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Journal of Materials Chemistry C

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Star-shaped D– π –A oligothiophenes with *tris*(2-methoxyphenyl)amine core and alkyldicyanovinyl groups: synthesis, physical and photovoltaic properties

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Abstract

Published on 20 June 2016. Downloaded by University of Cambridge on 20/06/2016 14:05:15.

Synthesis of a series of star-shaped oligomers having novel electron donating tris(2-methoxyphenyl)amine (m-TPA) core, which is linked through bithiophene or terthiophene π -bridge with electron-deficient alkyldicyanovinyl (alkyl-DCV) groups, is described. Comprehensive study of the oligomers revealed significant dependence of their physical properties, including absorption, molecular frontier energy levels, crystal packing, melting and glass transition temperatures upon the chemical structure. Comparison of their photophysical properties to the nearest analog having common dicyanovinyl (DCV) groups demonstrated a number of benefits to use alkyl-DCV units for the design of donor-acceptor small molecules: higher solubility, increased electrochemical stability, better photovoltaic performance, possibility to control the relative physical and photovoltaic properties by simple adjustment of alkyl and π -bridge lengths. Modification of well-known triphenvlamine (TPA) core in the star-shaped oligomers by 2-methoxy groups increases not only solubility, but also crystallinity of the oligomers, whereas their photovoltaic performance stays on the similar level to their analogs with TPA core. The study demonstrates that these design strategies represent interesting and simple tools for effective modulation of properties of star-shaped molecules.

1. Introduction

Solar cells based on organic semiconductors are developing as a promising cost-effective alternative to silicon-based solar cells due to easy fabrication by solution processing, lightweight, and compatibility with flexible substrates.^[1-3] Despite conjugated polymers have dominated the field of bulk heterojunction (BHJ) organic solar cells (OSCs),^[4] small molecules are received increasing attention due to their well-defined molecular structures, ease of functionalization, amenability to standard organic purification and characterization methods, and reduced

batch-to-batch variability. There has been significant recent progress in the development of small molecules for use in BHJ OSCs.^[5-7] The dynamic development in solution-processed small molecule OSCs has recently led to high power conversion efficiency (PCEs) of over 10%.^[8,9] Despite that, development of the cheap and stable photoactive materials as well as novel design strategies for small molecules is still a key to boost potential for commercial applications.

Oligothiophenes and their derivatives with well-defined structures possess extensive π -electron delocalization along the molecular backbone and are well known as good hole-transporting materials.^[10] Despite their excellent semiconducting properties, they do not absorb strongly in the red and near-infrared part of the spectrum where most solar photons are concentrated. Inclusion of electron-withdrawing units to the oligothiophene backbone can extend their absorption spectrum toward longer wavelengths by an intramolecular charge transfer (ICT) and thus leading to a better match with the solar spectrum. For this purpose, dicyanovinyl (DCV) unit is one of widely used acceptor groups due to its strong electron-accepting character. ^[11, 12] A main drawback of the DCV group is presence of an active vinyl hydrogen,^[13, 14] which decreases stability of the materials. A replacement the active hydrogen by an alkyl was found to be an efficient tool not only to increase the electrochemical stability of donor-acceptor small molecules,^[15,16] but also to control their solubility and a number of important solid-state physical properties by simple adjustment of alkyl chain length at DCV substitute.^[17,18]

To fine-tune the energy levels in small molecules, some additional electron-donating blocks such as dithienosilole,^[19-22] benzodithiophene,^[23,24] dithienopyrrole,^[25,] *etc.*, are often used. For design of star-shaped molecules, a triphenylamine (TPA) core is one of the widely used electron-donating block due to its low cost, high electrochemical stability and hole transporting ability.^[12, 26, 27] Moreover, the propeller-like structure of TPA prevents strong π - π interactions between neighboring groups, so that the vast majority of TPA derivatives are amorphous and highly soluble materials.In order to optimize photophysical properties of TPA-based star-shaped oligomers, a few attempts to modify TPA block were done, which were based mainly

on its planarization strategy.^[28-31] Nevertheless, an increase in performance of organic field-effect transistors (OFET),^[28] organic light-emitting diodes (OLEDs)^[29] and OSCs^[30,28] as compared to the devices based on non-modified analogs, revealed a great potential of TPA modification to moderately and effectively tune the properties of star-shaped molecules.

Meanwhile, alkoxy substituents at phenyl rings of TPA have been successfully used in design of unsymmetrical D-A molecules for organic and hybrid organic solar cells.[^{32, 33}] Alkoxy substituents at TPA core can increase solubility, change intra- and intermolecular interactions as well as energy levels of the molecules, and thus influence the solid-state properties of pristine oligomers and their blends. However, the first example of D-A star-shaped molecule with alkoxy groups at TPA, namely with *tris*(2-methoxyphenyl)amine (m-TPA) core, has been reported recently.^[34]

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In this work we report on the synthesis and comprehensive study of a series of four D- π -A oligomers having *tris*(2-methoxyphenyl)amine (m-TPA) core as donor and either alkyl-DCV or DCV as acceptor units, as well as either bi- or terthiophene as π -bridges (Scheme 1). Comparison of properties of these four molecules with those of their full analogs with TPA core ^[15-17, 35] reveals the benefits and drawbacks of this chemical design strategy. Furthermore, variation of π -bridge and alkyl chain length as well as type of substituent at DCV group allows elucidating the structure-property relationships in this series of star-shaped molecules systematically.



Scheme 1. Chemical structures of the star-shaped D- π -A oligomers investigated.

2. Results and discussion

2.1 Synthesis and chemical characterization

Synthesis of star-shaped oligomers with m-TPA and alkyl-DCV groups, N(Ph-OMe-2T-DCV)₃, N(Ph-OMe-2T-DCV-Me)₃,^[35] N(Ph-OMe-3T-DCV-Et)₃, N(Ph-OMe-3T-DCV-Hex)₃, was carried out using our recently developed approach for their analogs with TPA core.^[15,16] The synthetic routes outlined in Scheme 2 include several key reaction stages: preparation of the initial aldehyde or ketones (Scheme 2a and 2b), synthesis of organoboron derivative of bi- or terthiophene precursors (Scheme 2c), and preparation of star-shaped precursors with protective groups followed by deprotection reaction and substitution of carbonyl functions by DCV groups (Scheme 2d). However, in this work, several important optimizations of the initial steps were elaborated to simplify the synthesis. First, preparation of ketones,

1b-c, was carried out by Friedel-Crafts acylation of 2,2'-bithiophene in the presence of tin chloride in 80-86 % yields. This optimization allows using less expensive precursor and reagents as compared to manganese-catalyzed acylation of magnesium derivative of 5-bromo-2,2'-bithiophene.^[15,16] Nevertheless, it should be noted, that Friedel-Crafts acylation reaction was found to proceed with low reaction yields in the case of terthiophenes, probably, due to an oiling effect. Therefore, the extension of oligothiophene length (preparation of **4b-c**) was carried out via Suzuki cross coupling between organoboron derivatives of dioxane-protected bithiophene ketones (**3b-c**) and 2-bromothiophene in 71-74% yields. Second, protection of carbonyl functions of the ketones was found to be more convenient with 5,5-dimethyl-1,3-dioxane groups as compared to previously used 1,3-dioxolane ones, due to higher stability and better isolated yields of the protected compounds.

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Note that for the synthesis of the model star-shaped molecule with DCV groups, $N(Ph-OMe-2T-DCV)_3$, we have used for the first time the similar strategy as for the molecules with alkyl-DCV groups, whereas their common preparation is based on Vilsmeier–Haack formylation of star-shaped oligothiophenes followed by Knövenagel condensation.^[12,16] The main difference in the synthetic route for N(Ph-OMe-2T-DCV)₃, as compared to the molecules with alkyl-DCV groups, is preparation of the aldehyde precursor (1a) instead of the ketone one, which was done by lithiation of commercially available 2,2'-bithiophene followed by its reaction with dimethylformamide (DMF) in 94 % yield. In addition, there were also variations in the rates of protection, deprotection and Knövenagel reactions due to different activity of ketones and aldehydes (see Experimental Section for details).

As a result, all target star-shaped oligomers under discussion were prepared in good reaction yields, while their chemical structures and high purity were proved by 1 H-, and 13 C-NMR spectroscopy, elemental analysis, and mass-spectroscopy (see Electronic Supplementary Information (ESI), Figures S1 – S35). The low reaction yield of N(Ph-OMe-3T-DCV-Et)₃ can be explained by losses during purification by column chromatography, because of its insufficient solubility in dichloromethane, which was used as eluent. All these oligomers obtanied demonstrate reasonable

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solubility in common organic solvents such as THF, chloroform, 1,2-dichlorobenzene

Scheme 2. Synthesis of N(Ph-OMe-2T-DCV)₃, N(Ph-OMe-3T-DCV-Et)₃, and N(Ph-OMe-3T-DCV-Hex)₃.

2.2 Solubility and Thermal Properties.

1).

