

Novel Highly Fluorescent Triphenylamine-Based Oligothiophenes[†]

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A homologous series of novel amorphous oligothiophenyl-triphenylamines, comprised of head-to-tail coupled oligo(3-hexylthiophene)s covalently linked to a triphenylamine core, are disclosed. These hybrid systems, which differ by the length of the oligothiophene units from a monothiophene up to a quaterthiophene, were created via palladium-catalyzed cross-coupling reactions in good yields. The optical and electrochemical properties of these compounds were thoroughly investigated and are compared to the corresponding parent linear non-functionalized oligothiophenes, clearly demonstrating that these newly synthesized hybrid systems are characterized by outstanding absorption and emission properties. These molecules exhibit fluorescence quantum yields as high as 65%, which is unexpectedly high for thiophene-based materials. Based on this available data set, structure–property relationships were established, providing a deeper insight into the electronic nature of these materials and in this respect elucidating electronic differences between these star-shaped structures and their corresponding parent linear oligothiophenes.

Introduction

Organic molecules and polymers such as thiophene-based materials or triphenylamine-derivatives have gained much attention during the past decade as active materials in optoelectronic devices such as light emitting¹ and photovoltaic devices.² These materials have to fulfill the requirements of high absorptivities, high charge carrier mobilities, good film-forming properties, as well as good thermal- and photostabilities. However, it is known that the crystalline properties of the corresponding small molecular derivatives can aggravate their hole conducting properties.^{3,4} In this respect, dendritic structures received increasing attention as these materials exhibit interesting properties including energy transfer, photochemical antenna function, and stepwise metal assembling. Among the variety of dendritic semiconductive materials studied so far, triphenylamine and related derivatives exhibit as p-type conductors good spectral and transport properties^{5–10} and have been widely employed for the fabrication of organic field-effect transistors (OFET)¹¹ and

organic light emitting diodes (OLED).¹ These hole conductors have also been combined with the excellent properties of oligothiophenes to create star-shaped molecules with several oligothiophene chains attached to the central core,^{12–15} and due to their ability to form amorphous films with high glass-transition temperatures they are of special interest for the manufacturing of OLED devices. Besides their amorphous behavior, electronic and redox properties are also important and might be influenced by the dendritic type of structures. Therefore, it is of great interest to elucidate whether the optical and electronic properties can be influenced by changing the topologies of the corresponding conductive materials.¹⁶

In a recent approach, it has been found that the combination of regioregular dihexylbithiophene attached to a triphenylamine results in a novel class of oligothiophenyl-triphenylamines (TPA-OT₃) with astonishing emission properties,¹⁷ making this type of material a promising candidate for the application in OLEDs.

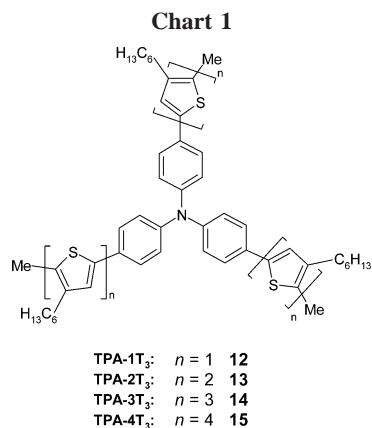
In this article, we focus on this class of compound in more detail as we thoroughly elucidate their optical and electrochemical properties in dependence of the chain length of the attached oligothiophene units. On the basis of this systematic investigation, we were able to set up new structure–property relationships, which give us further insight into the electronic properties of these substances. Furthermore, this allows us

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[†] This work is dedicated to Prof. Peter Bäuerle on the occasion of his 50th birthday.

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to emphasize distinct differences in the optical and electrochemical properties between the dendritic oligothiophenyl-triphenylamines and their related linear oligothiophenes.

Prior to the characterization, in the first steps we created a homologous series of α -methylated oligothiophenes, utilizing efficient α' -bromination and Suzuki-type cross-coupling reactions, which allows an easy scale-up of these reactions. Based on this first homologous series, the corresponding α' -brominated oligothiophenes were used as starting materials for the synthesis of the second series of oligothiophenyl-triphenylamines **12–15** (Chart 1), which in consequence are varied by the length of the regioregular oligo(3-hexylthiophene)s from a monothiophene ($n = 1$: TPA-1T₃) to a quaterthiophene ($n = 4$: TPA-4T₃). In this respect, we established an effective synthesis to obtain the oligothiophenyl-triphenylamines in good to excellent yields.

Synthesis

Prior to the synthesis of the oligothiophenyl-triphenylamines **12–15**, the parent brominated oligothiophenes **3**, **6**, **8**, and **10** were build-up by an iterative regioselective bromination and Suzuki cross-coupling sequence with monothiophene boronic ester **4**.¹⁸ The stepwise built-up of the oligothiophene was derived from 2-bromo-3-hexylthiophene **1**,¹⁹ which was converted into methylated thiophene **2** by a one-pot, two-step synthesis. First, a bromine–lithium exchange was achieved in THF at -80 °C with 1 equiv of *n*-BuLi. The lithiated intermediate was subsequently reacted with 1.05 equiv of methyl trifluoromethanesulfonate to give methylated compound **2** in 76% after distillation in vacuo. Next, a bromine function was introduced at the reactive α -position of thiophene **2**, using 1 equiv of *N*-bromosuccinimide (NBS) in dry DMF at 0 °C. In this manner, brominated thiophene **3** was accessible in 82% after distillation in vacuo.

For the palladium-catalyzed Suzuki reaction, DME and tripotassium phosphate were used as solvent and base, respectively. To achieve excellent yields, an effective catalytic system based on Pd₂(dba)₃ as the palladium source and [HP(*t*-Bu)₃]₂BF₄ as the ligand precursor was used,²⁰ which within 3 h gave a quantitative conversion of brominated thiophene **3** when reacted with boronic ester **4** at room

temperature. After the reaction was completed, the isomerically pure bithiophene **5** was distilled in vacuo with a yield of 89%.

Utilizing 1 equiv of NBS in dry DMF at 0 °C, the subsequent bromination in the free α -position of **5** was accomplished in a very clean way. Hence, brominated bithiophene was purely obtained in 97% yield after filtration over a short silica column. For further elongation of the oligothiophene chain, the Suzuki-type cross-coupling and NBS/DMF bromination steps were repeated. While for all Suzuki reactions the same reaction conditions were applied, the bromination procedures were slightly altered because no quantitative bromination in the α -position could be achieved for the longest analogues **7** and **9**. Therefore, a slight excess of 1.1 equiv of NBS was used, and a chromatographic workup was unavoidable. Furthermore, for the bromination of **9**, dry chloroform was added to the reaction mixture to increase the solubility of the quaterthiophenes. In this respect, methylated terthiophene **7** and brominated terthiophene **8** were obtained in 84% and 86% yield, respectively, while the corresponding quaterthiophenes **9** and **10** were accessible in 85% and 78% yield, respectively.

For the 3-fold Suzuki reaction of the brominated thiophenes **3**, **6**, **8**, and **10** with boronic ester **11**^{17,21} (Scheme 1), the same reaction conditions were applied as described for the build-up of the parent oligothiophenes; however, the reaction time was doubled to 6 h to get the reactions to full completion. Accordingly, the corresponding oligothiophenyl-triphenylamines **12–15** were afforded in good yields of greater than 70% (Scheme 2), corresponding to an efficiency for one cross-coupling step of 89%. In summary, TPA-1T₃ was obtained in 70%, TPA-2T₃ in 74%, TPA-3T₃ in 70%, and the longest homologue TPA-4T₃ in 73% yield after column chromatography. All of these materials were isolated as amorphous materials with wax-like properties, which do not crystallize even after a month.

Optical Properties

To compare the absorption and emission properties of the oligothiophenyl-triphenylamines **12–15**, the parent methylated-oligothiophenes **5**, **7**, and **9** as well as tri-*p*-tolyl-amine TPA-Me₃²² are taken as reference compounds. In the case of monothiophene **2**, no absorption bands down to 250 nm and no fluorescence could have been detected.

Absorption Properties

In the case of the reference materials, the spectra of the methylated oligothiophenes **5**, **7**, and **9** reveal a progressive bathochromic shift of the absorption maxima with increasing length of the conjugated system, exhibiting absorption maximum in the range from 308 nm (Me-2T) to 375 nm (Me-4T) (Figure 1). Simultaneously, the optical band gaps, which were determined from the lower-energy onset of the absorption bands, are gradually diminishing from 3.49 to 2.77

