Reflection of Molecular Twist in Unoccupied Molecular Orbitals in PTCDI Derivatives: A Density Functional Study

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ABSTRACT: In this work, the structural and electronic properties of perylene tetracarboxylic diimide (PTCDI) derivative molecules have been calculated using density functional theory simulations. Here, we have obtained the equilibrium geometry for certain PTCDI derivatives and calculated their occupied and unoccupied density of states separately for molecular orbitals lying in-plane (σ type) and orthogonal to the plane (π type) of the molecules. We have also simulated the X-ray absorption spectroscopy (XAS) spectra for these molecules separately for π- and σ-type orbitals. A comparison between the unoccupied density of states and XAS data has been made because both provide a description of the molecular orbitals above the Fermi level. We have observed the presence of shallow-lying σ orbitals in twisted molecules and have obtained an almost linear relationship between the abundance of these orbitals and the degree of molecular twist. Additionally, we have shown the possibility of an experimentally viable stereoisomerism in PTCDI-C3.

1. INTRODUCTION

Organic electronic technologies are emerging as prospective future options in recent years owing to their high application potential in electronic devices.1—11 Organic semiconductors are a class of organic solids, usually molecular crystals, amorphous thin films, or polymer films, which are normally insulators but become semiconducting when free charges are introduced through electrodes, doping, or photoexcitation. Their technological applications are manifold, including organic light emitting diodes, organic field effect transistors, and organic solar cells. Organic molecular crystal-based semiconductors have an advantage over conventional inorganic semiconductors, in that they are held together by relatively weaker van der Waals interactions. Compared to the more rigid ionic or covalent bonds in inorganic materials, the van der Waals bonds allow for a greater degree of flexibility, a fact that holds great promise vis-a-vis the manufacturing of advanced electronic devices. In principle, organic semiconductor materials have the ability to act as ambipolar semiconductors, capable of both p-type and n-type transport.12 However, it is observed in practice that the majority of organic semiconductors typically display p-type transport. This may be because the energetically high-lying lowest unoccupied molecular orbital (LUMO) in most organic semiconductor materials hinders the efficient injection of electrons from the contact to the LUMO. Additionally, it has been pointed out that n-type charge carriers are vulnerable to be trapped by ambient oxidants, such as O₂, H₂O, or O₃.12—15 Nevertheless, both n- and p-type semiconductors are essential for the fabrication of complementary integrated circuits, bipolar transistors, and organic p–n junctions with high speed operation, low power consumption and operating stability against the variation of operational parameters, as well as external noise.16,17 Hence, the development of high-performance n-type organic semiconductors has become one of the major challenges in the field of organic semiconductor and thin-film transistor research.

Perylene tetracarboxylic diimides (PTCDIs) are a class of perylene-based organic semiconductors with a high potential for optoelectronic applications, on account of their commercial availability, low cost, and electronic, optical, and charge transport properties. These properties may be conveniently tuned over a wide range by appropriate functionalization.14,18,19 Crucially, PTCDIs are n-type semiconductors by virtue of their high electron affinity and large electron mobility in the solid state.20—26 They have been significantly utilized as the electron-acceptor component in organic solar cells.27—32 Fairly recently, Bednorz et al. have reported the fabrication of a silicon/organic heterojunction-based IR photodetector capable of operation in the telecom regime, using PTCDI-C1, also known as MePTC.33—35 PTCDIs are typically arranged in π-stacks, consisting of π-conjugated perylene cores. The degree of overlap in the intermolecular π orbitals tends to vary greatly among the various PTCDI derivatives. These derivatives are formed using two main routes of functionalization: (i) end functionalization or substitution on the imide nitrogen18,22,25,26,34,35 and (ii) core functionalization or substitution in the so-called “bay area” positions 1, 6, 7, and/or 12 (see Figure 1).36—38 PTCDIs are a class of well-known...
organic dyes\textsuperscript{38} ranging in color from red to maroon to black. These materials display crystallochromy (dependence of color on crystal packing), which is relevant to their application as commercial dyes. This feature has been thoroughly investigated experimentally and theoretically. Klebe et al. developed an empirical model to explain the visible absorption maxima as a function of the $\pi-\pi$ orbital overlap area between stacked PTCDI molecules.\textsuperscript{39} Kazmaier and Hoffmann observed a strong correlation between the crystal color and both longitudinal and transverse intermolecular offsets, based on tight-binding extended Huckel calculations.\textsuperscript{40} More recently, it has been demonstrated by Zhao et al.\textsuperscript{41} using time dependent Hartree–Fock-based calculations that the electronically excited states of these materials, which determine the color of the pigments, have no significant charge-transfer character.

