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ORIGINAL PAPER

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Does the donor–acceptor concept work for designing synthetic metals?

III. Theoretical investigation of copolymers between quinoid acceptors and aromatic donors

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Abstract Homopolymers of quinoxaline (QX), benzothiadiazole (BT), benzobisthiadiazole (BBT), thienopyrazine (TP), thienothiadiazole (TT), and thienopyrazinothiadiazole (TTP) and copolymers of these acceptors with thiophene (TH) and pyrrole (PY) were investigated with density functional theory. Theoretical band-gap predictions reproduce experimental data well. For all but six copolymers, band-gap reductions with respect to either homopolymer are obtained. Four of the acceptors, BBT, TP, TT, and TTP, give rise to copolymers with band gaps that are smaller than that of polyacetylene. BBT and TTP copolymers with PY in 1:2 stoichiometry are predicted to be synthetic metals. Band-gap reductions result from upshifts of HOMO energies and much smaller upshifts of LUMO values. The smallest band gaps are predicted with TTP, since changes in LUMO energies upon copolymerization are particularly small. The consequence of the small interactions between LUMO levels of donor and acceptor are vanishingly small conduction bandwidths.

Keywords Conducting polymers · Donor–acceptor concept · Band gap · Band width · Conductivity · DFT

Introduction

Since the discovery of conducting organic polymers (COPs) in 1977, [1] enormous progress has been made in tailoring properties of COPs through chemical modification [2, 3]. One of the goals is decreasing band gaps, since zero-band-gap systems would be synthetic metals with intrinsic conductivity. Most COPs have band gaps between 1 and 4 eV and are semiconductors [4, 5]. Systems with band gaps above about 0.5 eV are insulating in their neutral ground state and require doping to conduct electricity. In general, oxidizing or p-doping is easier than reducing or n-doping. Thus, stable p-doped COPs with high conductivity are common. In contrast, n-doped polymers tend to loose electrons and show lower conductivities [6, 7]. To make organic transistors, materials that can be p- and n-doped are desirable. Therefore, there is interest in lowering conduction band energies of COPs, since n-type conductors as well as synthetic metals could be produced in this way. Tanaka, Yamashita, Yammamoto, and their coworkers [8–17] have succeeded in designing a series of low-band-gap materials with large electron affinities (EAs) by copolymerizing quinoxaline (QX), [8, 11, 14] benzothiadiazole (BT), [12, 14] benzobisthiadiazole (BBT), [12, 14] thienopyrazine (TP), [10, 14] thienothiadiazole (TT), [9, 12] and thienopyrazinothiadiazole (TTP) [17] (Scheme 1) with thiophene (TH) and pyrrole (PY) (Schemes 2 and 3). The smallest band gaps were achieved with BBT and TTP in combination with PY. Poly-PY-TTP-PY (Scheme 3) has no electrochemical band gap [17].

All acceptors shown in Scheme 1 have small HOMO-LUMO gaps, even as monomers. Their ionization potentials (IPs) are relatively close to that of thiophene but their EAs are much higher than those of thiophene or pyrrole. Therefore copolymers with thiophene and pyrrole were classified as donor–acceptor polymers [18]. The six acceptors can be divided into two groups. QX and BT adopt aromatic structures. Homopolymers of TP, TT, BBT, and TTP prefer quinoid conformations. In the quinoid form, rearrangement of the double bonds allows the sulfur atoms to form two single bonds with nitrogen and avoid the unfavorable non-classical structure with two double bonds between S and N. In this way the thiadiazole group forces the ring attached to it out of its preferred aromatic conformation. The strong preference for quinoid structures leads to a geometrical mismatch in copolymers with aromatic systems like thiophene and pyrrole. Since quinoid and aromatic polymers have their positions of single and double bonds reversed, copolymerization of quinoid and

Dedicated to Professor Dr. Paul von Ragué Schleyer on the occasion of his 75th birthday

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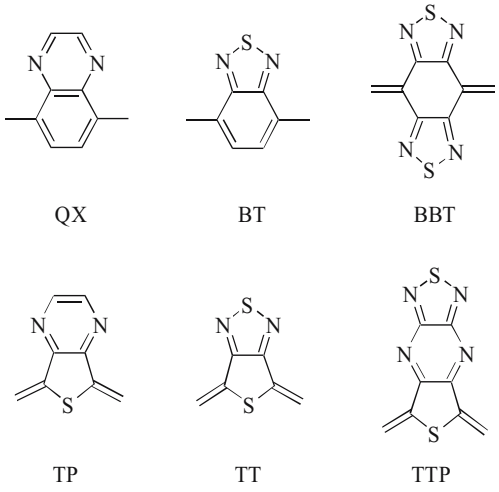


Scheme 1 Quinoxaline (QX), benzothiadiazole (BT), benzobisthiadiazole (BBT), thienopyrazine (TP), thienothiadiazole (TT), and thienopyrazinothiadiazole (TTP) monomers, shown in the conformation that is preferred in the polymers

aromatic units tends to reduce bond length alternation (BLA). Since BLA is one of the factors that increase band gaps, [2, 3] reduction of BLA could also contribute to the band-gap reductions observed for the copolymers [19]. The present investigation was carried out with the aim to analyze the electronic structures of these interesting systems and to evaluate the factors responsible for the band-gap reductions.

Materials and Methods

Theoretical level

Homo and cooligomers with between 1 and 8 repeat units shown in Schemes 2 and 3 were investigated. The necessary chain lengths were determined by the convergence properties. Cooligomers are named by using abbreviations of their names in the sequence of their connection. The calculations were carried out with density functional theory as implemented in Gaussian 98, revision A11 [20] and Gaussian 03, revision C.02 [21]. We used Becke's three-parameter hybrid functional [22] with Hartree-Fock exchange increased to 30% and Perdew's 86 [23] correlation functional. (The keywords to create this functional are: "BP86 IOP (5/45=10000300, 5/46=07200700, 5/47= 08101000, 5/42=406)" in G98 and "BP86 IOP (3/76=1000003000, 3/77=0720007000, 3/78=0810010000, 3/ 74=406)" in G03). Stevens Basch Krauss pseudopotentials [24] combined with polarized split-valence basis sets were employed throughout for all atoms (except hydrogen).

Structure determination

The thiadiazole unit is sometimes described as "non-classical" employing two double bonds between N and S. Such structures have been shown to be very unfavorable in a recent experimental and theoretical investigation [25]. In agreement with this conclusion, we find a high zwitterionic character in monomers of TT, BBT, and TTP. Adopting quinoid structures in the polymers relieves the unfavorable bonding situation between N and S that exists in the monomers. Therefore, oligomers that are terminated with H may be singlet biradicals and closed-shell calculations may lead to severe underestimation of the energy gaps. For such systems we performed closed- and open-shell calculations on oligomers end-capped with H, and closed-shell calculations on oligomers end-capped with CH2 groups. Open-shell calculations were carried out with the same functional as specified above in combination with the "guess=mix" keyword in G98 and G03.

