

Supplementary data

Design, Self-Assembly, and Photophysical Properties of Pentameric Metallomacrocycles: $[M_5(N\text{-hexyl}[1,2\text{-bis}(2,2':6',2''\text{-terpyridin-4-yl)]\text{carbazole})_5][M = \text{Fe(II)}, \text{Ru(II)}, \text{and Zn(II)}]$

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EXPERIMENTAL SECTION: GENERAL PROCEDURES

Chemicals were purchased from Aldrich and used without further purification. Thin layer chromatography (TLC) was conducted using flexible sheets (Baker-flex) precoated with Al_2O_3 (IB-F) or SiO_2 (IB2-F) and visualized by UV light. Column chromatography used neutral/basic Al_2O_3 , Brockman Activity I (60-325 mesh), or SiO_2 (60-200 mesh) from Fisher Scientific and used the stipulated solvent combination for elution. The melting points were determined with an Electrothermal 9100 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer using CDCl_3 , except where noted. Mass spectra were obtained using a Bruker Esquire Electrospray Ion Trap Mass Spectrometer (ESI-MS). UV/Vis absorption spectra were obtained on Hewlett-Packard UV/Vis spectrophotometer. Photoluminescence spectra were obtained using a Perkin-Elmer LS55 luminescence spectrometer. All the electrochemical experiments were performed with CHI 440 Electrochemical Workstation (CH Instruments Inc, Austin, Texas). 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6 , from Fluka) in DMF was used as the supporting electrolyte (degassed with argon). A platinum wire was employed as the counter electrode. A silver wire electrode was used as the reference. Ferrocene (Fc) was employed as an internal reference and all

the potentials were referenced relative to the Fc/Fc⁺ couple. A graphite electrode (CHI, 2 mm in diameter), polished with 1.0 and 0.3 μm aluminum paste and ultrasonicated in deionized water and DMF bath, was used as the working electrode. The scan rate for cyclic voltammetry (CV) was 100 mV/sec. All experiments were performed at 20 ± 2 °C.

***N*-Hexyl carbazole (1).** A stirred mixture of KOH (2.08 g, 35.88 mmol), 1-bromohexane (5.92 g, 35.88 mmol) and 9*H*-carbazole (5 g, 29.90 mmol) dissolved in DMF (40 mL) was refluxed for 12h. The reaction mixture was poured into distilled water and extracted with CH₂Cl₂. The combined extract was dried (MgSO₄), filtered, and concentrated in vacuo to a crude product, which was column chromatographed on SiO₂ eluting with a hexane/EtOAc (15:1; v/v) solvent mixture to afford (71%) **1**, as white solid: 5.34 g; m.p. 62-63 °C; ¹H NMR: δ 8.09 (d, *J* = 7.5 Hz, 5-Ar*H*, 2H), 7.42 (m, 3,4-Ar*H*, 4H), 7.21 (dd, *J* = 7.5, 6.6 Hz, 2-Ar*H*, 2H), 4.26 (t, *J* = 7.2 Hz, NCH₂, 2H), 1.84 (m, NCH₂CH₂, 2H), 1.37-1.26 [m, CH₂(CH₂)₃CH₃, 6H], 0.85 (t, *J* = 6.9 Hz, CH₃, 3H); ¹³C NMR: δ 140.63, 125.75, 123.02, 120.53, 118.87, 108.84, 43.27, 31.79, 29.13, 27.18, 22.75, 14.22; ESI-MS: *m/z* 274.1 [M + Na]⁺ (Calcd. *m/z* = 274.2).

***N*-Hexyl-3,6-diformylcarbazole (2).** To a stirred mixture of DMF (85 mL) and 1,2-dichloroethane (25 mL) cooled to 0 °C, phosphoryl chloride (79.29 g, 520 μmol) was added, then **1** (5.2 g, 20.69 mmol) was added. After stirring for 48 h at 90 °C, the mixture was poured into distilled water, extracted with CHCl₃, and dried (MgSO₄). The crude product was column chromatographed on SiO₂ eluting with a hexane/EtOAc (4:1; v/v) solvent mixture to afford (52%) **2**, as white solid: 3.31 g; m.p. 137-138 °C; ¹H NMR: δ 10.15 (s, CHO, 2H), 8.68 (s, 5-Ar*H*, 2H), 8.10 (d, *J* = 8.4 Hz, 3-Ar*H*, 2H), 7.56 (d, *J* = 8.4 Hz, 2-Ar*H*, 2H), 4.40 (t, *J* = 6.9 Hz, NCH₂, 2H), 1.92 (m, NCH₂CH₂, 2H), 1.40-1.29

