### Bis-Donor–Bis-Acceptor Tribranched Organic Sensitizers for Dye-Sensitized Solar Cells

### Alessandro Abbotto,\*<sup>[a,b]</sup> Valentina Leandri,<sup>[a]</sup> Norberto Manfredi,<sup>[a]</sup> Filippo De Angelis,\*<sup>[b]</sup> Mariachiara Pastore,<sup>[b]</sup> Jun-Ho Yum,<sup>[c]</sup> Mohammad K. Nazeeruddin,\*<sup>[c]</sup> and Michael Grätzel<sup>[c]</sup>

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A new class of tribranched dye-sensitized solar cell (DSC) sensitizers carrying two conjugated donors and two acceptor/ anchoring groups is introduced. The approach leads to significantly different optical properties and enhanced stability

efficiencies exceeding 11%.[4]

Introduction

Solar energy has not yet found widespread use due to the high cost of crystalline silicon panels, which are not competitive with electricity generated from fossil fuels.<sup>[1]</sup> Among the new approaches to solar energy conversion, dye-sensitized solar cells (DSCs) have one of the best potential for high conversion efficiency and low-cost manufacture.<sup>[2]</sup> One strategic route to improving cell efficiencies involves the optimization of the dye-sensitizer, which captures photons to generate an electron/hole pair at the interface with the inorganic semiconductor (TiO<sub>2</sub>) and the redox electrolyte, respectively. The Ru<sup>II</sup> complex bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) (N719)<sup>[3]</sup> is the most representative DSC sensitizer, with power conversion

One of the main drawbacks of Ru<sup>II</sup>–bipyridyl complexes is the modest molar absorptivity of the low-energy absorption band (14200 M<sup>-1</sup> cm<sup>-1</sup> at 530 nm for N719),<sup>[3]</sup> which hinders larger photocurrent densities and thus improved efficiencies.<sup>[5]</sup> In the last years, metal-free organic dyes have been proposed as alternative sensitizers to circumvent this problem.<sup>[6]</sup> Organic dyes are readily available, easier to purify, are relatively inexpensive to manufacture, and, most of

 [a] Department of Materials Science and Milano-Bicocca Solar Energy Research Center-MIB-Solar, Via Cozzi 53, 20125, Milano, Italy Fax: +39-02-64485400
 E-mail: alessandro.abbotto@mater.unimib.it
 [b] Ititive CNP, di Scienza a Tecnologia Molecolari (CNP, ISTM)



<sup>[</sup>c] Laboratory for Photonics and Interfaces, School of basic Sciences, Swiss Federal Institute of Technology, 1015 Lausanne, Switzerland E-mail: mdkhaja.nazeeruddin@epfl.ch

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with respect to related di- and monobranched dyes and yields power conversion efficiencies of up to 5.05%, which is possibly limited by the computed nonoptimal dye packing on the semiconductor surface.

all, are associated with an extended structural variety that can be adjusted to optimize the spectral absorption properties. Although their efficiencies are still lower than those of ruthenium sensitizers, very recently, values approaching, or even exceeding, 10% have been reported, showing the great potential of the new design.<sup>[7]</sup> The design of these efficient chromophores, in analogy with most organic sensitizers, has been based on a dipolar D- $\pi$ -A structural motif, where "D" is an electron-rich group, " $\pi$ " is a conducting bridge, and "A" an electron-poor moiety embedding the COOH anchoring functionality for grafting onto the TiO<sub>2</sub> surface. Triarylamine has been by far the most widely used D core.<sup>[8]</sup>

In the search for improved optical and structural properties, we,<sup>[9]</sup> and others,<sup>[10,11]</sup> have recently introduced a novel model class of dibranched dianchoring organic sensitizers composed of one donor and two anchoring groups (A- $\pi$ -D- $\pi$ -A). We have shown that the dibranched dye DB-1 (Scheme 1) offers improved optical properties (higher molar extinction coefficients and red-shifted absorption), increased photocurrent, and enhanced stability compared to its monobranched analogues.<sup>[9]</sup> Recently, a porphyrin pos-



Scheme 1. Reference photosensitizers.



sessing two anchoring groups has been successfully applied to DSC with a power conversion efficiency comparable to that of N719 under the same conditions.<sup>[12]</sup>

Here, we present an extension of this design, aimed at further expanding the possibility of improving the optical and energetic properties of the sensitizers. The new approach, based on a A- $\pi$ -D- $\pi$ '-D- $\pi$ -A tribranched structural motif (where  $\pi'$  is other than  $\pi$ ), implies the use of two donor and two acceptor/anchoring fragments and different  $\pi$  spacers, as pictorially depicted in Figure 1. Generally speaking, the tribranched approach should allow a much larger structural variety with respect both to the D- $\pi$ -A (Figure 1a) and A- $\pi$ -D- $\pi$ -A (Figure 1b) motifs due to the presence of two donor and two acceptor groups and three  $\pi$ -spacers. All of these constituent units can be fruitfully selected and combined to finely tune the donor and acceptor strength,  $\pi$ -framework extension and, ultimately, the optical, energetic, and photovoltaic response of the sensitizers.



Figure 1. Schematic representation of monobranched D- $\pi$ -A, dibranched A- $\pi$ -D- $\pi$ -A, and tribranched A- $\pi$ -D- $\pi$ '-D- $\pi$ -A (this work) structural motifs.

To design the new tribranched prototypes, we selected some of the most common donor and  $\pi$ -spacer groups. Namely, as donor cores we have adapted the common triarylamino group<sup>[8]</sup> by using the *trans*-4,4'-bis(diarylamino)stilbene and *trans*-4,4'-bis(diarylamino)distyrylbenzene building blocks. The simple thiophene-based  $\pi$ -A-COOH arm of L1<sup>[13]</sup> and C213<sup>[14]</sup> (Scheme 1), which we previously chose as reference monobranched dyes, and which have been used in other previously reported sensitizers,<sup>[15,16]</sup> was selected as a side-branch. Based on these premises, we designed the tribranched dyes TB-1 and TB-2 (Scheme 2).



Scheme 2. Investigated tribranched organic sensitizers.

Here, we wish to report the fabrication of DSCs with the novel sensitizers, and to disclose their photoelectrochemical properties and stability data, which were measured under various conditions. DFT/TDDFT calculations have been performed in order to highlight the main properties associated with the tribranched geometry, both in solution and on TiO<sub>2</sub> models.

