ESI to accompany:

**Combining phosphonic acid-functionalized anchoring ligands with asymmetric ancillary ligands in bis(diimine)copper(I) dyes for dye-sensitized solar cells**

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Syntheses of ligands 1–6

**Compound 1.** Compound 1 is prepared by deprotection of the corresponding diethylester and this step has previously been carried out using concentrated aqueous HCl and glacial acetic acid.1 A more convenient method is as follows. Tetraethyl ((6,6’-dimethyl-[2,2’-bipyridine]-4,4’-diyl)bis(4,1-phenylene))bis(phosphonate) (25 mg, 0.0341 mmol) and an excess of Me3SiBr (0.09 mL, 104 mg, 0.682 mmol, 20 eq.) were dissolved in dry CH2Cl2 (4 mL) and the solution was stirred for 22 h at room temperature. The reaction mixture was quenched with water (≈20 mL). An off-white solid precipitated which was collected by filtration and washed with water (≈10 mL). The organic phase was extracted with water (2 × 15 mL). The combined aqueous phases were concentrated under reduced pressure, and then toluene (50 mL) was added and solvent then removed. The residue was dried under high vacuum, yielding 1 as an off-white solid (12.4 mg, 0.0199 mmol, 58.6%). Spectroscopic data matched those reported.1

**Compound 3.** The preparation of 3 has been reported,2 but we find the following route more convenient. Compound 3a (1.89 g, 9.03 mmol) and 1-(2-oxopropyl)pyridinium chloride (1.55 g, 9.03 mmol) were dissolved in EtOH (40 mL). A solution of NH4OAc (20.9 g, 271 mmol) in EtOH (40 mL) was then added, and the reaction mixture was heated at reflux overnight (≈20 h). Solvent was then removed in vacuo and the residue dissolved in CH2Cl2, then extracted with CH2Cl2/H2O (3 × 100 mL) and the combined extracts dried over MgSO4. After separation from MgSO4 and removal of solvent, a brown oil was obtained which was purified by column chromatography (alumina, CH2Cl2). 3 was obtained as a sticky, off-white solid (1.77 g, 7.18 mmol, 79.5%). 270 MHz 1H NMR spectroscopic data have previously been reported.2 1H NMR (500 MHz, CD3CN) δ / ppm 8.67 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H, H\(^{A6}\)), 8.49 (m, 1H, H\(^{B3}\)), 8.45 (ddd, J = 8.0, 1.1, 1.1 Hz, 1H, H\(^{A3}\)), 7.89 (m, 1H, H\(^{A4}\)), 7.79 (m, 2H, H\(^{C2}\)), 7.54 (m, 3H, H\(^{C3+R5}\)), 7.48 (m, 1H, H\(^{C4}\)), 7.39 (m, 1H, H\(^{A5}\)), 2.64 (s, 3H, H\(^{Me}\)). 13C NMR (126 MHz, CD3CN) δ / ppm 159.7 (C\(^{B6}\)), 157.0 (C\(^{A2/B2}\)), 156.9 (C\(^{A2/B2}\)), 150.2 (C\(^{A6}\)), 150.15 (C\(^{B4}\)), 139.3 (C\(^{Cl}\)), 138.0 (C\(^{A4}\)), 130.1 (C\(^{C3}\)), 130.0 (C\(^{C4}\)), 127.9 (C\(^{C2}\)), 124.9 (C\(^{A5}\)), 122.1 (C\(^{R5}\)), 121.4 (C\(^{A1}\)), 116.4 (C\(^{R3}\)), 24.7 (C\(^{Me}\)).

**Compound 4.** Compound 4a (2.00 g, 6.94 mmol), 1-(2-oxopropyl)pyridinium chloride (1.19 g, 6.94 mmol) and NH4OAc (16.1 g, 208 mmol) were suspended in EtOH (120 mL). The reaction mixture was heated at reflux overnight (≈20 h). As the solution was allowed to cool to room temperature, a precipitate formed. Compound 4 was separated by
filtration, washed with cold MeOH and was isolated as an off-white solid (608 mg, 1.87 mmol, 26.8%). M.p. 125.0 °C. 1H NMR (500 MHz, CD3CN) δ / ppm 8.67 (ddd, J = 4.8, 1.8, 0.9 Hz, 1H, H^A6), 8.45 (overlapping m, 2H, H^B3+B3), 7.90 (td, J = 7.8, 1.8 Hz, 1H, H^A4), 7.70 (overlapping m, 4H, H^C2-C3), 7.52 (d, J = 1.4 Hz, 1H, H^B5), 7.39 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H, H^A5), 2.64 (s, 3H, H^Me). 13C NMR (126 MHz, CD3CN) δ / ppm 159.5 (C^A2), 156.8 (C^A3), 150.2 (C^A4), 148.9 (C^B4), 138.5 (C^C1), 138.0 (C^A6), 133.2 (C^C3), 129.9 (C^C2), 125.0 (C^A5), 123.8 (C^C4), 121.9 (C^B5), 112.7 (C^A3), 116.3 (C^B4), 24.7 (C^OMe). ESI-MS m/z 325.0 [M + H]^+ (calc. 325.0). Found C 62.90, H 4.02, N, 8.57; C_{13}H_{13}BrN_2 requires C 62.79, H 4.03, N, 8.61%.

