ESI to accompany

Hole-transport functionalized copper(I) dye sensitized solar cells

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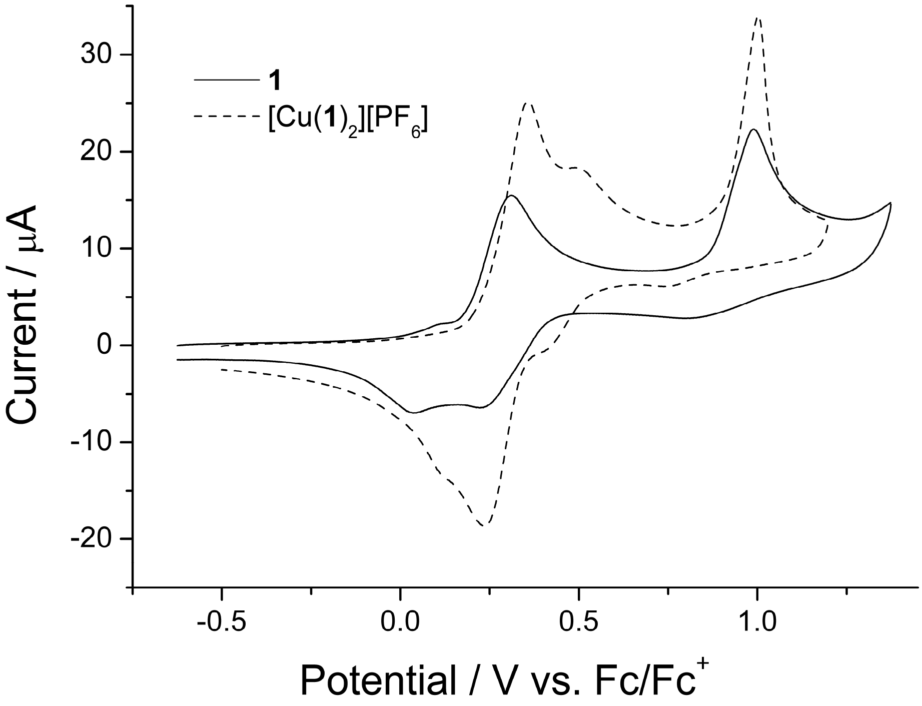
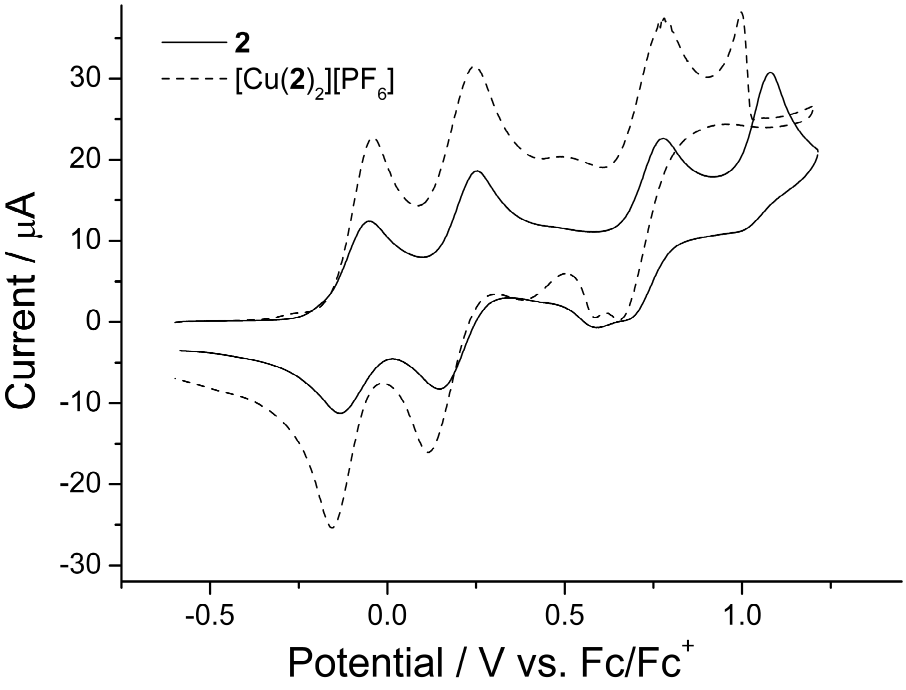


(a)



(b)

Figure S1 Cyclic voltammograms of CH_2Cl_2 (degassed) solutions of (a) **1** and [Cu(**1**)$_2$][PF$_6$] and (b) **2** and [Cu(**2**)$_2$][PF$_6$].

