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Molecular Engineering of the Internal Charge Transfer in Thiophene−Triphenylamine Hybrid π-Conjugated Systems

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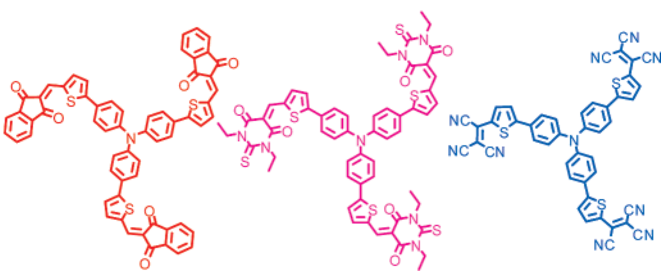

Introduction of electroaccepting groups at the periphery of triphenylamine-based derivatives leads to an internal charge-transfer band. Syntheses and spectroscopic, electrochemical, and theoretical studies of various derivatives which differ by the strength and the number of electroacceptor groups are presented. These various results show that the ICT band and the acceptor/donor abilities of derivatives can be finely tuned.

Introduction

Organic solar cells are subject to a considerable current interest motivated by the perspective of achieving large area, low-cost, lightweight, and flexible power sources.[1−7] Based on the intensive research effort invested in the optimization of multilayered and bulk heterojunctions solar cells during the past decade, power conversion efficiencies in the 4−5% range have been reached.[4,5]

Many materials used as donors in organic heterojunction solar cells are derived from linear π-conjugated systems such as acenes[6] or thiophene-based oligomers or polymers.[4,5,7−9] However, due to their one-dimensionality, these materials present anisotropic optical and charge transport properties[7−12] which pose specific problems for device fabrication. Thus, whereas a vertical orientation of the conjugated chains on the substrate improves the mobility of charge carriers in organic field-effect transistors,[10,11] such an orientation is detrimental for solar cells as it strongly reduces the absorption cross-section of the incident light as well as charge transport across the cell.[7−9]

Organic glasses derived from triphenylamine (TPA)-based compounds have been widely used as hole-transporting or electroluminescent material in OLEDs.[13] On the other hand, the amorphous character of these materials offers the possibility to develop organic semiconductors with isotropic optical and

