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## Metal-Free and Fluorescent Diketopyrrolopyrrole Fluorophores for Dye-Sensitized Solar Cells

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Novel metal-free and fluorescent dipyrrolopyrrole (DPP) dyes consisting of a central bis(lactam)-bearing pendent benzyl or branched hydrocarbon groups as solubilizing fragments and two orthogonal side arms (dimethylaminopropyne and benzoate anion) have been designed and synthesized. The UV/Vis absorption spectra recorded in THF are dominated by intense low-energy  $\pi$ - $\pi$ \* absorptions centered at 488 nm or 602 nm, respectively, for the phenyl- or thiophene-based DPP dyes. The fluorescence spectra also display broad bands at 555 nm ( $\Phi_F$ =

Introduction

The direct conversion of solar energy into electricity or chemical energy is one of the main scientific and technological challenges that humanity will have to face during this century.<sup>[1]</sup> The on-going depletion of fossil resources and the related environmental issues necessitate that the scientific community should find alternative sources of energy. Among these, solar energy lies at the forefront owing to its inexhaustible character. Silicon-based solar cell use is a well-established technology that requires massive amounts of energy to produce the silicon and thus its widespread development is technically limited. Dye-sensitized solar cells (DSSCs)<sup>[2,3]</sup> and bulk heterojunction solar cells (BHJSCs)<sup>[4,5]</sup> are alternatives which have received considerable attention as candidates for renewable energy devices. In this regard, metal-free sensitizers are interesting owing to their ease of preparation and purification, their high absorption coefficients and broad absorption wavelengths spanning from the near-UV to the near infrared, and they are easy to recycle at the end of their life cycle. Other advantages of organic dyes versus phosphorescent metal complexes are the wide range of readily modified molecular structures that are available and their particular optical and redox properties. The use of organic dyes to photosensitize mesoporous TiO<sub>2</sub> has blossomed over the last decades.<sup>[6]</sup> Indoline,<sup>[7]</sup> fluorene,<sup>[8]</sup> coumarin,<sup>[9]</sup> thienothiophene,<sup>[10]</sup> hemicyanines,<sup>[11]</sup> triarylamines,<sup>[12]</sup> heteropolycyclic,<sup>[13]</sup> porphyrin,<sup>[14,15]</sup> phthalocyanine,<sup>[16]</sup> blue squaraine<sup>[17]</sup> benzothiadiazole,<sup>[18]</sup> and thiophene-N,N-diphenylhydrazone<sup>[19]</sup> dyes have all been scrutinized.

In fact, most of these organic dyes have the same basic structure with a donor-( $\pi$ -conjugated spacer)-acceptor (D- $\pi$ -A) skeleton but in some cases remarkable solar-to-electric power conversion efficiencies reaching around 10% have been achieved.<sup>[6]</sup> In all cases, the donor belongs to the triarylamine family while the molecular anchor is an acrylic acid fragment. In these dyes, the fluorescence is heavily quenched by charge

0.57 and  $\tau_{\rm F}$ =4.6 ns) for the phenyl- and at 624 nm ( $\Phi_{\rm F}$ =0.31 and  $\tau_{\rm F}$ =3.5 ns) for the thiophene-based molecular structures. Under standard global AM 1.5G irradiation a maximum photon-to-electron conversion efficiency of 2.54% was achieved with dye-sensitized solar cells based on nanocrystalline TiO<sub>2</sub> ( $J_{sc}$ =7.5 mA cm<sup>-2</sup>,  $V_{oc}$ =0.49 V, and FF=0.70) for the phenyl-based DPP dye and 1.89% ( $J_{sc}$ =7.1 mA cm<sup>-2</sup>,  $V_{oc}$ = 0.41 V, and FF=0.65) for the thiophene-based DPP dye.

transfer or electron transfer. A push-pull zinc porphyrin sensitizer recently achieved very high power conversion efficiency.<sup>[20]</sup> Our research group has recently introduced the concept of using highly fluorescent borondipyrromethene (Bodipy) dyes to photosensitize semiconductor-based solar cells.<sup>[19,20]</sup> The absence of the donor (triphenylamine) but the presence of the anchor (carboxylate) provides highly fluorescent dyes capable of charge separation under appropriate cell conditions and the covalent linkage is provided by a carboxylate<sup>[21]</sup> or an acetylacetonate<sup>[22]</sup> unit. The absorption properties of the Bodipy dyes were tuned by changing the delocalization pathway on the organic dyes and by using double bond side-arms. We note that D- $\pi$ -A Bodipy dyes have also been used in DSSC solar cells.<sup>[23]</sup>

