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Quantum-Chemical Insights into the Prediction of Charge Transport Parameters for a Naphthalenetetracarboxydiimide-Based Copolymer with Enhanced Electron Mobility

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Supporting Information

ABSTRACT: Theoretical modeling has been applied to study the charge transport (CT) parameters of a high-electron-mobility (n-type) naphthalenetetracarboxydiimide copolymer that was recently synthesized and tested for organic field-effect transistor applications. To understand the physicochemical characteristics of such a material, the intra- and intermolecular CT properties of holes and electrons were investigated using different DFT functionals, evidencing the need of range-separated hybrid functionals to predict key parameters such as the hole and electron reorganization energies. Our calculations revealed clear differences between hole- and electron-charging processes, providing fundamental elements for the rationalization of their transport.

The synthesis of high-performance n-type polymers [electron transport (ET) materials] is paving the way for the development of innovative all-organic photovoltaic (OPV) cells, n-channel organic field-effect transistors (OFETs), and organic complementary logic circuits, which require both p- and n-type components.[1] To achieve optimal performance, ET materials must have (*i*) high electron affinity to facilitate electron injection, (*ii*) strong intermolecular electronic couplings to reach good charge mobility, and (*iii*) high environmental stability to limit degradation and susceptibility of the charge carrier to action by H_2O/O_2.[2] Following these design rules[3] and parallel quantum-chemical investigations,[4] Facchetti et al. recently synthesized the naphthalenetetracarboxydiimide−dithiophene copolymer poly{[*N*,*N*′-bis(2-octyldodecyl)-1,4,5,8-naphthalenedicarboximide-2,6-diyl]-*alt*-5,5′-(2,2′-bithiophene)} [P(NDI2OD-T2), Polyera ActivInk N2200; Figure 1a], which shows high electron field-effect mobility even under ambient conditions ($\mu = 0.10-0.85$ cm^2 V^{-1}s^{-1}) and strong processing versatility.[1,2,5]

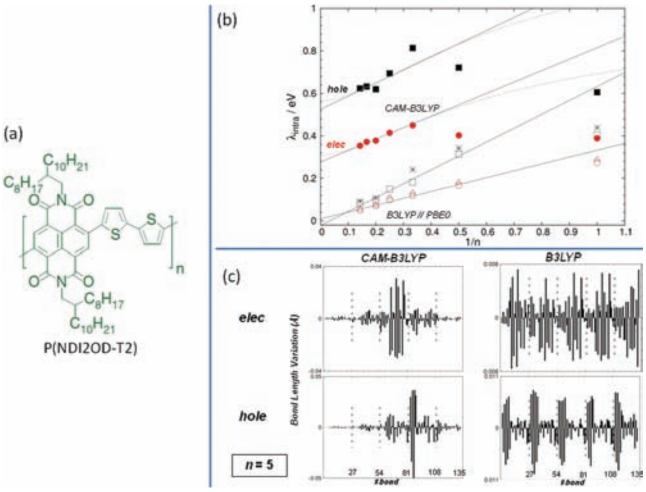

Figure 1. (a) Chemical structure of P(NDI2OD-T2). (b) $\lambda^{h/e}_{intra}$ as functions of $1/n$ ($n = 1-7$). Filled symbols: (red ●) λ^{e}_{intra} and (black ■) λ^{h}_{intra} evaluated at the (U)CAM-B3LYP/6-31G* level. Empty symbols: (red ○) λ^{e}_{intra} and (black □) λ^{h}_{intra} at the (U)B3LYP level; (red △) λ^{e}_{intra} and (black ∗) λ^{h}_{intra} at the (U)PBE0 level. Solid gray lines are linear fits (from $n = 2$ to $n = \infty$); dotted lines are asymptotic fits (from $n = 2$ to $n = \infty$) for (U)CAM-B3LYP data. (c) Bond length relaxations for electron and hole charging evaluated at the CAM-B3LYP and B3LYP levels for $n = 5$. Dashed vertical bars indicate the separation between nearest-neighbor polymer units. Numbers on the abscissa represent bonds along the polymer backbone (i.e., 1−27, first unit; 28−54, second unit; 55−81, third unit; 82−108, fourth unit; 109−135, fifth unit).

