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High-Performance Dipolar Organic Dyes with an Electron-Deficient Diphenylquinoxaline Moiety in the π -Conjugation Framework for **Dye-Sensitized Solar Cells**

Sie-Rong Li,^[a] Chuan-Pei Lee,^[b] Hui-Tung Kuo,^[a] Kuo-Chuan Ho,*^[b] and Shih-Sheng Sun^{*[a]}

Abstract: We report here the synthesis and electrochemical and photophysical properties of a series of easily prepared dipolar organic dyes and their application in dye-sensitized solar cells (DSSCs). For the six organic dyes, the molecular structures comprised a triphenylamine group as an electron donor, a cyanoacrylic acid as an electron acceptor, and an electron-deficient diphenylquinoxaline moiety integrated in the π -conjugated spacer between the electron donor and acceptor moieties. The incorporation of the electron-deficient diphenylquinoxaline moiety effectively reduces the energy gap of the dyes and broadly extends the spectral coverage. DSSCs based on dye 6 produced the best overall cell performance

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of 7.35%, which translates to approximately 79% of the intrinsic efficiency of the DSSCs based on the standard N719 dye under identical experimental conditions. The high performance of DSSCs based on dye 6 among the six dyes explored is attributed to the combined effects of high dye loading on a TiO₂ surface, rapid dye regeneration, and effective retardation of charge recombination.

Introduction

The development of efficient energy conversion materials has been a popular research topic for searching for an energy alternative for environmentally unfriendly fossil fuels.^[1-3] Dye-sensitized solar cells (DSSCs) represent a class of low-cost photovoltaics relative to the traditional solidstate semiconductor devices and have received considerable attention recently.^[4-6] Typically these devices are composed of three functional regions: a light-harvesting dye adsorbed on the nanocrystalline TiO₂ film as the photosensitizer, a Ptcoated counter electrode, and a liquid junction containing a reusable redox couple (most commonly I_3^{-}/I^{-}). Pioneered by Grätzel and co-workers,^[7-10] DSSCs with Ru^{II}-based sensitizers have shown the best photoconversion efficiency of up to 11.5%.[11-17] However, the consumption of precious metals for metal-complex dyes is still a concern in terms of cost and long-term availability. On the other hand, the efficiency of DSSCs based on metal-free organic dyes are rapid-

ly catching up and recently the best photoconversion efficiency of organic dye-sensitized solar cells up to 10% or higher was observed.[18-20]

One of the crucial components in a DSSC is the photosensitizer since it is responsible for light harvesting, funnelling excitation energy to the semiconductor surface, and eventually achieving charge separation. In recent years, many studies have focused on screening various organic dyes with a D- π -A system, which typically consists of an electron donor (D), a π -conjugated spacer (π) between the donor and acceptor, and an electron acceptor (A; most commonly a carboxylate group) for anchoring onto the TiO₂ surface. Photosensitizers possessing an extended π -conjugated spacer would expect to narrow their HOMO-LUMO gaps and increase the spectral coverage for the light harvesting.^[21-25] The structural design principle typically aims to facilitate efficient charge transfer upon light absorption, effectively tuning the spectral coverage with enhanced light-harvesting efficiency, and increasing thermal and photochemical stability.^[26-28] Many organic dyes featuring substituted triarylamine,^[29-34] coumarin,^[35-37] indoline,^[38] fluorene,^[39] and porphyrin^[20,40-42] have been intensively employed as sensitizers for DSSCs.

Alternatively, one way to extend the spectral coverage in DSSCs is to integrate an electron-deficient fragment in the π -conjugated spacer of organic dyes to form a low band gap chromophore, which enhances the degree of charge separation and extends the absorption range of the sensitizers. This strategy of reducing the HOMO-LUMO gap by introducing a linker to destabilize the HOMO and stabilize the

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LUMO has been widely employed for organic bulk heterojunction photovoltaic materials,^[43,44] but there are relatively few reports for DSSC-exploited organic dyes incorporating electron-deficient fragments. Notable examples for such electron-deficient chromophores incorporated in sensitizers for DSSCs include benzothiadiazole,[45,46] porphyrin-fused quinoxaline,^[47] boradiazaindacene,^[48,49] quinoxaline,^[50] and others.^[51] To explore the effect of an electron-deficient chromophore and its relative linkage position in the π -conjugated framework on the performance of the resulting DSSCs, we report herein the design and synthesis of a series of dipolar organic sensitizers imparted with an electron-deficient diphenylquinoxaline unit in the framework of the π -conjugated spacer to link the triphenylamine electron donor and cyanoacrylic acid electron acceptor. An appreciable efficiency of over 7.3% has been achieved with the dye 6 sensitized



DSSC. The high dye loading of dye **6** on the TiO_2 surface and effective retardation of charge recombination are attributed to the key factors for good DSSC performance, which correlates well with the relative position of the electron-deficient diphenylquinoxaline in the π -conjugated spacer.

Results and Discussion

Synthesis: The synthetic strategies for the preparation of the six new organic dyes with a diphenylquinoxaline moiety in

the π -conjugated spacer are illustrated in Scheme 1. After treating compound $7^{[52]}$ with *n*-butyllithium and DMF at -78°C to form monoformylated diphenylquinoxaline precursor 8, the aldehydes 9 and 10 were synthesized by conventional palladium-catalyzed Suzuki-Miyaura and Heck coupling reactions, respectively. Dyes 1 and 2 were obtained through a Knoevenagel condensation reaction by treating 9 and 10, respectively, with cyanoacetic acid in acetic acid at reflux. Dyes 3, 4, and 5 were synthesized in a similar manner by starting from 11,^[53] 12,^[53] and 13,^[53] respectively, by a series of boronation with n-butyllithium and excess B(OMe)₃ in THF, palladium-catalyzed Suzuki-Miyaura coupling reaction, and a final condensation reaction. Dye 6, which has a thiophene inserted between the diphenylquinoxaline and cyanoacrylic acid, was prepared from compound 7 through two successive Suzuki coupling reactions

followed by Knoevenagel condensation with cyanoacetic acid. All six dyes have been fully characterized by NMR spectroscopy, HRMS, and elemental analysis. All six dipolar dyes are air stable and possess fairly good solubility in highly polar solvents, especially in DMF.

