CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200601803

Cyanation: Providing a Three-in-One Advantage for the Design of *n*-Type Organic Field-Effect Transistors

Ming-Yu Kuo,[a] Hsing-Yin Chen,[a, b] and Ito Chao*[a]

Abstract: The theoretical work presented here demonstrates that, when substitution takes place at appropriate positions, cyanation could be a useful tool for reducing the internal reorganization energy of molecules. A molecular-orbital-based explanation is given for this fundamentally important phenomenon. Some of the cyanated pentacene derivatives (*n*CN-PENT-*n*) not only have internal reorganization energies for electron transfer (λ^-) smaller than that of pentacene, but the λ^- values are even of the same magnitude as the internal reorganization energy for hole transfer (λ^+) of pentacene, a small value that few organic compounds have surpassed. In addition, cyanation raises the electron affinity of the parent compound and may afford good electronic couplings between neighboring molecules, because of its ability in promoting π-stacking. For the design of high performance *n*-Type Organic field-effect transistors, high electron affinities, large intermolecular electronic couplings, and small reorganization energies are necessary. Cyanation may help in all three aspects. Two cyanated trialkylsilylethynyl pentacene derivatives with known π-stacking structures are predicted to provide reasonably small internal reorganization energies, large electronic couplings, and high electron affinities. They have the potential to outperform *N*-fluoroalkylated dicyanoperylene-3,4:9,10-bis(dicarboximides) (PDI-FCN_2) in terms of electron mobility.

Keywords: charge transfer · cyanation · density functional calculations · organic field-effect transistors · pentacenes · semiconductors

Introduction

Organic semiconductors have been investigated widely both in academia and in industry, due to their potential application for low-cost, light-weight, flexible, and large-area electronic devices, including organic field-effect transistors (OFETs)[1] and light-emitting diodes (OLEDs).[2] For the OFET application, the intrinsic charge mobility of the active layer depends largely on the solid-state order. Studies on solid-state order in relation to OFET performance showed that π-stacked arrays lead to OFETs with good charge mobility.[3] For example, unsubstituted polythiophene (PT) with a herringbone packing results in a low hole mobility of $10^{-5}\,cm^2V^{-1}s^{-1}$.[1c] In contrast to PT, regioregular poly(3-hexylthiophene) (P3HT) substituted by hexyl side chains changes its molecular packing from herringbone packing to π-stacking, and enhances the hole mobility up to $0.1\,cm^2V^{-1}s^{-1}$.[3e] However, pentacene (PENT), one of the most promising *p*-type organic compounds for OFETs,[4] has a herringbone packing structure.[5] This packing of PENT molecules does not provide optimal intermolecular π-orbital overlap,[6] which is a critical factor impacting the electronic coupling and hence the intrinsic charge mobility. Therefore, some research groups have attempted to obtain π-stacked oligoacene derivatives.[7] Anthony et al. showed that functionalization of PENT with two trialkylsilylethynyl groups is an effective method for facilitating π-stacking of pentacene.[7a–c] Swager et al. synthesized π-stacked tetracene derivatives with fluorine and alkyl/alkoxy functionalization.[7d] Bao et al. used dichloro substitution to switch the herringbone packing of tetracene to π-stacking, resulting in improved mobility.[7e]

For thin film OFETs, in which the structure is not as ordered as in single crystals, a hopping mechanism described

---

[a] Dr. M.-Y. Kuo, Dr. H.-Y. Chen, Prof. Dr. I. Chao
Institute of Chemistry, Academia Sinica
Taipei, 11529 (Taiwan)
Fax: (+886) 2-2783-1237
E-mail: ichao@chem.sinica.edu.tw

[b] Dr. H.-Y. Chen
Current address:
Faculty of Medicinal and Applied Chemistry
Kaohsiung Medical University
Kaohsiung, 807 (Taiwan)

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. The Supporting Information contains wave functions and Mulliken-type population analyses of LUMOs.

by Marcus theory[8] is believed to be involved in the charge-transport process at room temperature.[1b] According to Marcus theory, reducing the reorganization energy of the charge-transport process provides an additional possibility for pursuing semiconductors with large charge mobility. This may not be crucial for materials with poor intermolecular electronic coupling. However, for molecular frameworks already exhibiting sizeable electronic couplings, reducing the reorganization energy may turn them into high-performance OFET materials. In other words, to search for high-performance organic semiconductors that outperform current materials, it is desirable to design molecules with both the electronic coupling and the reorganization energy in mind. Currently, experimentalists address the former issue much more than the latter. Theoretical studies addressing the quest for small reorganization energy will clearly help to balance this disparity.

For complementary circuits, both *p*- and *n*-type organic semiconductors are necessary. In contrast to *p*-type organic semiconductors, *n*-type materials have been developed only in the last decade. The deficiency of *n*-type organic semiconductors is believed to be due to the high injection barrier of electrons and the intrinsic instability in air of organic radical anions, something which can be overcome by increasing the electron affinity (EA).[1b] Experimental and theoretical studies showed that functionalizing *p*-type semiconductors with electron-withdrawing groups is a promising way to convert them to *n*-type materials.[9,10] In 2004, Marks et al. demonstrated that electron-withdrawing imide substituents afford promising architectures for *n*-type naphthalene- and perylene-based semiconductors (e.g., NDI and PDI).[9f] Among these compounds, PDI-FCN$_2$ (see Figure 1) with core cyanation and *N*-fluoroalkylation exhibits excellent stability in air and a high electron mobility of 0.64 cm^{2}V^{-1}s^{-1} in air. Even without the *N*-fluoroalkyl group, PDI-CN$_2$ has also been found to be stable in air.[9f]

In the theoretical studies, Marks et al. showed with calculations that cyanation of oligothiophenes, oligopyrroles, and oligofurans can reduce internal reorganization energies for hole transfer (λ^+) compared to those of their parent compounds.[11] Other polar functional groups (−F, −OR, −CF$_3$, −NH$_2$) in the study did not provide this advantage. Unfortunately, λ^- was not discussed in the paper, so it is unclear whether cyanation is beneficial in terms of λ^-. On the other hand, our previous study demonstrated that perfluoropentacene (PF-PENT) and perfluorohexathiophene (PF-6T) have significantly larger λ^+ and λ^- values than those of PENT and hexathiophene (6T), respectively, due to the additional contribution of the C−F bond compression/stretching on oxidation and reduction.[10] It is fundamentally intriguing why CN-substitution has such a different impact on λ^+. With the comprehension of the origin of this unique tendency of CN, one may be able to design other chemical systems with the same behavior.