Related dipyrrolopyrrole (DPP) compounds exhibit pronounced absorption and intense emissive properties with exceptional outdoor photochemical, mechanical, and thermal stability which have led to industrial applications in paints, inks, and plastics.<sup>[24]</sup> We recently used soluble DPP scaffoldings to construct donor/acceptor dyads to promote intramolecular energy-transfer processes which appeared to be extremely fast (picosecond time scale).<sup>[25]</sup> The use of DDP subunits to link two different dyes also favors energy transfer by excitation in the

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DPP chromophore, the direction of which can be switched by changing the environment.<sup>[26]</sup>

A recent study on organic bulk heterojunction (BHJ) has demonstrated the viability of solution-processed heterojunctions composed entirely of small molecules.<sup>[4c, c, 27]</sup> Along these lines DPP dyes have been widely investigated as law-band-gap materials in solar cells.<sup>[28]</sup> When blended with  $PC_{61}BM$  (a modified fullerene as electron acceptor), BHJ solar cells generated photon-to-current conversion efficiencies (PCEs) up to 4.4% with high  $J_{sc} = 10 \text{ mA cm}^{-2}$  and  $V_{oc} =$ 0.92 V.<sup>[29]</sup> This incredible efficiency was ascribed to the good film morphology, to adequate HOMO/LUMO energy scaling of the DPP levels with respect to the electron acceptor and the working potential of the hole extracting electrode, but also to the hole mobility. Narrow-bandgap DPP polymers for solar cells



**Scheme 1.** Outline of the preparation of phenyl-based DPP dyes. Reaction conditions: 1) benzylbromide (10 equiv), DMF, K<sub>2</sub>CO<sub>3</sub> (11 equiv), 120 °C, 2 h (36% yield); 2) dimethylaminopropyne (1 equiv), benzene, triethylamine, [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (10 mol%), Cul (15 mol%), 40 °C, 60 h (35% (**3**) and 20% (**4**) yield); 3) benzene, ethanol, triethylamine, [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (10 mol%), CO flux, 70 °C, 15 h (90% yield); 4) NaOH, THF/H<sub>2</sub>O, 80 °C; 5) DMF, water, triethylamine, [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (10 mol%), CO flux, 110 °C, 15 h (47% yield). DMF = *N*,*N*-dimethylformamide.

have also been produced for high photovoltaic performances.  $^{\left[ 30\right] }$ 

To the best of our knowledge, there are only two recent contributions concerning DPP dyes based on the general concept of D- $\pi$ -A in DSSC applications.<sup>[31,32]</sup> Herein, we have built highly fluorescent DPP dyes through modification of the DPP periphery by introduction an acid function on one side for covalent linking to mesoporous TiO<sub>2</sub> and a dimethylaminopropyne fragment on the other side to disfavor aggregation of the dyes.

### **Results and Discussion**

#### Synthesis

The preparation of the target dyes is illustrated in Scheme 1 and Scheme 2. Solubilization of 1 was made feasible using excess benzylbromide. Orthogonal functionalization of 2 required the use of dimethylaminopropyne and Pd<sup>0</sup> catalysis. Owing to the high polarity imported by the dimethylamino fragment, the chromatographic separation of 3 and 4 was facile, and provided the pivotal monosubstituted derivative 3 in 35% yield. The disubstituted derivative 4 (more polar compound), was isolated pure during the same procedure in a yield of 20%. The yield ratio 3:4 depends on the reaction conditions and also on the stoichiometry of the reactants. It was anticipated that the most reliable way to generate the carboxylic acid would be to prepare first the diester 5 using a palladium(0)-catalyzed carboalkoxylation reaction,<sup>[33]</sup> and subsequent hydrolysis under basic conditions (Scheme 1). Unfortunately, here this protocol was not effective owing to the fact that the basic conditions destroyed the bis(lactam) framework. To reach the target molecule **6** we used a carboxylation reaction promoted by palladium catalysis under a flow of carbon monoxide, water as the nucleophile; and triethylamine as base to quench the nascent acid. Compound **6** was isolated by column chromatography in 47% yield.

A similar strategy was developed for the preparation of thiophene-based DPP dyes (Scheme 2).<sup>[34]</sup> Alkylation of the insoluble bis(lactam) compound **7** was achieved using 2-ethylhexyl bromide under basic conditions. Bromation of the thiophene subunit was possible using NBS and the use of dimethylaminopropyne allowed the preparation of a mixture of compounds **10** and **11**, which could be easily separated owing to the presence of the polar dimethylamino group. Unfortunately, the carboxylation conditions developed in Scheme 1 and applied to derivative **11** led to intractable mixtures of dyes which could not be separated by conventional chromatography. The solution came from the use of the benzoate derivative **12** which could be satisfactorily linked to the DDP dye through a palladium(0)-mediated cross-coupling reaction.

