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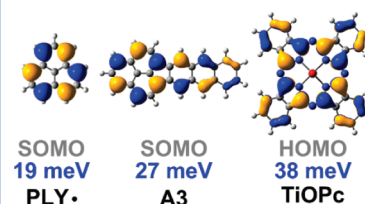
An Important Key to Design Molecules with Small Internal Reorganization Energy: Strong Nonbonding Character in Frontier Orbitals

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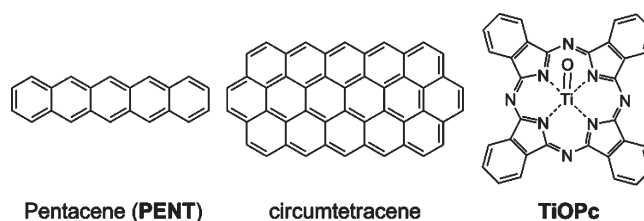
ABSTRACT For an electron to move between molecules (reactants), structural reorganizations of the reactants and their surrounding molecules are needed. The energy cost of the reorganizations, which is determined by structural and electronic features of molecules involved, contributes to the energy barrier of an electron transfer reaction. Finding the factors affecting the energy cost is of fundamental and technological importance. It is believed that extended π -conjugation and a rigid molecular framework are beneficial for minimizing the energy cost. We prove with phenalenyl and phthalocyanine derivatives that the extent of local nonbonding character in frontier molecular orbitals is in fact more crucial than extended π -conjugation; unprecedented small energy cost for reorganization has been found with the help of the nonbonding character. This finding provides a much better understanding of the literature data, as well as a new focus of the molecular design of cutting-edge organic electronics materials.

SECTION Electron Transport, Optical and Electronic Devices, Hard Matter



Contemporary development of electron transfer theory aids the understanding of the hole/electron transfer phenomenon and, therefore, provides directions for improving electron transfer in chemical and biochemical systems and materials.¹ According to the semiclassical Marcus theory,² one of the important factors governing the rate of electron transfer is reorganization energy, the energy needed for structural adjustments of the reactants (internal reorganization) and the surrounding molecules (external reorganization), to assume the configuration required for electron transfer. Small reorganization energy is highly desirable in the design of optoelectronic and electronic materials. For example, in artificial photosynthetic systems with long-lived charge-separated state, building blocks with small reorganization energies (e.g., fullerene, porphyrin, and phthalocyanine) have been used because they can accelerate charge separation while attenuating charge recombination.^{3–6} For organic electronic materials such as organic field-effect transistors (OFETs), the charge transport mechanism is not fully understood, so the application of Marcus theory is not always appropriate.^{7,8} Nevertheless, the consensus is that small reorganization energy and large electronic coupling afford high mobility of a charge carrier.^{7–9} With these requirements fulfilled, pentacene and titanyl phthalocyanine (TiOPc) have hole mobilities larger than $3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{10,11} the same order of magnitude as that of amorphous silicon ($0.1 - 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).¹² It is noted that internal reorganization energies for hole transport of these two compounds are less than 100 meV,^{13,14} significantly smaller than most organic compounds. An ideal way to assemble an electron transfer system is to use building blocks that have superior monomeric

properties (e.g., small internal reorganization energy) and a proper relationship with surrounding components (small external reorganization energy and large electronic coupling). Designing molecules/building blocks with superior monomeric properties is therefore a prerequisite step to assemble cutting-edge optoelectronic and electronic materials. In this study we ask the fundamental question of how to design molecules with small internal reorganization energy. Our study shows that with the use of molecular framework with a strong nonbonding character in their frontier orbitals, unprecedented small internal reorganization energies, only a fraction of that of pentacene and TiOPc, can be obtained.