The exact values of solubility for all star-shaped oligomers prepared were measured in ODCB at room temperature (Table 1). One can see that the solubility in this series of molecules depends significantly on the chemical structure and tends to decrease with elongation of the π -bridge length and to increase with elongation of the alkyl chain length. The lowest solubility was found for the model molecule without terminal alkyl groups, N(Ph-OMe-2T-DCV)₃, and for N(Ph-OMe-3T-DCV-Et)₃ having the longest 3T arms and short ethyl groups. Comparison of the solubility values for the series of m-TPA-based molecules to those obtained for their full analogs with TPA core revealed that usage of the former core can increase solubility by ca. 2-5 times (Table

Compounds	Solubility,	First heating		Seco	nd heating	TGA (air) TGA (N ₂)		
Compounds	mg/mL ^a	<i>T</i> _m , ℃	$\Delta H_{\rm m}$, J/g	T _g , ℃	dC_p , J/(g·K)	<i>T</i> _d , °C	$T_{\rm d}$, °C	
N(Ph-OMe-2T-DCV) ₃	9	200	32	147	0.33	403	408	
N(Ph-OMe-2T-DCV-Me) ₃	14	248	54	130	0.23	415	402	
N(Ph-OMe-3T-DCV-Et) ₃	8	243	50	119	0.27	403	391	
N(Ph-OMe-3T-DCV-Hex) ₃	20	173	30	76	0.33	386	400	
N(Ph-2T-DCV) ₃ ^b	2	276	28	145	0.17	405	405	
N(Ph-2T-DCV-Me) ₃ ^b	3	270	82	136	0.26	416	416	
N(Ph-3T-DCV-Hex) ₃ ^b	12	-	-	75	0.29	388	388	

Table 1. Solubility and thermal properties of the star-shaped oligomers

Notes: ^aMeasured in ODCB; ^b data from reference [16]; dC_p – heat capacity change at the glass transition; T_d corresponds to 5% weight losses.

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Thermal properties of the oligomers synthesized were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). One can see that all these oligomers possess very high stability both in the air and under inert atmosphere (Figure 1). Decomposition temperatures (T_d), corresponding to 5% weight losses, were found to be above 380°C in the air and under the inert atmosphere, as exhibited in Table 1. The residual weights vary from 50-75% at the heating up to 700 °C in the nitrogen. Comparison of the weight losses at very high temperatures indicates that it is caused mostly by decomposition of the aliphatic groups. Influence of the terminal hydrogen at DCV unit on the thermal stability of the oligomers cannot be evaluated by this technique, since the weight loss due to hydrogen elimination is around 0.2%, which is close to the experimental error.



Figure 1. TGA of star-shaped D- π -A oligomers (a) in air and (b) under nitrogen.

DSC analysis (Figure 2a and Table 2) reveals that all these oligomers as received are crystalline materials with the relatively high values of melting temperature ($T_{\rm m}$) and melting enthalpy ($\Delta H_{\rm m}$). However, the crystal structure was not restored after the first melting and subsequent cooling to the room temperature. One can observe a glass transition on the second heating scans only (Figure 2b), where a glass transition temperature ($T_{\rm g}$) lies in the range of 74-147°C. This peculiarity was used to simplify dissolution of these compounds, since materials in the amorphous state dissolve much better as compared to the crystalline one. Comparison of $T_{\rm m}$ and $\Delta H_{\rm m}$ values for the compounds studied allows concluding that elongation of the oligothiophene π -bridge or shortening of the alkyl chains lead to improved ordering in the bulk.



Figure 2. DSC first (a) and second (b) heating scans of star-shaped D- π -A oligomers with m-TPA core.

It is interesting to compare phase behavior of the molecules with m-TPA core to their full analogs having TPA core (see Table 1).^[15,16,34]N(Ph-3T-DCV-Hex)₃, being the full

analog of N(Ph-OMe-3T-DCV-Hex)₃ but with TPA core, is characterized by a hexagonal columnar mesophase.^[34] Meanwhile, N(Ph-2T-DCV)₃ and N(Ph-2T-DCV-Me)₃ can be also crystalline as received similar to their analogs with m-TPA core. Melting temperature and enthalpy in the pair of N(Ph-2T-DCV-Me)₃ and N(Ph-OMe-2T-DCV-Me)₃ are rather similar, while the melting temperature of N(Ph-2T-DCV)₃ is substantially higher than that of N(Ph-OMe-2T-DCV)₃, albeit their melting enthalpies being also close to each other.

2.3 X-Ray diffraction data

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X-ray studies of as-received samples of the compounds with m-TPA core revealed that all of them are highly crystalline materials with substantially different crystal lattices (Figure 3). However, small-angle region of diffractograms is dominated by a strong reflection corresponding to the periodicity of ~ 30 Å. Moreover, its fourth order reflection is also one of the strongest in the wide-angle region for all the compounds investigated. As the position of the mentioned reflection does not depend on the arm length of the specific star-shaped molecule, one can conclude, that this periodicity is due to the stacking of the molecules one above the other. Molecular modelling of the compounds with m-TPA core revealed that such discotic motifs form pairs in which methoxy groups of both partners are oriented outwards, the distance between the molecules being 5.8 Å (see discussion and Figures S38, S39 in the ESI). The same pairs are also the most specific feature of the crystal structure of m-TPA compound.^[36] Comparison of the experimental macroscopic densities with the calculated crystalline ones allows to suggest that molecular pairs form the columns with an inner 3_1 or 3_2 helical ordering which is rather common for the compounds with the molecules possessing rotary axis of symmetry of the third order.



Figure 3. X-Ray scattering patterns for $N(Ph-OMe-2T-DCV)_3$ (1), N(Ph-OMe-2T-DCV-Me)_3 (2), N(Ph-OMe-3T-DCV-Et)_3 (3) and N(Ph-OMe-3T-DCV-Hex)_3 (4).

Excluding reflections corresponding to the periodicity along the columns, one can obtain parameters of the columns ordering in lateral direction. Here two main criteria of the choice correctness were used – first, comparison of calculated and experimental densities and the arm length. We should though notify in advance that the macroscopic density was measured using the bulk samples after their melting and subsequent cooling, i.e. amorphous ones (**Table 2**). Thus, we allowed the calculated crystal density to be 10-15% higher than the experimental one. Second, all the reflections observed should have been indexed (see Tables S1 – S4 in ESI).

Table 2.	Crystal	lattice	parameters	calculated	and e	experimentally	measured	densities
			for comp	ounds with	m-TI	PA cores.		

Compounds	Туре	a, Å	b, Å	c, Å	ρ _{calc} , g/cm ³	ρ _{exp} , g/cm ³	L _{arm} , Å
N(Ph-OMe-2T-DCV) ₃	Orthorombic	25.3	20.9	30.7	1.296	1.322	14.9
N(Ph-OMe-2T-DCV-Me) ₃	Orthorombic	20.7	18.8	33.3	1.693	1.303	16.1
N(Ph-OMe-3T-DCV-Et) ₃	Orthorombic	32.9	17.7	28.4	1.557	1.319	22.1
N(Ph-OMe-3T-DCV-Hex) ₃	Orthorombic	33.9	31.2	27.7	1.411	1.227	26.5



Figure 4. Packing of the molecules in crystal lattices calculated based on X-ray scattering patterns for N(Ph-OMe-2T-DCV)₃ (1), N(Ph-OMe-2T-DCV-Me)₃ (2), N(Ph-OMe-3T-DCV-Et)₃ (3) and N(Ph-OMe-3T-DCV-Hex)₃ (4).

Figure 4 shows 001 cleaves of calculated crystal lattices. One should remember that every molecule on such a cleave represents the whole 3_1 helical column. However, every hand of the molecule has a face-to-edge π - π stacking with the molecule in the neighboring column, thus providing a helical pathway for charge carriers. The length of star's arm varies from 14.9 to 26.5 Å. All the lattices, with the exception of that formed by N(Ph-OMe-3T-DCV-Hex)₃, contain two columns with different type of rotation (one in the middle and four quarters in the corners). Thus, one can observe

the layers of the columns of particular orientation alternating with the layers of the columns of an opposite one. Crystal lattice formed by the compound $N(Ph-OMe-3T-DCV-Hex)_{3}$, contains three columns (two in the middle and four quarters in the corners) and correspondingly three different types of column layers. This fact could be due to a substantial length of hands of particular star-shaped molecule, so the packing of two different layers still leaves too much free space.

Summing up structural information concerning the star-shaped compounds with and without methoxy groups in their TPA cores, one can conclude that methoxy groups play definitive role in formation of pair aggregates inside the supramolecular columns, which are not observed in TPA-based analogs. Such aggregates are responsible for substantially higher ordering and formation of crystal structures in the materials with methoxy groups in the TPA cores. In comparison, formation of ordered structures in the compounds without methoxy groups in TPA cores is considerably hindered.

2.4. Optical and electrochemical properties

The UV-vis absorption spectra of the star-shaped oligomers in dilute ODCB solutions and thin films are shown in Figure 5. Samples used for the measurements of film absorption spectra were prepared by doctor-blading from ODCB solutions. The corresponding optical data are summarized in Table 3. In ODCB, all compounds demonstrate similar spectra: the weak UV absorption peak (370-412 nm) as generally accepted corresponds to the π - π * transition and the intensive visible peak (520-540 nm) is attributed to the ICT transition between the m-TPA-oligothiophene donor and the alkyl-DCV or DCV acceptor units.^[12] However, it has been shown that in fact both electronic excitations have a mixed character and the intensity of the high-energy absorption feature is a direct measure of the degree of conformational disorder in the star-shaped molecule.^[37] Indeed, with increasing of the π -conjugated bridge length from 2T to 3T the shorter wavelength region peaks are redshifted from 375 nm to 412 nm, which is attributed to the stronger localized π - π * transition for 3T π -bridge. Interestingly, that the expected redshifts of low energy bands for molecules with 3T π -bridges were not observed, since the extension of the conjugation cannot compensate a decrease in ICT between the core and terminal DCV units caused by longer distance between them and intramolecular distortions in 3T chain. Comparison to the absorption bands of the star-shaped molecules based on alkyl-DCV units as acceptor groups in films, the low energy absorption band is red-shifted by 16 nm for N(Ph-OMe-2T-DCV)₃ due to somewhat stronger electron-withdrawing ability of DCV groups.^[15] In thin films, the optical spectra of all these star-shaped molecules become broader and maxima of their absorption peaks (λ_{max}) shift to long-wave region as compared to those observed in solutions (Figure 5b).



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Figure 5. UV-vis absorption spectra of m-TPA-based oligomers in (a) dilute ODCB solutions and in (b) films casted from ODCB.