In this study, we investigate theoretically the effect of cyanation on the internal reorganization energy. As pentacene has shown good charge mobilities and is a widely studied organic semiconductor, we focus mainly on the effect of cyanation on this molecule. Both experimentally known and unknown cyanated pentacene derivatives are studied. Because cyanation will increase the electron affinity of a molecule,[12] we pay special attention to the calculated λ^- values, the ionization potentials (IP), and the electron affinities (EA) of these compounds. These last two properties are important

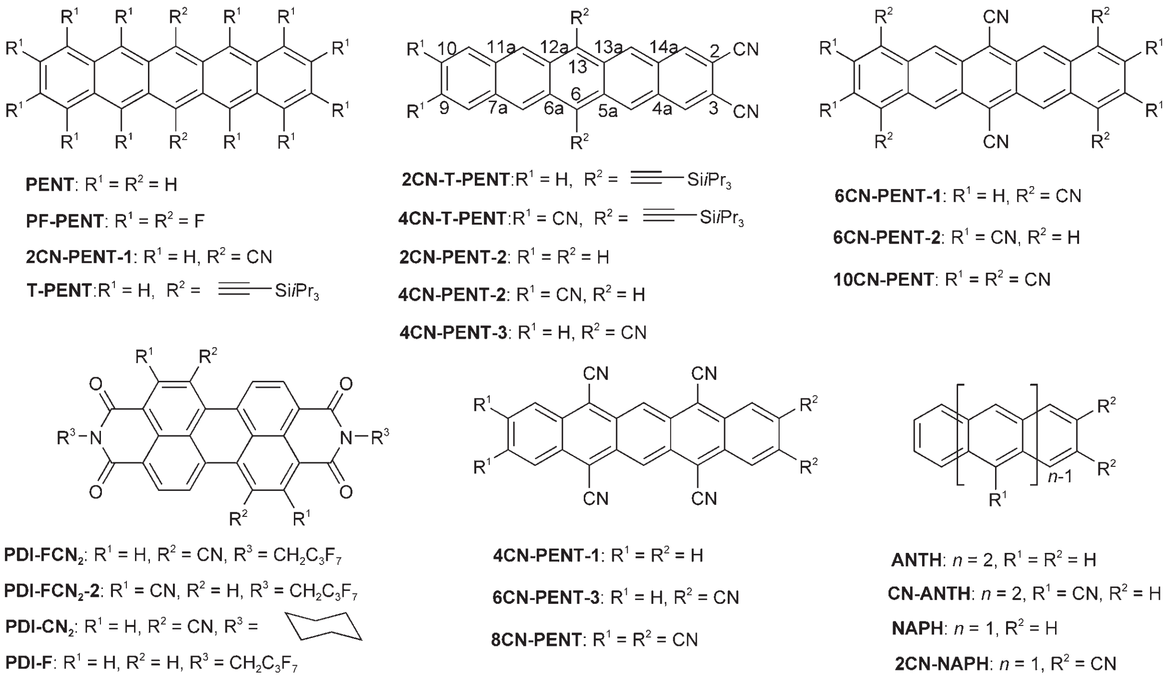

Figure 1. Chemical structures of the compounds investigated in this study and the atom labeling system.

because they are relevant to the stability, injection barrier, and polarity of the charge carrier. Besides the possibility of reducing the reorganization energy, cyanation is effective in promoting the π-stacking of oligothiophenes by CN···CN and CN···H interactions.[13] The crystal structures of cyanated oligoacenes are therefore searched and analyzed for their packing structures. For several molecules with known crystal structures, the electronic coupling between neighboring molecules is evaluated theoretically, and the charge mobility in this ideal situation estimated. The overall analysis reveals different facets of cyanation in terms of the molecular design of *n*-type organic semiconductors.

Results and Discussion

It is shown in Table 1 that the stronger electron-withdrawing group, CN, increases the EAs and IPs of PENT more effectively than F, as expected from their Hammett substituent constants.[14] The introduction of a few CN groups on PENT is enough to push the EA and IP values to be larger than those of PF-PENT, a known *n*-type OFET material. Therefore, many CN-substituted PENTs (*n*CN-PENT-*n*) studied herein may also be *n*-type materials. Among the *n*CN-PENT-*n* materials, 4CN-PENT-*n* and 6CN-PENT-*n* have EAs similar to those of PDI-CN_2 and PDI-FCN_2. As PDI-CN_2 and PDI-FCN_2 are known to be stable in air,[9f] it will be of interest to find out whether 4CN-PENT-*n* and 6CN-PENT-*n* also possess this stability. The calculated λ values of *n*CN-PENT-*n* (ca. 0.07–0.13 eV) are significantly smaller than those of PF-PENT (ca. 0.22 eV). In fact, the calculated λ^+ and λ^- values of *n*CN-PENT-*n* are mostly smaller than the corresponding values of the parent compound (PENT), as observed in the λ^+ values of the oligoheteroaromatic systems.[11] In particular, the small λ^+ values of *n*CN-PENT-*n* are impressive (0.069–0.093 eV at the B3LYP/6–31G** level). As 5,11-dichlorotetracene (calculated IP and λ^+ at the B3LYP/6–31G** level: 6.505 and 0.141 eV, respectively) could function as a *p*-type semiconductor,[7e] it is possible that 2CN-PENT-1, with an IP similar to that of dichlorotetracene, could also function as a *p*-type semiconductor in similar conditions, but with a significantly smaller λ^+. As for λ^-, 8CN-PENT and 10CN-PENT have λ^- values (0.095 and 0.087 eV, respectively) as small as λ^+ of PENT (0.094 eV). However, the EAs of 8CN-PENT and 10CN-PENT are larger than 4 eV at the B3LYP/6-31+G* level (this level has been shown to yield accurate EAs for polycyclic aromatic hydrocarbons)[15] and may impose an "air-dope" problem when these compounds are used to make devices.[1b] Comparing the λ^- values of *n*CN-PENT-*n* (0.087–0.135 eV) to that of PF-PENT (0.225 eV) by assuming the same extent of electronic coupling (t^-), it translates into a three- to sixfold increase of electron exchange rate (k_{et}) relative to that of PF-PENT.

Table 1. Internal reorganization energies (λ), adiabatic electron affinities (EA), and ionization potentials (IP) [all in eV] calculated at the B3LYP/6–31G** level. The adiabatic EAs calculated at the B3LYP/6-31+G* level are also given in parentheses.

Compound	λ^+	λ^-	EA	IP
PENT	0.094	0.133	1.136 (1.479)	5.899
PF-PENT	0.222	0.225	2.136	6.602
2CN-PENT-1	0.071	0.135	2.185	6.604
2CN-PENT-2	0.093	0.117	2.008	6.531
4CN-PENT-1	0.069	0.126	2.838 (3.181)	7.148
4CN-PENT-2	0.090	0.103	2.734 (3.050)	7.138
4CN-PENT-3	0.072	0.119	2.912 (3.250)	7.171
6CN-PENT-1	0.078	0.122	3.324 (3.662)	7.574
6CN-PENT-2	0.070	0.105	3.556 (3.888)	7.723
6CN-PENT-3	0.071	0.109	3.512 (3.846)	7.650
8CN-PENT	0.070	0.095	4.101 (4.431)	8.139
10CN-PENT	0.075	0.087	4.421 (4.743)	8.400
T-PENT	0.144	0.203	1.727	5.680
2CN-T-PENT	0.139	0.163	2.359	6.166
4CN-T-PENT	0.138	0.139	2.947	6.666
PDI-F	0.187	0.297	2.635	7.430
PDI-FCN_2	0.186	0.277	3.250 (3.655)	7.961
PDI-FCN_2-2	0.176	0.268	3.242	7.967
PDI-CN_2	0.171	0.260	2.958 (3.285)	7.637
NAPH	0.187	0.260	−0.129	7.608
2CN-NAPH	0.165	0.210	0.759	8.523
ANTH	0.140	0.200	0.124	6.816
CN-ANTH	0.120	0.202	0.876	7.252

