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Unsymmetrical donor–acceptor oligothiophenes end-capped with triphenylamine and phenyldicyanovinyl units

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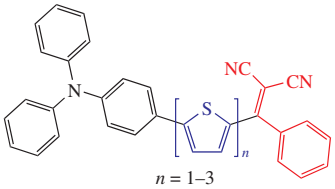
Highly stable unsymmetrical donor–acceptor oligothiophenes equipped with terminal electron-donating triphenylamine and an electron-withdrawing phenyldicyanovinyl groups have been synthesized. An influence of the length of conjugated oligothiophene π-spacer between the donor and acceptor blocks on solubility, thermal, optical and electrochemical properties of such compounds has been revealed.

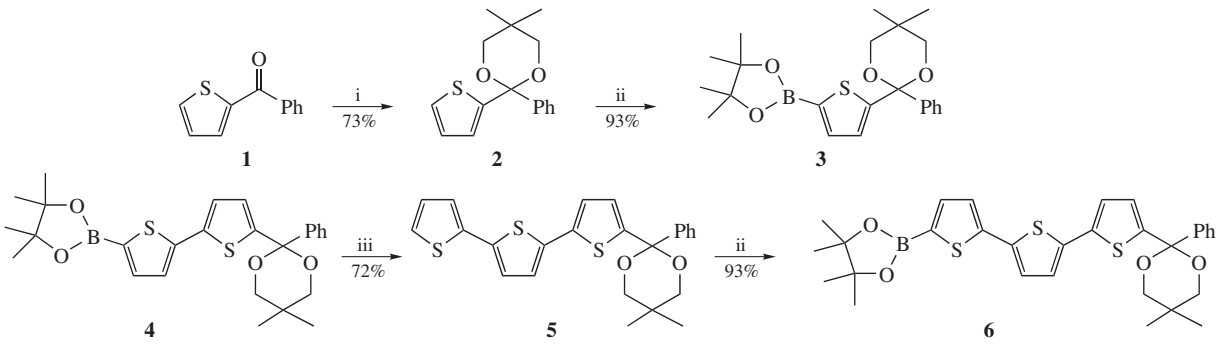


n = 1–3
TPA-nT-DCV-Ph

Among the huge amount of materials used in devices of organic electronics and photonics, donor–acceptor molecules containing oligothiophene units have the most interesting properties. They possess high mobility of charge carriers, stability, good light absorption and solubility in organic solvents. Various thiophene derivatives have been employed as functional components in organic electronics devices, ranging from sensors to organic solar cells.[1–5]

In this work, we investigated a series of donor–acceptor (DA) molecules differing in the length of the oligothiophene fragment between the electron-donating triphenylamine (TPA) and electron-withdrawing phenyldicyanovinyl (Ph-DCV) blocks. A preparation of relatively simple DA molecules with increased stability as compared to known analogues[6–8] was the main goal at design of such compounds. We have shown that the combination of Ph-DCV group and TPA unit allows one to obtain star-shaped DA compounds with unique properties and high stability.[9] Unsymmetrical linear analogues of such compounds have a number of advantages. They are synthetically available, their functional layers can be obtained by vacuum deposition[10] and the unsymmetrical structure favours to the appearance of nonlinear optical properties[11] and increased solubility. The first simplest unsymmetrical representative of DA oligomers with Ph-DCV group containing one thiophene unit was prepared by an alternative method and showed a number of promising properties including high photovoltaic efficiency and an unusually long exciton diffusion length.[12] That approach comprises lithiation step of the TPA-thiophene precursor which proceeds with a moderate yield. Apparently, this method may meet limitations for the synthesis of higher oligothiophenes, since the efficiency of the hydrogen–lithium exchange tends to decrease with increasing of the conjugation length. In this work, we demonstrate a more universal synthetic approach, which makes it possible to successfully prepare the series of DA unsymmetrical oligomers with different conjugation lengths of oligothiophene spacer between TPA and Ph-DCV units.

The Suzuki cross-coupling between (4-bromophenyl)diphenylamine **7** and thiophene-containing organoboron precursors **3**, **4** or **6** is the key stage of the developed protocol (Scheme 1). Since the organoboron precursors are produced *via* a lithium derivative, the synthetic scheme includes protection of the carbonyl



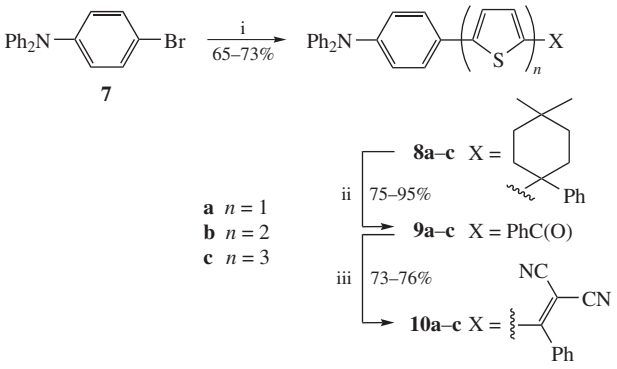
Scheme 1 *Reagents and conditions*: i, $HOCH_2CMe_2CH_2OH$, PhH, TsOH, reflux; ii, BuLi, THF, –78 °C, then IPTMDOB; iii, 2-bromothiophene, $Pd(PPh_3)_4$, aq. Na_2CO_3, PhMe, EtOH, reflux.