Table 3. Optical and electrochemical properties of the investigatedm-TPA-based oligomers.

	UV-v	is absorptic	n	cyclic voltammetry				
	solution ^a	1	film ^b		oxidation	reduction		
Compounds	λ_{max}	λ (nm)	λ_{onset}	$E_{\rm g}^{\ opt}$	$\varphi_{\rm ox}^{\ \ d}$ /HOMO	$\varphi_{\rm red}^{\rm d}/{\rm LUMO}$	E_{g}^{EC}	
e ompounde	(nm)	\mathcal{N}_{max} (IIIII)	(nm)	$(eV)^{c}$	(V)/(eV)	(V)/(eV)	(eV)	
N(Ph-OMe-2T-DCV) ₃	377/540	456/562	707	1.75	0.80/-5.20	-0.94/-3.46	1.74	
N(Ph-OMe-2T-DCV-Me) ₃	376/524	452/542	688	1.80	0.80/-5.20	-1.02/-3.38	1.82	
N(Ph-OMe-3T-DCV-Et) ₃	412/524	428/531	688	1.80	0.74/-5.14	-1.03/-3.37	1.77	
N(Ph-OMe-3T-DCV-Hex) ₃	412/524	432/535	688	1.80	0.74/-5.14	-1.03/-3.37	1.77	

^{*a*}Measured in ODCB solution. ^{*b*}Cast from ODCB solution. ^{*c*}Bandgap estimated from the onset wavelength (λ_{edge}) of the optical absorption: $E_g^{opt} = 1240/\lambda_{edge}$; ^{*d*}standard formal reduction (φ_{red}) and oxidation (φ_{ox}) potentials vs. SCE obtained for films of the oligomers.

View Article Online DOI: 10.1039/C6TC01530A

The electrochemical properties of the four star-shaped molecules and their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were examined by cyclic voltammetry (CV) (see Table 3 and Figure 6). From these data, it is clearly seen that all molecules demonstrate similar oxidation behavior, which appears as two consecutive and fully reversible waves. A decreased value of the first standard formal oxidation potentials (φ_{ox}) for N(Ph-OMe-3T-DCV-Et)₃ N(Ph-OMe-3T-DCV-Hex)₃, and as compared to 2T-containing analogs, revealed that elongation of π -bridge length facilitates the oxidation process. However, influence of π -bridge length on the first standard reduction potential (φ_{red}) was not observed, because in this process the reduction of DCV groups occurs firstly. Therefore, somewhat different φ_{red} value (-0.94 V vs. -1.03 V relatively to SCE) was observed for the N(Ph-OMe-2T-DCV)₃ having common DCV groups, which indicates its hindered reduction. Another important difference between the molecules having either DCV or alkyl-DCV groups is irreversibility of the reduction process for the former due to presence of active vinyl hydrogens in their structure. In Figure 6, one can see that the reduction of all compounds with alkyl-DCV groups proceeds with the first reversible and the second irreversible waves, whereas reduction of N(Ph-OMe-2T-DCV)₃ goes with the first irreversible wave only. These observations indicate less stability of anion radicals for oligomers having active hydrogen at DCV groups, whereas replacement of the vinyl hydrogens to alkyls stabilizes the anion radicals and increases their electrochemical stability.

HOMO and LUMO energy levels were calculated using first standard formal oxidation and reduction potentials according to the following equation: LUMO = $e(\phi_{red}+4.40)$ (eV) and HOMO = $-e(\phi_{ox}+4.40)$ (eV).^[38] For N(Ph-OMe-3T-DCV-Et)₃ and N(Ph-OMe-3T-DCV-Hex)₃ the LUMO was found to be -3.37 eV, which is similar to N(Ph-OMe-2T-DCV-Me)₃, whereas the HOMO was found to be -5.14 eV, which gives a bit lowered bandgap of 1.77 eV as compared to 1.82 eV for their 2T-containing analogue. The lowest electrochemical bandgap value (1.74 eV) was observed for N(Ph-OMe-2T-DCV)₃, which is in good agreement with its optical bandgap (see Table 1). Compared to their analogues with TPA core,^[16] this series of

star-shaped molecules shows somewhat higher HOMO levels due to the presence of additional electron donating methoxy substitutes in the m-TPA core.



Figure 6. Cyclic voltammograms of N(Ph-OMe-2T-DCV)₃ (1), N(Ph-OMe-2T-DCV-Me)₃ (2), N(Ph-OMe-3T-DCV-Et)₃ (3) and N(Ph-OMe-3T-DCV-Hex)₃ (4). Insets (dashed curves) correspond to the cyclic voltammogram of the first wave.

2.5 Charge transport

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Since the intended application of the star-shaped molecule under study is BHJ OSC as a donor component in their mixtures with the acceptor component PC₇₀BM, a space charge limited current (SCLC) method was used to map out hole and electron only mobilities of the oligomers/PC₇₀BM blended films. The *J-V* characteristics of both hole-only and electron-only diodes can be excellently fit to the Mott-Gurney model (Figure 7). We calibrated the hole (μ_h) and electron (μ_e) mobility by fitting the current-voltage curves over six diodes. The related average values of hole and electron only mobilities of the blended films are given in Table 4. All devices based on the star-shaped molecules with alkyl-DCV groups demonstrated slightly higher hole only mobilities, but lower electron only mobilities as compared to their analogue with DCV groups, N(Ph-OMe-2T-DCV)₃. Comparison of the devices based on N(Ph-OMe-2T-DCV-Me)₃ and N(Ph-OMe-3T-DCV-Et)₃ showed that elongation of the

oligomer π -bridge length from 2T to 3T does not influence significantly the mobility in blends. While the increase of alkyl chain length from ethyl to hexyl in N(Ph-OMe-3T-DCV-Et)₃/N(Ph-OMe-3T-DCV-Hex)₃ systems leads to obvious decrease of both the hole and electron mobility. This observation, on the one hand, explained by the blend morphology for can be poorer $N(Ph-OMe-3T-DCV-Hex)_3:PC_{70}BM$ system as shown below. On the other hand, elongation of alkyl chain results in weakening of the intra- and intermolecular interactions in the solid state, which is in agreement with our previous results as well as the thermal properties of pristine oligomers.^[34] Comparison of the hole only mobility for N(Ph-OMe-2T-DCV-Me)₃ and N(Ph-OMe-3T-DCV-Hex)₃ to the values obtained for their full analogs with TPA core,^[34] revealed a bit higher mobility for the blends based on the molecules with m-TPA core. These results in charge transport properties of blends will further influence the device performance as discussed below.

Table 4. Hole and electron only mobilities determined from the SCLC measurements.

	Thicknes	$ss \mu_h^a$	Thickne	ss μ _e ^a	
Semiconductor layers	(nm)	$[cm^2V^{-1}s^{-1}]$	(nm)	$[cm^2V^{-1}s^{-1}]$	μ_{e}/μ_{h}
N(Ph-OMe-2T-DCV) ₃ :PC ₇₀ BM (1:2.5)	81	4.58×10 ⁻⁴	70	1.27×10 ⁻³	2.77
N(Ph-OMe-2T-DCV-Me) ₃ :PC ₇₀ BM (1:2)	86	6.07×10 ⁻⁴	75	8.15×10 ⁻⁴	1.34
N(Ph-OMe-3T-DCV-Et) ₃ :PC ₇₀ BM (1:2)	78	5.87×10 ⁻⁴	75	9.91×10 ⁻⁴	1.69
N(Ph-OMe-3T-DCV-Hex) ₃ :PC ₇₀ BM (1:2.5) 85	4.86×10 ⁻⁴	74	6.73×10 ⁻⁴	1.38

^aThe reported mobility data are average values of the blended films over six devices.



Figure 7. The dark *J-V* characteristics of devices based on the m-TPA core oligomers including hole (a) and electron (b) only devices. The solid lines represent the best fitting using the SCLC modified Mott-Gurney model.

2.6. Photovoltaic properties of BHJ devices

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To study the effects of donor core, acceptor group, oligothiophene π -bridge length and alkyl chain length on the photovoltaic properties, BHJ OSCs with a configuration of ITO/PEDOT:PSS/oligomer:PC₇₀BM (wt%)/ZnO(25nm)/Al(100nm) were fabricated, and the detailed device fabrication process is described in the Experimental Section. The corresponding parameters of devices with the best blending ratios are shown in Figure S40, while optimized performances of these devices were achieved with the weight ratio of 1:2 or 1:2.5 without any treatments, as shown in Figure 8a and summarized in Table 5.