We have shown previously that frontier orbitals are useful for understanding the trends of reorganization energies of PF-PENT and PENT.[10] In this study, we checked the spin-density distribution of radial cations and anions of 4CN-PENTs and again found that the HOMOs and LUMOs of the neutral 4CN-PENTs correspond to the spin-density distributions of the radical cations and anions, respectively. Therefore, frontier orbitals of the neutral states are analyzed in an attempt to understand why reorganization energies are reduced in the cyanated species (Figure 2). To present the frontier orbitals in a more quantitative fashion, a Mulliken-type population analysis of HOMOs and LUMOs of PENT and 4CN-PENTs was performed.[16] The values from the analysis show how one electron, residing in a specific orbital, is distributed among the atoms; a large value reflects a large wave function amplitude on an atom. It can be seen that the HOMO and LUMO of PENT are primarily localized on the C atoms at the horizontal edge tip of the molecule (Figure 2a). The carbon atoms connecting the heavily populated tips show relatively small populations. In particular, the central vertical pair of edge-tip carbon atoms can be described as nonbonding atoms[17] and result in smaller bond length variations on oxidation or reduction.[18] In the presence of the cyano groups, the populations on both the tip and bridging C atoms of 4CN-PENTs are smaller than those of PENT in most cases (Figure 2b and c). This phenomenon has the effect of diminishing the strengths of bonding and antibonding interactions. More intriguingly, electron delocalization on the cyano groups has a strong nonbonding character. Therefore, even though the CN groups have been added to the PENT core, they may not contribute significantly to the geometric distortion upon oxidation or reduction, and hence contribute little to λ. We believe it is the combined

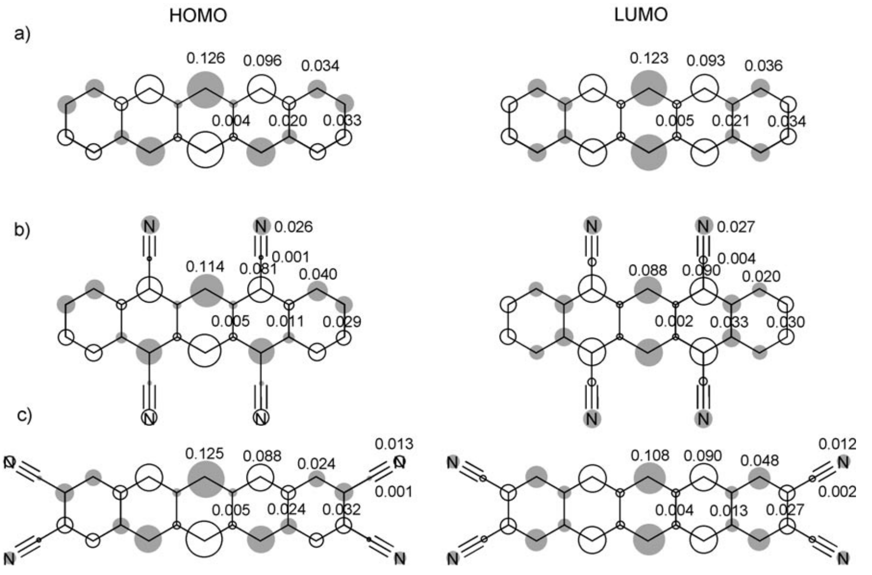

Figure 2. Molecular orbitals and Mulliken-type population analyses of HOMOs and LUMOs of a) PENT, b) 4CN-PENT-1, c) 4CN-PENT-2. The gray and white circles represent the positive and negative signs the of wave function, respectively.

effect of the reduced bonding/antibonding of the core structure and the nonbonding character of the CN groups in 4CN-PENTs that renders the λ values smaller than those of PENT.

To confirm this rationale based on frontier orbitals, the bond lengths of neutral, oxidized, and reduced forms of PENT and 4CN-PENT-1 were analyzed, see Figure 3. Upon oxidation, the changes in bond lengths compared to the neutral structure mainly occur in the C–C bonds of the core part, with average bond length differences of 0.0098 and 0.0082 Å for PENT and 4CN-PENT-1, respectively; for the C–C and C–N bonds involving the CN group of 4CN-PENT-1, the bond-length modifications are negligible (<0.001 Å). This is consistent with the fact that λ^+ of 4CN-PENT-1 (0.069 eV) is significantly smaller than that of PENT (0.094 eV). Upon reduction, the averaged bond-length modifications of the C–C bond in the cores of PENT and 4CN-PENT-1 are 0.0101 and 0.0095 Å, respectively; the bond-length modifications of substituted C–C and C–N bonds in 4CN-PENT-1 are 0.006 and 0.003 Å, respectively. Overall, the λ^- values of these two compounds are rather similar, with λ^- of 4CN-PENT-1 being smaller (see Table 1). For all 4CN-PENTs, the bond-length modifications of substituted C–C and C–N bonds induced by oxidation and reduction are in the range of 0.003–0.006 Å and 0.002–0.003 Å, respectively. For comparison, F substitution on PENT introduces additional C–F antibonding character in the HOMO and LUMO of PF-PENT; significantly, bond-length modifications of C–F bonds (0.010–0.018 Å) upon oxidation/reduction have been found and large λ values were observed.[10]

Conceivably, the nonbonding character of the cyano groups in the frontier orbitals shown in Figure 2b and c means that both bonding and antibonding orbitals of CN participate in the frontier orbitals, canceling out the population on the CN carbon atoms. This is confirmed by a computer-aided composition of atomic orbitals (CACAO)[19] calculation, shown in Figure 4. In this analysis based on the extended Hückel method, the antibonding and bonding orbitals of CN are both found to contribute to the molecular orbitals. However, the degrees of cancellation at the CN carbon atoms are less pronounced than in the DFT-calculated molecular orbitals (cf. mesh and solid orbitals shown in