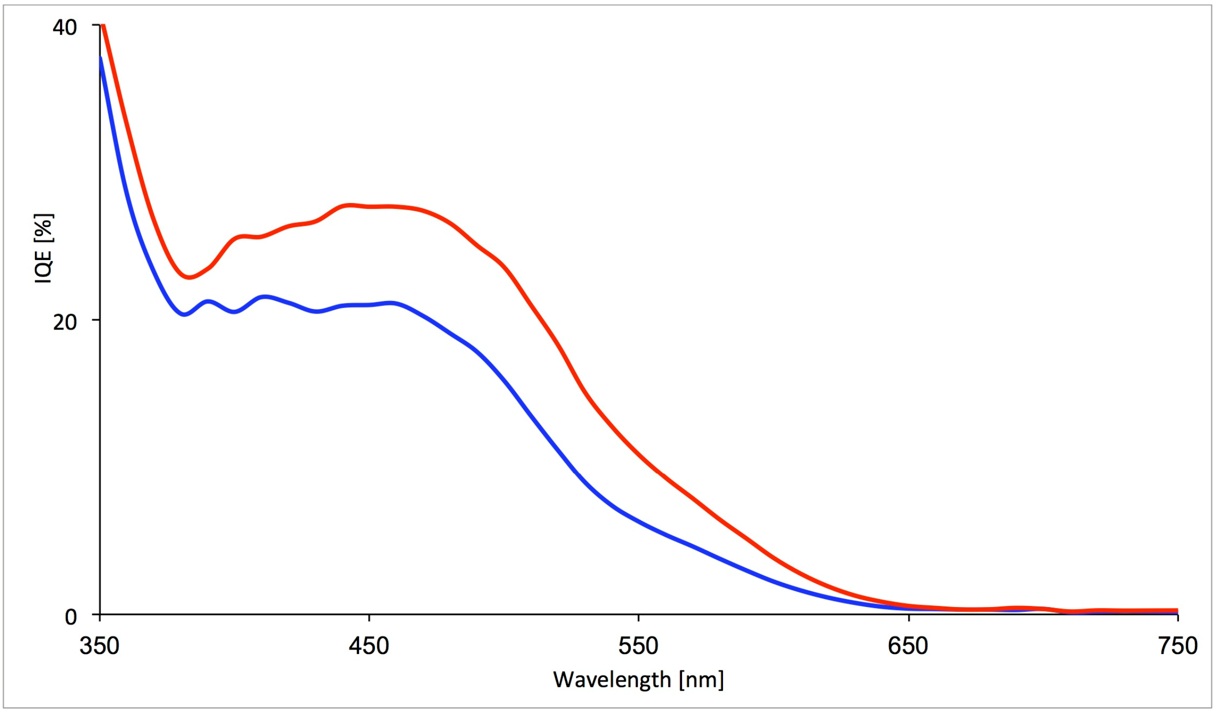
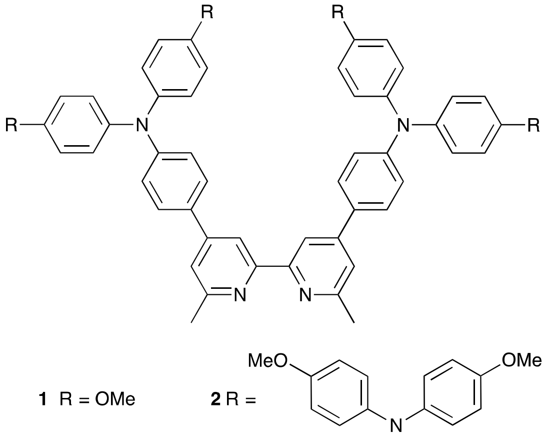


Figure S2: Internal quantum efficiency (IQE) spectra of the solar cells containing $[Cu(\mathbf{1})_2]^+/\mathbf{3}$ (blue line) and $[Cu(\mathbf{2})_2]^+/\mathbf{3}$ (red line).

Experimental Section



1 R = OMe **2** R =

General

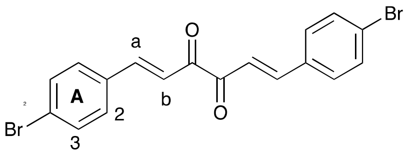
Bruker Avance III-400 or Avance III-500 NMR spectrometers were used to record ^{1}H and ^{13}C NMR spectra; chemical shifts were referenced to residual solvent peaks with respect to δ(TMS) = 0 ppm. Absorption spectra were recorded with an Agilent 8453 spectrophotometer, and FT-IR spectra on a Shimadzu 8400S instrument with a Golden Gate accessory for solid samples. Electron impact (EI), MALDI-TOF and electrospray ionization (ESI) mass spectra were recorded on Finnigan MAT 95Q instrument, Bruker Daltonics microflex and Bruker esquire 3000$^{\text{plus}}$ instruments, respectively.

