Panchromatic Push–Pull Dyes of Elongated Form from Triphenylamine, Diketopyrrolopyrrole, and Tetracyanobutadiene Modules

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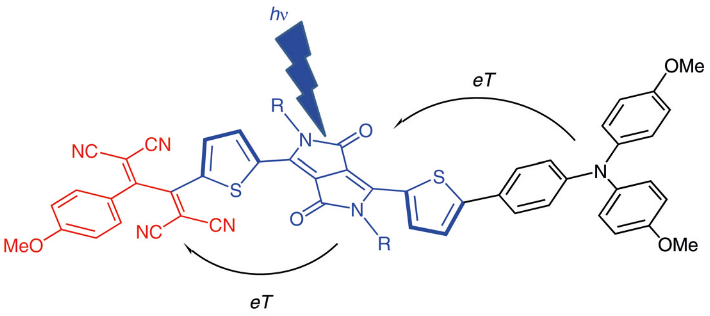

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Abstract Several symmetrical and unsymmetrical thiophene-functionalized diketopyrrolopyrrole chromophores bearing a bis(*p*-methoxyphenyl)-*p*-phenylamine substituent were synthesized through palladium-catalyzed cross-coupling reactions. Mono-substitution and di-substitution occur using either alkyne or borolane groups, allowing the preparation of mixed systems. The alkyne derivatives could be prepared in high yields, and are versatile building blocks for the [2+2] cycloaddition of tetracyanoethylene, leading to 1,1,4,4-tetracyanobuta-1,3-diene derivatives. These interesting push–pull molecules exhibit a rich redox activity, which is understandable in light of the behavior of appropriate reference compounds. These innovative and rationally designed scaffolds are highly colored, exhibiting high absorption coefficients and spanning an absorption range of more than 600 nm of the UV/Vis electromagnetic spectrum.

Key words cross-coupling reactions, cycloaddition reactions, push–pull molecules, panchromatic dyes, redox properties

Highly dipolar donor–acceptor substituted systems (also so called push–pull chromophores) are a fascinating set of synthetic targets that have a wide range of properties such as nonlinear optical (NLO) responses, significant two-photon absorption cross-sections for doubling the frequency of incident radiation, charge transport and charge separation abilities.[1] Potential applications of such sophisticated dyes for fluorescence enhancement, advanced microscopy techniques, biomedical analysis,[2] and for the construction of both organic photovoltaic materials[3] and field-effect transistors,[4] are foreseen.

An impressive number of donor groups are used in the design of push–pull systems and the complete list is too large to detail; however, among them, symmetric or dissymmetric triarylamines hold the lead.[5] Similarly, electron-withdrawing groups are numerous, with the most used being nitro- and cyano- (or polycyano) modules, which are suitable for promoting charge-transfer or electron-transfer along the main molecular axis.[6]

Of the common dyes, diketopyrrolopyrroles (DPPs) based on a bis-lactam backbone are interesting in regard to their synthetic availability, ease of modification, outstanding robustness, and attractive spectroscopic properties, making them excellent building blocks for a myriad of applications.[7] These chromophores are well known for their strong absorption bands in the UV/Vis region, high solubility in common organic solvents when adequately substituted on the bis-lactam core, high fluorescence quantum yields, and relatively long excited-state lifetimes (1–5 ns). These properties make DPPs promising candidates for OPV applications,[8,9] and for the engineering of dinuclear boron(III) complexes displaying unusual spectral properties.[10] Moreover, the construction of a push–pull system upon the DPP scaffold should engender some new properties, such as photochromism, enhanced charge transport, and recombination of π-conjugated electronic states. These could provide the basis for new developments in organic photovoltaic devices and fluorescent probes for biomedical applications.[11] Water-soluble conjugated and multi-cationic fluorene-DPP polymers have been used for the detection of DNA by fluorescence techniques.[12] The synthesis of anionic polyelectrolyte conjugates has also been investigated for their use as fluorescent bioprobes.[13,14] We reported the functionalization of DPP dyes with *N*,*N*-dimethylaminopropyne arms giving, after alkylation, weakly fluorescent, water-soluble dyes that are useful for cascade energy-transfer processes[15] and show lasing properties.[16] Protein labeling and high solubility in biological media has recently been demonstrated, confirming the proposed interest of these fluorescent probes in biology.[17]

In fact, the study of DPP-based push–pull systems is really rather limited and this has motivated our research program dedicated to the engineering of such interesting dyes. Herein, the design, synthesis and characterization of a series of DPP-based push–pull chromophores are described. The main strategy involved introduction of an electron-donor group and an electron-acceptor group through unsaturated (C≡C) or saturated (C–C) linkers to both sides of the DPP core (Figure 1). The linear optical and redox properties of these new compounds have been evaluated and are of particular interest.