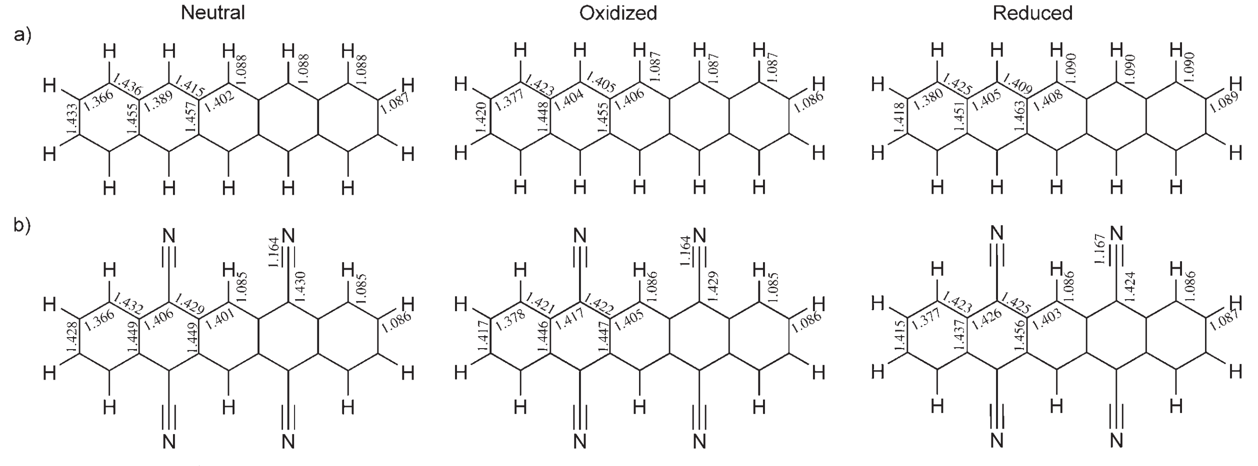

Figure 3. Bond lengths (in Å) of neutral, oxidized, and reduced forms of a) PENT, b) 4CN-PENT-1.

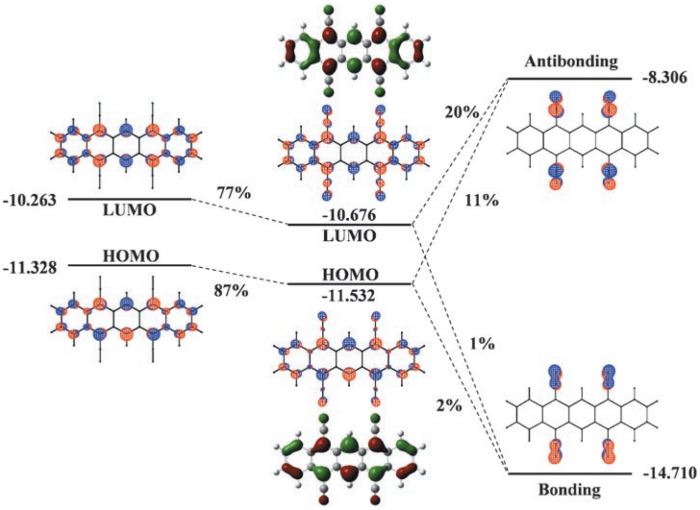

Figure 4. CACAO molecular orbital diagrams for 4CN-PENT-1 and the percentage of orbital contribution from the fragments (mesh). The DFT-optimized geometry was used for the CACAO analysis. Not all participating orbitals are shown. The DFT frontier orbitals are also shown for comparison (solid).

Figure 4). Nevertheless, the basic features of the Hückel- and DFT-calculated frontier orbitals are similar. For example, in the DFT orbitals, the cancellation is more complete in the HOMO than the LUMO (see population results in Figure 2b and c); the same trend is preserved in the Hückel molecular orbitals in that the low-lying CN bonding orbital participates in the LUMO with a smaller ratio (1:20) than in the HOMO (2:11; Figure 4). As a greater extent of electron delocalization leads to a smaller reorganization energy,[11] the nonbonding character of the cyano group provides an ideal way of extending electron delocalization.

Because the EAs of *n*CN-PENT-*n* are quite large and thus likely to be *n*-type semiconductors, we paid special attention to the λ^- values. It was found that λ^- of 4CN-PENT-2, with CN substituted at the terminal 2-, 3-, 9-, 10-positions, is further reduced by about 16–23 meV compared to those of other 4CN-PENTs. This is consistent with the observation that the total absolute bond-length variation between the neutral and reduced forms of 4CN-PENT-2 (0.256 Å) is smaller than that of 4CN-PENT-1 (0.296 Å). All of the other compounds with CN substitutions at these positions (i.e., 2CN-PENT-2, 6CN-PENT-2, 8CN-PENT and 10CN-PENT) have smaller λ^- values than their analogues with the same number of cyano groups. This phenomenon provides an empirical rule of thumb for the ideal functionalization positions in terms of λ^-. The reason for this phenomenon is not evident. However, one observation on the LUMO may be relevant. That is, after cyanation has taken place at the 2-, 3-, 9-, 10-positions, the wave function amplitudes of the nearby ring-fusing atoms (4a, 7a, 11a, 14a) decrease (cf. LUMOs in Figure 2a and c; see Figure 1 for atom numbering). In other words, upon reduction, the bond strengthening between 4a and 14a (and likewise between 7a and 11a) is smaller in 4CN-PENT-2 than in PENT. As the dislocation of ring-fusing atoms will affect two rings rather than one, it is possible that the smaller wave function amplitudes at the ring-fusing atoms may help to reduce the λ^-. In the present study, there are a total of four pairs of compounds (4CN-PENT-2 vs. PENT; 6CN-PENT-2 vs. 2CN-PENT-1; 8CN-PENT vs. 4CN-PENT-1; 10CN-PENT vs. 6CN-PENT-1) that provide the opportunity to check the effect of terminal cyanation on the closest ring-fusing atoms. All pairs show the same amplitude reduction effect and a smaller λ^- (by ca. 30 meV). On the other hand, when cyanation takes place at carbon atoms 6 and 13, the nearby ring-fusing atoms (5a, 6a, 12a, 13a) have increased amplitude. Therefore, it is not surprising to see that cyanation fails to reduce λ^- of 2CN-PENT-1 (0.135 eV) relative to PENT (0.133 eV), even though the cyano groups serve to extend the delocalization of the molecular orbital (see Supporting Information for the results of the Mulliken-type analysis on LUMOs of the compounds mentioned above). The same position effects are observed in the smaller systems; the terminally substituted 2CN-NAPH has a significantly smaller λ^- value (0.210 eV) than that of NAPH (0.260 eV), and the centrally substituted CN-ANTH (0.202 eV) has a similar λ^- value to that of ANTH (0.200 eV).

The crystal structures of CN-substituted compounds PDI-FCN$_2$, 2CN-T-PENT, and 4CN-T-PENT are known in the literature.[9f,g] Therefore, we checked whether cyanation brought about the same effect on λ in these three systems. As the CN groups in PDI-FCN$_2$ generate nonplanarity, and our previous study on 6T had shown that nonplanarity could increase λ values,[10] we also calculated λ for planar PDI-FCN$_2$-2. It is found that cyanation reduces the λ^+ and λ^- values from 0.187 and 0.297 eV for PDI-F to 0.176 and 0.268 eV for PDI-FCN$_2$-2, respectively. The λ^+ and λ^- values of PDI-FCN$_2$ are about 10 meV larger than those of PDI-FCN$_2$-2. Comparing 2CN-T-PENT and 4CN-T-PENT with T-PENT, cyanation also causes the λ values to drop, especially for λ^-. A decrease in λ^- of 0.064 eV is found for 4CN-T-PENT. As adding the triisopropylsilylethynyl groups to PENT increases λ (cf. λ values of PENT and T-PENT), the addition of the cyano groups counteracts this effect.

