Supporting Information

Ru complexes of thienyl-functionalized dipyrrins as NCS-free sensitizers for the dye-sensitized solar cell

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Experimental Section

All reactions were performed in an inert (N_2) atmosphere using standard Schlenk techniques, unless noted otherwise. All reagents were purchased from Aldrich, except for $RuCl_3\cdot3H_2O$ (Pressure Chemical Company), pyrrole (Alfa Aesar), and α-phellandrene (TCI), and they were used as received, except for pyrrole which was distilled prior to use. 5-(2-thienyl)-4,6-dipyrromethane, 4,4′-bis(methoxycarbonyl)-2,2′-bipyridine (dcmb), [(*p*-cymene)$RuCl_2$]$_2$, 2, 2′-bithiophene-5-carbaldehyde and 5′-hexyl-[2,2′]-bithiophene-5-carbaldehyde were prepared according to published procedures. Anhydrous commercial solvents were additionally purified by passing through a double-stage drying/purification system (Glass Contour Inc.). ^1H nuclear magnetic resonance (NMR) spectra were measured on Bruker 600 MHz spectrometer. Chemical shifts were referenced to the signals of residual protons in deuterated solvents (7.26 ppm in $CDCl_3$ and 3.31 ppm in CD_3OD).[28] Electrospray ionization (ESI) mass spectra were acquired on a Beckman Coulter System Gold HPLC BioEssential with Binary Gradient 125S pump and a UV/Vis 166 analytical detector. Electronic absorption (UV-Vis) spectra were collected in the 200-1000 nm range on a Perkin Elmer Lambda 950 UV/Vis/NIR spectrophotometer. Cyclic voltammograms (CV) were recorded on a CH Instruments 600D electrochemical analyzer at the sweep rate of 0.100 $V\cdot s^{-1}$, with 0.100 M $(TBA)PF_6$ electrolyte solution (TBA = tetrabutylammonium), Pt working electrode, and Ag^+(0.01 M $AgNO_3$)/Ag reference electrode. All the potentials initially were referenced to the standard Fc^+/Fc couple (Fc = ferrocene). Fc was added as an internal standard upon completion of each CV experiment. The obtained redox potentials were subsequently converted to the normal hydrogen electrode (NHE), assuming that the Fc^+/Fc couple has a redox potential of +0.630 V vs. NHE in acetonitrile/DMF.[29] Spectroelectrochemical measurements were performed on a CARY 50 Bio UV-Visible spectrophotometer, using a commercial thin-layer cell with a Pt mesh electrode (BASi). The spectra were collected for various applied potentials after reaching redox equilibrium at each specific potential value. Elemental analyses were performed by Atlantic Microlab Inc. (Atlanta, GA).

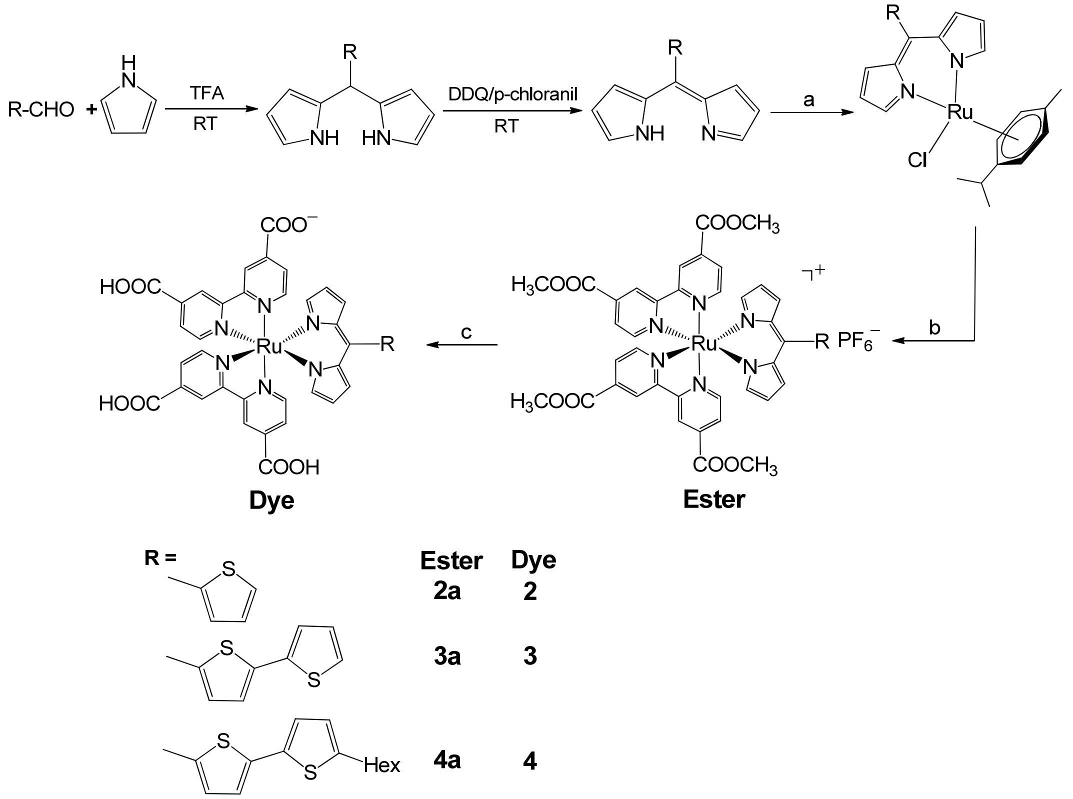
Cell Fabrication. Photoanodes were prefabricated by Dyesol, Inc. (Australia) with a screen-printable TiO_2 pastes (18-NRT, Dyesol™). The active area of the TiO_2 electrode is 0.88 cm^2 with a thickness of 12 μm (18-NRT) on fluorine-doped tin-oxide (FTO; TEC15 (15 Ω cm^{-2})). TiO_2 substrates were treated with $TiCl_{4(aq)}$ (0.05 M) at 70 °C for 30 min and subsequently rinsed with H_2O and dried prior to heating. The electrodes were heated to 450 °C for 20 min under ambient atmosphere and allowed to cool to 80 °C before dipping into the dye solution. The anode was soaked overnight for 16 h in a MeOH solution containing dye **2** (~0.25 mM) or ABS EtOH for N3. The stained films were rinsed copiously with the solvent they were dipped in and subsequently dried. The cells were fabricated using a Pt-coated counter-electrode (FTO TEC-15 (15 Ω cm^{-2}))

and sandwiched with a 30 µm Surlyn (Dupont) gasket by resistive heating. An acetonitrile electrolyte solution: A (1.0 M 1,3-dimethylimidazolium iodide (DMII), 0.06M I_2, 0.1M LiI and 0.1M guanidinium thiocyanate (GuSCN), B (1.0 M DMII, 0.06 M I_2, 0.3 M LiI and 0.1 M GuSCN), C (1.0 M DMII, 0.06 M I_2, 0.5 M LiI and 0.1 M GuSCN), D (1.0 M DMII, 0.06 M I_2, 1.0 M LiI and 0.1 M GuSCN), E (1.0 M LiI, 0.06 M I_2), F (1.0 M LiI, 0.06 M I_2, 0.5 M 4-tertbutylpyridine (^{t}BP)), G (1.0 M LiI, 0.06 M I_2, 0.1 M ^{t}BP), H (2.0 M LiI, 0.06 M I_2, 0.5 M ^{t}BP), I (2.0 M LiI, 0.06 M I_2, 1.0 M ^{t}BP) was introduced to the void via vacuum backfilling through a hole in the counter electrode. The hole was sealed with an aluminum-backed Bynel foil (Dyesol™). After sealing, silver bus bars were added to all cells.