### **Results and Discussion**

# Synthesis, Spectroscopic, and Electrochemical Characterization

TB-1 and TB-2 were synthesized according to Scheme 3. 4-[N-(4-Methoxyphenyl)-N-phenylamino]benzaldehyde (1a) <sup>[17]</sup> was brominated in high yields to **1b** using *N*-bromosuccinimide (NBS) in anhydrous N,N-dimethylformamide (DMF) while keeping the temperature between -5 and 0 °C. At temperatures below -10 °C the yields were much more modest (less than 50%) whereas at higher temperatures (0 °C to r.t.) a complex mixture of brominated products was recovered. After reduction to the corresponding brominated alcohol 2b, the phosphonate 3b was directly prepared in one step with I2, using P(OEt)3 as a solvent. Horner-Witting condensation between diethyl methylphosphonate 3b and aldehyde 1b afforded the electron-rich brominated trans-4,4'-bis(diarylamino)stilbene intermediate 4b. Similarly pphenylenevinylogue derivative 5b was prepared using tetraethyl 1,4-phenylenebis(methylene)diphosphonate<sup>[18]</sup> and two equivalents of aldehyde 1b. It should be noted that aromatic bromination of the corresponding precursors 4a and 5a, which were obtained in a similar manner to that described above from 1a and 3a, always lead to complex mixtures of mono- and polybrominated derivatives, regardless of reaction conditions. Unfortunately, this result prevented us from fully exploiting the high-yielding McMurry reaction of 1a, which easily allowed the isolation of gram-quantities of 4a in only one step. The two bromoderivatives 4b and 5b were then submitted to the same reaction sequence, involving the microwave-mediated Suzuki coupling reaction with 5-formyl-2-thienylboronic acid<sup>[13]</sup> to give the corresponding 2-thiophenecarbaldehydes 6 and 7. The final Knoevenagel condensation step with cyanoacetic acid and piperidine, under microwave irradiation (which led to improved yields), afforded the corresponding piperidinium carboxylate derivatives of TB-1 and TB-2. The corresponding carboxylic acids were then isolated after treatment with saturated aqueous NH<sub>4</sub>Cl.

The absorption and emission spectra of TB-1 and TB-2 are shown in Figure 2. The main optical parameters, together with those of reference mono- and dibranched dyes, are collected in Table 1. Both TB-1 and TB-2 present two bands in the visible region. Comparison with the absorption peak of the corresponding 4,4'-bis(diarylamino)stilbene **4a** and bis(diarylamino)distyrylbenzene **5a** building blocks (393 and 415 nm in CH<sub>2</sub>Cl<sub>2</sub>, respectively) shows that the higher energy visible band (393 and 421 nm in CH<sub>2</sub>Cl<sub>2</sub> for TB-1 and TB-2, respectively) is attributed to a local



Scheme 3. Synthesis of TB-1 and TB-2. Reagents and conditions: (i) NBS, DMF, -5 to 0 °C, 3 h; (ii) NaBH<sub>4</sub>, EtOH, 0 °C to r.t.; (iii) I<sub>2</sub>, P(OEt)<sub>3</sub>, 0 °C to r.t.; (iv) n = 0, 1a or 1b, *t*BuOK, THF, 0 °C to r.t.; (v) n = 1, tetraethyl 1,4-phenylenebis(methylene)diphosphonate, *t*BuOK, THF, 0 °C to r.t.; (vi) TiCl<sub>4</sub>, Zn, pyridine, THF; (vii) 5-formyl-2-thienylboronic acid, [Pd(dppf)Cl<sub>2</sub>], K<sub>2</sub>CO<sub>3</sub>, MeOH/toluene, 70 °C, 10 min, microwave irradiation; (viii) cyanoacetic acid, piperidine, EtOH or toluene, 100 °C, microwave irradiation followed by NH<sub>4</sub>Cl.

transition of the donor core (see the Supporting Information, Figure S1), whereas the lower energy band is associated to the  $\pi$ - $\pi$ \* intramolecular charge transfer (CT) tran-



Figure 2. Normalized absorption (solid line) and emission (dashed line) spectra of TB-1 and TB-2 in DMSO.

sition from the electron-rich bis(diarylamino) moieties to the 2-cyanoacrylic acid acceptor end-groups. Indeed, the absorption peaks are almost identical in the two dyes, as a consequence of the presence of the same donor–acceptor side arm. Upon addition of a small amount of HCl, the spectrum remains unchanged, confirming that both dyes are present as carboxylic acids.<sup>[9]</sup> This picture was con-

Table 1. Absorption and emission parameters of TB-1 and TB-2 compared to reference dyes.

| Compound            | $\lambda_{\rm abs}$ / nm ( $\varepsilon$ / M <sup>-1</sup> cm <sup>-1</sup> ) | $\lambda_{\rm em}$ / nm $(\Phi)^{[a]}$ |
|---------------------|---|--|
| TB-1 <sup>[b]</sup> | 397 (40 900)  | 485 (0.058) <sup>[c]</sup>             |
|                     | 478 (35 800)  |  |
| TB-2 <sup>[b]</sup> | 421 (54 000)  | 540 (0.013) <sup>[d]</sup>             |
|                     | 480 (40 200)  |  |
| DB-1 <sup>[e]</sup> | 494 (44 500)  |  |
| $L1^{[f]}$          | 410 (25 800)  | 549                                    |
| C213 <sup>[g]</sup> | 482 (27 500)  | 660                                    |
|                     |   |  |

[a] Fluorescence quantum yield; Coumarin 540A was used as a standard (0.58 in EtOH). [b] This work (DMSO). [c]  $\lambda_{exc} = 397$  nm. [d]  $\lambda_{exc} = 421$  nm. [e] Ref.<sup>[9]</sup> (EtOH). [f] Ref.<sup>[13]</sup> (*tert*-butyl alcohol/ acetonitrile, 1:1). [g] Ref.<sup>[14]</sup> (THF).

firmed by investigating the emission properties. Excitation at  $\lambda_{max}$  produced fluorescence spectra that were different in TB-1 and TB-2, according to their different donor cores, and resembled those of **4a** (473 nm in CH<sub>2</sub>Cl<sub>2</sub>) and **5a** (504 nm in CH<sub>2</sub>Cl<sub>2</sub>), respectively.

The donor-acceptor CT band of the tribranched dyes is hypsochromically shifted with respect to the monobranched dye C213, although the former chromophores have a more extended  $\pi$ -conjugated system. At the same time, TB-1 and TB-2 present a significant hyperchromic effect, likely for the same reason. Similar, albeit less pronounced, hypsochromic effects are observed when the optical properties of the tribranched dyes are compared with those of the dibranched sensitizer DB-1. In conclusion, the tribranched geometry induces a negligible blueshift but a substantial increase in absorbance with respect to mono- and dibranched dyes. In addition, a second and more intense visible band at higher energy is present due to local transitions of the donor core, thus enabling more efficient sunlight harvesting in this region.