Besides λ, the electronic coupling (*t*), dictated largely by orbital overlap, is also a key parameter for high-performance OFET materials. The crystal structures of cyanated naphthalene (NAPH) and anthracene (ANTH) show that cyanation changes the molecular packing from a herringbone arrangement to π-stacking (see Figure 5).[20] In the case of 2CN-NAPH, the dipole–dipole interactions between the cyano groups overcome the CH$\cdots\pi$ interactions that dominate in the herringbone arrangement to form a π-stacked structure. The connection between the π-stacked columns is built on CN$\cdots$H interactions (Figure 5b). A similar situation is observed for CN-ANTH. Just one cyano substitution on ANTH is enough to cause a significant change in the molecular packing by local dipole–dipole interactions between the cyano groups. The $\pi\cdots\pi$ distances in these CN systems are within 3.55 Å, which is promising for significant intermolecular electronic coupling.

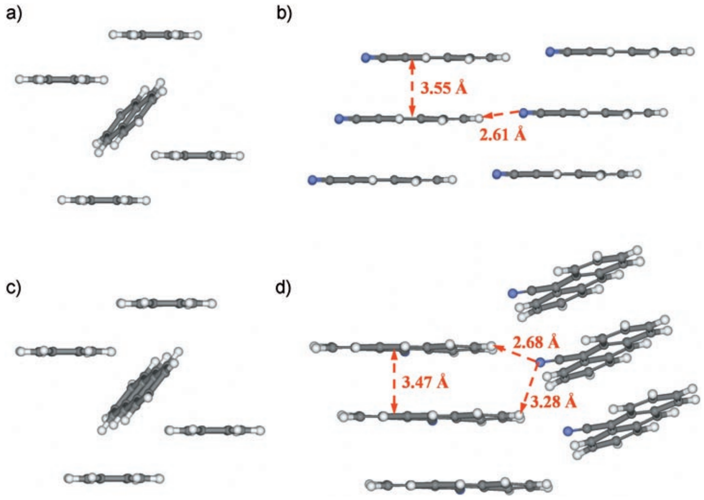

Figure 5. The influence of CN substitutions on molecular packing: a) NAPH viewed along the molecular axis, b) 2CN-NAPH viewed along the short axis of molecule, c) ANTH viewed along the molecular axis, d) CN-ANTH viewed along short axis of molecule. The dipole–dipole interaction between cyano groups promotes the change of the molecular packing from a herringbone arrangement to π-stacking.

Based on ADF calculations,[21] the electronic coupling of the LUMOs (t^-) between the CN-ANTH dimer taken from the crystal structure (83 meV) is larger than that for ANTH (46 meV). The difference in the electronic couplings of the HOMOs (t^+) is less pronounced (42 meV for CN-ANTH and 47 meV for ANTH). Troisi et al. have also shown that for functionalized PENTs with π-stacking it is easier to get greater couplings between LUMOs than HOMOs, because the nodal planes basically lie parallel to the short axis PENT for LUMOs, but parallel to both long and short axes for HOMOs.[7c] With nodal planes along both directions, it is easy to obtain ineffective coupling between the HOMOs. Therefore, functionalized PENTs with π-stacking and high enough EAs could be good candidates for *n*-type organic semiconductors. As the cyanated pentacene compounds in this study have larger mole fractions of the cyano group than that of CN-ANTH, we believe they are prone to form π-stacking structures. Furthermore, it has been shown in the literature that the incorporation of acceptor substitutions to the acenes would induce a strong molecular dipole moment. Strong molecular dipole–dipole interactions between neighboring molecules have also been shown to have a π-steering effect on the molecular packing. One example is the cofacially stacked 2,3-dimethyl-1,4-pentacene-quinone, in which an electron-rich acene portion stacks over an electron-poor quinone portion with a spacing (3.25 Å) smaller than the π···π distance in graphite by approximately 0.1 Å.[22] The dipole moment of 2,3-dimethyl-1,4-pentacene-quinone is 3.133 Debye, calculated by B3LYP/6–31G**. On the other hand, the asymmetrically cyanated 4CN-PENT-3 (10.560 Debye) and 6CN-PENT-3 (9.895 Debye) have dipole moments three to four times greater than that of 2,3-dimethyl-1,4-pentacene-quinone. The large molecular dipole moment and local cyano–cyano interaction should both promote π-stacking.

Based on a hopping mechanism for charge transport, Table 2 shows the calculated electronic couplings and electron mobility values of three CN systems with known crystal structures: PDI-FCN$_2$, 2CN-T-PENT, and 4CN-T-PENT.[9f–g] To our knowledge, PDI-FCN$_2$ is the *n*-type organic semiconductor with the highest electron mobility in air (0.64 cm^{2}V^{-1}s^{-1}).[9f] Compounds 2CN-T-PENT and 4CN-T-PENT, substituted by two/four cyano and two triisopropylsilylethynyl groups, have higher EAs than PF-PENT (Table 1) and can also be *n*-type organic semiconductors, but their electron mobilities have not been measured. Figure 6 shows several different types of dimers in the PDI-FCN$_2$, 2CN-T-PENT, and 4CN-T-PENT crystal structures, respectively.

Table 2. Center of mass distances (R_{CM}), electronic couplings (t^-) of LUMOs, and electron mobilities (μ^-) of different dimer type neighbors in PDI-FCN2, 2CN-T-PENT, and 4CN-T-PENT. Mobilities calculated based on π···π distances, rather than R_{CM}, are shown in parentheses.

Compound	Dimer	R_{CM} [Å]	t^- [meV]	t^- [meV][a]	μ^- [cm^{2}V^{-1}s^{-1}]	μ^- [cm^{2}V^{-1}s^{-1}][a]
PDI-FCN$_2$	D1	5.23	92	132	0.97 (0.41)	2.01 (0.85)
	D2	8.09	68	66	1.26 (0.20)	1.21 (0.19)
2CN-T-PENT	D1	6.45	168	136	19.30 (5.40)	12.73 (3.30)
	D2	9.71	142	141	31.58 (3.98)	31.00 (3.93)
	D3	9.04	58	82	4.61 (0.59)	9.09 (1.18)
4CN-T-PENT	D1	7.36	161	170	31.46 (6.79)	35.29 (7.57)

[a] The electronic couplings from half of the molecular orbitals splitting using intermediate neglect of differential overlap (INDO) calculation.