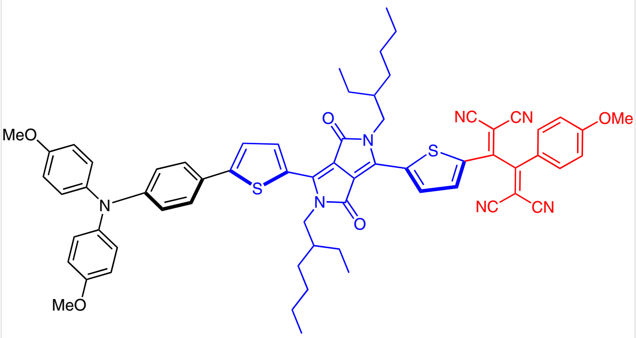


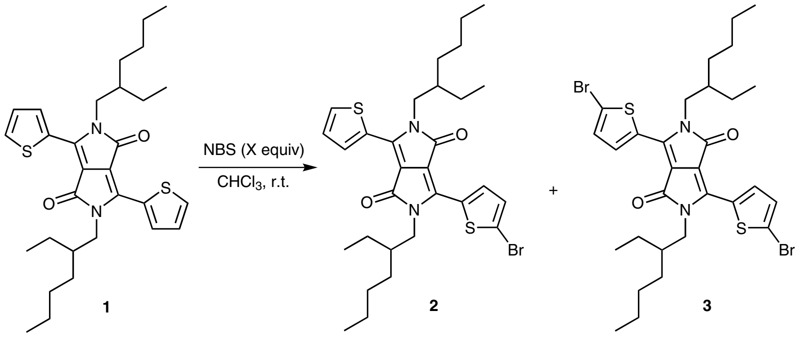
Figure 1 General molecular formula of the push–pull type of molecules synthesized and characterized in this work

For this purpose, thienyl-DPP derivative **1**[18] was selected as starting material. Electrophilic bromination led to a mixture of mono- (**2**), and di-bromo- (**3**) derivatives (Scheme 1). The isolated yields were clearly dependent on the reagent stoichiometry, however, the best yields of 53% for **2** and 73% for **3** were reproducible.

The next step consisted of the cross-coupling of derivative **2** with bis(*p*-methoxyphenyl)-*p*-phenylethynylamine (**4**), a reaction promoted by Pd(0) generated in situ from a Pd(II) precursor and CuI. Compound **5** was isolated and purified in excellent yield (87%). The donor-substituted alkyne group underwent a [2+2]cycloaddition reaction with tetracyanoethylene (TCNE), leading to an intermediate cyclobutene, which subsequently underwent ring opening, leading to 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivative **6** in good yield (Scheme 2).[19] The TCBD subunits exhibit a strong acceptor character and imparted good solubility in usual solvents because of the nonplanarity of the molecule,[20] which leads to efficient solvation and prevents the formation of aggregates.[21] Some TCBD derivatives connected with DPP,[22] thiophene,[23] and triphenylamine[24] have been reported previously.

The next challenge was to add further TCBD units to a single molecule in the hope that the molecule could accept more electrons with the reduced state and behave as an electron reservoir. One obvious synthetic strategy was to use the difunctionalized DPP-thienyl dye **3** first and to conduct a double cross-coupling reaction with bis(*p*-methoxyphenyl)-*p*-phenylethynylamine **4** (Scheme 3). This proved to be straightforward and enabled isolation of the doubly functionalized dye **7** in 72% yield. With TCNE in excess, the stable and highly colored octacyano dye **8** was isolated pure in 54% yield.

A subsequent test was to construct a triad with a triarylamine unit lacking a triple bond for reaction with TCNE on one side but a 4-ethynylanisole fragment on the other, which could give rise to a TCBD module in order to create a gradient of electronic density along the main molecular axis. This could involve linkage of either the triarylamine or the alkyne module first. Initial efforts with the triarylamine were unsuccessful because linking the boralane **9** to compound **3** was not regioselective, providing a mixture of **10** and **11** that was extremely difficult to separate on a preparative scale. The alternative of cross coupling to an alkyne proved more convenient, leading to compound **12** in 42% isolated yield. A side product was the bis-coupled molecule, which was isolated in 12% yield. Fortunately, Suzuki cross-coupling between **12** and borolane **9** proceeded in 92% yield, without any major difficulties, allowing the preparation of the novel product **13**. The final step of the [2+2] cy-