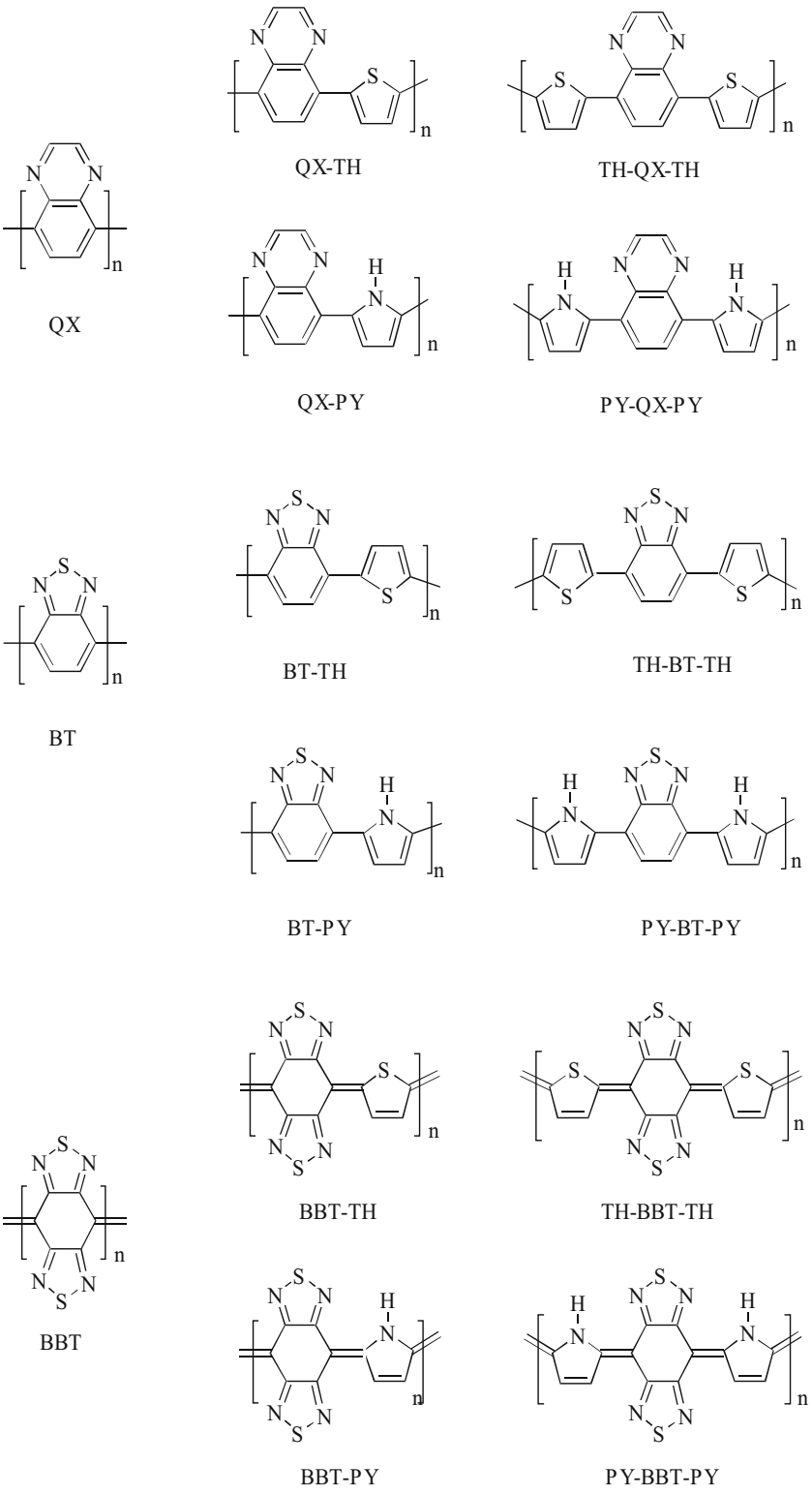
To determine whether quinoid or aromatic structures are preferred, energy differences were evaluated for fully optimized monomers and dimers end-capped with H and with CH_2. The energy of the inner fragment was estimated by subtracting energies of monomers from those of dimers. The procedure is shown in Scheme 4 for quinoxaline. In this way, the energies of the different end groups are removed. The lower-energy inner fragment (quinoid or aromatic) was used as repeat unit and the oligomers were terminated with the appropriate end-groups. Additional indications of the correct geometry are the bond lengths in the inner part of longer oligomers and speed of convergence of properties. Since end effects do not reach very far, inner fragments switch to the preferred conformation upon geometry optimization as the chain length increases. This is reflected in bond-length changes with increasing chain lengths if the wrong form is used. Switching to a different geometry is accompanied by discontinuities and slow convergence of IPs, EAs, and energy gaps.

In copolymers with pyrrole, the orientation of the pyrrole rings is fixed into the *trans* position by hydrogen bridges between the pyrrole N-H group and the nitrogen atoms of the acceptors. With thiophene, *cis* or *trans* forms are possible. We have checked the preference for the monomers and used the more stable conformation throughout. As a result, 1:1 copolymers with a *cis*-preference are non-linear and polymers would be helical. The relatively short oligomers considered here are planar. In 1:2 stoichiometry, the copolymers are linear since the adjacent thiophene rings adopt the *trans* conformation. Band gaps of *cis*- and *trans* forms are almost identical. The more stable conformers have slightly higher IPs and EAs. The differences are in the range of 0.1 eV.

Extrapolation

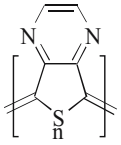
Polymer properties were obtained by extrapolation of oligomer data for increasing chain lengths. Geometries of all oligomers were fully optimized with appropriate symmetry constraints. It is common to employ linear fits using a couple of data points plotted vs inverse chain length [26]. Fig. 1. shows plots of HOMO-LUMO gaps and of time-dependent Hartree-Fock (TDHF) excitation energies vs

Scheme 2 Copolymers of QX, BT, and BBT with thiophene (TH) and pyrrole (PY) in 1:1 and 1:2 stoichiometry

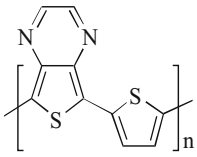


inverse chain lengths for oligomers of acetylene, thiophene, and pyrrole with up to 80 double bonds. The dependence is non-linear at either level of theory and saturation is reached for long oligomers. It is therefore evident that linear fitting will lead to different results depending on the number of data points and on the lengths of the oligomers. Therefore, it appears better to calculate oligomers of increasing size until the onset of saturation is reached and to fit only the data for the longest oligomers. We employ polynomial fitting to account for the saturation in the infinite-chain-length limit. In general, our longest oligomers have HOMO-LUMO gaps that are only 0.2–

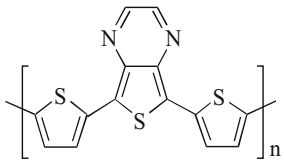
Scheme 3 Copolymers of TP, TT, and TTP with thiophene (TH) and pyrrole (PY) in 1:1 and 1:2 stoichiometry