As expected, OSCs based on N(Ph-OMe-2T-DCV)₃ and N(Ph-OMe-2T-DCV-Me)₃ show relatively high V_{oc} up to 0.9 V, due to their low-lying HOMO energy levels. With increasing of the π -conjugated oligothiophene bridge length, OSCs based on N(Ph-OMe-3T-DCV-Et)₃ and N(Ph-OMe-3T-DCV-Hex)₃ showed lower V_{oc} of 0.82 V and 0.86 V, respectively. These results are attributed to their HOMO level variations (Figure 8c) and also consistent with our previous results.^[16, 35] In addition, the slightly (N(Ph-OMe-2T-DCV-Me)₃ higher $V_{\rm oc}$ values (see Figure 8c) for and N(Ph-OMe-3T-DCV-Hex)₃ N(Ph-OMe-2T-DCV)₃ as compared to and $N(Ph-OMe-3T-DCV-Et)_3$ may be explained by presence of longer terminal alkyls

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for the former, leading to a weakening of the intermolecular interactions between the donor and acceptor moieties.^[17,39] Among these four systems, OSCs based on N(Ph-OMe-2T-DCV-Me)₃ exhibit the highest J_{sc} values (see Figure 8d), resulting from the high and balanced charge transport properties. N(Ph-OMe-3T-DCV-Hex)₃ system in contrast exhibits the poorest J_{sc} value, probably due to the longest alkyls at DCV, suppressing intramolecular and intermolecular interactions.[17] The corresponding J_{sc} values are consistent with the external quantum efficiency (EQE) measurements (see Figure 8b). In addition, these devices exhibited similar FF values of ca. 50% (see Table 5). Finally, the PCEs of these devices are 3.73% for 4.38% N(Ph-OMe-2T-DCV)₃, for N(Ph-OMe-2T-DCV-Me)₃, 3.55% for N(Ph-OMe-3T-DCV-Et)₃ and 3.18% for N(Ph-OMe-3T-DCV)₃, respectively. In general, the PCEs of OSCs based on molecules with m-TPA core and alkyl-DCV groups are slightly lower but comparable with those obtained for their analogs with TPA core.^[16, 35] However, obvious improvement of the photovoltaic performance from 2.31% for N(Ph-2T-DCV)₃ system to 3.73% for N(Ph-OMe-2T-DCV)₃ system was found, which is attributed to better molecular solubility and blend morphology of the latter. In addition, compared to the photovoltaic performance of the molecules with bithiophene as π -bridges, further extending of π -bridges to terthiophene did not lead to any improvement of the device performance. Nonetheless, the results of N(Ph-OMe-3T-DCV-Et)₃ and N(Ph-OMe-3T-DCV-Hex)₃ in devices demonstrated that the longer alkyl terminal chains resulted in the worse photovoltaic parameters due to the poor charge transport and worse blend morphology, which is in a good agreement with the previous research for TPA-based star-shaped molecules.^[17]

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Figure 8. Current density-voltage (*I-V*) curves (a) and EQE spectra (b) of solar cells based on N(Ph-OMe-2T-DCV)₃:PC₇₀BM (1:2.5, wt%), N(Ph-OMe-2T-DCV-Me)₃:PC₇₀BM (1:2, wt%), N(Ph-OMe-3T-DCV-Et)₃:PC₇₀BM (1:2, wt%), and N(Ph-OMe-3T-DCV-Hex)₃:PC₇₀BM(1:2.5, wt%), respectively, under the illumination of AM 1.5, 100 mWcm⁻²; Correlation between: (c) V_{oc} and experimental HOMO values of m-TPA based molecules and (d) V_{oc} and J_{sc} values of the OSCs based on these four systems.

Table 5.	Photovoltaic	Properties	of oligo	omer:PC ₇₀ BM	OSCs,	under	the	illuminatio	n
of AM 1	.5, 100 mW cr	m ⁻² .							

Donor	D:A [wt%]	$V_{\rm oc}$ [V]	$J_{\rm sc}$ [mAcm ⁻²]	FF [%]	PCE(^a) [%]
N(Ph-OMe-2T-DCV) ₃	1:2.5	0.90	8.52	48.6	3.73(3.62)
N(Ph-OMe-2T-DCV-Me) ₃	1:2	0.92	9.01	52.8	4.38(4.18)
N(Ph-OMe-3T-DCV-Et) ₃	1:2	0.82	8.65	50.0	3.55(3.44)
N(Ph-OMe-3T-DCV-Hex) ₃	1:2.5	0.86	7.78	47.6	3.18(3.02)

^athe average values of PCEs calculated from over six devices.

2.7 Film morphology

Absorption spectra and electronic structure of the components as well as their charge transport properties in blends are obviously important for device operation, but the role of film morphology cannot be ignored.^[20] The topographic AFM images of the blended films determined for the optimized OSCs are given in Figure 9.



Figure 9. Tapping mode AFM surface scans $(5 \times 5 \ \mu m^2)$ of blended films N(Ph-OMe-2T-DCV)₃:PC₇₀BM (1:2.5 wt%) (a), N(Ph-OMe-2T-DCV-Me)₃:PC₇₀BM (1:2 wt%) (b), N(Ph-OMe-3T-DCV-Et)₃:PC₇₀BM (1:2 wt%) (c), and N(Ph-OMe-3T-DCV-Hex)₃:PC₇₀BM (1:2.5 wt%) (d).

All the blended films are rather smooth with an average surface roughness (RMS) of 0.61 nm, 0.35 nm, 0.46 nm and 0.54 nm for N(Ph-OMe-2T-DCV)₃:PC₇₀BM,

N(Ph-OMe-2T-DCV-Me)₃:PC₇₀BM, N(Ph-OMe-3T-DCV-Et)₃:PC₇₀BM, and N(Ph-OMe-3T-DCV-Hex)₃:PC₇₀BM films, respectively. However, in all cases, the blended film morphologies were slightly different. It is evident from AFM studies that the variations in the molecular size, π -bridge and alkyl length can cause changes in the microstructure of the blended films. Among these four blended films, N(Ph-OMe-2T-DCV-Me)₃:PC₇₀BM system exhibited the smallest RMS value. In addition, the most pronounced nanoscale-aggregation of donor and acceptor phase was also found for the best performing N(Ph-OMe-2T-DCV-Me)₃:PC₇₀BM system, indicating that these nanoscale domains are beneficial to the exciton charge separation, charge transportation and in turn enhance the device performance. Thus, judicious choice of the core, oligothiophene π -bridge and alkyl chain length in star-shaped molecules is of crucial importance for fine-tuning the structure--morphology-property relationships.

3. Conclusions

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In summary, we synthesized a series of star-shaped oligomers with D- π -A structure and demonstrated the first comprehensive attempt to study the structure-property relationships depending on different substituents at donor and acceptor units as well as the length of either oligothiophene π -bridge or terminal alkyl chain length. All these oligomers with a novel m-TPA core exhibit good solution processability and high thermal and thermooxidation stability. Various properties, such as solubility in organic solvents, phase behavior, crystal packing, HOMO/LUMO levels, charge-transport ability in blends, morphological characteristics and photovoltaic performance can be fine-tuned simply by changing the π -bridge and alkyl terminal chain length. On the one hand, the main benefits of usage of the alkyl-DCV acceptor groups to design star-shaped molecules are confirmed significantly by their higher solubility, electrochemical stability and photovoltaic performance as compared to normal DCV units. On the other hand, the introduction of m-TPA core, as compared to TPA, not only leads to higher solubility, but also possesses the possibility to obtain molecules in a crystalline state without significant changing of other photophysical

and photovoltaic properties. Bearing the widespread usage of TPA-derivatives, we envisage that *tris*(2-methoxyphenyl)amine can find their own niche as a donor unit to design highly crystalline but still soluble semiconducting small molecules for organic and hybrid electronics.

4. Experimental Section

4.1. Characterization

¹H NMR spectra were recorded at a "Bruker WP-250 SY "spectrometer, working at a frequency of 250.13 MHz and utilising CDCl₃ signal (7.25 ppm) as the internal standard. ¹³C NMR spectra were recorded using a "Bruker Avance II 300" spectrometer at 75 MHz. In the case of ¹H NMR spectroscopy, the compounds to be analysed were taken in the form of 1% solutions in CDCl₃. In the case of ¹³C NMR spectroscopy, the compounds to be analysed were taken in the form of 1% solutions in CDCl₃. In the case of ¹³C NMR spectroscopy, the compounds to be analysed were taken in the form of 5% solutions in CDCl₃. The spectra were then processed on the computer using the ACD Labs software.

Mass-spectra (MALDI) were registered on the Autoflex II Bruker (resolution FWHM 18000), equipped with a nitrogen laser (work wavelength 337 nm) and time-of-flight mass-detector working in reflections mode. The accelerating voltage was 20 kV. Samples were applied to a polished stainless steel substrate. Spectrum was recorded in the positive ion mode. The resulting spectrum was the sum of 300 spectra obtained at different points of the sample. 2,5-dihydroxybenzoic acid (DHB) (Acros, 99%) and α -cyano-4-hydroxycinnamic acid (HCCA) (Acros, 99%) were used as matrices.

Elemental analysis of C, H and N elements was carried out using CHN automatic analyzer CE 1106 (Italy). The settling titration using BaCl₂ was applied to analyze sulphur. Experimental error for elemental analysis is 0.30-0.50%. The Knövenagel condensation was carried out in the microwave "Discovery", (CEM corporation, USA), using a standard method with the open vessel option, 50 watts.

Thermogravimetric analysis was carried out in dynamic mode in $30 \div 900^{\circ}$ C interval using *Mettler Toledo* TG50 system equipped with M3 microbalance. Heating/cooling rate was chosen to be 10°C/min. Every compound was studied twice: in air and in nitrogen flow of 200 ml/min. DSC scans were obtained with *Mettler Toledo* DSC30 system with 20°C/min heating/cooling rate in temperature range of +20 ÷ 250°C for all compounds. Nitrogen flow of 50 ml/min was used.

Cyclic voltammetry measurements were carried out using solid compact layers of the oligomers, which in turn were made by electrostatically rubbing the materials onto a glassy carbon electrode. Measurements were made in $CH_3CN:o-C_6H_4Cl_2=1:4$ solution using 0.1 M Bu₄NPF₆ as supporting electrolyte and using IPC-Pro M potentiostat. The scan rate was 200 mVs⁻¹. The glassy carbon electrode was used as a work electrode. Potentials were measured relative to a saturated calomel electrode (SCE).

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Absorption profiles were recorded with a Perkin Elmer Lambda-35 absorption spectrometer from 350 to 1100. AFM measurements were performed with a Nanosurf Easy Scan 2 in contact mode.

The structures of hole only and electron only devices were as Glass/ITO/PEDOT:PSS/semiconductor layer/MoO₃ (15 nm)/Ag (100 nm) and Glass/ITO/ ZnO/semiconductor layer/Ca (15nm)/Ag (100 nm).

