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PERYLENE-BASED, *BIS*(TERPYRIDINE)-Ru(II) COMPLEXES: SYNTHESIS, ELECTROCHEMICAL AND PHOTOVOLTAIC PROPERTIES

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Abstract – Perylene-based, terpyridine-Ru(II) complexes are synthesized and their electrochemical and photoelectrochemical properties are studied; their fabrication into dye-sensitized solar cells are described (DSSCs) and their resultant photovoltaic properties are evaluated.

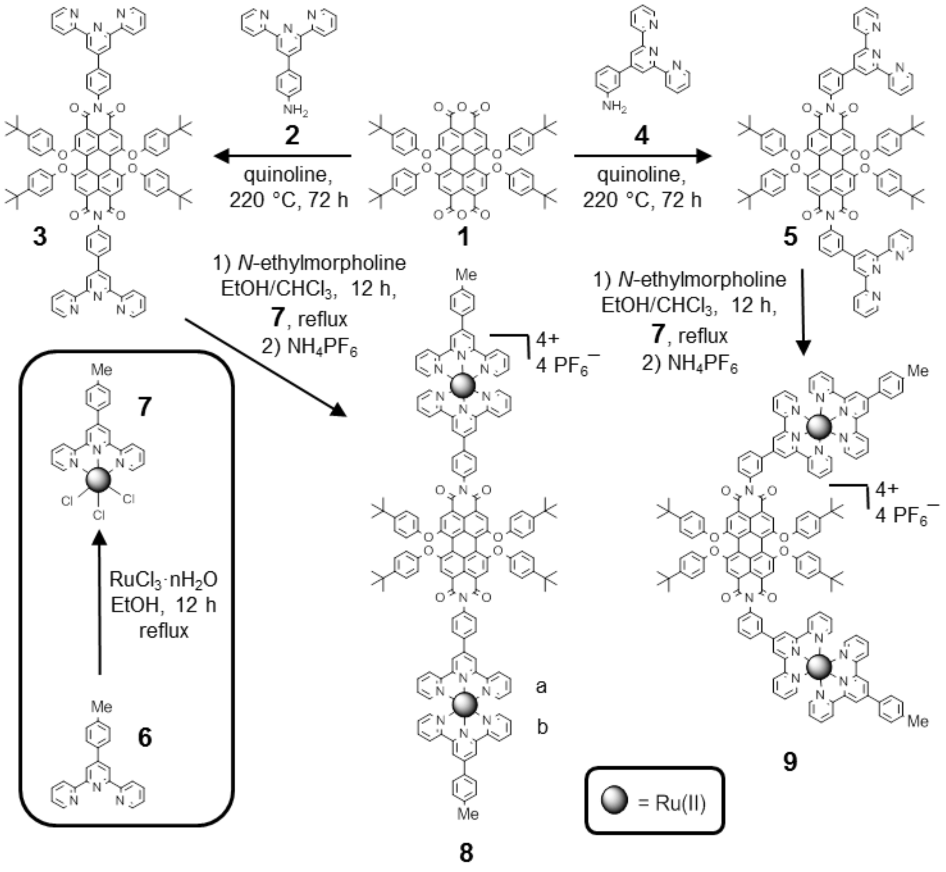
INTRODUCTION

Perylenediimides (PDIs) have been widely studied due to their stability and attractive electronic properties.[1-7] Elegant work by Würthner *et al*.[8,9] has resulted in the construction of numerous functional supramolecular architectures using ionic, *H*-bonding, π-π, and metal-ligand directed self-assembly.[10,11] Terpyridine-metal-terpyridine [<tpy-M^{2+}-tpy>, where tpy = 2,2':6',2"-terpyridine] connectivity[12,13] is an attractive approach to building functional materials due to the rich coordination chemistry and their incorporation of redox, photophysical, and electrochemical properties into the resulting supramolecules. As a result, terpyridine coordination has permitted the exploration of diverse materials used in construction of solar devices.[14,15] Their incorporation into a dendritic shell has given rise to unimolecular micelles[16-20] and bolaamphiphiles.[9,21] This, along with the unique properties of perylene provided the inspiration to synthesize perylene-containing tpy ligands[7] and their Ru^{II} complexes. Herein, we report the synthesis of heteroleptic, *bis*(terpyridinyl)perylene Ru^{II} complexes and their use in the fabrication of dye-sensitized solar cell (DSSC) devices.

RESULTS AND DISCUSSION

Synthesis began with the construction of aminoterpyridines **2** and **4**,[22] which were obtained from the reduction of the corresponding known nitroterpyridines[23] using Pd/C and hydrazine hydrate. The reaction of perylenetetracarboxylic acid dianhydride (**1**) with **2** gave (51%) the linear *bis*(terpyridine)perylene ligand[24] **3** (Scheme 1), which was confirmed with ^{1}H NMR by absorptions at 8.79 (3',5'-tpy*H*), 8.74 (6,6"-tpy*H*), 8.30 (per*H*), and 1.27 ppm [$C(CH_3)_3$] as well as with electrospray ionization mass spectrometry (ESI-MS) by a peak at *m/z* 1597.38 (calcd. $[M+H]^+$ = 1597.64). The isomeric **5**[25] was similarly synthesized (60%) and exhibited ^{1}H NMR peaks at 8.76 (3',5'-tpy*H*), 8.70 (6,6"-tpy*H*), 8.30 (per*H*), and 1.27 ppm [$C(CH_3)_3$] as well as ESI-MS peaks at *m/z* 1596.71 (calcd. $[M]^+$ = 1596.64).

