ESI to accompany

Copper(I) dye-sensitized solar cells with $[Co(bpy)_3]^{2+/3+}$ electrolyte

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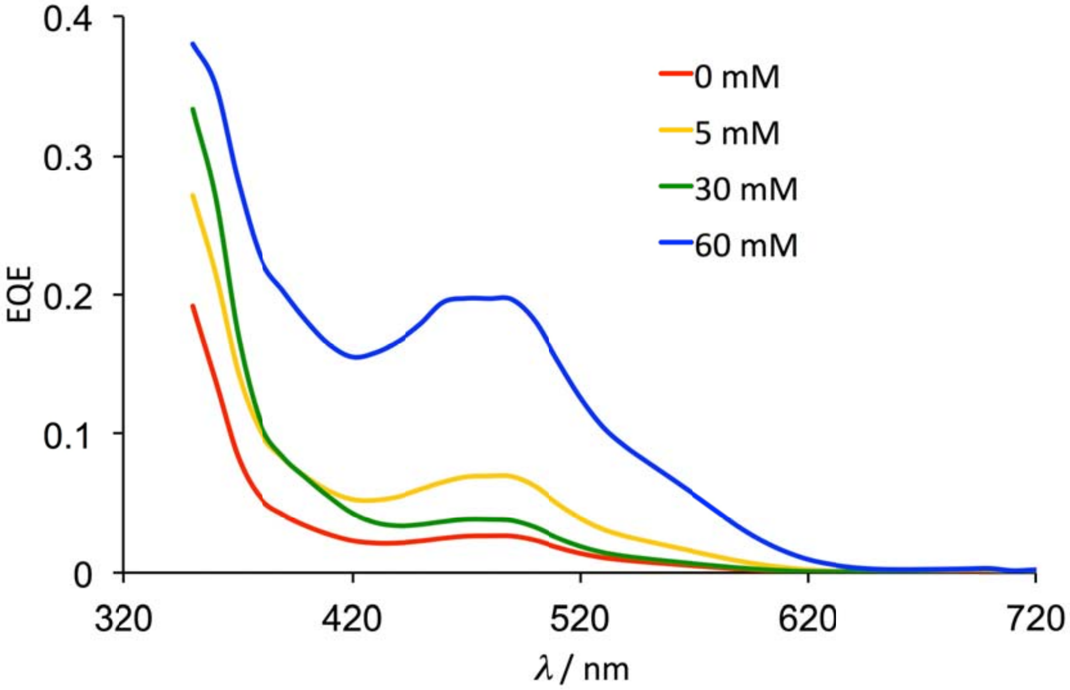


Fig. S1. EQE (IPCE) spectra for DSCs detailed at the top of Table 2 (main text) containing [Cu(**3**)(**4**)]$^{+}$ dye and [Co(bpy)$_3$]$^{2+}$/[Co(bpy)$_3$]$^{3+}$ electrolyte. In three cells (green, yellow and blue lines), the TiO_2 was post-treated with aqueous $TiCl_4$ using solutions of 5, 30 and 60 mmol dm^{-3}. The red line corresponds to no post-treatment.

Experimental Section

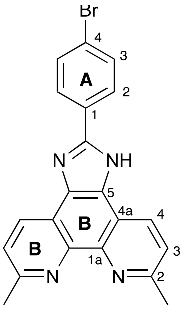
General

Bruker Avance III-400 and Avance III-500 NMR spectrometer was used to record ^{1}H and ^{13}C NMR spectra; chemical shifts were referenced to residual solvent peaks with respect to δ (TMS) = 0 ppm. Absorption spectra were recorded on a Perkin Elmer Lambda 25 spectrometer, and FT-IR spectra on a Shimadzu 8400S instrument using solid samples in a Golden Gate accessory. MALDI-TOF and Electrospray ionization (ESI) mass spectra were recorded using a Bruker Daltonics microflex and Bruker esquire 3000$^{\text{plus}}$ instruments, respectively.