Small-angle diffraction patterns of high resolution were recorded using SAXS- and WAXS camera S3-Micropix, manufactured by Hecus (CuK α , $\lambda = 1.542$ Å). Two detectors were used: two-dimensional Pilatus 100K and linear gas position sensitive detector PSD 50M. For shaping of X-ray beam the Fox 3D vacuum optics were used, the slits in the Kratky collimator were set to 0.1 and 0.2 mm correspondingly. The angular scale was between 0.003 Å⁻¹ and 1.9 Å⁻¹. The exposure varied from 600 to 5000 s while the Joule heater hot stages allowed heating the samples up to 300 °C.

The wide scattering angles were recorded at Protein crystallography station at

View Article Online DOI: 10.1039/C6TC01530A

Kurchatov Synchrotron with a 2D detector MarCCD165 at wavelength of 1.0402 Å $(dE/E = 2E^{-3})$. Station optics include a bending magnet with a 1.7 Tl (E_c = 7.1 keV), two-crystal monochromator with a focusing mirror resulting in a 2x1 mm² beam with a 10¹¹-10¹² fotons per mm² flux.

All devices were fabricated in the normal architecture. Photovoltaic devices were made by doctor-blading on indium tin oxide (ITO)-covered glass substrates (from Osram). These substrates were cleaned in toluene, water, acetone, and isopropyl alcohol. After drying, the substrates were bladed with 40 nm PEDOT:PSS (Heraeus Deutschland, PEDOT PH-4083). Photovoltaic layers, consisting of four different small molecules were dissolved in ODCB with PC₇₀BM as acceptor with various weight ratios, and bladed on top of PEDOT:PSS layer. The thicknesses of these blends are ca. 80-90 nm. After that, a ZnO layer (25 nm) was doctor-bladed on top of the active layer. Finally, an aluminum top electrode of 100 nm thickness was evaporated. The typical active area of the investigated devices was 10.4 mm². The current-voltage characteristics of the solar cells were measured under AM1.5G irradiation on an OrielSol 1A Solar simulator (100 mW/cm²). The EQE was detected with cary 500 Scan UV-Vis-NIR Spectrophotometer under monochromatic illumination, which was calibrated with a mono-crystalline silicon diode. Absorption profiles were recorded with a Perkin Elmer Lambda-35 absorption spectrometer from 350 to 1100.

4.2 Materials

Tetrakis(triphenylphosphine)palladium(0)Pd(PPh₃)₄, 2,2'-bithiophene, n-butyl lithium (1.6 M solution in hexane), isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (IPTMDOB), *p*-toluenesulfonic acid (p-TosH), heptanoyl chloride, acetyl chloride, DMF, 2,2-dimethylpropane-1,3-diol, 2-bromothiohene malononitrile were obtained from Sigma-Aldrich Co. and used without further purification. Pyridine, THF, toluene, benzene, were dried and purified according to the known techniques and then used as a solvent. *Tris*(4-bromo-2-methoxyphenyl)amine was obtained as described in reference.^[40] All reactions, unless stated otherwise, were carried out under an inert

atmosphere.

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4.3. Synthesis of the oligomers.

2,2'-bithiophene-5-carbaldehyde (1a). 1.6 M solution of butyllithium (13.27 mL, 21.2 mmol) in hexane was added dropwise to a solution of 2,2'-bithiophene (7.98 g, 48.0 mmol) in 220 mL of dry THF at -78 °C. Afterwards the reaction mixture was stirred for 60 min at -78 °C and then anhydrous DMF (5.26 mL, 72.0 mmol) was added in one portion. The reaction mixture was stirred for 1h at -78 °C, then the cooling bath was removed, and the stirring was continued for 1h. After completion of the reaction, 50 ml 1 M HCl to the reaction mixture were added to the reaction mixture followed by the addition of 300 mL of freshly distilled diethyl ether and 150 mL of distilled water. The organic phase was separated, washed with water, and dried over sodium sulfate and filtered to give product (8.8 g, 94%) as a red solid. M.p.: 55-56 °C. The product was used in the subsequent synthesis without further purification. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 7.05 (dd, 1H, $J_1 = 4.0$ Hz, $J_2 = 4.0$ Hz), 7.23 (d, 1H, J = 4.0 Hz), 7.34 (d, 2H, J = 4.3 Hz), 7.65 (d, 1H, J = 4.0 Hz), 9.85 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ [ppm] 124.26, 126.17, 127.12, 128.38, 136.03, 137.38, 141.68, 147.18, 182.59. Calcd (%) for C₉H₆OS₂: C, 55.64; H, 3.11; S, 33.01. Found: C, 55.79; H, 3.24; S, 32.97. MALDI MS: found *m/z* 194.27; calculated for [M]⁺ 194.21.

1-(2,2'-bithien-5-yl)propan-1-one (**1b**). SnCl₄ (33.43 g, 128.3 mmol) was added to a mixture of 2,2'-bithiophene (19.85 g, 119.4 mmol) and propionyl chloride (11.05 g, 119.4 mmol) in toluene (120 mL) at 0 °C. After stirring at 0 °C for about 2 h, an ice was added and the reaction mixture was diluted with CH₂Cl₂. The mixture was washed successively with water and a saturated aqueous solution of NaHCO₃, then dried over Na₂SO₄. Solvent was evaporated under vacuum, and the crude product was purified by recrystallization from hexane affording 1b as a white solid (26.2 g, 86% yield). M.p.: 96 °C. ¹H NMR (250 MHz, CDCl₃, d, ppm): 1.23 (t, 3H, *J* = 7.3 Hz), 2.90 (m, 2H, M = 4, *J* = 7.3 Hz), 7.05 (dd, 1H, *J*₁ = 3.7, *J*₂ = 1.1 Hz), 7.15 (d, 1H, *J* = 4.3 Hz), 7.28–7.33 (overlapping peaks, 2H), 7.58 (d, 1H, *J* = 4.3 Hz). ¹³C NMR (75

MHz, CDCl₃): d [ppm] 8.59, 32.16, 124.04, 125.46, 126.30, 128.16, 132.34, 136.38, 141.98, 145.11, 193.49. Calcd (%) for C₁₁H₁₀OS₂: C, 59.43; H, 4.53; S, 28.84. Found: C, 59.25; H, 4.44; S, 28.74. MALDI-MS: found m/z 222.43; calculated for [M]⁺ 222.33.

1-(2,2'-bithien-5-yl)heptan-1-one (**1c**). This compound was obtained by the method described above for compound **1b** using 2,2'-bithiophene (10 g, 60.1 mmol), SnCl₄ (16.83 g, 64.6 mmol), heptanoyl chloride (8.94 g, 60.1 mmol). Purification of crude product by column chromatography on silica gel (eluent hexane) gave compound **1c** (13.56 g, 80% yield) as a colorless liquid. ¹H NMR (250 MHz, CDCl₃, δ, ppm): 0.88 (t, 3H, J = 6.7Hz), 1.27-1.42 (overlapping peaks, 6H), 1.73 (m, 2H, M = 5, J = 7.3 Hz), 2.85 (t, 2H, J = 7.3 Hz), 7.05 (dd, 1H, $J_I = 3.7$ Hz, $J_2 = 1.1$ Hz), 7.15 (d, 1H, J = 4.3 Hz), 7.28-7.33 (overlapping peaks, 2H), 7.58 (d, 1H, J = 4.3 Hz). ¹³C NMR (125 MHz, CDCl₃): δ [ppm] 14.03, 22.48, 24.85, 28.99, 31.58, 39.02, 124.06, 125.48, 126.33, 128.18, 132.48, 136.38, 142.32, 145.24, 193.27. Calcd (%) for C₁₅H₁₈OS₂: C, 64.71; H, 6.52; S, 23.03. Found: C, 64.87; H, 6.58; S, 22.97. MALDI-MS: found m/z 278.49; calculated for [M]+ 278.44.

2-(2,2'-bithien-5-yl)-5,5-dimethyl-1,3-dioxane (**2a**). 2,2-dimethyl-1,3-propanediole (9.32 g, 89.6 mmol) and *p*-TosH (0.596 g, 3.1 mmol) were added to a solution of compound **1a** (8.7 g, 44.8 mmol) in dry benzene (90 mL). Afterwards, the mixture was stirred at reflux for 10 hours using water separator. After that, the mixture was extracted with toluene and washed with distilled water. The combined organic phases were dried over sodium sulfate and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. This crude product was purified by column chromatography on silica gel (eluent toluene) to give pure product (12.15 g, 97%) as a white solid. M.p.: 61-62 °C. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 0.79 (s, 3H), 1.28 (s, 3H), 3.61 (d, 2H, *J* = 11 Hz), 3.74 (d, 2H, *J* = 11 Hz), 5.61 (s, 1H), 6.98-7.05 (overlapping peaks, 3H), 7.14 (dd, 1H, *J*₁ = 1.0 Hz, *J*₂ = 3.7 Hz), 7.19 (dd, 1H, *J*₁ = 1.0 Hz, *J*₂ = 3.7 Hz). ¹³C NMR (125 MHz, CDCl₃): δ [ppm] 21.84, 22.99, 30.23, 77.54, 98.17, 123.12, 123.87, 124.53, 125.70, 127.79, 137.34, 137.72, 140.19. Calcd

(%) for C₁₄H₁₆O₂S₂: C, 59.97; H, 5.75; S, 22.87. Found: C, 60.11; H, 5.67; S, 22.80. MALDI MS: found *m/z* 280.15; calculated for [M]⁺ 280.41.

