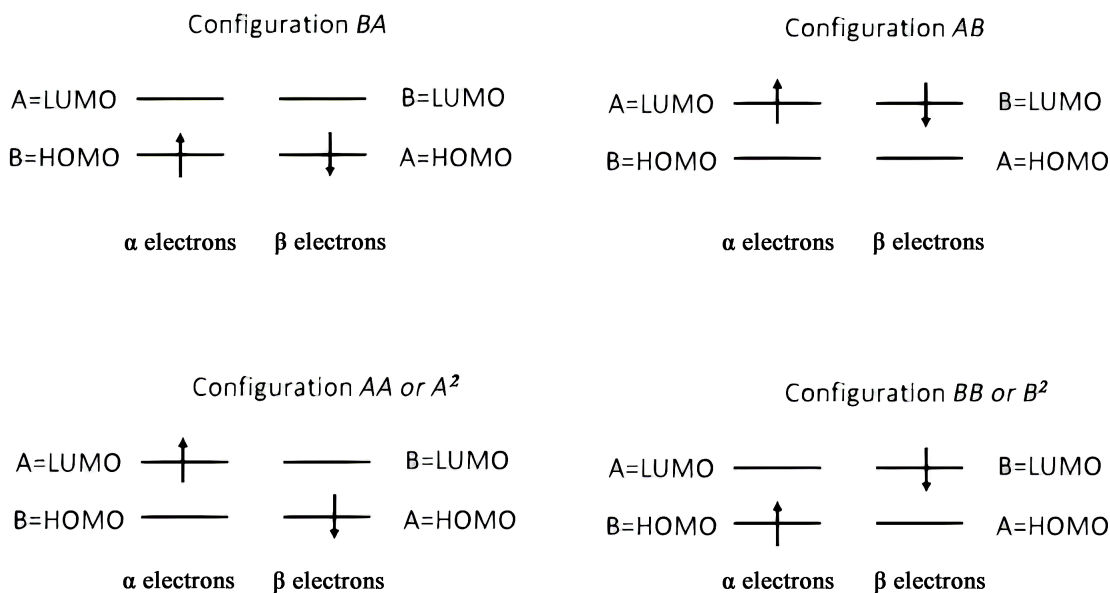


Figure 3.1: The 2e-2o model and localization case of α , β , HOMO, and LUMO orbitals [48].

BS-DFT is a very important method in the fields of computational chemistry and materials science [49], which focuses on the challenges faced by standard density functional theory in dealing with strongly correlated electron systems, particularly in antiferromagnetically coupled systems. This approach provides an efficient and reliable theoretical tool for studying molecular magnetism, bioinorganic chemistry, and magnetic materials.

For instance, for ferromagnetic states (e.g., when all spins are aligned upwards), the electronic structure can be accurately represented by a single determinant. In contrast, the situation is much more complex for antiferromagnetic states. The AFM state is es-

essentially a multireference state; for the simplest two-electron system, shown in Figure 3.1, it requires at least a linear combination of two determinants (the “up-down” and “down-up” configurations) to be accurately described, which exceeds the capabilities of standard DFT, as illustrated in Figure 3.1.

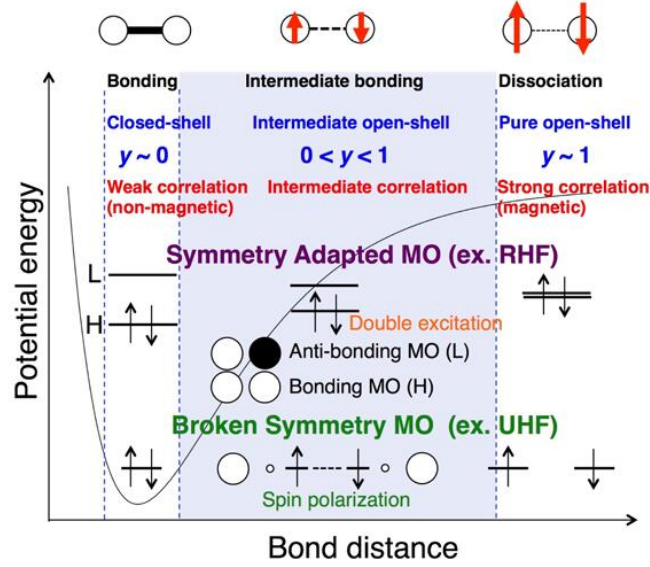


Figure 3.2: Schematic representation of the broken-symmetry approach in DFT [48].

For a deeper theoretical illustration, the key to describing molecular magnetism, namely, understanding the interactions between electron spins, is known as magnetic exchange interactions. For a system containing two magnetic centers (e.g., two transition metal ions, each with unpaired electrons), different spin states form depending on the arrangement of the electron spins. The simplest case involves the coupling of two spins S_A and S_B , whose energy difference can be described by the classical Heisenberg-Dirac-Van Vleck (HDVV) Hamiltonian [50]:

$$\hat{H} = -2J \mathbf{S}^A \cdot \mathbf{S}^B \quad (3-6)$$

where J denotes the magnetic exchange coupling constant. If $J > 0$, the system tends to form a ferromagnetic (FM) state with maximum total spin; if $J < 0$, the system tends to form an antiferromagnetic (AFM) state with minimum total spin. Accurately calculating the value of J is crucial for understanding and designing magnetic molecules.

All the approaches mentioned above aim to provide a more accurate description of ferromagnetically or antiferromagnetically coupled systems. In our work, we applied broken-symmetry density functional theory (BS-DFT) to OCRPs to explore static correlation effects in multireference systems within a single-reference framework by enforcing a spatially asymmetric distribution of spin orbitals (e.g., by breaking spin symmetry) [51],

particularly with respect to electron correlation and spin inhomogeneity [52]. For instance, Fazzi et al. described polarons in π -conjugated ladder-type polymers using BS-DFT, demonstrating that the BS-DFT scheme can yield reliable results in cases where a multiconfigurational approach would otherwise be required [39]. Here, the BS-DFT-based investigation reveals the diradical character of the system and electron unpairing behavior [53, 54], thus accurately describing the neutral states of PQL and SBBL.

3.1.2.4 Time dependent DFT

Time-dependent density functional theory (TDDFT) has become a vital method for investigating excited-state properties of molecular and extended systems due to its favorable balance between accuracy and computational efficiency. Unlike its ground-state counterpart, TDDFT allows for the treatment of time-dependent phenomena by introducing a time-dependent Kohn–Sham framework, in which the electronic density evolves under a time-dependent potential. This development was formalized by Runge and Gross in 1984, laying the theoretical foundation for TDDFT analogous to the Hohenberg–Kohn theorem in ground-state DFT [55]. The formalism enables the extraction of excitation energies via linear response theory, which has been widely implemented and applied in practical computations [56].

Classical TDDFT performs well only for (i) low-energy, (ii) single-electron excitations, (iii) those involving little or no charge transfer, and (iv) excitations that are not too delocalized [56], in terms of the exchange–correlation energy and exchange–correlation potential.

Here, Casida proposed a formula based on the Runge–Gross theorem and classical TDDFT, namely the Casida equation [57, 58], given below:

$$\left[\delta_{ij} \omega^2 - 4 \sqrt{\omega_i \omega_j} \langle \varphi_i | f_{xc} + v_{Coul} | \varphi_j \rangle \right] F_j = \omega^2 F_i \quad (3-7)$$

where ω_i are the Kohn–Sham orbital energy differences, f_{xc} is the exchange–correlation kernel, v_{Coul} is the Coulomb interaction operator, and F_i are the excitation amplitudes.

The Casida formulation allows TDDFT to compute excitation energies and optical spectra efficiently by transforming the problem into an eigenvalue equation. Herein, the relatively low computational cost of calculating vertical excitation energies and oscillator strengths for valence and Rydberg states of molecules has led to the widespread popularity of TDDFT in photochemistry, photovoltaics, and biological systems [59, 60].

Recently, applications of TDDFT have spanned from simulating UV/Vis spectra and excited-state absorption (ESA) to modeling nonadiabatic dynamics and photochemical reaction pathways [59]. Moreover, studies using TDDFT to calculate vertical transitions show strong correlation with experimental data [38].

In summary, TDDFT performs well for excited-state electronic structure calculations and can provide fairly accurate theoretical results in terms of both computational cost and accuracy.

3.1.2.5 Functionals

- ω B97X-D

The ω B97X-D functional is a range-separated hybrid density functional that includes empirical dispersion corrections, developed in 2008 by Chai [61]. ω is the range-separation parameter. B97 refers to the correlation functional developed by Becke in 1997. X and D denote 100% exact exchange at long range and Grimme’s dispersion (D) correction, respectively. The ω B97X-D functional combines two powerful concepts: long-range correction and an empirical dispersion correction, thus leading to a robust and widely applicable method that gives an accurate description from standard thermochemistry to non-covalent interactions.

Here, the mathematical form of the ω B97X-D exchange-correlation functional [61] is listed below:

$$E_{xc}^{\omega\text{B97X-D}} = E_x^{\text{SR-GGA}} + c_x E_x^{\text{SR-HF}} + E_x^{\text{LR-HF}} + E_c^{\text{GGA}} + E_D \quad (3-8)$$

As mentioned above, ω is the crucial range-separation parameter, defining the boundary between the short-range (SR) and long-range (LR) regimes. A small ω means the transition to 100% HF exchange happens at longer distances [61].

SR is the short-range exchange, shown below:

$$E_x^{\text{SR}} = E_x^{\text{SR-GGA}} + c_x E_x^{\text{SR-HF}} \quad (3-9)$$

$E_x^{\text{SR-GGA}}$ is based on a modified version of the B97 functional form [62]. The coefficient c_x determines the percentage of HF exchange included at $r_{12} = 0$. The value is approximately 15.9% in ω B97X-D [61].

LR is the long-range exchange, listed below:

$$E_x^{\text{LR}} = E_x^{\text{LR-HF}} \quad (3-10)$$

The second term from the partition represents the long-range interaction, which is treated with 100% exact HF exchange, critical for describing charge-transfer states, Rydberg states, and for eliminating the most pernicious effects of self-interaction error at long distances.

The last part of the equation is an empirical dispersion correction based on Grimme’s D2 model [63].

The ω B97X-D functional is widely applied and performs well for non-covalent interactions [64], thermochemistry and kinetics [61], as well as electronic excitations

and charge transfer [65]. For instance, the correct asymptotic potential in ω B97X-D largely resolves the issue that standard GGAs and global hybrids fail to describe charge-transfer (CT) excitations, often predicting their energies to be dramatically too low, thus providing a much more realistic description of CT states [65].

However, the ω B97X-D functional possesses heavy empiricism and potential transferability issues due to the large number of parameters fitted to specific datasets, leading to a risk that the functional may perform poorly for chemical systems fundamentally different from those in the training set [64]. The intricate interaction between the heavily parameterized GGA part and the separate dispersion term can sometimes lead to a cancellation of errors that produces a correct final energy but with an incorrect partitioning between different physical effects (e.g., exchange-repulsion vs. dispersion) [66], namely “right answer for the wrong reason.”

In summary, the ω B97X-D functional plays a pivotal role in the evolution of DFT. It demonstrated that by systematically combining physical insights (range separation) with empirical dispersion within a flexible and carefully optimized framework, it is possible to create a functional of remarkably broad utility and high accuracy. The functional largely delivers on the promise of a method that can reliably handle the energetics of both covalent and non-covalent systems.

- B3LYP

Becke’s three-parameter Lee–Yang–Parr (B3LYP) density functional [67], defined based on Becke’s insight for exchange and the correlation functional developed by Chengteh Lee, Weitao Yang, and Robert G. Parr [68, 69], is a hybrid functional that mixes exact exchange from Hartree–Fock theory with DFT exchange–correlation functionals, thus increasing the computational accuracy of a variety of molecular properties, including geometries, vibrational frequencies, and thermochemistry for main-group elements.

The form of the B3LYP exchange–correlation energy is shown below:

$$E_{\text{XC}}^{\text{B3LYP}} = E_{\text{XC}}^{\text{LSDA}} + a_0 \left(E_{\text{X}}^{\text{HF}} - E_{\text{X}}^{\text{LSDA}} \right) + a_X \Delta E_{\text{X}}^{\text{B88}} + a_C \Delta E_{\text{C}}^{\text{LYP}} \quad (3-11)$$

where $E_{\text{XC}}^{\text{LSDA}}$ is the local spin-density approximation exchange–correlation energy, E_{X}^{HF} is the exact Hartree–Fock exchange energy, $\Delta E_{\text{X}}^{\text{B88}}$ is the gradient correction to exchange [70], and $\Delta E_{\text{C}}^{\text{LYP}}$ is the gradient correction to correlation [69]. The standard B3LYP functional assigns the values 0.20, 0.72, and 0.81 to a_0 , a_X , and a_C , respectively, using semi-empirical fitting. $a_0 = 0.20$ means that 20% exact Hartree–Fock exchange is included, which provides a good balance between mitigating self-

interaction error and avoiding overestimation of reaction barriers that can occur with higher percentages of exact exchange [68].

Although B3LYP provides a relatively accurate description of electronic structure and chemical properties, it is known to systematically underestimate reaction energies [71], poorly describe van der Waals interactions [72], and incompletely eliminate the self-interaction error [73]. Therefore, other functionals or experimental data are often necessary to validate computational results.

- M06-2X

The M06-2X functional is a hybrid meta-generalized gradient approximation (meta-GGA) functional developed by the Truhlar group [zhao2002008m06]. It is specialized for demanding applications in main-group thermochemistry, kinetics, and non-covalent interactions [64], with the functional form shown below:

$$E_{\text{XC}}^{\text{M06-2X}} = \frac{X}{100} E_{\text{X}}^{\text{HF}} + \left(1 - \frac{X}{100}\right) E_{\text{X}}^{\text{M06-2X}} + E_{\text{C}}^{\text{M06-2X}} \quad (3-12)$$

where E_{X}^{HF} is the exact exchange energy from Hartree-Fock theory. The mixing parameter X is the percentage of HF exchange included, which equals 54 for the M06-2X functional. $E_{\text{X}}^{\text{M06-2X}}$ and $E_{\text{C}}^{\text{M06-2X}}$ are the meta-GGA exchange and correlation functionals, respectively.

Due to the 54% HF exchange, the functional is highly effective at reducing self-interaction error, leading to exceptionally accurate predictions of reaction barrier heights [zhao2002008m06, 64]. The combination of high accuracy for kinetics, thermochemistry, and non-covalent interactions (NCIs) makes the M06-2X functional particularly well suited for organic chemistry [74]. However, the high percentage of HF exchange can yield qualitatively incorrect results for geometries, spin states, and reaction energies in organometallic or coordination chemistry. Moreover, as a meta-GGA, M06-2X is more computationally demanding than GGAs or standard hybrid functionals.

In summary, the M06-2X functional provides top-tier accuracy for thermochemistry, kinetics, and non-covalent interactions, which is especially valuable in organic chemistry.

Herein, in our contribution, given the features mentioned above, we primarily adopted the ω B97X-D functional to comprehensively investigate the electrochemical properties of the OCRPs system. For support, the M06-2X and B3LYP functionals, both well-suited for describing polarons, molecular interactions, and covalent systems, were also employed. All

electrochemical properties computed using these different functionals were used to validate the rationality of the data and to avoid obtaining the “right answer for the wrong reason.”

3.2 Fractional Occupation Number Weighted Density

The Fractional Occupation Number Weighted Density (FOD, ρ^{FOD}) is a theoretical tool in computational chemistry designed to identify and analyze static electron correlation (SEC) effects in molecules. SEC arises from near-degenerate electronic states, leading to complex electronic structures that are challenging to describe with single-reference methods (e.g., Hartree-Fock or standard DFT) [75]. FOD provides a real-space visualization and quantification of "hot" electrons which are involved in strong correlation and chemical reactivity. The ρ^{FOD} is defined by the following equation:

$$\rho^{\text{FOD}}(\vec{r}) = \sum_i^N (\delta_1 - \delta_2 f_i) |\varphi_i(\vec{r})|^2 \quad (3-13)$$

where δ_1 and δ_2 are weighting parameters for fractionally occupied orbitals, and f_i denotes the fractional occupation numbers of molecular orbitals φ_i , obtained from finite-temperature density functional theory (FT-DFT) [76]. FOD relies on low-cost FT-DFT, suitable for large systems, in which electrons are distributed according to thermal equilibrium at an electronic temperature (T_{ele}). The quantity N^{FOD} , defined as the integral of ρ^{FOD} over all space, represents the number of "hot" electrons and is strongly correlated with the experimental and computational diradical character (y_0), thereby providing a computational measure of diradical character in materials [77], as discussed in the following subsection.

Grimme et al. explored this relationship by correlating N^{FOD} with y_{expt} or y_{comp} , which quantify diradical character via experimental or computational routes, respectively. The experimental diradical character (y_{expt}) is derived from two-photon absorption spectroscopy [78, 79] (see Equation 3-14), while the computed counterpart (y_{comp}) is based on unrestricted Hartree-Fock (UHF) natural orbital occupation numbers (UNOs) [80] (see Equation 3-15):

$$y_{\text{expt}} = 1 - \sqrt{1 - \left(\frac{E_{S_{1u}, S_{1g}} - E_{T_{1u}, S_{1g}}}{E_{S_{2g}, S_{1g}}} \right)^2} \quad (3-14)$$

and

$$y_{\text{comp}} = 1 - \frac{4(n_{\text{HOMO}} - n_{\text{LUMO}})}{4 + (n_{\text{HOMO}} - n_{\text{LUMO}})^2}. \quad (3-15)$$

The relevant excitation energies, $E_{S_{1u}, S_{1g}}$ and $E_{S_{2g}, S_{1g}}$, can be obtained from one- and two-photon absorption measurements, respectively. $E_{T_{1u}, S_{1g}}$ is accessible through phosphorescence and ESR measurements.

The conclusion is that the results for y_{expt} and y_{comp} are mutually consistent: for DBHZ1, $y_{\text{comp}} = 0.657$ and $N^{\text{FOD}} = 1.678$; for DBHZ2, $y_{\text{comp}} = 0.780$ and $N^{\text{FOD}} = 1.937$ [77]. Thus, the fractional occupation number weighted density (FOD) is employed

in this work as a tool to gauge diradical character in the characterization of materials.

3.3 Energy decomposition analysis

Energy decomposition analysis plays a vital role in quantum chemical analysis and is often based on various molecular force fields (FFs) [81, 82]. In FFs, non-bonded interactions consist of electrostatic and van der Waals contributions [83], with the latter further divided into repulsive and dispersion components. Most force fields employ a pairwise potential form to describe these interactions, electrostatics, repulsion, and dispersion, as outlined below.

The electrostatic interaction is given by:

$$E_{AB}^{\text{ele}} = \frac{q_A q_B}{r_{AB}} \quad (3-16)$$

The van der Waals interaction is expressed as:

$$E_{AB}^{\text{vdW}} = E_{AB}^{\text{rep}} + E_{AB}^{\text{disp}} \quad (3-17)$$

where the repulsive and dispersion terms are modeled using the Lennard-Jones 12-6 potential:

$$E_{AB}^{\text{rep}} = \epsilon_{AB} \left(\frac{R_{AB}^0}{r_{AB}} \right)^{12}, \quad (3-18)$$

$$E_{AB}^{\text{disp}} = -2\epsilon_{AB} \left(\frac{R_{AB}^0}{r_{AB}} \right)^6. \quad (3-19)$$

Here, A and B denote atomic indices, q represents the atomic partial charge, r_{AB} is the interatomic distance, ϵ_{AB} is the depth of the van der Waals potential well, and R_{AB}^0 is the equilibrium (non-bonded) distance at which the van der Waals interaction energy equals $-\epsilon_{AB}$ (i.e., the potential well minimum).

In molecular force fields, the parameters ϵ and R^0 are assigned based on atom types, which are defined according to the chemical environment of each atom. Most force fields define van der Waals parameters per atom type, and the effective parameters for an A - B pair are typically obtained via mixing rules.

For example, the Universal Force Field (UFF) uses geometric averaging for both parameters:

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}, \quad (3-20)$$

$$R_{AB}^0 = \sqrt{R_A^0 R_B^0}. \quad (3-21)$$

In contrast, the AMBER and GAFF force fields apply the same geometric mean for ϵ but define a non-bonded radius parameter R^* for each atom type. The equilibrium

distance R_{AB}^0 is then computed as the sum of the individual atomic radii:

$$\epsilon_{AB} = \sqrt{\epsilon_A \epsilon_B}, \quad (3-22)$$

$$R_{AB}^0 = R_A^* + R_B^*. \quad (3-23)$$

As shown in the equations above, calculating the nonbonded interaction energy between atoms is straightforward. To compute the nonbonded interaction between two molecular fragments, one simply sums the pairwise nonbonded interactions between all atoms in the respective fragments. This constitutes the principle of energy decomposition based on force fields.

The atomic charges used in such an energy decomposition must accurately reproduce the electrostatic potential near the van der Waals surface of the molecule; otherwise, the electrostatic interactions between fragments cannot be reliably estimated from atomic charges. Therefore, the preferred charges are those fitted to the electrostatic potential, the most common being Merz-Kollman (MK) and CHelpG charges [84].

Regarding the choice of force field for energy decomposition, AMBER or GAFF [85] are well suited for organic systems. Although the atom type nomenclatures differ between the two (a notable distinction being that AMBER uses uppercase labels while GAFF uses lowercase [85]), the van der Waals parameters in GAFF are largely inherited from AMBER. The primary differences lie in the bonded parameters; thus, either force field is acceptable for nonbonded energy decomposition.

Although Multiwfn’s energy decomposition also supports the Universal Force Field (UFF), its use is generally discouraged for this purpose. As demonstrated in the example below, UFF tends to grossly overestimate repulsive (Pauli) interactions, even for chemically reasonable structures, sometimes yielding positive total intermolecular interaction energies for systems that are inherently stable. While this issue can be partially mitigated by optimizing the geometry with UFF [86], the resulting energy decomposition is still inferior to that obtained with AMBER or GAFF. This is because UFF-optimized geometries of weakly interacting systems are often suboptimal. Nevertheless, UFF has the significant advantage of supporting a very broad range of elements, covering nearly the entire periodic table [86].

The geometries used for energy decomposition should be optimized at a reliable quantum chemical level. If derived from X-ray crystallographic data, they should undergo partial optimization. Specifically, hydrogen atom positions should be optimized while freezing the coordinates of the heavier atoms, whose positions are often determined empirically and may lack high accuracy.

In this work, energy decomposition analysis is employed in Chapter 4 (interlayer

interactions in graphdiyne) and Chapter 5 (alkali metals interacting with PQL and SBBL substrates) to thoroughly characterize the intermolecular interaction behavior in these systems.

3.4 Electron transfer theory

Chemical reactions are described by the motion of reactant atoms on a potential energy surface, which represents the electronic energy of the entire system plotted against the positions of all atoms. For a reaction like



the potential energy function can be plotted as constant-energy contours in a space defined by relevant relative coordinates.

Reacting systems start in the “valley of the reactants” on the potential energy contour plot. When they have sufficient energy, they can cross the “mountain pass” (saddle-point region), which is associated with the “transition state” of the reaction [87], shown in Figure 3.3. The line separating systems that flow into the reactants’ valley from those that flow into the products’ valley represents the transition state.

In transition state theory, a quasi-equilibrium between the transition state and the reactant is often postulated, and the reaction rate is calculated using equilibrium statistical mechanics [88]. Eugene Wigner provided a fundamental dynamical basis for this, stating that the quasi-equilibrium follows as a dynamical consequence if the reacting system’s trajectories do not recross the transition state and the reactants’ distribution is a Boltzmann one [89].

In practice, transition state theory is generalized to include more coordinates. When quantum mechanical tunneling through the potential energy barrier occurs, as in some H-transfer reactions at low energies, the treatment of the transition state region needs refinement due to the lack of “dynamical separability” of motions. Hydrogen transfer reactions involve the transfer of a hydrogen atom (H) from one molecule or ion to another. They hold great significance in chemistry and are often described by transition state theory in terms of their reaction processes.

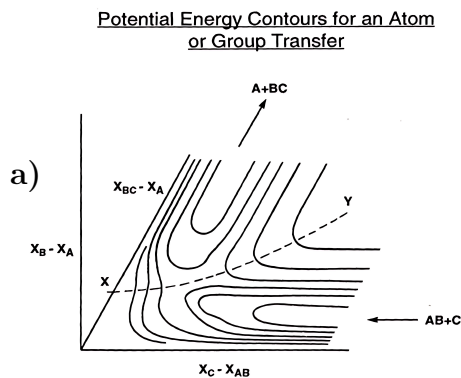


Figure 3.3: Potential energy contours for reaction $AB + C \rightarrow A + BC$.

Aiming to explore the energy barrier in the absence of external influences such as solvent or light effects, Marcus provided the primary formula listed below [90]:

$$k = A \exp \left\{ \frac{-\Delta G^*}{k_B T} \right\} \quad (3-25)$$

and

$$\Delta G^* = \frac{\lambda}{4} \left\{ 1 + \frac{\Delta G^0}{\lambda} \right\}^2 \quad (3-26)$$

where ΔG^0 is the standard free energy of reaction, and λ is a “reorganization term”.

3.4.1 Intramolecular reorganization energy

Here we shift our attention to the reorganization term, which can evaluate the electronic transfer rate of π -conjugated polymers. The reorganization energy is classified as inner and outer contributions. Inner (intramolecular) reorganization arises from changes in the equilibrium geometry of the donor (D) and acceptor (A) sites consecutive to the gain or loss of electronic charge upon electron transfer (ET). The outer reorganization energy results from the electronic and nuclear polarization/relaxation of the surrounding medium [91]. Also, it is worth emphasizing that owing to the weak van der Waals interactions between organic molecules, the division of reorganization energy into intermolecular and intramolecular components remains largely valid, even in the case of molecular crystals [22]. In our work, we stress the inner (intramolecular) reorganization energy. To describe the intramolecular reorganization energy, the system acceptor case illustration is shown in Figure 3.4.

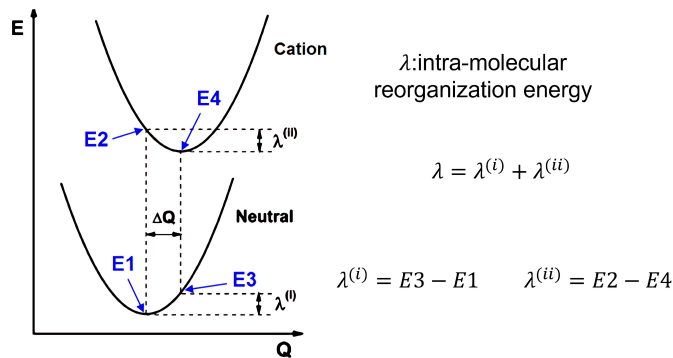


Figure 3.4: Illustration of intramolecular reorganization energy calculation.

E_1 and E_2 are the neutral state energy and cationic state energies of the donor/acceptor, respectively. E_3 and E_4 are the stable cationic state energy and the vertical transition energy of the stable cationic state, respectively.

The reorganization energy is strongly correlated to the electron transfer rate, shown

in Equation 3-27, especially for organic conjugated polymers. The lower the reorganization energy is, the faster the transfer rate is.

$$k = \frac{2\pi}{\hbar} |V_{if}|^2 \sqrt{\frac{1}{4\pi k_B T \lambda}} \exp \left[-\frac{(\Delta G^0 + \lambda)^2}{4\lambda k_B T} \right] \quad (3-27)$$

One notes that E_1 , E_2 , E_3 , and E_4 are the stable states computed by standard DFT and unrestricted DFT. However, once the BS-DFT solution is observed, the most stable states may change, emphasizing the importance of applying BS-DFT to the system, as shown in Figure 3.5.

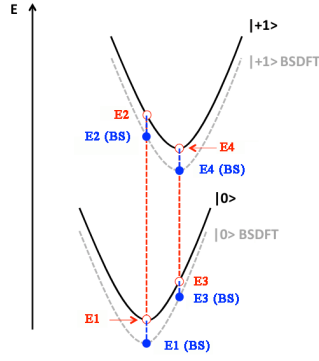


Figure 3.5: Four points method revisited in presence of BS points.

As we can see from Figure 3.5, the energies $E_{1\sim 4}$ (red label) and the energies $E_{1\sim 4}$ (BS) (blue label) are calculated by standard DFT and BS-DFT, respectively. A large energy difference was shown, thus strongly impacting the reorganization energy, which indirectly demonstrates the significance of adopting BS-DFT. Given the more accurate description for the reorganization energy of the system charge/discharge states, the deformation process of the polaron and bipolaron can be clearer, since reorganization energy influences the polaron deformation to some extent due to that low reorganization energy can easily lead to polaron deformation [92].

3.5.1 β measuring tool in multi-reference configuration interaction

Diradical properties have attracted remarkable attention over decades, as they strongly influence structural stability and unique electronic properties, such as narrow singlet–triplet gaps and high charge carrier mobilities in extended π -electron systems (EES) [48, 93–95]. Therefore, the investigation of diradical character is crucial for understanding and tuning the electrochemical properties of materials. A diradical system is defined as an even-electron molecular entity possessing two (possibly delocalized) radical centers that behave nearly independently [96, 97]. A schematic quantum-mechanical description of singlet and triplet states for such a system is shown in Figure 3.6.

$$\begin{array}{c}
 \varphi_2 \uparrow \\
 \hline
 \varphi_1 \uparrow
 \end{array}
 \quad \Bigg| \quad
 \left[\begin{array}{c} \varphi_2 \downarrow \\ \hline \varphi_1 \uparrow \end{array} \right] - \left[\begin{array}{c} \varphi_2 \uparrow \\ \hline \varphi_1 \downarrow \end{array} \right] = \left[\begin{array}{c} \chi_- \\ \hline \chi_+ \uparrow \downarrow \end{array} \right] - \left[\begin{array}{c} \chi_- \\ \hline \chi_+ \uparrow \downarrow \end{array} \right]$$

$$\chi_{\pm} = (\varphi_1 \pm \varphi_2) / \sqrt{2}$$

$${}^3\Psi = |\varphi_1 \varphi_2\rangle \quad {}^1\Psi = (|\varphi_1 \overline{\varphi_2}\rangle - |\overline{\varphi_1} \varphi_2\rangle) / \sqrt{2} = (|\chi_+ \overline{\chi_-}\rangle - |\chi_- \overline{\chi_+}\rangle) / \sqrt{2}$$

Figure 3.6: Triplet and singlet wavefunctions of two unpaired electrons occupying two different spatial orbitals, where arrows indicate the spin components.

In this schematic diagram, the triplet and singlet spin states are given by

$$^3\Psi = |\varphi_1 \uparrow \varphi_2 \uparrow\rangle, \quad (3-28)$$

and

$$^1\Psi = \frac{1}{\sqrt{2}} (|\varphi_1 \uparrow \varphi_2 \downarrow\rangle - |\varphi_1 \downarrow \varphi_2 \uparrow\rangle), \quad (3-29)$$

respectively, where the arrows $\uparrow$ and $\downarrow$ denote the spin-up and spin-down components of the spatial orbitals φ_k .

Following the orbital transformation illustrated in [Figure 3.6](#), the singlet state can equivalently be expressed in terms of the symmetric and antisymmetric spatial orbitals

$$\chi_{\pm} = \frac{\varphi_1 \pm \varphi_2}{\sqrt{2}}, \quad (3-30)$$

leading to the following representation of the singlet wavefunction [98]:

$$^1\Psi = \frac{1}{\sqrt{2}}(|\chi_+ \uparrow \chi_+ \downarrow\rangle - |\chi_- \uparrow \chi_- \downarrow\rangle), \quad (3-31)$$

where $\chi_{\pm}$ denote spatial orbitals and the arrows explicitly indicate the spin components.

Within the framework of multireference configuration interaction (MRCI), the singlet wavefunction can be written as a normalized linear combination of closed-shell and open-shell configurations,

$$\Psi = \frac{c_1 |\chi_+ \uparrow \chi_+ \downarrow\rangle - c_2 |\chi_- \uparrow \chi_- \downarrow\rangle}{\sqrt{c_1^2 + c_2^2}}, \quad (3-32)$$

where $c_1 > c_2$. Here, c_1 corresponds to the closed-shell configuration, whereas c_2 represents the diradical (open-shell) configuration. The diradical character is quantified by the index

$$\beta = \frac{2c_2^2}{c_1^2 + c_2^2}, \quad (3-33)$$

where $\beta = 0$ ($c_2 = 0$) indicates a pure closed-shell system and $\beta = 1$ corresponds to an ideal diradical.

3.5.2 y_0 diradical character

The y_0 index is a quantitative measure of diradical character, developed to evaluate the open-shell singlet nature of molecular systems within a computationally efficient framework. Originally formulated in the context of spin-unrestricted Hartree–Fock (UHF) or unrestricted DFT (UDFT) calculations [99, 100], it offers a simple and effective way to estimate the extent of electron pairing or unpairing using natural orbital occupations.

The derivation of y_0 stems from the two-electron-in-two-orbital (2e–2o) model, where a diradical ground state can be described as a mixture of closed-shell and biradical configurations [101, 102]. In practice, the y_0 value is computed from the occupation numbers of natural orbitals obtained from UHF or UDFT solutions, using the following formula:

$$y_i^{\text{PUHF}} = 1 - \frac{2T_i}{1 + T_i^2} \quad (3-34)$$

$$T_i = \frac{n_{\text{HONO}-i} - n_{\text{LUNO}+i}}{2} \quad (3-35)$$

where n_{HONO} and n_{LUNO} are the occupation numbers of the highest occupied and lowest unoccupied natural orbitals, respectively. The superscript PUHF stands for Projected Unrestricted Hartree–Fock, which utilizes a spin projection technique to avoid the spin-contaminated part [103]. When the two frontier orbitals are fully occupied and unoccupied (as in closed-shell systems), $T_0 = 1$ and $y_0 = 0$. Conversely, when both are half-occupied (as in ideal diradicals), $T_0 = 0$ and $y_0 = 1$.

The y_0 index provides a continuous scale from 0 to 1, enabling researchers to judge the diradical character of molecules. It is particularly advantageous for large π -conjugated systems [100, 104], where high-level multireference methods are computationally prohibitive.

Moreover, it correlates with HOMO–LUMO gaps and singlet–triplet energy differences [\[101\]](#), making it a useful diagnostic in materials design and theoretical studies of diradicals.

Chapter 4: Tailoring the Electronic Structure and Properties of Graphdiyne by Cyano Groups

4.1 Electrochemistry Properties Investigation

The electrochemical properties strongly impact the configuration and performance of materials. Within the electrochemical properties, energy band features characterize the structure, thus giving an electrical conductivity property distinction for the system. In this work, we calculate the electronic structure of GDY derivatives, cyano group doping in GDY, namely GDY, CN-GDY, *m*-CNGDY, and *p*-CNGDY, showing dissimilar bands and band gaps, depicted in Figure 4.1 (e–h). A small band gap means the electron is easily excited to the conduction band, therefore enhancing the conducting ability. Whereas, a large band gap effectively hinders electron excitation, thus reducing conducting ability.

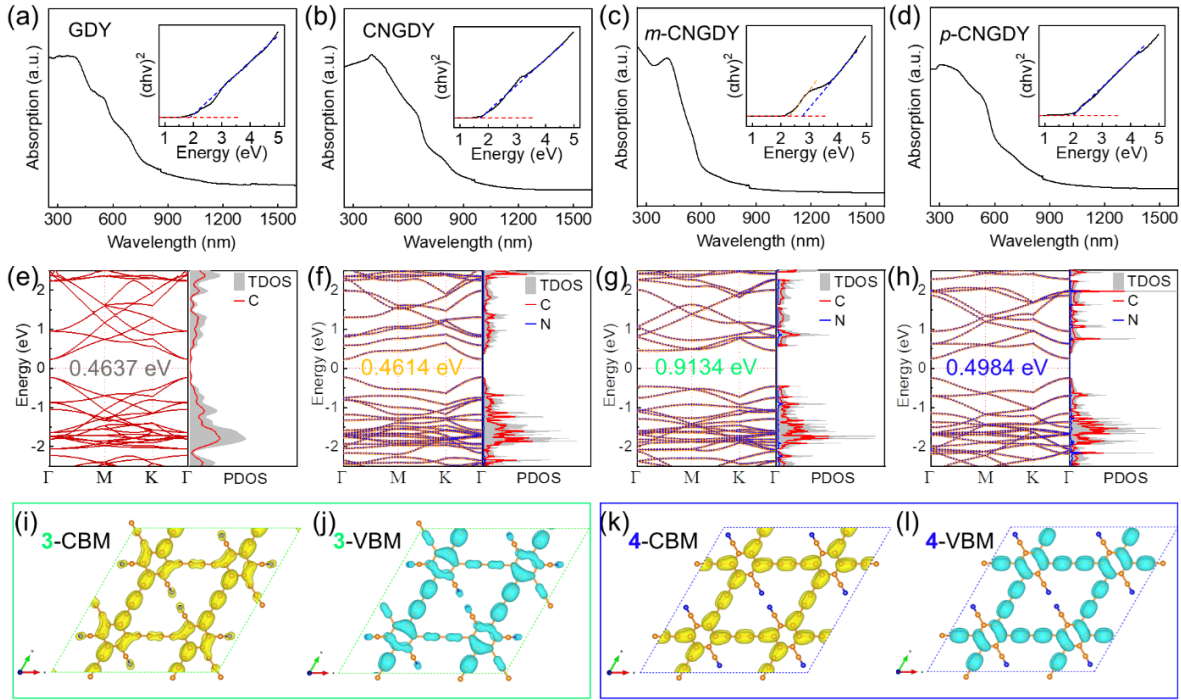


Figure 4.1: (a–d) show UV–vis absorption spectra with plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (inset). GDY derivatives' band gaps (e–h) and CBM and VBM of *m*-CNGDY and *p*-CNGDY (i–l).

As observed in Figure 4.1 (e–h), the direct electronic band gaps (energy difference between the conduction and valence bands at $k = 0$) for the GDY, CN-GDY, *m*-CNGDY, and *p*-CNGDY monolayers were calculated to be 0.4637, 0.4614, 0.9134, and 0.4984 eV, respectively. Although the cyano group possesses strong electron-withdrawing ability, the band gap still maintains a relatively constant width, indicating that the band gap depends not only on the cyano group with strong electron-withdrawing ability, but also

on the doping position and number of cyano groups. For a deeper understanding of the mechanism, we adopt the electron density of the conduction band minimum (CBM) and valence band maximum (VBM) and the projected density of states. Hereby, as depicted in Figure 4.1 (e–h), the doping N was found to change the distribution of electrons around C atoms, leading to promotion of the separation of electron–hole pairs. Based on the conclusion above, a detailed explanation is given to illustrate the electrochemical properties and provide an accurate description of the differing band gaps.

