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Structure–property relationship of acceptor-substituted oligothiophenes

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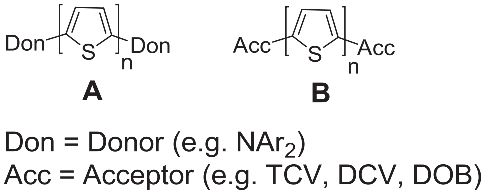
A series of oligothiophenes that are end-capped with dicyanovinyl (DCV) and 1,3,2-(2*H*)-dioxaborine (DOB) moieties has been prepared using standard procedures. Their optoelectronic properties have been investigated by cyclic voltammetry and optical absorption. The optical absorption has been measured both in solution and thin film state.

1. Introduction

Oligothiophenes represent a powerful class of functional materials, which are often used for manufacturing a variety of optoelectronic devices, such as organic light emitting diodes (OLEDs)[1,2] and organic solar cells (OSCs).[3–6] Their simple synthesis, high thermal stability, and strong optical absorption in the visible or near infrared region make them attractive as absorbers of OSCs.[7] Bandgap-engineering can be done both by enlarging the π-system and/or modifying the substituents at the α,ω-position of the thiophene chain.[8] The structural modification of a conjugated π-system by certain functional groups is one of the most common strategies with respect to their use as electronic materials (Scheme 1). For instance, by attaching diarylamino moieties at both ends of oligothiophenes, compounds of the general structure **A** (Don=NAr_2) exhibiting strong electron donating properties, indicated by low oxidation potentials and a high tendency to form stabilised radical cations and higher charged species, have been obtained.[9] By attaching tricyanovinyl (TCV) groups at both ends of oligothiophenes, compounds of the general structure **B** with Acc=–C(CN)=$C(CN)_2$ exhibiting a strong tendency to form stabilised radical anions have been obtained.[10,11] In recent studies, oligothiophenes end-capped with dicyanovinyl (DCV) groups and substituted by alkyl-chains at their backbone have been prepared and characterised by spectroscopic as well as electrochemical measurements.[5,6,12]



Scheme 1. Donor (Don) and acceptor (Acc) substituted oligothiophenes **A** and **B**.

Here, we have synthesised a series of alkyl-group free oligothiophenes end-capped with DCV and 1,3,2-(2*H*)-dioxaborine (DOB) moieties. Like the TCV and DCV groups, the DOB moieties have a relatively high electron affinity, which makes them suitable for tuning the electronic properties of oligothiophenes.[13] Until now, their potential for application in organic semiconducting devices is not fully explored. The absence of alkyl-chains has a significant influence on the packing density of the compounds in solid state and hence the morphology of thin films. Moreover, an influence on the active layer of an organic heterojunction device is expected, since the alkyl-chains can act as spacers between the molecules in the bulk. Therefore, this has an influence on the charge carrier transport in the layered systems.

Although oligothiophenes end-capped with DCV[14,15] and DOB[16] moieties are known, a detailed series of these compounds has not yet been studied. Therefore we have addressed this issue by preparing several new DOB substituted oligothiopenes DOB_2-*n*T (*n*=3,4) and DCV substituted oligothiophenes DCV_2-*n*T (*n*=3–6). The focus lies on the absorption in solution and thin film. Other important points are the electrochemical properties, investigated by cyclic voltammetry.