The electrochemical properties of TB-1 and TB-2 were examined by cyclic voltammetry in dimethylformamide (DMF). Using a glassy carbon working electrode, Pt counter electrode, and 0.05 M tetrabutylammonium hexafluorophosphate [TBA(PF<sub>6</sub>)] as a supporting electrolyte, the potentials measured vs. Fc<sup>+</sup>/Fc were converted into normal hydrogen electrode (NHE) potentials by addition of +0.63 V. TB-1 and TB-2 showed half-wave potentials corresponding to molecular oxidation potentials at +0.91 and +0.98 V vs. NHE, respectively. Their reduction potentials were detected at -0.87 and -0.97 V vs. NHE, respectively. By using the value of -4.5 eV vs. vacuum for NHE,<sup>[19]</sup> the HOMO/LUMO energies were calculated as -5.4/-3.6 and -5.5/-3.5 eV for TB-1 and TB-2, respectively.

#### **Computational Investigation**

To investigate the electronic structure of the representative TB-1 standalone dye and in relation to its constituent subunits, DFT/TDDFT calculations were performed on TB-1 and on the monobranched L1 and C213 systems. As shown in Figure 3, in which the energy levels of the Molecular Orbitals (MOs) are reported, the introduction of the  $\pi$ conjugated bridge linking the two monobranched subunits, induces a significant perturbation (mixing) among the occupied MOs. The strong mixing among the highest occupied MOs of the isolated building blocks is also evident by looking at the plots of the HOMO, HOMO-1, HOMO-2, LUMO, LUMO+1, and LUMO+2 of TB-1 reported in Figure 4. Taking the C213 dye as a reference monobranched unit, it can be seen that the HOMO, which is located at -5.90 eV in C213, is split in the tribranched system into three levels: the HOMO at -5.77 eV [mainly localized on the donor trans-4,4'-bis(diarylamino)stilbene core], the HOMO-1 at -6.18 eV (essentially extended on the two monobranched units), and the HOMO-2 at 6.91 eV (resulting from the strong mixing of the MOs of the linker and

of the C213 blocks). As expected, the interaction between the virtual orbitals is less pronounced, with the quasi-degenerate LUMO and LUMO+1, being the combinations of the LUMOs on the two monobranched units, and the LUMO+2 localized on the linking  $\pi$  bridge. Although a comparison between experimental electrochemical potentials and calculated HOMO/LUMO energy levels is not straightforward, we notice a rather good agreement between the calculated and experimental HOMO energy, whereas the calculated LUMO is substantially less negative than the electrochemical estimate. This is due to the employed exchange-correlation functional, which contains a large percentage of Hartree–Fock exchange (ca. 42%), but which, however, allows us to nicely reproduce the optical properties of the dyes.



Figure 3. Molecular orbital levels of L1, C213, and TB-1. The values were computed in the gas phase at the MPW1K/6-31G\* level.



Figure 4. Isodensity surfaces of the HOMO, HOMO–1, HOMO–2, LUMO, LUMO+1, and LUMO+2 of TB-1.

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The effect of the geometry of the tribranched dyes on the optical properties of the sensitizer is shown in Table 2, in which the lowest excitation energies and the corresponding oscillator strengths of the three dyes in the gas phase are compared. As could be expected on the basis of the molecular orbital energy diagram depicted in Figure 3, the lowest absorption peak moves to longer wavelengths on going from L1 to C213 as a consequence of HOMO destabilization induced by the two electron-donor hexyloxy substituents, coupled to only a slight LUMO energy upshift. Comparison of the calculated values with the experimentally determined band maxima is not straightforward because the deprotonated dye was measured for L1, whereas the protonation state of C213 is not clear. However, because protonation/deprotonation can shift the absorption maxima by up to 0.3 eV,<sup>[20]</sup> the data presented here can be considered to be in good overall agreement with the experimental values. An absorption maximum of 479 nm was calculated for C213, which can be compared with the 482 nm experimental value. For the protonated dye L1, a 461 nm absorption maximum was calculated, which can be compared to the 404 nm maximum measured for the deprotonated dye.

Table 2. Computed lowest excitation wavelengths and oscillator strengths in the gas phase and DMSO solution for TB-1, L1, and C213.

| Compound | $\lambda_{abs}$ / nm<br>vacuum/DMSO | Oscillator strength vacuum/DMSO |
|----------|-------------------------------------|---------------------------------|
| TB-1     | 457/495                             | 1.940/1.903                     |
| L1       | 421/461                             | 1.228/1.316                     |
| C213     | 436/479                             | 1.222/1.316                     |

In the tribranched structure, the computed lowest absorption band is slightly red-shifted compared with C213 both in vacuo and in solution, with an oscillator strength almost 70% larger than that of the monobranched systems. The calculated value in solution (495 nm) is in excellent agreement (within 0.1 eV) with the 478 nm experimental data. The lowest energy and most intense transition of TB-1 turns out to be a mixing of HOMO  $\rightarrow$  LUMO (65%), HOMO-1  $\rightarrow$  LUMO+1 (20%), and HOMO  $\rightarrow$  LUMO+2 (5%) orbital excitations. The mixed nature of the main TB-1 optical transition is responsible for the modest redshift computed for this system compared with C213 [495 vs. 479 nm in dimethyl sulfoxide (DMSO) solution], despite the sizeable reduction of the HOMO–LUMO gap computed for TB-1 compared with C213 (3.61 vs. 3.83 eV).

To gain insight into the possible interaction between the newly synthesized TB-1 dye and the nanostructured  $TiO_2$  semiconductor, we examined the optimized geometry of TB-1 and docked the resulting structure (with no further geometry optimization) onto extended  $TiO_2$  models. The optimized structure of TB-1 shows two conformers, a more stable conformer with a *transoid* arrangement of the two branches (Figure 5A) and a less stable conformer (Figure 5B) corresponding to a *cisoid* arrangement of the two branches. The A *transoid* conformer was calculated to be

5.3 kcal/mol more stable than the B *cisoid* conformer, possibly because of the preferential arrangement of the aromatic moieties around the N-terminated bridge.



Figure 5. Optimized molecular structures of the A and B TB-1 conformers.



Figure 6. Possible interaction of TB-1 conformers A and B with the  $TiO_2$  substrate.

As can be noticed from Figure 6, the more stable A conformer exhibits a non-optimal interaction with the  $TiO_2$ surface, which might reduce the dye molecular packing on  $TiO_2$ , which, in turn, may impact the photovoltaic performance, as discussed below. The less stable B conformer shows better dye packing on  $TiO_2$ , occupying essentially a similar space to that expected for two single branched dyes. The lower stability in solution, however, might imply that this conformer is present as a minor fraction upon adsorption onto  $TiO_2$ .