4.2 Cation/GDY interaction mechanism

The interaction behavior plays a vital role in electrodes while batteries function, thus influencing the performance, such as charge transfer, battery capacity, battery cycle life and so on. Here, firstly, we explore the favorable alkali metal adsorbing site by using the adsorption energy, defined as $E_{\text{ad}} = E_{\text{Li/substrate}} - E_{\text{Li}} - E_{\text{substrate}}$. The $E_{\text{Li/substrate}}$ is the energy of the adsorbed metal–substrate system, and E_{Li} and $E_{\text{substrate}}$ are the energies of isolated lithium and the substrate structure, respectively. Firstly, we need to distinguish the adsorption type, which includes physical adsorption and chemical adsorption, judging by the amount of electron transfer, here defined as N_{elect} . Generally, if $N_{\text{elect}} < 0.2e$, the adsorption type is physical adsorption, indicating that the unstable adsorption is easily prone to desorption when external conditions (temperature, pressure, solvents, stress, etc.) change. If $N_{\text{elect}} > 0.5e$, it is chemical adsorption empirically, demonstrating the adsorbing site during charging or discharging. Here, we check the amount of electron transfer by investigating the system containing lithium and substrate, shown in Figure 4.2 (a–d), validating the chemical adsorption.

As for the battery electrode interacting with cations (Li^+ , Na^+ , K^+), the cations hardly escape from the electrode substrate due to the strong chemical adsorption energy. Here, we utilize the adsorption equation to calculate the adsorption energy of the site, including: top site 1 of the benzene ring; side site 2 close to the carbon chain; side site 3 on the top of the carbon chain; side site 4 around the cyano group; and side site 5, which is located at the center between two cyano groups, especially for *m*-CNGDY and *p*-CNGDY, depicted in Figure 4.2. The favorable adsorbing site is side site 5 (adsorption energy: -1.829 eV) due to the strong electron affinity of the cyano group. The second favorable adsorbing site is side site 4 (adsorption energy: -1.581 eV), which is also close to the cyano group. Therefore, we simulated the electrode function as the battery works, where cations flow on the substrate and are trapped by specific sites that possess strong electron-accepting ability.

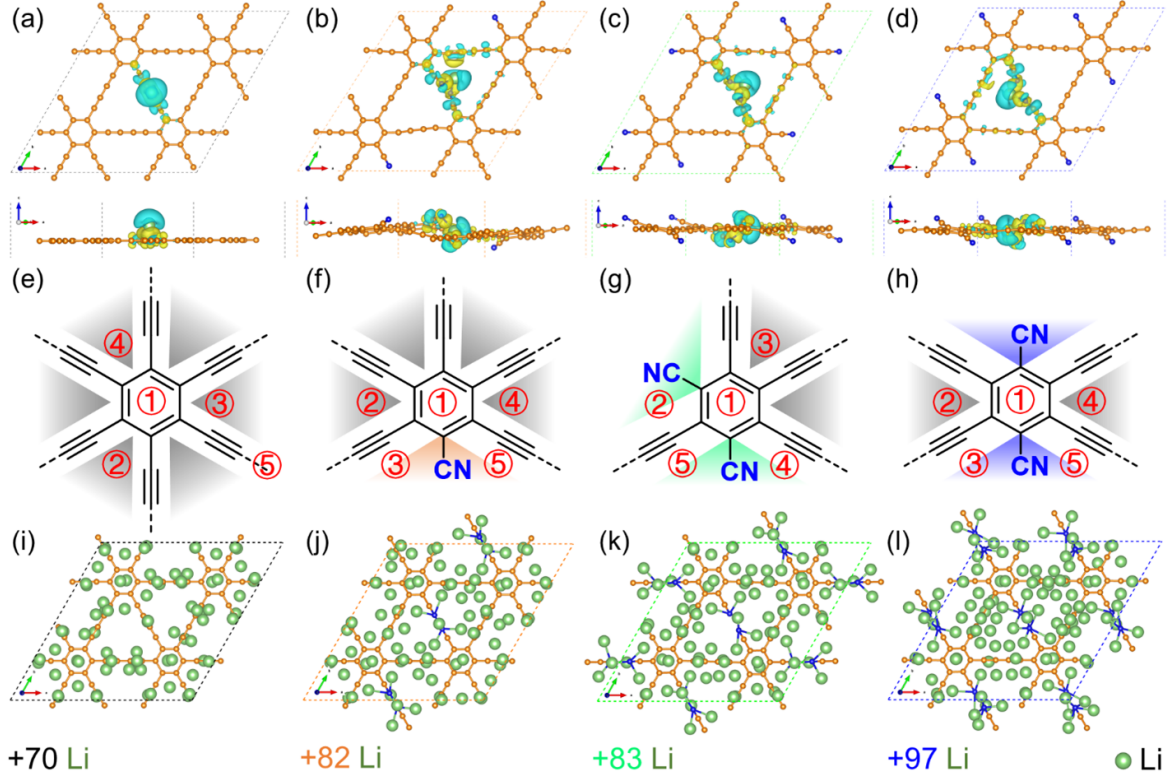


Figure 4.2: The adsorption behavior (a–d), adsorption scheme (e–h), and the theoretical capacity of GDY derivatives (GDY, CN-GDY, *m*-CNGDY, and *p*-CNGDY).

The capacity is another vital factor for the battery. In terms of the investigated lithium cation favorable site, lithium is orderly added to the substrate GDY derivatives. Based on the configurations, we compute the capacity of the battery electrode by using the theoretical maximum specific capacity equation:

$$C = \frac{n_{\max} z F}{M_{\text{substrate}}}.$$

Here, $n_{\max}$ denotes the maximum number of cations loaded; z is the valence number of Li cations; F is the Faraday constant (26.801 Ah g^{-1}); and $M_{\text{substrate}}$ is the mass of the substrate. As lithium is added, the integrity of the structure must be guaranteed to the greatest extent. The maximum theoretical lithium storage capacities of the GDY derivatives (GDY, CN-GDY, *m*-CNGDY, and *p*-CNGDY) are 2171.4, 2520.2, 2527.8, and 2954.0 Ah g^{-1} , respectively. All the theoretical capacity trends are in agreement with the experimental data (546.4 Ah g^{-1} for GDY, 861.5 Ah g^{-1} for CN-GDY, 1060.1 Ah g^{-1} for *m*-CNGDY, and 1224.2 Ah g^{-1} for *p*-CNGDY, measured under a current density of 10 A g^{-1} and a voltage window of 0.005–3 V). All the interaction mechanisms were explored to illustrate the interacting behaviors between the alkali metal cations and substrate materials, thus providing guidance for synthesis and doping in experiments.

4.3 Interlayer interaction investigation

For experimental comparison and stacking behavior exploration, we computationally simulate the stacking case with respect to GDY derivatives, shown in Figure 4.3. Here, we define three directions by the unit vectors **a**, **b**, and diagonal **c**. Along the different directions, by sliding the upper layer while constraining the bottom layer, the various configurations of the stacked structure are computed. Based on the method mentioned above, we observed the minimum energy of the configuration and figured out the most stable structure. Based on the structural energy values, the most stable configurations of the GDY derivatives (GDY, CN-GDY, *m*-CNGDY, and *p*-CNGDY) are shown in Figure 4.3 (a–d). The cyano group confers a huge impact on the structural stacking with respect to GDY, as observed, decreasing the interlayer gap. However, the trend is not linear as the number of doped cyano groups increases. The cyano group doping position also affects the interlayer gap, shown in Figure 4.3 (c–d), thus influencing the interlayer distance. Figure 4.3 (e–h), enlarged HRTEM images, illustrate the experimental interlayer gaps from HRTEM, which show good agreement with the theoretical interlayer gap trends.

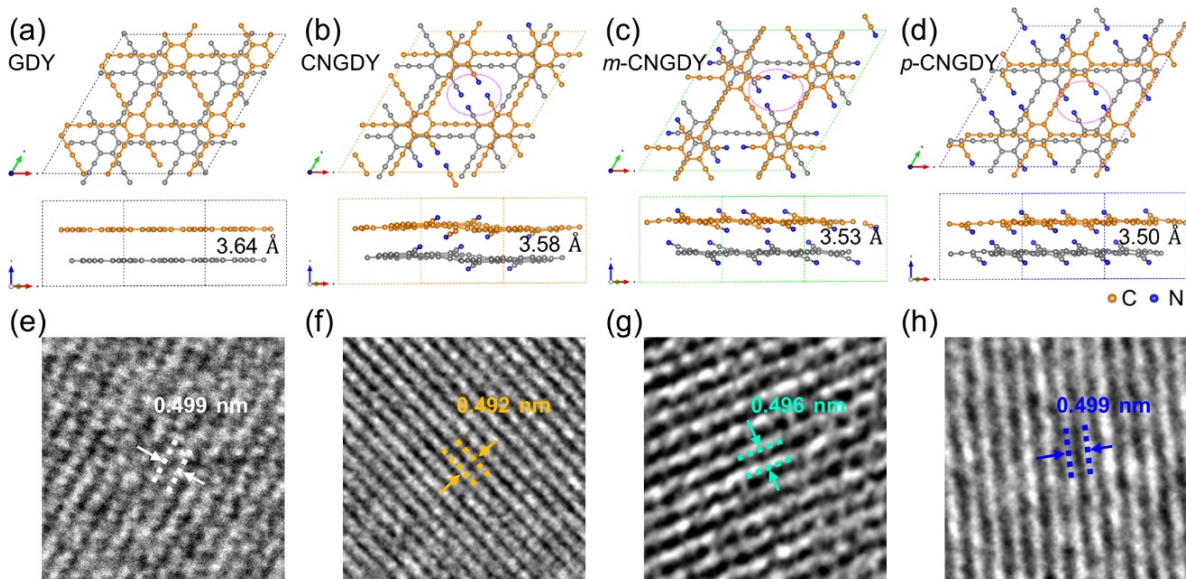


Figure 4.3: Optimal AB-type stacking positions and tested interplanar spacing of GDYs. (a–d) The most likely stacking states of samples 1–4 corresponding to the selected optimal stacking layer spacing, respectively. (e–h) Enlarged HRTEM images of the 1–4 crystal planes.

To deeply understand the stacking behavior, we utilize energy decomposition analysis (EDA), which includes the electrostatic energy, repulsion energy, and dispersion energy, by carrying out single-point DFT (B3LYP-D3/cc-pVTZ) calculations and force-field-based energy evaluation (UFF level) using Multiwfn to analyze an isolated large cluster. The

EDA shows that the (local) electrostatic contributions are very significant when CN groups are introduced at the *m*-CNGDY (3) and *p*-CNGDY (4) positions (electrostatic energy: $-223.20 \text{ kJ mol}^{-1}$ for *m*-CNGDY and $-46.84 \text{ kJ mol}^{-1}$ for *p*-CNGDY), thus inducing a shorter interlayer distance compared to the species GDY (1) and CN-GDY (2) (electrostatic energy: $-12.61 \text{ kJ mol}^{-1}$ for GDY and $20.01 \text{ kJ mol}^{-1}$ for CN-GDY), as observed. Here, the different effects of accurately adjusting the number and position of cyano groups to tune the stacking spacing of GDYs have been clearly reflected.

4.4 Manuscript I

All computational analyses in Publication I (Gao L, Wang S, Wang F, et al. Tailoring the Electronic Structure and Properties of Graphdiyne by Cyano Groups. *ACS Nano* **2024**, 18(44), 30368–30377.) were conducted by myself under the guidance of my supervisors. I wrote the initial manuscript draft and collaborated with the co-authors on subsequent revisions.

Tailoring the Electronic Structure and Properties of Graphdiyne by Cyano Groups

Lei Gao,[○] Shuailong Wang,[○] Fan Wang,[○] Ze Yang,^{*} Xiaodong Li, Jingchi Gao, Daniele Fazzi, Xiang Ye,^{*} Xuebin Wang, and Changshui Huang^{*}



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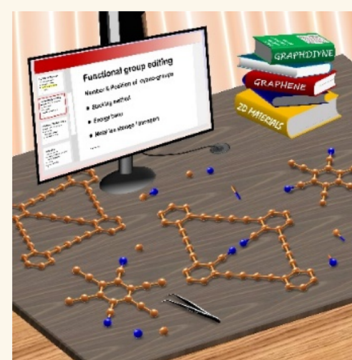
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Supporting Information

ABSTRACT: Two-dimensional (2D) materials, such as 2D carbon-based systems, have been recently the subject of intense studies, thanks to their optoelectronic properties and promising electronic performances. 2D carbon-based materials such as graphdiyne (GDY) represent an optimal platform for tuning the optoelectronic properties via precise chemical functionalization. Here, we report a synthetic strategy to precisely introduce cyano groups into the 2D GDY backbone in order to tune the electronic properties of GDY. Three kinds of cyano-modified GDY have been synthesized, namely, bearing one cyano group (CNGDY), two CN in meta (*m*-CNGDY), and two in para (*p*-CNGDY) positions. A variety of experimental data as well as first-principles calculations allowed us to elucidate the role of the cyano groups in tuning the structural and functional properties of GDYs. We found that an increase in the number of cyano groups reduces the interlayer spacing between GDY layers, increases the lithium adsorption amount, as well as impacts the lithium diffusion rate, while changes in meta- or para-position impact the energy band gap.

KEYWORDS: cyano groups, functional group editing, energy gap regulation, lithium-ion battery, graphdiyne



INTRODUCTION

Carbon-based materials are among the earliest and most important systems that human beings have studied and explored. The various hybrid forms of carbon greatly enrich the types of allotropes, bringing about different properties and applications. To meet the various needs of different stages of human development, scientists have never stopped exploring carbon materials, especially two-dimensional (2D) carbon materials. Typical 2D carbon materials, graphene¹ and graphdiyne^{2,3} (GDY), have been extensively studied in many fields such as chemistry, materials, energy, catalysis, medicine, sensing, and purification.^{4–17} There is also a wide variety of physical and chemical modification methods based on existing 2D carbon materials that are constantly emerging. Most of those methods are post-denaturation of the carbon skeleton, such as oxidation with strong acids, doping with heteroatoms, ball milling dispersion, *etc.* which are fast and straightforward.^{18–21} Dopants such as nitrogen, oxygen, boron, sulfur atoms, *etc.* have been reported to effectively regulate the properties of carbon materials, especially in the areas of catalysis and electrochemical energy storage.^{22–27} Among them, nitrogen doping is currently one of the most studied heteroatom doping methods to be adopted in enhancing the properties of carbon nanotubes, graphene, and graphdiyne.^{28,29} Generally, those doping methods are limited to surface structure modification or local defect generation and therefore

not easy to diffuse within the bulk of the materials. To produce uniform and controllable samples in large quantities, control over the synthesis procedure should be improved.

Another method is to perform a bottom-up approach, altering the electronic structure via accurate molecular reconstruction or heteroatom doping.^{30–33} For example, a series of two-dimension (2D) *N*-graphdiyne (*N*-GDY) nano-sheets with different numbers of nitrogen atoms on the benzene ring have been reported,³⁴ exhibiting that an increase in *N* content can enhance the hydrophilicity of GDY, thereby improving the metal-free photocatalysis used for coenzyme regeneration.^{35–38} Compared to heteroatom doping, adding functional groups with different electronegativity or conjugation properties to the GDY backbone offers a greater potential for structural manipulation, allowing for significant adjustments in charge density distribution, interlayer spacing, and morphology.³⁹ However, the introduction of functional groups imposes higher requirements for the synthesis and

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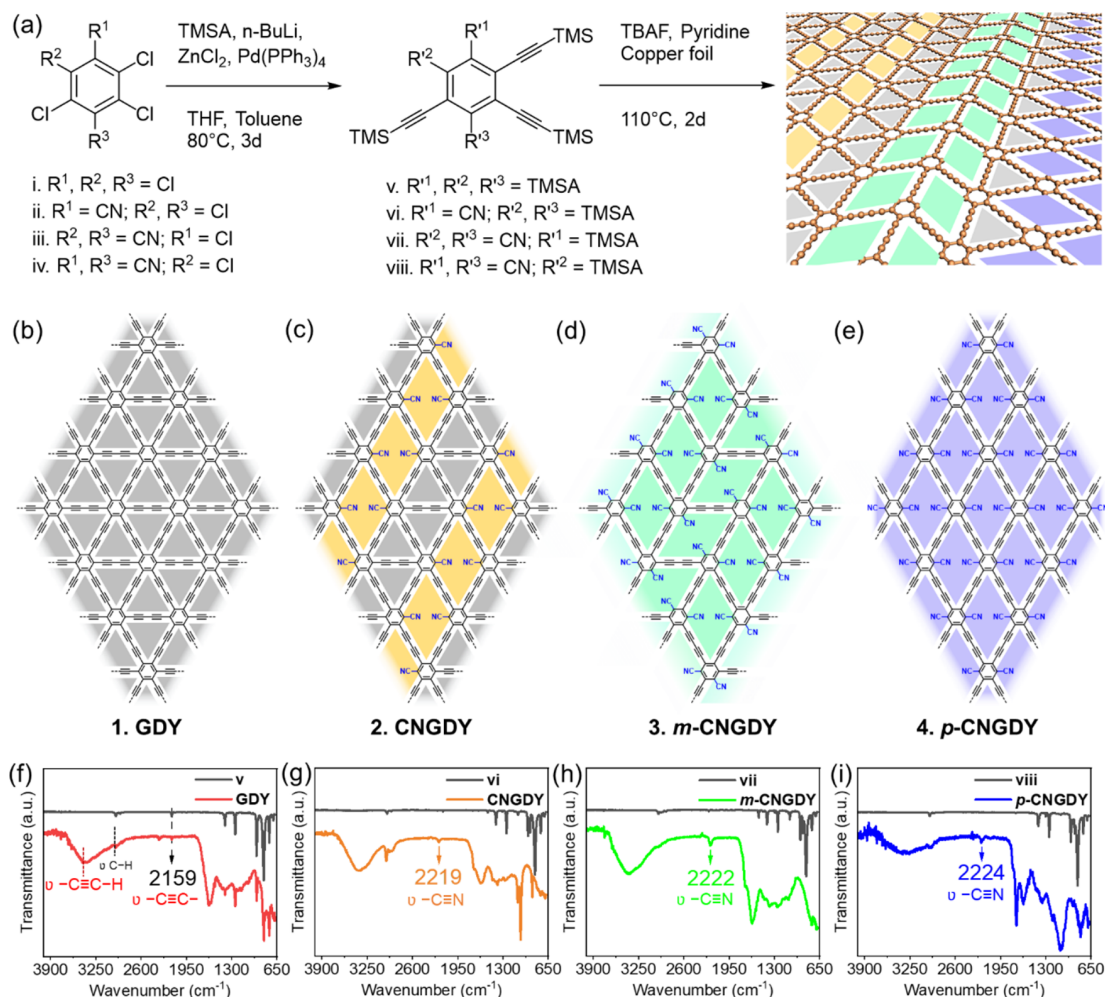


Figure 1. Synthesis and characterization of the series of GDYs. (a) Schematic of the synthetic route of GDY (1), CNGDY (2), m-CNGDY (3), and p-CNGDY (4). (b–e) Chemical structure of 1–4 repeating units, respectively. (f–i) FT-IR spectra of four precursor powders (v–viii) and their corresponding films of 1–4, respectively.

preparation process of carbon materials than doping procedures. The study of regulating GDY with different electron acceptor/donor groups (e.g., methyl, hydrogen, and cyano groups) displays that the microstructure, layer-to-layer spacing, and the morphology of GDY are related to the size of the functional group and the coplanarity between layers.⁴⁰ However, varying the number and the position of individual functional groups has a pronounced impact on the performance of GDYs, which have not been thoroughly investigated due to the challenges imposed by their synthesis. Herein, we developed a synthetic strategy to introduce strong electron acceptor cyano groups ($-CN$) into 2D GDY by precisely controlling their number and position, exhibiting a way to tailor the electronic structure and tune the optoelectronic properties of 2D carbon-based systems. The fine-tuning has been successfully achieved by varying the amount of cyano groups to replace acetylene groups at different positions on the precursor molecule, hexaethynylbenzene. Three GDY derivatives, namely with one cyano group (CNGDY), two cyano groups in meta (*m*-CNGDY), and two in para-position (*p*-CNGDY), were synthesized. The influence of changing the number and position of the cyano groups on the fundamental properties of GDY was systematically studied in combination with first-principles calculations. Experimental results and first-

principles calculations demonstrated that the planar morphology and interlayer spacing of GDY, as well as the optoelectronic properties, can be tuned by changing the position and number of cyano groups. Notably, when applied to the anode of lithium-ion batteries, even if the number of cyano groups in *m*-CNGDY was increased compared to that in CNGDY, the rate performance at high current density was not improved. *p*-CNGDY exhibited the best electrochemical performance, considering its comprehensive rate and long cycle performance. A high reversible capacity of 1264.1 mAh·g⁻¹ was achieved and well maintained at a current density of 20 mA·g⁻¹ after 100 cycles (tested for 350.8 days).

RESULTS AND DISCUSSION

Synthesis Method and Structural Characterizations.

Starting from a range of chlorides, as depicted in Figure 1a(i–iv) and drawing on the mature synthesis process of GDY, four precursors [Figure 1a(v–viii)], TMSA: (trimethylsilyl)-acetylene] were obtained: hexakis[(trimethylsilyl)ethynyl]benzene, cyanopentakis[(trimethylsilyl)ethynyl]benzene, meta-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene, and para-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene. As shown in Figures S1–S3, S5–S7, S9–S11, and S13–S15, the ¹H NMR, ¹³C NMR, and mass spectra indicate the successful

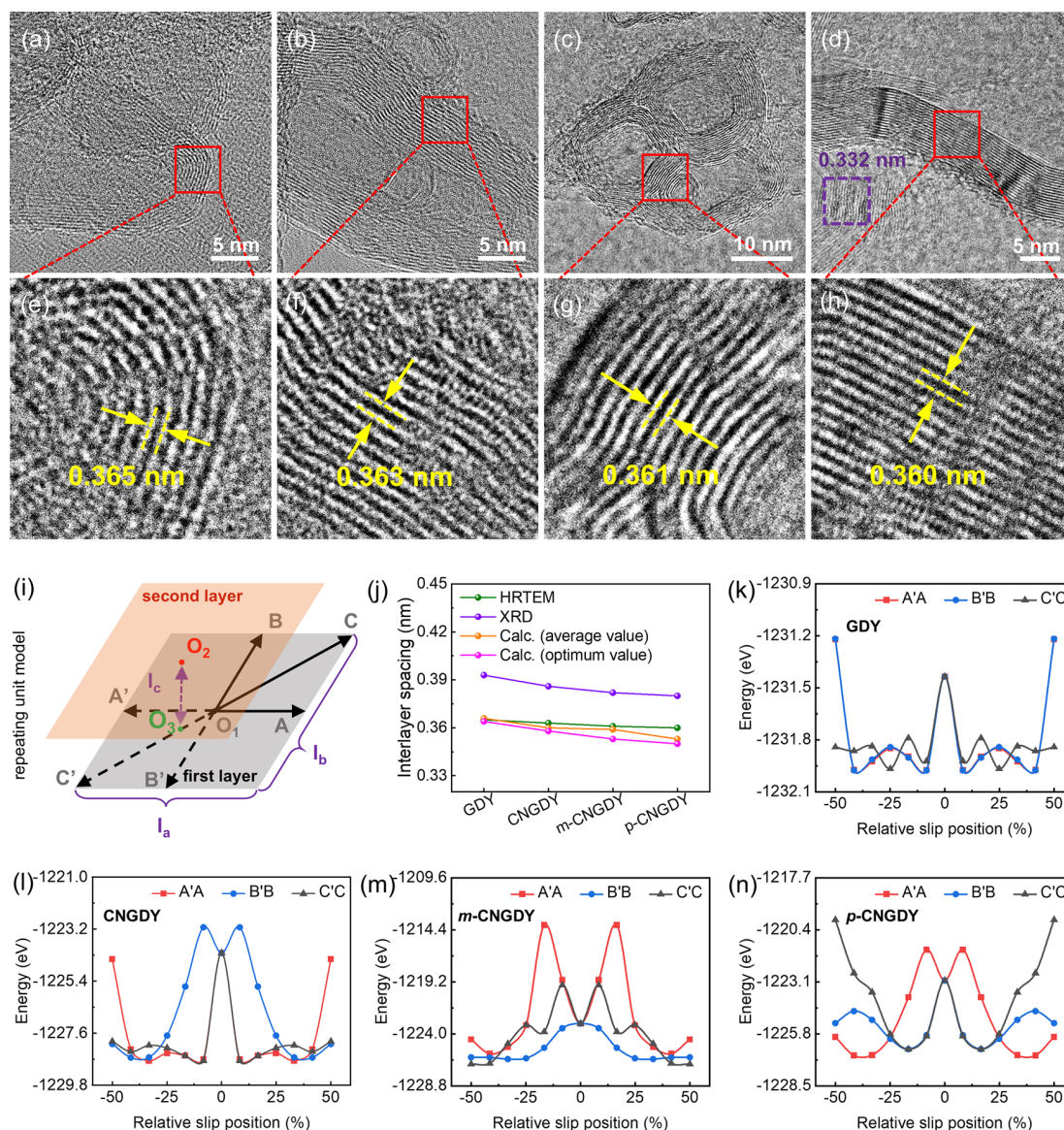


Figure 2. Layer spacing and theoretical stacking modes. (a–h) HRTEM images of GDY (1) (a, e), CNGDY (2) (b, f), m-CNGDY (3) (c, g), and p-CNGDY (4) (d, h). (i) Schematic diagram of the two-layer stacking model in cell units. (k–n) Computed total energy corresponding to different stacking positions of 1–4. (j) Experimental (HRTEM and XRD) and computational results about interlayer spacing for 1–4.

synthesis of all of the precursors. The tetrabutylammonium fluoride (TBAF) was used to remove the silane protective groups. After employing the copper foil as the template and catalyst for the coupling polymerization of the alkyne bond, the corresponding film products with different repeating unit structures (Figure 1b–e) were recorded as GDY (1), CNGDY (2), m-CNGDY (3), and p-CNGDY (4), respectively (see the Supporting Information for more details).

The low symmetry of precursor molecules caused by the substitution of a single cyano group for an alkyne bond leads to complex coupling modes in the actual acetylene polymerization process, resulting in multiple GDYs' configurations. Our previous work⁴⁰ had proved the composition and structure of CNGDY as shown in Figure 1c. While in Figure 1d, a cyano group was added in the meta position, the deprotection precursor molecule for m-CNGDY is axially symmetric. In contrast, the high central symmetry of precursors v and viii can greatly reduce their coupling diversity

(Figure 1b,e). Their precursors and corresponding films were characterized and compared by Fourier-transform infrared spectroscopy (FT-IR).^{41–43} The large infrared (IR) band at 3355–3412 cm^{-1} is assigned to terminal alkyne ($-\text{C}\equiv\text{C}-\text{H}$) groups in GDY (Figure 1f), CNGDY (Figure 1g), m-CNGDY (Figure 1h), or p-CNGDY (Figure 1i). GDY showed a band related to the terminal ethynyl group at 2159 cm^{-1} , while it may be hidden in 2–4 due to the increased proportion of the terminal cyano groups. The bands of 2219, 2222, and 2224 cm^{-1} were all assigned to the $-\text{C}\equiv\text{N}$ stretching in 2–4, respectively. Details and assignments of other peaks can be found in Figure S17. Raman spectrum is shown in Figure S25a. The characteristic peaks of these four GDYs assigned to acetylene bond appear at 2168, 2186, 2218, and 2223 cm^{-1} , respectively.⁴⁴ The D bands of GDY, CNGDY, m-CNGDY, and p-CNGDY are all located at 1369 cm^{-1} , representing the structural defect. Their G bands are located at 1553, 1577, 1567, and 1567 cm^{-1} , which correspond to the in-plane

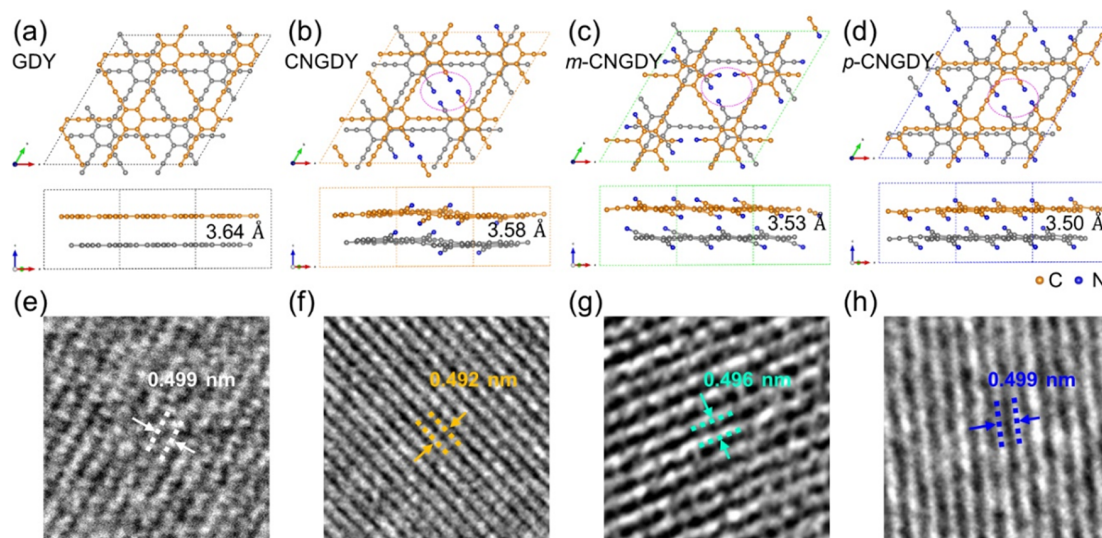


Figure 3. GDYs structures and crystal plane spacing. (a–d) DFT-optimized stacking positions of GDYs and interlayer distance. (e–h) Enlarged HRTEM images of 1–4 crystal planes.

stretching vibration of aromatic rings.⁴⁵ The thermogravimetry analysis (TGA) results of 1–4 (Figure S25b) showed that their thermal stability follows the sequence: 2 > 4 > 3 > 1.

Like GDY and CNGDY, *m*-CNGDY (Figure S18e) and *p*-CNGDY (Figure S18i) synthesized by the one-pot method are also centimeter-scale films. The root-mean-square roughness (R_q) and thickness of 1–4 films measured by AFM (Figure S19) are in the order 1 > 2 > 3 > 4. The surfaces of the films prepared by this low-temperature hydrothermal method are smoother, which can be directly reflected by the SEM image shown in Figure S20. It can be seen from the folds of the films that 1–4 presents a certain degree of flexibility and continuity. Transmission electron microscopy (TEM) images (Figure 2a–d) confirmed the layered 2D stacking details of 1–4. The High-resolution transmission electron microscopy (HRTEM) images clearly show the similar average layer spacing of 1–4: 0.365 nm for GDY (Figure 2e), 0.363 nm for CNGDY (Figure 2f), 0.361 nm for *m*-CNGDY (Figure 2g), and 0.360 nm of *p*-CNGDY (Figure 2h). Meanwhile, according to different peak angles of these four films in Figure S25c (GDY/CNGDY/*m*-CNGDY/*p*-CNGDY = 22.59, 23.02, 23.30, and 23.40°), the layer spacing order of 1–4 calculated by XRD diffraction (1 > 2 > 3 > 4) is consistent with the HRTEM result above.

Based on the comparison of HRTEM and X-ray diffraction (XRD) layer spacing results of 1–4, we found that the number of cyano groups and their relative positions have a prominent impact on the interlayer stacking of GDY-based networks. In order to evaluate the influence of cyano groups on the layer spacing and reduce the computational effort, we simplified first-principles calculations to study the stacking behaviors of 1–4 by considering two layers.

The two layers consisting of the repeating units of 1–4 are sketched in Figure 2i. Three directions are defined by the vectors *a*, *b*, and *c*, named O_1A , O_1B , and O_1C (bottom layer) and O_1A' , O_1B' , O_1C' (upper layer) for the upper layer. The rhombus side lengths were set to L_a and L_b , and L_c are the first (transparent gray rhombus) and second layer (transparent red rhombus) of 1–4 length, that is fixed as the distance measured by HRTEM (GDY: 0.365 nm; CNGDY: 0.363 nm; *m*-CNGDY: 0.361 nm; *p*-CNGDY: 0.360 nm). The second layer

was shifted parallel to the $A'A$, $B'B$, and $C'C$ directions, and the total energy along with 13 equidistant points in each of these three directions was computed. The energies corresponding to the different configurations in the stacked system are calculated via first-principles DFT-based simulations, by adopting the exchange-correlation functional PBE and by including the Grimme's dispersion corrections (scheme D3). We use the ratio of the distance shifted by the upper layer relative to the lower layer in different directions to the cell parameters to determine the stacking state (only by sliding the second layer). Since layers in 1–4 have different L_a and L_b , the horizontal coordinates represent the percentage of vector displacement of the upper layer relative to the lower layer, defined as the values of O_3O_1/O_1A , O_3O_1/O_1B , and O_3O_1/O_1C , respectively, as shown in Table S1.

As reported in Figure 2k–n, by varying the relative positions, the computed energy profile shows oscillations with relative minima and maxima. In particular for GDY, minima are observed by shifting the systems along the $A'A$ and $B'B$ directions (± 41 and $\pm 8\%$ slipped positions, respectively). By shifting the system along CC' , minima are computed at $\pm 25\%$ slipped positions.

The energy profiles are different when cyano groups are present, as for the case of CNGDY, depicted in Figure 2l, two minima of the CNGDY stacking are localized at $A'A \pm 8\%$ and $B'B \pm 33\%$ shifted position. The energy profile of the $C'C$ slipping is almost the same as the $A'A$ slipping, and the minima energies of the $C'C$ are calculated at $\pm 8\%$ slipped positions. For systems featuring more cyano groups, such as *m*-CNGDY and *p*-CNGDY, the energy profiles are rather different from GDY and CNGDY. The cyano group in meta- and para-positions changes the local symmetry; therefore, the translations along AA' , BB' , and CC' are different from the previous cases. For *m*-CNGDY, we computed a flat potential profile (around $\pm 25\%$ positions) when shifting the layers along BB' , with a broad maximum around 0%. In particular, the energy profiles of the *m*-CNGDY show minima at around ± 41 , ± 33 , and $\pm 50\%$ positions when displacing the two layers along $A'A$, $B'B$, and $C'C$ directions. As for *p*-CNGDY, the energy of the structures that are slipped at $\pm 19\%$ positions for $B'B$ and $C'C$

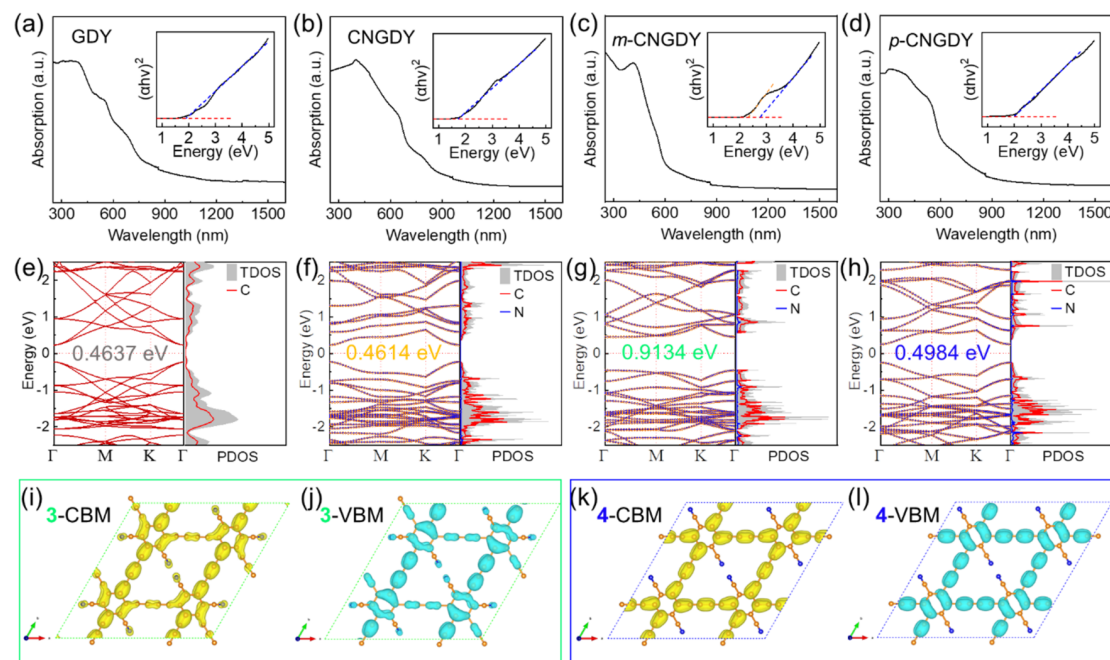


Figure 4. Optoelectronic properties of 1–4. (a–d) UV–vis absorption spectrum with plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) (inset). (e–h) Computed electronic band structures with the projected density of states (PDOSs, where the Fermi energy level is set to zero) of 1–4. (i–l) Top views of the conduction band minimum (CBM) and valence band maximum (VBM) of 3 and 4.

directions are computed and $\pm 41\%$ positions for A'A direction. While the almost perfect overlap of the layers (0% translation) is always a maximum for each system, the presence of cyano groups highly affects the energy minima, generally broadening the potential profile.

Based on the calculations, we selected two stacking points with the lowest relative energy and reoptimized the structure of the system, thus obtaining the relaxed atomic positions and interlayer spacing (see details in Figures S21–S24), which are also listed in Table S1.

Due to the steric hindrance between adjacent cyano groups, the layers deviate from planarity (Figure S26d–f). As the number and position of cyano groups change, the degree of bending also varies, reflecting the size of the spacing between nitrogen atoms (defined as $dN_3 > dN_2 > dN_4$, Figure S26a–c). According to the average values of the interlayer distance (GDY: 0.366 nm; CNGDY: 0.360; *m*-CNGDY: 0.359 nm; *p*-CNGDY: 0.353 nm) and size order ($1 > 2 > 3 > 4$) of the optimized layer spacing for 1–4, the HRTEM and XRD test results are in accordance with the simulations, as shown in Figure 2j.

