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Asymmetric Tribranched Dyes: An Intramolecular Cosensitization Approach for Dye-Sensitized Solar Cells

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A new multidonor and multianchoring asymmetric tribranched organic photosensitizer (i.e., TB-PT) for dye-sensitized solar cells containing three different (D– π –D, D– π_1 –A, and D– π_2 –A; D = electron-rich moiety, A = electron-poor moiety, π = conjugated bridge) polar branches, two donor cores, and two acceptor/anchoring groups to TiO₂ was investigated

Introduction

In the last decades, dye-sensitized solar cells (DSSCs)^[1] have become very attractive because of their easy and cheap manufacturing procedures combined with over 12% record efficiencies.^[2] Metal-free organic photosensitizers, providing several advantages over conventional metal complexes, typically own a linear dipolar D- π -A structure, in which the electron-rich (D) and the electron-poor (A) moieties are connected through a conjugated (π) bridge.^[3] Unfortunately, these compounds present a single, often narrow, absorption band in the visible region, related to intramolecular charge transfer, which limits sunlight harvesting. Cosensitization, that is, the use of two or more dyes having complementary absorption spectra, is an attractive strategy to reach a panchromatic absorption and to enhance light harvesting,^[3,4] as in the case of the recent record efficiency.^[2] However, conventional intermolecular cosensitization suffers from a number of drawbacks: (1) The concentration of each cosensitizing dye on the TiO₂ surface is about half of that in the absence of cosensitization, which thus negates the beneficial effects of improved optical properties. (2) Well-separated complementary absorption bands of the two dyes implies the presence of a region in the cosensitized spectrum in which the absorption intensity is very low.^[5] (3) Intermolecular charge- and energy-transfer processes decrease cell performances as a result of intimate mixing of the two dyes.^[4]

We here propose an original approach consisting of the use of a multibranched dye in which three π -conjugated

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and compared with the corresponding symmetric dyes. TB-PT combines the advantages arising from its π -extended tribranched architecture and the intramolecular cosensitization approach, which results in enhanced tailored optical and energetic properties and, eventually, photovoltaic performances.

branches possess complementary absorption properties (Figure 1, middle). Even if the dye is constituted by a single π -conjugated framework, the net result is equivalent to an intramolecular cosensitization effect. This architecture is the evolution of our previous design based on an A- π_1 -D- π -D- π_1 -A tribranched structural motif (Figure 1, left) in which the presence of two donor and two acceptor/anchoring^[6] fragments allowed enhanced optical and stability properties.^[7] To further improve the optical properties through an intramolecular cosensitization approach, we have now modified the design by introducing two different D- π -A side arms (D- π_1 -A and D- π_2 -A) with complementary absorption properties. The resulting dye can be regarded, in terms of intramolecular cosensitization, as a multichromophore structure that is derived from the combination of two linear D– π –A dyes linked through donor endcapping moieties by a conjugated bridge. We stress that our approach differs from the other reports of intramolecular cosensitization in that the two D- π -A arms are connected through saturated nonconjugated links, which thus limits π structure extension.^[8]



Figure 1. General design strategy for the multibranched dyes: symmetric tribranched (left), new geometry (middle), monobranched (right).

The new asymmetric dye TB-PT (see Figure 2) was designed on the basis of the most common building blocks for DSSC sensitizers, that is, D = triarylamino, A = 2-cyanoacrylic acid, and π_1 and π_2 = benzene and thiophene.

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Figure 2. Symmetric (i.e., TB-T, TB-P) and asymmetric tribranched (i.e., TB-PT) dyes and monobranched reference dyes (i.e., L1 and TC105).

The electron-donating strength of the D moiety was increased by donor alkoxy substituents (RO-), and long linear R chains were introduced to improve the solubility and to minimize cell recombination losses.^[9] TB-PT can thus be seen as the intramolecular combination of the linear dyes L1^[10] and TC105^[11] reported in the literature (Figure 2). The new dye was investigated in terms of its optical, electrochemical, and photovoltaic properties and compared with the corresponding symmetric tribranched dyes TB-P and TB-T (Figure 2). We will show how the optical response of the asymmetric dye TB-PT can be effectively obtained from a linear combination of the asym-

metric dyes TB-P and TB-T by validating the intramolecular cosensitization model.

Results and Discussion

Synthesis, Spectroscopic, and Electrochemical Characterization

TB-PT was conveniently prepared, with steps that provided products in yields from 70% to quantitative, by a convergent route characterized by the Horner–Emmons condensation of branched precursors 1 and 2 (Scheme 1, see



Scheme 1. Synthesis of TB-PT. Reagents and conditions: (i) Diphenylamine, 1,10-phenanthroline, CuCl, KOH, toluene, reflux; (ii) DMF, POCl₃, CH₂Cl₂, -5 °C to r.t.; (iii) *N*-bromosuccinimide (NBS), DMF, -18 °C; (iv) pinacol, *p*-toluenesulfonic acid (PTSA), toluene, reflux; (v) **4**, Pd(dppf)Cl₂ [dppf = 1,1'-bis(diphenylphosphanyl)ferrocene], K₂CO₃, toluene/MeOH, microwave; (vi) NaBH₄, THF, r.t.; (vii) P(OEt)₃, I₂; (viii) **4**, Pd(dppf)Cl₂, K₂CO₃, toluene/MeOH, microwave; (ix) *t*BuONa, THF, r.t.; (x) 10% HCl/THF, 50 °C; (xi) cyanoacetic acid, piperidine (cat.), CHCl₃, reflux.

the Supporting Information for the synthesis of symmetric dyes TB-P and TB-T). Asymmetric bis-aldehyde **3** was submitted, in the last step, to double Knoevenagel condensation with a 25-fold excess amount of cyanoacetic acid to afford pure TB-PT as a dark solid. Both side building blocks were prepared by starting from common triarylamine block **4** through a Suzuki–Miyaura cross-coupling reaction with the *p*-formylboronic esters of thiophene and benzene, in their protected forms **5** and **6**, respectively. A divergent approach, similar to that used for the previously described tribranched dyes,^[7b] was tested but discarded as a result of lower reproducibility and yields.

TB dyes exhibit two UV/Vis absorption bands (Figure 3), one more intense at lower energies (430-490 nm), which is due to intramolecular D- π -A charge transfer of the side arms, and one at higher energies (385-395 nm), which is due to a local transition of the donor core.^[6] The main quantitative optical parameters are collected in Table 1. In close agreement with the design strategy, the absorption spectrum of TB-PT nicely combines the optical features of the symmetric counterparts TB-P and TB-T. In particular, the intramolecular charge-transfer peak of the asymmetric chromophore is bathochromically and hypsochromically shifted relative to the corresponding band of TB-P and TB-T, respectively. Even more significant is the fact that the integrated intensity of the asymmetric dye absorption was higher than that of both symmetric compounds (see oscillator strengths in Table 1), and this suggests a cooperative enhancement effect of the two different side arms.