#### Photovoltaic Investigation in DSCs

The new sensitizers, TB-1 and TB-2, were used to fabricate DSCs to explore the current-voltage characteristics. The incident monochromatic photon-to-current conversion efficiency (IPCE) of TB-1 plotted as a function of excitation wavelength exhibits a high value at plateau (81%) and more than 70% from 400 to 560 nm (Figure 7). In contrast, although exhibiting a photoelectrochemical response in a similar wavelength range, the IPCE of TB-2 showed a slightly lower maximum value of 75%. The integrated current under the IPCE curve is 10.8 and 9.5 mA cm<sup>-2</sup>, for TB-1 and TB-2, respectively, which is consistent with the photocurrent of solar cells under standard global AM 1.5 solar conditions (see below). The main photovoltaic parameters are shown in Figure 8 and Table 3. The TB-1 cell showed a 10.9 mA cm<sup>-2</sup> short circuit current density ( $J_{sc}$ ), 641 mV of open circuit voltage ( $V_{oc}$ ), and 72.5% fill factor (ff) at standard global AM 1.5 solar conditions. Thus, the TB-1 power conversion efficiency  $\eta$ , derived from the equation  $\eta = J_{sc}$  $\times V_{\rm oc} \times ff$ , is 5.05%. Under similar conditions, the TB-2 cell performance showed a  $J_{\rm sc}$  value of 9.65 mA cm<sup>-2</sup>, 662 mV  $V_{\rm oc}$ , and a fill factor of 70.6, resulting in a power conversion efficiency ( $\eta$ ) of 4.51%. The different  $J_{\rm sc}$  value is consistent with the estimate obtained by IPCE integration. All devices showed a very linear response of  $J_{sc}$  and a slightly higher *ff* under a lower light intensity (see Table 3).



Figure 7. Photocurrent action spectra of TB-1 and TB-2 DSCs.



Figure 8. The J/V characteristics of DSCs based on TB-1 and TB-2 under various light intensities.

Table 3. Photovoltaic parameters of TB-1 and TB-2 compared with reference dyes.

| Compound             | $I_0$ / sun | $J_{\rm sc}$ / mA cm $^{-2}$ | $V_{\rm oc}$ / V | FF / % | η / % |
|----------------------|-------------|------------------------------|------------------|--------|-------|
| TB-1                 | 1           | 10.9                         | 641              | 72.5   | 5.05  |
|                      | 0.5         | 5.45                         | 616              | 74.5   | 5.01  |
|                      | 0.10        | 1.10                         | 558              | 76.6   | 4.75  |
| TB-2                 | 1           | 9.65                         | 662              | 70.6   | 4.51  |
|                      | 0.5         | 4.84                         | 640              | 72.6   | 4.50  |
|                      | 0.10        | 0.99                         | 584              | 73.6   | 4.30  |
| L1 <sup>[13]</sup>   | 1           | 5.42                         | 735              | 69     | 2.75  |
|                      | 1           | 12.8                         | 620              | 66     | 5.20  |
| C213 <sup>[14]</sup> | 1           | 11.9                         | 775              | 74.7   | 6.88  |

It is interesting to compare the photovoltaic data obtained for TB-1 and TB-2 with the previously reported device data obtained for the related L1 and C213 dyes. A survey of such data is reported in Table 3, showing that the difference between TB-1 and the better performing C213 is mainly related to an approximate 20% increase in  $V_{\rm oc}$  obtained for the latter, which, together with a 9% (3%) increase in  $J_{\rm sc}$  (ff), provides an overall 36% increase in  $\eta$ . The incorporated long alkoxy chain in C213 could also justify the higher  $V_{oc}$ . Indeed, Hagberg et al. have recently shown a correlation between  $V_{\rm oc}$  and bulky butoxy chains.<sup>[16]</sup> A similarly higher  $V_{\rm oc}$  is obtained for L1, despite the fact that a larger amount of LiI (0.1 and 0.05 M, respectively) was used than in the present investigation (0.05 M).<sup>[13,14]</sup> Thus, it is quite unlikely that the reduced  $V_{\rm oc}$  value obtained with TB-1 and TB-2 is due to the composition of the electrolyte, which renders the higher  $J_{\rm sc}$ . We could speculate that the unfavorable interaction with TiO<sub>2</sub> discussed on the basis of the structural parameters of the dye is responsible for the lower  $V_{\rm oc}$ , whereby the non-optimal dye packing on the semiconductor surface would allow the oxidized species in the electrolyte to approach the surface, thus increasing recombination between electrons injected into TiO<sub>2</sub> and the electrolyte. However, we did not observe increased recombination rates in TB-1 and TB-2 when compared with monobranched dye D5 (see the Supporting Information, Figure S6).<sup>[21]</sup> Moreover, the measured dye loadings<sup>[22]</sup> of TB-1 ( $4.8 \times 10^{-8} \text{ mol cm}^{-2}$ ) and TB-2 ( $4.1 \times 10^{-8} \text{ mol cm}^{-2}$ ) on 3- $\mu$ m TiO<sub>2</sub> films were 96 and 82% with respect to that of monobranched dye D5 ( $4.1 \times 10^{-8} \text{ mol cm}^{-2}$ ) under same conditions. In other words, neither overloaded dyes nor fast recombination were observed in TB-1 and TB-2.

We previously reported that dibranched dyes, having two anchoring groups, showed good stability data when employed in DSCs.<sup>[9]</sup> It was thus interesting to test the temporal stability of DSCs fabricated with the new TB-1 and TB-2 dyes. Figure 9 shows the photovoltaic performance changes during a long-term accelerated ageing of TB-1 and TB-2 sensitized solar cells using an ionic liquid electrolyte (1,3-dimethylimidazoliumiodide/1-ethyl-3-methylimidazoliumiodide/1-ethyl-3-methylimidazolium tetracyanoborate/iodine/N-butylbenzoimidazole/guanidinium thiocyanate

with molar ratio 12:12:16:1.67:3.33:0.67) under light soaking at full intensity (100 mW cm<sup>-2</sup>) at 60 °C. Values for  $J_{sc}$ ,  $V_{oc}$ , ff, and  $\eta$  were recorded over a period of 1000 h. The overall efficiencies of TB-1 and TB-2 remained at 88 and 74% of the initial value, respectively, after light soaking. These stabilities are an improvement over our previously reported dibranched dye DB-1, which exhibited a 67% residual value. The  $J_{sc}$  values of both TB-1 and DB-2 showed a drop at the initial ageing stage but recovered after 300 h of ageing. The reason for this drop of  $J_{sc}$  is not clear at this stage. The losses in  $\eta$  are mainly caused by the drop in  $V_{oc}$ , namely 68 and 55 mV for TB-1 and TB-2, respectively,



Figure 9. Photovoltaic parameter ( $J_{sc}$ ,  $V_{oc}$ , ff, and  $\eta$ ) variations with ageing time for the devices sensitized with TB-1 (closed symbols) and TB-2 (open symbols) based on ionic liquid electrolyte during successive light soaking for 1000 h.



which is likely caused by protonation processes that take place during light soaking, leading to a positive shift of the  $TiO_2$  band edge.<sup>[23]</sup>