Electrochemical measurements were made on a CH Instruments 900B potentiostat using glassy carbon, platinum wire and silver wire as the working, counter, and reference electrodes, respectively. Samples were dissolved in HPLC grade CH_2Cl_2 (10^{-4} to 10^{-5} mol dm^{-3}) containing 0.1 mol dm^{-3} [$^nBu_4N$][PF_6] as supporting electrolyte; all solutions were degassed with argon. Cp_2Fe was used as internal reference.

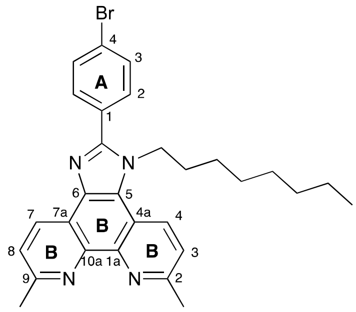
2,9-Dimethyl-1,10-phenanthroline-5,6-dione was prepared according to the literture method[1] starting from commercially available 2,9-dimethyl-1,10-phenanthroline. Anchoring ligand **4** was synthesized according to our previously published method.[2] [$Co(bpy)_3$][PF_6]$_2$ was prepared as described in the literature.[3]

Compound 1



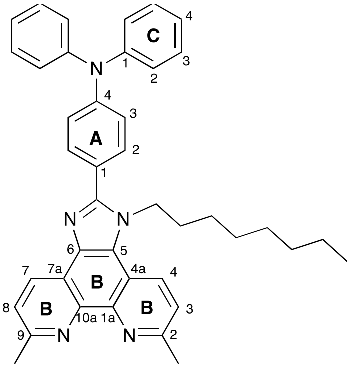
Under an atmosphere of argon, 4-bromobenzaldehyde (1.30 g, 7.01 mmol), 2,9-dimethyl-1,10-phenanthroline-5,6-dione (2.00 g, 8.40 mmol) and an excess of NH_4OAc (7.40 g, 96 mmol) were added to EtOH (45 mL). The yellow mixture was heated at reflux for 3 d, after which time the solvent was removed under reduced pressure. The brown residue was dissolved in CH_2Cl_2 and the organic layer was washed with water. A yellow precipitate formed, was separated by filtration and dried *in vacuo*. Compound **1** was isolated as a yellow solid (2.57 g, 6.38 mmol, 91%). ^1H NMR (400 MHz, DMSO-d_6) δ / ppm 13.70 (v br, H^{NH}), 8.76 (d, $J = 8.2$ Hz, 2H, H^{B3}), 8.21 (d, $J = 8.7$ Hz, 2H, H^{A3}), 7.82 (d, $J = 8.5$ Hz, 2H, H^{A2}), 7.68 (d, $J = 8.7$ Hz, 2H, H^{B4}), 2.79 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm 156.2 (C^{B2}), 149.0 (C^{A1}), 142.9 ($2C^{Q}$), 132.0 (C^{A2}), 129.9 (C^{B3}), 129.4 (C^{Q}), 128.0 (C^{A3}), 123.3 (C^{B4}), 122.7 (C^{A4}), 25.1 (C^{Me}); one C^{Q} not observed. ESI MS *m/z*: 405.1 $[M+H]^+$ (calc. 405.1). IR (solid, ν/cm^{-1}): 3360 (w), 3121 (w), 2915 (w), 1549 (w), 1475 (m), 1439 (m), 1370 (w), 1009 (m), 832 (s), 748 (m), 734 (m), 724 (m). UV-VIS (MeOH, 1.0×10^{-5} mol dm^{-3}) λ / nm 276 (ε / dm^3 mol^{-1} cm^{-1} 37200), 293 (37200), 317 sh (32600), 324 sh (28700).