Cell Characterization. Photovoltaic measurements were recorded with a Newport Oriel solar simulator (Model 9225A1) equipped with a class A 150 W xenon light source powered by a Newport power supply (Model 69907). The light output (area = 5 cm × 5 cm) was calibrated to AM1.5 using a Newport Oriel correction filter to reduce the spectral mismatch in the region of 350-700 nm to less than 1.5%. The power output of the lamp was measured to 1 Sun (100 mW cm^{-2}) using a certified Si reference cell. The current-voltage (I–V) characteristic of each cell was obtained by applying an external potential bias to the cell and measuring the generated photocurrent with a Keithley digital source meter (Model 2400). All cells were measured with a mask size of 0.88 cm^2. IPCE measurements were performed on a QEX7 Solar Cell Spectral Response Measurement System from PV Instruments, Inc. The system was calibrated with a photodiode that was calibrated against NIST standard I755 with transfer uncertainty less than 0.5% between 400-1000 nm and less than 1% at all other wavelengths. All measurements were made in AC mode at 4 Hz chopping frequency under a bias light between 0.01 to 0.1 Sun. The system was calibrated and operated in Beam Power mode.

Syntheses

2,2′-bithiophene-5-dipyrromethane. 6 mL of pyrrole was added to 2,2′-bithiophene-5-carbaldehyde (400 mg, 2.06 mmol) in a 50 mL Schlenk flask. The solution was degassed for 15 min, and 84 µL of TFA was added. The mixture was left to stir at RT for 1 h, after which time 30 mL of CH_2Cl_2 was added, and the mixture was washed with water (3×30 mL). The organic phase was collected and dried over anhydrous $MgSO_4$. The volatiles were removed under reduced pressure, and the crude product was loaded on a silica gel column (4 cm × 18 cm). The separation was achieved using CH_2Cl_2 : hexane eluent (1:1 *v/v*) . The first fraction (R_f = 0.26) was collected and evaporated to dryness to afford 1.151 g of brownish oil (yield = 84%). *^{1}H NMR* ($CDCl_3$, 600 MHz), δ, ppm: 8.02 (s, 2H), 7.18 (d, 1H, *J* = 5.2 Hz), 7.10 (d, 1H, *J* = 3.7 Hz), 7.02 (d, 1H, *J* = 3.6 Hz), 6.99 (dd, 1H, *J* = 5.0, 3.6 Hz), 6.80 (d, 1H, *J* = 3.4 Hz), 6.73-6.72 (m, 2H), 6.19 (q, 2H, *J* = 3.0 Hz), 6.10 (d, 2H, *J* = 3.2 Hz), 5.71 (s, 1H). *^{13}C NMR* ($CDCl_3$, 151 MHz), δ, ppm: 145.0, 137.5, 136.8, 131.7, 127.9, 126.4, 124.4, 123.7, 123.4, 117.7, 108.7, 107.3, 39.5.



Scheme 1. Synthesis of **2-4** and **2a-4a**: (a) [(p-cymene)RuCl$_2$]$_2$, NEt$_3$, MeCN, reflux, overnight; (b) dcmb, AgNO$_3$, NH$_4$PF$_6$, MeOH, reflux, 16h; (c) NEt$_3$: H$_2$O : DMF = 1:1:3 (*v*:*v*:*v*), reflux, 18h.

5′-hexyl-[2, 2′]-bithiophene-5-dipyrromethane. This compound was prepared in a fashion similar to that described above for 2, 2′-bithiophene-5-dipyrromethane, using 5′-hexyl-[2,2′]-bithiophene-5-carbaldehyde (962 mg, 3.46 mmol) as starting material. Yield = 84%. ^{1}*H NMR* (CDCl$_3$, 600 MHz), δ, ppm: 8.01 (s, 2H), 6.93 (d, 1H, *J* = 3.5 Hz), 6.89 (d, 1H, *J* = 3.4 Hz), 6.76 (d, 1H, *J* = 3.5 Hz), 6.72 (s, 2H), 6.64 (d, 1H, *J* = 3.3 Hz), 6.18 (d, 2H, *J* = 3.0 Hz), 6.08 (s, 2H), 5.69 (s, 1H), 2.77 (t, 2H, *J* = 7.7 Hz), 1.65 (q, 2H, *J* = 7.6 Hz), 1.38-1.36 (m, 2H), 1.34 – 1.27 (m, 4H), 0.92 – 0.84 (m, 3H). ^{13}*C NMR* (CDCl$_3$, 151 MHz), δ, ppm: 145.5, 144.2, 137.4, 134.9, 131.8, 126.3, 124.8, 123.3, 122.6, 117.6, 108.7, 107.3, 39.5, 31.71, 31.69, 30.3, 28.9, 22.7, 14.2.

[(p-cymene)Ru(2-TDP)Cl]. A solution of DDQ (866 mg, 3.82 mmol) in 10 mL of anhydrous THF was added dropwise to a solution of 2-thienyl-dipyrromethane (870 mg, 3.81 mmol) in 20 mL of anhydrous THF. The mixture was stirred at RT for 4 h, followed by filtration through a medium frit. The filtercake and [(p-cymene)RuCl$_2$]$_2$ (1.17 g, 1.911 mmol) were combined in a 100 mL Schlenk flask, and 1 mL of Et$_3$N and 50 mL of anhydrous MeCN were added sequentially. The mixture was refluxed overnight under N$_2$. After cooling down to RT, the reaction mixture was filtered through Celite. The filtrate was evaporated to dryness under reduced pressure and loaded on a silica column (4 cm × 20 cm). The separation was achieved using CH$_2$Cl$_2$:MeOH eluent (50:1 v/v). A bright-red fraction (R_f = 0.54) was collected and evaporated to dryness, affording 1.316 g of red solid (yield = 70%). *^{1}H NMR* ($CDCl_3$, 600 MHz), δ, ppm: 8.00 (t, 2H, *J* = 1.4 Hz), 7.45 (dd, 1H, *J* = 5.1, 1.3 Hz), 7.24 (dd, 1H, *J* = 3.5, 1.3 Hz), 7.09 (dd, 1H, *J* = 5.1, 3.5 Hz), 6.92 (dd, 2H, *J* = 4.4, 1.3 Hz), 6.49 (dd, 2H, *J* = 4.5, 1.5 Hz), 5.29 – 5.25 (m, 4H), 2.40 (sep, 1H, *J* = 6.9 Hz), 2.21 (s, 2H), 1.07 (d, 6H, *J* = 6.9 Hz). *^{13}C NMR* ($CDCl_3$, 151 MHz), δ, ppm: 155.4, 139.0, 138.4, 135.6, 131.3, 130.6, 127.1, 126.5, 118.6, 102.5, 100.4, 84.9, 84.8, 31.0, 30.7, 22.2, 18.7. *ESI-HRMS*: *m/z* = 461.06247 (calcd. for $[(p\text{-cymene})Ru(2\text{-}TDP)]^+$: 461.06254).