Electrochemical measurements were taken on a CH Instruments 900B potentiostat and performed using glassy carbon, platinum wire and silver wire as the working, counter, and reference electrodes, respectively. Substrates were dissolved in HPLC grade CH_2Cl_2 (ca. 10^{-4} to 10^{-5} mol dm^{-3}) containing 0.1 mol dm^{-3} [^{n}Bu$_4$N][PF$_6$] as the supporting electrolyte; all solutions were degassed with argon. Cp_2Fe was used as internal reference.

Anchoring ligands **3**, **4** and **5** were synthesized as previously described. [1,2]

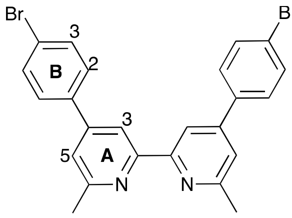
Abbreviation: Pd(bda)$_2$ = bis(dibenzylideneacetone)palladium(0).

(1*E*,5*E*)-1,6-bis(4-bromophenyl)hexa-1,5-diene-3,4-dione



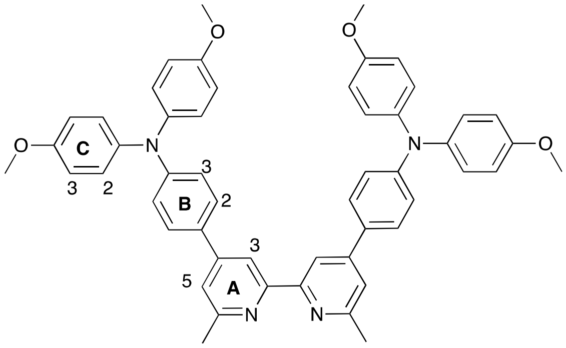
The synthesis is adapted from the general method of Krönhke.[3] To a vigorously stirred solution of 4-bromobenzaldehyde (20.6 mL, 200 mmol) and piperidine (2.00 mL, 20.0 mmol) in MeOH (50 mL), a solution of 2,3-butanedione (8.83 mL, 100 mmol) in MeOH (30 mL) was added dropwise using a dropping funnel over 30 min.. The reaction mixture was heated to reflux overnight. The solution was slowly cooled to room temperature while stirring and was cooled in an ice bath and the precipitate was removed by filtration and washed with Et_2O yielding (1*E*,5*E*)-1,6-bis(4-bromophenyl)hexa-1,5-diene-3,4-dione (2.36 g, 5.63 mmol, 5.63%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ / ppm: 7.81 (d, J = 16.1 Hz, 2H, H^a), 7.57 (d_{AB}, J = 9.0 Hz, 4H, $H^{A2/A3}$), 7.52 (d_{AB}, J = 8.9 Hz, 4H, $H^{A2/A3}$) overlapping with 7.49 (d, J = 16.1 Hz, 2H, H^b). EI MS *m/z*: 419.9 $[M]^+$ (calc. 419.9).

4,4'-Bis(4-bromophenyl)-6,6'-dimethyl-2,2'-bipyridine



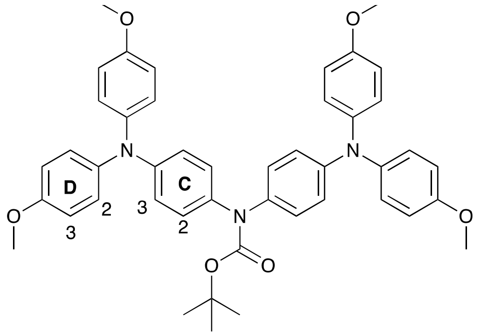
In a 1 L one-necked flask **1** (6.58 g, 15.7 mmol), 1-pyridiniopropanone chloride (5.37 g, 31.3 mmol) and ammonium acetate (24.1 g, 313 mmol) were suspended in EtOH (200 mL). The suspension was heated to reflux and EtOH (600 mL) was added until the reactants had dissolved. The solution was heated to reflux overnight, after which time the reaction mixture was allowed to cool to 70°C. The precipitate was was removed by filtration and was washed with Et_2O yielding 4,4'-bis(4-bromophenyl)-6,6'-dimethyl-2,2'-bipyridine (4.41 g, 8.92 mmol, 57%) as a colorless solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm: 8.48 (d, J = 1.8 Hz, 2H, H^{A3}), 7.63 (m, 8H, H^{B2+B3}), 7.37 (d, *J* = 1.6 Hz, 2H, H^{A5}), 2.73 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, CD_3Cl) δ / ppm: 158.5 (C^{A6}), 155.9 (C^{A2}), 148.5 (C^{A4}), 137.7 (C^{B1}), 132.2 ($C^{B2/B3}$), 128.6 ($C^{B2/B3}$), 123.3 (C^{B4}), 121.0 (C^{53}), 116.5 (C^{A3}), 24.1 (C^{Me}). EI MS (*m/z*): 494.0 $[M]^+$ (calc. 493.9). UV-VIS (CH_2Cl_2, 1.0 × 10^{-5} mol dm^{-3}) λ_{abs} / nm 255 (ε / dm^3 mol^{-1} cm^{-1} 59480), 302 (22343). Found: C, 58.19, H, 3.56, N, 5.61; $C_{24}H_{18}Br_2N_2$ requires C, 58.33, H, 3.67, N, 5.67.

