# Polarizability and Internal Charge Transfer in Thiophene–Triphenylamine Hybrid $\pi$ -Conjugated Systems

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#### Supporting Information

**ABSTRACT:** Extended star-shaped conjugated systems consisting of dicyanovinyl electron-acceptor units connected to a triphenylamine core by means of thiophene (T), thienylenevinylene (TV), and bithiophene (BT) conjugating spacers have been synthesized. The analysis of the electronic properties of the molecules by UV–vis absorption spectroscopy, cyclic voltammetry, and theoretical calculations shows that the electronic properties of the systems depend on the length and rigidity of the conjugating spacer.



## INTRODUCTION

Among the numerous classes of organic materials endowed with specific electronic properties, triphenylamine (TPA) derivatives have attracted sustained interest for many years.

Because of their high hole mobility, isotropic charge transport, and optical transparency in the visible region, these materials have been widely used for the design of hole injections and transporting layers in organic light-emitting diodes.<sup>1</sup>

The emergence of bulk heterojunction (BHJ) organic solar cells<sup>2</sup> based on soluble small molecules has triggered a renewal of interest in TPA derivatives as donor materials in such solar cells.<sup>4</sup> In this context, we have shown previously that the introduction of electron acceptor groups in the structure of a TPA-based molecular donor produces an internal charge transfer (ICT) which leads at the same time to the following: (i) the broadening of the absorption spectrum; (ii) a reduction of the optical band gap; and (iii) an increase in the oxidation potential and, hence, a decrease of the HOMO level.<sup>5</sup> When such compounds are used as donor material in molecular bulk heterojunction solar cells, this ICT leads to an improvement of the light-harvesting properties, a bathochromic extension of the external quantum efficiency spectrum, and an increase of the power conversion efficiency (PCE).<sup>5</sup>

During the past few years, many conjugated TPA derivatives have been used as molecular donors in BHJ solar cells, leading to a steady improvement of the PCE.<sup>6</sup> Values exceeding 4% have been reported for molecular BHJ solar cells based on TPA compounds and PC<sub>71</sub>BM or a new analogue of fullerene.<sup>7</sup>

In our continuing interest in the design of TPA-based donor materials for molecular BHJ solar cells, we report here an analysis of the effect of the chemical structure of the conjugating bridge between the TPA core and the peripheral electron acceptor groups on the electronic properties of the resulting star-shaped molecules. To this end, the electronic properties of three compounds involving dicyanovinyl acceptor units connected to the TPA core by means of thiophene (T), thienylenevinylene (TV), and bithiophene (BT) conjugating spacers have been investigated by cyclic voltammetry, UV—visible absorption spectroscopy, fluorescence emission spectroscopy, and quantum-chemical calculations.



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## EXPERIMENTAL METHODS

General. Solvents were purified and dried using standard protocols. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE DRX 300 spectrometer;  $\delta$  are given in ppm -(relative to tetramethylsilane), and coupling constants (J) are given in Hz. Matrix-assisted laser desorption ionization time-offlight (MALDI-TOF) mass spectra were recorded with a Bruker Biflex-III, equipped with a  $N_2$  laser (337 nm). For the matrix, dithranol in CH<sub>2</sub>Cl<sub>2</sub> was used. High resolution mass spectra were recorded under FAB mode on a Jeol JMS 700 spectrometer. UV-visible optical data were recorded with a Perkin-Elmer lambda 950 spectrophotometer. Thermal analyses were performed using a DSC 2010 CE (TA Instruments). For cyclic voltammetry (scan rate 100 mV cm<sup>-1</sup>), the electrochemical apparatus consisted of a potentiostat EG&G PAR 273A and a standard threeelectrode cell. As the working electrode and counterelectrode, a platinum foil and a platinum wire were used, respectively, while a SCE electrode was used as a reference.

