ARTICLES

Theoretical Study on the Correlation between Band Gap, Bandwidth, and Oscillator Strength in Fluorene-Based Donor−Acceptor Conjugated Copolymers

Ying-Chieh Hung,[†] Jyh-Chiang Jiang,[‡] Chi-Yang Chao,[§] Wei-Fang Su,[§] and Shiang-Tai Lin*,[†]

Department of Chemical Engineering, Department of Material Science and Engineering, National Taiwan University, Taipei, Taiwan, and Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

There is a growing interest in developing low-band gap conjugated polymers via synthesis of copolymers containing alternating units of different π-electron-donating/accepting capabilities. In this study, electronic and optical properties of conjugated copolymers containing fluorene and thiophene/cyclopentadithiophene derivatives are determined using density function theory and semiempirical ZINDO calculations. A remarkable linear correlation is found between the amount of charge transfer between the donor−acceptor pair, the band gap, the bandwidth, and the oscillator strength of $S_0 \rightarrow S_1$ electronic transition (ground state to first excited state) of the copolymers. Strong π-electron withdrawing substituents, such as dicyanoethenyl and carbonyl groups, on the thiophene moiety effectively reduce the band gap of the copolymers. However, the reduction of band gap is frequently accompanied by a linear reduction in bandwidths and in the oscillator strength of $S_0 \rightarrow S_1$ transition. For very strong π-electron withdrawing thiophene derivatives, the occurrence of maximum oscillator strength may even shift from $S_0 \rightarrow S_1$ to $S_0 \rightarrow S_{n>1}$ (ground state to a higher excited state), giving a blue shift in maxima absorption peak and a red shoulder in the UV−vis spectra as reported in recent experimental measurements. Therefore, the achievement of low band gap for conjugated polymers with alternating arrangement of π-electron-donating/accepting moieties may be achieved at a cost of lowering electron mobility and optical efficiency and sometimes a blue-shift in the major optical (UV−vis) absorption.

1. Introduction

Conjugated polymers have attracted great interests for their uses in photovoltaic cells, organic light-emitting diodes and semiconductor layers in field effect transistors.[1−9] Compared to silicon-based photovoltaic cells, organic photovoltaic cells have the merits of plastics, such as, flexibility, simple and low cost fabrication, and so forth. Low band gap conjugated polymers have been a very vigorous research field for their capability of harvesting more photons with long wavelengths so that the power conversion efficiency of the corresponding polymer solar cells could be improved. However, Scharber et al.[10] showed that in order to reach a 10% energy-conversion efficiency in bulk heterojunction solar cells with [6,6]-phenyl-C61-butyric acid methyl ester as electron acceptor, the photo-active material should have a lowest unoccupied molecular orbital (LUMO) no more than −3.9 eV and a band gap (Eg) around 1.5 eV (1.2∼1.8 eV). Near-zero band gap materials would in fact result in a lower energy-conversion efficiency[10] due to the reduction in open circuit voltage. It is therefore desirable to understand whether conjugated polymers could achieve the targeted LUMO and Eg to maximize the efficiency of photovoltaic devices.

Recently, thiophene-based conjugated polymers have received a great deal of attention because of the possibility to make synthetic materials with a very low band gap.[11−13] In addition, it may be possible to tune and optimize the desired electronic and optical properties of such polymers by selection of proper functional groups attached to the main chain. Nevertheless, many of the thiophene-based low band gap conjugated polymers exhibited poor solubility in common organic solvents so that further device fabrication and device performance were severely limited. In order to enhance the solubility of the low band gap polymers, fluorene units with long alkyl side chains have been incorporated into the polymer backbone. It is been reported that the fluorene-thiophene-based copolymers had relatively high quantum yield[14] and decent charge carrier mobility,[15] which enable them to serve as the photoactive material in photovoltaic devices.[10,16,17]

In addition to the improvement in solubility, the fluorene-thiophene-based copolymers resemble conjugated copolymers with alternating electron-donating and accepting units. The D−A molecular structure in the polymer backbone is well recognized as an effective approach to reduce the band gap.[18] The charge transfer between electron-donor and electron-acceptor leads to a mesomerism (D−A ↔ D$^+$=A$^−$) so that double-bond character between the units is increased. Generally, to achieve a small band gap, the highest occupied molecular orbital (HOMO) levels of strong donors and the LUMO levels of strong acceptors need to be very close.[19] Conjugated polymers synthesized by a weak

* To whom correspondence should be addressed: E-mail stlin@ntu.edu.tw.
† Department of Chemical Engineering, National Taiwan University.
‡ National Taiwan University of Science and Technology.
§ Department of Material Science and Engineering, National Taiwan University.

donor and acceptor might not show the small band gap as anticipated.[20]

Theoretical studies provide insights into these conjugated polymers and have been making a great contribution to support experimental results.[21−23] Comparing experimental results and theoretical studies indicates that some density functional theory calculations (DFT) consistently underestimate band gaps.[24,25] Nonetheless, Feng et al. successfully used DFT method with Gaussian-type orbital to calculate theoretical band gaps and obtained good agreement with experimental results for several fluorene-based copolymers.[26−28] Salzner et al.[29,30] designed several donor−acceptor copolymer systems theoretically. By analyzing energy level of molecular orbital, they concluded that donor−acceptor copolymers do not always result in low band gaps and wide bandwidth. Tachibana et al.[31] investigated very small band gap homopolymers of [1,2,5]thiadiazolo[3,4-b]thieno[3,4-e]pyrazine, which has previously been predicted to have a small band gap of 0.1 eV.

In this study, electronic and optical properties of conjugated copolymers comprised of alternating fluorene and thiophene/cyclopentadithiophene derivatives were investigated theoretically by using DFT and ZINDO calculations. By changing different functional groups on thiophene and cyclopentadithiophene, we further discuss substituent effect on fluorene-based copolymers and donor−acceptor concept on band gaps engineering in molecular design of low band gap conjugated polymers. By analyzing fifteen fluorene-thiophene derivatives copolymers we find that the band gap, the bandwidth, and the oscillator strength of $S_0 \rightarrow S_1$ electronic transition (ground state to first excited state) of the copolymer correlate almost linearly with the amount of charge transfer between the donor−acceptor moieties. The results presented here can serve as a useful guide to estimate the optoelectronic properties of donor−acceptor alternating copolymers.

