ESI to accompany:

The d^{10} route to Dye-Sensitized Solar Cells: Step-wise Assembly of Zinc(II) Photosensitizers on TiO_2 Surfaces

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Experimental

General

^{1}H and ^{13}C NMR spectra were measured on a Bruker DRX-500 MHz NMR spectrometer; chemical shifts are referenced to residual solvent peaks with TMS = δ 0 ppm, and spectra were assigned using COSY, NOESY, DEPT, HMQC and HMBC techniques. Electronic absorption and emission spectra were recorded using an Agilent 8453 spectrophotometer and Shimadzu RF-5301 PC spectrofluorometer, respectively. EI and electrospray (ESI) mass spectra were recorded on Finnigan MAT 95, or Bruker esquire 3000 plus mass spectrometer. IR spectra were recorded using a Shimadzu FTIR 8400 S Fourier-transform spectrophotometer with solid samples using a Golden Gate ATR. Microwave reactions were carried out in a Biotage Initiator^{TM} 8 reactor. Electrochemical measurements were carried out using a CHI 900B potentiostat with glassy carbon working and platinum auxiliary electrodes; a silver wire was used as a pseudo-reference electrode. Solvent was dry, purified MeCN and 0.1 M $[n\mathrm{Bu}_4\mathrm{N}][\mathrm{PF}_6]$ was used as supporting electrolyte. Cp_2Fe was used as external reference before each experiment. All solvents were dried before use.

Bis(dibenzylideneacetone)palladium(0) was used as received from Strem Chemicals. Ligand **4** was prepared as previously described.[1]

Ligand 1

Ligand **1** has previously been prepared in 59% using a Suzuki cross coupling.[3] A synthetic strategy based on that of Kim and coworkers for 2,2'-bipyridine-based ligands[2] gives an improved yield of **1**.

4'-(4-Bromophenyl)-2,2':6',2''-terpyridine (3.88 g, 10.0 mmol) and Ph_2NH (1.69 g, 10.0 mmol) were suspended in toluene (60 mL) under argon, and NaO^tBu (1.25 g, 13.0 mmol) was added. A suspension of bis(dibenzylideneacetone)palladium(0) (0.115 g, 0.200 mmol) and P^tBu_3 (0.041 g, 0.20 mmol) in toluene (4 mL) was prepared under argon and was added to the reaction mixture. The purple mixture was heated at 100 °C for 16 h, after which time it was filtered while hot and decolorizing charcoal was added to the filtrate. The product was purified by column chromatography (SiO_2, toluene then ethyl acetate), recrystallized from EtOH and isolated as a pale brown solid (3.43 g, 72.0%). ^1H and ^{13}C NMR spectroscopic data agree with literature data.[3] EI-MS: *m/z* 476.2 $[M]^+$ (calc. 476.2). UV-Vis (MeCN, 3.0×10^{-6} mol dm^{-3}) λ_{abs}/nm 239 (ε / dm^3 mol^{-1} cm^{-1} 28700), 285 (27700), 356 (19700). E^o / V (MeCN, $[nBu_4N][PF_6]$, vs Fc/Fc$^+$): +0.92/+0.88^{qr}, –2.16^{irr}, –2.57^{irr}. IR (solid, $\tilde{\nu}$ / cm^{-1}): 3045 (w), 1700 (w), 1581 (m), 1564 (m), 1545 (w), 1517 (m), 1490 (m), 1465 (m), 1441 (m), 1420 (w), 1389 (m), 1328 (m), 1275 (s), 1231 (w), 1116 (w), 1075 (w), 1030 (w), 988 (w), 889 (m), 835 (m), 828 (m), 789 (s), 757 (s), 734 (s), 692 (s), 661 (s), 609 (m). Found: C, 82.45, H, 5.18, N, 11.61; $C_{33}H_{24}N_4$ requires C, 83.17, H, 5.08, N, 11.76.

Ligand 2

Ligand **2** has previously been prepared in 23% yield by a one-pot Hantzsch synthesis.[4] A method analogous to that for **1** gives a significantly improved yield of **2**.