A major issue with n-type semiconductors investigated so far is the lack of air-stable operation. Lehmann et al. have shown the absence of an air-stable field effect in certain PTCDI derivatives.\textsuperscript{42} Various factors influencing the air-stability of organic thin-film transistor (OTFT) devices are still a matter of active research.\textsuperscript{13,14,36} Jones et al. in a recent study on cyano-perylene diimides (PDIs) have shown that the thermodynamic stability of charge carriers cannot explain the operational stability of devices manufactured from these materials.\textsuperscript{14,36} A kinetic approach towards air-stable n-type semiconductors involves the design of compounds in which segregated side chains prevent the intrusion of oxygen and moisture into the active layer.\textsuperscript{21,22,43,44} Klauk et al.,\textsuperscript{13} however, have recently demonstrated that this kinetic model cannot always explain the stability or instability of this class of materials. Oh et al. have suggested a subtle interplay between electronic and kinetic factors to determine the ambient stability of perylene bisimide semiconductors.\textsuperscript{45} It appears as of date that the optimal mobilities and stabilities in PDI-based organic semiconductors can be obtained by combining both electronic and kinetic concepts. Schmidt et al. have synthesized OTFTs from a broad spectrum of end- and core-halogenated perylene diimides by varying fluorinated imide substituents. The best OTFTs were obtained for PTCDI-C4F7. For distorted core tetrahalogenated (fluorine, chlorine, or bromine) perylene diimides, less advantageous solid state packing properties were found, and high performance OTFTs were obtained from only one tetrachlorinated derivative, PTCDI-F5Cl4.\textsuperscript{46}

In the present study, the structural and electronic properties of several PTCDI derivatives (Table 1) have been calculated using density functional theory (DFT) simulations. In this study, we have performed a geometry optimization on the molecules, the evaluation of the density of states (DOS) for occupied as well as unoccupied orbitals and the calculation of the X-ray absorption (XAS) spectra of these molecules have been performed. We have subsequently attempted to obtain a relation between molecular twisting and the electronic structure of the molecules.

### Table 1. Description of the Molecules and Their Dihedral Angles

| Name          | $R_3$     | $R_2$ | $R_1$ | Dihedral angle (degree) |
|---------------|-----------|-------|-------|-------------------------|
| PTCDI-C1      | CH$_3$    | H     | H     | 0.083                   |
| PTCDI-C2      | C$_2$H$_5$| H     | H     | 1.26                    |
| PTCDI-C3 (cis)| H$_2$C– H$_3$ | H | H | 7.04 |
| PTCDI-C3 (trans) | H$_2$C– H$_3$ | H | H | 1.478 |
| PTCDI-F2      | H         | F     | H     | 10.448                  |
| PTCDI-C4F7    | H$_2$C– CF$_3$ | H | H | 1.87 |
| PTCDI-F5Cl4   |            | Cl    | Cl    | 37.565                  |
2. COMPUTATIONAL APPROACH

Geometry optimization and calculation of DOS and XAS have been performed using the StoBe implementation of the deMon package. The structural properties of the molecules were obtained by optimizing their geometry. The geometry optimization process primarily involves taking ab initio coordinates for the molecule and then calculating the wavefunction using an iterative self-consistent field method. We have provided an ab initio set of coordinates for the molecule using Avogadro open-software (http://avogadro.cc/). The StoBe program is subsequently used to calculate the equilibrium geometry of the molecule, using a gradient-corrected Perdew–Burke–Ernzerhof (RPBE) exchange/correlation functional. The program applies small perturbations to the ab initio geometry and calculates the forces encountered by each coordinate, and the force constants are assigned to a matrix called the Hessian matrix. The geometry is again changed slightly so as to minimize these forces. A new wavefunction is then calculated and the Hessian matrix is updated using this new set of coordinates, by applying the quasi-Newton, Broyden–Fletcher–Goldfarb–Shanno method. This process is repeated until the forces have reached a previously assigned low threshold value, at which point the geometry is considered to have been optimized. In each case, the structural energy minimization was performed for a single molecule applying the gradient-corrected revised RPBE functional using a triple-$\zeta$ valence plus polarization basis set for all C, N, H, O, and Cl atoms and a double-$\zeta$ valence plus polarization basis for F. Auxiliary basis sets were applied to fit the electron density and the exchange/correlation potential.

