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High-Performance Organic Materials for Dye-Sensitized Solar Cells: Triarylene-Linked Dyads with a 4-*tert*-Butylphenylamine Donor

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Abstract: A series of organic dyes were prepared that displayed remarkable solar-to-energy conversion efficiencies in dye-sensitized solar cells (DSSCs). These dyes are composed of a 4-*tert*butylphenylamine donor group (D), a cyanoacrylic-acid acceptor group (A), and a phenylene-thiophene-phenylene (PSP) spacer group, forming a D- π -A system. A dye containing a bulky *tert*butylphenylene-substituted carbazole (CB) donor group showed the highest performance, with an overall conversion efficiency of 6.70%. The performance of the device was correlated to the structural features of the donor groups; that is, the presence of a *tert*butyl group can not only enhance the electron-donating ability of the donor, but can also suppress intermolecular aggregation. A typical device made with the **CB-PSP** dye afforded a maximum photon-to-current conversion ef-

Keywords: carbazoles • dyads • organic materials • solar cells • triarvlenes ficiency (IPCE) of 80% in the region 400–480 nm, a short-circuit photocurrent density $J_{sc} = 14.63 \text{ mA cm}^{-2}$, an open-circuit photovoltage $V_{oc} = 0.685 \text{ V}$, and a fill factor FF = 0.67. When chenodeoxycholic acid (CDCA) was used as a co-absorbent, the open-circuit voltage of **CB-PSP** was elevated significantly, yet the overall performance decreased by 16–18%. This result indicated that the presence of 4-*tert*-butylphenyl substituents can effectively inhibit self-aggregation, even without CDCA.

Introduction

Under the global strain of over-consumed fossil fuels and the need to reduce the greenhouse effect, there is an urgent demand for finding clean and renewable energy sources. Solar energy is widely recognized as a potential way to help solve this problem. Over the past two decades, dye-sensitized solar cells (DSSCs) have received considerable atten-

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tion owing to their improved efficiency and lower cost. Ever since the report by O'Regan and Grätzel in 1991 on highperformance dye-sensitized solar cells made with ruthenium complexes, research in this area has boomed.^[1] To date, three landmark polypyridyl ruthenium(II) complexes have achieved maximum power-conversion efficiencies of over 11 %: N3, N719, and the black dye.^[2] Compared to metallic materials, organic dyes have the advantages of environmental friendliness, higher structural flexibility, lower cost, and easier preparation. A wide variety of organic dyes have been reported in the literature, including derivatives of coumarin,^[3] indoline,^[4] cyanine,^[5] merocyanine,^[6] hemicyanine,^[7] perylene,^[8] dithiensilole,^[9] spirobifluorene,^[10] and porphyrin,^[11] whilst most of them exhibited energy-to-electricity conversion efficiencies in the range 5-9%. In our previous studies, we investigated a series of organic dyads with a donor-n-acceptor (D-n-A) structure, in which an amine donor group (D) was functionalized with a cyanoacrylic-acid acceptor group (A) through a triaryl linkage (π) .^[12] The DSSCs made with these D- π -A dyads exhibited remarkable quantum efficiency. Among others, the structure of the electron-donating group is one of the crucial factors that influence the conversion efficiency of solar energy into electricity in DSSCs. Herein, we report our efforts on the design of different electron donors, in particular those with bulky 4-tertbutylphenyl substituents. The fabrication process was also modified in order to obtain the highest efficiency with these new dyes.

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Results and Discussion

Synthesis and Chemical Characterization

The structures of the dyes are shown in Scheme 1. A 4-*tert*butylphenyl substituent is placed on the amine moiety of all of the compounds. Their synthetic sequences are outline in



Scheme 1. Structure of the dyes with a PSP triaryl linkage.

Scheme 2. Compound **DTB-PSP** is the only dye containing two 4-*tert*-butylphenyl substituents and its structure possesses a two-fold symmetry. The synthesis of **DTB-PSP** started from *para*-bromonitrobenzene, onto which a thiophene unit was added using the Stille coupling reaction. The nitro group of the product 2-(4-nitrophenyl)thiophene was subsequently reduced by sodium borohydride to give 4-(thiophen-2-yl)benzenamine. The amine group was then modified in the next step by the simultaneous addition of two 4-*tert*phenyl substituents using a Buchwald–Hartwig coupling reaction to produce compound **3-DTB** in 50% yield.^[13] The chain-length was further elongated by inserting another phenylene unit through a Stille coupling reaction with 4-bromobenzaldehyde to yield compound **4-DTB**. The formation of **DTB-PSP** was completed by a Knoevenagel condensation with a cyanoacetic acid to build up the cyanoacrylic acid acceptor unit.^[14]

Five compounds containing unsymmetrical amine groups were prepared according to a slightly modified procedure. All of these syntheses were started from the corresponding secondary amines, onto which a 4-tert-butylphenyl group was added, either through an Ullmann coupling reaction (for compound 1-CB) or through a Buchwald-Hartwig coupling reaction (for the other 1-X compounds, i.e. X = TB, 5TB, 6TB, and PT).^[15] The phenyl group of compound 1-X was brominated using N-bromosuccinimide to form compound 2-X,^[16] which was then transformed into compounds 3-X and 4-X through similar procedures to those used in the formation of compound **DTB-PSP** in yields of 63-90%. In the final step, the cyanoacrylic acid moiety was generated via Knoevenagel condensation to form the five X-PSP dyes.^[14] All of the final products crystallized as deep-colored solids, and their structures were confirmed by spectroscopic analysis.

Photophysical and Electrochemical Properties

The absorption spectra of the dyes in dilute tetrahydrofuran $(3 \times 10^{-5} \text{ M})$ are shown in Figure 1. Each of these compounds exhibit two or three major absorption bands in the ranges 302–307 nm, 341–356 nm, and 428–460 nm, respectively. The first two bands were assigned to localized aromatic π – π *



Scheme 2. Synthesis. 1) [PdCl₂(PPh₃)₂], 2-(tributylstannyl)thiophene, DMF, 90 °C; 2) SnCl₂·2H₂O, NaBH₄, EtOH; 3) [Pd₂(dba)₃], dppf, 4-bromo-*tert*-butyl-benzene, toluene, 90 °C; 4) NBS, DMF, RT; 5) (a) *n*BuLi, tributyltin chloride, THF, -78 °C; followed by aq. HCl, (b) [PdCl₂(PPh₃)₂], 4-bromobenzalde-hyde, DMF, 90 °C; 6) cyanoacetic acid, NH₄OAc, AcOH, ca. 90–100 °C. DMF = *N*,*N*-dimethylformamide, dba = dibenzylideneacetone, dppf = 1,1'-bis(diphenylphosphino)ferrocene, NBS = *N*-bromosuccinimide, THF = tetrahydrofuran.