**Compound 5.** Compound 5a (2.50 g, 10.4 mmol) and 1-(2-oxopropyl)pyridinium chloride (1.79 g, 10.4 mmol) were dissolved in EtOH (50 mL). Then a solution of NH4OAc (24.2 g, 313 mmol) in EtOH (50 mL) was added. The reaction mixture was heated at reflux overnight (≈20 h), then allowed to cool to room temperature. The product precipitated and was collected by filtration, washed with cold MeOH and isolated as an off-white solid (928 mg, 3.35 mmol, 32.3%). M.p. 95.2 °C. 1H NMR (500 MHz, CD3CN) δ / ppm 8.67 (ddd, J = 4.7, 1.8, 0.9 Hz, 1H, H^A6), 8.44 (overlapping m, 2H, H^A3+B3), 7.89 (td, J = 7.7, 1.8 Hz, 1H, H^A4), 7.75 (m, 2H, H^C2), 7.50 (d, J = 1.5 Hz, 1H, H^B5), 7.38 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H, H^A5), 7.06 (m, 2H, H^C3), 3.85 (s, 3H, H^OMe), 2.62 (s, 3H, H^Me). 13C NMR (126 MHz, CD3CN) δ / ppm 161.6 (C^C4), 159.6 (C^B6), 157.1 (C^A2), 156.8 (C^B2), 150.2 (C^A6), 149.6 (C^B4), 137.9 (C^A4), 131.4 (C^C1), 129.2 (C^C2), 124.8 (C^A5), 121.7 (C^A3), 121.4 (C^B5), 115.8 (C^B3), 115.5 (C^C3), 56.1 (C^OMe), 24.7 (C^Me). ESI-MS m/z 277.1 [M + H]^+ (calc. 277.1). Found C 78.11, H 5.86, N, 10.02; C_{10}H_{10}N_2O requires C 78.24, H 5.84, N, 10.14%.

**Compound 6.** Compound 6a (2.50 g, 8.35 mmol), 1-(2-oxopropyl)pyridinium chloride (1.43 g, 8.35 mmol) and NH4OAc (19.7 g, 251 mmol) were suspended in EtOH (120 mL). The reaction mixture was heated to reflux, and changed from a yellow suspension to an orange, then red solution. After heating at reflux was continued for 2 days, the mixture was cooled to room temperature and then stirred for a further 36 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography (alumina, CH2Cl2). Compound 6 was initially isolated as an orange-red oil which crystalized after standing for 24 h (2.32 g, 6.89 mmol, 82.5%). M.p. 98.0 °C. 1H NMR (500 MHz, CD3CN) δ / ppm 8.67 (ddd, J = 4.7, 1.8, 0.9 Hz, 1H, H^A6), 8.43 (overlapping m, 2H, H^A3+B3), 7.88 (td, J = 7.7, 1.8 Hz, 1H, H^A4), 7.53 (d, J = 1.4 Hz, 1H, H^B5), 7.38 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H, H^A5), 7.01 (s, 2H, H^C2), 3.90 (s, 6H, H^OMe-C3), 3.78 (s, 3H, H^OMe-C4), 2.63 (s, 3H, H^Me). 13C NMR (126 MHz, CD3CN) δ / ppm 159.5 (C^B6), 157.1 (C^A2), 156.9 (C^B2), 154.8 (C^C3), 150.2 (C^B4), 150.15 (C^A6), 139.9 (C^C4), 138.0 (C^A4), 135.1 (C^C1), 124.9 (C^A5), 122.2 (C^B5), 121.8 (C^A3), 116.4 (C^B3), 105.4 (C^C2), 60.9 (C^OMe-C4), 56.9 (C^OMe-C5), 24.7 (C^Me). ESI-MS m/z 337.1 [M + H]^+ (calc. 337.2). Found C 71.28, H 6.02, N, 8.26; C_{20}H_{20}N_2O_3 requires C 71.41, H 5.99, N, 8.33%.
**Fig. S1.** $J-V$ curves for sets of four DSCs containing the dyes (a) [Cu(2)(3)]$^+$, (b) [Cu(2)(4)]$^+$ and (c) [Cu(2)(5)]$^+$ measured on the day of cell assembly to confirm performance reproducibility.