The most representative stacking models of 1–4 for further research (Figure 3a–d) were selected, showing that as the number of cyano groups increases, the interlayer spacing of GDYs slightly decreases ($1 > 2 > 3/4$). When the number of cyano groups is the same, the change of the position from meta to para leads to small changes in the interlayer distance (0.03 Å), with the para species being the one with the shortest distance ($3 > 4$). The introduction of CN groups in the 2D network affects the local interlayer nonbonded interactions, namely, the electrostatic, repulsion, and dispersion contributions. We performed an energy decomposition analysis (EDA)⁴⁶ (by using the procedure implemented in Multiwfn⁴⁷) on supramolecular clusters of 1–4 (Table S2), by carrying out single-point DFT (B3LYP-D3/cc-pVTZ) calculations and force-field-based energy evaluation (UFF level). Such an

approach presents some limits being not purely based on quantum-chemical (wave function or DFT-based) calculations; however, it is an effective way to easily access the energetic contributions of supramolecular clusters. Further in-depth quantum-chemical studies will be reported in future investigations. EDA shows that the (local) electrostatic contributions are very relevant when CN groups are introduced in meta (3) and para (4) positions, thus inducing a shorter interlayer distance with respect to species 1 and 2, as observed. Here, the different effects of adjusting the number and position of the cyano groups to change the stacking spacing of GDYs are reflected. The crystal plane spacing of 0.499 nm shown in the enlarged HRTEM images (Figures 3e–h and S20i–l) with SAED patterns (Figure S20m–p) corresponds to the (002) plane indices (Figure S20q–t) of 1–4 in the stacking mode of Figure 3a–d.

The doping of nitrogen atoms, by tuning the number and the position of cyano groups, has not only a great influence on the 2D interlayer stacking of GDYs but also impacts tuning their intrinsic photoelectric properties. In terms of the electrode material, a small gap or a narrow band gap can enhance the electronic conductivity of the material. As shown in Figure 4a–d, the optical energy gaps of 1–4, which were determined using solid-state ultraviolet–visible (UV–vis) and the formula of $\alpha \propto (h\nu - E_g)^{1/2}/h\nu$,³⁰ were measured to be 1.9, 1.7, 2.7, and 2.0 eV, respectively. In Figure 4e–h, the direct electronic band gaps (energy difference between the conduction and valence band at $k = 0$) for the GDY, CNGDY, *m*-CNGDY, and *p*-CNGDY monolayers were calculated to be 0.4637, 0.4614, 0.9134, and 0.4984 eV, respectively. From the above results, we found that increasing the number of cyano groups does not necessarily result in narrowing the band gap. In fact, the largest band gaps are those of *m*-CNGDY and *p*-CNGDY species. Furthermore, the band gap is not only affected by the amount of cyano groups but also by the structural changes induced by their presence. This phenom-

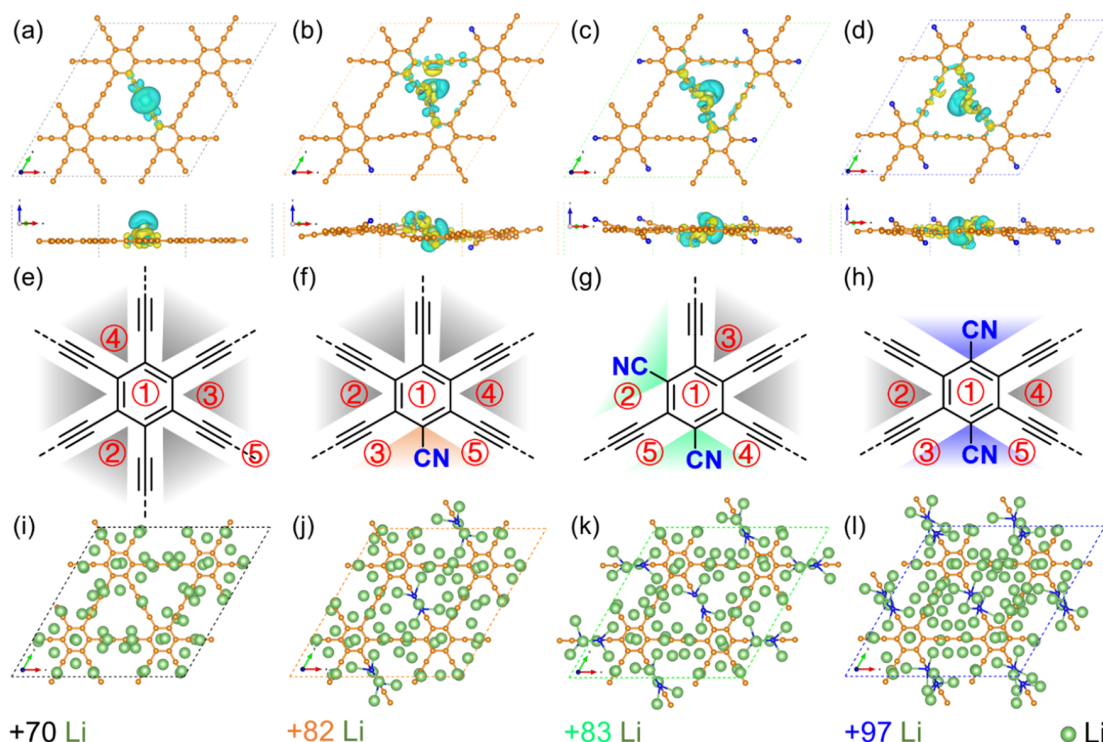


Figure 5. First-principles calculations of the lithium adsorption for 1–4. (a–d) Top and side views of charge density difference of adsorbed Li atoms of 1–4, and the density isosurface value is $0.002 \text{ e}/\text{\AA}^3$. (e–h) Selection of adsorption sites for the Li atoms of 1–4. (i–l) Under the premise of ensuring the integrity of the structure, the top view of the ball–stick model with the maximum amount of lithium attached to a single layer of 1–4 in theory.

enon was also found in the electrical conductivity test⁴⁸ of 1–4 as reported in Figure S2Sd (GDY: 0.185 s/m; CNGDY: 0.306 s/m; *m*-CNGDY: 0.015 s/m; *p*-CNGDY: 0.169 s/m).

Due to the doping as induced by the cyano groups, the conductivity of the material increases. Compared with *m*-CNGDY and *p*-CNGDY, GDY and CNGDY reserve the skeleton integrity to the greatest extent (refer to the molecular structures Figure 1b–e), contributing to the similar bandgap value. For *m*-CNGDY and *p*-CNGDY, the symmetry of the former is lower than that of the latter; thus, the bandgap widening is more significant.

As shown in Figure 4i–l, to study the changes in electronic bandgap and the effect of different doping sites on the structure, the electron density of the conduction band minimum (CBM) and valence band maximum (VBM), and the projected density of states are reported in Figure 4e–h. The N dopant was found to change the distribution of electrons around C atoms, leading to promoting the separation of electron–hole pairs.⁴⁹ As shown in Figure 4i,j, the N atoms serve as the acceptors of electrons from the C atoms in *m*-CNGDY, pushing the highest occupied states down in the VB (valence band). In contrast, only a few electrons localize around the N atoms in *p*-CNGDY (Figure 4k,l), leading to a big difference in optical bandgap between *m*-CNGDY and *p*-CNGDY. It can be seen that the optoelectronic properties of GDYs are affected not only by doping functional groups such as cyano groups but also by doping sites that have a great impact on structural integrity.

GDYs are here investigated as electrodes for electrochemical energy storage applications; therefore, the adsorbing characteristic has to be studied to judge the adsorption of lithium atoms.⁵⁰ We initially studied the physical or chemical

adsorption by calculating the charge density difference to examine the adsorption sites. Chemical adsorption is validated via the Mulliken charge analysis, corroborating the possibility to act as an electrode. The cyano group is usually the most favorite adsorption site for lithium atoms. The charge differences of 1–4 on adsorbing Li atoms are shown in Figure 5a–d, and it is clear that the charge density is more localized on the CN moieties. The lower electron density areas are the hollow, angular, and bridge sites for the next Li atom to be intercalated, which act as the suitable adsorption sites for Li atoms. The cyano group shows high electron-withdrawing and -polarization effects, thus contributing to the high capacity of the battery.

Electrode materials with high bandgap (*m*-CNGDY: 0.9134 eV) possess drawbacks for being battery electrodes because electrons need more energy to transfer from valence band to conduction band, reducing the performance of the battery. For long cycle battery systems, little effect can be produced in the case mentioned above. Because the intrinsic electronic properties of semiconductor electrode change with electron clusters around the substrate during charging and discharging process, thus leading to the conversion of intrinsic electronic properties from semiconductor to conductor.

The reasonable adsorption energy is the key factor between the adsorption ion and the host surface for a promising high-performance ion battery electrode material. Consequently, the adsorption energy was calculated for a single metal atom adsorbed on four different monolayers. According to Figure 5e–h, there were five adsorption sites (①–⑤) for each structure. Table S3 shows the calculation and comparison of the adsorption energy (E_{ad}) of lithium at different positions of 1–4 through formula (1). The electron density concentrates

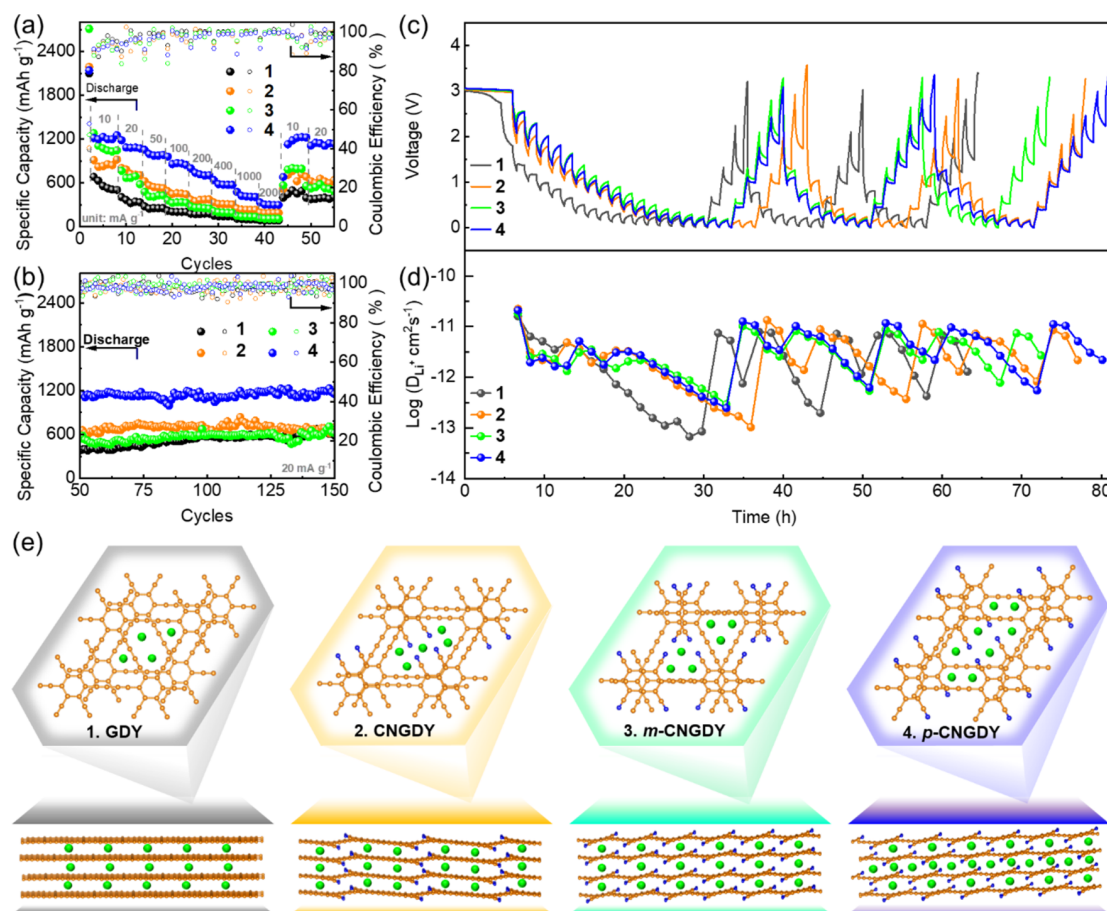


Figure 6. Lithium-ion storage and migration of 1–4. (a) Multiplication performances of 1–4 used as an anode material for lithium-ion batteries (half-cells). (b) Long cycle performances of 1–4. GITT profiles of three discharging (c) and charging processes with the diffusion coefficient (d) of 1–4. (e) Schematic diagrams of the adsorption/migration positions of Li atoms in the planar cavity (above) and the same lateral cavity (below) of 1–4 from left to right.

around the cyano group moieties, indicating that the CN moieties are the favorite sites with the adsorption energy as -1.581 eV (④/⑤), -1.829 eV (③), and -1.581 eV (④/⑤) for CNGDY, *m*-CNGDY, and *p*-CNGDY, respectively. And the adsorption energy of the favorite site (②/③/④) on the GDY monolayer is calculated as -0.837 eV. According to the definition, negative adsorption energy validates that the adsorption process is exothermic and spontaneous. As a result, the high reasonable negative adsorption energy is the advantage for the interaction between the substrate and adsorbing atoms.

The specific capacity is another crucial factor, together with the adsorption energies, to influence the electrode (battery) performance. According to formula (2) in the SI, the specific capacity is proportional to the number of adsorbing atoms on the substrate; therefore, the ionic concentration-dependent behaviors of the substrate have also been investigated. The substrate is provided first and the adsorbing Li atoms are added on the investigated adsorption sites on the surface, then the structural changes of the substrate are simulated. The upper and lower sides of the substrate can be fully covered by Li atoms, as shown in Figure S1–I. During the process of the Li atoms adsorption, the phase transitions of the substrate are investigated to explore the stability and integrity of the substrate structure. With the number of the adsorbing Li atoms increasing, the interatomic force increases and the structure

becomes folded. The factors affecting the volume expansion of 2D structures are related to surface area change as well as the distance change between two neighboring layers. These structures show excellent structural stability and lithium storage capacity due to the large space in the structure which benefits the long cycle lifetime of the battery. The maximum theoretical specific capacity is of great importance for the performance of battery. In the case where the integrity of the structures can be guaranteed to the greatest extent, as listed in Table S4, the maximum theoretical lithium storage quantities of 1–4 are 70, 82, 83, and 97. According to method 2 and formula (2), the capacities of the whole structural system are 2171.4, 2520.2, 2527.8, and 2954.0 mAh·g⁻¹ for GDY, CNGDY, *m*-CNGDY, and *p*-CNGDY ($4 > 3 > 2 > 1$), respectively.

In order to verify the theoretical findings, we used 1–4 as the anode of the lithium-ion half-cells for testing. When the loading amounts of the 1–4 were all 0.6 mg·cm⁻², as shown in Figure 6a, it was found that the reversible specific capacities obtained by them under 10 mA·g⁻¹ current density and 0.005–3 V voltage window are 546.4 (GDY), 861.5 (CNGDY), 1060.1 (*m*-CNGDY), and 1224.2 (*p*-CNGDY) mAh·g⁻¹, which match the sequences of theoretical values reported before. The test of rate performance showed the changes of the reversible specific capacity of 1–4 at different current densities, and it was obvious that *p*-CNGDY (4)

performed the best. However, the capacity of *m*-CNGDY decayed quickly, and it was already lower than that of CNGDY at a current density of 20 mA·g⁻¹. The *b* value ($4 > 1 > 2 > 3$) and capacitive contribution ratios ($2 > 4 > 1 > 3$) calculated by cyclic voltammetry curves at different scan rates also verified this phenomenon in Figure S28.^{51,52} The galvanostatic intermittent titration technique (GITT)^{53,54} was performed to evaluate the lithium-ion migration rate in the half-cells of 1–4 during three discharge/charge processes in Figure 6c,d, demonstrating that the incorporation of cyano groups indeed enhanced the Li-ion migration (the average values of Log (D_{Li^+} cm²·s⁻¹) for 1–4 were –11.82, –11.68, –11.58, and –11.55).

Based on the above stacking modes and the study of lithium adsorption, Figure 6e shows possible lithium-ion transport tunnels in the crystal plane (0 0 2) and interlayer (2 4 0) of 1–4, which can intuitively demonstrate that the transport rate of lithium can also be affected by changes in the number and position of cyano groups. 1–4 have an improved first coulomb efficiency (Table S4), which can be attributed to the fact that when the solid electrolyte SEI layer generated on the smooth surface, the consumption of electrolyte could be smaller than that on the rough surface. In contrast to Figures S20 and S27 intuitively proves this by the SEM images of each electrode after charging and discharging. The increase of the number of cyano groups of lithium affinity may also contribute to the rapid formation of a stable SEI layer. Meanwhile, the long cycle performances of 1–4 in Figure 6b show that GDYs, especially with the addition of cyano groups, can be used as the anode materials of lithium-ion batteries to improve the capacity and cycle stability.

CONCLUSIONS

Three different functionalized GDY derivatives have been synthesized by precisely controlling the amount and the position of cyano groups on the precursor. The effective tuning of GDY by varying the number and position of cyano group is shown and discussed in terms of microstructure, optoelectronic properties, and lithium storage applications. The interlayer spacing of GDY derivatives decreases by increasing the number of cyano groups or changing the position from meta to para, while the change of the bandgap does not follow this trend. Among them, *p*-CNGDY exhibited the best electrochemical performance considering its transfer rate and long cycle performance. While the number of cyano groups in *m*-CNGDY is larger than that in CNGDY, the rate performance at high current density did not improve. These findings suggest that increasing the number of cyano groups may not lead to improved lithium storage performance, rather adjusting their relative positions may be a more effective approach. Moreover, under the fine-grained control approach, the application potential of GDY derivatives with different energy gaps, electron mobilities, and interlayer spacing also needs to be explored in other application fields besides lithium-ion batteries. This work provides a more in-depth strategy for high-precision control of the structure and properties of carbon-based materials, and broadens the way for the development and application of 2D carbon materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsnano.4c07485>.

Details of methods; additional characterizations; and electrochemical performances (Figures S1–S28) (Tables S1–S4) (PDF)

AUTHOR INFORMATION

Corresponding Authors

Ze Yang – College of Energy Storage Technology, Shandong University of Science and Technology, Qingdao 266590, China; Email: yangze@sdust.edu.cn

Xiang Ye – Department of Physics, Shanghai Normal University, Shanghai 200234, China; orcid.org/0000-0002-9034-0046; Email: yexiang@shnu.edu.cn

Changshui Huang – Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0001-5169-0855; Email: huangcs@iccas.ac.cn

Authors

Lei Gao – Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; National Laboratory of Solid-State Microstructures (NLSSM), Collaborative Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory of Artificial Functional Materials, College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China

Shuailong Wang – Department of Physics, Shanghai Normal University, Shanghai 200234, China; Department of Chemistry “Giacomo Ciamician”, University of Bologna, Bologna 40129, Italy

Fan Wang – Science Center for Material Creation and Energy Conversion, Institute of Frontier and Interdisciplinary Science, Shandong University, Qingdao 266237, China

Xiaodong Li – Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Jingchi Gao – Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Daniele Fazzi – Department of Chemistry “Giacomo Ciamician”, University of Bologna, Bologna 40129, Italy; orcid.org/0000-0002-8515-4214

Xuebin Wang – National Laboratory of Solid-State Microstructures (NLSSM), Collaborative Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory of Artificial Functional Materials, College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China; orcid.org/0000-0002-7894-1922

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsnano.4c07485>

Author Contributions

○L.G., S.W., and F.W. contributed equally to this work. L.G., S.W., F.W., and C.H. performed the experiments and wrote the manuscript. S.W. and X.Y. performed the DFT calculations and analysis. X.L., J.G., D.F., X.W., and C.H. participated in the discussion of results. Z.Y., X.Y., and C.H. revised the manuscript. All authors discussed the results and commented on the manuscript.

Notes

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Chapter 5: Modelling redox properties and cation interaction mechanisms in organic redox conjugated polymers

5.1 Electrochemical properties

Organic materials have gained significant attention due to their environmental friendliness, low cost, and other advantageous properties. Among organic materials, ladder polymers represent a unique class of organic macromolecules characterized by a double-stranded backbone in which adjacent repeat units are covalently linked by bridging moieties, forming a rigid, planar "ladder"-like architecture. These polymers attract researchers' interest due to their exceptional thermal stability, mechanical rigidity, and other favorable properties. In this contribution, ladder organic conjugated redox polymers, namely PQL and SBBL, shown in Figure 5.1, are investigated to accurately describe their electrochemical properties.

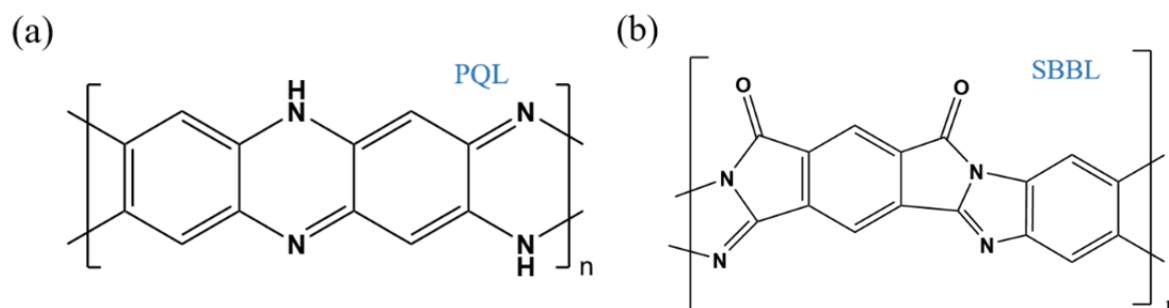


Figure 5.1: Chemical structure of PQL (a) and SBBL (b).

Electrochemical properties of electrode materials strongly impact EES performance. The Fractional Occupation Number Weighted Density (FOD) method was applied to gauge the correlation extent between electrons and the system. The FOD number (N_{FOD}) of the PQL and SBBL neutral states increases with polymer length based on the oligomer approach. Both PQL and SBBL display high N_{FOD} values, indicating that the conjugated system may exhibit biradicaloid or multiradicaloid electronic character. Furthermore, PQL exhibits higher electron correlation compared to SBBL based on N_{FOD} analysis.

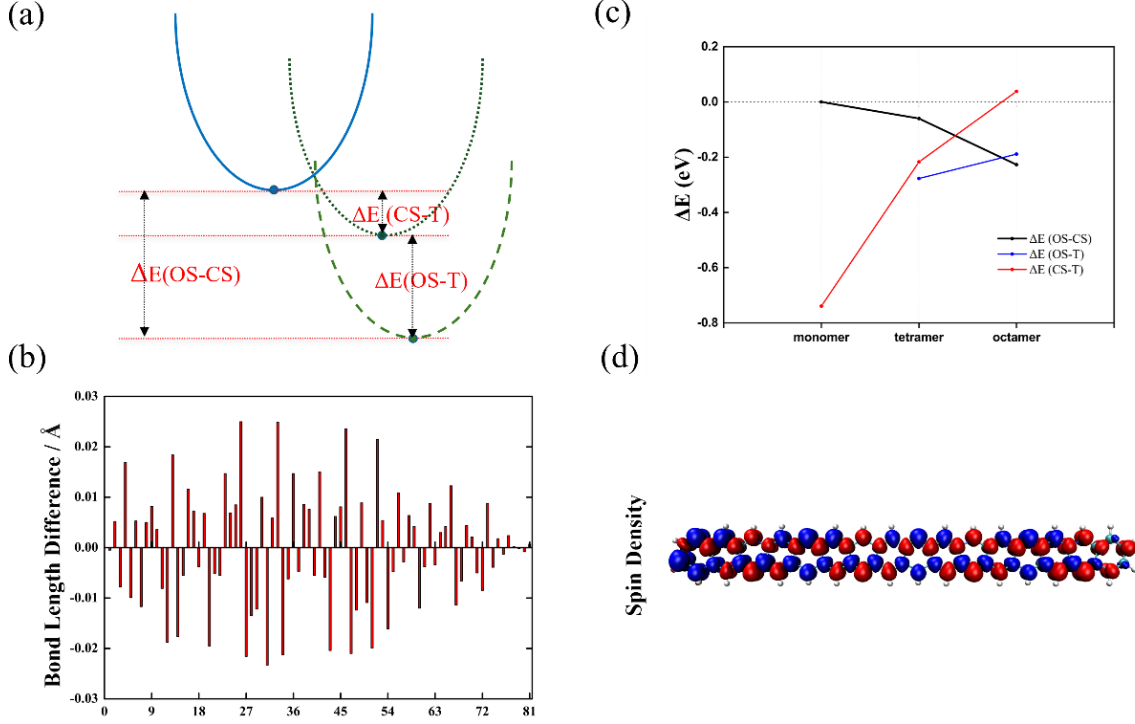


Figure 5.2: (a) The differences between OS, CS, and T states of the monomer (CS = closed-shell singlet, OS = open-shell singlet, T = closed-shell triplet), tetramer, and octamer of PQL. (b) The illustration for the relationship of the three states (CS, OS, and T). (c) The bond length difference (BLD) between the BS-UDFT-level neutral state and DFT-level neutral states of the PQL tetramer.

Considering the N_{FOD} analysis, we further investigated the neutral states of PQL and SBBL by combining standard Density Functional Theory (DFT), unrestricted Density Functional Theory (UDFT), and broken-symmetry (BS) DFT. The energy differences between singlet closed-shell and triplet states (ΔE_{CS-T}), singlet open-shell and closed-shell (ΔE_{OS-CS}), and singlet open-shell and triplet (ΔE_{OS-T}) were computed. As depicted in Figure 5.2, increasing the oligomer length stabilizes the triplet state by decreasing its energy, lowering the ΔE_{CS-T} gap, which may induce biradicaloid character in the singlet ground-state wavefunction. Notably, a broken-symmetry (open-shell singlet) solution was found to be more stable than the singlet CS for longer PQL oligomers, specifically for the tetramer and octamer. Additionally, the PQL bond length alternation (BLA) analysis shows that electrons delocalize over the entire oligomer, paralleling the electron delocalization of the open-shell spin density.

Beyond the ground states discussed above, we investigated multi-redox states to simulate battery operation processes. In multi-redox states, polarons (singly charged systems) and bipolarons (doubly charged systems) play vital roles, as detailed in the Abstract section. The deformation of polarons and bipolarons provides indirect insights into electron transfer rates.

In this work, intramolecular reorganization energy (λ) was employed to evaluate polaron and bipolaron deformation, thus reflecting charge transfer rates, as discussed in Chapter 3. λ , a fundamental parameter in redox and electron transfer theories, was used to evaluate charge transfer rates. We calculated λ based on singly charged states using both standard DFT and BS-DFT to investigate electron transfer rates in PQL and SBBL. As shown in Figure 5.3, standard DFT yields a completely different intramolecular reorganization energy trend compared to BS-DFT for PQL. λ computed by BS-DFT restores the physical trend of reorganization energy, showing a decrease with increasing oligomer length. Moreover, λ values for PQL are generally low, indicating good hole/electron transport properties.

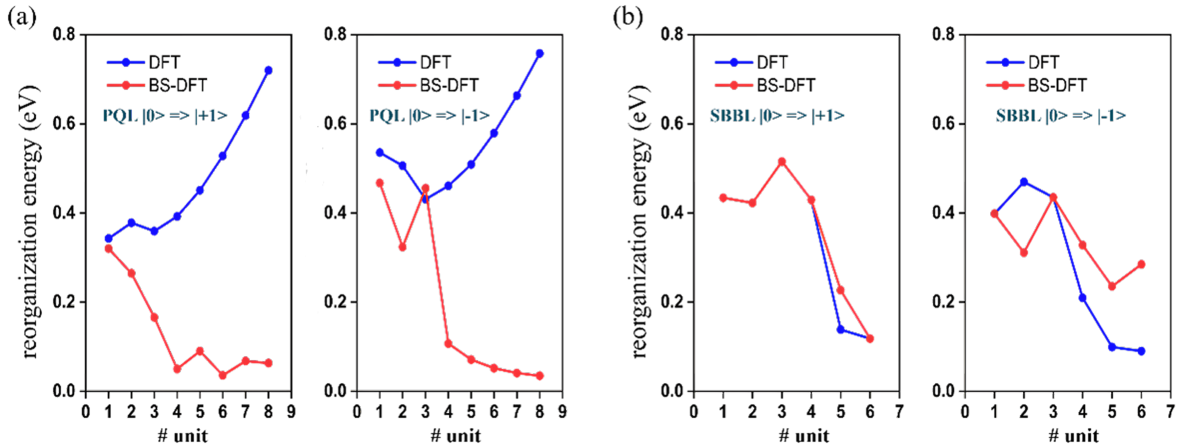


Figure 5.3: Reorganization energies for charging from neutral to singly charged states of PQL and SBBL calculated using standard DFT and BS-DFT.

For SBBL, no BS solution was found in the neutral state; however, BS solutions emerged when stability checks were performed on projected geometries for intramolecular reorganization energy calculations. In these cases, λ values are higher than for PQL, and generally λ_{BS} does not differ significantly from λ_{CS} , unlike PQL. Both hole and electron λ decrease with increasing oligomer length, with minor differences between hole and electron reorganization energies.

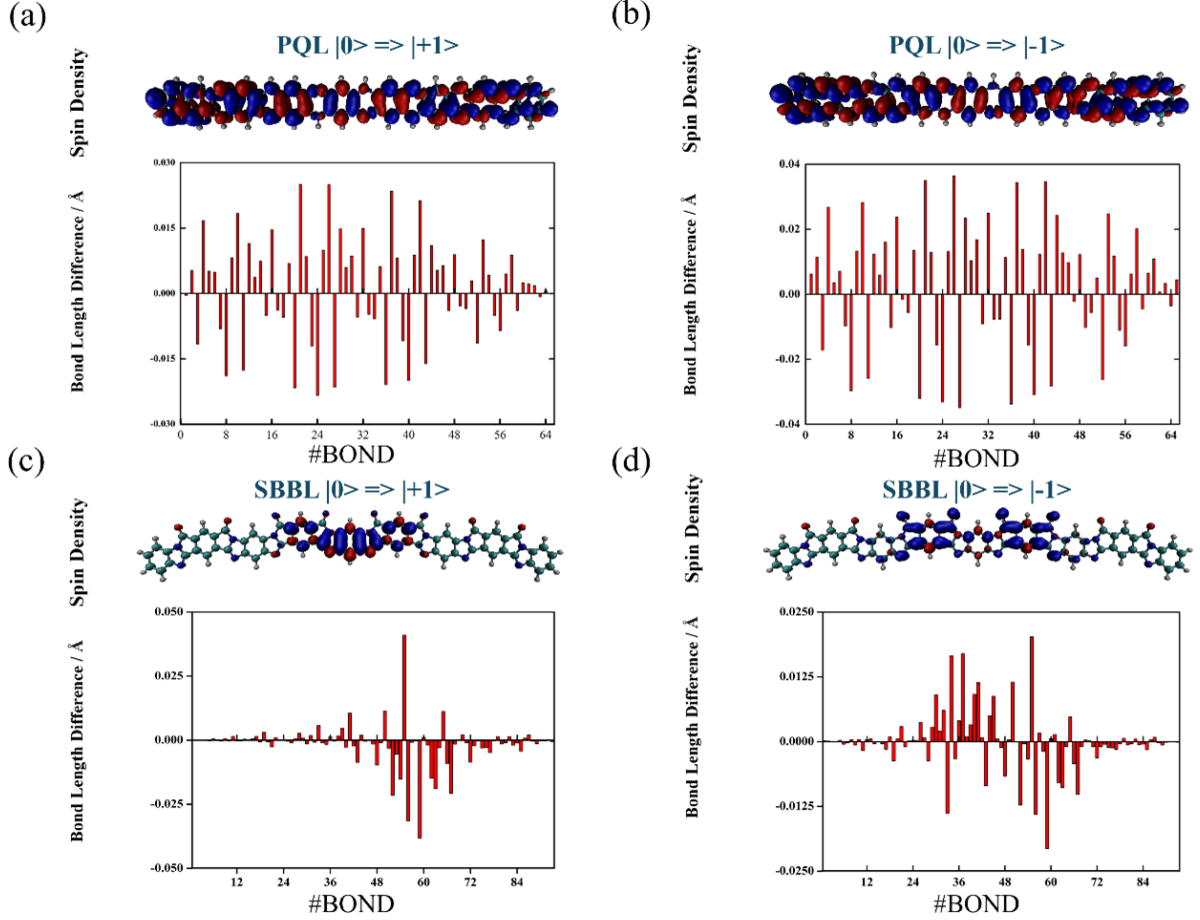


Figure 5.4: (a)–(d) The spin density of the PQL and SBBL polaron states and the BLDs of polaron and neutral states.

The chemical properties of multi-charged states were also explored to observe configuration variations. For each PQL and SBBL oligomer, multi-charged states, including singly and doubly charged states, were investigated using standard DFT and BS-DFT. Notably, doubly charged states exhibit both singlet and triplet configurations. N_{FOD} was employed to evaluate electron-system correlation, revealing that oxidized and reduced states display high electron correlation. Thus, we computed the energy difference between doubly charged singlet and triplet states to clarify this high electron correlation. Spin density analysis was utilized and displayed electron delocalization patterns for singly and doubly charged states, paralleling the BLD results for the PQL tetramer. In contrast, as depicted in Figure 5.4, for the SBBL tetramer, electrons localize over one unit, and the BLD agrees with this localization pattern.

As electrode materials, PQL and SBBL exhibit excellent electrochemical properties (ladder conjugated redox structure, high electron correlation, low intramolecular reorganization energy, etc.), indicating great promise for practical applications.

5.2 Interaction mechanism

To simulate realistic systems, we modeled alkali metal interactions with electrode materials. We identified several interacting sites for PQL and SBBL. For each adsorption site, the interaction energy was computed as $E_{\text{interaction}} = E_{\text{molecule/metal}} - E_{\text{molecule}} - E_{\text{metal}}$, where $E_{\text{molecule/metal}}$ is the total energy of the cluster, E_{molecule} is the total energy of the isolated molecule, and E_{metal} is the total energy of the isolated alkali metal. We observed the favorite adsorption sites are on top of the pyrazine plane for PQL and close to the Carbonyl Group and the nitrogen atom of imidazole ring for SBBL. Energy decomposition analysis, including electrostatic, repulsion, and dispersion energy components, was employed to investigate the main factors influencing the interaction between alkali metals and anode materials. Mulliken charge analysis provided additional details on the interaction mechanism. For different alkali metal cations, lithium cations exhibit greater electron transfer than sodium and potassium, as analyzed by Mulliken charge. Greater electron transfer correlates with more negative interaction energy, as detailed in [Manuscript II](#). We also considered the BLD between ideal and realistic systems to comprehensively illustrate the interaction between alkali metals and EES electrodes.

Various XC DFT functionals were considered: ω B97X-D enhances the biradicaloid character of the singlet configuration compared to B3LYP and M06-2X. However, range-separated functionals are necessary to mitigate electron delocalization and self-interaction errors.

Based on interaction analysis, we identified the optimal adsorption sites on PQL and SBBL polymer tetramer substrates, and partial charge analysis shows good agreement with interaction energy trends.

5.3 Manuscript II

All computational analyses in Publication II were conducted by myself under the guidance of my supervisors. I wrote the initial manuscript draft and collaborated with my supervisor on revisions.

Quantum chemical investigation of multi-redox states in organic conjugated redox ladder polymers for electrochemical energy storage systems

Shuailong Wang, Fabrizia Negri, Daniele Fazzi

*University of Bologna, Department of Chemistry “Giacomo Ciamician”, via P.
Gobetti 85, 40129, Bologna (Italy)*

Abstract

Electronic charged states play an imperative role in influencing the performance of organic electrode materials. We perform the standard Density Functional Theory (DFT), unrestricted density Functional Theory (UDFT) and broken symmetry (BS) DFT to explore the accurate description, which is crucial to understand the properties of the materials, for the organic conjugated redox ladder polymers PQL and SBBL in quantum-chemical level. Furthermore, the Fractional Occupation Number Weighted Density (FOD) was applied to evaluate the electron correlation for the system. The electronic charged states (polaron, bipolaron) of PQL and SBBL calculated by various DFT solutions manifest completely different properties and the BS DFT solution shows the most stable states compared to the electronic states investigated by standard DFT. The spin density and bond length analysis, combined the reorganization energy, illustrate the electronic states properties and electron transport parameters of the PQL and SBBL in DFT and BS DFT level. Besides, the charging system containing the alkali metal cations is also taken into consideration to explore the battery electrode mechanism while charging. The cation system shows obviously different situation in spin density, configuration and bond length, giving the proof that BS DFT is better description for the system. Our study sets deep descriptions for exploring electronic states, thus giving the correct understanding of the electronic mechanism behind and deeply illustrates the system mechanism while containing alkali metal cations.

Keyword: Energy storage system, organic material, DFT, BS DFT, alkali metal battery

Introduction

Organic electrode materials are gaining momentum in the last decades in the field of energy-storage devices thanks to their advantages with respect to the inorganic counterparts, which possess the toxic properties, environmental pollution, high cost, and so on.¹⁻⁵ Some positive aspects are related to their ease, flexible and environmental friendly, chemical design and synthesis, the low production costs, and the mechanical flexibility.^{6,7} However, the drawbacks of organic electrode materials with respect to inorganic are the low capacity and retention time,⁸ high solubility,⁹ low electronic conductivities,¹⁰ and volumetric energy densities.¹¹

Among different classes of organic electrode materials, organic conjugated redox polymers (OCRP) show low solubility, contain active functional group sites and possess stiff structures.^{12,13} OCRPs combine the benefit of having a π -conjugated backbone functionalized with redox centers. The π -conjugated system generally confers high electronic conductivity and good molecular packing, while the redox groups induce the required electrochemical functionalities to afford the redox process during the charging and discharging phases.¹² For instance, the biodegradable polydopamine (PDA) investigated by Zhang, etc. was experimented of possessing 1414 mAhg⁻¹ after 580 cycles and 900 mAhg⁻¹ at 3.2Ag⁻¹ indicating excellent capacity and cycle life.¹⁴ The diethyldihydrophenazine vinylene (CPP) cathode explored by Zhang, Etc. displays a high reversible specific capacity of 184 mAhg⁻¹ with excellent cycling stability.¹⁵

Ladder π -conjugated polymers are emerging OCRP due to their peculiar structural, electronic and electrochemical properties. They show a flat molecular structure without internal torsional degrees of freedom. Such structure confers short plane-to-plane packing distance, high crystalline or semi-crystalline degree at solid state and high electric conductivity. Short packing distances impact the intermolecular electron coupling, thus improving the electron transfer rate inside the molecular and structure stability and high crystallinity can provide transfer channels of migrating electron. The Tang etc. group gave an investigation on the poly(pentacenetrone sulfide) (PPTS) by exploring the stacking distance, giving the conclusion of fast-charge transport and high ionic conductivity based on the short stacking distance.¹⁶ Also, by modulating crystallinity of the PTzBI-dF, the efficiency of the material exceed 19%.¹⁷ Here, the organic ladder conjugated redox polymer, named polyazaacene analogue poly (1,6-dihydropyrazino [2,3g] quinoxalin e-2,3,8-triyl-7-6(2H)-ylidene-7,8-dimethylidene) (PQL), chemical structure shown in Figure 1a, confers the high reversible oxidation and reduction process.¹⁸ Wu et al. studied PQL as anode in lithium- and sodium-ion storage systems, demonstrating good electrode performances: high capacity (1750 mAh/g, 0.05C) and excellent cycle battery life (1000 cycles) for lithium-ion battery and initial discharged capacity of 1825 mAh/g at the current density of 100mA/g.^{19,20}

Besides PQL, another OCRP is SBBL, chemical structure shown in Figure 1, a derivative of the benzobisimidazobenzo phenanthroline (BBL)²¹⁻²³, which shows good thermal stability, low solubility, long-term cycling and substantial capacity.²³ Wu et al. demonstrated that SBBL possesses high capacity, sustaining at 922mAh/g after 50 cycles,¹⁹ which is almost higher than the capacity of other organic electrodes

(anthra[1',9',8'-b,c,d,e][4',10',5'-b',c',d',e']bis-[1,6,6a(6a-SIV)trithia]pentalene (ABTH) sustains at 180 mA/g after 7 cycles,²⁴ bis(2-aminophenyloxy)disulfide (APOD) sustains 230 mAh/g after 7 cycles,²⁵ tetrathiotetracene (TTT) and hexathiapentacene (HTP) sustain 257 mAh/g and 265 mAh/g after 30 cycles and 100 cycles,²⁶ respectively).