In contrast with most other available DFT-based programs, StoBe also has a dedicated functionality to simulate core-electron spectroscopies. Hence, it can be used to calculate both absorption [(XAS/near-edge X-ray absorption fine structure (NEXAFS)] and emission spectra arising because of X-ray absorption at, or emission from, certain given core levels of particular atomic sites within the molecule. This is implemented in the StoBe code by localizing the core holes, enabling a distinction between different excitation centers and allowing the calculation of partial XAS spectra for every excitation center that is symmetrically non-equivalent. While geometry optimization calculations are performed using identical all-electron basis sets for every atom, the spectroscopic simulations involving calculations for core-excited and -ionized states use different basis sets for the excited and spectator atoms, respectively. This is realized by describing the electrons in 1s orbitals of every other atom of the same element using effective core potentials, while the valence electrons are given by a [3s3p1d] valence basis set to prevent a mixing between the corresponding core orbitals. An IGLO-III basis set is used to describe the 1s electrons present at the excitation center in order to flexibly describe core-hole relaxation. The resulting transitions from core orbitals to unoccupied states including all excitation sites and both spin channels are calculated as XAS spectra. In these calculations, the polarization vector may be either p-polarized (perpendicular to the molecular plane) and hence resonant with $\pi^*$ states or s-polarized (parallel to the molecular plane) and hence resonant with $\sigma^*$ states. In case of the s-polarized vector, the incident polarized radiation is an average for every direction on the molecular plane.

In this study, the aforementioned RPBE functional was applied to evaluate ionized and electronically excited states to obtain the N k-edge XAS spectra for the different PTCDI derivatives. The N atom was chosen as there are two symmetrically equivalent N atoms in all the PTCDI derivative molecules, and thus, calculation with only one of them is sufficient. Closely following Klues et al., the nitrogen 1s (k-edge) XAS spectra was calculated using the transition potential approximation (TPA). This method gives a faithful description of NEXAFS spectra at low computational cost and provides an effective compromise in representing the excitation, relaxation, and dynamical correlation effects. It involves a self-consistent calculation of the electronic structure of the molecule, where the electronic relaxation during the excitation process is approximated by an N 1s orbital occupied by only half an electron. The unoccupied orbitals which are thus obtained then serve as approximations for final state orbitals in the dipole transition calculation from N 1s core orbitals. The spectral oscillator strengths and Kohn–Sham eigenvalue differences can be obtained from the transition moments, from which approximate excitation energies are calculated, giving an approximation for the theoretical NEXAFS spectrum. The nitrogen excitation site is then augmented by a large set of diffuse basis functions, $[19s19p19d]$, using a double basis set technique, to account for transitions into diffuse Rydberg states and final states beyond ionization. The XAS spectrum thus calculated is only a first order approximation and can be made more accurate. This may be done, firstly, by introducing a rigid shift of the order of 1 eV to the spectrum to account for the limitations in the electronic relaxation obtained through the TPA and, secondly, by obtaining more reliable excitation energies through explicit self-consistent calculations for excited states by transferring the electron of an N 1s core orbital to an unoccupied ground state. However, the present study has more to do with the qualitative nature of the NEXAFS spectrum than the absolute quantitative energy values, and as such we have avoided these further computational refinements. It may be noted therefore, to compare the calculated XAS spectra with experiments, a rigid shift may have to be applied on the energy axis.

3. RESULTS AND DISCUSSION

3.1. Structural Properties. Upon structural optimization, the molecules displayed varying degrees of twist in the perylene backbone. Following Delgado et al., this twist was measured using the dihedral angle $\theta$ defined by $C_6$–$C_6^*$–$C_7^*$–$C_7$ as shown in Figure 1.

The names, chemical formula, and dihedral angles obtained from geometry optimization for the different molecules are given in Table 1. The side-on view of the geometry optimized structure of the molecules is shown in Figure 2.

