Copper(I) complexes of 6,6'-disubstituted 2,2'-bipyridine dicarboxylic acids: new complexes for incorporation into copper-based dye sensitized solar cells (DSCs)[†]

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Synthetic approaches to 6,6'-disubstituted-2,2'-bipyridine ligands bearing carboxylic acid substituents at the 4,4' or 5,5'-positions are described. Copper(1) complexes with these ligands have been prepared for use in copper-based dye-sensitized solar cells. The single-crystal structures of 6,6'-dimethyl-2,2'-bipyridine-4,4'-dicarboxylic acid (H₂4), [H₃6][CF₃CO₂]·2CF₃CO₂H (H₂6 = 6,6'-diphenyl-2,2'-bipyridine-4,4'-dicarboxylic acid) and 4[Cu(H₂2)(H2)]·3H₂O (H₂2 = 6,6'-dimethyl-2,2'-bipyridine-5,5'-dicarboxylic acid) are described, as well as those of the intermediates (1*E*,5*E*)-1,6-di(2-furyl)hexa-1,5-diene-3,4-dione and 4,4'-di(2-furyl)-6,6'-dimethyl-2,2'-bipyridine (3), and the copper(1) complex [Cu(3)₂][PF₆]. The roles that classical and non-classical hydrogen bonding and π -stacking interactions play in determining the solid-state packing in these structures are discussed. Preliminary studies of DSCs with these complexes are reported.

Introduction

Carboxylate-functionalised complexes have become a popular choice for use in dye-sensitized solar cells (DSCs).1-4 While ruthenium(II) complexes dominate the dyes studied to date, we have recently shown that efficient DSCs can be fabricated using carboxylate-derivatised copper(I) bis(2,2'-bipyridine) complexes.⁵ This success has led us to a wider investigation of [CuL₂]⁺ complexes where L is a bpy ligand functionalised in the 4,4'or 5,5'-positions with carboxylic acid groups. A key structural requirement for the preparation of air-stable copper(I) complexes with 2,2'-bipyridine ligands is the presence of substituents at the 6- and 6'-positions⁶ and in this paper we report compounds with either methyl or phenyl substituents at these positions. From a structural point of view, these ligands and complexes are of interest in their own right because of the propensity for hydrogen bond formation between adjacent $CO_2H \cdots HO_2C$ units. In addition, it is well established that co-crystallisation of carboxylic acids with heterocyclic bases may lead to supramolecular assemblies based upon O-H · · · N and C-H · · · O interactions.7 In this paper, we describe the syntheses and copper(I) complexes of a series of 6,6'-dimethyl- or 6,6'-diphenyl-2,2'-bipyridines substituted in the 4,4'- or 5,5'-positions with carboxylic acid functionalities, as well as structural details for selected ligands and complexes.

Experimental

General

¹H and ¹³C NMR spectra were recorded at room temperature on Bruker Avance DRX 600 and 500 MHz spectrometers; chemical shifts are relative to residual solvent peaks with TMS δ 0 ppm. Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer with solid samples on a Golden Gate diamond ATR accessory. Electron impact (EI), electrospray ionisation (ESI), and MALDI-TOF mass spectra were recorded using Finnigan MAT 95 and MAT LCQ and PerSeptive Biosystems Voyager mass spectrometers, respectively. Electronic absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer. Electrochemical measurements were performed with an Eco Chemie Autolab PGSTAT 20 system using glassy carbon working and platinum auxiliary electrodes with a silver wire as pseudoreference electrode; solvents (see Experimental section) were purified. With the exception of $Na_3[Cu(6)_2]$, 0.1 M [^{*n*}Bu₄N][PF₆] was used as supporting electrolyte, and ferrocene (Fc) was added at the end of each experiment as an internal reference. For $Na_3[Cu(6)_2]$, the supporting electrolyte was 0.1M $NaClO_4$ and measurements were made relative to Ag/AgCl, then corrected to be with respect to Fc/Fc⁺.

Diethyl 6,6'-dimethyl-2,2'-bipyridine-5,5'-dicarboxylate (1)

The method is based on that reported for the synthesis of diethyl 4,4',6,6'-tetramethyl-2,2'-bipyridine-5,5'-dicarboxylate.⁸ Ethyl 2-methylnicotinate (9.34 cm³, 60.5 mmol) and Pd/C (5%, 1.35 g) were heated at reflux for 10 d under an inert atmosphere. After cooling the reaction mixture to room temperature, acetone (20 cm³) was added and the Pd/C was removed by filtration. The filtrate was evaporated to dryness. After standing overnight in the refrigerator, the brown–black solid was recrystallised

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from MeOH, and **1** was isolated as pale brown needles (0.31 g, 0.93 mmol, 1.5%). ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.41 (d, J = 8.1 Hz, 2H, H^{A3}), 8.33 (d, J = 8.1 Hz, 2H, H^{A4}), 4.41 (q, J = 7.1 Hz, 4H, H^{CH2CH3}), 2.92 (s, 6H, H^{Me}), 1.43 (t, J = 7.1 Hz, 6H, H^{CH2CH3}). ¹³C NMR (125 MHz, CDCl₃) δ /ppm 166.5 (C^{C=0}), 159.5 (C^{A6}), 156.6 (C^{A2}), 139.5 (C^{A4}), 125.7 (C^{A5}), 118.8 (C^{A3}), 61.3 (C^{CH2CH3}), 25.1 (C^{Me}), 14.3 (C^{CH2CH3}). MALDI-MS *m*/*z* 330.1 [M + 2H]⁺ (calc. 328.1). IR: *v*/cm⁻¹ 2976w, 2933w, 1716s, 1584s, 1547m, 1445m, 1428m, 1390m, 1353m, 1273s, 1249s, 1139m, 1114m, 1078s, 1020m, 986m, 8506s, 773s, 723m. Found: C, 65.89; H, 6.20; N, 8.54; C₁₈H₂₀N₂O₄ requires C, 65.84; H, 6.14; N, 8.53%.

6,6'-Dimethyl-2,2'-bipyridine-5,5'-dicarboxylic acid (H₂2)

Compound 1 (0.27 g, 0.82 mmol) was partially dissolved in a H_2O_{-} EtOH (20 cm³, 1 : 1 vol.) solution which contained KOH (0.46 g, 8.2 mmol). The mixture was heated at reflux for 12 h. After cooling to room temperature, the solution was partially evaporated under reduced pressure and the pH was adjusted to 2 with 1 M aqueous HCl to give a white precipitate. After filtration, H₂2 was collected as a white solid (0.221 g, 0.813 mmol, 99%). ¹H NMR (500 MHz, DMSO- d_6) δ /ppm 8.35 (m, 4H, H^{A3+A4}), 2.82 (s, 6H, H^{Me}). ¹³C NMR (126 MHz, DMSO- d_6) δ /ppm 167.6 (C^{C=0}), 158.6 (C^{A6}), 155.5 (CA2), 139.7 (CA4), 126.4 (CA5), 118.5 (CA3), 24.7 (CMe). EI-MS m/z 272.1 [M]⁺ (calc. 272.1). IR (ν/cm^{-1}) 3000w, 2893w, 2796w, 2645w, 2527w, 1688s, 1583s, 1544s, 1435m, 1404s, 1379m, 1349 (w), 1285s, 1258s, 1219m, 1140m, 1119m, 1079m, 1033w, 986w, 926m, 851s, 774s, 666s, 641m, 621w. UV-VIS (MeOH) λ_{max}/nm $(\varepsilon/dm^3 mol^{-1} cm^{-1})$ 212 (13000), 250 (13500), 305 (26000). Found: C, 59.50; H, 4.58; N, 9.82; C₁₄H₁₂N₂O₄·0.5H₂O requires C, 59.78; H, 4.66; N, 9.96%.