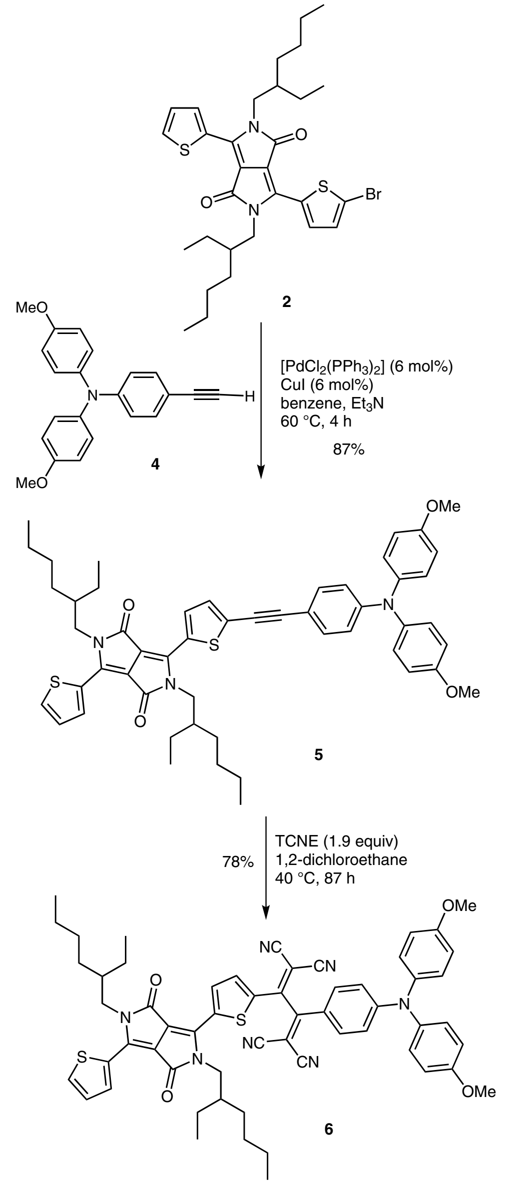
equivalents of NBS
X = 1.2 equiv; **2**, 53% and **3**, 26%
X = 1.6 equiv; **2**, 11% and **3**, 73%

Scheme 1 Preparation of the mono- and dibromo starting materials cloaddition reaction with TCNE provided the target compound **14** in 88% yield (Scheme 4).

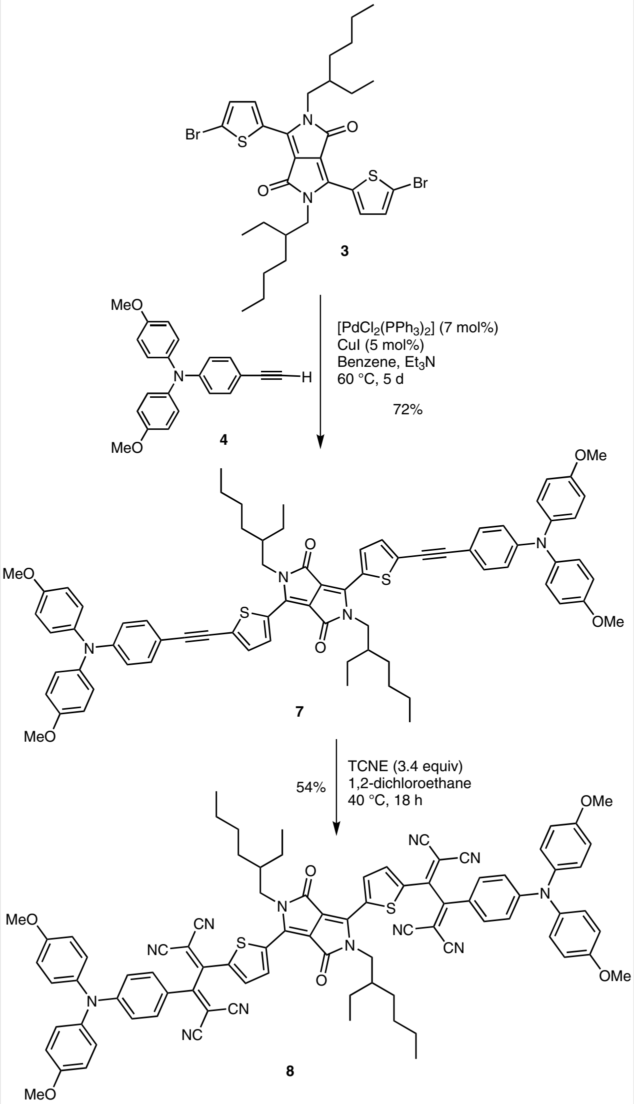
All the new compounds were isolated and purified by column chromatography. The chemical structures were assigned unambiguously by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analyses.

The optical properties of the push–pull chromophores were evaluated in fluid solution at room temperature. For clarity, the discussion will be limited to dyes **5**/**7** and **6**/**8**, which are the best representatives. The mono- and disubstituted dyes **5** and **7** display a broad and intense absorption at low energy centered at, respectively, 589 (ε = 55,000 $M^{-1}cm^{-1}$) and 634 nm (ε = 101,000 $M^{-1}cm^{-1}$) in toluene (Figure 2). These optical transitions are safely assigned, in the light of previous studies,[15] to the $S_0 \rightarrow S_1$ transition of the DPP chromophores.[28,29]

The weak transition about 460 nm, which is more pronounced in the presence of two TPA fragments in **7** (*ε* ca. 20,000 $M^{-1}cm^{-1}$) compared with **5** (*ε* ca. 10,000 $M^{-1}cm^{-1}$) is likely due to an internal charge transfer absorption induced by the strongly electron-donating TPA fragment and the π-accepting DDP fragment (Figure 2a and b). The intense transitions at higher energies near 360 nm are assigned to π–π* excitations of the TPA and thiophene subunits. By irradiation of both dyes in toluene, intense fluorescence is observed at 632 and 660 nm with quantum yields of 29 and 33%, respectively, for dyes **5** and **7**. This fluorescence is not