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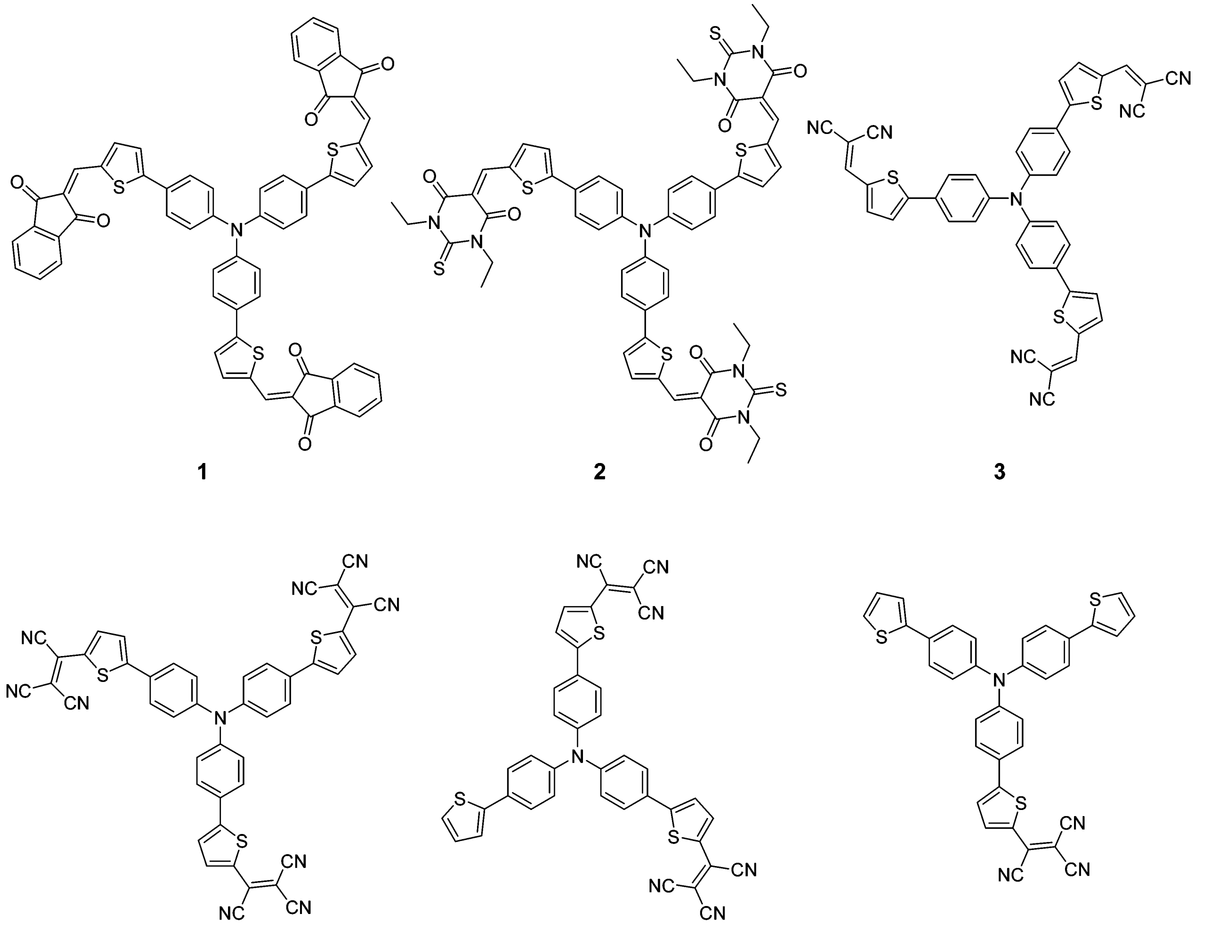
CHART 1



1 2 3

4 5 6

charge-transport properties. In the past few years, several groups have developed hybrid systems obtained by fixation of conjugated chains on a TPA core as active materials for the fabrication of OFETs or solar cells.[14] However, the absorption maximum of these materials in the 400−450 nm region is clearly insufficient to ensure an efficient harvesting of solar light. A possible solution to this problem consists in the covalent grafting of electron-acceptor groups on the hybrid TPA-conjugated system in order to increase the absorption in the visible region.[15] In this context, we have shown that the creation of an intramolecular charge transfer (ICT) by introduction of electron acceptors such as indan-1,3-dione or dicyanovinyl groups at the periphery of the hybrid TPA−thiophene systems leads to a considerable improvement of the performances of the resulting bilayer or bulk heterojunction solar cells thanks to the simultaneous increase of the open-circuit voltage and extension of the spectral response.[16]

We report here a further analysis of the structure−electronic property relationships in a new series of TPA-based compounds with ICT (**1**−**6**, Chart 1). The effects of different types of acceptor groups on the electronic properties of the system have been analyzed on compounds **1**−**4**, whereas the effect of the number of tricyanovinyl acceptor groups was analyzed on compounds **4**−**6** from both experimental and theoretical viewpoints.

Results and Discussion

Synthesis. Trialdehyde **7** was synthesized according to the already reported method.[16a] Compounds **1**−**3** have been synthesized by condensation of trialdehyde **7** with indandione, thiobarbituric acid, and malonodinitrile, respectively. The reaction carried out at room temperature in chloroform and in presence of triethylamine leads to derivatives **2** and **3** in good yields (Scheme 1). The compounds were precipitated by addition of methanol to the reaction mixture. The synthesis of **1** was much more complicated because of the polycondensation reactions of indandione,[17] and it was only after several purifications by chromatography that compound **1** could finally be isolated in ca. 1% yield.