Compound 1



4,4'-Bis(4-bromophenyl)-6,6'-dimethyl-2,2'-bipyridine (460 mg, 0.91 mmol) and bis(4-methoxyphenyl)amine (640 mg, 2.74 mmol) were suspended in toluene (60 mL) under argon, and NaO^{t}Bu (289 mg, 3.01 mmol) was added. A suspension of $Pd(bda)_2$ (21.0 mg, 4.0 mol%) and a 1M toluene solution of P^tBu_3 (0.029 mg, 0.036 mL, 4.0 mol%) in toluene (4 mL) was prepared under argon and was added to the reaction mixture. The mixture was heated at 100°C for 16 h, after which time it was filtered hot. The solvent of the filtrate was removed and the resulting solid was washed with boiling EtOH. Compound **1** was isolated as a greenish solid (543 mg, 0.69 mmol, 75%). Mp.: decomposition > 280 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm: 8.39 (d, *J* = 1.7 Hz, 2H, H^{A3}), 7.59 (d_{AB}, *J* = 8.7 Hz, 4H, H^{B2}), 7.33 (d, *J* = 1.7 Hz, 2H, H^{A5}), 7.11 (d_{AB}, *J* = 8.9 Hz, 8H, H^{C2}), 7.00 (d_{AB}, *J* = 8.7 Hz, 4H, H^{B3}), 6.86 (d_{AB}, *J* = 8.9 Hz, 8H, H^{C3}), 3.81 (s, 12H, H^{OMe}), 2.67 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm: 158.3 (C^{A6}), 156.8 (C^{A2}), 156.3 (C^{C4}), 149.6 (C^{B4}), 149.0 (C^{A4}), 140.6 (C^{C1}), 130.1 (C^{B1}), 127.8 (C^{B2}), 127.1 (C^{C2}), 120.2 (H^{A5+B3}), 116.0 (H^{A3}), 114.9 (C^{C3}), 55.6 (C^{OMe}), 25.0 (C$^{\text{Me}}$). ESI MS (*m/z*): 791.5 [M+H]$^+$ (calc. 791.4). UV-VIS (THF, 1.0 × 10^{-5} mol dm^{-3}) λ_{abs} / nm 245 (ε / dm^3 mol^{-1} cm^{-1} 50839), 294 (48100), 359 (50737). IR (solid, $\tilde{\nu}$ / cm^{-1}): 2954 (w), 2941 (w), 2831 (w), 1585 (s), 1495 (s), 1384 (m), 1322 (s), 1237 (s), 1107 (m), 1033 (s), 838 (s), 822 (s). Found: C, 77.84; H, 5.92; N, 7.21; $C_{52}H_{46}N_4O_4\cdot 1/2H_2O$ requires C, 78.07; H, 5.92; N, 7.00.

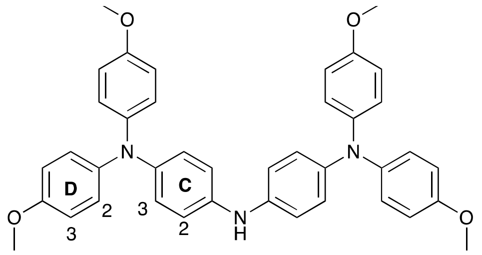
tert-Butyl bis(4-(bis(4-methoxyphenyl)amino)phenyl)carbamate