### Conclusions

We have introduced a novel design based on tribranched organic sensitizers, carrying two donors, two acceptors, three  $\pi$  spacers, and two anchoring points. Such molecular architecture should provide more variety in the sensitizer chemical structure, allowing further structural optimization that can be tailored to achieve the desired properties. Comparison of DSCs based on the tribranched dyes TB-1 and TB-2 with the corresponding monobranched system C213 shows a decrease in power conversion efficiency, mainly due to lower photovoltages in the former system. This was ascribed to the selected electrolyte for higher photocurrents, and to the computed non-optimal interaction with the  $TiO_2$ surface, which might reduce the molecular packing of the dye and favor detrimental recombination between the semiconductor and oxidized electrolyte. However, it should be noted that the twisted structure of the adsorbed transoid conformer is particularly suitable for efficient interaction with the chemisorption sites, for which a distance of 10.2 Å was measured.<sup>[24]</sup> Furthermore, such adsorption geometry inhibits aggregation as a result of steric hindrance. Indeed, the efficiency stabilities of DSCs based on TB-1 and TB-2 after light soaking are improved with respect to dibranched DB-1, which, in turn, offers increased stability with respect to the corresponding monobranched dyes.<sup>[9]</sup> Although the two first prototypes did not offer improved power conversion efficiencies with respect to the conventional uni-dimensional design, we believe that the tribranched design could trigger the development of optimized systems through the incorporation of appropriate new branches.

### **Experimental Section**

General: NMR spectra were recorded with a Bruker AMX-500 spectrometer operating at 500.13 MHz (<sup>1</sup>H). Coupling constants are given in Hz. High resolution mass spectra (HRMS) were recorded with a Bruker Daltonics ICR-FTMS APEX II spectrometer equipped with an electrospray ionization (ESI) source. Flash chromatography was performed with Merck grade 9385 silica gel 230-400 mesh (60 Å). Reactions were performed under nitrogen in oven-dried glassware and monitored by thin layer chromatography using UV light (254 and 365 nm) as a visualizing agent. All reagents were obtained from commercial suppliers at the highest purity grade and used without further purification. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Toluene and MeOH were dried with CaCl2 and MgSO<sub>4</sub>, respectively. Extracts were dried with Na<sub>2</sub>SO<sub>4</sub> and filtered before removal of the solvent by evaporation. Melting points are uncorrected. Absorption spectra were recorded with a V-570 Jasco spectrophotometer. Emission spectra were recorded with a FP6200 Jasco spectrofluorometer. Fluorescence spectra were collected by exciting at the maximum of absorption. Fluorescence quantum yields  $\Phi$  were recorded by using the relative comparative method with a standard sample of known  $\Phi$  value and optically dilute solu-

tions.<sup>[25]</sup> Coumarin 540A in EtOH ( $\Phi = 0.58$ ) was used to estimate fluorescence quantum yields.<sup>[26]</sup> The absorbance at excitation wavelengths were kept below 0.1. Refractive index (DMSO 1.477, EtOH 1.359) corrections were included in order to account for the different solvents of the test and the reference solutions. Infrared spectra (IR) were recorded with an ATR-FTIR Perkin–Elmer Spectrum 100 spectrometer.

**4-**[*N*-(**4-Bromophenyl**)-*N*-(**4-methoxyphenyl**)**aminolbenzaldehyde** (**1b**): A solution of NBS (0.65 g, 3.63 mmol) in anhydrous DMF (3 mL) was slowly added to a stirred solution of 4-[*N*-(4-methoxyphenyl)-*N*-phenylamino]benzaldehyde (**1a**)<sup>[17]</sup> (1.00 mg, 3.30 mmol) in the same solvent (10 mL). The solution was kept at -5 to 0 °C for 3 h. The reaction mixture was poured into water (50 mL) and the formation of a yellow precipitate was observed. The solid was filtered under reduced pressure to yield the pure product (1.12 g, 2.93 mmol, 89%) as a green gummy solid. <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 9.77 (s, 1 H), 7.72 (d, *J* = 8.8 Hz, 2 H), 7.56 (d, *J* = 8.8 Hz, 2 H), 7.18 (d, *J* = 8.9 Hz, 2 H), 7.13 (d, *J* = 8.8 Hz, 2 H), 7.02 (d, *J* = 8.9 Hz, 2 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 3.78 (s, 3 H) ppm.

**4-**[*N*-(**4-Methoxyphenyl**)-*N*-**phenylamino]benzyl** Alcohol (2a): A solution of NaBH<sub>4</sub> (0.22 g, 5.81 mmol) in THF (15 mL) was added to an ice-cold and stirred solution of 1a (1.48 g, 4.88 mmol) in the same solvent (25 mL). The mixture was warmed to r.t. and stirred overnight. The solvent was partially evaporated under reduced pressure, then Et<sub>2</sub>O (15 mL) and water (30 mL) were added. After separating the organic phase, the aqueous layer was extracted with Et<sub>2</sub>O (3×15 mL). The combined organic phases were dried and the solvent evaporated to afford the product as a yellow waxy solid (1.45 g, 4.75 mmol, 97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.24–7.19 (m, 4 H), 7.06 (d, *J* = 8.9 Hz, 2 H), 7.03 (d, *J* = 7.5 Hz, 2 H), 7.02 (d, *J* = 8.4 Hz, 2 H), 6.96 (t, *J* = 7.3 Hz, 1 H), 6.84 (d, *J* = 8.9 Hz, 2 H), 3.80 (s, 3 H) ppm.

**4-**[*N*-(**4-Bromopheny**])-*N*-(**4-methoxypheny**])amino]benzyl Alcohol (**2b**): A solution of NaBH<sub>4</sub> (0.23 g, 6.15 mmol) in EtOH (15 mL) was added to an ice-cold and stirred solution of **1b** (1.96 g, 5.13 mmol) in the same solvent (50 mL). The mixture was warmed to r.t. and stirred overnight. Et<sub>2</sub>O (15 mL) and water (30 mL) were then added, the organic phase was separated, and the aqueous layer was extracted with Et<sub>2</sub>O (3 × 15 mL). The combined organic phases were dried and the solvent was evaporated. The product was obtained as a yellow waxy solid (1.21 g, 3.14 mmol, 61%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.36 (d, *J* = 8.9 Hz, 2 H), 7.24 (d, *J* = 8.3 Hz, 2 H), 7.03 (d, *J* = 8.9 Hz, 2 H), 6.97 (d, *J* = 8.4 Hz, 2 H), 6.93 (d, *J* = 8.9 Hz, 2 H), 6.78 (d, *J* = 8.9 Hz, 2 H), 5.11 (t, *J* = 5.5 Hz, 1 H), 4.44 (d, *J* = 5.2 Hz, 2 H), 3.75 (s, 3 H) ppm.