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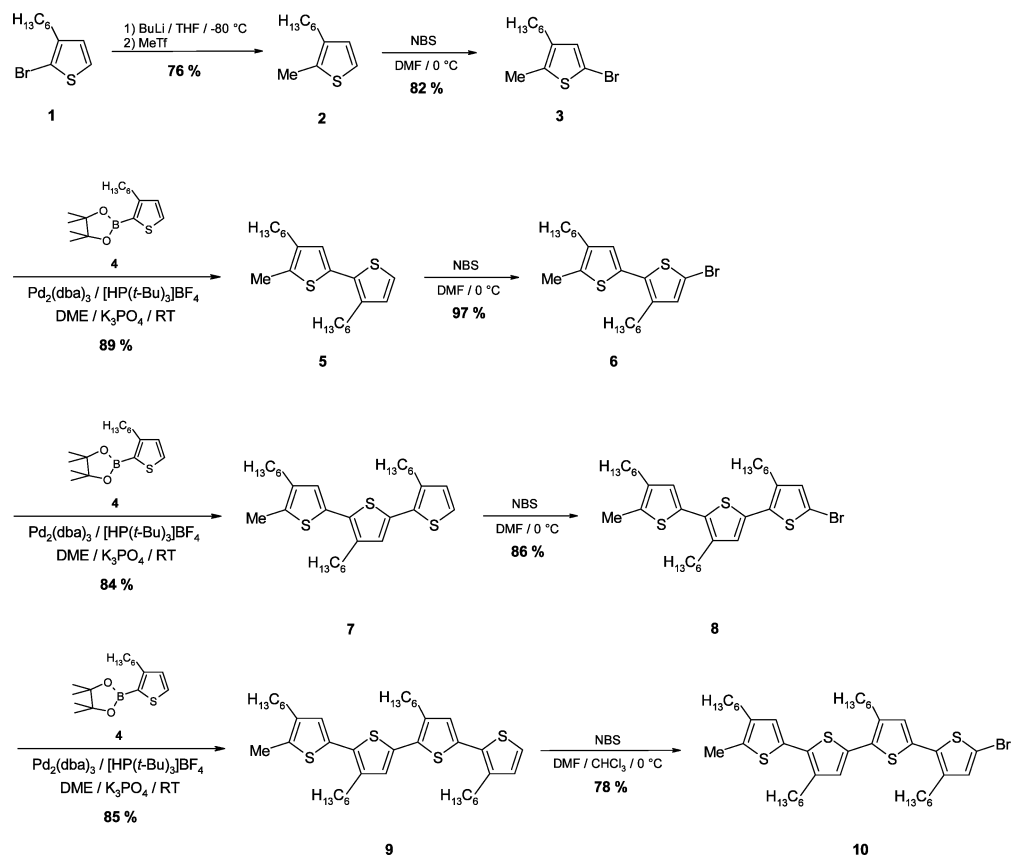
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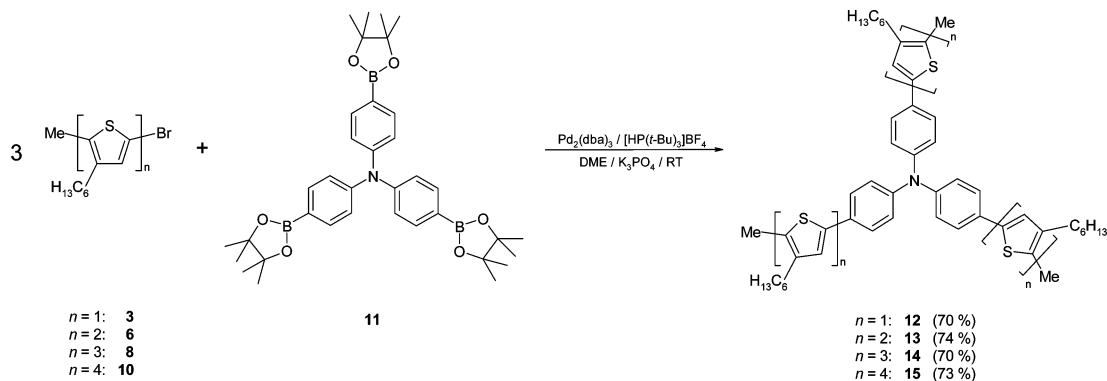
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Scheme 1



Scheme 2



eV, while the extinction coefficients are more than doubled by going from bithiophene **5** to quaterthiophene **9**. This trend is in accordance with previously reported homologous series of conjugated oligothiophenes.^{23–25} Further, the methylated triphenylamine **TPA-Me₃** shows a similar intense absorption as compared to the latter oligothiophenes with a maximum absorption wavelength of 305 nm.

In the case of the homologous series of oligothiophenyl-triphenylamines **12–15**, clear structure–property relationships can also be established (Table 1). As compared to the parent oligothiophenes **5**, **7**, and **9**, the absorption bands are significantly bathochromically shifted by 50–100 nm,

whereas the red-shifts are much more pronounced in the case of the smaller representatives [$\Delta\lambda_{\max}(\mathbf{5}–\mathbf{13}) = 92$ nm] than for the larger ones [$\Delta\lambda_{\max}(\mathbf{9}–\mathbf{15}) = 48$ nm]. At the same time, the optical band gaps are also strongly decreasing in energy when going from **TPA-1T₃** (3.02 eV) to **TPA-4T₃** (2.51 eV). As for the parent linear oligothiophenes, an increase in absorptivity is observed with elongation of the conjugated hybrid systems by going from **TPA-1T₃** to **TPA-4T₃**. Although the oligothiophenyl-triphenylamines **13–15** are characterized by generally larger absorptivities with respect to the corresponding oligothiophenes **5**, **7**, and **9**, the corresponding extinction coefficients are less amplified with enlargement of the conjugated systems. In this respect, the absorptivities of the oligothiophenyl-triphenylamines are stronger than expected from the 3-fold addition of the pure absorptivities of corresponding parent oligothiophenes and that of tri-*p*-tolyl-amine **TPA-Me₃**.

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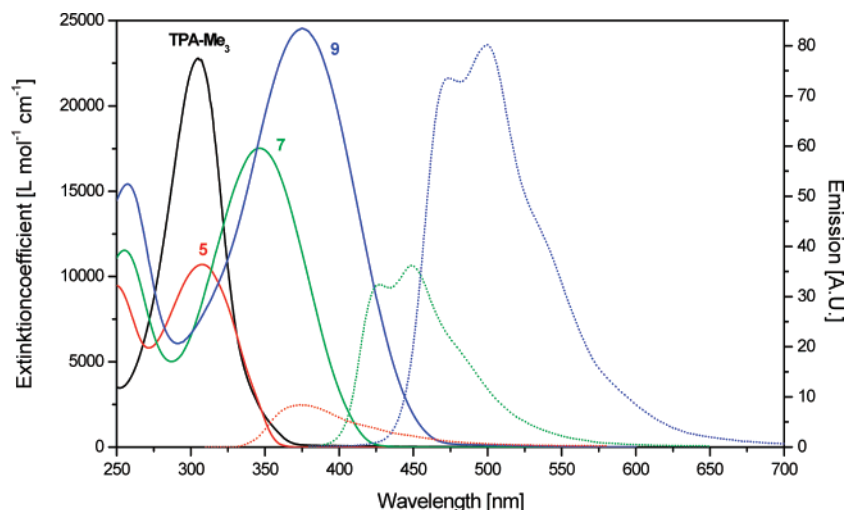


Figure 1. Absorption (solid lines) and emission (dotted lines) spectra of the parent oligothiophenes **5**, **7**, and **9** as well as **TPA-Me₃** in chloroform.

Table 1. Absorption Properties of the Oligothieryl-triphenylamines 12–15 in Comparison with the Parent Oligothiophenes 5, 7, 9, and TPA-Me₃ in Chloroform

compound	$\lambda_{\text{max}}^{\text{abs}}$ [nm] ^a	ϵ [L mol ⁻¹ cm ⁻¹] ^a	ΔE_{opt} [eV] ^b
TPA-Me ₃	305	22 800	3.70
Me-1T (2)	N/A	N/A	N/A
Me-2T (5)	308	10 700	3.49
Me-3T (7)	346	17 500	3.05
Me-4T (9)	375	24 500	2.77
TPA-1T ₃ (12)	371	51 500	3.02
TPA-2T ₃ (13)	400	81 400	2.74
TPA-3T ₃ (14)	416	105 800	2.59
TPA-4T ₃ (15)	423	119 300	2.51

^a $c = 5 \times 10^{-5}$ mol/L. ^b Determined from the onset of the absorption at the lower energy band edge.

The extinction coefficient of **TPA-2T₃** ($\epsilon = 81\,400$ L mol⁻¹ cm⁻¹) is almost 8 times as high as that of the corresponding **Me-2T** ($\epsilon = 10\,700$ L mol⁻¹ cm⁻¹). Consequently, the overall absorption of the pure bithiophene moiety is magnified by a factor of 1.8 upon the direct attachment to the triphenylamine core.²⁶ With ongoing enlargement of the conjugated system, a slight decline of this effect is observed as the absorption of the pure terthiophene in **TPA-3T₃** is only enhanced by a factor of 1.6 and, finally, the absorption of the pure quaterthiophene moiety of **TPA-4T₃** is only increased by a factor of 1.3. The strong bathochromic and hyperchromic shifts of the oligothieryl-triphenylamines **13–15** with respect to the corresponding parent oligothiophenes **5**, **7**, and **9** are due to the strong electronic influence of the electron-rich triphenylamine core on the electronic nature of the adjacent oligothiophene moieties (Figure 2). Nevertheless, this effect decreases with enlargement of the neighboring (oligo-)thiophene systems and therefore seems to be most pronounced in the case of **TPA-1T₃** rather than for **TPA-4T₃**.

For these reasons, it has to be assumed that the donor π -systems of the oligothieryl-triphenylamines **12–15** are larger than the corresponding pristine oligothiophene moieties

themselves. Accordingly, the four covalently connected p-type subunits are electronically coupled and form an extended star-shaped conjugated system, including the triphenylamine-core and the three adjacent (oligo-)thiophene chains. This assumption is further supported by the absence of any distinct absorption maxima in the region around 300 nm that could be ascribed to the absorption of a triphenylamine moiety.