In a three-necked round-bottomed flask, bis(4-methoxyphenyl)amine (3.49 g,15.2 mmol), sodium *tert*-butoxide (1.75 g, 18.3 mmol) and *N*-Boc-bis(4-bromophenyl)amine[4] (2.59 g, 6.09 mmol) were dissolved in dry toluene (20 mL). In a separate flask, flushed with N_2, ^{t}Bu$_3$P (0.30 mL, 1.0 M in toluene) and Pd(bda)$_2$ (175 mg, 0.30 mmol) were suspended in dry toluene (10 mL). The freshly prepared solution of the catalyst was added to the reaction mixture and heated to reflux overnight. The reaction mixture was filtered hot in order to remove insoluble solids. The solvent was removed. The resulting black oil was purified by column chromatography (Al_2O_3, EtOAc). The dark solid was recrystallized from hexane to give a white solid. A little acetone was added to the mother liquor and upon the addition of hexane, a white precipitate formed. These two fractions were collected to give *tert*-butyl bis(4-(bis(4-methoxyphenyl)amino)phenyl)carbamate as a colorless solid (3.66 g, 5.05 mmol, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm: 7.02 (m, 12H, H$^{\text{D2+C2}}$), 6.85 (d$_{\text{AB}}$, J = 8.9 Hz, 4H, H$^{\text{C3}}$), 6.81 (d$_{\text{AB}}$, J = 9.0 Hz, 8H, H$^{\text{D3}}$), 3.79 (s, 12H, C$^{\text{OMe}}$), 1.45 (s, 9H, C$^{\text{Me}}$). ^{13}C NMR (126 MHz, CD_3Cl) δ / ppm: 155.8 (C$^{\text{D4}}$), 154.5 (C$^{\text{C=O}}$), 146.3 (C$^{\text{C4}}$), 141.2 (C$^{\text{D1}}$), 136.1 (C$^{\text{C1}}$), 127.5

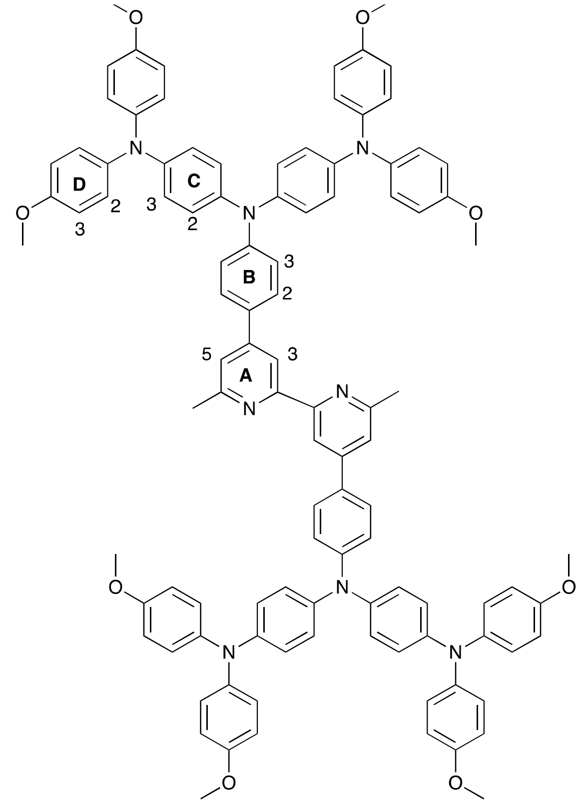
(C^{C2}), 126.5 (C^{D2}), 120.9 (C^{C3}), 114.7 (C^{D3}), 80.8 (C$^{\mathit{C}\mathrm{Me3}}$), 55.4 (C^{OMe}), 28.3 (C^{Me}). EI MS (*m/z*): 723.3 [M]$^+$ (calc. 723.3), 623.3 [M – Boc]$^+$ (calc. 623.3). IR (solid, $\tilde{\nu}$ / cm^{-1}): 3037 (w), 2965 (w), 2930 (w), 1696 (s), 1499 (s), 1234 (s), 1156 (s), 1034 (s), 825 (s), 690 (m).

N^1-(4-(bis(4-methoxyphenyl)amino)phenyl)-N^4,N^4-bis(4-methoxyphenyl)benzene-1,4-diamine (6)



