

Does the Donor–Acceptor Concept Work for Designing Synthetic Metals? 2. Theoretical Investigation of Copolymers of 4-(Dicyanomethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and 3,4-(Ethylenedioxy)thiophene

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Density functional theory (DFT) calculations were performed on oligomers of 3,4-(ethylenedioxy)thiophene (EDOT), 4-(dicyanomethylene)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CDM), and co-oligomers (CDM/EDOT). Oligomer data were extrapolated to polymer values. Theoretical band gaps reproduce λ_{\max} from UV spectroscopy for PEDOT and are about 1 eV larger than electrochemical band gaps. λ_{\max} of PCDM/EDOT is predicted to be 0.42 eV smaller than that of PEDOT and 0.15 eV smaller than that of PCDM. PCDM/EDOT has a wide valence and an extremely narrow conduction “band”. It is probably better not to refer to these localized states as a band at all. This rationalizes the mobility ratio of 500 between p-type and n-type charge carriers and the low n-type conductivity of PCDM/EDOT. The lack of dispersion of the conduction band is due to the very different EAs of EDOT and CDM.

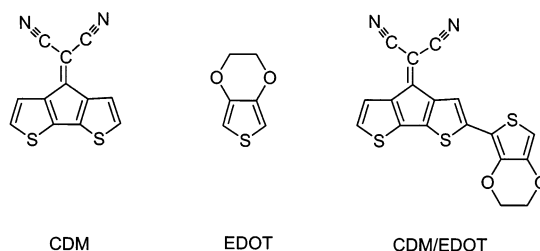
Introduction

In 1997 Huang and Pickup¹ reported on copolymers of CDM and EDOT (Chart 1) in various compositions. The lowest band gap was measured electrochemically for an EDOT rich copolymer. The precise band gap could not be determined but was estimated to be 0.16 eV or less and probably close to zero. Thus, poly-CDM-EDOT (PCDM/EDOT) might be the first zero-band gap conducting polymer produced since the discovery of poly-(sulfur nitride) and the first zero-band gap *organic* conducting polymer ever. The electrochemical band gaps of the homopolymers PCDM and PEDOT are 0.82³ and 1.2 eV,^{1,4} respectively. Compared to the homopolymers, the intrinsic conductivity is greatly increased in the copolymer ($\sigma_{\text{PCDM/EDOT}} = 10^{-3}$ S/cm, $\sigma_{\text{PCDM}} = 10^{-8}$ S/cm, $\sigma_{\text{PEDOT}} = 10^{-12}$ S/cm).¹ Like PCDM, PCDM/EDOT can be p- and n-doped but the conductivity of the n-doped form is poor. Since EDOT has a very low IP and CDM has a very high EA, the success with designing this new system was attributed by Huang and Pickup to the donor–acceptor concept.⁵ A summary of donor–acceptor systems is given in the preceding paper. For a recent review see van Mullekom et al.⁶

We are investigating donor–acceptor systems theoretically and have cast some doubt on the donor–acceptor concept.⁷ As shown in the preceding paper, systems with very different energies interact little. This is in agreement with principles of quantum mechanics. As a consequence, the decrease in energy gap and the increase in bandwidth with increasing chain length should be reduced for donor–acceptor polymers compared to homopolymers. The above results regarding the success of the donor–acceptor concept are therefore surprising from a theoretical point of view. Since understanding of all of the factors controlling band gaps and bandwidths is important for designing new conducting polymers, we investigated oligomers of CDM, EDOT, and CDM/EDOT theoretically. The aim is to determine whether the donor–acceptor concept is indeed useful for improving electrical properties of conducting polymers.