#### **Optical properties**

Photophysical measurements were performed on DPP dye **6** in THF solution. The absorption spectroscopic profile is broad and centered at 488 nm with a moderately high absorption coefficient log  $\varepsilon$  = 4.15 (Table 1). The breadth of the band is indi-

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**Scheme 2.** Outline of the preparation of thiophene-based DPP dyes. Reaction conditions: 1) 2-ethylhexylbromide (4.6 equiv), DMF,  $K_2CO_3$  (4 equiv), 145 °C, 15 h (49% yield); 2) NBS, anhydrous chloroform, RT, argon (42% yield); 3) dimethylaminopropyne (1 equiv), benzene, triethylamine,  $[Pd(PPh_3)_4]$  (10 mol%), 60 °C, 15 h (26% (**10**) and 46% (**11**) yield); 4) DMF, water, triethylamine,  $[Pd(PPh_3)_2Cl_2]$  (10 mol%), CO flux, 70 °C, 15 h, eventually followed by saponification; 5) DMF, triethylamine,  $[Pd(PPh_3)_2Cl_2]$  (10 mol%), 60 °C, 15 h (99% yield).

Table 1. Spectroscopic features of dyes 6 and 13								
Cmpd	$\lambda_{\max} \left[ nm  ight]^{[a]}$	$\log \epsilon_{max}$	$\lambda_{flu} \left[ nm  ight]$	$\varPhi_{\rm F}$	$ au_{ m S}$ [ns]	S <sup>+/0</sup> [V] <sup>[b]</sup>	$E_{0-0}  [eV]^{[c]}$	$S^{+/*} [V]^{[d]}$
6 13	488 602	4.15 4.57	555 624	0.57 0.31	4.6 3.5	+ 0.92 + 0.88	2.13 1.65	-1.21 -0.77

[a] Absorption peaks and molar extinction coefficients ( $\varepsilon$ ) were measured in THF. [b] Ground-state oxidation potentials,  $S^{+/0}$ , were determined by cyclic voltammetry in deoxygenated dichloromethane solutions, containing 0.1  $\times$  TBAPF<sub>6</sub> (TBA = tetrabutylammonium), at a solute concentration of approximately 1.5 mM and at room temperature. Potential was standardized versus ferrocene (Fc) as internal reference and converted to the SCE scale assuming that  $E_{1/2}$  (Fc/Fc<sup>+</sup>) = +0.38 V ( $\Delta E_p$  = 60 mV) vs. SCE. Error in half-wave potentials is ±10 mV. For irreversible processes the peak potentials ( $E_{ap}$  or  $E_{cp}$ ) are quoted. All reversible redox steps result from one-electron processes. [c] Optical energy gaps,  $E_{0-0}$ , were estimated from the 10% maximum absorption intensity of the absorption spectra on transparent TiO<sub>2</sub>. [d] Excited-state oxidation potentials,  $S^{+/*}$ , were calculated from the expression  $S^{+/*} = S^{+/0} - E_{0-0}$ .

cative that it involves two overlapping sets of transitions. There is a large Stokes shift of approximately 2470 cm<sup>-1</sup>, which indicates that the excited state may possess considerable charge-transfer character.<sup>[35]</sup> The fluorescence quantum yield is rather high but the emission lifetime is comparable to those recorded for the Bodipy dyes and lies in the nanosecond range.<sup>[36]</sup> The fluorescence spectroscopic profile is broad and can be analyzed in terms of a single transition with an average

conduction band of the  $TiO_2$  electrode and dye regeneration through electron donation from the electrolyte, a cyclic voltammogram was obtained in a typical three-electrode electrochemical cell in deoxygenated and anhydrous dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte (Table 2). A Pt microdisk was used as a working electrode and ferrocene was used as an internal reference. The ground-state oxidation potential

vibronic spacing of approximately 820 cm<sup>-1</sup>. On comparing the absorption spectroscopic profile with the emission profile, it is clear that there is a major reorganization in the excited state, confirming the possibility of charge transfer. This is in strong contrast with Bodipy dyes, which display emission profiles that mirror the absorption spectra (Figure 1).<sup>[37]</sup>

For the second dye 13, the low-energy absorption band is shifted to the red by about 114 nm with a larger absorption coefficient log  $\varepsilon = 4.57$  (Table 1). This bathochromic shift is induced by the thiophene moieties which favor delocalization along the thiophene-lactam main axis.[38] Remarkably, the absorption band is quite broad, spanning over 200 nm (Figure 2). Here the Stokes shift is weaker (586 cm<sup>-1</sup>) and the emission profile resembles the absorption with a vibronic sequence of approximately  $1363 \text{ cm}^{-1}$ . The short lifetime and the shape of the emission band are in keeping with the properties of a singlet emitter.