tert-Butyl bis(4-(bis(4-methoxyphenyl)amino)phenyl)carbamate (323 mg, 0.446 mmol) was dissolved in acetone (20 mL) and concentrated trifluoroacetic acid (5 mL, 7.40 g, 64.8 mmol, 145 eq.) was added. The reaction mixture was stirred at room temperature overnight. The solvent was then removed and the solid was purified by column chromatography (Al_2O_3, EtOAc). The resulting solid was suspended in hexane (50 mL) and the mixture was heated to reflux until a fine suspension was obtained. Compound **6** was isolated by filtration (243 mg, 0.39 mmol, 88%). ^{1}H NMR (500 MHz, acetone-d$_6$ + TFA) δ / ppm: 7.38 (d$_{AB}$, J = 9.0 Hz, 4H, H$^{C2/C3}$), 7.16 (d$_{AB}$, J = 8.9 Hz, 8H, H$^{D2/D3}$), 6.95 (d$_{AB}$, J = 8.9 Hz, 8H, H$^{D2/D3}$), 6.84 (d$_{AB}$, J = 9.0 Hz, 4H, H$^{C2/C3}$), 4.01 (br, H^{NH}), 3.79 (s, 12H, H^{OMe}). ^{13}C NMR (126 MHz, acetone-d$_6$ + TFA) δ / ppm: 158.4 (C^{D4}), 151.6 (C^{C4}), 139.9 (C^{D1}), 134.1 (C^{C1}), 129.0 (C^{D2}), 125.9 (C^{C2}), 118.4 (C^{C3}), 116.0 (C^{D3}), 55.6 (C^{OMe}). EI MS (EI, *m/z*): 623.3 [M]$^+$ (calc. 623.3). IR (ATR, $\tilde{\nu}$ / cm^{-1}): 3036 (w), 2999 (w), 2960 (w), 2900 (w), 2830 (w), 1587 (w), 1490 (s), 1266 (s), 1233 (s), 1101 (m), 815 (s), 798 (m), 572 (m).

Compound 2



In a three-necked round-bottomed flask N^1-(4-(bis(4-methoxyphenyl)amino)phenyl)-N^4,N^4-bis(4-methoxyphenyl)benzene-1,4-diamine (1.15 g, 1.85 mmol) was combined with sodium *tert*-butoxide (402 mg, 4.06 mmol) and 4,4'-bis(4-bromophenyl)-6,6'-dimethyl-2,2'-bipyridine (365 mg, 0.74 mmol) in dry toluene (60 mL). In a separate flask ^{t}Bu$_3$P (0.07 mL, 1.0 M in toluene) and Pd(bda)$_2$ (42.5 mg, 0.07 mmol) were suspended in dry toluene (20 mL). The freshly prepared solution of the catalyst was added to the reaction mixture which was then heated to reflux overnight. The reaction mixture was filtered hot to remove insoluble solids. The solvent was removed and the resulting solid was suspended in acetone and heated to reflux until a homogeneous suspension was obtained. After filtration, the product **2** was isolated as a fine yellow powder (865 mg, 0.547 mmol, 74%). ^{1}H NMR (250 MHz, CDCl$_3$) δ / ppm: 8.40 (d, J = 1.6 Hz, 2H, H^{A3}), 7.61 (d$_{AB}$, J = 8.7 Hz, 4H, H^{B2}), 7.33 (d, J = 1.6 Hz, 2H, H^{A5}), 7.09 (d$_{AB}$, J = 8.7 Hz, 4H, H^{B3}), 7.06 (d$_{AB}$, J = 8.9 Hz, 16H, H^{D2}), 6.98 (d$_{AB}$, J = 8.8

Hz, 8H, H^{C2}), 6.89 (d_{AB}, J = 8.9 Hz, 8H, H^{C3}), 6.83 (d_{AB}, J = 9.0 Hz, 16H, H^{D3}), 3.79 (s, 24H, H^{OMe}), 2.66 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm: 158.1 (C^{A6}), 156.6 (C^{A2}), 155.6 (C^{D4}), 149.0 ($C^{B4/A4}$), 148.9 ($C^{B4/A4}$), 144.7 (C^{C4}), 141.3 (C^{D1}), 140.3 (C^{C1}), 130.1 (C^{B1}), 127.6 (C^{B2}), 126.1 (C^{D2}), 126.0 (C^{C2}), 122.0 (C^{C3}), 120.7 (C^{B3}), 120.0 (C^{A5}), 115.8 (C^{A3}), 114.6 (C^{D3}), 55.4 (C^{OMe}), 24.7 (C^{Me}). Mp. decomposition > 220 °C. ESI MS *m/z*: 1580.5 $[M+H]^+$ (calc. 1580.7). UV-VIS (THF, 1.0×10^{-5} mol dm^{-3}) λ_{abs} / nm 239 (ε / dm^3 mol^{-1} cm^{-1} 91944), 305 (95260), 342 (78983). IR (solid, $\tilde{\nu}$ / cm^{-1}): 3045 (w), 3036 (w), 2931 (w), 2836 (w), 1589 (s), 1495 (s), 1318 (m), 1268 (m), 1239 (s), 1177 (m), 1109 (m), 1037 (s), 881 (m), 822 (s), 698 (m). Found: C, 76.48; H, 5.68; N, 6.41; $C_{104}H_{90}N_8O_8 \cdot 3H_2O$ requires C, 76.45; H, 5.92; N,6.86.