4'-(4-Bromophenyl)-2,2':6',2''-terpyridine (2.90 g, 7.47 mmol) and 4,4'-dimethoxydiphenylamine (1.71 g, 7.47 mmol) were suspended in toluene (60 mL) under argon and NaO^tBu (0.933 g, 9.71 mmol) was added. A suspension of bis(dibenzylideneacetone)palladium(0) (0.086 g, 0.149 mmol) and P^{t}Bu$_3$ (1 mol dm^{-3} solution in toluene, 0.149 mL, 0.20 mmol) in toluene (4 mL) was made up under argon and added to the reaction mixture. The purple mixture was heated at 100 °C for 16 h under argon, and was then filtered hot. Solvent was removed from the filtrate under reduced pressure and the residue was suspended in EtOH (10 mL), filtered and washed with cold EtOH (20 mL). Recrystallization from EtOH yielded **2** as pale brown solid (3.02 g, 75.3 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm: 8.72 (ddd, J = 4.8, 1.7, 0.9 Hz, 2H, H^{A6}), 8.69 (s, 2H, H^{B3}), 8.66 (ddd, J = 8.0, 1.0, 1.0 Hz, 2H, H^{A3}), 7.87 (td, J = 7.7, 1.7 Hz, 2H, H$^{A4)}$), 7.75 (d$_{AB}$, J = 8.8 Hz, 2H, H^{C2}), 7.34 (ddd, J = 7.5, 4.8, 1.2 Hz, 2H, H^{A5}), 7.11 (d$_{AB}$, J = 9.0 Hz, 4H, H^{D2}), 7.02 (d$_{AB}$, J = 8.8 Hz, 2H, H^{C3}), 6.87 (d$_{AB}$, J = 9.0 Hz, 4H, H^{D3}), 3.82 (s, 6H, H^{Me}). ^{13}C NMR (126 MHz, CD_3Cl) δ / ppm: 156.6 (C^{A2}), 156.3 (C^{D4}), 155.9 (C^{B2}), 150.0 (C$^{C4/B4}$), 149.8 (1C, C$^{B4/C4}$), 149.2 (C^{A6}), 140.6 (C^{D1}), 136.9 (C^{A4}), 129.8 (C^{C1}), 128.1 (C^{C2}), 127.1 (C^{D2}), 123.8 (C$^{A5)}$), 121.5 (C^{A3}), 120.1 (C^{C3}), 118.1 (C^{B3}), 114.9 (C^{D3}), 55.6 (C^{Me}). MS (EI, *m/z*): 536.2 [M]$^+$ (calc.: 536.2), 521.2 [M–Me]$^+$ (calc.: 521.2). UV-Vis (MeCN, 1.04 × 10^{-5} mol dm^{-3}) λ_{abs}/nm 240 (ε / dm^3 mol^{-1} cm^{-1} 31800), 286 (38500), 354 (24700). E^o / V (MeCN, [nBu$_4$N][PF$_6$], vs Fc/Fc$^+$): +1.00^{irr}, +0.42/+0.34^{qr}, –2.42^{irr}. IR (ATR, $\tilde{\nu}$ / cm^{-1}): 3039 (w), 2950 (w), 2832 (w), 1700 (w), 1601 (m), 1582 (m), 1565 (m), 1501 (s), 1460 (m), 1440 (m), 1391 (m), 1322 (m), 1268 (m), 1236 (s), 1178 (w), 1167 (w), 1105 (m), 1034 (s), 989 (m), 892 (m), 826 (s), 789 (s), 737 (m), 658 (s), 621 (m). Found: C, 78.48, H, 5.30, N, 10.45; $C_{35}H_{28}N_4O_2$ requires C, 78.34, H, 5.26, N, 10.44.

[Zn(1)$_2$][PF$_6$]$_2$

[Zn(1)$_2$][PF$_6$]$_2$ has been previously prepared in 73% yield under ambient conditions.^{5} The following procdeure gives near quantitative yield. Ligand **1** (100 mg, 0.210 mmol) and Zn(OAc)$_2$·2H$_2$O (28.2 mg, 0.126 mmol) were suspended in EtOH (5 mL) and the mixture was heated in a microwave reactor for 1 h at 120 °C. The precipitate that formed was dissolved in

EtOH (150 mL) and then an excess of aqueous NH_4PF_6 and water (50 mL) was added and an orange precipitate formed. This was separated by filtration, washed with H_2O and Et_2O, and then redissolved in MeCN (20 mL). After removal of solvent under reduced pressure, $[Zn(\mathbf{1})_2][PF_6]_2$ was isolated as an orange solid (134 mg, 97.5 %). ^{1}H NMR (500 MHz, CD_3CN) δ / ppm: 8.89 (s, 4H, H^{B3}), 8.68 (ddd, J = 8.0, 0.9, 0.9 Hz, 4H, H^{A3}), 8.14 (td, J = 7.8, 1.6 Hz, 4H, H^{A4}), 8.09 (d_{AB}, J = 8.9 Hz, 4H, H^{C2}), 7.81 (ddd, J = 5.1, 1.5, 0.8 Hz, 4H, H^{A6}), 7.44 (m, 8H, H^{D3}), 7.38 (m, 4H, H^{A5}), 7.25 (m, 12H, H^{D2+D4}), 7.22 (d_{AB}, J = 8.8 Hz, 4H, H^{C3}). ^{13}C NMR (126 MHz, CD_3CN) δ/ppm: 156.3 (C^{B4}), 152.0 (C^{C4}), 150.6 (C^{B2}), 149.0 (C^{A2}), 148.8 (C^{A6}), 147.6 (C^{D1}), 142.1 (C^{A4}), 130.8 (C^{D3}), 130.0 (C^{C2}), 128.4 (C^{C1}), 128.3 (C^{A5}), 126.9 (C^{D2}), 125.8 (C^{D4}), 124.0 (C^{A3}), 121.8 (C^{C3}), 121.0 (C^{B3}). ESI-MS: m/z 508.2 $[M - 2PF_6]^{2+}$ (calc. 508.2). UV-VIS (MeCN, 3.0×10^{-6} mol dm^{-3}) λ_{abs}/nm 205 (ε / dm^3 mol^{-1} cm^{-1} 170958), 243 (70888), 259 (63656), 284 (73148), 311sh (48742), 325 (43196), 407 (49060). E^o / V (MeCN, $[n\text{Bu}_4\text{N}][PF_6]$, vs Fc/Fc$^+$): +0.78/+0.70^{qr}, –2.42/–2.35^{qr}. IR (ATR, $\tilde{\nu}$ / cm^{-1}): 3066 (w), 1584 (m), 1572 (w), 1544 (w), 1516 (m), 1489 (m), 1471 (m), 1414 (m), 1363 (w), 1331 (m), 1262 (w), 1244 (w), 1201 (m), 1163 (w), 1116 (w), 1076 (w), 1024 (w), 1015 (w), 830 (s), 789 (s), 757 (m), 732 (m), 695 (s), 688 (s), 659 (m). Found: C, 57.49, H, 3.92, N, 8.27; $C_{66}H_{48}F_{12}N_8P_2Zn{\cdot}4H_2O$ requires C, 57.42, H, 4.09, N, 8.12.