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CHART 1



Methods

Monomer through pentamer of CDM, monomer through octamer of EDOT, and monomer through trimer of CDM/EDOT were optimized using density functional theory (DFT). Becke's three-parameter hybrid functional⁸ was combined with Perdew and Wang's correlation functional.⁹ Stevens–Basch–Krauss pseudopotentials¹⁰ and split valence plus polarization basis sets were employed.¹⁰ The weight of the Hartree–Fock exchange was increased to 30% since this type of functional yields highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gaps in close agreement with λ_{\max} values from UV spectroscopy.¹¹ IPs and EAs show a consistent error, but trends are reproduced correctly.

Polymer properties were evaluated by plotting data for oligomers with increasing chain length against $1/n$, n being the number of repeat units. The data were extrapolated using second-degree polynomial fits. All calculations were performed with Gaussian 98 Windows and UNIX versions.¹² Orbital contours were plotted with the g-openmol program.¹³

Results

Figure 1 shows the correlation of the energy levels of *cis*-bithiophene, CDM, and dicyanoethylene. All three molecules belong to the C_{2v} point group, and the π -orbitals have either A2 or B1 symmetry. The HOMO of dicyanoethylene has B1; the HOMO and HOMO-1 of bithiophene have A2 symmetry. The highest lying A2 orbital of dicyanoethylene is the HOMO-1

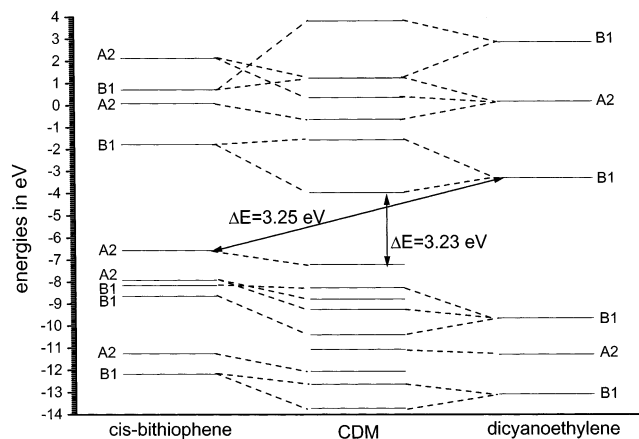


Figure 1. Orbital correlation diagram for the π -orbitals of *cis*-bithiophene, CDM, and dicyanoethylene.

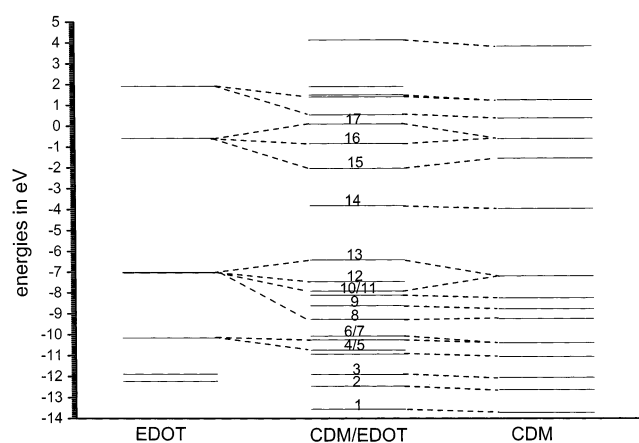


Figure 2. Orbital correlation diagram for the π -like orbitals of EDOT, CDM/EDOT, and CDM.

with an energy of -11.30 eV. The HOMO energy of bithiophene is -6.59 eV. Because of this large energy difference, there is no interaction between the HOMO or HOMO-1 of bithiophene and the dicyanoethylene group. Hence, the HOMO of CDM is similar to that of bithiophene.

The LUMOs of bithiophene and of dicyanoethylene have B1 symmetry but also quite different energies, -1.78 eV vs -3.32 eV. The result is an interaction that produces two new orbitals that lie only slightly above and below the original ones. The electron density in the LUMO of CDM is highest on the center part, carrying the dicyanoethylene group. The coefficients at the α -carbon atoms are small in the LUMO. CDM itself is a donor-acceptor system with an IP close to that of bithiophene and an EA close to that of dicyanoethylene. Note that there is almost no decrease in energy gap in CDM compared to the energy difference between the HOMO of bithiophene and the LUMO of dicyanoethylene.

