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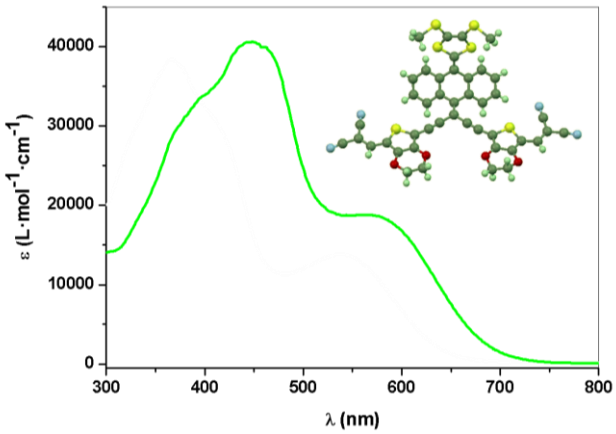
ABSTRACT



Three new push-pull chromophores based on the 10-(1,3-dithiol-2-ylidene)anthracene core were synthesized and fully characterized. The new chromophores display broad absorption spectra, nearly covering the whole visible region, with high extinction coefficients. Electrochemistry and theoretical calculations allowed the understanding of these singular electronic properties. The molecular structures were unambiguously confirmed by X-ray diffraction.

Solar energy represents nowadays one of the most realistic alternatives to the use of fossil fuels. Photovoltaic devices based on organic compounds (OPV) have experienced a tremendous development in the last years,[1] and recently efficiencies around 8-10% have been reported.[2] One of the crucial points to understand this improvement is the careful election of suitable organic materials able to fulfill some energetic and electronic requirements. Among these requisites, the ability of the material to harvest sunlight in a broad range of the visible and NIR spectrum is decisive in order to obtain a suitable photoresponse. In this regard, organic chromophores such as push-pull systems, displaying outstanding absorption

[1] (a) Thompson, B. C.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77. (b) Delgado, J. L.; Bouit, P.-A.; Filippone, S.; Herranz, M. A.; Martín, N. *Chem. Commun*. **2010**, *46*, 4853–4865. (c) Li, C.-Z.; Yip, H.-L.; Jen, A. K.-Y, *J. Mater. Chem.* **2012**, *22*, 4161–4177. (d) Lin ,Y.; Li, Y.; Zhan, X.; *Chem. Soc. Rev*. **2012**, *41*, 4245–4272.

[2] (a) Huo, L.; Zhang, S.; Guo, X.; Xu, F.; Li, Y.; Hou, J. *Angew. Chem. Int. Ed*. **2011**, *50*, 9697–9702. (b) Mishra, A.; Bäuerle, P., *Angew. Chem. Int. Ed.* **2012**, *51*, 2020–2068.

properties, are promising materials to obtain highly efficient OPV[3] and hybrid cells.[4]

In this communication, we report the synthesis and the optical and electrochemical properties of new push–pull molecules based on the 10-(1,3-dithiol-2-ylidene)anthracene core (see Scheme S1 in the Supporting Information (SI)), absorbing in a broad region of the visible spectrum. The chemical structures of the new push-pull materials have been unambiguously confirmed by single-crystal X-ray diffraction, and their electrochemical and optical properties have been characterized with the help of density functional theory (DFT) calculations. Recently, we have described the preparation of 10-(1,3-dithiol-2-ylidene)anthracene derivatives for their application in dye-sensitized solar cells.[5] Molecular engineering of this appealing core allows the design of materials with improved light-harvesting properties. The new dyes synthesized here bear the same electron-donor unit: the 10-(1,3-dithiol-2-ylidene)anthracene group, but a different conjugated π-bridge: 3,4-ethylenedioxythiophene (EDOT) for **6** or phenyl for **4** and **5**, as well as two kind of electro-accepting units: an ester group for **4** and a dicyanovinylene group for **5** and **6** (Figure 1).

The synthesis of the key synthon **1**, featuring two terminal alkyne groups (Scheme S1), was carried out in four steps with good yield.[6] The conjugated bridges were then introduced by the Sonogashira cross-coupling reaction using $PdCl_2(PPh_3)_2$ and CuI as catalysts. The introduction of the accepting units was achieved by two-fold Knoevenagel condensation of aldehydes **2**[5] and **3**[5] with malononitrile, to afford the new dyes **5** and **6** in good to moderate yields (75 and 50%, respectively, see the SI). Dye **4**, with the two decyl chains, displays excellent solubility in the main organic solvents. The structures of all the new compounds and the new sensitizers were confirmed by ^{1}H, ^{13}C NMR and High Resolution Mass Spectrometry.

