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Mendeleev Commun., 2019, **29**, 385–387

Mendeleev Communications

Effect of branching on the physical and photovoltaic properties of donor–acceptor oligomers based on triphenylamine

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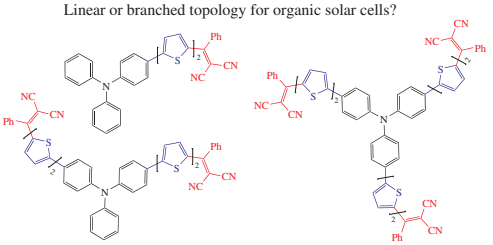
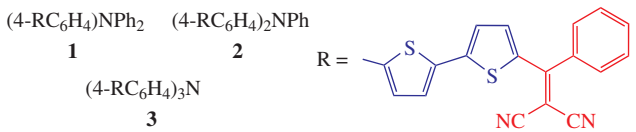
DOI: 10.1016/j.mencom.2019.07.008

A new donor–acceptor oligomer with two terminal electron-withdrawing phenyldicyanovinyl groups attached to the electron-donating triphenylamine core *via* π-conjugated bithiophene spacers has been synthesized and compared with its analogues containing one and three phenyldicyanovinyl groups. Influence of the number of electron-withdrawing substituents on the solubility, thermal, optical, electrochemical and photovoltaic properties of these compounds has been revealed.

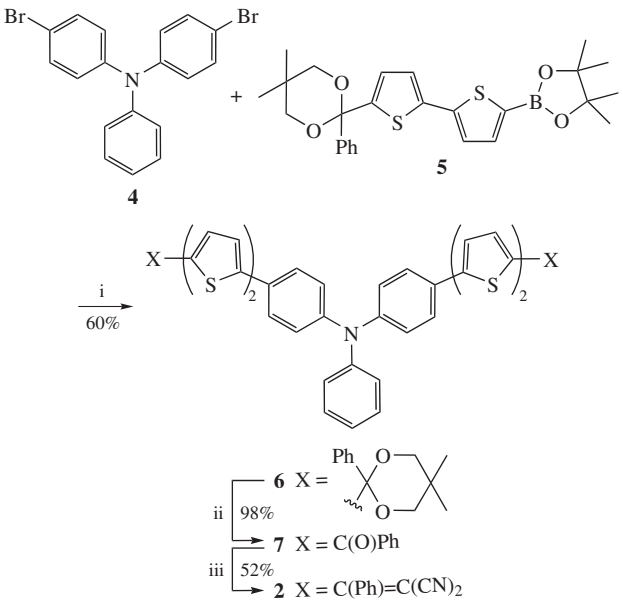


Among a huge amount of organic semiconductors used in organic optoelectronic devices, donor–acceptor (DA) compounds based on triphenylamine (TPA) core possess the most promising properties, such as good solubility in organic solvents, stability and high hole mobility.[1–6] In the last decade, numerous DA TPA-based molecules of linear and branched topology have been synthesized and employed as donor components in organic solar cells.[7] Although the influence of electron-withdrawing groups number in star-shaped TPA systems on their physicochemical and photovoltaic properties was analyzed,[1] a systematic investigation of this branching effect has not yet been reported.

Here we investigated a series of DA oligomers of various symmetry and degree of branching, which differ in the number of terminal phenyldicyanovinyl electron-accepting groups with conjugated bithiophene spacers (Ph-DCV-2T), attached to the electron-donating TPA core. Recently, we demonstrated that a combination of Ph-DCV-2T group and TPA core in asymmetric compound **1**[8] or its star-shaped counterpart **3**[9] provided their unique physicochemical properties, such as good solubility, crystallizability, high thermal, thermooxidation and electrochemical stability,[10,11] contrary to their analogues with active hydrogen in the dicyanovinyl groups.[12–15] In this work, we synthesized a new symmetrical TPA-core DA oligomer **2** with two Ph-DCV-2T branches and, for the first time, systematically investigated the influence of the number of branches on the solubility, thermal, optical, electrochemical and photovoltaic properties in the series of compounds **1**–**3**.