Compounds **4**−**6** substituted by one, two, and three tricyanovinyl groups were synthesized following two routes.[18] The first involves the reaction of **8** with an excess of tetracyanoethylene at 60 °C in DMF. Successive formation of **6**, **5**, and **4**

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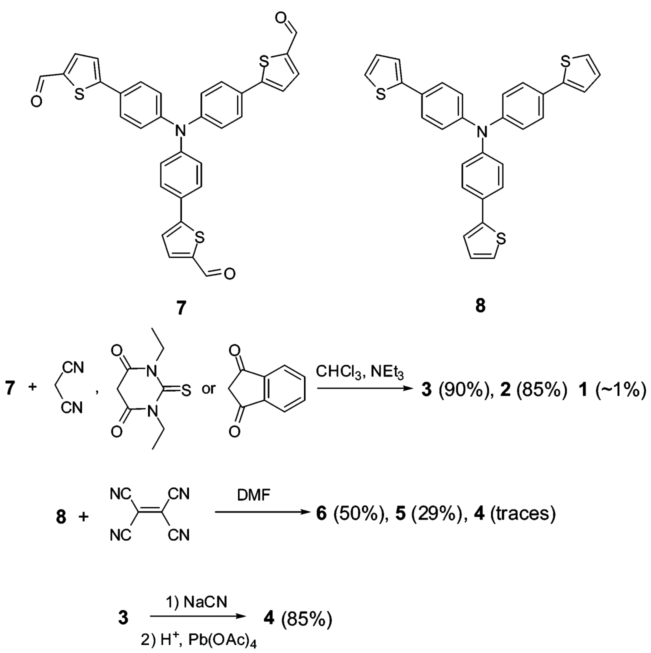
SCHEME 1. Synthetic Procedures for Synthesis of Derivatives 1−6



was followed by TLC. The best results were obtained after 1 week of reaction. Compounds **6** and **5** were isolated in 50 and 29% yield, respectively, while compound **4** was only observed in trace amounts. Increasing temperature, reaction time, and TCNE quantities only led to degradation. Compound **4** was finally obtained in 85% yield by treatment of compound **3** substituted by three dicyanovinyl groups, with successively NaCN and $Pb(OAc)_4$ in acidic conditions. All new compounds were isolated as glassy solids and satisfactorily characterized by NMR and mass spectrometry.

UV−vis Spectroscopy. The UV−vis spectrum of all compounds presents a first absorption band in the 370−430 nm region followed by a second transition at longer wavelengths. Based on the spectrum of reference compounds devoid of acceptor group,[14c] the first absorption band can be assigned to a $\pi-\pi^*$ transition and the second band to an intramolecular charge-transfer (ICT) transition between the TPA−thiophene donor block and the peripheral acceptors groups. The UV−vis data for the fully substituted compounds **1**−**4** show that the maximum of the ICT band increases from 528 nm for compound **1** substituted by indanedione acceptors to 613 nm for compound **4** bearing the tricyanovinyl groups. These results show that, as expected, the absorption maximum of the ICT band reflects the relative strength of the acceptor groups. Comparison of the data for compounds **6**, **5**, and **4** shows that increasing the number of tricyanovinyl acceptor groups produces a decrease of the intensity of the bands in the 300−450 nm region together an increase of the relative intensity of the ICT transition around 600 nm (Figure 1). As appears in Figure 1, these changes are accompanied with a hypsochromic shift of the ICT band. This later result probably reflects changes in the dipole moment of the molecules, but this question clearly requires further work.