Compound 2



NaH (60% oil dispersion, 255 mg, 6.38 mmol) were suspended in DMF (15 mL) under an atmosphere of argon. Compound **1** (857 mg, 2.13 mmol) was added and the brown suspension was heated to 40 °C. A 10-fold excess of 1-bromooctane (3.7 ml, 2.13 mmol) was added and the mixture was heated at reflux for 68 h. The black mixture was poured into an ice bath and a yellow precipitate formed. This was collected by filtration and purified by column chromatography (basic alumina, toluene/ethyl acetate 2:1) and recrystallized from toluene/ethyl acetate (3:1 by volume) to yield **2** as white needles (225 mg, 0.436 mmol, 21%). ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm 8.93 (d, J = 8.2 Hz, 1H, $H^{B4/B7}$), 8.45 (d, J = 8.5 Hz, 1H, $H^{B4/B7}$), 7.71 (m, 2H, $H^{A2/A3}$), 7.60 (m, 2H, $H^{A2/A3}$), 7.57 (m, 2H, H^{B3+B8}), 4.54 (m, 2H, H^{NCH2}), 2.98 (s, 3H, $H^{Me\text{-}phen}$), 2.96 (s, 3H, $H^{Me\text{-}phen}$), 1.91 (m, 2H, H^{CH2}), overlapping 1.24 and 1.18 (m, 10H, H^{CH2}), 0.85 (t, J = 7.0 Hz, 3H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm 158.1 ($C^{B2/B9}$), 156.9 ($C^{B2/B9}$), 152.3 (C^{NCN}), 144.2 (C^{Q}), 143.5 (C^{Q}), 136.5 (C^{Q}), 132.3 ($C^{A2/A3}$), 131.6 ($C^{A2/A3}$), 130.8 ($C^{B4/B7}$), 129.7 (C^{Q}), 128.5 ($C^{B4/B7}$), 124.9 (C^{B6}), 124.4 (C^{A1}), 124.0 ($C^{B3/B8}$), 123.0 ($C^{B3/B8}$), 122.1 (C^{A4}), 117.9 (C^{B5}), 46.9 (C^{NCH2}), 31.8 (C^{CH2}), 30.3 (C^{CH2}), 29.2 (C^{CH2}), 29.0 (C^{CH2}), 26.5 (C^{CH2}), 26.1 ($C^{Me\text{-}phen}$), 25.9($C^{Me\text{-}phen}$), 22.7 (C^{CH2}), 14.2 (C^{Me}). ESI MS *m/z*: 515.2 $[M+H]^+$ (calc. 515.2). IR (solid, ν/cm^{-1}): 2952 (w), 2925 (m), 2854 (m), 1585 (w), 1585 (w), 1533 (m), 1466 (m), 1402 (m), 1357 (m), 1185 (w), 1149 (w), 1008 (m), 837 (s), 817 (m), 748 (m), 719 (m). UV-VIS (CH_2Cl_2, 1.0×10^{-5} mol dm^{-3}) λ / nm 249 (ε / dm^3 mol^{-1} cm^{-1} 40012), 276 (41370), 292 (40950), 370 sh (2380).

