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Donor-π-Acceptors Containing the 10-(1,3-Dithiol-2-ylidene)anthracene Unit for Dye-Sensitized Solar Cells

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Dedicated to Professor Thomás Torres on the occasion of his 60th birthday

Abstract: Two donor–acceptor molecular tweezers incorporating the 10-(1,3-dithiol-2-ylidene)anthracene unit as donor group and two cyanoacrylic units as accepting/anchoring groups are reported as metal-free sensitizers for dye-sensitized solar cells. By changing the phenyl spacer with 3,4-ethylene-dioxythiophene (EDOT) units, the absorption spectrum of the sensitizer is red-shifted with a corresponding in-

crease in the molar absorptivity. Density functional calculations confirmed the intramolecular charge-transfer nature of the lowest-energy absorption bands. The new dyes are highly distorted from planarity and are bound to the

Keywords: absorption • dyes/pigments • optical properties • sensitizers • solar cells TiO_2 surface through the two anchoring groups in a unidentate binding form. A power-conversion efficiency of 3.7% was obtained with a volatile CH₃CN-based electrolyte, under air mass 1.5 global sunlight. Photovoltage decay transients and ATR-FTIR measurements allowed us to understand the photovoltaic performance, as well as the surface binding, of these new sensitizers.

Introduction

The increasing global energy demand has emerged as one of the key issues that need to be addressed, because this consumption enhances the depletion of fossil fuel reserves and leads to further aggravation of environmental pollution. A rational alternative to overcome this dependence on fossil fuels and their inherent pollution is the use of renewable energy sources, such as solar energy. In this context, dye-

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sensitized solar cells (DSCs) are amongst the best alternatives for exploiting solar energy and, therefore, the development of new organic dyes for the preparation of efficient DSCs is of utmost importance, as well as being a challenging research topic. Thus far, a few examples of DSCs that lead to power-conversion efficiencies (PCEs) of 11% have been reported;^[1] however, further research is needed to improve the PCE and the stability of such devices.

Within the field of organic sensitizers, a large variety of organic dyes have been reported,^[2] including coumarins,^[2a] indolines,^[2b] tetrahydroquinolines,^[2c] hemicyanines,^[2d] boron-dipyrromethenes,^[2e] oligothiophenes,^[2f] triarylamines,^[2g] and anthracenes and heteroanthracenes.^[2h] Recently, we introduced the use of π -extended tetrathiafulvalene (exTTF, 2-[9-(1,3-dithiol-2-ylidene)anthracen-10-(9 H)-ylidene]-1,3-dithiole)^[3] as a donor unit in a sensitizer (**1**, Figure 1) for the preparation of DSCs that exhibit efficient photovoltaic conversion, as well as unusual electrochemical and kinetic prop-



Figure 1. A previously reported exTTF-based sensitizer for DSCs (1) and a push-pull chromophore based on the 10-(1,3-dithiol-2-ylidene) anthracene core (2).

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erties.^[4] The donor ability of the exTTF unit increases the HOMO level of the organic dye and significantly lowers the required energy for the regeneration of the dye by the electrolyte to 150 mV. Stimulated by these results, we decided to explore the closely related 10-(1,3-dithiol-2-ylidene)anthracene group as an appealing electron-donor unit for the preparation of efficient DSCs.

Figure 1 shows the structure of a push-pull chromophore (2), which incorporates the 10-(1,3-dithiol-2-ylidene)anthracene electron-donor unit.^[5] Interestingly, molecule 2 is highly distorted from planarity owing to strong S…H steric repulsions, which is crucial for preventing dye aggregation. In addition, compound 2 shows strong UV/Vis absorption owing to the efficient intramolecular charge transfer (ICT) transition that takes place from the donor to the acceptor unit upon excitation. Molecular engineering by using the 10-(1,3-dithiol-2-ylidene)anthracene core allows the design of dyes that contain two anchoring groups; this feature was previously shown to enhance the performance and the stability of photovoltaic (PV) devices.^[6]

Taking all of these precedents into account, we designed two new push-pull sensitizers (6 and 7) that were based on the 10-(1,3-dithiol-2-ylidene)anthracene core, as electrondonor group, with two cyanoacrylic acid units, as acceptor/ anchor groups. To modulate the optical-absorption properties, each sensitizer contained a different π bridge between the donor group and the anchoring units: benzene rings in compound 6 and 3,4-ethylenedioxythiophene (EDOT) units in compound 7. EDOT spacers have previously been used for red-shifting the spectroscopic response and enhancing the molar extinction coefficient of triphenylamine and exTTF-based sensitizers.^[2g,4,7] Theoretical calculations have been carried out at the level of density functional theory (DFT) to gather information about the geometrical and electronic properties of these new sensitizers. Their photovoltaic potential in DSCs has been investigated by using J-Vmeasurements. The differences between the performances of these two molecules were scrutinized by using the transient-photovoltage technique. This technique supported the existence of enhanced recombination processes within devices that were functionalized by compound 7.