Figure 2 shows energy levels for EDOT, CDM/EDOT, and CDM. In Figure 3 selected orbitals of CDM/EDOT are plotted. EDOT has C_2 symmetry. CDM/EDOT has no symmetry since the ethylenedioxy group is twisted out of the molecular plane. Although symmetry does not enforce planarity for EDOT and CDM/EDOT oligomers, the backbones were found to be planar with full geometry optimizations. In a hypothetical fully planar CDM/EDOT, 23 p -orbitals would give rise to 23 π -molecular orbitals. With twisted ethylenedioxy groups, local π -symmetry is clearly visible for 21 orbitals (Figure 3). The frontier orbitals

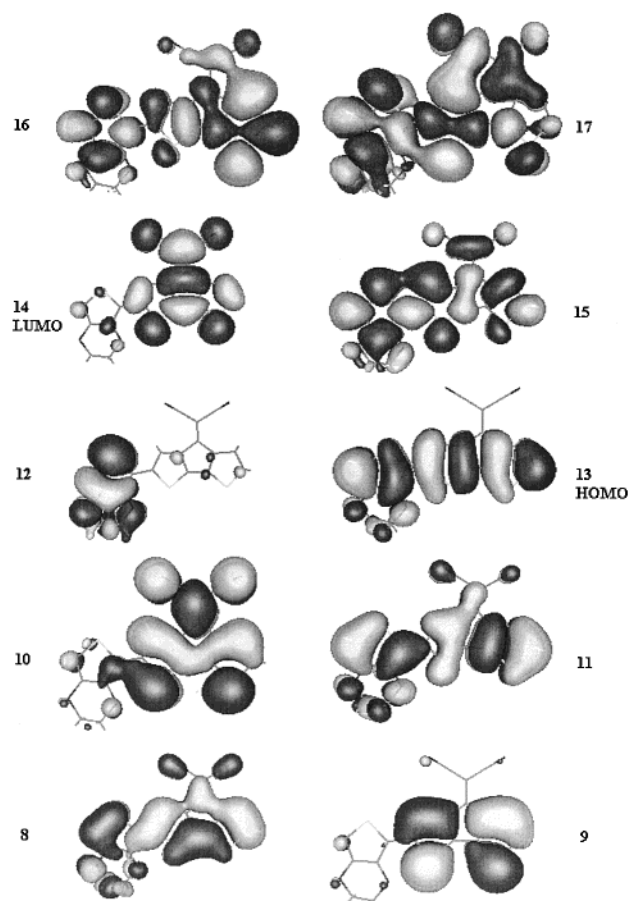


Figure 3. Orbital contour plots for the 6 highest occupied MOs and the 4 lowest unoccupied MOs of the CDM/EDOT monomer.

of CDM/EDOT could be correlated with those of EDOT and CDM. High and low lying orbitals of CDM mix significantly with EDOT σ -orbitals. For these orbitals assignment is difficult and is not indicated in Figure 2.

The HOMO and HOMO-1 of EDOT are shifted up in energy compared to those of thiophene and are almost degenerate. The HOMO and HOMO-1 of EDOT are close in energy to the HOMO of CDM (7.21 and 7.01 eV). The HOMO-1 of EDOT is similar to that of thiophene, the HOMO of CDM is virtually identical to that of bithiophene. Strong interaction between these two orbitals leads to HOMO and HOMO-2 of CDM/EDOT. Orbitals 13 and 11 (compare Figure 3) are very similar to HOMO and HOMO-2 of terthiophene. The HOMO of EDOT does not interact with CDM (compare orbital 12 in Figure 3) and becomes HOMO-1 in CDM/EDOT.