Compound 3



Compound **2** (119 mg, 0.231 mmol), Ph_2NH (43.0 mg, 0.254 mmol) and NaO^tBu (55.4 mg, 0.577 mmol) were added to toluene (10 mL) under an atmosphere of N_2. Bis(dibenzylideneacetone)palladium(0) (6.64 mg, 0.0115 mmol) and a 1.0 mol dm^{-3} solution of $^tBu_3P$ in toluene (0.012 ml, 0.0115 mmol) was added to the reaction mixture which was then heated at reflux overnight. The reaction mixture was filtered hot, the solvent removed and the remaining brown solid purified by column chromatography (basic aluminia, toluene/ethyl acetate 2:1). Compound **3** was isolated as a yellow solid (52.4 mg, 0.121 mmol, 52%). M. pt. 121 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ / ppm 8.97 (d, *J* = 8.2 Hz, 1H, $H^{B4/B7}$), 8.46 (d, *J* = 8.5 Hz, 1H, $H^{B4/B7}$), 7.57 (m, 4H, $H^{B3+B8+A2}$), 7.31 (m, 4H, H^{C3}), 7.21 (d, *J* = 8.6 Hz, 2H, H^{A3}), 7.18 (m, 4H, H^{C2}), 7.10 (m, 2H, H^{C4}), 4.60 (m, 2H, H^{NCH2}), 2.97 (s, 3H, $H^{Me\text{-}phen}$), 2.95 (s, 3H, $H^{Me\text{-}phen}$), 1.95 (m, 2H, H^{CH2}), overlapping 1.28 and 1.22 (m, 10H, H^{CH2}), 0.84 (t, *J* = 7.0 Hz, 3H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm 157.8 ($C^{B2/B9}$), 156.5 ($C^{B2/B9}$), 153.6 (C^{NCN}), 149.3 (C^Q), 147.3 (C^{C1}), 143.9 (C^Q), 143.3 (C^Q), 136.4 (C^Q), 130.8 (C^{A2}), 130.75 ($C^{B4/B7}$), 129.6 (C^{C3}), 128.5 ($C^{B4/B7}$), 125.3 (C^{C2}), 124.7 (C^Q), 124.0 ($C^{B3/B8}$), 123.9 (C^{C4}), 123.5 (C^Q), 122.9 ($C^{B3/B8}$), 122.5 (C^{A3}), 122.1 (C^Q), 118.0 (C^{B5}), 46.8 (C^{NCH2}), 30.3 (C^{CH2}), 29.8 (C^{CH2}), 29.2 (C^{CH2}), 29.0 (C^{CH2}), 26.4 (C^{CH2}), 26.0 ($C^{Me\text{-}phen}$), 25.8 ($C^{Me\text{-}phen}$), 22.7 (C^{CH2}), 14.2 (C^{Me}). ESI MS *m/z*: 604.3 $[M+H]^+$ (calc. 604.3). IR (solid, ν/cm^{-1}): 2923 (w), 2854 (w), 1588 (m), 1520 (w), 1488 (m), 1467 (m), 1316 (w), 1280 (m), 1180 (w), 820 (w), 749 (m), 695 (m). UV-VIS (CH_2Cl_2, 1.0 × 10^{-5} mol dm^{-3}) λ / nm 240 (ε / dm^3 mol^{-1} cm^{-1} 35850), 258 (31800), 295 (42300), 335 (29900).

[Cu(3)$_2$][PF$_6$]