Synthesis. Tris[4-(thiophen-2-ylvinyl)phenyl]amine (2). At room temperature and under inert atmosphere, 500 mg of tris-[4-formylphenyl]amine (1) (1.52 mmol) and 5 equiv of 2-(diethoxyphosphorylmethyl)thiophene (7.6 mmol, 1.78 g) were added to 70 mL of dry tetrahydrofuran. Then, 5 equiv of *t*-BuOK (20 wt %) in solution in tetrahydrofuran (3.8  $\times$  10<sup>-2</sup> mol, 4.6 mL) was added. The mixture was stirred overnight. After the evaporation of the solvent, the residue was purified by chromatography on silica gel, using a mixture of dichloromethane/petroleum ether 1:2 as eluent. Compound 2 was precipitated using a mixture of dichloromethane/petroleum ether and isolated as a yellow solid (yield: 580 mg, 67%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.37 (d, 2H,  ${}^{3}J = 8.5 \text{ Hz}$ ; 7.17 (d, 1H,  ${}^{3}J = 5.5 \text{ Hz}$ ); 7.15 (d, 1H,  ${}^{3}J = 16 \text{ Hz}$ ); 7.08 (d, 2H,  ${}^{3}J$  = 8.5 Hz); 7.045 (d, 1H,  ${}^{3}J$  = 3.5 Hz); 7.00 (dd, 1H,  ${}^{3}J$  = 5 Hz,  ${}^{3}J$  = 3.5 Hz); 6.89 (d, 1H,  ${}^{3}J$  = 16 Hz).  ${}^{13}C$  NMR (CDCl<sub>3</sub>, ppm): 146.5; 143.1; 131.8; 127.7; 127.6; 127.2; 125.7; 124.2; 124.0; 120.5.  $T_{\rm f}$  (DSC, °C): 181.  $T_{\rm d}$  (TGA, °C): 201. MALDI-TOF (calcd/found, [M<sup>+.</sup>], g mol<sup>-1</sup>): 569.13/569.41. HRMS (calcd/found, [M<sup>+.</sup>], g mol<sup>-1</sup>): 569.1300/569.1300.

Tris[4-(5-formyl-thiophen-2-ylvinyl)phenyl]amine (**3**). Under inert atmosphere, 280 mg of tris(4-(thiophen-2-ylvinyl)phenyl)amine (2) (0.49 mmol) was dissolved in 80 mL of 1,2-dichloroethane. Then, 4 equiv of dimethylformamide (1.96 mmol, 0.15 mL) and 4 equiv of phosphorus oxytrichloride (1.96 mmol, 0.18 mL) were added. The mixture was refluxed overnight under  $N_2$ . The mixture was allowed to cool to room temperature, and 50 mL of dichloromethane was added. The organic layer was washed with 150 mL of an aqueous solution of sodium acetate, and then it was washed three times with water. After the mixture was dried over anhydrous magnesium sulfate, and after the filtration and evaporation of the solvent, the residue was purified by chromatography on silica gel, using dichloromethane/ethyl acetate 95:5 as eluent. An orange powder was recovered (yield: 96 mg, 30%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 9.52 (s, 1H); 7.07 (m, 4H);  $6.92 (d, 1H, {}^{3}J = 16 Hz); 6.89 (d, 1H, {}^{3}J = 4 Hz); 6.78 (d, 1H, {}^{3}J =$ 16 Hz); 6.55 (d, 1H,  ${}^{3}J$  = 4 Hz).  ${}^{1}$ H NMR (CDCl<sub>3</sub>, ppm): 9.85 (s, 1H); 7.66 (d, 1H,  ${}^{3}J$  = 4 Hz); 7.42 (d, 2H,  ${}^{3}J$  = 8.5 Hz); 7.12 (m, 5H). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 181.8; 151.8; 147.5; 142.4; 136.6; 131.8; 128.5; 128.1; 126.3; 124.6; 120.3. <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 182.5; 152.7; 147.1; 141.2; 137.3; 132.1; 131.1; 128.1; 126.3; 124.4; 119.7. MALDI-TOF (calcd/found, [M<sup>+.</sup>], g mol<sup>-1</sup>): 653.10/ 653.17. HRMS (calcd/found, [M + Na]<sup>+</sup>, g mol<sup>-1</sup>): 676.10453/ 676.10450.  $T_d$  (Kofler, °C): 123. IR (cm<sup>-1</sup>): 1646 (-C=O).