The synthesis of oligomer **2** was carried out in three steps (Scheme 1). Diketal **6** was obtained by the Suzuki cross-coupling of *N*,*N*-bis(4-bromophenyl)phenylamine **4** and 5,5-dimethyl-2-phenyl-2-[5′-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2′-bithien-5-yl]-1,3-dioxane **5** in 60% yield. Then the protective groups of diketal **6** were removed by reflux in THF in the presence of 1 M hydrochloric acid to give the corresponding diketone **7** in 98% yield. Finally, the Knoevenagel condensation of diketone



Scheme 1 *Reagents and conditions*: i, $Pd(PPh_3)_4$, aq. Na_2CO_3, PhMe, EtOH, reflux, 12 h; ii, 1 M HCl, THF, reflux, 4 h; iii, $CH_2(CN)_2$, pyridine, reflux, 19 h.

Table 1 Solubility in *o*-dichlorobenzene as well as thermal, optical and electrochemical properties of compounds **1**–**3**.

Compound	Solubility/ g dm^{-3}	DSC			TGA in air/argon, T_d/°C	UV-VIS spectroscopy			Cyclic voltammetry		
						Solution		Film			
		T_m/°C	ΔH_m/J g^{-1}	T_g/°C		ε/dm^3 mol^{-1} cm^{-1}	λ_{max}/nm	λ_{max}/nm	HOMO/eV	LUMO/eV	E_g/eV
1[8]	30	183	69	76	423/437	46000	501	532	–5.34	–3.38	1.96
2	24	276	79	130	470/484	74000	510	543	–5.34	–3.42	1.92
3[9]	30	285	74	146	460/490	122000	515	545	–5.34	–3.43	1.91

7 with malononitrile in pyridine under microwave irradiation resulted in compound **2** in 52% yield. The chemical structure and purity of the intermediates and the product were confirmed by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry.†

Compound **2** was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the data obtained were compared with those for compounds **1** and **3** (Table 1). All the products demonstrated excellent stability both in air and under inert atmosphere [Figure 1(*a*) and Figure S7, Online Supplementary Materials]. The decomposition temperatures corresponding to 5% weight loss T_d were in the range of 423–490 °C, *i.e.*, represented high values for organic compounds.

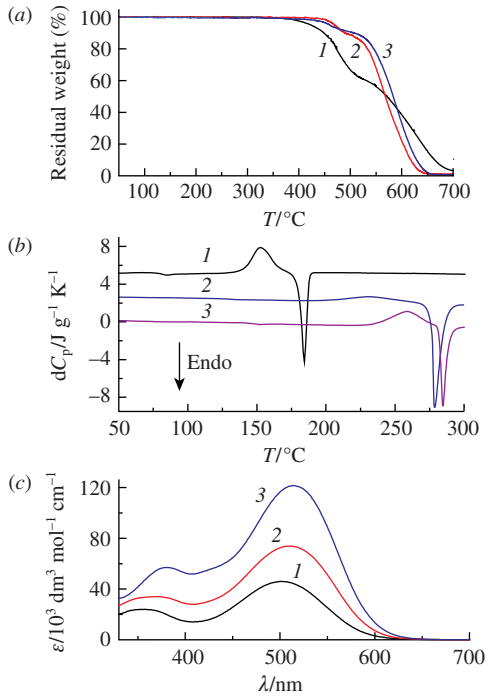


Figure 1 (*a*) TGA curves in air, (*b*) DSC curves of the first heating and (*c*) absorption spectra in diluted THF solutions for compounds (*1*) **1**, (*2*) **2** and (*3*) **3**.