Photophysical and electrochemical properties: The UV/Vis absorption spectra of the six dyes measured in DMF are plotted in Figure 1a and the related photophysical data are summarized in Table 1. The general features of the absorption spectra are composed of two broad bands in the near UV and visible region, which are assigned to a series of π - π * transitions and a low-energy intramolecular charge-transfer (ICT) transition, respectively. The lowest energy bands of the six dyes range from 433 to 483 nm with molar extinction coefficients between 1.2×10^4 and $2.4 \times$

 10^4 m⁻¹ cm⁻¹. The absorption spectral coverage follows the order of 5>3>4>2>6>1. As anticipated, dyes with a more extended π -conjugation network display lower energy absorption profiles and more extended spectral coverages. The presence of a hexyl group in the thiophene adjacent to the triphenylamine moiety in dye 4 results in a less planar conformation due to the steric hindrance, which may account for the higher energy absorption profile in dye 4 relative to dye 3. Dyes 3 and 6 contain the same π -conjugated fragments but differ in the relative position of thiophene and diphenylquinoxaline. Direct connection of an electron-







Scheme 1. Synthetic procedures for organic dyes **1–6**: a) *n*BuLi, DMF, -78 to 0°C, 2 h, 45%; b) 4-(diphenylamino)phenylboronic acid, [PdCl₂(PPh₃)₂], Na₂CO₃, H₂O/THF (3:2), RT, 16 h; c) 2-cyanoacetic acid, CH₃COOH, NH₄OAc, reflux, 12 h; d) *N*,*N*-diphenyl-4-vinylaniline, Pd(OAc)₂, Na₂CO₃, DMF, 120°C, 16 h; e) 1) *n*BuLi, THF, B(OCH₃)₃, -78°C to RT, 5 h; 2) [PdCl₂(PPh₃)₂], Na₂CO₃, **8**, THF/H₂O (3:2), RT, 16 h; f) 5-formylthiophen-2-ylboronic acid, [PdCl₂(PPh₃)₂], THF/H₂O (3:2), Na₂CO₃, RT, 16 h.

Table 1. Photophysical and electrochemical data and dye loading on a TiO2 surface.

Dye	$\begin{array}{c} \lambda_{max} \ [nm] \\ (10^{-4} \ \text{m}^{-1} \text{cm}^{-1})^{[a]} \end{array}$	λ_{em} $[nm]^{[a]}$	Dye loading [10 ⁻⁷ mol cm ²]	<i>E</i> (S ⁺ /S) [V] ^[b]	$E_{0-0} \ [eV]^{[c]}$	E (S ⁺ /S [*]) [V] ^[d]	$E_{\rm gap}$ $[V]^{[e]}$
1	433 (1.2)	628	6.4	1.19	2.34	-1.15	0.65
2	463 (2.4)	665	5.2	1.06	2.21	-1.15	0.65
3	483 (1.9)	681	3.6	1.07	2.12	-1.05	0.55
4	466 (1.8)	675	2.7	1.07	2.15	-1.08	0.58
5	483 (2.0)	682	2.2	1.00	2.14	-1.14	0.64
6	460 (2.2)	630	7.9	1.12	2.29	-1.17	0.67

[a] Absorption and emission spectra were measured in DMF. [b] The oxidation potentials (vs. the normal hydrogen electrode (NHE)) of dyes were measured in DMF with tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte. [c] E_{0-0} values were estimated from the intersection of the normalized absorption and emission spectra. [d] E (S⁺/S^{*}) (vs. NHE) values were calculated from E (S⁺/S) $-E_{0-0}$. [e] The energy gap between the excited-state oxidation potential and the TiO₂ conduction band edge.

rich thiophene to the triphenylamine donor site facilitates a stronger ICT effect and more bathochromic shift of the absorption profile in dye 3 relative to the less effective ICT in dye 6 in which an electron-deficient diphenylquinoxaline is connected to the triphenylamine donor site. All six dyes

FULL PAPER

show fairly strong emission with maxima between 628 to 682 nm. The emission maximum also follows the same trend as the absorption spectra with more π -conjugated molecules showing red-shifted emission profiles.

The absorption spectra of all dyes adsorbed on a transparent TiO₂ film are depicted in Figure 1b. Relative to the spectra measured in DMF, apparent bathochromic shifts and broadening of the absorption profiles were observed for all six dyes adsorbed on the TiO₂ surface. In particular, the spectral coverage of dye 5 is extended over 700 nm upon adsorption on the TiO₂ surface. Although the exact nature of the dye aggregate on the TiO₂ surface is not clear, the observed bathochromic shift in the absorption spectra is likely due to the coordination of the carboxylate group to the surface Ti⁴⁺ that lowers the π^* level of the organic dyes.^[54] The amount of dye loadings on the TiO₂ surface estimated by changes of absorbance of the mother liquid of dyes before and after adsorption are collected in Table 1. It generally correlates well with the molecular size of the dyes in which the

smaller dyes displayed larger amounts of dye loading on the TiO₂ surface. Dye **6** shows the highest dye loading on the TiO₂ surface among the six dyes even though its molecular size is larger than dyes **1** and **2**. It is possible that the less space demanding thiophene directly attached to cyanoacrylic acid dramatically increases the number of dye molecules that can be adsorbed on the TiO₂ surface when compared to other dyes with the more stericly demanding diphenylquinoxaline near the TiO₂ surface (see Table 1 and Figure 2). The orientation of the adsorbed dyes on the TiO₂ surface may also contribute to the ultimate density of dye loading. The dense packing of dye **6** on the TiO₂ surface may also prevent the bulky I_3^- approaching closely to

the surface and retard the charge recombination (vide infra).

The redox potentials of dyes **1–6** were measured in DMF by square-wave voltammetry and the results are also summarized in Table 1. The first oxidation potential of the dyes,

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Figure 1. a) Absorption spectra measured in DMF and b) absorption spectra measured with dyes adsorbed on a TiO₂ surface.

E (S⁺/S), which occurs at the triphenylamine site, falls in the range between 1.00 to 1.19 V versus NHE and follows the order of $1 > 6 > 2 \approx 3 \approx 4 > 5$. The higher oxidation potentials observed for dyes 1 and 6 relative to the others are attributed to the direct connection of an electron-deficient diphenylquinoxaline moiety to the electrochemically active triphenylamine site, which lowers the HOMO level. The 0-0 transition energy (E_{0-0}) of the dyes, which was estimated at the intersection of the normalized absorption and emission spectra, follows the trend of π -conjugation length with 1 > 6 > 2 > 4 > 5 > 3. The E (S⁺/S^{*}) values, corresponding to the LUMO levels of the dyes, were calculated from E (S⁺/S)- E_{0-0} and fall in the range between -1.05 to -1.17 V. As illustrated in Figure 3, the HOMO and LUMO levels of all six dyes exhibit sufficient driving force for the charge injection to the TiO_2 conduction band (-0.5 V vs. NHE), as well as the dye regeneration by iodide reduction (0.4 V vs. NHE).

Molecular orbital calculations: Theoretical studies based on DFT calculations by using the Gaussian 09 program package at the B3LYP/6-31G* level of theory were carried out for the six dyes to gain insight into the geometric electronic strucutres.^[55] Table 2 summarizes the frontier molecular orbitals for the six dyes. In Table 2 it can clearly be seen that the electron density of the HOMOs is predominantly localized on the triphenylamine donor moiety and diffusively distributed over the π -conjugation onto the diphenylquinoxa-



Figure 2. A cartoon illustration of the steric demands of the dyes on adsorption on a TiO_2 surface.