Results and Discussion

Synthesis: The synthesis of the two new sensitizers was accomplished according to a multistep synthetic procedure (for experimental details, see the Supporting Information). Intermediate **3**, which featured two terminal alkyne groups (Scheme 1), was synthesized in four steps in good yield according to a modified literature procedure.^[9]

The conjugated bridges were introduced by means of the Sonogashira cross-coupling reaction with $[PdCl_2(PPh_3)_2]$ and CuI as catalysts. Thus, the reaction of compound **3** with either 4-iodobenzaldehyde or 7-bromo-3,4-ethylenedioxy-thiophene-5-carbaldehyde^[XXX] afforded compounds **4** and **5** in moderate yields (both 50%). The introduction of the ac-



Scheme 1. Synthesis of new sensitizers 6 and 7; reagents and conditions: a),b) $[PdCl_2(PPh_3)_2]$, CuI, THF/Et₃N 4:1, reflux overnight; c),d) cyanoacetic acid, NH₄(CH₃COO), CH₃COOH, reflux overnight.

ceptor/anchor units was achieved by the twofold Knoevenagel condensation of aldehydes **4** and **5** with cyanoacetic acid to afford the new sensitizers (**6** and **7**) in moderate yields (40 and 64%, respectively). The structures of all of the new compounds, were confirmed by ¹H and ¹³C NMR spectroscopy.

Optical and electrochemical properties: The optical properties of sensitizers **6** and **7** were studied by UV/Vis spectroscopy. The absorption spectra of both compounds display two absorption bands (Figure 2). The first band, with



Figure 2. UV/Vis absorption spectra of sensitizers 6 (solid line) and 7 (dotted line) in dilute DMSO solution $(2 \times 10^{-5} \text{ M})$.

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maxima at 354 nm and 440 nm for compounds 6 and 7, respectively, is in the region of the π - π * transitions of the anthracene core.^[5] The weaker, broad band in the visible region, with absorption maxima at 495 and 540 nm for compounds 6 and 7, respectively, is assigned to an ICT transition from the donor to the acceptor moieties.^[5] As expected, extending the conjugation with EDOT in compound 7 allowed a red-shift of the absorption up to 700 nm. Compared to the previously reported exTTF sensitizers, which mainly absorb in the 400–500 nm region,^[4] this extension represents a significant improvement in the optical properties of the sensitizer.

Electrochemical characterization of the new dyes was performed by using cyclic voltammetry and differential pulse voltammetry in DMF. Both molecules show reversible redox behavior. According to the optical measurements, a decrease of the gap is observed when the phenyl spacer in $\mathbf{6}$ is replaced by the EDOT in $\mathbf{7}$ (Table 1), The oxidation potential for both compounds (Table 1), which is related to their

Table 1. Redox potentials and experimental/theoretical HOMO-LUMO energy gaps (E_g) for dyes 6 and 7.

Dye	$E_{ m ox}$ $[V]^{[a]}$	$E_{ m red} \ [{ m V}]^{[a]}$	$E_{\rm g}({ m elect})$ $[{ m eV}]^{[{ m b}]}$	$E_{\rm g}({ m opt})$ $[{ m eV}]^{[{ m c}]}$	$E_{\rm g}({ m DFT})$ $[{ m eV}]^{[{ m d}]}$
6	0.25	-1.76	2.01	2.10	2.25
7	0.23	-1.69	1.92	1.95	2.11

[a] Values determined by differential pulse voltammetry in DMF versus Fe⁺/Fe. [b] Estimated as $E_{\rm ox}-E_{\rm red}$. [c] Taken as the intersection of the absorption and emission spectra. [d] Obtained from DFT calculations (B3LYP/6-31G^{**}) in DMF.

HOMO, is around 0.25 V versus the ferrocenium/ferrocene (Fc⁺/Fc) couple and is sufficiently more-positive than the redox potential of the I^-/I_3^- electrolyte (-0.21 V versus Fc⁺/Fc in an ionic liquid)^[10] for efficient dye-regeneration. The reduction potential of the dyes, which is related to their LUMO, is considerably more-negative than the TiO₂ conduction band, thereby providing enough of a driving force for electron-injection.

ATR-FTIR studies: The surface-binding mode of the sensitizer on titania is an interesting aspect for investigation, because two anchoring groups are present in dyes 6 and 7, which may allow these dyes to attach onto the semiconductor surface through either one or both anchoring groups. ATR-FTIR measurements that were performed on the dye powders and on the sensitized films (Figure 3 and Figure 4) revealed that, most likely, both dyes 6 and 7 were bound to the surface through both anchoring groups. In the ATR-FTIR spectra of the dye powders, the peaks at 1680-1720 cm⁻¹ are attributed to the carboxylic acid groups. The spectra for the dyes adsorbed onto transparent TiO₂ films did not contain these peaks; this result indicates that both anchoring groups form bonds with the surface of titania. Moreover, the symmetric stretching modes of the carboxylate groups can be identified at $1340-1380 \text{ cm}^{-1}$ and the



Figure 3. FTIR spectra of dye **6** as a powder (dotted line) and adsorbed onto a transparent TiO_2 layer (solid line); the spectra were corrected for residual CO₂, surface-adsorbed water, and TiO₂ itself.