[(p-cymene)Ru(BTDP)Cl]. A solution of *p*-chloranil (135 mg, 0.55 mmol) in 10 mL of anhydrous THF was added dropwise to a solution of 2,2′-bithiophene-5-dipyrromethane (168 mg, 0.54 mmol) in 10 mL of anhydrous THF. The reaction was stirred for 4 h at RT, after which time the solvent was evaporated to dryness. The obtained product was added to a 100 mL Schlenk flask charged with $[(p\text{-cymene})_2RuCl_2]_2$ (168 mg, 0.27 mmol), followed by 1 mL of Et_3N and 25 mL of anhydrous MeCN. The mixture was refluxed overnight. After cooling to RT, the solvent was evaporated to dryness under reduced pressure. The crude product was loaded on a silica column (2.5 cm × 20 cm) and eluted with a CH_2Cl_2:MeOH mixture (50 : 1, v/v). A bright-red fraction (R_f = 0.57) was collected and evaporated to dryness to afford 273 mg of red solid (yield = 87%). *^{1}H NMR* ($CDCl_3$, 600 MHz), δ, ppm: 8.01 (s, 2H), 7.22 (d, 1H, *J* = 3.6 Hz), 7.17 (q, 2H, *J* = 3.7 Hz), 7.05-7.03 (m, 3H), 6.52 (d, 2H, *J* = 4.4 Hz), 5.29 – 5.25 (m, 4H), 2.42 (sep, 1H, *J* = 7.1 Hz), 2.22 (s, 3H), 1.08 (d, 6H, *J* = 6.9 Hz). *^{13}C NMR* ($CDCl_3$, 151 MHz), δ, ppm: 155.5, 139.5, 138.4, 137.3, 136.9, 135.4, 131.6, 131.2, 128.1, 125.1, 124.3, 123.3, 118.7, 102.5, 100.4, 84.9, 84.8, 31.1, 30.7, 22.3, 18.7. *ESI-HRMS*: *m/z* = 543.05044 (calcd. for $[(p\text{-cymene})Ru(BTDP)]^+$: 543.05026).

[(p-cymene)Ru(5-HBTDP)Cl]. The complex was prepared in a fashion similar to that described above for [(p-cymene)Ru(5-HBTDP)Cl], using 5′-hexyl-[2,2′]-bithiophene-5-dipyrromethane (205 mg, 0.52 mmol) and *p*-chloranil (130 mg, 0.53 mmol) as starting materials. The crude product obtained was passed through a silica gel column (2.5 cm × 20 cm) using CH_2Cl_2:MeOH eluent (100:1, v/v). A bright-red fraction (Rf = 0.38) was collected and evaporated to dryness, affording 290 mg of red solid (yield = 84%). *^{1}H NMR* ($CDCl_3$, 600 MHz), δ, ppm: 8.00 (s, 2H), 7.14 (d, 1H, *J* = 3.7 Hz), 7.09 (d, 1H, *J* = 3.8 Hz), 7.05 (d, 2H, *J* = 4.4 Hz), 7.03 (d, 1H, *J* = 3.4 Hz), 6.70 (d, 1H, *J* = 3.4 Hz), 6.51 (d, 2H, *J* = 4.5 Hz), 5.28 – 5.24 (m, 4H), 2.80 (t, 2H, *J* = 7.6 Hz), 2.40 (sep, 1H, *J* = 6.9 Hz), 2.21 (s, 3H), 1.69 (p, 2H, *J* = 7.6 Hz), 1.41-1.36 (m, 2H), 1.34 – 1.29 (m, 4H), 1.07 (d, 6H, *J* = 6.9 Hz), 0.93 – 0.87 (m, 3H). *^{13}C NMR* ($CDCl_3$, 151 MHz), δ, ppm: 155.4, 146.3, 140.2, 138.6, 136.5, 135.4, 134.2, 131.6, 131.2, 125.1, 124.0, 122.5, 118.6, 102.4, 100.4, 84.9, 84.8, 31.7, 30.7, 30.3, 28.8, 22.7, 22.2, 18.7, 14.2. *ESI-HRMS*: *m/z* = 627.14569 (calcd. for $[(p\text{-cymene})Ru(5\text{-}HBTDP)]^+$: 627.14416).

$[Ru(dcmb)_2(2\text{-}TDP)]PF_6$ (2a). A 100 mL Schlenk flask containing [(p-cymene)Ru(2-TDP)Cl] (150 mg, 0.30 mmol), dcmb (206 mg, 0.76 mmol), $AgNO_3$ (60 mg, 0.35 mmol), and 30 mL of anhydrous MeOH was heated at reflux for 14 h under reduced light. After that time, the heating was suspended and the reaction mixture was concentrated to ~5 mL and filtered through a fine porosity frit to remove the remaining dcmb and precipitated AgCl. To the filtrate was added 2 mL of a methanolic solution of NH_4PH_6 (148 mg, 0.90 mmol), and the mixture was stirred vigorously at RT for 1 h to complete the anion exchange. The solid that formed was recovered by filtration through a medium porosity frit, washed with diethyl ether (3 × 10 mL), and dried in vacuo to afford 243 g of black powder (yield = 79%). *^{1}H NMR* ($CDCl_3$, 600 MHz), δ, ppm: 8.90 (d, 2H, *J* = 1.3 Hz), 8.88 (d, 2H, *J* = 1.3 Hz), 8.00 (d, 2H, *J* = 6.1 Hz), 7.96 (d, 2H, *J* = 5.6 Hz), 7.90 (ddd, 4H, *J* = 9.0, 5.9, 1.7 Hz), 7.50 (dd, 1H, *J* = 5.1, 1.2 Hz), 7.25 (dd, 1H, *J* = 3.5, 1.2 Hz), 7.12 (dd, 1H, *J* = 5.1, 3.5 Hz), 6.95 (dd, 2H, *J* = 4.4, 1.2 Hz), 6.30 (dd, 2H, *J* = 4.5, 1.5 Hz), 6.27 – 6.25 (m, 2H), 4.04 (s, 6H), 4.00 (s, 6H). *^{13}C NMR* ($CDCl_3$, 151 MHz), δ, ppm: 164.13, 164.11, 158.2, 157.4, 152.6, 152.4, 149.5, 140.2, 138.7, 137.7, 137.2, 136.2, 132.8, 131.0, 127.5, 126.8, 126.5, 126.0, 123.2, 122.8, 119.0, 53.55, 53.48. *ESI-HRMS*: *m/z* = 871.11370 (calcd. for $[Ru(dcmb)_2(2\text{-}TDP)]^+$: 871.11241). *Elem. anal.* Calcd. (found) for $RuSPF_6O_{8.5}N_6C_{41}H_{34}$ (**2a**·$0.5H_2O$) (%): C, 48.05 (47.97); H, 3.34 (3.32); N, 8.20 (8.37).