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Figure 3. Comparison of the ground- and excited-state oxidation potentials of dyes 1-6 witt the conduction band of TiO₂ and the oxidation potential of iodide.

line moiety, which holds a small fraction of the overall electron density. In contrast, the electron density of the LUMOs is extended over the diphenylquinoxaline and cyanoacrylic acid acceptor moiety. It is notable that, by careful scrutiny of the frontier MOs, dyes 1 and 6 exhibit more localized electron density distribution than dyes 2–5, which implies a 4 more prominent charge separation in dyes 1 and 6 than dyes 2–5 upon photoexcitation. This subtle difference, in conjunction with other physical parameters, may contribute to the different DSSC performance based on these six dyes.^[56,57]

Photovoltaic performance: Figure 4 depicts the J-V curves and action spectrum of incident photon-to-electron conversion efficiency (IPCE) plots as a function of wavelength for 5 the DSSCs based on the six dyes studied in this work under AM 1.5 illumination. The device performance and the relevant data of the assembled DSSCs are summarized in Table 3. The power conversion efficiencies are in the range of 2.38–7.35% and in the order of 1 < 2 < 4 < 3 < 5 < 6 with the best efficiency of dye 6 up to approximately 79% of intrinsic performance of the standard N719 dye under the 6 same experimental conditions. It is interesting to note that

Table 3. Photovoltaic	performance	parameters	of the	dyes.[a]
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Dye	$V_{ m oc}$ [V]	$J_{\rm sc}$ [mA cm ²]	ff	η [%]	τ_{e} [ms] ^[b]
1	0.57	5.97	0.70	2.38	0.95
2	0.53	6.99	0.70	2.61	0.77
3	0.56	9.90	0.71	3.94	0.87
4	0.57	8.84	0.71	3.58	1.02
5	0.59	12.34	0.69	5.01	1.65
6	0.70 ± 0.004	15.40 ± 0.26	0.68 ± 0.02	7.35 ± 0.10	2.29
N719	0.74 ± 0.003	18.10 ± 0.27	0.69 ± 0.01	9.35 ± 0.08	3.56

[a] $V_{\rm oc}$ is the open-circuit voltage, $J_{\rm sc}$ is the short-circuit photocurrent density, *ff* is the fill factor, and η is the power conversion efficiency. Working areas on an FTO substrate were 0.16 cm². The cell parameters for dye **6** and N719 were averages with five measurements. [b] Electron lifetimes (τ_e) in the TiO₂ film were obtained from the transient photovoltage decay measurements.



FULL PAPER

replacing the diphenylquinoxaline unit in dye **6** with either a phenyl or thiophene group resulted in DSSCs with lower power conversion efficiencies than the device fabricated based on dye $6^{[58,59]}$

The spectral coverage of the IPCE plots becoming broader toward the red region, consistent with the trend of the π conjugation of the organic dyes, generally matches well with the absorption spectra of dyes adsorbed on the TiO₂ surface. In particular, the IPCE of dye **5** has extended into the near-IR region. A similar trend of J_{sc} also follows the same order with more extended π -conjugation network dyes generally showing higher short-circuit current density. A notable ex-

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Figure 4. a) The J-V characteristics of DSSCs based on the dye sensitizers. b) Incident photon-to-current efficiency (IPCE) spectra for the sensitized DSSCs.

ception is dye **6**, which exhibits the highest J_{sc} among all six dyes. A DSSC based on dye **6** produced the maximum IPCE of approximately 95% at 480 nm and maintained 80% or higher over the spectral range from 400 to 570 nm. Those based on other dyes produced maximum IPCE values below 60%. The outstanding IPCE of the DSSC based on dye **6** is probably due to the combined effects of a particularly high surface dye loading, a large driving force from the LUMO level of the dye to the conduction band edge of TiO₂, a high molar extinction coefficient, and the efficient charge separation that led to a greater electron injection efficiency and higher light-harvesting efficiency (LHE) than DSSCs based on the other dyes studied here.^[60,61]

Dye **6** exhibits a larger V_{oc} than other dyes in the assembled DSSCs. It is quite phenomenal that the V_{oc} value from a DSSC based on dye **6** is nearly comparable to that based on N719.^[4b,62] The bulky diphenylquinoxaline adjacent to the triphenylamine donor in dye **6** forms a hydrophobic barrier preventing the hydrophilic I_3^- ions approaching the TiO₂ surface, thereby retarding the charge recombination.^[23] Controlled experiments with DSSCs containing co-adsorb-

ent chenodeoxycholic acid (CDCA) with dye 6 showed no improvement of V_{oc} but a reduced J_{SC} , which is indicative of dense packing of dyes on the TiO₂ surface. The high dye loading for dye 6 that results in a thick aggregate on the TiO₂ surface contributes not only to the improved light harvesting, but may also contribute to the effective retardation of charge recombination and enhanced V_{oc} . The dark current measured with DSSCs based on dyes 1-6 also displayed a reverse trend to the V_{oc} values (see Figure S27 in the Supporting Information). The incorporation of hydrophobic hexyl groups in the π -conjugated framework of dyes 4 and 5 slightly increases the resulting $V_{\rm oc}$ values relative to dyes 1– 3. On the contrary, dye 5 with two hydrophobic hexylthiophene units in the structure shows a lower $V_{\rm oc}$ value and shorter electron lifetime than dye 6 with a shorter conjugated spacer. A similar reduced V_{oc} value has been reported in organic dyes with the π -conjugated hexylthiophene unit increasing from three to four and six.^[63] Compared with the tightly packed layer of dye 6, the more loosely packed layer of dye 5 on the TiO₂ surface may produce large interstices that allows I_3^- to infuse close to the TiO₂ surface and results in faster charge recombination. The electron lifetimes (τ_e) , obtained from the transient photovoltage decay measurements, correlate well with the measured $V_{\rm oc}$ value (see Figure 5 and Table 3).^[64] A longer electron lifetime indicates



Figure 5. Traces of the transient photovoltage decay of DSSCs based on dyes **1–6** and N719.

a suppressed charge recombination arising from electrons in the TiO_2 film with the I_3^- ion in the electrolyte and, therefore, an enhanced open-circuit photovoltage was observed.

Electrochemical impedance spectroscopy (EIS) was further employed to investigate the interfacial charge-transfer dynamics in DSSCs.^[65] In general, the EIS spectrum of an FTO/TiO₂/dye/electrolyte/Pt/FTO device (FTO=fluorinedoped SnO₂ conducting glass) shows three semicircles in the frequency range of 10 mHz to 65 kHz. The ohmic serial resistance (R_s) corresponds to the overall series resistance (see Figure S28 in the Supporting Information for the equivalent circuit of an assembled DSSC). The first and second semicircles correspond to the charge-transfer resistances at the counter electrode (R_{ct1}) and the TiO₂/dye/electrolyte interface (R_{ct2}) , respectively. The Warburg diffusion process of I^{-/I₃⁻ in the electrolyte (Z_w) is associated with the third semicircle. However, in this work most of the conventional diffusion resistance of the redox couple is apparently greatly overlapped by R_{ct2} due to a short length for I⁻ ion diffusion available with the thin spacer used (25 µm thick), and owing to the low viscosity of the solvents used in our electrolyte. The Nyquist plots for DSSCs based on dyes **1–6** under AM 1.5 illumination are illustrated in Figure 6. The TiO₂/dye/ electrolyte interface resistance decreased in the order of **1**}



Figure 6. EIS Nyquist plots for DSSCs based on dyes 1-6 under AM 1.5 illumination.