The conventional wisdom to reduce the reorganization energy of organic molecules includes extending the π -conjugation and employing a rigid molecular framework. Extensive π -conjugation leads to a delocalized charge distribution, so that local structural adjustments for electron transfer are less severe than smaller π -systems. A rigid molecular

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framework restrains the molecule from large structural changes for electron transfer. The small reorganization energy of C_{60} has been ascribed to extended π -conjugation and its rigid molecular framework.¹⁵ On the other hand, in the search of pentacene-based n -channel OFETs (aiming at large electron affinity (EA) and small internal reorganization energy (λ)), we found several useful guidelines to achieve the goal:^{16–18} (1) Increase EA by functionalizing pentacene with weak C–X bonds (–X: Cl or Br) rather than the strong C–F bond, because the relatively strong C–F bond contributes significantly to λ .^{16,17} (2) Increase EA by directly replacing some C atoms in pentacene with N atoms to avoid the introduction of extra degrees of freedom, since extra degrees of freedom may increase λ .¹⁷ (3) Employ an electron-withdrawing substituent (e.g., –CN) that contributes to the frontier orbitals of pentacene in a nonbonding fashion.¹⁸ This is because the local structural adjustment for electron/hole transfer often correlates with the local bonding character in the frontier molecular orbitals, where an electron is added to or removed from. The local bonding characters between two neighboring atoms in a molecular orbital include bonding, antibonding, and nonbonding. When populated, bonding and antibonding cause change in bond order, but nonbonding only involves one atom, so it will not cause change in bond order. Therefore, nonbonding induces much less bond length adjustment than the other two bonding types upon electron/hole transfer, and is beneficial for the reduction of λ . For example, the cyano and chloro substituents contribute to the lowest unoccupied molecular orbital (LUMO) of pentacene in a nonbonding and antibonding fashion, respectively (Figure 1). Therefore, λ^- values for electron transfer of 2,3,5,7,9,10,12,14-octacyanopentacene, pentacene, and 2,3,5,7,9,10,12,14-octachloropentacene at the B3LYP/6-31G(d,p) level are 95, 133, and 159 meV, respectively.^{17,18}

The three guidelines mentioned above are about how to functionalize a core structure. For the third guideline, it is of great interest to explore how small λ could be if the frontier orbitals of the core structure have a strong nonbonding character. Phenalenyl radical (PLY•) is an ideal species for this purpose, as revealed by its singly occupied molecular orbital (SOMO) shown in Figure 2a. In this SOMO, there is no presence of bonding or antibonding relationships between any two atoms. PLY• is rigid, and is yet a relatively small π -system compared to pentacene, porphyrin, or C_{60} . It provides an opportunity to compare the importance of nonbonding character in frontier orbitals versus extended π -conjugation. Therefore, we have calculated λ of PLY• and related compounds for the self-exchange electron transfer reaction shown in eq 1 at the B3LYP/6-31G(d,p) level, which has been shown to reproduce the experimental values obtained from the gas-phase photoelectron spectra.^{19–22} In addition to the calculated λ of PLY• and related compounds, subsequent examination of literature data of phthalocyanine compounds also confirms the important role of the nonbonding character in the reduction of λ .

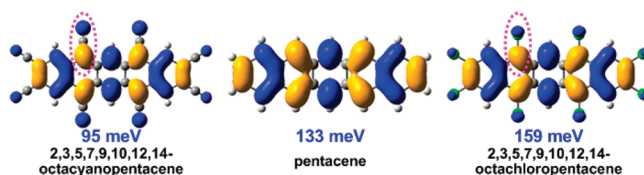
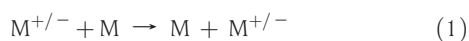


Figure 1. LUMOs (0.020 au) for 2,3,5,7,9,10,12,14-octacyanopentacene (left), pentacene (middle), and 2,3,5,7,9,10,12,14-octachloropentacene (right) at the B3LYP/6-31G(d,p) level. λ^- values are shown in blue.

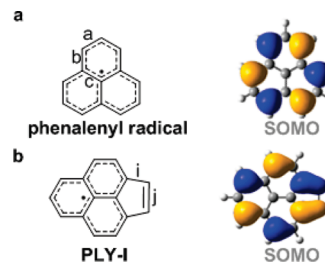


Figure 2. Structures and SOMO (0.025 au) for (a) neutral PLY• (D_{3h} symmetry) and (b) PLY-I (C_{2v} symmetry) at the UB3LYP/6-31G(d,p) level.