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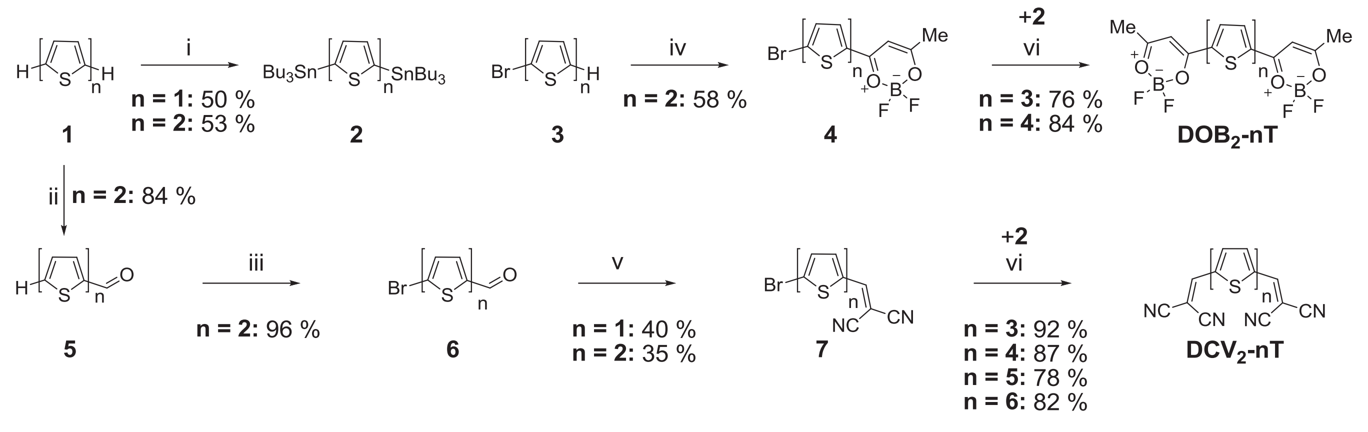
2. Results and discussion

2.1. Synthesis

The synthesis of both types of acceptor-substituted oligothiophenes starts from the parent thiophene **1** (Scheme 2). By using standard procedures, it has been functionalised at first by reaction with 2 equiv of BuLi in THF at −78 °C, followed by addition of 2 equiv of tributylstannylchloride to yield **2**.[17,18] The DOB derivative **4** was synthesised by reacting the bromo compound **3** with acetic anhydride in presence of BF_3 etherate.[19] Compound **5b** was realized by using the Vilsmeier reagent, $POCl_3$ and DMF in the first step with a yield of 84%.[20] To obtain the corresponding bromo compound **6b**, the bromination was carried out with NBS in DMF to yield **6b** (96%).[20] The DCV compounds **7** have been synthesised by reaction with malonodinitrile in acetonitrile catalysed by triethylamine.[21] The reaction has yields between 35 and 40% and results in dark red products. Subsequently, the DOB derivative **4** and the DCV compounds **7** were transformed into the target compounds DOB_2-*n*T (*n*=3,4) and DCV_2-*n*T (*n*=3–6) (with *n* as the number of thiophene rings) by Stille-coupling with **2** as reagents and $Pd(PPh_3)_4$ as catalyst.[22]



i: a) BuLi, b) Bu_3SnCl; ii: DMF/$POCl_3$; iii: NBS; iv: Ac_2O/BF_3; v: $CH_2(CN)_2$, Et_3N; vi: $Pd(PPh_3)_4$.

Scheme 2. Reaction scheme for the synthesis of DOB_2-*n*T and DCV_2-*n*T.

2.2. Optical and electronic properties

The optical and electronic properties of organic materials are important parameters to determine their application in electronic devices. The compounds listed in Table 1 are designed for working in the absorbing (intrinsic) layer of an organic small molecule solar cell.[23,24]

Table 1
Absorption maxima in solution and thin film, HOMO and LUMO energy levels from CV for the compounds DOB_2-*n*T and DCV_2-*n*T

Compd	λ_{max} [nm]		Oxidation[a]		Reduction[a]	
	in DCM (ε [L mol^{-1} cm^{-1}])	in thin-film	$E_{1/2}$ [V]	E_{HOMO} [eV]	$E_{1/2}$ [V]	E_{LUMO} [eV]
DOB_2-3T	470 (454,000)	410	1.39	−5.9	−0.78	−3.7
DOB_2-4T	482 (343,000)	486	1.07	−5.5	−1.07	−3.4
DCV_2-3T	488 (72,000)	495	1.42	−5.9	−0.89	−3.6
DCV_2-4T	517 (78,000)	547	1.02	−5.5	−0.92	−3.4
DCV_2-5T	—	558	—	—	—	—
DCV_2-6T	—	538	—	—	—	—

[a] Conditions: Pt-tip-electrode, Ag/AgCl, Pt wire; dry CH_3CN (oxidn) and dry CH_2Cl_2 (red); 0.1 mol L^{-1} Bu_4NPF_6; 100 mV s^{-1}; $E_{1/2}$ recalculated to Fc (HOMO −4.78 eV).[27]

The absorption measurements were performed in dichloromethane (DCM). Thin films were prepared by thermal evaporation in vacuum. To ensure the thermal stability of the compounds we investigated them by DSC and found a thermal stability up to 320 °C for the DCV-materials and 275 °C for the DOB-materials. The electrochemical reduction potentials were measured by cyclic voltammetry in DCM and the oxidation potentials in acetonitrile using tetrabutylammonium hexafluorophosphate as electrolyte. The data derived from these measurements are depicted in Table 1 and in Figs. 1 and 2.