Scheme 2 Preparation of the thienyl-DPP-substituted triarylamine and its TCBD derivative[25]

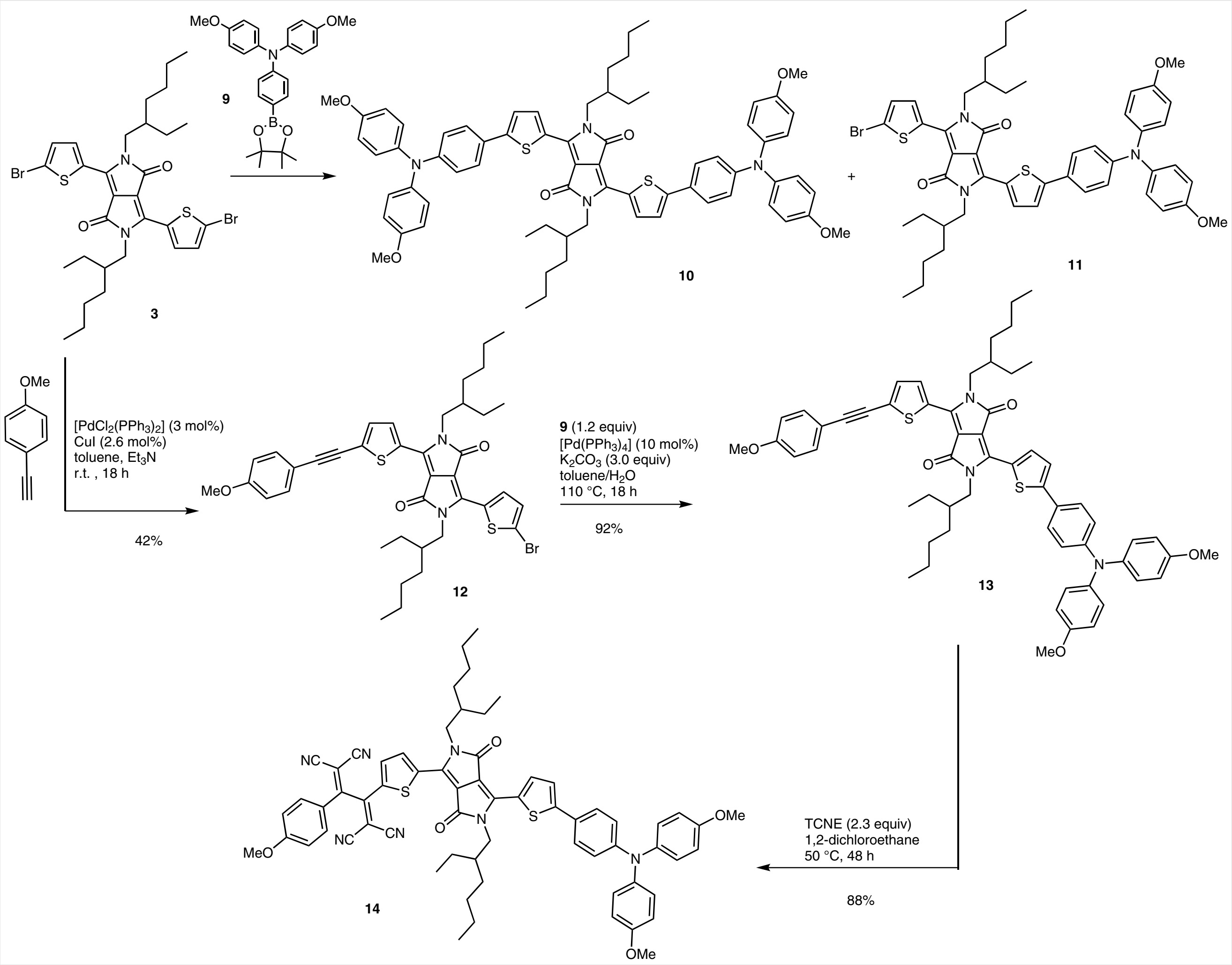


Scheme 3 Preparation of the thienyl-DPP disubstituted triarylamine and its TCBD derivative[26]

dependent on the excitation wavelength, and the excitation spectra match perfectly the absorption spectra over the entire wavelength range (red curve in Figure 2), indicating that no aggregates are formed in solution and that no fluorescent impurities are present in the samples. Interestingly, the fluorescence profile is highly structured, as usually observed for DPP dyes, and the short excited state lifetimes (2.7 and 5.8 ns for **5** and **7**, respectively) favor a singlet emitting state. Little solvent influence is observed, which is an observation that is in keeping with such a conclusion.[30] In addition, no degradation of the dyes is observed during the course of the fluorescence analysis.