**Diethyl 4-[N-(4-Methoxyphenyl)-N-phenylamino]benzylphosphonate** (3a): Alcohol 2a (1.45 g, 4.75 mmol) was dissolved in P(OEt)<sub>3</sub> (10 mL) at 0 °C and I<sub>2</sub> (1.27 g, 5.00 mmol) was added in one pot. The reaction mixture was warmed to r.t. and stirred overnight. The excess of P(OEt)<sub>3</sub> was distilled off under reduced pressure and the pure product was obtained after filtration through silica gel (*n*hexane to AcOEt/petroleum ether, 8:2) as a clear oil (1.24 g, 2.91 mmol, 62%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 7.19 (t, *J* = 8.5 Hz, 2 H), 7.13 (dd, *J* = 8.6, 2.5 Hz, 2 H), 7.04 (d, *J* = 8.9 Hz, 2 H), 7.00 (d, *J* = 7.6 Hz, 2 H), 6.97 (d, *J* = 8.0 Hz, 2 H), 6.92 (t, *J* = 7.3 Hz, 1 H), 6.82 (d, *J* = 8.9 Hz, 2 H), 4.06 (quintet, *J* = 7.1 Hz, 4 H), 3.79 (s, 3 H), 3.08 (d, *J* = 21.3 Hz, 2 H), 1.26 (t, *J* = 7.1 Hz, 6 H) ppm.

**Diethyl 4-**[*N*-(**4-Bromophenyl**)-*N*-(**4-methoxyphenyl**)**amino**]**benz-ylphosphonate (3b):** Alcohol **2b** (1.21 g, 3.14 mmol) was dissolved in P(OEt)<sub>3</sub> (10 mL) at 0 °C and I<sub>2</sub> (0.96 g, 3.78 mmol) was added

in one pot. The reaction mixture was warmed to r.t. and stirred overnight. The excess of P(OEt)<sub>3</sub> was distilled off under reduced pressure and the pure product was obtained after filtration through silica gel (*n*-hexane to EtOH), as a clear oil (1.50 g, 2.98 mmol, 94%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.37 (d, *J* = 8.9 Hz, 2 H), 7.19 (dd, *J* = 8.5, 2.3 Hz, 2 H), 7.03 (d, *J* = 8.8 Hz, 2 H), 6.94 (d, *J* = 8.8 Hz, 4 H), 6.69 (d, *J* = 8.8 Hz, 2 H), 4.01 (quintet, *J* = 8.2 Hz, 4 H), 3.75 (s, 3 H), 3.16 (d, *J* = 21.3 Hz, 2 H), 1.25 (t, *J* = 7.1 Hz, 6 H) ppm.

#### p,p'-Bis[N-(4-methoxyphenyl)-N-phenylamino]stilbene (4a)

Route A (Scheme 3, step iv): tBuOK (0.18 g, 1.60 mmol) was added to an ice-cold and stirred solution of diethyl benzylphosphonate 3a (0.48 g, 1.12 mmol) in THF (20 mL). After 30 min, a solution of benzaldehyde 1a (0.34 g, 1.12 mmol) in the same solvent (10 mL) was added dropwise and the resulting mixture was stirred at r.t. for 24 h. The solvent was partially evaporated under reduced pressure, then AcOEt (20 mL) and water (50 mL) were added. After collecting the organic phase, the aqueous layer was extracted with AcOEt  $(3 \times 20 \text{ mL})$ , and the combined organic phases were dried and the solvent was evaporated under reduced pressure to afford an orange oil, which was submitted to flash chromatography (Et<sub>2</sub>O/cyclohexane, 3:7). The pure product was obtained as a yellow-orange solid (0.14 g, 0.24 mmol, 22%), m.p. 161–162 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ = 7.30 (d, J = 8.6 Hz, 4 H), 7.22 (t, J = 7.5 Hz, 4 H), 7.08 (d, J = 8.9 Hz, 4 H), 7.06 (d, J = 8.6 Hz, 4 H), 6.99 (d, J = 8.1 Hz, 4 H), 6.95 (t, J = 7.3 Hz, 2 H), 6.91 (s, 2 H), 6.85 (d, J = 8.9 Hz, 4 H), 3.81 (s, 6 H) ppm.

**Route B (Scheme 3, step vi):** Zn (2.16 g, 32.9 mmol) was suspended in anhydrous THF (50 mL) and the suspension was cooled to -20 °C. TiCl<sub>4</sub> (3.13 g, 16.5 mmol) was added dropwise (formation of a yellow precipitate was observed). The suspension was heated to reflux for 30 min (gradual darkening was observed). The mixture was cooled to -15 °C and a solution of benzaldehyde **1a** (2.50 g, 8.2 mmol) and anhydrous pyridine (1.69 g, 21.4 mmol) in anhydrous THF (20 mL) was added dropwise. The resulting suspension was heated to reflux for 2 h and then poured into a 3:2 mixture of water and CH<sub>2</sub>Cl<sub>2</sub> (100 mL). The dark suspension was filtered through a pad of Celite. The organic phase was separated, extracted with water (3 × 30 mL), dried, and the solvent evaporated under reduced pressure to yield the pure product as a yellow solid (2.00 g, 3.48 mmol, 84%).

*p*,*p*′-**Bis**[*N*-(bromophenyl)-*N*-(4-methoxyphenyl)amino]stilbene (4b): tBuOK (0.42 g, 3.70 mmol) was added to an ice-cold and stirred solution of diethyl benzylphosphonate **3b** (1.50 g, 2.97 mmol) in anhydrous THF (20 mL). After 30 min, a solution of aldehyde **1a** (1.22 g, 3.20 mmol) in the same solvent (10 mL) was added dropwise and the resulting mixture was stirred at r.t. for 24 h. The solvent was partially evaporated under reduced pressure, then Et<sub>2</sub>O (20 mL) and water (50 mL) were added. After collecting the organic phase, the aqueous layer was extracted with Et<sub>2</sub>O (3 × 20 mL). The combined organic phases were dried and the solvent evaporated to afford the pure product as a yellow-orange solid (0.99 g, 1.35 mmol, 46%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.60 (d, *J* = 8.8 Hz, 4 H), 7.52 (d, *J* = 8.8 Hz, 4 H), 7.16 (d, *J* = 8.9 Hz, 4 H), 7.08 (d, *J* = 8.8 Hz, 4 H), 7.01 (s, 2 H), 7.00 (d, *J* = 8.9 Hz, 4 H), 6.88 (d, *J* = 8.8 Hz, 4 H), 3.78 (s, 6 H) ppm.