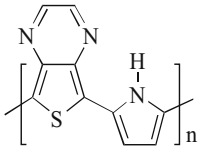
TP



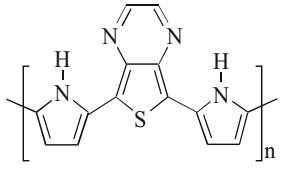
TP-TH



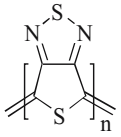
TH-TP-TH



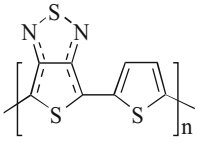
TP-PY



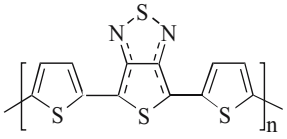
PY-TP-PY



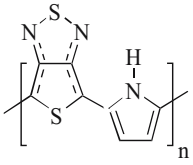
TT



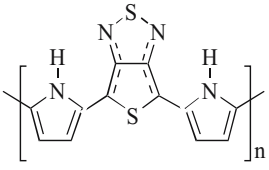
TT-TH



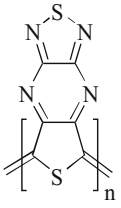
TH-TT-TH



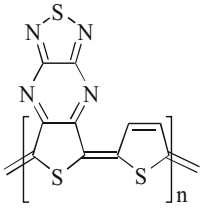
TT-PY



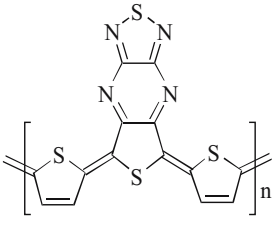
PY-TT-PY



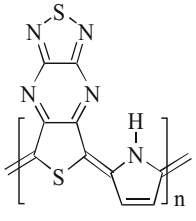
TTP



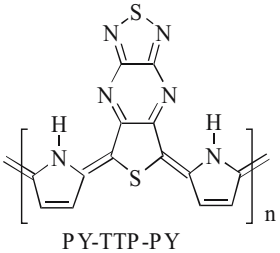
TTP-TH



TH-TTP-TH

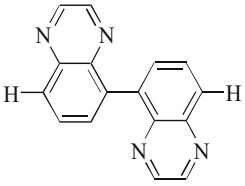


TTP-PY

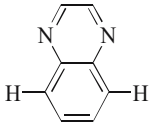


PY-TTP-PY

Scheme 4 Determination of the preferred conformation of a polymer from oligomer calculations. Monomers and dimers are calculated in aromatic and quinoid conformation. Energies of end groups are removed by subtracting total energies of monomers from those of dimers. The form with the lower energy difference is the preferred conformation

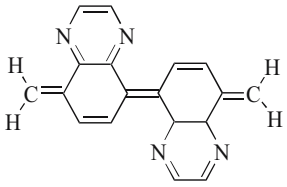


E = - 138.369957 au

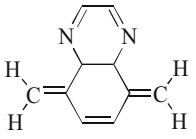


E = - 69.810712 au

ΔE = -68.559245 au



E = -151.063819 au



E = - 82.523041 au

ΔE = -68.540778 au

ΔΔE = -0.018467 au = -11.59 kcal mol^{-1}

0.4 eV larger than the extrapolated values. Therefore, little error is introduced due to extrapolation.

Accuracy of the band gaps

The accuracy of DFT HOMO-LUMO gaps for predicting band gaps of conducting polymers has been studied in detail by one of us [27–30]. With the above functional, HOMO-LUMO gaps give reasonable estimates for λ_{max} in gas-phase spectra of medium-sized polyenes. HOMO-LUMO gaps converge to a limiting value of 1.7 eV for polyacetylene in the gas phase. The same value is obtained with one-dimensional periodic boundary calculations. More accurate time-dependent Hartree-Fock (TDHF) calculations lead to a limiting value of 2.2 eV. Polyenes are the only systems for which experimental gas phase data are available. In solution the excitation energies are about

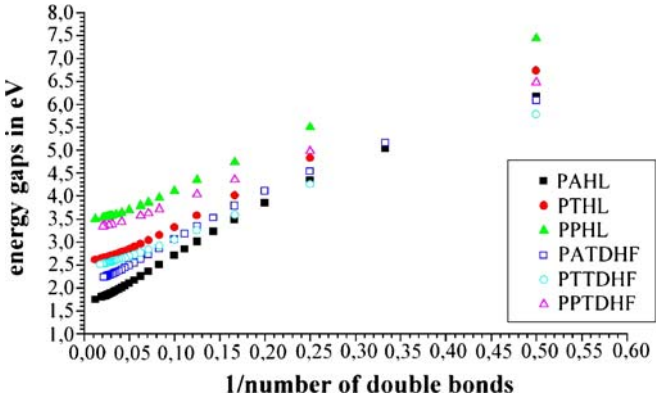


Fig. 1 DFT HOMO-LUMO gaps (*filled symbols*) and TDHF excitation energies (*open symbols*) in electron volts (eV) for acetylene, thiophene and pyrrole oligomers with up to 80 double bonds plotted vs. inverse number of double bonds

0.3–0.4 eV lower [31]. In the solid-state inter-chain interactions lower the lowest excitation energy due to Davydov splitting compared to solution data. The exact amount of Davydov splitting in the long-chain limit is unknown but it is predicted [32] be smaller than for medium-sized thiophene oligomers, which show Davydov splittings of about 0.4 eV and lowering of the lowest excitation energies of 0.1–0.2 eV [33]. Since the lowering of excitation energies due to Davydov splitting is small, we do not consider it here. Thus, from experiment we deduce that gas-phase values should be around 0.4 eV higher than solution data. λ_{max} of PA films occurs at 1.9 eV [34, 35]. TDHF, which gives a gas-phase value of 2.2 eV, is therefore quite accurate but HOMO-LUMO gaps underestimate λ_{max} of PA by about 0.7 eV.

There are no gas-phase data for thiophene and pyrrole oligomers and for the systems shown in Schemes 2 and 3. We assume therefore that solvent effects are the same as for polyenes, ~0.4 eV. Comparison between RT solutions and low-temperature solid solutions of thiophene oligomers [36–38] showed that thiophene oligomers are non-planar in liquid solution. Cooling leads to a lowering of the excitation energies by about 0.4 eV. Cooling has no such effect on polyene spectra. Thus, at room temperature, effects due to solvent and non-planarity cancel roughly for thiophene oligomers. This is reflected in the fact that TDHF reproduces excitation energies of thiophene oligomers in RT solution very accurately. The limiting values in the long-chain limit are 2.5 eV at the TDHF level and 2.6 eV with DFT HOMO-LUMO gaps. λ_{max} of PT occurs at 2.5–2.6 eV [39, 40]. Thus, both levels of theory agree nicely for PT and are close to experiment. The error is thus much smaller than for PA. λ_{max} of polypyrrole (PPy) converges to 3.3 eV with TDHF and to 3.5 eV with DFT HOMO-LUMO gaps. Since pyrrole oligomers are non-planar in the gas phase, effects of non-planarity should cancel solvent

effects roughly. Therefore, HOMO-LUMO gaps overestimate λ_{max} by 0.3 eV (3.5 vs. 2.9–3.2 eV [40, 41]). Thus, the overall accuracy of DFT HOMO-LUMO gaps is about ±0.3 eV for aromatic polymers. Since the systems investigated here are ring systems and since they are planar, we expect that HOMO-LUMO gaps overestimate condensed-phase values of oligomers by about 0.4 eV. This correction is applied when theory and experiment are compared.

Experimental band gaps are obtained as differences between oxidation and reduction potentials or as the onset of optical absorptions. For many polymers, both coincide. [42] Onset of absorption and λ_{max} usually differ by about 0.5 eV [34, 39, 43]. Adding the correction for the solvent effect of 0.4 eV, our HOMO-LUMO gaps should be about 0.9 eV higher than experimental band gaps. We will refer to the theoretical estimates as HOMO-LUMO or *energy* gaps in order to distinguish them from experimental *band* gaps. When a comparison is made, 0.9 eV is subtracted from the theoretical gas-phase values.

IPs and EAs

IPs and EAs are obtained as negative HOMO and LUMO energies, respectively. Using Koopmans' theorem [44] in connection with density functional theory (DFT) is controversial [29, 45–50] but experience shows that LUMO energy levels are much better approximations to EAs than virtual orbital energies obtained with the HF approximation [48]. In contrast HOMO energies are too high to give good IPs. The error is about 1 eV and similar for HOMO and LUMO, which is the reason for the good energy gaps [29]. The error is also roughly the same for different systems. Therefore, we will use HOMO and LUMO energies chiefly to compare IPs and EAs of homo- and copolymers. We will not try to produce absolute values.