The absorption spectra of the highly soluble TCBD dyes **6** and **8** display similar broad bands between 580–780 nm and 580–870 nm, respectively, with absorption coefficients in the 37,000 to 47,000 $M^{-1}cm^{-1}$ range (Figure 3). Notably, the intensity of this absorption is considerably reduced (by ca. 50%) in comparison with that of the alkyne derivatives **5** and **7**. This decrease has previously been observed with Bodipy derivatives.[31] As would be expected by increasing the strength of the electron-accepting TCBD fragment, the internal charge transfer band (ICT) at 480 nm should be markedly enhanced. Indeed the intensity of this ICT band is similar to the main $S_0 \rightarrow S_1$ transition of the DPP chromophores, reaching 53,000 and 31,500 $M^{-1}cm^{-1}$, respectively, for chromophores **8** and **6**. No fluorescence was observed in either case at any excitation wavelength. This may be a result of an intramolecular electron transfer from the strongly electron-donating DPP* (excited state) to the strongly accepting TCBD fragment (see below).

The electrochemical properties of both sets of dyes **5**/**6** and **7**/**8** were investigated in deoxygenated dichloromethane solution at r.t. by using tetrabutylammonium hexafluorophosphate as supporting electrode; the data are shown in Figure 4 and Figure 5 and are summarized in Table 1. For



Scheme 4 Preparation of the hybrid thienyl-DPP-triarylamine/anisole and its TCBD derivative[27]

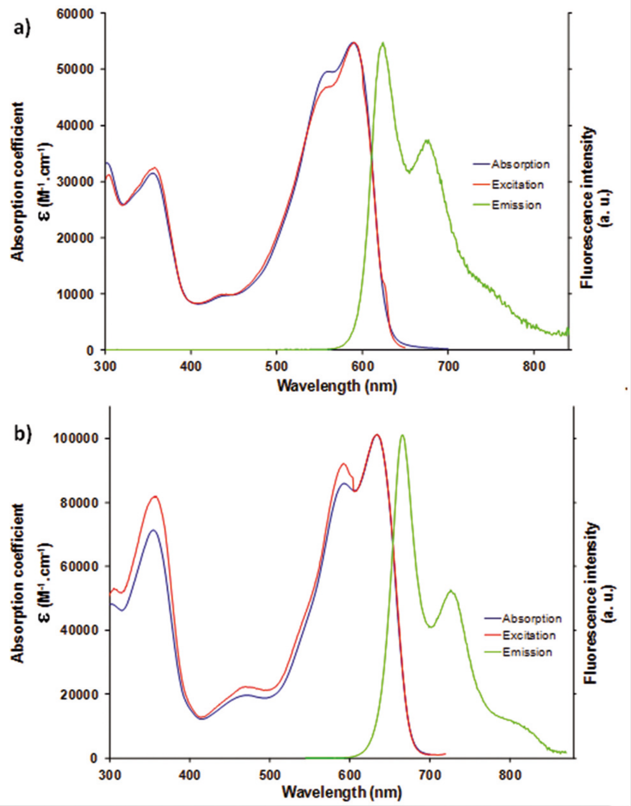


Figure 2 Absorption, emission, and excitation spectra of dyes **5** (a) and **7** (b) at r.t. in toluene

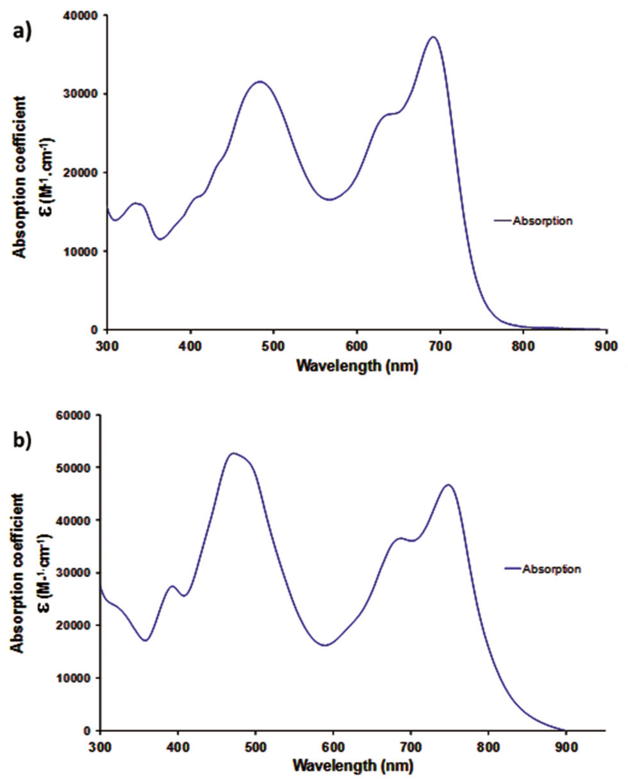


Figure 3 Absorption spectra of dyes **6** (a) and **8** (b) at r.t. in toluene

dye **5** (DPP linked TPA), three reversible steps and one irreversible step were observed on the oxidation scans (Figure 4). On the reductive scans, a single reduction step is found at –1.14 V. Assignment of these oxidation waves is feasible with the help of reference compounds **1** and **4**. It clearly appears that oxidation of TPA(OMe)$_2$ is easier than oxidation of thienyl-DPP by 260 mV and that the TPA(OMe)$_2$ is inactive in reduction, whereas thienyl-DPP is reversibly reduced around –1.18 V. Cycloaddition of TCNE to the triple bond of compound **5** leading to **6** resulted in a cathodic shift of the oxidation potential by approximately 260 mV and the emergence of two new reversible signals at –0.42 and –0.62 V (Figure 4). The *gem*-dicyanovinyl groups strongly stabilize a radical anion on each side of the TCBD.[32] As a consequence of these multiple reduction processes, the reduction of the DPP-thiophen is shifted anodically by approximately 340 mV.