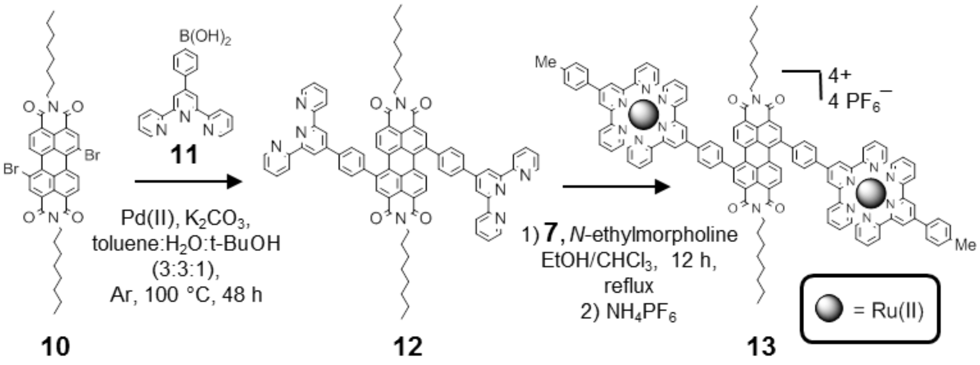
The known Ru^{III} adduct **7**[24] was obtained (88%) from terpyridine **6** by reaction with $RuCl_3 \cdot nH_2O$ (Scheme 1). Complexes **8** and **9** were subsequently generated from adduct **7** (2.2 eq.) by treatment with *bis*terpyridine ligands **3** and **5**, respectively, in a MeOH:$CHCl_3$ mixture and *N*-ethylmorpholine, as a reducing agent. After counter ion exchange to give the PF_6^- salt, the desired complexes were isolated (78%), as dark red solids.



Scheme 1

The ^{1}H NMR spectrum for *bis*-complex **8** revealed a pair of singlets at 9.53 (3',5'-tpy*H*^{a}) and 9.45 (3',5'-tpy*H*^{b}) ppm [where, "a = inner" tpy*H*s and "b = outer" tpy*H*s; Scheme 1] that, as expected, were shifted downfield ($\Delta\delta$ = +0.65 Hz) in comparison to that of the free ligands **3** and **6**. It also revealed a multiplet at 9.14 (3,3"-tpyH^{a} and 3,3"-tpyH^{b}) ppm, a peak at 7.80 (6,6"-tpyH^{a} and 6,6"-tpyH^{b}) ppm, with a significant upfield shift resulting from the ring current shielding effect upon complexation, as well as two singlets with an integration ratio of 1:6 at 2.90 (Ph-CH_3) and 1.66 [C(CH_3)$_3$] ppm. In the case of the isomeric **9**, the ^{1}H NMR spectrum showed three singlets with an integration ratio of 1:1 at 9.04 (3',5'-tpyH^{a}), 9.02 (3',5'-tpyH^{b}), and 8.18 (per*H*) ppm along with two doublets at 8.66 (3,3"-tpyH^{a}) and 8.63 (3,3"-tpyH^{b}) ppm. The spectrum also revealed a multiplet at 7.41 (6,6"-tpyH^{a} and 6,6"-tpyH^{b}) ppm, in addition to two singlets at 2.57 (Ph-CH_3) and 1.32 [C(CH_3)$_3$] ppm, with an integration ratio of 1:6, respectively. The structure was further confirmed by MALDI-TOF-MS peaks at *m/z* 2881.01 [M-PF$_6^-$]$^{1+}$ (Calcd. *m/z* = 2881.2) for **9**.

In contrast, complex **13** was synthesized *via* a Suzuki coupling of dibromide **10** (Scheme 2) with 4'-terpyridinylphenylboronic acid (**11**) in a solvent mixture of toluene:H$_2$O:*t*-BuOH (3:3:1) at 100 °C for 3 days. The solvent was evaporated *in vacuo* and the residue was column chromatographed (Al$_2$O$_3$) eluting with CHCl$_3$ and then recrystallized (5x) CHCl$_3$:MeOH (1:1 v/v) to eliminate the isomeric 1,6-*bis*(terpyridine)-substituted perylene to afford (55 %) the pure 1,7-*bis*(terpyridine)perylene ligand **12**, as a red solid. The ^{1}H NMR spectrum of **12** showed the following resonances: 8.88 (3',5'-tpy*H*), 8.79 (6,6"-tpy*H*), 8.74 (3,3"-tpy*H*), and 8.69 ppm (per*H*), in addition to the ESI-MS peak at *m/z* 1229.64 [M+H]$^+$ (Calcd. *m/z* = 1229.54). Finally, *bis*terpyridine **12** was reacted with **7** in refluxing EtOH/CHCl$_3$ (2:1) solution with a catalytic amount of *N*-ethylmorpholine for 12 h, followed by counter ion exchange (NO$_3^-$ to PF$_6^-$) to afford (78%) **13**, as a dark red solid. The ^{1}H NMR of *bis*-complex **13** exhibited three singlets at 9.35 (3',5'-tpyH^{a}) and 9.18 (3',5'-tpyH^{b}), and 8.69 (per*H*) ppm, two doublets at 8.91 (3,3"-tpyH^{a}) and 8.83 (3,3"-tpyH^{b}) ppm, and a multiplet at 7.54 (6,6"-tpyH^{a} and 6,6"-tpyH^{b}) ppm. A singlet at 2.54 ppm was assigned to the Ph-CH_3 moieties. ESI-MS further confirmed **13** with peaks at *m/z* 519.70 [M-4PF$_6^-$]$^{4+}$ (Calcd. *m/z* = 519.65), 741.28 [M-3PF$_6^-$]$^{3+}$ (Calcd. 741.19). Finally, complex **14** (Figure 1) was synthesized according to the literature procedure.