(1E,5E)-1,6-Di(2-furyl)hexa-1,5-diene-3,4-dione

The synthesis followed a literature method,⁹ although spectroscopic data have not previously been reported. (1E,5E)-1,6-di(2-furyl)hexa-1,5-diene-3,4-dione was isolated as an orange crystalline solid in 11.7% yield. ¹H NMR (500 MHz, CDCl₃, ring B = furan) δ /ppm 7.61 (d, J = 15.9 Hz, 2H, H¹), 7.57 (dd, J = 1.7, 0.4 Hz, 2H, H^{B5}), 7.31 (d, J = 15.9 Hz, 2H, H²), 6.80 (d, J = 3.5 Hz, 2H, H^{B3}), 6.53 (dd, J = 3.5, 1.8 Hz, 2H, H^{B4}). ¹³C NMR (126 MHz, CDCl₃) δ /ppm 188.7 (C^{C=0}), 151.6 (C^{B2}), 146.2 (C^{B5}), 133.1 (C¹), 117.9 (C^{B3}), 117.4 (C²), 113.1 (C^{B4}). EI-MS m/z 242.1 [M]⁺ (calc. 242.1). IR (ν /cm⁻¹) 3123w, 1662m, 1585m, 1543m, 1471m, 1388w, 1289m, 1265m, 1200m, 1068w, 995m, 974s, 926s, 881m, 850m, 831m, 811m, 746s, 637s, 588s, 548s. Found: C, 69.23; H, 4.20; C₁₄H₁₀O₄ requires C, 69.42; H, 4.16%.

4,4'-Di(2-furyl)-6,6'-dimethyl-2,2'-bipyridine (3)

The preparation of **3** was based on the reported method,^{10,11} although few characterisation data for **3** were available. (1*E*,5*E*)-1,6-Di(2-furyl)hexa-1,5-diene-3,4-dione (0.500 g, 2.07 mmol), 1-acetonylpyridinium chloride (0.708 g, 4.132 mmol) and ammonium acetate (1.0 g, 13 mmol) were heated at reflux in MeOH (20 cm³) for 12 h. The solution was allowed to cool to room temperature, and the off-white precipitate was collected by filtration and washed with cold MeOH. **3** was isolated as a white solid (0.361 g, 1.14 mmol, 55%). ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.61 (s, 2H, H^{A3}), 7.58 (dd, J = 1.7, 0.6 Hz, 2H, H^{B5}),

7.49 (d, J = 1.1 Hz, 2H, H^{A5}), 7.12 (d, J = 1.4 Hz, 2H, H^{B3}), 6.56 (dd, J = 3.5, 1.7 Hz, 2H, H^{B4}), 2.75 (s, 6H, H^{Me}). ¹³C NMR (126 MHz, CDCl₃) δ /ppm 158.3 (C^{A6}), 151.5 (C^{B2}), 143.9 (C^{B5}), 139.4 (C^{A4}), 117.6 (C^{A5}), 113.7 (C^{A3}), 112.3 (C^{B4}), 109.9 (C^{B3}), 24.3 (C^{Me}) (C^{A2} not observed). EI-MS *m/z* 316.1 [M]⁺ (calc. 316.1). IR (ν /cm⁻¹) 3115w, 2370w, 1603m, 1574m, 1548s, 1485m, 1410m, 1374m, 1359m, 1218m, 1161m, 1016s, 985m, 930m, 865m, 848m, 813s, 744s, 700s, 669m, 595s. Satisfactory analysis could not be obtained.

6,6'-Dimethyl-2,2'-bipyridine-4,4'-dicarboxylic acid (H₂4)

Compound H₂4 was prepared from **3** as previously described, and the ¹H NMR and UV-VIS spectra agreed with literature data.¹¹ ¹³C NMR (126 MHz, DMSO- d_6) δ /ppm 166.3 (C^{C=0}), 159.3 (C^{A6}), 155.1 (C^{A2}), 139.4 (C^{A4}), 122.8 (C^{A5}), 116.8 (C^{A3}), 24.2 (C^{Me}). EI-MS *m*/*z* 272.1 [M]⁺ (calc. 272.1), 228.1 [M – COO]⁺ (calc. 228.1). IR (*v*/cm⁻¹) 3093w, 2916w, 2854w, 2615w, 2545w, 1836w, 1697s, 1566s, 1427s, 1396m, 1296s, 1218m, 1095w, 910m, 763m. Found: C, 61.17; H 4.90; N, 10.38; C₁₄H₁₂N₂O₄ requires C, 61.76; H, 4.44; N, 10.29%.

4,4'-Di(2-furyl)-6,6'-diphenyl-2,2'-bipyridine (5)

1,6-Di(2-furyl)hexa-1,5-diene-3,4-dione (0.500 g, 2.07 mmol), Nphenacylpyridinium bromide (1.149 g, 4.132 mmol) and ammonium acetate (1.0 g, 13 mmol) were heated at reflux in EtOH (20 cm³) for 12 h. The solution was allowed to cool to room temperature, and the off-white precipitate was collected by filtration and washed with cold EtOH. 5 was collected as a white solid (0.464 g, 1.05 mmol, 51%). ¹H NMR (500 MHz, CDCl₃) δ /ppm 8.82 (d, J = 1.4 Hz, 2H, H^{A3}), 8.23 (d, J = 7.4 Hz, 4H, H^{C2}), 8.07 (d, J = 1.4 Hz, 2H, H^{A5}), 7.63 (d, J = 1.6 Hz, 2H, H^{B5}), 7.57 (m, 4H, H^{C3}), 7.49 (m, 2H, H^{C4}), 7.11 (d, J = 3.4 Hz, 2H, H^{B3}), 6.60 (dd, J = 3.4, 1.7 Hz, 2H, H^{B4}). ¹³C NMR (126 MHz, CDCl₃) δ/ppm 157.1 (C^{A6}), 156.1 (C^{A2}), 151.9 (C^{B2}), 143.8 (C^{B5}), 139.4 (C^{C1}), 139.2 (C^{A4}), 129.2 (C^{C4}), 128.8 (C^{C3}), 127.1 (C^{C2}), 114.8 (C^{A5}), 114.2 (C^{A3}), 112.2 (C^{B4}), 109.1 (C^{B3}). EI-MS *m*/*z* 440.2 [M]⁺ (calc. 440.2). IR (v/cm⁻¹) 3040w, 1601m, 1570w, 1543m, 1489w, 1404w, 1366w, 1215w, 1153w, 1007m, 918w, 868m, 814w, 772m, 729m, 687s, 590s, 513s, 486s, 455s, 409s. Found: C 78.87, H 4.42, N 6.02; C₃₀H₂₀N₂O₂·H₂O requires C 78.59, H 4.84, N 6.11%.