A solution of [Cu(NCMe)$_4$][PF$_6$] (17.3 mg, 0.0464 mmol) in MeCN (2 mL) was added dropwise to a solution of **3** (56.0 mg, 0.0927 mmol) in CHCl$_3$ (2 mL). The dark red solution was stirred for 1h and then solvent was removed. The dark red solid was purified by filtration through silica to yield [Cu(**3**)$_2$][PF$_6$] as a dark red solid (65.0 mg, 0.0459 mmol, 99%). ^{1}H NMR (500 MHz, CDCl$_3$) δ / ppm 9.22 (d, J = 8.2 Hz, 1H, H$^{B4/B7}$), 8.85 (d, J = 8.6 Hz, 1H, H$^{B4/B7}$), 7.95 (d, J = 8.5 Hz, 1H, H$^{B3/B8}$), 7.79 (d, J = 8.4 Hz, 1H, H$^{B3/B8}$), 7.61 (d, J = 8.6 Hz, 2H, H^{A2}), 7.34 (m, 4H, H^{C3}), 7.24 (d, J = 8.7 Hz, 2H, H^{A3}), 7.20 (m, 4H, H^{C2}), 7.13 (m, 2H, H^{C4}), 4.78 (m, 2H, H^{NCH2}), 2.46 (s, 3H, H$^{Me\text{-}phen}$), 2.43 (s, 3H, H$^{Me\text{-}phen}$), 2.01 (m, 2H, H^{CH2}), overlapping 1.32 and 1.23 (m, 10H, H^{CH2}), 0.84 (t, J = 7.0 Hz, 3H, H^{Me}). ^{13}C NMR (126 MHz, CDCl$_3$) δ / ppm 155.3 (C$^{B2/B9}$), 155.1 (C$^{B2/B9}$), 154.9 (C^{NCN}), 149.6 (C^Q), 147.0 (C^{C1}), 141.2 (C^Q), 141.0 (C^Q), 136.1 (C^Q), 131.7 (C$^{B4/B7}$), 130.8 (C^{A2}), 130.1 (C$^{B4/B7}$), 129.7 (C^{C3}), 125.7 (C$^{B3/B8}$), 125.4 (C$^{B3/B8}$), 125.2 (C^{C2}), 124.9 (C^Q), 124.1 (C^{C4}), 123.1 (C^Q), 122.3 (C^{A3}), 121.8 (C^Q), 119.2 (C^{B5}), 46.7 (C^{NCH2}), 31.8 (C^{CH2}), 30.1 (C^{CH2}), 29.2 (C^{CH2}), 28.9 (C^{CH2}), 26.1 (C^{CH2}), 25.8 (C$^{Me\text{-}phen}$), 25.6 (C$^{Me\text{-}phen}$), 22.5 (C^{CH2}), 14.2 (C^{Me}). MALDI MS: m/z 1271.6 [M–PF$_6$]$^+$ (calc. 1269.6), 666.9 [M – **3** – PF$_6$]$^+$ (calc. 666.3). IR (solid, ν/cm^{-1}): 2924 (w), 2854 (w), 1588 (m), 1489 (m), 1468 (m), 1282 (m), 836 (s), 746 (m), 695 (s), 557 (s). UV-VIS (CH$_2$Cl$_2$, 1.0 × 10^{-5} mol dm^{-3}) λ / nm 266 (ε / dm^3 mol^{-1} cm^{-1} 74200), 299 (89300), 342 (61700), 476 (15150). Found C 69.61, H 6.17, N 9.42; $C_{82}H_{82}CuF_6N_{10}P$ requires C 69.55, H 5.84, N 9.89%.

Crystallography

Data were collected on a Bruker APEX-II diffractometer with data reduction, solution and refinement using the programs APEX[4] and SHELX-13.[5] The ORTEP-type diagram and structure analysis used Mercury v. 3.0.[6,7]

Compound 2: $C_{29}H_{31}BrN_4$, M = 515.48, colourless block, triclinic, space group P–1, a = 7.6353(3), b = 10.3601(3), c = 17.3511(6) Å, α □ 92.5970(10□□□β = 100.6550(10), γ= 109.1290(10)°, U = 1266.05(8) Å^3, Z = 2, D_c = 1.352 Mg m^{-3}, μ(Cu-Kα) = 2.388 mm^{-1}, T = 123 K. Total 18891 reflections, 4507 unique, R_{int} = 0.0266. Refinement of 4410 reflections (310 parameters) with $I > 2\sigma(I)$ converged at final $R1$ = 0.0299 ($R1$ all data = 0.0304), $wR2$ = 0.0788 ($wR2$ all data = 0.0792), gof = 1.064. CCDC 945455.