Tris[4-(5-dicyanomethylidenemethyl-thiophen-2-ylvinyl)phenyl]amine (**TV**). At room temperature and under inert atmosphere, 250 mg of the aldehyde (3) (0.383 mmol) was dissolved in 300 mL of chloroform. Then, 10 equiv of malonodinitrile (3.83 mmol, 253 mg) and ca. 30 drops of triethylamine were added. The mixture was stirred at room temperature overnight under nitrogen atmosphere after 100 mL of chloroform was added. The organic phase was washed three times with 150 mL of a solution of sodium hydroxide (1 M) and then with water. After the mixture was dried over anhydrous magnesium sulfate and after the filtration and evaporation of the solvent, the residue was purified by chromatography on silica gel using dichloromethane as eluent. A purple powder was isolated (yield: 265 mg, 87%). <sup>1</sup>H NMR (DMSO $-d^6$ , ppm): 8.61 (s, 1H); 7.87 (d, 1H,  $^3J = 4$  Hz); 7.67 (d, 2H,  ${}^{3}J = 8.5 \text{ Hz}$ ); 7.55 (d, 1H,  ${}^{3}J = 16 \text{ Hz}$ ); 7.5 (d, 1H,  ${}^{3}J =$ 4.5 Hz); 7.36 (d, 1H,  ${}^{3}J$  = 16 Hz); 7.08 (d, 2H,  ${}^{3}J$  = 8.5 Hz).  ${}^{1}H$ NMR (CDCl<sub>3</sub>, ppm): 7.76 (s, 1H); 7.60 (d, 1H,  ${}^{3}J$  = 4 Hz); 7.46 (d, 2H,  ${}^{3}J = 9$  Hz); 7.19–7.13 (m, 5H).  ${}^{13}C$  NMR (CDCl<sub>3</sub>, ppm): 155.2; 150.1; 147.4; 140.3; 134.0; 133.5; 131.0; 128.5; 126.8; 124.5; 119.1; 114.4; 113.6; 75.8. MALDI-TOF (calcd/ found, [M<sup>+.</sup>], g mol<sup>-1</sup>): 797.15/797.20. HRMS (calcd/found,  $[M + Na]^+$ , g mol<sup>-1</sup>): 820.1382/820.1380.  $T_f$  (DSC, °C): 259.  $T_{\rm d}$  (TGA, °C): 357. IR (cm<sup>-1</sup>): 2219 (-CN).

(5'-Dimethoxymethyl-[2,2']bithiophen-5-yl)-trimethyl-stannane (4). Under inert atmosphere, 6 g of 2,2'-bithienyl-5-carboxaldehyde (30.9 mmol) and 0.1 equiv of PTSA (3.09 mmol, 533 mg) were introduced in a three-neck flask. A catalytic amount of molecular sieves and 5 equiv of trimethyl orthoformate (1.55  $\times$  $10^{-1}$  mol, 16.9 mL) were introduced in 35 mL of dry methyl alcohol. The mixture was refluxed overnight under inert atmosphere. Then, the mixture was allowed to cool to room temperature, and 200 mL of a solution of sodium hydroxide at  $10^{-3}$  M was added. The mixture was extracted with 200 mL of dichloromethane. The organic phases were washed three times with water  $(3 \times 200 \text{ mL})$  and dried over anhydrous magnesium sulfate. After the evaporation of the solvent, 7.18 g of crude acetal was recovered. This was later dissolved in 105 mL of dry tetrahydrofuran, and the mixture was cooled to -78 °C under inert atmosphere. To the mixture was added 1.1 equiv of *n*-BuLi (2.5 M in hexanes,  $3.27 \times 10^{-2}$  mol, 13.15 mL). The mixture was stirred for 2 h under inert atmosphere at -78 °C. Then, 1.1 equiv of a solution of trimethyltin chloride (1 M) in tetrahydrofuran (32.87 mmol, 32.9 mL) was added dropwise at -78 °C, and the mixture was maintained at this temperature for 2 h. The mixture was stirred overnight at room temperature. The crude product was then washed with 200 mL of water and extracted with dichloromethane. The organic phase was washed three times with water  $(3 \times 200 \text{ mL})$  and then dried over anhydrous magnesium sulfate. After the evaporation of the solvent, 10.8 g of product was recovered and used without any further purification (yield: 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.26 (d, 1H, <sup>3</sup>J = 4 Hz); 7.08 (d, 1H,  ${}^{3}J = 3.5 \text{ Hz}$ ; 7.06 (d, 1H,  ${}^{3}J = 3.5 \text{ Hz}$ ); 6.96 (d, 1H,  ${}^{3}J = 4 \text{ Hz}$ ); 5.61 (s, 1H); 3.38 (s, 6H); 0.38 (s, 9H); 0.09 (m, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 142.8; 139.97; 137.9; 137.6; 135.8; 126.1; 124.97; 123.1; 99.9; 52.6; -8.22.