Similarly, the shift is larger in the anodic regime with dye **8**, carrying two TCBD fragments (anodic shift of 480 mV). Interestingly, for **8**, three additional signals are observed at –0.23, –0.31, and –0.74 V, the two first signals each integrate for one electron, whereas the last integrates for two electrons (Figure 5). Here the tetraradical anion (or dianion) is stabilized by the four *gem*-dicyanovinyl fragments present at the periphery of the thienyl-DPP framework.

By using these redox potentials and the energy of the calculated optical transition (E_{00} for dyes **6** and **8** at 1.74 and 1.60 eV, respectively)[33] we can estimate, within the frame of the Rehm–Weller theory,[34] a driving force of ΔG_0 of –640 meV for the tetracyano dye **6** and of –420 meV for the octacyano dye **8**. These calculations thus support a photoinduced electron transfer from the excited state of the chromophores towards the cyano groups. This highly favorable process is presumed to be responsible for the fluorescence quenching in solution at room temperature.

In conclusion, we have prepared and characterized stable 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivatives of DPP-thienyl chromophores bearing triarylamine substituents. The interesting electrochemical properties and strong absorption features in the 280–680 nm range, and excellent solubility (ca. 10 to 15 mg of **6** or **8** per mL of chlorinated solvent) make these dyes interesting candidates for incorporation in optoelectronic devices. Further investigations on the synthetic methodology are in progress to shift the absorption features further to the near-infrared portion of the solar spectrum. Replacement of the standard fullerene

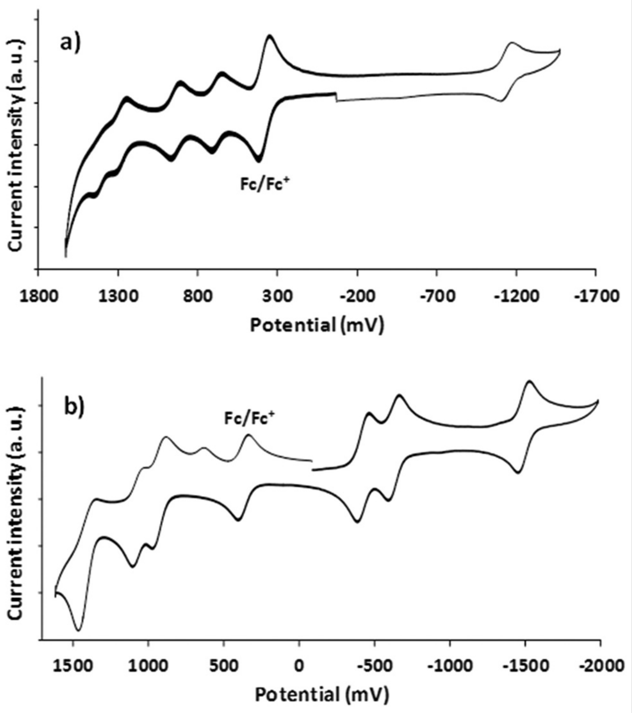


Figure 4 Cyclic voltammograms of dyes **5** (a) and **6** (b) in dichloromethane solution using $TBAPF_6$ as supporting electrolyte on a platinum electrode; ferrocene was used as internal reference and calibrated at +0.38 V using a saturated calomel electrode