There are two types of dimers in the PDI-FCN$_2$ system: dimer 1 (D1) and dimer 2 (D2), with centers of mass separated by R_{CM} of 5.23 and 8.09 Å, respectively. The electronic couplings (t^-) of the LUMOs in D1 and D2 are 92 and 68 meV, respectively, calculated by ADF. The corresponding electron-mobility values of D1 and D2 are 0.97 and 1.26 cm^{2}V^{-1}s^{-1}, respectively. These values are of the same order as the experimental value of 0.64 cm^{2}V^{-1}s^{-1} measured for the thin film. There are three types of dimers in the 2CN-T-PENT crystal: D1, D2, and D3, with electron-mobility values of 19.30, 31.58, and 4.61 cm^{2}V^{-1}s^{-1}, respectively. For 4CN-T-PENT, the calculated electron mobilities are 31.46 cm^{2}V^{-1}s^{-1}. These values are larger than the 1.26 cm^{2}V^{-1}s^{-1} for PDI-FCN$_2$ and await experimental confirmation. The relatively smaller electron mobility of PDI-FCN$_2$ is due to the large reorganization energy (λ^- = 277 meV) and small electronic coupling caused by large lateral (short-axis) slip of 2.15 Å (Figure 6a). We also calculated t^- from the molecular orbital splitting derived from an intermediate neglect of differential overlap (INDO) calcula-

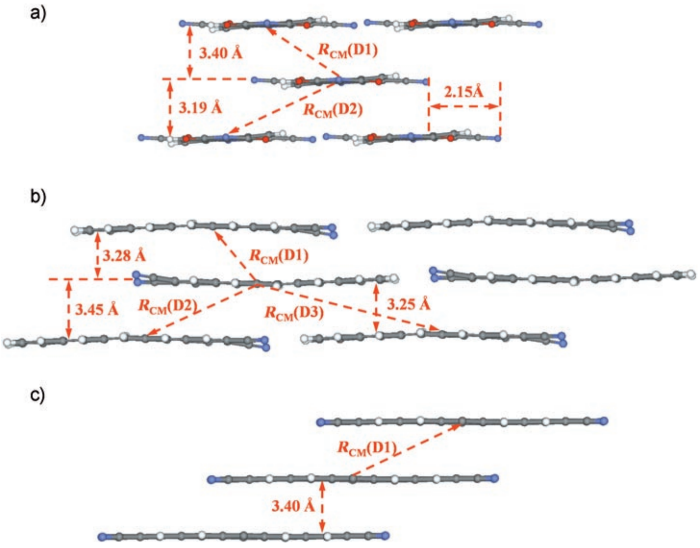

Figure 6. Dimer type neighbors in crystals: a) PDI-FCN_2 viewed along the long axis of the molecule, b) 2CN-T-PENT viewed along the short axis of the molecule, c) 4CN-T-PENT viewed along the short axis of the molecule. Fluoropropyl and triisopropylsilyl groups are deleted for clarity.

tion. The resultant μ^- again showed that *n*CN-T-PENT compounds should be better electron-transport materials than PDI-FCN_2 (Table 2). When the π···π distances are used to replace R_{CM} in the calculation of mobility, no conclusion is changed (Table 2). Even if the hopping mechanism cannot fully describe these systems, the large t^- values of the *n*CN-T-PENT materials will make them very competitive in terms of a band-like motion for charge transport, and they still warrant experimental investigation.

In real thin-film OFET devices, molecules cannot be so perfectly packed as in the crystal structure. Optimization of fabrication processes generally makes a difference in device performance. Before going through the time-consuming tests for device optimization, it is desirable to first identify promising molecules. We feel that if molecules are intrinsically superior for charge transport, calculations based on ordered structures may be a worthwhile reference for screening molecules of good potential. To test this notion, we calculated the mobilities of rubrene, PENT, tetracene, PF-PENT, and hexathiophene, based on their crystal structures.[5,9b,23] Even though the assumption is crude, the calculated results are in reasonable agreement with currently available experimental values.[9b,24] This result reflects that calculations may serve the purpose of screening molecules. It may also imply that the external reorganization energy does not play an essential role in the cases we studied. In a similar treatment based on the hopping mechanism, Zhu et al. reproduced the mobility trend observed for aryl amines.[25] As the calculated mobilities of *n*CN-T-PENT are one order of magnitude larger than that of PDI-FCN_2, *n*CN-T-PENT materials should certainly be examined experimentally.

Conclusion

In this study, we have proven that cyanation has a favorable impact on the internal reorganization energy of several commonly employed molecular frameworks for organic semiconductors. A rationale based on molecular-orbital arguments is provided: cyanation extends electron delocalization in a nonbonding fashion. Fluorination also extends electron delocalization, but in an antibonding fashion. Therefore, fluorination results in increased reorganization energies. For the pentacene framework, we have found the 2-, 3-, 9-, and 10-terminal substitution positions are superior for reducing λ^-. Evidence of the advantages of cyanation on molecular packing and electronic coupling is provided by small cyanated acene compounds. For high performance *n*-type OFETs, high EAs, large t^- values, and small λ^- values are necessary. Cyanation may help in all three aspects. Therefore, cyanation bears multiple functions in terms of the molecular design of *n*-type organic semiconductors. For molecule-based organic semiconductors, high mobility and good stability are intensively sought-after goals. With a fundamental understanding of the impacts of cyanation on different aspects, we provide the possibility for the design of superior functional materials. The predicted good stability of several *n*CN-PENT-*n* compounds and the high mobility of *n*CN-T-PENT await experimental exploration. As the internal reorganization energy is a fundamental property of molecules, the insights gained from this study will benefit the design of other systems in which electron or hole transfer is of importance.

Computational Methods

At very low temperature, the charge carriers are delocalized in the materials and the charge transport is a coherent band-like motion. In this case, the charge mobility was determined by the bandwidths of the valence (hole-transport) and conduction (electron-transport) bands.[6] At higher temperatures (and probably at room temperature), the charge carriers are localized, due to the interaction with molecular vibrations. In this situation, the charge transport becomes a sequential electron hopping-process between neighboring molecules that can be described by Marcus electron-transfer theory.[6,26] According to Marcus theory,[8] the rate of the electron self-exchange process is expressed as shown in Equation (1).

$$k_{\mathrm{et}} = \frac{4\pi^2}{h}\frac{1}{\sqrt{4\pi\lambda k_{\mathrm{B}}T}}t^2\exp\left(-\frac{\lambda}{4k_{\mathrm{B}}T}\right) \tag{1}$$

The rate of this process governed by two key parameters: the reorganization energy (λ) due to geometric relaxation accompanying charge transfer, and the electronic coupling (t) between the two molecules, dictated largely by orbital overlap. The geometry optimization, frequency, and reorganization energy were calculated at the density functional theory (DFT) level using the B3LYP functional with 6–31G** basis sets; this method has been employed widely for calculating reorganization energies of charge-transport processes.[27] All λ values were calculated by the Gaussian 03 program without considering the external reorganization energy.[28] The calculated expectation values of the spin operator $\langle S^2\rangle$ for the open-shell ionic states are in the range of 0.7610–0.7705 at the

UB3LYP/6-31G** level, deviating only slightly from the exact value of 0.75 for doublet electronic states.