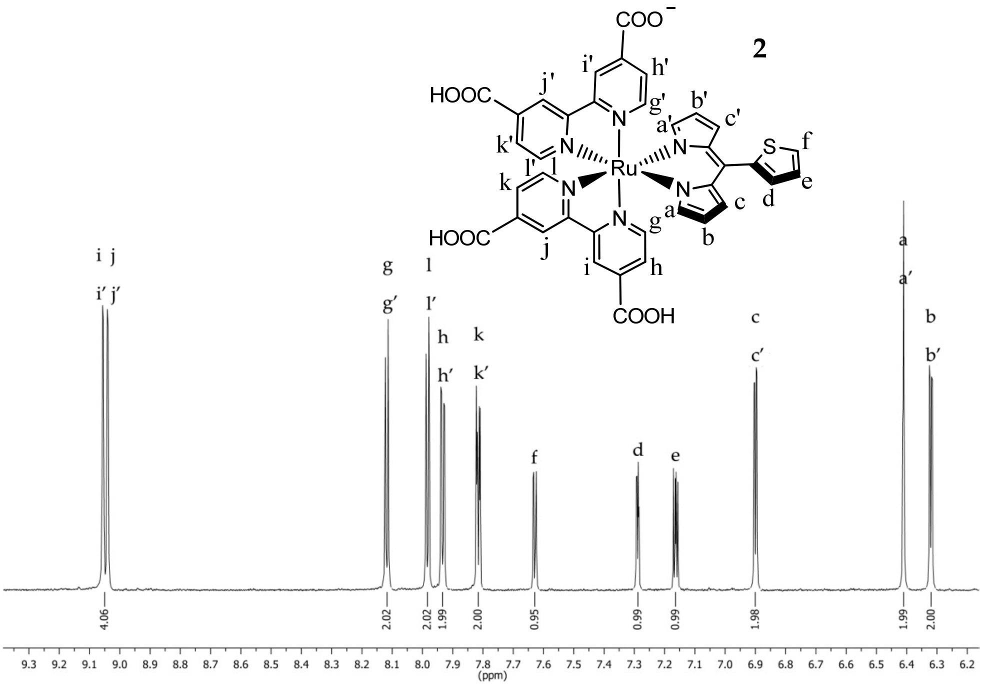
$[Ru(dcmb)_2(BTDP)]PF_6$ (3a). The complex was prepared in a fashion similar to that described above for **2a**, using [(p-cymene)Ru(BTDP)Cl] (173 mg, 0.30 mmol) as starting material. Yield = 80%. *^{1}H NMR* ($CDCl_3$, 600 MHz), δ, ppm: 8.91 (d, 2H, *J* = 1.1 Hz), 8.88 (d, 2H, *J* = 1.1Hz), 7.99 – 7.96 (m, 4H), 7.92 – 7.89 (m, 4H), 7.28 (dd, 1H, *J* = 5.2, 1.0 Hz), 7.22 (dd, 1H, *J* = 3.6, 1.0 Hz), 7.20 (d, 1H, *J* = 3.7 Hz), 7.18 (d, 1H, *J* = 3.7 Hz), 7.10 (dd, 2H, *J* = 4.5, 1.1 Hz), 7.05 (dd, 1H, *J* = 5.1, 3.6 Hz), 6.33 (dd, 2H, *J* = 4.5, 1.5 Hz), 6.28 – 6.26 (m, 2H), 4.05 (s, 6H), 4.01 (s, 6H). *^{13}C NMR* ($CDCl_3$, 151 MHz), δ, ppm: 164.1, 158.2, 157.4, 152.6, 152.4, 149.6, 140.0, 139.6, 137.7, 137.4, 137.2, 136.6, 136.0, 132.6, 131.9, 128.2, 126.9, 126.0, 125.4, 123.2, 123.2, 122.9, 119.1, 53.6, 53.5. *ESI-HRMS*: *m/z* = 953.10251 (calcd. for $[Ru(dcmb)_2(BTDP)]^+$: 953.10013). *Elem. anal.* Calcd. (found) for $RuS_2PF_6O_{8.5}N_6C_{45}H_{36}$ (**3a**·$0.5H_2O$) (%): C, 48.83 (49.04); H, 3.28 (3.28); N, 7.59 (7.39).

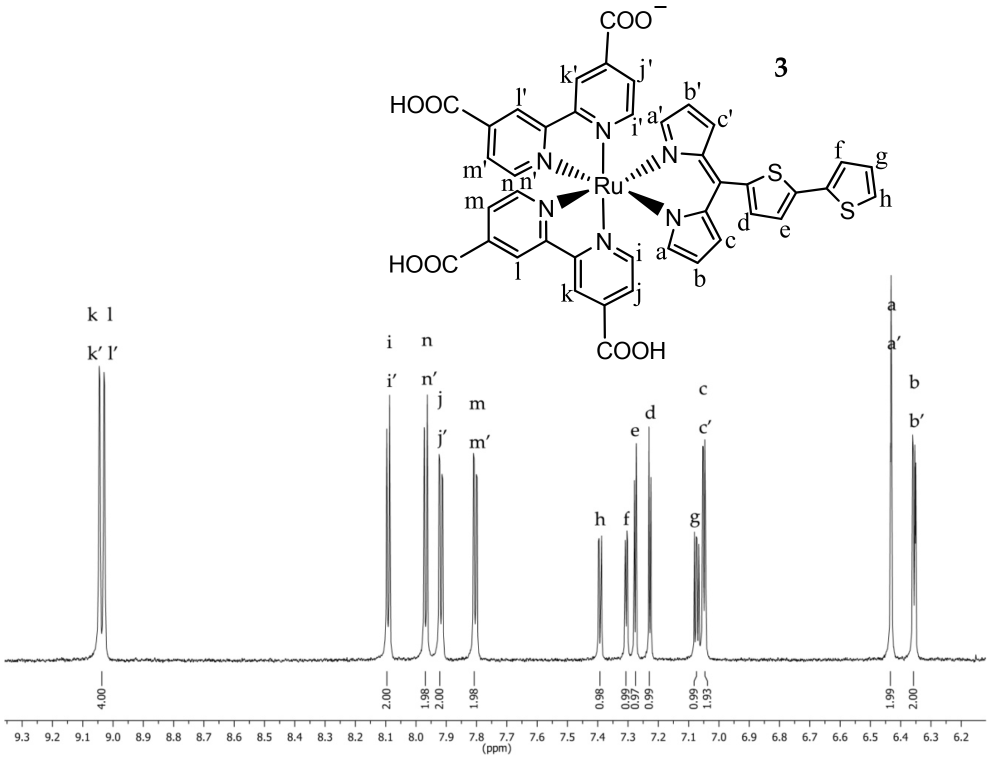
$[Ru(dcmb)_2(5\text{-}HBTDP)]PF_6$ (4a). The complex was prepared in a fashion similar to that described above for **2a**, using [(p-cymene)Ru(5-HBTDP)Cl] (178 mg, 0.27 mmol) as starting material. Yield = 72%. *^{1}H NMR* ($CDCl_3$, 600 MHz), δ, ppm: 8.90 (d, 2H, *J* = 1.6 Hz), 8.88 (d, 2H, *J* = 1.9 Hz), 7.97 (d, 4H, *J* = 5.9 Hz), 7.90 (ddd, 4H, *J* = 6.0, 4.5, 1.7 Hz), 7.15 (d, 1H, *J* = 3.7 Hz), 7.13 – 7.09 (m, 3H), 7.03 (d, 1H, *J* = 3.6 Hz), 6.71 (d, 1H, *J* = 3.5 Hz), 6.32 (dd, 2H, *J* = 4.5, 1.5 Hz), 6.27-7.26 (m, 2H), 4.05 (s, 6H), 4.01 (s, 6H), 2.81 (t, 2H, *J* = 7.6 Hz), 1.69 (p, 2H, *J* = 7.6 Hz), 1.41 – 1.36 (m, 2H), 1.34 – 1.29 (m, 4H), 0.89 (t, 3H, *J* = 6.9Hz). *^{13}C NMR* ($CDCl_3$, 151 MHz), δ, ppm: 164.1, 158.2, 157.4, 152.6, 152.4, 149.4, 146.6, 140.7, 139.8, 137.7, 137.1, 136.6, 136.0, 133.9, 132.7, 132.0, 126.8, 126.0, 125.2, 124.2, 123.2, 122.9, 122.4, 119.1, 53.6, 53.5, 31.7, 30.4, 28.9, 22.7, 14.2. *ESI-HRMS*: *m/z* = 1037.19115 (calcd. for $[Ru(dcmb)_2(5\text{-}HBTDP)]^+$: 1037.19403). *Elem. anal.* Calcd. (found) for $RuS_2PF_6O_{8.5}N_6C_{51}H_{48}$ (**4a**·$0.5H_2O$) (%): C, 51.43 (51.22); H, 4.06 (4.09); N, 7.06 (7.06).

