Supplementary Information:

5,10,15,20-Tetrakis[4'-(terpyridyl)phenyl]porphyrin and its Ru^{II} complexes: Synthesis, photovoltaic properties, and self-assembled morphology

Tae Joon Cho,[a] Carol D. Shreiner,[a] Seok-Ho Hwang,[a] Charles N. Moorefield,[b] Brandy Courneya,[a] Luis A. Godínez,[c] Juan Manríquez,[c] Kwang-Un Jeong,[a] Stephen Z. D. Cheng,[a] and George R. Newkome*[a,b]

[a] *Department of Polymer Science, The University of Akron, Akron, OH 44325, USA; E-mail: newkome@uakron.edu; http://www.dendrimers.com*

[b] *Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325, USA;*

[c] *Centro de Investigación y Desarrollo Tecnológico en Electroquímica, Querétaro, 76700, México*

Selected data for materials. **2**: ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.42 (t, 8H, *J* = 6.3 Hz, 5,5" tpy*H*), 7.95 (t, 8H, *J* = 7.5 Hz, 4,4" tpy*H*), 8.35 (d, 8H, *J* = 8.1 Hz, 3',5' Ph*H*), 8.44 (d, 8H, *J* = 8.1 Hz, 2',6' Ph*H*), 8.79 (d, 8H, *J* = 8.4 Hz, 3,3" tpy*H*), 8.81 (d, 8H, *J* = 6.6 Hz, 6,6" tpy*H*), 9.00 (s, 8H, py*H*), 9.10 (s, 8H, 3',5' tpy*H*), -2.64 (s, 2H, N*H*); UV/Vis (CHCl$_3$): λ_{max} (ε) = 423 (370150), 519 (17700), 554 (11540), 593 (6730), 652 nm (5080).

3: ^{1}H NMR (CD$_3$CN, 300 MHz): δ 7.26 (m, 16H, 5,5" tpy*H*, both), 7.53 (d, 8H, *J* = 5.4 Hz, 6,6" tolyltpy*H*), 7.60 (m, 16H, 6,6" porphyrin-tpy*H* + 3,5 tolyl*H*), 8.02 (m, 16H, 4,4" tpy*H*, both), 8.16 (d, 8H, *J* = 8.1 Hz, 2,6 tolyl*H*), 8.73 (m, 16H, 3,3" tolyltpy*H*

+ 3',5' Ph*H*), 8.81 (d, 8H, *J* = 8.1 Hz, 2',6' Ph*H*), 8.93 (d, 8H, *J* = 8.1 Hz, 3,3'' porphyrin-tpy*H*), 9.08 (s, 8H, 3',5' tolyltpy*H*), 9.23 (s, 8H, py*H*), 9.49 (s, 8H, 3',5' porphyrin-tpy*H*), -2.54 (s, 2H, N*H*); ^{13}C NMR (CD_3CN, 75 MHz): 21.53, 120.98, 122.53, 122.95, 125.68, 125.80, 127.58, 128.60, 128.69, 128.79, 131.42, 135.01, 135.97, 136.73, 137.82, 139.21, 142.21, 144.95, 148.97, 149.60, 153.64, 156.51, 156.90, 156.95, 159.43; UV/Vis (CH_3CN): λ_{max} (ε) = 430 (240000), 496 (172500), 518 (97500, shoulder), 551 (47500, shoulder), 592 (24250), 645 nm (15750).

4: ^{1}H NMR (CD_3CN, 300 MHz): δ 7.26 (m, 16H, 5,5'' tpy*H*, both), 7.52 (d, 8H, *J* = 5.7 Hz, 6,6'' tolyltpy*H*), 7.60 (m, 16H, 6,6'' porphyrin-tpy*H* + 3,5 tolyl*H*), 8.01 (m, 16H, 4,4'' tpy*H*, both), 8.16 (d, 8H, *J* = 7.8 Hz, 2,6 tolyl*H*), 8.74 (m, 24H, 3,3'' tolyltpy*H* + 3',5' Ph*H* + 2',6' Ph*H*), 8.90 (d, 8H, *J* = 8.1 Hz, 3,3'' porphyrin-tpy*H*), 9.08 (s, 8H, 3',5' tolyltpy*H*), 9.15 (s, 8H, py*H*), 9.46 (s, 8H, 3',5' porphyrin-tpy*H*); ^{13}C NMR (CD_3CN, 75 MHz): 22.08, 121.84, 123.09, 123.48, 126.23, 126.36, 127.78, 129.17, 129.23, 129.35, 131.97, 133.71, 135.60, 137.28, 137.80, 139.76, 142.75, 149.94, 149.66, 150.14, 151.65, 154.20, 157.09, 157.47, 160.01; UV/Vis (CH_3CN): λ_{max} (ε) = 435 (245800), 496 (169100), 568 (39100), 611 nm (27230).