Our calculated internal reorganization energies of PLY• for hole (λ^+ ; 19 meV) and electron (λ^- ; 35 meV) transfer at the B3LYP/6-31G(d,p) level hit record low values, unexpected for a molecule of this size. Haddon had previously shown that PLY• had small structural change upon oxidation and reduction with semiempirical calculations, but the λ for a self-exchange reaction were not estimated.²³ It has been shown in the literature that λ values for a self-exchange reaction are rather insensitive to the size of the basis set employed.^{16,24,25} This is proven in the case for PLY•. At the B3LYP/6-31G(d) and B3LYP/6-311+G(d,p) levels, λ^+ are 20 and 21 meV, respectively, and λ^- are 35 and 32 meV, respectively. Compared to the λ of anthracene (138 and 200 meV for λ^+ and λ^-),²⁴ λ of PLY• are many times smaller, even though the two molecules have similar numbers of carbon atoms. Using λ^+ as an example to compare with the literature data of organic molecules, we found the value of PLY• is only one-fifth of that of pentacene (93 meV)¹⁶ and one-half of that of TiOPc (38 meV) at the B3LYP/6-31G(d) level.¹⁴ One of the latest theoretical studies concerning small λ^+ is on circum(oligo)acenes, the prototype molecules for graphene nanoribbons.²⁶ The λ^+ value of circumtetracene (a molecule with 48 carbon atoms) calculated at both the B3LYP/cc-pCVDZ²⁶ and B3LYP/6-31G(d,p) (our result) levels was 57 meV, a value 3 times that of the more atom-economic PLY• (a molecule with 13 carbon atoms). The much smaller PLY• with a record-low λ^+ signifies the importance of the design concept of employing nonbonding character in frontier orbitals to achieve a small λ , in contrast to the conventional wisdom of pursuing extended π -conjugation.

To examine whether the structural adjustments for electron/hole transfer correlate with the spatial distribution of frontier orbitals of PLY•, we defined the bond length alteration (BLA) as the absolute value of the bond length difference between the neutral and charged species ($BLA = |\Delta_{C-N}|$ and $|\Delta_{A-N}|$ for λ^+ and λ^- , respectively). As shown in Table 1,

Table 1. Bond lengths (Å) and Absolute BLAs ($|\Delta_{C-N}|$ and $|\Delta_{A-N}|$) of Selected Bonds of **PLY•** and **PLY-I** Optimized at the B3LYP/6-31G(d,p) Level

molecule	bond	neutral	cationic	anionic	$ \Delta_{C-N} $	$ \Delta_{A-N} $
PLY•	<i>a</i>	1.392	1.394	1.392	0.002	0.000
	<i>b</i>	1.418	1.417	1.422	0.001	0.004
	<i>c</i>	1.431	1.422	1.444	0.009	0.013
PLY-I	<i>i</i>	1.469	1.497	1.434	0.028	0.035
	<i>j</i>	1.371	1.354	1.402	0.017	0.031

bonds *a* and *b* (Figure 2a), which connect to the atoms with nonbonding character, show only negligible BLA (< 0.004 Å). Compared to the neutral geometry, the cationic geometry shrinks toward the center via shortening bonds *c* and the anionic geometry expands via lengthening of the same bonds. As there is no electron density populated on bond *c* in the SOMO, it may seem surprising that bond *c* changes significantly relative to bonds *a* and *b*. However, because the local nonbonding orbitals are out of phase with their neighbors (Figure 2a), similar to the out-of-phase situation in antibonding, it is not surprising that removing/adding an electron will cause the molecule to shrink/expand. It is conceivable if nonbonding atomic orbitals are further apart in a frontier molecular orbital, a λ value smaller than 19 meV should be possible. Attaching a double bond to the **PLY•** framework (**PLY-I** in Figure 2b) introduces bonding (bond *i*) and antibonding (bond *j*) characters to the frontier orbitals and raises the values of λ^+ and λ^- to 87 and 154 meV at the B3LYP/6-31G(d,p) level, respectively. For bonds *i* and *j*, the BLA values are ca. 0.02–0.03 Å (Table 1), significantly larger than other bonds in **PLY-I** (< 0.015 Å; see Supporting Information). It is noted that the values of $|\Delta_{A-N}|$ are mostly larger than that of $|\Delta_{C-N}|$ (Table 1), so do the values of λ^- relative to λ^+ . This reflects the different extents of structural impact upon removing and adding an electron to a molecule.