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Figure 1. Absorption spectra in THF.

transitions, and the last one to a charge-transfer (CT) transition. The major absorption band of DTB-PSP is slightly red-shifted to that of TB-PSP, owing to the presence of the extra tert-butyl substituent. The influence of ring-size was investigated by comparing compounds 5TB-PSP and 6TB-**PSP**, which have extinction coefficients of $\varepsilon = 2.89 \times$ $10^4 \text{ m}^{-1} \text{ cm}^{-1}$ and $2.64 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1}$, respectively (Table 1). These values are consistent with their oscillator strengths as determined by TDDFT (0.82 and 0.79, respectively). In the series of CB-PSP, TB-PSP, and PT-PSP, the λ_{max} value of the major absorption band appeared at 428, 433, and 446 nm, respectively. The longest-wavelength absorption of PT-PSP was ascribed to the additional electron-donating effect of the sulfur atom. The dihedral angles between the aminophenyl and thiophenyl rings were calculated to be -26.44°, -22.93°, and -22.89° for compounds CB-PSP, TB-PSP, and PT-PSP, respectively, and this indicated that a good amount of planarity had persisted. Of all the compounds tested, CB-PSP showed the highest molar-extinction coefficient $(4.00 \times 10^4 \text{ m}^{-1} \text{ cm}^{-1})$, which correlated well with its highest oscillator strength (0.92, calculated by TDDFT). The absorption spectra of the dyes, after they were chemisorbed onto the surface of TiO₂, displayed a mild blue shift with respect to those in solution (Figure 2). Such a phenomenon has been observed previously, and was attributed to the decrease in electron-accepting ability of the cyanoacry-



Figure 2. Adsorption spectra of the dyes adsorbed on the surface of TiO2.

late group comparing to a free carboxylic acid.^[17] The absorption band of **CB-PSP** on TiO₂ possesses the longest wavelength (λ_{max} =418 nm) and displayed the smallest blue shift with respect to its absorption in solution. However, in the excited state, their conformation may be readjusted to a different geometry from those in the ground state. The presence of a conformational twist in the excited state may benefit the quantum efficiency of the DSSC, as a non-planar geometry could retard the rate of charge-recombination and therefore increase the photocurrent.

The first oxidation potentials (E_{ox}), corresponding to the HOMO level of dyes, were measured by cyclic voltammetry (CV) in tetrahydrofuran, and the results are shown in Table 1. The relative potentials decrease in the order **CB-PSP** (0.91) > **TB-PSP** (0.73) > **DTB-PSP** (0.69) > **PT-PSP** (0.56) > **6TB-PPS** (0.54) > **5TB-PSP** (0.51). The LUMO levels of the sensitizers were estimated by the values of E_{ox} and the 0–0 band gaps, whilst the latter values were obtained at the intersection of the absorption and emission spectra. The band-gap energies decrease along with the electron-donating power of the substituents in the trend: TB-PSP (2.49) > **DTB-PSP** (2.46), **CB-PSP** (2.46) > **5TB-PSP** (2.28), and **PT-PSP** (2.39) > **6TB-PSP** (2.26). The estimated LUMO levels of all of dyes tested are sufficiently higher than the conductive band level of TiO₂ (ca. -0.5 V vs.

Table 1. Calculated (TDDFT/B3LYP) and experimental parameters of all of the dyes.^[a]

Dye	HOMO/LUMO ^[b] [eV]	Band gap ^[b]	<i>f</i> ^[b]	$\lambda_{abs}^{[c]}nm$	λ_{abs} (film) [nm]	HOMO ^[d] /LUMO ^[e] [eV]	$E_{\mathrm{ox}}^{\mathrm{[f]}}[\mathrm{V}]$	$E_{0-0}^{[g]}[V]$	$E_{\rm red}^{\rm [h]} [V]$
				$[\varepsilon/M^{-1}cm^{-1}]$					
DTB-PSP	-4.98/-2.58	2.40	0.71	439 (34000)	405	-5.19/-2.73	0.69	2.46	-1.77
TB-PSP	-5.03/-2.61	2.42	0.70	433 (32600)	401	-5.23/-2.74	0.73	2.49	-1.76
5TB-PSP	-4.96/-2.52	2.44	0.82	460 (28900)	415	-5.01/-2.73	0.51	2.28	-1.77
CB-PSP	-5.29/-2.58	2.71	0.92	428 (40000)	418	-5.41/-2.95	0.91	2.46	-1.55
6TB-PSP	-4.95/-2.53	2.42	0.79	454 (26400)	406	-5.04/-2.78	0.54	2.26	-1.72
PT-PSP	-5.04/-2.61	2.43	0.49	446 (33900)	408	-5.06/-2.67	0.56	2.39	-1.83

[a] f=Oscillator strength for the lowest-energy transition; ε =absorption coefficient; E_{ox} =oxidation potential; E_{0-0} =0–0 transition energy measured at the intersection of absorption and emission spectra. [b] TDDFT/B3LYP calculated values. [c] Absorptions measured in THF. [d] Oxidation potentials of dyes (10⁻³ M) in THF, 0.1 M (n-C₄H₉)₄NPF₆, scan rate 50 mV s⁻¹ (vs. Fc⁺/Fc). [e] LUMO calculated by HOMO+ E_{0-0} . [f] E_{ox} calculated by HOMO+4.5 (eV) (vs. NHE). [g] E_{0-0} determined from the intersection of absorption and emission in THF. [h] E_{red} calculated by E_{ox} - E_{0-0} .

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NHE; NHE = normal hydrogen electrode, whilst their HOMO levels are sufficiently lower than that of the electrolyte ion pair I^-/I_3^- (ca. 0.4 V vs. NHE).^[18] The electronic structures thus ensure a favorable exothermic flow of charge throughout the photoelectronic conversion (Figure 3). In



Figure 3. Potential energy levels of the dyes.

particular, the lowest HOMO potential-energy level was found in **CB-PSP**, which implies that the device made with it may show the most efficient charge regeneration.

Theoretical Calculations

To gain a better understanding of the electronic configurations, the compounds were examined by theoretical models using a Gaussian 03 program.^[19] The molecular geometries were optimized by a B3LYP hybrid functional with a 6-31G* basis set, and then the electronic configurations of both the ground and excited states were computed by timedependent density functional theory (TDDFT) with the B3LYP functional. The HOMO/LUMO energy levels and the corresponding band-gaps are listed in Table 1 (see the Supporting Information, Tables S1–S3 and Figures S33–S35) and they are remarkably consistent with the experimental values. According to the optimized molecular geometry, the bridge conformations of 5TB-PSP and 6TB-PSP are more coplanar than CB-PSP and PT-PSP (S35). The moieties with strongly electron-donating substituents displayed larger oscillator strengths as well as lower oxidation potentials. The molecular dipole moment of compound 5TB-PSP (11.00 debye) was about equal to that of compound 6TB-**PSP** (10.95 debye) in the ground state. The dipole moment of compound TB-PSP (9.58 debye) was somewhat smaller than those of compounds CB-PSP (10.99 debye) and PT-PSP (11.05 debye). The latter two also exhibited higher molar extinction coefficients for more-efficient light-harvesting. Compared to compound TB-PSP, the presence of two tert-butyl substituents in dye DTB-PSP exhibits not only a smaller band-gap owing to a stronger electron-donating

effect, but also a stronger dipole moment and a higher absorptivity. The electron-density distributions in the HOMO and LUMO are illustrated in the Supporting Information, Figure S34. The electron density of the HOMO is mainly localized on the amine moiety, whilst that of the LUMO is mainly localized on the cyanoacrylic acid group. Upon photoexcitation, an electron migrates from the donor (D) to the acceptor (A), thereby forming a charge-shifted dipolar state. In both of the ground and excited states, the electron densities of D and A are heavily coupled with the orbitals in the central bridge linkage (B). The difference in Mülliken charge shift surrounding the D, B, and A segments, before (S₀ state) and after (S₁ state) the photoexcitation, can be clearly depicted in a bar chart (see the Supporting Information, S33).