[m, CH₂(CH₂)₃CH₃, 6H], 0.87 (t, *J* = 6.6 Hz, CH₃, 3H); ¹³C NMR: δ 191.72, 145.01, 129.89, 128.06, 124.51, 123.40, 109.99, 44.05, 31.66, 29.12, 27.08, 22.69, 14.15; ESI-MS: *m/z* 330.2 [M + Na]⁺ (Calcd. *m/z* = 330.1).

***N*-Hexyl-[1,2-bis(2,2':6,2''-terpyridin-4-yl)]carbazole (3).** To a stirred mixture of dialdehyde **2** (2.3 g, 7.48 mmol) and EtOH (100 mL), 2-acetylpyridine (3.99 g, 32.92 mmol) was added, followed after 2 min. by NaOH powder (1.3 g, 32.5 mmol). After the dark pink solution had been stirred at 25 °C for 24 h, the solvent was evaporated in vacuo to yield the intermediate, as a dark brown solid. Ammonium acetate (23 g, excess) and glacial AcOH (100 mL) were added to this solid, then this mixture was refluxed for 12 h. After cooling, the dark brown solution was neutralized with aqueous Na₂CO₃. The crude product was extracted with CH₂Cl₂. The combined extract was dried (MgSO₄), concentrated in vacuo, and the resultant residue was column chromatography on Al₂O₃ eluting with a hexane/CH₂Cl₂ (1:1; v/v) solvent mixture to afford (34%) **3**, as off-white solid: 1.82 g; m.p. 204-205 °C; ¹H NMR: δ 8.93 (s, 3',5'-tpyH, 4H), 8.81-8.79 (m, 6,6''-tpyH, 5-ArH, 6H), 8.72 (d, *J* = 7.8 Hz, 3,3''-tpyH, 4H), 8.11 (d, *J* = 8.4 Hz, 3-ArH, 2H), 7.90 (dd, *J* = 7.8, 7.5 Hz, 4,4''-tpyH, 4H), 7.54 (d, *J* = 8.4 Hz, 2-ArH, 2H), 7.37 (dd, *J* = 5.1, 6.9 Hz, 5,5''-tpyH, 4H), 4.38 (t, *J* = 6.9 Hz, NCH₂, 2H), 1.96 (m, NCH₂CH₂, 2H), 1.46-1.34 [m, CH₂(CH₂)₃CH₃, 6H], 0.89 (t, *J* = 6.9 Hz, CH₃, 3H); ¹³C NMR: δ 156.78, 156.10, 151.13, 149.37, 141.76, 137.02, 129.81, 125.75, 123.89, 123.84, 121.61, 119.92, 118.99, 109.52, 43.68, 31.78, 29.25, 27.20, 22.77, 14.24; ESI-MS: *m/z* 715.2 [M + H]⁺ (Calcd. *m/z* = 714.9).

[Fe₅(3**)₅][10PF₆⁻] (4).** A solution of one equivalent of FeCl₂·4H₂O (54 mg, 270 μmol) in MeOH, was added to a stirred solution of ligand **3** (195 mg, 270 μmol) in