 $(44.9) > 2 (33.0) > 4 (23.8) > 3 (23.0) > 5 (21.4) > 6 (17.0 \Omega)$, which is in good agreement with the trend of the cell performance. It is evident that an improved electron generation and transport occurred in the cell due to the smaller TiO₂/ dye/electrolyte interface resistance under illumination.^[66]

Conclusion

We reported the synthesis of a series of dipolar organic dyes with an electron deficient diphenylquinoxaline moiety incorporated within the π -conjugation framework and the performance of standard DSSCs sensitized by these organic dyes. DSSCs based on these dyes have shown photo-to-electrical energy conversion efficiency up to 7.35% under simulated AM 1.5 irradiation, which translates to approximately 79% of the intrinsic performance of a DSSC sensitized by the N719 dye. The presence of the diphenylquinoxaline moiety effectively lowers the energy gaps of organic dyes and extends the absorption spectral coverage to the near-IR region. The bulky and hydrophobic nature of diphenylquinoxaline could suppress the infusion of I₃⁻ ions toward the TiO₂ surface and retard the charge recombination. The performance of the DSSC sensitized by dye 6 was the best among the six dyes investigated. In particular, dye 6 shows an outstanding light-harvesting ability and cell performance, which are attributed to the combined effects of high dye loading on the TiO_2 surface, efficient charge injection, and dye regeneration. Further improvement of DSSCs with organic sensitizers based on the structure of dye **6** by molecular engineering aiming for better cell performance is in progress.

Experimental Section

Materials and general procedures: The starting materials, *N*,*N*-diphenyl-4-vinylaniline,^[67] 5,8-dibromo-2,3-diphenylquinoxaline (**7**),^[52] *N*,*N*-diphenyl-4-(thiophen-2-yl)benzenamine (**11**),^[53] 4-(3-hexylthiophen-2-yl)-*N*,*N*-diphenylbenzenamine (**12**),^[53] and 4-[3-hexyl-5-(3-hexylthiophen-2-yl)thiophen-2-yl]-*N*,*N*-diphenylbenzenamine (**13**),^[53] were prepared according to literature procedures. All other chemical reagents were commercially available and were used without further purification unless otherwise noted. Reactions were monitored by TLC using aluminum plates precoated with a 0.25 mm layer of silica gel containing a fluorescent indicator.

8-Bromo-2,3-diphenylquinoxaline-5-carbaldehyde (8): Under a nitrogen atmosphere, a solution of 7 (1.0 g, 2.3 mmol) in THF (10 mL) was cooled to -78°C. After addition of 2.5 M n-butyllithium in hexane (1.0 mL, 2.3 mmol) the reaction was stirred at a low temperature for 30 min and slowly warmed to -10°C. The reaction mixture was cooled to -78°C again and treated with DMF (0.2 mL, 2.6 mmol). The resulting mixture was stirred for another 2 h followed by hydrolyzing with 1 M HCl. The mixture was extracted, dried over MgSO4, and purified by column chromatography (ethyl acetate/hexane 1:5). Compound 8 (0.4 g, 45%) was obtained as a colorless solid. M.p. 186-190 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.34-7.44$ (m, 6H), 7.61 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 6.0 Hz, 7.65 (d, J7.6 Hz, 2 H), 8.18 (s, 2 H), 11.38 ppm (s, 1 H); ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 128.6$, 129.4, 129.9, 130.0, 130.2, 130.4, 131.2, 132.0, 133.3, 138.2, 138.3, 138.6, 141.0, 154.4, 154.7, 191.0 ppm; HRMS (ESI): m/z calcd for C₂₁H₁₃BrN₂O: 389.0284 [M+H]+; found: 389.0283; elemental analysis calcd (%) for C₂₁H₁₄BrN₂O: C 64.80, H 3.37, N 7.20; found: C 64.81, H 3.35, N 7.24.

General procedure for the syntheses of 9, 17, and 18: Under a nitrogen atmosphere, a degassed mixture of THF (30 mL) and H₂O (20 mL) was added to a flask charged with the bromo-substituted compound (7, 8, or 17; 2.0 mmol), the aryl-substituted boronic acid (3.0 mmol), Na₂CO₃ (0.64 g, 6.0 mmol), and [PdCl₂(PPh₃)₂] (84 mg, 0.12 mmol), and the resulting mixture was stirred for 16 h at room temperature. The solution was extracted with ethyl acetate, dried over MgSO₄, and purified by column chromatography (ethyl acetate/*n*-hexane or dichloromethane/*n*-hexane) to obtain the desired product.

8-[4-(Diphenylamino)phenyl]-2,3-diphenylquinoxaline-5-carbaldehyde

(9): The crude product was purified by column chromatography (ethyl acetate/hexane 1:5) to yield pure compound **9** (1.07 g, 97%) as a red solid. M.p. 238–241 °C; ¹H NMR (400 MHz, CDCl₃): δ =7.07 (t, *J*=7.2 Hz, 2H), 7.18–7.20 (m, 6H), 7.27–7.31 (m, 6H), 7.33–7.41 (m, 4H), 7.56 (d, *J*=8.0 Hz, 2H), 7.65 (d, *J*=7.6 Hz, 2H), 7.77 (d, *J*=8.0 Hz, 2H), 7.94 (d, *J*=7.6 Hz, 1H), 8.38 (d, *J*=8.0 Hz, 1H), 11.44 ppm (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =122.2, 123.7, 125.3, 128.5, 128.6, 129.1, 129.3, 129.4, 129.6, 129.7, 130.0, 130.2, 130.3, 130.8, 132.1, 138.1, 138.9, 141.2, 146.3, 147.6, 148.7, 152.6, 153.2, 191.5 ppm; HRMS (ESI): *m/z* calcd for C₃₉H₂₇N₃O: C 84.61, H 4.92, N 7.59; found: C 84.73, H 5.21, N 7.20.

4-(8-Bromo-2,3-diphenylquinoxalin-5-yl)-*N*,*N***-diphenylaniline (17)**: The crude product was purified by column chromatography (ethyl acetate/ hexane 1:7) to yield compound **17** (0.46 g, 38%) as a red solid. M.p. 256–257°C; ¹H NMR (400 MHz, CDCl₃): δ =7.05 (t, *J*=7.6 Hz, 2H), 7.17–7.19 (m, 6H), 7.26–7.30 (m, 6H), 7.33–7.38 (m, 4H), 7.55 (d, *J*=7.6 Hz, 2H), 7.66–7.70 (m, 5H), 8.08 ppm (d, *J*=8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ =122.6, 122.8, 123.4, 125.0, 128.4, 128.5, 129.3,

Chem. Eur. J. **2012**, 00, 0–0

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129.5, 129.8, 130.3, 130.4, 131.3, 131.8, 133.2, 138.8, 138.9, 139.4, 139.9, 147.8, 147.9, 152.6, 153.0 ppm; elemental analysis calcd (%) for C38H26BrN3: C 75.50, H 4.33, N 6.95; found: C 75.36, H 4.23, N 6.81.