6,6'-Diphenyl-2,2'-bipyridine-4,4'-dicarboxylic acid (H₂6)

KMnO₄ (4.95 g, 31.3 mmol) was added to a warmed mixture of **5** (1.06 g, 2.42 mmol), 'BuOH (145 cm³) and H₂O (30 cm³). After heating at reflux overnight, the mixture was filtered through Celite. The filtrate was evaporated to *ca*. 50 cm³, the pH adjusted to 2 with 2 M HCl, and the white precipitate that formed was separated by filtration. H₂**6** was isolated as a white solid (0.62 g, 1.55 mmol, 64%). ¹H NMR (600 MHz, CF₃CO₂D) δ /ppm 9.22 (s, 2H, H^{A3}), 9.00 (s, 2H, H^{A5}), 8.19 (d, *J* = 7.2 Hz, 4H, H^{C2}), 7.82 (t, 2H, *J* = 7.3 Hz, H^{C4}), 7.77 (t, *J* = 7.4 Hz, 4H, H^{C3}). ¹³C NMR (151 MHz, CF₃CO₂D) δ /ppm 169.2 (C^{C=0}), 160.3 (C^{A6}), 148.2 (C^{A2}), 146.4 (C^{A4}), 135.6 (C^{C4}), 134.0 (C^{C1}), 132.3 (C^{C3}), 129.4 (C^{C2}), 128 1 (C^{A5}), 123.5 (C^{A3}). ESI-MS *m/z* 397.2 [M + H]⁺ (calc. 397.1). IR (*v*/cm⁻¹) 2978w, 2831w, 2561w, 2361 w), 1690s, 1551s, 1427m, 1389s, 1296m, 1250s, 1142m, 895m, 756s, 679s. Satisfactory elemental analysis could not be obtained.

[Cu(H₂2)₂]Cl

The procedure was adapted from the literature.⁸ An aqueous solution (2 cm³) of H₂2 (0.090 g, 0.33 mmol) was warmed to 70 °C, and 15 drops of 1 M aqueous NaOH were added to the solution. An aqueous solution (2 cm³) of CuSO₄ \cdot 5H₂O (0.042 g, 0.17 mmol) was then added, followed by a further addition of 20 drops of 1 M aqueous NaOH. An aqueous solution (0.3 cm³) of ascorbic acid (0.044 g, 0.25 mmol) was added to the reaction mixture and the solution immediately turned dark red. The pH of the solution was adjusted to 2 by adding 1 M aqueous HCl to precipitate the product. After filtration, [Cu(H₂2)₂]Cl was isolated as a red solid (0.070 g, 0.11 mmol, 33%). ¹H NMR (500 MHz, CD₃OD) δ/ppm 8.54 (s, 8H, H^{A3+A4}), 2.57 (s, 12H, H^{Me}). ESI-MS m/z 605.1 [M - Cl]⁺ (calc. 607.1). IR (ν/cm^{-1}) 3526w, 2916w, 1712m, 1582m, 1404w, 1381w, 1265m, 1157s, 1095w, 980w, 957w, 926w, 849m, 772s, 664w, 579m, 502m, 463s, 447s. UV-VIS (MeOH) $\lambda_{\rm max}/{\rm nm} (\epsilon/{\rm dm}^3 \,{\rm mol}^{-1} \,{\rm cm}^{-1}) 214 (74400), 274 (47000), 314 (60000),$ 482 (8000). E°(MeOH)/V vs. Fc: +0.53 (quasi-reversible). Found: C 52.94, H 4.25, N 8.62; C₂₈H₂₄ClCuN₄O₈ requires C 52.26, H 3.76, N 8.71%.

[Cu(3)₂][PF₆]

A solution of [Cu(CH₃CN)₄][PF₆] (19 mg, 0.050 mmol) in CH₃CN (2 cm³) was added to a solution of 3 (31.6 mg, 0.100 mmol) in CHCl₃ (5 cm³) resulting in a change from colourless to red. Upon addition of Et₂O to the solution, a red precipitate formed. After filtration, $[Cu(3)_2][PF_6]$ was isolated as a red solid (39 mg, 0.046 mmol, 46%). ¹H NMR (500 MHz, CDCl₃) δ/ppm 8.42 (s, 4H, H^{A3}), 7.68 (m, 8H, H^{A5+B5}), 7.24 (d, J = 3.6 Hz, 4H, H^{B3}), 6.66 (dd, J = 2.9, 1.5 Hz, 4H, H^{B4}), 2.29 (s, 12H, H^{Me}). ESI-MS m/z 695.8 [M – PF₆]⁺ (calc. 695.2). IR (v/cm^{-1}) 3115w, 2949w, 2912w, 2361w, 2334w, 1610m, 1547m, 1489m, 1441w, 1371w, 1250w, 1221w, 1159w, 1078w, 1020m, 937w, 932w, 885w, 872w, 835s, 739s, 704m, 673w. UV-VIS (CH₃CN) $\lambda_{\rm max}/\rm nm~(\epsilon/dm^3~mol^{-1}~cm^{-1})$ 274 (67000), 289 (71000), 493 (4100). *E*°(MeCN)/V vs. Fc: +0.29 (reversible). Found: C, 55.83; H, 3.77; N, 6.36; $C_{40}H_{32}CuF_6N_4O_4P\cdot H_2O$ requires C, 55.91; H, 3.99; N, 6.52%.

[Cu(H₂4)₂]Cl

The procedure was as for $[Cu(H_22)_2]Cl$, using H_24 (89.7 mg, 0.33 mmol) and CuSO₄·5H₂O (0.042 g, 0.17 mmol). $[Cu(H_24)_2]Cl$ was isolated as a red solid (58 mg, 0.090 mmol, 27%). ¹H NMR (500 MHz, CD₃OD) δ /ppm 8.91 (s, 4H, H^{A3}), 8.12 (s, 4H, H^{A5}), 2.32 (s, 12H, H^{Me}). ESI-MS *m*/*z* 607.2 [M – Cl]⁺ (calc. 607.1). IR (ν /cm⁻¹) 3180w, 1712s, 1558s, 1434m, 1388m, 1265m, 1218m, 894m, 763s, 671 m. UV-VIS (MeOH) λ_{max} /nm (ε /dm³ mol⁻¹ cm⁻¹) 202 (34300), 252 (27200), 268 (25000), 319 (35400), 483 (9900). *E*°(MeOH)/V *vs*. Fc +0.42 (quasi-reversible). Found: C, 47.46; H, 3.99; N, 7.90; C₂₈H₂₄ClCuN₄O₈·4H₂O requires C, 47.00; H, 4.51; N, 7.83%.

[Cu(5)₂][PF₆]

The method was as for $[Cu(3)_2][PF_6]$, starting with $[Cu(CH_3CN)_4][PF_6]$ (84.6 mg, 0.227 mmol) in CH₃CN (3 cm³) and 5 (200 mg, 0.455 mmol) in CHCl₃ (7 cm³). $[Cu(5)_2][PF_6]$ was