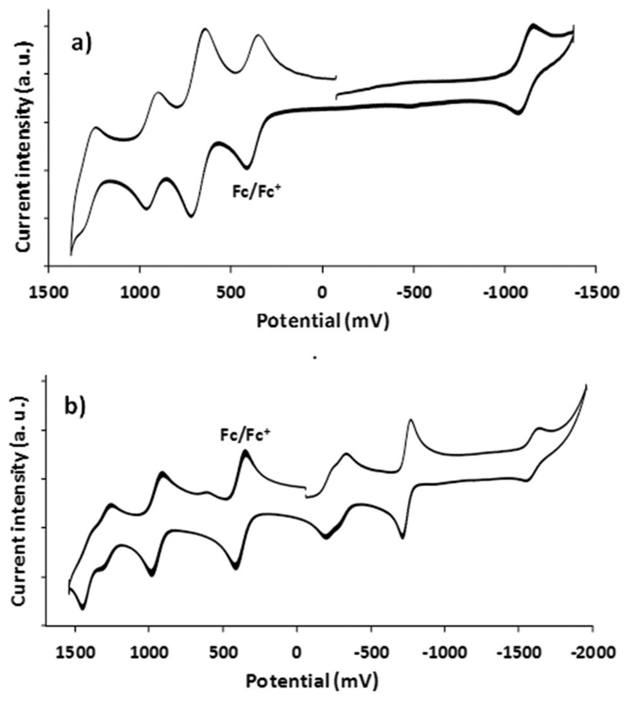


Figure 5 Cyclic voltammograms of dyes **7** (a) and **8** (b) in dichloromethane solution using $TBAPF_6$ as supporting electrolyte on a platinum electrode; ferrocene was used as internal reference and calibrated at +0.38 V using a saturated calomel electrode

Table 1 Electrochemical Data for the New Compounds[a]

Cmpd	E_{ox} (V) (ΔE, mV)	E_{red} (V) (ΔE, mV)	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[b]
5	+0.68 (60) +0.94 (60) +1.28 (60) +1.42 (60)	−1.14 (60)	−5.46	−3.64
6	+0.94 (60) +1.08 (60) +1.42 (irr)	−0.42 (70) −0.62 (70) −1.48 (60)	−5.71	−4.35
7	+0.67[c] (60) +0.93 (60) +1.28 (60) +1.40 (irr)	−1.12 (60)	−5.46	−3.66
8	+0.95[c] (70) +1.29 (60) +1.42 (irr)	−0.23 (60) −0.31 (60) −0.74[c] (60) −1.60 (70)	−5.73	−4.56
14	+0.65 (70) +1.05 (70) +1.42 (irr)	−0.36 (70) −0.61 (60) −1.45 (70)	−5.43	−4.42

[a] All potentials were measured in CH_2Cl_2 at r.t. with a Pt electrode and Bu_4NPF_6 (0.1 M) as supporting electrolyte; Fc/Fc+ (+0.38 V vs. SCE) was used as internal reference.
[b] Calculated assuming that ferrocene (Fc) has an ionization potential of −4.78 eV below the vacuum level.
[c] Assigned as a two-electron process; peak potentials (E_{ap} or E_{cp}) were used for irreversible processes.

type of electron acceptor in bulk heterojunction solar cells is another interesting option for these TCBD derivatives that deserves investigation.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1378818.

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(25) **Compound 6:** Tetracyanoethylene (41.0 mg, 0.320 mmol, 1.9 equiv) was added to a solution of **5** (144.3 mg, 0.169 mmol) in 1,2-dichloroethane (25 mL). The reaction medium was stirred at 40 °C for 87 h, then evaporated to dryness. Purification by column chromatography (SiO_2, CH_2Cl_2–petroleum ether, 80:20 to 100:0 with 2% Et_3N), followed by recrystallization (THF–*n*-pentane) afforded **6** (129.6 mg, 78%) as a black powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.91 (m, 12 H), 1.21–1.40 (m, 16 H), 1.78–1.92 (m, 2 H), 3.84 (s, 6 H), 4.00–4.06 (m, 4 H), 6.81 (d, ^3J = 9.2 Hz, 2 H), 6.92 (d, ^3J = 8.9 Hz, 4 H), 7.16 (d, ^3J = 8.9 Hz, 4 H), 7.33 (dd, ^3J = 5.0, 4.8 Hz, 1 H), 7.67 (d, ^3J = 9.2 Hz, 2 H), 7.77 (dd, ^3J = 5.0 Hz, ^4J = 1.0 Hz, 1 H), 7.84 (d, ^3J = 4.5 Hz, 1 H), 9.06 (d, ^3J = 4.5 Hz, 1 H), 9.17 (dd, ^3J = 4.1 Hz, ^4J = 0.8 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.5, 14.1, 23.2, 23.5, 23.6, 28.3, 28.4, 30.1, 30.2, 39.1, 39.8, 46.2, 46.4, 55.7, 80.1, 108.6, 112.0, 113.0, 113.0, 113.1, 113.9, 115.5, 116.8, 120.0, 125.4, 128.3, 129.1, 129.4, 132.1, 133.3, 135.6, 136.0, 137.1, 137.7, 138.1, 140.2, 144.4, 154.8, 157.5, 158.5, 161.0, 161.9, 162.1. UV/Vis (toluene): λ (ε, $M^{-1}cm^{-1}$) = 691 (37 200), 636 (27 300), 483 (31 500), 333 (16 000) nm. MS (EI): *m*/*z* (%) calcd for $C_{58}H_{57}N_7O_4S_2$: 979.39 (100); found 979.2 (100), 953.2 (25). Anal. Calcd for $C_{58}H_{57}N_7O_4S_2$ (980.25): C, 71.07; H, 5.86, N, 10.00. Found: C, 70.84; H, 5.47; N, 9.77.