Photovoltaic Performance

The performances of the devices under solar conditions (AM 1.5) are listed in Table 2. The J-V curves for each of the individual dyes are shown in Figure 4. A comparison be-

Table 2. Photovoltaic parameters of devices for different donor of PSP series under AM 1.5 conditions. $^{\rm [a]}$

Dye	$J_{\rm sc} [{\rm mA cm^{-2}}]$	$V_{ m oc} \left[{ m V} ight]$	FF	$\eta^{\left[b ight] }\left[\% ight]$	$\tau^{[c]}$ [ms]
DTB-PSP	13.96	0.67	0.66	6.14	17.76 (4.97)
TB-PSP	13.32	0.66	0.61	5.43	17.17 (4.68)
5TB-PSP	12.60	0.63	0.61	4.87	16.66 (4.30)
CB-PSP	14.63	0.685	0.67	6.70	19.44 (7.23)
6TB-PSP	8.48	0.57	0.65	3.14	14.85 (3.98)
PT-PSP	14.12	0.68	0.64	6.32	18.56 (5.68)
N719	15.95	0.73	0.62	7.24	22.11 (19.9)

[a] J_{sc} =short-circuit photocurrent density; V_{oc} =open-circuit photovoltage; FF=fill factor; η =total-power-conversion efficiency. [a] Performance of DSSC measured in a 0.25 cm² working area on an FTO (8 Ω / square) substrate. [b] Lifetime of injected electrons measured by transient photovoltage at open circuit in the presence of LiI electrolyte (0.5 M) in MeCN. Values in parantheses were obtained by fitting the middle-frequency in the Bode phase plots through the expression $\tau = 1/(2\pi f)$, where *f* is the frequency.

tween the performances of **DTB-PSP** and **TB-PPS** is worth mentioning. The former exhibited a higher short-circuit current, a higher open-circuit voltage, and a higher field factor $(J_{\rm sc} = 13.96 \,\mathrm{mA}\,\mathrm{cm}^{-2}, V_{\rm oc} = 0.68 \,\mathrm{V}, \,\mathrm{FF} = 0.66)$ than the latter $(J_{\rm sc} = 13.32 \,\mathrm{mA\,cm^{-2}}, V_{\rm oc} = 0.66 \,\mathrm{V}, \,\mathrm{FF} = 0.61)$. As a result, the overall conversion efficiency of the former is better than the latter (6.26% vs. 5.43%). In the IPCE plot of **DTB-PSP**, the spectrum covers a broader wavelength range than TB-PSP, and also shows a higher conversion efficiency (Figure 5). A comparison between 5TB-PSP and 6TB-PSP indicated that a five-membered ring is preferable owing to a more-planar geometry. The current density of **5TB-PSP** $(12.60 \text{ mA cm}^{-2})$ is significantly higher than that of **6TB-PSP** $(8.48 \,\mathrm{mA}\,\mathrm{cm}^{-2})$, as is the conversion efficiency 4.87% vs. 3.14%. For compounds CB-PSP and PT-PSP, their short-circuit currents maintain a constant value in the range of 14.12-14.63 mA cm⁻², which was slightly better than that of **TB**-



Figure 4. Comparison of the J-V curves of DSSCs made from the dyes with N719.



Figure 5. Comparison of the IPCE plots of DSSCs made from the dyes with N719.

PSP (13.32 mA cm⁻²). This result complies well with their higher absorptivity in the charge-transfer transitions (Table 1, also see the Supporting Information, Figure S2). The open-circuit voltages of CB-PSP and PT-PSP (0.685 V and 0.68 V, respectively) were also higher than that of TB-**PSP** (0.66 V). These values benefited from the reduction in the rate of charge recombination at the nanocrystalline/dye/ redox-electrolyte interface, and was demonstrated by the trend in dark currents, which appeared in the order CB-**PSP** < **PT-PSP** < **TB-PSP** (Figure 4). Further support was found by examining the decay in the transient photovoltages of the assembled devices. The measurements were done on an open circuit in the presence of LiI electrolyte in acetonitrile using a pulsed Nd:YAG laser (see the Supporting Information, Figure S42). The decay lifetimes of the dyes are listed in Table 2, and compound CB-PSP indeed showed the longest lifetime (19.44 ms). A longer electron lifetime indicates a slower charge recombination, and therefore leads to a larger V_{oc} value. This rationale is also true for compound **PT-PSP**, whose high value of V_{oc} is also supported by its long decay lifetime (18.56 ms).^[20] It is noteworthy that the fill factors of dyes **CB-PSP** (0.67) and **PT-PSP** (0.64) were again higher than that of compound **TB-PSP** (0.61). Among all of the dyes tested, the best performance was found with **CB-PSP**, which showed a maximal IPCE value of 80% and an overall conversion efficiency of 6.70%, which is quite close to that of the well-known ruthenium complex N-719. The incident photon to current conversion efficiency (IPCE) was higher than 70% in the 390–540 nm region (Figure 5).

Electrochemical Impedance Spectra and the Influence of CDCA

Electrochemical impedance spectroscopy (EIS) was performed to further elucidate the photovoltaic properties of these dyes.^[21] EIS analysis of the DSSCs made with these sensitizers were taken under a forward bias of -0.73 V in the dark. In the Nyquist plot (Figure 6) a major semicircle



Figure 6. *J*--*V* curves of DSSC made from **CB-PSP** with and without CDCA.

was observed in the frequency range 20-100 Hz, which is related to the transport process of injected electrons at the interfaces between TiO_2 and the electrolyte/dye.^[22] The charge-recombination resistance (R_{rec}) can be deduced by fitting the curves using Z-view software.^[23] The resistance value is related to the charge recombination rate at the TiO₂ surface of the DSSC; for example, a smaller R_{rec} value indicates a faster charge recombination and therefore a larger dark current (Figure 5). The radius of the semicircle increasorder **6TB-PSP** (23.9 ohm) < 5TB-PSP es in the (30.5 ohm) < TB-PSP (33.1 ohm) < DTB-PSP (40.4 ohm) <**PT-PSP** (46.3 ohm) < CB-PSP (47.1 ohm) in the dark. This trend appears to be consistent with the V_{oc} values of **6TB**-**PSP** (0.57 V) < 5TB-PSP (0.63 V) < TB-PSP $(0.66 \text{ V}) \approx$ **DTB-PSP** $(0.67 \text{ V}) < \text{PT-PSP} (0.68 \text{ V}) \approx \text{CB-PSP} (0.685 \text{ V}).$ In Bode phase plots, the peak position of the middle frequency is related to the electron lifetime, for example, a shift to low frequency corresponds to a longer electron lifetime. The injected electron lifetime (τ) can be estimated directly by fitting the plots into the equation $\tau = 1/(2\pi f)$, where *f* is the frequency. The lifetimes estimated by EIS were compared with those obtained by the transient photovoltages. The trends in both series are consistent with one another, as shown in Table 2.