Figure 3. Absorption spectra of symmetric (i.e., TB-T, TB-P) and asymmetric (i.e., TB-PT) tribranched dyes in THF (solid line); calculated spectrum of TB-PT according to Equation (1) (dashed line).

The premise of the strategy proposed here was to demonstrate that the new molecule is actually equivalent to an intramolecular mixture of two different molecules with complementary absorption properties. Indeed, we found that both the position and intensity of the experimental spectrum of TB-PT could be nicely predicted (dashed line in Figure 3) by simply applying a 1:1 linear combination of the spectra of the symmetric dyes, as shown in Equation (1). in which ε is the molar absorptivity at each wavelength. The calculated and the experimental spectra nicely match in

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Table 1. Optical and electrochemical parameters of the dyes.^[a]

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Dye	$\lambda_{\rm abs} [{\rm nm}] \ (\varepsilon imes 10^{-4} { m M}^{-1} { m cm}^{-1})$	f ^[b]	HOMO ^[c] [eV]	LUMO ^[c] [eV]
TB-T	388 (4.6) 482 (6.1)	1.96	-5.7	-3.5
TB-P	401 (4.8) 439 (5.3)	1.58	-5.5	-3.1
TB-PT	394 (5.2) 460 (5.5)	1.98	-5.6	-3.4

[a] In THF. [b] Oscillator strength measured in the 350–800 nm range. [c] From cyclic voltammetry potential measurements vs. ferrocene/ferrocenium (Fc/Fc⁺); energy levels were calculated by using a value of -5.2 eV vs. vacuum for Fc/Fc⁺ (-4.5 eV vs. vacuum for NHE).

$$\varepsilon_{\text{TB-PT}} = 0.50\varepsilon_{\text{TB-P}} + 0.50\varepsilon_{\text{TB-T}} \tag{1}$$

shape, and the difference in intensity is within experimental error. The optical response of the target dye TB-PT can thus be effectively obtained from a linear combination of the absorption bands of the symmetric dyes, in agreement with the proposed intramolecular cosensitization model. The perfect matching between the experimental and the predicted spectrum of TB-PT is valuable in terms of the design of new panchromatic dyes with predefined optical properties once the absorption properties of the two constituting monobranched units are properly selected and investigated.

The electrochemical properties and HOMO/LUMO energies of dyes TB-P, TB-T, and TB-PT were measured by cyclic voltammetry (CV) and spectroelectrochemical measurements. The current potential profiles are shown in Figure 4 and the derived HOMO and LUMO energies are collected in Table 1 and graphically depicted in Figure S1 (Supporting Information) and compared to DSSC reference energies (conduction band of TiO₂ and Nerst potential of the redox pair I₃⁻/I⁻). All the observed oxidative waves were reversible. It is clearly seen from the electrochemical data that, similarly to the optical properties, TB-PT combines the energetic properties of TB-P and TB-T. In particular, the HOMO/LUMO energies of TB-PT lie in between those of the two symmetric dyes. Spectroelectrochemical analysis,



Figure 4. Cyclic voltammetry traces (vs. Fc) of dyes TB-P, TB-T, and TB-PT.

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showing the change in the absorption properties of dye TB-PT upon oxidation, is described in the Supporting Information (Figure S2). The potential (0.45 V vs. Fc) was applied until no change in the optical properties was observed.

Photovoltaic Investigation in DSSCs

The dyes were used as photosensitizers in DSSCs by using a double-layer TiO₂ film (20 nm particles 10 µm layer + scattering 4 µm layer) in the presence of chenodeoxycholic acid (CDCA)^[12] as a deaggregating co-adsorbent agent (Table 2). Two electrolyte solutions were tested by varying the concentrations of LiI. The best average power conversion efficiencies were measured by using the electrolyte Z960 (1.0 м 1,3-dimethylimidazolium iodide, 0.03 м I₂, 0.05 м LiI, 0.10 м guanidinium thiocyanate, and 0.50 м 4*tert*-butylpyridine in acetonitrile/valeronitrile, 85:15). Table 2 summarizes the photovoltaic parameters in comparison with the DSSC benchmark dye N719 [bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) bis(tetrabutylammonium) salt].^[13] The overall conversion efficiencies PCE were derived from the equation PCE = $J_{sc} \times V_{oc} \times FF$, in which $J_{\rm sc}$ is the short circuit current density, $V_{\rm oc}$ is the open circuit voltage, and FF is the fill factor. Figure 5 shows the photocurrent-voltage curves of the devices.

Table 2. Photovoltaic parameters for TB-based DSSCs.

Dye	CDCA/dye	$J_{ m sc}$ [mA cm ⁻²]	V _{oc} [mV]	FF	PCE [%]
TB-P TB-T	100:1	10.0	722	0.66	4.8
TB-PT N719	100:1 1:1	10.9 11.7 14.4	708 707	0.66 0.69	5.4 7.1



Figure 5. Current–voltage characteristics of DSSCs sensitized by TB-P, TB-T, and TB-PT.

In agreement with the superior optical properties and oscillator strength (Table 1), the asymmetric dye TB-PT exhibited the highest current and approximately 10% improved power conversion efficiency relative to the two symmetric dyes. The absolute efficiency of TB-PT is not very high if compared to recent values on organic sensitizers.^[3] However, it should be noted that our goal was to demonstrate, in addition to enhanced optical properties, improved photovoltaic efficiencies relative to the symmetric counterparts, as achieved. The very simple structure of the conventional donor, spacer, and acceptor groups and the nature of the monobranched reference dyes L1 and TC105 were not selected with the goal of reaching, at this time, higher efficiencies close to those of present record dyes.

The incident monochromatic photon-to-current conversion efficiencies (IPCE, 0-100%) of the devices based on the three dyes are shown in Figure 6. TB-PT summarizes the conversion proprieties of the two symmetric molecules over the whole range. To investigate this term in deeper detail, we separately examined the two constituting factors of IPCE according to the equation IPCE(λ) = LHE(λ) × APCE(λ) (Figure 7) in which LHE (0–100%) is the lightharvesting efficiency associated to the ability of the cell to harvest light and APCE (0-100%) is the absorbed monochromatic photon-to-current conversion efficiency; this term gives the true quantum efficiency of the cell of generating electric current (internal quantum efficiency), and it is related to the electron injection efficiency from the dve to the semiconductor oxide, the dye regeneration efficiency, and the charge collection efficiency.^[1] IPCE and LHE are experimentally determined. APCE is thus derived by dividing the IPCE number by LHE. Given that LHE can be directly measured only for transparent dye-coated films, as similarly performed for previous representative studies,^[2] the whole set of comparative IPCE, LHE, and APCE spectra was recorded and derived for transparent 9 µm thick nanocrystalline TiO₂ monolayers. It is evident that APCE is excellent ($\approx 100\%$) for almost the entire range of visible light, whereas the external quantum efficiency IPCE is much more modest, limited by the low LHE.