Results

Quinoxaline QX

Quinoxaline oligomers prefer aromatic structures. The energy difference ΔΔE obtained by subtracting the energy differences between dimer and monomer in aromatic conformations end-capped with H and in quinoid conformations end-capped with CH_2 (Scheme 4), is 11.59 kcal mol^{-1} in favor of the aromatic form. Since TH and PY oligomers prefer aromatic structures as well, all copolymers are assumed to be aromatic and only closed-shell calculations were performed. With pyrrole, hydrogen bridges between pyrrole hydrogen and quinoxaline nitrogen atoms determine the orientation of the rings. With thiophene, the opposite orientation of the rings is conceivable. Geometry optimizations show, however, that the structures in Scheme 2 are preferred by 0.35 kcal mol^{-1} for the 1:1 and by 1.1 kcal mol^{-1} for the 1:2 monomer. The effect on the energy gap is below 0.1 eV.

Energy gaps, IPs and EAs for the oligomers of the QX series are summarized in Table 1. The extrapolated energy gap of p-QX is the same as that of p-PT, 2.6 eV. IP and EA are 0.3 eV higher than those of p-PT. Copolymerization with PT and PY in 1:1 and 1:2 ratio leads to band-gap reductions of up to 0.67 eV, which are due to lowering of the IPs. Experimentally, λ_{max} of the QX homopolymer was determined to be 3.81 eV, the onset of absorption was estimated to occur at 2.6 eV [8]. Correcting our data as described in the methods section would predict a value of 2.2 eV for λ_{max} and 1.7 eV for the onset of absorption. These are unusually large discrepancies. The experimental difference of 1.2 eV between λ_{max} and the onset of absorption is also unusually large.

The copolymer with one TH unit has a band gap of 1.7 eV; with two TH units the band gap is 1.4 eV [51, 52]. Our predictions of 1.2 eV are in much better agreement with experimental values than those for the homopolymer. For pyrrole systems, the theoretical energy gaps are about 0.2 eV lower than with thiophene. Although the band gaps

Table 1 Energy gaps, IPs, and EAs according to Koopmans' theorem for oligomers of the QX system

Number of units		QX	QX-TH	TH-QX-TH	QX-PY	PY-QX-PY
1	Eg	5.40	4.06	3.45 (3.06) [14]	3.64 (2.95) [51]	3.00 (2.47) [51]
	IP	7.79	6.70	6.31	6.24	5.78
	EA	2.39	2.64	2.86	2.60	2.79
2	Eg	4.24	3.13	2.76	2.83 (2.32) [51]	2.43
	IP	7.00	6.09	5.82	5.68	5.31
	EA	2.76	2.96	3.07	2.85	2.89
3	Eg	3.72	2.76	2.52	2.51	2.24
	IP	6.67	5.86	5.69	5.47	5.18
	EA	2.95	3.10	3.16	2.96	2.94
4	Eg	3.43		2.42		2.15
	IP	6.49		5.63		5.12
	EA	3.06		3.21		2.96
inf	Eg	2.63	2.08 (1.7) [52]	2.14 (1.4) [52]	1.88	2.13
	IP	5.98	5.47	5.48	5.10	4.96
	EA	3.35	3.28	3.34	3.13	3.03

Experimental values are quoted in brackets. For oligomers these are λ_{max} values obtained in solution, for polymers they are onsets of absorption. All values are given in electron volts (eV)

are lowered upon copolymerization, all QX systems are predicted to have larger energy gaps than polyacetylene (PA).

Benzothiadiazole BT

Due to the influence of the thiadiazole side group, the benzene ring is strongly distorted. It contains a butadiene fragment and a relatively long bond between the carbon atoms attached to the thiadiazole group. In long oligomers, the inter-ring bond has a similar bond length as in p-TH and p-PY. Therefore, p-BT is aromatic. There are no major geometry changes upon copolymerization with TH and PY. Although BT is structurally very similar to QX, the thiophene rings prefer opposite orientations in the co-polymers. The 1:2 monomer, for instance, is 1.92 kcal mol^{-1} more stable in the orientation shown in Scheme 2 than in the conformation analogous to TH-QX-TH. With pyrrole the hydrogen bridges require the opposite orientation.

The agreement between theory and experiment is very good for the BT systems, as can be seen from Table 2. The BT homopolymer has a very small band gap but there are only small band-gap reductions upon copolymerization. With one or two thiophene rings, there is practically no change in band gaps. With pyrrole, the band gap decreases by 0.5 with 1:1 stoichiometry and 0.5 eV with 1:2 stoichiometry. Table 2 reveals that HOMO and LUMO are affected by copolymerization with thiophene but the upshift of the HOMO is stronger than that of the LUMO with pyrrole. While copolymers with thiophene are predicted to have similar energy gaps to those of QX, the pyrrole-BT copolymers have about 0.3 and 0.5 eV smaller energy gaps than those with QX.

Benzobisthiadiazole BBT

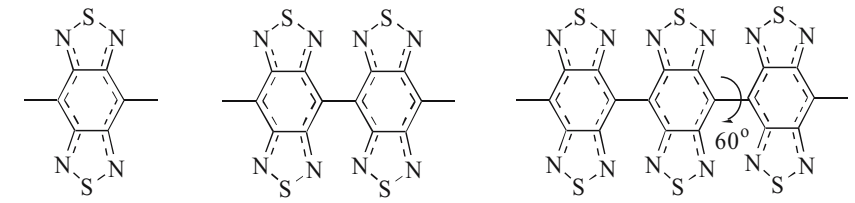
With two thiadiazole groups, the benzene ring cannot form double bonds at four of its six carbon atoms. Therefore, a quinoid structure with an inter-ring double bond is favorable. However, a planar BBT polymer would be a highly strained because of repulsions between the nitrogen lone pairs in the thiadiazole units. Frequency calculations show that aromatic and quinoid forms are twisted around the inter-ring bonds. The optimized dihedral angles are 60° in the aromatic and 40° in the quinoid form. Since the inter-ring double bond is weakened in the quinoid form, the aromatic form turns out to be 3.1 kcal mol^{-1} more stable when evaluated between dimer and monomer. The preference for the aromatic form, however, decreases when longer oligomers are considered (Scheme 5). For oligomers

Table 2 Energy gaps, IPs, and EAs according to Koopmans' theorem for oligomers of the BT system

Number of repeat units		BT	BT-TH	TH-BT-TH	BT-PY	PY-BT-PY
1	Eg	4.92	3.84 (3.18) [51]	3.27 (2.77) [51] (2.66) [14]	3.38 (2.81) [51]	2.73 (2.33) [51]
	IP	7.76	6.85	6.44	6.35	5.86
	EA	2.84	3.01	3.16	2.97	3.12
2	Eg	3.86	2.90	2.66 (2.38) [51]	2.59	2.17
	IP	7.11	6.24	6.05	5.82	5.41
	EA	3.25	3.34	3.39	3.23	3.24
3	Eg	3.33	2.61	2.44	2.26	1.98
	IP	6.81	6.15	5.94	5.62	5.27
	EA	3.48	3.54	3.50	3.36	3.29
4	Eg	3.03	2.44	2.34	2.08	1.89
	IP	6.65	6.07	5.89	5.52	5.21
	EA	3.61	3.63	3.55	3.44	3.32
5	Eg	2.85	2.34		1.97	
	IP	6.54	6.02		5.46	
	EA	3.70	3.68		3.49	
6	Eg	2.72	2.28		1.91	
	IP	6.48	6.00		5.43	
	EA	3.76	3.72		3.52	
8	Eg	2.57				
	IP	6.40				
	EA	3.83				
inf	Eg	2.11	2.05	2.07 (1.2) [14]	1.61	1.63
	IP	6.15	5.93	5.85	5.31	5.05
	EA	4.05	3.91	3.71	3.65	3.40