PTCDI-C1 and PTCDI-C2 were observed to have planar structures. Of the halogenated molecules, the end-substituted PTCDI-C4F7 was found to have a planar structure, whereas the core-substituted PTCDI-F2 molecule displays an intermediate level of twisting, and the PTCDI-F5Cl4 with halogen substitution in both core and end positions was found to have a highly twisted backbone. This is mainly due to the Coulomb repulsion between the four large chlorine atoms situated in the “bay area”.

Interestingly, PTCDI-C3 displays two very distinct structures, depending on the selection of the ab initio coordinates. A cis structure and a trans structure have been obtained, with the...
energy difference between the two stereoisomers being of the order of $6 \times 10^{-3}$ eV. This small difference in energy suggests that the two stereoisomers are equally energetically viable, and the samples of PTCDI-C3 may contain both in equal measures. This stereoisomerism in PTCDI-C3 has not been previously reported in the literature.

3.2. Unoccupied Density of States Calculation. The frontier molecular orbitals of the various molecules, along with their corresponding energies, are given in Figure 3. Though the present form of DFT calculation usually underestimates the highest occupied molecular orbital (HOMO)−LUMO gap, the qualitative changes are reliable.59,60

In concurrence with Delgado et al.,58 both the HOMO and LUMO are found to be $\pi$-type orbitals, spread out over the entire molecule core, with multiple nodes observed along the long molecular axis and on the imide nitrogens. The molecules with hydrocarbon end-substituents are observed to have HOMOs and LUMOs of identical values, whereas the halogenated molecules, both core- and end-substituted, display frontier molecular orbitals at somewhat different energies. The DOS structure was calculated using the Doscalc utility provided with StoBe. A component-resolved analysis of the unoccupied molecular orbitals has been performed separately for $\sigma$-type and $\pi$-type orbitals as shown in Figure 4. In the perylene core, the carbon molecules exist in an sp² hybridized state. A mixture of $s$, $p_x$, and $p_y$ orbitals contribute to the in-plane $\sigma$-type orbitals. The delocalized $p_z$ orbitals are of the $\pi$-type and remain orthogonal to the molecular plane, forming the $\pi$ conjugated structure of the perylene core which allows the semiconductor action. In principle, it is expected that the $\sigma$-type orbitals should be obtained at higher binding energies, whereas the $\pi$-type orbitals should occur at lower binding energies. While this has been found to be the case in general, low-intensity signatures for $\sigma$-type orbitals in regions of $\pi$-dominance have been observed at low binding energies close to the Fermi level.

The intensity of $\sigma$-type orbitals at lower binding energies for the relatively planar PTCDI-C1, PTCDI-C2, the trans isomer of PTCDI-C3, and PTCDI-C4F7 has been found to be comparatively low. However, with an increase in the degree of twisting of the molecular backbone, the signature becomes significant at lower energies, as observed in the twisted cis isomer of PTCDI-C3 as well as the core-halogenated PTCDI-F2 and PTCDI-F5Cl4 molecules. A systematic, almost linearly increasing relationship has been observed between the intensities of these low binding energy $\sigma$ orbitals and the twisting, as measured by the dihedral angle in the perylene core of the molecules. Because the height as well as intensity of peaks in the partial density of states (PDOS) curve for $s$, $p_x$, and $p_y$ orbitals (given by the area under the curve) is a measure of the densities of $\sigma$-type orbitals, hence plotting the area under the curve representing the PDOS of each molecule at low binding energies, against the dihedral angle measured in the molecular core, gives the relation between low lying $\sigma$ orbitals and molecular twisting. It may be noted here that the aforementioned low binding energies have been defined as regions where there is a clear dominance of $\pi$-type orbitals over the $\sigma$-type.

The area under the $\sigma$-type orbitals ($s$, $p_x$, and $p_y$) close to the Fermi level is plotted against the dihedral angles of various molecules and is presented in Figure 5. The intensity is found to increase systematically with the increase of the twisting of the molecules. As can be seen from the figure, an exception to this almost linear relation is found in the fluorinated molecules PTCDI-C4F7 and PTCDI-F2. It may be noted that the fluorinated molecules are unlikely to follow the same trend as the non-fluorinated molecules because of the inverse linear dichroism observed in fluorinated planar aromatic molecules by
de Oteyza et al.\textsuperscript{6} We have also calculated the component resolved DOS for the unoccupied states of fluorine, carbon, and nitrogen in PTCDI-C4F7 and PTCDI-F2, as shown in Figure 6 (data for PTCDI-F2 not shown for similarity).