Scheme 2

ELECTROCHEMISTRY

The CV responses of complexes **8** and **9** (Figure 2A and 2B, respectively) each show two reversible waves between -2.2 and -1.4 V associated with one-electron consecutive reductions for the two pairs of inner and outer tpy moieties.[26] Two additional reversible waves were also observed between -1.3 and -0.6 V that are associated with two-electron consecutive reduction processes for perylene.[27] Similarly, CV responses for **14** and **13** (Figures 2C and 2D, respectively) show irreversible waves for the consecutive reduction events previously described for the tpy moieties (from -2.2 to -1.4 V) and perylene (from -1.3 to -0.6 V).

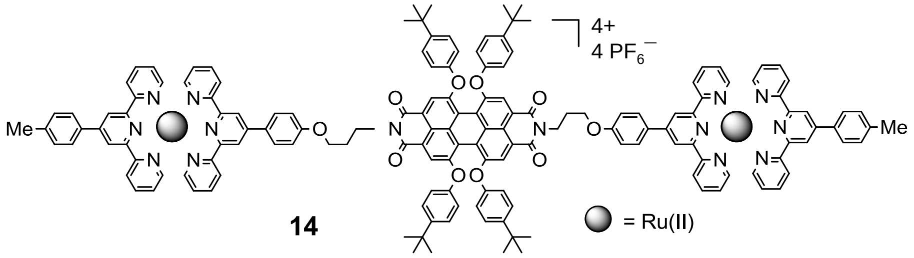


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Figure 1

Comparison of the cathodic behavior for the isomers **8** and **9** to that of **13** and **14** (Figures 2A and 2B *vs* 2C and 2D) strongly suggests that the reversible electrochemical responses for tpy and perylene moieties are observed only if the π-orbitals of these two types of groups are able to communicate electronically through the *peri*-positions on the perylene units.[27] Inspection of the oxidation processes (Figures 2A and 2B) reveals consecutive one-electron oxidations for the perylene and phenoxy moieties between 0 and +0.50 V and a one-electron oxidation for the <tpyRu^{II}tpy> moieties between +0.50 and +0.75 V, respectively.[25]

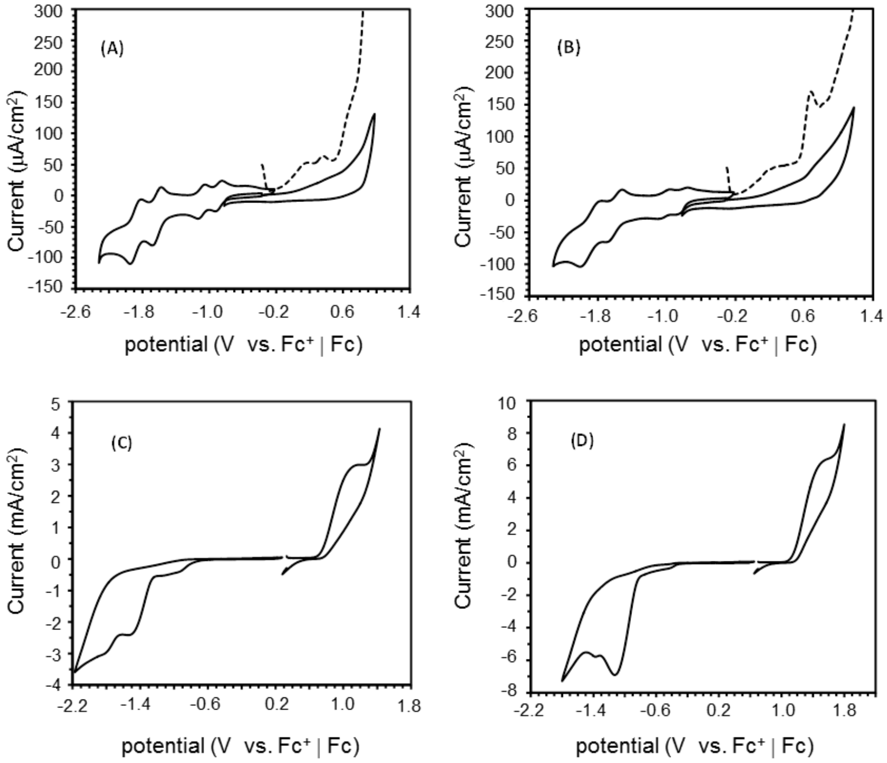

Figure 2. CV responses for **8** (A), **9** (B), **14** (C), and **13** (D) using a glassy carbon electrode at 25°C (dE/dt = 25 mVs^{-1}). Dashed lines in (A) and (B) are the differential pulse voltammetry (DPV) responses for the oxidative scans of **8** and **9**, respectively.

Thus, the low intensities observed for these two types of oxidation could be associated with very short life-times for the perylene radical anions due to favorable *e*-transfer to Ru^{III}tpy units. In contrast, a comparison between Figures 2C and 2D show irreversible overlapped signals between +0.6 and +1.4 V, possibly due to the consecutive oxidation reactions previously described for perylene and <tpyRu^{II}tpy>.

PHOTOELECTROCHEMISTRY

As predicted by their electrochemical responses, a comparison between Figures 3A and 3B, indicates that the output power obtained from DSSC assembled with **14** or **13** are higher than for **8** or **9**. This behaviour is reflected by the photovoltaic parameters compiled in Table 1; whereas, the global photovoltaic efficiencies (η) follow the same tendencies. Despite the well-known photophysical and electrochemical properties of both <tpyRu^{II}tpy> and perylene, the observed low efficiencies of the DSSC can be attributed to the presence of the two strong electron-withdrawing imide groups leading to a non-directional transfer[7] of the generated photoelectrons. As well, for all of the dyes studied, there is an absence of anchoring groups (*i.e.*, CO_2H) that are known to promote an efficient injection of photo-generated electrons into TiO_2 photoanodes.[29]

Photo-stability for the sensitizers was studied by means of open-circuit-potential transients (*ocp vs*. time plots) obtained for all the DSSC upon repetitive illumination-dark (ON-OFF) cycles. Figures 4-*i* and 4-*ii* show the *ocp* transients obtained for **8** and **9** (Figures 4-*i*A and 4-*i*B) and for **14** and **13** (Figures 4-*ii*A and 4-*ii*B), respectively.