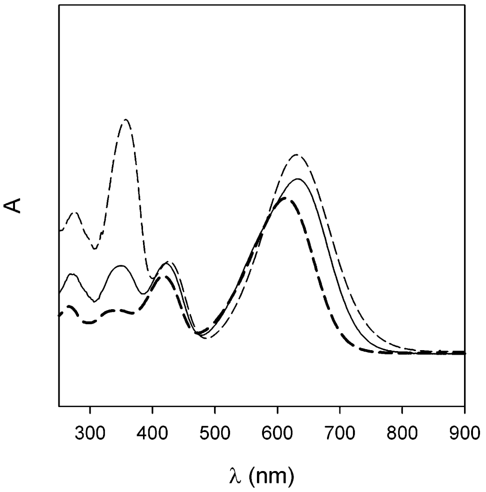


FIGURE 1. UV−vis absorption spectra of compounds **4** (bold dashed), **5** (solid line), and **6** (dashed) in methylene chloride.

TABLE 1. UV−vis Absorption Data (in CH_2Cl_2) and Cyclic Voltammetric Data (in 0.10 M Bu_4NPF_6/CH_2Cl_2, Scan Rate 100 mV s^{-1}, Ref SCE) for Compounds 1−6

	$\lambda\ \pi-\pi^*$	λ ICT	E_{pa} (V)	E_{pr} (V)	ΔE_{op}[b] (eV)	ΔE_{el}[c] (eV)
1	396	528	0.91	−1.11[a]	2.35	2.02
2	420	557	1.05	−0.95[a]	2.23	2.00
3	368	538	1.06	−1.23[a]	2.30	2.29
4	417	613	1.19	−0.56	2.02	1.75
5	422	632	1.00	−0.63	1.96	1.63
6	426	633	0.88	−0.64	1.96	1.52

[a] Irreversible process. [b] Optical gap based on λ_{ICT}. [c] Electrochemical gap $\approx E_{pa} - E_{pr}$.

Electrochemical Experiments. Compounds **1**−**6** have been analyzed by cyclic voltammetry in methylene chloride in the presence of tetrabutylammonium hexafluorophosphate 0.10 M as supporting electrolyte. The cylic voltammogram of all compounds shows a reversible oxidation process indicative of stable cation radical. As shown in Table 1, the potential of the anodic peak (E_{pa}) of the trisubstituted compounds increases with the strength of the acceptor groups and shifts from 0.91 V for indandione to 1.19 V for the strongest tricyanovinyl acceptor. Comparison of the data for compounds **4**−**6** shows that the increase of the number of tricyanovinyl acceptor groups from 1 to 3 leads to a 0.31 V positive shift of E_{pa}. As for oxidation, all compounds can be reduced at a potential which depends on the strength and on the number of acceptor groups. Whereas compounds **1**−**3** undergo irreversible reduction, the process is fully reversible for compounds **4**−**6** (Figure 2). As shown in Table 1, the potential of the corresponding cathodic peak (E_{pr}) shifts toward more positive values from −0.64 to −0.56 V when the number of acceptor groups increases. The deconvoluted CV of compounds **4**−**6** (Figure 2) show that the intensity of the reduction wave relatively to that of the oxidation one increases with the number of acceptor groups. Assuming a monoelectronic oxidation process, integration of the reduction wave shows that the reduction process involves one, two, and three electrons for compounds **6**, **5**, and **4** respectively.

Theoretical Calculations. The electronic properties of compounds **4**−**6** have been investigated by means of theoretical calculations. Ab initio quantum calculations have been performed with the Gaussian 03 package of programs at a hybrid density functional theory (DFT) level. Calculations were done using the restricted B3LYP/6-31G(d)* functions. HOMO and

