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Synthesis and properties of acceptor–donor–acceptor molecules based on oligothiophenes with tunable and low band gap

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ABSTRACT

A series of acceptor–donor–acceptor molecules (**DCN3T**, **DCN5T** and **DCN7T**) based on oligothiophenes with low band gap are synthesized. The UV–vis absorption spectra of solution show that the introduction of electron-accepting groups results in a shift of the absorption onset towards longer wavelengths. Moreover, the optical spectra of their films show a large bathochromic shift and broadening of the bands with respect to the spectra in solution. The optical band gaps of film of these A–D–A molecules are 1.90, 1.74 and 1.68 eV, respectively. Cyclic voltammetry shows that all these compounds present a reversible first oxidation process whose potential decreases with the lengthening of oligothiophene cores. Electrochemical band gaps are 2.14, 1.88 and 1.71 eV, respectively.

1. Introduction

Currently, thiophene-based π-conjugated oligomers have been widely used in optoelectronic devices such as field-effect transistors,[1–3] light emitting diodes[4,5] and photovoltaic devices.[6,7] The advantages of oligomers are that finite-size systems can be obtained with high purity and a well-defined chemical structure, thus offers the advantages to investigate the relationship between the chemical structures with device performance by changing the number of thiophene rings and/or chemical modifications or substitutions.[8–11] Oligothiophenes possess extensive π-electron delocalization along the molecular backbone and are well known as high hole-transporting materials. Dipolar push–pull chromophores with a highly polarizable π-electron systems involving a donor group and an acceptor group, have been widely investigated for their nonlinear optical[12–15] and other optoelectronic properties.[16–19] These properties result from the existence of a photoinduced intramolecular charge transfer at relatively low energies, which depends on the efficiency of the π-electron delocalization along the conjugated systems and the electron donating and accepting capability.[20–22]

Dicyanovinyl group has strong electron-accepting properties and its double bond can also participate in the conjugation of the whole backbone π-system and lead to efficient intermolecular interactions. Some dicyanovinyl substituted oligothiophenes have been synthesized and used for solar cells,[23–26] but the relationship of their properties with the number of units (length) of oligothiophenes for this class is rarely studied.[27]

In this paper, we report the synthesis of a series of dicyanovinyl endcapped π-conjugated oligothiophenes (Fig. 1) with low and tunable band gap, and investigate their thermal, optical and electrochemical properties. The characterization of various acceptor–donor–acceptor (A–D–A) molecules based on oligothiophenes has led to a clear understanding, at a molecular level, of the structure–property relationships in this new class of materials.

2. Results and discussion

The synthesis of the target molecules is depicted in Scheme 1. The starting materials, 2-bromo-3-octylthiophene, 2-(3-octylthienyl)magnesium bromide and 3,3″-dioctyl-2,2′:5′,2″-terthiophene **1**, were synthesized according to the literature.[28] Terthiophene **1** and quinquethiophene **3** were brominated with NBS in $CHCl_3$–AcOH at 0 °C to give the corresponding brominated derivative **2** and **4**. For the nickel-catalyzed Kumada cross-coupling reaction,[29] diethyl ether was used as solvent and $Ni(dppp)Cl_2$ was used as the catalyst. For a better yield, an excess of 3.0 equiv of 2-(3-octylthienyl)magnesium bromide was used when reacted with dibromoterthiophene **2** under reflux conditions, which gave a 83% yield of oligothiophene **3** as a golden oil. Using the same method, septithiophene **5** was obtained as a brick red solid in 72% yield. Diformyl oligothiophenes, **6**, **7** and **8**, were prepared similarly by utilizing Vilsmeier–Haack reaction.[23,30,31] Finally, the target molecules **DCN3T**, **DCN5T** and **DCN7T** were obtained by Knoevenagel condensation[23–25,32] of malononitrile with the corresponding aldehydes.

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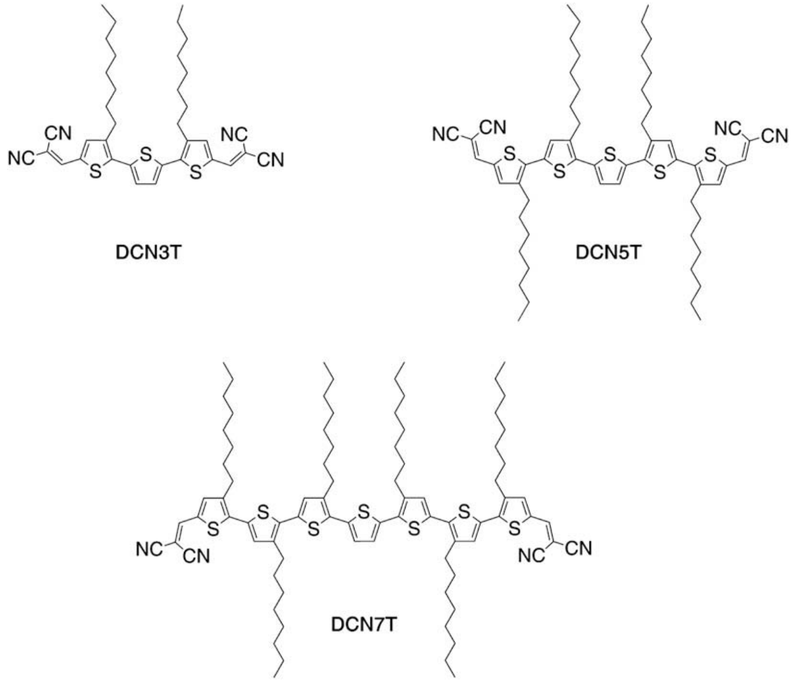