Great attention has been recently devoted to understanding the physicochemical and optoelectronic properties of P(NDI2OD-T2) in order to draw out suitable structure−property relationships for the attractive class of naphthalenediimide−dithiophene copolymers.[5,6] Numerous investigations have been carried out to analyze the microstructure of the polymer films, the crystalline/amorphous content ratio, and the lamellar packing in order to rationalize the relationship between the high electron mobility and the film texture.[7] We can summarize the main structural results obtained to date as follows: (*i*) A certain percentage of P(NDI2OD-T2) films exhibit in-plane lamellar ordering with face-on packing, thus presenting the conjugated cores lying flat or quasi-parallel to the substrate. Consequently, the π-stacking direction assumes an uncommon texture, being normal to the substrate, in contrast to the usual edge-on orientation found for high-mobility p-type materials.[7a] (*ii*) A significant fraction of each film is amorphous, without evidence for a preferred in-plane or out-of-plane orientation of the conjugated cores and side chains at the top surface.[7b] Moreover, recent X-ray analysis by Salleo and co-workers[7c] revealed a change in the bulk crystallographic texture from prevalent face-on to edge-on structures when the material was annealed up to the melting point and then slowly cooled to ambient conditions.

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A general insensitivity of the OFET μ to such structural variations was also demonstrated, a challenging result that has not found precise explanation to date. As a possible model mechanism to rationalize the high electron mobility, an extensive intergrain connectivity through polymer chains has been suggested to play an important role.[7a,c]

Parallel to structural characterizations, variable-temperature electrical experiments, contact resistance measurements, and charge modulation spectroscopy studies[8] have been performed to provide information about the electric properties of P(NDI2OD-T2). These investigations evidenced efficient electron injection even from high-work-function metals (e.g., Au),[8a] consistent with high bulk mobility due to the face-on orientation[8b] and an unusually uniform energetic landscape of sites for ET along the OFET channel.[8c]

To help rationalize the evidence acquired through the relevant experimental studies,[1b,2a,5,6] detailed theoretical and quantum-chemical investigations of the charge transport (CT) properties of naphthalenetetracarboxydiimide copolymers are strongly needed. We presented a preliminary and qualitative study[8c] based on semiempirical (AM1 and ZINDO/S) and density functional theory (DFT) approaches, proposing an interesting correlation between the measured electron-mobility activation energy and the corresponding intramolecular reorganization energy (λ_{intra}).

Here we report a detailed quantum-chemical study of P(NDI2OD-T2) focusing on evaluation of the main parameters involved in the CT processes, such as λ_{intra} and the CT integrals (V).[9] We investigated both hole and electron CT properties using DFT calculations with the aim of justifying from a molecular point of view the high electron mobility of P(NDI2OD-T2). Values of λ_{intra} for holes/electrons ($\lambda_{\text{intra}}^{\text{h/e}}$) were calculated through an oligomer approach and the relative polymer-limit values of $\lambda_{\text{intra}}^{\text{h/e}}$ extracted. Comparison of different DFT functionals revealed various and *anomalous* trends in the electronic properties as functions of chain length (n) upon variation of the exchange-correlation contribution. This screening may be useful in guiding the choice of the best DFT functional to be used for the prediction of CT properties in polymer semiconductors. 2D maps of the hole and electron coupling integrals ($V^{\text{H/L}}$) were computed, taking into account the possible intermolecular positions and orientations of NDI2OD-T2 oligomers. In this way, the calculated fluctuations in $V^{\text{H/L}}$ can been correlated with modulation of the charge-carrier mobility possibly induced by thermal disorder and ordered/disordered supramolecular structures.[9b]

For the calculation of $\lambda_{\text{intra}}^{\text{h/e}}$, we considered (NDI2OD-T2)$_n$ oligomers with n = 1−7. The CAM-B3LYP, B3LYP, and PBE0 functionals with 6-31G* basis set were employed[10] in the restricted and unrestricted formalisms. The use of range-separated hybrid functionals (e.g., CAM-B3LYP) is fundamental for a correct evaluation of the polymer-limit properties. The adiabatic potential (AP) method[11] was adopted for the evaluation of $\lambda_{\text{intra}}^{\text{h/e}}$ [see the Supporting Information (SI)]. $V^{\text{H/L}}$ were computed using the direct approach[12] for three different model dimers made from (NDI2OD-T2)$_n$ oligomers with n = 1−3 (see the SI for details) at a fixed intermolecular distance (d) of ~4.0 Å.[7a] In each case, we analyzed a wide range of in plane (xy) and out-of-plane (z) displacements, obtaining 2D maps.