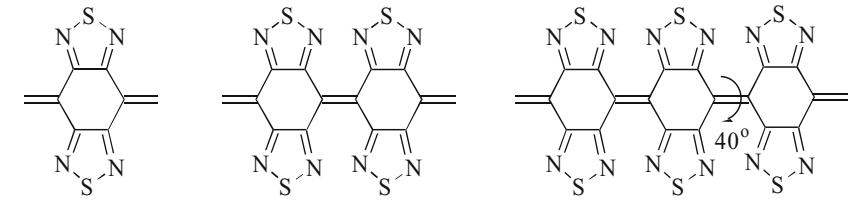
Experimental values are quoted in brackets. For oligomers these are λ_{max} values obtained in solution, for polymers they are onsets of absorption. All values are given in electron volts (eV)

Scheme 5 Determination of the preferred conformation of poly-BBT from oligomer calculations. Although BBT is inherently quinoid, steric strain prevents formation of a planar structure. As a result, the preference for the aromatic conformation decreases on chain length increase and converges to about 1.2 kcal/mol per BBT unit for longer oligomers



E = - 96.404798 E = - 191.569682 E = - 286.734484

$\Delta E_{1\text{-}2}$ = - 95.164884 $\Delta E_{2\text{-}3}$ = - 95.164802 $\Delta E_{3\text{-}4}$ = - 95.164766



E = - 109.161519 E = - 204.321409 E = - 299.484237

$\Delta E_{1\text{-}2}$ = - 95.159890 $\Delta E_{2\text{-}3}$= - 95.162828 $\Delta E_{3\text{-}4}$ = - 95.162824

$\Delta\Delta E_{1\text{-}2}$ = - 3.13 kcal/mol $\Delta\Delta E_{2\text{-}3}$ = - 1.24 kcal/mol $\Delta\Delta E_{3\text{-}4}$ = - 1.22 kcal/mol

Table 3 Energy gaps, IPs, and EAs according to Koopmans' theorem for oligomers of the BBT system

Number of repeat units		BBT	BBT-TH	TH-BBT-TH	BBT-PY	PY-BBT-PY
1	Eg	3.24	3.32	q 2.99/a 2.01 (1.77) [14]	3.27	q 2.84/a 1.73
	IP	7.34	6.51	6.10	6.29	5.75
	EA	4.11	3.19	3.11	3.02	2.91
2	Eg	2.76	2.42	1.89	2.32	1.66
	IP	6.99	6.19	5.77	5.93	5.38
	EA	4.23	3.77	3.89	3.61	3.71
3	Eg	2.50	2.16	1.65	2.08	1.43
	IP	6.80	6.07	5.68	5.81	5.27
	EA	4.30	3.91	4.03	3.73	3.84
4	Eg	2.19	2.03	1.54	1.96	1.32
	IP	6.43	6.02	5.64	5.76	5.23
	EA	4.23	3.99	4.10	3.80	3.91
5	Eg	2.02				
	IP	6.34				
	EA	4.32				
6	Eg	1.90				1.22
	IP	6.28				5.20
	EA	4.38				3.98
8	Eg					1.18
	IP					5.19
	EA					4.01
inf	Eg	1.30	1.66	1.36 (0.5) [14]	1.60	1.05
	IP	5.98	5.83	5.57	5.65	5.17
	EA	4.70	4.23	4.26	4.01	4.12

Experimental values are quoted in brackets. For oligomers these are λ_{max} values obtained in solution, for polymers they are onsets of absorption. All values are given in electron volts (eV)

longer than trimer, the quinoid form is more stable. In Table 3, data are given accordingly. For extrapolation, tetramers and longer oligomers of the quinoid form are used. Extrapolated energy gaps for p-BBT are as follows: aromatic closed-shell: 1.9 eV, aromatic open-shell: 2.4 eV, quinoid 1.3 eV. Applying the correction for using gas-phase λ_{max} values, the band gap of the quinoid form is 0.4 eV.

The inherent preference for the quinoid form comes to the fore upon copolymerization, since this increases the separation of the nitrogen lone pairs and allows formation of strong double bonds between the rings. The preference for the quinoid form is 7.4 kcal mol^{-1} for BBT-TH, 3.6 kcal mol^{-1} for TH-BBT-TH, and 8.0 kcal mol^{-1} for BBT-PY. The TH-BBT-TH monomer has a λ_{max} value of 1.77 eV in $CHCl_3$. Our value of 2.99 eV for the quinoid monomer, even after correction for the solvent effect, is 0.8 eV too high. We therefore checked the energy gap of the aromatic form and found it to be in much better agreement with experiment. The energy gap is 2.01 eV and after correction for the solvent effect our prediction is 1.6 eV. This suggests that quinoid structures develop only at longer chain lengths.

All copolymers of BBT are quinoid and energy gaps were evaluated for oligomers end-capped with CH_2. For extrapolation, the aromatic monomers are not included. Copolymerization tends to increase the energy gaps. 1:2 Stoichiometry is more favorable with respect to small energy gaps than 1:1 stoichiometry. Poly-TH-BT-TH is predicted to have a 0.06 eV larger band gap than p-BBT. Only with PY in 1:2 stoichiometry does the energy gap decrease (by 0.25 eV) compared to p-BBT. The band-gap reduction is due to lowering of IP and EA, but the latter is smaller. Correcting the energy gap as described in the methods section suggests that p-PY-BBT-PY has a band gap of about 0.15 eV. There is no direct experimental comparison since BBT was copolymerized only with N-methylpyrrole. It turned out that the methyl groups lead to steric hindrance and non-planarity. The band gap was 0.6, 0.1 eV larger than that of p-TH-BBT-TH [14].

Thienopyrazine TP

In TP, pyrazine and thiophene rings compete for aromaticity. The energy difference between quinoid and aromatic forms is evaluated in the same way as shown for QX in Scheme 4. For the homopolymer, there is a slight preference (3.5 kcal mol^{-1}) for the quinoid structure. Therefore, all data for the homopolymer are obtained for the quinoid oligomers, terminated with CH_2 groups. Copolymerization with aromatic TH and PY induces a change from quinoid to aromatic structures. For p-TP-TH, the preference for the aromatic conformation amounts to 2.1 kcal mol^{-1}, for p-TP-PY it is 4.12 kcal mol^{-1}. Copolymers with 1:2 stoichiometry are therefore assumed to be aromatic as well. The orientation of the pyrrole and thiophene rings is *trans* with respect to the central unit. The agreement with experimental data is good (compare Table 4).

Table 4 Energy gaps, IPs, and EAs according to Koopmans' theorem for oligomers of the TP system

Number of repeat units		TP	TP-TH	TH-TP-TH	TP-PY	PY-TP-PY
1	Eg	4.37	3.54	2.93 (2.35) [14] (2.79) [12]	3.27	2.62
	IP	6.78	6.50	6.07	6.14	5.63
	EA	2.41	2.96	3.14	2.88	3.00
2	Eg	3.31	2.54	2.30	2.38	2.10
	IP	6.18	5.86	5.68	5.54	5.23
	EA	2.86	3.32	3.38	3.15	3.13
3	Eg	2.78	2.13	2.06	2.03	1.91
	IP	5.89	5.62	5.55	5.31	5.11
	EA	3.12	3.49	3.48	3.27	3.19
4	Eg	2.47	1.92	1.95	1.85	1.83
	IP	5.73	5.50	5.49	5.20	5.05
	EA	3.26	3.58	3.53	3.34	3.22
5	Eg		1.80			
	IP		5.43			
	EA		3.63			
6	Eg	2.15				
	IP	5.56				
	EA	3.41				
8	Eg	1.99				
	IP	5.47				
	EA	3.48				
inf	Eg	1.55	1.41	1.66 (1.0) [14]	1.32	1.58
	IP	5.23	5.14	5.29	4.85	4.84
	EA	3.68	3.82	3.69	3.53	3.32

Experimental values are quoted in brackets. For oligomers these are λ_{max} values obtained in solution, for polymers they are onsets of absorption. All values are given in electron volts (eV)