From Figure 6, it can be clearly seen that in the case of fluorine, the $\sigma$ orbital dominates over the $\pi$ orbital at lower energies close to the Fermi level, contrary to what is seen in carbon and nitrogen. This is indicative of inversed linear dichroism as observed by de Oteyza et al. This unusually large $\sigma$ intensity due to fluorine is the reason why these two molecules display overall larger $\sigma$-peak intensities at lower energies compared to the other molecules. This argument can also be used to explain the similar trend observed for the XAS results in Figure 8.

Figure 4. Component resolved unoccupied molecular orbitals for various molecules. The energy values are as obtained from the calculation.

Figure 5. Density of $\sigma$ orbitals at low binding energies as a function of molecular twisting for various molecules.
3.3. Calculation of X-ray Absorption Spectra. In the absence of experimental results in the literature, a simulation of the X-ray absorption spectra for the molecules has been performed to provide corroboration for the results obtained in the DOS calculations because the XAS spectrum, specifically, of the NEXAFS, provides a detailed description of the unoccupied molecular orbitals above the Fermi level, albeit for excited states in the presence of a core hole. The XAS spectra were calculated using the Xrayspec utility available with StoBe. Two separate modes were taken for the calculation of the spectra—one where the polarization vector of the incident radiation was simulated to be at right angles to the plane of the molecular core and the second where the polarization vector is parallel with respect to the same molecular core. In this second mode, the average of all possible directions in the plane is taken. These two modes thus allow the XAS spectra of the molecule to be calculated for both normal and grazing incidence of radiation. The normally incident radiation, with its electric field orthogonal to the molecular plane, is expected to resonate with the in-plane σ-type orbitals (σ polarization), whereas the grazing radiation with its electric field orthogonal to the molecular plane will excite the similarly oriented π-type orbitals (π polarization).

In Figure 7, the calculated N k-edge XAS spectra with σ and π polarization for all the molecules are shown. In the case of PTCDI-C1 with its almost perfectly planar core, the lower energy π orbitals were seen to dominate the resonance at lower photon energies just above the Fermi level, whereas the σ type orbitals did not dominate until ~6 eV above the Fermi level. A similar observation was made for the similarly planar PTCDI-C2 molecule, where σ-type orbitals start to dominate at around 4.5 eV above the Fermi level. This result is in clear agreement with PDOS for the PTCDI-C1 and PTCDI-C2 molecules (Figure 4a,b), where the π orbitals were seen to dominate at lower binding energies and the σ orbitals at higher binding energies. The two stereoisomers of PTCDI-C3 gave almost identical XAS spectra, with the π orbitals dominating at lower photon energies and the σ orbitals at higher energies. However, in contrast to the planar PTCDI-C1 molecule, both the cis and trans isomers displayed small, low intensity σ polarized peaks at energies very close to the Fermi level. In fact, these low intensity peaks were seen to overlap with the much higher intensity π polarized peaks at these energies. The size of the low energy σ polarized peaks in the twisted cis isomer was observed to be distinctly greater than in the relatively planar trans isomer. This difference is in agreement with the corresponding low energy signatures for σ-type orbitals observed in the DOS calculations for these molecules (Figure 4c,d). The trend for low energy signatures for the σ-type orbitals with increasing twisting has been further corroborated with the observation of a significant σ polarized peak in PTCDI-F2, overlapping with the lowest energy π polarized peak. This is replicated in PTCDI-F5Cl4, the most twisted molecule within our set, which has the largest low energy σ polarized peak of all, overlapping with the second π polarized peak.

It can thus be argued that here, as in the case of the unoccupied DOS, a distinct positive correlation exists between the abundance of relatively shallow, or weakly bound σ-type molecular orbitals, and the degree of twisting in the molecular core. This is further demonstrated in Figure 7 by plotting the area under the low energy signatures against the degree of twisting of each molecule, as done for the DOS.