5-{8-[4-(Diphenylamino)phenyl]-2,3-diphenylquinoxalin-5-yl}thiophene-2carbaldehyde (18): Compound 18 was purified by column chromatography (dichloromethane/hexane 1:1) to yield a red solid (1.04 g, 82%). M.p. 251–252 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.06$ (t, J = 7.2 Hz, 2H), 7.19-7.21 (m, 6H), 7.27-7.34 (m, 8H), 7.40 (br, 3H), 7.59 (d, J= 7.2 Hz, 2H), 7.72–7.73 (m, 2H), 7.75 (t, J=8.4 Hz, 2H), 7.81 (d, J= 3.2 Hz, 1 H), 7.88 (d, J=7.6 Hz, 1 H), 7.93 (d, J=3.6 Hz, 1 H), 8.22 (d, J= 7.6 Hz, 1 H), 9.97 ppm (s, 1 H); 13 C NMR (100 MHz, CDCl₃): $\delta = 122.6$, 123.5, 125.1, 127.2, 128.4, 128.5, 128.6, 129.3, 129.6, 129.5, 129.9, 130.3, 130.6, 131.3, 131.9, 135.9, 137.7, 138.6, 138.8, 138.9, 140.7, 145.1, 147.8, 148.1, 148.9, 152.2, 152.2, 183.6 ppm; HRMS (MALDI): m/z calcd for C43H30N3OS: 636.2104 [M+H]+; found: 636.2164; elemental analysis calcd (%) for $C_{43}H_{29}N_3OS \cdot H_2O$: C 78.99, H 4.78, N 6.43; found: C 79.02, H 4.71. N 6.43.

(E) - 8 - [4 - (Diphenylamino) styryl] - 2, 3 - diphenylquinoxaline - 5 - carbaldehyde(10): Under a nitrogen atmosphere, degassed DMF (10 mL) was added to a 50 mL flask containing 8 (0.20 g, 0.51 mmol), N,N-diphenyl-4-vinylaniline (0.17 g, 0.63 mmol), Na2CO3 (0.11 g, 1.02 mmol), and Pd(OAc)2 (5 mg, 0.02 mmol). The mixture was stirred at 120 °C for 12 h. The mixture was extracted with ethyl acetate, dried over MgSO4, and purified by column chromatography (ethyl acetate/hexane 1:5). Compound 10 (0.28 g, 94 %) was obtained as a red solid. M.p. 241–242 °C; $^1\mathrm{H}\,\mathrm{NMR}$ (400 MHz, CDCl₃): $\delta = 7.04-7.08$ (m, 4H), 7.13 (d, J = 7.6 Hz, 4H), 7.25-7.29 (m, 4H), 7.33–7.40 (m, 6H), 7.52 (d, J=8.0 Hz, 2H), 7.55 (d, J= 16.0 Hz, 1 H), 7.61-7.63 (m, 4 H), 8.11 (d, J=7.6 Hz, 1 H), 8.33 (d, J= 7.6 Hz, 1H), 8.36 (d, J=16.4 Hz, 1H), 11.38 ppm (s, 1H); ¹³C NMR $(100 \text{ MHz}, \text{ CDCl}_3): \delta = 120.9, 123.0, 123.7, 124.1, 125.2, 128.5, 128.6,$ 129.3, 129.4, 129.5, 129.6, 130.2, 131.0, 133.8, 138.0, 138.9, 139.1, 141.2, 142.8, 147.5, 148.7, 152.4, 153.8, 191.3 ppm; HRMS (MALDI): m/z calcd for C₄₁H₃₀N₃O: 580.2384 [*M*+H]⁺; found: 580.2395; elemental analysis calcd (%) for $C_{41}H_{29}N_3O$ ·1.5 H_2O : C 81.17, H 5.32, N 6.93; found: C 81.53, H 5.12, N 6.87.

General procedure for the syntheses of 14, 15, and 16: Under a nitrogen atmosphere, a solution of a thiophene derivative (11, 12, and 13; 2.5 mmol) in THF (12 mL) was cooled to -78 °C. After addition of 2.5 M n-butyllithium in hexane (1 mL, 2.5 mmol), the reaction was stirred for 1 h at -78 °C and gently warmed to -10 °C. The solution was cooled to -78°C again and treated with B(OMe)₃ (0.85 mL, 7.5 mmol). This was then followed by gently warming to room temperature and the mixture was stirred for another 5 h and then quenched with water. The mixture was extracted with ethyl acetate, dried over MgSO4, and purified by flash column chromatography (ethyl acetate/hexane 1:1). The boronic acid derivatives thus obtained were not further purified and were instead used directly for the subsequent reactions. A degassed solution of THF (12 mL) and H₂O (8 mL) was added to a flask containing the boronic acid derivative (0.48 mmol), compound 8 (0.16 g, 0.40 mmol), Na₂CO₃ (0.13 g, 1.20 mmol), and [PdCl₂(PPh₃)₂] (14 mg, 0.02 mmol). The resulting mixture was stirred for 16 h at room temperature under a nitrogen atmosphere. The mixture was extracted with dichloromethane, dried over MgSO₄, and purified by column chromatography to yield the desired aldehydes (14, 15, and 16).

8-{5-[4-(Diphenylamino)phenyl]thiophen-2-yl}-2,3-diphenylquinoxaline-5carbaldehyde (14): Compound 14 was obtained as a red solid (0.19 g, 51%) after purification by column chromatography (ethyl acetate/hexane 1:4). M.p. 136–137 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.03-7.10$ (m, 4H), 7.12-7.14 (m, 4H), 7.26-7.30 (m, 4H), 7.31 (d, J=4.0 Hz, 1H), 7.35-7.42 (m, 6H), 7.55 (d, J=7.6 Hz, 2H), 7.65 (d, J=7.6 Hz, 2H), 7.73 (d, J=7.2 Hz, 2 H), 7.99 (d, J=4.0 Hz, 1 H), 8.23 (d, J=8.0 Hz, 1 H), 8.34(d, J = 8.0 Hz, 1 H), 11.38 ppm (s, 1 H); ¹³C NMR (100 MHz, CDCl₃): $\delta =$ 122.6, 123.6, 125.0, 125.5, 126.8, 128.3, 128.5, 128.6, 129.2, 129.4, 129.6, 129.7, 130.0, 130.2, 130.7, 136.4, 136.5, 138.6, 138.8, 138.9, 141.3, 147.6, 148.1, 149.9, 152.5, 153.7, 191.0 ppm; HRMS (MALDI): m/z calcd for $C_{43}H_{30}N_3OS:$ 636.2104 [*M*+H]⁺; found: 636.2117; elemental analysis calcd (%) for $C_{43}H_{29}N_3OS$: C 81.23, H 4.60, N 6.61; found: C 81.07, H 4.71, N 6.59.