Table 5 Energy gaps, IPs, and EAs according to Koopmans' theorem for oligomers of the TT system

Number of repeat units		TT	TT-TH	TH-TT-TH	TT-PY	PY-TT-PY
1	Eg	4.38	3.38	2.72 (2.00) [12]	3.18	2.47 (1.74) [52]
	IP	7.06	6.28	6.12	5.93	5.68
	EA	2.68	2.90	3.40	2.75	3.21
2	Eg	3.54	2.56	2.33	2.25	2.07
	IP	6.60	5.92	5.87	5.46	5.39
	EA	3.06	3.36	3.54	3.20	3.32
3	Eg		2.27	2.19	1.94	1.95
	IP		5.80	5.79	5.27	5.29
	EA		3.53	3.60	3.34	3.34
4	Eg	3.01	2.11	2.13	1.76	1.89
	IP	6.30	5.74	5.76	5.18	5.25
	EA	3.29	3.63	3.63	3.42	3.36
6	Eg	2.82				
	IP	6.20				
	EA	3.39				
inf	Eg	2.40	1.61	1.97 (0.9) [12]	1.17	1.73
	IP	5.97	5.59	5.71	4.90	5.14
	EA	3.57	3.92	3.73	3.63	3.40

Experimental values are quoted in brackets. For oligomers these are λ_{max} values obtained in solution, for polymers they are onsets of absorption. All values are given in electron volts (eV)

P-TP has a small theoretical energy gap as a homopolymer, 1.6 eV. Therefore, the band gap would be around 0.7 eV. Copolymerization in 1:1 stoichiometry with TH and with PY leads to reductions of the energy gap. As always, the effect of pyrrole is stronger than that of thiophene. In contrast to most of the other systems, increasing the content of TH and PY increases the energy gaps.

TP is the only acceptor for which the homopolymer has a lower IP (5.23 eV) than p-TH (5.66 eV at the same level of theory). Therefore, the valence band is pushed up compared to p-TH, not down as for the other systems. With one TH ring and with one and two PY rings, the IPs of the copolymers are smaller than those of either homopolymer. The small energy gap of p-TH-TP is due to a slight increase in EA and a slight decrease in IP. For p-TP-PY the reason is the stronger decrease of the IP compared to that of the EA.

Table 6 Energy gaps, IPs, and EAs according to Koopmans' theorem for oligomers of the TTP system

Number of repeat units		TTP	TTP -TH	TH- TTP -TH	TTP -PY	PY- TTP -PY
1	Eg	q 3.29/a 3.01 (2.13) [17]	2.63	q 2.28/a 1.71 (1.25) [17]	2.52	q 2.20/a 1.31 (0.92) [17]
	IP	q 7.19/a 7.32	6.45	q 6.03/a 6.09	6.16	q 5.66/a 5.68
	EA	q 3.90/a 4.31	3.82	q 3.66/a 4.38	3.64	q 3.46/a 4.37
2	Eg	2.59	1.98	1.58	1.78	1.27
	IP	6.81	6.19	5.73	5.76	5.33
	EA	4.22	4.21	4.15	3.98	4.07
3	Eg	2.41	1.82	1.45	1.63	1.14
	IP	6.64	6.12	5.66	5.62	5.27
	EA	4.23	4.29	4.20	3.99	4.13
4	Eg	2.31	1.75	1.40	1.56	1.10
	IP	6.56	6.10	5.63	5.56	5.26
	EA	4.26	4.35	4.23	4.01	4.16
5	Eg	2.26				
	IP	6.52				
	EA	4.26				
6	Eg	2.22				
	IP	6.49				
	EA	4.27				
inf	Eg	2.11	1.57	1.29 (0.3) [52]	1.30	1.02 (0) [52]
	IP	6.39	6.07	5.57	5.43	5.22
	EA	4.34	4.50	4.32	4.07	4.25

Experimental values are quoted in brackets. For oligomers these are λ_{max} values obtained in solution, for polymers they are onsets of absorption. All values are given in electron volts (eV)

Thienothiadiazole TT

P-TT prefers the quinoid conformation by 11.2 kcal mol^{-1}. In 1:1 stoichiometry, copolymers are quinoid. Copolymers with thiophene prefer the *cis*-conformation. The band gaps are lowered by 0.8 eV with thiophene and by 1.2 eV with pyrrole (Table 5). In the case of thiophene, this is due to a decrease of the IP and increase of the EA. Pyrrole has only a small influence on the EA of TT but lowers the IP by 1 eV. It is remarkable that such a strong mixing of the EAs occurs with TT since TT has the second smallest EA of all the acceptors in this investigation. The increase of the EAs of the copolymers compared to p-TT of up to 0.35 eV (with TH) seems to be possible since the difference between the EAs of p-TT and p-TH is only 0.5 eV. According to the donor–acceptor concept, the smallest band gaps are expected when the energy differences between the energy levels are largest.

With two thiophene rings, there is only a very small energy difference between quinoid and aromatic structures, 0.24 kcal mol^{-1} in favor of the quinoid form. For PY-TT-PY, the energy difference is 1.23 kcal mol^{-1}. When open-shell (unrestricted) calculations are used for comparison, aromatic forms are preferred but there is increasing spin contamination with increasing chain length, which may artificially lower the energies. It is therefore difficult to decide from a theoretical point of view which structure is correct. Since energy gaps depend strongly on the choice of structure, we evaluated aromatic, quinoid and open-shell aromatic forms for the 1:2 oligomers. For quinoid as well as for closed-shell aromatic forms, HOMO-LUMO gaps extrapolate to very small energy gaps, around 1 eV. Quinoid p-PY-TT-PY has an energy gap of 0.34 eV. The band gaps of the 1:2 copolymers would therefore be close to zero. Poly-PY-TT-PY, in particular, would be a metal. For p-TH-TT-TH, the experimental band gap is known, 0.9 eV [12]. Thus, the theoretical energy gap of 1.1 eV is too small since it leads to a predicted band gap of 0.2 eV. With open-shell calculations the energy gaps increase. For p-TH-TT-TH we obtain a value of 1.97 eV, so that the predicted band gap, 1.07 eV, agrees with experiment. Thus, it seems that symmetry breaking occurs when the mismatch between quinoid and aromatic structure leads to no clear structural preference.

Thienopyrazinothiadiazole TTP

The homopolymer is planar and has a strong preference (12.2 kcal mol^{-1}) for the quinoid conformation. Even if copolymerized with two TH and two PY rings, the preference for the quinoid form, 4.0 and 5.8 kcal mol^{-1}, respectively, remains and TH and PY are forced to adopt quinoid structures as well. As a result of the geometrical mismatch, bond-length alternation in the TH or PY fragments is very small. The longest bond along the conjugated pathway is the C–C bond attached to the pyrazine group in the thiophene ring of the TTP fragment. With one thiophene ring, the *cis*-conformation is more stable. With two thiophene rings, the monomer prefers the *cis*-conformation but longer oligomers are more stable in the *trans* form. The energetic preferences are subtle and the effect on the energy gaps is small.

As for monomers in the BBT system, the energy gap of the quinoid PY-TTP-PY monomer is much larger than the experimental value, 2.20 vs 0.92 eV (Table 6). Using the aromatic form leads to good agreement. The HOMO-LUMO gap is 1.31 eV. The TDHF excitation energy is 1.28 eV. If 0.4 eV is subtracted to account for the solvent effect, the agreement is almost perfect. To obtain polymer values, the aromatic monomers were excluded from the extrapolation.

TTP copolymers have very small band gaps and p-PY-TTP-PY is predicted to have the smallest energy gap of all systems in this investigation, 1.02 eV. After correction of 0.9 eV, the experimental zero band gap is confirmed. This is interesting since residual doping was suggested as a possible reason for the absence of an electrochemical band gap [51, 52].