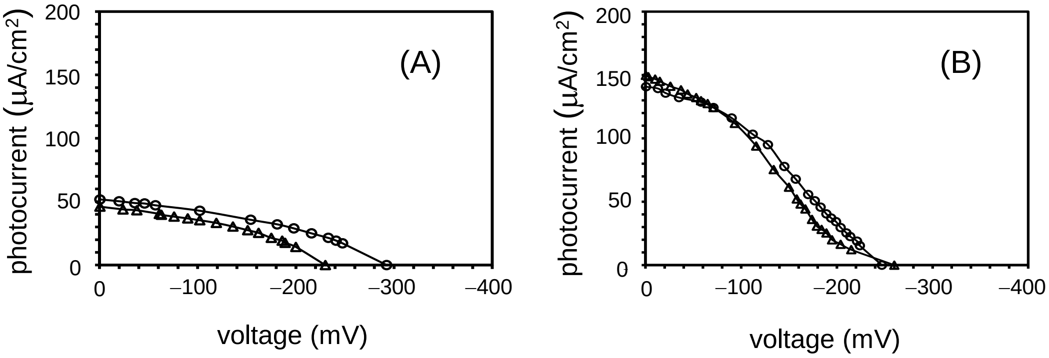

Figure 3. Discharge curves obtained using DSSCs containing the dyes couples (A): **8** (-o-) and **9** (-Δ-); and (B): **14** (-o-) and **13** (-Δ-) as sensitizers

These results indicate that the *ocp* for the DSSC containing **8** (Figure 4-*i*A) or **14** (Figure 4-*ii*A) is constant under illumination, as function of time; however, the *ocp* for photocells sensitized by **9** (Figure 4-*i*B) and **13** (Figure 4-*ii*B) is rapidly deactivated under the same condition. These last results indicate that the oxidized states for the dyes **9** and **13** are not efficiently reduced by I^- ions contained in the cell electrolyte.

Table 1. Performance data obtained for DSSC having **8**, **9**, **13** or **14**-dyed TiO_2 electrodes

Photoanode	$-E_{OC}$(V)	$j_{sc}/\mu A\ cm^{-2}$	^{a}ff	$^{b}\eta$ (%)
TiO_2/8	0.29	51.78	0.38	0.08
TiO_2/9	0.23	46.07	0.39	0.05
TiO_2/13	0.26	149.64	0.28	0.14
TiO_2/14	0.24	140.71	0.36	0.16
TiO_2(bare)	0.03	1.07	0.21	3.5×10^{-4}

[a] Fill-factor was calculated using $ff = P_{max}/|E_{oc}\times j_{sc}|$, where P_{max} is the maximum output power cell and j_{sc} is the short-circuit photocurrent.[26] [b] Global photovoltaic conversion was calculated using η (%) = $[P_{max}/(0.82\times P_0)]\times100$, where P_0 is the power of the incident photon flux (9.21 mW/cm^2)[26] and the constant 0.82 represents the effective transmittance when the photon flux passes through the OTE.

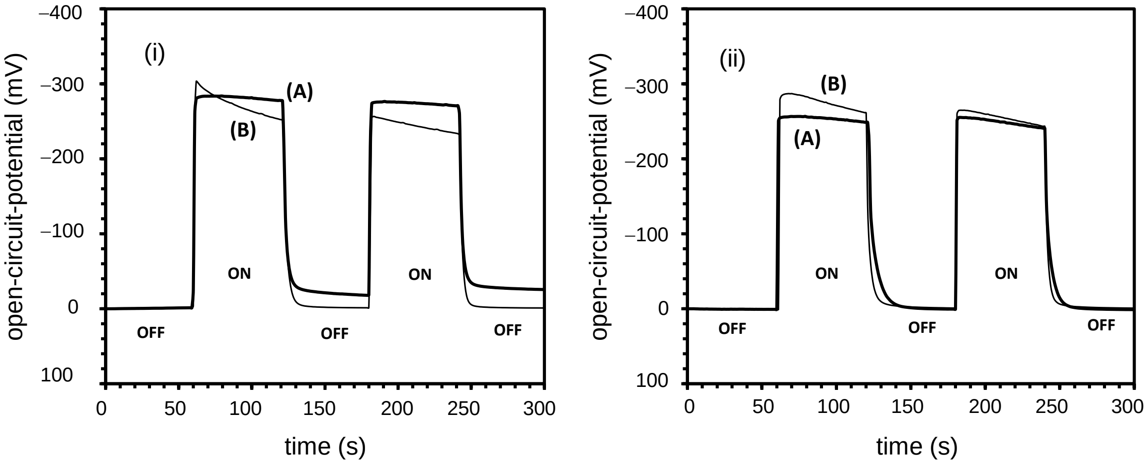

Figure 4. Open-circuit-potential (*ocp*) transients obtained for DSSC containing the dyes (i): **8** (A) and **9** (B) or (ii): **14** (A) and **13** (B), as sensitizers