In a previous report, it has been shown that co-depositing chenodeoxycholic acid (CDCA) with organic dyes on TiO₂ can effectively retard the charge recombination, and consequently increase the electron lifetime. CDCA also an effect of preventing intermolecular aggregation of the dyes, thereby enhancing the short-circuit current.^[22] This method was applied to our compound CB-PSP. With the addition of CDCA, we observed an increase of the open circuit, yet surprisingly we found a decrease in the short-circuit current (Table 3). With 1 mm and 10 mm co-absorptions of CDCA, the J_{sc} values decreased from 14.63 mA cm⁻² to 12.52 and 11.40 mA cm⁻², respectively, as did the FF values (from 0.67 to 0.63 and 0.66, respectively). The overall quantum efficiency dropped to 5.47-5.61 %. The addition of CDCA to CB-PSP did not have a favorable influence on device performance (Figure 6 and Figure 7). The reason for this phenomenon can be explored more clearly by examining the EIS spectra. When the dye was co-absorbed with CDCA, the diameter of the major semicircles in the Nyquist plot was enlarged along with the increase in CDCA concentration (Figure 7). The low-frequency peak in the Bode plot was also shifted to lower frequency. Therefore, the effect of de-

Table 3. Photovoltaic parameters of devices made with **CB-PSP** with and without CDCA.^[a]

Dye ^[b]	CDCA [mm]	$J_{\rm sc} [{ m mA}{ m cm}^{-2}]$	$V_{\rm oc} \left[{ m V} ight]$	FF	$\eta^{[c]}$ [%]
CB-PSP	0	14.63	0.685	0.67	6.70
	1	12.52	0.71	0.63	5.61
	10	11.40	0.72	0.66	5.47

[a] J_{sc} =short-circuit photocurrent density; V_{oc} =open-circuit photovoltage; FF=fill factor; η =total-power-conversion efficiency. [b] Concentration of dye is 3×10^{-4} m in THF. [c] Performance of DSSC measured in a 0.25 cm² working area on an FTO (8 Ω /square) substrate under AM 1.5 conditions.



Figure 7. EIS Nyquist plots of **CB-PSP** with and without CDCA at -0.73 V bias in the dark.

pressing dark current was clear, and consequently the $V_{\rm oc}$ value was increased. However, the $J_{\rm sc}$ values decreased substantially in the presence of CDCA, presumably caused by a reduction in the loading amount of the dye on the TiO₂ surface. This result indicated that self-aggregation of **CB-PSP** did not happen to a significant degree, even without CDCA. The addition of bulky *tert*-butyl substituents did have a profound effect in preventing aggregation.

Conclusions

The organic dyes reported here have several advantages: 1) easy handling and preparation from low-cost starting materials, 2) intense absorption in the visible-light region owing to efficient intramolecular-charge-transfer transitions, 3) stable charge-separated states with long lifetimes, and 4) depressed dark-current because of the presence of bulky 4-*tert*-butylphenyl substituents.

Among the series of dyes tested, some structural factors can be correlated with device performance. The dyes may be divided into three groups based on their structural features: 1) those with two aryl substituents on the nitrogen donor atom (**5TB-PSP** and **6TB-PSP**) 2) those with three aryl substituents on the nitrogen donor atom (**TB-PSP** and **DTB-PSP**); and 3) those with a fused ring between the aryl groups (**CB-PSP** and **PT-PSP**). The DSSC performance was found to be in the order of group 3>group 2>group 1, whilst the highest performance was observed for compound **CB-PSP**.

In the group 1 dyes, the current density of compound **5TB-PSP** (12.60 mA cm⁻²) is significantly higher than that of **6TB-PSP** (8.48 mA cm^{-2}), as a result of higher ring planarity. The conversion efficiencies of the two compounds are 4.87% and 3.14%, respectively. For the dyes in groups 2 and 3, the addition of an additional aryl substituent on the nitrogen atom lowered the HOMO levels substantially, thus promoting the injection efficiency of electrons from the electrolyte to the oxidized dyes. The dyes in groups 2 and 3 also exhibited higher absorptivity, which led to better IPCE values than those in group 1.

In the group 2 dyes, a comparison between compounds **DTB-PSP** and **TB-PPS** indicated that the former exhibited higher values in all three parameters, that is, short-circuit current, open-circuit voltage, and field factor. The presence of two bulky 4-*tert*-butyl substituents in compound **DTB-PSP** provided better shielding between the electrolyte and the TiO₂ surface, so that the dark current was reduced and the V_{oc} value increased. The electron-donating nature of the 4-*tert*-butyl group also elevated the HOMO level, narrowed down the band gap, and widened the absorption spectrum of the dye. The IPCE plot of **DTB-PSP** covered a broader wavelength range than that of **TB-PSP**. As a result, the overall conversion efficiency of the former is better than the latter (6.26% vs. 5.43%).

Among all of the dyes tested, **CB-PSP** (group 3) showed the highest molar extinction coefficient $(4.00 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$,

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which is consistent with the high oscillator strength (0.92) calculated by TDDFT. The two phenyl moieties in the carbazole moiety maintained a better planar geometry than the isolated phenyl groups in the triarylamine group. **CB-PSP** possesses the lowest oxidation potential of all of the dyes, which thus affords an increased efficiency for charge regeneration in the device. The V_{oc} values of **CB-PSP** and **PT-PSP** were among the highest observed (0.685 V and 0.68 V, respectively). These values benefited by reducing the charge-recombination rate in the nanocrystalline/dye/redoxelectrolyte interface. This phenomenon can be rationalized by the long electron lifetimes measured by both the decay of transient photovoltage (Table 2; also see the Supporting Information, Figure S42) and the large R_{rec} values obtained by EIS analyses (Figure 8). The device made with **CB-PSP**



Figure 8. EIS Nyquist plots of the dyes at -0.73 V bias in the dark (i.e., minus the imaginary part of the impedance -Z" vs. the real part of the impedance Z' when sweeping the frequency).

showed the lowest dark current (Figure 4). Therefore, the **CB-PSP** dye exhibited the highest J_{sc} value of 14.63 mA cm⁻², a V_{oc} value of 0.685 V, and a FF value of 0.67, corresponding to a conversion efficiency (η) value of 6.7%.

In particular, the prevention of aggregation by the bulky 4-*tert*-butyl substituents was clearly demonstrated by the coabsorption experiment with CDCA. The open-circuit voltage increased upon the addition of CDCA, whilst the shortcircuit current decreased. This decrease in the short circuit current was caused by a decrease in loading amount. We also found that self-aggregation on the surface of TiO_2 did not occur to a significant degree on these dyes.

Experimental Section

General Procedures

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were distilled freshly according to standard procedures. ¹H and ¹³C NMR spectra were recorded on a Brucker (AV 400/AV 500 MHz) spectrometer in CDCl₃ or [D₆]DMSO. Chemical shifts are reported downfield of tetramethylsilane. Absorption spectra were recorded on a Jasco-550 spectrophotometer. Emission spectra were obtained on a Hitachi F-4500 spectrofluorimeter. The emission spectra in solution were measured in spectroscopy grade solvent at a detection angle of 90°. The redox potentials were measured using cyclic voltammetry on a CHI 620 analyzer. The data were collected and analyzed using electrochemical analysis software. All measurements were carried out in THF containing 0.1 M tetrabutylammonium hexaflourophosphate (TBAPF₆) as the supporting electrolyte under ambient conditions after purging for 10 min with N2. The conventional three-electrode configuration was employed, which consisted of a glassy-carbon working electrode, a platinum counter electrode, and a Ag/AgNO₃ (0.1 M) reference electrode calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference with a scan rate of 50 Vs⁻¹. Mass spectra were recorded on a VG70-250S mass spectrometer. The cell containing the solution of the sample (1 mM) and the supporting electrolyte were thoroughly purged with nitrogen gas before measurements were taken. The oxidation potentials of organic dyes were estimated by averaging the anode and cathode peak potentials. The HOMO and LUMO values were calculated with reference to the ferrocene oxidation potential by using the following equations: HOMO = E_{ox} +4.8 eV; LUMO = HOMO - E_{0-0} , where the HOMO of ferrocene was set at 4.8 eV.