Due to a restricted solubility, the optical absorption of DCV_2-5T and DCV_2-6T could only be measured in thin films (Fig. 1 (right)). The absorption maxima of the DCV derivatives in solution are found at longer wavelengths than the maxima of the DOB derivatives with the same number *n* of thiophene units (Fig. 1 (left), Fig. 2). In general, a bathochromic shift is observed by increasing the number *n* of thiophene units. In contrary, hypsochromic shifts are observed in thin films by going from DCV_2-5T (558 nm) to DCV_2-6T (538 nm) as well as going from solution to thin film for the DOB_2-3T (470 nm in DCM, 410 nm in thin film). This indicates that the molecular interaction between oligothiophene molecules in solid state is different from solution and that in thin films, this interaction can vary significantly. The broadening of the absorptions in the solid state also indicates that there are more types of molecular interactions (such as J-aggregates or H-aggregates[25,26]) in thin films than in solution. The effect of the DOB compound can also be explained by a strong solvatochromism. Measurements in different solvents (polar and nonpolar) exhibit a wide range for the absorption maxima from 411 nm (in THF) to 493 nm (in DMSO). It is worth mentioning that the DOB compounds have an extinction coefficient about six times higher than the DCV compounds. Calculation of the transition dipole moment (TDM) is part of future investigation to explain this phenomenon.

To characterise the redox properties of the prepared compounds, CV measurements were performed and the results are listed in Table 1. For the compounds, which were sufficiently soluble in DCM or acetonitrile, a reversible oxidation and reduction peak was observed (exemplarily shown for DCV_2-4T in Fig. 3). The oxidation potentials decrease with growing *n*, whereas the reduction potentials increase simultaneously to a smaller extent. These data indicate that the increase in donor strengths with growing *n* is more distinctive than the decrease in acceptor strength.

The HOMO and LUMO energy levels were calculated from the reduction and oxidation half-wave potential with reference

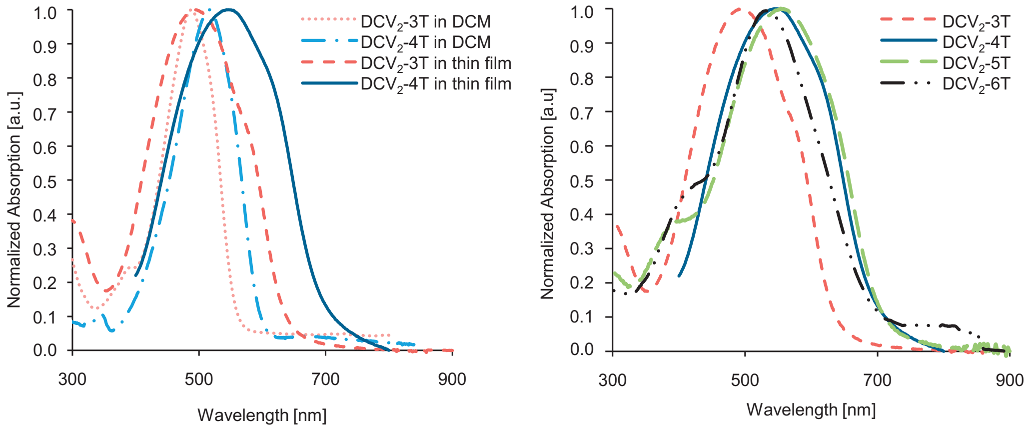


Fig. 1. Absorption spectra of DCV$_2$-3T and DCV$_2$-4T in solution (DCM) and thin film (left) and DCV$_2$-nT (with n=3–6) in vacuum processed thin films (right).