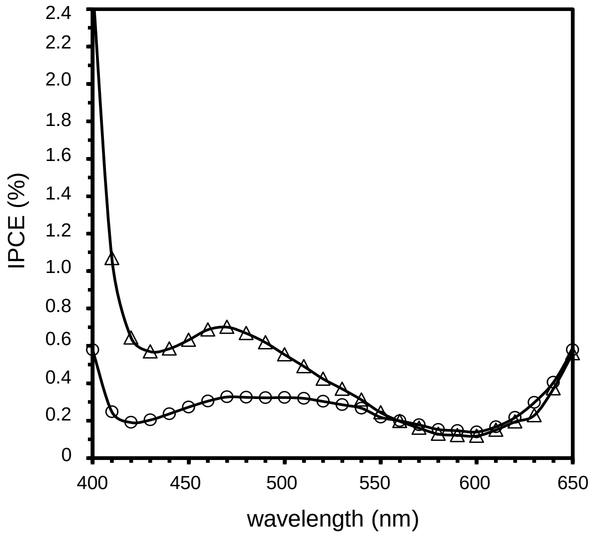

Figure 5. Steady-state photocurrent spectra obtained from the DSSC containing **8** (-o-) and **14** (-Δ-), as sensitizers

To support the results shown in Figures 4-*i*A and 4-*ii*A, steady-state-photocurrent spectra (IPCE *vs*. wavelength plots, Figure 5) were obtained and compared for the DSSCs containing the dyes. The photocurrents subsequently obtained from photocells constructed with **8** and **14** predominately resulted from injection by perylene at 470, 500, and 550 nm, respectively.[30] Finally, the spectra shown in Figure 5 demonstrates that <tpyRu^{II}tpy> units contained in **8** and **14** have no direct contribution to the photocurrent generation, thereby suggesting that only perylene groups can establish a successful electronic connection with Ti bonding orbitals in the TiO_2 photoanodes.

In summary, dyes **8**, **9**, **13**, and **14** were synthesized, their structures were confirmed using ^{1}H and ^{13}C NMR, COSY, and ESI-MS. As well, their electrochemical, photoelectrochemical, and photovoltaic properties were studied. These complexes were successfully implemented in the assembly of DSSCs for which global conversion efficiencies were obtained. Photovoltaic results demonstrated that the perylene moieties of these dyes were responsible for the photoactivated electron injection into the TiO_2 collectors. As well, the <tpyRu^{II}tpy> complexes were simultaneously deactivated by the presence of the perylene radical cations newly formed by photoactivation, thus inhibiting charge injection into the TiO_2.

EXPERIMENTAL

Starting materials were commercially purchased and used without further purification. Thin layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) percolated with Al_2O_3 (IB-F) or SiO_2 (IB2-F) and visualized by UV light. Column chromatography was conducted using basic Al_2O_3, Brockman Activity I (60-325 mesh) or SiO_2 (60-200 mesh) from Fisher Scientific. Melting points were determined on an Electrothermal 9100 heater. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Mercury 300 or a Varian NMRS 500 spectrometer. Mass spectra were obtained on a Synapt HDMS quadrupole/time-of flight (Q/TOF) mass spectrometer (Waters Corp., Milford, MA); the sprayed solution was prepared by dissolving 1 mg of sample in 1 mL of a MeCN/MeOH (1:1) solvent mixture.

Preparation of the 8-, 9-, 13-, and 14-Sensitized Solar Cells. Nanoparticulate TiO_2 electrodes (523-roughness factor, η, and 5 μm thick, d, estimated according to measurements of the electroactive area, A_e, and perfilometry, respectively) were obtained by electrophoretic deposition of TiO_2 nanoparticles (P25 Degussa, 21 nm diameter), as previously reported. Cathodes were obtained, as follows: 8 μL/cm^2 of a 10 mM $H_2PtCl_6 \cdot 6H_2O$ (Strem Chemicals, 99.9%-Pt) solution in Me_2CHOH (J.T. Baker, 99.97%) was homogeneously spread on the surface of optically transparent electrodes (OTE) based on indium-doped tin oxide (TEC15, Hartford Glass Co., USA). The cathodes were subsequently dried at 25 °C and finally annealed in air at 380 °C for 30 min. TiO_2 electrodes were dyed by immersion in 0.40 mM solutions of (a) **8** and **9** both in MeOH (J. T. Baker, HPLC grade), (b) **14** in MeOH/$CHCl_3$ (3:1) or (c) **13** in MeOH/$CHCl_3$ (5:1), at 25 °C for 6 days. DSSCs were assembled in a sandwich arrangement using a 160 μm-thick o-ring (6 mm i.d.), home-made from a commercial transparency sheet

(CG3700 *3M*, typically used as projecting transparencies) in order to avoid premature short circuit. A solution of 0.3 M LiI (Aldrich, 99.9%) + 0.015 M I_2 (J.T. Baker, ACS reagent) in propylene carbonate (Aldrich, 99.7%) was employed as the electrolytic medium in the photovoltaic cells. An effective geometric area of 0.28 cm^2 was illuminated for all the photoelectrochemical experiments.

Electrochemistry. Cyclic voltammetry (CV) experiments were performed at 25 °C and 25 mV/s by means of a BAS Epsilon potentiostat-galvanostat. A glassy carbon working-disc-electrode (1.5 mm-diameter) was immersed in a typical three-electrode cell containing DMF (99.8 %, J.T. Baker) + 0.1M Bu_4NPF_6 (Fluka, 98%) for testing complexes **8** and **9**. Electrolytic mixtures of MeOH/$CHCl_3$ (5:1) + 0.1M Bu_4NPF_6 and MeOH/$CHCl_3$ (3:1) + 0.1M Bu_4NPF_6 were used for obtaining the CV responses for samples **13** and **14**, respectively. Experimental setup was completed when silver and platinum wires were inserted in the electrochemical cell as pseudo- and counter-electrodes, respectively. All solutions were purged with ultra-pure nitrogen (Praxair, 99.999%) for 15 min. prior to conducting the experiments. Potentials were referenced to the ferrocinium/ferrocene redox scale (denoted as Fc^+ | Fc). PDIs are stable, electron-deficient molecules, which are difficult to oxidize and easy to reduce. Scheme SI-A shows the one electron-reversible oxidation (as revealed by CV) and Scheme S1-B shows the reduction process reported for PDI.[31]