Carbazole, *para*-bromonitrobenzene, 1,2,3,4-tetrahydroquinoline, 2-methylindoline, 4-bromo-*tert*-butylbenzene, palladium(II) acetate (Pd(OAc)₂), 1,1'- bis(diphenylphosphanyl) ferrocene (dppf), 1,4-dibromobenzene, 10*H*-phenothiazine, *n*-butyllithium (1.6 m in *n*-hexane), *trans*-dichlorobis(triphenylphosphine) palladium(II) ([PdCl₂(PPh₃)₂]), *N*,*N*-dimethylformamide, 2-(tributylstannyl)thiophene, 4-bromobenzaldehyde, *N*-bromosuccinimide (NBS), diphenylamine, tin(II) chloride dihydrate (SnCl₂·2 H₂O), sodium borohydride, tri-*n*-butyltin chloride, cyanoacetic acid, ammonium acetate, and glacial acetic acid, were purchased from ACROS, Alfa, Merck, Lancaster, TCI, Sigma–Aldrich, and Showa, and purified where necessary. Chromatographic separations were carried out by using silica gel from Merck, Kieselgel si 60 (40–63 µm). The synthesis of compounds **1-X, 2-X**, and **3-X**, along with their spectra are provided in the Supporting Information.

Synthesis2-(4-Nitrophenyl)thiophene

To a three-necked flask containing a mixture of *para*-bromonitrobenzene (6.22 g, 30.95 mmol), [PdCl₂(PPh₃)₂] (0.65 g, 0.9 mmol), and 2-tributylstannylthiophene (26.5 mL, 71.0 mmol) was added DMF (50 mL). The reaction mixture was stirred at 90 °C for 24 h. After cooling, the reaction was quenched by adding MeOH and saturated KF (aq., 45 mL). The mixture was extracted with CH₂Cl₂ and the organic layer dried over anhydrous MgSO₄. Evaporation of the solvent gave a crude product that was purified by column chromatography on silica gel (CH₂Cl₂/*n*-hexane, 1:3). The yellow solid was isolated in 80% yield (5.07 g, 24.76 mmol), m.p.: 138–140 °C. ¹H NMR (500 MHz, CDCl₃): δ =8.21 (dt, 2H, *J*=9.0, 2.5 Hz), 7.71 (dt, 2H, *J*=9.0, 2.5 Hz), 7.45 (dd, 1H, *J*=4.0, 1.0 Hz), 7.42 (dd, 1H, *J*=4.0, 1.0 Hz), 7.13 ppm (dd, 1H, *J*=5.0, 3.5 Hz). ¹³C NMR (125 MHz, CDCl₃): δ =146.5, 141.5, 140.5, 128.6, 127.6, 125.9, 125.6, 124.3 ppm. MS (EI, 70 eV): *m/z* (%): 205 [*M*⁺] (100); HRMS calcd for C₁₀H₇O₂NS: 205.0197; found: 205.0196.

4-(Thiophen-2-yl)aniline

A mixture of SnCl₂·2H₂O (19.26 g, 85.35 mmol) and 2-(4-nitrophenyl)thiophene (3.5 g, 17.07 mmol) in degassed absolute EtOH was placed in a three-necked flask under a nitrogen atmosphere, and heated to reflux. Following this, a suspension of NaBH₄ (323 mg, 8.54 mmol) in EtOH was slowly added dropwise to this reaction and the mixture was heated to reflux with stirring. After cooling, the reaction was quenched by adding deionized water in an ice bath. To the resulting solution was added NaOH (1 M) to render it strongly basic, and the mixture extracted with EtOAc. The organic layer was dried over anhydrous MgSO₄ and evaporated under vacuum. The product was purified by column chromatography on silica gel (CH₂Cl₂/*n*-hexane, 1:1). Yellow-green solid was obtained in 90% yield (2.69 g, 15.36 mmol), m.p. 72–74°C. ¹H NMR (400 MHz, CDCl₃): δ =7.44 (d, 2H, *J*=8.4 Hz), 7.19 (d, 1H, *J*=4.8 Hz), 7.17 (d, 1H, *J*=3.2 Hz), 7.06 (t, 1H, *J*=4.0 Hz), 6.69 ppm (d, 2H, *J*=8.4 Hz). ¹³C NMR (100 MHz, CDCl₃): δ =146.0, 145.0, 127.8, 127.1, 125.1, 123.1, 121.3, 115.3 ppm. MS (EI, 70 eV): *m*/*z* (%): 175 [*M*⁺] (100); HRMS calcd for C₁₀H₉NS: 175.0456; found: 175.0456.

(N,N-Di-tert-butylphenyl)-4-(thiophen-2-yl)aniline (3-DTB)

A mixture of 4-(thiophen-2-yl)aniline (1.5 g, 8.56 mmol), $[Pd_2(dba)_3]$ (296 mg, 0.32 mmol), dppf (284 mg, 0.51 mmol), 1-*tert*-butyl-4-bromobenzene (4.54 mL, 21.4 mmol), and sodium *tert*-butoxide (4.11 g, 42.8 mmol) in dry toluene was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 90°C for 15 h. After cooling, the reaction was quenched by adding H₂O, and then was extracted with EtOAc. The organic layer was dried over anhydrous MgSO₄ and evaporated under vacuum. The product was purified by column chromatography on silica gel (*n*-hexane). Compound **3-DTB** was obtained in 50% yield as a yellow solid, m.p. 208–210°C. ¹H NMR (400 MHz, CDCl₃): δ =7.47 (d, 2H, J=8.4 Hz), 7.29 (d, 4H, J=8.0 Hz), 7.23 (d, 2H, J=4.0 Hz), 7.08– 7.05 (m, 7H), 1.34 ppm (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ =147.6, 145.8, 144.8, 144.5, 127.9, 127.7, 126.6, 126.0, 124.0, 123.7, 122.9, 121.9 ppm. MS (EI, 70 eV): *m*/z (%): 439 [*M*⁺] (100); HRMS calcd for C₃₀H₃₃NS: 439.2334; found: 439.2331.

4-(5-(4-(Bis(4-tert-butylphenyl)amino)phenyl)thiophen-2-yl)benzaldehyde (4-DTB)