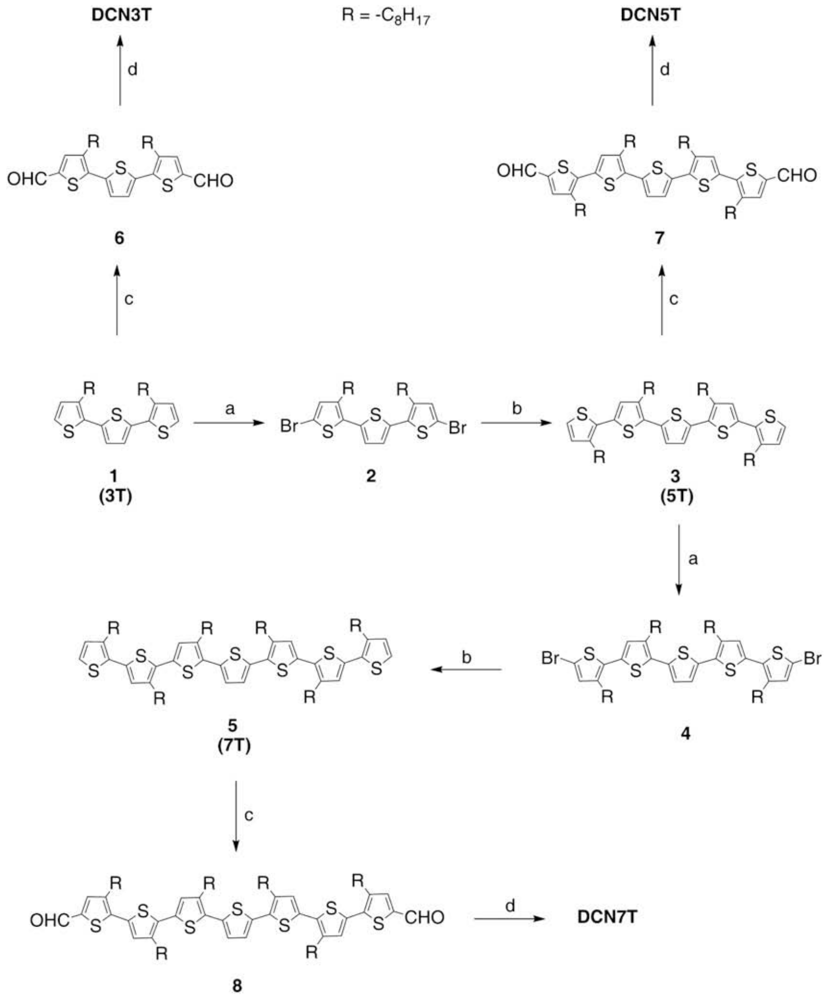
Figure 1. Chemical structures of **DCN3T**, **DCN5T** and **DCN7T**.

The thermal behaviours of A–D–A molecules were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen. TGA analysis revealed that these three A–D–A molecules exhibited an onset degradation temperature above 200 °C under nitrogen. DSC analysis (Fig. 2) revealed that **DCN3T**, **DCN5T** and **DCN7T** had different melting peaks, which were 135, 152 and 168 °C, respectively. It is interesting to point out that only **DCN7T** among these three dicyanovinyl-substituted oliogothiophenes exhibited a glass transition temperatures (T_g) (~89 °C) during DSC analysis, which is believed due to the increasing length of the oligomers.

The absorption spectra of **DCN3T**, **DCN5T** and **DCN7T** in $CHCl_3$ solution are displayed in Figure 3, and the corresponding data are presented in Table 1. For comparison purposes between dicyanovinyl-substituted and unsubstituted analogues, the absorption spectra of **3T**, **5T** and **7T** are also included in Figure 3, and the corresponding data are also presented in Table 1. The absorption spectra show that the absorption peaks of the oligothiophene cores are gradually red-shifted to longer wavelengths with increasing number of thiophene units. This can be rationalized by better intermolecular π–π interaction with expanding π-conjugation size. Two prominent absorption features were observed in the spectra of all the A–D–A molecules: a lower intensity band in the 488–517 nm range and a higher intensity band in the 304–403 nm range. In all molecules, the lowest-energy peaks have larger extinction coefficients (ε) compared to that of the high-energy peak. The high-energy absorption bands are associated with the π–π* transitions of the oligothiophene cores. Meanwhile, the lowest-energy absorption band can be assigned to the intramolecular charge transfer (ICT) between the aromatic ring donor part and the acceptor end groups.[18,23,24,33] Compared with unsubstituted oligothiophenes, **DCN3T**, **DCN5T** and **DCN7T** exhibit a rather large bathochromic shift (151, 126 and 107 nm, respectively) of the absorption maximum, which is attributed to the introduction of electron-accepting dicyanovinyl end groups, leading to a conjugated A–D–A system.