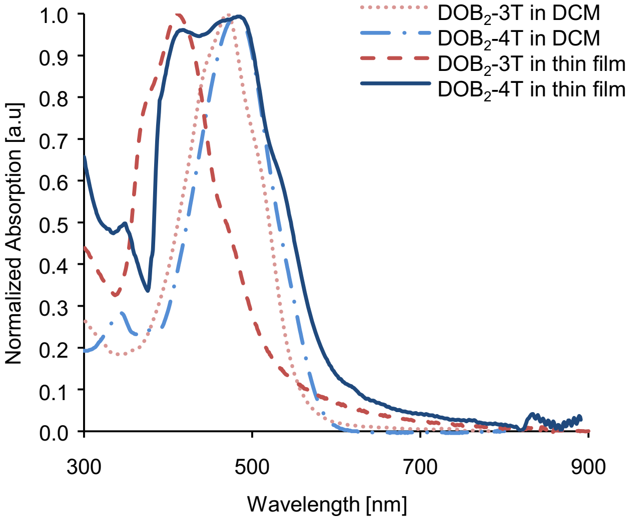


Fig. 2. Absorption spectra of DOB$_2$-nT (n=3,4) in solution (DCM) and thin film.

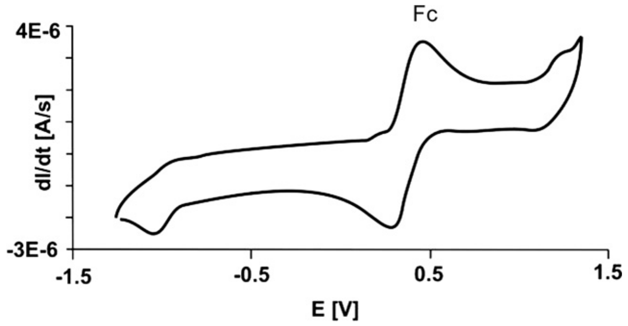


Fig. 3. Voltammogram of DCV$_2$-4T.

to ferrocene. The HOMO value of ferrocene is −4.78 eV in DCM and −4.84 eV in acetonitrile (e.g., for DCM: $E_{FMO}=-4.78-[E_{1/2}-E_{1/2}(Fc)]$).[27]

The electron affinity is nearly the same for both acceptor groups. The LUMO level is in a range between −3.4 eV for the substituted quaterthiophene and −3.6 eV (DCV$_2$-3T) to −3.7 eV (DOB$_2$-3T) for the terthiophene. The HOMO energy level of both terthiophenes DOB$_2$-3T and DCV$_2$-3T is at −5.9 eV, the CV measurement reveals values of −5.5 eV for the quaterthiophenes DOB$_2$-4T and DCV$_2$-4T.

3. Conclusion

We have investigated the relationship between structure, optical and electronic properties of a series of acceptor-substituted oligothiophenes, which are prepared for the absorbing (intrinsic) layer of organic small molecule solar cells. Our work included the investigation of two different acceptor groups—dicyanovinyl (DCV) and 1,3,2-(2*H*)-dioxaborine (DOB). The synthesis of several acceptor-substituted thiophenes with chain-lengths varying from three to six thiophene units for the case of the DCV compounds and three and four for the DOB compounds was achieved.

A constant bathochromic tendency in relation to the chain-length from three to five thiophene rings can be observed for the DCV compounds. DCV$_2$-6T shows a hypsochromic shift compared to DCV$_2$-4T and DCV$_2$-5T in vacuum processed thin film.

Compared to the DCV compounds, the DOB compounds show an outstandingly large extinction coefficient. Comparing the absorption of the DOB compounds with respect to their chain-lengths, we discovered a smaller bathochromic shift than our studies revealed from the DCV compounds. In solution and in thin film, the DOB compounds showed a hypsochromic shift, that comes from a strong solvatochromic behaviour of the molecules in solution.

The compounds with chain-length of three and four for both acceptors have been investigated by CV, which yields information about reversibility and that enlarging the chain-lengths of an oligomer has larger influences on the HOMO energy level of the molecules than on the LUMO energy level. Due to a restricted solubility of the compounds with five and six thiophene rings, a CV analysis was not possible.