Figure 4. FTIR spectra of dye 7 as a powder (dotted line) and adsorbed onto a transparent TiO_2 layer (solid line); the spectra were corrected for residual CO_2 , surface-adsorbed water, and TiO_2 itself.

asymmetric stretching mode can be observed at about 1600 cm^{-1} . The position of these frequencies is consistent with the unidentate form of binding of the carboxylate to the TiO₂ surface.^[11]

Theoretical calculations: The molecular geometries of the two dyes were fully relaxed, both as isolated systems and in the presence of the solvent, by using DFT calculations that were performed at the B3LYP/6-31G** level. Among the various possible conformations, owing to internal rotation and to the relative orientation of the cyanoacrylic acid groups (see the Supporting Information, Figures S7 and S8), Figure 5 shows the calculated minimum-energy structures for dyes **6** and **7** that favored the unidentate anchoring of both carboxylate groups. As shown in Figure 5b, for dye **6**, the molecule adopts the typical butterfly- or saddle-like shape that is observed for exTTFs.^[5,12,13] To relieve the short-range interactions of the *peri* hydrogen atoms of the anthracene core with both the sulfur atoms of the dithiol





Figure 5. Optimized B3LYP/6-31G** structures: a) front view and b) side view of dye 6, which show the distortion from planarity, and c) dye 7.

ring and the carbon atoms of the acetylene units, the central ring of the anthracene unit folds in a boat conformation along the C9–C10 vector by an average angle of 36.9° for both dyes **6** and **7** in the gas phase. This value is very similar to that determined by X-ray crystallography for tetramethylthio–exTTF (38°),^[5] for which an almost identical value (38.3°) was calculated at the B3LYP/6-31G** level.^[13] The dithiol ring and the diacetylene unit are tilted by 33.3 and 31.9°, respectively, with respect to the plane that is defined by anthracene atoms C11–C12–C13–C14. Almost-identical tilting angles were computed for compound **7** (34.0 and 31.2°, respectively). Therefore, the molecular structures of dyes **6** and **7** are highly distorted from planarity, which helps to prevent molecular aggregation.

Figure 6 shows the atomic orbital (AO) composition of the highest occupied (HOMO-2 to HOMO) and lowest unocupied (LUMO and LUMO+1) molecular orbitals calcu-



Figure 6. Electron-density contours $(0.025 \text{ ebohr}^{-3})$ and orbital energies for the HOMOs and LUMOs of dye **6** calculated in DMF at the B3LYP/ 6-31G** level. H and L denote the HOMO and LUMO, respectively.

lated for dye 6 in DMF. Identical MO topologies are obtained for the isolated dye in the gas phase. The HOMO (-5.14 eV) is mainly localized on the electron-donor dithiol unit and is calculated at lower energy than the HOMO of the tetramethylthio-exTTF molecule (-4.90 eV), which contains two dithiol units.^[14] The HOMO-1 (-5.75 eV) spreads over the dithiol and the diacetylene units and is separated by 0.64 eV from HOMO-2 (-6.39 eV), which is fully localized over the acceptor part of the molecule. The LUMO (-2.89 eV) and LUMO+1 (-2.63 eV) levels are close in energy and correspond to the symmetric and antisymmetric combination of the LUMOs of the two molecular arms that constitute the acceptor moiety, respectively. An equivalent MO distribution is obtained for molecule 7. Therefore, dyes 6 and 7 present small HOMO-LUMO energy gaps of 2.25 and 2.11 eV, respectively, and low-energy charge-transfer (CT) absorption bands are expected, in agreement with that observed in the electronic spectra (Figure 2).

The nature of the HOMO and LUMO indicates that oxidation should mainly affect the dithiole moiety, whereas reduction concerns the acetylene/benzene/cyanoacrylic-acid units (Figure 6). DFT calculations support the observed experimental trends for the redox potentials (Table 1): On passing from dye 6 to dye 7, the HOMO increases in energy slightly from -5.14 to -5.10 eV, which is in good agreement with the small cathodic shift of 0.02 V that is observed experimentally for the first oxidation potential. In contrast, the LUMO decreases in energy from -2.89 eV (6) to -2.99 eV (7), which justifies the less-negative reduction potential for dye 7 (-1.69 V) compared with dye 6 (-1.76 V). The shift of the HOMO to higher energy and of the LUMO to lower energy leads to a narrowing of the HOMO-LUMO gap on going from compound 6 (2.25 eV) to compound 7 (2.11 eV), which is in good accordance with the electrochemical (6: 2.01 eV; 7: 1.92 eV) and spectroscopic estimates (**6**: 2.10 eV; **7**: 1.95 eV).