Thin films of the **DCN3T**, **DCN5T** and **DCN7T** were obtained by spin-coating of corresponding $CHCl_3$ solutions (c=8 mg mL^{-1}) onto a glass substrate. For a comparison purpose, the absorption spectra data of thin film of oligomer **7T** is also presented in Table 1. Oligomers **3T** and **5T** are oil at room temperature, and their thin films spectra were not measured. Absorption spectra in the solid state (Fig. 4) show the same trends and compared to the solution spectra, and in general, a broadening and bathochromic shift of the bands are visible. The overall spectra show a clear red-shift with increasing the units of the oligomers. As in solution, the lowest-energy absorption band in the solid state is of charge-transfer character. Compared with solution absorption spectra, the absorption maxima of film of **DCN3T**, **DCN5T** and **DCN7T** exhibit a large bathochromic shift, which is 107, 138 and 144 nm, respectively. Optical band gaps (Table 1) in solution and solid state were approximated by extrapolation of the low energy edge of each absorption spectra.[34] The optical band gaps of film of these A–D–A molecules are 1.90, 1.74 and 1.68 eV, respectively. The results show that the optical band gaps decrease with increasing units of oligomers. The wide and strong absorption of the longer members, **DCN5T** and **DCN7T** in the series, covering a broad range of the visible spectra (400–900 nm), has important implications in particular for their applications in photovoltaic devices. Because of the strong intermolecular interaction between π-electrons in the solid state, we ascribe this broadening and bathochromic shift of the bands to the coplanarization of the conjugated systems and a formation of more ordered packing in the film state as observed in many other cases.[25,26] It is important to note that the thin film in the absorption spectra of A–D–A molecules shows a sub/shoulder peak structure at longer wavelength, suggesting a vibronic progression. This is commonly understood in terms of a rigid coplanarization of the conjugated systems enforced by the crystal packing.[26,35]

Fluorescence emission spectra for the whole series of compounds were measured in chloroform (Fig. 5), and the corresponding data are presented in Table 1. The A–D–A molecules exhibit less structured and broader emission bands whose maxima absorptions with respect to the unsubstituted analogues are significantly shifted to the red due to the electron-accepting nature of the end groups. For the A–D–A molecules, the intensity of the emission bands decreased with the enlargement of the conjugated backbone, while the pure unsubstituted oligothiophenes show



Scheme 1. Synthesis route to **DCN3T**, **DCN5T** and **DCN7T**. Reagents and conditions: (a) NBS, AcOH, $CHCl_3$; (b) 2-(3-octylthienyl)magnesium bromide, Ni(dppp)Cl_2, Et_2O; (c) $POCl_3$, DMF, dichloroethane; (d) malonitrile, NEt_3, $CHCl_3$.

a structured emission whose intensity increases and maximum bathochromic shifts with the enlargement of the conjugated backbone. **DCN7T** exhibits a weak fluorescence emission at 698 nm because of its strong charge-transfer character. These results are in accordance with an expected intramolecular charge transfer from the oligothiophene donor to the dicyanovinyl acceptor.

To investigate the electrochemical properties of these A–D–A molecules and estimate their band gap, we performed cyclic voltammetry (CV) measurements on solutions of the molecules under

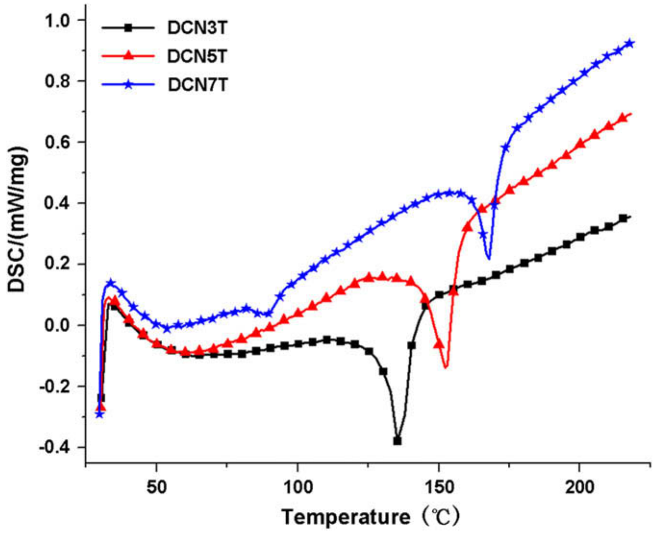


Figure 2. DSC curves of **DCN3T**, **DCN5T** and **DCN7T** with a heating rate of 5 °C min^{-1} under N_2.

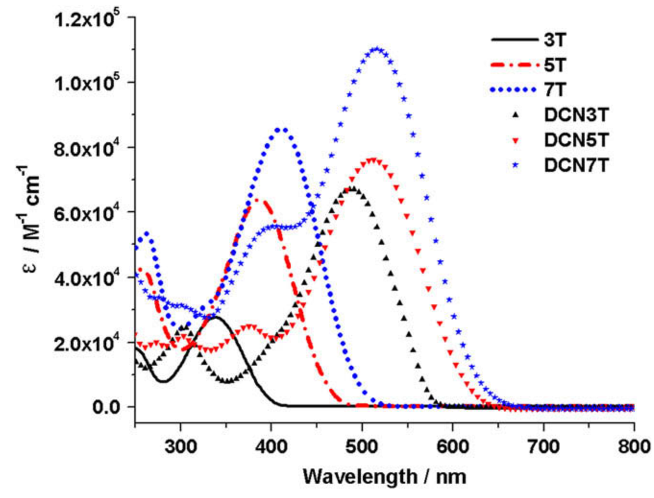


Figure 3. UV–vis spectra of 10^{-5} mol L^{-1} of **3T**, **5T**, **7T**, **DCN3T**, **DCN5T** and **DCN7T** in $CHCl_3$.