To validate and justify our approach, we fully optimized (at the M06-2X/6-311G** level[10g]) molecular dimers made from two NDI2OD-T2 monomers. We found peculiar packing structures and intermolecular orientations, thus shining light on the possible supramolecular organization of P(NDI2OD-T2) fragments inside the crystalline lamellae phases. We considered two cases: (i) monomers with alkyl chains on the dicarboxydiimide moieties and (ii) monomers with only methyl groups. For each optimized dimer, we evaluated the binding energy [with the basis-set superposition error (BSSE) method[13]] and $V^{\text{H/L}}$. All of the calculations were performed using Gaussian 09.[14]

In Figure 1b we report the calculated values of $\lambda_{\text{intra}}^{\text{h/e}}$ for (NDI2OD-T2)$_n$ with n = 1−7. CAM-B3LYP predicts $\lambda_{\text{intra}}^{\text{e}}$ to be lower than $\lambda_{\text{intra}}^{\text{h}}$ at each oligomer length. For both holes and electrons, there is a peak in the λ_{intra} values at $n = 3$[8c] followed by a decreasing trend until n = 7 (as expected for increasing π-electron conjugation[15]). Analysis of CAM-B3LYP structural relaxations, evaluated as the differences in the bond lengths for the charged and neutral species (Figure 1c; also see the SI) shows the following: (i) electrons induce a relaxation mainly upon the naphthalenetetracarboxydiimide units (the electron-withdrawing groups), while holes primarily affect the bithiopene groups; (ii) with increasing chain length, the polaron defect is mainly located over three repeat units for both holes and electrons (see Figure 1c for n = 5), and for longer oligomers (n > 5), the geometric relaxations remain localized within the central three units, with negligible variations for the other polymer units; (iii) the hole-charging process causes planarization of the bithiophene groups, while electron charging does not consistently affect the torsion angle between thiophene rings, slightly changing only the angle between the NDI2OD and T2 units (see the SI). The polymer-limit values for $\lambda_{\text{intra}}^{\text{h/e}}$ (Figure 1b) calculated at CAM-B3LYP level are 0.52 eV (linear fit) to 0.56 eV (asymptotic fit) for holes and 0.27 eV (linear) to 0.30 eV (asymptotic) for electrons. These results may be slightly overestimated because of stiffness in the CAM-B3LYP description of the bond-length alternation in poly-conjugated sequences, but they are consistent with the usual λ_{intra} values predicted for various well-known organic semiconductors.[9,16−18] The CAM-B3LYP data indicate that holes induce strong variations within the bithiophene units of P(NDI2OD-T2), e.g. the chemical groups featuring low π-electron conjugation and thus giving a high λ_{intra}. In contrast, ET affects the more conjugated naphthalenetetracarboxydiimide cores, resulting in lower λ_{intra}. This first DFT result provides theoretical support for the enhanced transfer of electrons in P(NDI2OD-T2) relative to holes, which we believe is reflected in the measured carrier mobilities in field-effect devices.[1b,8a,8b]

An important computational issue is a comparison of different DFT functionals in predicting structural relaxations and CT properties of polymeric semiconducting materials. As shown in Figure 1c (also see the SI), the range-separated DFT functional (CAM-B3LYP) localizes the charge defect within the oligomer backbone, whereas hybrid GGA functionals (e.g., B3LYP, PBE0) tend to delocalize it over the whole oligomer backbone (as illustrated for the case of n = 5). Moreover, in Figure 1b, we also compare the trend and extrapolated polymer-limit values of $\lambda_{\text{intra}}^{\text{h/e}\to\infty}$. In contrast to data obtained with the CAM-B3LYP functional, both B3LYP and PBE0 predict $\lambda_{\text{intra}}^{\text{e}\to\infty}$ to vanish or at least be very small (<0.005 eV, linear fit), whereas $\lambda_{\text{intra}}^{\text{h}\to\infty}$ is predicted to be *negative* (linear fit) or less than 0.04 eV (asymptotic fit). These values are highly underestimated and directly reflect the continuous increase of the delocalization of the polaron defect (Figure 1c, B3LYP data) with increasing n. The unphysical trends obtained using hybrid GGA functionals such as B3LYP and PBE0 show the inaccuracy of these methods for the evaluation of reorganization energies in polymeric semiconducting materials.