In the TTP system (Table 6), small energy gaps are due to large gap reductions upon copolymerization. Copolymerization decreases the relatively high IP of the homopolymer without lowering the EA. This is due to the fact that the LUMO of TTP is localized on the pyrazino thiadiazole side group. The thiophene rings contribute little and the overlap between the rings upon polymerization is small. Therefore, the EA of p-TTP, 4.34 eV, is not much larger than that of the monomer, 3.90 eV, and the conduction band is flat. The EAs of the copolymers are close to that of p-TTP, independent of whether TH or PY is used and independent of the stoichiometry.

Discussion

There are three main questions we wish to answer with this investigation. Firstly, do theoretical gas-phase calculations reproduce the experimental findings of dramatic band-gap lowering upon copolymerization of donor and "non-classical" acceptor units? Secondly, is the donor–acceptor concept as proposed by Havinga [18] responsible? Thirdly, what is the influence of the geometrical mismatch when quinoid and aromatic units are copolymerized?

In Fig. 2, our best estimates as discussed in the previous sections for λ_{max} values (HOMO-LUMO gaps −0.4 eV) and band gaps (extrapolated HOMO-LUMO gaps −0.9 eV) are plotted vs experimental values. The straight line corresponds to perfect agreement between theory and experiment. Open circles are oligomer data; closed circles are polymer band gaps. The overall accuracy is good. Thus, theory reproduces the small experimental band gaps. The good agreement justifies using DFT calculations to analyze electronic structures of these systems.

In Table 7, the band-gap changes upon copolymerization of the acceptors with thiophene and pyrrole in 1:1 and in 1:2 stoichiometry are summarized. We note large band-gap reductions with QX, TT, and with TTP. With BT there is no effect with thiophene but substantial lowering with pyrrole.

The band gaps of TP and BBT are affected much less and may decrease or increase depending on donor and stoichiometry. In general the band-gap reductions are larger with pyrrole than with thiophene. The general trend is that band gaps are smaller in 1:2 copolymers, only with TP and TT, the 1:1 copolymers have smaller band gaps.

The acceptors can be divided into three groups, QX and BT homopolymers are aromatic, p-TP and p-TT are quinoid but switch to aromatic structures when copolymerized with aromatic donors, TTP and BBT are quinoid and force thiophene and pyrrole units to become quinoid upon copolymerization. In each of the three groups, one system exhibits strong band-gap reduction upon copolymerization (QX, TTP, and TT) and one does not (BT, BBT, and TP). There is thus no clear indication that quinoid acceptors are required for band-gap reductions of copolymers with aromatic donors. It will be shown below that small band gaps are obtained, however, when the energetic preference for either form is small. Neither the pyrazino group nor the thiadiazole group is crucial for band-gap reduction, as the comparison between QX, BT, TP, and TT shows.

Changes in IPs and EAs upon copolymerization are listed in Tables 8 and 9. The general trend is that copolymerization decreases IPs and EAs. This can be attributed to the fact that pyrrole and thiophene have lower IPs and EAs than the acceptors. The changes range from +0.06 to −1.17 eV for IPs and from +0.35 to −0.69 eV for EAs. Smaller reductions of EAs are responsible for the band-gap reductions. The effects are larger with pyrrole than with thiophene, especially on the IPs. The exceptionally large band-gap reductions in the TTP system are due to the nearly constant EAs of all of the polymers involving TTP. Only two acceptors with relatively low EAs interact strongly with unoccupied levels of TH and PY. The corresponding copolymers may even have increased EAs compared to the homopolymers. In summary, strong interactions arise only between similar energy levels. Interactions between levels of very different energy are small as predicted by perturbation theory.

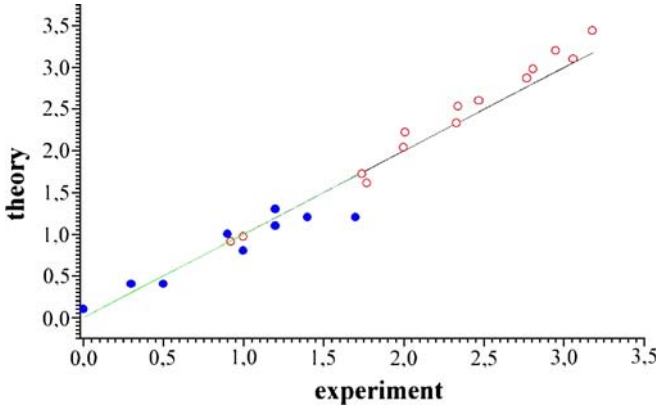


Fig. 2 Theoretical λ_{max} and band gap estimates plotted vs. measured values. *Open circles* are oligomer data, *closed circles* are extrapolated polymer band gaps. All energies are in electron volts (eV)

Table 7 Band gap changes of copolymers with respect to the corresponding acceptor homopolymers in electron volt (eV)

	TH		PY	
	1:1	1:2	1:1	1:2
QX	−0.44	−0.49	−0.67	−0.50
BT	−0.06	−0.04	−0.50	−0.48
BBT	+0.36	+0.06	+0.30	−0.25
TP	−0.14	+0.11	−0.23	+0.03
TT	−0.79	−0.47	−1.23	−0.68
TTP	−0.54	−0.82	−0.81	−1.09

The smallest band gaps are predicted to be those of p-PY-TTP-PY ~ p-PY-BBT-PY< p-TT-PY<TH-TTP-TH ~ TTP-PY ~ TP-PY< TH-BBT-TH< TP-TH. With TP and BBT the small band gaps do not result from band-gap reductions but from small band gaps of the homopolymers. BBT is unusual since the small band gap of the homopolymer is probably caused by steric strain. It is noteworthy that small band gaps result for copolymers of acceptors that strongly prefer quinoid structures in 1:2 stoichiometry and of acceptors that weakly prefer quinoid structures in 1:1 stoichiometry with aromatic donors. Thus, the smallest band gaps are found when energetic differences between quinoid and aromatic forms are small. The trend is continued with the 1:2 polymers of the TT system, for which we obtained extremely small energy gaps with closed-shell calculations. However, in these systems symmetry breaking increases the energy gap.

Since the original prediction of the donor–acceptor concept is that band gaps are smallest when electronegativity differences are largest, we tried to find correlations between band-gap reductions and energy differences between IPs and EAs of donors and acceptors. No such correlation could be established in a variety of plotting schemes. In contrast, the crucial factor for band-gap lowering is that the mixing between HOMO levels must be large, so that the IPs are lowered, and mixing between LUMO levels must be small, so that the large EAs of the homopolymers are preserved.

Small mixing between energy levels has a negative effect on band width. In Table 10 we show estimates for band widths. The numbers are not true band widths but energy differences between the four highest occupied orbitals and between the four lowest unoccupied orbitals

Table 8 IP changes of copolymers with respect to the corresponding acceptor homopolymers in electron volts (eV)

	TH		PY	
	1:1	1:2	1:1	1:2
QX	−0.51	−0.50	−0.88	−1.02
BT	−0.22	−0.30	−0.84	−1.10
BBT	−0.15	−0.41	−0.33	−0.81
TP	−0.09	+0.06	−0.38	−0.39
TT	−0.38	−0.32	−1.07	−0.85
TTP	−0.32	−0.82	−0.96	−1.17

Table 9 EA changes of copolymers with respect to the corresponding acceptor homopolymers in electron volts (eV)

	TH		PY	
	1:1	1:2	1:1	1:2
QX	−0.07	−0.01	−0.22	−0.32
BT	−0.14	−0.34	−0.40	−0.65
BBT	−0.47	−0.44	−0.69	−0.58
TP	+0.15	+0.02	−0.14	−0.35
TT	+0.35	+0.16	+0.06	−0.16
TTP	+0.16	−0.02	−0.27	−0.09

for tetramers. For a valid comparison, the same four levels are taken for thiophene and pyrrole octamers and dodecamers. Octamers can be considered to be tetramers of dimeric, dodecamers of trimeric repeat units. Dimers have the same number of double bonds as 1:1 and trimers as 1:2 comonomers. Since the repeat units of 1:2 are larger than those of 1:1 polymers, their "band widths" are smaller. The valence "band widths" of cooligomers are comparable to those of TH and PY systems. The conduction "band widths" tend to be smaller, about half of those of the TH and PY tetramers. Aromatic polymers have wider valence and conduction bands than quinoid polymers.