Table 1
Photophysical properties of **3T**, **5T**, **7T**, **DCN3T**, **DCN5T** and **DCN7T**

Oligomer	Absorption spectral data			Emission spectral data		
	Solution[a]		Thin film	Optical band gap		Solution[a]
	λ_{max}^{abs}, nm (ΔE, eV)	ε_{max}, L mol^{-1} cm^{-1}	λ_{max}^{abs}, nm (ΔE, eV)	Solution, eV	Film, eV	λ_{max}^{em}, nm (ΔE, eV)
3T	337 (3.68)	2.76×10^4	[b]	3.12	[b]	435 (2.85)[c]
5T	385 (3.22)	6.38×10^4	[b]	2.69	[b]	492 (2.52)[c]
7T	410 (3.02)	8.59×10^4	427 (2.90)	2.49	2.36	531 (2.34)[c]
DCN3T	487 (2.55)	6.70×10^4	551 (2.25); 594 (2.09)	2.16	1.90	576 (2.15)[d]
DCN5T	511 (2.43)	7.63×10^4	599 (2.07); 649 (1.91)	2.02	1.74	658 (1.88)[d]
DCN7T	517 (2.40)	1.10×10^5	613 (2.02); 661 (1.88)	1.96	1.68	696 (1.78)[d]

[a] Measured in dry dichloromethane.
[b] Both **3T** and **5T** are oil.
[c] Excited at 352 nm for **3T**, 397 nm for **5T**, and 419 nm for **7T**.
[d] Excited at 467 nm.

Argon. Cyclic voltammograms of all compounds in anhydrous CH_2Cl_2 in the presence of Bu_4NPF_6 as supporting electrolyte are shown in Figure 6, and all the electrochemical data are summarized in Table 2. For comparison purposes between dicyanovinyl-substituted and unsubstituted analogues, the electrochemical data of **5T** and **7T** are also included in Table 2. The CV of **3T** only shows irreversible oxidation processes, as the literature reported,[28] while **5T** displays two reversible oxidations with $E^\circ_{1+/0}$=0.78 V and $E^\circ_{2+/1+}$=0.95 V, and **7T** mainly show one reversible oxidation with $E^\circ_{1+/0}$=0.75 V. Upon introducing the electron-accepting dicyanovinyl-substituent end groups, the oligomers display oxidations with more positive potentials and new irreversible reduction processes were observed. The CV of **DCN3T** shows a reversible oxidation process at a redox potential E° of 1.43 V, corresponding to the formation of the cation radical. With increasing chain length of the oligothiophenes, both **DCN5T** and **DCN7T** show two reversible oxidation waves, which has E°=1.02 V and E°=1.24 V for **DCN5T**, and E°=0.83 V and E°=0.95 V for **DCN7T**, corresponding to the formation of the cation radical and dication, respectively. It is clear that easy oxidations can be achieved for dicyanovinyl-substituted oligothiophenes with increasing the length of the oligothiophenes and their ionization energy are dependent on the length of the conjugated systems.

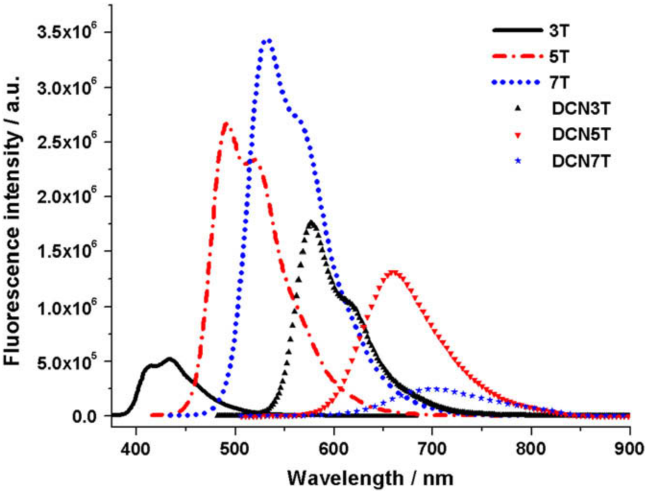


Figure 5. Fluorescence emission spectra of 10^{-5} mol L^{-1} of **3T**, **5T**, **7T**, **DCN3T**, **DCN5T** and **DCN7T** in $CHCl_3$.

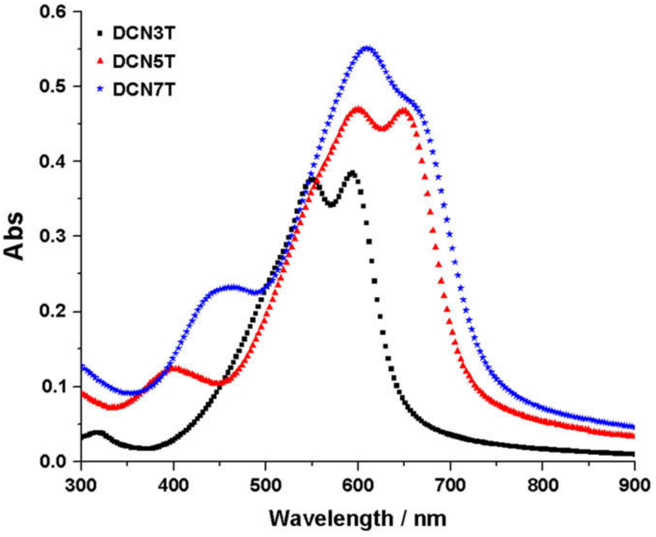


Figure 4. UV–vis-NIR spectra of film of **DCN3T**, **DCN5T** and **DCN7T**.