function of the corresponding ketones with 5,5-dimethyl-1,3-dioxane group. The total synthesis of the target molecules **1a–c** involves two general stages. First, thiophene-containing precursors with the protective group (compounds **3**, **4** and **6**) were obtained (see Scheme 1). Organoboron reactant **3** was produced in two reaction steps. Its precursor **2** was prepared by protection of ketone **1** with 2,2-dimethyl-1,3-propanediol in 73% yield. Second, compound **3** was synthesized in 93% yield *via* reaction of the monolithium derivative of **2** with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB).

Terthiophene organoboron reactant **6** was prepared by 'elongation' of the thiophene chain of the previously described[9] compound **4**. The addition of thiophene was carried out by the Suzuki cross-coupling between **4** and commercial 2-bromothiophene to give compound **5** in 72% yield. Product **6** was obtained *via* lithiation reaction of the latter followed by subsequent treatment with IPTMDOB in 93% yield.

At the second stage, cross-coupling of thiophene-containing organoboron precursors **3**, **4** or **6** and (4-bromophenyl)diphenylamine **7** afforded adducts **8a–c** in 70, 68 and 65% yields, respectively. The ketal protective group was removed by their reflux in THF in the presence of 1 M hydrochloric acid to give ketones **9a–c** in 75–95% yields. Finally, the Knoevenagel condensation of the ketones with malononitrile led to the desired compounds **10a–c** in 73, 76 and 73% yields, respectively (Scheme 2). ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry were used to characterize the structure of the precursors and the target compounds (Figures S1–S26, Online Supplementary Materials).

The thermal properties of the DA oligomers **10a–c** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All compounds (Table 1) demonstrate excellent stability both in air and under inert atmosphere [Figures 1(*a*) and S27]. The decomposition temperatures corresponding to 5% of the weight loss (T_d) reach 448 °C, which is a very high value for this type of compounds. In addition, T_d tends to increase with elongation of the thiophene spacer. It is also of interest that a proportion of the Ph-DCV group in the mass of the DA molecule affects the solid residue (see TGA curves in argon, Figure S27). The smaller proportion of the Ph-DCV group in the mass of the DA molecule, the greater solid residue we have, suggesting that this group starts to destroy first at high temperatures and then initiates further decomposition of the molecule.



Scheme 2 *Reagents and conditions*: i, **3**, **4** or **6**, $Pd(PPh_3)_4$, aq. Na_2CO_3, PhMe, EtOH, reflux; ii, 1 M HCl, THF, reflux; iii, $CH_2(CN)_2$, Py, reflux.

An investigation of the phase behavior of synthesized compounds by the DSC has shown that the increase in length of the thiophene π-spacer hinders crystallization of the molecules and raises glass transition temperature (T_g). The DSC studies of compounds **10a**,**b** revealed that both of them have a quite complex phase behavior [Figure 1(*b*)]. At the first heating, they show a glass transition followed by cold crystallization and melting processes, while compound **10c** demonstrates only a glass transition. Such behavior of the molecules with one and two thiophene units in the π-spacer suggests that these oligomers as-received are a mixture of amorphous and crystalline materials. The preliminary annealing of **10a** and **10b** above the glass transition temperature allowed converting them to the crystalline state only (Figure S28). Compound **10a** has a higher melting enthalpy and temperature than compound **10b** (see Table 1), which indirectly indicates that oligomer **10a** forms a more ordered crystalline phase. The subsequent heating showed that both materials become amorphous after melting, which is typical of other known analogous molecules based on the propeller-shaped TPA core.[13,14] Note that T_g tends to increase from **10a** to **10c** due to growing molecular weight of the oligomers.

All three DA molecules exhibit good solubility in THF, chloroform and *o*-dichlorobenzene. The measured exact solubility values in *o*-dichlorobenzene increase from 25 to 41 g dm^{-3} with elongation of the conjugated thiophene π-bridge (see Table 1). This is in a good agreement with DSC data, which revealed a decrease

Table 1 Solubility in *o*-dichlorobenzene and thermal, optical, electrochemical properties of DA oligomers **10a–c**.