Emission Properties

The fluorescence spectra of parent oligothiophenes **5**, **7**, and **9** exhibit broad and structured emission bands with at least one distinct maximum and a pronounced shoulder. In the case of the **Me-4T**, vestiges of a second shoulder arise at the low-energy band edge. In analogy to the absorption properties, the methylated oligothiophenes **5**, **7**, and **9** show clear trends with respect to the corresponding emission behavior as their emission maxima are gradually red-shifted with increasing length of the conjugated backbone, ranging from 375 nm for **Me-1T** to finally 500 nm in the case of the longest homologue **Me-4T**. At the same time, the fluorescence quantum yields are increasing from 2% to 15%, which is consistent with other homologous series of conjugated oligothiophenes,^{25,27} whereas in contrast the Stokes shifts are almost constant. These relatively high values in the range of 5500 cm⁻¹ are characteristic for conjugated oligothiophenes and are due to a large structural difference between the non-excited ground state and corresponding excited state. In the case of oligothiophenes, the ground state is characterized by a prevalent aromatic structure, whereas the excited state has a predominant quinoidic character. As a consequence of the latter rigid quinoidic structure, the emission bands are much more structured as compared to the corresponding absorption bands, which have their origin in the more flexible ground state.

In the series of the oligothieryl-triphenylamines **12–15**, the trends observed for the emission properties are comparable to those of the parent oligothiophenes **5**, **7**, and **9** (Table

(26) To calculate the absorptivity increase for the hypothetical non-functionalized oligothiophene in the oligothieryl-triphenylamines, the absorptivity of the pure triphenylamine is subtracted from the overall value of that specific hybrid system, divided by a factor of 3, and then compared to the parent methylated oligothiophene.

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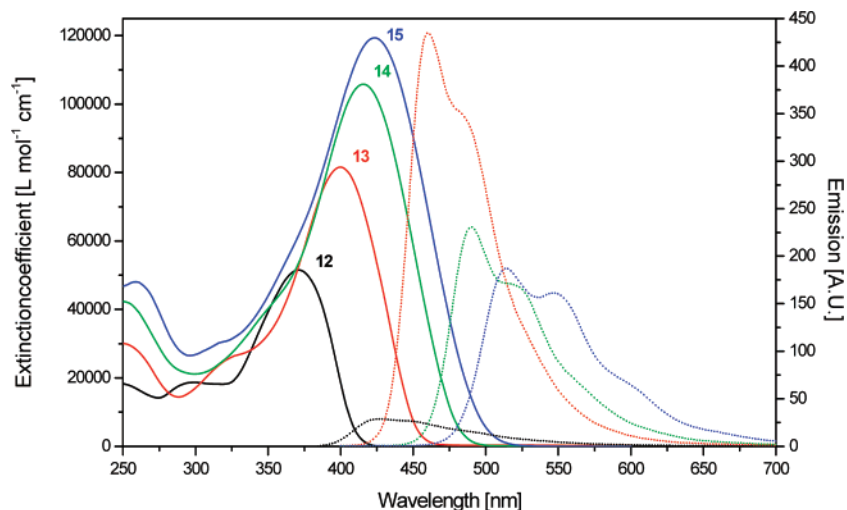


Figure 2. Absorption (solid lines) and emission (dotted lines) spectra of the oligothieryl-triphenylamines **12–15** in chloroform.

Table 2. Emission Properties of the Oligothieryl-triphenylamines **12–15** in Comparison with the Parent Oligothiophenes **5, 7, 9, and TPA-Me₃** in Chloroform

compound	$\lambda_{\text{max}}^{\text{em}}$ [nm] ^a	Φ [%]	Stokes shift [cm ⁻¹ (eV)] ^b
TPA-Me ₃	N/A	N/A	N/A
Me-1T (2)	N/A	N/A	N/A
Me-2T (5)	375 ^c	2 ^e	5801 (0.72)
Me-3T (7)	427, 449 ^d	6 ^f	5483 (0.68)
Me-4T (9)	474, 500, 535 ^d	15 ^f	5570 (0.69)
TPA-1T ₃ (12)	426, 446 ^d	6 ^f	3480 (0.43)
TPA-2T ₃ (13)	460, 483 ^d	65 ^f	3261 (0.40)
TPA-3T ₃ (14)	490, 520 ^d	36 ^f	3630 (0.45)
TPA-4T ₃ (15)	517, 547, 600 ^d	37 ^f	4298 (0.53)

^a Maxima italicized. ^b Stokes shifts measured as $\lambda_{\text{max}}^{\text{em}} - \lambda_{\text{max}}^{\text{abs}}$. ^c Excitation wavelength $\lambda^{\text{ex}} = 300$ nm. ^d Excitation wavelength $\lambda^{\text{ex}} = 375$ nm. ^e Quantum yields determined with respect to anthracene.²⁸ ^f Quantum yields determined with respect to 9,10-diphenylanthracene.²⁹

2). Besides the fact that the shapes of the corresponding emission band are also structured with one distinct emission maximum and one pronounced shoulder, they are generally bathochromically shifted. This effect, however, is most pronounced in the case of **TPA-2T₃** ($\Delta\lambda_{\text{max}}^{\text{em}} = 85$ nm) and becomes less emphasized for the longer analogues, and accordingly the maximum emission of **TPA-4T₃** ($\Delta\lambda_{\text{max}}^{\text{em}} = 17$ nm) is rather comparable to that of the parent **Me-4T**. In contrast to the linear oligothiophenes **2, 5, 7, and 9**, all oligothieryl-triphenylamines **12–15** show strongly enhanced fluorescence quantum yields with values as high as 65%. The smallest representative of this series **TPA-1T₃** only exhibits a quantum yield of 6%, which seems to be negligible as compared to the next higher homologue **TPA-2T₃**, being characterized by an exceptionally high quantum yield of 65%. Nevertheless, it has to be considered that the corresponding building blocks of **TPA-1T₃**, triphenylamine **TPA-Me₃** and monothiophene **Me-1T**, have to be regarded as completely nonfluorescent. In this respect, the quantum yield of 6% for the enlarged conjugated system of **TPA-1T₃** alludes to a significant enhancement of the emission properties with respect to that of the corresponding monothiophene **2**. The next larger conjugated systems **TPA-3T₃** and **TPA-4T₃** exhibit quantum yields of 36% and 37%, respectively, which in turn is considerably larger as compared to that of the parent oligothiophenes **Me-3T** and **Me-4T**. As a third trend, the

Stokes shifts increase from 3500 to 4300 cm⁻¹ with elongation of the conjugated systems, approaching values that are more comparable to those of the pristine oligothiophenes.

In accordance with the corresponding absorption properties, the emission behavior of the oligothieryl-triphenylamines **12–15** leads to the conclusion that these materials consist of largely conjugated systems, which are fully delocalized over the triphenylamine core and the adjacent three (oligo-)thiophene units. In this respect, the electron-donating triphenylamine moiety has a strong electronic effect on the overall conjugated system; however, its influence vanishes with enlargement of the overall conjugated system. Accordingly, the emission maxima and the Stokes shifts approach values that are more comparable to those of the corresponding pristioliogothiophenes in the case of the longest analogues. To draw a conclusion, the combination of the triphenylamine core with the three (oligo-)thiophene units attached reaches an optimum synergetic effect, especially with respect to quantum yields, in the case of the attached bithiophenes.

A similar effect has already been demonstrated for a linear system comprised of an oligothiophene linked to two terminal triphenylamines.¹⁵ In that case, the absorption maximum for a quaterthiophene was shifted to 453 nm and the emission maximum to 532 nm, leading to much more pronounced red-shifts as compared to **TPA-4T₃**. However, it has to be considered that the influence of the triphenylamine moieties in the comparative example is twice as high, and a better comparison would be the corresponding bithiophene, exhibiting maximum absorption and emission at 423 and 491 nm, respectively. In another study, a terthiophen with only one terminal triphenylamine unit was described, which exhibits absorption and emission maxima at 413 and 500 nm, respectively,³⁰ being rather comparable to our **TPA-3T₃**, while the extinction coefficient is only in the order of $\epsilon = 48\,000$ L mol⁻¹ cm⁻¹ (**TPA-3T₃**: $\epsilon = 105\,800$ L mol⁻¹ cm⁻¹). Nevertheless, all of those linear systems described earlier are characterized by relatively low emission quantum

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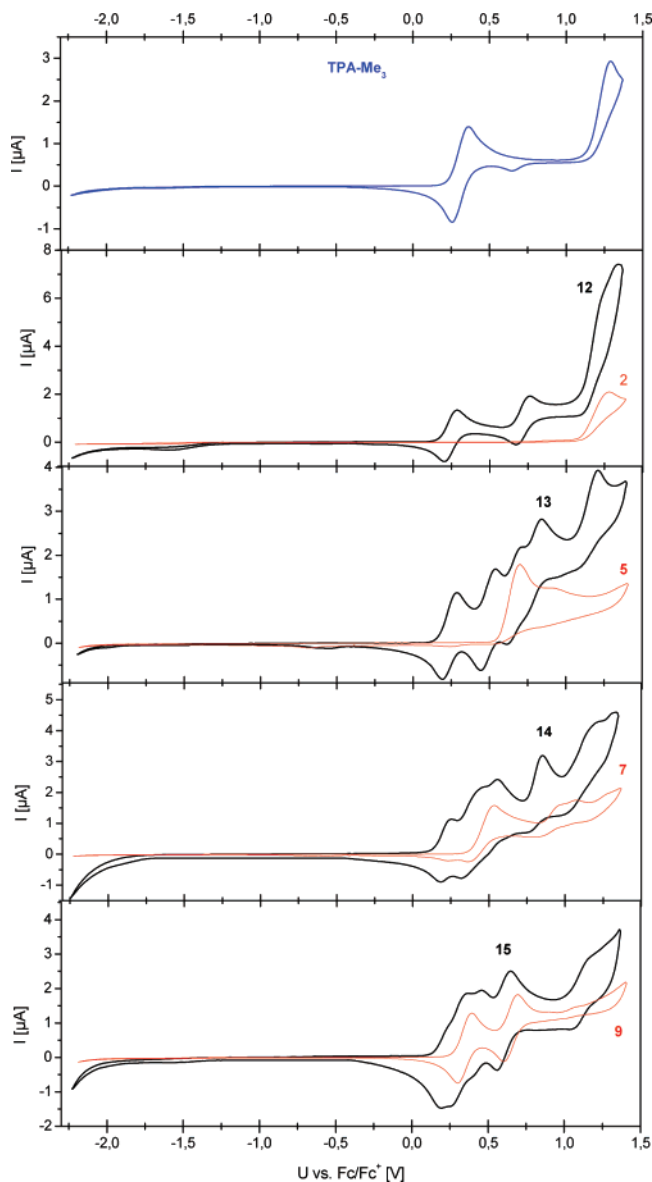