*Tris*[4-(5-formyl-2,2'-bithiophen-5-yl)phenyl]amine (**5**). Under inert atmosphere, 1.9 g of tris-(4-bromo)phenylamine (3.9 mmol) was dissolved in a three-neck flask in 300 mL of dry toluene. Then, 6 equiv of stannic compound 4 (23.7 mmol, 9.6 g) was added. The mixture was degassed for 10 min using  $N_2$ , and 10 mol % of catalyst Pd(PPh<sub>3</sub>)<sub>4</sub> was added. The mixture was then refluxed overnight under inert atmosphere. Then, the mixture was allowed to

cool to room temperature, and 200 mL of an aqueous solution of sodium hydrogenocarbonate was added. The organic phase was washed three times with water (3 × 200 mL) and then dried over anhydrous magnesium sulfate. After the evaporation of the solvent, the residue was purified by chromatography on silica gel, using a mixture of dichloromethane and dichloromethane/ethyl acetate 95:5 as eluent. An orange powder was recovered (yield: 2.32 g, 72%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 9.86 (s, 1H), 7.68 (d, 1H, <sup>3</sup>*J* = 4 Hz), 7.53 (d, 2H, <sup>3</sup>*J* = 8.5 Hz), 7.34 (d, 1H, <sup>3</sup>*J* = 4 Hz), 7.26 (d, 1H, <sup>3</sup>*J* = 4 Hz), 7.22 (d, 1H, <sup>3</sup>*J* = 4 Hz), 7.17 (d, 2H, <sup>3</sup>*J* = 8.5 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 182.5; 147.2; 146.8; 145.6; 141.4; 137.5; 134.6; 128.6; 127.2; 126.9; 124.5; 123.9; 123.6. MALDI-TOF (calcd/found, [M<sup>+-</sup>], g mol<sup>-1</sup>): 821.0315/821.0300. Elemental anal. (calcd/found, %): C (65.82/65.89); H (3.95/3.76); N (1.57/1.54); S (21.52/22.59). *T*<sub>f</sub> (DSC, °C): 155. *T*<sub>d</sub> (TGA, °C): 211. IR (cm<sup>-1</sup>): 1652 (—C=O).

Tris[4-(5-dicyanomethylidenemethyl-2,2'-bithiophen-5yl)phenyl]amine (**BT**). At room temperature and under inert atmosphere, 150 mg of aldehyde 5 (0.182 mmol) was dissolved in 150 mL of chloroform. Then, 10 equiv of malonodinitrile (1.82 mmol, 121 mg) and four drops of triethylamine were added. The mixture was refluxed overnight. The mixture was allowed to cool to room temperature, and 50 mL of chloroform was added. The organic phase was washed three times with 150 mL of an aqueous solution of sodium hydroxide (10% molar) and washed once with water, and then it was dried over anhydrous magnesium sulfate. After the filtration and evaporation of the solvent, the residue was purified by chromatography on silica gel, using dichloromethane as eluent, leading to 100 mg of a purple powder (yield: 57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 7.75 (s, 1H); 7.63 (d, 1H,  ${}^{3}J = 4$  Hz); 7.51 (d, 2H,  ${}^{3}J = 8.5$  Hz); 7.41 (d, 1H,  ${}^{3}J$  = 4 Hz); 7.18 (m, 2H); 7.13 (d, 2H,  ${}^{3}J$  = 8.5 Hz). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, ppm): 150.2; 149.1; 146.9; 142.9; 140.4; 134.9; 133.7; 133.2; 128.4; 127.9; 126.7; 126.5; 124.2; 124.1; 114.2; 113.5. MALDI-TOF (calcd/found,  $[M + H]^+$ , g mol<sup>-1</sup>): 966.06/966.04. HRMS (calcd/found, [M<sup>+.</sup>], g mol<sup>-1</sup>): 965.06467/ 965.0638. *T*<sub>f</sub> (DSC, °C): 181. *T*<sub>d</sub> (TGA, °C): 201.