When absorbed on a transparent thin TiO<sub>2</sub> film, dyes **6** and **13** show broad absorption spectra similar to that in solution, whereas the absorption peaks are slightly red-shifted owing to the interaction between the carboxylate group and TiO<sub>2</sub> (Figure 3). This broadening of the absorption spectrum is desirable for harvesting the solar spectrum and leads to a large photocurrent.

To evaluate the thermodynamics of electron injection from the excited-state of the dye to the



Figure 1. Absorption (black line), emission (dashed line), and excitation (dotted line) spectra of dye  ${\bf 6}$  in THF at room temperature.



Figure 2. Absorption (black line), emission (dashed line), and excitation (dotted line) spectra of dye 13 in THF at room temperature.



Figure 3. Absorption spectra of dyes 6 (——) and 13 (----) anchored on a transparent TiO<sub>2</sub> film.

Table 2. Photovoltaic performance of DSCs based on dye 6.						
Cmpd	TBP (M)/Lil (M)	$J_{\rm sc}$ [mA cm <sup>-2</sup> ]	<i>V</i> <sub>oc</sub> [V]	FF	η [%]	
6	0:0.5	8.0	0.44	0.67	2.36	
6	0:0.1	7.5	0.49	0.70	2.54	
6	0.5:0.1	4.0	0.53	0.78	1.66	
13	0:0.5	7.1	0.41	0.65	1.89	
13	0:0.1	5.1	0.46	0.68	1.60	
13	0.5:0.1	3.6	0.52	0.74	1.39	

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values,  $S^{+/0}$ , of dye 6 and 13 were measured to be 0.92 and 0.88 V (vs SCE), respectively, and these values were low enough for efficient regeneration of the oxidized dyes through reaction with iodide (0.07 V vs SCE).<sup>[39]</sup> The onset of the optical energy gap ( $E_{0-0}$ ) of dye **6** was approximately 2.13 eV, determined from the 10% maximum absorption intensity of the absorption spectrum on transparent TiO<sub>2</sub> films, whereas this gap is estimated to 1.65 eV for dye 13. The excited-state oxidation potentials,  $S^{+/*}$ , of dye 6 and 13 were estimated to -1.21 V and -0.77 V (versus SCE), respectively. The S<sup>+/\*</sup> of dye **6** lies above the conduction band edge (approximately -0.82 V vs SCE)<sup>[40]</sup> of the nanocrystalline TiO<sub>2</sub>. Therefore, an efficient excited-state injection into the conduction band of TiO<sub>2</sub> is expected to occur with dyes 6. For dye 13,  $S^{+/*}$  lies about 0.1 eV lower than the conduction band edge of TiO<sub>2</sub>. Hence, the excited state of dye 13 is not energetically favorable for efficient electron injection.

The photovoltaic performance parameters of cells sensitized by dyes **6** and **13** were studied using electrolytes **E1**, **E2**, and **E3** with various Lil and TBP (4-*tert*-butylpyridine) concentrations under standard AM 1.5G irradiation (100 mW cm<sup>-2</sup>). The short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factors (*FF*), and overall solar-to-electric energy conversion efficiencies ( $\eta$ ) for TiO<sub>2</sub> electrodes coated with dyes **6** and **13** are summarized in Table 2. The IPCEs for the solar cells, plotted as a function of excitation wavelength, were calculated from Equation (1),

$$IPCE(\lambda) = 1240(I_{sc}/\lambda\varphi)$$
(1)

where  $I_{\rm sc}$  is the photocurrent density at short circuit (mAcm<sup>-2</sup>) under monochromatic irradiation,  $\lambda$  is the wavelength of incident radiation (nm) and  $\varphi$  is the incident radiative flux (Wm<sup>-2</sup>).