The parent **PLY•** is not a stable species in ambient condition.²⁷ Nevertheless, its stability can be enhanced by introducing bulky groups or further delocalization of the radical. Therefore, many PLY-based molecules are stable enough to be actively explored for their unique magneto-, electronic, and optical properties.^{28–31} For example, while a lot of OFET devices have to be operated under nitrogen, PLY-based OFET devices have been shown to operate in air.³¹ Because, in the crystal structures of PLY-based molecules, the six atoms on which the SOMO is populated in a **PLY•** unit (Figure 2a) is often on top of the populated atoms of the other **PLY•** unit, strong electronic coupling between **PLY•** units has been reported.³²

Oligoacenes and oligothiophenes are two structural motifs that often appear in organic electronic materials. It is of interest to investigate the influence of these motifs on λ if incorporated into PLY-based molecules. These compounds may also be used to confirm the relative importance of π -conjugation and nonbonding character. With joint **PLY•** and acene/thiophene structural units, model compounds (**An** and **Tn**) up to roughly the sizes of pentacene (**PENT**) and sexithiophene (**Th6**) have been calculated. To mimic the solid state planar geometry of oligothiophenes and to make a fair comparison about the impact of nonbonding character

Table 2. Internal Reorganization Energies of Acene and Thiophene Derivatives (λ^+ and λ^- ; meV) at the B3LYP/6-31G(d,p) Level

acene ^a	λ^+	λ^-	thiophene ^c	λ^+	λ^-
A1	38	102	T0	54	121
A2	28	87	T1	158	134
A3	27	80	T2	215	151
PENT ^b	94	133	Th6 ^b	256	221

^a **A1–A3** are of C_{2v} symmetry. ^b Reference 16. ^c Planar structure of C_s symmetry.

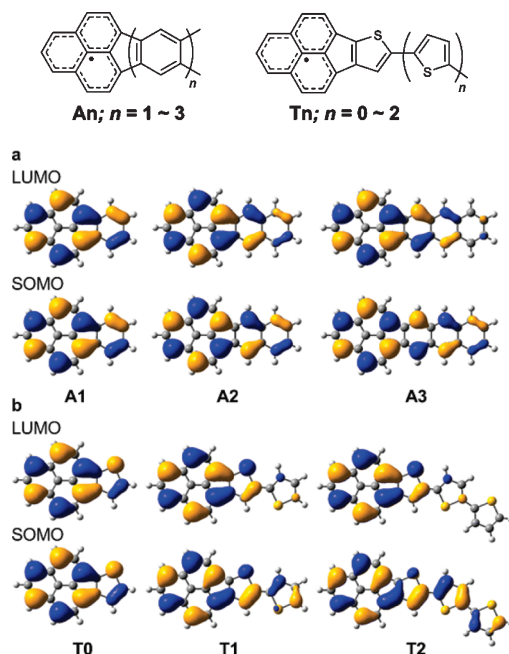


Figure 3. Frontier orbitals (0.025 au) for (a) neutral **A1–A3** (top), (b) **T0–T2** (bottom) at the UB3LYP/6-31G(d,p) level.

among rigid structures, only planar **Tn** and **Th6** were studied. Results in Table 2 confirm the benefit of introducing nonbonding character into the design of new compounds; all calculated λ^\pm of **An** and **Tn** are smaller than that of **PENT** and **Th6**, respectively (Table 2). The λ^+ of **A1–A3** are among the smallest values found in the literature. The λ^- of each **An** is again significantly larger than the corresponding λ^+ as in **PLY•** and **PLY-I**. However, different from the smaller **PLY•** and **PLY-I** systems where frontier orbitals resemble each other, the spatial similarity between the α -highest occupied molecular orbital (α -HOMO) (SOMO) and the β -LUMO (LUMO) lessens for the larger acene and thiophene analogs. As shown in Figure 3a for **An**, the percentage of nonbonding character is smaller in β -LUMO than in α -HOMO. Therefore, this factor should also contribute to the larger values of λ^- than that of λ^+ . Another observation from the results in Table 2 is that the trend of λ^\pm for **Tn** does not follow the notion that larger analogs (more extended π -conjugation) have smaller λ values as found in calculation results of planar oligothiophenes.³³ As shown by the SOMO of **Tn** in Figure 3b, when the more extended delocalization is accompanied by losing the nonbonding character to bonding/antibonding character