8-{5-[4-(Diphenylamino)phenyl]-4-hexylthiophen-2-yl}-2,3-diphenylquinoxaline-5-carbaldehyde (15): Compound 15 was obtained as a red solid (0.20 g, 48%) after purification by column chromatography (ethyl acetate/hexane 1:4). M.p. 113–114 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 0.88$ (t, J=6.8 Hz, 3 H), 1.27-1.39 (m, 6 H), 1.68-1.74 (m, 2 H), 2.73 (t, J= 7.6 Hz, 2 H), 7.05 (t, J=7.6 Hz, 2 H), 7.11 (d, J=8.4 Hz, 2 H), 7.16 (d, J= 7.6 Hz, 4H), 7.28 (t, J = 7.6 Hz, 4H), 7.33–7.42 (m, 8H), 7.65 (d, J =8.0 Hz, 2 H), 7.72 (d, J=8.0 Hz, 2 H), 7.94 (s, 1 H), 8.20 (d, J=8.0 Hz, 1H), 8.34 (d, J=8.4, 1H), 11.38 ppm (s, 1H); ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 14.3, 22.8, 29.1, 29.5, 31.2, 31.9, 123.1, 123.5, 125.0, 125.6,$ 128.4, 128.5, 129.1, 129.3, 129.5, 129.6, 129.7, 129.9, 130.2, 130.7, 132.0, 135.3, 136.6, 138.6, 138.8, 138.9, 141.2, 144.1, 147.6, 147.7, 152.4, 153.5, 190.9 ppm; HRMS (MALDI): m/z calcd for $C_{49}H_{42}N_3OS$ [*M*+H]⁺: 720.3044; found: 720.3055; elemental analysis calcd (%) for C₄₉H₄₁N₃OS: C 81.75, H 5.74, N 5.84; found: C 81.45, H 5.82, N 5.77.

8-{5'-[4-(Diphenylamino)phenyl]-3,4'-di-n-hexyl[2,2']bithiophen-5-yl}-2,3diphenylquinoxaline-5-carbaldehyde (16): Compound 16 was obtained as a red solid (0.29 g, 63%) after purification by column chromatography (ethyl acetate/hexane 1:4). M.p. 145-146°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 0.89$ (t, J = 6.8 Hz, 6 H), 1.30–1.45 (m, 12 H), 1.64–1.76 (m, 4 H), 2.69 (t, J=7.6 Hz, 2 H), 2.85 (t, J=7.6 Hz, 2 H), 7.04 (t, J=7.6 Hz, 2 H), 7.09-7.15 (m, 7H), 7.27 (t, J=8.0 Hz, 4H), 7.33 (d, J=8.8 Hz, 2H), 7.36-7.42 (m, 6H), 7.66 (d, J=7.2 Hz, 2H), 7.75 (d, J=7.2 Hz, 2H), 7.85 (s, 1H), 8.17 (d, J = 7.6 Hz, 1H), 8.30 (d, J = 8.0 Hz, 1H), 11.35 ppm (s, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.3$, 14.4, 22.85, 22.86, 29.1, 29.5, 29.6, 29.7, 30.8, 31.2, 32.0, 123.2, 123.4, 124.9, 125.3, 128.2, 128.4, 128.6, 129.0, 129.3, 129.5, 129.6, 129.7, 130.0, 130.2, 130.8, 131.9, 133.9, 134.8, 136.5, 137.8, 138.5, 138.6, 138.7, 138.9, 139.1, 141.2, 147.4, 147.7, 152.4, 153.6, 190.9 ppm; HRMS (MALDI): m/z calcd for $C_{59}H_{56}N_3OS_2$: 886.3860 $[M+H]^+$; found: 886.3884; elemental analysis calcd (%) for C59H55N3OS20.5H2O: C 79.16, H 6.31, N 4.69; found: C 79.02, H 6.19, N 5.02.

General procedure for syntheses of dyes 1-6: Under a nitrogen atmosphere, the aldehyde (9, 10, 14, 15, 16, or 18; 0.3 mmol), cvanoacetic acid (0.08 g, 0.9 mmol), ammonium acetate (9 mg), and glacial acetic acid (5 mL) were mixed together and heated at reflux for 12 h. The red solution was then cooled to room temperature to yield dark-red precipitates, which were collected by filtration and thoroughly washed with cold acetic acid (2×10 mL), water (3×10 mL), and diethyl ether (2×10 mL). The collected solids were further purified by washing with the dichloromethane/hexane mixture and subsequent recrystallization from dichloromethane/ethanol to yield the pure product.

(E)-2-Cyano-3-{8-[4-(diphenylamino)phenyl]-2,3-diphenylquinoxalin-5-

yl}acrylic acid (1): A dark-red solid (160 mg, 84%). M.p. 251-252°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.08$ (t, J = 7.2 Hz, 2H), 7.19–7.21 (m, 6H), 7.28–7.32 (m, 7H), 7.35–7.42 (m, 3H), 7.56 (d, J=7.6 Hz, 2H), 7.66 (d, J=7.2 Hz, 2H), 7.80 (d, J=8.0 Hz, 2H), 7.97 (d, J=8.0 Hz, 1H), 8.99 (d, J = 7.6 Hz, 1 H), 9.93 ppm (s, 1 H); ¹³C NMR (100 MHz, [D₆]DMSO): $\delta\!=\!104.8,\,116.3,\,120.9,\,123.8,\,124.9,\,127.4,\,128.1,\,128.3,\,129.0,\,129.1,\,129.3$ 129.6, 129.7, 129.9, 132.0, 137.6, 138.3, 139.0, 143.5, 146.7, 147.8, 148.1, 152.2, 152.6, 163.2 ppm; HRMS (FAB): m/z calcd for $C_{42}H_{28}N_4O_2$: 620.2207; found: 620.2206; elemental analysis calcd (%) for $C_{42}H_{28}N_4O_2{\textbf{\cdot}}0.5\,H_2O\colon C$ 80.11, H 4.64, N 8.90; found: C 79.77, H 4.55, N 8.59.

(E)-2-Cyano-3-{8-[(E)-4-(diphenylamino)styryl]-2,3-diphenylquinoxalin-

5-yl}acrylic acid (2): A dark-red solid (160 mg, 82%). M.p. 236-238°C; ¹H NMR (400 MHz, $[D_6]$ DMSO): $\delta = 7.00$ (d, J = 8.4 Hz, 2H), 7.09 (d, J =8.0 Hz, 4 H), 7.11 (t, J=7.2 Hz, 2 H), 7.36 (t, J=8.0 Hz, 4 H), 7.40–7.45 (m, 6H), 7.55–7.64 (m, 6H), 7.86 (d, J=16.4 Hz, 1H), 8.28 (d, J=16.4 Hz, 1 H), 8.46 (d, J=8.0 Hz, 1 H), 8.80 (d, J=8.0 Hz, 1 H), 9.51 ppm (s, 1 H); ¹³C NMR (125 MHz, [D₆]DMSO): δ =104.1, 116.5, 120.0, 122.0, 123.8, 124.7, 126.9, 128.2, 128.5, 129.1, 129.3, 129.7, 129.8, 129.9, 130.3, 134.1, 137.4, 138.4, 139.0, 140.4, 146.6, 147.9, 148.0, 152.5, 153.0, 163.3 ppm; HRMS (MALDI): m/z calcd for $C_{44}H_{31}N_4O_2$ [M+H]⁺: 647.2241; found: 647.2458; elemental analysis calcd (%) for $C_{44}H_{30}N_4O_2$: C 81.71, H 4.68, N 8.66; found: C 81.52, H 4.70, N 8.64.