7: ^{1}H NMR (CD_3CN, 300 MHz): δ 0.92 (t, 12H, $-CH_2CH_3$), 1.33 – 1.60 (aliphatic region, 64H), 4.19 (t, 8H, $-OCH_2R$), 7.26 (m, 16H, 5,5'' tpy*H*, both), 7.30 (d, 8H, *J* = 9.0 Hz, 3,5 O-Ph*H*), 7.53 (d, 8H, *J* = 6.0 Hz, 6,6'' O-Ph-tpy*H*), 7.57 (d, 8H, *J* = 6.0 Hz, 6,6'' porphyrin-tpy*H*), 8.02 (m, 16H, 4,4'' tpy*H*, both), 8.21 (d, 8H, *J* = 9.0 Hz, 2,6 O-Ph*H*), 8.70 (d, 8H, *J* = 8.1 Hz, 3,3'' O-Phtpy*H*), 8.76 (m, 16H, 3',5' Ph*H* + 2',6' Ph*H*), 8.83 (d, 8H, *J* = 8.1 Hz, 3,3'' porphyrin-tpy*H*), 9.02 (s, 8H, 3',5' O-Ph-tpy*H*), 9.23 (s, 8H, py*H*), 9.39 (s, 8H, 3',5' porphyrin-tpy*H*), -2.53 (s, 2H, N*H*); ^{13}C NMR (CD_3CN, 75 MHz):

14.50, 23.51, 26.84, 30.05 - 30.45 (aliphatic), 32.76, 69.47, 116.67, 120.99, 122.03, 122.93, 125.65, 125.79, 127.60, 128.56, 128.70, 129.74, 130.33, 136.75, 137.82, 139.19, 144.91, 148.80, 149.30, 151.08, 153.65, 156.41, 156.99, 159.49, 162.47; UV/Vis (CH_3CN): λ_{max} (ε) = 424 (345000), 496 (216000), 514 (121000, shoulder), 556 (57400, shoulder), 592 (18400), 651 nm (13000).

8: ^{1}H NMR (CD_3CN, 300 MHz): δ 0.92 (t, 12H, R-C*H$_3$*), 1.34 – 1.60 (aliphatic region, 64H), 4.19 (t, 8H, -PhOC*H$_2$*CH$_2$-), 7.27 (m, 16H, 5,5" tpy*H*, both), 7.54 (m, 16H, 6,6" tpy*H*, both), 7.62 (d, 8H, *J* = 7.8 Hz, 3,5 O-Ph*H*), 8.01 (m, 16H, 4,4" tpy*H*, both), 8.21 (d, 8H, *J* = 7.8 Hz, 2,6 O-Ph*H*), 8.71 (m, 24H, 3,3" O-Phtpy*H* + 3',5' Ph*H* + 2',6' Ph*H*), 8.83 (d, 8H, *J* = 8.1 Hz, 3,3" porphyrin-tpy*H*), 9.02 (s, 8H, 3',5' O-Phtpy*H*), 9.20 (s, 8H, py*H*), 9.40 (s, 8H, 3',5' porphyrin-tpy*H*); ^{13}C NMR (CD_3CN, 75 MHz): 14.50, 23.51, 26.84, 30.05 - 30.45 (aliphatic), 32.76, 69.45, 116.66, 121.27, 122.01, 122.91, 125.65, 125.78, 127.21, 128.54, 128.68, 129.76, 130.33, 133.15, 136.74, 139.19, 145.02, 149.00, 149.40, 151.08, 153.64, 156.42, 156.94, 159.49, 162.46; UV/Vis (CH_3CN): λ_{max} (ε) = 432 (278500), 496 201000), 568 (44700), 611 nm (28700).