The solar cell sensitized by dye 6 showed high power conversion efficiency, with  $J_{sc}$  of 7.5 mA cm<sup>-2</sup>,  $V_{oc}$  of 0.49 V, FF of 0.70, corresponding to an overall conversion efficiency ( $\eta$ ) of 2.54% with electrolyte composition of 0.6м dimethylpropylimidazolium iodide (DMPII), 0.05 M I<sub>2</sub> and 0.1 M Lil (E1; Figure 4 and Table 2). The J<sub>sc</sub> of the dye-sensitized solar cell (DSC; 8.0 mA cm<sup>-2</sup>) with an electrolyte composition of 0.6 M DMPII, 0.05 M I<sub>2</sub> and 0.5 M Lil (E2) was slightly higher than that of the DSC with E1, owing to the higher concentration of Lil compared to that of E1. However, both  $V_{oc}$  and FF with E2 were lower than those with **E1**, resulting in a lower  $\eta$  value (2.36%) for E2. The open-circuit voltage increased at a TBP concentration of 0.5 м with electrolyte composition E3 (0.6 м DMPII, 0.05 м I<sub>2</sub>, 0.1 м Lil, 0.5 м TBP). The TBP probably adsorbed on the bare TiO<sub>2</sub> surface and suppressed the recombination between the injected electrons and  $\boldsymbol{I_3}^-$  ions. In contrast, the short-circuit photocurrent decreased significantly as the TBP concentrations increased owing to higher energy shift of the TiO<sub>2</sub> conduction band edge. The solar cell sensitized by dye 13 showed poor power conversion efficiency compare to that of dye 6. Photovoltaic parameters  $J_{sc}$ ,  $V_{ocr}$ , FF, and  $\eta$  of the dye 13 with **E2** were 7.1 mA cm<sup>-2</sup>, 0.41 V, 0.65, and 1.89%, respectively. Although dye 13 has better light harvesting efficiency than

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**Figure 4.** Photocurrent voltage characteristics of DSCs sensitized with the dye **6** at AM 1.5G irradiation (light intensities: 100 mW cm<sup>-2</sup>). The redox electrolyte consisted of a solution of (**E1**) 0.6 M DMPII, 0.05 M I<sub>2</sub>, 0.1 M Lil in acetonitrile (solid line); (**E2**) 0.6 M DMPII, 0.05 M I<sub>2</sub>, 0.5 M Lil in acetonitrile (dashed line); and (**E3**) 0.6 M DMPII, 0.05 M I<sub>2</sub>, 0.1 M Lil, 0.5 M TBP in acetonitrile (dashed-dotted line).

dye **6**, it shows a lower cell performance compared to that of dye **6** because of poor excited-state electron injection to the  $TiO_2$  conduction band. The concentration of Lil in the electrolyte has strong effect on electron injection of this dye in DSCs.

Figure 5 shows the monochromatic incident photon-to-current conversion efficiency (IPCE) for DSCs based on dyes **6** and **13** with an electrolyte having a Lil concentration of 0.5 M (**E2**). The newly developed material **6** shows excellent sensitization of nanocrystalline TiO<sub>2</sub> from 350 to 600 nm with a maximum value of 78% in the plateau region. The action spectrum of dye **6** is consistent with the absorption spectrum on a transparent TiO<sub>2</sub> film (Figure 3). Taking into account the reflection and absorption losses by the conducting glass, the photon-to-cur-



**Figure 5.** Photocurrent action spectrum obtained with dye 6 (——) and **13** (-----) attached to a nanocrystalline  $TiO_2$  film. The incident photon-to-current conversion efficiency is plotted as a function of wavelength. A sandwich-type sealed cell configuration was used to measure this spectrum. The electrolyte composition was 0.6 M DMPII, 0.05 M  $I_{2r}$  and 0.5 M Lil in acetonitrile (**E2**).

rent conversion efficiency in this range reaches about 90%. The onset of the IPCE spectrum of dye **6** is close to 650 nm. As shown in Figure 5, dye **13** achieved moderate sensitization of nanocrystalline  $TiO_2$  across the whole visible range and into the near-IR region as far as 900 nm, and displayed an IPCE value of about 40% between 350 and 650 nm.

### Conclusion

Novel fluorescent DPP dyes have been synthesized with two orthogonal functions. The dimethylaminopropyne group introduces solubility and polarity which facilitates the purification procedure and the acid function is required for anchoring to transparent thin TiO<sub>2</sub> films. The novel dyes are fluorescent and not constructed on a push-pull principle. The redox potential of the excited dye is such as to allow injection of an electron into the conduction band of nanocrystalline TiO<sub>2</sub>. The best device is produced with a TBP/Lil ratio of 0:0.1, providing a conversion of 2.54% with a  $J_{sc}$  of 7.5 mA cm<sup>-2</sup> and a  $V_{oc}$  of 0.49 V. The absorption of dye 6 is not optimal above 600 nm on the nanocrystalline TiO<sub>2</sub> film, and the absorption of dye 13 provides a larger light absorption cross-section. Unfortunately, dye 13 shows lower incident-photon-to-current conversion efficiency (IPCE) compared to dye 6, resulting in a total solar-toelectric conversion efficiency ( $\eta$ ) of 1.89%. An efficiency improvement has not yet been attained for dye 13 owing to poor excited-state electron injection to the TiO<sub>2</sub> conduction band. However, this study demonstrates that a DPP-based fluorescent molecule could be used as a photosensitizer in dyesensitized solar cells. The development of highly efficient organic sensitizers should be feasible through improved molecular design, and the fact that a strong luminescence is maintained in the dyes is not detrimental for the photosensitization process. Results from this study strongly indicate that the application of this class of DPP-based organic dyes as panchromatic sensitizers for DSCs is interesting, and opens new avenues for the design of more efficient dyes by fine-tuning of the ground and excited states through structural changes.