Photoelectrochemistry. Discharge curves were obtained for the DSSCs utilizing a variable resistance of 52 kΩ upon polychromatic illumination emitted by a MR16 50W 12V lamp (GE) equipped with an EXN dichroic reflector to diffuse the light. Power of the light source was 9.21 mW/cm^2 (*ca*. 0.1 Sun). Steady-state photocurrent spectra were obtained upon monochromatic illumination (400 - 650 nm) using a 6257 100W Xe lamp coupled to a 77250 monochromator, both purchased from Thermo-Oriel and calibrated by means of a 17043 Eppley Thermopile. Incident-photon-to-current efficiencies (IPCE) were estimated according to Eq. 1, where λ, $j_{ph,\lambda}$ and $I_{0,\lambda}$ denote incident photon wavelength (in nm) photocurrent density (in μA/cm^2), and incident photon flux (in W/cm^2), respectively. The constant 0.82 corresponds to the effective transmittance of the incident photon flux through the OTE. All these experiments were conducted on an IM6 BAS-Zahner potentiostat-galvanostat in order to measure open-circuit-potentials or steady-state-photocurrents.

(Equation 1) $$IPCE(\lambda)=\frac{(1240\,eV\cdot nm)j_{ph,\lambda}}{0.82\lambda I_{0,\lambda}}$$

General procedure for the synthesis of terpyridine-perylene ligands 3 and 4. A mixture of 1,6,7,12-tetra(*p*-*t*-butylphenoxy)perylene-3,4:9,10-tetracarboxylic acid *bis*(anhydride) **1** (500 mg, 0.5 mmol), 4- or 3-aminophenylterpyridine **2** or **4** (1.31 g, 4.06 mmol) in quinoline (50 mL) was stirred at 220 ºC under argon for 3 days. The mixture was cooled to 25 ºC, precipitated with AcOH (50 mL), filtered, and washed with water, and then MeOH. The product was column chromatographed (Al_2O_3)

eluting with a mixture of $CHCl_3$/hexane (2:1).

***N,N'-Bis*[4-([2,2':6',2"]terpyridin-4'-yl)phenyl]-1,6,7,12-tetra(*p*-*t*-butylphenol)perylene-3,4:9,10-tetracarboxylic acid *bis*anhydride (3)**: red powder, 51%; mp > 350 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 4H, 3',5'-tpy*H*), 8.74 (d, 4H, *J* = 4.2 Hz, 6,6"-tpy*H*), 8.68 (d, 4H, *J* = 7.8 Hz, 3,3"-tpy*H*), 8.30 (s, 4H, per*H*), 8.06 (d, 4H, *J* = 8.4 Hz, Ph*H*), 7.89 (dd, 4H, $J_1 = J_2$ = 7.8 Hz, 4,4"-tpy*H*), 7.43 (d, 4H, *J* = 8.4 Hz, Ph*H*), 7.36 (dd, J_1 = 7.8 Hz, J_2 = 4.2 Hz 4H, 5,5"-tpy*H*), 7.25 (d, 8H, *J* = 9.0 Hz, Ar*H*), 6.88 (d, 8H, *J* = 9.0 Hz, Ar*H*), 1.27 (s, 36 H, C*H*$_3$); ^{13}C NMR δ 163.75, 156.40, 156.28, 153.07, 149.68, 149.37, 147.70, 139.19, 137.09, 136.21, 133.41, 129.44, 128.46, 126.93, 124.06, 122.79, 121.61, 121.08, 120.51, 120.05, 119.60, 119.27, 105.23, 34.59, 31.65; ESI-MS: *m/z* 1597.38 (calcd. $[M+H]^+$ = 1597.64).

***N,N'-Bis*[3-([2,2':6',2"]terpyridin-4'-yl)phenyl]-1,6,7,12-tetra(*p*-*t*-butylphenol)perylene-3,4:9,10-tetracarboxylic acid *bis*anhydride (5)**: red powder, 60%; mp > 350 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (s, 4H, 3',5'-tpy*H*), 8.70 (d, 4H, *J* = 4.7 Hz, 6,6"-tpy*H*), 8.66 (d, 4H, *J* = 7.8 Hz, 3,3"-tpy*H*), 8.3 (s, 4H, per*H*), 8.02 (d, 2H, *J* = 7.1 Hz, Ph*H*), 7.86 (dd, 4H, $J_1 = J_2$ = 7.8 Hz, 4,4"-tpy*H*), 7.83 (s, 2H, Ph*H*), 7.67 (dd, 2H, $J_1 = J_2$ = 7.1 Hz, Ph*H*), 7.37 (d, 2H, *J* = 7.1 Hz, Ph*H*), 7.33 (dd, J_1 = 7.8 Hz, J_2 = 4.7 Hz, 4H, 5,5"-tpy*H*), 7.25 (d, 8H, *J* = 9.1 Hz, Ar*H*), 6.89 (d, 8H, *J* = 9.1 Hz, Ar*H*), 1.27 (s, 36 H, *CH*$_3$); ^{13}C NMR δ 163.54, 156.16, 156.03, 152.90, 149.21, 149.11, 147.39, 139.92, 136.77, 136.05, 133.18, 129.85, 129.18, 126.67, 123.78, 122.56, 121.30, 119.37, 118.91, 105.02, 34.35, 31.42; ESI-MS: *m/z* 1596.71 (calcd. $[M]^+$ = 1596.64).

[Ru(6)Cl$_3$] (7). 4'-(4-Methylphenyl)[2,2':6',2"]terpyridine (**6**; 200 mg, 890 μmol) was treated with $RuCl_3 \cdot 3H_2O$ (251.7 mg, 1.21 mmol) in EtOH (20 mL), then the suspension was refluxed for 12 h. After the mixture was cooled, the resultant dark brown solid was filtered, washed with cold EtOH, and dried *in vacuo* to give **7**: 290 mg (88%). This material was used without further purification.