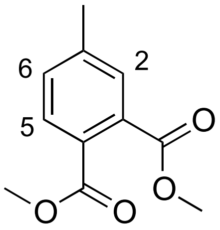
$[Zn(\mathbf{2})_2][PF_6]_2$

Ligand **2** (100 mg, 0.186 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (24.5 mg, 0.112 mmol) were suspended in EtOH (5 mL) and the mixture was heated in a microwave reactor for 1 h at 120 °C. The precipitate that formed was dissolved in EtOH (150 mL) and then an excess of aqueous NH_4PF_6 and water (50 mL) was added and an orange precipitate formed. This was separated by filtration, washed with H_2O and Et_2O, and then redissolved in MeCN (20 mL). Solvent was removed under reduced pressure to give an orange glassy solid. This was dissolved in CH_2Cl_2 (20 mL) and then toluene (10 mL) was added. The solvents were evaporated under reduced pressure and [Zn(**2**)$_2$][PF$_6$]$_2$ was isolated as an orange solid (130 mg, 97.6 %). ^{1}H NMR (500 MHz, CD$_3$CN) δ/ppm: 8.85 (s, 4H, H^{B3}), 8.66 (dt, *J* = 8.3, 0.8 Hz, 4H, H^{A3}), 8.13 (td, *J* = 7.9, 1.6 Hz, 4H, H^{A4}), 8.03 (d$_{AB}$, *J* = 9.0 Hz, 4H, H^{C2}), 7.79 (ddd, *J* = 5.1, 1.5, 0.8 Hz, 4H, H^{A6}), 7.36 (m, 4H, H^{A5}), 7.24 (d$_{AB}$, J = 9.0 Hz, 8H, H^{D2}), 7.01 (m, 12H, H^{D3+C3}), 3.83 (s, 12H, H^{Me}). ^{13}C NMR (126 MHz, CD$_3$CN) δ / ppm: 158.5 (C^{D4}), 156.5 (C$^{B4/C4}$), 153.1 (C$^{B4/C4}$), 150.5 (C^{A2}), 149.2 (C^{B2}), 148.9 (C^{A6}), 142.1 (C^{A4}), 140.2 (C^{D1}), 129.9 (C^{C2}), 129.2 (C^{D2}), 128.3 (C^{A5}), 126.2 (C^{C1}), 123.9 (C^{A3}), 120.6 (C^{B3}), 118.6 (C^{C3}), 116.1 (C^{D3}), 56.2 (C^{Me}). ESI-MS *m/z*: ESI-MS: *m/z* 568.2 [M – 2PF$_6$]$^{2+}$ (calc. 568.2), 537.3 [**2** + H]$^+$ (base peak, calc. 537.2). UV-VIS (MeCN, 3.0 × 10^{-6} mol dm^{-3}) λ_{abs} / nm 231 (ε / dm^3 mol^{-1} cm^{-1} 65158), 283 (71034), 313sh (49669), 325 (44219), 420 (48338). *E*^{o} / V (MeCN, [*n*Bu$_4$N][PF$_6$], vs Fc/Fc$^+$) +1.03^{irr}, +0.49/+0.40^{qr}, –2.44^{irr}. IR (ATR, ṽ / cm^{-1}): 1700 (w), 1595 (m), 1572 (w), 1502 (s), 1474 (m), 1465 (w), 1437 (w), 1418 (w), 1366 (w), 1325 (w), 1285 (w), 1237 (s), 1198 (w), 1162 (w), 1106 (w), 1069 (w), 1015 (w), 824 (s), 788 (s), 744 (w), 730 (s), 667 (w), 659 (s), 639 (w). Found: C, 57.41; H, 4.13; N, 7.65; C$_{70}$H$_{56}$F$_{12}$N$_8$O$_4$P$_2$Zn·2H$_2$O requires C, 57.52; H, 4.24; N,7.78.

Synthesis of anchoring ligand 3

The precursor to **3** was dimethyl 4-formylphthalate. Although previously utilized, its synthesis is not accessible in the non-patent literature.

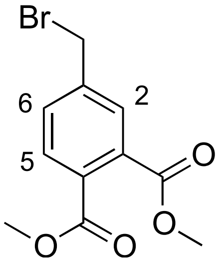
Compound I



I

4-Methylphthalic acid anhydride (4.00 g, 24.67 mmol) was suspended in MeOH (35 mL). Sulfuric acid (98%, 2 mL) was added and the suspension was heated at reflux overnight. The solvent was evaporated, the residue was dissolved in Et_2O and neutralized with saturated aqueous $NaHCO_3$. The aqueous phase was extracted three times with Et_2O and dried over Na_2SO_4. After evaporation of the Et_2O, **I** was isolated (4.39 g , 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm: 7.66 (d, *J* = 7.9 Hz, 1H, H^5), 7.46 (s, 1H, H^2), 7.31 (d, *J* = 7.9 Hz, 1H, H^6), 3.89 (s, 3H, H^{OMe}), 3.87 (s, 3H, H^{OMe}), 2.39 (s, 3H, H^{CMe}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm : 168.8 (C^{CO}), 168.7 (C^{CO}), 142.2 (C^{C1}), 132.8 (C^{C3}), 131.5 (C^{C6}), 129.3 (C^{C5}), 129.25 (C^{C2}), 128.4 (C^{C4}), 52.7 (C^{OMe}), 52.6 (C^{OMe}), 21.4 (C^{CMe}). EI-MS *m/z*: 208.1 $[M]^+$ (calc. 208.1).