The LUMOs of EDOT and CDM differ in energy by 3.4 eV and do not interact appreciably, although symmetry would allow such an interaction. Orbital plot 14 (Figure 3) confirms that there is little electron density on EDOT in the LUMO of CDM/EDOT. In contrast, the LUMO of EDOT interacts strongly with the LUMO+1 through the LUMO+3 of CDM. The resulting MOs are of similar character as the LUMO and LUMO+1 of bithiophene.

Figure 4 shows band formation upon chain length increase for CDM/EDOT. The HOMO of CDM/EDOT gives rise to a band (compare the lowest three MOs in Figure 5) that is similar in position and has character similar to that of polybithiophene.¹⁴ The low lying LUMO level forms a "band" with almost no dispersion and the EA increases by only 0.1 eV upon polymerization. There is very little electron density on EDOT in the

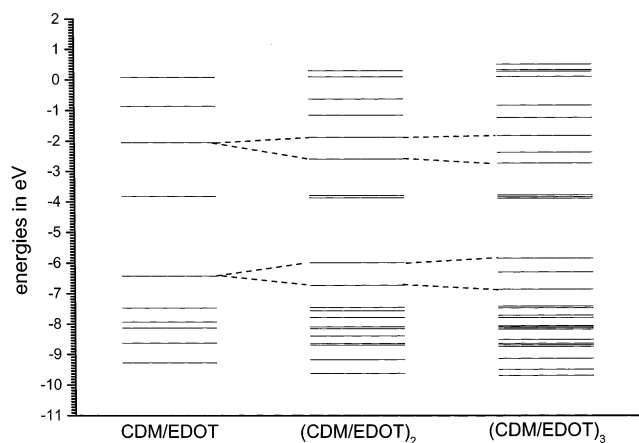


Figure 4. Energy levels for monomer, dimer, and trimer of CDM/EDOT. Onset of band formation is indicated by dashed lines.

conduction “band” (MOs 4–6 in Figure 5). Therefore, it seems more appropriate to consider these to be localized levels rather than a band. A true band forms involving the LUMO of EDOT and the LUMO+1 of CDM. Comparison with energy levels of polybithiophene¹⁴ shows that the resulting band lies 0.3 eV higher in energy than the conduction band of polybithiophene and has similar dispersion. Orbital contour plots (MOs 7–9 in Figure 5) confirm the similarity of this band with the conduction band of polybithiophene.¹⁴ PCDM/EDOT, therefore, appears to be a substituted polybithiophene with low-lying unoccupied localized energy levels within the band gap.

In Table 1, DFT orbital energies of HOMOs and LUMOs and of orbitals leading to upper and lower valence and conduction band edges are compared for oligomers of CDM, EDOT, and CDM/EDOT. The data are ordered according to matching numbers of thiophene rings and not according to number of repeat units, since the sizes of the repeat units differ. In the last three lines extrapolated values for band edges, IPs, EAs, band gaps, and for valence and conduction bandwidths are given. Extrapolations are done with second-degree polynomial fits. For some of the data the dependence on inverse chain lengths is close to linear but correlation improved with polynomial fitting compared to linear fitting for all data. Correlation coefficients are 0.999 or better. Bandwidths of EDOT were evaluated using the EDOT dimer as the repeat unit, so that the bandwidths can be compared to those of PCDM.

IP and EA of PCDM are high, 6.36 and 4.55 eV. IP and EA of PEDOT are low, 4.38 and 2.34 eV. The IP of PCDM/EDOT is 5.58 eV, the EA is 3.94 eV. Extrapolated band gaps are 1.81, 2.06, and 1.64 eV for PCDM, PEDOT, and PCDM/EDOT, respectively. Thus, the band gap of the copolymer is 0.15 eV smaller than that of PCDM and 0.42 eV smaller than that of PEDOT. PCDM and PEDOT have similar valence bandwidths, the valence bandwidth of the copolymer is smaller, but this is mainly due to the larger repeat unit, containing three rather than two thiophene rings. EDOT has a wide conduction band, but PCDM and the copolymer have very narrow conduction bands. Again, the decrease in conduction bandwidth of the copolymer compared to PCDM can be attributed to its larger repeat unit.