All these A–D–A molecules display irreversible reduction processes. The CV of **DCN3T** shows two irreversible reduction wave, while **DCN5T** and **DCN7T** show only one irreversible reduction wave and their E_{pc} are about the same. The positive shift of the first reduction potential in **DCN7T** (E_{pc}=−1.06 V) or **DCN5T** (E_{pc}=−1.06 V) as compared to that of **DCN3T** (E_{pc}=−1.10 V) is very small. The similarity of these reduction potentials suggests that the reductions are happening around the dicyanovinyl groups.[36,37] Thus, the electron affinity remains almost constant, mainly dependent on the dicyanovinyl end groups.

The data of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of

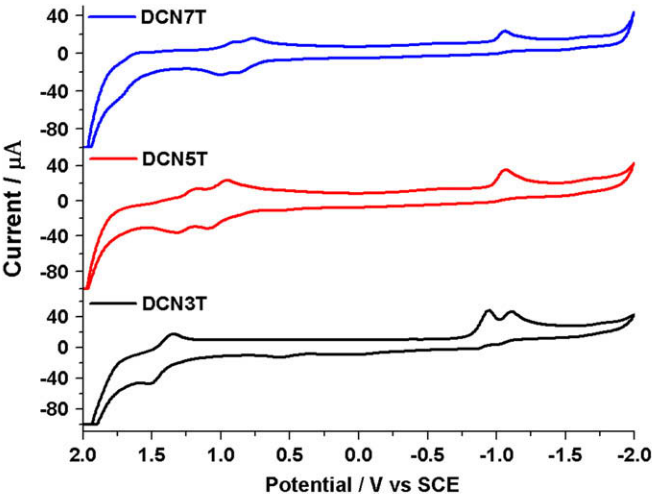


Figure 6. Electrochemical characterization of **DCN3T**, **DCN5T** and **DCN7T** in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as supporting electrolyte and a scan speed of 100 mV s^{-1}.

Table 2
Redox properties of **5T**, **7T**, **DCN3T**, **DCN5T** and **DCN7T**

Oligomer	Oxidation processes		Reduction processes		Energy level (eV)		Electrochemical band gap
	$E°$ (V)	$E^{\mathrm{ox}}_{\mathrm{onset}}$ (V)	$E°$ (V)	$E^{\mathrm{red}}_{\mathrm{onset}}$ (V)	HOMO	LUMO	$E^{\mathrm{CV}}_{\mathrm{g}}$ (eV)
5T	0.78; 0.95	0.71	[a]	[a]	−5.11		
7T	0.75	0.63	[a]	[a]	−5.03		
DCN3T	1.43	1.33	−0.94[b]; 1.10[b]	−0.81	−5.73	−3.59	2.14
DCN5T	1.02; 1.24	0.92	−1.06[b]	−0.96	−5.32	−3.44	1.88
DCN7T	0.83; 0.95	0.73	−1.06[b]	−0.98	−5.13	−3.42	1.71

[a] No observable reduction processes.

[b] Irreversible process; E_{pc} value provided.

the compounds were calculated from the onset oxidation potential and the onset reduction potential.[38–40] Thus, in this article, $E_{\mathrm{HOMO}}=-e(E^{\mathrm{ox}}_{\mathrm{onset}}+4.4)$ (eV) and $E_{\mathrm{LUMO}}=-e(E^{\mathrm{red}}_{\mathrm{onset}}+4.4)$ (eV), where E_{LUMO} is the LUMO energy level, E_{HOMO} is the HOMO energy level and all electrode potential values are versus SCE as the reference electrode. Electrochemical band gaps $E^{\mathrm{CV}}_{\mathrm{g}}$ were calculated from the energy difference of HOMO and LOMO levels calculated as above, which are 2.14, 1.88 and 1.71 eV, respectively. These results demonstrate that the electrochemical band gaps $E^{\mathrm{CV}}_{\mathrm{g}}$ (Table 2) decreases also throughout the series with increasing oligothiophene units and can be compared to the optical band gaps $E^{\mathrm{opt}}_{\mathrm{g}}$ (Table 1). As a result, these materials, with low and tunable band gap and thus a good match with the solar spectra, are expected to have improved energy conversion efficiency for solar cells.[41,42]

3. Conclusions

In conclusion, a series of A–D–A molecules based on oligothiophenes that exhibit interesting electronic and solid-state properties have been synthesized and characterized. For all the A–D–A molecules, we found that the band gap and ionization energy are dependent on the length of the conjugated systems while the electron affinity remains almost constant, being dominated by the electron-accepting end groups. By controlling the oligomer units, their band gap can be clearly tuned and a low band gap of 1.68 eV was achieved. These properties, coupled with their good solubility and stability, are prompting us to study their applications for light harvesting and solar energy conversion in various optoelectronic devices.