2. Computational Details

All theoretical calculations in this study are carried out using quantum mechanical package Gaussian 03.[32] Equilibrium structure for each fluorene-based copolymer is determined using DFT with the B3LYP functional and the 6-31G* basis set. It has been shown that B3LYP/6-31G* gives decent ground state structures of conjugated polymers.[33] The equilibrium geometry is ensured to be in a minimal energy state by checking the energy second derivatives (NIMAG = 0). All such calculations were done for monomer $((F\text{-}X)_1)$ to tetramer $((F\text{-}X)_4)$ of alternating fluorene and thiophene/cyclopentadithiophene derivatives. Properties including HOMO/LUMO energies, vertical ionization potentials (IP)/electron affinities (EA), and band gap are derived through single point energy calculations performed at B3LYP/6-31+G* level and are compared with experimental results when available.[34] Note that the IP (and EA) is determined from difference in the ground-state energy of the neutral and ionized molecule using the geometry of the neutral molecule.[27] Optical transition properties such as the oscillator strength and electronic transition energy were obtained from semiempirical ZINDO[35] calculations and only singlet states were considered in our calculations. The properties of a polymer $((F\text{-}X)_\infty)$ were determined by linear extrapolation of the property of corresponding oligomers $((F\text{-}X)_1$ to $(F\text{-}X)_4)$, that is, each property was plotted against the inverse of the total number of rings on the backbone and the intercept at origin (finite number of rings) represents the property of a polymer with a degree of polymerization of infinity.
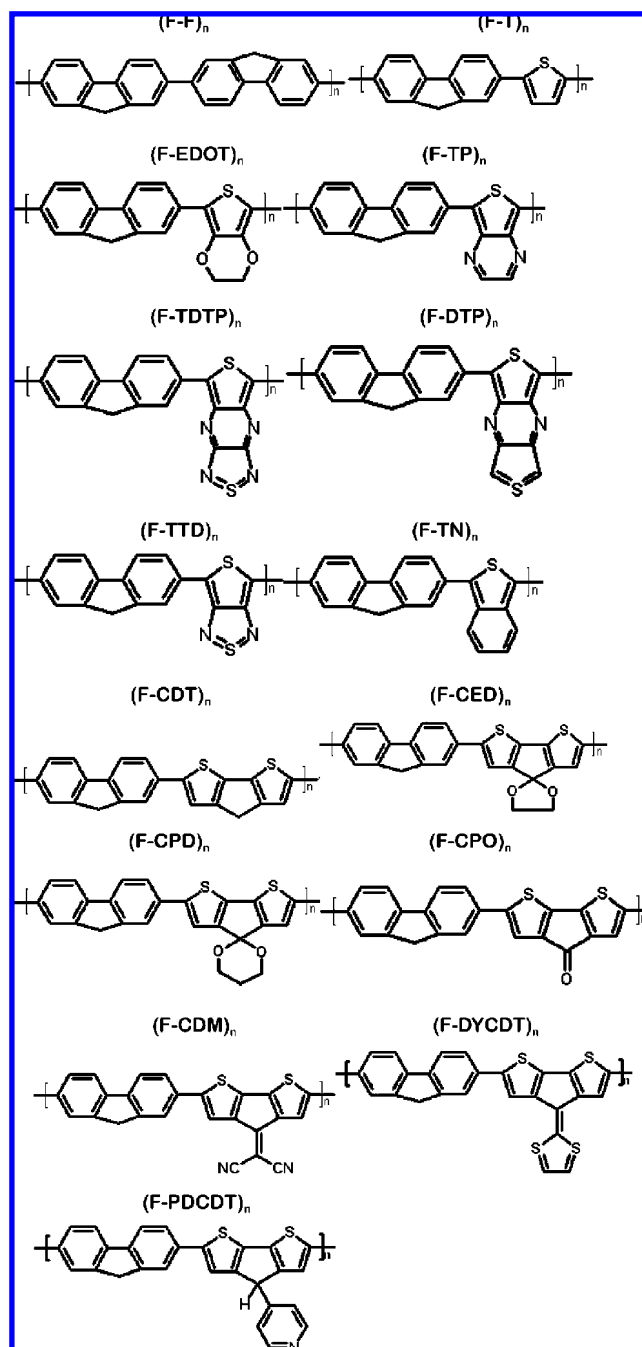

Figure 1. Sketch of chemical structures of fluorene-thiophene/cyclopentadithiophene-based copolymers studied in this work.

3. Results and Discussion

The chemical structures of 15 fluorene thiophene derivatives based copolymers considered in this work are summarized in Figure 1. For convenience, we classify the thiophene derivatives into the following two categories: thiophene-based units and cyclopentadithiophene-based units. The thiophene-based units include thiophene (T), ethylenedioxythiophene (EDOT), thienopyrazine (TP), thiadiazolothienopyrazine (TDTP), dithienopyrazine (DTP), thianaphthene (TN), and thienothiadiazole (TTD). The cyclopentadithiophene-based units include cyclopentadithiophene (CDT), ethylenedioxycyclopentadithiophene (CED), propylenedioxycyclopentadithiophene (CPD), cyclopentadithiophenone (CPO), dicyanomethylenecyclopentadithiophene (CDM), 4-(1,3-dithiol-2-ylidene) cyclopentadithiophene (DYCDT), and 4-*N*-methylpyridinium-cyclopentadithiophenes (PDCDT). In the

TABLE 1: Properties of Monomers (X), Comonomers ((F-X)₁), and Copolymers ((F-X)∞) from Quantum Mechanical Calculations

X	X				(F-X)$_1$			(F-X)$_\infty$				BW of VB	BW of CB
	-E_{HOMO}	-E_{LUMO}	IP	EA	π_{eF}	$\Delta\pi$	L_B (Å)	IP	EA	E_g(H-L)[a]	E_g(ZIN)[b]		
F	6.04	1.09	7.24	0.01	12.897	0.000	1.484	5.70[5.8][a]	1.71[2.12][a]	3.23[3.68⁴¹][a]	3.19 [3.11⁴²][b]	1.56	1.17
TDTP	6.43	4.01	8.15	2.31	12.841	−0.056	1.460	5.35	3.82	0.76	2.40(0.39)	1.82	0.28
TTD	6.27	3.03	8.22	1.13	12.847	−0.050	1.456	5.12	3.07	1.18	0.68	1.94	0.61
TP	6.51	2.60	8.05	1.16	12.862	−0.035	1.464	5.33 [5.6][a]	2.64 [3.31][a]	1.78 [1.80][a]	1.73 [1.82⁴³][b]	1.79	0.71
DTP	5.54	3.32	7.17	1.69	12.866	−0.031	1.459	4.92	3.24	0.92	0.65	1.45	0.38
TN	5.65	1.68	7.49	−0.06	12.879	−0.019	1.467	5.25	1.95	2.38	2.07	1.78	0.96
T	6.62	0.63	8.64	−1.09	12.881	−0.016	1.468	5.47 [5.49][a]	1.79 [2.84][a]	2.66 [2.70][a]	2.55 [2.5⁴⁴][b]	1.70	1.63
EDOT	5.80	0.04	7.69	−0.63	12.913	0.017	1.465	5.08 [5.21][a]	1.63 [2.83][a]	2.47 [2.38][a]	2.41 [2.47⁴⁵][b]	1.68	1.85
CDM	6.31	3.70	7.32	2.74	12.857	−0.039	1.464	5.70 [6.14][a]	3.44 [3.43][a]	1.55 [2.71][a]	2.74(1.32) [2.56¹⁶][b]	1.49	0.17
DYCDT	5.33	1.92	6.83	0.53	12.877	−0.020	1.463	4.95	2.02	2.22	2.98(1.87)	1.37	0.63
CPO	6.01	2.86	7.21	1.65	12.876	−0.019	1.464	5.50 [5.47][a]	2.71 [3.36][a]	2.05 [2.11][a]	3.02(1.64) [2.59(1.91)¹⁶][b]	1.39	0.30
PDCDT	5.69	1.54	7.29	0.04	12.886	−0.011	1.464	5.80	2.05	2.39	2.22	1.44	1.48
CPD	5.50	1.55	6.48	0.66	12.887	−0.01	1.464	5.10 [5.35][a]	1.99 [3.53][a]	2.33 [1.82][a]	2.18 [2.30¹⁶][b]	1.28	1.26
CED	5.51	1.60	6.52	0.67	12.891	−0.005	1.464	5.12 [5.79][a]	2.01 [3.49][a]	2.32 [2.30][a]	2.18 [2.39¹⁶][b]	1.29	1.23
CDT	5.48	1.34	6.81	0.06	12.897	0.001	1.464	5.08 [6.13][a]	1.92 [3.57][a]	2.38 [2.56][a]	2.21 [2.49¹⁶][b]	1.29	1.50

[a] Experimental data shown in [] are determined from CV measurements using the empirical relationship proposed by de Leeuw et al.:[46] Ip(HOMO) − (Eonset, ox + 4.39) (eV), Ea(LUMO) − (Eonset, red + 4.39) (eV). [b] Experimental data shown in [] are determined from UV−vis measurements. In the experiment, electrochemical gaps were approximated by the difference of HOMO (or IP) and LUMO (or EA) energy in CV measurements. Optical energy gaps for F-T, F-EDOT, F-TP were estimated from the absorption onset of UV−vis spectra. The intersection point of UV−vis spectra and fluorescence was used as optical gap for F-CDT, F-CED, F-CPD, F-CPO, and F-CDM.

following discussions, these units are denoted as X and fluorene is denoted as F. (F-X)₁ is referred to as the repeat unit or comonomer, (F-X)$_n$ represents the oligomer with a degree of polymerization of n, while (F-X)∞ represents the conjugated copolymer with a degree of polymerization of infinity.