4. Experimental section

4.1. General

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. The chemicals (standard and thiophene **1a**, 2,2′-bithiophene **1b**, 2-bromothiophene **3** and 5-bromo-2-carbaldehyde **6a**) were purchased from commercial sources (Aldrich, Alfa-Aeser and ABCR) and used without further purification. The solvents were dried according to standard procedures.

2,5-Bis(tributylstannyl)thiophene **2a**,[17] 5,5′-bis(tributylstannyl)-2,2′-bithiophene **2b**,[18] 2,2-bithiophene-5-carbaldehyde **5b**,[20] 5′-bromo-2,2′-bithiophene-5-carbaldehyde **6b**[20] and 4-(2-bromothienyl)-2,2-difluoro-6-methyl-1,3,2-(2*H*)-dioxaborine **4**[19] were prepared using literature procedures.

4.1.1. General analytic methods. ^{1}H and ^{13}C NMR spectra were recorded at room temperature with a Bruker DRX 500 P instrument at 500.13 and 125.76 MHz. The assignment of quaternary C, CH, CH_2, CH_3 was completed using DEPT spectra. Elemental analysis was done with a Eurovektor Hekatech EA-3000 elemental analyzer. The UV–vis spectra were measured with a Perkin–Elmer λ 25 spectrometer. The IR spectra were recorded with a Thermo Nicolet AVATAR 360 FTIR. The characteristic peaks are listed with an intensity of s=strong, m=medium and w=weak. Mass spectra were recorded with a Bruker Esquire-LC 00084 instrument. Melting points were measured with a Stuart apparatus and are uncorrected. DSC measurements were performed with a Netzsch STA 449 C under nitrogen atmosphere and with a heating rate of 10 K/min.

4.1.2. CV-measurements. CV measurements were performed with a Ag/AgCl-electrode in a typical three-electrode set-up. The conducting salt was tetrabutylammoniumhexafluorophosphat (0.1 M/L) (recrystallised from ethanol) and ferrocene as an internal standard. The reduction potentials were measured in dichloromethane, the oxidation potentials in acetonitrile. The step potential rate was 100 mV s^{-1}. The redox potentials were recalculated in reference to the HOMO level of ferrocene.[27]

4.1.3. Thin film preparation. The thin films were deposited on quartz glass by thermal evaporation in vacuum. The base pressure of the vacuum chamber was better than 10^{-6} mbar and the film thickness monitored by a quartz crystal microbalance.

4.2. Synthesis

4.2.1. General instruction for the synthesis of **7**. The carbaldehydes **6a** or **6b** and malononitrile (1.1 equiv) were suspended in acetonitrile. The mixture was warmed to 50–60 °C and a small amount of triethylamine was added. The suspension was dissolved and promptly a red precipitation was formed. After cooling to room temperature the precipitation could be filtered and washed with acetonitrile to give **7a** and **7b** in 35–40% yield.

4.2.2. 2-Bromo-5-dicyanovinylthiophene ***7a***. Compound **7a** was prepared from **6a**; mp: 156–158 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.66 (s, 1H), 7.75 (d, *J*=4.1, 1H), 7.56 (d, *J*=4.1, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=152.5 (CH), 141.3 (CH), 136.9 (C), 132.8 (CH), 125.5 (C), 114.2 (C), 113.7 (C), 76.8 (C).

4.2.3. 5′-Bromo-5-dicyanovinyl-2,2′-bithiophene ***7b***. Compound **7b** was prepared from **6b**; mp: 194–196 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ=8.65 (s, 1H), 7.89 (d, *J*=4.1, 1H,), 7.61 (d, *J*=4.1, 1H), 7.52 (d, *J*=4.0, 1H), 7.35 (d, *J*=4.0, 1H); ^{13}C NMR (125 MHz, DMSO-d_6): δ=152.6 (CH), 146.1 (C), 142.3 (CH), 136.3 (C), 133.9 (C), 132.6 (CH), 128.5 (CH), 126.0 (CH), 114.8 (C), 114.6 (C), 113.9 (C), 75.2 (C).