BuLi (5.4 mL, 8.54 mmol, 1.6 m in n-hexane) was added dropwise to a solution of 3-DTB (2.5 g, 5.69 mmol) in dry THF at -78°C in a threenecked flask under a nitrogen atmosphere. The solution was cooled to -40°C and stirred with a magnetic bar for 30 min. The solution was cooled again to -78°C and to it was added tri-n-butyltin chloride (2.8 mL, 16.1 mmol). The reaction was warmed to room temperature and stirred overnight. The reaction mixture was quenched by the addition of H2O, and was extracted with CH2Cl2. The combined organic solution was dried over anhydrous MgSO4, and dried under vacuum. The crude product was dissolved in dry DMF, then to it was added 4-bromobenzaldehyde (1.0 g, 5.41 mmol) and [PdCl₂(PPh₃)₂] (119 mg, 0.17 mmol). The solution was heated to 90 °C for 24 h and then cooled. The reaction was quenched by the addition of MeOH and saturated KF (aq., 15 mL). The mixture was extracted with CH2Cl2, and the organic layer dried over anhydrous MgSO₄. Evaporation of the solvent gave a crude product, which was purified by column chromatography on silica gel (CH2Cl2/n-hexane, 1:1). 4-DTB was obtained as a yellow solid in 90% yield (2.78 g, 5.12 mmol), m.p. 235–237 °C. ¹H NMR (400 MHz, CDCl₃): $\delta = 10.01$ (s, 1H), 7.90 (d, 2H, J=8.0 Hz), 7.77 (d, 2H, J=8.4 Hz), 7.49 (d, 2H, J= 8.4 Hz), 7.44 (d, 1 H, J=4.0 Hz), 7.31 (d, 4 H, J=8.8 Hz), 7.24 (d, 1 H, J= 4.0 Hz), 7.09 (d, 4H, J=8.8 Hz), 7.07 (d, 2H, J=8.4 Hz), 1.35 ppm (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ = 191.4, 148.2, 146.2, 144.5, 140.3, 140.2, 134.7, 130.5, 126.7, 126.4, 126.1, 125.4, 124.4, 123.1, 122.3, 34.3, 31.4 ppm. MS (FAB, 70 eV): m/z (%): 544 [M+H+ (100); HRMS calcd for C₃₇H₃₈NOS: 544.2674; found: 544.2682.

4-(5-(9-(4-tert-Butylphenyl)-9H-carbazol-3-yl)thiophen-2-yl)benzaldehyde (4-CB)

Compound **4-CB** was synthesized according to the same procedure as compound **4-DTB**. A yellow solid of **4-CB** was obtained in 75% yield, m.p. 251–253 °C. ¹H NMR (400 MHz, CDCl₃): δ = 10.02 (s, 1H), 8.42 (s, 1H), 8.21 (d, 1H, *J* = 7.6 Hz), 7.92 (d, 2H, *J* = 8.4 Hz), 7.83 (d, 2H, *J* = 8.4 Hz), 7.71 (d, 1H, *J* = 8.4 Hz), 7.65 (d, 2H, *J* = 8.4 Hz), 7.52–7.44 (m, 6H), 7.41 (d, 1H, *J* = 3.6 Hz), 7.36–7.32 (m, 1H), 1.46 ppm (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ = 191.4, 150.7, 147.4, 141.6, 140.8, 140.5, 140.3, 134.8, 134.5, 130.5, 126.8, 126.5, 126.3, 126.1, 125.9, 125.4, 124.1, 123.8, 123.4, 123.0, 120.4, 120.1, 117.6, 110.4, 110.2, 34.8, 31.4 ppm. MS (FAB, 70 eV): *m/z* (%) 485 [*M*⁺] (100); HRMS calcd for C₃₃H₂₇NOS: 485.1813; found: 485.1814.

4-(5-(4-(4-tert-Butylphenyl)phenyl)amino)phenyl)thiophen-2yl)benzaldehyde (4-TB)

Compound **4-TB** was synthesized according to the same procedure as compound **4-DTB**. Compound **4-TB** was obtained as a yellow solid in 71% yield, m.p. 157–159°C. ¹H NMR (500 MHz, CDCl₃): δ =9.97 (s,

1 H), 7.86 (d, 2H, J=8.5 Hz), 7.74 (d, 2H, J=8.0 Hz), 7.47 (d, 2H, J=8.5 Hz), 7.41 (d, 1H, J=4.0 Hz), 7.27 (d, 2H, J=8.5 Hz), 7.25 (d, 2H, J=8.0 Hz), 7.21 (d, 1H, J=4.0 Hz), 7.11 (d, 2H, J=8.5 Hz), 7.06–7.04 (m, 5H), 1.31 ppm (s, 9H). ¹³C NMR (125 MHz, CDCl₃): $\delta = 191.2$, 147.9, 147.3, 146.5, 146.1, 144.4, 140.4, 140.1, 134.8, 130.4, 129.2, 127.1, 126.4, 126.1, 126.0, 125.4, 124.5, 124.4, 123.2, 123.0, 122.8, 34.3, 31.3 ppm. MS (FAB, 70 eV): m/z (%) 488 [M+H⁺] (100); HRMS calcd for C₃₃H₃₀NOS: 488.2048; found: 488.2053.

4-(5-(1-(4-tert-Butylphenyl)-2-methylindolin-5-yl)thiophen-2yl)benzaldehyde (4-5TB)

Compound **4-5TB** was synthesized according to the same procedure as compound **4-DTB**. Compound **4-5TB** was obtained as an orange solid in 70% yield, m.p. 159–161 °C. ¹H NMR (400 MHz, CDCl₃): δ =10.00 (s, 1H), 7.89 (d, 2H, *J*=8.0 Hz), 7.77 (d, 2H, *J*=8.0 Hz), 7.44–7.41 (m, 4H), 7.34 (d, 1H, *J*=8.4 Hz), 7.21 (d, 2H, *J*=8.8 Hz), 7.19 (d, 1H, *J*=4.0 Hz), 6.80 (d, 1H, *J*=8.4 Hz), 4.46–4.41 (m, 1H), 3.39 (dd, 1H, *J*=15.2, 8.8 Hz), 2.82 (dd, 1H, *J*=15.6, 8.8 Hz), 1.37 (s, 9H), 1.35 ppm (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ =191.4, 149.2, 147.4, 146.3, 140.4, 140.0, 139.2, 134.5, 130.5, 130.2, 126.2, 126.1, 125.2, 124.2, 122.4, 122.1, 121.6, 108.0, 60.2, 36.8, 34.3, 31.4, 20.1 ppm. MS (FAB, 70 eV): *m/z* (%): 451 [*M*⁺] (100); HRMS calcd for C₃₀H₂₉NOS: 451.1970; found: 451.1967.

4-(5-(10-(4-tert-Butylphenyl)-10 H-phenothiazin-3-yl)thiophen-2-yl)benzaldehyde (4-PT)

Compound **4-PT** was synthesized according to the same procedure as compound **4-DTB**. Compound **4-PT** was obtained as an orange solid in 81% yield, m.p. 199–201°C. ¹H NMR (500 MHz, CDCl₃): δ =7.85 (dd, 2H, *J*=8.4, 1.6 Hz), 7.71 (d, 2H, *J*=8.4 Hz), 7.60 (dd, 2H, *J*=8.4, 2.0 Hz), 7.37 (d, 1H, *J*=3.9 Hz), 7.29 (dd, 2H, *J*=8.4, 2.0 Hz), 7.24 (s, 1H), 7.14 (d, 1H, *J*=3.9 Hz), 7.07 (dd, 1H, *J*=8.6, 2.1 Hz), 6.99 (dd, 1H, *J*=7.4, 1.8 Hz), 6.78–6.85 (m, 2H), 6.17 (d, 1H, *J*=7.8 Hz), 6.15 (d, 1H, *J*=8.5 Hz), 1.40 ppm (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ =191.3, 151.7, 145.0, 144.2, 143.8, 140.6, 140.0, 137.7, 134.9, 130.4, 130.2, 128.1, 127.7, 127.0, 126.6, 126.0, 125.5, 124.3, 123.6, 123.2, 122.5, 120.4, 119.0, 115.9, 34.8, 31.4 ppm. MS (FAB, 70 eV): *m*/z (%) 517 [*M*⁺] (100); HRMS calcd for C₃₃H₂₇NOS₂: 517.1534; found: 517.1529.