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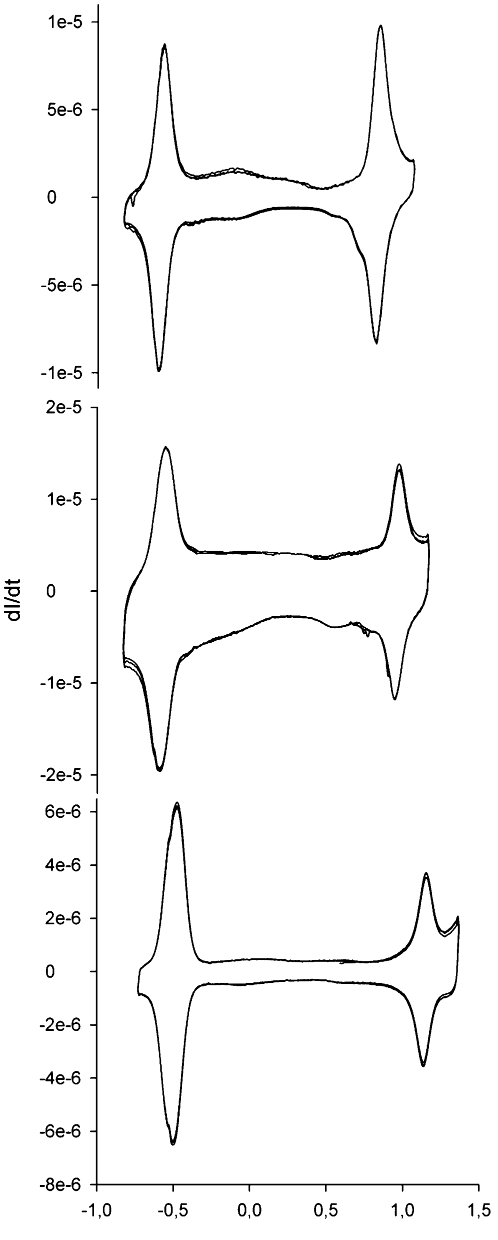

FIGURE 2. Deconvoluted CV of compounds **6**, **5**, and **4** (from top to bottom) in CH_2Cl_2, $TBAPF_6$ 0.1 M 100mV/S vs SCE.

LUMO levels of neutral molecules **4**−**6** are shown in Figure 3 (larger pictures of HOMO−LUMO levels are available in ESI).

As generally observed for TPA derivatives, the three N−C bonds are coplanar which is characteristic of enamines and indicates a certain degree of conjugation between the arms. Steric hindrance between the phenyl rings grafted on the central nitrogen atom generates the typical propeller shape of the molecule. The HOMO is mainly located on the central node with a significant contribution of the unsubstituted branches in **5** and **6**. The LUMO is localized on the peripheral electron-withdrawing groups and on the adjacent thiophene rings. Distributions of HOMO and LUMO levels are separated in all compounds indicating that the HOMO−LUMO transition can be consider as a charge-transfer transition. As expected, the HOMO and LUMO levels decrease when increasing the number of electron-withdrawing groups on the molecule, in agreement with electrochemical results. For compounds **5** and **4**, the localization of the LUMO at the terminal acceptor groups leads to a 2- and 3-fold degenerated LUMO, respectively (Figure 3). This indication of independent terminal acceptor groups agrees well with the two- and three-electron reduction processes indicated by electrochemical results for compounds **5** and **4**. In contrast, the persistence of a relatively delocalized HOMO for all compounds is consistent with the observed one-electron oxidation process. Calculations also show that the HOMO−LUMO gap ΔE increases with the number of electro-acceptor groups on the molecule, in agreement with optical and electrochemical results.

Conclusions

Star-shaped conjugated systems consisting of a hybrid TPA−thiophene core substituted by electron-acceptor groups have been synthesized. Optical and electrochemical data and theoretical calculations provide a coherent picture showing that the electronic properties of this class of compounds can be controlled over a wide range by varying the nature and the number of acceptor groups. Comparison of the characteristics of compounds containing indandione, barbiturate, and dicyano- and tricyanovinyl acceptor groups shows that the latter leads to the systems with the smallest HOMO LUMO gap and the lowest LUMO level.