isolated as a dark green solid (336 mg, 0.309 mmol, 68%). ¹H NMR (600 MHz, CD₂Cl₂ with added K₂CO₃) δ /ppm 8.13 (s, 4H, H^{A3}), 7.77 (d, J = 1.1 Hz, 4H, H^{B5}), 7.75 (s, 4H, H^{A5}), 7.58 (d, J = 7.4 Hz, 8H, H^{C2}), 7.21 (d, J = 3.4 Hz, 4H, H^{B3}), 7.06 (t, J = 7.4 Hz, 4H, H^{C4}), 6.91 (t, J = 7.6 Hz, 8H, H^{C3}), 6.73 (dd, J 3.3, 1.7 Hz, 4H, H^{B4}). ¹³C NMR (151 MHz, CD₂Cl₂) δ/ppm 157.8 (C^{A6}), 153.9 (CA2), 150.9 (CB2), 145.7 (CB5), 139.7 (CA4), 138.8 (CC1), 129.9 (C^{C4}) , 128.1 (C^{C2+C3}) , 119.2 (C^{A5}) , 115.5 (C^{A3}) , 113.5 (C^{B4}) , 111.5 (C^{B3}). ESI-MS m/z 943.0 [M – PF₆]⁺ (calc. 943.2). IR (ν /cm⁻¹) 3122w, 3059w, 1735w, 1608s, 1540m, 1486m, 1454w, 1440w, 1429w, 1407w, 1371w, 1308w, 1244w, 1222m, 1157w, 1076w, 1016m, 937w, 920w, 884m, 833s, 769s, 738s, 692s, 642m, 590m, 554s. UV-VIS (CHCl₃) λ_{max} /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 244 (35000), 282 (36000), 313 (48000), 432 (4000), 587 (2400). E°(MeCN)/V vs. Fc: +0.27 (reversible). Found: C, 63.63; H, 3.72; N, 4.79; C₆₀H₄₀CuF₆N₄O₄P·2.4H₂O requires C, 63.62; H, 3.99; N, 4.95%.

$[Cu(H_26)_2]Cl$

The procedure was as for $[Cu(H_22)_2]Cl$, using H_26 (39.6 mg, 0.100 mmol) and $CuSO_4$ ·5H₂O (12.5 mg, 0.0500 mmol). $[Cu(H_26)_2]Cl$ was isolated as a green solid (31.1 mg, 0.035 mmol, 35%). ¹H NMR (see text) (600 MHz, D₂O) δ /ppm 8.08 (s, 4H, H^{A3}), 6.99 (m, 12H, H^{A5+C2}), 6.49 (m, 4H, H^{C4}), 6.40 (m, 8H, H^{C3}). MS see text. IR (ν/cm^{-1}) 3059w, 2357w, 1716s, 1608w, 1553s, 1456m, 1437m, 1377m, 1296w, 1217s, 1026w, 999w, 901m, 841m, 764s, 737m, 692s, 640m. UV-VIS (see text, H₂O): λ_{max}/nm (ε/dm^3 mol⁻¹ cm⁻¹) 296 (10000), 343 (11000), 437 (2000), 608 (1170). E° (see text, H₂O)/V νs . Fc: 0.00 (reversible). Found: C, 62.82; H, 3.86; N, 6.05; C₄₈H₃₁ClCuN₄O₈·1.7H₂O requires C, 62.57; H, 3.76; N, 6.08%.

Crystal structure determinations

Data were collected on a Bruker-Nonius Kappa CCD instrument; data reduction, solution and refinement used the programs COLLECT,¹² DENZO/SCALEPACK,¹³ SIR92,¹⁴ and CRYSTALS.¹⁵ The positions of the H atoms bonded to O or N atoms were located in the difference maps. Structures have been analysed using Mercury v. 1.4.2.¹⁶ ORTEP figures were drawn using Ortep-3 for Windows.¹⁷

(1E,5E)-1,6-Di(2-furyl)hexa-1,5-diene-3,4-dione

C₁₄H₁₀O₄, M = 242.23, colourless plate, monoclinic, space group C2/c, a = 37.426(1), b = 3.7745(2), c = 18.0118(7) Å, $\beta = 118.174(2)^{\circ}$, U = 2242.96(18) Å³, Z = 8, $D_c = 1.435$ Mg m⁻³, μ (Mo-K α) = 0.106 mm⁻¹, T = 173 K, 2556 reflections collected. Refinement of 1651 reflections (164 parameters) with $I > 1.9\sigma(I)$ converged at final R1 = 0.0470 (R1 all data = 0.0717), wR2 = 0.0519 (wR2 all data = 0.0648), $R_{int} = 0.026$, gof = 1.138.

4,4'-Di(2-furyl)-6,6'-dimethyl-2,2'-bipyridine (3)

 $C_{20}H_{16}N_2O_2$, M = 316.36, colourless plate, orthorhombic, space group *Pcab*, a = 6.5194(1), b = 12.1847(2), c = 19.5707(3) Å, U = 1554.64(4) Å³, Z = 4, $D_c = 1.352$ Mg m⁻³, μ (Mo-K α) = 0.089 mm⁻¹, T = 173 K, 1855 reflections collected. Refinement of 1101 reflections (109 parameters) with $I > 2.5\sigma(I)$ converged at final R1 = 0.0408 (R1 all data = 0.0641), wR2 = 0.0349 (wR2 all data = 0.0416), $R_{int} = 0.071$, gof = 1.121.

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6,6'-Dimethyl-2,2'-bipyridine-4,4'-dicarboxylic acid (H₂4)

 $C_{14}H_{12}N_2O_4$, M = 272.26, colourless plate, triclinic, space group $P\bar{1}$, a = 3.8591(6), b = 8.111(1), c = 10.607(2) Å, $\alpha = 73.344(9)$, $\beta = 84.983(7)$, $\gamma = 77.881(10)^{\circ}$, U = 310.83(8) Å³, Z = 1, $D_c = 1.454$ Mg m⁻³, μ (Mo-K α) = 0.109 mm⁻¹, T = 173 K, 1468 reflections collected. Refinement of 1461 reflections (91 parameters) with $I > 2.0\sigma(I)$ converged at final R1 = 0.0513 (R1 all data = 0.0834), wR2 = 0.0870 (wR2 all data = 0.1174), $R_{int} = 0.030$, gof = 1.040.

4,4'-Di(2-furyl)-6,6'-diphenyl-2,2'-bipyridine (5)

 $C_{30}H_{20}N_2O_2$, M = 440.50, colourless plate, trigonal, space group $R\bar{3}$, a = b = 33.495(2), c = 5.1499(3) Å, U = 5003.7(5) Å³, Z = 9, $D_c = 1.316$ Mg m⁻³, μ (Mo-K α) = 0.083 mm⁻¹, T = 173 K, 2084 reflections collected. Refinement of 2064 reflections (155 parameters) with $I > 2.0\sigma(I)$ converged at final R1 = 0.0375 (R1 all data = 0.0773), wR2 = 0.0554 (wR2 all data = 0.0800), $R_{int} = 0.050$, gof = 1.018.

$4[Cu(H_22)(H2)] \cdot 3H_2O$

C₁₁₂H₉₈Cu₄N₁₆O₃₅, M = 2482.28, purple plate, monoclinic, space group C2/c, a = 19.3405(4), b = 19.6142(4), c = 15.5801(3) Å, $\beta = 114.0211(9)^{\circ}$, U = 5398.4(2) Å³, Z = 2, $D_c = 1.527$ Mg m⁻³, μ (Mo-K α) = 0.871 mm⁻¹, T = 173 K, 6190 reflections collected. Refinement of 4532 reflections (449 parameters) with $I > 2.0\sigma(I)$ converged at final R1 = 0.0360 (R1 all data = 0.0468), wR2 = 0.0364 (wR2 all data = 0.0394), $R_{int} = 0.033$, gof = 1.044.