5,5-dimethyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithien-5-yl] -1,3-dioxane (3a). 2.5 M solution of n-butyllithium (15.59 mL, 39.0 mmol) in hexane was added dropwise to a solution of compound 2a (10.93 g, 39.0 mmol) in 270 mL of dry THF at -78 °C. Afterwards the reaction mixture was stirred for 60 min at -78 °C and then isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (7.3 mL, 39.0 mmol) was added in one portion. The reaction mixture was stirred for 1h at -78 °C, then the cooling bath was removed, and the stirring was continued for 1h. After completion of the reaction, 400 mL of freshly distilled diethyl ether and 150 mL of distilled water and 21.2 mL of 1 M HCl were added to the reaction mixture. The organic phase was separated, washed with water, and dried over sodium sulfate and filtered. The solvent was evaporated to give 15.68 g (99 %) of the pure product as a gray solid. M.p.: 164-166 °C. The product was used in the subsequent synthesis without further purification. ¹H NMR (250 MHz, CDCl₃, δ, ppm): 0.79 (s, 3H), 1.27 (s, 3H), 1.33 (s, 12H), 3.61 (d, 2H, J = 11 Hz), 3.73 (d, 2H, J = 11 Hz), 5.60 (s, 1H), 7.01 (d, 1H), 7. 3.7 Hz), 7.09 (d, 1H, J = 3.7 Hz), 7.20 (d, 1H, J = 3.7 Hz), 7.49 (d, 1H, J = 3.7 Hz). ¹³C NMR (125 MHz, CDCl₃): δ [ppm] 21.83, 22.95, 24.75, 30.21, 77.51, 84.16, 98.09, 123.79, 125.07, 125.81, 137.54, 137.91, 140.81, 144.03. Calcd (%) for C₂₀H₂₇BO₄S₂: C, 59.11; H, 6.70; S, 15.78. Found: C, 59.25; H, 6.82; S, 15.70. MALDI-MS: found m/z 406.43; calculated for $[M]^+$ 406.37.

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2-(2,2'-bithien-5-yl)-2-ethyl-5,5-dimethyl-1,3-dioxane (**2b**). This compound was obtained by the method described for compound **2a** using **1b** (26.1 g, 117.3 mmol), 1,3-dimethyl-1,3-propanediol (73.36 g, 704.8 mmol) and p-TosH (1.56 g, 8.2 mmol). Purification by column chromatography on silica gel (eluent toluene : hexane : triethylamine 49.95: 49.95 : 0.1) gave pure compound **1b** (31.4 g, 81%) as a colorless liquid. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 0.65 (s, 3H), 0.9 (t, 3H, *J* = 7.3 Hz), 1.22 (s, 3H), 1.84 (m, 2H, M = 4, *J* = 7.3 Hz), 3.69 (d, 2H, *J* = 11 Hz), 3.70 (d, 2H, *J* = 11 Hz), 6.85 (d, 1H, *J* = 3.7 Hz), 6.98 (dd, 1H, *J*₁ = 3.7Hz, *J*₂ = 3.7 Hz), 7.05 (d, 1H, *J* = 3.7 Hz), 7.12-7.21 (overlapping peaks, 2H). ¹³C NMR (75 MHz, CDCl₃): δ [ppm]

7.66, 21.96, 22.81, 29.88, 37.77, 71.92, 100.56, 123.33, 123.56, 124.32, 126.97, 127.80, 137.49, 137.64, 143.33. Calcd (%) for $C_{16}H_{20}O_2S_2$: C, 62.30; H, 6.54; S, 20.79. Found: C, 62.45; H, 6.65; S, 20.72. MALDI-MS: found m/z 308.56; calculated for $[M]^+$ 308.46.

2-ethyl-5,5-dimethyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bithi en-5-yl]-1,3-dioxane (3b). This compound was obtained by the method described for compound **3a** using **2b** (31.1 g, 101 mmol), 1.6 M solution of butyllithium (62.01 mL, 101 mmol) in hexane, IPTMDOB (18.76 g, 101 mmol) to give 41.5 g (95%) of the pure product (purity was 98% according to ¹H NMR) as a blue solid. M.p.: 119-120 °C. The product was used in the subsequent synthesis without further purification. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 0.65 (s, 3H), 0.9 (t, 3H, *J* = 7.3 Hz), 1.22 (s, 3H), 1.34 (s, 12H), 1.84 (m, 2H, M = 4, *J* = 7.3 Hz), 3.39 (d, 2H, *J* = 11 Hz), 3.69 (d, 2H, *J* = 11 Hz), 6.85 (d, 1H, *J* = 3.7 Hz), 7.10 (d, 1H, *J* = 3.7 Hz), 7.19 (d, 1H, *J* = 3.7 Hz), 7.50 (d, 1H, *J* = 3.7 Hz). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 7.67, 21.96, 22.80, 24.62, 24.81, 29.88, 37.78, 71.93, 84.22, 100.54, 124.06, 124.78, 127.12, 137.51, 137.98, 144.03, 144.19. Calcd (%) for C₂₂H₃₁BO₄S₂: C, 60.83; H, 7.19; S, 14.76. Found: C, 60.49; H, 7.25; S, 14.70. MALDI-MS: found m/z 434.27; calculated for [M]⁺ 434.49.

2-ethyl-5,5-dimethyl-2-(2,2':5',2''-terthien-5-yl)-1,3-dioxane (4b). In an inert atmosphere, degassed solutions of 2-bromthiopene (3.75 g, 23 mmol) and compound **3b** (8 g, 18 mmol) in toluene/ethanol mixture (100/10 mL) and 2M solution of aq. Na₂CO₃ (14 mL) were added to Pd(PPh₃)₄ (399 mg, 0.35 mmol). The reaction mixture was stirred under reflux for 20 h, and then it was cooled to room temperature and poured into 100 mL of water and 100 mL of toluene. The organic phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel (eluent toluene : triethylamine 99.9 : 0.1) to give pure compound **4b** (5,39 g, 74%) as a yellow solid. M.p.: 93-94 °C. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 0.66 (s, 3H), 0.92 (t, 3H, *J* = 7.3 Hz), 1.22 (s, 3H), 1.86 (m, 2H, M = 2, *J* = 7.3 Hz), 3.41 (d, 2H, *J* = 11 Hz), 3.71 (d, 2H, *J* = 11 Hz), 6.86 (d, 1H, *J* = 3.7

Hz), 6.98–7.08 (overlapping peaks, 4H), 7.15 (dd, 1H, $J_1 = 1$ Hz, $J_2 = 1$ Hz), 7.20 (dd, 1H, $J_1 = 1$ Hz, $J_2 = 1$ Hz). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 7.65, 21.91, 22.75, 29.84, 37.72, 71.87, 100.49, 123.25, 123.65, 124.08, 124.30, 124.46, 127.06, 127.87, 136.13, 136.17, 137.10, 137.28, 143.39. Calcd (%) for C₂₀H₂₂O₂S₃: C, 61.50; H, 5.68; S, 24.63. Found: C, 61.31; H, 5.75; S, 24.42. MALDI-MS: found m/z 389.56; calculated for [M]+ 390.59

2-ethyl-5,5-dimethyl-2-[5''-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2':5',2' '-terthien-5-yl]-1,3-dioxane (5b). This compound was obtained by the method described for compound **3a** using **4b** (5.39 g, 14 mmol), 2.5 M solution of n-butyllithium (5.52 mL, 14 mmol) in hexane, IPTMDOB (2.57 g, 14 mmol) to give 6.92 g (98%) of the pure product (purity was 98% according to ¹H NMR) as a blue liquid. The product was used in the subsequent synthesis without further purification. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 0.65 (s, 3H), 0.91 (t, 3H, *J* = 7.3 Hz), 1.22 (s, 3H), 1.34 (s, 12H), 1.86 (dd, 2H, *J*₁ = 7.3 Hz), 7.04 (t, 2H, *J* = 3.7 Hz), 7.12 (d, 1H, *J* = 3.7 Hz), 7.21 (d, 1H, *J* = 3.7 Hz), 7.51 (d, 1H, *J* = 3.7 Hz). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 7.62, 21.92, 22.76, 24.75, 25.60, 29.85, 37.72, 71.90, 84.20, 100.50, 123.44, 124.23, 124.82, 125.00, 127.07, 135.99, 136.89, 137.20, 137.96, 143.68, 143.75. Calcd (%) for C₂₆H₃₃BO₄S₃: C, 60.46; H, 6.44; S, 18.62. Found: C, 60.18; H, 6.28; S, 18.09. MALDI-MS: found m/z 515.61; calculated for [M]⁺ 516.55.

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2-(2,2'-bithien-5-yl)-2-hexyl-5,5-dimethyl-1,3-dioxane (**2c**). This compound was obtained by the method described above for compound **2a** using 1c (16.7 g, 60.1 mmol), 1,3-dimethyl-1,3-propanediol (37.56 g, 360.7 mmol), p-TosH (0.8 g, 4.2 mmol) to give the crude product. It was purified by a column chromatography on silica gel (eluent toluene : hexane : triethylamine 49.95: 49.95 : 0.1) to give pure compound (15.07 g, 71%) as a colorless liquid. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 0.65 (s, 3H), 0.84 (t, 3H, *J* = 6.7 Hz), 1.21–1.46 (overlapping peaks, 12H), 1.82–1.89 (overlapping peaks, 2H), 3.39 (d, 2H, *J* = 11 Hz), 3.71 (d, 2H, *J* = 11 Hz), 6.85 (d, 1H, *J* = 3.7 Hz), 6.97-7.02 (dd, 1H, *J*₁ = 3.7 Hz, *J*₂ = 3.7 Hz), 7.12-7.17 (dd, 1H, *J*₁ = 1 Hz, *J*₂ = 1 Hz), 7.17-7.23 (dd, 1H, *J*₁ = 1 Hz, *J*₂ = 1 Hz). ¹³C

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NMR (75 MHz, CDCl₃): δ [ppm] 14.05, 21.89, 22.59, 22.80, 23.11, 29.29, 29.80, 31.79, 44.98, 71.84, 100.29, 123.27, 123.49, 124.26, 126.78, 127.75, 137.43, 137.51, 143.62. Calcd (%) for C₂₀H₂₈O₂S₂: C, 65.89; H, 7.74; S, 17.59. Found: C, 65.45; H, 7.95; S, 17.32. MALDI-MS: found m/z 364.83; calculated for [M]⁺ 364.56.