3.1. Measures for π-Electron Donating/Accepting Capability. 3.1.1. Charge Transfer between Donor−Acceptor Moieties. The strength of π-electron-donating (or accepting) in a (F-X)∞ copolymer can be measured by the excess of π-electrons ($\Delta\pi$) in fluorene of a (F-X)₁ molecule from that in a (F-F)₁ molecule

$$\Delta\pi = (\pi_{eF}^{(FX)_1} - \pi_{eF}^{(FF)_1}) \tag{1}$$

where π_{eF} is total number of π-electrons (obtained by Mulliken population analysis[36]) in orbital perpendicular to the plane of the fluorene unit (i.e., from all the 13 carbon atoms). We use the excess of π-electrons ($\Delta\pi$) on the fluorene unit as a measure for the relative electron-donating/withdrawing strength between F and X. A large negative value of $\Delta\pi$ would indicate a strong π-electron-donating power of X relative to F, and vice versa.

From the results listed in Table 1 (7th column), thiophene derivatives having pyrazine-fused rings as substituent are classified as π-electron-accepting units while connected with fluorene.[37] Comparing $\Delta\pi$ for F-T comonomers (including (F-T)₁, (F-EDOT)₁, (F-TP)₁, (F-TDTP)₁, (F-DTP)₁, (F-TN)₁, (F-TTD)₁), we find that pyrazine-containing substituents on thiophene (TDTP, TP, DTP) lead to larger values in $\Delta\pi$ when compared to benzene substituents (TN). Nonetheless, TN is slightly stronger in π-electron withdrawing compared with T due to increased quinoid properties by the additional fused ring. The only case of increasing π-electrons on fluorene, that is, F as a π-electron-accepting unit is the combination of F and EDOT due to donation of π-electrons from two electron-rich oxygen atoms on EDOT.

On the other hand, the $\Delta\pi$ on fluorene of F-CDT series comonomers (including (F-CDT)₁, (F-CED)₁, (F-CPD)₁, (F-CPO)₁, (F-CDM)₁, (F-DYCDT)₁, (F-PDCDT)₁) increase in the following order: F-CDM < F-DYCDT < F-CPO < F-PDCDT < F-CPD < F-CED < F-CDT. CDM with substituent of dicyano-

ethenyl on CDT is the strongest π-electrons withdrawing group among the all cyclopentadithiophene derivatives, causing the least amount of $\Delta\pi$ on fluorene.

It is worth noting that although both EDOT and CED/CPD have electron-donating ethylenedioxy linked to the backbone, EDOT appears to be a π-electron-donor while CED behaves as a π-electron-acceptor. This is because that the oxygen atoms of ethylenedioxy are almost on the same plane as the backbone in EDOT. The increasing of coplanarity between lone pairs of oxygen atoms (on ethylenedioxy group) and the backbone would enhance the delocalization of π-electrons from ethylenedioxy to thiophene and then to fluorene. Unlike EDOT, the oxygen atoms on ethylenedioxy in CED are perpendicular to the coplanar atoms of backbone. The weak interactions between π-electrons of oxygen and the backbone make CED unfavorable to donate π-electrons and become a π-electron-acceptor in (F-CED).

3.1.2. Ionization Potential, Electron Affinity, and Molecular Orbital Energy. The IP and EA of an atom or a molecule are the energy needed to remove or gain an electron and therefore can be regarded as the molecule's ability for donating and accepting electrons. X in a (F-X)₁ comonomer has a high EA (easily gain an electron from donor) and high IP (hardly lose an electron to donor) is recognized as an acceptor. IP and EA are sometimes approximated as the negative of HOMO and LUMO energy, respectively. Table 1 (columns 2 to 5) shows the DFT energy levels compared with IPs and EAs for different X. It can be seen that most HOMO energies vary in the range of −5.5 to approximately −6.5 eV, while LUMO energies vary significantly (from −0.04 to −4.01 eV). As shown in Figure 2, we find a linear relationship between the direct calculated vertical IPs and the HOMO energies calculated from DFT (with a correlation coefficient $r^2 = 0.82$) and between the direct calculated vertical EA with the DFT LUMO energies ($r^2 = 0.91$). Such a linear correlation has also been reported previously.[38]