**Computational Study.** The geometries of the molecules under study have been first optimized at the DFT (Density Functional Theory) level with the B3LYP functional and the 6-31G(d,p) basis set by imposing a  $C_3$  symmetry.<sup>8</sup> On the basis of the optimized geometries, absorption spectra have been calculated by the time-dependent DFT (TD-DFT) formalism with the BHandHLYP functional and a 6-31G(d,p) basis set. The use of the hybrid BHandHLYP functional has been motivated by the presence of electronic transitions with a strong intramolecular charge transfer character to cope with the inherent deficiency of pure TD-DFT in dealing with such excited states.<sup>9</sup>

## RESULTS AND DISCUSSION

**Syntheses.** Compound T was prepared as already reported.<sup>5c,d</sup> Tris(*p*-formylphenyl)amine (1) was obtained in two steps from triphenylamine using a known procedure.<sup>10</sup> A 3-fold Wittig—Horner olefination of compound 1, with an excess of the phosphonate anion of thiophene, gave compound tris(4-(thiophen-2-ylvinyl)-phenyl)amine (2) in 67% yield. Vilsmeier formylation of 2, using POCl<sub>3</sub>/DMF in refluxing 1,2-dichloroethane, led to the corresponding trialdehyde 3 in 30% yield. Compound TV was finally obtained in 87% yield by Knoevenagel condensation of 3, with malonodinitrile in the presence of triethylamine in chloroform at room temperature (see Scheme 1).

Vilsmeier—Haack formylation of bithiophene led quantitatively to 5-formyl-2,2'-bithiophene. This later compound was acetalized with trimethyl orthoformate in the presence of a catalytic amount of *p*-toluene sulfonic acid and molecular sieves. The acetal was used for the next step without further purification; the addition of *n*-BuLi and trimethyltin chloride at -78 °C led to the stannic derivative 4 in 89% overall yield.<sup>11</sup> A Stille coupling between compound 4 and trisbromophenylamine followed by a hydrolysis with a NaHCO<sub>3</sub> solution led to trialdehyde 5 in 72% yield. Knoevenagel condensation of trialdehyde 5 and malonodinitrile gave the target **BT** compound in 57% yield. All compounds were satisfactorily characterized by NMR and mass spectrometry.

**Spectroscopic Measurements.** The optical and electrochemical properties of the compounds have been analyzed by UV-vis absorption spectroscopy, fluorescence emission spectroscopy, and cyclic voltammetry in methylene chloride in the presence of tetrabutylammoniumhexafluorophosphate (TBAHP) as supporting electrolyte. The corresponding results are listed in Table 1.

While the UV—vis absorption spectrum of compound **2** presents a single broad absorption band with a maximum at 402 nm, the spectra of all other compounds that contain electronwithdrawing end groups exhibit two absorption bands. Examination of the data in Table 1 shows that replacing the carboxaldehyde end group with the stronger electron-acceptor dicyanovinyl leads to a bathochromic shift of the first and second absorption maximum of 64 and 87 nm between **3** and **TV**, respectively, and of 61 and 83 nm between **5** and **BT**, respectively.

On the other hand, comparison of the data for the three target compounds **T**, **TV**, and **BT** shows that, as expected, the extension of the conjugation length leads to a red shift of the absorption maxima (see Figure 1). However, although **BT** possesses, in principle, the longest topological conjugation length, **TV** absorbs at the longest wavelength and thus presents the most extended electron delocalization. This result can be explained by the combined effects of the lower overall aromatic character of thienylenevinylene systems and by the limitation of inter-ring rotational disorder inherent to oligothiophenes.<sup>12</sup>

To gain more detailed information on the nature of the two optical transitions observed in the spectrum of the donor-acceptor compounds, the UV-vis absorption spectra of compounds T, TV, and BT have been recorded in a series of solvents, presenting a large variation of polarity (toluene, THF, chlorobenzene, and chloroform) and Kamlet–Taft  $\pi^*$  constants.<sup>13</sup> When a correlation with the empirical Taft polarity scale is found, an almost linear relationship is observed between the transition energy (expressed in kcal mol<sup>-1</sup>) and  $\pi^*$ ,  $E = E^\circ + S\pi^*$ . The values of  $E^\circ$ and S give valuable information on the nature of electronic transitions.  $E^{\circ}$  corresponds to the transition energy in a nonpolar solvent so that two compounds of comparable polarity present similar  $E^{\circ}$ values. S models the solvatochromic sensibility of the compound; a negative value of S indicates a positive solvatochromism. The absolute value of S increases with the polarizability of the compound. Figure 2 shows the variation of the energy of the long wavelength absorption band of the three compounds vs the Kamlet-Taft constant. For all compounds, a negative S coefficient is observed, suggesting high polarizabilities and an internal charge transfer character associated with the transition. The  $E^{\circ}$ values of T and BT are very close (62.0 and 61.8 kcal mol<sup>-1</sup>, respectively; see the Supporting Information), indicating analogous polarities. The lower value of  $E^{\circ}$  for TV (59.1 kcal mol<sup>-1</sup>)