(26) **Compound 8:** Tetracyanoethylene (23.3 mg, 0.182 mmol, 3.4 equiv) was added to a solution of **7** (64.2 mg, 0.054 mmol) in 1,2-dichloroethane (15 mL). The reaction medium was stirred at 40 °C for 18 h, then evaporated to dryness. Purification by column chromatography (Al_2O_3; CH_2Cl_2–petroleum ether, 70:30 to 80:20), followed by recrystallization (THF–*n*-pentane) afforded **8** (41.6 mg, 54%) as a brownish black powder. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.83–0.91 (m, 12 H), 1.21–1.36 (m, 16 H), 1.78–1.84 (m, 2 H), 3.82 (s, 12 H), 4.02 (d, ^3J = 7.9 Hz, 4 H), 6.81 (d, ^3J = 9.2 Hz, 4 H), 6.91–6.95 (m, 8 H), 7.13–7.18 (m, 8 H), 7.66 (d, ^3J = 9.4 Hz, 4 H), 7.85 (d, ^3J = 4.6 Hz, 2 H), 9.20 (d, ^3J = 4.6 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.4, 14.1, 23.2, 23.4, 28.2, 30.0, 39.7, 46.6, 55.7, 76.5, 81.8, 111.6, 112.7, 112.9, 113.1, 113.8, 115.5, 116.9, 119.8, 128.3, 132.1, 137.1, 137.3, 137.7, 138.8, 139.0, 140.0, 154.9, 157.7, 158.6, 161.1, 161.6.

UV/Vis (toluene): λ (ε, $M^{-1}cm^{-1}$) = 749 (48 100), 689 (36 500), 472 (52 700), 393 (27 400) nm. MS (EI): *m*/*z* (%) calcd for $C_{86}H_{74}N_{12}O_6S_2$: 1434.53 (100), 1435.53 (99.3); found: 1435.4 (100), 1408.4 (35), 1382.4 (15). Anal. Calcd for $C_{86}H_{74}N_{12}O_6S_2$ (1434.71): C, 71.94; H, 5.20, N, 11.71. Found: C, 71.72; H, 4.84; N, 11.49.

(27) **Compound 14:** Tetracyanoethylene (31.0 mg, 0.242 mmol, 2.3 equiv) was added to a solution of **13** (100.4 mg, 0.105 mmol) in 1,2-dichloroethane (25 mL). The round-bottom flask was equipped with a condenser and the mixture was stirred at 50 °C for 48 h. The reaction medium was extracted with CH_2Cl_2, washed with H_2O, and dried with brine and over Na_2SO_4. Purification by column chromatography (SiO_2; petroleum ether–EtOAc, 85:15 to 75:25), followed by precipitation from CH_2Cl_2–MeOH afforded **14** (100.0 mg, 88%) as a black powder. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.84–0.93 (m, 12 H), 1.21–1.40 (m, 16 H), 1.81–1.87 (m, 1 H), 1.92–1.99 (m, 1 H), 3.82 (s, 6 H), 3.92 (s, 3 H), 4.02–4.08 (m, 4 H), 6.88 (d, ^3J = 8.9 Hz, $Dn_{AB\ syst}$ = 94.0 Hz, 4 H), 6.91 (d, ^3J = 8.8. Hz, 2 H), 7.05 (d, ^3J = 9.1 Hz, 2 H), 7.11 (d, ^3J = 8.9 Hz, $Dn_{AB\ syst}$ = 94.0 Hz, 4 H), 7.41 (d, ^3J = 4.4 Hz, 1 H), 7.49 (d, ^3J = 8.8 Hz, 2 H), 7.82 (d, ^3J = 9.1 Hz, 2 H), 7.83 (d, ^3J = 4.7 Hz, 1 H), 9.08 (d, ^3J = 4.6 Hz, 1 H), 9.35 (d, ^3J = 4.3 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.52, 10.61, 14.15, 14.21, 23.2, 23.5, 23, 7, 28.3, 28, 5, 30.1, 30.4, 39.3, 39.8, 46.3, 46.5, 55.7, 56.1, 77.9, 78.8, 83.4, 108.5, 111.8, 112.2, 112.5, 113.1, 114.1, 115.0, 115.1, 115.9, 119.3, 123.4, 123.7, 123.9, 126.4, 127.4, 127.5, 127.6, 132.3, 133.8, 135.1, 135.9, 137.8, 139.8, 141.3, 145.0, 150.5, 154.9, 156.0, 156.9, 160.9, 162.3, 165.0, 165.4. UV/Vis (toluene): λ (ε, $M^{-1}cm^{-1}$) = 796 (61 200), 549 (6 300), 372 (39 200) nm. UV/Vis (THF): λ (ε, $M^{-1}cm^{-1}$) = 763 (52 600), 541 (3 400), 370 (38 900) nm. MS (EI): *m*/*z* (%) calcd for $C_{65}H_{63}N_7O_5S_2$: 1085.2 (100), 1086.44 (71); found: 1085.2 (100), 1086.2 (75). Anal. Calcd for $C_{65}H_{63}N_7O_5S_2$ (1085.43): C, 71.86; H, 5.85, N, 9.03. Found: C, 71.60; H, 5.69; N, 8.77.

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