Figure 3. Cyclic voltammograms of the oligothieryl-triphenylamines **11–15** (black) in comparison with **TPA-Me₃** (blue) and the corresponding parent oligothiophenes **2**, **5**, **7**, and **9** (red) in dichloromethane/*n*Bu₄NPF₆ (0.1 M) vs Fc/Fc⁺ at 100 mV/s.

yields with values around 0.2, whereas our star-shaped systems exhibit quantum yields as high as 0.65 and for the largest systems with the smallest influence of the TPA core still values in the range of 0.35.

In summary, linear systems consisting of oligothiophenes attached to a triphenylamine also show a significant redshift reported here, which can be achieved by attaching oligothiophenes to triphenylamines units. However, not all optical properties are enhanced in this manner, and hence it seems to be important to create a large fully π -conjugated system for maximizing quantum yields and overall absorptivity.³¹

Electrochemical Properties

For comparison of the electrochemical properties, **TPA-Me₃** has been chosen as the triphenylamine reference because

Table 3. Electrochemical Properties of the Oligothieryl-triphenylamines 12–15 in Comparison with the Parent Oligothiophenes 2, 5, 7, 9, and TPA-Me₃

compound	E°_{ox1} [V] ^a	E°_{ox2} [V] ^a	E°_{ox3} [V] ^a	E°_{ox4} [V] ^a	E°_{ox5} [V] ^a
TPA-Me₃	0.34	1.28 ^b			
Me-1T (2)	1.25 ^b				
Me-2T (5)	0.67 ^b				
Me-3T (7)	0.45	0.91			
Me-4T (9)	0.35	0.65			
TPA-1T₃ (12)	0.25	0.72	1.19 ^b		
TPA-2T₃ (13)	0.23	0.49	0.66	0.79	1.17 ^b
TPA-3T₃ (14)	0.22	0.38	0.51	0.81	1.16 ^b
TPA-4T₃ (15)	0.21	0.30	0.42	0.60	1.13 ^b

^a In dichloromethane/*n*Bu₄NPF₆ (0.1 M) vs Fc/Fc⁺ at 100 mV/s.
^b Irreversible redox process, E° determined at $I^{\circ} = 0.855 \times I_p$.³²

it shows a fully reversible first oxidation in contrast to pristine triphenylamine (Figure 3). However, this process is considerably shifted to a potential of $E^{\circ}_{\text{ox1}} = 0.34$ V with respect to that of pure triphenylamine ($E^{\circ}_{\text{ox1}} = 0.53$ V)¹⁷ as a consequence of the incorporation of the terminal methyl groups, which tend to stabilize the formed radical cation. As a further dissimilarity, **TPA-Me₃** exhibits a second irreversible oxidation at $E^{\circ}_{\text{ox1}} = 1.28$ V.

In the series of methylated oligothiophenes, the first oxidation potential is progressively shifted to more negative values with increasing size of the conjugated backbone and in addition becomes more and more reversible. While for **Me-1T** the first oxidation process is completely irreversible at $E^{\circ}_{\text{ox1}} = 1.28$ V, quaterthiophene **9** show a fully reversible oxidation at $E^{\circ}_{\text{ox1}} = 0.35$ V. Moreover, for the two longest homologues **7** and **9**, a second oxidation step arises at $E^{\circ}_{\text{ox2}} = 0.91$ V and $E^{\circ}_{\text{ox2}} = 0.65$ V, respectively, which is quasi-reversible in the case of terthiophene **7** and reversible for quaterthiophene **9**. This tendency is due to the fact that radical cations are better stabilized on larger conjugated systems and, in this respect, the electrochemical properties are comparable to a series of homologous non-functionalized oligothiophenes.^{24,25} However, in the latter case due to the absence of the corresponding α -methyl groups, the resulting radical cations are less stabilized, and consequently significant higher first oxidation potentials are observed ($E^{\circ}_{\text{ox1}}(2T) = 0.83$ V and $E^{\circ}_{\text{ox1}}(4T) = 0.43$ V).^{24,25}

In the series of the oligothieryl-triphenylamines **12–15**, the same general electrochemical trends can be observed as compared to the parent oligothiophenes **2**, **5**, **7**, and **9** (Table 3). Accordingly, the first oxidation potential is gradually negatively shifted with enlargement of the conjugated system. However, this course is much smoother as these potentials differ only in the range from $E^{\circ}_{\text{ox1}} = 0.25$ V to $E^{\circ}_{\text{ox1}} = 0.21$ V, whereas for the parent oligothiophenes this potential lies between $E^{\circ}_{\text{ox1}} = 1.25$ V and $E^{\circ}_{\text{ox1}} = 0.35$ V. As compared to the first oxidation potential of either the reference **TPA-Me₃** or the parent oligothiophenes **2**, **5**, **7**, and **9**, the significantly lower E°_{ox1} of the oligothieryl-triphenylamines **12–15** alludes to the fact that the corresponding radical cations are delocalized over a conjugated system larger than that of either pure triphenylamine or the corresponding non-functionalized oligothiophenes. For the second oxidation process of the oligothieryl-triphenylamines, a clear progressive shift from $E^{\circ}_{\text{ox2}} = 0.72$ V in the case of **TPA-1T₃** to $E^{\circ}_{\text{ox2}} = 0.30$ V for **TPA-4T₃** can be found, being comparable

(31) Optical properties determined in the solid state and the characterization of corresponding light emitting devices are currently under investigation and will be published in a forthcoming paper.

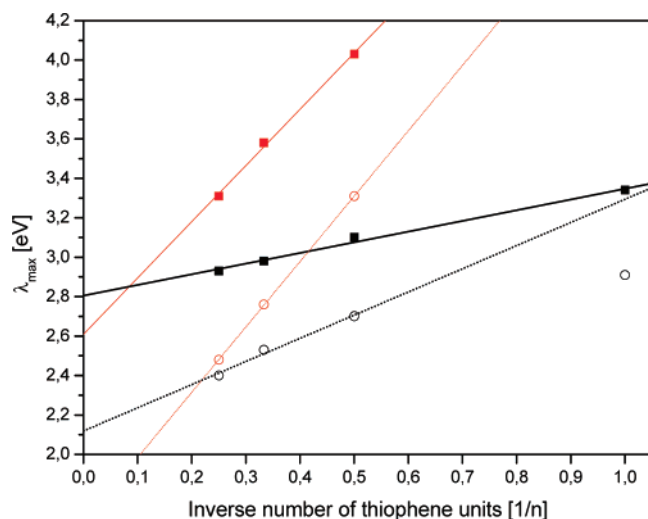


Figure 4. $1/n$ -Correlation of the optical properties of the oligothiophenyl-triphenylamines **12–15** (black) and the parent oligothiophenes **5**, **7**, and **9** (red). Here, the maximum absorption (■) and emission (○) energies are correlated versus the inverse number of oligothiophene units.

to the series of the parent oligothiophenes, whereas in contrast to the latter series, with elongation of the oligothiophenyl-triphenylamines almost no increase in the number of redox waves is observed. While the smallest representative **TPA-1T₃** only shows three oxidation processes, of which two are reversible and one being irreversible, all of the other oligothiophenyl-triphenylamines **13–15** exhibit four reversible and one irreversible ($E_{\text{ox}5}^{\circ} \approx \sim 1.15$ V) oxidation step.

A comparison of the electrochemical behavior of **TPA-3T₃** to a linear terthiophene with an adjacent triphenylamine ($E_{\text{ox}1}^{\circ} = 0.29$ V; $E_{\text{ox}2}^{\circ} = 0.47$ V) as it has been described in the literature earlier³⁰ reveals that the star-shaped system **TPA-3T₃** exhibits significantly reduced oxidation potentials and a larger number of oxidation steps due to the larger conjugated system.

In conclusion, the electrochemical properties of the oligothiophenyl-triphenylamines **12–15** show greater deviations from those of the corresponding parent linear oligothiophenes than expected at first instance. Consequently, the assumption of completely delocalized conjugated systems, being in accordance with the optical properties, can be confirmed. If the donor system would be fully electronically decoupled into a triphenylamine core and three discrete surrounding (oligo-)thiophene subunits, a one-electron oxidation step of the triphenylamine core and several additional oxidation waves similar to those of the parent linear oligothiophenes would be observed as three-electron processes.