### **Experimental Section**

#### Synthesis

Compounds  $3^{[23]}_{,} 9^{[41]}_{,}$  and  $12^{[42]}_{,}$  were prepared and purified according to the literature.

Preparation of compound **5**: A solution of **3** (100.0 mg, 1 equiv, 0.159 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (5.6 mg, 0.05 equiv, 0.008 mmol) in benzene/EtOH/triethylamine (10:2:1 mL) was heated to 70 °C overnight (15 h) under a flux of CO at atmospheric pressure. After cooling to RT, the solvents were removed under vacuum. The residual solid was dissolved in dichloromethane. The solution was washed with H<sub>2</sub>O (1 × 30 mL) and the combined water washes back-extracted with dichloromethane (3 × 30 mL). The combined organic phases were dried over magnesium sulfate. The solution was filtered and evaporated to dryness. The residue was purified by column chromatography on silica gel, eluting with dichloromethane then dichloromethane/EtOH (from 98:2 to 95:5) to give 88.6 mg of orange compound **5** (yield 90%). <sup>1</sup>H NMR (300 MHz,

CDCl<sub>3</sub>):  $\delta$  = 8.01 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 6.99–7.29 (10 lines m, 10 H), 4.89 (s, 4H), 4.30 (q, J = 7.3 Hz, 2H), 3.40 (s, 2H), 2.27 (s, 6H), 1.30 ppm (t, J = 7.1 Hz, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.51, 162.55, 162.37, 149.04, 147.35, 137.08, 137.07, 132.48, 131.97, 131.63, 129.82, 128.89, 128.85, 128.77, 128.48, 128.32, 127.45, 126.88, 126.61, 126.57, 110.64, 109.86, 88.11, 84.70, 61.23, 48.53, 45.64, 45.56, 44.17, 14.18 ppm; ESI-MS (CH<sub>2</sub>Cl<sub>2</sub> + 1% TFA) *m/z* (intensity, molecular peak): 622.2 (100, [*M*+H]<sup>+</sup>); elemental analysis (%) calcd for C<sub>40</sub>H<sub>35</sub>N<sub>3</sub>O<sub>4</sub>: C 77.27, H 5.67, N 6.76; found: C 77.04, H 5.32, N 6.43.

Preparation of compound **6**: A solution of **3** (102.0 mg, 1 equiv, 0.162 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (5.7 mg, 0.05 equiv, 0.008 mmol) in DMF/H<sub>2</sub>O/triethylamine (6:2:1 mL) was heated at 110 °C overnight (15 h) under a flux of CO at atmospheric pressure. After cooling to RT, the solution was taken to dryness under vacuum. The crude residual solid was purified by column chromatography on silica gel, eluting with dichloromethane (+1% formic acid) then dichloromethane/EtOH (+1% formic acid, from 98:2 to 8:2) to give 45.2 mg of orange/red compound **6** (yield 47%). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>):  $\delta$ =8.04 (d, *J*=8.3 Hz, 2H), 7.58–7.82 (3 lines m, 4H), 7.48 (d, *J*=8.3 Hz, 2H), 6.94–7.34 (m, 10H), 4.91 (s, 4H), 3.57 (s, 2H), 2.85 ppm (s, 6H), ESI-MS (CH<sub>2</sub>Cl<sub>2</sub>+1% TFA) *m/z* (intensity, molecular peak): 594.1 (100, [*M*+H]<sup>+</sup>); elemental analysis (%) calcd for C<sub>38</sub>H<sub>31</sub>N<sub>3</sub>O<sub>4</sub>: C 76.88, H 5.26, N 7.08; found: C 76.46, H 5.07, N 6.82.