To investigate the nature of the electronic transitions that give rise to the absorption bands in the electronic spectra, the lowest-energy singlet-excited states (S_n) of dyes 6 and 7 were calculated by using the time-dependent DFT (TDDFT) approach and the B3LYP/6-31G**-optimized ground-state geometries. The TDDFT calculations predict that the low-energy absorption band that is observed experimentally at 495 nm (2.50 eV) for dye 6 and at 540 nm (2.30 eV) for dye 7 (Figure 2) mainly results from the electronic transition to the first excited singlet state (S_1) at 2.12 eV (6) and 1.94 eV (7) with oscillator strengths (f) of 0.34 and 0.54, respectively. The calculated $S_0 \rightarrow S_1$ transition supports both the shift to the red and the higher intensity of the low-enery absorption band for 7. The second excited singlet state (S_2) , which is computed at slightly higher energy (6: 2.34 eV, f=0.26; 7: 2.25 eV, f=0.16), could also contribute to that band. The S_1 and S_2 states originate from the HOMO-JLUMO and HOMO-JLUMO+1 monoexcitations, respectively, and imply an electron-density transfer from the dithiol moiety, where the HOMO mainly resides, to the acceptor part of the molecule, where the LUMO and LUMO+1 are located (Figure 6). Therefore, the calculations confirm the CT nature of the low-energy absorption band in the electronic spectra of the new dyes (6 and 7). The higher intensity that was experimentally observed and theoretically calculated for this band in compound 7 can be ascribed to the better electronic communication existing between the donor and acceptor units through the EDOT bridge. The high-energy absorption band that was recorded in the spectra of 6 and 7 (Figure 2) results from the excited states that are associated with the HOMO-2→LUMO excitation, which is localized on the acceptor part of the molecule, and the HOMO-1→LUMO and LUMO+1 excitations, which also imply some intramolecular electron-density transfer (Figure 6).

The calculations clearly show that molecules **6** and **7** become more polarized in the S_1 state (see the molecular electrostatic potentials calculated for **6** in Figure S11). The acceptor part of dye **6** accumulates a charge of -0.54e in the S_1 state, which is extracted from the anthracene moiety (+0.31 e) and the dithiol unit (+0.23 e). The charge transfer that is associated with the S_1 state is also reflected by the computed value for the molecular dipole moment, which increases from 1.41 D in S_0 to 12.94 D in S_1 . The charge that is transferred from the donor unit to the acceptor unit in the S_1 state is slightly smaller for dye **7** (acceptor unit: -0.43e; anthracene moiety: +0.27e; dithiol unit: +0.16e). The polarization of the dye in the excited S_1 state facilitates the electron injection in the semiconductor TiO₂ surface.

Photovoltaic performance: The photovoltaic performance of dyes **6** and **7** was tested with a volatile CH_3CN -based electrolyte and a solvent-free ionic-liquid electrolyte. Device-fabrication methods and -conditions, as well as the compositions of the electrolytes, are described in the Experimental Section.

The J-V curves for the volatile systems are shown in Figure 7. The devices that were sensitized with dye **6** showed improved photovoltaic performance, owing to higher J_{sc} and V_{oc} values. This result seems somewhat surprising because the absorption spectra of the dyes, either in solution (Figure 2) or adsorbed on a transparent TiO₂ layer (Figure 8), show a better spectroscopic response for dye **7**. The bathochromic shift of 40 nm, which is accompanied by a significant broadening of the spectra on the film, would suggest a better performance for the device that contained compound **7**. However, the J_{sc} value is $1.3-2.5 \text{ mA cm}^{-2}$ lower, depending on the electrolyte used, than that obtained for the device that contained dye **6**. Detailed photovoltaic parameters of both devices are given in Table 2.

The absorption spectrum of dye **6** adsorbed onto the titania surface is notably broadened in the complete device (filled with electrolyte). The incident photon-to-current-conversion efficiency (IPCE) spectra of the complete devices are also shown in Figure 8. The integrated current that was obtained from the IPCE spectrum of the device that contained dye **7** (35%) was significantly smaller than that measured for the device that incorporated dye **6** (60%). This



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Figure 7. J-V plots of the DSCs that were sensitized with dyes 6 (black) and 7 (gray) measured under 1 sun (AM 1.5G, 100 MW cm⁻²) conditions (solid line) and in the dark (dashed line).



Figure 8. Comparison of the absorption spectra of dyes **6** (black) and **7** (gray), which were adsorbed onto a transparent 1.9 μ m TiO₂ film (dashed line, right axis), and the IPCE spectra of the devices with a 5.5 μ m TiO₂ layer (solid line, left axis).

Table 2. Photovoltaic parameters of devices with volatile- and ionicliquid electrolytes under simulated AM 1.5G illumination (100 mW cm^{-2}) .