Structure–Property Relationships

To establish clear structure–property relationships, the optical and electrochemical properties are correlated to the inverse number of oligothiophene units (Figures 4 and 5). In this respect, the methylated-oligothiophenes **2**, **5**, **7**, and **9** as well as the oligothiophenyl-triphenylamines **12–15** exhibit perfect $1/n$ -correlations. Therefore, the corresponding properties of hypothetical higher homologous can be estimated;³³

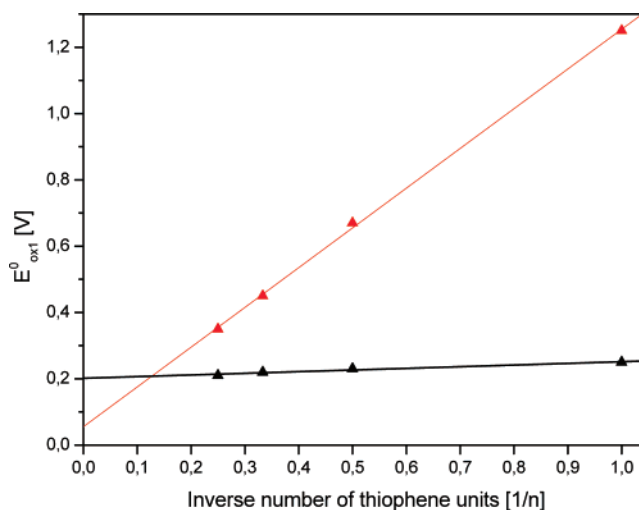


Figure 5. $1/n$ -Correlation of the electrochemical properties of the oligothiophenyl-triphenylamines **12–15** (black) and the parent oligothiophenes **2**, **5**, **7**, and **9** (red). Here, the first oxidation potentials (▲) are correlated versus the inverse number of oligothiophene units.

however, it has to be considered that beyond a specific length of the conjugated system, these properties will deviate from linearity and approach saturation.

According to the correlated maximum absorption energies (Figure 4), the oligothiophenyl-triphenylamines exhibit a less pronounced dependence on the inverse chain length as compared to the corresponding parent oligothiophenes, concluding that the triphenylamine core has a predominant electronic impact on the overall conjugated hybrid systems rather than the surrounding oligothiophenes on their own. A similar effect can be observed for the regression of the maximum emission energies (Figure 4); however, in contrast to the absorption properties the oligothiophene units have a significant stronger influence on the emission properties of the hybrid systems **12–15** as the $1/n$ -correlation is much steeper. To draw a conclusion, the electronic influences of the corresponding electrophoric subunits are unequally distributed in the ground and in the excited state.

In the case of the electrochemical properties, the $1/n$ -correlation (Figure 5) of the first oxidation potential reveals strong discrepancies between the oligothiophenyl-triphenylamines **12–15** and the parent oligothiophenes **2**, **5**, **7**, and **9** also. While a strong dependence on the inverse chain length can be found for the oligothiophenes, almost no influence of the oligothiophene chain length is observable for the oligothiophenyl-triphenylamines. This can be explained by the fact that the radical cation located on an oligothiophene backbone is more stable the longer the conjugation length is, whereas in the case of all hybrid systems the corresponding radical cation predominantly resides on the central triphenylamine and just three adjacent monothiophene units, even if there are further thiophene units in vicinity. Moreover, it can be assumed that the next higher valent radical cations are mainly located on one of the three oligothiophene arms, respectively. Because of the mutual electronic influence mediated by the conjugated triphenylamine core, the overall hybrid system becomes less electron-rich when an additional

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(33) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomeric Approach*; Wiley-VCH: Weinheim, 1998.

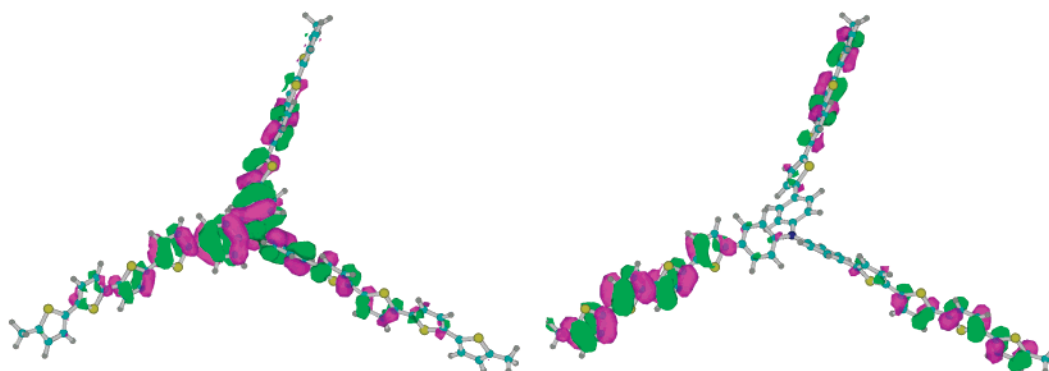


Figure 6. Electron density distributions of **TPA-4T₃** (hexyl-side chains are omitted for clarity) based on semiempirical calculations (AM1). In the electronic ground state (left), the electron density of the HOMO level is predominantly located on the core of the hybrid system, whereas in the dipositive state (right) the HOMO is moved toward the outer oligothiophene units.

charge is generated on one of the surrounding oligothiophene units, impeding the next oxidation process, which in turn leads to a corresponding positively shifted oxidation potential. In this respect, the fifth irreversible oxidation process of the highest oligothiophenyl-triphenylamines **13–15** seems to be more comparable to the second oxidation step of the reference **TPA-Me₃**, concluding that the fifth positive charge is mainly located on the central triphenylamine core. Therefore, one has to imagine that in the case of **13–15** the overall conjugated system is large enough to accommodate five charges, and that in this quintuply charged state three radical cations are mainly located on one of the three oligothiophene units, respectively, and one dication resides mainly on the triphenylamine core.

The fact that the radical cation, being generated during the first oxidation process, predominantly dwells on the central triphenylamine and the first units of three adjacent oligothiophene moieties, respectively, can be supported by semiempirical calculations. The electron density distribution of the **TPA-4T₃**-HOMO in the ground state (Figure 6) illustrates that the electron density is mainly located on the triphenylamine core and fades out toward the end of neighboring oligothiophene units. Accordingly, only the thiophene units next to triphenylamine significantly contribute to the HOMO, whereas the other thiophene units are almost excluded. As a result, the first oxidation processes of the oligothiophenyl-triphenylamines **12–15**, which originate from the HOMO level of the ground state, are characterized by comparable potentials with a small decline toward the larger homologues. In contrast, the third oxidation step of these hybrid systems, which originates from the HOMO level of the corresponding dipositive state (Figure 6), is primarily influenced by the electronic properties of the adjacent oligothiophene units, and, therefore, a considerable dependence of $E^{\circ}_{\text{ox}3}$ on the size of the conjugated hybrid systems is immanent.

Conclusions

Based on an effective, iterative, palladium-catalyzed cross-coupling and bromination protocol, a homologous series of α -methyl-substituted head-to-tail coupled oligo(3-hexylthiophene)s up to a quaterthiophene have been obtained in good yields. The corresponding α' -brominated oligothiophenes

were utilized for the efficient synthesis of star-shaped oligothiophenyl-triphenylamines, consisting of three oligothiophene units attached to a triphenylamine core. These novel hybrid-systems exhibit fully donor-type conjugated systems and, in this respect, are characterized by intriguing optical and electrochemical properties. In particular, they show intense absorptivities and unexpected high fluorescence quantum yields for thiophene-based materials, which reach values of up to 65%, making these materials suitable for optoelectronic applications. In this respect, these star-shaped oligothiophenyl-triphenylamines show strongly amplified electronic properties as compared to their linear analogues as a result of the enlarged conjugated systems. Furthermore, to gain these enhanced properties it is of great importance to incorporate the electron-donating triphenylamine as a central core. In addition and based on the data set obtained from the optical and electrochemical measurements, structure–property relationships have been established, which give further information about the nature of these hybrid systems and elucidate differences in the corresponding properties as compared to those of the parent oligothiophenes.