(E)-2-Cyano-3-(8-{5-[4-(diphenylamino)phenyl]thiophen-2-yl}-2,3-diphenylquinoxalin-5-yl)acrylic acid (3): A dark-red solid (170 mg, 80%). M.p.

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264–266 °C; ¹H NMR (400 MHz, [D₆]DMSO): δ =7.03 (d, *J*=8.4 Hz, 2 H), 7.09 (d, *J*=7.6 Hz, 4 H), 7.11 (t, *J*=7.6 Hz, 2 H), 7.35 (t, *J*=8.0 Hz, 4 H), 7.42–7.48 (m, 6 H), 7.56 (d, *J*=3.2 Hz, 1 H), 7.59 (d, *J*=7.6 Hz, 2 H), 7.64 (d, *J*=7.6 Hz, 2 H), 7.68–7.69 (m, 2 H), 8.21 (d, *J*=3.6 Hz, 1 H), 8.62 (d, *J*=8.0 Hz, 1 H), 8.80 (d, *J*=8.4 Hz, 1 H), 9.49 ppm (s, 1 H); ¹³C NMR (125 MHz, [D₆]DMSO): δ =104.1, 116.6, 122.7, 123.6, 124.5, 125.6, 126.3, 126.5, 127.3, 128.2, 128.3, 129.4, 129.6, 129.8, 130.2, 130.4, 135.0, 135.6, 136.1, 137.7, 138.2, 139.0, 146.7, 147.2, 147.3, 149.1, 152.3, 152.8, 163.3 ppm; HRMS (MALDI): *m/z* calcd for C₄₆H₃₁N₄O₂S: 703.2162 [*M*+H]⁺; found: 703.2178.

(E)-2-Cyano-3-(8-{5-[4-(diphenylamino)phenyl]-4-hexylthiophen-2-yl}-

2,3-diphenylquinoxalin-5-yl)acrylic acid (4): A dark-red solid (210 mg, 89%). M.p. 258–260 °C; ¹H NMR (500 MHz, [D₆]DMSO): δ =0.84 (t, *J*= 6.5 Hz, 3 H), 1.23–1.30 (m, 6 H), 1.59–1.65 (m, 2 H), 2.63 (t, *J*=7.5 Hz, 2 H), 7.00 (d, *J*=8.5 Hz, 2 H), 7.05 (d, *J*=8.5 Hz, 4 H), 7.10 (t, *J*=7.0 Hz, 2 H), 7.33 (t, *J*=8.5 Hz, 4 H), 7.32–7.37 (m, 4 H), 7.39–7.42 (m, 3 H), 7.45 (t, *J*=7.0 Hz, 1 H), 7.54 (d, *J*=8.0 Hz, 2 H), 7.59 (d, *J*=8.0 Hz, 2 H), 8.06 (s, 1 H), 8.44 (d, *J*=8.5 Hz, 1 H), 8.72 (d, *J*=8.5 Hz, 1 H), 9.44 ppm (s, 1 H); the ¹³C NMR spectrum was not acquired due to the low solubility in CDCl₃ and [D₆]DMSO; HRMS (MALDI): *m/z* calcd for C₅₂H₄₃N₄O₂S [*M*+H]⁺: 787.3101; found: 787.3111; elemental analysis calcd (%) for C₅₂H₄₂N₄O₂S-0.5 H₂O: C 78.46, H 5.44, N 7.04; found: C 78.13, H 5.28, N 7.37.

(E)-2-Cyano-3-(8-{5'-[4-(diphenylamino)phenyl]-3,4'-di-n-hexyl[2,2']bi-

thiophen-5-yl}-2,3-diphenylquinoxalin-5-yl}acrylic acid (5): A dark-red solid (240 mg, 82%). M.p. 246–247°C; ¹H NMR (400 MHz, CDCl₃): δ = 0.89 (t, *J*=6.8 Hz, 6H), 1.30–1.45 (m, 12H), 1.60–1.77 (m, 4H), 2.69 (t, *J*=7.6 Hz, 2H), 2.87 (t, *J*=7.6 Hz, 2H), 7.04 (t, *J*=7.2 Hz, 2H), 7.10 (d, *J*=8.4 Hz, 2H), 7.14 (d, *J*=7.2 Hz, 4H), 7.28 (t, *J*=7.6 Hz, 4H), 7.33 (d, *J*=8.8 Hz, 2H), 7.38–7.44 (m, 6H), 7.67 (d, *J*=7.2 Hz, 2H), 7.76 (d, *J*= 6.0 Hz, 2H), 7.89 (s, 1H), 8.24 (d, *J*=8.4 Hz, 1H), 8.97 (d, *J*=8.8 Hz, 2H), 9.86 ppm (s, 1H); the ¹³C NMR spectrum was not acquired due to the low solubility in CDCl₃ and [D₆]DMSO; HRMS (FAB): *m/z* calcd for C₆₂H₅₆N₄O₂S₂: 952.3840 [*M*]⁺; found: 952.3844.

(E)-2-Cyano-3-(5-{8-[4-(diphenylamino)phenyl]-2,3-diphenylquinoxalin-

5-yl}thiophen-2-yl}acrylic acid (6): A dark-red solid (180 mg, 85%). M.p. 277–284°C; ¹H NMR (500 MHz, $[D_6]DMSO$): δ =7.04 (d, J=8.5 Hz, 2H), 7.06–7.10 (m, 6H), 7.29–7.35 (m, 7H), 7.38–7.39 (m, 3H), 7.49 (d, J=7.5 Hz, 2H), 7.72–7.74 (m, 5H; ArH), 7.84 (d, J=7.5 Hz, 1H), 8.20 (s, 1H), 8.35 ppm (d, J=8.0 Hz, 1H); ¹³C NMR (125 MHz, $[D_6]DMSO$): δ =119.0, 127.1, 127.9, 128.1, 128.4, 129.0, 129.2, 129.4, 129.6, 129.7, 130.2, 130.8, 131.7, 134.4, 136.2, 137.5, 137.8, 138.5, 138.6, 139.8, 141.2, 143.1, 146.9, 147.1, 151.2, 151.6, 163.6 ppm; HRMS (MALDI): m/z calcd for C₄₆H₃₁N₄O₂S: 703.2162 [M+H]⁺; found: 703.2181; elemental analysis calcd (%) for C₄₆H₃₀N₄O₂S: C 78.61, H 4.30, N 7.97; found: C 78.46, H 4.27, N 7.89.

Analytical instruments and measurements: Absorption and emission spectra were recorded according to previously published procedures.^[68] Cyclic voltammetry experiments were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum working electrode, a platinum wire auxiliary electrode, and a non-aqueous Ag/AgNO₃ reference electrode.^[69] The potentials were quoted against the ferrocene/ferrocenium internal standard and converted to NHE by addition of 0.63 V. The solvent contained 1.0 mM of the dye and 0.1 m tetrabutylammonium hexafluorophosphate as the supporting electrolyte in all experiments. The geometry and electronic properties of the dyes were calculated with the Gaussian program package.^[55] All calculations were performed by using DFT with the B3LYP/6-31G* basis set.