4. Experimental section

4.1. Materials and reagents

All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. Diethyl ether was distilled from Na/benzophenone under argon atmosphere. Dichloromethane and chloroform were distilled from calcium hydride under argon atmosphere. All starting materials were purchased from commercial suppliers (Alfa Aesar and Aldrich) and used without further purification. 2-Bromo-3-octylthiophene, 2-(3-octylthienyl)magnesium bromide and 3,3-dioctyl-2,2′:5,2″-terthiophene were prepared according to the literature procedures.[28]

4.2. Instruments and measurements

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV400 Spectrometer. High resolution MALDI spectra were collected with a Fourier transform-ion cyclotron resonance mass spectrometer instrument (Varian 7.0T FTICR-MS). Elemental analyses were performed on an Elementar Vario EL analyzer. FTIR spectra were obtained with a BRUKER TENSOR 27 instrument. All IR samples were prepared as thin films using spectroscopic grade KBr. Only significant absorptions (ν_{max}) were reported in wavenumbers (cm^{-1}). The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis studies were carried out on a NETZSCH STA 409PC instrument under purified nitrogen gas flow with a 5 °C min^{-1} heating rate. UV–vis spectra were obtained with a JASCO V-570 spectrophotometer. Fluorescence spectra were obtained with a FluoroMax-P instrument. Cyclic voltammetry (CV) experiments were performed with a LK98B II Microcomputer-based Electrochemical Analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6, 0.1 M) in dichloromethane was used as the supporting electrolyte, and the scan rate was 100 mV s^{-1}.

4.2.1. *5,5″-Dibromo-3,3″-dioctyl-2,2′:5′,2″-terthiophene (**2**)*

N-Bromosuccinimide (0.96 g, 5.39 mmol) was added in small portions to a solution of terthiophene **1** (1.20 g, 2.54 mmol) in chloroform and acetic acid (60 mL, 1:1, v/v) at 0 °C. After being stirred for 3 h at room temperature, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2. The organic layer was thoroughly washed with water, aqueous sodium bicarbonate, brine and again with water, and then dried over Na_2SO_4. After removal of solvent it was chromatographied on silica gel using petroleum ether as eluant to afford dibromoterthiophene **2** (1.60 g, 100%) as a yellow oil. ^{1}H NMR (400 MHz, $CHCl_3$): 6.99 (s, 2H), 6.91 (s, 2H), 2.72 (t, *J*=7.8 Hz, 4H), 1.63 (m, 4H), 1.29 (m, 20H), 0.91 (t, *J*=6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 140.43, 135.18, 132.73, 131.67, 126.41, 110.71, 31.94, 30.64, 29.52, 29.46, 29.31, 22.74, 14.18. HRMS (MALDI-FTICR): calcd for $C_{28}H_{38}Br_2S_3$ $[M]^+$ 628.0502; found 628.0507.

4.2.2. *3,3′,3‴,3⁗-Quadrioctyl-2,5′:2′,5″:2″,2‴:5‴,2⁗-quinquethiophene (**3**)*

A solution of 2-(3-octylthienyl)magnesium bromide prepared from 2-bromo-3-octylthiophene (2.00 g, 7.27 mmol) was added dropwise into a mixture of dibromoterthiophene **2** (1.54 g, 2.44 mmol) and Ni(dppp)Cl_2 (90 mg, 0.17 mmol) catalyst in diethyl ether (20 mL) over 0.5 h. After refluxing for additional 20 h, the solution was cooled to room temperature and quenched with HCl (20 mL, 1 M), followed by the addition of water (100 mL). The mixture was extracted with CH_2Cl_2, washed with water, brine and dried over Na_2SO_4. After removal of solvent it was chromatographied on silica gel using petroleum ether as eluant to afford quinquethiophene **3** (1.75 g, 83%) as a golden oil. ^{1}H NMR (400 MHz, $CHCl_3$): 7.18 (d, *J*=5.2 Hz, 2H), 7.09 (s, 2H), 6.96 (s, 2H), 6.93 (d, *J*=5.2 Hz, 2H), 2.78 (t, *J*=7.7 Hz, 8H), 1.67 (m, 8H), 1.28 (m, 40H), 0.88 (m, 12H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 139.83, 139.62, 135.74, 134.28, 130.47, 130.25, 130.08, 128.73, 125.86, 123.59, 31.92, 30.71, 30.64, 29.63, 29.57, 29.50, 29.46, 29.31, 22.71, 14.13. HRMS (MALDI-FTICR): calcd for $C_{52}H_{76}S_5$ $[M]^+$ 860.4551; found 860.4540.