2-hexyl-5,5-dimethyl-2-[5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bith ien-5-yl]-1,3-dioxane (3c). This compound was obtained by the method described above for compound **3a** using **2c** (7.94 g, 22 mmol), 2.5 M solution of butyllithium (8.71 mL, 22 mmol) in hexane, IPTMDOB (4.05 g, 22 mmol) to give 9.91 g (92%) of the pure product (purity was 98% according to ¹H NMR) as a blue liquid. The product was used in the subsequent synthesis without further purification. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 0.64 (s, 3H), 0.81 (t, 3H, *J* = 6.7 Hz), 1.22 (s, 12H), 1.33– 1.46 (overlapping peaks, 12H), 1.82–1.86 (overlapping peaks, 2H), 3.38 (d, 2H, *J* = 11 Hz), 3.69 (d, 2H, *J* = 11 Hz), 6.85 (d, 1H, *J* = 3.7 Hz), 7.10 (d, 1H, *J* = 3.7 Hz), 7.19 (d, 1H, *J* = 3.7 Hz), 7.49 (d, 1H, *J* = 3.7 Hz). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 14.04, 21.88, 22,58, 22.78, 23.09, 24.73, 29.27, 29.80, 31.78, 44.97, 71.84, 84.14, 100.26, 124.00, 127.70, 126.91, 137.39, 137.90, 144.13, 144.36. Calcd (%) for C₂₆H₃₉BO₄S₂: C, 63.66; H, 8.01; S, 13.07. Found: C, 63.18; H, 8.48; S, 12.89. MALDI-MS: found m/z 490.96; calculated for [M]+ 490.54.

2-hexyl-5,5-dimethyl-2-(2,2':5',2''-terthien-5-yl)-1,3-dioxane (**4c**) was obtained by the method described above for compound **4b** using **3c** (8,7 g, 18 mmol), 2-bromthiopene (3.62 g, 22 mmol), 2M solution of aq. Na₂CO₃ (14 mL), Pd(PPh₃)₄ (384 mg, 0.33 mmol) to give a crude product. It was purified by column chromatography on silica gel (eluent toluene : hexane : triethylamine 49.95: 49.95 : 0.1) to give pure compound **4c** (5.56 g, 71%) as a as yellow solid. M.p. 78-80 °C. ¹H NMR (250 MHz, CDCl₃, δ , ppm): 0.65 (s, 3H), 0.84 (t, 3H, *J* = 6.7 Hz), 1.22–1.46 (overlapping peaks, 12H), 1.82–1.89 (overlapping peaks, 2H), 3.40 (d, 2H, *J* = 11 Hz), 3.70 (d, 2H, *J* = 11 Hz), 6.85 (d, 1H, *J* = 3.7 Hz), 7.00–7.07 (overlapping peaks, 4H), 7.16 (dd, 1H, *J*₁ = 1 Hz, *J*₂ = 1 Hz), 7.20 (dd, 1H, *J*₁ = 1 Hz, *J*₂ = 1 Hz). ¹³C NMR (75 MHz, CDCl₃): δ [ppm] 14.10, 21.92, 22.63, 22.81, 23.15, 29.32, 29.85, 31.82, 45.00, 77.44, 100.31, 123.28, 123.66, 124.09, 124.31, 124.47, 126.92, 127.88, 136.14,

136.21, 137.13, 137.24, 143.81. Calcd (%) for C₂₄H₃₀O₂S₃: C, 64.53; H, 6.77; S, 21.53. Found: C, 64.87; H, 6.63; S, 21.12. MALDI-MS: found m/z 447.07; calculated for [M]⁺ 446.70.

2-hexyl-5,5-dimethyl-2-[5''-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2':5',2 ''-terthien-5-yl]-1,3-dioxane (5c) was obtained by the method described above for compound **5b** using **4c** (4.33 g, 10 mmol), 2.5 M solution of n-butyllithium (3.87 mL, 10 mmol) in hexane, IPTMDOB (1.8 g, 10 mmol) to give 5.45 g (98%) of the pure product (purity was 98% according to ¹H NMR) as a dark green liquid. The product was used in the subsequent synthesis without further purification. ¹H NMR (250 M Hz, CDCl₃, δ , ppm): 0.65 (s, 3H), 0.81 (t, 3H, *J* = 6.7 Hz), 1.22 (s, 12H), 1.33–1.46 (overlapping peaks, 12H), 1.82–1.87 (overlapping peaks, 2H), 3.39 (d, 2H, *J* = 11 Hz), 3.69 (d, 2H, *J* = 11 Hz), 6.85 (d, 1H, *J* = 3.7 Hz), 7.03–7.07 (overlapping peaks, 2H), 7.12 (d, 1H, *J* = 3.7 Hz), 7.21 (d, 1H, *J* = 3.7 Hz), 7.51 (d, 1H, *J* = 3.7 Hz). ¹³C NMR (75 M Hz, CDCl₃): δ [ppm] 14.04, 21.88, 22.78, 23.09, 24.75, 29.27, 29.80, 31.78, 44.98, 71.90, 84.20, 100.50, 123.44, 124.23, 124.82, 125.00, 127.07, 135.99, 136.89, 137.20, 137.96, 143.68, 143.75. Calcd (%) for C₃₀H₄₁BO₄S₃: C, 62.92; H, 7.22; S, 16.80. Found: C, 63.38; H, 7.54; S, 16.97. MALDI-MS: found m/z 572.67; calculated for [M]⁺ 572.66.

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tris{4-[5'-(5,5-dimethyl-1,3-dioxan-2-yl)-2,2'-bithien-5-yl]-2-methoxyphenyl}amin e (6a). In an inert atmosphere, degassed solutions of tris(4-bromo-2-methoxyphenyl) amine (2.5 g, 4.37 mmol) and compound **3a** (6.39 g, 15.7 mmol) in toluene/ethanol mixture (110/11 mL) and 2M solution of aq. Na₂CO₃ (23.6 mL) were added to Pd(PPh₃)₄ (545 mg, 0.47 mmol). The reaction mixture was stirred under reflux for 11 h, and then it was cooled to room temperature and poured into 100 mL of water and 100 mL of toluene. The organic phase was separated, washed with water, dried over sodium sulfate and filtered. The solvent was evaporated in vacuum and the residue was dried at 1 Torr. The product was purified by column chromatography on silica gel (eluent toluene : ethyl acetate : trimethylamine = 20 : 1 : 0.02) to give pure compound **6a** (4.25 g, 83%) as a yellow solid. M.p. = 239-241°C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 0.8 (s, 9H), 1.29 (s, 9H), 3.62 (d, 6H, *J* = 11 Hz), 3.65 (s, 9H), 3.74 (d, 6H, *J* =

11 Hz), 5.61 (s, 3H), 6.77-6.92 (overlapping peaks, 3H), 7.02-7.09 (overlapping peaks, 12H), 7.10 (d, 3H, J = 3.7 Hz), 7.12-7.20 (overlapping peaks, 3H). Calcd (%) for C₆₃H₆₃NO₉S₆: C, 64.64; H, 5.42; N, 1.20; S, 14.43. Found: C, 64.87; H, 5.63; N, 1.17; S, 14.32. MALDI-MS: found m/z 1169.47; calculated for [M]⁺ 1170.57.

5',5'',5'''-[nitrilotris(3-methoxy-4,1-phenylene)]tris(2,2'-bithiophene-5-carbaldeh yde) (7a). 1M HCl (9 mL) was added to a solution of compound 6a (3.4 g, 2.9 mmol) in THF (90 mL) and then the reaction mixture was stirred for 4 hours at reflux. During the reaction, the product was gradually formed orange precipitate. The organic phase was separated using diethyl ether, washed with water and filtered off. After completion of the reaction the organic phase was separated using diethyl ether, washed with water and filtered off to give pure compound 7a (2.5 g, 95%) as orange crystals. M.p. = 194-196 °C. ¹H NMR (250 MHz, DMSO-d6): δ [ppm] 3.62 (s, 9H), 6.67 (d, 3H, *J* = 8.3 Hz), 7.16 (dd, 3H, *J*₁ = 1.82 Hz, *J*₂ = 1.82 Hz), 7.30 (d, 3H, *J* = 2.14 Hz), 7.53 (d, 6H, *J* = 3.7 Hz), 7.61 (dd, 3H, *J*₁ = 3.7Hz, *J*₂ = 3.7Hz), 7.98 (d, 3H, *J* = 3.7 Hz), 9.87 (s, 3H). Calcd (%) for C₄₈H₃₃NO₆S₆: C, 63.20; H, 3.65; N, 1.54; S, 21.09. Found: C, 63.31; H, 3.56; N, 1.58; S, 21.18. MALDI-MS: found m/z 911.75; calculated for [M]⁺ 912.17.

tris{4-[5'-(1,1-dicyanoeth-1-en-2-yl)-2,2'-bithien-5-yl]-2-methoxyphenyl}amine

N(Ph-OMe-2T-DCV)₃. Compound **7a** (0.738 g, 0.8 mmol), malononitrile (0.32 g, 4.9 mmol) and dry pyridine (14.7 mL) were placed in a reaction vessel and stirred under argon atmosphere for 6 hours at 105°C using the microwave heating. After completeness of the reaction, the pyridine was evaporated in vacuum and the residue was dried at 1 Torr. This crude product was purified by column chromatography on silica gel (eluent dichloromethane). Further purification included precipitation of the product from its THF solution with toluene and hexane to give pure product as a black solid (0.43 g, 51%). M.p. = 200 °C. ¹H NMR (250 MHz, DMSO-d6): δ [ppm] 3.62 (s, 9H), 6.75 (d, 3H, J = 8.6 Hz), 7.18–7.24 (overlapping peaks, 3H), 7.29–7.34 (overlapping peaks, 3H), 7.61 (t, 6H, J = 3.7 Hz), 7.70 (d, 3H, J = 3.7 Hz), 7.88 (d, 3H, J = 4.3 Hz), 8.61 (s, 3H). Calcd (%) for C₅₇H₃₃N₇O₃S₆: C, 64.81; H, 3.15; N, 9.28; S, 18.21. Found: C, 64.72; H, 3.16; N, 9.22; S, 18.18. MALDI-MS: found m/z

1056.26; calculated for $[M]^+$ 1056.21.