p,p'-Bis[*N*-(4-methoxyphenyl)-*N*-phenylamino]distyrylbenzene (5a): *t*BuOK (0.11 g, 0.99 mmol) was added to an ice-cold and stirred solution of the tetraethyl 1,4-phenylenebis(methylene)diphosphonate<sup>[18]</sup> (0.15 g, 0.41 mmol) in anhydrous THF (20 mL). After 30 min, a solution of aldehyde **1a** (0.25 g, 0.82 mmol) in the same



solvent (5 mL) was added dropwise and the resulting mixture was stirred at r.t. for 36 h. The solvent was partially evaporated under reduced pressure, then AcOEt (50 mL) and water (100 mL) were added. After collecting the organic phase, the aqueous layer was extracted with AcOEt (3 × 30 mL). The combined organic phases were dried and the solvent was evaporated to afford an orange oil. The crude product was purified by flash chromatography (Et<sub>2</sub>O/ cyclohexane, 7:3) to give the product as a yellow-orange solid (0.15 g, 0.22 mmol, 54%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.55 (s, 4 H), 7.48 (d, *J* = 8.9 Hz, 4 H), 7.29 (t, *J* = 8.6 Hz, 4 H), 7.20 (d, *J* = 16.2 Hz, 2 H), 7.08 (d, *J* = 16.2 Hz, 2 H), 7.07 (d, *J* = 9.0 Hz, 4 H), 7.01 (t, *J* = 6.3 Hz, 2 H), 7.00 (d, *J* = 8.4 Hz, 4 H), 6.96 (d, *J* = 9.0 Hz, 4 H), 6.89 (d, *J* = 8.4 Hz, 4 H), 3.90 (s, 6 H) ppm.

*p*,*p*′-**Bis**[*N*-(**bromopheny**])-*N*-(4-methoxyphenyl)amino]distyrylbenzene (5b): *t*BuOK (0.49 g, 4.32 mmol) was added to an ice-cold and stirred solution of the tetraethyl 1,4-phenylenebis(methylene) diphosphonate<sup>[18]</sup> (0.68 g, 1.80 mmol) and **1b** (1.38 g, 3.61 mmol) in anhydrous THF (30 mL). The resulting mixture was stirred at r.t. for 6 h. The solvent was partially evaporated under reduced pressure, then AcOEt (30 mL) and water (50 mL) were added. The combined organic phases were dried and the solvent removed under reduced pressure to afford an orange oil, which was purified by flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:1) to give the product as a yellow solid (0.97 g, 1.16 mmol, 65%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 7.56 (s, 4 H), 7.51 (d, *J* = 8.7 Hz, 4 H), 7.42 (d, *J* = 8.9 Hz, 4 H), 7.22 (d, *J* = 16.3 Hz, 2 H), 7.11 (d, *J* = 16.4 Hz, 2 H), 7.08 (d, *J* = 8.9 Hz, 4 H), 6.89 (d, *J* = 8.9 Hz, 4 H) 3.77 (s, 6 H) ppm.

*p*,*p*'-Bis{*N*-[(5-formyl-thien-2-yl)phenyl]-*N*-(4-methoxyphenyl)amino}stilbene (6): A solution of 5-formyl-2-thienylboronic acid (213 mg, 1.36 mmol) and K<sub>2</sub>CO<sub>3</sub> (481 mg, 3.75 mmol) in anhydrous MeOH (3 mL) was added to a solution of dibromo derivative **4b** (250 mg, 0.34 mmol) and [Pd(dppf)Cl<sub>2</sub>] (55.7 mg, 0.068 mmol) in anhydrous toluene (2.5 mL). The mixture was heated by microwave irradiation at 70 °C for 10 min. After adding water (30 mL), the mixture was extracted with  $CH_2Cl_2$  (3 × 30 mL), the combined organic extracts were dried, and the solvent was removed by rotary evaporation leaving a residue that was taken up with hot EtOH. The product was obtained as a brown solid (210 mg, 0.26 mmol, 78%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 9.87 (s, 2 H), 8.01 (d, J = 4.0 Hz, 2 H), 7.68 (d, J = 8.7 Hz, 4 H), 7.61 (d, J = 4.0 Hz, 2 H), 7.53 (d, J = 8.7 Hz, 4 H), 7.12 (d, J = 8.7 Hz, 4 H), 7.11 (s, 2 H), 7.04 (d, J = 8.6 Hz, 4 H), 6.99 (d, J = 8.9 Hz, 4 H), 6.95 (d, J = 8.7 Hz, 4 H) 3.78 (s, 6 H) ppm.

p,p'-Bis{N-[(5-formyl-thien-2-yl)phenyl]-N-(4-methoxyphenyl)amino}distyrylbenzene (7): A solution of 5-formyl-2-thienylboronic acid (220 mg, 1.44 mmol) and K<sub>2</sub>CO<sub>3</sub> (510 mg, 3.95 mmol) in anhydrous MeOH (3 mL) was added to a solution of dibromo derivative 5b (303 mg, 0.36 mmol) and [Pd(dppf)Cl<sub>2</sub>] (59 mg, 0.072 mmol) in anhydrous toluene (2.5 mL). The mixture was heated by microwave irradiation at 70 °C for 10 min. The reaction was quenched by the addition of water (30 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub>  $(3 \times 30 \text{ mL})$ . The combined organic extracts were dried and the solvent removed by evaporation under reduced pressure, leaving a residue that was taken up with hot EtOH. The product was obtained as a brown solid (290 mg, 0.32 mmol, 89%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$ = 9.87 (s, 2 H), 8.01 (d, J = 4.0 Hz, 2 H), 7.69 (d, J = 8.7 Hz, 4 H), 7.61 (d, J = 3.9 Hz, 2 H), 7.58 (s, 4 H), 7.56 (d, J = 8.6 Hz, 4 H), 7.25 (d, J = 16.4 Hz, 2 H), 7.15 (d, J = 16.4 Hz, 2 H), 7.13 (d, J = 8.8 Hz, 4 H), 7.05 (d, J = 8.5 Hz, 4 H), 7.00 (d, J = 8.9 Hz, 4 H), 6.97 (d, J = 8.7 Hz, 4 H), 3.78 (s, 6 H) ppm.