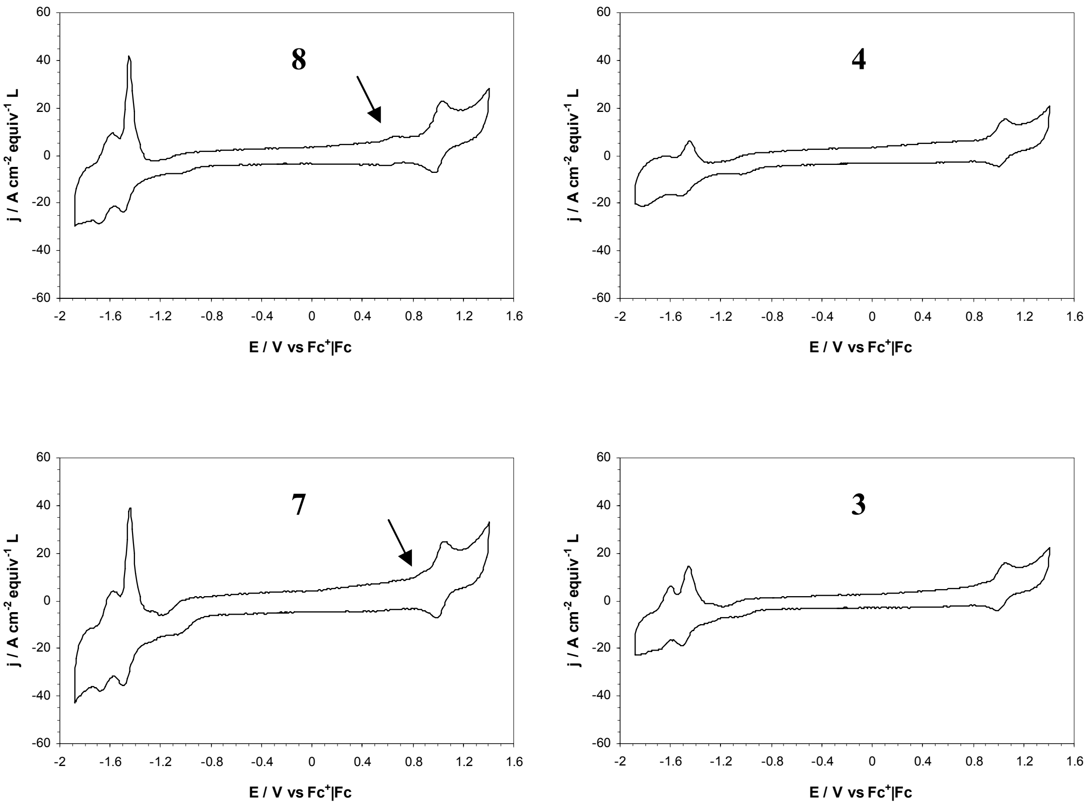
Electrochemistry

Cyclic voltammetry experiments were carried out using an IM6 BAS-Zahner potentiostat connected to a 3mL three-electrode cell at 298K. A glassy carbon disk (diameter = 1mm) was used as working electrode, while a Pt and a Ag wire were used as counter and pseudo-reference electrodes, respectively (all potentials were referenced to the ferrocinium | ferrocene couple, denoted as $Fc^+|Fc$). All voltammograms were obtained in MeCN + 0.1M Bu_4NPF_6 as electrolytic medium, a scan rate of dE/dt = 100mV/s and an ohmic compensation of 1.5kΩ were used. All solutions were bubbled with ultra-pure nitrogen during 15 minutes before each experiment.

S1 contains electrochemical data obtained from cyclic voltammograms (S2), where peaks around 1.0V can be associated to the redox couple $Ru^{III}|Ru^{II}$, and peaks around -1.47V and -1.60V can be associated to redox processes in the terpyridyl moeties (tpy) [1]. Small anodic peaks were also observed for samples **8** and **7** at 0.65V and 0.85V, respectively, probably due to the irreversible oxidation of aryl ether groups formed between porphyrinic cores (PorO) and the aliphatic groups (R) [2]. It is important to point out that the corresponding peak potentials are strongly related to the presence or absence of Zn^{II} in the porphyrinic cores (PorOR). Therefore, since the oxidation of PorOR groups in sample **8** takes place at a more negative potential (0.65V), compared to the one observed for **7** (0.85V), it is clear that Zn^{II} atoms promote an electronic charge shift on the aryl ether groups.

Dye	**$E^{\theta'}(Ru^{III}\|Ru^{II})$ / V**	**$E_p(PorO^{+}R\|PorOR)$ / V**	**$E^{\theta'}(tpy^{-}\|tpy)$ / V**	**$E^{\theta'}(tpy^{-}\|tpy^{2-})$ / V**
8	1.00	0.65	-1.47	-1.62
4	1.02	—	-1.47	-1.65
7	1.01	0.85	-1.47	-1.62
3	1.02	—	-1.47	-1.65

S1. Electrochemical data obtained for **8**, **4**, **7** and **3** in MeCN + 0.1M Bu_4NPF_6 at 298K



S2. Cyclic voltammograms (normalized to concentration) obtained for **8**, **4**, **7**, and **3** in MeCN + 0.1M Bu_4NPF_6 at 298K. Arrows are pointing out small anodic waves probably related to the oxidation of the aryl ether groups of samples **7** and **8**.