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tris{4-[5''-(2-ethyl-5,5-dimethyl-1,3-dioxan-2-yl)-2,2':5',2''-terthien-5-yl]-2-metho xyphenyl}amine (6b). This compound was obtained by the method described for compound 6a using *tris*(4-bromo-2-methoxyphenyl)amine (1.71 g, 2.99 mmol), compound 5b (5.56 g, 10.8 mmol), 2M solution of aq. Na₂CO₃ (16.1 mL), Pd(PPh₃)₄ (0.37 g, 0.32 mmol). The crude product was purified by column chromatography on silica gel (eluent toluene : triethylamine = 1000 : 1) to give pure compound 6b (4.06 g, 89%) as a yellow solid. M.p. = 185-187 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 0.67 (s, 9H), 0.93 (t, 9H, *J* = 7.3 Hz), 1.24 (s, 9H), 1.87 (dd, 6H, *J*₁ = 7.3Hz, *J*₂ = 7.3 Hz), 3.41 (d, 6H, *J* = 11 Hz), 3.67 (s, 9H), 3.72 (d, 6H, *J* = 11 Hz), 6.81–6.98 (overlapping peaks, 6H), 7.02–7.21 (overlapping peaks, 21H). Calcd (%) for C₈₁H₈₁NO₉S₉: C, 64.81; H, 5.44; N, 0.93; S, 19.22. Found: C, 64.57; H, 5.63; N, 0.95; S, 19.11. MALDI-MS: found m/z 1501.82; calculated for [M]⁺ 1501.12.

1,1',1''-{nitrilotris[(3-methoxy-4,1-phenylene)-2,2':5',2''-terthiene-5'',5-diyl]}trip ropan-1-one (**7b**). This compound was obtained by the method described for compound **7a** using 1M HCl (4.5 mL), **6b** (3.35 g, 2.23 mmol) and THF (67 mL) to yield pure compound **7b** (2.48 g, 91 %) as orange crystals. M.p. = 256-257 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 1.21 (t, 9H, *J* = 7 Hz), 2.84-3.00 (m, 6H, M = 4, *J* = 7.3 Hz), 3.67 (s, 9H), 6.85 (d, 3H, *J* = 8.5 Hz), 7.04–7.24 (overlapped peaks, 21H), 7.59 (d, 3H, *J* = 4 Hz). Calcd (%) for C₆₆H₅₁NO₆S₉: C, 63.79; H, 4.14; N, 1.13; S, 23.22. Found: C, 63.31; H, 4.26; N, 1.22; S, 23.58. MALDI-MS: found m/z 1241.16; calculated for [M]⁺ 1242.72.

tris{4-[5''-(1,1-dicyanobut-1-en-2-yl)-2,2':5',2''-terthien-5-yl]-2-methoxyphenyl}a mine N(Ph-OMe-3T-DCV-Et)₃. This compound was obtained by the method described for N(Ph-OMe-2T-DCV)₃ using compound **7b** (2.11 g, 1.7 mmol) and malononitrile (0.56 g, 8.5 mmol) to give pure product as a black solid (0.4 g, 18%). M.p. = 243°C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 1.34 (t, 9H, *J* = 7.3 Hz), 2.92 (m, 6H, M = 4, *J* = 7 Hz), 3.68 (s, 9H), 6.86 (d, 3H, *J* = 8.6 Hz), 7.04–7.13 (overlapping peaks, 6H), 7.14 (d, 3H, *J* = 3.7 Hz), 7.18–7.23 (overlapping peaks, 6H), 7.26-7.28 (overlapping peaks, 3H), 7.29 (d, 3H, *J* = 3.7 Hz), 7.96 (d, 3H, *J* = 3.7 Hz). Calcd (%)

for C₇₅H₅₁N₇O₃S₉: C, 64.95; H, 3.71; N, 7.07; S, 20.81. Found: C, 64.34; H, 3.92; N, 6.85; S, 20.37. MALDI-MS: found m/z 1385.62; calculated for [M]⁺ 1386.86.

tris{4-[5''-(2-ethyl-5,5-dimethyl-1,3-dioxan-2-yl)-2,2':5',2''-terthien-5-yl]-2-metho xyphenyl}amine (6c). This compound was obtained by the method described above for compound 6a using *tris*(4-bromo-2-methoxyphenyl)amine (1.00 g, 1.75 mmol), compound 5c (3.6 g, 6.29 mmol), 2M solution of aq. Na₂CO₃ (9.4 mL), Pd(PPh₃)₄ (218 mg, 0.19 mmol). The crude product was purified by column chromatography on silica gel (eluent toluene: triethylamine = 1000 : 1) to give pure compound 6c (2.04 g, 70%) as a yellow solid. M.p. 92-93 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 0.66 (s, 9H), 0.82 (t, 9H, *J* = 6.7 Hz), 1.19–1.48 (overlapped peaks, 33H), 1.72–2.01 (overlapped peaks, 6H), 3.40 (d, 6H, *J* = 11 Hz), 3.67 (s, 9H), 3.70 (d, 6H, *J* = 11 Hz), 6.87 (d, 6H, *J* = 3.7 Hz), 7.04–7.20 (overlapped peaks, 21H). Calcd (%) for C₉₃H₁₀₅NO₉S₉: C, 66.91; H, 6.34; N, 0.84; S, 17.29. Found: C, 66.87; H, 6.53; N, 0.89; S, 17.12. MALDI-MS: found m/z 1669.32; calculated for [M]+ 1669.41.

1,1',1''-{nitrilotris](3-methoxy-4,1-phenylene)-2,2':5',2''-terthiene-5'',5-diyl]}trih eptan-1-one (**7c**). Compound **7c** was obtained by the method described above for compound **7b** using 1M HCl (2.7 mL), compound **6c** (1.52 g, 0.91 mmol) and THF (35 mL) to give pure compound **7c** (1.17 g, 91%) as orange crystals. M.p. = 245-247 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm] 0.85 (t, 9H, J = 6.7 Hz), 1.22–1.47 (overlapped peaks, 24H), 2.00 (t, 6H, J = 7.3 Hz), 3.67 (s, 9H), 6.89 (d, 3H, J = 3.7Hz), 6.98–7.09 (overlapped peaks, 9H), 7.11–7.18 (overlapped peaks, 12H), 7.48 (d, 3H, J = 4.1 Hz). Calcd (%) for C₇₈H₇₅NO₆S₉: C, 66.40; H, 5.36; N, 0.99; S, 20.45. Found: C, 66.48; H, 5.49; N, 1.08; S, 21.01. MALDI-MS: found m/z 1411.07; calculated for [M] + 1411.05.

tris{4-[5''-(1,1-dicyanooct-1-en-2-yl)-2,2':5',2''-terthien-5-yl]-2-methoxyphenyl}a mine N(Ph-OMe-3T-DCV-Hex)₃. This compound was obtained by the method described above for N(Ph-OMe-2T-DCV)₃ using compound 8c (1 g, 0.7 mmol), malononitrile (0.327 g, 5.0 mmol) and pyridine (20 mL) to give pure product as a black solid (0.77 g, 70%). M.p. = 173 °C. ¹H NMR (250 MHz, CDCl₃): δ [ppm]

0.87 (t, 9H, J = 6.7 Hz), 1.29–1.51 (overlapping peaks, 18H), 1.63–1.76 (overlapping peaks, 6H), 2.88 (t, 6H, J = 7.3 Hz), 3.68 (s, 9H), 6.86 (d, 3H, J = 8.6 Hz), 7.06–7.25 (overlapping peaks, 18H), 7.29 (d, 3H, J = 3.7 Hz), 7.94 (d, 3H, J = 4.3 Hz). Calcd (%) for C₈₇H₇₅N₇O₃S₉: C, 67.19; H, 4.86; N, 6.30; S, 18.56. Found: C, 67.09; H, 4.93; N, 6.22; S, 18.31. MALDI-MS: found m/z 1555.53; calculated for [M]+ 1555.19.

5. Acknowledgements

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The part of this work including the synthesis and characterization of the oligomers was carried out under financial support from the Russian Science Foundation (grant 14-13-01380). The preparation and characterization of blends and the photovoltaic devices was financed by the Cluster of Excellence "Engineering of Advanced Materials" at the University of Erlangen-Nuremberg, which is funded by the German Research Foundation (DFG) within the framework of its "Excellence Initiative". This work has been partially funded by the the Sonderforschungsbereich 953 "Synthetic Carbon Allotropes", and we also thank the support of "Solar Technologies go Hybrid" (SolTech) project and the Energy Campus Nürnberg (EnCN) financed by the Bavarian state government.

Electronic Supplementary Information

Electronic Supplementary Information (ESI) available: ¹H and ¹³C NMR spectra, molecular modeling and X-ray diffraction data, and photovoltaic data.

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Synthesis of a series of D- π -A star-shaped oligomers having *tris*(2-methoxyphenyl)amine core and alkyldicyanovinyl groups is described. The optical, electrochemical, thermal, structural and photovoltaic properties were investigated and compared to those of the analogs with pristine triphenylamine core and dicyanovinyl group.