Preparation of compounds 10 and 11: To a degassed solution of 9 (214.8 mg, 1 equiv, 0.314 mmol) and [Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>] (11.0 mg, 0.05 equiv, 0.016 mmol) in benzene/triethylamine (18:3 mL) was added Cul (2.9 mg, 0.05 equiv, 0.016 mmol) and 1-dimethylamino-2-propyne (34 mL, 1 equiv, 0.314 mmol). The reaction mixture was heated to 60°C overnight (15 h) then cooled to RT. The reaction mixture was filtered through Celite then taken to dryness under reduced pressure. The residue was dissolved in dichloromethane and the solution was washed with saturated aqueous NaCl (1×20 mL). The combined washes were back-extracted with dichloromethane (3×30 mL) and the combined organic phases then dried over MqSO<sub>4</sub>. The solution was filtered and evaporated to dryness. The residue was purified by column chromatography on silica gel, eluting with dichloromethane then dichloromethane/EtOH (gradient from 99:1 to 97:3) to give 11 (99 mg, 46%) and then dichloromethane/EtOH (gradient from 95:5 to 85:15) to give 10 (57 mg, 26%).

Compound 11: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.76–0.97 (m, 12 H), 1.10–1.47 (m, 16 H), 1.76–1.94 (m, 2 H), 2.72 (s, 6 H), 3.82–4.09 (m, 6 H), 7.25 (d, *J* = 4.1 Hz, 1 H), 7.38 (d, *J* = 4.1 Hz, 1 H), 8.70 (d, *J* = 4.1 Hz, 1 H), 8.77 ppm (d, *J* = 4.1 Hz, 1 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.42, 13.99, 23.01, 23.51, 28.29, 30.13, 39.08, 43.93, 46.00, 48.66, 78.96, 108.16, 108.60, 119.05, 127.79, 128.39, 128.55, 130.34, 131.12, 131.45, 131.88, 131.92, 132.01, 132.14, 133.20, 135.20, 135.44, 139.32, 139.61, 161.45 ppm; ESI-MS in dichloromethane/ methanol + 1% TFA, positive mode, *m/z* (%): 684.1 (90), 686.1 (100); elemental analysis (%) calcd for C<sub>35</sub>H<sub>46</sub>BrN<sub>3</sub>O<sub>2</sub>S<sub>2</sub>: C 61.39, H 6.77, N 6.14; found: C 61.13, H 6.53, N 5.82.

Compound **10**: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.66–0.98 (m, 12 H), 1.05–1.52 (m, 16 H), 1.76–1.95 (m, 2 H), 2.47 (s, 12 H), 3.65 (s, 4 H), 3.84–4.09 (m, 4 H), 7.31 (d, *J* = 4 Hz, 2 H), 8.83 ppm (d, *J* = 4 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.62, 10.42, 13.99, 23.01, 23.50, 28.29, 29.67, 30.11, 39.09, 46.02, 108.78, 127.91, 130.27, 133.17, 135.28, 139.57, 161.48 ppm; ESI-MS in dichloromethane/methanol + 1% TFA, positive mode, *m/z* (%): 687.2 (100); elemental analysis (%) calcd for C<sub>40</sub>H<sub>54</sub>N<sub>4</sub>O<sub>2</sub>S<sub>2</sub>: C 69.93, H 7.92, N 8.16; found: C 69.74, H 7.75, N 7.85. Compound 13: To a degassed solution of 11 (99.2 mg, 1 equiv, 0.145 mmol) and 12 (29.2 mg, 1.2 equiv, 0.174 mmol) in DMF/triethylamine (20;14 mL) was added [Pd(PPh<sub>3</sub>)<sub>4</sub>] (8.4 mg, 0.05 equiv, 0.007 mmol). The reaction mixture was heated to 60 °C overnight (15 h) then was cooled to RT. The maximum amount of DMF was removed under vacuum. The residue was dissolved in a water/ methanol mixture and slow addition of diethyl ether resulted in the precipitation of compound 13 as a violet solid (111.8 mg, quantitative yield). <sup>1</sup>H NMR (400 MHz, DMSO):  $\delta = 0.71 - 0.91$  (m, 12 H), 1.07-1.38 (m, 16H), 1.64-1.84 (m, 2H), 2.25 (s, 6H), 3.58 (s, 2H), 3.85-4.03 (m, 4H), 7.55 (d, J=4.1 Hz, 1H), 7.67 (d, J=8.2 Hz, 2H), 7.71 (d, J=4.1 Hz, 1H), 7.96 (d, J=8.6 Hz, 2H), 8.71 (d, J=4.1 Hz, 1 H), 8.74 ppm (d, J=4.1 Hz, 1 H); ESI-MS in dichloromethane/methanol+1% TFA, negative mode, m/z (%): 748.2 (100); elemental analysis (%) calcd for C<sub>44</sub>H<sub>50</sub>N<sub>3</sub>NaO<sub>4</sub>S<sub>2</sub>H<sub>20</sub>: C 66.89, H 6.63, N 5.32; found: C 66.63, H 6.42, N 5.19.