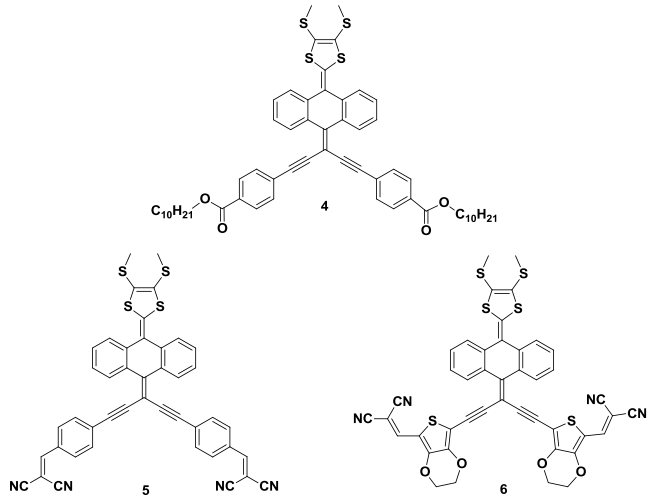


Figure 1. Push–pull systems **4**, **5**, and **6**.

Slow evaporation of chloroform solutions of **2**, **5**, and **6** allowed the obtention of single crystals suitable for its study by X-ray diffraction (Figure 2 and S7 and S8 in the SI).[7] The compounds adopt the typical butterfly- or saddle-like shape observed for exTTF (2-[9-(1,3-dithiol-2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole) derivatives.[8] The existence of several C−H···π and π···π stacking interactions plus other weaker C−H···N≡C and C−H···S hydrogen bonds led to the formation of supramolecular networks of compounds **2**, **5,** and **6**.

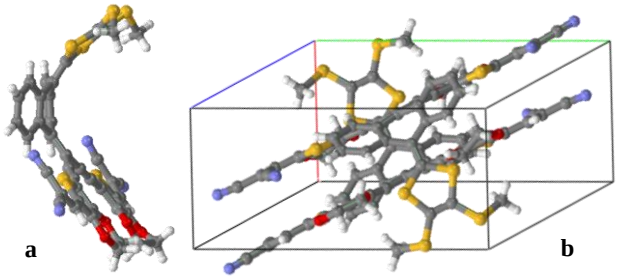


Figure 2. a) X-ray crystal structure of **6**. b) Unit cell.

The molecular geometries of the three push–pull systems were optimized using DFT calculations at the B3LYP/6-31G** level (see the SI for computational details). The decyl chains in **4** were replaced by a simple

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[4] (a) Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J. H.; Fantacci, S.; De Angelis, F.; Di Censo, D.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701–16707. (b) Wenger, S.; Bouit, P.-A.; Chen, Q.; Teuscher, J.; Di Censo, D.; Humphry-Baker, R.; Moser, J. E.; Delgado, J. L.; Martín, N; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2010**, *132*, 5164–5169.

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[6] Chen, G.; Wang, L.; Thompson, D. W.; Zhao, Y. *Org. Lett.* **2008**, *10*, 657–660.

[7] CCDC 900353 (**2**) , CCDC 890337 (**5**), and CCDC 890785 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

[8] Batsanov, A. S.; Bryce, M. R.; Coffin, M. A.; Green,; A.; Hester, R. E.; Howard, J. A. K.; Lednev, I. K.; Martín, N.; Moore, A. J.; Moore, J. N.; Ortí, E.; Sánchez, L.; Savirón, M.; Viruela, P. M.; Viruela, R.; Ye, T.-Q. *Chem. Eur. J.* **1998**, *4*, 2580–2592.

methyl group to simplify the calculation. As obtained from X-ray analysis, theoretical calculations predict concave saddle-like structures, in which the central ring of the anthracene unit folds up in a boat conformation and the dithiole rings are tilted down. The planes defined by the external benzene rings of the anthracene unit are predicted to form an angle of 40.5º for **5** and 38.6º for **6** slightly underestimating the angles obtained by X-ray diffraction (36.2 and 34.5º, respectively) due to the packing forces present in the crystal that tend to reduce the folding. The dihedral angles of 35.5º computed for the dithiole tilting in **5** and **6** nicely fit the X-ray values of 34.2º (**5**) and 34.1º (**6**). Same considerations apply for the tilting of the acceptor moiety (see Table S1 in the SI). The acceptor arms remain mostly planar in all dyes thus favouring the π-electron communication along the acceptor moiety. This planarity is even more pronounced in the crystal due to the efficient π–π coplanar interactions in the packing (see Figure 2b and Table S1).