The energy levels for F and X are illustrated in Figure 3. The difference between LUMO of F and LUMO of X increased when X has strong π-electron withdrawing substituents of pyrazine derivatives (TDTP, DTP, TP), and of dicyanoethenyl (CDM) and carbonyl (CPO) groups. Meanwhile, the LUMO+1
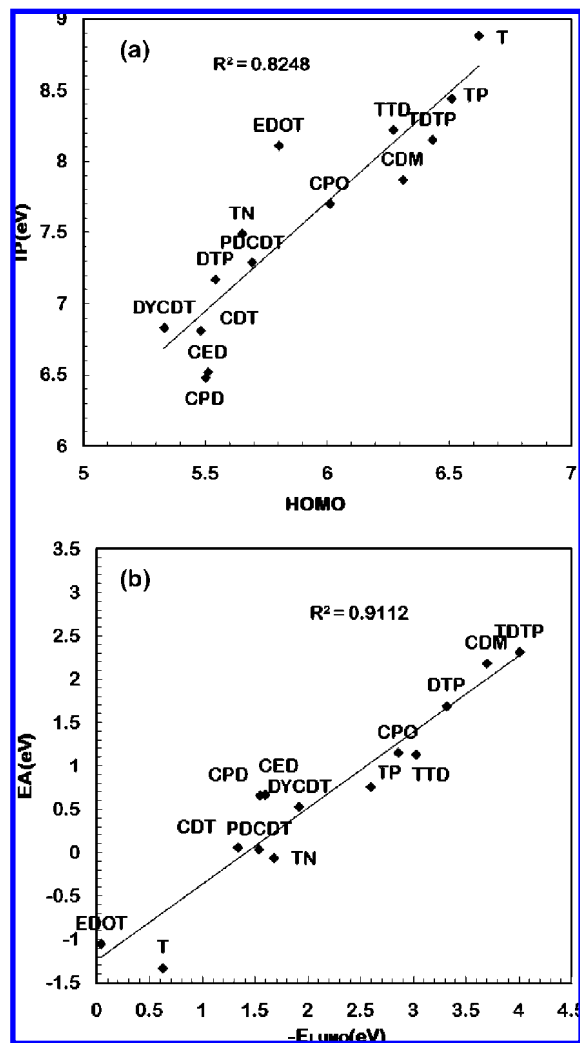
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Figure 2. Plot of (a) HOMO energy level versus ionization potential (b) LUMO energy level versus electron affinity of different monomers from DFT calculations at B3LYP/6-31+G* level.
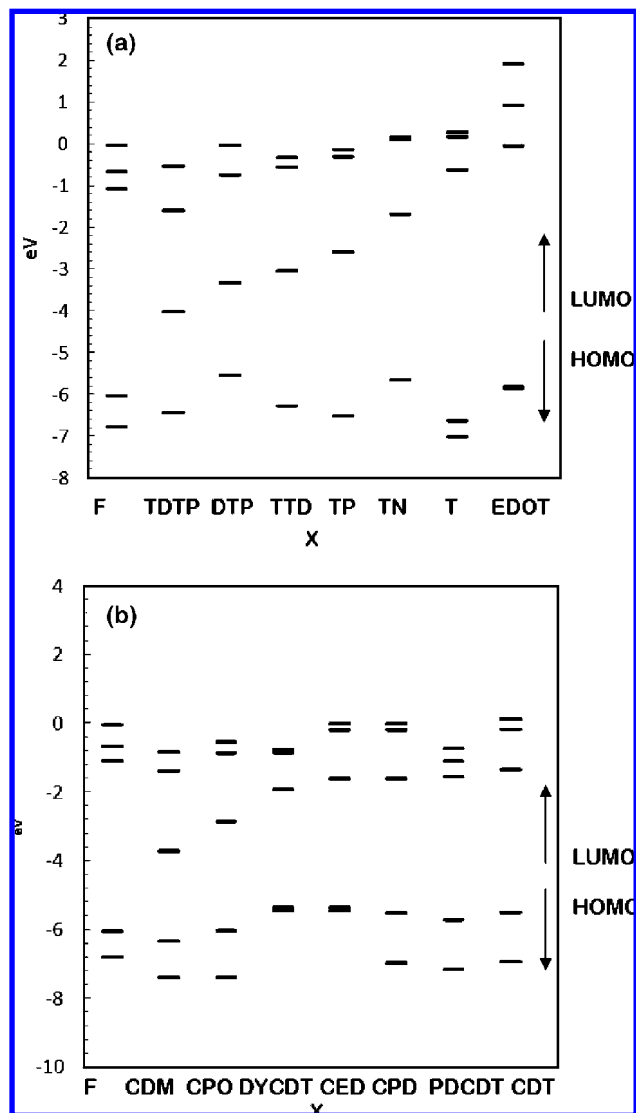

Figure 3. Energy level of frontier orbitals of different monomers from DFT calculations at B3LYP/6-31+G* level. (a) fluorene and thiophene derivatives and (b) fluorene and cyclopentadithiophene derivatives.
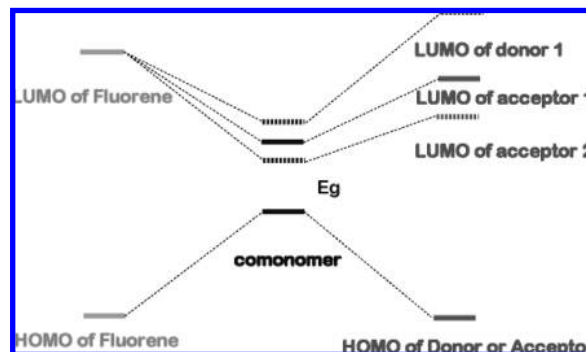

Figure 4. Schematic diagram showing the variation of the LUMO energy level of a comonomer F-X by varying substituents on thiophene derivative.

level of X become closer to the LUMO of fluorene, implying that the interactions between LUMO+1 of X with LUMO of F are strong. On the other hand, weak π-electron-donating or withdrawing substituents on X have little influence on the energy levels of LUMO orbital of X. For example, LUMO of TN is close to that of T.

For all X studied in this paper, the energy levels of HOMO vary within a small range of 1 eV; thus, the band gap of the comonomer F-X is mainly determined by the LUMO levels of X, as shown in Figure 4. Therefore, we may define ΔLUMO to be another measure for the π-electron-donating power compared to fluorene, that is

$$\Delta\text{LUMO} = (E_{\text{LUMO}}^{\text{X}} - E_{\text{LUMO}}^{\text{F}}) \qquad (2)$$

where $E_{\text{LUMO}}^{\text{F}}$ and $E_{\text{LUMO}}^{\text{X}}$ represent the energy level of LUMO of F and of X, respectively. The more negative value of ΔLUMO represents that the moiety X has a higher ability to accept π-electron from fluorene.

As shown in Figure 5, there is a good linear correlation between $\Delta\pi$ (listed in Table 1) and ΔLUMO for comonomers (F-X)$_1$ with $r^2 = 0.79$. The comonomers at the bottom-right side with higher ΔLUMO generally correspond to more negative values of $\Delta\pi$, indicating X in F-X are strong π-electron acceptors.

3.1.3. Bond Length between Fluorene and Thiophene Derivatives.
The bond length (L_{B}) between F and X (either a strong π-electron-donor or a strong π-electron-acceptor) in a (F-X)$_1$ comonomer is reduced, indicating an enhancement of double-bond character due to their increasing π-electron delocalization.[39] In our calculated results (Table 1, eighth column), L_{B} of F-F shows a largest length of 1.484 Å. The L_{B} of
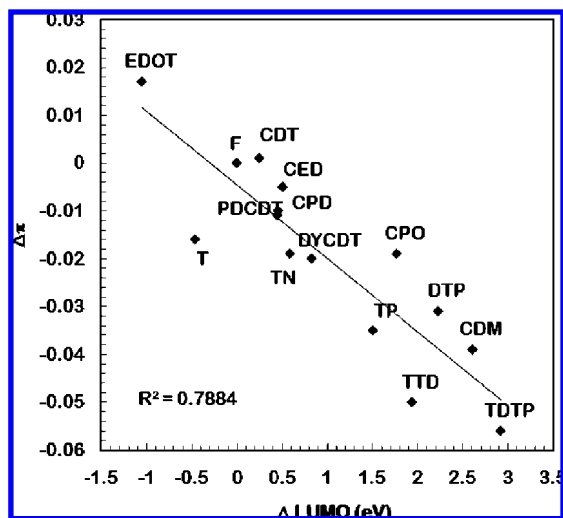
Figure 5. Correlation between the amount of charge transfer ($\Delta\pi$, defined in eq 1) and the difference in the LUMO energies (ΔLUMO, defined in eq 2) in comonomers (F-X)$_1$.

comonomers is reduced by about 0.02 Å. The order of L_B of F-T series comonomers is F-DTP $\approx$ F-TTD < F-TDTP < F-TP < F-EDOT < F-TN < F-T. The results indicate that the presence of strong π-electron-withdrawing groups on thiophene increases the quinoid characters, induced by intramolecular charge transfer between F and X. On the other hand, for F-X comonomers with X being cyclopentadithiophene, the change of substituents on cyclopentadithiophene does not significantly influence the L_B. This might suggest that the delocalization of π-electrons between F and cyclopentadithiophene derivatives is poorer than that between F and thiophene derivatives.

3.2. Electronic States and Optical Transitions. 3.2.1. Electron Excitation Energies and HOMO–LUMO Band Gaps. The energetic properties such as HOMO–LUMO gaps and electron transition energies should vary with the chain length of the polymer. It is found that these properties of a certain oligomer (F-X)$_n$ showed linear relations against the inverse of the total number of rings of the oligomer (two rings in a fluorene or a cyclopentadithiophene unit, one ring in a thiophene unit). As a reference, we determine the properties of polymers with an infinite chain length by linearly extrapolation to infinite rings (as shown in Figure 6).