A comparison between Figures 7 and 5 readily displays a noteworthy similarity in the nature of both plots. This is particularly highlighted in the case of the PTCDI-F5Cl4 molecule, which is significantly more twisted than all the other molecules; yet, in both plots it faithfully contributes to the almost linear trend. The close matching in the linear trends of Figures 5 and 7 seems to provide convincing evidence in favor of a linear relationship between the abundance of σ-type orbitals in σ-dominated energy regions close to the Fermi level, and the degree of twisting of the perylene core, in PTCDI derivatives. It may be noted that in the case of XAS results, the spectra in the π and σ resonances are the result of the electronic structure of the unoccupied orbitals as well as the effect of the cross-section of the orbitals with respect to radiation, whereas the results obtained from unoccupied DOS are purely related to the chemical nature of the unoccupied orbitals of the molecules.

3.4. Occupied Density of States Calculation. For completeness of the study, we have also calculated the component resolved density of states for the occupied molecular orbitals of the molecules and investigated the comparative intensities of the σ- and π-type orbitals at energies close to the Fermi level, as shown in Figure 9. A similar attempt in line with the analysis performed for the unoccupied states as discussed above has been made with the intensities of the occupied levels. No systematic relation was observed in the intensities of either type of orbital with the
degree of twisting in the molecule. This shows an absence of any discernible signal for twisting in the occupied molecular orbitals closest to the Fermi level, in contrast with what has been observed in the unoccupied molecular orbitals. Because the occupied molecular orbitals are determined by the inter-atomic interactions within the molecules, they are not quite as susceptible to physical features such as twisting. It may be noted that the bond lengths and angles are fixed for specific bonds in a molecule. There is a negligible change of about 0.04—0.06% in the bond lengths and the angles because of twisting in PTCDI-C3, for example. Therefore the inter-atomic interactions remain essentially unchanged for twisting. Because the occupied DOS depends on these parameters, they are also unlikely to be affected for twisting in an optimized geometry. Consequently, no effect of twisting was observed in the occupied DOS. It may thus be argued that the occupied DOS for the molecules is mainly determined by the chemical nature of the molecule, whereas the unoccupied DOS of a molecule is

**Figure 7.** Component-resolved XAS spectra for different molecules.

**Figure 8.** Intensity of low energy σ polarized peaks in XAS spectra as a function of molecular twisting for various molecules.
specified by chemical as well as physical properties, such as twisting.

4. CONCLUSIONS

In this study, we have obtained the equilibrium geometry for certain PTCDI derivatives and calculated their occupied and unoccupied density of states separately for the molecular orbitals lying in-plane (\(\sigma\)-type) and orthogonal to the plane (\(\pi\)-type) of the molecules. We have also simulated the XAS spectrum for these molecules separately for radiation polarized normal as well as parallel to the molecular plane. These angles of incidence led to resonance of \(\pi\)- and \(\sigma\)-type molecular orbitals, respectively. We have thus been able to effect a comparison between the unoccupied DOS and XAS results because both provide a description of the molecular orbitals above the Fermi level. We have observed the presence of \(\sigma\) orbitals close to the Fermi level and have obtained an almost linear relationship between the abundance of these orbitals in \(\pi\)-dominated regions and the degree of molecular twist. While the signature for weakly bound \(\sigma\) orbitals in XAS data might be explained by suggesting that a twisting of the molecular core might physically change the orientation of the molecular orbitals, thereby increasing the cross-section of certain orbitals with respect to radiation incident at particular angles, a

Figure 9. Component resolved occupied molecular orbitals for various molecules. The energy values are as obtained from the calculation.
replication of these results in the unoccupied DOS data seems to point to a more fundamental change in the energy distribution of the unoccupied molecular orbitals because of twisting. A similar relationship has not been observed in the occupied molecular orbitals, which indicates that the effect of twisting reflects more on the unoccupied levels compared to the occupied ones. We conclude from this observation that the occupied DOS is almost exclusively determined by the chemical structure of the molecule, while the nature of the unoccupied DOS can be significantly affected by physical properties such as molecular twisting.

Additionally, we have observed a hitherto unobserved stereoisomerism in PTCDI-C3. We have shown that both the molecular twisting and the nature of the unoccupied molecular orbitals because of replication of these results in the unoccupied DOS data seems to point to a more fundamental change in the energy distribution of the unoccupied molecular orbitals because of twisting. A similar relationship has not been observed in the occupied molecular orbitals, which indicates that the effect of twisting reflects more on the unoccupied levels compared to the occupied ones. We conclude from this observation that the occupied DOS is almost exclusively determined by the chemical structure of the molecule, while the nature of the unoccupied DOS can be significantly affected by physical properties such as molecular twisting.

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