4.3. General instruction for the synthesis of DOB$_2$-*n*T and DCV$_2$-*n*T

The acceptor-substituted bromo compounds **4** or **7** (2 equiv) were dissolved in DMF and the catalyst ($Pd(PPh_3)_4$ 3 mol %) was added. The resulting mixture was heated to 80 °C before adding the stannylcompound **2** (1 equiv) and refluxed for 5–6 h. A precipitation was formed, which could be filtered after cooling to room temperature and washed with DMF. The compounds were purified by sublimation.

4.3.1. 5,5″-Bis(2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborin-4-yl)-2,2′:5′,2″-terthiophene (DOB$_2$-3T). Compound (DOB$_2$-3T) was prepared from **2a** and **4**; mp: 270 °C; $C_{20}H_{14}B_2F_4O_4S_3$: calculated: C 46.90, H 2.76, S 18.78; found: C 46.83, H 2.71, S 18.53; IR (ATR): ν=3094 (w), 1618 (w), 1558 (m), 1529 (m), 1455 (w), 1424 (m), 1378 (m), 1350 (m), 1284 (w), 1155 (m), 1031 (s), 976 (m), 803 (m), 727 (m), 690 (m), 580 (m), 543 (m) cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.04 (dd, *J*=3.9, 1.0, 2H), 7.85 (dd, *J*=4.9, 1.0, 2H), 7.25 (dd, *J*=4.8, 4.0, 2H), 6.77 (s, 1H), 1.55 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=191.6 (C), 174.9 (C), 138.1 (CH), 137.3 (C), 135.3 (CH), 132.7 (CH), 128.4 (CH), 126.8 (C), 96.7 (CH), 25.6 (CH_3); MS (ESI, −10 V): *m*/*z*: 510.8 [M$^-$].

4.3.2. 5,5‴-Bis(2,2-difluoro-6-methyl-1,3,2-(2H)-dioxaborin-4-yl)-2,2′:5′,2″:5″,2‴-quaterthiophene (DOB$_2$-4T). Compound DOB$_2$-4T was prepared from **2b** and **4**; mp: >300 °C; $C_{24}H_{16}B_2F_4O_4S_4$: calculated: C 48.51, H 2.71, S 21.58; found: C 48.75, H 2.68, S 21.12; IR (ATR): ν=3137 (w), 3090 (w), 2873 (w), 1979 (w), 1548 (s), 1500 (m), 1434 (s), 1377 (m), 1353 (s), 1286 (m), 1256 (m), 1221 (m), 1132 (s), 1036 (s), 976 (m), 877 (m), 788 (s), 723 (m), 699 (s), 659 (m), 578 (m) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 363 K): δ=8.37 (d, *J*=4.3, 2H), 7.71 (d, *J*=3.9, 2H), 7.68 (d, *J*=4.3, 2H,), 7.43 (d, *J*=3.9, 2H,), 7.08 (s, 2H), 2.39 (s, 6H); ^{13}C NMR (125 MHz, DMSO-d_6, 363 K): δ=191.2 (C), 176.7 (C), 137.4 (C), 135.2 (CH), 134.3 (C), 132.7 (CH), 130.9 (C), 128.6 (CH), 126.3 (C), 125.7 (CH), 96.8 (CH), 24.7 (CH_3); MS (ESI, −10 V): *m*/*z*: 593.8 [M$^-$].

4.3.3. 5,5″-Di(2,2-dicyanovinyl)-2,2′:5′,2″-terthiophene (DCV$_2$-3T). Compound (DCV$_2$-3T) was prepared from **2a** and **7a**; mp: 255 °C; $C_{20}H_8N_4S_3$: calculated: C 59.98, H 2.01, N 13.99, S 24.02; found: C 59.73, H 1.84, N 12.89, S 23.31; IR (ATR): ν=3081 (w), 3023 (w), 2982 (w), 2219 (m), 1573 (m), 1522 (m), 1474 (m), 1458 (w), 1424 (s), 1363 (m), 1334 (s), 1266 (m), 1237 (m), 1145 (m), 1073 (m), 1058 (m), 937 (m), 896 (w), 856 (m), 799 (m), 773 (s), 733 (m), 694 (m), 606 (m), 536 (m) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ=8.65 (s, 2H), 7.90 (d, *J*=4.3, 2H), 7.73 (m, 4H); ^{13}C NMR (125 MHz, DMSO-d_6): δ=152.3 (CH), 146.2 (C), 142.4 (CH), 136.7 (C), 134.4 (C), 129.6 (CH), 126.2 (CH), 114.6 (C), 113.9 (C) 75.3 (C); MS (ESI, −10 V): *m*/*z*: 398.8 [M$^-$], 798.8 [(2M)$^-$].