The theoretical 2.06 eV band gap for PEDOT matches λ_{\max} from absorption spectroscopy, which is reported to be between 2.00 and 2.15 eV.^{15–25} The onset of absorption lies between 1.5 and 1.7 eV.^{15–17,20,22–24,26} The electrochemical band gap is still smaller, 1.2 eV.¹⁴ Thus, there is a difference of 0.3–0.5 eV between optical and electrochemical band gap and a difference of almost 1 eV between λ_{\max} and the electrochemical

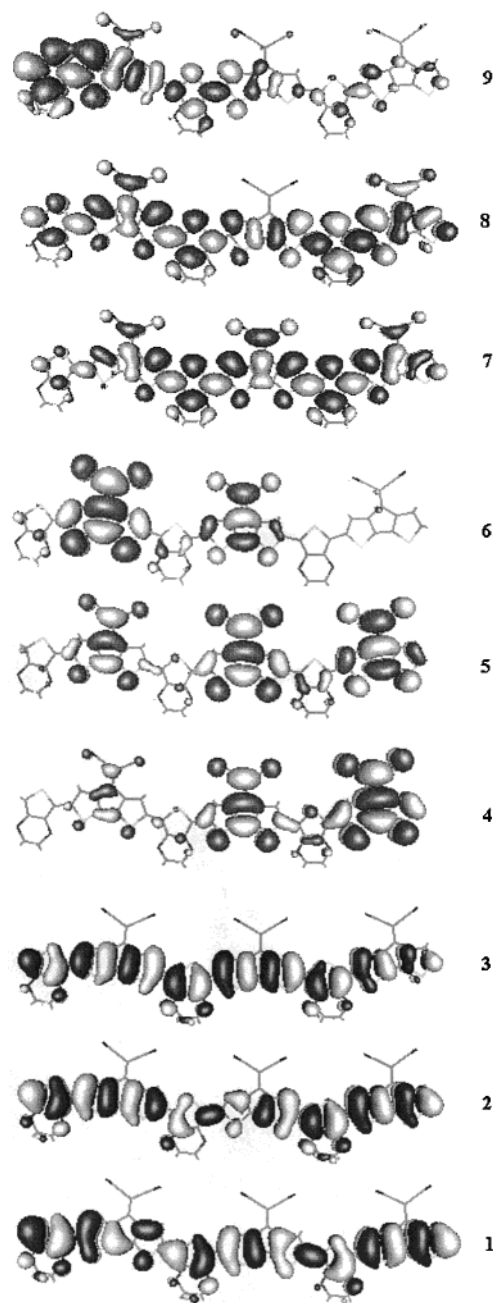


Figure 5. Orbital contour plots of the 3 highest occupied and the 6 lowest unoccupied MOs of the CDM/EDOT trimer. Since a band contains as many levels as the polymer has repeat units, there are only three levels per “band” in the trimer. The first three MOs correspond to the valence band, the second three levels to the localized states in the band gap, and the third three levels to the conduction band of PCDM/EDOT.

band gap for PEDOT. For polythiophene optical and electrochemical band gaps differ by only 0.2 eV.²⁷

For PCDM electrochemical and optical band gaps match. The experimental value is 0.8 eV.^{2,3} Our theoretical estimate for λ_{\max} is 1.81 eV. If λ_{\max} and the onset of absorption of PCDM differ by about 0.30–0.65 eV, like those of EDOT, we are overestimating the band gap by 0.36–0.71 eV. The origin for the larger error in the PCDM calculations is not clear. Our λ_{\max} value for the copolymer is 1.64 eV, the electrochemical band gap would therefore be around 1 eV. Huang and Pickup¹ found band gaps ranging from 0.33 to 0 eV for EDOT rich copolymers. The band gap decreased with the increasing amount of EDOT.