[H₃6][CF₃CO₂]·2CF₃CO₂H

C₃₀H₁₉F₉N₂O₁₀, M = 738.47, colourless needle, triclinic, space group $P\bar{1}$, a = 9.0489(7), b = 9.8221(8), c = 17.542(1) Å, $\alpha = 93.451(5)$, $\beta = 98.501(5)$, $\gamma = 95.971(5)^{\circ}$, U = 1529.1(2) Å³, Z = 2, $D_c = 1.604$ Mg m⁻³, μ (Mo-K α) = 0.155 mm⁻¹, T = 173 K, 9445 reflections collected. Refinement of 4614 reflections (505 parameters) with $I > 1.0\sigma(I)$ converged at final R1 = 0.0833(R1 all data = 0.1798), wR2 = 0.0638 (wR2 all data = 0.0966), $R_{int} = 0.075$, gof = 1.285.

[Cu(3)₂][PF₆]

C₄₀H₃₂CuF₆N₄O₄P, M = 841.23, orange plate, triclinic, space group $P\bar{1}$, a = 8.9016(2), b = 10.9570(3), c = 19.0865(4) Å, $\alpha = 81.724(1)$, $\beta = 81.0409(1)$, $\gamma = 88.743(1)^{\circ}$, U = 1819.78(8) Å³, Z = 2, $D_c = 1.535$ Mg m⁻³, μ (Mo-K α) = 0.724 mm⁻¹, T = 173 K, 13054 reflections collected. Refinement of 7298 reflections (505 parameters) with $I > 3.0\sigma(I)$ converged at final R1 = 0.0378(R1 all data = 0.0715), wR2 = 0.0408 (wR2 all data = 0.0594), $R_{int} = 0.051$, gof = 1.106.

Preparation and evaluation of solar cells

Nanocrystalline titanium dioxide electrodes were prepared by doctor blading a colloidal TiO₂ paste (Solaronix Nanooxide-T, colloidal anatase) on the conductive transparent surface of a piece of glass (F-doped SnO₂, FTO, Hartford glass company, Tec 8, 8Ω cm⁻²) that had been cut to 0.9 × 2.0 cm and cleaned with water and ethanol. The FTO-coated glass was covered with two layers

Compound (solvent)	$J_{\rm sc}/{ m mA}$ cm ⁻²	$V_{\rm oc}/{ m mV}$	FF	$\eta_{ ext{global}} \ (\%)$	λ_{\max}/nm (soln)	$\lambda_{\rm max}/\rm nm$ (dye)
[Cu(H ₂ 2) ₂]Cl (MeOH)	1.21	570	0.65	0.45	482	480
$[Cu(H_24)_2]Cl$ (MeOH)	1.15	530	0.68	0.41	483	492
$[Cu(H_26)_2]Cl^a$ (DMSO)	0.69	484	0.63	0.21	437, 608	494, 604
$[Cu(3)_2][PF_6]$ (CHCl ₂)	0.46	490	0.62	0.14	493	494
N719 (MeCN)	11.3	750	0.67	5.0	534	392, 530
^a Solution UV-VIS data are for the sodium salt, see text.						

of parallel adhesive tape 0.5 cm apart to control the thickness and the area of the TiO₂ film (0.9×0.5 cm). The colloidal paste was applied between the tapes by rolling a glass rod on the surface. The film thickness was measured with a profilometer (Dektak) and was $6.0 \pm 0.5 \,\mu\text{m}$. After annealing at 450 °C for 30 min, the slides were dipped into a solution of the dye in an appropriate solvent (see Table 1) for several hours. The cells were constructed using 0.5 M LiI, 0.05 M I₂, 0.5 M 1-methylbenzimidazole and 0.6 M 1-butyl-3-methylimidazolinium iodide in 3-methoxypropionitrile as electrolyte. The electrolyte was chosen to give the best possible comparison to the state-of-the-art optimized systems based on N719. Cathode electrodes were constructed from FTO glass pieces of the same dimensions as the anodes platinized by treatment with 5 mM H₂[PtCl₆] in propan-2-ol followed by heating to 380 °C for 15 min. The anode and cathode were assembled using Surlyn (Dupont) plastic and the seal made by heating to 110-120 °C while pressing the two together. Measurements were made with irradiation from the rear using a lamp with intensity 100 mW cm⁻² (1 sun). The standard dye N719 was purchased from Solaronix.

Results and discussion

Ligand synthesis and characterisation

Entry into the 6,6'-dimethyl-5,5-dicarboxylic acid series is achieved through the convenient (but low-yielding) oxidative dimerisation of ethyl 2-methylnicotinate with palladium/ charcoal.^{8,18,19} Ligand H₂**2** was prepared in near quantitative yield by the saponification of **1**⁸ under basic conditions, and was fully characterised by routine spectroscopic and mass spectrometric methods. For H₂**4** and H₂**6**, the strategy outlined in Scheme 2 was employed; this has previously been applied to the synthesis of H₂**4**. For H₂**4**, our ¹H NMR and UV-VIS spectroscopic data agreed with those published,¹¹ and the ¹³C NMR spectrum exhibited the number of resonances expected and was fully assigned by 2D NMR techniques.

X-Ray quality crystals of the dione precursor shown in Scheme 2 readily formed from an ethanol solution of the compound, and a search of the CSD¹⁶ revealed that its structure had not previously been reported. The molecular structure of the dione is shown in Fig. 1. The asymmetric unit contains two independent, centrosymmetric molecules, and all bond distances and angles are unexceptional. Each molecule is planar (deviations of atoms



Fig. 1 Structure of one of the independent molecules of (1E,5E)-1,6-di(2-furyl)hexa-1,5-diene-3,4-dione; ellipsoids are plotted at the 50% level. Selected bond distances (Å): C5–C6 1.336(3), C4–C5 1.429(3), C6–C7 1.467(3), C7–C7^a 1.532(4), C7–O2 1.220(2), C1–O1 1.373(2), C4–O1 1.376(2); symmetry code a = 1 – x, 1 – y, -z. Bond lengths in the second independent molecule are similar.

from the least squares plane through each molecule < 0.2 Å), and the planes through the two independent molecules are almost parallel (angle subtended = 3.4°). The molecules are stacked in an offset manner, and continuation of this stacking arrangement generates columns. Molecules in adjacent stacks interact with each other through weak $O \cdots H-C$ contacts (C1H11 $\cdots O4^{i} = 2.68$, $O2 \cdots H91^{i}C9^{i} = 2.61$, C2H21 $\cdots O4^{ii} = 2.63$ Å) and C-H $\cdots \pi_{alkene}$ interactions (C3H31 \cdots C13ⁱⁱⁱ = 2.89, C3H31 \cdots C12ⁱⁱⁱ = 3.24 Å) (symmetry codes i = x, 1 + y, z; ii = $\frac{1}{2} - x$, $\frac{1}{2} + y$, $-\frac{1}{2} - z$; iii = x, $-y, -\frac{1}{2} + z$). Such weak interactions are well established as important components in solid-state supramolecular assemblies.²⁰⁻²⁵ The overall supramolecular assembly is a herring-bone like array (Fig. 2), with an angle of 58.4° between the planes through molecules in adjacent stacks.



Fig. 2 Packing of dione molecules (see text).