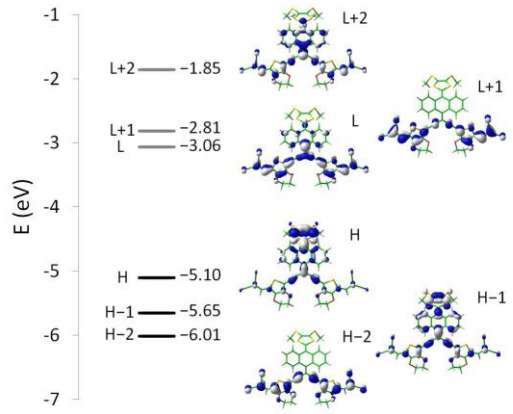

Figure 3. Electron-density contours (0.03 e bohr^{-3}) and orbital energies calculated for the frontier molecular orbitals of **6** at the B3LYP/6-31G** level. H and L denote HOMO and LUMO, respectively.

Figure 3 shows the atomic orbital (AO) composition of the highest-occupied (HOMO−2 to HOMO) and lowest-unoccupied (LUMO to LUMO+2) molecular orbitals of **6**, as a representative example, The HOMO (−5.10 eV) and HOMO−1 (−5.65 eV) are localized on the electron-donor 10-(1,3-dithiol-2-ylidene)anthracene unit, hereafter named hemi-exTTF, whereas the HOMO−2 (−6.01 eV) spreads over the electron-acceptor moiety with no participation of hemi-exTTF. The LUMO (−3.06 eV) and LUMO+1 (−2.81 eV) are located on the electron-acceptor arms and the LUMO+2 (−1.85 eV) comprises both the hemi-exTTF moiety and the acceptor fragment. Identical topologies are predicted for the frontier molecular orbitals of **4** and **5** (see Figure S10). A pronounced stabilization of the LUMO is predicted in passing from **4** (−2.46 eV) to **5** (−3.01 eV) and **6** (−3.06 eV) due to the higher electronegative character of the dicyanovinylene group compared to the ester unit. The presence of the electron-donor EDOT fragment in **6** slightly increases the energy of the HOMO (−5.10 eV) compared to **5** (−5.17 eV). Theoretical calculations therefore predict small HOMO−LUMO energy gaps of −2.64, −2.16, and −2.04 eV for **4**, **5**, and **6**, respectively, and suggest the presence of low-energy charge-transfer (CT) absorption bands in the electronic spectrum.

The redox properties of **4**–**6** were examined by cyclic voltammetry (CV) (Table 1). The anodic region of dye **4** is characterized by one reversible wave ($E°_{ox}$ = 0.27 V) attributed to the hemi-exTTF unit, whereas no reduction is observed in the experimental conditions. The presence of the stronger electro-accepting dicyanovinylene groups in **5** shifts the reduction potential to −1.31 V, whereas the oxidation potential is only weakly affected ($E°_{ox}$ = 0.29 V). This trend nicely correlates with the slight stabilization of the HOMO (0.07 eV) and the significant stabilization of the LUMO (0.55 eV) predicted by theoretical calulations in passing from **4** to **5** (Figure S10). The presence of the auxiliary electron-donor EDOT groups in **6** slightly reduces the oxidation ($E°_{ox}$ = 0.25 V) and reduction ($E°_{red}$ = −1.26 V) potentials. CV measurements therefore obtain a decrease of the electrochemical gap along the series **4** (> 2.07 V), **5** (1.60 V), and **6** (1.51 V), which is in perfect agreement with theoretical predictions and with the trend observed from optical data (see below).

Table 1. Electrochemical and optical data for **4**–**6.**

Compd	$E°_{ox}$ (V)[a]	$E°_{red}$ (V)[a]	E_g^{cv} (V)[b]	λ_{max} (nm)[c]	ε (L·mol^{-1}·cm^{-1})
4	0.27	<–1.80	>2.07	491	19000
5	0.29	–1.31	1.60	536	14000
6	0.25	–1.26	1.51	590	19000

[a] Measured by CV (CH_3CN, 0.1 M Bu_4ClO_4, v = 100 mV·s^{-1}, V vs. $Ag/AgNO_3$). [b] Electrochemical gap determined as $E_{ox} - E_{red}$. [c] Measured in DCM, 10^{-5} mol·L^{-1}.

The absorption properties of compounds **4**–**6** were measured in dichloromethane solution (Figure 4a). **4** displays two main absorption bands in the UV and the visible range (λ_1 = 364 nm; λ_2 = 491 nm). Both transitions are red-shifted, first when a better acceptor is inserted in the molecule (**5**, λ_1 = 366 nm; λ_2 = 536 nm), then with the presence of the EDOT units (**6**, λ_1 = 443 nm; λ_2 = 590 nm). As expected, a decrease of the optical bandgap is observed when the push–pull effect in the compound is reinforced.