(e.g., **T2** vs **T0**), extended delocalization does not lead to the reduction of λ . The same rationale also explains the fact that λ^+ are larger than λ^- for **T1** and **T2**. Two things should be noted here. First, the frontier orbitals in Figure 3 were drawn in a rather contracted form to reveal the local nonbonding character; therefore, orbital distribution with small wave function amplitude was not shown. This compromises the predicting power of β -LUMO for the λ^- trend of **T2** > **T1** > **T0**. Second, the HOMO (LUMO) of the anionic (cationic) species corresponds well to the β -LUMO (α -HOMO) of the neutral species in the molecules we have examined in this study. That is why one can judge the trends of λ^\pm values in terms of the frontier orbitals of the neutral species.

Recently, phthalocyanine-based OFET material (**TiOPc** in Figure 4) has been reinvestigated by Zhu et al.¹¹ The authors found a large hole mobility of **TiOPc** in α -phase, in which effective solid-state π - π interactions were found. Contrary to the phenalenyl-based derivatives, **TiOPc** is a closed-shell species. A theoretical study conducted by Brédas et al. showed large electronic couplings and that the λ^+ of 38 meV for **TiOPc** was remarkably low.¹⁴ As to the reason for the low λ^+ value, no comment has been given. In their paper, the HOMO was drawn with a loose isosurface (simulated in the middle of Figure 4). When scaling the HOMO isosurface to a reasonably contracted size, the nonbonding character in the central ring area becomes evident (right of Figure 4). Thus, we believe that the small λ^+ of **TiOPc** should be ascribed to extended charge delocalization plus a good percentage of nonbonding character in the HOMO. The BLAs ($|\Delta_{C-N}|$) upon charge extraction are less than 0.01 Å (Table 3). The most acute BLAs (0.008 Å) appear in the four peripheral phenyl rings (bonds *g* in Figure 4 and Table 3), where the bonding character of small wave function amplitude resides. Theoretical calculations of other metal phthalocyanine compounds also showed small λ^+ values.³⁴ The molecular orbitals presented in that paper again show strong nonbonding character in the HOMO as what is shown in Figure 4. In the LUMO the bonding character of the central ring increases, in line with the significantly larger λ^- values (> 160 meV³⁴).

In this study, it is demonstrated with phenalenyl and phthalocyanine units (both have been shown to afford effective electronic coupling) that a large percentage of nonbonding character in frontier orbitals plays a very crucial role in pushing the limit for the reduction of internal reorganization energy. In the literature, nonbonding character in the frontier orbitals has been employed to explain small values of internal reorganization energy in cases such as derivatives of pentacene, benzo[1,2-*k*;4,5-*k'*]difluoranthene, and tetraceno[2,3-*c*]thiophene.^{18,35,36} However, in terms of molecular design, it is much less often included in the design principles, searching specifically for structures with strong nonbonding character. With this study focusing on the role of nonbonding character in frontier orbitals, it is demonstrated that the conventional wisdom (design principles) for small internal reorganization energy should be modified to include rigidity, strong nonbonding character in frontier orbitals, and extended π -conjugation. With this in mind, in-depth understanding of the literature data and the design of superior new compounds can be facilitated.

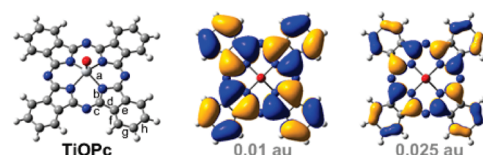


Figure 4. Optimized geometry of neutral **TiOPc** (C_{4v} symmetry) and HOMO for **TiOPc** at the RB3LYP/6-31G(d,p) level.

Table 3. Bond Lengths (Å) and Absolute BLAs ($|\Delta_{C-N}|$) of **TiOPc** Optimized at the B3LYP/6-31G(d,p) level

index	neutral	cationic	$ \Delta_{C-N} $
<i>a</i>	2.092	2.090	0.002
<i>b</i>	1.378	1.379	0.001
<i>c</i>	1.327	1.327	0.000
<i>d</i>	1.457	1.461	0.004
<i>e</i>	1.409	1.407	0.002
<i>f</i>	1.396	1.390	0.006
<i>g</i>	1.393	1.401	0.008
<i>h</i>	1.408	1.402	0.006