Ligands H₂4 and H₂6 were prepared by permanganate oxidation of 4,4'-di(2-furyl)-6,6'-dimethyl-2,2'-bipyridine (3) and 4,4'-di(2furyl)-6,6'-diphenyl-2,2'-bipyridine (5), respectively.²⁶ The intermediate compounds were fully characterised. Each exhibited a parent ion in the EI mass spectrum (m/z 316.1 for 3, and m/z 440.2for 5). The ¹H NMR spectra of 3 and 5 are readily distinguished by the presence of a signal at δ 2.75 ppm for the methyl groups in 3, and diagnostic signals for the phenyl substituents (ring C, Scheme 1) in the spectrum of 5. The chemical shifts of the resonances assigned to the bipyridine rings (A, Scheme 1) and furan rings (B) are similar in 3 and 5, with the exception of the signal for proton H^{A5} which appears at δ 7.49 ppm in **3** and at δ 8.07 ppm in **5**. This observation is consistent with the deshielding effect of the 6phenyl substituent on HA5. The 13C NMR spectra were assigned using 2D techniques. Both compounds yielded X-ray quality crystals, grown by slow evaporation of chloroform solutions of the ligands. The centrosymmetric structures are shown in Fig. 3(a) and 4(a), respectively. The bpy unit in each compound adopts the expected *trans*-configuration. Both **3** and **5** are close to being planar. In **3**, the angle between the least squares planes of the pyridine and



Scheme 1 Ligand structures and ring labelling for NMR spectroscopy.



Fig. 3 (a) Molecular structure of compound **3** with ellipsoids plotted at the 40% level. Selected bond parameters (Å and °): C7–C8 1.503(2), C9–C9ⁱ 1.493(3), C4–C5 1.455(2), O1–C1 1.358(2), O1–C4 1.370(2), C1–C2 1.326(3), C2–C3 1.449(3), C3–C4 1.349(3); C1–O1–C4 106.8(2) (symmetry code: i = 2 - x, -y, 1 - z). (b) Packing of molecules of **3** is dominated by π -stacking.



Fig. 4 (a) Molecular structure of **5**, with ellipsoids plotted at the 40% level. Selected bond parameters (Å and °): C11–C11^a 1.486(4), C6–C7 1.490(3), C9–C12 1.461(3), O1–C12 1.375(2), O1–C15 1.370(3), C12–C13 1.353(3), C13–C14 1.431(3), C14–C15 1.340(4); C12–O1–C15 106.9(2) (symmetry code a = 1 - x, 1 - y, 1 - z). (b) Packing of molecules of **5** in the unit cell.

furan rings is $10.3(1)^\circ$, while in 5 it is $1.0(1)^\circ$. In 5, the phenyl ring is twisted $10.7(1)^{\circ}$ out of the plane of the pyridine ring to which it is bonded. Compounds 3 and 5 crystallise in orthorhombic (Pcab) and trigonal (R3) space groups, respectively. In 3, the principal packing forces are π -stacking interactions between bpy units. Pairs of pyridine rings in adjacent molecules are aligned so as to generate an offset stack (Fig. 3(b)), the distance between rings containing atoms N1 and N1ⁱ being 3.39 Å, symmetry code i = 1 - x, -y, 1 - z). The dominant attractive forces between molecules of 5 involve weak edge-to-face π -interactions and $N_{\text{pyridine}} \cdots H-C_{\text{furan}}$ non-classical hydrogen bonds, and are in stark contrast to the π -stacking observed in 3. The edge-to-face π -interactions feature both phenyl...phenyl and furan...furan contacts. The shortest phenyl \cdots phenyl contact is C3 \cdots H51ⁱ-C5ⁱ (2.81 Å, symmetry code $i = \frac{2}{3} + x + y$, $\frac{1}{3} + x$, $1\frac{1}{3} - z$); the distance from the ring centroid to H51ⁱ is 3.19 Å. Although not directly aligned, each C13–H131 bond points towards the C14–C15 π bond of an adjacent furan ring $(C13-H131\cdots C15^{ii} = 3.02, C13-$ H131 ··· C14ⁱⁱ = 3.46 Å, symmetry code ii = $\frac{1}{3} - x + y$, $\frac{2}{3} - x$, $-\frac{1}{3} + z$), and these weak interactions complement the edge-to-face aromatic interactions. The relative orientations of planar molecules of 5 that follow from the plethora of edge-to-face interactions place each nitrogen atom within close proximity of a furan hydrogen atom $(N1 \cdots H151^{iii}C15^{iii} = 2.68 \text{ Å}, N1 \cdots C15^{iii} = 3.605(4) \text{ Å},$ $N1 \cdots H151^{iii} - C15^{iii} = 170^{\circ}$; symmetry code iii $= \frac{2}{3} + x + y, \frac{1}{3} + x,$ $\frac{1}{2} - z$). The high symmetry that crystallisation in the R3 space group imparts on packing of molecules of 5 and the dominance of edge-to-face interactions are illustrated in Fig. 4(b).



Scheme 2 Synthetic strategy for the formation of ligands H_24 and H_26 .

Compounds 3 and 5 were oxidised to dicarboxylic acids H_24^{11} and H₂6 (Scheme 2) using KMnO₄. The highest mass peak in the ESI mass spectrum of H_26 appeared at m/z 397.2 and was assigned to $[M + H]^+$. The NMR spectra of H₂6 were recorded in CF₃CO₂D because the compound is not soluble in common organic solvents. Although it is difficult to compare the ¹H NMR spectra of 5 in CDCl₃ and H₂6 in CF₃CO₂D (which may be protonated, see below), the significant changes in chemical shift for protons $H^{\scriptscriptstyle A3}$ (§ 8.82 to 9.22 ppm) and $H^{\scriptscriptstyle A5}$ (§ 8.07 to 9.00 ppm), and the disappearance of signals for the furan ring, confirm the replacement of the substituent in the 4- and 4'-positions of the bpy unit. In the ¹³C NMR spectrum, a signal at δ 169.2 ppm was assigned to the carboxylic acid carbon atom. Single crystals of H₂4 suitable for a X-ray diffraction study were grown from a methanol solution of the compound, and the centrosymmetric structure is shown in Fig. 5. The trans-configuration is as expected, and the molecule is planar (maximum deviation of a framework atom from the least squares plane through the molecule is 0.07 Å for C3). The difference in C5-O1 and C5-O2 bond distances (see figure caption) is consistent with carboxylic acid (rather than carboxylate) functionalities. The trans-arrangement of the two CO₂H groups is ideal for the formation of hydrogen-bonded polymeric chains (O1H1 · · · O2ⁱ = 1.78, O1 · · · O2ⁱ = 2.645(2) Å, $O1-H1\cdots O2^{i} = 177^{\circ}$, symmetry code i = 1 - x, 1 - y, 1 - yz), and Fig. 6(a) illustrates that these all run in the same direction through the lattice. Adjacent chains assemble into sheets (Fig. 6(b)) by virtue of $C=O \cdots H_{methyl}$ attractive contacts



Fig. 5 Molecular structure of H₂**4**, with ellipsoids plotted at the 50% level. Selected bond parameters (Å and °): C4–C5 1.489(3), O2–C5 1.234(3), O1–C5 1.306(3), C7–C7^a 1.482(4), C1–C2 1.496(3); C4–C5–O1 115.8(2), C4–C5–O2 121.2(2), O1–C5–O2 122.9(2) (symmetry code a = -x, -y, -z).



Fig. 6 (a) Hydrogen-bonded polymeric chains of H_24 molecules. (b) Adjacent chains assemble into 2D sheets.

 $(O2 \cdots H13^{ii}C1^{ii} = 2.60 \text{ Å}, O2 \cdots C1^{ii} = 3.428(3) \text{ Å}, O2 \cdots H13^{ii}-C1^{ii} = 143^{\circ}$, symmetry code ii = -1 + x, 1 + y, z). A methyl group from an adjacent molecule nestles into the cavity defined in Fig. 5 by atoms O2, C6–H61 and N1^a.