4.3.4. 5,5‴-Di(2,2-dicyanovinyl)-2,2′:5′,2″:5″,2‴-quaterthiophene (DCV$_2$-4T). Compound (DCV$_2$-4T) was prepared from **2b** and **7a**; mp: 298 °C; $C_{24}H_{10}N_4S_4$: calculated: C 59.73, H 2.09, N 11.61, S 26.58; found: C 59.62, H 1.79, N 10.53, S 26.79; IR (ATR): ν=3352 (w), 3087 (w), 3029 (w), 2217 (s), 1617 (w), 1565 (s), 1529 (s), 1508 (m), 1496 (w), 1418 (s), 1347 (m), 1323 (s), 1264 (s), 1144 (m), 1062 (s), 939 (m), 901 (w), 805 (m), 791 (s), 742 (m), 682 (w), 646 (m), 603 (s), 548 (m) cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6, 353 K): δ=8.54 (s, 2H), 7.93 (d, 4H, *J*=4.2), 7.65 (d, 2H, *J*=4.0), 7.63 (d, 2H, *J*=4.1), 7.52 (d, 2H, *J*=3.9); ^{13}C NMR (125 MHz, DMSO-d_6, 353 K): δ=151.5 (CH), 150.0 (C), 149.1 (C), 138.1 (C), 137.5 (C), 135.2 (C), 134.1 (C), 131.5 (CH), 130.1 (CH), 126.6 (CH), 125.5 (CH), 64.7 (C); MS (ESI, +10 V): *m*/*z*: 482.9 [M$^+$].

4.3.5. 5,5⁗-Di(2,2-dicyanovinyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene (DCV$_2$-5T). Compound DCV$_2$-5T was prepared from **2a** and **7b**; mp: 285 °C; $C_{28}H_{12}N_4S_5$: calculated: C 59.55, H 2.14, N 9.92, S 28.39; found: C 59.28, H 2.11, N 9.74, S 28.66; IR (ATR): ν=3332 (w), 3098 (w), 3018 (w), 2811 (w), 2456 (w), 2199 (s), 2047 (w), 1617 (w), 1561 (s) 1519 (w), 1496 (m), 1474 (m), 1459 (w), 1408 (s), 1385 (s), 1343 (s), 1314 (s), 1262 (s), 1226 (s), 1133 (s), 1047 (s), 926 (s), 786 (s), 648 (s), 596 (s), 528 (s) cm^{-1}.

4.3.6. 5,5′′′′′-Di(2,2-dicyanovinyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′′-sexithiophene (DCV$_2$-6T). Compound (DCV$_2$-6T) was prepared from **2b** and **7b**; mp: 300 °C; $C_{32}H_{14}N_4S_6$: calculated: C 59.42, H 2.18, N 8.66, S 29.74; found: C 58.61, H 2.17, N 8.47, S 29.66; IR (ATR): ν=3144 (w), 3066 (w), 3025 (w), 2220 (m), 2051 (w), 1607 (w), 1569 (m), 1484 (w), 1424 (m), 1343 (m), 1260 (m), 1218 (m), 1144 (m), 1071 (m), 921 (m), 856 (m), 832 (s), 791 (s), 714 (s), 606 (s), 553 (s) cm^{-1}.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.09.004.