Construction of dye-sensitized solar cells (DSSC)

Nanocrystalline TiO_2 electrodes were synthesized by electrophoretic deposition. Experimental details were previously reported. [3] The counter-electrode was constructed using a glass plate covered with a conductive film of indium tin oxide (ITO). Then, 8 μL/cm^2 of a 10mM H_2PtCl_6 solution in isopropanol was spread on the ITO surface. Fresh electrodes were dried at 25 ºC and annealed in air at 380 ºC for 30 min.

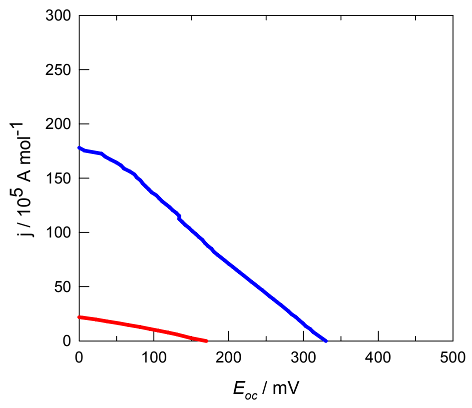
Modification of TiO_2 electrodes was carried out by immersion in 0.2 mM solutions of each dye in pure MeCN during 12h. Then, these electrodes were rinsed with MeCN and dried in air before their use in DSSC. Surface coverage for each dye was estimated by means of UV-Vis spectroscopy.

DSSC were assembled in a sandwich fashion using a Teflon™ gap between the photo-anode and the cathode in order to avoid short circuit. A solution of 0.3 M KI + 0.015 M I_2 in propylene carbonate was used as the electrolyte medium in DSSC. An area of 0.1781cm^2 was used to illuminate the cell with a polychromatic light source (2.2mW/cm^2).

Photocurrent spectroscopy and discharge of DSSC

IPCE (Incident-Photon-to-Current-Efficiency) *vs* wavelength plots were obtained using a 100W Xe lamp and a monochromator (300–650nm) for illuminating the previously assembled DSSC under short circuit conditions.

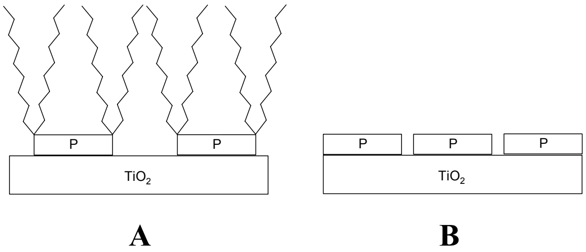
Discharge of DSSC (S3) was carried out using a variable resistance of 52 kΩ under polychromatic illumination (400-800nm, 2.2mW/cm^2).



S3. Normalized j-E plots for DSSC assembled using modified TiO_2 electrodes with **8** (blue line) and **4** (red line).

Surface conformation of porphyrins on TiO_2 electrodes

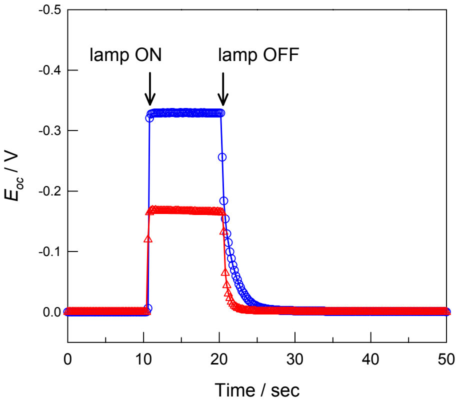
Comparison of the theoretical coverage for a well-packaged monolayer of dyes (9.5×10^{-11} mol/cm^2) [4] with the reported values in Table 1 in the manuscript, a parallel conformation of these molecules on the TiO_2 surface (S4) can be assumed. Surface coverage values also suggest that dyes without large aliphatic chains (**4** and **3**, S4-A) are more closely packaged than those containing these groups (**8** and **7**, S4-B).



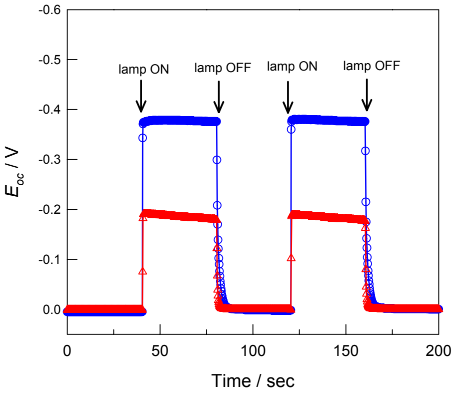
S4. Scheme showing surface conformation of porphyrins, P, with (A) or without (B) large aliphatic chains, adsorbed on TiO_2 electrodes.