Solar cell fabrication

The fabrication of DSCs was based on the method of Grätzel and coworkers.[8] Each working electrode was made from an FTO glass plate (Solaronix TCO22-7, 2.2 mm thickness, sheet resistance ≈7 Ω square^{-1}) which was cleaned by sonicating in a 2% surfactant solution in miliQ water (Sonoswiss cleaner, SW-C L2), and rinsed with milliQ water and EtOH. After surface activation in a UV-O_3 system (Model 256-220, Jelight Company Inc) for 18 min, the FTO plates were immersed in aqueous $TiCl_4$ (40 mmol dm^{-3}) at 70 °C for 30 min, and then washed with milliQ water and EtOH. The electrodes were dried in N_2 and a layer of TiO_2 paste (Dyesol, DSL 90-T) was screen printed (90T, Serilith AG, Switzerland). The printed plates were kept in an EtOH chamber for 1.5 min, and 3 min for the following printing cycles, to reduce surface irregularities of the printed layer and dried for 6 min at 125 °C on a heating plate. The screen printing process was repeated 2 or 3 times, respectively and then a final scattering layer was printed on top (Dyesol, WER2-O). The electrodes were gradually heated at 75 °C for 30 min, at 135 °C for 15 min, at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min. After the final sintering, the thickness of the TiO_2 layer was 12-15 μm (measured with Tencor Alpha-Step 500 profilometer). The annealed TiO_2 film was post-treated with 0-60 mmol dm^{-3} aqueous $TiCl_4$ solution, rinsed with milliQ water and EtOH and sintered at 500 °C for 30 min. The electrodes were cooled to ca. 80°C and immersed in a 1 mM DMSO solution of the anchoring ligand for ca. 20 h. The colourless electrodes were removed from the solution, washed with DMSO and EtOH and dried in a stream of N_2. The electrodes with adsorbed anchoring ligand were immersed in a 0.1 mM MeCN solution of $[Cu(\mathbf{3})_2][PF_6]$ for 24, 64 or 110 h to produce red-orange coloured electrodes. The electrodes were removed from the solution and were washed with MeCN and dried under a stream of N_2.

Each counter electrode was prepared from an FTO glass plate (Solaronix TCO22-7, 2.2 mm thickness, sheet resistance ≈7 Ω square–1) with a previously drilled hole. Residual organic impurities were removed by heating for 15 min at 500 °C on a heating plate and the perforated plate was washed with miliQ water, 0.1 M HCl solution in EtOH and finally ultrasonicated in an acetone bath for 15 min. The electrodes were dried on a heating plate at 500 °C for 15 min. After letting cool down to room temperature, the Pt catalyst was deposited on the FTO glass plates by coating the surface with Platisol T (2 × 25.0 μL, Solaronix) and drying on a heating plate at 500 °C for 15 min.

The TiO_2 electrodes and Pt counter-electrodes were assembled using thermoplast hot-melt sealing foil (Solaronix, Meltonix 1170-60 Series, 60 microns thick) by heating while pressing them together. The I_2/I_3^- electrolyte comprised of LiI (0.1 mol dm^{-3}), I_2 (0.05 mol dm^{-3}), 1-methylbenzimidazole (0.5 mol dm^{-3}) and 1-butyl-3-methylimidazolinium iodide (0.6 mol dm^{-3}) in methoxypropionitrile, and the Co^{2+}/Co^{3+} electrolyte consisted of $[Co(bpy)_3][PF_6]_2$ (0.2 mol dm^{-3}), $[Co(bpy)_3][PF_6]_3$ (0.05 mol dm^{-3}), $LiClO_4$ (0.1 mol dm^{-3}) and 4-*tert*-butylpyridine (0.2 mol dm^{-3}) in MeCN. The electrolytes were introduced into the cell by vacuum backfilling. The hole on the counter electrode was finally sealed using hot-melt sealing foil and a cover glass.

The solar cell measurements and testing protocol was performed using fully masked cells. A black coloured copper sheet was used for masking with a single aperture of an average area of 0.06012 cm^2 (with a standard deviation of 1%) placed over the screen printed dye-sensitized TiO_2 circle. The area of the aperture in the mask was smaller than the active area of the dye-sensitized TiO_2 (0.288 cm^2). For complete masking, tape was also applied over the edges and rear of the cell. Current density-voltage (JV) measurements were made by irradiating from behind using a light source SolarSim 150 (100 mW cm^{-2} = 1 sun). The power of the simulated light was calibrated by using a reference Si photodiode. The standard dye N719 was purchased from Solaronix.

The quantum efficiency measurements were performed on a Spe-Quest quantum efficiency setup from Rera Systems (Netherlands) equipped with a 100 W halogen lamp (QTH) and a lambda 300 grating monochromator from Lot Oriel. The monochromatic light was modulated to 3Hz using a chopper wheel from ThorLabs. The cell response was amplified with a large dynamic range IV converter from CVI Melles Griot and then measured with a SR830 DSP Lock-In amplifier from Stanford Research.

References

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