For the TiO₂ colloid solution, the TiO₂ precursor was prepared by the sol-gel method as in the following processes. Ti^{IV} tetraisopropoxide (72 mL, TTIP, Aldrich, >98%) was added to a 0.1 m nitric acid (430 mL, 70%, J. T. Baker) aqueous solution with constant stirring and heated to 85 °C simultaneously for 8 h. When the mixture was cooled to room temperature, the resultant colloid was transferred to an autoclave (PARR 4540, USA), and then heated at 240 °C for 12 h to allow the TiO₂ particles to grow uniformly (ca. 20 nm). Consequently, the TiO₂ colloid was concentrated to 8 wt% (with respect to the TiO₂). The first type of TiO₂ paste (transparent layer) was prepared by the addition 25 wt% (with re-

FULL PAPER

spect to the TiO₂) of PEG to the above solution to control the pore diameters and to prevent the film from cracking during drying. For the second type of TiO₂ paste (scattering layer), the first type of TiO₂ paste was incorporated with 50 wt % of light scattering TiO₂ particles (PT-501A, 15 m²g⁻¹, 100 nm, 99.74%, Ya Chung Industrial, Taiwan; with respect to the 20 nm TiO₂) for reducing the light loss by back scattering. A fluorine-doped SnO₂ conducting glass (FTO, $7 \Omega sq^{-1}$, visible transmittance $\geq 80\%$, NSG America, USA) was first cleaned with a neutral cleaner, and then washed with deionized water, acetone, and isopropyl alcohol (IPA), sequentially. The conducting surface of the FTO was treated with a solution of TTIP (1 g) in 2-methoxyethanol (3 g, 99.5%, Sigma-Aldrich) for obtaining a good mechanical contact between the conducting glass and TiO₂ film, and to isolate the conducting glass surface from the electrolyte. TiO2 pastes were coated onto the treated conducting glass by using the doctor blade technique. For each coating TiO₂ layer, the dried TiO2 film was gradually heated to 500 °C in an oxygen atmosphere, and subsequently sintered at that temperature for 30 min. Before the next coating, the sintered TiO2 film was treated with UV/Ozone for 15 min. The TiO₂ photoanodes of the DSSCs employed in the experiments were composed of a 12 µm thick transparent TiO₂ layer and with a scattering layer of 4 µm thickness. The prepared TiO2 photoanode was treated with UV/Ozone for 30 min and heated to 80°C, and then it was immersed in a 5×10^{-4} M N719 dye solution at room temperature for 24 h. N719 (Solaronix S.A., Switzerland) was dissolved in acetonitrile (ACN, 99.99%, Aldrich) and tert-butyl alcohol (tBA, 96%, Acros; volume ratio of 1:1) as a standard dye solution. Various organic dye solutions were prepared in dichloromethane (>99.8%, Sigma-Aldrich). The TiO₂/dye electrode thus prepared was placed on a platinum-sputtered conducting glass electrode (FTO), keeping the two electrodes separated by a 25 µmthick surlyn (SX1170-25, Solaronix S.A., Switzerland). The two electrodes were then sealed by heating. A mixture of 0.1 M lithium iodide (LiI, synthetic grade, Merck), 0.6 M DMPII (Solaronix S.A., Switzerland), 0.05 m iodine (I2, synthetic grade, Merck), and 0.5 m 4-tert-butylpyridine (TBP, 96%, Acros) in 3-methoxypropionitrile (MPN, Fluka)/ACN (volume ratio of 1:1) was used as the electrolyte. The electrolyte was injected into the gap between the electrodes by capillarity. The surface of the DSSC was covered by a mask with a light-illuminated area of 0.16 cm² and then illuminated by a class-A quality solar simulator (XES-301S, AM 1.5G, SAN-EI ELECTRIC). Incident light intensity (100 mW cm $^{-2}$) was calibrated with the reference solar cell and meter (Oriel Instrument, model 91105).

Photocurrent-density-voltage curves of the DSSCs were obtained with a potentiostat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, the Netherlands). Electrochemical impedance spectra (EIS) were obtained by the aforementioned potentiostat/galvanostat, equipped with an FRA2 module, under a constant light illumination of 100 mW cm⁻². The frequency range explored was 10 mHz to 65 kHz. The applied bias voltage was set at the open-circuit voltage of the DSSC, between the counter electrode and the FTO-TiO2-dye working electrode by starting from the short-circuit conditions; the corresponding ac amplitude was 10 mV. The impedance spectra were analyzed by using an equivalent circuit model. Incident photo-to-current conversion efficiency (IPCE) curves were obtained at short-circuit conditions. The light source was a class A quality solar simulator (PEC-L11, AM1.5G, Peccell Technologies, Inc.); light was focused through a monochromator (Oriel Instrument, model 74100) onto the photovoltaic cell. The monochromator was incremented through the visible spectrum to generate the IPCE (λ) as defined in Equation (1) in which λ is the wavelength, J_{SC} is the short-circuit photocurrent (mA cm⁻²) recorded with a potentiostat/galvanostat, and ϕ is the incident radiative flux (W m⁻²) measured with an optical detector (Oriel Instrument, model 71580) and power meter (Oriel Instrument, model 70310).

IPCE
$$(\lambda) = 1240 \ (J_{\rm SC}/\lambda\phi)$$
 (1)

Photovoltage transients of the assembled devices were recorded with a digital oscilloscope (model LT322, LeCroy, USA). Pulsed laser excitation was applied by a frequency-doubled Q-switched Nd:YAG laser (model Quanta-Ray GCR-3-10, Spectra-Physics laser) with a 2 Hz repetition rate at 532 nm, and a 7 ns pulse width at half-height. The average electron

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lifetime (τ_{ac}) was determined by a laser-induced photovoltage transient technique. The transients were measured under a continuous bias illumination of approximately 60 mW cm⁻² (white light) and a low voltage pulse.^[64] The average electron lifetime could approximately be estimated by fitting a decay of the open-circuit voltage transient with $\exp(-t\tau_{ac}^{-1})$, in which *t* is the time and τ_{ac} is an average time constant before recombination.

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Solar Cells -

S.-R. Li, C.-P. Lee, H.-T. Kuo, K.-C. Ho,* S.-S. Sun*...... **IIII**-**IIII**

High-Performance Dipolar Organic Dyes with an Electron-Deficient Diphenylquinoxaline Moiety in the π-Conjugation Framework for Dye-Sensitized Solar Cells

Donor–acceptor systems: Six organic dyes comprised of a triphenylamine group as an electron donor, a cyanoacrylic acid as an electron acceptor, and an electron-deficient diphenylquinoxaline moiety integrated into the π -conjugated spacer between the electron

1000

donor and acceptor were synthesized (see figure). Dye-sensitized solar cells (DSSCs) based on one of the dyes produced an overall cell performance of 7.35%, which translates to about 79% of the intrinsic efficiency of the DSSC based on standard N719.

п -conjugated spacer