[Ru(H_2dcbpy)(Hdcbpy)(2-TDP)] (2). A solution containing [Ru(dcmb)$_2$(2-TDP)]PF_6 (40 mg, 0.04 mmol), 3 mL of Et_3N, 3 mL of H_2O, and 9 mL of DMF was heated at reflux for 18 h. After cooling down to RT, the mixture was evaporated to dryness under reduced pressure, and 30 mL of CH_2Cl_2 was added to remove unreacted starting materials and byproducts. The obtained product was washed with diethyl ether and dried in vacuo, affording 28 mg of black solid (yield = 74%). *^{1}H NMR* (CD_3OD, 600 MHz), δ, ppm: 9.05 (dd, 4H, *J* = 9.3, 1.7 Hz), 8.12 (d, 2H, *J* = 5.9 Hz), 7.98 (d, 2H, *J* = 5.8 Hz), 7.93 (dd, 2H, *J* = 5.9, 1.8 Hz), 7.82 (dd, 2H, *J* = 5.8, 1.7 Hz), 7.63 (dd, 1H, *J* = 5.2, 1.4 Hz), 7.29 (dd, 1H, *J* = 3.7, 1.4 Hz), 7.16 (dd, 1H, *J* = 5.2, 3.5 Hz), 6.90 (dd, 2H, *J* = 4.5, 1.4 Hz), 6.43 – 6.40 (m, 2H), 6.32 (dd, 2H, *J* = 4.4, 1.6 Hz). *ESI-HRMS*: *m/z* = 815.04800 (calcd. for [Ru(H_2dcbpy)$_2$(2-TDP)]$^+$: 815.04981). *Elem. anal.* Calcd. (found) for $RuSO_{12}N_6C_{37}H_{32}$ (**2**·4H_2O) (%): C, 50.17 (49.91); H, 3.64 (3.47); N, 9.49 (9.41).

[Ru(H_2dcbpy)(Hdcbpy)(BTDP)] (3). The dye was prepared in a fashion similar to that described above for **2**, using **3a** (120 mg, 0.11 mmol) as starting material. Yield = 76%. *^{1}H NMR* (CD_3OD, 600 MHz), δ, ppm: 9.04 (dd, 4H, *J* = 9.4, 1.6 Hz), 8.09 (d, 2H, *J* = 6.0 Hz), 7.97 (d, 2H, *J* = 5.9 Hz), 7.92 (dd, 2H, *J* = 5.8, 1.7 Hz), 7.80 (dd, 2H, *J* = 5.8, 1.7 Hz), 7.39 (dd, 1H, *J* = 5.3, 1.2 Hz), 7.31 (dd, 1H, *J* = 3.6, 1.0 Hz), 7.28 (d, 1H, *J* = 3.7 Hz), 7.23 (d, 1H, *J* = 3.7 Hz), 7.09 – 7.06 (m, 1H), 7.05 (dd, 2H, *J* = 4.5, 1.3 Hz), 6.45 – 6.41 (m, 2H), 6.36 (dd, 2H, *J* = 4.5, 1.5 Hz). *ESI-HRMS*: *m/z* = 897.03742 (calcd. for [Ru(H_2dcbpy)$_2$(BTDP)]$^+$: 897.03753). *Elem. anal.* Calcd. (found) for $RuS_2O_{11}N_6C_{41}H_{32}$ (**3**·3H_2O) (%): C, 51.84 (52.25); H, 3.40 (3.35); N, 8.85 (9.00).

[Ru(H_2dcbpy)(Hdcbpy)(5-HBTDP)] (4). The dye was prepared in a fashion similar to that described above for **2**, using **4a** (77 mg, 0.065 mmol) as starting material. Yield = 75%. *^{1}H NMR* (CD_3OD, 600 MHz), δ, ppm: 9.08 – 9.04 (dd, 4H, *J* = 9.4, 1.6 Hz), 8.11 (d, 2H, *J* = 5.9 Hz), 7.99 (d, 2H, *J* = 5.8 Hz), 7.95 (dd, 2H, *J* = 5.9, 1.6 Hz), 7.82 (dd, 2H, *J* = 5.9, 1.6 Hz), 7.20 (q, 2H, *J* = 3.7 Hz), 7.10 (d, 1H, *J* = 3.5 Hz), 7.06 (dd, 2H, *J* = 4.4, 1.1 Hz), 6.76 (d, 1H, *J* = 3.6 Hz), 6.44-6.42 (m, 2H), 6.36 (dd, 2H, *J* = 4.5, 1.5 Hz), 2.83 (t, 2H, *J* = 7.5 Hz), 1.70 (p, 2H, *J* = 7.6 Hz), 1.48 – 1.37 (m, 2H), 1.38 – 1.31 (m, 4H), 0.96 – 0.89 (m, 3H). *ESI-HRMS*: *m/z* = 981.13620 (calcd. for [Ru(H_2dcbpy)$_2$(5-HBTDP)]$^+$: 981.13143). *Elem. anal.* Calcd. (found) for $RuS_2O_{11}N_6C_{47}H_{44}$ (**4**·3H_2O) (%): C, 54.49 (54.32); H, 4.29 (4.15); N, 8.13 (8.07).