*4.2.3. 5,5⁗-Dibromo-3,3′,3‴,3⁗-quadrioctyl-2,5′:2′,5″:2″,2‴:5‴,2⁗-quinquethiophene (**4**)*

N-Bromosuccinimide (0.50 g, 2.81 mmol) was added in small portions to a solution of quinquethiophene **3** (1.15 g, 1.33 mmol) in chloroform and acetic acid (60 mL, 1:1 v/v) at 0 °C. After being stirred for 3 h at room temperature, the reaction mixture was poured into water (100 mL) and extracted with CH_2Cl_2. The organic layer was thoroughly washed with water, aqueous sodium bicarbonate, brine and again with water, and then dried over Na_2SO_4. After removal of solvent it was chromatographied on silica gel using petroleum ether as eluant to afford dibromoquinquethiophene **4** (1.22 g, 90%) as a yellow oil. ^{1}H NMR (400 MHz, $CHCl_3$): 7.10 (s, 2H), 6.92 (s, 2H), 6.91 (s, 2H), 2.81 (t, J=7.5 Hz, 4H), 2.75 (t, J=7.6 Hz, 4H), 1.61–1.73 (m, 8H), 1.32 (m, 40H), 0.90 (m, 12H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 140.15, 139.88, 135.68, 132.96, 132.73, 132.07, 130.78, 129.04, 125.99, 110.41, 32.02, 30.88, 30.68, 30.63, 29.72, 29.58, 29.56, 29.53, 29.44, 29.38, 29.34, 22.81, 14.22. HRMS (MALDI-FTICR): calcd for $C_{52}H_{74}Br_2S_5$ $[M]^+$ 1016.2761; found 1016.2763.

*4.2.4. 3,3′,3″,3⁗,3⁗′,3⁗″-Sexioctyl-2,5′:2′,5″:2″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗″-septithiophene (**5**)*

A solution of 2-(3-octylthienyl)magnesium bromide prepared from of 2-bromo-3-octylthiophene (1.00 g, 3.63 mmol) was added dropwise into a mixture of dibromoquinquethiophene **4** (1.24 g, 1.22 mmol) and Ni(dppp)Cl_2 (59 mg, 0.11 mmol) catalyst in diethyl ether (20 mL) over 0.5 h. After refluxing for additional 20 h, the solution was cooled to room temperature and quenched with HCl (20 mL, 1 M), followed by the addition of water (100 mL). The mixture was extracted with CH_2Cl_2, washed with water, brine and dried over Na_2SO_4. After removal of solvent it was chromatographied on silica gel using petroleum ether as eluant to afford septithiophene **5** (1.09 g, 72%) as a brick red solid. ^{1}H NMR (400 MHz, $CHCl_3$): 7.17 (d, J=5.2 Hz, 2H), 7.12 (s, 2H), 7.00 (s, 2H), 6.97 (s, 2H), 6.95 (d, J=5.2 Hz, 2H), 2.81 (m, 12H), 1.70 (m, 12H), 1.30 (m, 60H), 0.90 (m, 18H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 139.96, 139.86, 139.65, 135.77, 134.16, 133.98, 130.53, 130.31, 130.12, 128.79, 128.60, 125.93, 123.61, 31.94, 30.71, 30.67, 30.60, 29.66, 29.58, 29.52, 29.47, 29.34, 22.72, 14.15. HRMS (MALDI-FTICR): calcd for $C_{76}H_{112}S_7$ $[M]^+$ 1248.6809; found 1248.6809.

*4.2.5. 5,5″-Diformyl-3,3″-dioctyl-2,2′:5′,2″-terthiophene (**6**)*

A Vilsmeier reagent, which was prepared with $POCl_3$ (0.71 mL, 7.78 mmol) in DMF (3.00 mL, 38.76 mmol), was added to a cold solution of **3T** (1.22 g, 2.58 mmol) in 1,2-dichloroethane (30 mL) at 0 °C under Ar. After being stirred at 60 °C for 12 h, the mixture was poured into ice water (200 mL), neutralized with Na_2CO_3, and then extracted with dichloromethane. The combined organic layer was washed with water and brine, dried over Na_2SO_4. After removal of solvent it was chromatographied on silica gel using a mixture of dichloromethane and petroleum ether (1:1) as eluant to afford diformylterthiophene **6** (1.13 g, 83%) as a coral solid. ^{1}H NMR (400 MHz, $CHCl_3$): 9.84 (s, 2H), 7.61 (s, 2H), 7.27 (s, 2H), 2.82 (t, J=7.6 Hz, 4H), 1.69 (m, 4H), 1.29 (m, 20H), 0.87 (t, J=5.8 Hz, 6H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 182.51, 140.99, 140.84, 140.07, 138.91, 136.70, 127.96, 31.86, 30.32, 29.50, 29.40, 29.24, 22.67, 14.10. HRMS (MALDI-FTICR): calcd for $C_{30}H_{40}O_2S_3$ $[M]^+$ 528.2190; found 528.2191.

*4.2.6. 5,5⁗-Diformyl-3,3′,3‴,3⁗-quadrioctyl-2,5′:2′,5″:2″,2‴:5‴,2⁗-quinquethiophene (**7**)*

Compound **7** was prepared from **3** with a method similar to that described earlier for **6**. Yield: 85%. Dark orange solid. ^{1}H NMR (400 MHz, $CHCl_3$): 9.83 (s, 2H), 7.59 (s, 2H), 7.14 (s, 2H), 2.82 (m, 8H), 1.70 (m, 8H), 1.28 (m, 40H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 182.48, 141.01, 140.47, 140.39, 140.19, 139.01, 135.74, 132.94, 132.47, 130.46, 126.55, 31.88, 30.55, 30.27, 29.56, 29.43, 29.38, 29.28, 29.24, 22.67, 14.10. HRMS (MALDI-FTICR): calcd for $C_{54}H_{76}O_2S_5$ $[M]^+$ 916.4449; found 916.4441.