### Scheme 1



Scheme 1

Table 1. Data of $UV - V$ is Spectroscopy, Cyclic Voltammetry and Fluorescence Emission Spectroscopy for T, TV, B
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	$\lambda_{ m max} \ ( m nm)^a$	$\log \\ (\varepsilon)^a$	$\lambda_{ m max} \ ( m nm)^b$	$E_{\mathrm{pa1}}{}^{c}$	$E_{\mathrm{pa2}}{}^{c}$	$E_{\rm pc}^{\ \ c}$	$\lambda_{ m em} \ ({ m nm})^d$	$\Phi_{ m em}\ (\%)^d$
Т	370-510	4.66-5.02	377-539	1.08	$1.67^{e}$	$-1.2^{e}$	635/559	15/25
TV	407-541	4.45-4.76	360-576	0.90	$1.40^{e}$	$-1.1^{e}$	700/604	0.3/2
BT	415-527	4.73-4.92	358-548	0.88	1.28	$-1.1^{e}$	703/599	0.4/31
2	402	4.88		0.68				
3	343-454	4.54-4.84		0.84				
5	354-444	4.70-4.99		0.82	1.23			
$a 10^{-5} \text{ M} i$	n CH <sub>2</sub> Cl <sub>2</sub> , <sup>b</sup> In the	solid state, spin-cast f	rom CH <sub>2</sub> Cl <sub>2</sub> 2.5 mg	/mL, 2000 rnd/	/min. <sup>c</sup> 0.10 M T	BAHP methylen	e chloride, scan rate	$100 \text{ mV s}^{-1}$

"10 ° M in CH<sub>2</sub>Cl<sub>2</sub>. "In the solid state, spin-cast from CH<sub>2</sub>Cl<sub>2</sub> 2.5 mg/mL, 2000 rnd/min. "0.10 M TBAHP methylene chloride, scan rate 100 mV s  $^{\circ}$ , ref SCE. <sup>d</sup> In CH<sub>2</sub>Cl<sub>2</sub>/toluene against rhodamine B in ethanol as standard. <sup>e</sup> Nonreversible processes.

reflects a higher polarity. The *S* values of three compounds are very close. Nevertheless, despite high standard deviations, one can observe a slightly higher value for **TV** (S = -9.1) when compared with **T** (S = -8.2) and **BT** (S = -8.8), which may indicate a higher polarizability. These two observations may indicate a better conjugation between the triphenylamine node and the outer electron withdrawing moieties in **TV**. The same measurements performed on the high energy transition band lead to a weaker linearity of results and lower *S* coefficients, which indicates a moderate effect of the solvent on this transition.

Thin films of the target compounds have been spun-cast on glass from methylene chloride solutions. The UV-vis absorption

spectra of the films (Table 1, Figure 1) reveal bathochromic shifts of the absorption maxima as a result of intermolecular interactions and/or planarization of the conjugated backbone. **T**, **BT**, and **TV** present a maximum of absorption at 540, 548, and 576 nm, respectively (Table 1).

The photoluminescence of the three compounds has been investigated by fluorescence emission spectroscopy; the results are reported in Table 1. In methylenechloride, only T presents a decent fluorescent quantum yield, while the other two compounds, TV and BT, only fluoresce scarcely. On the contrary, in toluene, T, TV, and BT present fluorescent quantum yields attaining 25, 31, and 32%, respectively. This solvent-dependent



Figure 1. UV-vis absorption spectra of compounds T (long dash), TV (short dash), and BT (solid line). (Left)  $10^{-5}$  M in methylene chloride. (Right) In the solid states (spin-cast films).