The DSC investigation of compounds **1**–**3** revealed their similar phase behavior pattern, regardless of the number of branches, and occurrence of the crystalline state with high melting temperature T_m and enthalpy ΔH_m [see Table 1, Figures 1(*b*) and S8]. During the first heating, compounds **1**–**3** revealed a glass transition, followed by cold crystallization and melting [see Figure 1(*b*)], which testified that they were obtained as mixtures of amorphous and crystalline states. Preliminary annealing of these compounds above the glass transition temperature resulted in their conversion into the crystalline state (see Figure S8). The T_m value increases with the number of branches, which indicates improved ability to form ordered crystalline phase. Note, that after the first melting and the subsequent cooling to the room temperature, none of the compounds restored the crystalline phase, which is typical of the known related molecules based on the propeller-shaped TPA core.[16,17] During the second heating, only bending of the DSC curve was observed due to the glass transition. Moreover, a pronounced increase in the glass transition temperature was detected in a series of compounds from **1** to **3**, following the molecular weight increase.

All three DA compounds exhibit good solubility in THF, chloroform and *o*-dichlorobenzene, with no evident trend for the last solvent (see Table 1). The lower solubility for compound **2** bearing two branches agrees well with its high T_m and ΔH_m values, testifying to the strong intermolecular interaction in the crystalline phase.

Optical properties of compounds **1**–**3** were examined using absorption spectroscopy in solutions as well as thin films, and the compounds revealed effective sunlight absorption in 350–650 nm range. The absorption spectra of diluted THF solutions have similar shapes [see Figure 1(*c*)] with two absorption bands having a mixed character due to the π–π* transition in the conjugated phenylene–bithiophene moiety as well as intramolecular charge transfer between the electron-donor and the electron-withdrawing groups.[15,18] Increase in the number of Ph-DCV-2T branches results in a noticeable enlargement of molar extinction coefficient ε, namely *ca.* 1.6 times per each added branch. The absorption spectra of thin films are broadened compared with their solution counterparts, and the absorption maxima are red-shifted by 30–33 nm (Figure S9). The values of the absorption maxima for both the solutions and thin films are red-shifted with increase in the number of branches [see Figures 1(*c*), S9 and Table 1], which can be attributed to partial conjugation of the branches through the central nitrogen atom, and has been confirmed by DFT-based modelling data for compounds **1**–**3** (Figure S10).

Electrochemical properties of compounds **1**–**3** were studied by cyclic voltammetry. It was found that their oxidation did not depend on the number of branches and occurred at the same values of the electrode potential. Since the oxidation proceeds mainly through the triphenylamine–thiophene moiety, the number of electron-withdrawing groups does not affect this process. However, it has been revealed that the values of reduction potentials have a weak dependence on the number of Ph-DCV-2T branches, and the reduction process is facilitated by the increase

† For synthesis and characteristics of compounds **6** and **7**, see Online Supplementary Materials.

N,N-*Bis{4-[5'-(2,2-dicyano-1-phenylvinyl)-2,2'-bithien-5-yl]phenyl} phenylamine* **2**. Compound **7** (1.29 g, 1.6 mmol), malononitrile (0.44 g, 6.6 mmol) and dry pyridine (25.0 ml) were stirred and refluxed under agron atmosphere for 19 h using microwave heating. Then pyridine was evaporated, the residue was dried *in vacuo* (1 Torr), purified by column chromatography on silica gel (eluent dichloromethane) and further purified by precipitation from THF solution with toluene and hexane. Yield 0.75 g (52%), black solid, mp 276 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.05–7.18 (overlapping peaks, 7H), 7.19 (d, 2H, *J* 4.0 Hz), 7.22 (d, 2H, *J* 4.3 Hz), 7.28–7.36 (overlapping peaks, 4H), 7.41–7.60 (overlapping peaks, 14H), 7.60 (d, 2H, *J* 4.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 75.88, 114.22, 114.88, 123.68, 123.90, 124.33, 124.55, 125.41, 126.78, 127.69, 127.92, 128.85, 129.37, 129.66, 131.61, 133.54, 135.99, 136.10, 138.55, 146.61, 146.84, 147.52, 148.88, 163.78. MS (MALDI), *m/z*: 878.21 $[M]^+$ (calc. for $C_{54}H_{31}N_5S_4$, *m/z*: 878.12). Found (%): C, 73.85; H, 3.54; N, 7.84; S, 14.49. Calc. for $C_{54}H_{31}N_5S_4$ (%): C, 73.86; H, 3.56; N, 7.98; S, 14.61.