Crystals of $[H_36][CF_3CO_2]\cdot 2CF_3CO_2H$ were grown over a period of two days by dissolving the ligand in CF_3CO_2H and placing the vial containing the solution into a sample bottle containing a small amount of water. Fig. 7 shows the structure of the $[H_36]^+$ cation. The bpy unit adopts a *cis*-conformation, consistent with protonation at one of the nitrogen atoms and the formation of an N–H…N hydrogen bond (the H atom being located in the difference map). The angle between the least squares planes of the two pyridine rings is $1.7(1)^\circ$. The difference between the two



Fig. 7 Molecular structure of the $[H_36]^+$ cation in $[H_36][CF_3CO_2]$. 2CF₃CO₂H; ellipsoids are plotted at the 50% level. Selected bond parameters (Å and °): O1–C11 1.304(3), O2–C11 1.203(3), O3–C12 1.307(3), O4–C12 1.204(3), N1····N2 2.599(3); O1–C11–O2 125.5(2), O3–C12–O4 123.7(2).

C-O bond distances in each carboxylic acid group (see caption to Fig. 7) confirms the protonation state. One phenyl substituent is twisted out of the plane of the bpy unit more than the other (angles between the least squares planes of rings containing atoms N1 and C13, and N2 and C19 are 31.3(1) and 7.2(1)°, respectively). Although the distance between the least squares planes through the bpy units of symmetry-related molecules in the triclinic unit cell is only 3.39 Å, there is little overlap of the rings and π stacking interactions are therefore negligible. Packing within the lattice is controlled primarily by hydrogen bonding as illustrated in Fig. 8. The $[CF_3CO_2]^-$ ion and CF_3CO_2H solvate molecules are distinguished by a comparison of the C-O bond distances: C29–O9 and C29–O10 =1.221(3) and 1.249(3) Å, respectively, C25–O5 and C25–O6 = 1.195(4) and 1.287(4) Å, respectively, and C27–O7 and C27–O8 = 1.189(4) and 1.294(4) Å, respectively. The $[CF_3CO_2]^-$ ion and one of the CF_3CO_2H molecules are disordered. In the anion, each F atom position has been modelled over two sites with 65 and 35% occupancies. In the CF₃CO₂H molecule, two of the F atoms are disordered, and each position has been modelled over two sites with 70 and 30% occupancies.



Fig. 8 Hydrogen bonding between cations, anions and solvate molecules in $[H_36][CF_3CO_2]\cdot 2CF_3CO_2H$. Symmetry codes: i = 1 - x, 1 - y, 1 - z; ii = 1 - x, -y, 1 - z; iii = x, 1 + y, z.

Copper(I) complexes

Copper(I) complexes of ligands 3 and 5 were prepared by treating [Cu(CH₃CN)₄][PF₆] with each ligand, and the hexafluoridophosphate salts of $[Cu(3)_2]^+$ and $[Cu(5)_2]^+$ were isolated as red and green solids, respectively, in moderate to good yields. The electronic absorption spectra of acetonitrile solutions of $[Cu(3)_2][PF_6]$ and $[Cu(5)_2][PF_6]$ exhibited MLCT bands at 493 and 587 nm, respectively, consistent with the observed colours. The spectra also showed intense, higher energy absorptions assigned to ligand centred $\pi^* \leftarrow \pi$ transitions. Each complex is redox active, and undergoes a reversible Cu⁺/Cu²⁺ process at +0.29 V for $[Cu(3)_2][PF_6]$, and +0.27 V for $[Cu(5)_2][PF_6]$. The highest mass peaks in the ESI mass spectra of $[Cu(3)_2][PF_6]$ and $[Cu(5)_2][PF_6]$ corresponded to $[M - PF_6]^+$ (*m*/*z* 695.8 for $[Cu(3)_2]^+$ and 943.0 for $[Cu(5)_2]^+$). Coordination of ligand 3 to copper(I) results in only small changes to the ¹H NMR spectrum (both in CDCl₃). Similarly, on going from 5 (in CDCl₃) to $[Cu(5)_2]^+$ (in CD₂Cl₂), the chemical shifts of the signals assigned to the bpy and furan protons undergo small perturbations. However, the signals for the phenyl protons are significantly shifted to lower frequency (H^{C2} from δ 8.23 to 7.58 ppm, H^{C3} from δ 7.57 to 6.91 ppm, and H^{C4} from 7.49 to 7.06 ppm). This is a consequence of the shielding resulting from each phenyl substituent lying over the π -cloud of a bpy domain of the second ligand, enforced by the near tetrahedral copper(I) coordination sphere (see structural discussion below).

The electronic spectra of $[Cu(3)_2][PF_6]$ and $[Cu(5)_2][PF_6]$ exhibit intense absorptions in the UV region assigned to ligand-based $\pi^* \leftarrow \pi$ transitions, in addition to absorptions arising from MLCT transitions (493 nm for $[Cu(3)_2]^+$ and 432 and 587 nm for $[Cu(5)_2]^+$). The introduction of phenyl substituents in the 6- and 6'-positions results in the observation of a second MLCT band, extends the range of the absorption spectrum into the red.²⁷

Crystals of $[Cu(3)_2][PF_6]$ suitable for X-ray analysis were grown by slow diffusion of Et_2O into a CHCl₃ solution of the complex. The structure of the $[Cu(3)_2]^+$ cation is shown in Fig. 9 and confirms that the two ligands are close to being orthogonal (angle between the least squares planes through the



Fig. 9 Molecular structure of the $[Cu(3)_2]^+$ cation in $[Cu(3)_2][PF_6]$; ellipsoids are plotted at the 40% level and H atoms are omitted. The furan rings containing O3 and O4 are disordered and only the major occupancy atoms are shown (see text). Selected bond parameters (Å and °): Cu1–N1 2.024(2), Cu1–N2 2.011(2), Cu1–N3 2.000(2), Cu1–N4 2.026(2); N1–Cu1–N2 81.27(7), N1–Cu1–N3 130.31(7), N2–Cu1–N3 128.77(7), N1–Cu1–N4 113.72(6), N2–Cu1–N4 126.03(6), N3–Cu1–N4 81.94(6).

two bpy units = $81.11(5)^{\circ}$; the bite angle of each bpy ligand is ≈81°. Two of the furan rings are disordered and have been modelled with O/C mixed occupancy sites (O3 and C54 75%) occupancy, and C134 and O30 25%; O4 and C58 70% occupancy, and C138 and O40 30%). Each ligand is close to being planar, with the maximum deviation being for the furan ring containing atom O2 (angle between the least squares planes of rings with O2 and $N2 = 14.1(1)^{\circ}$). The packing of the cations is noteworthy. One near-planar ligand stacks over a ligand of an adjacent cation. The interplane distances are appropriate for π -stacking (distances between planes containing N1/N2 and N1ⁱ/N2ⁱ = 3.43 Å, N3/N4 and $N3^{ii}/N4^{ii} = 3.37$ Å, symmetry codes: i = 1 - x, 1 - y, 1 - z; ii = 2 - x, -y, -z). However, the two ligands of each complex interact with their neighbours in different ways. Stacking between ligands containing N1/N2 and N1ⁱ/N2ⁱ involves the whole face of each ligand. In contrast, half of each N3/N4 ligand stacks with half of a symmetry-related ligand in an adjacent molecule; Fig. 10(a) shows the stacking involving pyridine rings $N3 \cdots N3^{ii}$ and illustrates that face-to-face pyridine ... furan stacking occurs. The remaining half of the ligand stacks with another cation (represented as N4...N4ⁱⁱⁱ, symmetry code iii = 1 - x, 1 - y, -z) leading to the overall evolution of stacked chains of cations running in parallel directions through the lattice (Fig. 10(b)). The $[PF_6]^-$ ions reside in the cavities between the cations, and there are extensive $C-H \cdots F-P$ weak interactions.