4-(5-(1-(4-tert-Butylphenyl)-1,2,3,4-tetrahydroquinolin-6-yl)thiophen-2-yl)benzaldehyde (4-6TB)

Compound **4-6TB** was synthesized according to the same procedure as compound **4-DTB**. Compound **4-6TB** was obtained as a yellow solid in 64% yield, m.p. 177–179°C. ¹H NMR (500 MHz, CDCl₃): δ =9.96 (s, 1H), 7.85 (d, 2H, *J*=8.3 Hz), 7.72 (d, 2H, *J*=8.3 Hz), 7.37–7.39 (m, 3H), 7.30 (s, 1H), 7.16–7.19 (m, 3H), 7.13 (d, 1H, *J*=3.8 Hz), 6.67 (d, 1H, *J*=8.5 Hz), 3.64 (t, 2H, *J*=5.6 Hz), 2.89 (t, 2H, *J*=6.3 Hz), 2.04–2.09 (m, 2H), 1.33 ppm (s, 9H). ¹³C NMR (125 MHz, CDCl₃): δ =1913, 147.5, 147.2, 145.0, 144.8, 140.4, 139.3, 134.5, 130.4, 126.8, 126.4, 126.0, 125.2, 124.9, 124.1, 123.8, 123.2, 122.1, 115.1, 51.1, 34.4, 31.4, 27.8, 22.5 ppm. MS (FAB, 70 eV): *m/z* (%): 451 [*M*⁺] (100); HRMS calcd for C₃₀H₂₉NOS: 451.1970; found: 451.1970.

(E)-3-(4-(5-(4-(Bis(4-tert-butylphenyl)amino)phenyl)thiophen-2yl)phenyl)-2-cyanoacrylic acid (**DTB-PSP**)

A mixture of compound **6-DTB** (1.05 g, 1.93 mmol), cyanoacetic acid (165 mg, 1.93 mmol), and ammonium acetate (38 mg, 0.48 mmol) in acetic acid was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 90–100 °C for 12 h. After cooling, the reaction was quenched by adding distilled water and extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and evaporated under vacuum. The product was purified by column chromatography on silica gel (CH₂Cl₂/acetic acid, 19:1). The black solid was isolated in 61% yield (718 mg, 1.17 mmol), m.p. 278–280 °C. ¹H NMR (400 MHz, [D₆]DMSO): δ =8.26 (s, 1H), 8.07 (d, 2H, *J*=8.4 Hz), 7.46 (d, 1H, *J*=3.6 Hz), 7.36 (d, 1H, *J*=4.0 Hz), 7.59 (d, 2H, *J*=8.8 Hz), 7.46 (d, 1H, *J*=3.6 Hz), 7.36 (d, 1H, *J*=8.8 Hz), 7.00 (d, 4H, *J*=8.8 Hz), 6.93 (d, 2H, *J*=8.4 Hz), 1.28 ppm (s, 18H).¹³C NMR (100 MHz, [D₆]DMSO): δ =163.7, 148.0, 146.4, 145.3, 144.5, 140.3, 137.9, 131.8, 131.0, 127.6, 126.9, 126.8, 126.6,

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125.7, 124.7, 124.5, 122.1, 34.5, 31.6 ppm. MS (FAB, 70 eV): m/z (%) 611 [M+H⁺] (100); HRMS calcd for $C_{40}H_{30}N_2O_2S$: 611.2732; found: 611.2741.

(E)-3-(4-(5-(9-(4-tert-Butylphenyl)-9H-carbazol-3-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (**CB-PSP**)

Compound **CB-PSP** was synthesized according to the same procedure as compound **DTB-PSP**. Compound **CB-PSP** was obtained as a dark-red solid in 70% yield, m.p. 298–300 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.66 (s, 1H), 8.36 (d, 1H, *J*=7.6 Hz), 8.32 (s, 1H), 8.12 (d, 2H, *J*= 8.0 Hz), 7.93 (d, 2H, *J*=8.0 Hz), 7.83 (d, 1H, *J*=4.0 Hz), 7.80 (d, 1H, *J*= 8.4 Hz), 7.72 (d, 2H, *J*=8.0 Hz), 7.67 (d, 1H, *J*=4.0 Hz), 7.59 (d, 2H, *J*= 8.0 Hz), 7.49–7.39 (m, 3H), 7.34 (t, 1H, *J*=7.2 Hz), 1.41 ppm (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ =163.8, 153.6, 150.7, 146.6, 141.2, 140.4, 140.2, 138.3, 134.4, 132.1, 130.6, 127.9, 127.4, ,127.2, 126.6, 126.0, 125.7, 124.7, 124.6, 123.7, 123.0, 121.4, 120.8, 117.9, 116.9, 110.8, 110.4, 35.0, 31.6 ppm. MS (FAB, 70 eV): *m/z* (%): 552 [*M*⁺] (100); HRMS calcd for C₃₆H₂₈N₂O₂S: 552.1871; found: 552.1869.

(E)-3-(4-(5-(4-(N-(4-tert-butylphenyl)-N-phenyl)amino)phenyl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (**TB-PSP**)

Compound **TB-PSP** was synthesized according to the same procedure as compound **DTB-PSP**. Compound **TB-PSP** was obtained as a dark-red solid in 64% yield, m.p. 274–276 °C. ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 8.30$ (s, 1H), 8.09 (d, 2H, J = 8.0 Hz), 7.88 (d, 2H, J = 8.0 Hz), 7.76 (d, 1H, J = 3.6 Hz), 7.61 (d, 2H, J = 8.4 Hz), 7.49 (d, 1H, J = 3.6 Hz), 7.61 (d, 2H, J = 8.4 Hz), 7.49 (d, 1H, J = 3.6 Hz), 7.38–7.31 (m, 4H), 7.09–7.05 (m, 3H), 7.02 (d, 2H, J = 8.4 Hz), 6.97 (d, 2H, J = 8.4 Hz), 1.29 ppm (s, 9H). ¹³C NMR (100 MHz, [D₆]DMSO): $\delta = 163.7$, 147.8, 147.2, 146.6, 145.2, 144.4, 140.3, 138.1, 131.9, 130.8, 130.0, 127.8, 127.0, 126.9, 125.7, 124.9, 124.7, 124.6, 123.8, 122.7, 34.5, 31.6 ppm. MS (FAB, 70 eV): m/z (%) 555 [M+H⁺] (100); HRMS calcd for C₃₆H₃₁N₂O₂S: 555.2106; found: 555.2113.

(E)-3-(4-(5-(1-(4-tert-Butylphenyl)-2-methylindolin-5-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (**5TB-PSP**)

Compound **5TB-PSP** was synthesized according to the same procedure as compound **DTB-PSP**. Compound **5TB-PSP** was obtained as a black solid in 65% yield, m.p. 267–269°C. ¹H NMR (400 MHz, [D₆]DMSO): δ =8.29 (s, 1H), 8.08 (d, 2 H, *J*=8.4 Hz), 7.85 (d, 2 H, *J*=8.4 Hz), 7.72 (d, 1H, *J*=3.6 Hz), 7.50 (s, 1H), 7.44–7.35 (m, 4H), 7.22 (d, 2 H, *J*=8.4 Hz), 6.74 (d, 1H, *J*=8.4 Hz), 4.53–4.44 (m, 1H), 3.40–3.36 (m, 1H), 2.76 (dd, 1H, *J*=16.2, 7.6 Hz), 1.30 (s, 9H), 1.25 ppm (s, 3 H).¹³C NMR (100 MHz, [D₆]DMSO): δ =163.8, 148.9, 146.7, 145.8, 139.9, 138.8, 132.0, 130.8, 127.7, 127.4, 126.5, 125.5, 125.4, 124.0, 123.2, 122.5, 121.5, 107.8, 59.6, 36.4, 34.5, 31.6, 20.2 ppm. MS (FAB, 70 eV): *m/z* (%) 518 [*M*⁺] (100); HRMS calcd for C₃₃H₃₀N₂O₃S: 518.2028; found: 518.2026.