$[Cu(\mathbf{1})_2][PF_6]$

Compound **1** (102 mg, 0.129 mmol) was dissolved in $CHCl_3$ (5 mL) and a MeCN (4 mL) solution of $[Cu(MeCN)_4][PF_6]$ (24.0 mg, 0.064 mmol) was added. The solution turned dark red and was stirred at room temperature for 1 h. The volume of the solvent was reduced and the product was precipitated by adding Et_2O. The product was separated by filtration and was washed with Et_2O. $[Cu(\mathbf{1})_2][PF_6]$ was isolated as a red solid (76.2 mg, 0.0426 mmol, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm: 8.25 (s, 2H, H^{A3}), 7.59 (s, 2H, H^{A5}) overlapping with 7.58 (m, 4H, H^{B2}), 7.13 (d_{AB}, J = 8.7 Hz, 8H, H^{C2}), 7.02 (m, 4H, H^{B3}), 6.89 (d_{AB}, J = 8.8 Hz, 8H, H^{C3}), 3.83 (s, 12H, H^{OMe}), 2.31 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm: 157.1 (C^{A6}), 152.1 (C^{A2}), 156.2 (C^{C4}), 150.5 (C^{B4}), 139.7 (C^{C1}), 127.7 (C^{A5}), 127.4 (C^{C2}), 127.1 (C^{B1}), 122.3 (C^{B2}), 119.3 (C^{B3}), 115.9 (C^{A3}), 114.5 (C^{C3}), 55.4 (C^{OMe}), 25.4 (C^{Me}); signal for C^{A4} not resolved. ESI MS: *m/z* 1644.6 $[M{-}PF_6]^+$ (calc. 1644.6), 791.5 $[\mathbf{1} + H]^+$ (base peak, calc. 791.4). UV-VIS (MeCN, 1.0×10^{-5} mol dm^{-3}) λ_{abs} / nm 304 (ε / dm^3 mol^{-1} cm^{-1} 78390), 368 (76950), 486 (16900). IR (solid, $\tilde{\nu}$ / cm^{-1}): 3052 (w), 3032 (w), 1591 (s), 1498 (s), 1324 (m), 1239 (s), 1171 (m), 1030 (m), 822 (s), 746 (s), 691 (s). Found: C, 67.54; H, 5.14; N, 6.34; $C_{104}H_{92}CuF_6N_8O_8P\cdot3H_2O$ requires C, 67.72; H, 5.36; N, 6.08.

$[Cu(\mathbf{2})_2][PF_6]$

Compound **2** (586 mg, 0.371 mmol) was dissolved in $CHCl_3$ (15 mL) and a MeCN (15 mL) solution $[Cu(MeCN)_4][PF_6]$ (69.1 mg, 0.185 mmol) was added. The solution turned red and was stirred overnight at ambient temperature. The volume of solvent was reduced and the product was precipitated by adding Et_2O. $[Cu(\mathbf{2})_2][PF_6]$ was separated by filtration and was washed with Et_2O; it was isolated as red solid (601 mg, 0.179 mmol, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm: 8.26 (s, 2H, H^{A3}), 7.62 (d_{AB}, J = 8.6 Hz, 4H, H^{B2}), 7.57 (s, 2H, H^{A5}), 7.11 (d_{AB}, J = 8.6 Hz, 4H, H^{B3}), 7.07 (d_{AB}, J = 8.9 Hz, 16H, H^{D2}), 7.01 (d_{AB}, J = 8.8 Hz, 8H, H^{C2}), 6.90 (d_{AB}, J = 8.9 Hz, 8H, H^{C2}), 6.83 (d_{AB}, J = 9.0 Hz, 8H, H^{D3}), 3.78 (s, 24H, H^{OMe}), 2.31 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm 157.1 (C^{A6}), 155.7 (C^{D4}), 152.3 (C^{A2}), 150.3 (C^{A4}), 150.0 (C^{B4}), 145.2 (C^{C4}), 141.0 (C^{D1}), 139.4 (C^{C1}), 127.7 (C^{B2}), 127.4 (C^{B1}), 126.3 (C^{D2}), 126.3 (C^{C2}), 121.6 (C^{C3}), 120.0 (C^{B3}), 122.3 (C^{A5}), 115.9 (C^{A3}), 114.6 (C^{D3}), 55.4 (C^{OMe}), 25.3 (C^{Me}). MALDI-TOF MS *m/z*: 3223.9 $[M - PF_6]^+$ (calc. 3222.3), 1580.0 $[L+H]^+$ (calc. 1580.7). UV-VIS (MeCN, 1.0×10^{-5} mol dm^{-3}) λ_{abs} / nm 308 (ε / dm^3 mol^{-1} cm^{-1} 153200), 332 sh (141100), 505 (22300). IR (ATR, $\tilde{\nu}$ / cm^{-1}): 3036 (w), 2949 (w), 2836 (w), 1591 (s), 1495 (s), 1313 (m), 1266 (m), 1235 (s), 1178 (m), 1105 (m), 1033 (s), 881 (m), 821 (s). Found: C, 71.89; H, 5.29; N, 6.90; $C_{208}H_{180}CuF_6N_{16}O_{16}P\cdot CHCl_3\cdot CH_3CN$ requires C, 71.82; H, 5.26; N, 6.75.