TB-1: Cyanoacetic acid (0.26 g, 3.02 mmol) and a catalytic amount of piperidine were added to a solution of bis-aldehyde 6 (80 mg, 0.10 mmol) in EtOH (5 mL). The mixture was heated by microwave irradiation at 100 °C for 1 h and then water (30 mL) was added. The formed precipitate was collected and dissolved in CH<sub>2</sub>Cl<sub>2</sub>. After extracting the solution with saturated aqueous NH<sub>4</sub>Cl, the organic phase was separated, dried, and the solvent removed by rotary evaporation to afford the crude product, which was purified as a dark-red solid by recrystallization (AcOH) (0.021 g, 0.02 mmol, 23%); m.p. > 200 °C (dec.). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$ = 8.09 (s, 2 H), 7.69 (d, J = 3.9 Hz, 2 H), 7.59 (d, J = 8.7 Hz, 4 H), 7.50 (d, J = 8.7 Hz, 4 H), 7.48 (d, J = 3.9 Hz, 2 H), 7.10 (d, J= 8.9 Hz, 4 H), 7.08 (s, 2 H), 7.01 (d, J = 8.6 Hz, 4 H), 6.98 (d, J= 8.8 Hz, 4 H), 6.97 (d, J = 8.5 Hz, 4 H) 3.78 (s, 6 H) ppm. IR (neat):  $\tilde{v} = 3500-2000$  (s), 2217 (m), 1712 (s), 1571 (vs), 1502 (vs), 1424 (vs), 1317 (vs), 1283 (s), 1239 (vs), 1178 (vs), 1059 (s), 1027 (s), 797 (s) cm<sup>-1</sup>. HRMS-ESI: m/z = 463.11390 [(M - 2H)/2 requires)463.11164], 419.12302 [(M - 2COOH)/2 requires 419.12181]. C<sub>56</sub>H<sub>40</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>: calcd. C 72.39, H 4.34, N 6.03; found C 72.28, H 4.76, N 6.29.

TB-2: Cyanoacetic acid (0.33 g, 3.89 mmol) and a catalytic amount of piperidine were added to a solution of bis-aldehyde 7 (0.174 g, 0.19 mmol) in toluene (5 mL). The mixture was heated by microwave irradiation at 100 °C for 40 min. The reaction was quenched by the addition of saturated aqueous NH<sub>4</sub>Cl (30 mL). The formed solid was collected to afford, after recrystallization (AcOH), the pure product as a dark-red solid (0.081 g, 0.08 mmol, 41%); m.p. > 200 °C (dec.). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta$  = 8.43 (s, 2 H), 7.97 (d, J = 3.9 Hz, 2 H), 7.68 (d, J = 8.7 Hz, 4 H), 7.63 (d, J = 3.9 Hz, 2 H), 7.59 (s, 4 H), 7.56 (d, J = 8.7 Hz, 4 H), 7.25 (d, J = 16.3 Hz, 2 H), 7.15 (d, J = 16.3 Hz, 2 H), 7.14 (d, J = 8.7 Hz, 4 H), 7.06 (d, J = 8.4 Hz, 4 H), 7.00 (d, J = 8.8 Hz, 4 H), 6.99 (d, J = 8.5 Hz, 4 H), 3.78 (s, 6 H) ppm. IR (neat):  $\tilde{v} = 3260-2000$  (s), 2215 (m), 1685 (s), 1565 (vs), 1506 (vs), 1408 (vs), 1318 (vs), 1287 (vs), 1243 (vs), 1220 (vs), 1193 (vs), 1181 (vs), 1063 (m), 828 (w), 801 (w) cm<sup>-1</sup>. HRMS-ESI: m/z = 514.13783 [(M - 2H)/2 requires 514.13512], 470.14602 [(M - 2COOH)/2 requires 470.14529]. C<sub>64</sub>H<sub>46</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>·4H<sub>2</sub>O: calcd. C 69.67, H 4.93, N 5.08; found C 70.03, H 4.67, N 5.07.

**Computational Details:** DFT and TDDFT calculations were carried out using the Gaussian03 suite of programs.<sup>[27]</sup> Following the previously proposed successful strategy,<sup>[20]</sup> the ground state geometries were optimized in the gas phase using the B3LYP exchange-correlation functional<sup>[28]</sup> and a standard 6-31G\* basis set, whereas the hybrid MPW1K functional<sup>[29]</sup> was employed for the excited state calculations. Finally, the solvation effects were taken into account by applying the non-equilibrium C-PCM method<sup>[30]</sup> as implemented in Gaussian03.

**Preparation and Characterization of DSCs:** FTO glass plates (Nippon Sheet Glass, Solar 4 mm thickness) were immersed in aqueous TiCl<sub>4</sub> (40 mM) at 70 °C for 30 min and washed with water and ethanol. A paste composed of 20 nm anatase TiO<sub>2</sub> particles for the transparent nanocrystalline layer was coated on the FTO glass plates by screen printing. The coating-drying procedure was repeated to increase the thickness to that required. The TiO<sub>2</sub> electrodes were made of an approximate 6 µm transparent layer and were gradually heated under a flow of air. After a second TiCl<sub>4</sub> treatment, the TiO<sub>2</sub> electrodes were immersed in a 0.3 mM solution of TB-1 or TB-2 in tetrahydrofuran (THF) and kept at r.t. for 18 h. The liquid electrolyte consisted of 0.6 M *N*-methyl-*N*-butyl imidazolium iodide, 0.04 M iodine, 0.05 M LiI, 0.05 M guanidinium thiocyanate, and 0.28 M *tert*-butylpyridine in 15:85 (v/v) mixture of va-

leronitrile and acetonitrile. The dye-adsorbed TiO<sub>2</sub> electrode and counter electrode were assembled into a sealed sandwich-type cell with a gap of a hot-melt ionomer film, Surlyn (25 µm, Du-Pont). For stability evaluation, the TiO<sub>2</sub> electrodes were made of an approximate 7 µm transparent layer (20 nm diameter) and approximate 5 µm scattering layer (400 nm diameter, CCIC, HPW-400). The ionic liquid electrolyte consisted of 1,3-dimethylimidazoliumiodide, 1-ethyl-3-methylimidazoliumiodide, 1-ethyl-3-methylimidazolium tetracyanoborate, iodine, N-butylbenzoimidazole, and guanidinium thiocyanate (molar ratio 12:12:16:1.67:3.33:0.67).<sup>[31]</sup> The other procedure was identical to that mentioned above. In order to reduce scattered light from the edge of the glass electrodes of the dyed TiO<sub>2</sub> layer, a light shading mask was used on the DSCs, so the active area of DSCs was fixed to 0.2 cm<sup>2</sup>. For photovoltaic measurements of the DSCs, the irradiation source was a 450 W xenon light (Osram XBO 450, Germany) fitted with a filter (Schott 113), the power of which was regulated to the AM 1.5 G solar standard by using a reference Si photodiode equipped with a colormatched filter (KG-3, Schott) in order to reduce the mismatch in the region of 350-750 nm between the simulated light and AM 1.5 G to less than 4%. The measurement of incident photon-tocurrent conversion efficiency (IPCE) was plotted as a function of excitation wavelength by using the incident light from a 300 W xenon lamp (ILC Technology, USA), which was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd.). The measurement settling time between applying a voltage and measuring a current for the I-V characterization of DSCs was fixed to 40 and 200 ms for liquid and ionic liquid electrolytes, respectively.

**Supporting Information** (see footnote on the first page of this article): Absorption spectra of **4a** and **5a**, <sup>1</sup>H NMR and FT-IR spectra of TB-1 and TB-2, recombination rates of TB-1 and TB-2.

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