Figure 2. Energy transitions of the low energy band for compounds T (triangle), TV (square), and BT (circle) vs Taft constants of solvents.

behavior remains unexplained up to now and deserves to be cleared up by further photophysical experiments. Analogously to  $\lambda_{max}$ , the  $\lambda_{em}$  values of compounds **T**, **TV**, and **BT** all present a large sensibility to solvent polarity. For example, in toluene and methylenechloride, derivative **TV** emits at 604 and 700 nm, respectively. This behavior is characteristic of a photoinduced intramolecular charge transfer. In the series, compound **BT** presents larger Stokes' shifts than **T** and **TV**, probably because of larger conformation changes between fundamental and excited states.

**Electrochemical Measurements.** The cyclic voltammograms of compounds **2**, **3**, **5**, **TV**, and **BT** exhibit a first reversible oneelectron oxidation wave, corresponding to the formation of a stable cation radical (Figure 3). The potential of the first anodic peak  $(E_{pa1})$  depends on the extension of the conjugated system as well as on the nature of the terminal substituent. Thus, the introduction of substituents of increasing electron-acceptor character produces a positive shift of  $E_{pa1}$  from 0.68 V for compound **2** to 0.84 V for **3** and 0.90 V for **TV**. Conversely, the lengthening of the conjugated branches produces the reverse



Figure 3. CV traces of compounds T (top), TV (middle), and BT (bottom) in 0.10 M TBAHP/CH<sub>2</sub>Cl<sub>2</sub>; scan rate 100 mV s<sup>-1</sup>.



Figure 4. DFT-calculated orbitals of compound TV: (a) HOMO, (b) HOMO-1, (c) HOMO-2, (d) LUMO, (e) LUMO+1, and (f) LUMO+2.

Table 2. DFT-Calculated O	ccupied (H: HOMC	) and Unoccupied	(L:LUMO)	) Molecular Orbital E	nergies of T,	TV, BT, 2, 3	3, and 5
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cmpd	H-3 (eV)	H-2 (eV)	H-1 (eV)	H (eV)	L (eV)	L+1 (eV)	L+2 (eV)	L+3 (eV)
Т	-8.16	-7.46	-7.46	-6.61	-2.30	-2.30	-2.10	-0.42
TV	-7.79	-7.09	-7.09	-6.40	-2.42	-2.42	-2.25	-0.94
BT	-7.51	-6.92	-6.92	-6.33	-2.38	-2.38	-2.31	-1.00
2	-7.22	-6.33	-6.33	-5.51	-0.63	-0.06	-0.18	0.70
3	-7.69	-6.85	-6.85	-6.03	-1.52	-1.52	-1.24	0.01
5	-7.36	-6.68	-6.68	-6.00	-1.49	-1.49	-1.34	-0.24

effect as a result of the extended charge delocalization. Thus, while T, which contains the shortest conjugated branches, oxidizes

at 1.08 V, compounds **TV** and **BT** show  $E_{\rm pa1}$  values at 0.90 and 0.88 V, respectively.

	1 <sup>st</sup> peak(exptl) (eV)	$2^{nd}$ peak(exptl) (eV)	$1^{st}$ peak(theor) (eV)	$2^{nd}$ peak(theor) (eV)	$\Delta E(exptl)$ (eV)	$\Delta E(\text{theor}) (\text{eV})$		
Т	2.43	3.34	2.98	3.95	0.91	0.964		
TV	2.29	3.07	2.73	3.63	0.78	0.90		
ВТ	2.35	2.99	2.74	3.54	0.64	0.80		
2	3.07	3.94	3.37	4.41	0.87	1.04		
3	2.72	3.61	3.12	4.12	0.89	1.01		
5	2.79	3.51	3.12	3.99	0.72	0.87		
<sup>a</sup> The experimental and theoretical energy difference between the two transitions is also reported.								

Table 3. Experimental (exptl) and Theoretical (theor) Transition Energies for the Lowest Two Absorption Peaks of Compounds T, TV, BT, 2, 3, and 5<sup>*a*</sup>



Figure 5. Experimental  $(10^{-5} \text{ M in methylenechloride, top})$  and theoretical (bottom) spectra for T (black), BT (blue), and TV (red).

Compound **BT**, which contains the longest conjugated branches, undergoes a second reversible oxidation process to form a dication at 1.28 V, while for **T** and **TV** the second oxidation process is quasi-irreversible.