In parallel, we also studied the trends of the optical properties of (NDI2OD-T2)$_n$ as a function of n for n = 1−5 by carrying out time-dependent DFT (TDDFT) calculations for each DFT functional considered above (Table 1; also see the SI). The data in Table 1 indicate that PBE0 is the best functional for modeling the optical properties, as it gives a low $S_0 \rightarrow S_1$ excitation energy

Table 1. Experimental Absorption-Maximum Wavelength[1a] and TDDFT/6-31G* Vertical Excitation Energies (CAM-B3LYP, B3LYP, PBE0) for (NDI2OD-T2)$_5$

	exptl	PBE0	B3LYP	CAM-B3LYP
λ_{max} (nm) [eV]	697 [1.78]	726 [1.71]	795 [1.56]	492 [2.52]
CI coeffs for $S_0 \rightarrow S_1$ transition		$H \rightarrow L$ (50%)	$H \rightarrow L$ (51%)	$H \rightarrow L$ (50%)

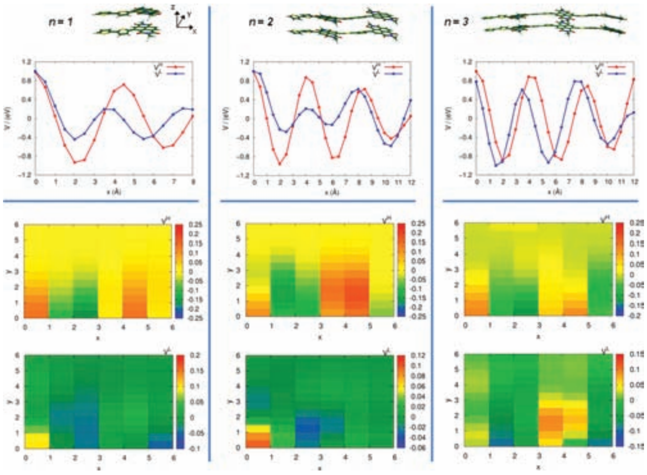

Figure 2. Hole (V^H) and electron (V^L) coupling integrals evaluated at the CAM-B3LYP/6-31G* level for stacked (NDI2OD-T2)$_n$ dimers with $n = 1-3$. Upper panels: dimer structures and 1D maps (shift along the x axis) of V^H (red) and V^L (blue). The $V^{H/L}$ values have been normalized to the maximum value. Lower panels: 2D maps (shifts along the xy plane) of V^H and V^L. Color bars are shown for each map indicating the values of $V^{H/L}$ in eV. Displacements are in Å.

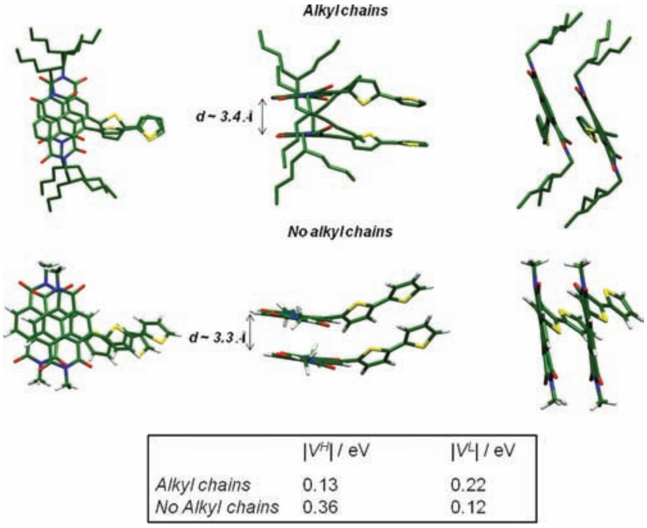

Figure 3. Fully M06-2X/6-311G**-optimized structures of NDI2OD-T2 dimers: (left) top, (center) front, and (right) side views of NDI2OD-T2 dimers with (top) alkyl chains ($-C_4H_9$) and (bottom) methyl groups. H atoms have been omitted for clarity. Inset: CAM-B3LYP/6-31G** hole and electron coupling integrals (absolute values) as evaluated for both structures.

close to the experimental value while CAM-B3LYP and B3LYP over- and underestimate this energy, respectively.

The above intramolecular DFT studies not only reveal significant physical trends (e.g., for λ_{intra}) but also show the importance of choosing the proper DFT functional for the accurate study and prediction of the optoelectronic properties of polymeric semiconducting materials;[18] in particular, we stress here the relevance of considering range-separated DFT functionals[18b] (e.g., CAM-B3LYP, wB97XD) for calculating and predicting reorganization energies of π-conjugated polymers (Figure 1b).