Open-circuit photovoltage transients

Open-circuit photovoltage (E_{oc}) responses upon polychromatic illumination (2.2mW/cm^2) of the DSSC (S5) showed that photopotential generation was instantaneous and rapidly reached a steady-state for modified TiO_2 samples. For instance, a potential of ~330mV for TiO_2/**8** system and ~170mV for TiO_2/**4** (Table 1) was observed. When the illumination was turned off, the photovoltage fell back to zero within a few seconds. Decay was faster for TiO_2/**4** system than for TiO_2/**8** and it is important to note that the photovoltage was stable during several on/off cycles of illumination (S6).



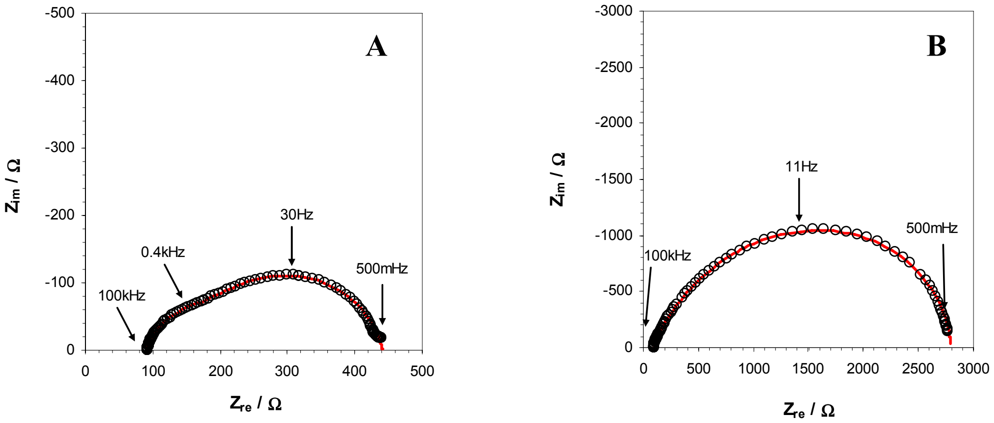
S5. Open-circuit photovoltage transient observed upon an on/off cycle of polychromatic illumination (2.2mW/cm^2) on a DSSC, previously assembled with modified TiO_2 electrodes with (O) **8** and (Δ) **4**.



S6. Open-circuit photovoltage transients observed upon two on/off cycles of polychromatic illumination on a DSSC, assembled with modified TiO_2 electrodes with (O) **8** and (Δ) **4**.

Electrochemical impedance spectroscopy under illumination

Electrochemical impedance spectroscopy experiments were carried out following the methodology previously reported by Bisquert et al. [5] and Grätzel et al. [6]. In order to calculate electron lifetimes (τ_n) in DSSC, measurements were performed using an IM6 BAS-Zahner potentiostat connected to DSSC in a two-electrode array. EIS spectra were obtained under polychromatic illumination (400-800nm), using an a.c. potential of 10mV and a frequency range between 100kHz-500mHz. d.c. potentials were equal to open-circuit potentials (E_{OC}). Electron lifetimes were obtained by fitting the spectra to the equivalent circuit (see S7) previously reported by Bisquert and co-workers [5] (Table 1).



S7. EIS spectra (O) under illumination for DSSC assembled with modified TiO_2 electrodes with (A) **8** and (B) **4**, and fitted to the model previously reported by Bisquert and co-workers (red line).

References

[1] G.R. Newkome, E. He, L.A. Godínez and G.R. Baker, *J. Am. Chem. Soc.* 2000, **122**, 9993-10006.

[2] V.D. Parkers in *Encyclopedia of Electrochemistry of the Elements*, A.J. Bard and H. Lund (Eds.), Vol. XI, Marcel Dekker, New York, 1978, 276.

[3] S.-H. Hwang, P. Wang, C. N. Moorefield, L. A. Godínez, J. Manríquez, E. Bustos, G.R. Newkome, *Chem. Commun.* 2005, 4672-4674

[4] N. Araki, M. Obata, A. Ichimura, Y. Amao, K. Mitsuo, K. Asai and S. Yano, *Electrochim. Acta,* 2005, **51**, 677.

[5] F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo and A. Hagfeldt, *Sol. Energy Mater. Sol. Cells*, 2005, **87**, 117-131.

[6] Q. Wang, J.-E. Moser and M. Grätzel, *J. Phys. Chem. B*, 2005, **109**, 14945-14953.