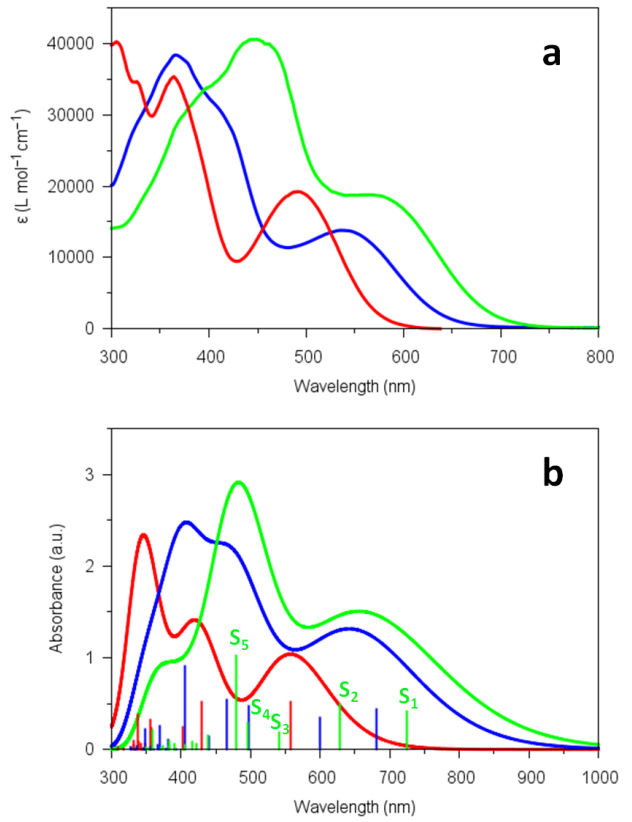

Figure 4. a) Absorption spectra of **4** (red) **5** (blue), and **6** (green) recorded in dichloromethane at room temperature. b) Theoretical simulation of the UV-Vis absorption spectra for push-pull compounds **4**–**6**. Vertical lines indicate the vertical excitation energies and oscillator strengths calculated for the electronic transitions to the different singlet excited states S_n. States S_1 to S_5 are explicitly denoted for compound **6**.

To investigate the nature of the electronic transitions that give rise to the absorption bands observed in the electronic spectra, the lowest-energy singlet excited states (S_n) were calculated for **4**–**6** using the time-dependent DFT (TDDFT) approach. TD-DFT calculations predict that the lowest-energy absorption band observed for **5** and **6** above 500 nm is due to electronic transitions to the first two excited singlets S_1 and S_2 (see Table S2 and Figure 4b). These states originate from the HOMO→LUMO and HOMO−1→LUMO monoexcitations, respectively, and imply an electron density transfer from the hemi-exTTF moiety, where the HOMO and HOMO−1 reside, to the acceptor moiety, where the LUMO is mainly located (Figure 3). In compound **4**, S_2 stands higher in energy (2.89 eV) due to the higher energy of the LUMO+1 (Figure S10) and does not contribute to the lowest-energy band at 491 nm (Figure 4b). Calculations therefore confirm the CT nature of the lowest-energy absorption band of **4**–**6**. The moderately high intensities observed for this band are in agreement with the oscillator strengths (*f*) around 0.4−0.5 calculated for S_1 and S_2 (Table S2), and are due to the significant overlap between the HOMO/HOMO−1 and the LUMO.

The intense absorption band observed at higher energies mainly results from the HOMO−2→LUMO excitation (state S_6 for **5** and S_5 for **6**, Table S2 and Figure 4b), which mainly implies the electron-acceptor part of the molecule (Figure 3). This electronic transition is predicted to have a high intensity (f ~ 1.00) and shifts to lower energies in passing from **5** to **6** due to the EDOT groups that destabilize the HOMO−2 from −6.46 (**5**) to −6.01 eV (**6**). For compound **4**, the transition is calculated to show a lower intensity (f = 0.33) in good agreement with the experimental spectra (Figure 4a). The HOMO→LUMO+2 excitation involving the hemi-exTTF moiety and the CT HOMO−1→LUMO and HOMO−1→LUMO+1 excitations also contribute to this intense absorption band (Table S2).

In summary, a series of push–pull chromophores has been synthesized and fully characterized. The new chromophores possess a broad optical absorption, being dye **6** the best light harvester covering the visible spectrum from 300 to 750 nm. The broad absorption is due to the efficient electronic connection between the donor and acceptor units, which determines the appearance of high-intensity charge-transfer bands extending into the near-infrared. These low bandgap molecules may be used as new molecular materials in the field of photovoltaics.[9] Molecular engineering is currently in progress in the laboratory in order to take advantage of the outstanding optical properties of these compounds in molecular bulk heterojunction devices.[10]

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Supporting Information Available Synthetic procedure, chemical characterization, X-ray structures, and computational details (geometrical data and TD-DFT results). This material is available free of charge via the Internet at http://pubs.acs.org.

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