Figure 6. Incident photon-to-electric current conversion efficiencies as a function of wavelength of DSSCs sensitized by TB-P, TB-T, and TB-PT.

Electrochemical impedance spectroscopy (EIS) was used to further investigate the comparative behavior of the three dyes in DSSC.^[14] In this experiment, a small sinusoidal voltage stimulus of a fixed frequency was applied to an electrochemical cell and its current response was measured. The alternating current (ac) behavior of an electrochemical sysDate: 20-08-13 11:41:22

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Figure 7. LHE (top) and APCE (bottom) as a function of wavelength of the DSSCs sensitized by TB-P, TB-T, and TB-PT.

tem can be investigated by sweeping the frequency over several orders of magnitude (generally from a few mHz to several MHz). The analysis of the impedance spectra is usually performed in terms of Nyquist plots in which the imaginary part of the impedance is plotted as a function of the real part over the range of frequencies. The impedance of the cell can be described by an equivalent circuit model (Figure 8, inset), in which the different cell components and their interfaces are treated as discrete electrical elements.^[14] Under illumination under open-circuit voltage conditions, the DSSC Nyquist plot shows three arcs corresponding to the I^-/I_3^- redox process at the counter electrode in the highfrequency region $(10^4 \div 10^2 \text{ Hz})$, the TiO₂/dye/electrolyte interface at intermediate frequencies $(1 \div 10 \text{ Hz})$, and the Nernst diffusion within the electrolyte of the ionic species (I⁻) in the low-frequency region $(0.01 \div 1 \text{ Hz})$.^[14] Under these conditions, the properties of the TiO₂/electrolyte interface can be derived from the central arc in terms of recombination resistance (R_{rec}) and chemical capacitance for charge accumulation (C_{μ}) . Both parameters are associated to charge-transfer (recombination) phenomena and represent detrimental back processes between the injected electrons in the oxide and the oxidized form of the electrolyte.[15]

Figure 8 shows the Nyquist plots for the DSSC devices obtained by EIS at the open circuit voltage under 250 Wm^{-2} (0.25 sun) illumination. The data can be fitted by using the equivalent circuit reported in the inset of the



Figure 8. Nyquist plots of DSSCs sensitized by TB-P, TB-T, and TB-PT. Continuous lines represent the data fitting by using the equivalent circuit shown in the onset.

figure in which, in addition to the TiO₂/electrolyte interface parameters, R_S is the serial resistance [mainly due to the fluorine-doped tin oxide (FTO) layers], Z_D is the Warburg diffusion of the ionic species (I⁻) in the electrolyte, and R_{CE} and C_{CE} are the charge-transfer resistance and double-layer capacity at the counter electrode, respectively. The results of the EIS investigation are summarized in Table 3. R_{rec} values can be determined by the width of the central arc, whereas the capacitance C_{μ} can be deduced by fitting the data with the equivalent circuit in Figure 8. The apparent electron lifetime in the oxide, τ_n , can thus be calculated from $\tau_n = R_{rec}C_{\mu}$ and corresponds to the angular frequency at the top of the middle arc.^[14]

Table 3. Parameters calculated from EIS data plots of DSSCs based on TB-P, TB-T, and TB-PT sensitizers in comparison with the benchmark dye N719.

Dye	$R_{\rm rec} \left[\Omega {\rm cm}^2\right]$	$C_{\mu} [\mathrm{F}\mathrm{cm}^{-2}]$	$\tau_{\rm n} [{\rm ms}]$
TB-P	25	5.8×10^{-4}	15
ТВ-Т	14	8.1×10^{-4}	11
TB-PT	17	5.7×10^{-4}	10
N719	15	1.1×10^{-3}	16

Yet again, asymmetric sensitizer TB-PT exhibited intermediate properties between those of symmetrical TB-P and TB-T. For the three dyes, the most relevant parameter, that is, the recombination resistance, R_{rec} , was comparable, or even slightly higher, than that of the benchmark dye N719. Therefore, detrimental charge recombination from TiO₂ to the electrolyte is equally or less efficient in the DSSCs by using the three organic dyes than for the N719 sensitizer. This result is consistent with their APCE spectra. However, the corresponding capacitances, which probe the charge carrier accumulation in the oxide film and the density of states in the band gap, are lower than the reference DSSC by one order of magnitude. The net result is lower electron lifetimes, which affects cell performance.

Conclusions

In conclusion, a new multidonor-multiacceptor/anchoring tribranched asymmetric dye, TB-PT, with two different Date: 20-08-13 11:41:22

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side dipolar branches having complementary absorption properties was designed and investigated as a DSSC sensitizer. The optical, electrochemical, and photovoltaic properties were compared with those of the corresponding symmetric counterparts, TB-P and TB-T. The results suggested a cooperative enhancement of the two different branches in terms of light-harvesting properties. Indeed, the measured current density of the DSSC based on TB-PT was higher than those of cells based on the symmetric dyes, resulting in an approximately 10% increase in the power conversion efficiency.

A novel intramolecular cosensitization strategy to enhance the optical response and, ultimately, the photovoltaic efficiency of DSSCs was demonstrated. In particular, we believe that the experimental validation of Equation (1), which shows that the panchromatic behavior of a new sensitizer can be built by appropriately selected constituting molecules with complementary optical and photovoltaic properties, will facilitate the search for new efficient sensitizers.^[16]

Experimental Section

General: NMR spectra were recorded with an instrument operating at 500.13 (¹H) and 125.77 MHz (¹³C). ¹³C signals were assigned on the basis of the results of J-MOD experiments. HRMS measurements were performed by using a ESI source and an ion trap (Fourier transform ion cyclotron resonance FT-ICR) as a mass analyzer. Flash chromatography was performed with silica gel 230– 400 mesh (60 Å). Reactions performed under a nitrogen atmosphere were performed in oven-dried glassware and monitored by thin-layer chromatography by using UV light (254 and 365 nm) as a visualizing agent. All reagents were obtained from commercial suppliers at the highest purity and used without further purification. Anhydrous solvents were purchased from commercial suppliers and used as received. Extracts were dried with anhydrous Na₂SO₄ and filtered before removal of the solvent by evaporation.