Experimental Section

General Procedures. ¹H NMR spectra were recorded in CDCl₃ on a Bruker AMX 400 at 400 MHz. ¹³C NMR spectra were recorded in CDCl₃ on a Bruker AMX 400 at 100 MHz. Chemical shifts are denoted in δ unit (ppm) and were referenced to internal tetramethylsilane (0.0 ppm). The splitting patterns are designated as follows: s (singlet), d (doublet), t (triplet), quin (quintet), and m (multiplet), and the assignments are Ph (phenyl) and TPA (triphenylamine) for ¹H NMR. Mass spectra were recorded with a Varian Saturn 2000 GC-MS and with a MALDI-TOF MS Bruker Reflex 2 (dithranol as the matrix). Elemental analyses were performed on an Elementar Vario EL. Gas chromatography was carried out using a Varian CP-3800 gas chromatograph. HPCL analyses were performed on a Shimadzu SCL-10A equipped with a SPD-M10A photodiode array detector and a SC-10A solvent delivery system using a LiChrospher column (Silica 60, 5 μ m, Merck). Thin-layer chromatography was carried out on silica gel 60 F₂₅₄ aluminum plates (Merck). Developed plates were dried and examined under a UV lamp. Preparative column chromatography was carried out on glass columns of different sizes packed with silica gel Merck 60 (40–63 μ m). UV–vis spectra were taken on a Perkin-Elmer Lambda 19 in 1 cm cuvettes. Fluorescence spectra were measured with a Perkin-Elmer LS 55 in 1 cm cuvettes. Fluorescence quantum

yields were determined with respect to 9,10-diphenylanthracene ($\Phi = 0.9$ in cyclohexane²⁸) and anthracene ($\Phi = 0.36$ in cyclohexane²⁹). Cyclic voltammetry experiments were performed with a computer-controlled EG&G PAR 273 potentiostat in a three-electrode single-compartment cell (5 mL). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of $A = 0.785 \text{ mm}^2$, which was polished down to $0.5 \mu\text{m}$ with Buehler polishing paste prior to use to obtain reproducible surfaces. The counter electrode consisted of a platinum wire, and the reference electrode was an Ag/AgCl secondary electrode. All potentials were internally referenced to the ferrocene/ferricenium couple. For the measurements, concentrations of 10^{-3} mol/L of the electroactive species were used in freshly distilled and deaired dichloromethane (Lichrosolv, Merck) and 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{Bu}_4\text{NPF}_6$, Fluka), which was twice recrystallized from ethanol and dried under vacuum prior to use. Solvents and reagents were purified and dried by usual methods prior to use and typically used under inert gas atmosphere. The following starting materials were purchased and used without further purification: *n*-Butyllithium (*n*-BuLi, Merck) was a 1.6 M solution in *n*-hexane, *N*-bromosuccinimide (NBS, Merck), methyl trifluoromethanesulfonate (Aldrich), and tripotassium phosphate (Fluka). $[\text{HP}(t\text{-Bu})_3\text{BF}_4]$,²⁰ $\text{Pd}_2(\text{dba})_3$,³⁴ and tri-*p*-tolyl-amine **TPA-Me**₃²² were prepared according to literature procedures.

Synthesis. 3-Hexyl-2-methyl-thiophene (2). To thiophene **1** (5.19 g, 21 mmol) in THF (21 mL) at -80°C was added *n*-BuLi (13.2 mL, 21 mmol). After the mixture was stirred at -80°C for 15 min, methyl trifluoromethanesulfonate (3.6 g, 22 mmol) was added and the solution was allowed to warm to room temperature. Next, 1 mL of a 1 molar sodium hydroxide solution was added to deactivate the excessive methyl triflate before the solvent was completely removed by rotary evaporation. The remaining residue was suspended in 50 mL of *n*-hexane, and the resulting suspension was poured into 200 mL of water. The water phase was extracted with *n*-hexane (three times 50 mL), and, subsequently, the combined organic phases were washed with water and were dried over sodium sulfate. Next, the solvent was removed by rotary evaporation, and the crude product was distilled in vacuo to yield methylated thiophene **2** (2.89 g, 76%) as a colorless liquid. bp: 72°C ($1.8 \times 10^{-1} \text{ mbar}$). ¹H NMR (CDCl_3): $\delta = 6.97$ (d, $J = 5.2 \text{ Hz}$, 1H, 5-*H*), 6.80 (d, $J = 5.2 \text{ Hz}$, 1H, 4-*H*), 2.50 (t, $J = 7.6 \text{ Hz}$, 2H, α -*H*), 2.35 (s, 3H, T- CH_3), 1.55 (quin, $J = 7.5 \text{ Hz}$, 2H, β -*H*), 1.34–1.26 (m, 6H, $-\text{CH}_2-$), 0.88 (t, $J = 6.8 \text{ Hz}$, 3H, $-\text{CH}_3$). ¹³C NMR (CDCl_3): $\delta = 138.34, 128.86, 120.66, 100.01, 31.75, 30.51, 29.12, 28.22, 22.64, 14.09, 12.87$. MS (EI): m/z [M^+] = 182. Anal. Calcd for $\text{C}_{11}\text{H}_{18}\text{S}$: C, 72.46; H, 9.95; S, 17.59. Found: C, 72.41; H, 9.90; S, 17.70.

5-Bromo-3-hexyl-2-methyl-thiophene (3). Thiophene **2** (2.60 g, 14.3 mmol) was dissolved in 14 mL of dry DMF and was cooled down to 0°C . In the absence of light, a NBS solution (2.55 g, 14.3 mmol dissolved in 5 mL of dry DMF) was added, and the reaction mixture was stirred for another hour at 0°C . Next, it was poured into 100 mL of a 1 molar potassium hydroxide solution. The water phase was extracted with *n*-hexane (three times 20 mL), and the combined organic phases were washed with a 1 molar potassium hydroxide solution (100 mL). After the organic phase was dried over sodium sulfate, the solvent was removed by rotary evaporation and the crude product was distilled in vacuo to yield brominated thiophene **3** (3.00 g, 82%) as a colorless liquid. bp: 101°C ($1.3 \times 10^{-1} \text{ mbar}$). ¹H NMR (CDCl_3): $\delta = 6.73$ (s, 1H, 4-*H*), 2.43 (t, $J = 7.6 \text{ Hz}$, 2H, α -*H*), 2.27 (s, 3H, T- CH_3), 1.52 (quin, $J = 7.5 \text{ Hz}$, 2H, β -*H*), 1.35–1.23 (m, 6H, $-\text{CH}_2-$), 0.88 (t, $J = 6.8 \text{ Hz}$, 3H,

$-\text{CH}_3$). ¹³C NMR (CDCl_3): $\delta = 139.10, 134.05, 131.47, 106.63, 31.69, 30.35, 28.98, 22.61, 14.08, 12.89$. MS (EI): m/z [M^+] = 260. Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{BrS}$: C, 50.58; H, 6.65; S, 12.27. Found: C, 50.65; H, 6.71; S, 12.25.

4,3'-Dihexyl-5-methyl-2,2'-bithiophene (5). A solution of bromothiophene **3** (2.62 g, 10 mmol) and boronic ester **4** (3.23 g, 11 mmol) in 20 mL of DME was carefully degassed prior to the addition of 16.5 mL (33 mmol) of a 2 molar tripotassium phosphate solution. The resulting emulsion was degassed, and the catalyst system (Pd_2dba_3 [51.8 mg, 0.05 mmol], $[\text{HP}(t\text{-Bu})_3\text{BF}_4]$ [29.2 mg, 0.1 mmol]) was added. Next, the mixture was degassed and was stirred at room temperature for 3 h. It was then poured into water (100 mL) and was extracted with *n*-hexane (three times 20 mL). The organic phase was dried with magnesium sulfate, and the solvent was taken off before the crude product was distilled in vacuo to yield bithiophene **5** (3.10 g, 89%) as a pale yellow, viscous liquid. bp: 147°C ($1.1 \times 10^{-2} \text{ mbar}$). ¹H NMR (CDCl_3): $\delta = 7.11$ (d, $J = 5.2 \text{ Hz}$, 1H, 5'-*H*), 6.90 (d, $J = 5.2 \text{ Hz}$, 1H, 4'-*H*), 6.81 (s, 1H, 3-*H*), 2.72 (t, $J = 7.8 \text{ Hz}$, 2H, α' -*H*), 2.49 (t, $J = 7.7 \text{ Hz}$, 2H, α -*H*), 2.34 (s, 3H, T- CH_3), 1.65–1.55 (m, 4H, β, β' -*H*), 1.42–1.28 (m, 12H, $-\text{CH}_2-$), 0.92–0.85 (m, 6H, $-\text{CH}_3$). ¹³C NMR (CDCl_3): $\delta = 138.82, 138.73, 132.70, 131.31, 131.24, 129.82, 127.82, 122.90, 31.72, 31.67, 30.70, 40.41, 29.22, 29.15, 29.09, 28.23, 22.63, 22.61, 14.07, 14.06, 12.86$. MS (EI): m/z [M^+] = 348. Anal. Calcd for $\text{C}_{21}\text{H}_{32}\text{S}_2$: C, 72.35; H, 9.25; S, 18.39. Found: C, 72.41; H, 9.37; S, 18.23.

5-Bromo-3,4'-dihexyl-5'-methyl-2,2'-bithiophene (6). Bithiophene **5** (2.09 g, 6 mmol) was dissolved in 6 mL of dry DMF and was cooled down to 0°C . In the absence of light, a NBS solution (1.07 g, 6 mmol dissolved in 3 mL of dry DMF) was added, and the reaction mixture was stirred for another hour at 0°C . Next, it was poured into 50 mL of a 1 molar potassium hydroxide solution. The water phase was extracted with *n*-hexane (three times 20 mL), and the combined organic phases were washed with a 1 molar potassium hydroxide solution (50 mL). After the organic phase was dried over sodium sulfate, the solvent was removed by rotary evaporation, and the crude product has been filtrated over a short column (silica/*n*-hexane) to yield brominated bithiophene **6** (2.50 g, 97%) as a pale yellow, viscous liquid. ¹H NMR (CDCl_3): $\delta = 6.84$ (s, 1H, 3'-*H*), 6.75 (s, 1H, 4-*H*), 2.65 (t, $J = 7.8 \text{ Hz}$, 2H, α' -*H*), 2.48 (t, $J = 7.7 \text{ Hz}$, 2H, α -*H*), 2.34 (s, 3H, T- CH_3), 1.61–1.50 (m, 4H, β, β' -*H*), 1.38–1.25 (m, 12H, $-\text{CH}_2-$), 0.91–0.85 (m, 6H, $-\text{CH}_3$). ¹³C NMR (CDCl_3): $\delta = 139.45, 138.87, 133.39, 132.82, 132.46, 130.02, 128.24, 109.47, 31.72, 31.63, 30.57, 30.39, 29.10, 29.08, 28.20, 22.63, 22.59, 14.08, 14.06, 12.89$. MS (EI): m/z [M^+] = 427. Anal. Calcd for $\text{C}_{21}\text{H}_{31}\text{BrS}_2$: C, 59.00; H, 7.31; S, 15.00. Found: C, 59.21; H, 7.42; S, 14.79.