In regard to the intermolecular properties, Figure 2 shows the calculated hole and electron coupling matrix elements ($V^{H/L}$) for stacked (NDI2OD-T2)$_n$ dimers ($n = 1-3$). These data reveal that for each oligomer length considered, large values of the CT integrals for both holes and electrons ($V^{H/L} \approx 100-200$ meV) similar to those predicted for other high-mobility CT organic materials were obtained.[9] Moreover, holes on average show stronger couplings than electrons. From the 2D maps in the xy plane at fixed $z \approx 4.0$ Å, the maximum values [V^H/eV vs V^L/eV at (x/Å,y/Å)] are: $n = 1$, 0.25 vs 0.16 at (0.0,0.0); $n = 2$, 0.25 at (4.0,1.5) vs 0.12 at (0.0,0.0); $n = 3$, 0.21 at (0.0,0.0) vs 0.13 at (4.0,1.5). In particular, from the analysis of the 2D maps, the variances of V for holes (σ_h/eV^2) vs electrons (σ_e/eV^2) are: $n = 1$, 0.077 vs 0.040; $n = 2$, 0.099 vs 0.027; $n = 3$, 0.075 vs 0.057. Interestingly σ_h was found to be larger than σ_e, whereas the coherence parameter $C = \langle V \rangle^2/\langle V^2 \rangle$,[19] which quantifies the amplitude of the fluctuations,[19b] is smaller for holes than electrons ($C^h = 0.0004$ vs $C^e = 0.0014$ for $n = 3$; see the SI). Thus, V^H fluctuates more than V^L (also see the normalized values in the 1D maps in the upper panels of Figure 2). These data, even though they were not obtained from molecular dynamics simulations,[20] are in agreement with recent experimental results[21] showing that the hole-site energy distribution is wider than that for electrons.[8c]

As a concluding remark about the electronic couplings obtained on model systems, we can observe that comparing the root-mean-square (rms) values of $V^{H/L}$ (V_{rms}) with the polymer-limit $\lambda_{intra}^{h/e}$ values (see the SI), we obtained $V_{rms}/\lambda_{intra} \approx 0.2$. According to the Marcus CT theory,[22] this V/λ ratio implies a CT regime, as outlined also by Troisi in a recent review,[9b] where the hypothesis of nonadiabaticity for the hopping CT reaction is not valid anymore and a modified version of the Marcus transfer-rate equation has to be considered in predicting the transfer rates.[9b] Furthermore, the role of defect states[23a] and the effects of the environment[23b,c] on the charge mobility have not yet been fully analyzed, and any quantitative theoretical prediction about the CT rates must be carried out with caution, especially for the case of polymeric CT materials with unknown supramolecular structures, as the case of P(NDI2OD-T2).

To gain insight into the packing of P(NDI2OD-T2) we performed full DFT optimizations on NDI2OD-T2 dimers, considering monomers carrying either alkyl chains (a more realistic model of the polymer chemical structure) or methyl groups. In Figure 3 the optimized structures are reported. In both cases, the stabilizing driving force is the $\pi-\pi$ interaction between the NDI cores, which results in very small intermolecular distances of 3.3−3.4 Å. An intermolecular stabilization energy of ~10 kcal/mol (BSSE value in vacuum) was calculated for the dimer with alkyl chains, which shows slightly distorted packing of both the NDI and T2 cores in comparison with the case of methyl groups only.

The calculated hole and electron CT couplings (Figure 3 inset) are on the same order of magnitude and in good agreement with the 1D and 2D $V^{H/L}$ values discussed above (Figure 2). These data justify our previous model system approach and reinforce the trends and predictions discussed before.

In conclusion, we have investigated the CT properties of P(NDI2OD-T2), a recently synthesized and very relevant n-type copolymer showing enhanced electron mobility whose features are still a challenge for the understanding of efficient CT in polymeric semiconductors. Range-separated DFT functionals (e.g., CAM-B3LYP) must be considered for the prediction of the polymer-limit values of intramolecular reorganization energies. λ^{h}_{intra} is predicted to have a high value (~0.56 eV) that is greater than λ^{e}_{intra} (~0.30 eV). These data suggest low hole mobility in contrast to enhanced electron mobility. Hole and electron coupling integrals were evaluated on both model dimers and fully DFT-optimized dimers. Both V^H and V^L were found to be quite large (0.1−0.2 eV), and V^L showed a lower degree of fluctuations than to V^H, suggesting a more uniform energetic landscape for electrons. Stabilizing $\pi-\pi$ interactions were calculated for the fully optimized dimers; stacking of the quasi-planar NDI cores and good packing of the alkyl chains were found, providing reasonable structural models that may be useful as guess structures in solving the supramolecular geometry of P(NDI2OD-T2).

ASSOCIATED CONTENT

Ⓢ Supporting Information. Details concerning the quantum-chemical calculations and complete ref 14. This material is available free of charge via the Internet at http://pubs.acs.org.

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