(E)-3-(4-(5-(10-(4-tert-Butylphenyl)-10H-phenothiazin-3-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (**PT-PSP**)

Compound **PT-PSP** was synthesized according to the same procedure as compound **DTB-PSP**. Compound **PT-PSP** was obtained as a dark-red solid in 60% yield, m.p. 302–304°C. ¹H NMR (500 MHz, [D₆]DMSO): δ =7.85 (s, 1H), 7.80 (d, 2H, *J*=8.5 Hz), 7.65–7.68 (m, 5H), 7.43 (d, 1H, *J*=3.9 Hz), 7.37 (d, 1H, *J*=2.2 Hz), 7.33 (d, 2H, *J*=8.5 Hz), 7.22 (dd, 2H, *J*=8.5, 2.1 Hz), 7.05 (dd, 1H, *J*=7.6, 1.5 Hz), 6.91 (td, 1H, *J*=7.6, 1.5 Hz), 6.83 (td, 1H, *J*=7.3, 1.0 Hz), 6.08 (d, 1H, *J*=8.5 Hz), 6.07 (d, 1H, *J*=5.8 Hz), 4.70 (s, 2H), 1.34 ppm (s, 9H). ¹³C NMR (125 MHz, [D₆]DMSO): δ =193.4, 167.7, 166.8, 151.7, 143.8, 143.7, 143.6, 140.7, 137.7, 136.3, 133.6, 132.2, 132.0, 130.4, 128.3, 128.2, 127.9, 127.3, 127.1, 126.1, 125.0, 124.9, 123.5, 123.3, 121.6, 120.2, 118.7, 116.4, 116.2, 45.6, 35.0, 31.6 ppm. MS (FAB, 70 eV): *m/z* (%) 584 [*M*⁺] (100); HRMS calcd for C₃₆H₂₈N₂O₂S₂: 584.1592; found: 584.1594.

(E)-3-(4-(5-(1-(4-tert-Butylphenyl)-1,2,3,4-tetrahydroquinolin-6-yl)thiophen-2-yl)phenyl)-2-cyanoacrylic acid (**6TB-PSP**)

Compound **6TB-PSP** was synthesized according to the same procedure as compound **DTB-PSP**. Compound **6TB-PPS** was obtained as a black solid in 52% yield, m.p. 234–236°C. ¹H NMR (500 MHz, $[D_6]DMSO$): δ =8.24 (s, 1H), 8.03 (d, 2H, J=8.5 Hz), 7.81 (d, 2H, J=8.5 Hz), 7.67 (d,

1 H, J = 3.8 Hz), 7.39 (d, 2 H, J = 8.5 Hz), 7.31–7.34 (m, 2 H), 7.21 (dd, 1 H, J = 8.5, 2.0 Hz), 7.16 (d, 2 H, J = 8.5 Hz), 6.51 (d, 1 H, J = 8.5 Hz), 3.56 (t, 2 H, J = 5.5 Hz), 2.82 (t, 2 H, J = 5.5 Hz), 1.95 (m, 2 H), 1.27 ppm (s, 9 H). ¹³C NMR (125 MHz, [D₆]DMSO): $\delta = 163.8$, 153.2, 147.3, 146.5, 145.1, 145.0, 139.0, 138.3, 132.0, 130.5, 127.7, 126.8, 125.5, 125.1, 124.4, 124.3, 123.2, 123.0, 117.2, 115.0, 51.1, 34.6, 31.6, 27.6, 22.4 ppm. MS (FAB, 70 eV): m/z (%) 518 [M^+] (100); HRMS calcd for C₃₃H₃₀N₂O₂S: 518.2028; found: 518.2024.

Fabrication and Characterization of DSSCs

The FTO-conducting glass (FTO glass, fluorine-doped tin-oxide overlayer, transmission > 90 % in the visible region, sheet resistance 8Ω square⁻¹), titanium dioxide pastes of titanium-nanoxide T/SP and titanium-nanoxide R/SP were purchased from Solaronix. A thin film of TiO_2 (ca. 16-18 µm thick) was coated onto a 0.25 cm² FTO glass substrate, and the thickness was measured by Veeco Dektak 150. The substrate was immersed in a THF solution containing 3×10^{-4} M dye sensitizers for at least 12 h, then rinsed with anhydrous acetonitrile and dried. Another piece of FTO that was covered with sputtered platinum (100 nm thick) was used as a counter electrode. The active area was controlled at a dimension of 0.25 cm² by adhering polyester tape (60 µm thick) onto the platinum electrode. The photocathode was placed on top of the counter electrode and was tightly clipped together to form a cell. Electrolyte was then injected into the seam between two electrodes. An acetonitrile solution containing LiI (0.5 M), I₂ (0.05 M), and 4-tert-butylpyridine (0.5 M) was used as the electrolyte. A device made from a commercial dye (N719) under the same conditions (3×10⁻⁴ M, Solaronix S.A., Switzerland) was used as a reference. The cell parameters were obtained under an incident beam of light (intensity 100 mW cm⁻², measured by a thermopile probe; Oriel 71964) that was generated by a 300 W Xe lamp (Oriel 6258) passing through an AM 1.5 filter (Oriel 81088). The current-voltage parameters of DSSCs were recorded by a potentiostat/galvanostat model CHI650B (CH Instruments, USA). The light intensity was further calibrated by an Oriel reference solar cell (Oriel 91150) and adjusted to be 1.0 sun. The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100) at short-circuit condition. Electrochemical impedance spectra of DSSCs were recorded by an Impedance/Gain-Phase analyzer (SI 1260, Solartron). The frequencies explored were in the range of 10 mHz to 65 kHz. The alternating current (ac) amplitude was set at 20 mV. The photovoltage transients of assembled devices were recorded using a digital oscilloscope (Tektronix, TDS 3012b). Pulsed-laser excitation was applied by a Q-Switched Nd:YAG laser (Quanrel, brilliant B) with a 10 Hz repetition rate at 532 nm and a 7 ns pulse width at halfheight. The laser energy of 3 mJ cm⁻² to cover the area of the device size was slightly larger than 0.25 cm². The recombination lifetime of injected electrons with oxidized dyes was measured by transient photovoltages on an open circuit in the presence of LiI electrolyte (0.5 M) in acetonitrile. The average electron lifetime can be approximately estimated by fitting a decay of the open-circuit voltage transient to $\exp(-t/\tau)$, in which t is time and τ is an average time constant before recombination.

Quantum Chemistry Computation

All organic dyes were optimized by using B3LYP/6–31G* hybrid functional. Geometry optimizations were performed to locate the minima on the potential energy surface, in order to predict the equilibrium structure of a given molecule. For the excited states, a time-dependent densityfunctional theory (TDDFT) with the B3LYP functional was employed. All analyses were performed under Q-Chem 3.0 software. The frontierorbital plots of HOMO and LUMO were drawn by using Gaussian 03. All calculations were performed using the Gaussian 03 suite of programs.

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