Despite the remarkable experimental evidence, showing ladder polymers as a promising class of OCP, little is known about their fundamental properties, in particular the electronic structure of neutral and multi-charged (redox) states, and their interactions with ionic species at the base of the electrochemical energy storage technologies (e.g., batteries, supercapacitors), such as Li⁺, Na⁺ and K⁺.

Investigating the electronic properties of charged (redox) states is of paramount importance to address the electron-transfer (ET) mechanism occurring in the organic electrodes.^{27,28} In its simple form, an ET event oxidizes (reduces) the organic species, creating a radical cation (anion), also known as a molecular polaron. Polarons in organic semiconductors have been largely investigated since the early stages of organic electronics, however the physical-chemical properties of polarons in ladder pi-conjugated redox polymers have been only recently explored and no clear structure-function properties emerge.

In this study we apply density functional theory (DFT) and broken-symmetry DFT methods to describe the electronic structure of PQL and SBBL in their neutral and multi-charged (redox) states. We modelled both *ideal* systems, where fragments of a polymer chain (i.e., oligomers) are both oxidized and reduced, and more *realistic* systems, namely oligomers in the presence of cations (Li⁺, Na⁺, K⁺). We found that PQL and SBBL confer completely different electrochemical properties, possessing different electron correction to system, electron distribution in charging and discharging cases, obvious reorganization energy difference based on different methods, leading to different electrochemical performance as electrodes in ideal system. Also, cations on the PQL and SBBL substrates exhibit huge impact, bending structures and truncating spin density of structures and electronic structures of substrates. Deeply investigating the system with cations, energy decomposition analysis (EDA) is adopted to give more energy details by means of electrostatic energy, repulsion energy and dispersion energy, fully understanding the complex mechanism while system functioning.

Computational details

An oligomer approach was used to explore the electronic properties of PQL and SBBL, considering oligomer lengths ranging from 1 (monomer) up to 8 (octamer) for PQL and 1 (monomer) up to 6 (hexamer) for SBBL. The range-separated-corrected DFT functional (ω B97X-D), was considered to optimize the ground state (neutral) structures, combined with double-zeta split valence polarized Pople's basis set 6-31G* (for optimization, frequency, reorganization energy...). The electronic states, including the neutral ($q=0$), singly charged states (both positive $q=1$ and negative $q=-1$) and doubly charged states ($q=2$ and $q=-2$) were investigated. Singly charged species are here referred as polarons, while doubly charged species as bipolarons. The spin

multiplicity of polarons is doublet, while bipolarons can show both singlet (S) and triplet (T) states. We used the unrestricted (U)DFT method to describe polarons, whereas for singlet bipolarons we used RDFT and for triplet bipolarons the UDFT method was applied. For every charged state ($q=0, \pm 1, \pm 2$), a stability analysis of the electronic wavefunction was carried out to check the presence of possible broken symmetry solutions (BS-UDFT method). If an instability of the wavefunction was found, the electronic and molecular structure of the system were re-optimized at the BS-UDFT level. No imaginary frequencies were found for every oligomer in each electronic state, indicating stable equilibrium geometries.

To quantify strong electron correlation and multireference effects in the systems, the Fractional Occupation Number Weighted Density (FOD) method was adopted to calculate the FOD number (N_{FOD}) by using ORCA²⁹ for each electronic state.³⁰

As for the reorganization energy, determining the electron transfer rate, which includes internal (intramolecular) reorganization energy and external (intermolecular) reorganization energy,³¹ we adopt the internal reorganization energy to explore electron transfer rate of PQL and SBBL. The equations are listed:

$$\lambda = \lambda^{(i)} + \lambda^{(ii)} \quad (1)$$

$$\lambda^{(i)} = E_3 - E_1 \quad (2)$$

$$\lambda^{(ii)} = E_4 - E_2 \quad (3)$$

Where E_1 , E_2 , E_3 and E_4 denote energy from different system states, shown in Supporting Information 1. The energy decomposition analysis is an important component of quantum chemical analysis methods. It can decompose the total interaction energy between fragments into physically meaningful energy terms, facilitating the examination of the nature of the interaction. Here are the equations:

$$E_{AB}^{\text{ele}} = \frac{q_A q_B}{r_{AB}} \quad (4)$$

$$E_{AB}^{\text{vdW}} = E_{AB}^{\text{rep}} + E_{AB}^{\text{disp}} \quad (5)$$

$$E_{AB}^{\text{rep}} = \epsilon_{AB} \left(\frac{R_{AB}^0}{r_{AB}} \right)^{12} \quad E_{AB}^{\text{disp}} = -2\epsilon_{AB} \left(\frac{R_{AB}^0}{r_{AB}} \right)^6 \quad (6)$$

Among them, A and B are atomic labels, q represents the atomic charge, r is the inter - atomic distance, ϵ is the depth of the van der Waals interaction potential well, and R^0 is the non-bonding distance between atoms. When $r = R^0$, the van der Waals interaction energy between atoms is exactly equal to the depth of the potential well. In this work, we utilized the energy decomposition analysis to investigate the interaction energy between the cation and substrate on the basis of UFF force field processed by the Multiwfn software.^{32,33}

We also use y_0 to describe diradical character of the system by calculating according to the following equation:

$$y_0 = 1 - \frac{2T_i}{1 + T_i^2} \quad (7)$$

$$T_i = \frac{n_{\text{HONO}-i} - n_{\text{LUNO}+i}}{2} \quad (8)$$

Where the n_{HONO-i} and is the n_{LUNO+i} are the occupied number of the highest occupied natural orbital and lowest unoccupied natural orbital. Normally, $y_0=0$ for closed-shell and $0 < y_0 < 1$ for open shell singlet states.³⁴

Almost the calculations were performed with the program package Gaussian16.³⁵

Results and discussion

PQL and SBBL electronic structure of ground neutral state.

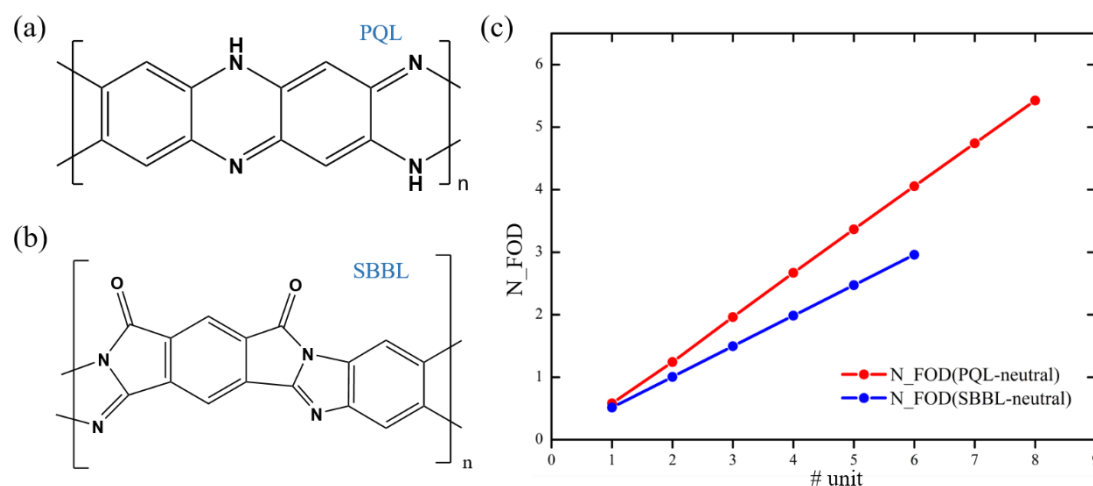


Figure 1 Chemical structure of PQL (a) and SBBL (b). (c) Computed FOD number (N_{FOD}) for PQL ($n=1-8$, red) and SBBL ($n=1-6$, blue) oligomers in their neutral electronic state.

Fig. 1(c) shows the trend of N_{FOD} by varying the oligomer length for PQL (red) and SBBL (blue) in their neutral ($q=0$) electronic state. The longer the oligomer length is, the higher N_{FOD} is, for both PQL and SBBL. According to reference,^{24,36} large N_{FOD} ($> 1.0-2.0$) indicates systems with strongly correlated electrons characterized by high static electron correlation effects, possibly leading to multi-reference characters of the electronic wavefunction. Moreover, as well documented in literature,³⁷ high N_{FOD} on extended conjugated systems can lead to biradicaloid or multiradicaloid electronic configurations. Both PQL and SBBL oligomers display high N_{FOD} , the former showing values larger than the latter and scoring $N_{\text{FOD}} > 4$ for long oligomers ($n > 6$). For comparison, considering the oligomer length $n = 4$ (tetramer), the corresponding N_{FOD} are 2.67 for PQL and 1.98 for SBBL.

Giving the high N_{FOD} s, we further explored the electronic structure of neutral PQL and SBBL oligomers by computing open shell (broken symmetry) singlet and triplet states. Figure 2 are reported the calculations for the PQL monomer ($n = 1$), tetramer ($n = 4$) and octamer ($n = 8$). We computed the energy differences between singlet closed shell and triplet states ($\Delta(\text{CS-T})$) (blue line), singlet open and closed shell ($\Delta(\text{OS-CS})$) (black line), singlet open shell and triplet ($\Delta(\text{OS-T})$) (red line). By increasing the oligomer length, the triplet state stabilizes by decreasing its energy, lowering the $\Delta(\text{CS-T})$ gap. A low-lying triplet state might induce a biradicaloid character to the singlet ground state wavefunction. A broken-symmetry (open shell singlet) solution was indeed found to be more stable than the singlet CS for long PQL oligomers, specifically for tetramer and octamer, as reported by the negative $\Delta(\text{OS-CS})$ values in Figure 2a. The

OS singlet is the most stable state for long PQL oligomers, being circa 0.2 eV lower than T. The result is relevant, showing that already the neutral state of PQL displays a complex (radicaloid) electronic structure with a spin density delocalized over the whole oligomer length, as reported in Figure 2d. Figure 2c shows the structural relaxations by comparing the high energy CS to the low energy OS singlet. In particular, we report for each bond length difference between the CS and the OS state. The bond-length difference pattern shows that structural relaxation is delocalized over all the oligomer, paralleling the delocalization of the open shell spin density.

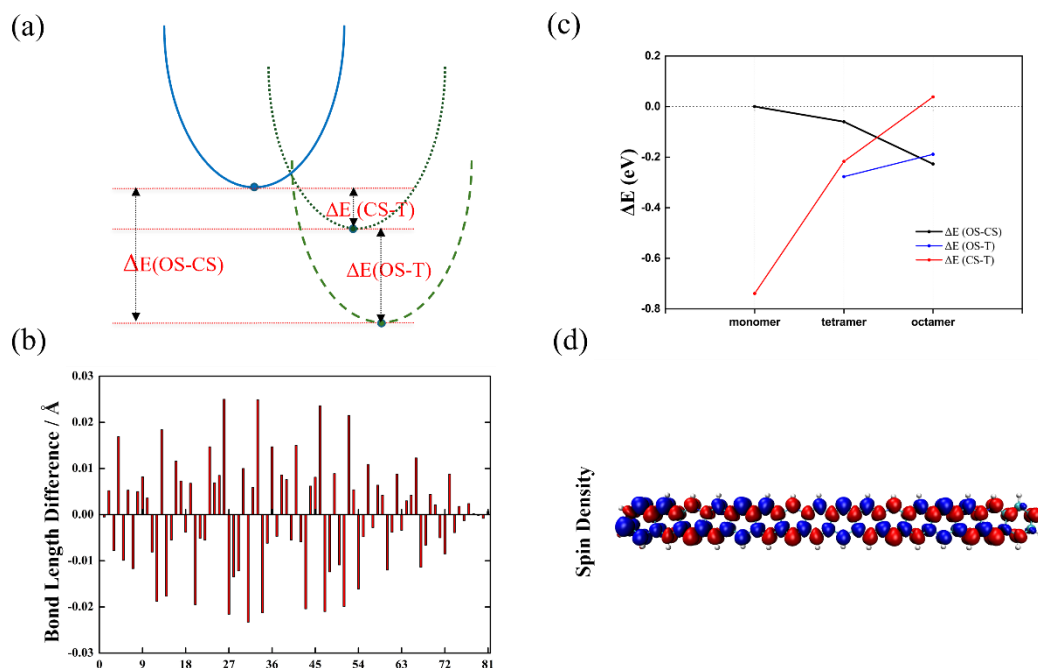


Figure 2 (a) The differences between OS, CS and T states of the monomer (CS => close shell singlet, OS => open shell singlet, T => close shell triplet) tetramer and octamer of PQL. (b) The illustration for the relationship of three states (CS, OS and T.) (c), the bond length difference (BLD) of the BS-UDFT level neutral state and DFT level neutral states of PQL tetramer.

The energy difference of tetramer between OS and CS states, OS and T, CS and T are -0.06 eV, -0.28 eV and -0.22 eV, respectively, shown in Figure 2 (c). Furthermore, the trend shown in Figure 2 (c) reveals that OS states is more stable configuration by enlarging the oligomer length known from the growing energy difference of OS and CS and decreasing energy difference of OS and T, provided in Supporting Information Table 1 and Table 2, indicating that PQL has strong radicaloid properties. On the contrary, SBBL system shows no BS DFT solutions. To validate reliability of data produced by ω B97-XD function, we adopted other functions named B3LYP and M06-2X to PQL and SBBL systems. The same conduct procedures are functioning on the basis of two functions mentioned above. PQL growing neutral energy differences, based on ω B97-XD, B3LYP and M06-2X, are represented in Supporting Information 2 by increasing the oligomer length, ascribed to variations in approached of handling the exchange energy and correction energy. On the contrary, the bond length differences of

PQL and SBBL in Supporting Information 3 computed by different functions show similar trends, indicating functions confer the resembling electrons distributions. The reorganization energy of $|-1\rangle$ state of PQL and SBBL are listed in the Supporting Information 4, showing narrowing gap between PQL and SBBL by expanding length. Afterward, the value of y_0 computed to check the biradicaloid properties shown in Supporting Information 5 is increasing by expanding the oligomer length, paralleling to the FOD trend. Brief speaking, the ω B97-XD function provides relatively reliable values considering BLD and reorganization energy under the comparison of B3LYP and M062X functions. We also calculated the trans-PQL to distinguish the differences between the cis-PQL and trans-PQL by the FOD analysis. It is worthy to note that the cis-PQL show non BS-DFT solution and the FOD is slightly lower than that of trans_PQL, shown in Supporting Information 6.

PQL and SBBL electronic structure of charged states.

For each PQL and SBBL oligomer, we computed the electronic and molecular structures of singly and doubly charged states, considering both oxidized ($q = +1, +2$) and reduced ($q = -1, -2$) cases. Figure 3 shows the N_{FOD} for each case. Moving to the charged states N_{FOD} increases with respect to the neutral state for both oligomer s. PQL shows very high N_{FOD} for both positive and negative polaron ($q = \pm 1$) and bipolaron ($q = \pm 2$), however the increase with respect to the neutral state is small. For SBBL the increment of N_{FOD} , moving from neutral to charged states, is larger than PQL, scoring higher N_{FOD} for the same oligomer length. For comparison, considering the case of $n = 4$, PQL shows N_{FOD} in the range of 2.82 to 3.26 for $q = \pm 1$ and ± 2 , slightly larger than the neutral case. SBBL instead shows a marked variation from neutral to charged states, featuring N_{FOD} in the range of 2.83-4.15 for both oxidized and reduced species. Another interesting feature is that for PQL there are no differences (for almost all chain lengths) between singly and doubly charged oxidized/reduced states and referring to $q = \pm 2$ (bipolarons) singlet and triplet multiplicities result in similar N_{FOD} . A different scenario

holds for SBBL, where bipolarons ($q = \pm 2$) show higher N_{FOD} than polarons ($q = \pm 1$).

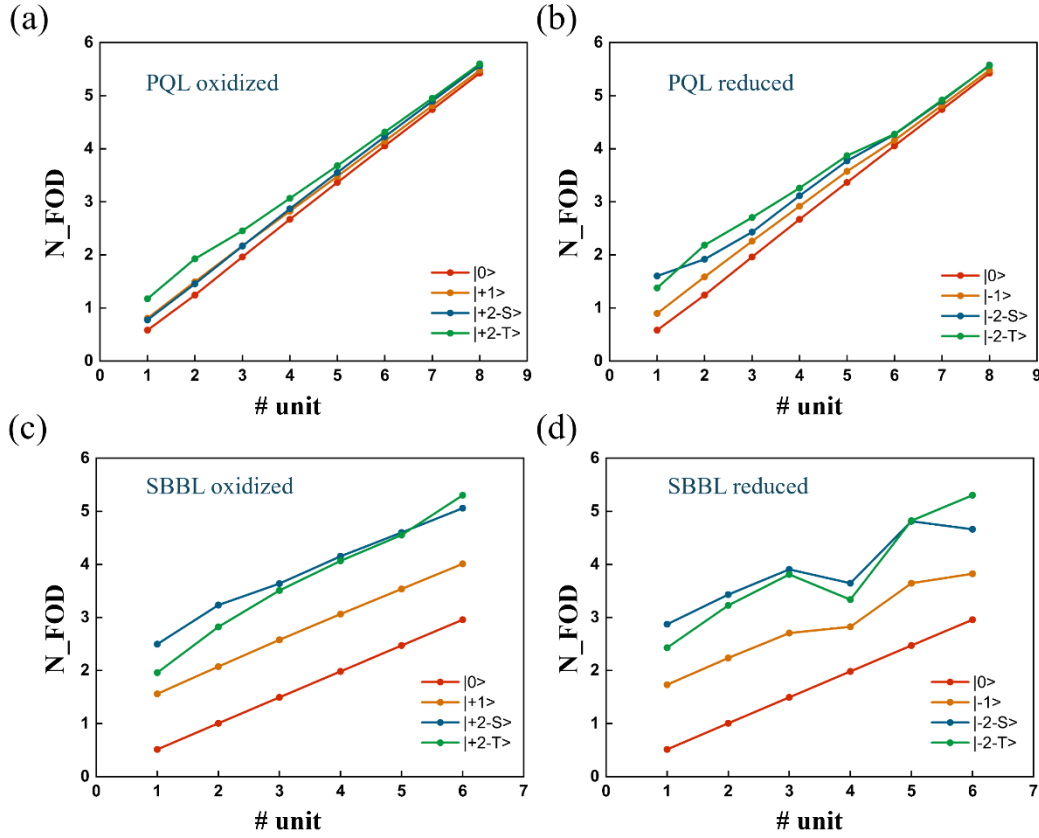


Figure 3. Computed N_{FOD} for singly (green) and doubly charged states (singlet (red), triplet (blue) states) for PQL oxidized ($q = +1, +2$) (a) and reduced ($q = -1, -2$) states (b), and for SBBL oxidized ($q = +1, +2$) (c) and reduced ($q = -1, -2$) (d) states.

Generally, the doubly charged oxidized/reduced states show higher electron correlation than singly charged states for each system.³⁷

Giving the high N_{FOD} , for the doubly charged states ($q = \pm 2$) we verified the presence broken symmetry singlet open-shell state. PQL oligomers show a broken symmetry singlet OS solution for both $q = +2$ and -2 charged states, with $\Delta E(\text{OS-CS})$ ranging from 0.10 eV up to 0.4 eV for $n > 3$ (see Supporting Information 8). Analogously, SBBL singlet bipolaron species feature broken-symmetry OS solutions more stable than the CS singlet up to 1 eV (neutral $|+2-S\rangle$ species 1.23 eV).

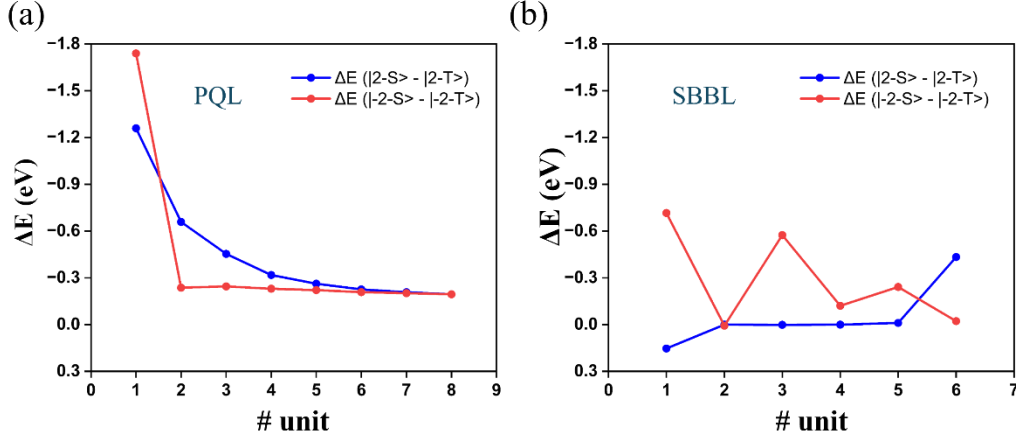


Figure 4. (a) and (b) The PQL trend of the N_{FOD} and the energy difference of the doubly charged singlet and triplet states. (c) and (d) The SBBL trend of the N_{FOD} and the energy difference of the doubly charged singlet and triplet states.

Given the presence of broken-symmetry OS singlet for both oxidized and reduced bipolaronic species, we checked the energy of triplet states with respect to the singlet OS. In Figure 4 we report the energy difference between singlet OS and triplet for PQL and SBBL, both +2 and -2 charge. For PQL the $\Delta E(\text{OS-T})$ decreases by increasing the oligomer length, paralleling the trend of the N_{FOD} in Figure 3a, b. For SBBL the trend is less linear showing a different behavior between doubly charged oxidized and reduced species.

In this part, we pay our focus on the electronic structure of PQL and SBBL, featuring different properties on neutral as well as charged states. Generally, we observe the BS DFT solution presence from PQL instead of SBBL, demonstrating that for neutral species, PQL possess radicaloid properties instead of SBBL. N_{FOD} grows by increasing the oligomer length, indicating both PQL and SBBL confer strong electron system correlation. PQL shows a slightly stronger correlation ascribed to the bigger N_{FOD} compared to SBBL based on charged states.

Structural analysis of polarons and bipolarons in PQL and SBBL

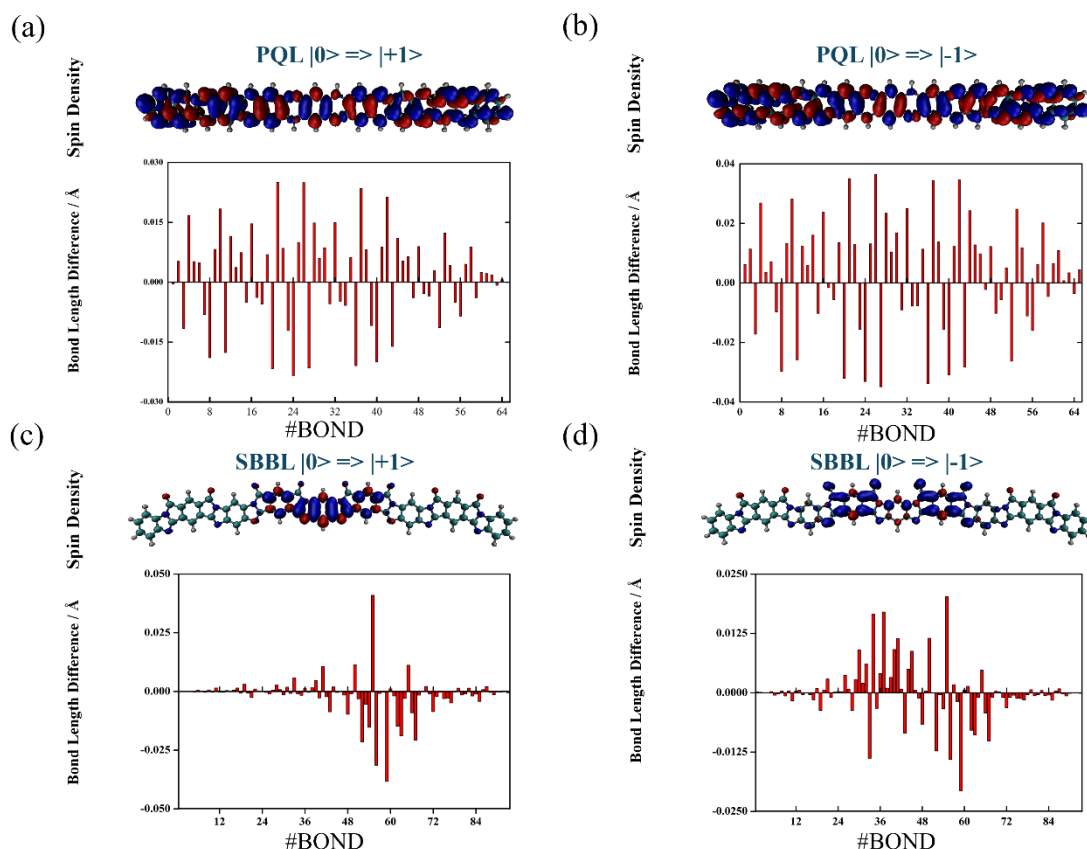


Figure 5. (a) (b) (c) (d) The spin density of the PQL and SBBL polaron states and the BLDs of polaron and neutral state.

As shown in Figure 5 (a) and (b), both hole ($q = +1$) and electron ($q = -1$) polaron are delocalized over the entire PQL molecular structure. The spin density is distributed along with the molecular backbone reflecting the structural change (i.e., bond length difference) upon charging. The situation is remarkably different for SBBL where the carbonyl groups locally perturb electronic and structural relaxation upon charging. Polarons in SBBL are highly localized over one/two units, as reflected by the BLD and the spin density (Figure 5 c,d). Giving the heterogeneous units constituting SBBL, hole and electron polaron localized over different donor and acceptor moieties, paralleling the case of SBBL.³⁶

Whereas, for reduction singly doublet states, the electrons are only localized on the edges of the SBBL oligomer, which can explain the phenomenon that the energy differences between CS (doubly charged singlet states) and OS (doubly charged triplet states) solution of oxidation and reduction doubly charged states are completely different. (I want to give a relationship between the localized spin density and doubly singlet and triplet states. There is no correlation between these two factors.) And the electrons are localized on one almost unit, which is a good match to the BLDs. Noteworthy, as seen in Figure. 9, for oxidation doubly charged singlet and triplet states, the electrons are localized on the center and edge of the oligomer. However, the electrons are localized on the edge of the oligomer for reduction singlet state and on the

center and edge of the SBBL for triplet state, which has a strong impact on the ion transferring. (The being localized electron over one unit is benefit for ion transfer process.)

Similarly, we analyzed the structural and spin density relaxations by moving from polaron to bipolaron ($q = \pm 1 \rightarrow \pm 2$), results are reported in Supporting Information 9. As observed for polaron, bipolarons (both singlet and triplet states) are completely delocalized in PQL and localized in SBBL.

Hole and electron intra-molecular reorganization energy of PQL and SBBL

A fundamental parameter in redox and electron transfer theories is the intra-molecular reorganization energy (λ). By considering Marcus theory for homogeneous charge transfer reaction, high (low) λ leads to high (low) activation energy and consequently low (high) charge transfer rates. The evaluation of λ within the adiabatic method involves the assessment of the equilibrium geometries of both neutral and charged states, and their vertical projections. Therefore, an accurate description of the stable electronic states is crucial for the calculation of the reorganization energy. In such frame, the presence of broken symmetry OS singlet states for PQL neutral state can indeed impact the quantitative evaluation of λ .

In Figure 6 we report the computed intra-molecular reorganization energies for PQL (Figure 6a) and SBBL (Figure 6b). As discussed previously, PQL shows a broken symmetry OS singlet neutral state, lower in energy than the CS. Reorganization energy computed by considering OS or CS solutions differ quite dramatically each other. λ CS show very high value (>0.4 eV) and an increase trend for long oligomers. λ BS, on the contrary, restore the physical trend of the reorganization energy, namely a decrease by increasing the oligomer length. λ BS change by varying the oligomer size and they start to reach a plateau for $n > 4$, assessing to very low values (< 0.1 eV).

We stress here, that the decrease of the reorganization energy by increasing the oligomer length and the low values, can be obtained only by considering the open-shell character of the neutral, ground state of the oligomer.

λ values for PQL are generally low featuring good hole/electron transport properties as observed from the experiments. From the only calculation of the reorganization energy, hole and electron can be equivalently transported from PQL.

The situation is slightly different for SBBL. SBBL shows stable CS solution in the neutral state, however BS solutions are found when the stability check is performed on the projected geometries for the calculation of the reorganization energy. For such reason, also for SBBL – and for some oligomer length – BS reorganization energies are computed. SBBL shows higher λ than PQL and generally λ BS do not differ much from λ CS as for the case of PQL. Both hole and electron λ decrease by increasing the

oligomer length and minor differences are computed for hole and electron.

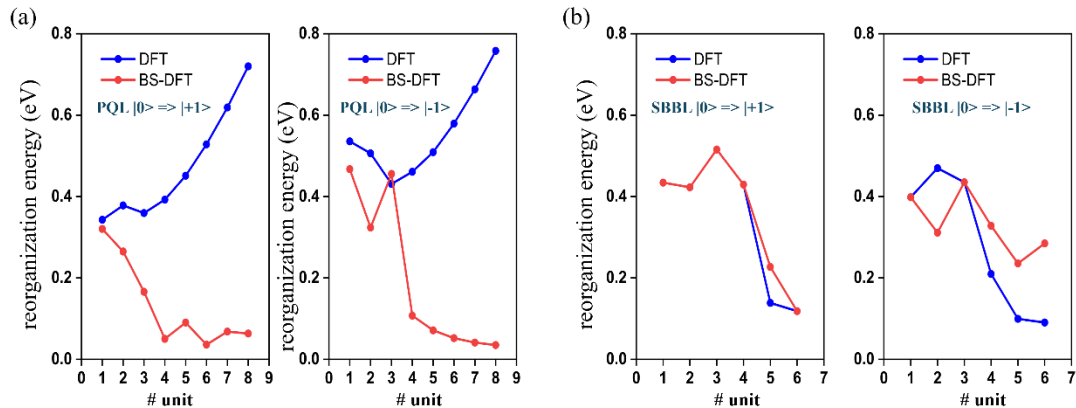


Figure 6. Reorganization energies for charging from neutral to singly charged states of PQL and SBBL calculated using standard DFT and BS-DFT.

Besides, we switch to the doubly charge species, considering the high N_{FOD} of PQL and SBBL. Similarly, as PQL neutral species situation, λ trends of OS and BS differ each other by increasing the oligomer length and λ value is gradually decreasing to circa 0.1 eV. The doubly triplet states, without the presence of BS solution, show CS λ values circa 0.3 eV. However, the λ trends of SBBL doubly charged states present an oscillating situation. The doubly charged species is generally growing as the oligomer length increases, and the values stay circa 0.5 eV except SBBL hole doubly singlet states (+2-S).

The BS solution show a dramatically different λ trend compared to CS solution on the basis of PQL charge species, which holds physical trend. And the λ value of PQL neutral states reaches circa 0.1 eV with the increase in length. Furthermore, the PQL hole doubly species (+2-S, +2-T) λ value under the BS solution represent decreasing trend instead of SBBL charge states. All the results are concluded from the ideal system. Considering the electrode functioning process metal cation interacts with electrode material, we explore the interactions between metal cation and oligomer by utilizing the following constructing metal-ion-substrate system.

The interaction effects with alkali metal

Up to now ideal systems, namely isolated oligomers, have been considered in order to characterize the intrinsic electronic and structural properties of both PQL and SBBL in their neutral and multi-charged (polaron, bipolaron) states. In operating electrochemical energy devices (e.g., batteries) electrodes are in contact with an electrolyte and upon a redox event ions can migrate into organic materials. Therefore, it is relevant to model the interactions between the OCRP and the ions. Typical ions

considered for the applications are Li^+ , Na^+ and K^+ .^{38–40}

In a bottom-up atomistic spirit, we considered for both PQL and SBBL an oligomer interacting with one alkali metal atom, the latter placed on multiple positions with respect to the oligomer in order to explore a variety of interaction sites. In such way, for each OCRP, we built many possible oligomer/alkali metal interacting configurations.

Figure 7 shows the multiple adsorption sites investigated in our study for both PQL (Figure 7a-c) and SBBL (Figure 7d). For PQL we identified six classes of configurations named *-1, *-2, *-3 and *-1', *-2', *-3', responding to Figure 7a-7c. *-1 and *-1' is the site where the alkali metal is located on top of the benzene ring, while in *-2 and *-2', *-3 and *-3' the alkali metal is interacting with the pyrazine moiety, precisely on the side close to the nitrogen atom (*-2, *-2'), or on top of the pyrazine plane(*-3, *-3').

To address the interaction energies in PQL, we considered the tetramer ($n = 4$) and the symbol * in our notation refers to the monomer repeat unit where the metal is located. For instance, 2-1 represents an alkali metal located on top of the benzene ring in the third monomer unit, while 2-3 an alkali metal on top of the pyrazine ring in the second monomer unit.

We introduced a similar notation for SBBL, however in such case we considered only one monomer. The choice would be clear later and it is directly related to the polaron localization reported in the previous section. Since SBBL is the symmetrical configuration, we number the sites from 1-1 to 1-8 and 2-1 to 2-8, which are equivalent sites. And the middle site of the SBBL is named 2-9.

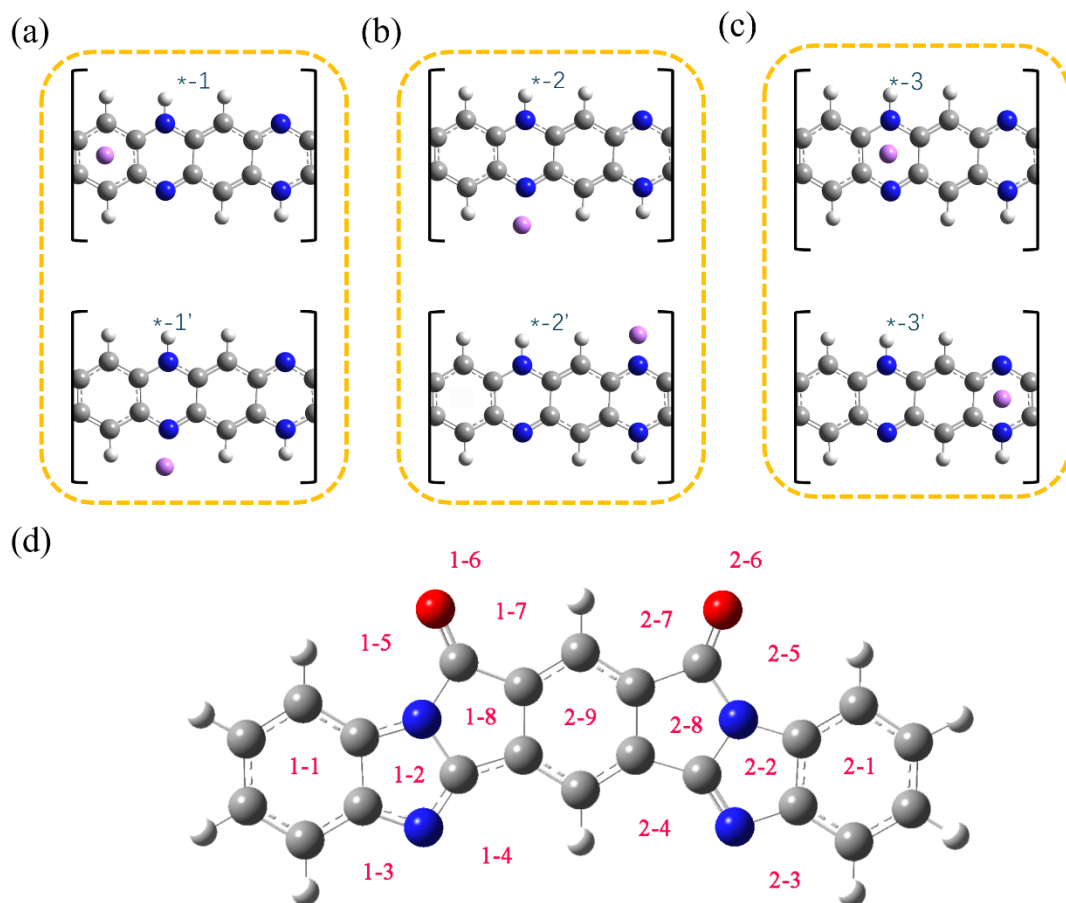


Figure 7. The lithium cation illustration adsorption site on PQL and SBBL.