`	/				
Dye	Electrolyte	$J_{\rm sc} [{ m mAcm^{-2}}]$	$V_{\rm oc} [{ m V}]$	FF	η [%]
6	Z960	8.8	0.56	0.75	3.7
	Z952	7.4	0.52	0.71	2.8
7	Z960	6.3	0.50	0.70	2.2
	Z952	6.1	0.49	0.70	2.1

result is consistent with the lower current densities as measured from the J-V curves for the device that contained dye 7 (Figure 7 and Table 2). To calculate the amount of dye that was adsorbed onto the surface of TiO₂, we stained transparent 2 µm-thick films with the dyes and measured their optical density by using UV/Vis spectroscopy. By using

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the Lambert–Beer law, we calculated the concentration of the dye within this 2 μ m-thick volume, assuming that the film porosity and the surface area were exactly the same for all of the samples. This result enabled us to compare the calculated concentrations: 150 mM for dye **6** and 158 mM for dye **7**. Because the dye-loading results show that there is no difference between the number of molecules that effectively sensitize the semiconductor, the differences between the performances of devices based on dyes **6** and **7** should originate from other factors that affect the processes in the cell, such as charge recombination.

In addition to the above-observed difference in the J_{sc} value, there is also a substantial difference between the V_{oc} values of the two devices: at 1 sun illumination, the V_{oc} value for the cell that is sensitized with dye **6** is 60 mV (Z960 electrolyte) higher than that with dye **7**. This difference is even-more-pronounced when comparing the dark currents: the logarithmic plot of the dark currents of both devices (Figure 9) reveals that there is a tenfold difference



Figure 9. Dark currents of the DSCs that incorporated dyes 6 (solid line) and 7 (dotted line), which show the undesired behavior ("leak") of the dark current in the case of the device that was sensitized with dye 7, thus indicating the presence of additional channels for recombination.

between the currents, which can be interpreted as a sign of enhanced charge-recombination in the device that is sensitized with dye 7. To investigate this behavior, transient photovoltage-decay measurements were performed on both devices. The apparent electron lifetimes, which were measured at the same density of states level, were much shorter for the DSCs that incorporated dye 7 (Figure 10). By assuming that the position of TiO₂ conduction band remains at the same level in both cases, these results support the previous suggestion that a much-faster recombination takes place in the device that is sensitized with dye 7 and explains the lower photovoltaic performances that are obtained when using this dye.



Figure 10. Apparent electron lifetime plotted against the density of states for DSCs that contained dyes $6 (\bullet)$ and $7 (\bullet)$.

Conclusions

Herein, we focused on the investigation of the synthesis, characterization, and applications of new dye molecules that were based on the 10-(1,3-dithiol-2-ylidene)anthracene core. These molecules were designed to improve their spectroscopic response, thereby making them more attractive for incorporation into DSCs. The insertion of EDOT into their structure led to an extension of the absorption spectrum of the dye up to 700 nm, which, in comparison with previously reported analogous molecules, gave an additional 200-300 nm of red-shift. FTIR measurements revealed that both dyes are bound to the TiO₂ surface through the two anchoring groups in a unidentate binding form. The preferable conformations that were obtained from DFT calculations support this binding and showed that the molecular geometry is highly distorted from planarity owing to the saddle-likeshaped exTTF-like core, with the anthracene unit being folded into a boat-type structure. Owing to this spatial arrangement, less aggregation is expected. Optical and electrochemical characterization of these new materials satisfied the criteria for their successful incorporation into photovoltaic devices. The highest efficiency (3.7%) in which the IPCE was stretched out beyond 700 nm, was obtained for the device that contained dye 6. Dye 7, which is an EDOTcontaining molecule, despite exhibiting a slightly broader UV/Vis spectrum, was inferior to the phenyl-substituted dye in terms of overall PV performance. The main reason for this lower overall PV performance for dye 7 is its higher recombination rate, as witnessed by a higher dark current and a shorter electron-lifetime.

Experimental Section

General: NMR spectra (¹H, ¹³C) were recorded at RT on a Bruker DPX 300 MHz spectrometer. Data are listed in parts per million (ppm) and are reported relative to tetramethylsilane; residual solvent peaks were used as an internal standard (CDCl₃; ¹H: 7.26 ppm, ¹³C: 77.36 ppm). High-resolution mass spectrometry measurements were performed at the Unidad de Espectrometría de Masas of the Universidad Complutense de Madrid. Column chromatography was performed on Merck 60 (40-63 µm) silica gel. UV/Vis spectra were recorded on a Varian Cary 50 spectrometer at a constant temperature of 25°C in dilute DMSO solution (about $10^{-5} \text{ mol } L^{-1}$).