Solar cell fabrication

DSCs were prepared adapting the method of Grätzel and coworkers.[5] The TiO_2 paste was prepared following the published method with adaptations: a porcelain (in place of alumina) mortar, sonicator bath (in place of an ultrasonic horn), and terpineol (CAS: 8000-41-7, in place of α-terpineol). Each working electrode was prepared from an FTO glass plate (Solaronix TCO22-7, 2.2 mm thickness, sheet resistance ≈7 Ω square^{-1}) which was cleaned by sonicating in Hellmanex® surfactant (2% in milliQ water), and rinsed with milliQ water and EtOH. After a surface activation in a UV-O_3 system (Model 256-220, Jelight Company Inc) for 20 min, the FTO plate were immersed in aqueous $TiCl_4$ solution (40 mmol dm^{-3}) at 70 ^{o}C for 30 min, and then washed with milliQ water and EtOH. The FTO plate was dried and a layer of TiO_2 paste was screen printed (90T, Serilith AG, Switzerland). The printed plate was kept in an EtOH chamber for 3 min to reduce surface irregularities of the printed layer and dried for 6 min at 125 ^{o}C on a heating plate. The screen printing process was repeated 6 times and then 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 μm (measured with Tencor Alpha-Step 500 profilometer). The annealed TiO_2 film was post-treated with 40 mmol dm^{-3} aqueous $TiCl_4$ solution (see above), rinsed with milliQ water and EtOH and sintered at 500^{o} C for 30 min. The electrodes were cooled to ca. 80^{o}C and immersed in a 1 mM DMSO solution of the anchoring ligand **3**, **4** or **5** for 20 h. The colourless electrode was removed from the solution, washed with DMSO and EtOH and dried under a stream of N_2. The electrode with adsorbed anchoring ligand was immersed in a 1 mM CH_2Cl_2 solution of [Cu(**1**)$_2$][PF$_6$] or [Cu(**2**)$_2$][PF$_6$] for 20 h, and during this time, the electrodes turned red-orange. The electrodes were removed from the solution and were washed with CH_2Cl_2 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 previously drilled hole. Residual organic impurities were removed by heating for 15 min at 500 ^{o}C on a heating plate and the perforated plate was washed with water, then 0.1 M HCl solution in EtOH and finally ultrasonicated in an acetone bath for 10 min. It was dried on the heating plate at 500 °C for 15 min. The Pt catalyst was deposited on the FTO glass plate by coating with Platisol T (2 × 10.0 μL), Solaronix, and dried on a heating plate at 500 °C for 15 min.

The dye-covered TiO_2 electrode and Pt counter-electrode were assembled using thermoplast hot-melt sealing foil (Solaronix, Meltonix 1170-25 Series, 25 microns thick) by heating while pressing them together. The electrolyte comprised 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 was introduced into the cell by vacuum backfilling. The hole on the counter electrode was finally sealed using the hot-melt sealing foil and a cover glass. The solar cell measurements and testing protocol was performed using unmasked, top-masked and fully masked cells. Non-transparent black tape was used for masking (see Figure 3 in the main paper) with a single aperture of area 0.126 cm^2 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 dot (0.288 cm^2). For complete masking, tape was also applied over the edges and rear of cell. Current density-voltage (IV) 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. Internal quantum efficiency measurements were obtained by measuring the external quantum efficiency and correcting the incoming light from absorption and reflective losses of the complete cell. This was achieved by subtracting the measured transmission (T) and reflection (R) of the complete cells from the incoming light of the light source according to:

$$IQE = \frac{EQE}{(1 - T - R)}$$

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