Table 2 Photovoltaic characteristics of selected bulk heterojunction organic solar cells based on DA compounds **1**–**3**.[a]

Compound	Mass ratio DA compound: $PC_{71}BM$	J_{sc}/mA cm^{-2}	V_{oc}/V	FF (%)	η (%)
1	1:3	8.73	0.97	39.9	3.38
2	1:2.5	9.74	0.99	45.2	4.36
3	1:2	9.88	1.00	46.5	4.61

[a] J_{sc} is reduced short-circuit current density, V_{oc} is open-circuit voltage, FF is fill factor, η is power conversion efficiency.

in this number from 1 to 3. The HOMO and LUMO energies were calculated using the first standard formal oxidation and reduction potentials (see Table 1). It has been found that the value of the electrochemical band gap E_g slightly decreases from 1.96 to 1.91 eV, which agrees well with the absorption data, where absorption maxima and absorption edges are red-shifted with increase in the number of Ph-DCV-2T branches.

Photovoltaic properties of DA compounds **1**–**3** were investigated for the samples of bulk heterojunction organic solar cells with the following architecture: glass/ITO/PEDOT:PSS/active layer/Ca/Al. The active layer comprised the DA compound as a donor and [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as an acceptor, with their ratio being varied for the purpose of optimization (see Figure S11). Photovoltaic data for the selected solar cells with optimized donor–acceptor ratio are shown in Table 2 and their current–voltage characteristics are presented in Figure S12.

The highest power conversion efficiency 4.61% was demonstrated by solar cells based on oligomer **3**. A gradual decrease in the efficiency is observed with lowering the number of branches, especially going from compound **2** to **1**. The reduced short-circuit current density J_{sc} of the solar cells based on compound **1** may originate from its blue-shifted absorption and the resulting less effective transformation of solar light. Open-circuit voltage V_{oc} values of the solar cells are almost identical for all DA compounds, which corresponds to the identity of their HOMO levels. Slightly less value of the fill factor (FF) for photovoltaic cells based on compound **1** may be due to non-optimal morphology of the active layer. Thus, decrease in the number of branches in compounds **1**–**3** results in lowering the efficiency of solar cells based on them.

In summary, new DA oligomer **2** based on electron-donating TPA with two bithiophene branches terminating in Ph-DCV electron-withdrawing groups has been synthesized. Its thermal, optical, electrochemical, and photovoltaic properties were investigated and compared with its analogues **1** and **3** bearing one and three branches, respectively. The effect of the number of electron-withdrawing groups and the branching of the molecule on the properties of compounds and on power conversion efficiency of solar cells based on them has been revealed. All the compounds investigated have high thermal stability and similar phase behavior. However, evident trends in increase of the thermal stability as well as the glass transition and melting temperatures with the number of branches have been established. The bathochromic shift in the absorption spectra and noticeable enlargement of molar extinction coefficients with increase in this number are also observed. Solar cells based on star-shaped oligomer **3** with three branches demonstrate the best power conversion efficiency 4.61%, whereas decrease in the number of branches to one results in lowering the efficiency to 3.38%.

The synthesis and investigation of compounds **1** and **3** were supported by the Russian Science Foundation (grant nos. 17-73-10485 and 14-13-01380, respectively). The synthesis and investigation of compound **2** were supported by the Global Energy Association. The work was performed in the framework of leading science school NSh-5698.2018.3. The authors thank S. A. Pisarev for DFT calculations. NMR and absorption spectroscopic analysis of compound **2** was supported by the Ministry of Science and Higher Education of the Russian Federation and was performed using the equipment of Collaborative Access Center 'Center for Polymer Research' of N. S. Enikolopov Institute of Synthetic Polymeric Materials, Russian Academy of Sciences. The solar cells investigation was performed using the equipment acquired from the Development Program of M. V. Lomonosov Moscow State University.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.07.008.

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Received: 12th December 2018; Com. 18/5771