The analysis of the effect of the number of tricyanovinyl groups shows that increasing the number of acceptor groups leads to a decrease of the HOMO and LUMO levels and to an increase of the energy gap. On the other hand these three compounds present a reduction potential higher than that of fullerene C_{60}. While these results show that these compounds cannot be used as donor in bulk heterojunction solar cells, they suggest that they could eventually behave as n type or as ambipolar organic semiconductors. Work aiming at the confirmation of this hypothesis is now underway and will be reported in future publications.

Experimental Section

Synthesis of *N,N,N*-Tris[4-[5-(1,3-dioxoindan-2-ylidenemethyl)-2-thienyl]phenyl]amine (1). To a solution of tris[4-(5-formyl-2-thienyl)phenyl]amine **7** (0.2 g 0.35 mmol) in 10 mL of CH_2Cl_2 were added 3.3 equiv of indandione and one drop of triethylamine. After 24 h of stirring, 3 equiv of indandione were added, and the mixture was stirred again for 24 h. Addition of petroleum ether led to the precipitation of a crude product which was dissolved in CH_2Cl_2. The organic phase was washed with 0.10 M aqueous sodium hydroxide and water and dried over magnesium sulfate. After solvent removal, the mixture was chromatographed twice on a silica gel column using CH_2Cl_2 as eluent and once on a preparative plate using the same eluent. Pure **6** was obtained in ca. 1% yield as a purple glassy solid. ^1H NMR ($CDCl_3$) attributed by 2D COSY: 7.98 (m, 12H, 4, 5, 6 and 6′), 7.79 (m, 6H, 7 and 7′), 7.75 (d, 6H, 2, $^3J = 8.5$ Hz), 7.45 (d, 3H, 3, $^3J = 4$ Hz), 7.23 (d, 6H, 3, $^3J = 8.5$ Hz). ^{13}C NMR ($CDCl_3$): 190.4, 189.8, 156.8, 147.5, 143.8, 142.0, 140.5, 136.3, 136.2, 135.0, 134.8, 128.7, 127.8, 124.7, 124.3, 123.7, 123.0, 122.8. MS (MALDITOF): $C_{60}H_{33}NO_6S_3$ M^+ 960.0. HRMS: $M^{+\bullet}$ (calcd) (959.1470) 959.1495.

Synthesis of Compounds 2 and 3. To a solution of tris[4-(5-formyl-2-thienyl)phenyl]amine **7** (0.2 g, 0.35 mmol) in 10 mL of CH_2Cl_2 were added 3.3 equiv of malonodinitrile or thiobarbiburic acid and one drop of triethylamine. The condensation was followed by TLC: mono-, di-, and trifunctionnalized compounds appeared successively. After 4 h (for **3**) to 10 h (for **2**) of reaction, addition of petroleum ether allowed the precipitation of a crude product.