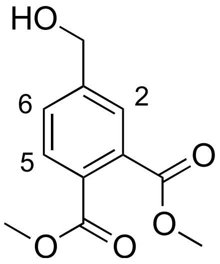
Compound II



II

Dibenzoyl peroxide (100 mg, 0.41 mmol) and NBS (5.51 g, 30.95 mmol) were added to a solution of **I** (5.86 g, 28.14 mmol) in CCl_4 (75 mL). The mixture was heated at reflux for 3 h and after cooling to room temperature, the solid product was separated by filtration. The solvent was evaporated yielding 7.61 g of crude product. Column chromatographic purification (silica, hexanes/CH_2Cl_2, 5:1) yielded **II** contaminated with 30-35% dibromo derivative. **II**: ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm: 7.73 (d, *J* = 1.8 Hz, 1H, H^2), 7.70 (d, *J* = 8.0 Hz, 1H, H^5), 7.54 (dd, *J* = 8.0, 1.8 Hz, 1H, H^6), 4.47 (s, 2H, H^{CH2}), 3.90 (s, 3H, H^{OMe}), 3.89 (s, 3H, H^{OMe}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm: 167.7 (C^{CO}), 167.2 (C^{CO}), 140.7 (C^{C1}), 132.7 (C^{C3}), 131.8 (C^{C4}), 131.4 (C^{C5}), 129.4 (C^{C6}), 129.1 (C^{C2}), 52.9 (C^{OMe}), 52.8 (C^{OMe}), 31.4 (C^{CH2}). EI-MS *m/z*: 287.0 (with diagnostic Br pattern, calc. 286.0). The impure compound was used for the next step without further purification.

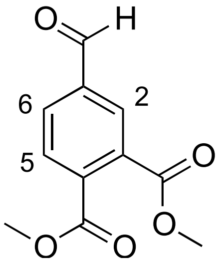
Compound III



III

Compound **II** (11.7 g crude with 65% **II**, see above) was dissolved in acetone/water (100 mL, 1:1 by vol.) and Na_2CO_3 (17.326 g, 163.47 mmol) was added. The mixture was heated at reflux for 16 h after which time it was cooled, and neutralized by addition of 1M HCl. Acetone was evaporated and the organic compounds were extracted three times in ethyl acetate. Column purification (SiO_2, hexane/ethyl acetate 1:1) yielded **III** (2.60 g, ~43%). ^1H NMR (500 MHz, $CDCl_3$) δ / ppm 7.70 (d, $J = 7.9$ Hz, 1H, H^5,), 7.65 (m, 1H, H^2) 7.49 (m, 1H, H^6), 4.73 (d, $J = 5.7$ Hz, 2H, H^{CH2}), 3.89 (s, 3H, H^{OMe}), 3.89 (3H, H^{OMe}) 2.39 (t, $J = 6.0$ Hz, 1H, H^{OH}). ^{13}C NMR (126 MHz, $CDCl_3$) δ / ppm 168.4 (C^{CO}), 167.9 (C^{CO}), 144.9 (C^{C1}), 132.5 (C^{C3}) , 130.5 (C^{C4}), 129.4 (C^{C5}), 128.9 (C^{C6}), 126.8 (C^{C2}), 64.1 (C^{CH2}), 52.85 (C^{OMe}), 52.8 (C^{OMe}). EI-MS *m/z*: 224.1 $[M]^+$ (calc. 224.1). IR (neat, cm^{-1}) 3647 (m), 3568 (m), 3547 (m), 3448 (m), 3367 (m), 3218 (m), 3206 (m), 3191 (m), 3097 (m), 3030 (m), 3001 (m), 2994 (m), 2954 (m), 2876 (m), 2843 (m), 2841 (m), 2735 (m), 2602 (m), 1721 (s), 1716 (s), 1693 (m), 1609 (w), 1435 (m), 1417 (w), 1289 (s), 1199 (m), 1127 (m), 1071 (m), 1022 (w), 980 (w), 960 (w), 631 (s).