Synthesis: Synthesis of compound 4: 3 (240 mg, 0.55 mmol, 1 equiv) and p-iodobenzaldehyde (385 mg, 3 equiv) were dissolved in THF/NEt₃ (30 mL, 4:1). Then, the solution was degassed for 20 min and [PdCl₂-(PPh₃)₂] (39 mg, 0.1 equiv) and CuI (20 mg, 0.2 equiv) were added, and the solution was refluxed overnight. After cooling down to RT, the mixture was filtrated and washed with CH2Cl2. The organic layer was washed with saturated NH₄Cl solution and water, dried over MgSO₄, and the solvents were evaporated. The crude mixture was purified by column chromatography on silica gel (eluent: CH₂Cl₂) to afford 4 as a red solid (170 mg, 50%). ¹H NMR (300 MHz, CDCl₃): $\delta = 2.41$ (s, 6H), 7.37 (ddd, ${}^{3}J=7.5$ Hz, ${}^{3}J=7.5$ Hz, ${}^{4}J=1.5$ Hz, 2H), 7.45 (ddd, ${}^{3}J=7.5$ Hz, ${}^{3}J=7.5$ 7.5 Hz, ${}^{4}J = 1.5$ Hz, 2H), 7.62 (d, ${}^{3}J = 8$ Hz, 4H), 7.69 (dd, ${}^{3}J = 7.5$ Hz, ${}^{4}J =$ 1.5 Hz, 2 H), 7.86 (d, ${}^{3}J = 8$ Hz, 4 H), 8.35 ppm (dd, ${}^{3}J = 7.5$ Hz, ${}^{4}J = 1.5$ Hz, 2H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 19.2$, 92.2, 92.8, 98.7, 122.4, 125.3, 125.8, 126.3, 127.6, 128.4, 129.3, 129.6, 132.0, 132.7, 134.1, 135.6, 135.7, 148.9, 191.3 ppm; MS (ESI): m/z calcd for $C_{38}H_{24}O_2S_4 + Na^+$: 663.1 $[M+Na]^+$; found: 633.1; IR (KBr): $\tilde{\nu}_{C=0} = 1696 \text{ cm}^{-1}$.

Synthesis of compound 5: 3 (350 mg, 0.81 mmol, 1 equiv) and 7-bromo-3,4-ethylenedioxythiophene-5-carbaldehyde (605 mg, 3 equiv) were dissolved in THF/NEt₃ (50 mL, 4:1). Then, the solution was degassed for 20 min and [PdCl₂(PPh₃)₂] (56 mg, 0.1 equiv) and CuI (28 mg, 0.2 equiv) were added, and the solution was refluxed overnight. After cooling down to RT, the mixture was filtrated and washed with CH2Cl2. The organic layer was washed with saturated NH₄Cl solution and water, dried over MgSO₄, and the solvents were evaporated. The crude mixture was purified by column chromatography on silica gel (eluent: CH2Cl2/ethyl acetate 9:1) and then recrystallized in methanol to afford 5 as a red solid (170 mg, 50%). ¹H NMR (300 MHz, CDCl₃): $\delta = 2.43$ (s, 6H), 4.40 (m, 8H), 7.33 (ddd, ${}^{3}J=7.5$ Hz, ${}^{3}J=7.5$ Hz, ${}^{4}J=1.5$ Hz, 2H), 7.44 (ddd, ${}^{3}J=$ 7.5 Hz, ${}^{3}J=7.5$ Hz, ${}^{4}J=1.5$ Hz, 2H), 7.66 (dd, ${}^{3}J=7.5$ Hz, ${}^{4}J=1.5$ Hz, 2H), 8.33 (dd, ³*J*=7.5 Hz, ⁴*J*=1.5 Hz, 2H), 9.91 ppm (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ=19.7, 65.2, 65.5, 84.4, 98.6, 99.8, 109.3, 119.0, 123.0, 125.6, 126.4, 126.7, 128.0, 128.8, 132.8, 134.5, 135.8, 144.6, 147.8, 148.8, 180.0 ppm; MS (MALDI): m/z calcd for $C_{38}H_{24}O_6S_6$: 767.990 $[M]^+$; found: 767.878; IR (KBr) $\tilde{\nu}_{C=O} = 1654 \text{ cm}^{-1}$.