4,3',3''-Trihexyl-5-methyl-2,2';5',2''-terthiophene (7). A solution of bromo-bithiophene **6** (1.28 g, 3 mmol) and boronic ester **4** (0.97 g, 3.3 mmol) in 9 mL of DME was carefully degassed prior to the addition of 5 mL (10 mmol) of a 2 molar tripotassium phosphate solution. The resulting emulsion was degassed, and the catalyst system (Pd_2dba_3 [15.5 mg, 0.015 mmol], $[\text{HP}(t\text{-Bu})_3\text{BF}_4]$ [8.8 mg, 0.03 mmol]) was added. Next, the mixture was degassed and was stirred at room temperature for 3 h. It was then poured into water (50 mL) and was extracted with *n*-hexane (three times 10 mL). The organic phase was dried with magnesium sulfate, and the solvent was taken off before the crude product was purified by flash column chromatography (silica/*n*-hexane) to yield terthiophene **7** (1.30 g, 84%) as a yellow oil. ¹H NMR (CDCl_3): $\delta = 7.14$ (d, $J = 5.2 \text{ Hz}$, 1H, 5''-*H*), 6.91 (d, $J = 5.2 \text{ Hz}$, 1H, 4''-*H*), 6.90 (s, 1H, 4'-*H*), 6.84 (s, 1H, 3-*H*), 2.77 (t, $J = 7.9 \text{ Hz}$, 2H, α'' -*H*), 2.72 (t, $J = 7.9 \text{ Hz}$, 2H, α' -*H*), 2.47 (t, $J = 7.7 \text{ Hz}$, 2H, α -*H*), 2.36 (s, 3H, T- CH_3), 1.68–1.60 (m, 4H, β', β'' -*H*), 1.54 (quin, $J = 7.6,$

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Hz, 2H, β -H), 1.45–1.25 (m, 18H, $-CH_2-$), 0.91–0.87 (m, 9H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 139.36, 138.90, 138.83, 133.30, 132.84, 131.15, 131.00, 130.71, 130.03, 128.59, 127.64, 31.74, 31.68, 30.67, 30.59, 30.44, 29.25, 22.23, 29.11, 28.23, 22.64, 14.11, 12.03. MS (EI): m/z [M^+] = 515. Anal. Calcd for $C_{31}H_{46}S_3$: C, 72.31; H, 9.00; S, 18.68. Found: C, 72.18; H, 8.91; S, 18.74.

5-Bromo-3,4,4'-trihexyl-5''-methyl-2,2';5',2''-terthiophene (8). Terthiophene **7** (773 mg, 1.5 mmol) was dissolved in 7 mL of dry DMF and was cooled down to 0 °C. In the absence of light, a NBS solution (294 mg, 1.65 mmol dissolved in 1 mL of dry DMF) was added dropwise, and the reaction mixture was stirred for another hour at 0 °C. Next, it was poured into 30 mL of a 1 molar potassium hydroxide solution. The water phase was extracted with *n*-hexane (three times 10 mL), and the combined organic phases were washed with a 1 molar potassium hydroxide solution (50 mL). After the organic phase was dried over sodium sulfate, the solvent was removed by rotary evaporation and the crude product was purified by flash column chromatography (silica/*n*-hexane) to yield brominated terthiophene **8** (770 mg, 86%) as a yellow oil. 1H NMR ($CDCl_3$): δ = 6.86 (s, 1H, 4''-H), 6.84 (s, 1H, 4'-H), 6.83 (s, 1H, 3-H), 2.71 (t, J = 7.8 Hz, 2H, α' -H), 2.70 (t, J = 7.8 Hz, 2H, α -H), 2.49 (t, J = 7.7 Hz, 2H, α -H), 2.36 (s, 3H, T- CH_3), 1.67–1.55 (m, 6H, β - β'' -H), 1.40–1.28 (m, 18H, $-CH_2-$), 0.90–0.87 (m, 9H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 138.90, 133.12, 132.64, 132.25, 131.92, 131.74, 130.72, 128.97, 127.82, 109.98, 31.73, 31.67, 31.62, 30.55, 30.43, 29.23, 29.10, 28.23, 22.64, 14.10, 12.94. MS (EI): m/z [M^+] = 593. Anal. Calcd for $C_{31}H_{45}BrS_3$: C, 62.71; H, 7.64; S, 16.20. Found: C, 62.56; H, 7.45; S, 16.33.

4,3',3'',3'''-Tetrahexyl-5-methyl-2,2';5',2'';5'',2'''-quaterthiophene (9). A solution of bromo-terthiophene **8** (515 mg, 1 mmol) and boronic ester **4** (323 mg, 1.1 mmol) in 3 mL of DME was carefully degassed prior to the addition of 1.6 mL (3.2 mmol) of a 2 molar tripotassium phosphate solution. The resulting emulsion was degassed, and the catalyst system (Pd_2dba_3 [5.2 mg, 5 μ mol], $[HP(t-Bu)_3]BF_4$ [2.9 mg, 10 μ mol]) was added. Next, the mixture was degassed and was stirred at room temperature for 3 h. It was then poured into water (20 mL) and was extracted with *n*-hexane (three times 10 mL). The organic phase was dried with magnesium sulfate, and the solvent was taken off before the crude product was purified by column chromatography (silica/*n*-hexane) to yield quaterthiophene **9** (570 mg, 85%) as an orange oil. 1H NMR ($CDCl_3$): δ = 7.14 (d, J = 5.2 Hz, 1H, 5'''-H), 6.93 (s, 1H, 4'-H), 6.92 (s, 1H, 4''-H), 6.91 (d, J = 5.2 Hz, 1H, 4'''-H), 6.84 (s, 1H, 3-H), 2.80–2.71 (m, 6H, α' - α'' - CH_2), 2.50 (t, J = 7.7 Hz, 2H, α - CH_2), 2.36 (s, 3H, T- CH_3), 1.70–1.55 (m, 8H, β - β''' - CH_2), 1.45–1.25 (m, 24H, $-CH_2-$), 0.92–0.87 (m, 12H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 139.57, 139.56, 139.01, 138.88, 133.86, 133.04, 132.92, 131.28, 131.04, 130.65, 130.63, 130.08, 128.75, 128.45, 127.69, 123.51, 31.75, 31.70, 30.64, 30.59, 30.54, 30.44, 29.41, 29.31, 29.26, 29.25, 19.23, 19.12, 28.26, 22.64, 14.10, 12.93. MS (MALDI-TOF): m/z [$M + H^+$] = 681. Anal. Calcd for $C_{41}H_{60}S_4$: C, 72.29; H, 8.88; S, 18.83. Found: C, 72.36; H, 8.99; S, 18.73.

5-Bromo-3,4,4',4'''-tetrahexyl-5''''-methyl-2,2';5',2'';5'',2'''-quaterthiophene (10). Quaterthiophene **9** (370 mg, 0.54 mmol) was dissolved in 2 mL of dry chloroform and was cooled to 0 °C. In the absence of light, a NBS solution (105 mg, 0.59 mmol dissolved in 1 mL of dry DMF) was added dropwise, and the reaction mixture was stirred for another hour at 0 °C. Next, the chloroform was removed by rotary evaporation, and the residual solution was poured into 30 mL of a 1 molar potassium hydroxide solution. The water phase was extracted with *n*-hexane (three times 10 mL), and the combined organic phases were washed with water (three times 50 mL). After the organic phase was dried over sodium

sulfate, the solvent was removed by rotary evaporation and the crude product was purified by flash column chromatography (silica/*n*-hexane) to yield brominated quaterthiophene **10** (320 mg, 78%) as an orange oil. 1H NMR ($CDCl_3$): δ = 6.92 (s, 1H, 4'-H), 6.88 (s, 1H, 4''-H), 6.86 (s, 1H, 4'''-H), 6.85 (s, 1H, 3-H), 2.78–2.68 (m, 6H, α' - α''' - CH_2), 2.50 (t, J = 7.7 Hz, 2H, α - CH_2), 2.37 (s, 3H, T- CH_3), 1.70–1.53 (m, 8H, β - β''' - CH_2), 1.45–1.25 (m, 24H, $-CH_2-$), 0.93–0.85 (m, 12H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 140.06, 139.53, 138.98, 138.88, 132.98, 132.68, 132.66, 132.37, 132.12, 131.47, 131.16, 130.90, 129.07, 128.57, 127.69, 110.15, 31.74, 31.69, 31.67, 31.63, 31.60, 30.59, 30.52, 30.45, 29.34, 29.26, 29.22, 29.11, 28.24, 22.65, 22.61, 14.11, 12.93. MS (MALDI-TOF): m/z [$M + H^+$] = 758. Anal. Calcd for $C_{41}H_{59}BrS_4$: C, 64.79; H, 7.82; S, 16.87. Found: C, 64.95; H, 8.00; S, 16.95.