The calculated band gaps are compared to experimental ones as shown in Table 1 (columns 11 and 12). In general, the calculated band gaps are in good agreement with experimental data. Note that the calculations were done for oligomers in the gas phase, while experiments were performed for polymers in dilute solutions. The good agreement between our calculation and experiment could be a result of error cancellation or an indication that the solvent has little impact on the electronic properties of the systems studied here. The discrepancies between experimental band gaps from cyclic voltammetry (CV) measurements and HOMO–LUMO gap from DFT calculation (E_g(H-L)) of (F-X)$_\infty$ with X = F, T, TP, and EDOT, are 0.45, 0.04, 0.02, and 0.09 eV, respectively; meanwhile, the discrepancies between experimental band gaps from UV–vis measurements and the major optical absorption from ZINDO calculations (E_g(ZIN)) are 0.08, 0.05, 0.05, and 0.06 eV. In the cases of copolymers (F-X)$_\infty$ with X as cyclopentadithiophene derivatives, the discrepancies between experimental band gaps of copolymers (F-X)$_\infty$ with X = CDT, CED, CPD, CPO, and CDM and E_g(H-L) of those copolymers are 0.11, 0.07, 0.03, 0.54, and 1.01 eV, respectively, while the errors for E_g(ZIN) are 0.28,
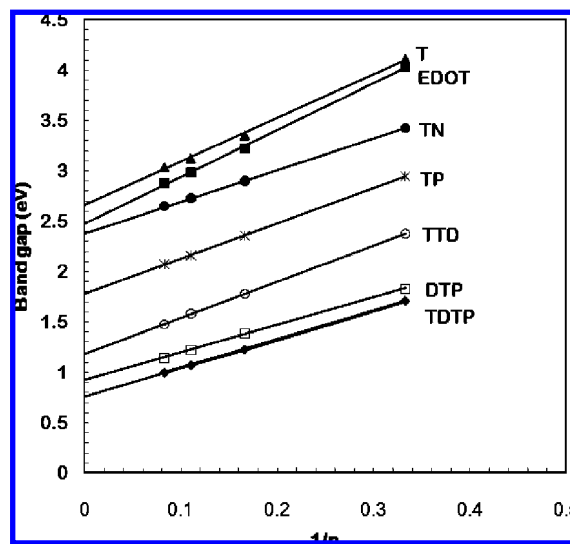

Figure 6. Variation of DFT calculated HOMO–LUMO gaps with the inverse chain length (indicated by the number of rings n) of oligomers (F-X)$_n$.

0.21, 0.12, 0.43, and 0.18 eV. Except for CDM and CPO, both DFT method and ZINDO semiempirical method are in good agreement with the experimental band gaps. The much larger discrepancies between E_g(UV–vis) and E_g(ZIN) for CDM and CPO result from the stronger optical absorption from $S_0{\rightarrow}S_{n>1}$ electronic transitions, which will be detailed in a later section.

Figure 7 shows the comparison of calculated gaps and available experimental data as functions of ΔLUMO. It is seen that optical transition gap determined from ZINDO calculations, E_g(ZIN), are consistently lower than the HOMO–LUMO energy gap, E_g(H-L) by less than 0.5 eV. Large discrepancies between E_g(ZIN) with E_g(H-L) occur while X is thiophene derivative with strong π-electron withdrawing substituent. For F-T series copolymers, F-TDTP with the largest ΔLUMO results in the largest discrepancies between E_g(ZIN) and E_g(H-L). For F-CDT series copolymers, similarly results are also observed for F-DYCDT, F-CPO, and F-CDM.

The optical transition gap E_g(ZIN) is determined as a linear combination of several ground-state and excited configurations. Therefore, only for the $S_0{\rightarrow}S_1$ transition with the largest oscillator strength can the HOMO–LUMO gap be regarded as a rough approximation to electron transition energy. For the case where $S_0{\rightarrow}S_1$ electronic transition is not the main transition, an obvious deviation would be observed between HOMO–LUMO and optical transition gaps.

3.2.2. Electronic Transition Properties (Detailed ZINDO Analysis). The detailed electronic transitions, including excitation energies, oscillator strength, and configurations for the main and the $S_0{\rightarrow}S_1$ electronic transitions of (F-X)$_4$, are presented in Table 2. The calculated excitation energies with the largest oscillator strength are compared to the maximum absorption in UV–vis spectrum (denoted as λ_{max} hereafter).[40] The configurations for $S_0{\rightarrow}S_1$ electronic transition are given (underlined) if it does not correspond to the largest oscillator strength (shown in bold type). It can be seen that for (F-F)$_4$, (F-T)$_4$, (F-TTD)$_4$, (F-TD)$_4$, (F-TN)$_4$ [F-T series conjugated copolymers], (F-CDT)$_4$, (F-CED)$_4$ and (F-CED)$_4$ [F-CDT series conjugated copolymers], the $S_0{\rightarrow}S_1$ electronic transition has the largest oscillator strength, corresponding to absorption maxima in UV–vis spectra. The detailed configurations for the transition also show that HOMO$\rightarrow$LUMO transition mainly dominates the transition.

For copolymers (F-X)$_\infty$ with X having a much stronger π-electron withdrawing group (e.g., TDTP, CDM, CPO) or

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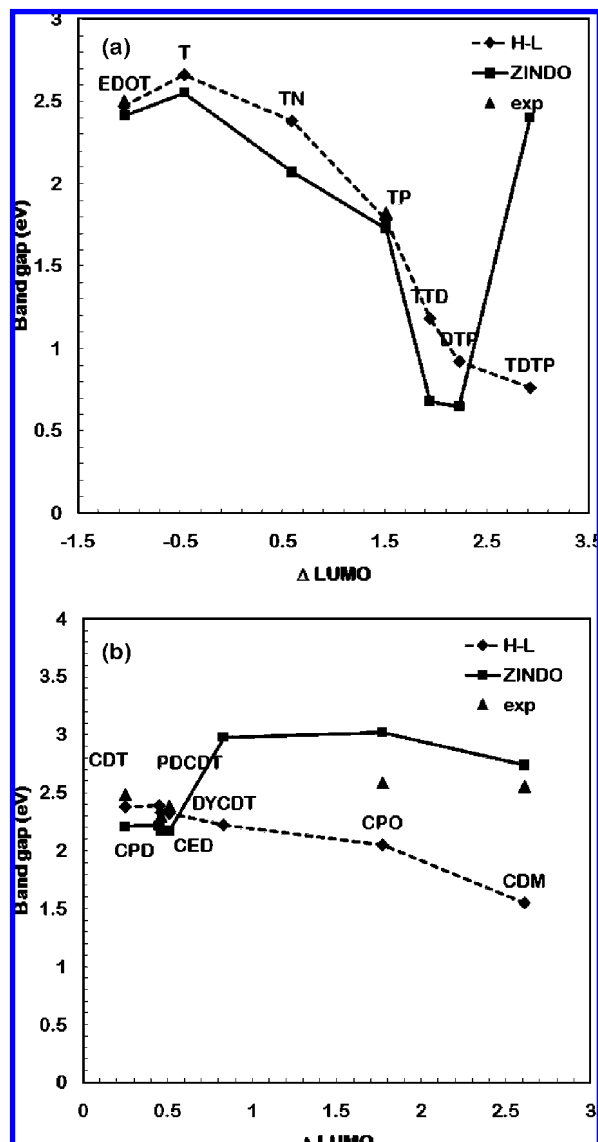**Figure 7.** Comparisons of band gaps from DFT (E_g(H-L)) and ZINDO (E_g(ZIN)) calculations with available experimental data for different copolymers (F-X)$_\infty$. (a) F-T-based conjugated copolymers. (b) F-CDT-based conjugated copolymers.