1-(Hexyloxy)-4-iodobenzene (7): A procedure reported in the literature was adapted with some modifications.^[17] 1-Bromohexane (3.81 mL, 27.30 mmol) and K₂CO₃ (12.56 g, 90.91 mmol) were added at room temperature to a solution of 4-iodophenol (9.99 g, 45.43 mmol) in dry acetone (50 mL). After stirring at reflux for 30 h, the mixture was filtered to remove the solid, and the solvent was evaporated under reduced pressure. The residual oil was extracted (CH₂Cl₂) and washed with 3 M NaOH, water, and brine. The organic phase was dried, filtered, and concentrated in vacuo to give the desired product as a colorless oil (6.64 g, 21.82 mmol, 85%).

4-(Hexyloxy)-*N*,*N***-diphenylaniline (8):** A procedure reported in the literature was adapted with some modifications.^[18] A two-necked, round-bottomed flask equipped with a Dean–Stark apparatus was charged with diphenylamine (4.59 g, 27.10 mmol) and toluene (50 mL). Then, **7** (5.51 g, 18.12 mmol), 1,10-phenanthroline (652 mg, 3.61 mmol), cuprous chloride (358 mg, 3.61 mmol), and potassium hydroxide (4.06 g, 72.30 mol) were added. The reaction mixture was heated at reflux for 20 h, and then, water (150 mL) was added. The crude product was extracted with CH₂Cl₂, and the organic layer was washed with water, dried, and filtered. After removing the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/CH₂Cl₂, 1:1) on silica gel to obtain a colorless oil (4.39 g, 12.71 mmol, 70%).

4-{[4-(Hexyloxy)phenyl](phenyl)amino}benzaldehyde (9): Phosphorus oxychloride (0.752 mL, 8.21 mmol) was added dropwise to dry DMF (0.634 mL, 8.22 mmol) at -5 °C. The formation of a white solid was observed, and the reaction was kept at -5 °C for 15 min. CH₂Cl₂ (30 mL) was added, and the solid was allowed to reach room temperature. After complete dissolution, 8 (2.04 g, 5.91 mmol) was added, and the mixture was stirred for 24 h. The reaction was quenched by the addition of water saturated with K_2CO_3 , and the organic phase was washed with water (3× 120 mL), dried, and filtered. Purification by column chromatography over silica gel (CH₂Cl₂/cyclohexane, 1:1) resulted in a yellow oil (2.10 g, 5.63 mmol, 95%). ¹H NMR (CDCl₃): δ = 9.78 (s, 1 H), 7.64 (d, J = 8.8 Hz, 2 H), 7.32 (dd, J = 7.5, 7.4 Hz, 2 H), 7.17 (d, J = 7.5 Hz, 2 H), 7.14 (t, J = 7.4 Hz, 1 H), 7.1 (d, J = 8.9 Hz, 2 H), 6.94 (d, J = 8.8 Hz, 2 H), 6.89 (d, J = 8.9 Hz, 2 H), 1.46–1.44 (t, 2 H), 3.91 (t, J = 6.6 Hz, 2 H), 1.81-1.71 (m, 2 H), 1.52-1.42(m, 2 H), 1.40–1.30 (m, 4 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. ¹³C NMR (CDCl₃): δ = 190.35 (CH), 157.08 (C), 153.66 (C), 146.11 (C), 138.52 (C), 131.33 (CH), 129.60 (CH), 128.43 (CH), 128.39 (C), 125.79 (CH), 124.77 (CH), 118.05 (CH), 115.62 (CH), 68.25 (CH₂), 31.57 (CH₂), 29.24 (CH₂), 25.73 (CH₂), 22.60 (CH₂), 14.04 (CH₃) ppm. HRMS (ESI): calcd. for [M + Na]⁺ C₂₅H₂₇NNaO₂ 396.19340; found 394.19267.

4-{(4-Bromophenyl)[4-(hexyloxy)phenyl]amino}benzaldehyde (4): A solution of freshly recrystallized NBS (863 mg, 4.85 mmol) in DMF (10 mL) was added dropwise to a stirred solution of 9 (1.81 g, 4.85 mmol) in DMF (15 mL). The mixture was left at -18 °C for 15 h and then poured into water (50 mL). Diethyl ether was added, and the resulting organic phase was washed with water $(4 \times 120 \text{ mL})$, dried, and filtered. Removal of the solvent under reduced pressure yielded the pure product (2.06 g, 4.55 mmol, 94%) as a yellow gummy oil. ¹H NMR (CDCl₃): $\delta = 9.80$ (s, 1 H), 7.66 (d, J = 8.8 Hz, 2 H), 7.41 (d, J = 8.8 Hz, 2 H), 7.08 (d, J = 8.9 Hz, 2 H), 7.03 (d, J = 8.8 Hz, 2 H), 6.96 (d, J = 8.7 Hz, 2 H), 6.89 (d, J = 8.9 Hz, 2 H), 3.91 (t, J = 6.6 Hz, 2 H), 1.81–1.71 (m, 2 H), 1.52-1.42 (m, 2 H), 1.40-1.31 (m, 4 H), 0.90 (t, J = 7.1 Hz, 3 H) ppm. ¹³C NMR (CDCl₃): δ = 190.38 (CH), 157.25 (C), 153.14 (C), 145.35 (C), 138.16 (C), 132.61 (CH), 131.35 (CH), 128.95 (C), 128.36 (CH), 126.86 (CH), 118.69 (CH), 117.24 (C), 115.73 (CH), 68.28 (CH₂), 31.57 (CH₂), 29.22 (CH₂), 25.73 (CH₂), 22.61 (CH₂), 14.05 (CH₃) ppm. HRMS (ESI): calcd. for $[M + Na]^+$ C₂₅H₂₆NNaO₂Br 474.10391; found 474.10369.

4,4,5,5-Tetramethyl-2-[5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl]-1,3,2-dioxaborolane (5): A solution of 5-formyl-2-thienylboronic acid (802 mg, 5.14 mmol), 2,3-dimethyl-butane-2,3diol (3.02 g, 25.70 mmol), and a catalytic amount of p-toluenesulfonic acid in toluene (40 mL) was heated at reflux by using a Dean-Stark receiver for 2 h. The reaction mixture was then washed with water $(3 \times 100 \text{ mL})$, dried, and filtered, and the solvent was evaporated under reduced pressure. The product was purified over silica gel (petroleum ether/ethyl acetate, 4:1) to give the desired product as light yellow needle-shaped crystals (1.22 g, 3.60 mmol, 71%); m.p. 128.5–129.5 °C. ¹H NMR (CDCl₃): δ = 7.49 (d, J = 3.5 Hz, 2 H), 7.194 (d, J = 3.5 Hz, 2 H), 6.20 (s, 1 H), 1.32 (s, 12)H), 1.29 (s, 6 H), 1.28 (s, 6 H) ppm. ¹³C NMR (CDCl₃): δ = 151.00 (C), 136.82 (CH), 127.22 (CH), 96.48 (CH), 84.07 (C), 83.09 (C), 24.73 (CH₃), 24.20 (CH₃), 22.07 (CH₃) ppm; the signal for the carbon atom directly attached to boron was not observed owing to quadrupolar relaxation. C₁₇H₂₇BO₄S (338.27): calcd. C 60.36, H 8.06; found C 60.38, H 7.83.