General procedure for the synthesis of complexes 8, 9, and 13: *Bis*(terpyridine) ligand (**3**, **5** or **12**) (40 mg, 31 μmol) was added to a suspension of Ru^{III}tpy **7** (25 mg, 69 μmol) in a mixed solvent (20 mL) of EtOH/$CHCl_3$ (2:1), then *N*-ethylmorpholine (500 μL) was added. The mixture was refluxed for 12 h. After cooling, the resulting deep red solution was filtered (Celite), solvent was removed *in vacuo* and the residue was column chromatographed (SiO_2), eluting with H_2O: KNO_3:MeCN (1:1:35). The counter ion was exchanged by adding NH_4PF_6, and then the product was filtered, washed with water and dried *in vacuo*.

[(3)Ru$_2$(6)$_2$][PF$_6$]$_4$ (8): red powder, 50 mg (78%), mp > 350 °C; ^{1}H NMR (500 MHz, CD_3OD) δ: 9.53 (s, 4H, 3',5'-tpy*H*), 9.45 (s, 4H, 3',5'-tpy*H*), 9.14 (m, 8H, 3,3"-tpy*H*), 8.71 (d, 4H, *J* = 8.0 Hz, Ph*H*), 8.67 (s, 4H, per*H*), 8.45 (d, 4H, *J* = 8.0 Hz, Ph*H*), 8.36 (m, 8H, 4,4"-tpy*H*), 8.02 (d, 4H, *J* = 8.0 Hz, Ph*H*), 7.90 (d, 4H, *J* = 8.0 Hz, Ph*H*), 7.80 (m, 8H, 6,6"-tpy*H*), 7.65 (m, 16H, Ar*H*, 5,5"-tpy*H*), 7.31 (d, 8H, *J* = 8.0 Hz, Ar*H*), 2.90 (s, 6H, C*H*$_3$), 1.66 (s, 36H, C*H*$_3$); ^{13}C NMR δ: 163.56, 157.86, 157.80, 155.01, 151.63, 149.36, 147.99, 147.45, 141.14, 138.30, 138.25, 137.17, 136.80, 133.14, 133.03, 130.19, 129.88, 127.82, 127.70, 126.46, 124.72, 124.63, 121.54, 121.04, 121.01, 120.99, 120.08, 120.05, 119.69, 119.15, 34.04, 30.92, 29.31; ESI-MS (*m/z*): 2881.1 $[M - PF_6^-]^{1+}$ (Calcd. *m/z* = 2881.5), 863.5 $[M - 3PF_6^-)]^{3+}$ (Calcd. *m/z* = 863.6), 611.4 $[M - 4PF_6^-)]^{4+}$ (calcd. *m/z* = 611.5).

$[(5)Ru_2(6)_2][PF_6]_4$ (9): red powder, 50 mg (78%), mp > 350 °C; ^{1}H NMR (500 MHz, CD_3CN) δ 9.04 (s, 4H, 3',5'-tpy*H*), 9.02 (s, 4H, 3',5'-tpy*H*), 8.66 (d, 4H, *J* = 8.0 Hz, 3,3"-tpy*H*), 8.63 (d, 4H, *J* = 8.0 Hz, 3,3"-tpy*H*), 8.32 (d, 2H, *J* = 7.5 Hz, Ph*H*), 8.18 (s, 4H, per*H*), 8.14 (m, 8H, Ph*H*), 7.92 (m, 8H, 4,4"-tpy*H*), 7.64 (d, 2H, *J* = 7.5 Hz, Ph*H*), 7.58 (d, 4H, *J* = 8.0 Hz, Ph*H*), 7.41 (m, 8H, 6,6"-tpy*H*), 7.36 (d, 8H, *J* = 7.5 Hz, Ar*H*), 7.16 (m, 8H, 5,5"-tpy*H*), 6.96 (d, 8H, *J* = 7.5 Hz, Ar*H*), 2.57 (s, 6H, CH_3), 1.32 (s, 36H, CH_3); ^{13}C NMR δ: 163.50, 157.80, 157.73, 156.05, 155.26, 154.95, 152.61, 151.57, 149.29, 147.38, 141.08, 138.18, 137.10 136.73, 133.07, 132.6, 130.13, 129.81, 128.42, 127.75, 127.67, 127.19, 126.42, 124.57, 122.12, 12.47, 120.97, 120.92, 120.01, 119.62, 119.08, 33.97, 30.93, 29.24; MALDI-TOF-MS (*m/z*): 2881.0 $[M - PF_6^-]^{1+}$ (calcd. *m/z* = 2881.2).

1,6/1,7-Dibromo-3,4,9,10-perylenetetracarboxylic dianhydride.[31] A mixture of 3,4,9,10-perylenetetracarboxylic dianhydride (4 g, 10 mmol) and H_2SO_4 (60 mL) was stirred at 55 ºC for 18 h. Next I_2 (80 mg, 300 μmol) was added and the mixture was stirred for 5 h at 55 ºC. Br_2 (3.5 g, 20 mmol) was added, the reaction mixture was stirred for 48 h at 85 ºC, followed by cooling to 0 ºC. Excess Br_2 was removed using air stream in the hood. The product was precipitated with cold water (30 mL), filtered, washed with water, EtOH and then dried *in vacuo* to afford (89%) an orange powder: 5 g. The product was used in the next step without further purification.