TABLE 2: Electronic Transition Data from ZINDO Calculation for all Fluorene Based Conjugated Copolymers (with a Degree of Polyrization of 4) at the B3LYP/6-31G* Optimized Geometry[a]

copolymers	electronic transition	band gaps	F	configurations
(a) F-T Conjugated Copolymers		ZINDO		
(F-F)$_4$	**$\underline{S_0 \rightarrow S_1}$**	**$\underline{3.33}$**	**$\underline{5.97}$**	**HOMO→LUMO(0.43)**
				HOMO-1→LUMO+1(0.31)
	$S_0 \rightarrow S_2$	3.45	0.46	HOMO→LUMO+1(0.34)
				HOMO-1→LUMO(0.33)
(F-T)$_4$	**$\underline{S_0 \rightarrow S_1}$**	**$\underline{2.83}$**	**$\underline{4.00}$**	**HOMO→LUMO(0.49)**
				HOMO-1→LUMO+1(0.32)
	$S_0 \rightarrow S_3$	3.24	0.22	HOMO→LUMO+1(0.36)
				HOMO-2→LUMO(0.34)
(F-TTD)$_4$	**$\underline{S_0 \rightarrow S_1}$**	**$\underline{0.85}$**	**$\underline{1.74}$**	**HOMO→LUMO(0.50)**
				HOMO-1→LUMO+1(0.30)
	$S_0 \rightarrow S_{11}$	2.71	0.82	HOMO→LUMO+4(0.37)
				HOMO-1→LUMO(0.22)
(F-TB)$_4$	**$\underline{S_0 \rightarrow S_1}$**	**$\underline{2.26}$**	**$\underline{2.70}$**	**HOMO→LUMO(0.47)**
				HOMO-1→LUMO+1(0.32)
	$S_0 \rightarrow S_2$	2.41	0.43	HOMO→LUMO+1(0.37)
				HOMO-1→LUMO(0.37)
(F-EDOT)$_4$	**$S_0 \rightarrow S_2$**	**2.90**	**2.20**	**HOMO→LUMO+1(0.39)**
				HOMO-1→LUMO(0.38)
	$\underline{S_0 \rightarrow S_1}$	$\underline{2.69}$	$\underline{2.00}$	HOMO→LUMO(0.50)
				HOMO-1→LUMO+1(0.32)
(F-TP)$_4$	**$S_0 \rightarrow S_2$**	**1.98**	**1.19**	**HOMO→LUMO+1(0.38)**
				HOMO-1→LUMO(0.36)
	$\underline{S_0 \rightarrow S_1}$	$\underline{1.83}$	$\underline{1.18}$	HOMO→LUMO(0.49)
				HOMO-1→LUMO+1(0.32)
(F-DTP)$_4$	**$S_0 \rightarrow S_2$**	**0.90**	**0.77**	**HOMO→LUMO+1(0.38)**
				HOMO-1→LUMO(0.36)
	$\underline{S_0 \rightarrow S_1}$	$\underline{0.76}$	$\underline{0.65}$	HOMO→LUMO(0.48)
				HOMO-1→LUMO+1(0.30)
(F-TDTP)$_4$	**$S_0 \rightarrow S_{16}$**	**2.50**	**1.00**	**HOMO-1→LUMO+4(0.25)**
				HOMO→LUMO+6(0.20)
	$\underline{S_0 \rightarrow S_1}$	$\underline{0.53}$	$\underline{0.38}$	HOMO→LUMO(0.47)
				HOMO-1→LUMO+1(0.29)
(b) F-CDT Conjugated Copolymers				
(F-CDT)$_4$[b]	**$\underline{S_0 \rightarrow S_1}$**	**$\underline{2.37}$**	**$\underline{4.70}$**	**HOMO→LUMO(0.44)**
				HOMO-1→LUMO+1(0.31)
	$S_0 \rightarrow S_4$	2.80	0.39	HOMO-3→LUMO+3(0.29)
				HOMO-3→LUMO+1(0.25)
(F-CED)$_4$	**$\underline{S_0 \rightarrow S_1}$**	**$\underline{2.32}$**	**$\underline{4.36}$**	**HOMO→LUMO(0.44)**
				HOMO-1→LUMO+1(0.31)
	$S_0 \rightarrow S_8$	3.67	0.49	HOMO→LUMO+7(0.22)
				HOMO-1→LUMO+6(0.18)
(F-CPD)$_4$	**$\underline{S_0 \rightarrow S_1}$**	**$\underline{2.32}$**	**$\underline{4.34}$**	**HOMO→LUMO(0.44)**
				HOMO-1→LUMO+1(0.32)
	$S_0 \rightarrow S_8$	3.67	0.50	HOMO→LUMO+7(0.22)
				HOMO-1→LUMO+6(0.19)
(F-PDCDT)$_4$	**$\underline{S_0 \rightarrow S_1}$**	**$\underline{2.37}$**	**$\underline{4.34}$**	**HOMO→LUMO(0.44)**
				HOMO-1→LUMO+1(0.31)
	$S_0 \rightarrow S_4$	2.79	0.38	HOMO-3→LUMO+7(0.22)
				HOMO-1→LUMO+6(0.19)
(F-CPO)$_4$[b]	**$S_0 \rightarrow S_9$**	**3.09**	**3.83**	**HOMO→LUMO+6(0.37)**
				HOMO-1→LUMO+5(0.22)
	$\underline{S_0 \rightarrow S_1}$	$\underline{1.71}$	$\underline{1.32}$	HOMO→LUMO(0.39)
				HOMO-1→LUMO+1(0.28)
(F-CDM)$_4$[b]	**$S_0 \rightarrow S_5$**	**2.88**	**4.71**	**HOMO→LUMO+4(0.39)**
				HOMO-1→LUMO+5(0.22)
	$\underline{S_0 \rightarrow S_1}$	$\underline{1.39}$	$\underline{0.57}$	HOMO→LUMO(0.34)
				HOMO-2→LUMO+2(0.32)
(F-DYCDT)$_4$	**$S_0 \rightarrow S_5$**	**3.08**	**2.79**	**HOMO→LUMO+6(0.32)**
				HOMO−1→LUMO+5(0.20)
	$\underline{S_0 \rightarrow S_1}$	$\underline{1.95}$	$\underline{2.20}$	HOMO→LUMO(0.42)
				HOMO-1→LUMO+1(0.32)

[a] The electronic transitions corresponding to the largest oscillator strength are shown in **bold type**. The ground-to-first-excited-state ($S_0 \rightarrow S_1$) transitions are underlined. [b] The values for F-CDM, F-CPO, and F-CPD were reported previously in ref 16.