References and notes

1. Mitschke, U.; Baeuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471.
2. Mazzeo, M.; Pisignano, D.; Favaretto, L.; Barbarella, G.; Cingolani, R.; Gigli, G. *Synth. Met.* **2003**, *139*, 671.
3. Videlot, C.; Kassmi, A. E.; Fichou, D. *Sol. Energy Mater. Sol. Cells* **2000**, *63*, 69.
4. Wynands, D.; Levichkova, M.; Riede, M.; Pfeiffer, M.; Baeuerle, P.; Rentenberger, R.; Denner, P.; Leo, K. *J. Appl. Phys.* **2010**, *107*, 014517.
5. Schulze, K.; Uhrich, C.; Schüppel, R.; Leo, K.; Pfeiffer, M.; Brier, E.; Reinold, E.; Bäuerle, P. *Adv. Mater.* **2006**, *18*, 2872.
6. Schulze, K.; Riede, M.; Brier, E.; Reinold, E.; Baeuerle, P.; Leo, K. *J. Appl. Phys.* **2008**, *104*, 074511.
7. Mishra, A.; Ma, C.-Q.; Baeuerle, P. *Chem. Rev.* **2009**, *109*, 1141.
8. Xia, P. F.; Feng, X. J.; Lu, J.; Tsang, S.-W.; Movileanu, R.; Tao, Y.; Wong, M. S. *Adv. Mater.* **2008**, *20*, 4810.
9. Rohde, D.; Dunsch, L.; Tabet, A.; Hartmann, H.; Fabian, J. *J. Phys. Chem.* **2006**, *110B*, 8223.
10. Papenfus, T. M.; Burand, M. W.; Janzen, D. E.; Mann, K. R. *Org. Lett.* **2003**, *5*, 1535.
11. Xia, P. F.; Feng, X. J.; Lu, J.; Movileanu, R.; Tao, Y.; Baribeau, J.-M.; Wong, M. S. *J. Phys. Chem. C* **2008**, *112*, 16714.
12. Liu, Y.; Zhou, J.; Wan, X.; Chen, Y. *Tetrahedron* **2009**, *65*, 5209.
13. Fabian, J.; Hartmann, H. *J. Phys. Org. Chem.* **2004**, *17*, 359.
14. Pfeiffer, M.; Schueppel, R.; Uhrich, C.; Petrich, A.; Leo, K.; Baeuerle, P.; Kilickiran, P.; Brier, E. WO 2006092135, 2006; *Chem. Abstr.* **2006**, *145*, 317960.
15. Halik, M.; Schmid, G.; Davis, L. DE 2001-10152938 2001, US 2002-281828 2002, US 2004-993117, 2004; *Chem. Abstr.* **2002**, *137*, 378622.
16. Zotti, G.; Zecchin, S.; Vercelli, B.; Berlin, A.; Grimoldi, S.; Pasini, M. C.; Raposo, M. M. M. *Chem. Mater.* **2005**, *17*, 6492.
17. Hou, J.; Tan, Z.; Yan, Y.; He, Y.; Yang, C.; Li, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4911.
18. Huang, J.; Miragliotta, J.; Becknell, A.; Katz, H. E. *J. Am. Chem. Soc.* **2007**, *129*, 9366.
19. Goerlitz, G.; Hartmann, H.; Nuber, B.; Wolff, J. J. *J. Prakt. Chem.* **1999**, *341*, 167.
20. Chen, R.; Yang, X.; Tian, H.; Wang, X.; Hagfeldt, A.; Sun, L. *Chem. Mater.* **2007**, *19*, 4007.
21. Raposo, M. M. M.; Fonseca, A. M. C.; Kirsch, G. *Tetrahedron* **2004**, *60*, 4071.
22. Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
23. Maennig, B.; Drechsel, J.; Gebeyehu, D.; Simon, P.; Kozlowski, F.; Werner, A.; Li, F.; Grundmann, S.; Sonntag, S.; Koch, M.; Leo, K.; Pfeiffer, M.; Hoppe, H.; Meissner, D.; Sariciftci, N. S.; Riedel, I.; Dyakonov, V.; Parisi, J. *Appl. Phys.* **2004**, *79*, 1.
24. Riede, M.; Mueller, T.; Tress, W.; Schueppel, R.; Leo, K. *Nanotechnology* **2008**, *19*, 424001/1.
25. Plekhanov, A. I.; Gorkovenko, A. I.; Orlova, N. A.; Simanchuk, A. E.; Shelkovnikov, V. V. *High Energy Chem.* **2009**, *43*, 607.
26. Li, Y.-X.; Tao, X.-T.; Wang, F.-J.; He, T.; Jiang, M.-H. *Org. Electron.* **2009**, *10*, 910.
27. Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.