For each adsorption sites, we computed the Basis Set Superposition Error (BSSE) corrected interaction energy and uncorrected interaction energy as $E_{\text{interaction}} = E_{\text{molecule/metal}} - E_{\text{molecule}} - E_{\text{metal}}$, with $E_{\text{molecule/metal}}$ is the total energy of the cluster, E_{molecule} is the total energy of the isolated molecule and E_{metal} is the total energy of the isolated alkali metal. The isolated molecular is the taken from the molecular-metal optimized system. It is noteworthy that the molecule from optimized PQL system is bent, rather than SBBL system substrate, ascribed to the metal cation interaction to the molecular and redistributed electron of the molecular. Interaction energies were computed for both PQL and SBBL oligomers, considering lithium, sodium and potassium in each interaction site and the results are reported in Figure 8 (a) and (b). As shown in Figure 8, the most stable interaction sites for PQL are $*-3$, indicating a stabilizing interaction between alkali metal and the pyrazine ring. The less stable interaction sites are $*-1$, showing a less favorable coordination between alkali metal and the benzene ring. Considering SBBL case, $*-5$ features favorable adsorption site, located around the nitrogen and oxygen atoms. For both PQL and SBBL interaction cases, Li interacting with substrates confers lowest interaction energy for BSSE corrected and uncorrected situation. In addition, we observed the BSSE correction value of Li in PQL is 2.49 kcal/mol, 0.34 kcal/mol higher than that in SBBL (2.15 kcal/mol) on average; for Na, the BSSE correction value in PQL (2.37 kcal/mol) exceeds that in SBBL (2.24 kcal/mol) by 0.13 kcal/mol on average,

indicating a higher degree of basis set overlap between the PQL ligand which leads to more pronounced interference from the basis set superposition effect, which is shown in SI 11.

Such interactions can be further rationalized via energy decomposition analysis procedure, where the electrostatic, repulsion and dispersion energy terms can be evaluated (see Supporting Information 11). From Supporting Information Figure 14 PQL case, it is clear the strong electrostatic interaction term stabilizing the configuration *-3 over *-1. Such strong electrostatic terms arise also from the (partial) charge transfer between the conjugated oligomer and the alkali metal. As shown in Supporting Information Figure 15 the positive partial charge on the alkali metal is higher in *-3 configuration (circa 0.5e) than in *-1 site (circa 0.4e). Sodium and potassium show lower total interaction energies as lithium with configuration *-3, generally the most stable one. Also, SBBL case confers the similar corresponding trend that high value of the electrostatic energy of the adsorption features high value partial charge.

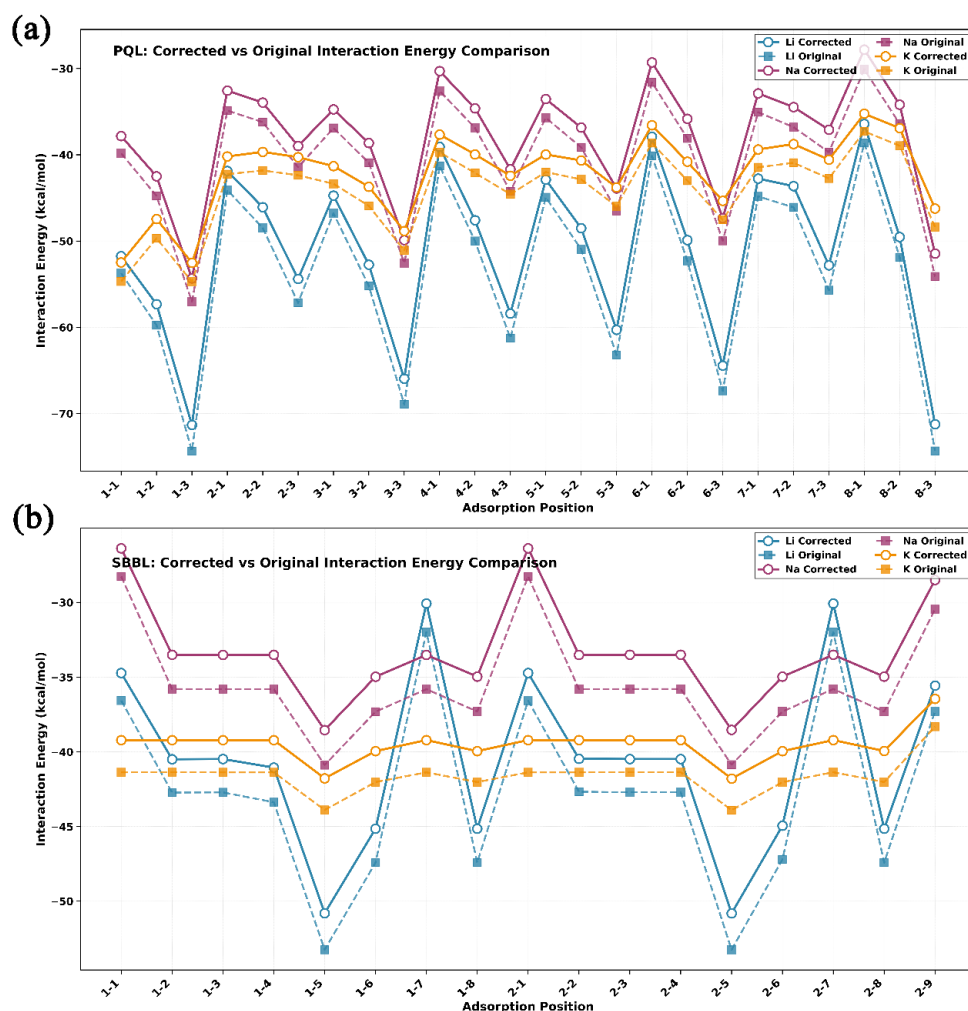


Figure 8. Comparison of interaction energies with (solid lines) and without (dashed lines) BSSE correction for Li (blue), Na (magenta), and K (orange) on (A) PQL and (B) SBBL substrates.

The bond length difference between the charge and cation adsorption states

After the finding of favorable interaction site, we adopted the BLD of ideal system (electron projecting system) (Figure 9 blue bar graph) and realistic system (cation charged system) (Figure 9 orange bar graph) to distinguish the difference from various systems. Also, the spin density of the realistic system is listed in the paralleling BLD bar graphs.

To mitigate the edge effect and correspond to the favorable interaction site in Figure 7, the 3-1, 3-2 and 3-3 configurations from PQL tetramer and 2-1, 2-5 and 2-7 configurations from SBBL tetramer are carried out for comparison. The conclusion differs a lot in two types of BLDs, especially for the interacting sites. Cation interacts the molecule leading to modifying bond length ascribed to the electrostatic energy between cation and molecule, as concluded above. As the matter of course, spin density redistributes among the PQL and SBBL oligomer, reflecting the obvious BLDs in Figure 9. Thus, it can be seen the necessity of considering both isolated system and cation-molecule system, especially investigating electrochemical properties of the electrode materials.

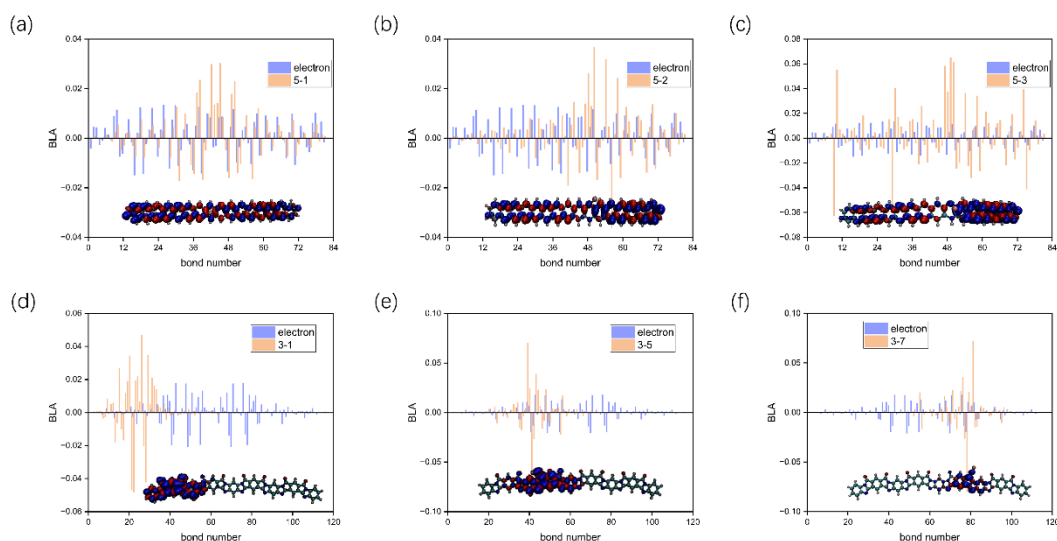


Figure 9. The BLD comparison between the electron charge and cation adsorption states. Electron denotes that the charge state is -1 and 5-1, 5-2 and 5-3 are the adsorption sites.

Conclusion

In brief, the calculation results demonstrate that PQL and SBBL manifest excellent electrochemical properties as electrodes. We explored the electronic structures of PQL and SBBL to investigate the mechanism behind by UDFT and DFT approaches under the oligomer approach. And the BS-DFT solution are applied for the stability of the wavefunction for the optimization and frequency calculations, which can lead to more

stable structures for the electronic structures (like polaron, bipolaron). And for singly charged states, as the length of the oligomer increases, the N_{FOD} of the PQL and SBBL increases, indicating that the length of the oligomer strengthens the radicaloid properties of the PQL and SBBL. BS DFT solution shows more stable wavefunction for the system than applying standard DFT. Additionally, the results of comparison between the trans-PQL and cis-PQL illustrate that trans-PQL manifests better electronic structure. For doubly charged states, the progressively decreasing value of the energy difference between the doubly charged singlet and triplet states validates that the radicaloid properties get strengthened as the length of the oligomer increases. Charged transfer rates is the vital role for the energy storage system. ET parameter inner reorganization λ^i was calculated for PQL and SBBL oligomer. By increasing the length of the PQL oligomer, the trend of λ^i is reasonable calculated by the BS DFT solution, indicating that the BS DFT solutions show more stable wavefunction than the standard DFT wavefunction. Compared to PQL, the λ^i of SBBL is slightly higher, indicating that the performance of the PQL is better than that of SBBL, which is proved by the experimental data mentioned above.

Also, the electrode cation system is explored and shows the periodic trend for PQL in interaction energy, relative energy and symmetric trend for SBBL ascribed to the SBBL symmetric structure. And compared to the electron charge system, the electrode cation system shows the bending angle of the structure and different spin density for PQL. As for SBBL, the electron charge system and the electrode cation system exhibit almost the same situation in different properties like bond length difference, structure planarity and others. Our study offers a better understanding of the electronic charged states and electrode cation system of PQL and SBBL and provides a strategy for exploring the mechanism behind charging, exciton, spin and heat transport states.

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Chapter 6: Investigating Electrochemical Properties and Cation Interaction Behavior for HATCOOH and its Derivatives HATCOOM (M=Na/K) as Anodes

6.1 Introduction

Over decades, organic materials have emerged as promising electrodes for electrochemical energy storage (EES) due to their environmental friendliness, low cost, and sustainable production [105], in contrast to inorganic EES electrodes, which often suffer from high cost and toxicity [106, 107]. Organic materials confer considerable advantages: abundant resources (C, H, O, N) and, notably, a flexible design space for tuning electrochemical properties [108]. Thus, researchers shifted their attention toward organic materials. Considering EES performance improvement, we investigate factors affecting battery performance, focusing on organic electrode materials (cathode and anode) which primarily impact battery performance metrics such as capacity, cycling life and charge transfer rate [109]. Therefore, it is crucial to explore organic electrode materials and elucidate their mechanisms, including structural formation, deformation, and charge/discharge processes.

Lithium batteries have flourished over decades [110] due to lithium's smaller ionic radius compared to other alkali metals and its higher energy density, facilitating extensive application and ease of ion transport [111, 112]. However, with rapid societal and technological development and increasing human and industrial demands, finding substitutes for lithium is urgent due to its rapidly depleting resources. Alkali metals such as sodium and potassium have entered research focus since they feature more abundant Earth resources and greater environmental friendliness for sodium batteries, and lower standard electrode potential and higher output voltage for potassium batteries [113, 114].

Based on the advantages of organic electrodes and alkali metal (Na- and K-) batteries mentioned above, we focus on organic electrode materials for alkali (Na- and K-) batteries. Among organic materials, hexaazatriphenylene-hexacarboxylic acid (HATCOOH) has emerged as a highly promising option for next-generation organic electrode materials in rechargeable batteries owing to multiple redox sites (six redox-active carboxyl groups), structural rigidity, and stability (conjugated framework) [115], as shown in Figure 6.2. In the work of Xia et al., π -conjugated N-containing heteroaromatic hexacarboxylate (Li₆-HAT), where hydrogen of the carboxyl group in HATCOOH is replaced by lithium, exhibits an ultrahigh initial capacity of 1126.3 mAh g⁻¹ at a current density of 100 mA g⁻¹ [115]. In our contribution, we have observed crystalline materials synthesis based on HATCOOM (M=Na/K) molecules via crystal growth in different solvents ex-

perimentally, shown in Figure 6.1, which act as anodes for sodium- and potassium-ion batteries. The same small molecules form crystalline materials with different configurations in different solvents, exhibiting distinct advantages such as long cycle life and high capacity.

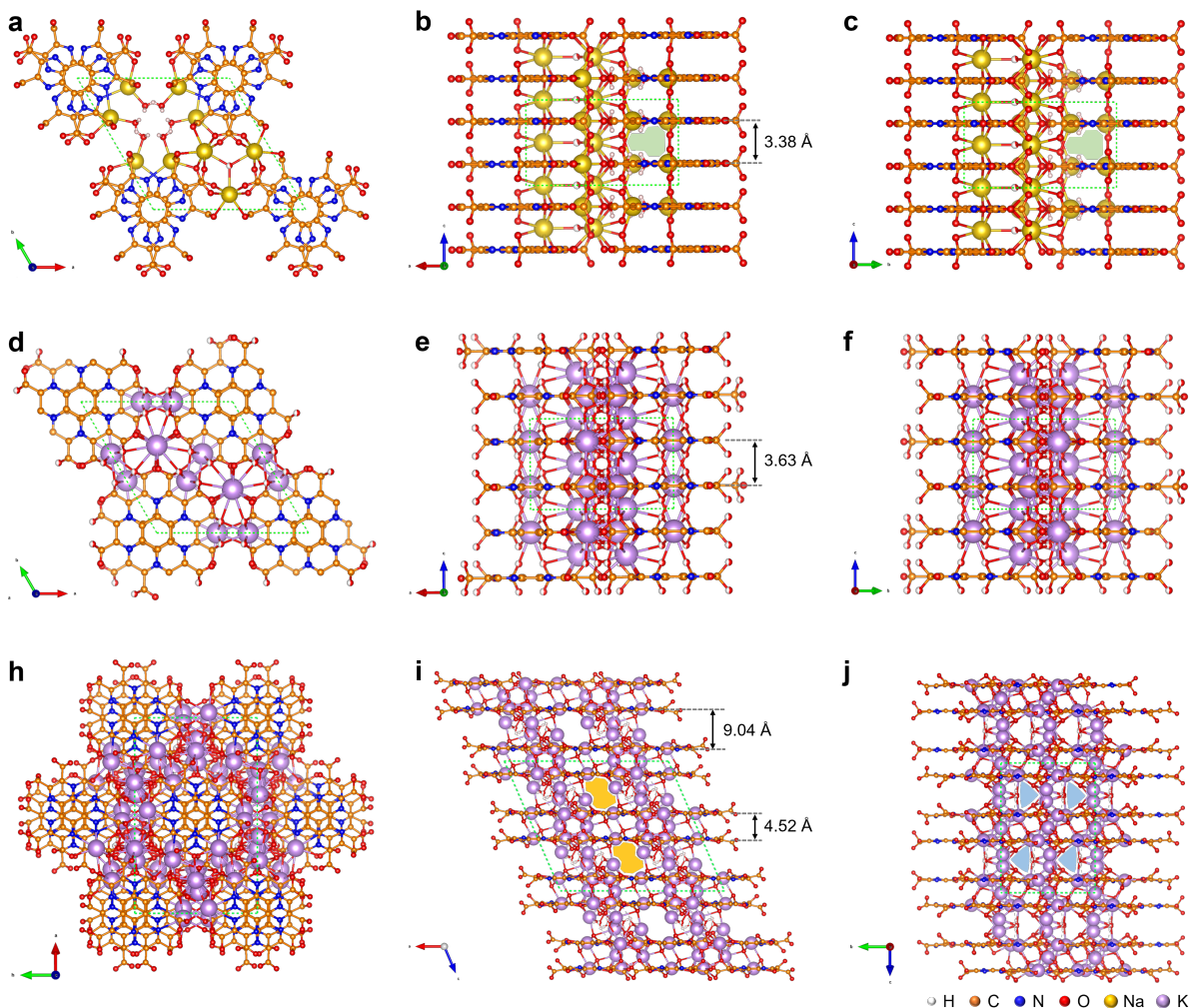


Figure 6.1: Various views for crystalline materials HATCOOM (M=Na/K).

We aim to investigate the formation mechanism of different configurations based on HATCOOM (M=Na/K). Firstly, the investigation starts from the HATCOOH molecule, which was adopted for electrochemical properties exploration and illustrates structural properties contributing to the material's obvious merits via DFT calculations. Additionally, to simulate the operation process, the model of alkali metal cation interaction with the substrate was simulated to illustrate the underlying operation mechanism. The formation mechanism of HATCOOM (M=Na/K) was computed based on deprotonation of HATCOOH. We employed electrostatic potential analysis to explore optimal adsorption sites and probe the reaction between alkali metal and substrate based on the deprotonation case. After that, H atoms are subsequently removed in the deprotonated case and

Na/K is incorporated into the HATCOOH molecule. The independent gradient model based on Hirshfeld partition (IGMH) is used to analyze various structural clusters to observe interlayer interactions affecting the interlayer gap. Considering battery operation, we utilized the Nudged Elastic Band (NEB) method ^[116] to analyze alkali metal cation migration within the configurations. The corresponding procedure and data analysis are still in progress.

6.2 Computational details

Standard DFT is utilized for structure optimization and electronic properties investigation. Electrostatic potential (ESP) is adopted for analyzing electron distribution. The ESP definition is as follows ^[117]:

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{r} - \mathbf{R}_A|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \quad (6-1)$$

where Z_A is the charge number of the A -th atomic nucleus (total number of protons, positively charged); $\mathbf{R}_A$ denotes the position vector of the A -th atomic nucleus in space; $\rho(\mathbf{r}')$ represents the electron density function, describing the distribution density of electrons at spatial point $\mathbf{r}'$ (negatively charged).

For molecules, the Gaussian ^[30] package is used for structure optimization and vibrational frequency calculations at the ω B97X-D/6-31G* level. For clusters, given unit cells containing over one hundred atoms, structures are optimized using xTB ^[32] to visualize electronic structure.

The Independent Gradient Model based on Hirshfeld partition (IGMH) enables the visualization of atom-atom, atom-molecule, and molecule-molecule interactions. IGMH is a real-space quantum chemical method for visualizing and quantifying non-covalent interactions. It improves upon the original Independent Gradient Model (IGM) by incorporating Hirshfeld atomic partitioning, enabling physically meaningful assignment of interaction contributions to individual atoms or fragments ^[118, 119].

In IGMH framework, the total electron density $\rho(\mathbf{r})$ is decomposed using Hirshfeld weight functions:

$$w_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r})}{\sum_B \rho_B^0(\mathbf{r})}, \quad (6-2)$$

where $\rho_A^0(\mathbf{r})$ denotes the promolecular electron density of atom A . The Hirshfeld-partitioned density for atom A is then $\rho_A(\mathbf{r}) = w_A(\mathbf{r})\rho(\mathbf{r})$.

The central quantity in IGMH is the following function:

$$\delta g(\mathbf{r}) = |\nabla \rho(\mathbf{r})| - \sum_A |\nabla \rho_A^0(\mathbf{r})|, \quad (6-3)$$

which measures the deviation between the actual gradient norm and the sum of non-interacting fragment gradient norms. Regions with $\delta g(\mathbf{r}) \approx 0$ correspond to covalent bonding or atomic cores, while positive values indicate non-covalent interactions [118].

For enhanced chemical insight, IGMH introduces a signed density overlap descriptor:

$$\delta g_{\text{inter}}^{\text{H}}(\mathbf{r}) = \delta g(\mathbf{r}) \cdot \text{sgn}(\lambda_2(\mathbf{r})) \cdot \rho(\mathbf{r}), \quad (6-4)$$

where $\lambda_2(\mathbf{r})$ is the second eigenvalue of the electron density Hessian matrix. The sign of λ_2 distinguishes attractive ($\lambda_2 < 0$) from repulsive ($\lambda_2 > 0$) interactions, while $\rho(\mathbf{r})$ ensures chemical relevance [118, 119].

A key advantage of IGMH is its ability to decompose interactions atom-by-atom. The pairwise interaction strength between atoms A and B is quantified by:

$$\delta G_{AB} = \int_{\Omega_{AB}} \delta g_{\text{inter}}^{\text{H}}(\mathbf{r}) d\mathbf{r}, \quad (6-5)$$

where Ω_{AB} denotes the spatial domain influenced by atoms A and B . This approach provides robust analysis of weak interactions in complex systems such as supramolecular assemblies and biomolecules [119].

Considering cation migration within anode materials, the climbing-image nudged elastic band (CI-NEB) method [116] was employed to illustrate migration mechanisms.

The climbing-image nudged elastic band (CI-NEB) method was employed to locate the minimum-energy path (MEP) and transition state (TS) for alkali metal cation diffusion between adjacent interstitial sites [120, 121]. Within the CI-NEB formalism, a discrete chain of P images $\{\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_P\}$ is constructed between fixed end-points $\mathbf{R}_{\text{IS}}$ (initial state) and $\mathbf{R}_{\text{FS}}$ (final state). The total effective force acting on image i is given by

$$\mathbf{F}_i = \mathbf{F}_i^{\text{true}} - (\mathbf{F}_i^{\text{true}} \cdot \hat{\boldsymbol{\tau}}_i) \hat{\boldsymbol{\tau}}_i + \mathbf{F}_i^{\text{spring}} - (\mathbf{F}_i^{\text{spring}} \cdot \hat{\boldsymbol{\tau}}_i) \hat{\boldsymbol{\tau}}_i, \quad (6-6)$$

where $\mathbf{F}_i^{\text{true}} = -\nabla E(\mathbf{R}_i)$ is the true atomic force (negative energy gradient), and $\hat{\boldsymbol{\tau}}_i$ is the unit tangent vector to the path at image i , estimated using the improved tangent scheme of Henkelman *et al.* [121]:

$$\hat{\boldsymbol{\tau}}_i = \frac{\mathbf{R}_{i+1} - \mathbf{R}_{i-1}}{\|\mathbf{R}_{i+1} - \mathbf{R}_{i-1}\|}. \quad (6-7)$$

The spring force is defined as:

$$\mathbf{F}_i^{\text{spring}} = k (\|\mathbf{R}_{i+1} - \mathbf{R}_i\| - \|\mathbf{R}_i - \mathbf{R}_{i-1}\|) \hat{\boldsymbol{\tau}}_i, \quad (6-8)$$

where the spring constant $k = 5.0 \text{ eV } \text{\AA}^{-2}$ ensures uniform spacing between images while introducing no artificial force component perpendicular to the reaction path [121]. For

the highest-energy image, the climbing-image protocol is applied, reversing the parallel component of the true force while preserving the perpendicular component:

$$\mathbf{F}_{\text{climb}} = -\mathbf{F}_{\text{true}}^{\parallel} + \mathbf{F}_{\text{true}}^{\perp} = \mathbf{F}_{\text{true}} - 2(\mathbf{F}_{\text{true}} \cdot \hat{\boldsymbol{\tau}}) \hat{\boldsymbol{\tau}}, \quad (6-9)$$

thereby driving this image precisely to the first-order saddle point [120]. All intermediate images were relaxed using the conjugate-gradient optimizer from the VTST tools for VASP [122] until the maximum component of the residual force fell below $0.03 \text{ eV } \text{\AA}^{-1}$. The migration barrier ΔE_{m} was computed as the energy difference between the transition state and initial state:

$$\Delta E_{\text{m}} = E_{\text{TS}} - E_{\text{IS}}. \quad (6-10)$$

6.3 Results and discussion

According to the ESP definition, it reflects electron distribution: negative ESP regions are mainly around nitrogen atoms (“pocket site”) and carboxyl groups, while positive ESP regions are located on benzene and pyrazine ring surfaces. Cations Na^+ and K^+ are more strongly attracted to the “pocket site” and carboxyl groups. Additionally, yellow and green points on the ESP denote maximum and minimum ESP values, indicating the most attractive and repulsive sites, respectively.

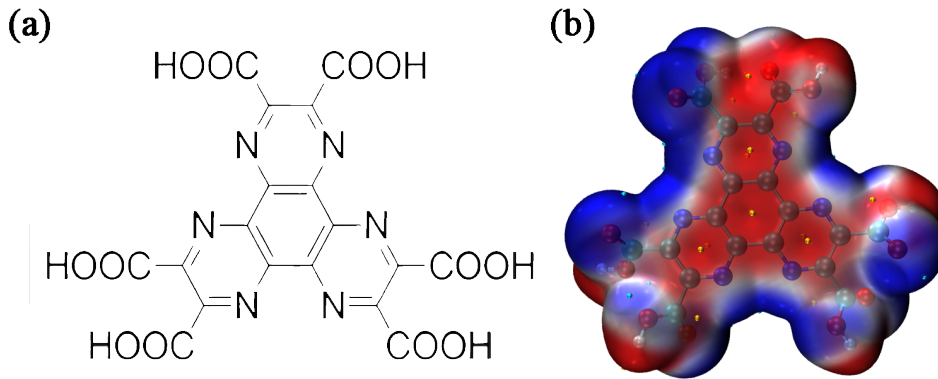


Figure 6.2: The chemical structure of HATCOOH and its molecular electrostatic potential.

Based on adsorption site investigation, we modeled Na^+ and K^+ adsorption systems to validate the above conclusion. Metal ions were successively positioned at optimal adsorption sites identified from ESP, with one ion placed at a time in the deprotonated

case, obtaining total system energy and interaction energy via the equation

$$E_{\text{interaction}} = E_{\text{molecule/metal}} - E_{\text{molecule}} - E_{\text{metal}}, \quad (6-11)$$

where $E_{\text{molecule/metal}}$ is the total energy of the cluster, E_{molecule} is the total energy of the isolated molecule, and E_{metal} is the total energy of the isolated alkali metal.

Based on computed interaction energies, the pocket site is confirmed as the optimal adsorption site for both Na^+ and K^+ . Furthermore, we calculated ESP of optimal adsorption configurations for Na^+ and K^+ and applied the independent gradient model based on Hirshfeld partitioning (IGMH), along with energy decomposition analysis (EDA) performed with Multiwfn [123–125], to illustrate the mechanism in detail, as shown in Figure 6.3.

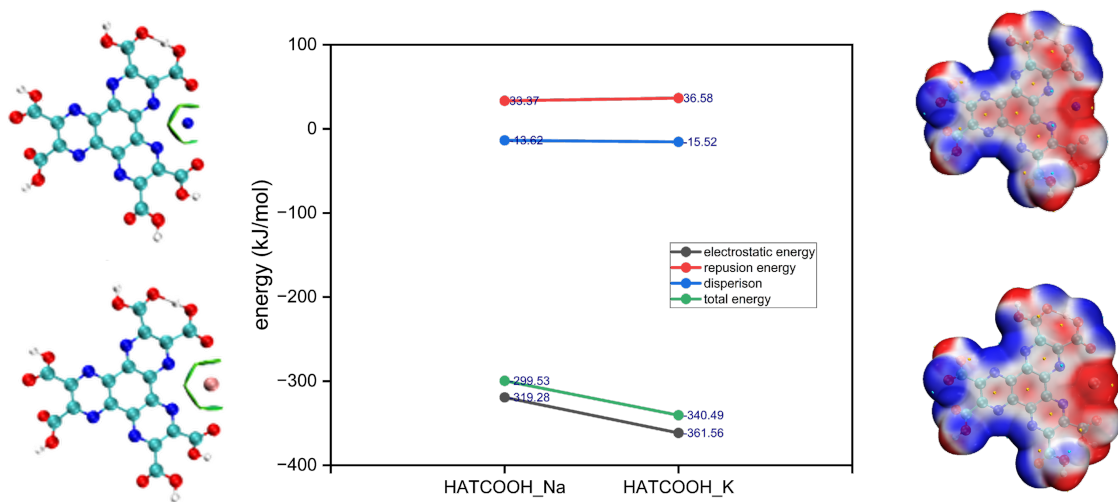


Figure 6.3: The Na^+ and K^+ –HATCOOH systems, IGMH, energy decomposition analysis and ESP.

As shown in the left panel of Figure 6.3, IGMH reveals predominantly attractive interactions between Na^+ and K^+ cations and nitrogen atoms of the pyrazine ring, which exhibit strong attractiveness. Energy decomposition analysis agrees with IGMH: dispersion energy of the K^+ –HATCOOH system is $-15.52 \text{ kJ mol}^{-1}$, larger in magnitude than that of the Na^+ –HATCOOH system ($-13.62 \text{ kJ mol}^{-1}$). After exploring the most stable configurations of alkali metal systems, as seen from the right panel in Figure 6.3, other negative ESP sites also attract additional alkali metal cations. Therefore, we consider continuous deprotonation with sequential addition of Na^+ and K^+ cations based on previously obtained stable adsorption configurations, constructing an adsorption stepwise energy profile. The procedure proceeds as follows: Initially, one H atom is removed from HATCOOH, and one Na/K atom is incorporated at sites proximal to the H-removed location. It should be stressed that H atom removal sites were selected randomly. The

resulting structure is optimized to obtain its most stable configuration. Subsequently, building upon this optimized stable structure, a second H atom (also from a random site) is removed and the procedure is repeated: one Na/K atom is introduced near the newly formed H vacancy, followed by structural optimization for new stable configurations. This stepwise substitution (removing one random H atom and incorporating one adjacent Na/K atom, then optimizing) continues until all H atoms in HATCOOH are replaced. Ultimately, 6 H atoms are removed and 6 Na/K atoms are incorporated, with the objective of identifying the most stable configuration of the modified HATCOOH structure. This approach allows observation of HATCOOM (M=Na/K) formation process, thereby understanding crystalline material structure formation. This work is currently in progress.

The next step involves calculating Gibbs free energy to evaluate energy requirements for continuous deprotonation and metal ion adsorption. Subsequently, we will move to larger clusters, focusing on chemical properties such as thermal stability, electronic structure, cation diffusion pathways, etc., to describe charge/discharge processes. This contribution aims to accurately describe crystalline structure formation from molecules and alkali cation migration pathways and diffusion behavior within crystalline structures.

Chapter 7: Conclusions

Electrochemical Energy Storage (EES) devices, such as batteries and supercapacitors, are key technologies for future applications. EES materials, constituting the electrodes that are the active components of EES devices, play a fundamental role in determining the device efficiency and durability. Among electrode materials, an emerging class is that of organic functional materials, which generally feature low costs, sustainable production methods, and good mechanical and thermal properties. The current work centers on three classes of organic materials, namely para-graphdiyne (*p*-CNGDY), hexaazatriphenylene-hexacarboxylic acid (HATCOOH), and conjugated redox polymers (OCRPs), summarily outlined as follows:

- **Graphdiyne and its derivatives**

Graphdiyne (GDY) and its cyano-based derivatives, two-dimensional (2D) carbon-based materials, have been computationally and experimentally investigated as EES materials. Three different GDY derivatives have been considered, differing by the position and number of cyano groups inserted into their structure. CN-GDY has been defined as the species with one cyano group (located at the para positions of the peripheral benzene rings, i.e., at the vertices of the hexagonal 2D conjugated framework). *m*-CNGDY and *p*-CNGDY possess two cyano groups in meta (*m*) and para (*p*) positions, respectively. One of the main goals of the study was to address the structural changes induced by varying the insertion of cyano groups in the GDY structure. Via solid-state quantum chemical calculations, we computed the bulk structure, the packing, and the relative orientation of each GDY species, and found that an increase in the number of cyano groups reduces the interlayer spacing between GDY planes, increases the lithium adsorption capacity, and impacts the lithium diffusion rate. In particular, we found that adding CN groups in various amounts and at different positions on the GDY frameworks decreases the interlayer distance and alters the stacking arrangement by sliding the planes relative to each other. Furthermore, we explored the intercalation of lithium cations within the bulk GDY structures. We found that lithium prefers positions close to the cyano groups. The greater the number of cyano groups, the higher the amount of lithium cations stored. Finally, from the calculations we were able to compute the band gap of these 2D materials, finding that meta substitution opens the gap, while para substitution does not significantly affect the band gap compared to pristine GDY. The quantum-chemical calculations well supported and confirmed the experimental studies.

- **Organic Conjugated Redox Polymer (PQL and SBBL)**

Among the organic conjugated redox polymers (OCRPs), the ladder-type OCRPs we investigated are polyquinoxalines (PQL) and SBBL, which is a simplified derivative of benzobisimidazobenzophenanthroline (BBL), a well-known polymer with high charge capacity, thermal stability, and ion mobility. By combining density functional theory (DFT), broken-symmetry DFT (BS-DFT), and fragment orbital density (FOD) analysis, we revealed the polyradicaloid character of the electronic structure of neutral and multi-redox states for pristine polymers (i.e., not interacting with alkali metals). For multi-redox states, polarons (i.e., singly charged systems) and bipolarons (i.e., doubly charged systems) were modelled. The polaron/bipolaron structural deformations were modelled by considering both negative (electron) and positive (hole) charges, aiming to mimic the reduction and oxidation processes. The intramolecular reorganization energy, a fundamental charge transfer parameter governing the transfer rate, was computed for each charged state and for each polymer. Due to the polyradicaloid nature of the electronic structure, we found that standard DFT leads to unphysical results, while BS-DFT mitigates these errors, thus yielding physical values and trends for the reorganization energy, as computed at the polymer limit. Different XC DFT functionals were considered (e.g., ω B97X-D, which enhances the biradicaloid character of singlet configurations compared to B3LYP and M06-2X) to validate the reliability of the computational results. The interplay between singlet and triplet neutral and multi-charged redox states is then discussed and analysed. The action of alkali metals is studied by modelling, via a supramolecular approach, the interaction between polymer segments and cations. DFT and force-field-based energy decomposition analysis revealed that different polymer sites lead to different interaction energies. We found that the regions around the nitrogen-rich sites for PQL and the carbonyl units for SBBL are the most favourable locations for cation interaction, and more electrons migrate from Li to the substrate compared to Na and K. The project aims to shed light on the theoretical investigation of OCRPs and to offer guidance for experimental material synthesis.

- **HATCOOH**

We investigated the structural, electronic, and interaction properties of hexaazatriphenylene-hexacarboxylic acid (HATCOOH) and simulated the interaction mechanism with multiple potassium cations using the range-separated functional ω B97X-D. We observed the most favorable adsorption site (located near the nitrogen atoms of two adjacent pyridine rings). For the next steps, we will switch to a larger cluster in-

stead of the HATCOOH molecule to focus on the diffusion pathway of K^+ cations on the substrate and the electrochemical performance capacity for potassium-ion batteries.

The current work paved the way for an accurate bottom-up modelling of the structure-property relationships for organic conjugated redox active materials. Their electrochemical (redox) states and intermolecular interactions with alkali metals have been investigated by combining DFT and Molecular Mechanics (MM) approaches in order to unlock the molecular mechanisms behind the operating processes of EES systems.

Appendix

Supporting Information Manuscript I

Supporting Information

Tailoring the Electronic Structure and Properties of Graphdiyne by Cyano Groups

Lei Gao,^{†, ‡, ∇} Shuailong Wang,^{¶, ⊥, ∇} Fan Wang,^{§, ∇} Ze Yang,^{Ⓛ, *} Xiaodong Li,[†] Jingchi Gao,[†] Daniele Fazzi,[Ⓛ] Xiang Ye,^{¶, *} Xuebin Wang,[‡] and Changshui Huang,^{†, Φ, *}

[†]Beijing National Laboratory for Molecular Sciences, Organic Solids Laboratory, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

[‡]National Laboratory of Solid-State Microstructures (NLSSM), Collaborative Innovation Center of Advanced Microstructures, Jiangsu Key Laboratory of Artificial Functional Materials, College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China

[¶]Department of Physics, Shanghai Normal University, Shanghai 200234, China

[§]Science Center for Material Creation and Energy Conversion, Institute of Frontier and Interdisciplinary Science, Shandong University, Qingdao 266237, China

[Ⓛ]College of Energy Storage Technology, Shandong University of Science and Technology, Qingdao 266590, China

[Ⓛ]Department of Chemistry "Giacomo Ciamician", University of Bologna, via P. Gobetti 85, 40129 Bologna, Italy

^ΦUniversity of Chinese Academy of Sciences, Beijing 100049, China

*Corresponding Authors: yangzejuly10th@163.com, yexiang@shnu.edu.cn, huangcs@iccas.ac.cn

[∇]These authors contributed equally to this work.

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Part 1. Supplemental Experimental Section

Note S1. Reagent and experiment conditions

Cu foils were purchased from Sinopharm Chemical Reagent Co., Ltd. (SCRC) and pretreated by sonicating in 1M HCl and acetone and ethanol, sequentially, for 5 min, dried under a flow of argon, and used immediately for growing four kinds of GDYs films. All the solvents and reagents such as pyridine, tetrahydrofuran, toluene, butyllithium (2.5 M solution in hexanes), dichloromethane, (trimethylsilyl)acetylene, hexachlorobenzene, pentachlorobenzonitrile, tetrachloroisophthalonitrile, tetrachloroterephthalonitrile and tetrabutylammonium fluoride (TBAF) were purchased from ArcosOrganics, Alfa Aesar or J&K Scientific Ltd. and used directly in the experiment unless otherwise stated. Toluene and tetrahydrofuran were further dried by boiling with sodium scraps in argon atmosphere before use. All reactions were performed under nitrogen (N₂) condition unless otherwise noted.

Note S2. Methods

Synthesis of meta-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene (compound vii):

TMSA (56.5 mL, 400 mmol), *n*-BuLi (160 mL, 2.5 M), ZnCl₂ (68.1 g, 500 mmol), Pd (PPh₃)₄ (2.9 g, 2.5 mmol), toluene (100 mL), and tetrachloroisophthalonitrile (compound iii, 13.3 g, 50 mmol) were added to 150 mL of THF in sequence. The mixture was stirred under a nitrogen atmosphere at 80°C for 3 days in a tube sealing. Saturated sodium chloride aqueous solution (100 mL) was used as the quenching agent. After the insoluble matter was filtered, the organic matter was extracted with dichloromethane (100 mL) and the solvents were evaporated. Then the residue was purified by column chromatography (silica gel, hexane/CH₂Cl₂, v/v, 8:1) to obtain white powdery solid (21.8 g, 85.1%). ¹H NMR (600 MHz, CDCl₃) δ /

S3

ppm = 0.32 (s, 9H), 0.31 (s, 18H), 0.30 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 133.25 (s), 129.71 (s), 128.93 (s), 118.93 (s), 114.86 (s), 113.20 (s), 113.00 (s), 110.04 (s), 99.40 (s), 98.67 (s), 97.26 (s), 0.23 (s), 0.00 (s), -0.15 (s); HRMS (ESI, positive mode) m/z 512.2091 $[\text{M}]^+$, calculated for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{Si}_4$: m/z = 512.1956.