Dimethyl 4-formylphthalate (IV)



IV

Compound **III** (2.60 g, 11.6 mmol) was dissolved in CH_2Cl_2 and MnO_2 (10.1 g, 116 mmol) was added. The suspension was stirred in the dark for 5 d, and then the mixture was filtered over Celite to remove the MnO_2 and washed 3 times with CH_2Cl_2. Solvent was evaporated *in vacuo* and **IV** was isolated as a pale yellow liquid (2.00 g 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ / ppm : 10.07 (s, 1H, H^{CHO}), 8.27 (dd, *J* = 1.6, 0.5 Hz, 1H, H^2), 8.05 (dd, *J* = 7.9, 1.6 Hz, 1H, H^6), 7.82 (d, *J* = 7.8 Hz, 1H, H^5), 3.94 (s, 6H, H^{OMe}). ^{13}C NMR (126 MHz, $CDCl_3$) δ/ppm: 190.6 (C^{CHO}), 167.6 (C^{CO}), 166.6 (C^{CO}), 137.7 (C^{C1}), 137.6 (C^{C4}), 132.2 (C^{C3}), 132.0 (C^{C6}), 130.6 (C^{C2}), 129.6 (C^{C5}), 53.2 (C^{OMe}), 53.1 (C^{OMe}). EI-MS *m/z*: 222.0 $[M]^+$ (calc. 222.1). IR (neat, cm^{-1}) 3650 (w), 3223 (w), 3178 (w), 3001 (w), 2992 (w), 2954 (w), 2884 (w), 2844 (w), 2808 (w), 2619 (w), 2584 (w), 2468 (w), 2323 (w), 1723 (s), 1700 (s), 1696 (s), 1685 (s), 1661 (w), 1648 (w), 1642 (w), 1607 (m), 1574 (w), 1551 (w), 1519 (w), 1515 (w), 1490 (w), 1474 (w), 1434 (s), 1420 (w), 1385 (w), 1373 (w), 1277 (s), 1197 (s), 1178 (s), 1122 (s), 1068 (s), 1024 (w), 1015 (w), 978 (w), 958 (m), 919 (w), 900 (m), 847 (m), 821 (m), 804 (s), 791 (m), 765 (m), 700 (m), 686 (m), 658 (m), 601 (s).

Ligand 3

Aldehyde **IV** (1.34 g, 6.03 mmol) and 2-acetylpyridine (1.46 g, 12.05 mmol) were dissolved in EtOH (30 mL). Solid KOH (677 mg, 12.1 mmol) and aqueous NH_3 (25%, 1.5 mL, 20.0 mmol) were added and stirred overnight. Water (50 mL) was poured into the reaction mixture and the product was precipitated with concentrated aqueous HCl. The precipitate was separated by filtration, washed with H_2O and EtOH, suspended in EtOH (50 ml) and heated at reflux for 15 min. After cooling, the mixture was filtered, dried over P_2O_5 and **3** was isolated as a white solid (1.03 g, 43%). ^{1}H NMR (500 MHz, DMSO-d$_6$) δ / ppm 8.78 (ddd, *J* = 4.8, 1.7, 0.9 Hz, 2H, H^{A6}), 8.76 (s, 2H, H^{B3}), 8.67 (d, *J* = 7.9 Hz, 2H, H^{A3}), 8.45 (br, H$^{C2/C6}$), 8.13 overlapping 8.12 (br, 2H$^{C5+C2/C6}$), 8.04 (td, J = 7.6, 1.8 Hz, 2H, H^{A4}), 7.54 (m, 2H, H^{A5}). ^{13}C NMR (126 MHz, DMSO-d$_6$) δ / ppm 168.0 (C^{CO}), 167.9 (C^{CO}), 155.9 (C^{B2}), 154.7 (C^{A2}), 149.4 (C^{A6}), 147.9 (C^{B4}), 139.2 (C^{C1}), 137.6 (C^{A4}), 134.9 (C^{C3+C4}), 131.9 (C$^{C2/C6}$), 128.8 (C^{C5}), 128.72 (C$^{C2/C6}$), 124.7 (C^{A5}), 121.0 (C^{A3}), 117.9 (C^{B3}). ESI-MS *m/z*: 379.1 $[M - H_2O]^+$ (base peak, calc. 379.1). IR (neat, cm^{-1}) 3474 (w), 3443 (w), 3222 (w), 3081 (w), 1717 (w), 1712 (m), 1699 (m), 1586 (w), 1410 (w), 1366 (m), 1362 (m), 1259 (w), 1242 (w), 1171 (w), 1122 (w), 1070 (w), 1043 (w), 991 (w), 917 (w), 893 (w), 854 (w), 844 (w), 789 (m), 764 (m), 733 (w), 668 (m).

Solar cell preparation

TiO_2 paste was prepared by a procedure based on that descibed by Grätzel and coworkers.[6] The adaptations to the published procedure were use of a porcelain mortar, a sonicator bath, and terpineol (CAS: 8000-41-7) in place of α-terpineol, and the omission of the three roller mill treatment. The FTO glass (Solaronix TCO22-7, 2.2 mm thickness, sheet resistance ≈7 Ω square^{-1}) was cleaned by sonicating in acetone, EtOH, Hellmanex® surfactant (2% in water), water and EtOH bath sequentially for 10 min. After treatment in a UV-O_3 system (Model 256-220, Jelight Company Inc), the FTO plates were immersed into 40 mM aqueous $TiCl_4$ solution at 70°C for 30 min, and washed with water and EtOH. Nanocrystalline TiO_2 electrodes were made by doctor blading the TiO_2 paste onto a conducting glass slide and kept at room temperature for 10 min so that the paste could mature to reduce the surface irregularity. The electrode coated with the TiO_2 paste was gradually heated under an air flow at 70°C for 30 min, 135°C for 5 min, 325°C for 5 min, 375°C for 5 min, 450°C for 15 min, and 500°C for 15 min. After annealing, the TiO_2 film was treated with 40 mM $TiCl_4$ solution as described above, rinsed with water and EtOH and sintered at 500°C for 30 min. After cooling to about 80°C, each slide was immersed in a DMSO solution of ligand **3**, **4** or **5** (1 mmol dm^{-3}) for 24 h. The colourless slide was moved from the solution, washed with DMSO and EtOH, and dried. The electrode was next immersed in an EtOH solution of $Zn(OAc)_2$ or $ZnCl_2$ (0.5 mmol dm^{-3}) for 24 h. The electrode was removed from the solution and was washed with EtOH. Finally, the electrode was immersed in a CH_2Cl_2 solution of ligand **1** or **2** (0.5 mmol dm^{-3}) for 64 h during which time the slide turned from colourless to orange.