4-([4-(Hexyloxy)phenyl]{4-[5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl]thiophen-2-yl]phenyl}amino)benzaldehyde (1b): Pd(dppf)-

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Cosensitization Approach for Dye-Sensitized Solar Cells

Cl₂·CH₂Cl₂ (91 mg, 0.110 mmol), 5 (400 mg, 1.18 mmol), and K_2CO_3 (628 mg, 4.55 mmol) were added to a solution of 4 (0.411 g, 0.910 mmol) in toluene/MeOH (1:1, 6 mL) in a microwave vial. The resulting mixture was heated in a microwave reactor at 75 °C for 20 min. After cooling to room temperature, the reaction mixture was poured into water and extracted with diethyl ether. The organic phase was washed with water $(3 \times 100 \text{ mL})$, dried, filtered, and concentrated under reduced pressure. Flash chromatography purification (cyclohexane/ethyl acetate, 9:1) gave the product as an orange sticky oil (414 mg, 0.710 mmol, 78%). ¹H NMR (CDCl₃): $\delta = 9.78$ (s, 1 H), 7.67 (d, J = 8.7 Hz, 2 H), 7.52 (d, J = 8.6 Hz, 2 H), 7.16–7.08 (m, 6 H), 7.00 (d, J = 8.7 Hz, 2 H), 6.90 (d, J =8.9 Hz, 2 H), 6.18 (s, 1 H), 3.96 (t, J = 6.5 Hz, 2 H), 1.83–1.72 (m, 2 H), 1.52–1.42 (m, 2 H), 1.38–1.30 (m, 10 H), 1.29 (s, 6 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. ¹³C NMR (CDCl₃): $\delta = 190.11$ (CH₃), 157.22 (C), 153.24 (C), 145.55 (C), 144.32 (C), 142.91 (C), 138.34 (C), 131.28 (CH), 130.63 (C), 128.90 (C), 128.39 (CH), 127.04 (CH), 126.90 (CH), 125.46 (CH), 122.33 (CH), 118.75 (CH), 115.76 (CH), 96.72 (CH), 83.02 (C), 68.27 (CH₂), 31.57 (CH₂), 29.25 (CH₂), 25.74 (CH₂), 24.27 (CH₃), 22.59 (CH₂), 22.08 (CH₃), 14.05 (CH₃) ppm. HRMS (ESI): calcd. for $[M + Na]^+ C_{36}H_{41}NNaO_4S$ 606.26485; found 606.26500.

[4-([4-(Hexyloxy)phenyl]{4-[5-(4,4,5,5-tetramethyl-1,3-dioxolan-2yl)thiophen-2-yl]phenyl]amino)phenyl]·MeOH (1a): A solution of NaBH₄ (63.0 mg, 1.65 mmol) in THF (5 mL) was added dropwise to a solution of **1b** (740 mg, 1.27 mmol) at -10 °C in THF (25 mL). The mixture was stirred for 5 h at room temperature and then quenched by the addition of water. Ethyl acetate was added, and the resulting organic phase was washed with water $(3 \times 110 \text{ mL})$, dried, filtered, and concentrated under reduced pressure. The pure product was isolated as a light yellow sticky oil (709 mg, 1.21 mmol, 95.2%). ¹H NMR (CDCl₃): δ = 7.41 (d, J = 8.7 Hz, 2 H), 7.23 (d, J = 8.5 Hz, 2 H), 7.10–7.03 (m, 6 H), 6.99 (d, J =8.7 Hz, 2 H), 6.84 (d, J = 8.9 Hz, 2 H), 6.17 (s, 1 H), 3.95 (t, J = 6.5 Hz, 2 H), 1.82–1.73 (m, 2 H), 1.52–1.42 (m, 2 H), 1.40–1.33 (m, 10 H), 1.31 (s, 6 H), 0.93 (t, J = 7.0 Hz, 3 H) ppm. ¹³C NMR $(CDCl_3): \delta = 156.00 (C), 147.56 (C), 147.25 (C), 145.26 (C), 141.60$ (C), 139.99 (C), 134.71 (C), 128.25 (CH), 127.72 (C), 127.43 (CH), 127.21 (CH), 126.57 (CH), 123.23 (CH), 122.32 (CH), 121.47 (CH), 115.38 (CH), 96.83 (CH), 83.04 (C), 68.23 (CH₂), 64.94 (CH₂), 31.63 (CH₂), 29.32 (CH₂), 25.79 (CH₂), 24.30 (CH₃), 22.65 (CH₂), 22.08 (CH₃), 14.12 (CH₃) ppm. HRMS (ESI): calcd. for [M + Na]⁺ C₃₆H₄₃NNaO₄S 608.28050; found 608.28059.

Diethyl-4-([4-(Hexyloxy)phenyl]{4-[5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl|phenyl}amino)benzylphosphonate (1): Alcohol 1a (709 mg, 1.21 mmol) was dissolved in P(OEt)₃ (15 mL) at -5 °C, and a solution of I₂ (1.27 g, 5.01 mmol) in P(OEt)₃ (5 mL) was added dropwise. The reaction mixture was stirred for 24 h at room temperature. The excess amount of P(OEt)₃ was distilled off under reduced pressure, and the pure product was obtained after flash chromatography on silica gel (CH₂Cl₂/ethyl acetate, 5:5) as a dark yellow oil (615 mg, 0.871 mmol, 72%). ¹H NMR (CDCl₃): δ = 7.38 (d, J = 8.7 Hz, 2 H), 7.15 (d, J = 8.6 Hz, 2 H), 7.07–7.01 (m, 4 H), 6.99 (d, J = 8.3 Hz, 2 H), 6.95 (d, J = 8.6 Hz, 2 H), 6.82 (d, J = 8.9 Hz, 2 H), 6.14 (s, 1 H), 4.05 (m, 4 H), 3.92 (t, J =6.5 Hz, 2 H), 3.07 (d, J = 21.3 Hz, 2 H), 1.82–1.73 (m, 2 H), 1.52– 1.42 (m, 2 H), 1.40–1.33 (m, 10 H), 1.31 (s, 6 H), 1.26 (t, J = 7.1 Hz, 6 H) 0.93 (t, J = 7.0 Hz, 3 H) ppm. ¹³C NMR (CDCl₃): δ = 156.02 (C), 147.54 (C), 146.53 (C), 145.24 (C), 141.71 (C), 139.98 (C), 130.54/130.50 (³ $J_{13C,31P}$ = 5.0 Hz, CH), 127.73 (C), 127.43 (CH), 127.08 (CH), 126.55 (CH), 125.08/125.02 (${}^{2}J_{{}^{13}C},{}^{31}P$ = 6.3 Hz, C), 123.25 (CH), 122.28 (CH), 121.45 (CH), 115.37 (CH), 96.82 (CH), 82.99 (C), 68.24 (CH₂), 62.11,62.06 (${}^{2}J_{{}^{13}C,{}^{31}P}$ = 6.3 Hz, CH₂), 33.58/