TABLE 1: HOMO (H) and LUMO (L) Energies and Energy Levels Leading to Valence and Conduction Band Edges upon Extrapolation^a

no. of rings	CDM				EDOT				CDM/EDOT			
	edge	H	L	edge	edge	H	L	edge	edge	H	L	edge
1						-7.01	-0.58					
2	-7.21	-7.21	-3.98	-3.98	-6.00	-6.00	-1.32	-1.32				
3						-5.53	-1.63		-6.42	-6.42	-3.83	-3.83
4	-7.89	-6.72	-4.19	-4.15	-6.37	-5.26	-1.80	-0.81				
5						-5.10	-1.91					
6	-8.17	-6.55	-4.34	-4.19	-6.50	-4.99	-1.97	-0.61	-6.73	-5.99	-3.88	-3.80
8	-8.32	-6.48	-4.40	-4.22	-6.55	-4.84	-2.05	-0.49				
9									-6.86	-5.85	-3.90	-3.79
10	-8.41	-6.45	-4.44	-4.23								
∞	-8.79	-6.36	-4.55	-4.30	-6.73	-4.38	-2.34	-0.13	-7.15	-5.58	-3.94	-3.77
E_g		1.81				2.06				1.64		
B_w	2.43		0.25		2.35		2.19		1.57		0.17	

^a Extrapolated band gaps and band width for CDM, EDOT, and CDM/EDOT. All values in eV.

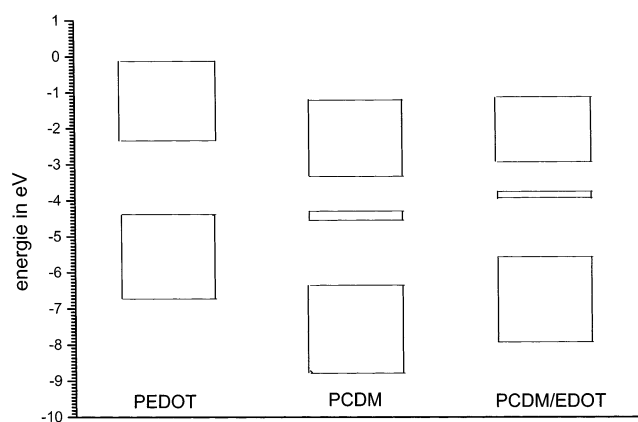


Figure 6. Extrapolated valence and conduction bands of PEDOT, PCDM, and PCDM/EDOT. The valence band of PEDOT bridges the energy gap of PCDM. Nonetheless, the copolymer PCDM/EDOT has an only slightly smaller band gap than PCDM. The conduction “bands” of PCDM and PCDM/EDOT are very flat and are better considered to be localized states within the band gap.

Discussion

The donor–acceptor concept suggests that copolymers made of alternating electron donors and acceptors should have lower band gaps and wider bandwidths than either of the corresponding homopolymers.⁵ The reasoning is that the IP of the copolymer should be close to the low IP of the polymer of the electron donor and that the EA of the copolymer should be close to the high EA of the polymer of the electron acceptor. The small band gap and high intrinsic conductivity of PCDM/EDOT were attributed to the donor–acceptor concept.¹ Figure 6 compares calculated bands of PEDOT, PCDM, and the copolymer. Bandwidths of the copolymer are multiplied by $3/2$ to remove the bandwidths decrease that is caused solely by the larger size of the repeat unit of the copolymer. IPs and EAs of PEDOT and PCDM differ by 1.98 and 2.21 eV, respectively. In fact, the EA of PCDM is larger than the IP of PEDOT. If the band edges would shift little for the copolymer, PCDM/EDOT would be a synthetic metal. We think, however, that it is incorrect to consider a copolymer to consist of two homopolymers. A copolymer consists of the repeat units of the two homopolymers and band development upon chain length increase depends on the properties of and interactions between the repeat units. These repeat units are CDM and EDOT monomers.