Synthesis of para-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene (compound viii):

TMSA (56.5 mL, 400 mmol), *n*-BuLi (160 mL, 2.5 M), ZnCl_2 (68.1 g, 500 mmol), $\text{Pd}(\text{PPh}_3)_4$ (2.9 g, 2.5 mmol), toluene (100 mL), and tetrachloroterephthalonitrile (compound iv, 13.3 g, 50 mmol) were added to 150 mL of THF in sequence. The mixture was stirred under a nitrogen atmosphere at 80°C for 3 days in a tube sealing. Saturated sodium chloride aqueous solution (100 mL) was used as the quenching agent. After the insoluble matter was filtered, the organic matter was extracted with dichloromethane (100 mL) and the solvents were evaporated. Then the residue was purified by column chromatography (silica gel, hexane/ CH_2Cl_2 , v/v, 8:1) to obtain white powdery solid (18.3 g, 71.5%). ^1H NMR (600 MHz, CDCl_3) δ / ppm = 0.18 (s, 36H); ^{13}C NMR (150 MHz, CDCl_3) δ 129.39 (s), 122.62 (s), 114.88 (s), 111.70 (s), 98.32 (s), 0.00 (s); HRMS (ESI, positive mode) m/z 512.2093 $[\text{M}]^+$, calculated for $\text{C}_{28}\text{H}_{36}\text{N}_2\text{Si}_4$: m/z = 512.1956.

Generic preparation of GDY, CNGDY, m-CNGDY and p-CNGDY films:

Six pieces of copper foil (5×10 cm) was placed in a 300 mL polytetrafluoroethylene tank and submerged with refrigerated pyridine (0~5°C). After the alkyne polymer precursor was added and stirred evenly (v: 909.35 mg / vi: 803.16 mg / vii or viii: 698.87 mg), 2 ml TBAF was added rapidly and the hydrothermal kettle was installed. After reaction at 80°C for one day, the copper foils with alkyne polymer film were obtained. Soak them in 6 M HCl to peel the film, then wash it with ethanol and deionized water for five times, and vacuum dry it for standby.

Note S3. Characterizations

^1H NMR, ^{13}C NMR were recorded on Bruker AVANCE-III 600 (600 MHz for ^1H , 150 MHz for ^{13}C) instrument in CDCl_3 with tetramethylsilane as an internal standard. Solid-state ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AVANCEIII/WB-400. Mass spectrum (MS) was obtained on a Bruker Solarix 7.0T high resolution Fourier transform mass spectrometer. The XRD pattern was obtained by Bruker D8 ADVANCE diffractometer with $\text{Cu K}\alpha$ irradiation at $\lambda = 1.5406 \text{ \AA}$. FT-IR

images were taken from Thermo-Fisher Nicolet iN10 in the frequency range of 4000~650 cm^{-1} . The Raman spectra were recorded at room temperature using a Thermo Scientific DXRXI system with excitation from an Ar laser at 532 nm. The ultraviolet-visible (UV-Vis) spectra were measured on a Varian Cary 50. Thickness and roughness measurements were performed on an atomic force microscope (AFM) using the Bruker Multimode 8 instrument. Field emission scanning electron microscopy (FESEM, Hitachi S-4800) and transmission electron microscopy (TEM, H-7650 or FEI Tenna F20) were used to obtain the microscopic morphology of all the GDY films. A Rubotherm DynTHERM instrument was used to perform thermogravimetry analysis (TGA). The semiconductor analyzer (Keithley 4200SCS) was used to analyze the conductivity and transfer characteristics.

Note S4. Theoretical Calculations

In this work, the calculations were performed by the Vienna ab initio Simulation Package (VASP)¹ based on the density functional theory (DFT), within the generalized gradient approximation of the Perdew-Burke-Ernzerhof (PBE)^{2,3}. The interaction between ion cores and valence electrons is handled using the projector augmented wave method (PAW)⁴. The kinetic energy cutoff is set as 350 eV. And the value of threshold convergence for energy and atomic forces are set as 10^{-5} eV and 2×10^{-2} eV/Å, respectively. $3 \times 3 \times 1$ k-point mesh produced by Monkhorst-Pack scheme are used in the structure optimization, and the calculation of the electronic band structure and density of state (DOS). Also, the van der Waals (vdW) (DFT-D3 method with Becke-Johnson damping function) corrections have been utilized for the structure optimization and stacking optimization. The charge transfer between ion and electrode is calculated by the Bader charge analysis.⁵ And the DFT calculations for energy decomposition analysis (EDA) were performed by using the Gaussian 16.⁶ The adsorption energy of the ion on the GDY monolayer is obtained by:

$$E_{ad} = E_{Li\text{substrate}} - E_{Li} - E_{\text{substrate}} \quad (1)$$

where $E_{Li\text{substrate}}$ donates the energy of the ion adsorbed GDY, and $E_{\text{substrate}}$ and E_{Li} are the energies of the pristine GDY substrate and single Li atom, respectively.

The theoretical maximum specific capacity is calculated by:

$$C = \frac{n_{\max} z F}{M_{\text{substrate}}} \quad (2)$$

where the n_{max} is the maximum number of the ions loaded; z is the valence number of Li ion; F is the Faraday constant (26.801 Ah g⁻¹); $M_{substrate}$ is the mass weight of substrate.

Note S5. Electrochemical Measurements

The LIB half-cell tests were assembled in standard CR2032-type coin cells and used lithium metal foil as counter electrodes. For the preparation of lithium-ion anode, the slurry containing GDY/CNGDY/*m*-CNGDY/*p*-CNGDY (80w%), super P (10w%) and PVDF (10w%) in 1-methyl-2-pyrrolidone (NMP) is uniformly coated on the copper foil by doctor blade. After then, it is dried at 80°C in a vacuum oven overnight. The as-prepared electrodes were cut into small round pieces with the diameter of 1.2 centimeter. The mass load of active substances of these four alkyne polymers was controlled at 0.6 mg cm⁻¹, so as to compare the magnification performance (Figure 4m) and long cycle performance horizontally (Figure 4n). The electrolyte was 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1, v/v), the separator was a Celgard ® 2300 membrane. The LAND battery testing system was used to monitor the button cells in the voltage range of 0.005~3V (GITT: 0.01~3V, 100 mA g⁻¹, τ = 3600 s). Installation or disassembly of the cells was carried out in an Ar-filled glove box with both O₂ and H₂O content below 0.1 ppm. Cyclic voltammograms (I-V) were recorded using a CHI 760 D apparatus.

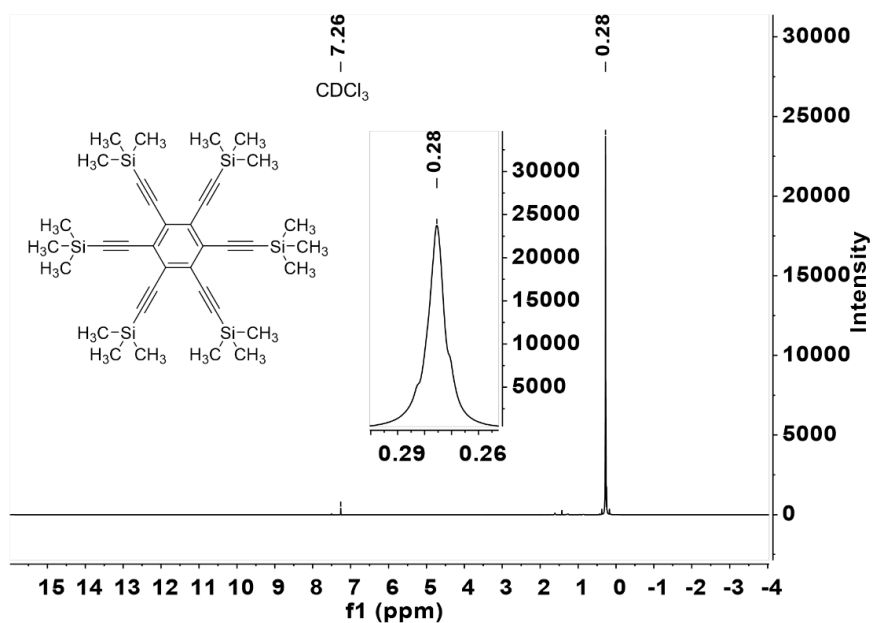
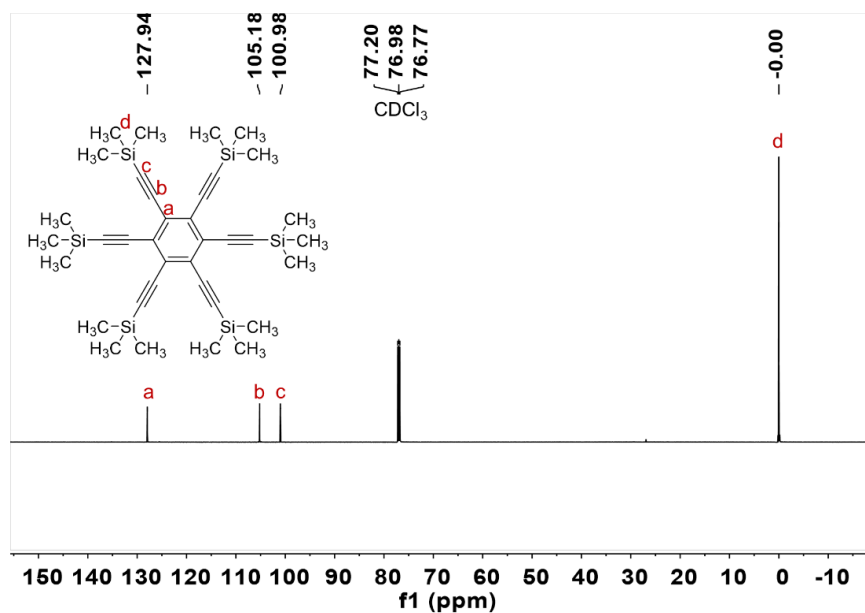
Note S6. Galvanostatic intermittent titration technique (GITT)

A galvanostatic intermittent titration technique (GITT) was conducted to examine D_{Li^+} during Li-ion intercalation/deintercalation through the following formula:

$$D = \frac{4L^2}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (3)$$

where L is the Li⁺ diffusion length (equal to the electrode thickness, cm), τ represents the relaxation time (s), ΔE_s stands for the steady-state potential change via the current pulse, and ΔE_t is the potential change in current pulse after subtracting the iR drop.

Part 2. Supplemental Figures and Tables

**Figure S1.** ^1H NMR spectrum of hexakis[(trimethylsilyl)ethynyl]benzene.**Figure S2.** ^{13}C NMR spectrum of hexakis[(trimethylsilyl)ethynyl]benzene.

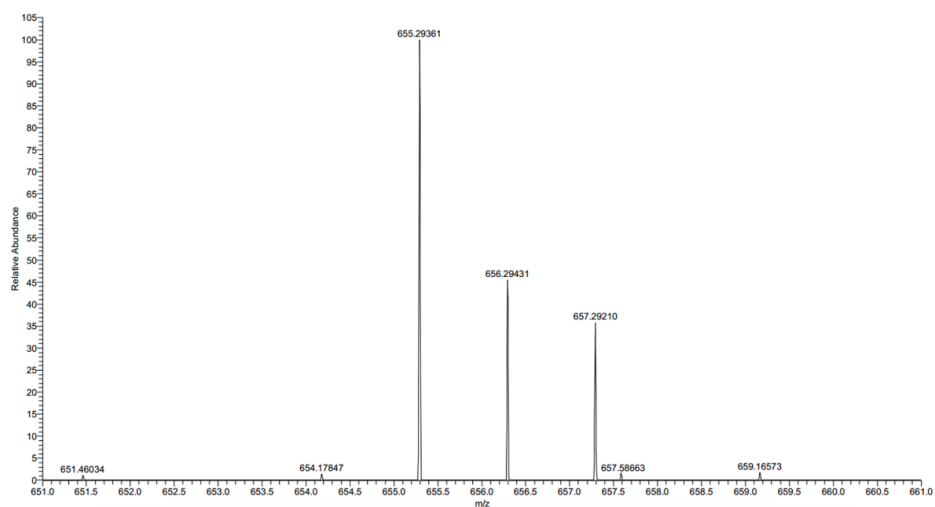


Figure S3. Mass spectrum of hexakis[(trimethylsilyl)ethynyl]benzene.

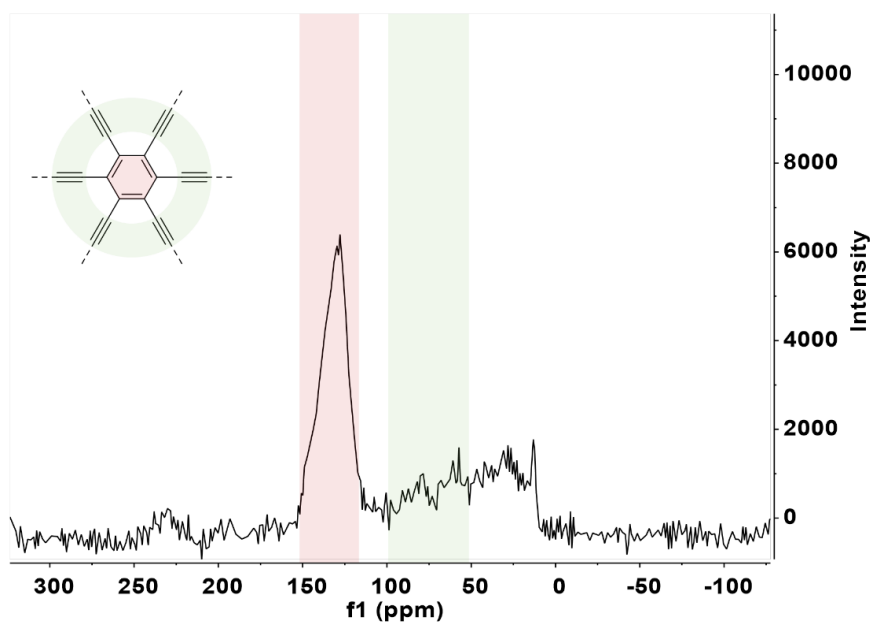


Figure S4. Solid-state ^{13}C NMR spectrum of GDY.

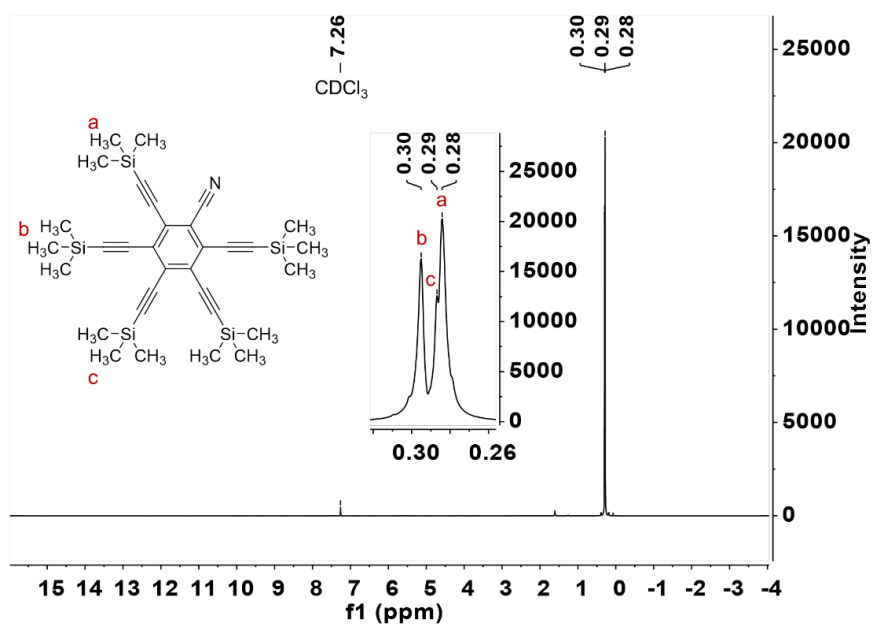


Figure S5. ^1H NMR spectrum of cyanopentakis[(trimethylsilyl)ethynyl]benzene.

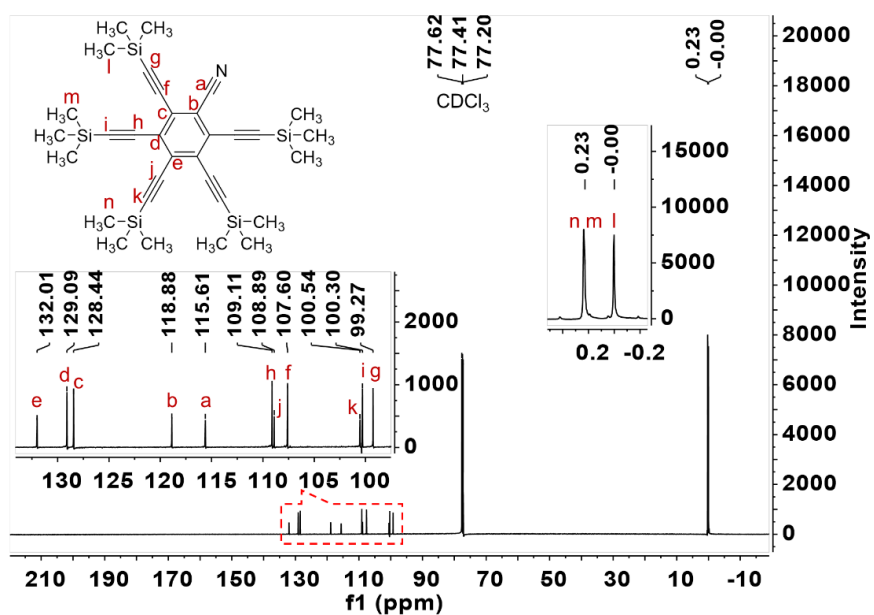


Figure S6. ^{13}C NMR spectrum of cyanopentakis[(trimethylsilyl)ethynyl]benzene.

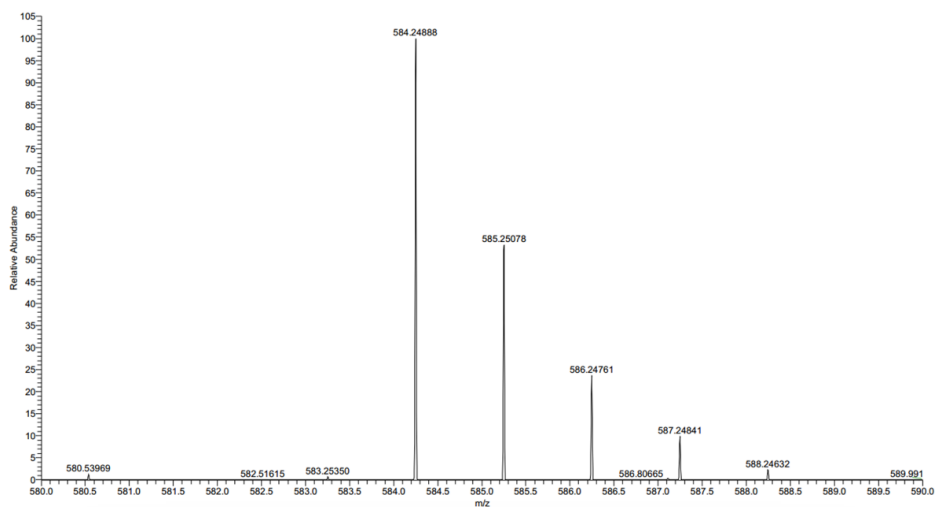


Figure S7. Mass spectrum of cyanopentakis[(trimethylsilyl)ethynyl]benzene.

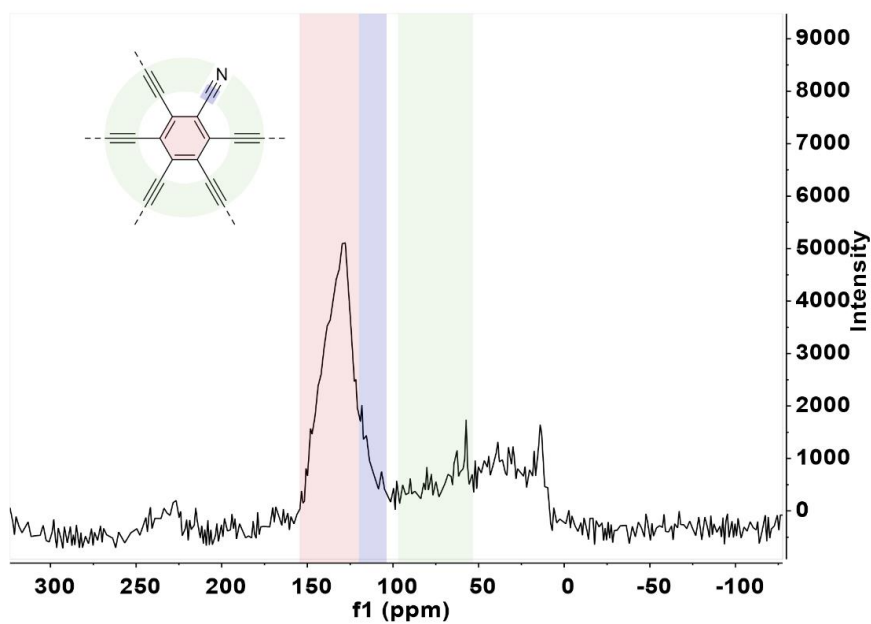


Figure S8. Solid-state ^{13}C NMR spectrum of CNGDY.

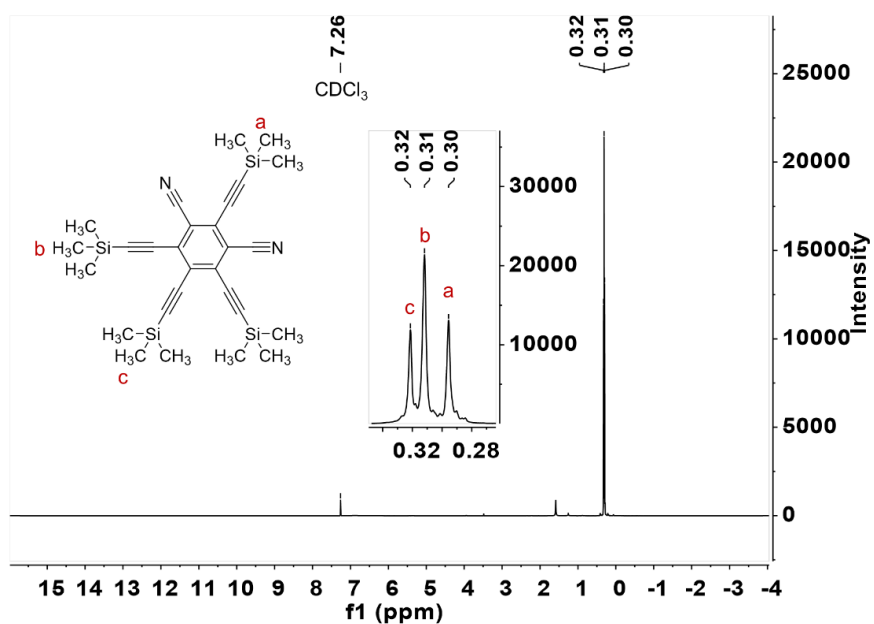


Figure S9. ^1H NMR spectrum of meta-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene.

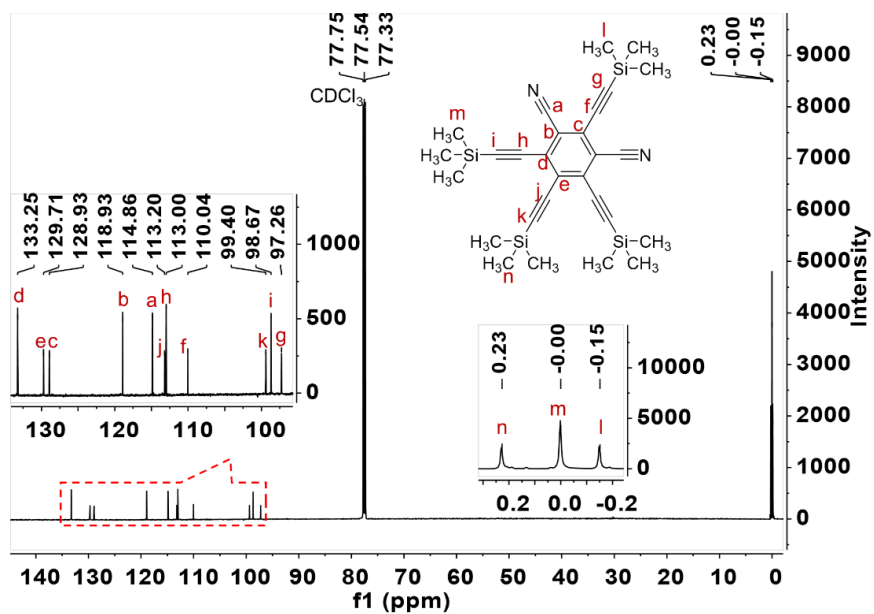


Figure S10. ^{13}C NMR spectrum of meta-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene.

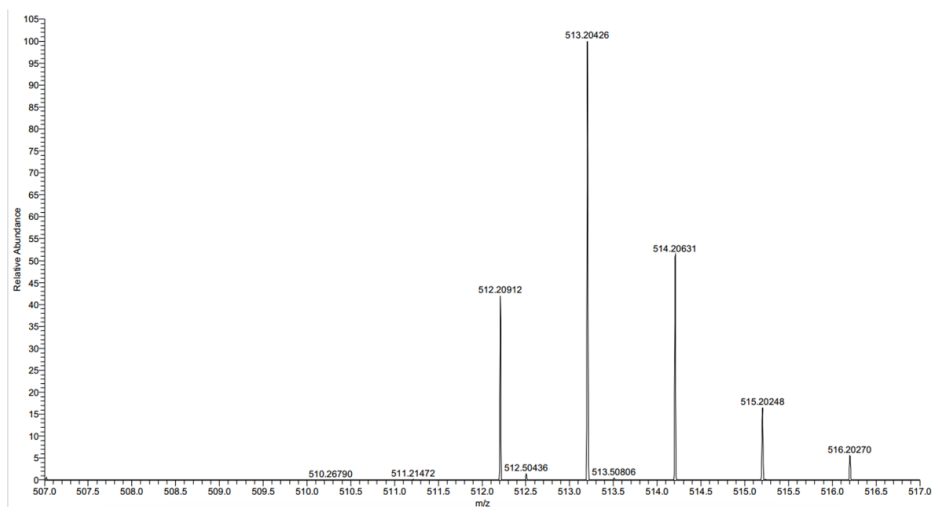


Figure S11. Mass spectrum of meta-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene.

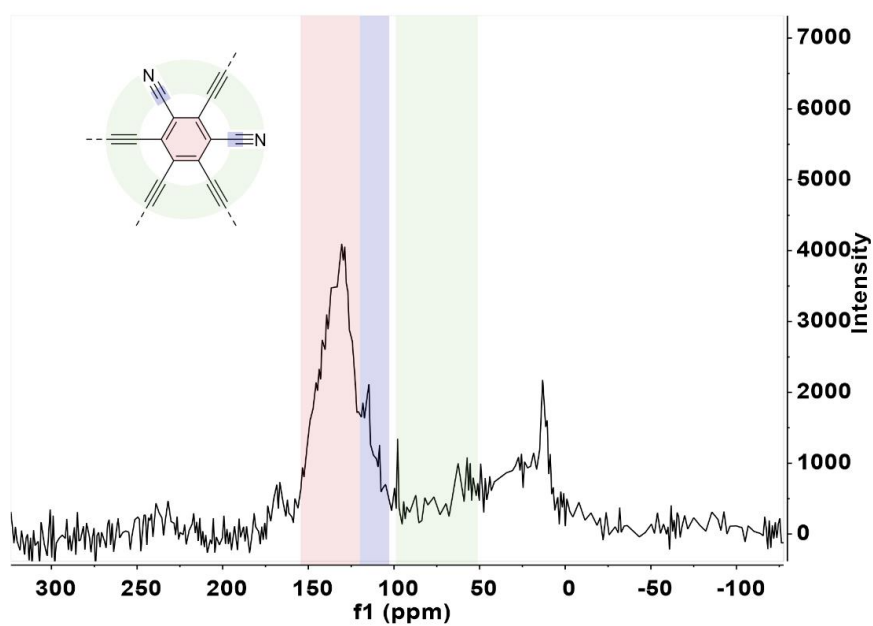


Figure S12. Solid-state ^{13}C NMR spectrum of *m*-CNGDY.

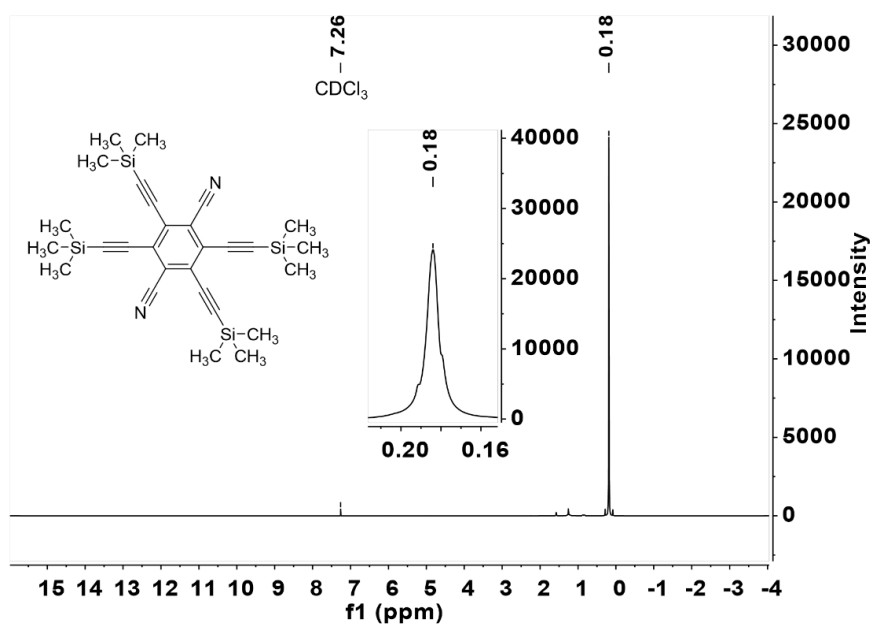


Figure S13. ^1H NMR spectrum of para-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene.

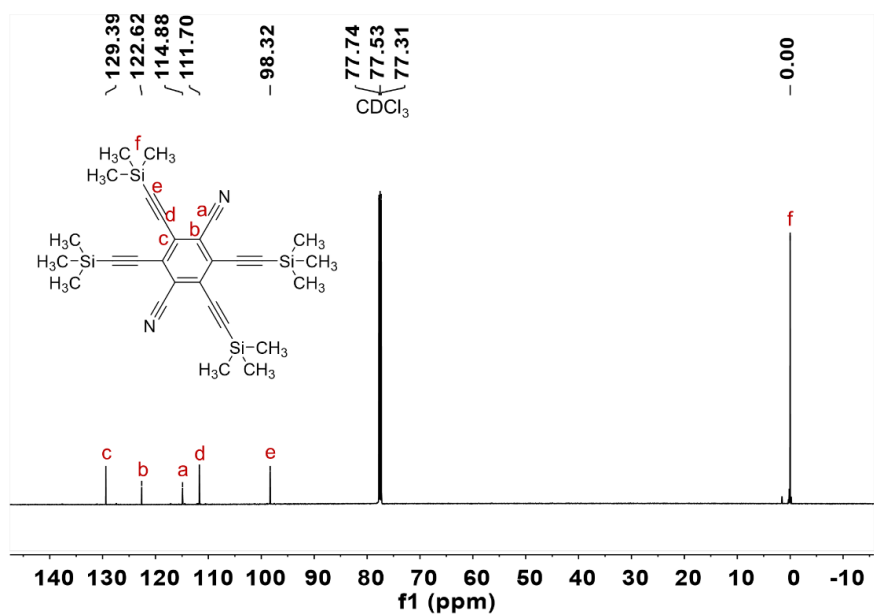


Figure S14. ^{13}C NMR spectrum of para-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene.

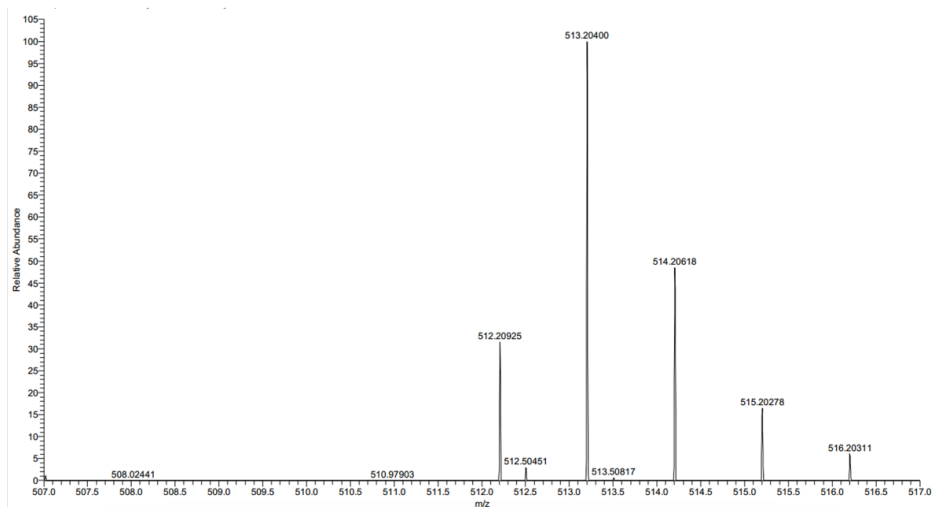


Figure S15. Mass spectrum of para-dicyanotetrakis[(trimethylsilyl)ethynyl]benzene.

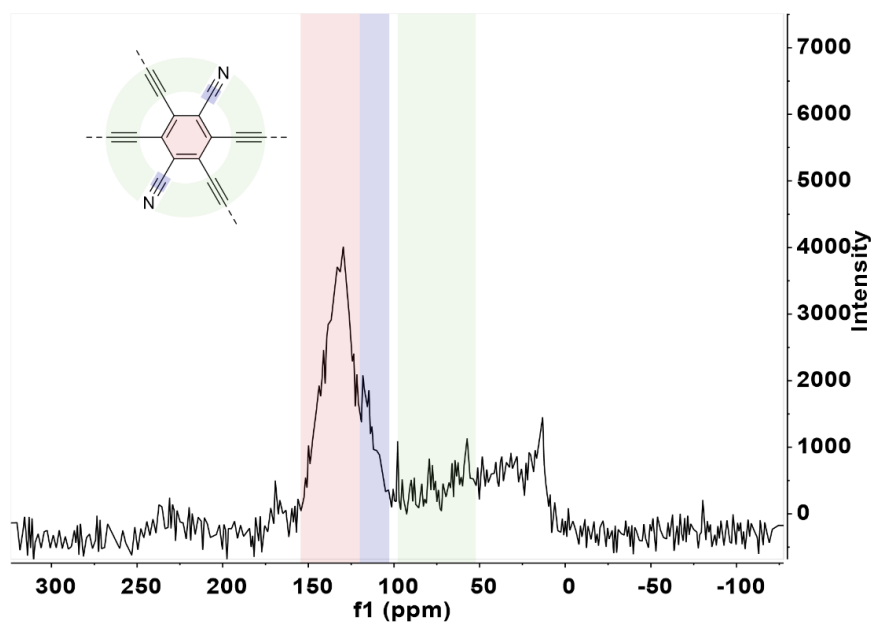


Figure S16. Solid-state ^{13}C NMR spectrum of *p*-CNGDY.

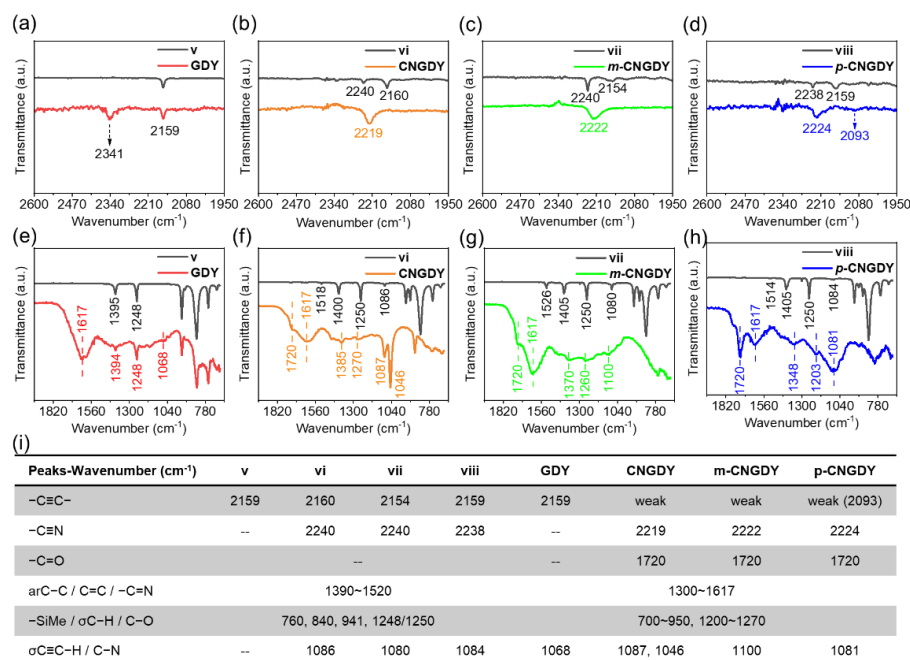


Figure S17. The enlarged FT-IR spectra (a-h) of **1~4** in **Figure 1f-1i** with their characteristic peak assignment list (i).