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32.47 (${}^{1}J_{^{13}C,^{31}P}$ = 139.6 Hz, CH₂), 31.59 (CH₂), 29.29 (CH₂), 25.74 (CH₂), 24.27 (CH₃), 22.60 (CH₂), 22.06 (CH₃), 16.42/16.37 (${}^{3}J_{^{13}C,^{31}P}$ = 6.3 Hz, CH₃), 14.03 (CH₃) ppm. HRMS (ESI): calcd. for [M + Na]⁺ C₅₀H₄₂NNaO₆SP 728.31452; found 728.31367.

4,4,5,5-Tetramethyl-2-[4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)phenyl]-1,3,2-dioxaborolane (6): A solution of 4-formylphenylboronic acid (610 mg, 6.67 mmol), 2,3-dimethyl-butane-2,3-diol (3.94 g, 33.34 mmol), and a catalytic amount of p-toluenesulfonic acid in toluene (40 mL) was heated at reflux by using a Dean-Stark receiver for 3 h. The reaction mixture was then washed with water $(3 \times 100 \text{ mL})$, dried, and concentrated. The product was purified over silica gel (petroleum ether/ethyl acetate, 9:1) to give the desired product as colorless needle-shaped crystals (1.73 g, 5.20 mmol, 70%); m.p. 143.6–144.0 °C. ¹H NMR (CDCl₃): δ = 7.81 (d, J = 8.0 Hz, 2 H), 7.49 (d, J = 8.0 Hz, 2 H), 6.0 (s, 1 H), 1.32 (s, 12 H), 1.29 (s, 6 H), 1.23 (s, 6 H) ppm. ¹³C NMR (CDCl₃): δ = 142.99 (C), 134.69 (CH), 125.33 (CH), 99.66 (CH), 83.71 (C), 82.62 (C), 24.87 (CH₃), 24.17 (CH₃), 22.17 (CH₃) ppm; the signal for the carbon atom directly attached to boron was not observed owing to quadrupolar relaxation. $C_{19}H_{29}BO_4$ (332.25): calcd. C 68.69, H 8.80; found C 68.77, H 8.77.

4-{[4-(Hexyloxy)phenyl][4'-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)biphenyl-4-yllamino}benzaldehyde (2): Pd(dppf)Cl₂·CH₂Cl₂ (111 mg, 0.137 mmol), 6 (682 mg, 2.05 mmol), and K₂CO₃ (946 mg, 6.85 mmol) were added to a solution of 4 (620 mg, 1.37 mmol) in toluene/MeOH (1:1, 10 mL) in a microwave vial. The resulting mixture was heated in a microwave reactor at 75 °C for 20 min. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate. The organic phase was washed with water (3×150 mL), dried, filtered, and concentrated under reduced pressure. Flash chromatography purification (cyclohexane/ethyl acetate, 4:1) gave the product as a yellow sticky oil (633 mg, 1.10 mmol, 82%). ¹H NMR (CDCl₃): δ = 9.80 (s, 1 H), 7.67 (d, J = 8.9 Hz, 2 H), 7.69–7.51 (m, 6 H), 7.21 (d, J = 8.6 Hz, 2 H), 7.14 (d, J = 8.9 Hz, 2 H), 7.01 (d, J = 8.2 Hz, 2 H), 6.91 (d, J = 8.9 Hz, 2 H), 3.96 (t, J = 6.5 Hz, 2 H), 1.85–1.74 (m, 2 H), 1.52-1.42 (m, 2 H), 1.39-1.32 (m, 10 H), 1.29 (s, 6 H), 0.90 (t, J = 7.0 Hz, 3 H) ppm. ¹³C NMR (CDCl₃): δ = 190.32 (CH), 157.18 (C), 153.49 (C), 145.46 (C), 140.57 (C), 138.70 (C), 138.47 (C), 137.05 (C), 131.32 (CH), 128.66 (C), 128.47 (CH), 128.16 (CH), 126.78 (CH), 126.70 (CH), 125.64 (CH), 118.49 (CH), 115.70 (CH), 99.72 (CH), 82.72 (C), 68.29 (CH₂), 31.57 (CH₂), 29.24 (CH₂), 25.73 (CH₂), 24.37 (CH₃), 22.59 (CH₂), 22.20 (CH₃), 14.01 (CH₃) ppm. C₃₈H₄₃NO₄ (577.76): calcd. C 79.00, H 7.50, N 2.42; found C 79.20, H 7.57, N 2.43.

(E)-N-[4-(Hexyloxy)phenyl]-N-{4-[4-([4-(hexyloxy)phenyl]{4-[5-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)thiophen-2-yl]phenyl}amino)styryl]phenyl}-4'-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)biphenyl-4amine (3a): Under a nitrogen atmosphere, tBuOK (147 mg, 1.30 mmol) was added to a -10 °C, stirred solution of 1 (615 mg, 0.871 mmol) and 2 (503 mg, 0.871 mmol) in anhydrous THF (30 mL). The reaction immediately became red and was stirred at room temperature for 5 h. The mixture was poured into water saturated with NH₄Cl, and ethyl acetate was added. The organic layer was separated, washed with water (3 \times 120 mL), dried, and filtered. The solvent was removed under reduced pressure, and purification by column chromatography (petroleum ether/ethyl acetate, 4:1) gave the pure product as a yellow solid (757 mg, 0.670 mmol, 77%); m.p. 85.3–86.0 °C. ¹H NMR (CDCl₃): δ = 7.59–7.51 (m, 4 H), 7.46 (d, J = 8.7 Hz, 2 H), 7.43 (d, J = 8.7 Hz, 2 H), 7.37 (d, J = 8.7 Hz, 2 H), 7.13-7.01 (m, 14 H), 6.94 (s, 2 H), 6.90-6.84 (m, 4 H), 6.18 (s, 1 H), 6.02 (s, 1 H), 3.95 (m, 4 H), 1.82–1.76 (m, 4 H), 1.51–1.42