**Theoretical Calculations.** *Electronic Structure.* The calculated occupied and unoccupied molecular orbital energies in the gas phase are collected in Table 2 for **2**, **3**, **5**, **T**, **TV**, and **BT**. As a consequence of the imposed  $C_3$  symmetry, the occupied HOMO-1 and HOMO-2 and unoccupied LUMO and LUMO +1 levels are degenerate. Compounds **TV** and **BT** do show an increase (a decrease) in their HOMO (LUMO) energies compared to **T** as a result of the increase in conjugation length, as

observed experimentally. When comparing the energies of the frontier orbitals of **TV** vs **3** as well as **BT** vs **5**, we notice a significant stabilization of the LUMO (0.9 eV in both cases) and a weaker stabilization of the HOMO level (around 0.35 eV in both cases) as a result of the strong withdrawing character of the cyano groups.

The optimized geometry and shape of the frontier electronic levels of **TV** are shown in Figure 4. As generally observed for TPA derivatives, the three central N–C bonds are coplanar, which is characteristic of enamines. Steric hindrance between the phenyl rings grafted on the central nitrogen atom generates the typical propeller shape of the molecules.<sup>14</sup> In the case of **T** and **BT**, the steric hindrances between the hydrogen atoms grafted on the central phenyl ring and the lateral thiophene lead to a twist angle of ca. 24°. On the contrary, in compound **TV**, which presents a vinylene-linkage between the heterocycles, each conjugated branch appears planar.

The HOMO is delocalized over the whole molecule with large coefficients on the central node and a smaller weight on the lateral dicyanovinyl systems (Figure 4a), while the LUMO (LUMO+1, Figure 4d-e) is localized on two branches and presents large coefficients on the lateral electron withdrawing groups. Interestingly, the orbital features of TV described above are reproduced for compounds T and **BT**, although the chemical structures are different (see the Supporting Information).

UV-Vis Spectra. Experimental and theoretical transition energies of the two main electronic transitions are collected in Table 3. Experimental and theoretical results, though being systematically shifted by ca. 0.5 eV, are very consistent. The lengthening of the conjugated spacer going from T to TV-BT leads, in both cases, to a decrease in the difference of energy between the two transitions and to a bathochromic shift of the low energy band. Moreover, the reinforcement of the acceptor strength from aldehyde to dicyanovinyl group leads to a further bathochromic shift of the lowest band by 0.4-0.5 eV.

Figure 5 presents the calculated and experimental UV—vis spectra of **T**, **TV**, and **BT** in electronvolts. The detailed description of the different transitions provided by the calculations is given in the Supporting Information. In both cases, the low energy band corresponds mainly to two degenerate excited states mostly described by HOMO–LUMO and HOMO–LUMO+1 transitions, respectively. As seen from Figure 4, these transitions correspond to charge transfer transitions, with both an intrabranch character due to the different localizations of the HOMO/LUMO–LUMO+1 levels on a given branch (vide supra) and interbranch character (likely to dominate the solvatochromic effects) due to the different spatial extent of the HOMO/LUMO–LUMO+1 levels on the whole molecular backbone; this fully rationalizes the solvatochromism observed experimentally.

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The second peak is described at the TD-DFT level by a large mixing of transitions; the reduced solvatochromism might be rationalized by the fact that the interbranch charge transfer character is reduced by an increased intrabranch character (as a result of a similar spatial localization of the orbitals involved in the one-electron transitions) and/or by compensation effects between the existing interbranch charge transfer processes associated with the individual transitions.

## CONCLUSION

A new series of star-shaped chromophores constituted by a TPA core substituted by conjugated branches of variable conjugation length and constitution bearing terminal electron-withdrawing groups has been synthesized, and their electronic properties have been analyzed by UV—vis spectroscopy and cyclic voltammetry. The nature of the low energy optical transition has been investigated using TD-DFT calculations, confirming the charge transfer character of this transition. The synthesis of more soluble analogues of this series of compounds is now in progress and will be reported in due time.

## ASSOCIATED CONTENT

**Supporting Information.** Taft constants of solvents,  $E^{\circ}$  and *S* values, absorption maxima, and corresponding transition energy in kcal/mol. Theoretical description of the optical transitions. Shape of the molecular orbitals for **BT** and **T**. This material is available free of charge via the Internet at http://pubs.acs.org.

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