Computational Details

The λ of a self-exchange electron transfer reaction (eq 1) was calculated with Nelson's four-point method.³⁷ The total internal reorganization energy (λ^\pm) is the sum of the λ_1^\pm and λ_2^\pm (eqs 2–4; also see Figure S1 in the Supporting Information):

$$\lambda^\pm = \lambda_1^\pm + \lambda_2^\pm \quad (2)$$

$$\lambda_1^\pm = E_\pm(Q_N) - E_\pm(Q_\pm) \quad (3)$$

$$\lambda_2^\pm = E_N(Q_\pm) - E_N(Q_N) \quad (4)$$

where $E_\pm(Q_N)$ is the total energy of the charged state in the neutral geometry, $E_\pm(Q_\pm)$ is the total energy of the charged state in the charged state geometry, $E_N(Q_\pm)$ is the total energy of the neutral state in the charged state geometry, and $E_N(Q_N)$ is the total energy of the neutral state in the neutral geometry. All the structures were optimized at the DFT-B3LYP/6-31G(d,p) level of theory, and frequency calculations were performed to confirm whether the optimized geometry was an energy minimum on the potential energy surface with Gaussian 03.³⁸ Basis sets other than 6-31G(d,p) were also employed for selected molecules. To mimic the solid state planar geometry of oligothiophenes, C_s symmetry was applied to **T0**–**T2**. All the optimized geometries were shown to be a local minimum with frequency analysis ($N_{\text{imag}} = 0$), except for the neutral state of **T1** ($N_{\text{imag}} = 1$) and **T2** ($N_{\text{imag}} = 2$). Molecular orbitals were drawn with GaussView.^{39,40} The values of $\langle S^2 \rangle$ for the open-shell species were in the range of 0.7542–0.8026.