To prepare the counter electrode, a hole was drilled in the FTO glass, and the perforated sheet was heated in air for 15 min at 450°C to remove organic residues and was then washed as described for the working electrode. The Pt catalyst was deposited on the FTO glass by coating with a drop of H_2PtCl_6, 5 mmol dm^{-3} in propan-2-ol and heated to 400°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 was a mixture 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 MeCN, and was introduced into the cell via vacuum backfilling. The hole on the counter electrode was finally sealed using the hot-melt sealing foil and a cover glass. 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.

References

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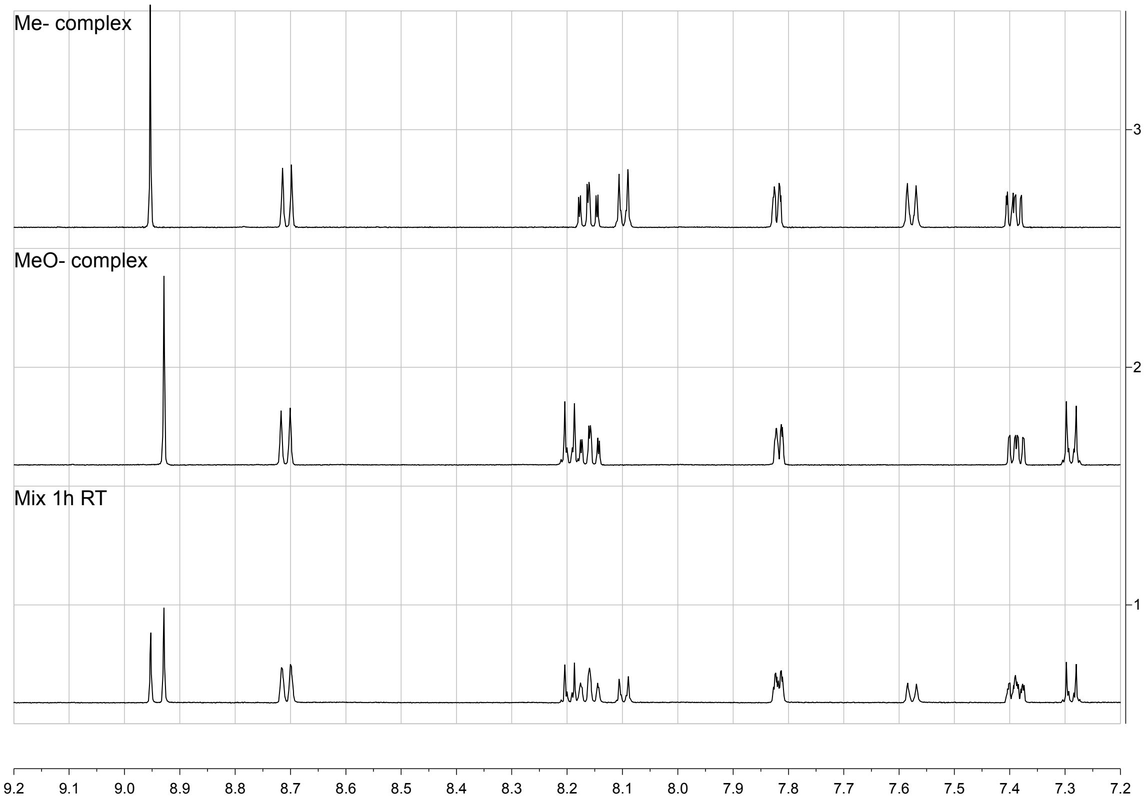


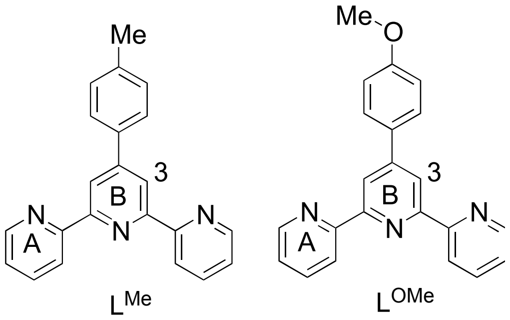


Figure S1(a). 500 MHz ^{1}H NMR spectra of CD_3CN solutions of (top to bottom): $[Zn(L^{Me})_2][PF_6]_2$, $[Zn(L^{OMe})_2][PF_6]_2$ and 1 : 1 mixture of $[Zn(L^{Me})_2][PF_6]_2$ and $[Zn(L^{OMe})_2][PF_6]_2$ after standing at room temperature for 1 hour.