donating group (e.g., EDOT), the oscillator strength for $S_0 \rightarrow S_1$ electronic transition becomes smaller. For X containing a strong π-electron withdrawing group, electronic transition from S_0 to a higher energy state becomes the major transition. The detailed transition configurations for such a transition are no longer dominated by HOMO→LUMO transition but by HOMO→LUMO+n transition. The energy level analysis in Figure 5 shows that strong π-electron withdrawing groups significantly lower the energy levels of LUMO, resulting in weaker interactions between LUMO orbital of fluorene and LUMO orbital of X. Stronger interactions between LUMO of fluorene and LUMO+n of strong π-electron accepting X would increase their contribution to electronic transition. Therefore fluorene and strong acceptors such as CPO and CDM can result in a small band gap and at the same time in a reduction of the oscillator strength of $S_0 \rightarrow S_1$ electronic transition. These results are in agreement with the blue shift in λ_{max} and a shoulder on the red edge in experimental UV−vis absorption spectra.[16]

3.2.3. Bandwidth and Frontier Orbital. Even though the donor−acceptor concept is an effective strategy for designing low band gap conjugated polymers, it has been cautioned that

donor−acceptor concept might result in a narrowed bandwidth of the valence and conduction bands due to weak interactions between HOMO and LUMO energy levels for conjugated copolymers based on thiophene derivatives.[30] The narrow bandwidth of conduction and valence bands would result in a lowered carrier mobility in both bands.[30]
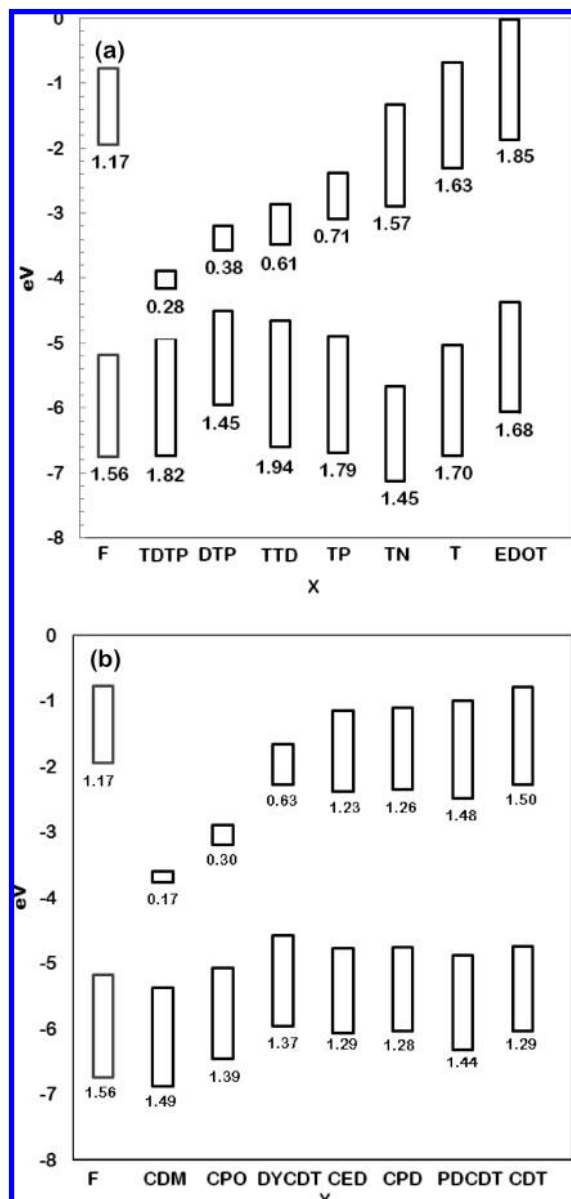
Figure 8. Valence and conduction bands of different copolymers (F-X)∞ from DFT calculations. (a) F-T-based conjugated copolymers. (b) F-CDT-based conjugated copolymers.
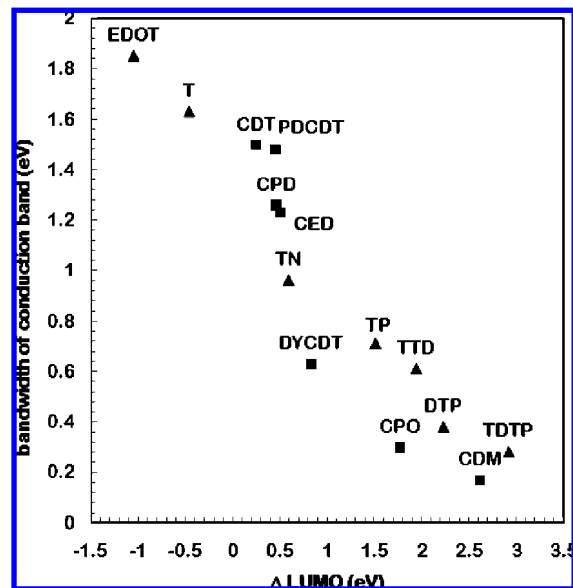

Figure 9. Correlation between the bandwidth of the conduction band of copolymers (F-X)∞ and the difference between LUMO of F and LUMO of X (ΔLUMO, defined in eq 2).

Figure 8 shows that the extrapolated valence and conduction bands of (F-X)∞ copolymers. To remove the bias resulting from the difference in the size of the copolymers, bandwidths for F-T series copolymer (F-T, F-EDOT, F-TP) are multiplied by 3/2 and bandwidths for F-CDT series copolymers (CDT, CED, CPD, CPO, CDM) are multiplied by 2.[30] It can be seen that the bandwidths of both bands are mainly determined by the discrepancies between HOMO/LUMO levels of F and those of X. Large difference between energy levels would weaken the interactions between the corresponding orbital. In Figure 8 the bandwidth of valence band is similar for each (F-X)∞ copolymers because there is no significant difference between HOMO energy level of F and that of X. When X is a strong π-electron acceptor, a narrow bandwidth of conduction band of (F-X)∞ copolymers is observed. For F-CDT series copolymers, the bandwidth of conduction band for (F-CDM)∞, (F-CPO)∞, and (F-DYCDT)∞ are 0.17, 0.30, and 0.63 eV, respectively (Table 1, column 14). On the other hand, for F-T series copolymers the bandwidths are 0.28, 0.61, 0.71, and 0.38 eV for (F-TDTP)∞, (F-TTD)∞, (F-TP)∞, (F-DTP)∞, respectively. These narrow

conduction bands are attributed to the low LUMO level of strong π-electron acceptors. Conjugated copolymers of fluorene with weaker π-electron acceptors or π-electron donors would have a wider conduction band, due to the similarity in EA (or LUMO) between fluorene and X. As a result, there exists a remarkable correlation between the conduction bandwidth and the energy differences in LUMO as shown in Figure 9.

These results can be further confirmed by the calculated frontier molecular orbital shown in Figure 10. Frontier orbital of HOMO spreads over the whole backbone for fluorene homopolymer (F-F)₂ and all (F-X)₂ copolymer, demonstrating that strong interactions between HOMO energy levels of F and that of X. The electron density distribution of HOMO orbital also displays bonding character (rather than a node in the electron wave function) between the bridging carbon atom and its conjoint atom of intraring.

The LUMO orbital of (F-F)₂, (F-T)₂, (F-EDOT)₂, (F-CDT)₂, (F-CED)₂, and (F-CPD)₂ have similar shapes of bonding character between two linking carbon atoms of inter-ring. This is because fluorene, thiophene, and cyclopentadithiophene have similar energy levels of their LUMO orbital. The additional fused rings such as ethylenedioxy and propylenedioxy in CED and CPD only slightly change the LUMO energy level in comparison with CDT. The coplanarity of these copolymers at excited state is better than that at ground state due to the bonding character between F and X. Upon photoexcitation, the aromatic like structure will deform to a quinoidlike structure.[27]

Comparatively, for F-X copolymers with X as a strong π-electron acceptor, such as TP, CDM, CPO, and TDTP, the LUMO orbital almost locates on X, inconsistent with the large difference between the LUMO energy levels of F and X. The much weaker interactions between the energy levels of LUMO orbital, therefore, reduce the oscillator strength for S₀→S₁ transition.