***N,N*'*-Bis*(*n*-octyl)-1,6/1,7-dibromo-3,4,9,10-perylenetetracarboxydiimide**[32,33] **(10)**. To a mixture of 1,6/1,7-dibromo-3,4,9,10-perylenetetracarboxylic dianhydride (2.5 g, 4.5 mmol) and *n*-octylamine (5.8 g, 44.8 mmol), was added a mixture of 2-BuOH:H_2O (80 mL, 1:1). The reaction mixture was stirred under argon at 65 ºC for 12 h, cooled to 25 ºC, precipitated with MeOH (150 mL), and filtered. The product was dried *in vacuo* and column chromatographed (SiO_2) eluting with $CHCl_3$ to give **10**, as an orange powder: 5 g (89 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.43 (d, 4H, *J* = 8.0 Hz, per*H*), 8.87 (s, 4H, per*H*), 8.65 (d, 4H, *J* = 8.0 Hz, per*H*), 4.20 (m, 8H, CH_2), 1.75 (m, 8H, CH_2), 1.44-1.26 (m, 48H, CH_2), 0.89 (t, 12H, CH_3); ^{13}C NMR δ 163.39, 163.01, 162.51, 162.14, 138.27, 138.15, 133.32, 133.08, 132.93, 132.52, 130.16, 130.02, 129.36, 128.64, 128.27, 127.88, 127.08, 123.54, 123.35, 122.92, 122.61, 121.79, 120.97, 41.16, 41.04, 40.93, 32.04, 29.54, 29.43, 28.30, 27.38, 27.33, 27.29, 22.86, 14.31; MALDI-TOF-MS: *m/z* 770.20 (calcd. M^+ = 770.13).

***N,N*'*-Bis*(*n*-octyl)-1,7-di[4-([2,2':6',2"]terpyridin-4'-yl)phenyl]-3,4,9,10-perylenetetracarboxydiimide (12).** To a mixture of **10** (250 mg, 500 μmol) and 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine **11** (485 mg, 1.3 mmol) in toluene: *t*-BuOH:H_2O (2:1:1; 80 mL), was added K_2CO_3 (3.5 g, 27.4 mmol). The system was freeze-pump-thawed three times and backfilled with argon; then $Pd(PPh_3)_2Cl_2$ (16 mg) was added. After refluxing for 72 h under argon, the mixture was cooled to 25 °C, solvent was removed *in vacuo* and the residue was dissolved in $CHCl_3$ and filtered. After concentration *in vacuo*, the residue was purified by column chromatography (Al_2O_3) eluting with $CHCl_3$, followed by recrystallization from $CHCl_3$/MeOH (5x) to give (31%) **15**, as a red solid: mp > 300 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 4H, 3',5'-tpy*H*), 8.79 (d, 4H, *J* = 4.5 Hz, 6,6"-tpy*H*), 8.74 (d, 4H, *J* = 8.0 Hz, 3,3"-tpy*H*), 8.69 (s, 2H, per*H*), 8.23 (d, 2H, *J* = 8.0 Hz, per*H*) , 8.11 (d, 4H, *J* = 8.0 Hz, Ph*H*), 7.95 (m, 6H, per*H*, 4,4"-tpy*H*), 7.76 (d, 4H, *J* = 8.0 Hz, Ph*H*), 7.42 (dd, J_1 = 8.0 Hz, J_2 = 4.5 Hz, 4H, 5,5"-tpy*H*), 4.20 (t, 4H, *J* = 8 Hz, CH_2), 1.43-1.27 (m, 23H, CH_2), 0.87 (m, 6H, CH_3); ^{13}C NMR δ 163.55, 163.42, 140.44, 135.30, 134.90, 133.36, 132.88, 130.60, 130.12, 129.86, 129.46, 129.42, 127.98, 124.71, 122.66, 122.34, 40.81, 31.99, 29.51, 29.36, 28.32, 27.29, 22.79, 14.23; ESI-MS: *m/z* 1229.64 (calcd. $[M+H]^+$ = 1229.54).

$[(10)Ru_2(6)_2][PF_6]_4$ (13): red powder, (78%), mp > 350 °C; ^{1}H NMR (500 MHz, CD_3OD): δ 9.35 (s, 4H, 3',5'-tpy*H*), 9.18 (s, 4H, 3',5'-tpy*H*), 8.91 (d, 4H, *J* = 8.0 Hz, 3,3"-tpy*H*), 8.83 (d, 4H, *J* = 8.0 Hz, 3,3"-tpy*H*), 8.69 (s, 2H, per*H*), 8.49 (d, 4H, *J* = 8.0 Hz, Ph*H*), 8.26 (d, 2H, *J* = 8.0 Hz, per*H*), 8.13 (d, 4H, *J* = 8.0 Hz, Ph*H*), 8.02-7.96 (m, 14H, Ph*H*, per*H*, 4,4"-tpy*H*), 7.54 (m, 8H, 6,6"-tpy*H*), 7.51 (d, 4H, *J* = 8.0 Hz, Ph*H*), 7.30 (m, 8H, 5,5"-tpy*H*), 4.23 (t, 4H, CH_2), 2.54 (s, 6H, CH_3), 1.77 (m, 8H, CH_2), 1.46-1.25 (m, 23H, CH_2), 0.86 (m, 6H, CH_3); ^{13}C NMR δ 162.72, 157.84, 157.75, 155.14, 155.12, 154.84, 151.62, 151.35, 148.88, 140.62, 137.94, 137.87, 137.78, 137.77, 137.74, 133.09, 127.42, 127.36, 126.75, 126.68, 124.64, 124.31, 121.37, 121.35, 120.76, 31.24, 28.71, 28.60, 28.54, 27.44, 26.53, 21.96, 20.18, 13.03; ESI-MS (*m/z*): 519.70 $[M-4PF_6^-]^{4+}$ (calcd. *m/z* = 519.65), 741.20 $[M-3PF_6^-]^{3+}$ (calcd. *m/z* = 741.19).

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