For EA calculations, both B3LYP/6-31G** and B3LYP/6-31+G* levels have been used. It has been shown that the latter level, although without correction of the zero-point energy, can reproduce experimental EAs of polycyclic aromatic hydrocarbons of different systems.[15] We calculated the EAs of 9-cyanoanthracene (CN-ANTH), 2-cyanonaphthalene, 1-trifluoromethylbenzonitrile at this level (1.283, 0.626, and 0.701 eV, respectively) and also found the values correspond to the experimental values very well (1.271, 0.649, and 0.672 eV, respectively).

The electronic coupling (t) can be calculated directly from the spatial overlap (S_{RP}), charge transfer integrals (H_{RP}), and site energies (H_{RR}, H_{PP}). The electronic coupling, t, is given by Equation (2).

$$t = \frac{H_{RP} - S_{RP}(H_{RR} + H_{PP})/2}{1 - S_{RP}{}^{2}} \qquad (2)$$

All electronic couplings were performed using the Amsterdam density functional (ADF) theory program,[21] which has been used successfully for calculating electronic coupling.[29] The DZP basis set in ADF was used and the local density functional VWN[30] was employed in conjunction with the PW91 gradient corrections.[31]

Once the electron transfer rate k_{et} was obtained according to Equation (1), the diffusion coefficient D of charge carriers was estimated by Equation (3), in which L is the effective length of electron transfer.

$$D = L^2 k_{et}/2 \qquad (3)$$

The parameter L can be approximated by the center of mass distance (R_{CM}) in a dimer. This allows us to evaluate the drift mobility of charge from the Einstein relation,[32] as given in Equation (4), in which e is the electronic charge.

$$\mu = eD/k_B T \qquad (4)$$

This method has been employed for the calculation of the charge carrier mobility in π-stacked organic semiconductors.[27f,33]

Acknowledgements

We thank the Academia Sinica for financial support and the National Center for High-performance Computing and the Computing Center of Academia Sinica for providing computational resources.

---

[1] a) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.* **2002**, *14*, 99; b) C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J. L. Brédas, P. C. Ewbank, K. R. Mann, *Chem. Mater.* **2004**, *16*, 4436; it is mentioned in this review that with EA much greater than 4 eV, a material may have an air-dope problem; c) A. Tsumura, H. Koezuka, T. Ando, *Appl. Phys. Lett.* **1986**, *49*, 1210.

[2] a) C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913; b) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. dos Santos, J. L. Brédas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121; c) M. A. Baldo, M. E. Thompson, S. R. Forrest, *Nature* **2000**, *403*, 750.

[3] a) X. C. Li, H. Sirringhaus, F. Garnier, A. B. Holmes, S. C. Moratti, N. Feeder, W. Clegg, S. J. Teat, R. H. Friend, *J. Am. Chem. Soc.* **1998**, *120*, 2206; b) F. Garnier, G. Horowitz, D. Fichou, D. Yassar, *Synth. Met.* **1996**, *81*, 163; c) C. D. Dimitrakopoulos, B. K. Furman, T. Graham, S. Hegde, S. Purushothaman, *Synth. Met.* **1998**, *92*, 47; d) J. G. Laquindanum, H. E. Katz, A. J. Lovinger, A. Dodabalapur, *Adv. Mater.* **1997**, *9*, 36; e) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielson, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685.

[4] a) C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, J. M. Shaw, *Science* **1999**, *283*, 822; b) C. D. Dimitrakopoulos, J. Kymissis, S. Purushothaman, D. A. Neumayer, P. R. Duncombe, R. B. Laibowitz, *Adv. Mater.* **1999**, *11*, 1372.

[5] D. Holmes, S. Kumaraswamy, A. J. Matzger, K. P. C. Vollhardt, *Chem. Eur. J.* **1999**, *5*, 3399.

[6] a) J. Cornil, D. Beljonne, J. P. Calbert, J. L. Brédas, *Adv. Mater.* **2001**, *13*, 1053; b) J. Cornil, J. P. Calbert, J. L. Brédas, *J. Am. Chem. Soc.* **2001**, *123*, 1250; c) J. L. Brédas, J. Cornil, D. A. da Silva Filho, J. Cornil, *Proc. Natl. Acad. Sci. USA* **2002**, *99*, 5804.

[7] a) J. E. Anthony, D. L. Eaton, S. R. Parkin, *Org. Lett.* **2002**, *4*, 15; b) M. M. Payne, S. R. Parkin, J. E. Anthony, C. C. Kuo, T. N. Jackson, *J. Am. Chem. Soc.* **2005**, *127*, 4986; c) A. Troisi, G. Orlandi, J. E. Anthony, *Chem. Mater.* **2005**, *17*, 5024; d) Z. Chen, P. Müller, T. M. Swager, *Org. Lett.* **2006**, *8*, 273; e) H. Moon, R. Zies, E. J. Borkent, C. Besnard, A. J. Lovinger, T. Siegrist, C. Kloc, Z. Bao, *J. Am. Chem. Soc.* **2004**, *126*, 15322.

[8] R. A. Marcus, *Rev. Mod. Phys.* **1993**, *65*, 599.

[9] a) S. B. Heidenhain, Y. Sakamoto, T. Suzuki, A. Miura, H. Fujikawa, T. Mori, S. Tokito, Y. Taga, *J. Am. Chem. Soc.* **2000**, *122*, 10240; b) Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato, S. Tokito, *J. Am. Chem. Soc.* **2004**, *126*, 8138; c) Y. Sakamoto, S. Komatsu, T. Suzuki, *J. Am. Chem. Soc.* **2001**, *123*, 4643; d) A. Facchetti, M. Mushrush, H. E. Katz, T. J. Marks, *Adv. Mater.* **2003**, *15*, 33; e) A. Facchetti, M. H. Yoon, C. L. Stern, H. E. Katz, T. J. Marks, *Angew. Chem.* **2003**, *115*, 4030; *Angew. Chem. Int. Ed.* **2003**, *42*, 3900; f) B. A. Jones, M. J. Ahrens, M. H. Yoon, A. Facchetti, T. J. Marks, M. R. Wasielewski, *Angew. Chem.* **2004**, *116*, 6523; *Angew. Chem. Int. Ed.* **2004**, *43*, 6363; g) C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer, G. G. Malliaras, *Org. Lett.* **2005**, *7*, 3163.

[10] H. Y. Chen, I. Chao, *Chem. Phys. Lett.* **2005**, *401*, 539.

[11] G. R. Hutchison, M. A. Ratner, T. J. Marks, *J. Am. Chem. Soc.* **2005**, *127*, 2339.

[12] X. Zhang, Q. Li, J. B. Ingels, A. C. Simmonett, S. E. Wheeler, Y. Xie, R. B. King, H. F. Schaefer III, *Chem. Commun.* **2006**, 758.

[13] T. M. Barclay, A. W. Cordes, C. D. Mackinnon, R. T. Oakley, R. W. Reed, *Chem. Mater.* **1997**, *9*, 981.

[14] J. Bromilow, R. T. C. Brownlee, V. O. Lopez, R. W. Taft, *J. Org. Chem.* **1979**, *44*, 4766.