IPs of EDOT and CDM are close in energy, 7.01 and 7.21 eV. Therefore, the valence band is not expected to exhibit donor–acceptor character. The closeness of IPs of CDM and

EDOT is a coincidence. EDOT has a low IP compared to thiophene because of the presence of electron-donating oxygen atoms. CDM has an IP close to that of EDOT because of two competing factors: it contains two thiophene rings, which decreases the IP, and it is substituted with the dicyanoethylene group, which increases the IP.

The valence band of PCDM/EDOT that is formed from the strongly interacting HOMO levels with similar energies looks perfectly comparable to those of polythiophene, PEDOT, and PCDM. The somewhat smaller bandwidth, 1.57 eV, in the copolymer compared to 2.36 eV in PEDOT can be accounted for by the larger size of the repeat unit (three rather than two thiophene rings). A crude estimate by multiplying the copolymer bandwidth by $3/2$ (as done in Figure 6), gives a bandwidth of 2.36 eV and shows that the bandwidths are equivalent if the polymers are treated on equal footing.

EAs of EDOT and CDM differ considerably, 0.58 eV vs 3.98 eV. Thus, a donor–acceptor type interaction is to be expected for the conduction band. According to the donor–acceptor concept, this should give rise to a low-lying wide band. According to second-order perturbation theory, the two levels should hardly interact and a flat band at approximately 3.98 eV, the EA of the monomer, should be found. Data in Table 1 and Figure 4 confirm that the latter is the case. The extrapolated EA of PCDM/EDOT is 3.94 eV, the width of the conduction “band” is only 0.17 eV. Compared to CDM, the LUMO levels of the oligomers are slightly pushed up and decrease in energy by only 0.1 eV upon polymerization.

Figure 6 shows that the conduction band is already narrow in PCDM. The reason is that PCDM itself is a donor–acceptor system consisting of *cis*-bithiophene and dicyanoethylene. Figures 1–3 illustrate how the difference in orbital energies between *cis*-bithiophene and dicyanoethylene leads to charge localization in CDM and how this results in virtually zero electron density on EDOT in the LUMO of CDM/EDOT. The donor–acceptor character of the LUMO of CDM/EDOT leads to localized states rather than to a band upon polymerization. Above these localized levels, a band similar to the conduction band of polybithiophene forms. These are the additional bands shown in Figure 6 for PCDM and PCDM/EDOT. The small “band” gap of the PCDM/EDOT copolymer is due to a combination of a normal valence band with no donor–acceptor character and the presence of low lying localized states within the band gap.

The problem with the donor–acceptor concept is the following. Band gaps of polymers can be considered to depend on two factors: the first factor is the size of the HOMO–LUMO

gap in the monomer, the second factor is the shift of the HOMO and LUMO levels upon polymerization. The donor–acceptor concept can be used to decrease the HOMO–LUMO gap of the monomer. If IPs and EAs of the donor and acceptor are sufficiently different, the corresponding orbitals do not interact much. In such a case, IP and EA of the donor–acceptor repeat unit, are close to the IP of the monomeric donor and to the EA of the monomeric acceptor. Such a repeat unit has a small HOMO–LUMO gap. CDM/EDOT, for instance, has a smaller HOMO–LUMO gap than terthiophene, 2.59 eV vs 4.00 eV. However, the second factor, which is responsible for the decrease of the energy gap upon chain length increase, is adversely affected by donor–acceptor substitution. Since orbitals with very different energies will also not interact strongly upon polymerization, the energy gap decrease upon chain length increase and the resulting bandwidth of the copolymer must be smaller than for homopolymers. These considerations are in perfect agreement with experimental findings on PCDM/EDOT¹ and other donor–acceptor systems²⁸ and confirm that the donor–acceptor concept does not lead to small band gaps and wide bands at the same time.