Compound	Solubility/ g dm^{-3}	DSC			TGA, T_d/°C		UV-VIS absorption, λ/nm		Cyclic voltammetry		
		T_m/°C	ΔH_m/J g^{-1}	T_g/°C	In air	In argon	In THF solution	Films cast from THF	HOMO/ eV	LUMO/ eV	Band gap/ eV
10a	25	223	106	73	390	400	489	514	–5.40	–3.38	2.02
10b	30	183	69	76	423	437	501	532	–5.34	–3.38	1.96
10c	41	–	–	78	448	428	509	543	–5.27	–3.38	1.89

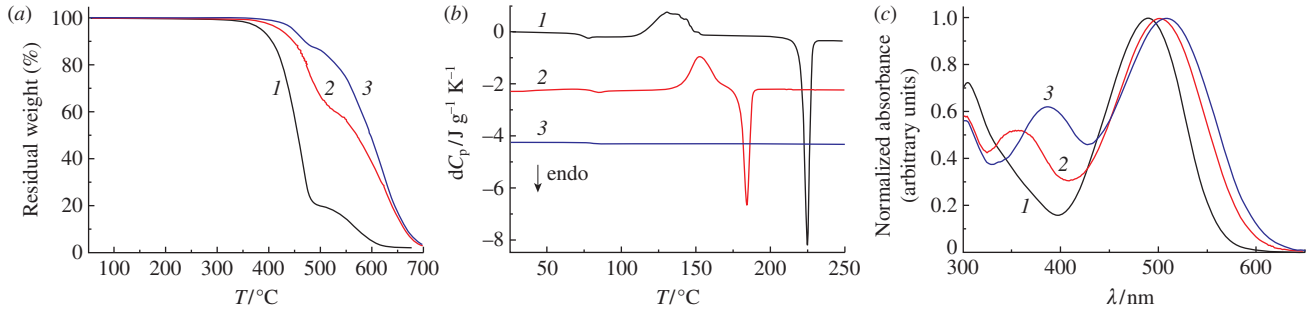


Figure 1 (*a*) TGA curves in air, (*b*) DSC curves of the first heating, (*c*) normalized absorption spectra in diluted solutions of THF for (*1*) **10a**, (*2*) **10b** and (*3*) **10c**.

in the ability of molecules to form highly ordered crystalline phases with increasing the number of thiophene units. Note that the observed tendency of solubility increase with the elongation of the thiophene fragment is not typical of oligothiophenes, whose solubility usually diminishes with increasing the conjugation length.[15]

The optical properties of synthesized oligomers were studied by absorption spectroscopy in both solutions and thin films. All compounds reveal an effective sunlight absorption in the range of 350–650 nm. The absorption spectra of the synthesized oligomers in diluted solutions of THF have a similar shape [Figure 1(*c*)]. Two types of absorption bands are observed in the spectra, where the bands in 300–410 nm region are usually ascribed to π–π* transition in the conjugated phenyloligothiophene fragment and the intensive bands in long-wave region (400–600 nm) are mainly attributed to an intramolecular charge transfer (ICT) between electron-donating and electron-withdrawing blocks.[6,8] The bathochromic shift of the high-energy absorption bands with increasing the number of thiophene fragments has a pronounced character due to the increase in π-conjugation length in the oligothiophene fragment. However, bathochromic shift of the low-energy absorption bands with increasing the number of thiophene fragments is less pronounced and has a tendency of saturation, due to both the known intramolecular distortion of the torsional angles in oligothiophenes[16,17] and a decreased efficiency of ICT process with elongation of distance between D and A blocks.[17–19] As compared to solution, the absorption spectra in thin films are broadened and the absorption maxima are shifted to the long-wave region by 25–34 nm (Figure S29).

The electrochemical properties of the oligomers were investigated by the cyclic voltammetry. Their reduction proceeds at the same values, since in these compounds the electron-withdrawing Ph-DCV group is mainly responsible for the reduction and the length of the π-bridge has no effect on that. However, the oxidation potentials were found to be dependent significantly on the length of the thiophene π-bridge, since the oxidation occurs mainly through the triphenylamine-thiophene fragment. Therefore, we observe a facilitation of the oxidation process with increasing the number of the thiophene fragments from 1 to 3. The HOMO and LUMO energies were calculated using the first standard formal oxidation and reduction potentials (see Table 1). Values of the LUMO energy levels for this series of molecules are similar, whereas values of the HOMO energy levels increase in the row **10a < 10b < 10c**. The latter leads to a corresponding decrease in the electrochemical band gap from 2.02 to 1.89 eV, which agrees well with the absorption spectra of molecules, since their absorption maxima and absorption edges are shifted to long-wave region with increasing the number of thiophene units in the π-spacer.

In conclusion, a universal synthetic approach was developed and used for the preparation of the series of unsymmetrical DA oligothiophenes based on electron-donating TPA and an electron-withdrawing Ph-DCV group. An effect of the length of the conjugated oligothiophene π-spacer on solubility and thermal, optical, electrochemical properties of the molecules was evaluated. Compounds with one and two thiophene units in the π-spacer can be obtained both in a crystalline and amorphous state, while that with three thiophene units in the π-spacer does not show any capability of forming a crystalline phase. All the compounds synthesized demonstrate an effective sunlight absorption in the visible region of the spectrum. However, their absorption maxima shift to the long-wave region with increasing the number of thiophene units. The elongation of the oligothiophene fragment also increases values of the HOMO energy level and reduces the band-gap from 2.02 to 1.89 eV. In addition, all the compounds obtained have excellent thermal stability and high solubility in organic solvents, which makes them promising materials for organic electronics and photonics.

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A.N.S. and Yu.N.L. contributed equally to this study.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.07.025.

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