Synthesis of compound 6: 4 (100 mg, 0.15 mmol, 1 equiv) was dissolved in glacial acetic acid (5 mL), and then cyanoacetic acid (133 mg, 10 equiv) and ammonium acetate (100 mg) were added. The solution was refluxed for 6h and precipitated in cold water. The solid was filtrated, dissolved in CH₂Cl₂, washed with water, and diluted in a solution of hydrochloric acid. The organic layer was dried with MgSO4 and evaporated. The crude mixture was then dissolved in a minimum quantity of CH2Cl2 and precipitated in pentane to afford 6 as a dark brown solid (50 mg, 40%). ¹H NMR (300 MHz, [D₆]DMSO): $\delta = 2.40$ (s, 6H), 7.50–7.60 (m, 4H), 7.65–7.70 (m, 6H), 8.08 (d, ${}^{3}J=8$ Hz, 4H), 8.30–8.40 ppm (m, 4H); $^{13}\mathrm{C}\,\mathrm{NMR}$ (75 MHz, CDCl₃): $\delta\!=\!18.3,$ 79.1, 91.5, 92.5, 98.1, 104.6, 115.9, 118.4, 121.7, 121.8, 125.1, 125.8, 126.5, 127.3, 128.1, 128.8, 128.9, 130.8, 131.6, 131.8, 131.9, 133.4, 134.5, 147.8, 152.8, 163.0 ppm; UV/Vis: λ (ε) = 354 (40000), 440 nm (14000); HRMS (MALDI): m/z calcd for C₄₄H₂₆N₂0₂S₄: 774.077 $[M]^+$; found: 774.051; IR (KBr): $\tilde{\nu}_{C=0} = 1711$, $\tilde{\nu}_{\text{C=N}} = 2183, \, \tilde{\nu}_{\text{COO-H}} = 3000 \, \text{cm}^{-1}.$

Synthesis of compound 7: 5 (100 mg, 0.13 mmol, 1 equiv) was dissolved in glacial acetic acid (5 mL), and then cyanoacetic acid (110 mg, 10 equiv) and ammonium acetate (100 mg) were added. The solution was refluxed for 12h and precipitated in cold water. The crude mixture was then dissolved in a minimum quantity of THF and precipitated in diethyl ether to afford 7 as a dark brown solid (75 mg, 64%). ¹H NMR (300 MHz, $[D_6]$ DMSO): $\delta = 2.42$ (s, 6H), 4.45–4.50 (m, 8H), 7.44 (ddd, ${}^{3}J = 7.5$ Hz, ${}^{3}J = 7.5$ Hz, 2H), 7.55 (dd, ${}^{3}J = 7.5$ Hz, ${}^{3}J = 7.5$ Hz, 2H), 7.70 (d, ${}^{3}J =$ 7.5 Hz, 2H), 8.17 (s, 2H), 8.27 ppm (d, ${}^{3}J=7.5$ Hz, 2H); ${}^{13}C$ NMR $(75 \text{ MHz}, \text{ CDCl}_3): \delta = 19.3, 65.8, 66.4, 85.4, 97.7, 98.3, 100.3, 101.7, 106.0,$ 113.1, 117.5, 118.8, 122.4, 126.0, 127.3, 128.2, 130.0, 132.2, 134.9, 135.3, 140.5, 148.1, 144.5, 164.3 ppm; UV/Vis: λ (ϵ)=495 (45000), 540 nm (20000); HRMS (MALDI): m/z calcd for $C_{44}H_{26}N_20_8S_6$: 902.001 $[M]^+$;

found: 901.964; IR (KBr): $\tilde{v}_{C=0} = 1706$; $\tilde{v}_{C=N} = 2213$; $\tilde{v}_{COO-H} = 3000 \text{ cm}^{-1}$ Fluorescence measurements: Steady-state excited-state emission was measured on a FluoroLog-322 (Horiba) that was equipped with a 450W Xe arc lamp. Dye powders were dissolved in CH2Cl2 and diluted to a concentration of about 10⁻⁵ M. The samples were excited at a wavelength that corresponded to the absorption maximum.

Electrochemical measurements: A standard three-electrode setup was employed to determine the redox potentials of the dyes. Measurements were performed on a PC-controlled Autolab system (PGSTAT-10, Eco Chimie). A glassy carbon electrode (Metrohm) was used as a working electrode, a Pt plate was used as an auxiliary electrode, and Pt wire was used as a quasi-reference electrode. Ferrocene was used as an internal standard in each case. Dye solutions were prepared by dissolving 0.5 mm of the powder in DMF and adding 0.1 M of tetrabutylammonium hexafluorophosphate (TBAPF₆) as a supporting electrolyte.

ATR-FTIR measurements: ATR-FTIR spectra were measured on an FTS 7000 FTIR spectrometer (Digilab) that was equipped with a "Golden Gate" diamond anvil. The final spectra were integrated from 64 individual scans at a resolution of 2 cm⁻¹. A similar force, which led to an intimate contact between the anvil and the sample (powder or dye adsorbed onto the film), was exerted on the specimen during the experiment. The films were rinsed with CH3CN and dried before the measurements were recorded.