According to the donor–acceptor concept, maximizing the electronegativity difference decreases band gaps and increases band widths. Thus copolymers with pyrrole should have wider valence and conduction bands than with thiophene. The opposite is the case for the conduction bands of the QX, BT, and TP systems. Only the quinoid polymers seem to have wide conduction bands, even wider than those of pyrrole and thiophene oligomers. Closer inspection of the energy levels shows that for the quinoid tetramers, the first three unoccupied orbitals are virtually degenerate. The fourth level has a substantially higher energy and is localized at the ends of the chains. This is probably an end-effect due to the CH_2 groups, which are

Table 10 Valence and conduction "band" width of tetramers in eV

	TH		PY	
	1:1	1:2	1:1	1:2
	1.70	1.02	1.72	0.99
	1.44	0.90	1.15	0.70
QX	1.62	1.13	1.60	1.17
	0.75	0.47	0.56	0.25
BT	1.56	1.03	1.65	1.18
	0.70	0.44	0.57	0.26
BBT	1.31	1.10	1.41	1.21
	0.72 (0.19)	0.88	0.72	0.92 (0.22)
TP	1.84	1.07	1.86	1.11
	0.81	0.49	0.62	0.29
TT	1.58	0.92	1.82	0.98
	0.60 (0.33)	0.32	0.69 (0.30)	0.19
TTP	1.38	1.10	1.55	1.15
	0.60 (0.13)	0.64 (0.05)	0.69 (0.11)	0.83 (0.08)

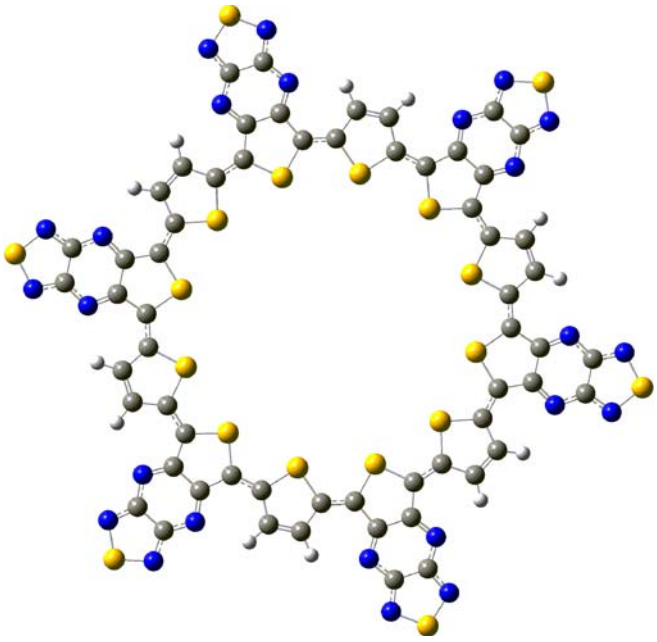


Fig. 3 Six-membered ring of *cis*-TTP-TH used as a model for p-TTP-TH avoiding end groups

needed to terminate the oligomers properly. For aromatic tetramers, the four levels are equally spaced. Without this last level, homo- and copolymers of BBT and TTP have negligible conduction-band dispersions. The corresponding values are given in parentheses for some of the systems in Table 10. To check whether this approach is valid, a test calculation on a symmetric 6-TTP-TH ring (Fig. 3) was performed. The TTP-TH system prefers the *cis*-conformation and leads to an unstrained six-membered ring. IP (6.12 eV), EA (4.46 eV), and band gap (1.66 eV) are close to those of the tetramer and of the polymer. Valence and conduction band widths estimated as the energy range of the six highest occupied MOs and the six lowest unoccupied MOs are 1.74 and 0.24 eV, respectively. This confirms that the conduction band widths of the TTP system is very small. Without end groups, no high-lying unoccupied level exists.

A totally flat conduction band was observed also for the only other zero-band-gap conducting polymer ever synthesized, p-CDM-EDOT [6]. This polymer has high intrinsic conductivity but the ratio between the mobilities of p- and n-type charge carriers is 500. Theoretical investigation revealed that the low mobility of the electrons is due to the lack of interaction between the high-lying unoccupied energy levels of EDOT and the low-lying unoccupied levels of CDM [53]. Because of their narrow conduction bands, we expect copolymers of BBT and TTP to have poor n-conductivities as well.

Conclusions

Estimates of λ_{max} values of oligomers and of band gaps of polymers obtained from DFT HOMO-LUMO gaps reproduce experimental values reliably if corrections for

solvent effects and for the difference between E_g and λ_{max} are applied. Care must be taken to consider the correct conformations (aromatic vs. quinoid) since the band gaps are dramatically underestimated when the wrong geometry is used. We used comparison with experiment for several systems to select the proper structures. Purely theoretical predictions require great care.

Poly-PY-TTP-PY is predicted to have no band gap. This supports the experimental finding and indicates that this system is a zero-band-gap material in its neutral form, without residual doping. We predict p-PY-BBT-PY and p-TT-PY to have almost the same low band gaps. Thus, synthesizing p-PY-BBT-PY without methyl groups on the pyrrole rings could be worthwhile. For p-TH-TTP-TH, p-TTP-PY, p-TH-BBT-TH, p-TP-PY, and p-TP-TH, we predict band gaps of about 0.4–0.5 eV.

Band-gap reductions are a result of smaller upshifts of EAs as compared to IPs. The smaller general effect of copolymerization on EAs is due to reduced interactions between donor and acceptor because of large LUMO energy differences. This leads to smaller conduction-band widths compared to homopolymers for aromatic polymers and vanishingly small conduction-band widths of polymers involving TTP and BBT. This makes the low-band-gap quinoid polymers like p-PY-TTP-PY good candidates for intrinsic conductors. We predict their p-type conductivities to be comparable to those of homopolymers and n-type conductivities to be very low.

Since band-gap reductions do not correlate with IPs or EAs of monomer or homopolymers, we believe that the origin of the band-gap reductions is not due to the donor–acceptor concept. On the contrary, the reduced interactions between the energetically different LUMOs of donors and acceptors prevent averaging of the EAs. At the same time, the HOMOs of more similar energies interact and average their values. Thus, the two predictions of the donor–acceptor concept, namely that band gaps are smaller the larger the electronegativity difference and that polymerizing donor with acceptors leads to increase in band widths, are both wrong.

Geometrical mismatch between quinoid and aromatic form seems to be an important factor when the structural preferences of donor and acceptor are opposite and about of equal size. This is shown when comparing TP, TT, and TTP. TP and TT have a weak preference for the quinoid form and the band gap is smaller in 1:1 stoichiometry than in 1:2 stoichiometry with TH and PY. TTP has a strong preference for the quinoid form. Here, increasing the amount of donor additionally lowers the energy gap. When there is no clear preference for either structure as with 1:2 copolymers involving TT, closed-shell calculations predict vanishingly small energy gaps. However, symmetry breaking may occur, which increases the band gap.

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