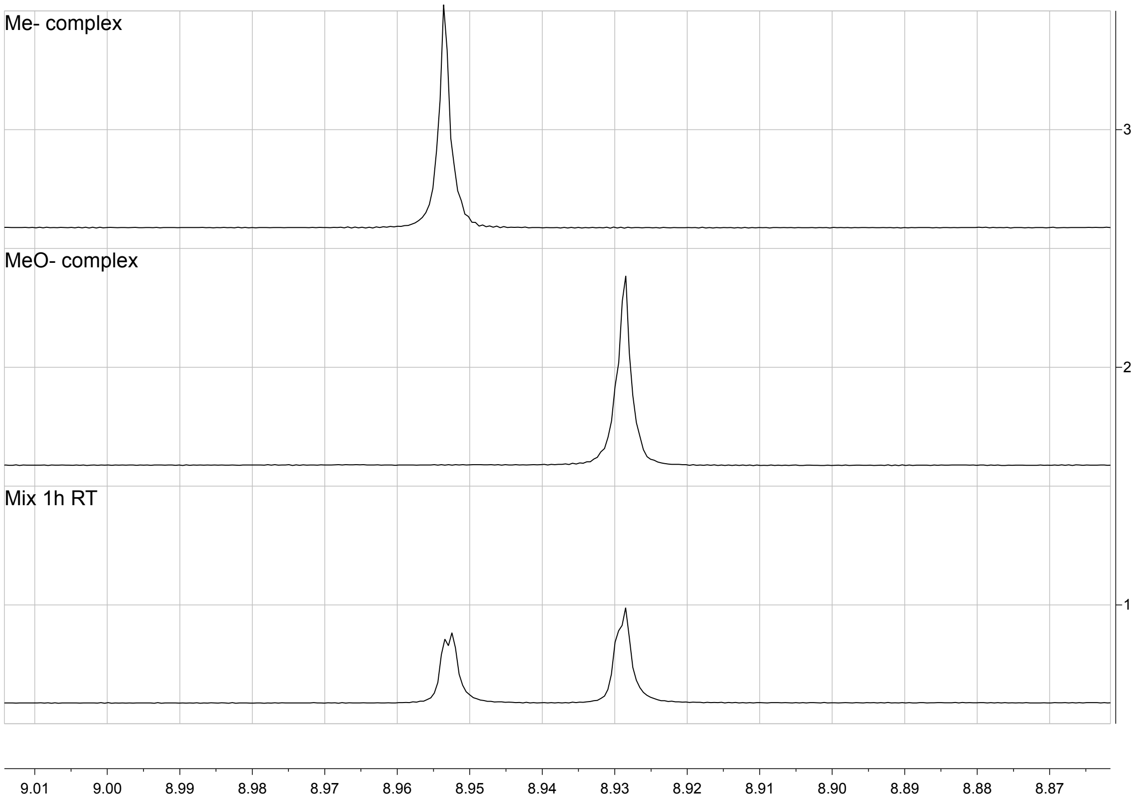
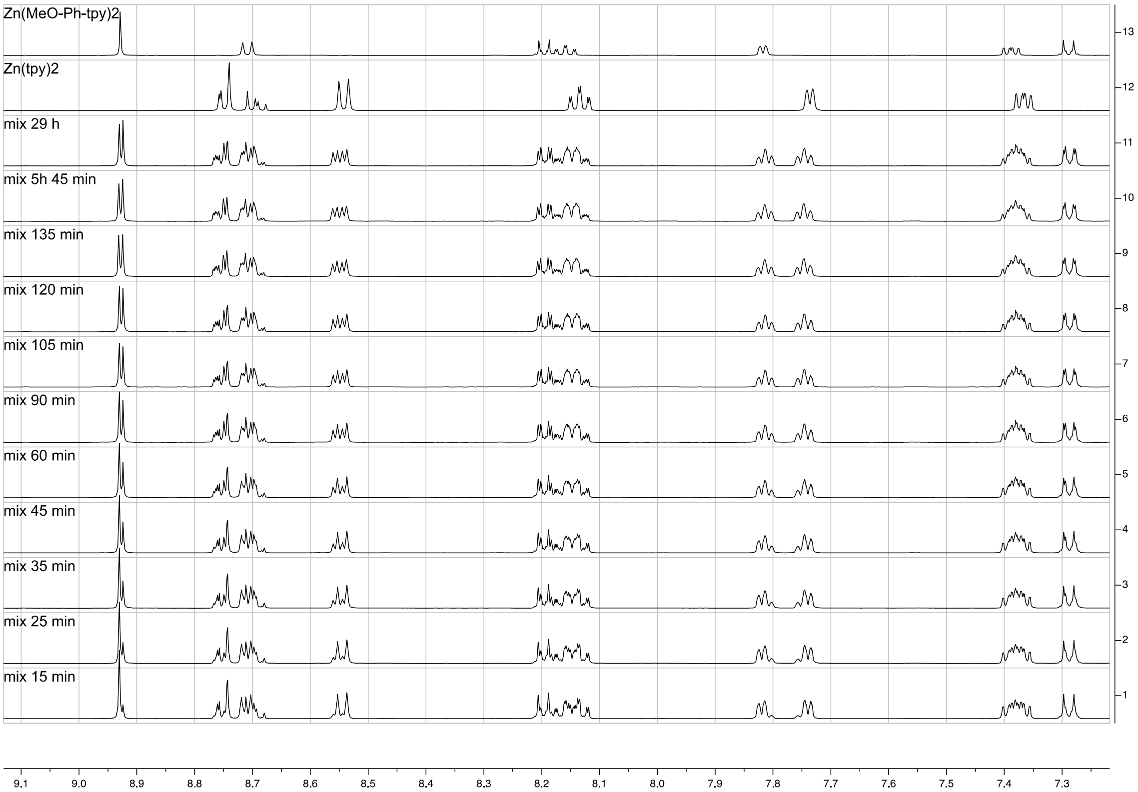


Fig. S1(b) Expansion of the signals for protons H^{B3} (see scheme above) in the 500 MHz ^1H NMR spectra of CD_3CN solutions of (top to bottom): $[Zn(L^{Me})_2][PF_6]_2$, $[Zn(L^{OMe})_2][PF_6]_2$ and 1 : 1 mixture of $[Zn(L^{Me})_2][PF_6]_2$ and $[Zn(L^{OMe})_2][PF_6]_2$ after standing at room temperature for 1 hour.