Theoretical calculations: All theoretical calculations were carried out by using density functional theory (DFT) with the A.02 revision of the Gaussian 09 program package.^[15] Geometry optimizations were performed with Becke's three-parameter B3LYP exchange functional^[16] and the 6-31G** basis set.^[17] The molecular conformations (Figure 5) for dyes 6 and 7 were optimized within C_s symmetry constraints. Geometry optimizations were performed both in the gas phase and in the presence of the solvent (DMF and DMSO). Solvent effects were considered within the self-consistent reaction field (SCRF) theory by using the SMD keyword, which performs polarized continuum model (PCM)^[18] calculations by using the solvation model of Truhlar and co-workers.^[19] The SMD solvation model is based on the polarized continuous quantum-chemical charge density of the solute (the "D" in the name stands for "density"). The solvent had no relevant effect on the geometrical parameters but it significantly affected the relative energy of the molecular conformations that could be present in solution (see the Supporting Information). Molecular orbitals were plotted by using Molekel 4.3.^[20]

Vertical electronic-transition energies were computed at the B3LYP/6-31G** level by using the TDDFT approach[21] with the optimized ground-state molecular geometries. The vertical excitation energies were also calculated by using the hybrid PBE0 functional,^[22] which provided a similar description (energies and nature) of the lowest-energy excited states. Both the B3LYP and PBE0 functionals underestimated the energy of the HOMO-JLUMO CT excited state. This shortcoming of standard global hybrid functionals has been reported for donor-acceptor compounds for which there is a small overlap between the HOMO and the LUMO,^[23] as is the case for dyes 6 and 7 (Figure 6). To solve this problem, the use of long-range corrected functionals, such as the CAM-B3LYP functional,^[24] is recommended. The CAM-B3LYP approach completely fails in reproducing the optical spectra of dyes 6 and 7 because the CT states are calculated too high in energy and mixed with the $\pi \rightarrow$ π^* states of the donor and acceptor units of the molecule. A summary of the TDDFT results for dye 6 by using the B3LYP and PBE0 functionals is given in the Supporting Information, Table S1.

Cell fabrication: The devices were fabricated by using a transparent 5.5 µm-thick TiO₂ layer (nanoparticle size: 200 nm). The layer was screen-printed onto FTO glass (NSG-10, Nippon Sheet Glass) and sin-



tered according to a literature procedure.^[25] The photoanodes that were prepared in this way were immersed in the dye solutions (0.3 mm in DMSO/EtOH, 1:9 v/v, with 10 mM chenodeoxycholic acid) for 2 h after prior heating at 500 °C for 30 min. TEC-15 glass (Pilkington) with a predrilled hole was covered with Pt by drop-casting an 8 mm solution of hexachloroplatinic acid in isopropanol and heated at 450 °C for 15 min. This procedure was repeated twice. The electrodes were then sealed by using a 25 µm-thick Surlyn gasket. Electrolyte was introduced into the space between the electrodes by using a vacuum back-filling system. In this study, two types of electrolyte were used: volatile electrolyte Z960 (1.0 M 1,3-dimethylimidazolium iodide, 0.03 м iodine, 0.1 м guanidinium thiocyanate, 0.5 M tert-butylpyridine, 0.05 M lithium iodide in CH3CN/valeronitrile, 85:15 v/v) and ionic-liquid-based electrode Z952 (1,3-dimethylimidazolium-iodide/1-ethyl-3-methylimidazolium-iodide/1-ethyl-3-methylimidazolium-tetracyanoborate/iodine/N-butylbenzoimidazole/guanidiniumthiocyanate, 12:12:16:1.67:3.33:0.67). Metal contacts were placed on the edges of the device to ensure good conductivity during the measurements. A UV-light-filtering, self-adhesive foil (AKTOP, Asahi Glass) was placed on top of the device.

Photovoltaic characterization: A 450 W Xe light source (Oriel, USA) was used to characterize the devices. The spectroscopic output of the lamp was matched in the region 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated- and actual solar spectra to less than 2%. The current–voltage characteristics of the cell under these conditions were obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). A similar data-acquisition system was used to control the incident photon-to-current conversion efficiency (IPCE) measurements. Under computer control, light from a 300 W Xe lamp (ILC Technology, USA) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd., UK) onto the photovoltaic cell. The devices were masked to attain an illuminated active area of 0.159 cm².

Photovoltage transient measurements: Transient decays were measured under a white-light bias with superimposed red-light perturbation pulses (both light sources were LEDs). The voltage dynamics were recorded by using a Keithley 2400 source meter. Variation of the intensity of white-light bias allowed us to estimate the recombination rate constant (and hence the apparent electron lifetime) at different open-circuit potentials by controlling the concentrations of the free charges in TiO₂. Red-light perturbation pulses were adjusted to a very low level to maintain single-exponential voltage decay.

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Optical Properties -

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Donor-π-Acceptors Containing the 10-(1,3-Dithiol-2-ylidene)anthracene Unit for Dye-Sensitized Solar Cells



Housing the rising sun: The optical properties of metal-free sensitizers that were composed of 10-(1,3-dithiol-2-ylidene)anthracene-unit-based molecular tweezers were tuned for dye-sensitized solar cells. With the use of 3,4-ethylenedioxythiophene (EDOT) units, the absorption spectrum of the sensitizer was red-shifted. A power-conversion efficiency value of 3.7% was obtained, under air mass 1.5 global sunlight.