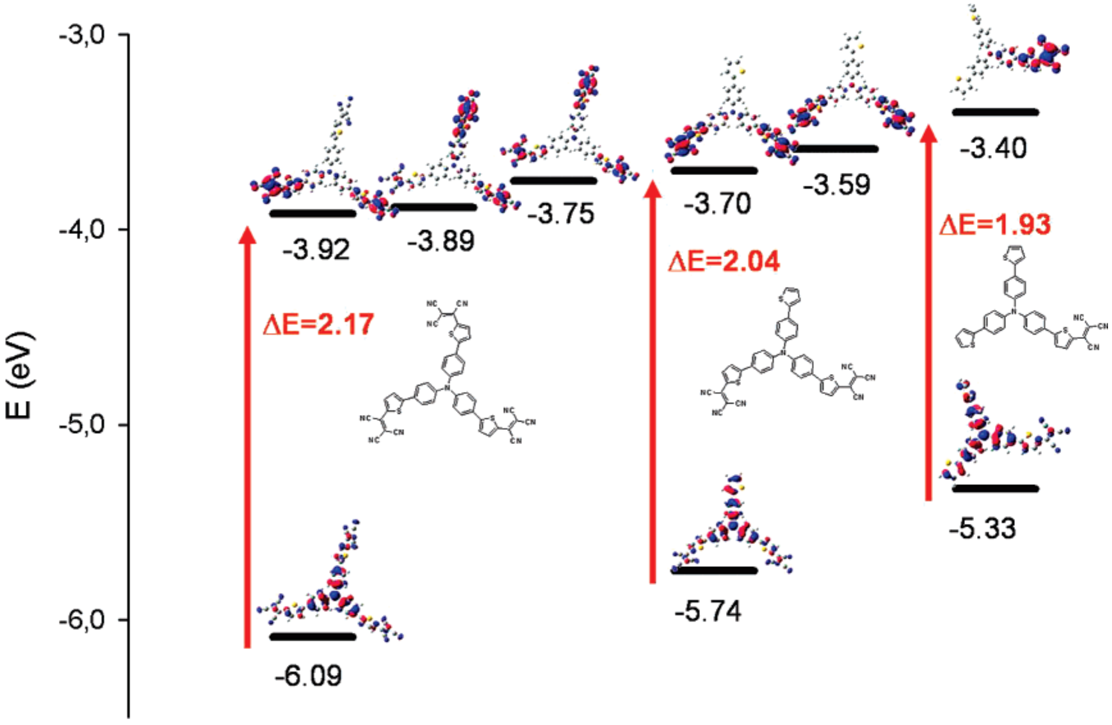

FIGURE 3. Calculated HOMO and LUMO levels for compounds **4**−**6**.

Compound **3** was isolated pure in 90% yield as a red solid. In the case of **2**, the crude product was dissolved in CH_2Cl_2 and washed with an aqueous solution of sodium hydroxide 0.1 M and then three times with water after the organic phase was dried on magnesium sulfate. After evaporation of the solvent, the pure derivative **2** was isolated in 85% yield as a purple glassy solid.

***N,N,N*-Tris[4-[5-(2-thioxodihydropyrimidin-4,5-oxo-5-ylidenemethyl)-2-thienyl]phenyl]amine (2).** ^{1}H NMR ($CDCl_3$): 8.67 (s, 3H), 7.89 (d, 3H, $^3J = 4.5$ Hz), 7.78 (d, 6H, $^3J = 8.5$ Hz), 7.51 (d, 3H, $^3J = 4$ Hz), 7.21 (d, 6H, $^3J = 8.5$ Hz), 4.61 (m, 12H), 1.34 (m, 18H). ^{13}C NMR ($CDCl_3$): due to very poor solubility, several signals were not observed (see the Supporting Information). MS (MALDITOF): $C_{57}H_{51}N_7O_6S_6$ M$^+$ 1121.0. HRMS: M$^{+\bullet}$ (calcd) (1121.2225) 1121.2213.

***N,N,N*-Tris[4-[5-(2,2-dicyanoethen-1-yl)-2-thienyl]phenyl]amine (3).** Spectroscopic data are identical to those already published.[16]

Synthesis of *N,N,N*-Tris[4-(5-tricyanoethenyl-2-thienyl)phenyl]amine (4). To a solution of compound **3** (60 mg, 0.083 mmol) dissolved at 0 °C under nitrogen atmosphere in 5 mL of dry DMF was added 5 equiv of NaCN dissolved in 2 mL of 1:1 water−DMF. The mixture turned brown immediately. After 15 min of stirring at 0 °C, two drops of acetic acid and one drop of concentrated hydrochloric acid were added followed by portionwise addition of 3 equiv of $Pb(OAc)_4$, and the solution turned blue. The mixture was stirred for 2 h at 0 °C, and 100 mL of water was added. The suspension was filtered on a Hyflo supercell. The solid collected on the top of the column was dissolved in methylene chloride and the solution dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel (eluent 3:1 CH_2Cl_2/PE) to give 65 mg (85%) of a blue coruscant glassy solid. ^{1}H NMR ($CDCl_3$): 8.08 (d, 3H, $^3J = 4.5$ Hz), 7.70 (d, 6H, $^3J = 9$ Hz), 7.51 (d, 3H, $^3J = 4.5$ Hz), 7.23 (d, 6H, $^3J = 9$ Hz). ^{13}C NMR is not available due to the extremely low solubility. MS (MALDITOF): $C_{45}H_{18}N_{10}S_3$, 794.0. HRMS: M$^{+\bullet}$ (calcd) (794.0878) 794.0854.