2
COO⁻
HOOC
HOOC
COOH
Ru
S
i j
i′ j′
g
g′
l
l′
h
h′
k
k′
f
d
e
c
c′
a
a′
b
b′
4.06
2.02
2.02
1.99
2.00
0.95
0.99
0.99
1.98
1.99
2.00
9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2
(ppm)


3
COO⁻
HOOC
HOOC
COOH
Ru
S
S
k l
k′ l′
i
i′
n
n′
j
j′
m
m′
h
f
e
d
g
c
c′
a
a′
b
b′
4.00
2.00
1.98
2.00
1.98
0.98
0.99
0.97
0.99
0.99
1.93
1.99
2.00
9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2
(ppm)

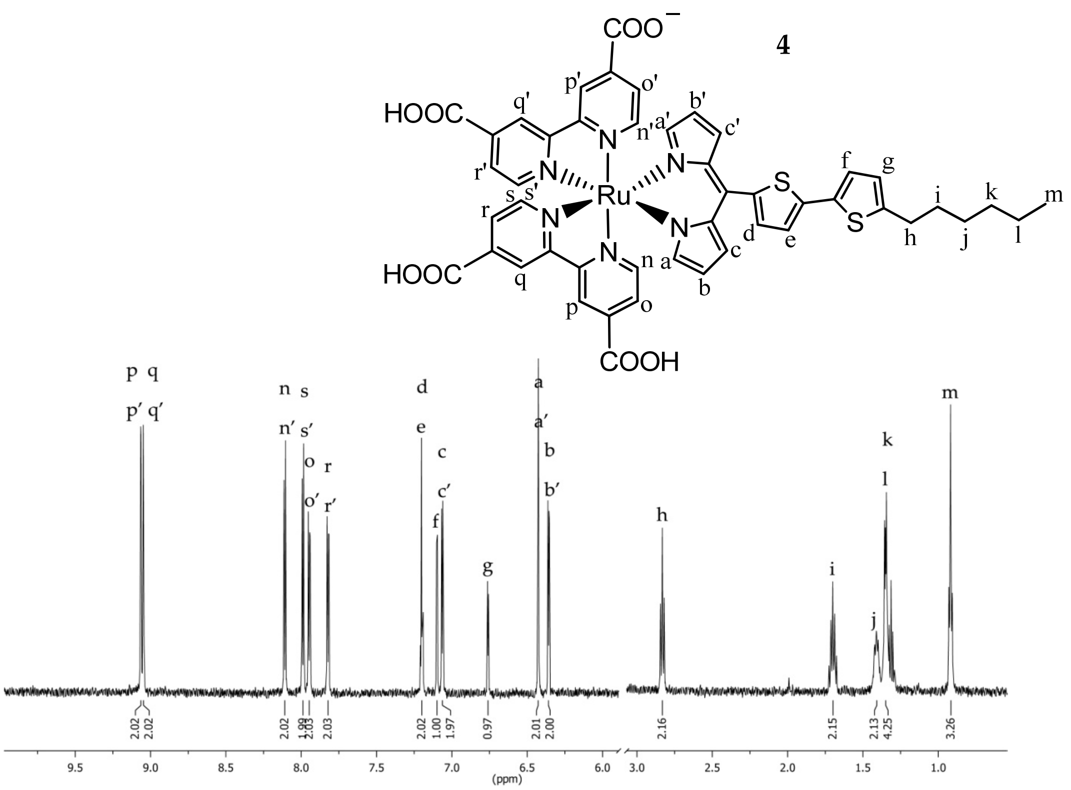

4
COO⁻
HOOC
HOOC
COOH
Ru
S
S
p q
p′ q′
n s
n′ s′
o r
o′ r′
d
e
c
c′
f
g
a
a′
b
b′
h
i
j
k
l
m
2.02
2.02
2.02
2.03
2.03
2.02
1.00
1.97
0.97
2.01
2.00
2.16
2.15
2.13
4.25
3.26
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
3.0
2.5
2.0
1.5
1.0
(ppm)

Table S1. Energies and composition (%) of frontier molecular orbitals for **2**.

Orbital	Energy, eV	Ru	2-TDP	bpy
LUMO+5	-2.31	0.7	4.8	94.5
LUMO+4	-2.56	2.8	0.1	97.1
LUMO+3	-2.58	0.7	0.0	99.3
LUMO+2	-2.73	1.3	92.9	5.9
LUMO+1	-3.13	8.5	0.4	91.1
LUMO	-3.20	3.9	1.0	95.1
HOMO	-5.89	0.5	99.2	0.3
HOMO-1	-6.00	66.2	25.2	8.6
HOMO-2	-6.06	62.0	28.6	9.4
HOMO-3	-6.34	76.2	6.0	17.8
HOMO-4	-6.75	0.1	99.9	0.0

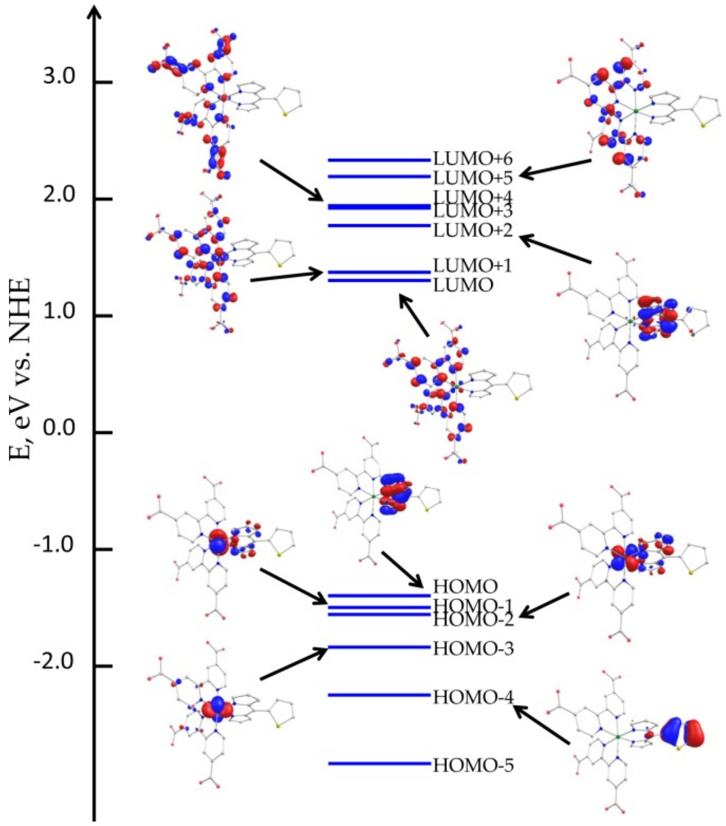


Figure S1. Frontier molecular orbitals of **2**. Hydrogen atoms have been omitted for the sake of clarity. All energies have been converted to the NHE scale assuming that the NHE potential is −4.5 V vs vacuum level.