*4.2.7. 5,5⁗″-Diformyl-3,3′,3″,3⁗,3⁗′,3⁗″-sexioctyl-2,5′:2′,5″:2″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′,2⁗″-septithiophene (**8**)*

Compound **8** was prepared from **5** with a method similar to that described earlier for **6**. Yield: 81%. Brown solid. ^{1}H NMR (400 MHz, $CHCl_3$): 9.82 (s, 2H), 7.58 (s, 2H), 7.12 (s, 2H), 7.11 (s, 2H), 7.01 (s, 2H), 2.81 (m, 12H), 1.69 (m, 12H), 1.30 (m, 60H), 0.87 (m, 18H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 182.49, 141.18, 140.27, 140.24, 140.16, 140.04, 139.10, 135.71, 133.28, 132.80, 132.57, 130.97, 130.47, 129.13, 126.14, 31.90, 30.92, 30.63, 30.50, 30.26, 29.71, 29.62, 29.54, 29.47, 29.42, 29.39, 29.32, 29.26, 22.69, 14.12. HRMS (MALDI-FTICR): calcd for $C_{78}H_{112}O_2S_7$ $[M]^+$ 1304.6707; found 1304.6707.

*4.2.8. 5,5″-Bi(dicyanovinyl)-3,3″-dioctyl-2,2′:5′,2″-terthiophene (**DCN3T**)*

Diformylterthiophene **6** (70 mg, 0.13 mmol) was dissolved in a solution of malonitrile (66 mg, 1.00 mmol) in dry $CHCl_3$ (10 mL) and then three drops of triethylamine were added and the resulting solution was stirred overnight, under argon, at room temperature. The reaction mixture was then diluted with ethyl acetate, washed with water and brine, After removal of solvent it was chromatographied on silica gel using dichloromethane as eluant to afford **DCN3T** as a maroon solid (73 mg, 88% yield). ^{1}H NMR (400 MHz, $CHCl_3$): 7.74 (s, 2H), 7.57 (s, 2H), 7.36 (s, 2H), 2.83 (t, J=7.4 Hz, 4H), 1.68 (m, 4H), 1.25 (m, 20H), 0.86 (t, J=6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 149.95, 142.09, 141.71, 141.53, 136.72, 133.03, 129.00, 114.08, 113.21, 31.81, 30.90, 30.09, 29.68, 29.45, 29.34, 29.19, 22.63, 14.07. IR (KBr): 2923, 2853, 2821, 1568, 1408, 1333, 1269, 1182. Anal. Calcd for $C_{36}H_{40}N_4S_3$: C, 69.19; H, 6.45; N, 8.97. Found: C, 69.31; H, 6.90; N, 8.53.

*4.2.9. 5,5⁗-Bi(dicyanovinyl)-3,3′,3‴,3⁗-quadrioctyl-2,5′:2′,5″:2″,2‴:5‴,2⁗-quinquethiophene (**DCN5T**)*

DCN5T was prepared from **7** with a method similar to that described earlier for **DCN3T**. Yield: 85%. Black solid. ^{1}H NMR (400 MHz, $CHCl_3$): 7.70 (s, 2H), 7.53 (s, 2H), 7.23 (s, 2H), 7.18 (s, 2H), 2.83 (m, 8H), 1.69 (m, 8H), 1.28 (m, 40H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 149.97, 143.70, 141.88, 140.94, 140.80, 135.81, 133.82, 132.16, 132.07, 131.48, 126.87, 114.37, 113.50, 31.87, 31.84, 30.56, 30.06, 29.70, 29.62, 29.46, 29.42, 29.34, 29.28, 29.22, 22.67, 14.10. IR (KBr): 2924, 2853, 2218, 1568, 1421, 1377, 1327, 1180. HRMS (MALDI-FTICR): calcd for $[M]^+$ 1012.4674; found 1012.4675. Anal. Clacd for $C_{60}H_{76}N_4S_5$: C, 71.10; H, 7.56; N, 5.53. Found: C, 71.16; H, 7.11; N, 5.31.

*4.2.10. 5,5⁗″-Bi(dicyanovinyl)-3,3′,3″,3⁗,3⁗′,3⁗″-sexioctyl-2,5′:2′,5″:2″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′, 2⁗″-septithiophene (**DCN7T**)*

DCN7T was prepared from **8** with a method similar to that described earlier for **DCN3T**. Yield: 83%. Black solid. ^{1}H NMR (400 MHz, $CHCl_3$): 7.69 (s, 2H), 7.52 (s, 2H), 7.21 (s, 2H), 7.13 (s, 2H), 7.04 (s, 2H), 2.81 (m, 12H), 1.69 (m, 12H), 1.28 (m, 60H), 0.88 (m, 18H). ^{13}C NMR (100 MHz, $CHCl_3$): δ 149.90, 144.00, 141.92, 140.62, 140.31, 135.72, 134.33, 132.99, 131.99, 131.62, 131.50, 131.39, 129.42, 126.27, 114.46, 113.54, 31.90, 30.62, 30.53, 30.02, 29.63, 29.60, 29.47, 29.41, 29.35, 29.30, 22.68, 14.12. IR (KBr): 2924, 2853, 2818, 1564, 1423, 1377, 1325, 1182. HRMS (MALDI-FTICR): calcd for $[M]^+$ 1400.6932; found 1400.6935. Anal. Calcd for $C_{84}H_{112}N_4S_7$: C, 71.95; H, 8.05; N, 4.00. Found: C, 72.43; H, 8.33; N, 4.01.

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