### Cell fabrication and characterization

The DSCs were fabricated as follows: A double-layer TiO2 photoelectrode (thickness 15 µm; area 0.25 cm<sup>2</sup>) was used as a working electrode. A 10 µm main transparent layer with titania particles  $(\approx 25 \text{ nm})$  and a 5  $\mu$ m scattering layer with titania particles ( $\approx$ 400 nm) were screen-printed on a fluorine-doped tin oxide conducting glass substrate.<sup>[43]</sup> A solution of dye 6,  $(3 \times 10 - 4 \text{ M})$  in dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) was used to coat the TiO<sub>2</sub> film with the dye. The electrodes were immersed in the dye solutions and then kept at 25 °C for 24 h to adsorb the dye onto the TiO<sub>2</sub> surface. Photovoltaic measurements were performed in a two-electrode sandwich-type sealed-cell configuration. The dye-coated TiO<sub>2</sub> film was used as the working electrode, and platinum-coated conducting glass was used as the counter-electrode. The two electrodes were separated by a Surlyn spacer (40 µm thick) and sealed by heating the polymer frame. The electrolytes were composed of (E1) 0.6 M dimethylpropylimidazolium iodide (DMPII), 0.05 м I2 and 0.1 м Lil in acetonitrile; (E2) 0.6 м DMPII, 0.05 м I2, and 0.5 м Lil in acetonitrile; and (E3) 0.6 м DMPII, 0.05 м I2, 0.1 м Lil, and 0.5 м TBP in acetonitrile. The current-voltage characteristics were measured using a black metal mask with an aperture area of 0.25 cm<sup>2</sup> under standard AM 1.5G irradiation (100 mW cm<sup>-2</sup>, WXS-155S-10: Wacom Denso Co. Japan).<sup>[44]</sup> Monochromatic incident photon-to-current conversion efficiency spectra were measured with monochromatic incident light of  $1 \times 1016$  photons cm<sup>-2</sup> under 100 mW cm<sup>-2</sup> in director current mode (CEP-2000BX, Bunko-Keiki).

#### **Electrochemical measurements**

Electrochemical studies employed cyclic voltammetry with a conventional three-electrode system using a BAS CV-50W voltammetric analyzer equipped with a Pt microdisk (2 mm<sup>2</sup>) working electrode and a silver wire counter-electrode. Ferrocene was used as an internal standard and was calibrated against a saturated calomel reference electrode (SCE) separated from the electrolysis cell by a glass frit presoaked with electrolyte solution. Solutions contained the electro-active substrate (about 1.5 mm) in deoxygenated and anhydrous dichloromethane containing tetra-*n*-butylammonium hexafluorophosphate (0.1 m) as supporting electrolyte. The quoted half-wave potentials were reproducible within approximately 15 mV. See Table 3 for data.

# **CHEMPLUSCHEM**

Table 3. s. <sup>[a]</sup>	Electrochemical data for	dyes 6 and 13 and related	l compound-
Cmpd	$E^{0'}(\text{ox, soln}) [V], \Delta E [mV]$	$E^{0'}$ (red, soln) [V], $\Delta E$ [mV]	Electro-gap
3	+ 1.23 (70) + 1.11 (irr.) onset potential + 1.03 V	-1.10 (70) -1.74 (irr.) onset potential -1.00 V	2.03 V
6	+ 1.32 (80) + 1.01 (irr.) onset potential + 0.92 V	—1.17 (80) - onset potential —1.05 V	1.97 V
11	+ 1.32 (80) + 1.16 (irr.) + 1.00 (60) onset potential + 0.89 V		1.89 eV
13	+ 1.30 (70) + 0.95 (60) onset potential + 0.88 V	—1.09 (70) — onset potential —0.95 V	1.83 eV

[a] Potentials determined by cyclic voltammetry in deoxygenated dichloromethane solution, containing  $0.1 \,\mathrm{m}$  TBAPF<sub>6</sub>, [electrochemical window from +1.6 to -2.2 V], at a solute concentration of approximately  $1.5 \,\mathrm{mm}$  and at room temperature. Potentials were standardized versus ferrocene (Fc) as internal reference and converted to the SCE scale assuming that  $E_{1/2}$  (Fc/Fc<sup>+</sup>) = +0.38 V ( $\Delta Ep = 60$  mV) vs. SCE. Error in halfwave potentials is  $\pm 10$  mV. For irreversible processes the peak potentials ( $E_{ap}$  or  $E_{cp}$ ) are quoted. All reversible redox steps result from one-electron processes. irr. = irradiation

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