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 Me_3SiBr (0.09 mL, 104 mg, 0.682 mmol, 20 eq.) were dissolved in dry CH_2Cl_2 (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 NH_4OAc (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 CH_2Cl_2, then extracted with CH_2Cl_2/H_2O (3 × 100 mL) and the combined extracts dried over $MgSO_4$. After separation from $MgSO_4$ and removal of solvent, a brown oil was obtained which was purified by column chromatography (alumina, CH_2Cl_2). **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, CD_3CN) 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+B5}), 7.48 (m, 1H, H^{C4}), 7.39 (m, 1H, H^{A5}), 2.64 (s, 3H, H^{Me}). ^{13}C NMR (126 MHz, CD_3CN) 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^{C1}), 138.0 (C^{A4}), 130.1 (C^{C3}), 130.0 (C^{C4}), 127.9 (C^{C2}), 124.9 (C^{A5}), 122.1 (C^{B5}), 121.4 (C^{A3}), 116.4 (C^{B3}), 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 NH_4OAc (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. ^{1}H NMR (500 MHz, CD$_3$CN) δ / ppm 8.67 (ddd, *J* = 4.8, 1.8, 0.9 Hz, 1H, H^{A6}), 8.45 (overlapping m, 2H, H^{B3+A3}), 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}). ^{13}C NMR (126 MHz, CD$_3$CN) δ / ppm 160.0 (C^{B6}), 157.0 (C^{B2}), 156.8 (C^{A2}), 150.2 (C^{A6}), 148.9 (C^{B4}), 138.5 (C^{C1}), 138.0 (C^{A4}), 133.2 (C^{C3}), 129.9 (C^{C2}), 125.0 (C^{A5}), 123.8 (C^{C4}), 121.9 (C^{B5}), 121.7 (C^{A3}), 116.3 (C^{B3}), 24.7 (C^{Me}). ESI-MS *m/z* 325.0 [M + H]$^+$ (calc. 325.0). Found C 62.90, H 4.02, N, 8.57; $C_{17}H_{13}BrN_2$ 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 NH$_4$OAc (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 **5** 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. ^{1}H NMR (500 MHz, CD$_3$CN) 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}). ^{13}C NMR (126 MHz, CD$_3$CN) 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; $C_{18}H_{16}N_2O$ 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 NH$_4$OAc (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, CH$_2$Cl$_2$). 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. ^{1}H NMR (500 MHz, CD$_3$CN) 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$^{OMe\text{-}C3}$), 3.78 (s, 3H, H$^{OMe\text{-}C4}$), 2.63 (s, 3H, H^{Me}). ^{13}C NMR (126 MHz, CD$_3$CN) 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$^{OMe\text{-}C4}$), 56.9 (C$^{OMe\text{-}C3}$), 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%.

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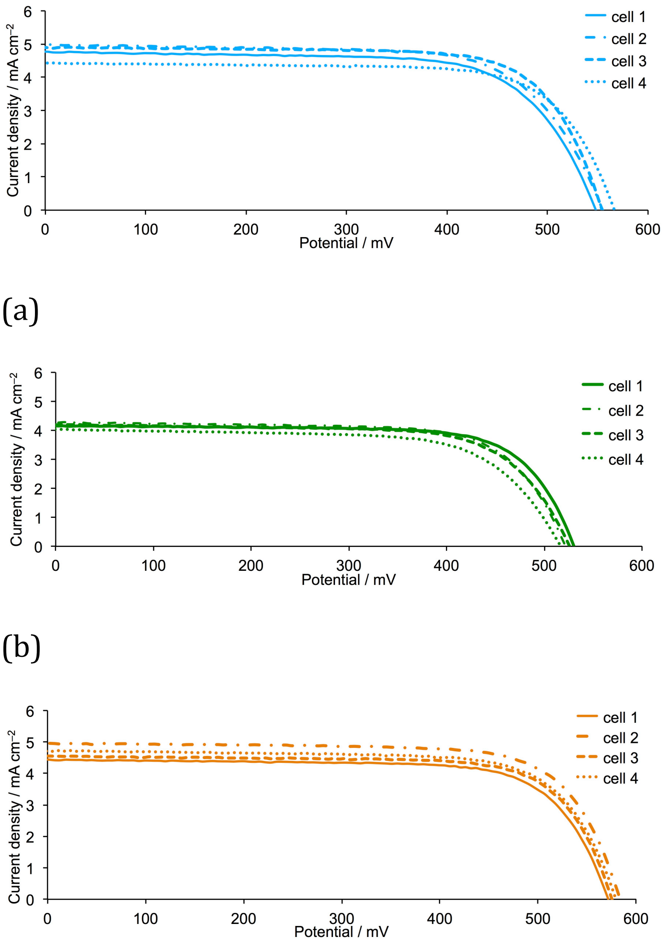
[1] S. Y. Brauchli, F. J. Malzner, E. C. Constable and C. E. Housecroft, *RSC Adv.*, 2015, **5**, 48516.

[2] K. Shibata, I. Katsuyama, H. Izoe, M. Matsui and H. Muramatsu, *J. Heterocyclic Chem.*, 1993, **30**, 277.



(a)

(b)

(c)

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.