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(m, 4 H), 1.38–1.33 (m, 20 H), 1.31–1.29 (m, 12 H), 0.92 (m, 6 H) ppm. ¹³C NMR (CDCl₃): δ = 156.12 (C), 156.07 (C), 147.37 (C), 147.27 (C), 147.12 (C), 146.88 (C), 145.23 (C), 141.77 (C), 141.02 (C), 140.04 (C), 139.87 (C), 138.11 (C), 134.21 (C), 131.61 (C), 131.39 (C), 127.97 (C), 127.71 (CH), 127.54 (CH), 127.51 (CH), 127.16 (CH), 126.32 (CH), 126.74 (CH), 126.00 (CH), 126.51 (CH), 126.48 (CH), 126.32 (CH), 122.99 (CH), 122.91 (CH), 122.82 (CH), 122.67 (CH), 121.53 (CH), 115.40 (CH), 99.86 (CH), 96.86 (CH), 83.02 (C), 82.69 (C), 68.24 (CH₂), 31.64 (CH₂), 29.34 (CH₂), 26.94 (CH₂), 25.80 (CH₂), 24.42 (CH₃), 24.31 (CH₃), 22.66 (CH₂), 22.25 (CH₃), 22.10 (CH₃), 14.11 (CH₃) ppm. C₇₄H₈₄N₂O₆S (1129.55): calcd. C 78.69, H 7.50, N 2.48; found C 78.66, H 7.62, N 2.41.

(E)-5-(4-{[4-(4-{(4'-Formylbiphenyl-4-yl)[4-(hexyloxy)phenyl]amino}styryl)phenyl][4-(hexyloxy)phenyl]amino}phenyl)thiophene-2-carbaldehyde (3): Compound 3a (757 mg, 0.670 mmol) was dissolved in 10% HCl/THF (1:2, 30 mL). The mixture was heated at 50 °C for 3 h and then poured into water. Ethyl acetate was added, and the organic layer was washed with water until neutral pH, dried with anhydrous Na₂SO₄, and filtered. The solvent was removed under reduced pressure, and purification by column chromatography (cyclohexane/ethyl acetate, 4:1) followed by crystallization from THF gave the pure product as an orange solid (517 mg, 0.553 mmol, 81%); m.p. 182.4–183.3 °C. ¹H NMR (CDCl₃): δ = 10.03 (s, 1 H), 9.85 (s, 1 H), 7.92 (d, J = 8.3 Hz, 2 H), 7.72 (d, J = 8.3 Hz, 2 H), 7.71 (d, J = 4.0 Hz, 1 H), 7.51 (m, 4 H), 7.49 (m, 4 H), 7.29 (d, J = 4.0 Hz, 1 H), 7.16–7.02 (m, 12 H), 6.97 (s, 2 H), 6.88 (m, 4 H), 3.95 (m, 4 H), 1.82–1.75 (m, 4 H), 1.51–1.43 (m, 4 H), 1.39–1.33 (m, 8 H), 0.91 (m, 6 H) ppm. ¹³C NMR (CDCl₃): δ = 191.78 (CH), 182.52 (CH), 156.59 (C), 156.40 (C), 154.69 (C), 149.17 (C), 148.42 (C), 146.81 (C), 146.62 (C), 146.29 (C), 141.19 (C), 139.64 (C), 139.28 (C), 137.69 (CH), 134.63 (C), 132.47 (C), 132.25 (C), 131.87 (C), 130.32 (CH), 127.95 (CH), 127.85 (CH), 127.75 (CH), 127.21 (CH), 126.90 (CH), 126.79 (CH), 126.50 (CH), 125.62 (C), 123.91 (CH), 123.42 (CH), 122.68 (CH), 122.22 (CH), 121.48 (CH), 115.57 (CH), 115.52 (CH), 68.30 (CH₂), 31.59 (CH₂), 29.30 (CH₂), 29.28 (CH₂), 25.75 (CH₂), 22.60 (CH₂), 14.02 (CH₃) ppm. $C_{62}H_{60}N_2O_4S$ (929.23): calcd. C 80.14, H 6.51, N 3.01; found C 80.26, H 6.52, N 3.07.

3-[5-(4-{[4-((E)-4-{[4'-(2-Carboxy-2-cyanovinyl)biphenyl-4-yl][4-(hexyloxy)phenyl]amino}styryl)phenyl][4-(hexyloxy)phenyl]amino}phenyl)thiophen-2-yl]-2-cyanoacrylic acid (TB-PT): Cyanoacetic acid (192 mg, 2.26 mmol) and a catalytic amount of piperidine were added to a solution of 3 (210 mg, 0.226 mmol) in CHCl₃ (15 mL). The reaction mixture was heated at refluxed for 18 h, poured into 15% HCl (100 mL), and stirred overnight at room temperature. After evaporation of the solvent, a dark precipitate was formed. Isolation of the precipitate by vacuum filtration afforded the pure product as a dark-red solid (233 mg, 0.220 mmol, 97.3%); m.p. > 200 °C (decomp.). ¹H NMR ([D₆]DMSO): δ = 8.45 (s, 1 H), 8.32 (s, 1 H), 8.10 (d, J = 8.6 Hz, 2 H), 7.92 (d, J = 4.1 Hz, 1 H), 7.88 (d, J = 8.5 Hz, 2 H), 7.72 (d, J = 8.8 Hz, 2 H), 7.67 (d, J = 8.8 Hz, 2 H), 7.63 (d, J = 4.1 Hz, 1 H), 7.54–7.50 (m, 4 H), 7.13– 7.08 (m, 6 H), 7.16-6.99 (m, 6 H), 6.98-94 (m, 6 H), 3.96 (m, 4 H), 1.75-1.67 (m, 4 H), 1.47-1.38 (m, 4 H), 1.36-1.27 (m, 8 H), 0.89 (m, 6 H) ppm. ¹³C NMR ([D₆]DMSO): δ = 164.25 (C), 163.91 (C), 156.64 (C), 156.47 (C), 154.04 (CH), 153.87 (C), 149.15 (C), 148.37 (C), 146.95 (CH), 146.57 (C), 146.04 (C), 144.36 (C), 142.11 (CH), 139.34 (C), 138.99 (C), 133.79 (C), 132.81 (C), 132.16 (C), 131.94 (CH), 131.42 (C), 130.17 (CH), 128.31 (CH), 128.29 (CH), 128.23 (CH), 127.88 (CH), 127.81 (CH), 127.15 (CH), 126.82 (CH), 126.75 (CH), 125.18 (C), 124.22 (CH), 123.58 (CH), 121.90 (CH), 121.21 (CH), 117.12 (C), 116.90 (C), 116.14 (CH), 116.12 (CH), 102.96 (C), 97.60 (C), 68.12 (CH₂), 31.48 (CH₂), 29.17 (CH₂), 25.69 (CH₂),

22.54 (CH₂), 14.37 (CH₃) ppm. $C_{68}H_{62}N_4O_6S$ (1063.32): calcd. C 76.81, H 5.88, N 5.27; found C 76.51, H 6.13, N 5.29.