Table S2. Spin-allowed absorption bands calculated for **2**.[a]

Wavelength, nm	Oscillator strength	Excitation
620.1	0.0006	H-1→L+1(+91%)
615.7	0.0077	H-1→L+0(+90%) H-2→L+1(5%)
588.9	0.026	H-2→L+1(+81%) H-3→L+0(+7%)
577.8	0.0027	H-2→L+0(+82%) H-3→L+1(+8%)
573.2	0.0085	H-0→L+0(+92%) H-2→L+1(6%)
513.2	0.1327	H-3→L+0(+87%) H-2→L+1(5%)
487.8	0.0859	H-3→L+1(+56%) H-2→L+2(26%)
467.1	0.0182	H-2→L+2(+66%) H-1→L+4(21%)
444.6	0.0376	H-1→L+3(+81%) H-2→L+4(+16%)
441.4	0.0326	H-3→L+2(+81%) H-0→L+2(+15%)
437.6	0.011	H-0→L+3(+93%)
435.4	0.1121	H-2→L+4(+72%) H-1→L+3(15%)
420	0.1538	H-0→L+2(+54%) H-0→L+5(27%)
410.7	0.0262	H-1→L+5(+96%)
400.6	0.0236	H-2→L+5(+75%) H-3→L+4(21%)
396.7	0.0173	H-3→L+3(+83%) H-0→L+5(+13%)
392.1	0.0443	H-1→L+6(+54%) H-4→L+0(24%)
391.6	0.0708	H-1→L+6(+42%) H-4→L+0(+30%)
390.9	0.1541	H-4→L+0(+40%) H-0→L+5(33%)
386.1	0.0252	H-0→L+6(+45%) H-3→L+4(30%)
384.5	0.0106	H-2→L+6(+89%)
383.9	0.0373	H-0→L+6(+43%) H-4→L+1(22%)
383.3	0.0197	H-4→L+1(+72%) H-0→L+6(+9%)
374.6	0.066	H-4→L+2(+89%)
372.1	0.0189	H-3→L+5(+94%)
351.5	0.0254	H-5→L+0(+53%) H-2→L+10(17%)
351	0.019	H-2→L+10(+42%) H-5→L+0(+23%)
334.1	0.0296	H-7→L+1(+67%) H-6→L+1(+16%)
311.6	0.0992	H-8→L+0(+94%)
309.1	0.0234	H-6→L+2(+95%)
308.8	0.1096	H-9→L+0(+88%)
306.3	0.2775	H-8→L+1(+86%)
305.3	0.1162	H-9→L+1(+86%)

[a] Transitions in the visible and near-UV region (10,000–30,000 cm^{-1}). Excitation contributions greater than 20% are shown, smaller contributions are omitted.

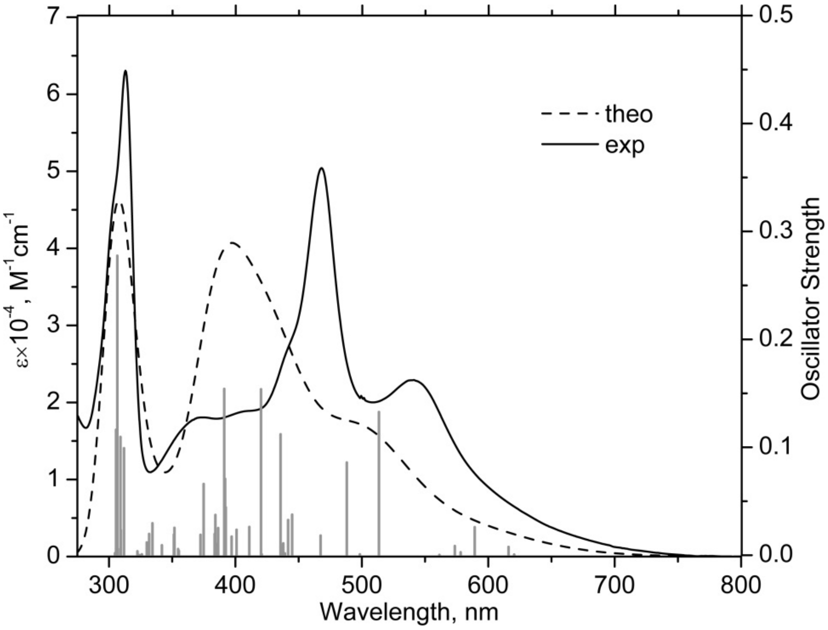


Figure S2. Experimental (solid line) and simulated (dashed line) absorption spectra of **2**. The gray bars indicate the energy and oscillator strength of each electronic excitation.

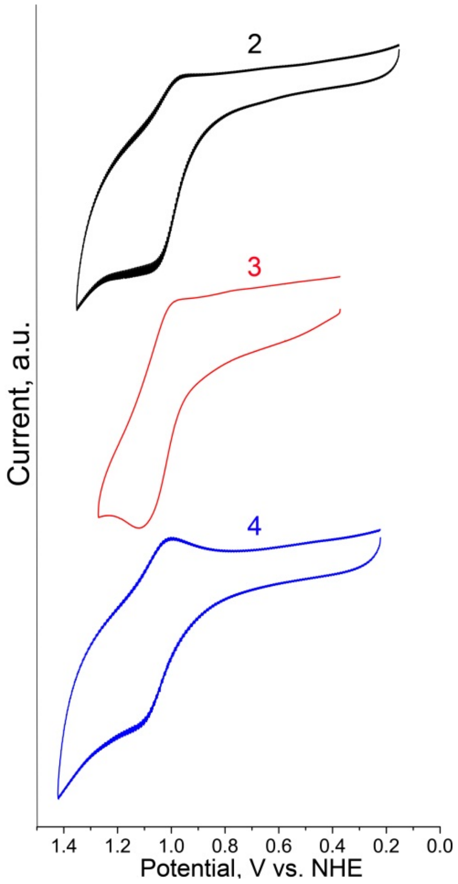


Figure S3. Cyclic voltammograms of **2-4** recorded in 0.100 M solutions of (TBA)PF_6 in DMF.

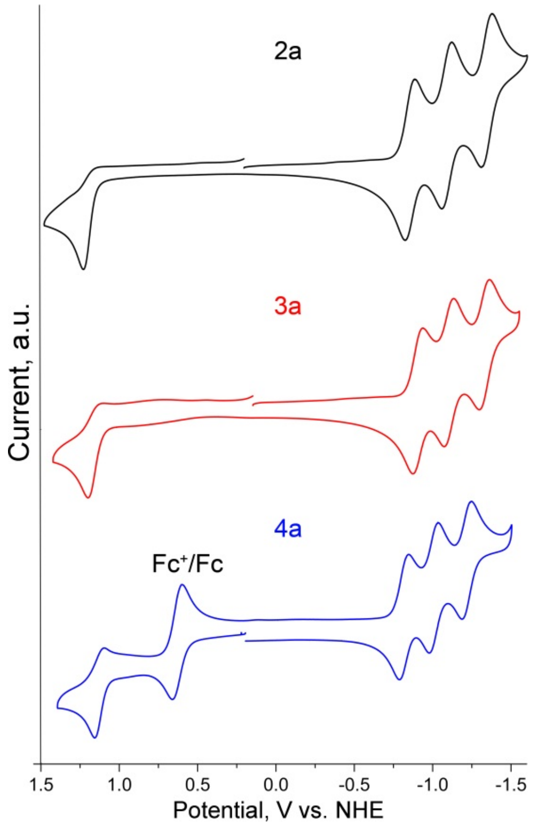


Figure S4. Cyclic voltammograms of **2a-4a** recorded in 0.100 M solutions of $(Bu_4N)PF_6$ in MeCN.