[15] a) C. E. H. Dessent, *Chem. Phys. Lett.* **2000**, *330*, 180; b) G. Malloci, G. Mulas, G. Cappellini, V. Fiorentini, I. Porceddu, *Astron. Astrophys.* **2005**, *432*, 585; c) A. Modelli, L. Mussoni, D. Fabbri, *J. Phys. Chem. A* **2006**, *110*, 6482.

[16] The Mulliken-type population analysis of HOMOs and LUMOs was carried out without multiplying by two for the number of electrons per orbital. The same procedure was used in reference [10].

[17] T. Kato, T. Yamabe, *J. Chem. Phys.* **2004**, *120*, 3311.

[18] a) T. Kato, T. Yamabe, *J. Phys. Chem. A* **2004**, *108*, 11223; b) H. Y. Chen, I. Chao, *ChemPhysChem* **2006**, *7*, 2003.

[19] C. Mealli, D. M. Proserpio, *J. Chem. Educ.* **1990**, *67*, 399.

[20] a) M. Colapietro, A. Domenicano, G. Portalone, G. Schultz, I. Hargittai, *J. Mol. Struct.* **1984**, *112*, 41; b) J. Janczak, R. Kubiak, *J. Mol. Struct.* **2000**, *516*, 81; c) H. Rabaud, J. Clastre, *Acta Crystallogr.* **1959**, *12*, 911.

[21] G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. Fonseca Guerra, S. J. A. van Gisbergen, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931.

[22] Q. Miao, M. Lefenfeld, T. Q. Nguyen, T. Siegrist C. Kloc, C. Nuckolls, *Adv. Mater.* **2005**, *17*, 407.

[23] a) I. Bulgarovskaya, V. Vozzhennikov, S. Aleksandrov, V. Belsky, *Latv. PSR Zinat. Akad. Vestis, Khim. Ser.* **1983**, 53; b) C. C. Matheus, A. B. Dros, J. Baas, A. Meetsma, J. L. de Boer, T. T. M. Palstra, *Acta Crystallogr. Sect. C* **2001**, *57*, 939; c) T. Siegrist, R. M.

Fleming, R. C. Haddon, R. A. Laudise, A. J. Lovinger, H. E. Katz, P. Bridenbaugh, D. D. Davis, *J. Mater. Res.* **1995**, *10*, 2170.

[24] The calculated charge mobilities based on R_{CM} are in the order of rubrene ($\mu^+ = 6.95\,cm^2V^{-1}s^{-1}$) > PENT ($\mu^+ = 5.43\,cm^2V^{-1}s^{-1}$) > tetracene ($\mu^+ = 3.39\,cm^2V^{-1}s^{-1}$) > PF-PENT ($\mu^- = 0.93\,cm^2V^{-1}s^{-1}$) > hexathiophene ($\mu^+ = 0.19\,cm^2V^{-1}s^{-1}$), which is consistent with the experimental trends (rubrene ($\mu^+ = 15.3\,cm^2V^{-1}s^{-1}$), PENT ($\mu^+ = 3.0\,cm^2V^{-1}s^{-1}$), tetracene ($\mu^+ = 1.3\,cm^2V^{-1}s^{-1}$), PF-PENT ($\mu^- = 0.22\,cm^2V^{-1}s^{-1}$), hexathiophene ($\mu^+ = 0.03\,cm^2V^{-1}s^{-1}$)). Only the best mobility calculated from all dimer pairs is reported. a) V. C. Sundar, J. Zaumseil, V. Podzorov, E. Menard, R. L. Willett, T. Someya, M. E. Gershenson, J. A. Rogers, *Science* **2004**, *303*, 1644; b) H. Klauk, M. Halik, U. Zschieschang, G. Schmid, W. Radlik, W. Weber, *J. Appl. Phys.* **2002**, *92*, 5259; c) C. Goldmann, S. Haas, C. Kreliner, K. P. Pernstich, D. J. Gundlach, B. Batlogg, *J. Appl. Phys.* **2004**, *96*, 2080; d) L. Torsi, A. Dodabalapur, L. J. Rothberg, A. W. P. Fung, H. E. Katz, *Science* **1996**, *272*, 1462.

[25] Y. Song, C. Di, X. Yang, S. Li, W. Xu, Y. Liu, L. Yang, Z. Shuai, D. Zhang, D. Zhu, *J. Am. Chem. Soc.* **2006**, *128*, 15 940.

[26] a) M. Mas-Torrent, P. Hadley, S. T. Bromley, X. Ribas, J. Tarrés, M. Mas, E. Molins, J. Veciana, C. Rovira, *J. Am. Chem. Soc.* **2004**, *126*, 8546; b) S. T. Bromley, M. Mas-Torrent, P. Hadley, C. Rovira, *J. Am. Chem. Soc.* **2004**, *126*, 6544.

[27] a) K. Sakanoue, M. Motoda, M. Sugimoto, S. Sakaki, *J. Phys. Chem. A* **1999**, *103*, 5551; b) M. Malagoli, J. L. Brédas, *Chem. Phys. Lett.* **2000**, *327*, 13; c) B. C. Lin, C. P. Cheng, Z. P. M. Lao, *J. Phys. Chem. A* **2003**, *107*, 5241; d) N. E. Gruhn, D. A. da Silva Filho, T. G. Bill, M. Malagoli, V. Coropceanu, A. Kahn, J. L. Brédas, *J. Am. Chem. Soc.* **2002**, *124*, 7918; e) V. Coropceanu, M. Malagoli, D. A. da Silva Filho, N. E. Gruhn, T. G. Bill, J. L. Brédas, *Phys. Rev. Lett.* **2002**, *89*, 275 503; f) V. Lemaur, D. A. da Silva Filho, V. Coropceanu, M. Lehmann, Y. Geerts, J. Piris, M. G. Debije, A. M. van de Graats, K. Senthilkumar, L. D. A. Siebbeles, J. M. Warman, J. L. Brédas, J. Cornil, *J. Am. Chem. Soc.* **2004**, *126*, 3271; g) O. Kwon, V. Coropceanu, N. E. Gruhn, J. C. Durivage, J. G. Laquindanum, H. E. Katz, J. Cornil, J. L. Brédas, *J. Chem. Phys.* **2004**, *120*, 8186.

[28] Gaussian 03, Revision B.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**..

[29] a) K. Senthilkumar, F. C. Grozema, F. M. Bickelhaupt, L. D. A. Siebbeles, *J. Chem. Phys.* **2003**, *119*, 9809; b) P. Prins, K. Senthilkumar, F. C. Grozema, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, L. D. A. Siebbeles, *J. Phys. Chem. B* **2005**, *109*, 18 267.

[30] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200.

[31] J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13 244.

[32] P. W. Atkins, *Physical Chemistry*, 4th ed., Oxford University Press, Oxford **1990**.

[33] J. Cornil, V. Lemaur, J. P. Calbert, J. L. Brédas, *Adv. Mater.* **2002**, *14*, 726.

Received: December 15, 2006