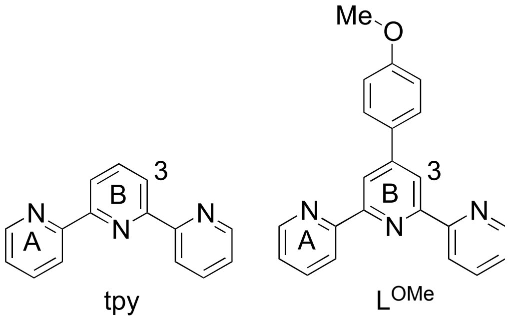


Figure S2(a). 500 MHz ^{1}H NMR spectra of CD$_3$CN solutions of [Zn(L^{OMe})$_2$][PF$_6$]$_2$ and [Zn(tpy)$_2$][PF$_6$]$_2$ (top two spectra) and (from bottom upwards) a 1 : 1 mixture of [Zn(tpy)$_2$][PF$_6$]$_2$ and [Zn(L^{OMe})$_2$][PF$_6$]$_2$ after standing at room temperature for periods of 15 minutes to 29 hours.

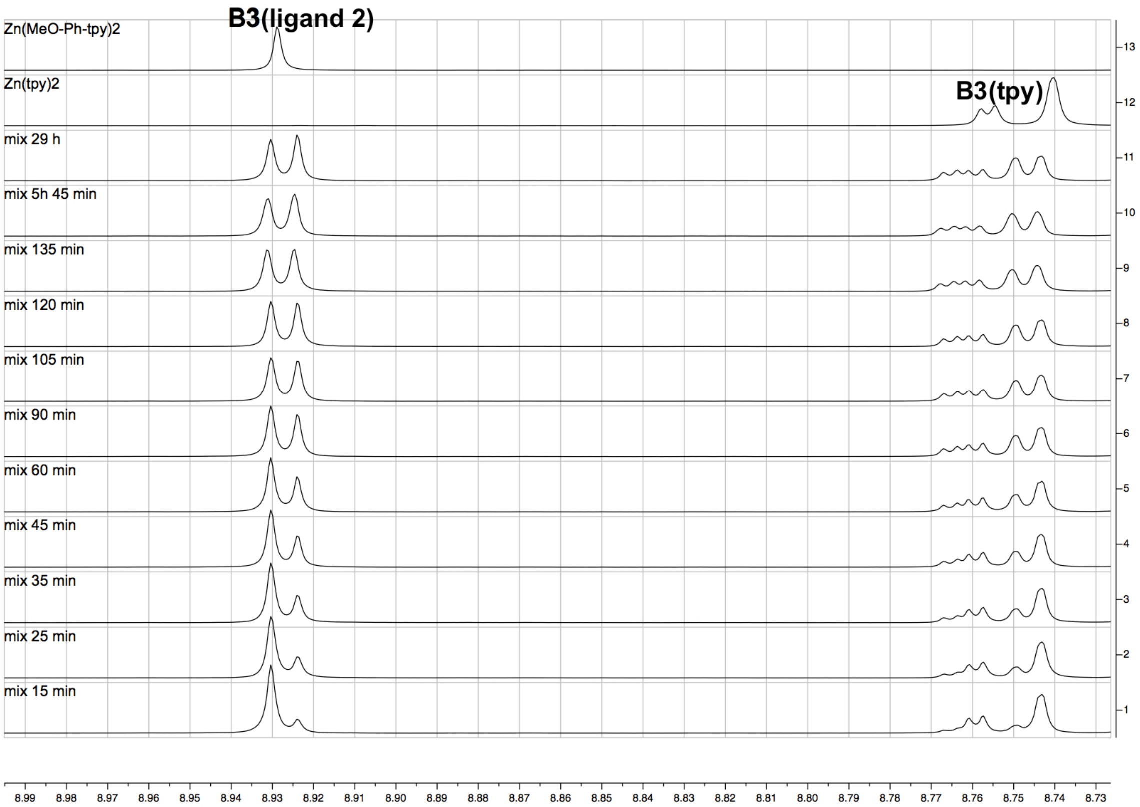


Figure S2(b). Expansion of the signals for the protons H^{B3} (see scheme above) in the 500 MHz ^{1}H NMR spectra of CD_3CN solutions of $[Zn(L^{OMe})_2][PF_6]_2$ and $[Zn(tpy)_2][PF_6]_2$ (top two spectra) and (from bottom upwards) a 1 : 1 mixture of $[Zn(tpy)_2][PF_6]_2$ and $[Zn(L^{OMe})_2][PF_6]_2$ after standing at room temperature for periods of 15 minutes to 29 hours.