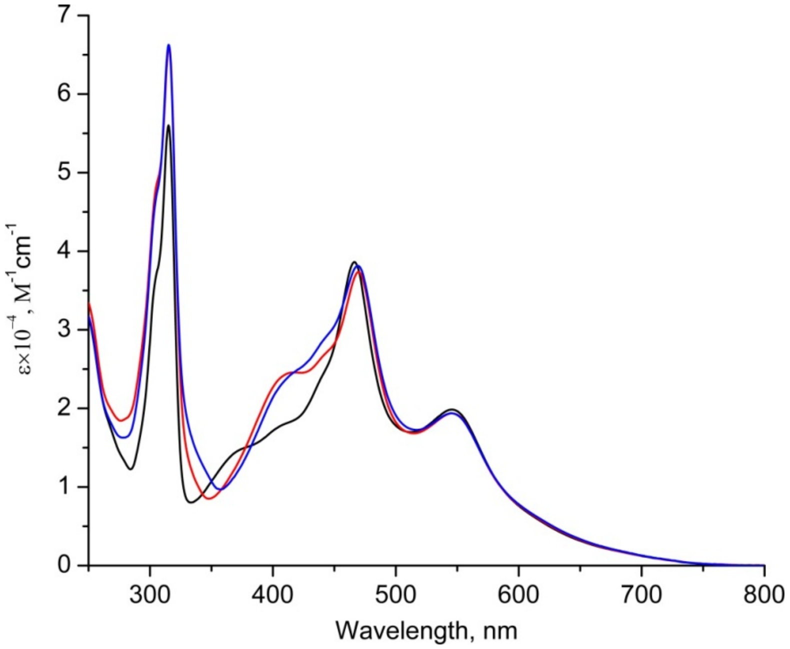


Figure S5. Absorption spectra of **2a** (black), **3a** (red) and **4a** (blue) in MeCN at room temperature.

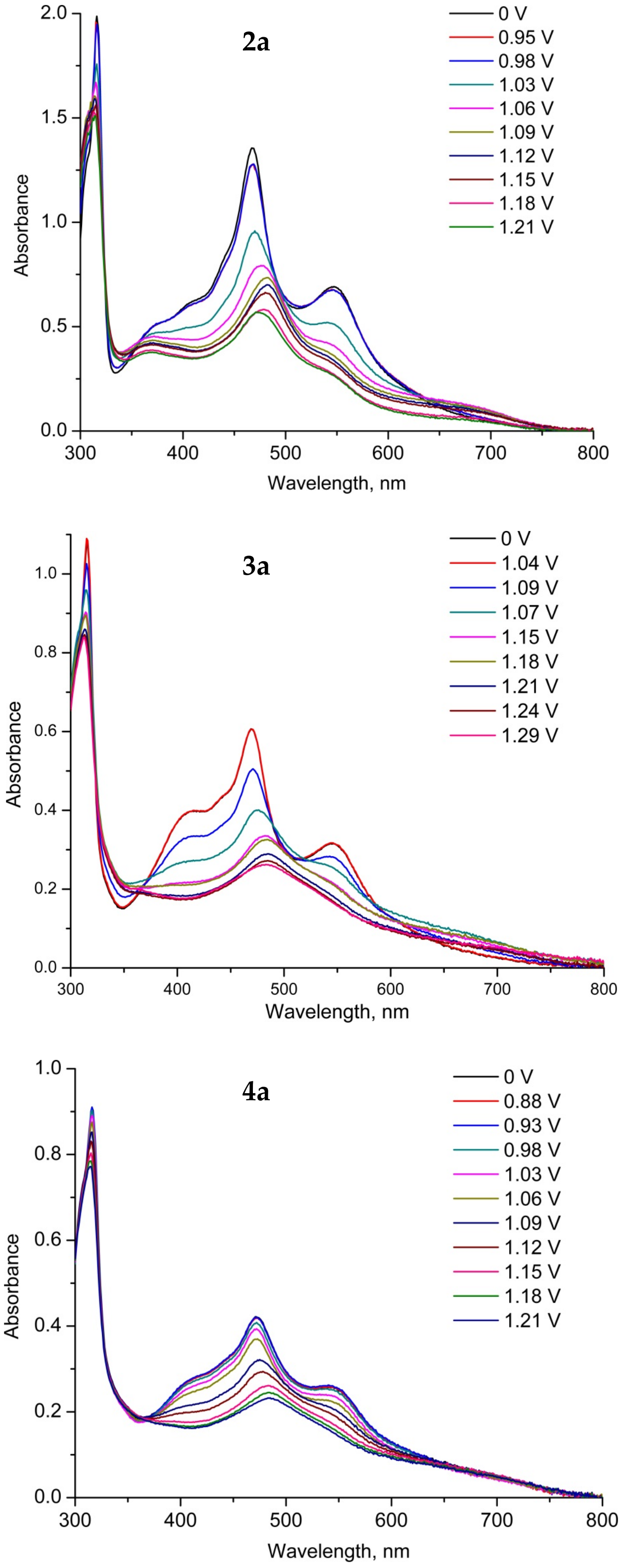


Figure S6. Thin-layer absorption spectra of **2a**-**4a** recorded in acetonitrile solutions at different applied potentials (vs. NHE).

Table S3. Photovoltaic characteristics of DSSCs containing dye **3** under AM 1.5 illumination.

Entry	Electrolyte composition (M)					V_{oc}, V	J_{sc}, mA cm $^{-2}$	*FF*	η%
	DMII[a]	LiI	I_2	GuSCN	tBP				
a	1	0.1	0.06	0.1		0.34	2.36	0.44	0.36
b	1	0.3	0.06	0.1		0.36	2.94	0.46	0.48
c	1	0.5	0.06	0.1		0.34	3.39	0.42	0.48
d	1	1	0.06	0.1		0.30	6.76	0.38	0.77
e		1	0.06			0.28	7.07	0.33	0.66
f		1	0.06		0.1	0.32	4.94	0.39	0.62
g		1	0.06		0.5	0.35	1.99	0.47	0.33
h		2	0.06		0.5	0.36	2.29	0.46	0.38
i		2	0.06		1	0.36	2.25	0.47	0.38

[a] DMII = 1,3,-dimethylimidazolium iodide.

Table S4. Photovoltaic characteristics of DSSCs containing dye **4** under AM 1.5 illumination.

Entry	Electrolyte composition (M)					V_{oc}, V	J_{sc} mA/cm^2	FF	η%
	DMII	LiI	I_2	GuSCN	tBP				
a	1	0.1	0.06	0.1		0.26	1.07	0.41	0.11
b	1	0.3	0.06	0.1		0.27	1.82	0.41	0.21
c	1	0.5	0.06	0.1		0.27	1.51	0.42	0.17
d	1	1	0.06	0.1		0.31	5.66	0.42	0.73
e		1	0.06			0.31	6.45	0.38	0.76
f		1	0.06		0.1	0.29	5.27	0.41	0.63
g		1	0.06		0.5	0.36	1.97	0.47	0.34
h		2	0.06		0.5	0.33	2.46	0.44	0.36
i		2	0.06		1	0.34	1.79	0.43	0.27