The band gap of PCDM/EDOT is decreased compared to those of the homopolymers, since the valence band does not have donor–acceptor character. EDOT units push the upper valence band edge up but do not shift the lower conduction band edge due to lack of interaction between the LUMOs of EDOT and CDM. If there was such an interaction, the conduction band would be pushed up due to the EDOT units and the band gap would be about average between those of the homopolymers. The band gap reduction compared to PCDM is rather small because there is almost no increase in EA with increasing chain length. Thus, the donor–acceptor concept can lead to band gap reduction in special cases where only one of the bands has donor–acceptor character or where there is almost no energy difference between IP and EA of *monomers* of donor and acceptor. A copolymer of the latter two having two narrow “bands” would be useless as a conductor, since carrier mobility would be low in both bands. If only one band is sacrificed to produce localized states, conduction is still possible in the other band.

The experimental results¹ for PCDM/EDOT are in agreement with the above analysis. Copolymers are electrochemically found to have smaller band gaps than either PCDM or EDOT. The band gap decreases with the increasing content of EDOT. Our calculations agree with this, since copolymerization CDM and EDOT decreases the EA compared to CDM by only 0.6 eV whereas it decreases the IP by 1.98 eV. Hence, increasing the amount of EDOT will result in a smaller band gap. However, since the HOMO of an EDOT rich copolymer would lie lower than that of PEDOT (4.38 eV) and the LUMO would lie a little higher than that of the 1:1 copolymer (3.94 eV), a zero difference in λ_{\max} appears to be impossible. Since the band gap is smaller than λ_{\max} , a zero band gap seems plausible. The experimentally observed 5 orders of magnitude increase in intrinsic conductivity of the copolymer compared to PCDM can thus be attributed to a vanishingly small band gap. However, the mobility of n-type carriers was found to be about 500 times less than that of the p-type carriers. This is due to the lack of dispersion of the conduction “band”. The intrinsic conductivity of PCDM/EDOT is almost exclusively due to movement of holes in the valence band. Conductivity upon p-doping was determined to be 0.5 S/cm, which is no improvement over that of polythiophene or of PEDOT, which have conductivities up to 2000²⁹ and 600 S/cm,^{4,15,22,25,26,30,31} respectively.

Thus, the CDM/EDOT copolymer turns out to be a hybrid of a normal conducting polymer with a wide valence band and a donor–acceptor polymer with vanishingly small dispersion of its conduction band. This combination of strong interactions in one band and weak interactions in the other one can be used to design a kind of self-doped system, in which the “band” gap is so small that the low lying localized states can act as acceptor levels. One might speculate whether a system could be constructed with relatively high lying localized donor states that can provide electrons for the conduction band and lead to n-type conductivity. The starting point would have to be a system with high IP and EA because otherwise stability problems would have to be expected.

Conclusions

Theoretical results regarding band gap and bandwidths of copolymers of CDM and EDOT agree with electrochemical properties of PCDM/EDOT. The copolymer has a wide valence band that gives rise to p-type conductivity. The IP of PCDM/EDOT is average between those of PCDM and PEDOT. The actual conduction band of the copolymer lies 0.3 eV higher than that of polythiophene and has similar dispersion. n-doping, however, reduces localized states that lie in the band gap. These states are localized on the central ring of CDM. They do not interact, they do not form a band, and therefore n-doping of these states does not result in n-type conductivity.

Although PCDM/EDOT was presented as a success story for the donor–acceptor concept, we believe that this polymer gives further evidence to our claim that the donor–acceptor concept cannot be used to design organic conductors with small band gaps and wide bands. The more the energy levels of the donor and the acceptor differ in energy, the less they interact. The smaller the interaction, the smaller the energy gap decrease and bandwidth increase with increasing chain length. That PCDM/EDOT has a small band gap and is a p-type conductor is due to the fact that only the conduction band has donor–acceptor character but not the valence band. Otherwise PCDM/EDOT would be a small band gap insulator.

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