MeOH (100 mL), and then maintained at 25 °C for 24 h. After the resultant deep purple solution was filtered with Celite, a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed on SiO₂ eluting with a H₂O/MeCN/sat. aq. KNO₃ (1:10:1; v/v/v) solvent mixture to afford (>50%) **4**, as a purple solid: m.p. > 400 °C; ¹H NMR (CD₃CN): δ 9.39 (s, 3',5'-tpyH, 5-ArH, 6H), 8.75 (d, *J* = 8.1 Hz, 3,3''-tpyH, 4H), 8.56 (d, *J* = 8.7 Hz, 3-ArH, 2H), 8.08 (d, *J* = 8.4 Hz, 2-ArH, 2H), 7.92 (dd, *J* = 7.8, 7.5 Hz, 4,4''-tpyH, 4H), 7.31 (d, *J* = 5.1 Hz, 6,6''-tpyH, 4H), 7.12 (dd, *J* = 6.6, 6.0 Hz, 5,5''-tpyH, 4H), 4.71 (t, *J* = 6.6 Hz, NCH₂, 2H), 2.09 (m, NCH₂CH₂, 2H), 1.49-1.38 (m, CH₂(CH₂)₃CH₃, 6H), 0.95 (t, *J* = 6.9 Hz, CH₃, 3H); ¹³C NMR (CD₃CN): δ 161.27, 159.35, 154.16, 152.57, 143.77, 139.74, 129.46, 128.35, 127.43, 125.03, 124.89, 122.59, 121.99, 112.14, 44.59, 32.44, 29.93, 27.68, 23.45, 14.42; UV/vis(CH₃CN): λ_{max} (ε) 239(9.65 × 10⁴), 285(1.25 × 10⁵), 319(1.08 × 10⁵), 573 nm(5.80 × 10⁴ dm³·mol⁻¹·cm⁻¹); ESI-MS: *m/z* 914.7 [M – 5PF₆⁻]⁵⁺(Calcd. *m/z* = 914.7), 702.8 [M – 4PF₆⁻ – 4PF₅⁻ + 2H]⁶⁺(Calcd. *m/z* = 702.8), 622.7 [M – 3PF₆⁻ – 4PF₅⁻]⁷⁺(Calcd. *m/z* = 622.8), 519.2 [M – 7PF₆⁻ – PF₅⁻]⁸⁺(Calcd. *m/z* = 519.7), 460.6 [M – PF₆⁻ – 8PF₅⁻]⁹⁺(Calcd. *m/z* = 460.6), 384.8 [M – 10PF₆⁻]¹⁰⁺(Calcd. *m/z* = 384.9).

[Ru₅(3**)₅][10PF₆⁻] (**5**).** To a stirred solution of **3** (131 mg, 180 μmol) in MeOH, RuCl₂·(DMSO)₄ (89 mg, 180 μmol) was added; the mixture was refluxed for 48 h. After cooling, the resultant deep red solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed on SiO₂ eluting with a combination of a H₂O/MeCN/sat. aq. KNO₃ (1:7:1; v/v/v) to afford (>35%) **10**, as a dark red solid: m.p. > 400 °C; ¹H NMR

(CD₃CN): δ 9.30 (s, 5-ArH, 2H), 9.24 (s, 3',5'-tpyH, 4H), 8.79 (d, $J = 8.1$ Hz, 3,3''-tpyH, 4H), 8.48 (d, $J = 8.4$ Hz, 3-ArH, 2H), 8.03-7.95 (m, 4,4''-tpyH, 2-ArH, 6H), 7.54 (d, $J = 5.0$ Hz, 6,6''-tpyH, 4H), 7.22 (dd, $J = 5.8, 5.7$ Hz, 5,5''-tpyH, 4H), 4.66 (t, $J = 6.1$ Hz, NCH₂, 2H), 2.07 (m, NCH₂CH₂, 2H), 1.49-1.26 [m, CH₂(CH₂)₃CH₃, 6H], 0.91 (t, $J = 6.9$ Hz, CH₃, 3H); ¹³C NMR (CD₃CN): δ 159.57, 156.58, 153.55, 150.22, 143.61, 139.08, 129.39, 128.55, 127.37, 125.63, 124.99, 122.42, 121.62, 112.05, 44.35, 32.44, 29.92, 27.67, 23.45, 14.41; UV/Vis (CH₃CN) λ_{\max} (ϵ) 237 (1.56×10^5), 285 (1.94×10^5), 308 (2.49×10^5), 504 nm (1.21×10^4 dm³·mol⁻¹·cm⁻¹); ESI-MS: m/z 545.7 [M - 8PF₆⁻]⁸⁺ (Calcd. $m/z = 545.6$), 644.4 [M - 7PF₆⁻]⁷⁺ (Calcd $m/z = 644.3$), 775.3 [M - 6PF₆⁻]⁶⁺ (Calcd. $m/z = 775.8$), 960.7 [M - 5PF₆⁻]⁵⁺ (Calcd. $m/z = 960.0$).