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SUPPORTING INFORMATION AVAILABLE Full list of reference 38, illustration for the estimation of internal reorganization energy, tables of BLAs, and Cartesian coordinates for B3LYP/6-31G(d,p) optimized geometries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, Germany, 2001.
- (2) Marcus, R. A. Electron Transfer Reactions in Chemistry: Theory and Experiment (Nobel Lecture). *Angew. Chem., Int. Ed.* **1993**, *32*, 1111–1121.
- (3) Imahori, H.; Tamaki, K.; Guldi, D. M.; Luo, C.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. Modulating Charge Separation and Charge Recombination Dynamics in Porphyrin–Fullerene Linked Dyads and Triads: Marcus-Normal versus Inverted Region. *J. Am. Chem. Soc.* **2001**, *123*, 2607–2617.
- (4) Fukuzumi, S. Development of Bioinspired Artificial Photosynthetic Systems. *Phys. Chem. Chem. Phys.* **2008**, *10*, 2283–2297.
- (5) D'Souza, F.; Ito, O. Photoinduced Electron Transfer in Supramolecular Systems of Fullerenes Functionalized with Ligands Capable of Binding to Zinc Porphyrins and Zinc Phthalocyanines. *Coord. Chem. Rev.* **2005**, *249*, 1410–1422.
- (6) El-Khouly, M. E.; Ito, O.; Smith, P. M.; D'Souza, F. Intermolecular and Supramolecular Photoinduced Electron Transfer Processes of Fullerene–Porphyrin/Phthalocyanine Systems. *J. Photochem. Photobiol. C* **2004**, *5*, 79–104.
- (7) Troisi, A. Prediction of the Absolute Charge Mobility of Molecular Semiconductors: The Case of Rubrene. *Adv. Mater.* **2007**, *19*, 2000–2004.
- (8) Cheung, D. L.; Troisi, D. A. Modelling Charge Transport in Organic Semiconductors: From Quantum Dynamics to Soft Matter. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5941–5952.
- (9) da Silva Filho, D. A.; Olivier, Y.; Coropceanu, V.; Brédas, J.-L.; Cornil, J. In *Organic Field-Effect Transistors*; Bao, Z., Locklin, J., Eds.; Optical Science and Engineering Series; CRC Press: Boca Raton, FL, 2007; Chapter 1, pp 1–26.
- (10) Tan, H. S.; Kulkarni, S. R.; Cahyadi, T.; Lee, P. S.; Mhaisalkar, S. G.; Kasim, J.; Shen, Z. X.; Zhu, F. R. Solution-Processed Trilayer Inorganic Dielectric for High Performance Flexible Organic Field Effect Transistors. *Appl. Phys. Lett.* **2008**, *93*, 183503/1–183503/3.
- (11) Li, L.; Tang, Q.; Li, H.; Yang, X.; Hu, W.; Song, Y.; Shuai, Z.; Xu, W.; Liu, Y.; Zhu, D. An Ultra Closely π -Stacked Organic Semiconductor for High Performance Field-Effect Transistors. *Adv. Mater.* **2007**, *19*, 2613–2617.
- (12) Mas-Torrent, M.; Rovira, C. Novel Small Molecules For Organic Field-Effect Transistors: Towards Processability and High Performance. *Chem. Soc. Rev.* **2008**, *37*, 827–838.
- (13) Deng, W.-Q.; Goddard, W. A. Predictions of Hole Mobilities in Oligoacene Organic Semiconductors from Quantum Mechanical Calculations. *J. Phys. Chem. B* **2004**, *108*, 8614–8621.
- (14) Norton, J. E.; Brédas, J.-L. Theoretical Characterization of Titanyl Phthalocyanine as a P-Type Organic Semiconductor: Short Intermolecular π – π Interactions Yield Large Electronic Couplings and Hole Transport Bandwidths. *J. Chem. Phys.* **2008**, *128*, 034701/1–034701/7.
- (15) Imahori, H.; Mori, Y.; Matano, Y. Nanostructured Artificial Photosynthesis. *J. Photochem. Photobiol. C* **2003**, *4*, 51–83.
- (16) Chen, H.-Y.; Chao, I. Effect of Perfluorination on the Charge-Transport Properties of Organic Semiconductors: Density Functional Theory Study of Perfluorinated Pentacene and Sexithiophene. *Chem. Phys. Lett.* **2005**, *401*, 539–545.
- (17) Chen, H.-Y.; Chao, I. Toward the Rational Design of Functionalized Pentacenes: Reduction of the Impact of Functionalization on the Reorganization Energy. *ChemPhysChem* **2006**, *7*, 2003–2007.
- (18) Kuo, M.-Y.; Chen, H.-Y.; Chao, I. Cyanation: Providing a Three-in-One Advantage for the Design of n-Type Organic Field-Effect Transistors. *Chem.—Eur. J.* **2007**, *13*, 4750–4758.
- (19) Gruhn, N. E.; da Silva Filho, D. A.; Bill, T. G.; Malagoli, M.; Coropceanu, V.; Kahn, A.; Brédas, J.-L. The Vibrational Reorganization Energy in Pentacene: Molecular Influences on Charge Transport. *J. Am. Chem. Soc.* **2002**, *124*, 7918–7919.
- (20) Coropceanu, V.; Malagoli, M.; da Silva Filho, D. A.; Gruhn, N. E.; Bill, T. G.; Brédas, J.-L. Hole- and Electron-Vibrational Couplings in Oligoacene Crystals: Intramolecular Contributions. *Phys. Rev. Lett.* **2002**, *89*, 275503/1–275503/4.
- (21) Kwon, O.; Coropceanu, V.; Gruhn, N. E.; Durivage, J. C.; Laquindanum, J. G.; Katz, H. E.; Cornil, J.; Brédas, J.-L. Characterization of The Molecular Parameters Determining Charge Transport in Anthradithiophene. *J. Chem. Phys.* **2004**, *120*, 8186–8194.
- (22) Malagoli, M.; Coropceanu, V.; da Silva Filho, D. A.; Brédas, J. L. A Multimode Analysis of the Gas-Phase Photoelectron Spectra in Oligoacenes. *J. Phys. Chem.* **2004**, *108*, 7490–7496.
- (23) Haddon, R. C. Quantum Chemical Studies in the Design of Organic Metals III. Odd-Alternant Hydrocarbons-The Phenalenyl (ply) System. *Aust. J. Chem.* **1975**, *28*, 2343–2351.
- (24) Winkler, M.; Houk, K. N. Nitrogen-Rich Oligoacenes: Candidates for n-Channel Organic Semiconductors. *J. Am. Chem. Soc.* **2007**, *129*, 1805–1815.
- (25) Zhang, Y.; Cai, X.; Bian, Y.; Li, X.; Jiang, J. Heteroatom Substitution of Oligothiophenes: From Good p-Type Semiconductors to Good Ambipolar Semiconductors for Organic Field-Effect Transistors. *J. Phys. Chem. C* **2008**, *112*, 5148–5159.
- (26) Sancho-García, J. C.; Pérez-Jiménez, A. J. Charge-Transport Properties of Prototype Molecular Materials for Organic Electronics Based on Graphene Nanoribbons. *Phys. Chem. Chem. Phys.* **2009**, *11*, 2741–2746.
- (27) Hicks, R. G. What's New in Stable Radical Chemistry? *Org. Biomol. Chem.* **2007**, *5*, 1321–1338.
- (28) Itkis, M. E.; Chi, X.; Cordes, A. W.; Haddon, R. C. Magneto-Opto-Electronic Bistability in a Phenalenyl-Based Neutral Radical. *Science* **2002**, *296*, 1443–1445.
- (29) Pal, S. K.; Itkis, M. E.; Tham, F. S.; Reed, R. W.; Oakley, R. T.; Haddon, R. C. Resonating Valence-Bond Ground State in a Phenalenyl-Based Neutral Radical Conductor. *Science* **2005**, *309*, 281–284.
- (30) Kamada, K.; Ohta, K.; Kubo, T.; Shimizu, A.; Morita, Y.; Nakasuji, K.; Kishi, R.; Ohta, S.; Furukawa, S.-i.; Takahashi, H.; Nakano, M. Strong Two-Photon Absorption of Singlet Diradical Hydrocarbons. *Angew. Chem., Int. Ed.* **2007**, *46*, 3544–3546.
- (31) Chikamatsu, M.; Mikami, T.; Chisaka, J.; Yoshida, Y.; Azumi, R.; Yase, K.; Shimizu, A.; Kubo, T.; Morita, Y.; Nakasuji, K. Ambipolar Organic Field-Effect Transistors Based on a Low Band Gap Semiconductor with Balanced Hole and Electron Mobilities. *Appl. Phys. Lett.* **2007**, *91*, 043506/1–043506/3.