In each precursor, the stretching vibrations of the alkynyl (v~viii: 2159, 2160, 2154 and 2159 cm⁻¹) and cyano groups (vi~viii: 2240, 2240 and 2238 cm⁻¹) are readily observable. However, upon the removal of the silane protecting groups^{7, 8} (v~viii: 760, 840, 941 and 1248/1250 cm⁻¹), the infrared activity of the alkynyl groups diminishes significantly compared to the cyano group (**2~4**: 2219, 2222 and 2224 cm⁻¹), owing to the coupling effect.⁹ The aromatic-ring breathing modes combined C=C chain stretching modes (1300~1617 cm⁻¹) indicates the intactness of diyne groups in **1~4**. Given the utilization of 6 M HCl for the removal of copper foil, despite rigorous washing with ample amounts of deionized water and ethanol, it remains challenging to prevent acidification, which may lead to the oxidation (-C=O: 1720 cm⁻¹, C-O: 1200~1270 cm⁻¹) or cyclization of cyano and alkynyl groups present on the surface or edges.^{10, 11} The adsorption of O₂ or CO₂ (**1~4**: 2341 cm⁻¹) in the air may also lead to the presence of oxygen-containing functional groups.¹² Affected by these complex factors and their own structural arrangement (content at the edge or surface), the performance of C-N peaks (1046~1110 cm⁻¹) may vary greatly.¹³

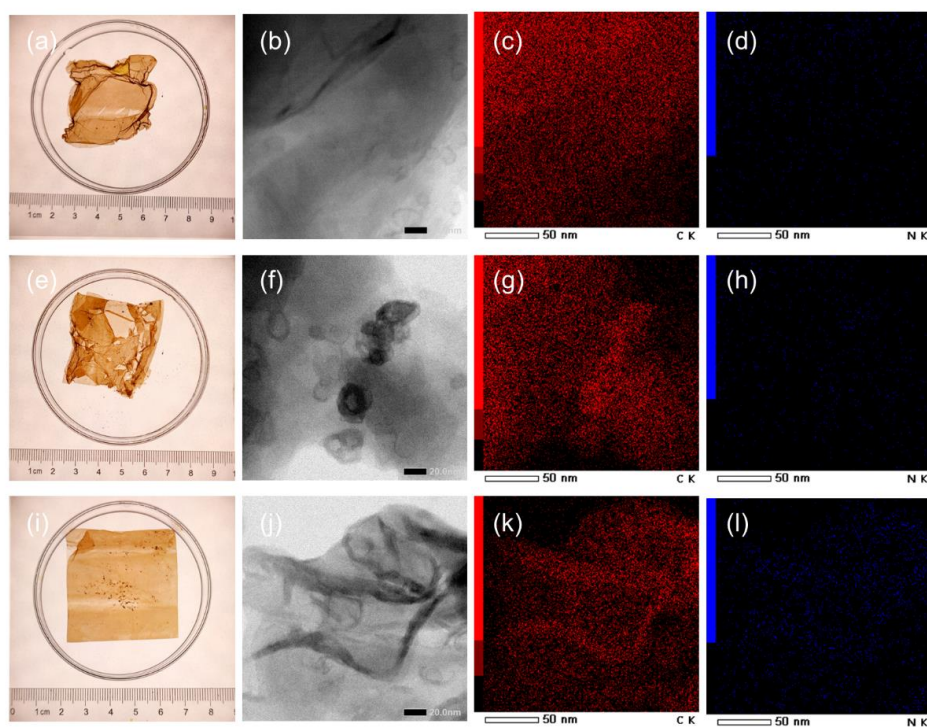


Figure S18. Photos (first column) and TEM (second column) with mapping images (last two columns). (a–d) CNGDY. (e–h) *m*-CNGDY. (i–l) *p*-CNGDY.

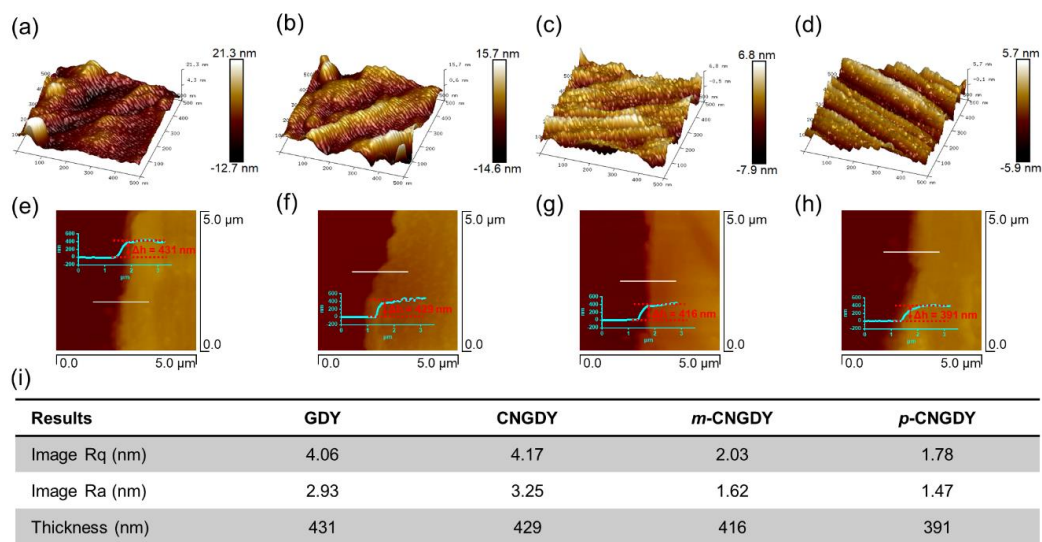


Figure S19. Atomic force microscopy (AFM) images of 1~4. (a–d) Three-dimensional diagram of surface roughness measurement of 1~4 (500 × 500 nm). (Rq: root mean square roughness; Ra: arithmetic mean roughness). (e–h) Thickness measurement of 1~4 on silicon wafer (5 × 5 μm). (i) The data list of roughness and thickness tests in the selected areas of 1~4.

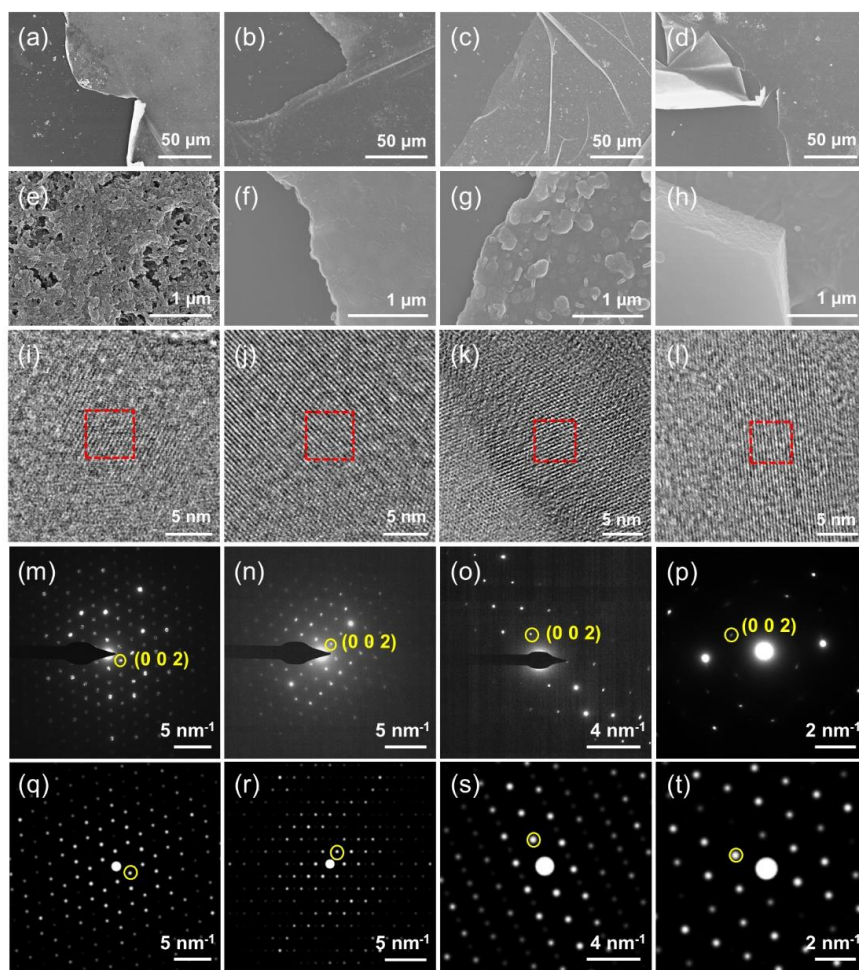


Figure S20. SEM and HRTEM images with SAED patterns. SEM images of **1~4**: (a, e) GDY, (b, f) CNGDY, (c, g) *m*-CNGDY and (d, h) *p*-CNGDY. HRTEM images and SAED patterns with the simulated ones from the proposed theoretical models in Figure 3: (i, m, q) GDY, (j, n, r) CNGDY, (k, o, s) *m*-CNGDY and (l, p, t) *p*-CNGDY.

According to the theoretical stacking structure in Figure 3d, the crystal plane index of *p*-CNGDY at 0.333 nm in Figure 2d is (0 0 3).

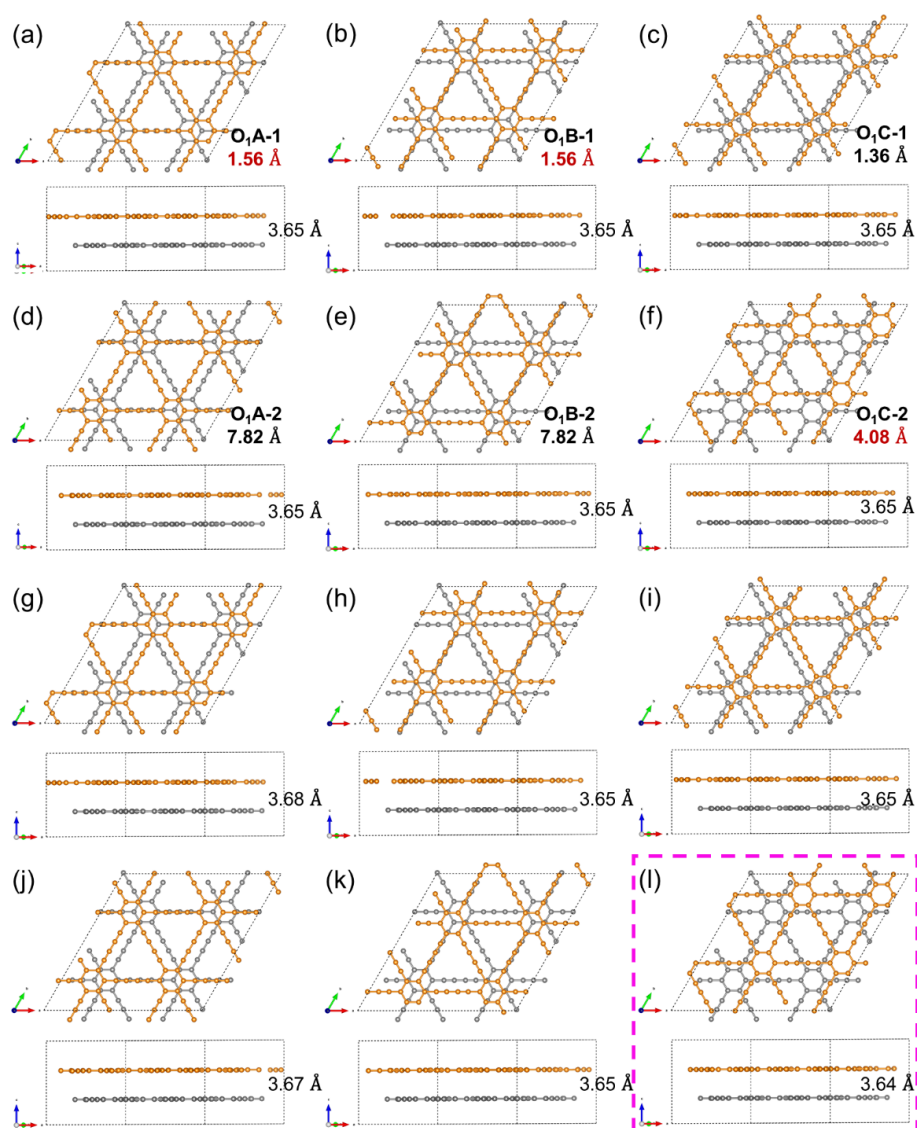


Figure S21. Theoretical stacking modes of GDY. Compared with the fixed first layer below, the second layer at a distance of 0.365 nm was displaced in the directions of O_1A , O_1B , and O_1C to reach the first (a–c) and second (d–f) positions of the lowest energy points of the system in Figure 2k. (g–l) The optimized front view (upper) and side view (lower) after loosening constraints in all directions including layer spacing at each low point position, sequentially.

After unraveling and optimizing the interlayer constraints at each position in Figure S7a–7f, the relative stacking position of the two layers does not change significantly, nor does the layer spacing.

The pink dotted box shows the optimal stacking state at the best stacking position (lowest energy point) in the O_1C direction.

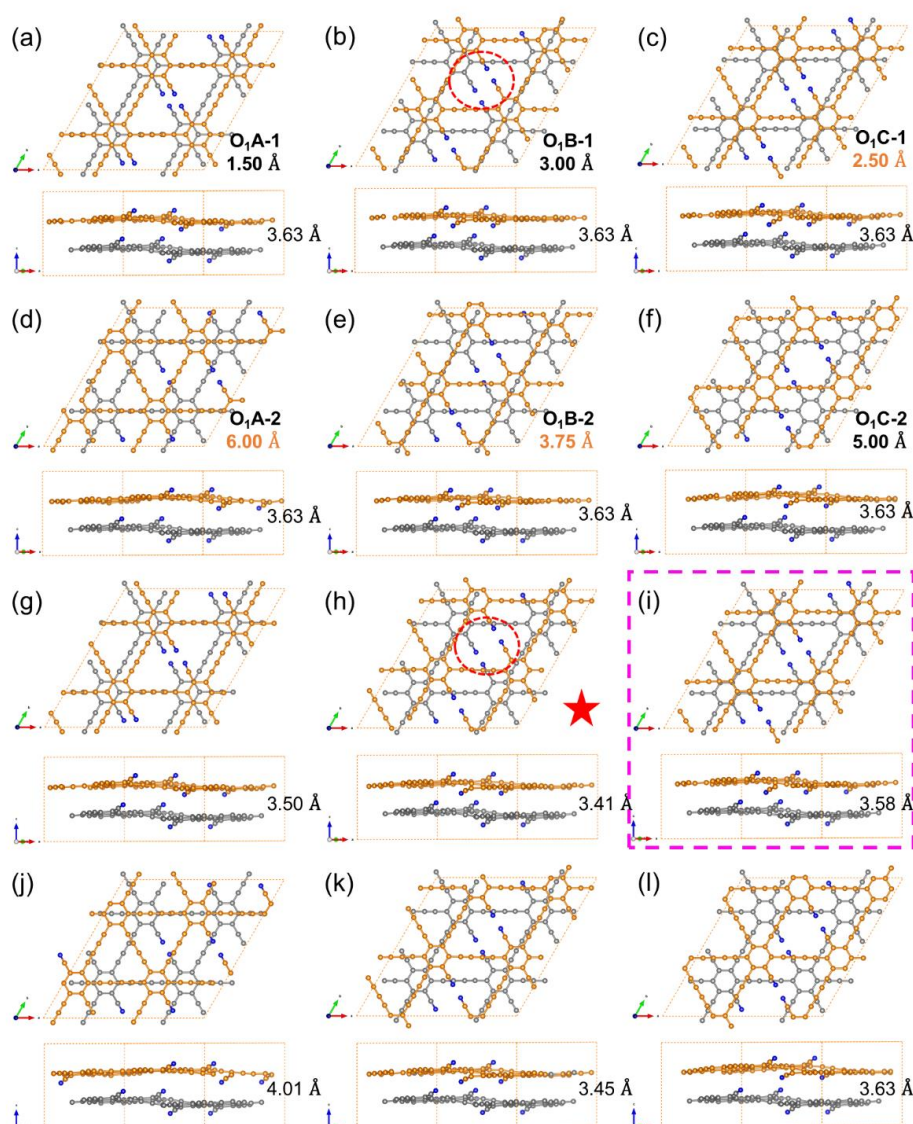


Figure S22. Theoretical stacking modes of CNGDY. Compared with the fixed first layer below, the second layer at a distance of 0.363 nm was displaced in the directions of O₁A, O₁B, and O₁C to reach the first (a–c) and second (d–f) positions of the lowest energy points of the system in Figure 2l. (g–l) The optimized front view (upper) and side view (lower) after loosening constraints in all directions including layer spacing at each low point position, sequentially.

After unraveling and optimizing the interlayer constraints at each position in Figure S8a–8f, the relative stacking position of the two layers changes slightly (as indicated by the relative position of the cyano groups in the red dotted circle).

The red five-pointed star marked the diagram where the relative position of the two layers changes has changed significantly after the structure was released and optimized.

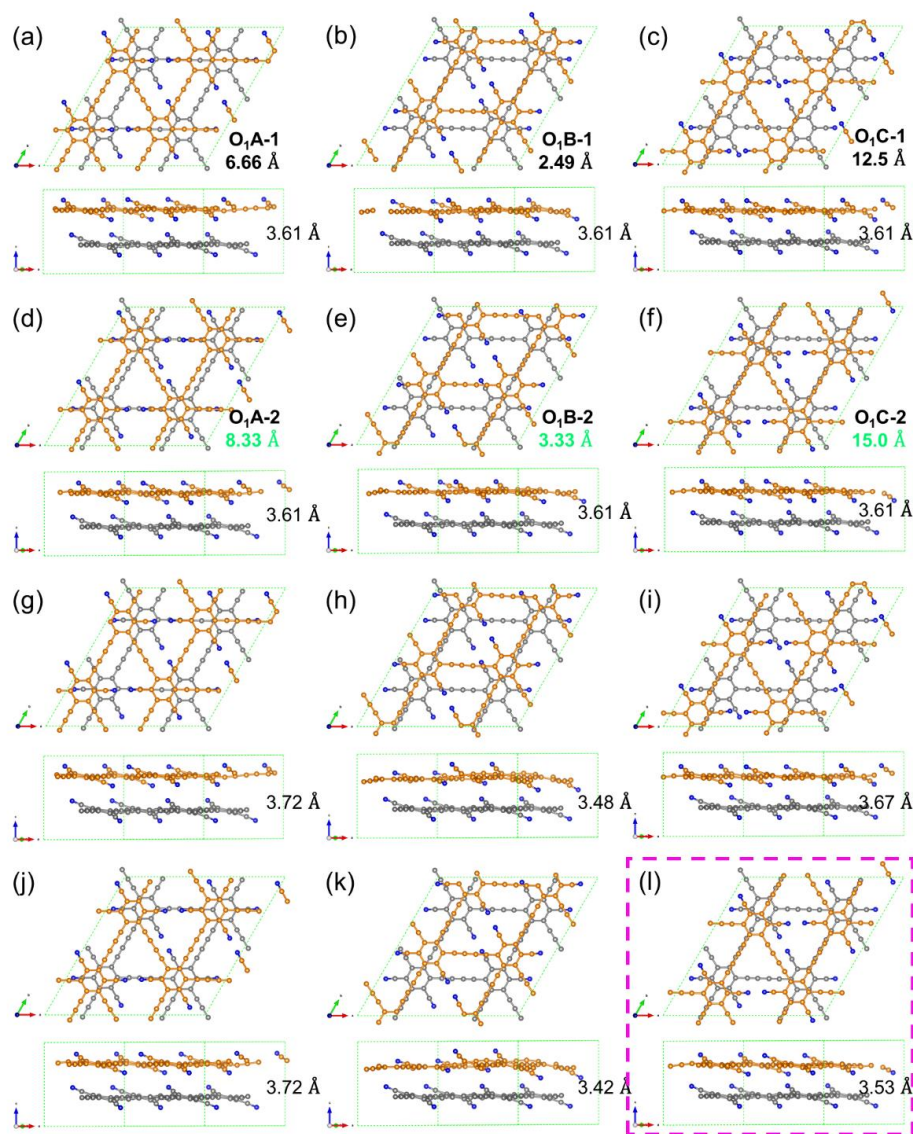


Figure S23. Theoretical stacking modes of *m*-CNGDY. Compared with the fixed first layer below, the second layer at a distance of 0.361 nm was displaced in the directions of O_1A , O_1B , and O_1C to reach the first (a–c) and second (d–f) positions of the lowest energy points of the system in Figure 2m. (g–l) The optimized front view (upper) and side view (lower) after loosening constraints in all directions including layer spacing at each low point position, sequentially.

After unraveling and optimizing the interlayer constraints at each position in Figure S9a–9f, the relative stacking position of the two layers does not change significantly.

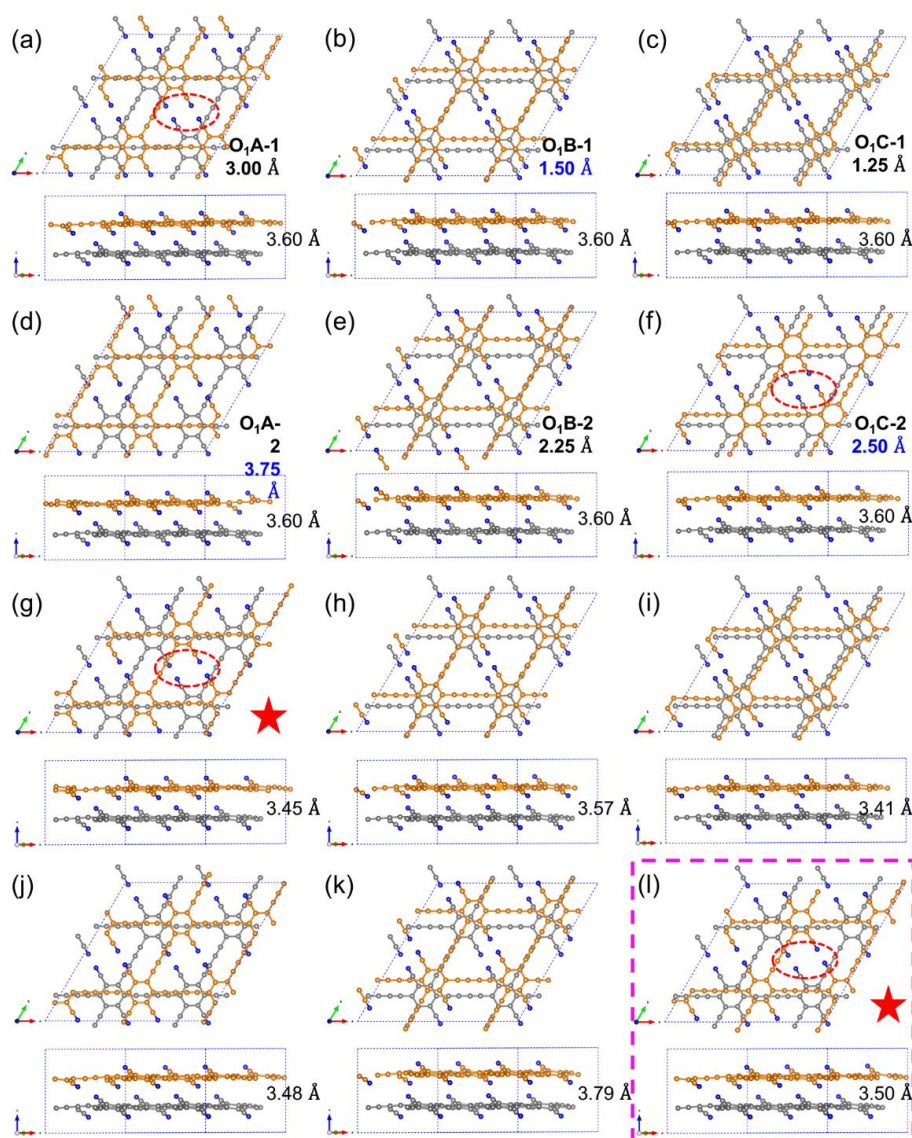


Figure S24. Theoretical stacking modes of *p*-CNGDY. Compared with the fixed first layer below, the second layer at a distance of 0.360 nm was displaced in the directions of O₁A, O₁B, and O₁C to reach the first (a–c) and second (d–f) positions of the lowest energy points of the system in Figure 2n. (g–l) The optimized front view (upper) and side view (lower) after loosening constraints in all directions including layer spacing at each low point position, sequentially.

After unraveling and optimizing the interlayer constraints at each position in Figure S10a–10f, the relative stacking position of the two layers changes slightly (as indicated by the relative position of the cyano groups in the red dotted circle).

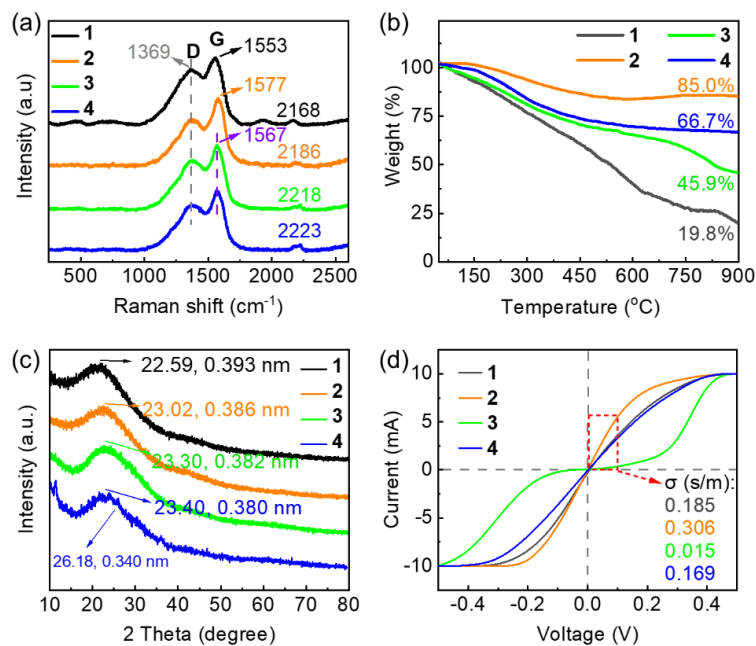


Figure S25. Characterization of 1~4. (a) Raman. (b) TGA ($5.0^{\circ}\text{C min}^{-1}$, from 50°C to 900°C , Ar). (c) XRD. (d) Conductivity.

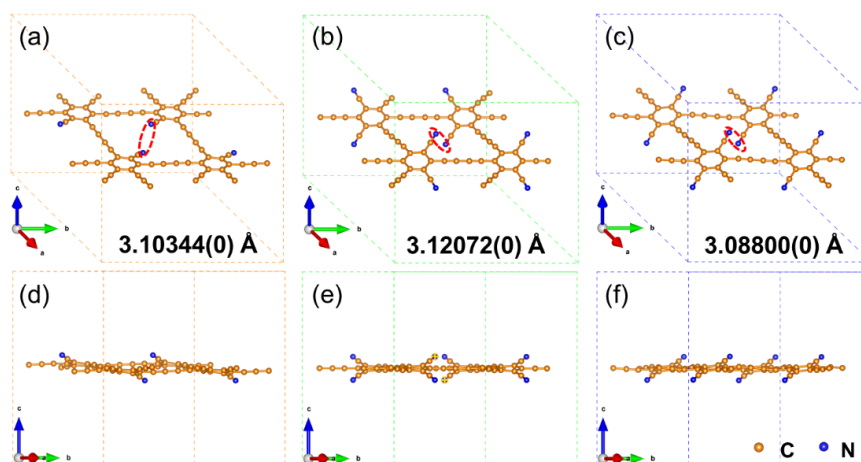


Figure S26. Single layer theoretical structures of 2~4. Different views of the structures of (a, d) CNGDY, (b, e) m-CNGDY and (c, f) p-CNGDY.

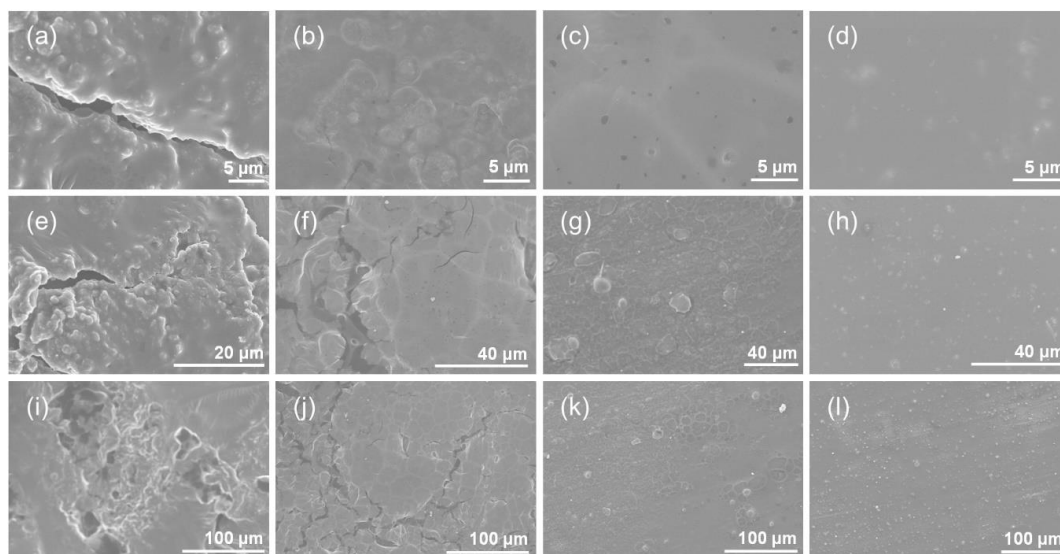


Figure S27. SEM images of **1~4** as lithium-ion battery anode after undergoing the magnification test in Figure 6b. (a, e, i) GDY. (b, f, j) CNGDY. (c, g, k) *m*-CNGDY. (d, h, l) *p*-CNGDY.

In order to observe the interface changes of the alkyne polymer films, **1~4** films grown on copper foil were directly used as the anode for charge-discharge tests. After the half cells were disassembled in the glove box, the electrodes were sealed and characterized within half an hour.

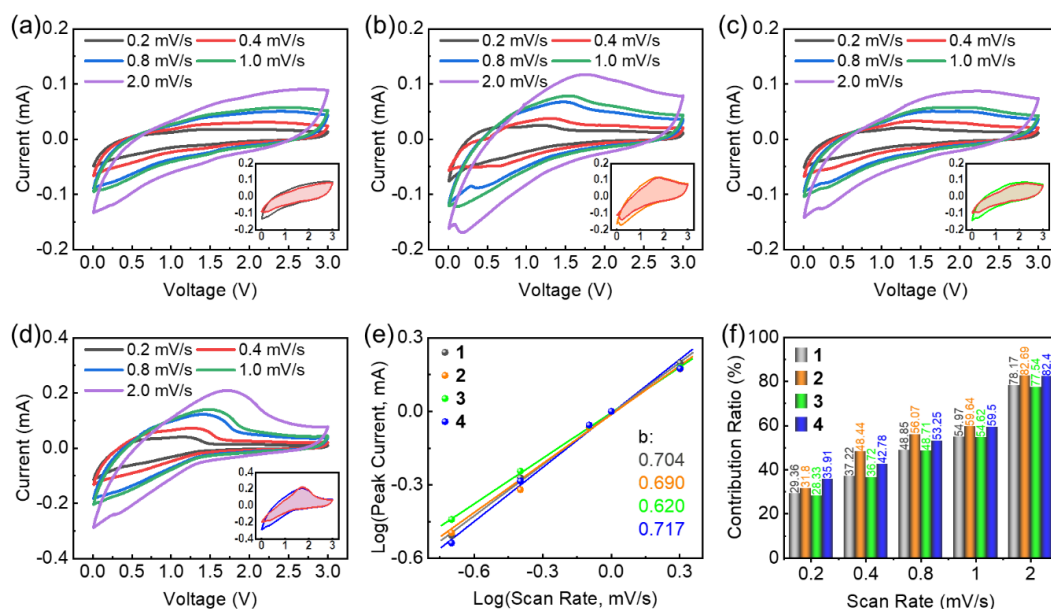


Figure S28. Pseudo capacitance analysis. (a-d) CV curves at different scan rates (0.2~2.0 mV/s, 0.01~3V) for **1~4**. (e) Log(*i*) versus log(*v*) plots at specific peaks. (f) Capacitive contribution ratios at different scan rates of **1~4**.

Table S1. Stacking parameters and calculation data of **1~4** in Figure S7–S10 (unit: Å).

GDYs	1	2	3	4
$ O_1A / O_1B / O_1C $	19/19/16	18/9/30	20/10/30	9/9/15
$ O_3O_1 _1$ in $O_1A/O_1B/O_1C$ ^[a]	1.56/1.56/1.36	1.50/3.00/2.50	6.66/2.49/12.5	3.00/1.50/1.25
$ O_3O_1 _2$ in $O_1A/O_1B/O_1C$ ^[b]	7.82/7.82/4.08	6.00/3.75/5.00	8.33/3.33/15.0	3.75/2.25/2.50
$ O_3O_2 _1$ in $O_1A/O_1B/O_1C$ ^[c]	3.68/3.65/3.65	3.50/3.41/3.58	3.72/3.48/3.67	3.45/3.57/3.41
$ O_3O_2 _2$ in $O_1A/O_1B/O_1C$ ^[d]	3.67/3.65/3.64	4.01/3.45/3.63	3.72/3.42/3.53	3.48/3.79/3.50
Average layer spacing ^[e]	3.66	3.60	3.59	3.53

[a, b] The displacement values of the second layer relative to the first layer in three different directions, [a] and [b] correspond to two different energy nadirs.

[c, d] The stacking layer spacing in three different directions, [c] and [d] correspond to two different energy minimum points selected in [a] and [b], respectively.

[e] Summed average interlayer spacing values calculated from $|O_3O_2|_1$ and $|O_3O_2|_2$.

Table S2. Energy Decomposition Analysis (EDA) terms (B3LYP-D3/cc-pVTZ, UFF) for **1~4** (unit: kJ/mol).

	Electrostatic	Repulsion	Dispersion	Total
GDY	-12.61	119.54	-397.14	-290.20
CNGDY	20.01	76.03	-239.15	-143.11
<i>m</i> -CNGDY	-223.20	133.70	-331.33	-420.84
<i>p</i> -CNGDY	-46.84	130.79	-327.19	-243.24

Table S3. The adsorption energy of lithium in different positions of **1~4**.

E_{ad} at Ad-sites ^[a]	①	②	③	④	⑤
GDY	-0.170	-0.837	-0.837	-0.837	2.022
CN-GDY	-0.883	-0.750	-1.575	-1.581	-1.581
<i>m</i> -CNGDY	-0.218	-1.826	-1.829	-1.782	-1.782
<i>p</i> -CNGDY	-0.088	-0.750	-1.576	-1.581	-1.581

[a] The adsorption energy (E_{ad}) of **1~4** at ①~⑤ calculated by formula (1) above.

Table S4. Some data of the 1~4 electrode tests and related theoretical calculations.

GDYs	1	2	3	4
Unit atoms	C72	C68N4	C64N8	C64N8
Molecular weight (M)	864.0	872.0	880.0	880.0
Cal. Li _{max} adsorbed (n) ^[a]	70,	82,	83,	97,
Cal. Specific capacity (mAh g ⁻¹) ^[b]	2171.4	2520.2	2527.8	2954.0
Real Test Specific Capacity (mAh g ⁻¹)	546.4	861.5	1060.1	1224.2
First coulomb efficiency	39.7%	40.6%	47.2%	52.9%

[a] The number of lithium intercalation when the bond structure of acetylene polymer is destroyed.

[b] The maximum amount of lithium intercalation before the bond structure of acetylene polymer is destroyed.

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Supporting Information Manuscript II

Supporting Information

Quantum chemical investigation of multi-redox states in organic conjugated redox ladder polymers for electrochemical energy storage systems

Shuailong Wang, Fabrizia Negri, Daniele Fazzi

*University of Bologna, Department of Chemistry “Giacomo Ciamician”, via P. Gobetti
85, 40129, Bologna (Italy)*

Supporting Information

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SI 1

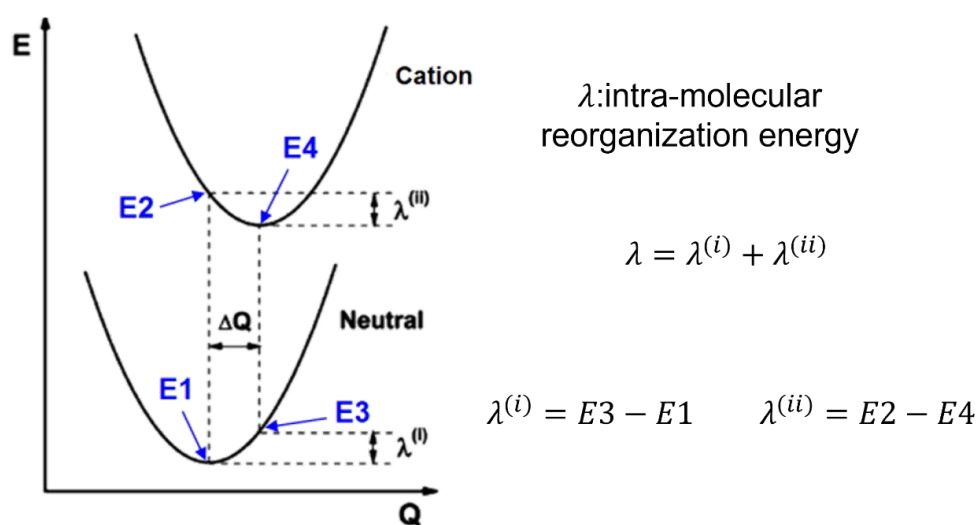


Figure 1 The intra-reorganization energy illustration.

Figure 1 demonstrates the intra molecular reorganization energy. E1 denotes the stable equilibrium energy of the investigated material neutral states ($|0\rangle$). Then, we project one electron to the neutral states, named E2 ($|-1\rangle$ states). Based on E2, the optimized process is carried on getting E4 (equilibrium energy of $|-1\rangle$ states). Finally, we calculate the single points of taking one electron from E4 states. The energy computed from different states is utilized for the reorganization energy.

The data for various charged states ($0 \pm 1 \pm 2$) of PQL and SBBL.