Tris-[4-(4-hexyl-5-methyl-thien-2-yl)-phenyl]-amine [TPA-T₃] (12). A solution of bromo-bithiophene **3** (87 mg, 0.33 mmol) and boronic ester **11** (62 mg, 0.1 mmol) in 3 mL of DME was carefully degassed prior to the addition of 0.45 mL (0.9 mmol) of a 2 molar tripotassium phosphate solution. The resulting emulsion was degassed, and the catalyst system (Pd_2dba_3 [1.6 mg, 1.5 μ mol], $[HP(t-Bu)_3]BF_4$ [0.9 mg, 3 μ mol]) was added. Next, the mixture was degassed and was stirred at room temperature for 6 h. It was then poured into water (30 mL) and was extracted with dichloromethane (three times 10 mL). The organic phase was dried with magnesium sulfate, and the solvent was taken off before the crude product was purified by column chromatography (silica/*n*-hexane:dichloromethane [10:1]) to yield TPA-T₃ (**12**) (55 mg, 70%) as a yellow wax. 1H NMR ($CDCl_3$): δ = 7.42–7.40 (m, 6H, TPA-3H,5H), 7.07–7.05 (m, 6H, TPA-2H,6H), 6.95 (s, 3H, 3-H), 2.48 (t, J = 7.6 Hz, 6H, α -H), 2.35 (s, 9H, Th- CH_3), 1.56 (quin, J = 7.5, Hz 6H, β -H), 1.35–1.25 (m, 18H, $-CH_2-$), 0.89 (t, J = 6.7 Hz, 9H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 146.02, 139.43, 138.96, 131.68, 129.45, 126.12, 124.23, 31.76, 30.50, 29.10, 28.38, 22.65, 14.13, 13.06. MS (MALDI-TOF): m/z [$M + H^+$] = 786. Anal. Calcd for $C_{51}H_{63}NS_3$: C, 77.91; H, 8.08; N, 1.78. Found: C, 78.06; H, 8.12; N, 1.85.

Tris-[4-(3,4'-dihexyl-5'-methyl-2,2'-bithien-5-yl)-phenyl]-amine [TPA-T₂] (13). A solution of bromo-bithiophene **6** (141 mg, 0.33 mmol) and boronic ester **11** (62 mg, 0.1 mmol) in 3 mL of DME was carefully degassed prior to the addition of 0.45 mL (0.9 mmol) of a 2 molar tripotassium phosphate solution. The resulting emulsion was degassed, and the catalyst system (Pd_2dba_3 [1.6 mg, 1.5 μ mol], $[HP(t-Bu)_3]BF_4$ [0.9 mg, 3 μ mol]) was added. Next, the mixture was degassed and was stirred at room temperature for 6 h. Next, it was poured into water (30 mL) and was extracted with dichloromethane (three times 10 mL). The organic phase was dried with magnesium sulfate, and the solvent was taken off before the crude product was purified by column chromatography (silica/*n*-hexane:dichloromethane [10:1]) to yield TPA-T₂ (**13**) (95 mg, 74%) as an orange wax. 1H NMR ($CDCl_3$): δ = 7.48–7.44 (m, 6H, Ph-3H,5H), 7.11–7.08 (m, 6H, Ph-2H,6H), 7.05 (s, 3H, 3'-H), 6.85 (s, 3H, 4-H), 2.73 (t, J = 7.8 Hz, 6H, α' -H), 2.49 (t, J = 7.7 Hz, 6H, α -H), 2.35 (s, 9H, Th- CH_3), 1.66 (quin, J = 7.6 Hz, 6H, β' -H), 1.58 (quin, J = 7.6 Hz, 6H, β -H), 1.41–1.26 (m, 36H, $-CH_2-$), 0.91–0.87 (m, 18H, $-CH_3$). ^{13}C NMR ($CDCl_3$): δ = 146.32, 140.68, 139.68, 138.82, 132.65, 131.48, 130.37, 129.13, 127.51, 126.36, 125.37, 124.36, 31.75, 31.71, 30.62, 30.44, 29.48, 29.28, 29.12, 28.26, 22.65, 14.10, 12.90. MS (MALDI-TOF): m/z [$M + H^+$] = 1284. Anal. Calcd for $C_{81}H_{105}NS_6$: C, 75.70; H, 8.24; N, 1.09. Found: C, 75.86; H, 8.31; N, 1.13.

Tris-[4-(3,4,4'-trihexyl-5''-methyl-2,2';5',2''-terthien-5-yl)-phenyl]-amine [TPA-T₃] (14). A solution of bromo-terthiophene **8** (196 mg, 0.33 mmol) and boronic ester **11** (62 mg, 0.1 mmol) in 3 mL of DME was carefully degassed prior to the addition of 0.45

mL (0.9 mmol) of a 2 molar tripotassium phosphate solution. The resulting emulsion was degassed, and the catalyst system (Pd_2dba_3 [1.6 mg, 1.5 μmol], $[\text{HP}(t\text{-Bu})_3]\text{BF}_4$ [0.9 mg, 3 μmol]) was added. Next, the mixture was degassed and was stirred at room temperature for 6 h. It was then poured into water (30 mL) and was extracted with dichloromethane (three times 10 mL). The organic phase was dried with magnesium sulfate, and the solvent was taken off before the crude product was purified by column chromatography (silica/*n*-hexane:dichloromethane [10:1]) to yield **TPA-T3** (**14**) (125 mg, 70%) as an orange wax. ^1H NMR (CDCl_3): $\delta = 7.50\text{--}7.47$ (m, 6H, *Ph-3H,5H*), 7.14–7.11 (m, 6H, *Ph-2H,6H*), 7.08 (s, 3H, 3''-H), 6.95 (s, 3H, 3'-H), 6.85 (s, 3H, 4-H), 2.78 (t, $J = 7.9$ Hz, 6H, $\alpha''\text{-H}$), 2.73 (t, $J = 7.8$ Hz, 6H, $\alpha'\text{-H}$), 2.50 (t, $J = 7.7$ Hz, 6H, $\alpha\text{-H}$), 2.37 (s, 9H, *Th-CH3*), 1.72–1.64 (m, 12H, $\beta'\text{-}\beta''\text{-H}$), 1.65 (quin, $J = 7.6$ Hz, 6H, $\beta\text{-H}$), 1.41–1.31 (m, 54H, $-\text{CH}_2-$), 0.91–0.88 (m, 27H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): $\delta = 146.37, 141.07, 140.30, 138.98, 138.87, 133.38, 132.87, 131.04, 129.80, 129.00, 128.27, 127.63, 126.40, 125.54, 124.38, 31.74, 31.70, 30.60, 30.56, 30.45, 29.60, 29.28, 29.12, 28.66, 14.12, 12.94$. MS (MALDI-TOF): m/z [$\text{M} + \text{H}^+$] = 1782. Anal. Calcd for $\text{C}_{111}\text{H}_{147}\text{NS}_9$: C, 74.73; H, 8.31; N, 0.79. Found: C, 74.89; H, 8.43; N, 0.88.

Tris-[4-(3,4',4'',4'''-tetrahexyl-5'''-methyl-2,2';5',2'';5'',2'''-quaterthien-5-yl)-phenyl]-amine [TPA-T4₃] (15). A solution of bromo-quaterthiophene **10** (76 mg, 0.1 mmol) and boronic ester **11** (19 mg, 0.03 mmol) in 2 mL of DME was carefully degassed prior to the addition of 0.14 mL (0.28 mmol) of a 2 molar tripotassium phosphate solution. The resulting emulsion was

degassed, and the catalyst system (Pd_2dba_3 [0.9 mg, 0.9 μmol], $[\text{HP}(t\text{-Bu})_3]\text{BF}_4$ [0.5 mg, 1.8 μmol]) was added. Next, the mixture was degassed and was stirred at room temperature for 6 h. It was then poured into water (20 mL) and was extracted with dichloromethane (three times 10 mL). The organic phase was dried with magnesium sulfate, and the solvent was taken off before the crude product was purified by column chromatography (silica/*n*-hexane:dichloromethane [10:1]) to yield **TPA-T4₃** (**15**) (50 mg, 73%) as an orange wax. ^1H NMR (CDCl_3): $\delta = 7.52\text{--}7.48$ (m, 6H, *Ph-3H,5H*), 7.16–7.12 (m, 6H, *Ph-2H,6H*), 7.09 (s, 3H, 3'-H), 6.97 (s, 3H, 3''-H), 6.94 (s, 3H, 3'''-H), 6.85 (s, 1H, 4-H), 2.82–2.70 (m, 18H, $\alpha'\text{-}\alpha'''\text{-CH}_2$), 2.50 (t, $J = 7.7$ Hz, 6H, $\alpha\text{-CH}_2$), 2.37 (s, 9H, *Th-CH3*), 1.74–1.63 (m, 18H, $\beta'\text{-}\beta'''\text{-CH}_2$), 1.63–1.53 (m, 6H, $\beta\text{-CH}_2$), 1.46–1.26 (m, 72H, $-\text{CH}_2-$), 0.94–0.83 (m, 36H, $-\text{CH}_3$). ^{13}C NMR (CDCl_3): $\delta = 146.40, 141.22, 140.48, 139.60, 139.00, 138.88, 133.86, 133.00, 132.91, 131.24, 131.00, 130.46, 129.67, 128.98, 128.40, 127.66, 126.44, 125.60, 124.39, 31.70, 30.60, 30.54, 30.45, 29.63, 29.43, 29.27, 29.12, 28.25, 22.66, 14.12, 12.95$. MS (MALDI-TOF): m/z [$\text{M} + \text{H}^+$] = 2280. Anal. Calcd for $\text{C}_{141}\text{H}_{189}\text{NS}_{12}$: C, 74.19; H, 8.35; N, 0.61. Found: C, 74.37; H, 8.50; N, 0.56.

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