- (32) Huang, J.; Kertesz, M. Intermolecular Covalent π – π Bonding Interaction Indicated by Bond Distances, Energy Bands, and Magnetism in Biphenalenyl Biradicaloid Molecular Crystal. *J. Am. Chem. Soc.* **2007**, *129*, 1634–1643.
- (33) Zade, S. S.; Bendikov, M. Study of Hopping Transport in Long Oligothiophenes and Oligoselenophenes: Dependence of Reorganization Energy on Chain Length. *Chem.—Eur. J.* **2008**, *14*, 6734–6741.
- (34) Cai, X.; Zhang, Y.; Qi, D.; Jiang, J. Density Functional Theory Study on the Semiconducting Properties of Metal Phthalocyanine Compounds: Effect of Axially Coordinated Ligand. *J. Phys. Chem. A* **2009**, *113*, 2500–2506.
- (35) Liu, W.-S.; Liu, C.-C.; Kuo, M.-Y. High-Performance p-Channel Organic Semiconducting Candidates Based on Benzo[1,2-*k*;4,5-*k'*]difluoranthene Derivatives. *Chem.—Eur. J.* **2009**, *15*, 5896–5900.
- (36) Kuo, M.-Y.; Liu, C.-C. Molecular Design toward High Hole Mobility Organic Semiconductors: Tetraceno[2,3-*c*]thiophene Derivatives of Ultrasmall Reorganization Energies. *J. Phys. Chem. C* **2009**, *113*, 16303–16306.
- (37) Nelsen, S. F.; Blackstock, S. C.; Kim, Y. Estimation of Inner Shell Marcus Terms for Amino Nitrogen Compounds by Molecular Orbital Calculations. *J. Am. Chem. Soc.* **1987**, *109*, 677–682.
- (38) Frisch, M. J. et al. ; *Gaussian 03*, revisions D.02 and E.01; Gaussian, Inc.: Wallingford, CT, 2004.
- (39) Dennington, R., II; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R.; *GaussView*, version 3.09; Semichem, Inc.: Shawnee Mission, KS, 2003.
- (40) Dennington, R., II; Keith, T.; Millam, J.; *GaussView*, version 4.1; Semichem, Inc.: Shawnee Mission, KS, 2007.