Since the interaction between energy levels are significantly influenced by the difference of energy levels, we use the absolute value of ΔLUMO, denoted by |ΔLUMO|, as an indication of the strength of interactions between LUMO level of F and LUMO of X. Figure 11 shows there exists a remarkable correlation between |ΔLUMO| and oscillator strength of S₀→S₁

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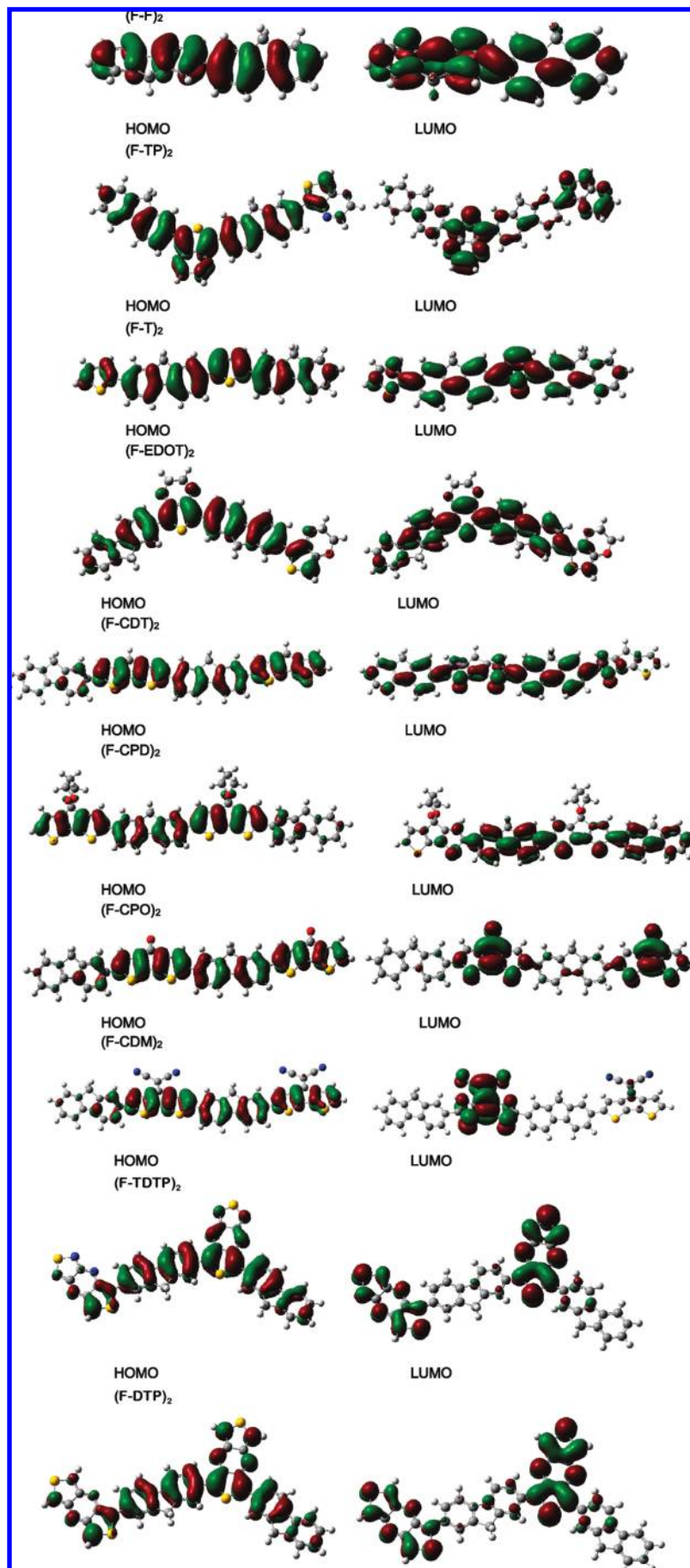*J. Phys. Chem. B, Vol. 113, No. 24, 2009* **8275**

Figure 10. Electron distribution in HOMO (left figures) and LUMO (right figures) orbitals of selected oligomers (F-X)₂.
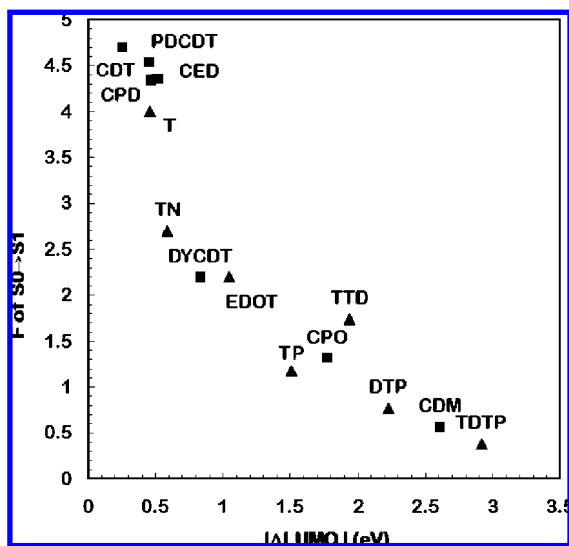
Figure 11. Correlation between the oscillator strength of $S_0 \rightarrow S_1$ transition for $(F-X)_4$ and the difference between LUMO of F and LUMO of X (ΔLUMO, defined in eq 2).

transition. The copolymers with a larger $|\Delta LUMO|$ show smaller oscillator strength of $S_0 \rightarrow S_1$ transition. In other words, too large discrepancies between HOMO/LUMO energy levels of donor and those of acceptor will result in a weak adsorption for $S_0 \rightarrow S_1$ transition. When F and X have similar HOMO/LUMO energy levels, the F-X copolymers will have a large oscillator strength for $S_0 \rightarrow S_1$ transition, however, at a cost of the scarification of low-band gap.

4. Conclusion

In summary, our calculation results show that low-band gap conjugated polymers can be obtained via donor–acceptor conjugation of alternating fluorene and thiophene/cyclopenta-dithiophene derivatives. Copolymers of fluorene and thiophene/cyclopentadithiophene derivatives with strong π-electrons with-drawing substituents such as CPO, CDM, and TDTP exhibit significantly reduced band gap of 2.05, 1.55, and 0.76 eV, respectively. However, increasing the π-electron withdrawing ability in thiophene/cyclopentadithiophene derivatives could lead to a higher energy gap in optical transition and a narrower bandwidth that could lead to the reduction of the efficiency of a photovoltaic device.

Theoretical analysis on ZINDO-based calculations suggests that larger differences between HOMO/LUMO energy levels of donor and those of acceptor would reduce the oscillator strength of $S_0 \rightarrow S_1$ electronic transition. Furthermore, the electronic transition from the ground state (S_0) to a higher excited state (S_n, $n > 1$) might dominate the total transition. The theoretical observations are consistent with the blue shift in the absorption maxima in UV–vis spectra observed experi-mentally from F-CPO and F-CDM copolymers. Therefore, acceptors with too strong π-electron withdrawing/donating capability might not be good candidates for fluorene-based D–A conjugated copolymers. In addition, the large difference between HOMO/LUMO energy levels also results in narrow bandwidth of conduction bands, thus reducing the charge carrier mobility of these polymers.

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