SI 2

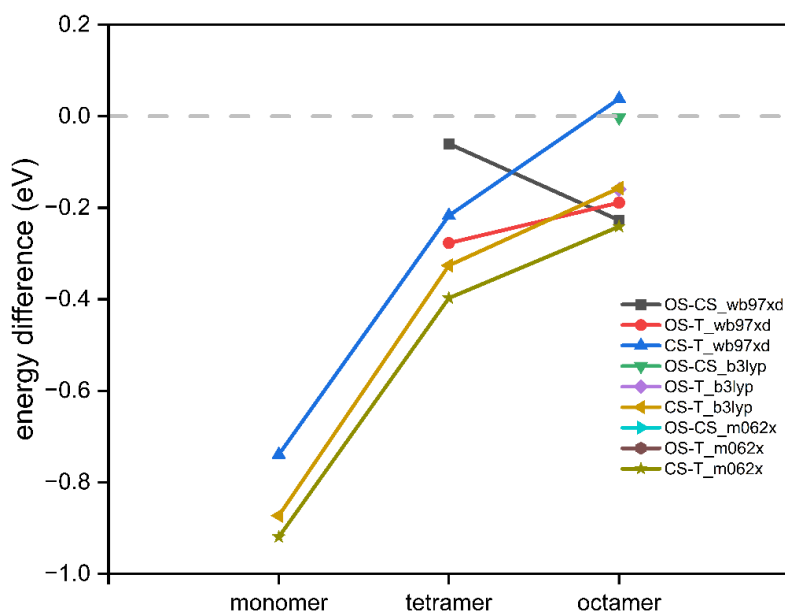


Figure 2 Energy difference between OS, CS and T based on wb97xd, b3lyp and m062x functions.

To validate description accuracy of neutral states computed by different functions, we plot Figure 2 to distinguish the energy difference based on CS neutral, OS neutral and neutral T states. The B3LYP functional combines 20% of the Hartree - Fock exchange, Becke's three - parameter non - local exchange functional (80%), and the Lee - Yang - Parr correlation function better performing on geometric structures, vibrational frequencies, and thermochemical properties of a series of small molecules.¹ The wb97xd functional is a long-range corrected hybrid functional combining long-range exchange correction with empirical dispersion correction (D), and performs outstandingly when dealing with systems containing long-range interactions such as dispersion forces.² The m062x function is a range-separated double hybrid functional. It employs different mixing ratios for short-range and long-range exchange interactions. This function is specifically designed for calculations in thermochemistry, kinetics, and non-covalent interactions. When dealing with organic, inorganic, and main group chemical systems, it exhibits high computational accuracy for properties such as bond energies, reaction heats, and activation energies.³ We notice the absence of BS for monomer and tetramer describing by b3lyp and m062x functions until octamer. All the energy difference values decrease as expanding the oligomer length with respect to increasing E_{OS-CS_wb97xd} considering length under octamer. And the E_{OS-CS_b3lyp} is circa 0 eV with respect to -0.24 eV

of E_{OS-CS_m062x} , which is close to E_{OS-CS_wb97xd} : -2.2 eV. The energy difference between CS and T states calculated by different functionals demonstrate the similarity that value decreases as length increases. However, the value given wb97xd is positive indicating (the function is not suitable for describing this system). Since the function not only gives electron distribution but also the bond analysis. Thus, we shift our attention to the bond computed by functions.

SI 3

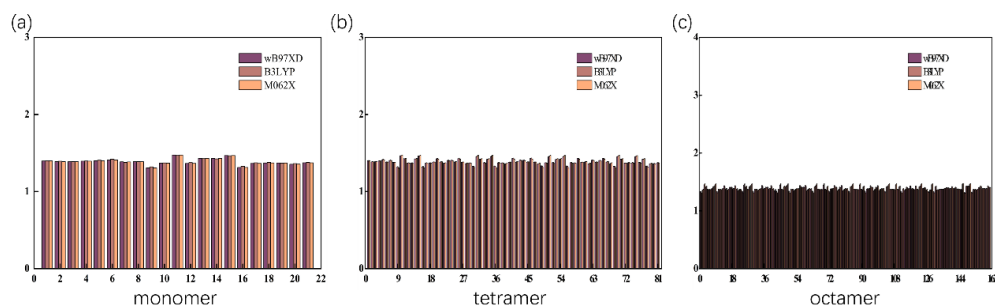


Figure 3 The bond length computed by wb97xd, b3lyp and m062x functions.

With respect to energy, the bond length from various oligomer length shows similar value calculated by each function, shown in Figure 3. And the bond length difference are less than 0.05 angstroms. For more detailed data, the panel a), b) and c), hold the view that every function gives similar electron description of the system considering the oligomer length, which determines the bond length, bond angle and so on.

SI 4

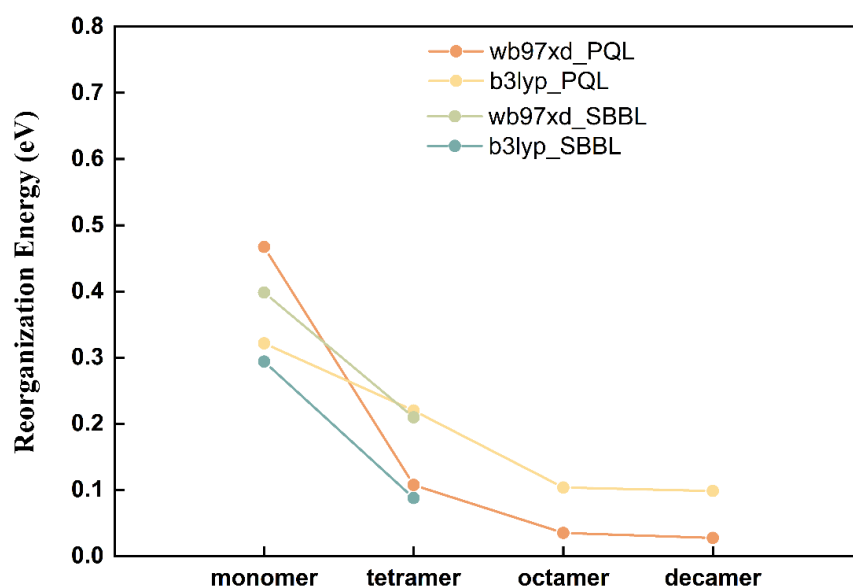


Figure 4 reorganization energy calculated by wb97xd and b3lyp functions

Given the PQL and SBBL as electrodes, charge transfer (CT) plays a paramount role, determining the electron transfer rate. We therefore carry the same functions (wb97xd and b3lyp) for the computation of the reorganization energy. The reorganization energy trend to close to 0 eV by increasing the oligomer length. However, for PQL system, the reorganization energy computed by b3lyp is slightly higher than that of wb97xd as the length beyond 4, indicating that wb97xd function perform better for PQL system which holds weak interaction moieties. The SBBL reorganization energy shows higher value on wb97xd than that of b3lyp circa 0.1 eV.

SI 5

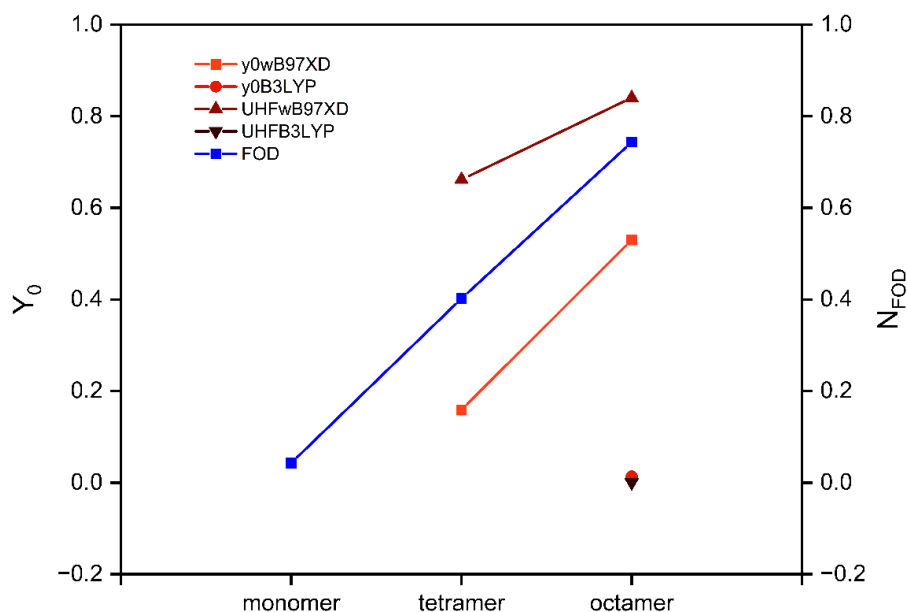


Figure 5 The y_0 (left axis) and N_{FOD} (right axis) of the PQL based on wb97xd, b3lyp, UHFwb97xd and UHFb3lyp.

We also investigated the diradical properties (y_0) of PQL by utilizing wb97xd, b3lyp, uhfwb97xd and uhfb3lyp. The UHFwb97xd and UHFb3lyp is the function within the framework of the unrestricted Hartree - Fock method. Also, the N_{FOD} of the PQL is taken into consideration for electron system correlation, paralleling to y_0 . Figure 5 demonstrates that the PQL shows high electron multireference to the system on the basis of different functions by increasing the oligomer length. It is noteworthy that PQL shows the high y_0 computed by wb97xd compared the value by b3lyp as the length exceeds 4. Within the unrestricted Hartree-Fock framework, the UHFwb97xd features high value compared to UHFb3lyp.

SI 6

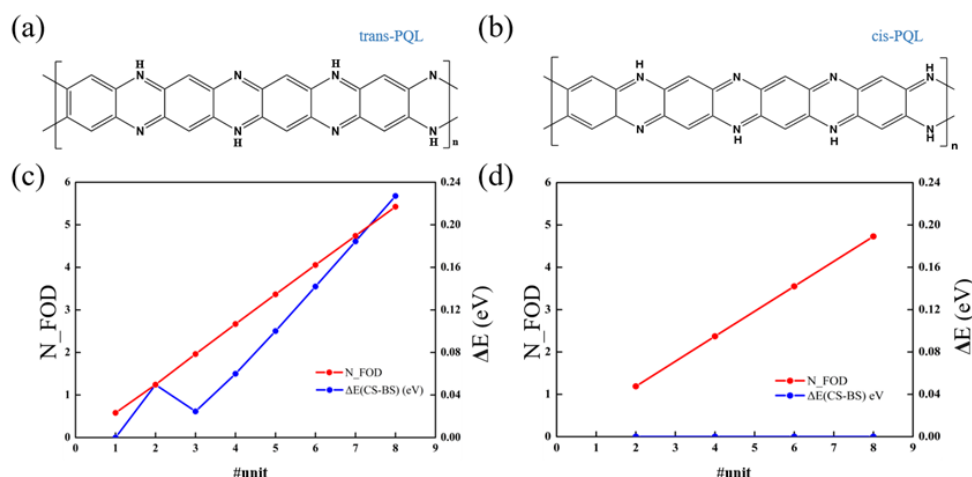


Figure 6 (a) and (b) The chemical structure of trans-PQL and cis-PQL. (c) and (d) The N_{FOD} of the cis-PQL and trans-PQL neutral states and the energy differences of the CS neutral and OS (BS) neutral states.

We also calculated the trans-PQL to distinguish the differences between the cis-PQL and trans-PQL by the FOD analysis. For trans_PQL and cis_PQL, the difference is the protonation site, seen from Figure 6 panel a) and b). However, protonation features big difference to electron correlation of the system and stable wavefunctions to describe electronic structure holding that the cis-PQL show non BS-DFT solution and the FOD is slightly lower than that of trans_PQL, shown in Figure 6. N_{FOD} of trans_PQL and cis_PQL grows up as the length expands. The N_{FOD} of cis_PQL is slightly smaller than that of trans_PQL.

SI 7

Table.1 The value of Singlet–Triplet Energy Gap (ΔE_{S-T}) Values Computed by DFT.

Length	Spin contamination		ΔE between close shell and triplet neutral states	Energy gap value	
	CS-BS (after)	Triplet (after)		Before	After
1	0	0	-0.027171201	-0.739347399	-0.739347399
4	0	0	-0.00797815	-0.217091046	0.228100931
8	0	0	0.00140472	0.038223415	-0.032659304

Table.2 The value of Singlet–Triplet Energy Gap (ΔE_{S-T}) Values Computed by BS DFT.

Length	Value of spin contamination		ΔE between neutral single open shell and triplet states	Energy gap value	
	Before	After		Before	After
1	0	0	-0.027171201		-0.739366038
4	1.454	4.3994	-0.01018332	-0.277102251	0.291155635
8	3.438	13.1826	-0.0069407	-0.188866067	0.161373191

Table 1 and Table 2 give the spin contamination and the neutral singlet and triplet states energy gap (ΔE_{S-T}) calculated by standard DFT and broken symmetry DFT (BS-DFT). Normally, “before” column refers to the expected value of the square of the spin angular momentum $\hat{S}^2$ obtained at a certain step in the calculation process and “after” column denotes the finally obtained expected value of $\hat{S}^2$. It reflects the degree of spin contamination of the wave function at the end of the calculation. The “before” column and “after” column from the energy gap value are the calculated value concluded by different spin contamination situation and “after” column named corrected energy gap is calculated by following equation:⁴

$$\Delta E_{S-T} = (E_{OS} - E_T) \frac{\langle S^2 \rangle_T}{\langle S^2 \rangle_T - \langle S^2 \rangle_{OS}} \quad 1$$

SI 8

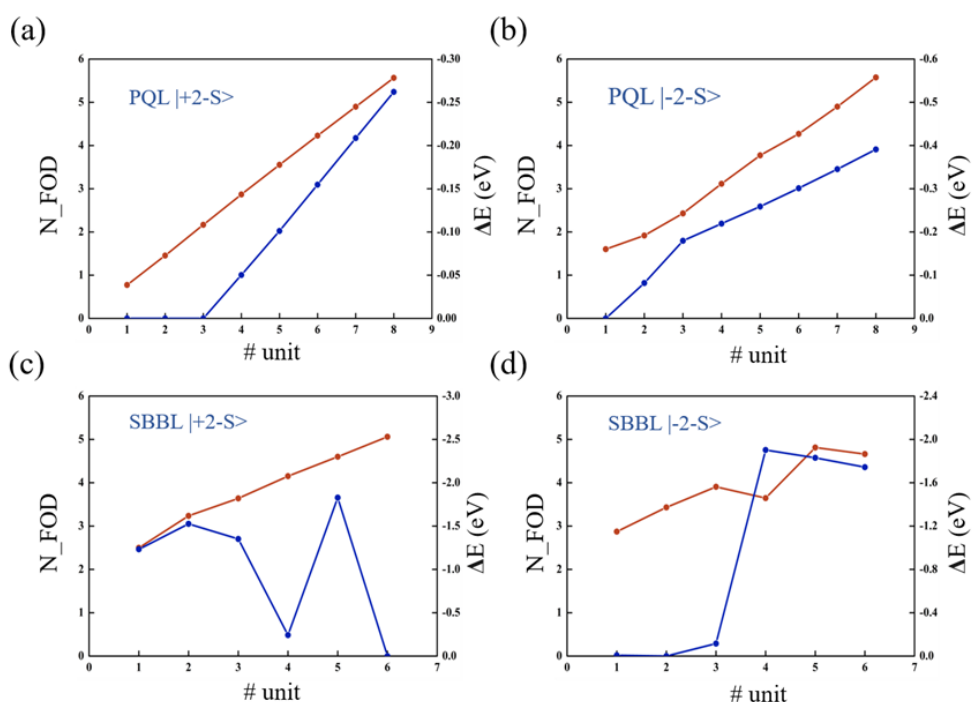


Figure 7 The relationship between energy difference of the doubly charged OS singlet and CS singlet and N_{FOD} . (a), (c) for the oxidation states and (b) (d) for reduction states of PQL and SBBL oligomer. Red line for N_{FOD} and blue line for the energy difference. The unit of the energy difference is eV.

The PQL and SBBL doubly charged states show completely different situations for oxidation and reduction states. The energy gap grows up by increasing the oligomer length. However, for SBBL system, the difference energy of oxidation doubly charged singlet charged states calculated by DFT and BS DFT is getting progressively smaller as the length increases. While, for reduction doubly charged singlet charged states, the energy difference increases as the unit and the N_{FOD} increase, indicating that the radicaloid properties of the oxidation and reduction doubly charged states are completely different.

SI 9

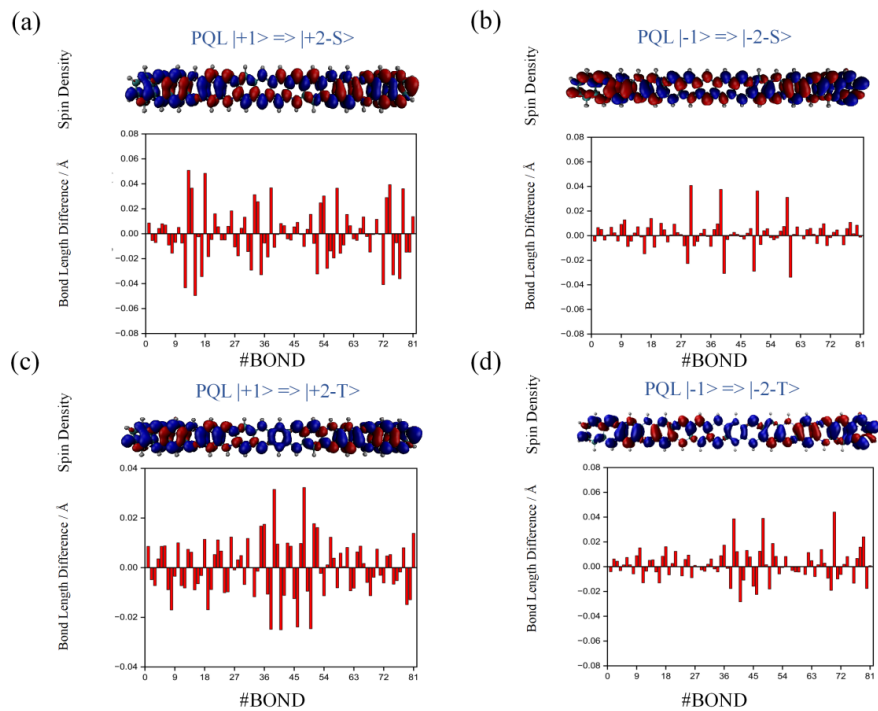


Figure 8 The spin density of the PQL oxidation and reduction doubly charged singlet and triplet states and the BLDs of bipolaron and polaron.

In terms of the complex charged states and the properties shown during charging and discharging, we also investigate the relationship of doubly charged singlet and triplet states of every unit state. As shown in Fig. 8, the electrons delocalize the PQL tetramer oxidation and reduction doubly charged singlet states. The doubly charged singlet states of oxidation and reduction demonstrate a greater degree of delocalization.

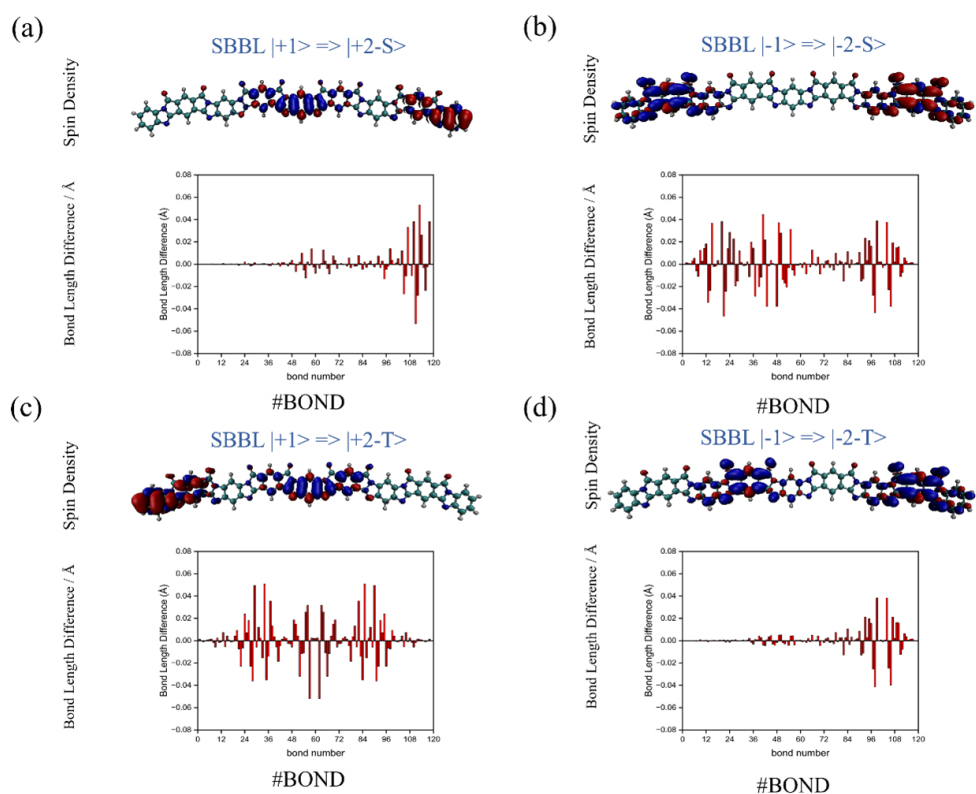


Figure 9 The spin density of the SBBL oxidation and reduction doubly charged singlet and triplet states and the BLDs for these states.

For SBBL doubly charged species, the BLD better reflects to the spin density. And the electron localizes over one SBBL unit for all the doubly charged species.

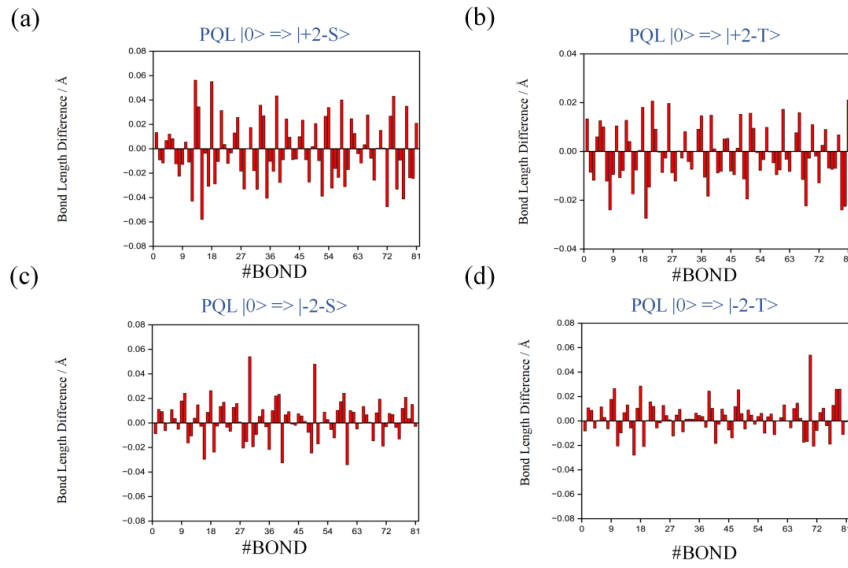


Figure 10 The BLDs between PQL bipolaron and neutral state.

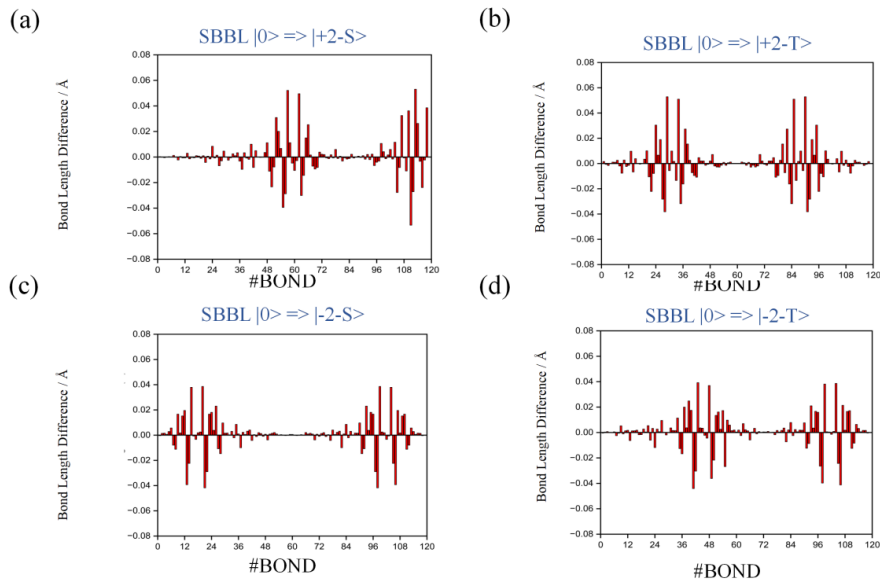


Figure 11 The BLDs between SBBL bipolaron and neutral state.

For Figure 10 and 11, the BLDs between PQL and SBBL neutral states are plotted to overview the distinction once system projected two electrons. Electrons are delocalized over the PQL resulting to substantial changes to the whole system, thus minoring changes

of the local part appear. As for SBBL, electrons are localized on one or two repeat unit of the system, leading to enlarge the BLDs of the moiety of SBBL.

SI 10

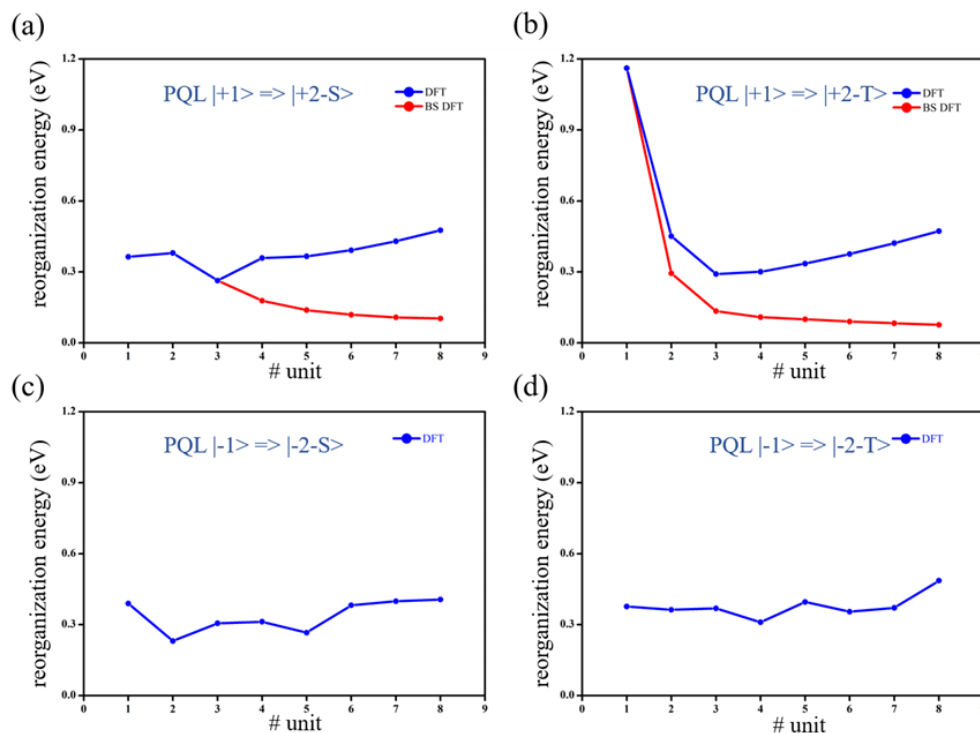


Figure 12 The reorganization energy for oxidation and reduction states for PQL.

Taking the doubly charged states (± 2 -singlet/triplet states) into consideration, the doubly charged states λ^i is generally higher than the singly charged states λ^i . For doubly charged singlet states, the results of λ^i calculated by DFT show unreasonable values (-1.0 eV). As the length of the PQL increases, the result of the λ^i presents an oscillating trend as the charged states are oxidation states. By increasing the length of the oligomer, the reorganization energy of the PQL charged states (± 1 , ± 2 -singlet/triplet states) is reasonable calculated by the BS wavefunction, indicating that the BS solutions show more stable wavefunction than standard DFT wavefunction.

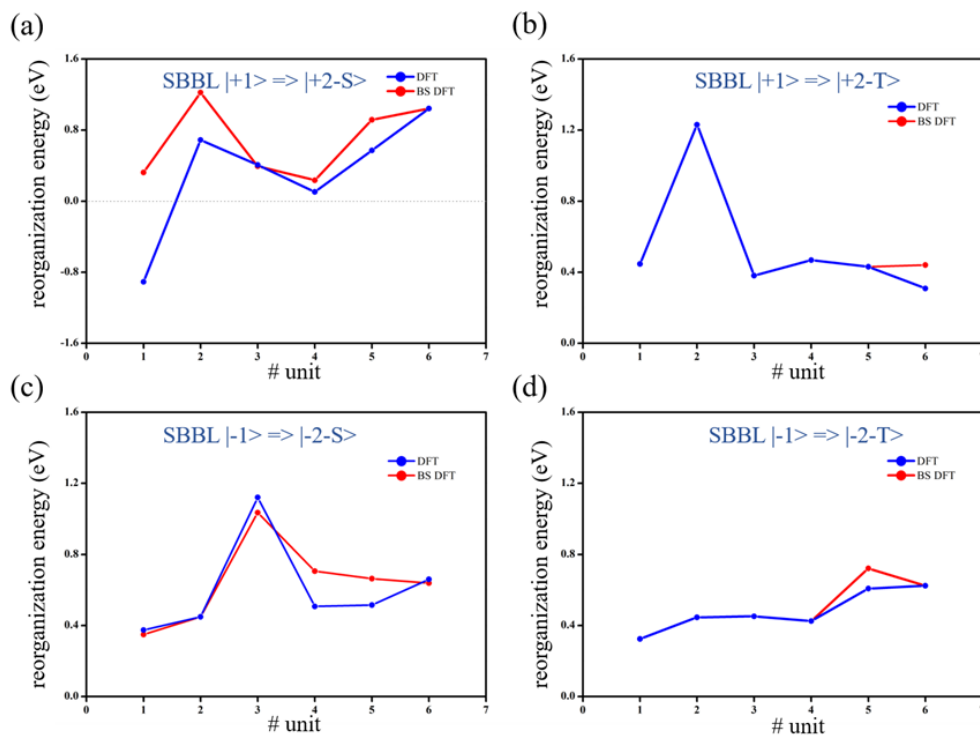


Figure 13 The reorganization energy for oxidation and reduction states for SBBL.

By increasing the length of the oligomer, the reorganization energy of the SBBL singly charged states, calculated by the standard DFT and BS-DFT, is getting small. However, the reorganization energy of the doubly charged states is slightly higher than the reorganization energy of the singly charged states. It seems that the trend of reorganization energy for oxidation doubly charged states shows not a gentle curve instead of a curve which oscillates up and down. Additionally, the energy differences between doubly charged singlet and triplet, shown in Fig. 6, also present oscillation line, which can be the factors for the value fluctuation of reorganization energy. In the context of reorganization energy trend of these two-oligomer s PQL and SBBL, as we compare with Fig. 13 and Fig. 14, the total reorganization energies of the PQL for the various electronic states are slightly lower than that of the SBBL. The spin density of various electronic states of PQL and SBBL elucidates the mechanism for the different value of the λ^i . For almost all electronic states of the PQL, the spin densities of oxidation and reduction states are completely delocalized over the oligomer chain, whereas the cases of the SBBL oxidation and reduction states are roughly different, which is that spin densities are

localized on the oligomer. The situations mentioned above illustrate the mechanism which the λ^i of PQL is smaller than that of SBBL. Noteworthy, the value of SBBL λ^i is roughly ideal (average 0.3 eV), owing to that for SBBL, by increasing the oligomer length, the spin density (both hole and electron) localizes over roughly one unit.

SI 11

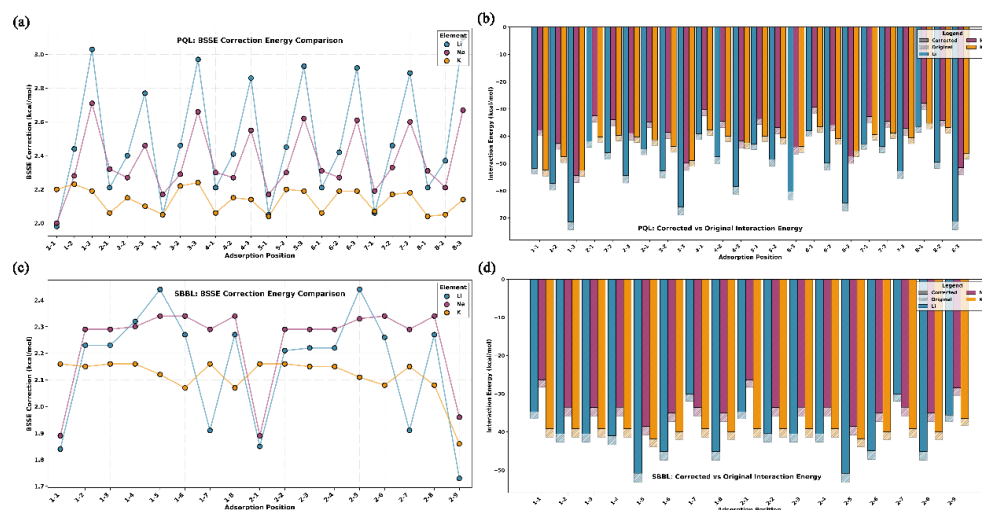


Figure 14 (a) and (c): The difference value of the BSSE corrected interaction energy and uncorrected interaction energy of PQL and SBBL. (b) and (d): the bar comparison

To identify the accuracy of the computed interaction energy, we adopted the BSSE correction to detailly evaluate the interaction energy based on 6-31G* basis set. As shown in Figure 14, the BSSE corrected interaction energy of Li-PQL system is slower than that of uncorrected interaction energy and as the radius of the atom increases, the difference value of BSSE corrected interaction energy decreases, demonstrating that for bigger radius atoms, the BSSE effect slightly influences the interaction. However, the trend of the BSSE corrected interaction energy shows the similarity of the uncorrected interaction energy trend, indicating that the special position confers the same effect interaction. For instance, the *-3 position of PQL displays the relatively highest magnitude of interaction energy.

SI 12

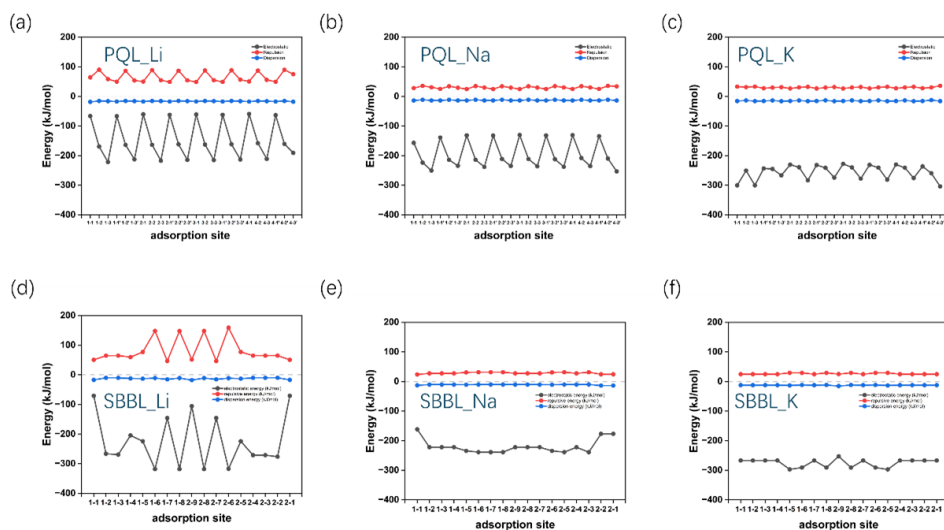


Figure 15 The electrostatic energy, repulsion energy and dispersion energy of the PQL and SBBL adsorbing alkali metal cations.

Here we adopt the energy decomposition analysis to analyze interaction between metal cation and substrate. The average electrostatic energy increases by expanding the radius of metal cation for both PQL and SBBL. Panel a), b) and c) feature the electrostatic energy dominates the cation-molecule system and repulsion energy impact the substrate less considered Li cation on PQL. The Na and K cation perform less repulsive interaction, and the values of dispersion interaction are close to 0. Also, metal cation performs similarly behaviors on SBBL.

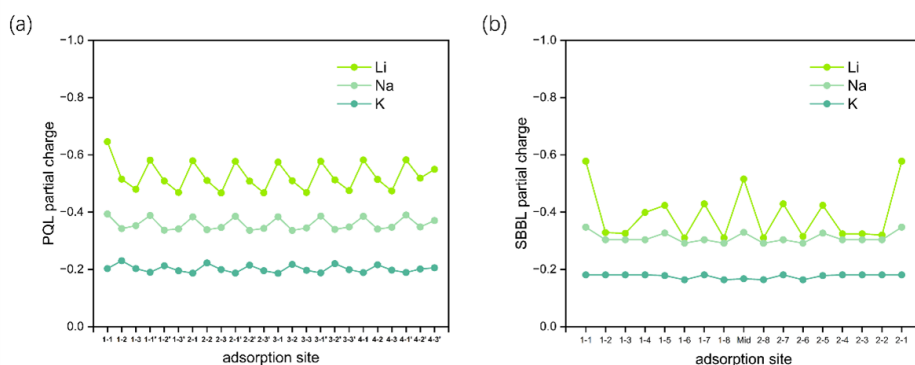


Figure 16 Substrate partial charge from PQL and SBBL system.

The Li-molecule system interacts more electrons compared to Na/K-molecule system, better reflecting interaction energy shown in Figure 8.

SI 13

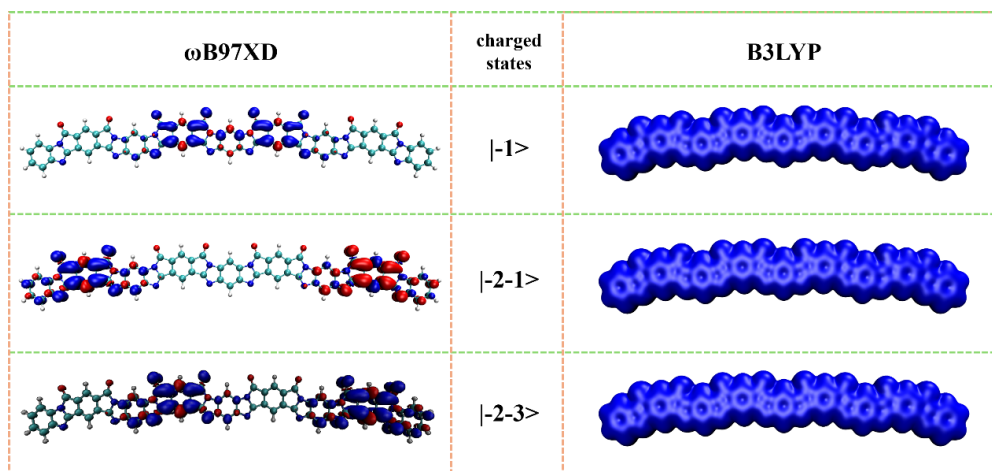


Figure 17 Spin density of neutral and multicharged species calculated by ω B97XD and B3LYP.

Electrons localize around one SBBL unit described by ω B97XD function. Whereas the B3LYP function features complete delocalization for all SBBL charged species.

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