Synthesis of Compounds 5 and 6. To a solution of tris[4-(2-thienyl)phenyl]amine **8** (100 mg, 0.2mmol) was added 4 equiv of TCNE dissolved in 5 mL of DMF. The mixture was stirred for 1 week at 60 °C under nitrogen atmosphere followed by addition of 100 mL of methylene chloride. The organic phase was washed 10 times with water and dried over magnesium sulfate. After evaporation of the solvent, the residue was chromatographed on silica gel using methylenechloride/petroleum ether 1/1 (compound **1**) and then methylenechloride/EP 3/1 (compound **2**) as eluent. Compounds **1** and **2** were isolated in 50 and 29 yields, respectively, as green glassy solids. Note that compound **3** was observed in trace amounts.

***N*-[4-(5-Tricyanoethenyl-2-thienyl)phenyl]-*N,N*-bis[4-(2-thienyl)phenyl]amine (6).** ^{1}H NMR ($CDCl_3$): 8.03 (d, 1H, $^3J = 4.5$ Hz), 7.59 (d, 2H, $^3J = 9$ Hz), 7.58 (d, 4H, $^3J = 8.5$ Hz), 7.44 (d, 1H), 7.29 (m, 4H, $^3J = 4.5$ Hz), 7.17 (d, 2H, $^3J = 9$ Hz), 7.11 (d, 2H, $^3J = 8.5$ Hz), 7.09 (dd, 2H, $^3J = 5$, 3.5 Hz). ^{13}C NMR ($CDCl_3$): 160.0, 150.3, 145.1, 143.5, 141.8, 131.9, 131.7, 131.1, 128.2, 128.1, 127.2, 125.9, 124.9, 124.2, 123.0, 121.7, 112.9, 112.8, 112.5, 80.1. MS (MALDITOF): $C_{35}H_{20}N_4S_3$ MS M$^+$ 592.1. HRMS: M$^{+\bullet}$ (calcd) (592.0850) 592.0833.

***N,N*-Bis[4-(5-tricyanoethenyl-2-thienyl)phenyl]-*N*-[4-(2-thienyl)phenyl]amine (5).** ^{1}H NMR ($CDCl_3$): 8.06 (d, 2H, $^3J = 4.5$ Hz), 7.65 (d, 4H, $^3J = 8.5$ Hz), 7.62 (d, 2H, $^3J = 8.5$ Hz), 7.48 (d, 2H, $^3J = 4.5$ Hz), 7.32 (m, 2H), 7.21 (d, 4H, $^3J = 9$ Hz), 7.17 (d, 2H, $^3J = 8.5$ Hz), 7.11 (dd, 1H, $^3J = 5$, 3.5 Hz). ^{13}C NMR ($CDCl_3$): 159.0, 149.1, 144.4, 143.1, 141.6, 132.3, 132.2, 132.0, 128.4, 128.3, 127.4, 126.6, 126.1, 125.3, 124.8, 123.8, 123.4, 112.8, 112.5, 112.2, 81.4. MS (MALDITOF): $C_{40}H_{19}N_7S_3$ MS M$^{+\bullet}$ 693.0. HRMS: (calcd) (693.0864) 693.0854.

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Supporting Information Available: ^{1}H NMR spectra of compounds **1**, **2**, **4**−**6**; HOMO−LUMO figures and calculated bond length for compounds **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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