Electrochemical and Spectroelectrochemical Characterization: Dyes TB-P, TB-T, and TB-PT were submitted to electrochemical characterization. Each sample was dissolved (10⁻⁴ M) in a 0.1 M solution of tetrabutylammonium perchlorate (Fluka, electrochemical grade, 99.0%) in anhydrous THF (Aldrich) as the supporting electrolyte. Cyclic voltammetry (CV) was performed at a scan rate of 50 mV s⁻¹ by using a PARSTA2273 potentiostat in a two-chamber three-electrode electrochemical cell in a glove box filled with argon ([O₂] < 1 ppm). The working, counter, and pseudoreference electrodes were a glassy carbon (GC) pin, a Pt flag, and an Ag/AgCl wire, respectively. The working electrode disc was well polished with a 0.1 µm alumina suspension, sonicated for 15 min in deionized water and washed with 2-propanol before use. The Ag/AgCl pseudoreference electrode was calibrated by adding ferrocene (10⁻³ M) to the test solution.

Spectroelectrochemical analysis of TB-PT was performed by using a three-electrode cell arranged in a thin layer quartz glass cell. The gold gauze working electrode was confined in the thin portion of the cell (wall thickness 0.5 mm) to minimize the diffusion length of the electroactive molecule. The change in the absorption properties of TB-PT upon oxidation is depicted in Figure S2 (Supporting Information). The potential (0.45 V vs. Fc) was applied until no change in the optical properties was observed.

Fabrication of the DSSCs: The DSSCs were prepared by adapting a procedure reported in the literature.^[19] To exclude metal contamination, all of the containers were glass or Teflon and were treated with EtOH and 10% HCl prior to use. Plastic spatulas and tweezers were used throughout the procedure. FTO glass plates (Solaronix TCO 22–7, 2.2 mm thickness, 7 Ω square⁻¹) were cleaned in a detergent solution for 15 min by using an ultrasonic bath, and then rinsed with pure water and EtOH. After treatment in a UV-O₃ system (Novascan PSD Pro Series - Digital UV Ozone System) for 18 min, the FTO plates were treated with a freshly prepared 40 mM aqueous solution of TiCl₄ for 30 min at 70 °C and then rinsed with water and EtOH. A first transparent nanocrystalline layer (20 nm particles, Dyesol 18NR-T) was screen-printed and dried at 125 °C for 6 min. The working electrodes were screen-printed and dried again with the same procedure to obtain a 10 µm transparent double layer. A scattering 4 µm layer containing optically dispersing anatase particles (Dyesol WER2-O) was screen-printed on the previous electrodes. The coated films were kept in a cabinet for 5 min and then thermally treated under an air flow at 125 °C for 6 min, 325 °C for 10 min, 450 °C for 15 min, and 500 °C for 15 min. The heating ramp rate was 5–10 °Cmin⁻¹. The thickness of the layers was measured by using a VEECO Dektak 8 Stylus Profiler. The sintered layer was treated again with 40 mM aqueous TiCl₄ (70 °C for 30 min), rinsed with EtOH, and heated at 500 °C for 30 min. After cooling down to 80 °C the TiO2 coated plate was immersed into a 2.0×10^{-4} M solution of organic dyes in THF/EtOH (1:1) containing 2.0×10^{-2} M chenodeoxycholic acid (CDCA) for 20 h at room temperature in the dark. For the reference devices with N719, the plate was immersed into a 5.0×10^{-4} M solution of the dye in EtOH containing equimolar CDCA under the same experimental conditions. Counter electrodes were prepared according to the following procedure: A 1 mm hole was made in a FTO plate by using diamond drill bits. The electrodes were then cleaned with a detergent solution for 15 min by using an ultrasonic bath, 10% HCl, and finally acetone for 15 min by using an ultrasonic bath. After treatment in the UV-O₃ system for 18 min, a drop of a 5×10^{-3} M solution of H₂PtCl₆ in EtOH was added and the thermal treatment at 400 °C for 15 min was repeated.

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Cosensitization Approach for Dye-Sensitized Solar Cells

The dye-adsorbed TiO₂ electrode and Pt counter electrode were assembled into a sealed sandwich-type cell by heating with a hotmelt ionomer-class resin (Surlyn 25- μ m thickness) as a spacer between the electrodes. A drop of the electrolyte solution (Z960: 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M I₂, 0.05 M LiI, 0.10 M guanidinium thiocyanate, and 0.50 M 4-*tert*-butylpyridine in acetonitrile/valeronitrile, 85:15; for N719-based cells the standard electrolyte A6141 was used: 0.6 M *N*-butyl-*N*-methylimidazolium iodide, 0.03 M I₂, 0.10 M guanidinium thiocyanate, and 0.5 M 4-*tert*-butylpyridine in acetonitrile/valeronitrile, 85:15) was added to the hole and introduced inside the cell by vacuum backfilling. Finally, the hole was sealed with a sheet of Bynel and a cover glass. A reflective foil at the back side of the counter electrode was taped to reflect unabsorbed light back to the photoanode.

Photovoltaic and Photoelectrical Characterization of DSSCs: Photovoltaic measurements of the DSSCs were performed with an antireflective layer on top of the cells under a 500 W xenon light source (ABET Technologies Sun 2000 class ABA Solar Simulator). The power of the simulated light was calibrated to AM 1.5 (100 mW cm⁻²) by using a reference Si cell photodiode equipped with an IR cutoff filter (KG-5, Schott) to reduce the mismatch in the region of 350-750 nm between the simulated light and the AM 1.5 spectrum. Values were recorded after 3 and 24 h and 3 and 7 d of ageing in the dark. Curves I-V were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. Incident photonto-current conversion efficiencies (IPCE) was recorded as a function of excitation wavelength by using a monochromator (Omni 300 LOT ORIEL) with single grating in Czerny-Turner optical design, in AC mode by using a chopping frequency of 1 Hz and a bias of white light (0.3 sun). EIS spectra were obtained by using an Eg&G PARSTAT 2263 galvanostat potentiostat. The measurements were performed in the frequency range from 100 kHz to 100 mHz under ac stimulus with an amplitude of 10 mV and no applied voltage bias. The obtained Nyquist plots were fitted by a nonlinear least-square procedure by using the equivalent circuit model in Figure 8.

Supporting Information (see footnote on the first page of this article): Synthesis of TB-P and TB-T, ¹H NMR and ¹³C NMR spectra for all new compounds, HOMO and LUMO energy levels of the dyes (pictorial view), and spectroelectrochemical curves.

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Dye-Sensitized Solar Cells

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Asymmetric Tribranched Dyes: An Intramolecular Cosensitization Approach for Dye-Sensitized Solar Cells

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