[Zn₅(3**)₅][10PF₆⁻] (**6**).** To a stirred solution of **3** (95 mg, 130 μ mol) in MeCN, Zn(BF₄)₂ · 8H₂O (51 mg, 130 μ mol) was added, then the mixture was refluxed for 48 h. After cooling, the resultant solution was filtered through Celite, then a slight excess of methanolic ammonium hexafluorophosphate was added to precipitate the complex, which was column chromatographed on Al₂O₃ eluting with a H₂O/MeCN/sat. aq. KNO₃ (1:7:1; v/v/v) solvent mixture to afford (>35 %) **10**, as a light-yellow solid: m.p. > 400 °C; ¹H NMR (CD₃CN): δ 9.24 (s, 5-ArH, 2H), 9.17 (s, 3',5'-tpyH, 4H), 8.84 (d, $J = 8.1$ Hz, 3,3''-tpyH, 4H), 8.45 (d, $J = 8.4$ Hz, 3-ArH, 2H), 8.20 (dd, $J = 7.8, 7.8$ Hz, 4,4''-tpyH, 4H), 8.02 (d, $J = 8.7$ Hz, 2-ArH, 2H), 7.93 (d, $J = 4.2$ Hz, 6,6''-tpyH, 4H), 7.43 (dd, $J = 5.4, 5.4$ Hz, 5,5''-tpyH, 4H), 4.66 (t, $J = 6.1$ Hz, NCH₂, 2H), 2.07 (m, NCH₂CH₂, 2H), 1.52-1.31 [m, CH₂(CH₂)₃CH₃, 6H], 0.92 (t, $J = 7.2$ Hz, CH₃, 3H); ¹³C NMR (CD₃CN): δ 158.23, 150.83, 149.22, 149.10, 144.07, 142.03, 128.82, 128.54, 127.65, 124.90, 124.24, 122.24, 122.23, 112.18, 42.07, 32.41, 29.89, 27.63, 23.43, 14.39; UV/Vis (CH₃CN) λ_{\max}

(ϵ) 240 (2.64×10^5), 285 (2.50×10^5), 316 (1.79×10^5), 398 nm ($1.29 \times 10^5 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$); ESI-MS: m/z 924.3 [$\text{M} - 5\text{PF}_6^-$] $^{5+}$ (Calcd $m/z = 924.2$), 745.2 [$\text{M} - 6\text{PF}_6^-$] $^{6+}$ (Calcd $m/z = 746.0$), 466.0 [$\text{M} - 8\text{PF}_6^- - \text{PF}_5^-$] $^{9+}$ (Calcd $m/z = 465.9$), 389.8 [$\text{M} - 10\text{PF}_6^-$] $^{10+}$ (Calcd $m/z = 389.6$).

Fabrication of the photovoltaic cell devices. Nanocrystalline semiconductor TiO_2 electrodes were prepared applying a 4V d.c. potential difference across a stainless steel sheet (anode) and an ITO conducting glass plate (cathode)¹ for 40s in a colloidal suspension containing 0.5g P25 TiO_2 powder (Degussa, nominal particle diameter 21nm) per each 10mL of 5% 2-propanol in water (v/v). These electrodes were then taken out from the electrophoretic apparatus and sintered at 450 °C in air for 30 min. According to RAMAN spectroscopy studies, an anatase phase was mainly exhibited by these oxide surfaces, while an average thickness value of 2 μm and a roughness factor of 80 were estimated by profilometry and cyclic voltammetry, respectively. Surface confinement of the relevant dyes, was carried out by dipping the electrode for 12h in a MeCN solution (0.2mM). Photovoltaic devices were assembled in a sandwich arrangement², using a sensitized nanocrystalline semiconductor electrode as a photo anode pressed with a Ti plate covered with a film of colloidal graphite as cathode, both of them separated by a Teflon™ tape (0.5mm gap) in order to avoid electrical contact. An electrolytic solution of carbonate propylene containing 20% carbonate ethylene (w/v) + 0.3M KI + 0.015M I_2 was previously incorporated between the two electrodes.³ Discharge experiments were carried out using a 1.5 mW cm^{-2} incident light source and a variable resistance, as described by Cherepy et al.⁴

References

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