Fig. 10 Packing of cations in $[Cu(3)_2][PF_6]$.

The copper(I) complexes of H_22 , H_24 and H_26 were prepared by the addition of copper(II) sulfate to aqueous solutions of the sodium salts of the acids, followed by reduction with ascorbic acid.⁸ After work-up in aqueous HCl, $[Cu(H_22)_2]Cl$ and $[Cu(H_24)_2]Cl$ were isolated as red solids, and $[Cu(H_26)_2]Cl$ as a

green solid. The cations in $[Cu(H_22)_2]Cl$ and $[Cu(H_24)_2]Cl$ are isomers, and ESI mass spectra showed ions corresponding to $[CuL_2]^+$ at m/z 607. The electronic spectra of methanol solutions of [Cu(H₂2)₂]Cl and [Cu(H₂4)₂]Cl exhibit MLCT bands at 482 and 483 nm, respectively, in addition to more intense, higher energy ligand-based absorptions arising from $\pi^* \leftarrow \pi$ transitions (Fig. 11). Upon formation of the complexes, signals in the ¹H NMR spectra undergo minor perturbations, although the change in solvent from DMSO-d₆ to CD₃OD makes detailed comparisons difficult. The elemental analysis of the bulk sample of $[Cu(H_26)_2]Cl$ confirmed the formulation, but mass spectrometric and solution spectroscopic characterisation of [Cu(H₂6)₂]Cl proved to be difficult. Attempts to obtain an ESI mass spectrum of the complex led only to the observation of a peak envelope at m/z 396 assigned to the free ligand. Unlike $[Cu(H_22)_2]Cl$ and $[Cu(H_24)_2]Cl$ which are slightly soluble in MeOH, [Cu(H₂6)₂]Cl is insoluble in water and common organic solvents with the exception of DMSO. The ¹H NMR spectrum of a DMSO- d_6 solution of [Cu(H₂6)₂]Cl showed only broad peaks at room temperature. Initially we wondered if this were due to restricted bond rotation around the C_{pv}-C_{phenyl} bond but the signals did not sharpen upon increasing the temperature of the solution. Since DMSO is not ideal for crystal growth at room temperature, we attempted to grow crystals of $[Cu(H_26)_2]Cl$ by leaving the crude reaction mixture (still containing an excess of NaOH) to stand for several days. Single crystals of $Na_3[Cu(6)_2]$ (see below) were isolated. The sodium salt was water-soluble, and the ¹H NMR spectrum of a D₂O solution of the complex was well-resolved. We noted earlier that on going from 5 to $[Cu(5)_2]^+$, signals for the phenyl protons shift to lower frequency, and the same phenomenon is observed on going from H_26 (in CF₃CO₂D) to [Cu(6)₂]³⁻ (in D₂O) (H^{C2} from δ 8.19 to 6.99 ppm, H^{C3} from δ 7.77 to 6.40 ppm, and H^{C4} from δ 7.82 to 6.49 ppm). Preliminary structural data for Na₃[Cu(6)₂].nH₂O confirm that the coordination geometry of the copper(I) centre is distorted tetrahedral and that each phenyl substituent lies over the bpy unit of the second ligand, consistent with the shielding effects noted in the ¹H NMR spectrum. Unfortunately, the structure was severely disordered with respect to the positions of the Na⁺ ions and solvate molecules, and attempts to grow better quality crystals were unsuccessful.



Fig. 11 Comparison of part of the electronic spectra of $[Cu(H_22)_2]Cl$ (\Box , MeOH), $[Cu(H_24)_2]Cl$ (\blacksquare , MeOH) and Na₃ $[Cu(6)_2]$ (\triangle , H₂O, lowest extinction coefficients).

Attempts to obtain the electronic spectrum of a DMSO solution of $[Cu(H_26)_2]Cl$ were hampered by the fact that the complex is not stable in this solvent. Therefore, the spectrum of an aqueous solution of Na₃[Cu(6)₂] was recorded. In addition to high energy absorptions assigned to ligands-centred $\pi^* \leftarrow \pi$ transitions, the spectrum exhibited two MLCT bands at 437 and 608 nm. The spectrum is compared with those of $[Cu(H_22)_2]Cl$ and $[Cu(H_24)_2]Cl$ in Fig. 11, and illustrates the decrease in intensity of the MLCT bands on going from the complexes with ligands H₂2 or H₂4 to [6]⁻, and, by inference, H₂6.

Crystals of 4[Cu(H₂2)(H2)]·3H₂O grew after a methanol solution of [Cu(H₂2)₂]Cl had been standing at room temperature for several weeks. The molecular structure is shown in Fig. 12 and selected bond parameters are given in the caption. The disordering leads to large estimated standard deviations, but the bond distances are consistent with the protonation states shown in the figure. The fully protonated ligand is ordered, while the CO₂H and CO_2 units of the second ligand are disordered and have been modelled (each with the CO₂ units constrained to being planar) over two sites, each with equal occupancy. One methyl group is also disordered (C28 in Fig. 12) and has been modelled over two sites of fractional occupancies of 75% and 25%. The compound crystallises as a hydrate, and one water molecule resides on a twofold axis. The copper(I) centre is in the expected pseudo-tetrahedral environment, the angle between the least squares planes of the two bpy units being $84.49(7)^{\circ}$. The packing of $[Cu(H_22)(H2)]$ molecules is worthy of note and involves both π -stacking between bpy domains and extensive hydrogen bonding between carboxylate and carboxylic acid groups. The bpy unit containing N1 and N2 stacks over that containing N3ⁱ and N4ⁱ (symmetry code i = x, $1 - y, \frac{1}{2} + z$) of an adjacent molecule. The stacking is not ideal, and while the bpy units overlap effectively, their planes are not parallel. The distance from the centroids of the rings containing N1 and N2 to the least squares plane through the bpy unit with



Fig. 12 Structure of the $[Cu(H_22)(H2)]$ molecule in $4[Cu(H_22)(H2)]$. 3H₂O; H atoms except those in the CO₂H groups are omitted, and ellipsoids are plotted at the 30% level. For disordered atoms, one (if 50 : 50) or major occupancy (for C28) sites only are shown. Selected bond parameters (Å and °): Cu1–N1 2.057(1), Cu1–N2 2.045(1), Cu1–N3 2.036(1), Cu1–N4 2.052(2), C11–O3 1.272(3), C11–O4 1.228(3), C14–O1 1.311(3), C14–O2 1.211(3), C36–O50 1.25(3), C36–O60 1.29(2), C37–O70 1.208(8), C37–O80 1.283(8); N1–Cu1–N2 81.30(6), N1–Cu1–N3 128.59(6), N2–Cu1–N3 133.40(6), N1–Cu1–N4 121.97(6), N2–Cu1–N4 115.34(6), N3–Cu1–N4 81.12(6), O3–C11–O4 127.3(2), O1–C14–O2 124.1(2), O50–C36–O60 118(2), O70–C37–O80 125.7(6).

N3ⁱ and N4ⁱ are 3.24 and 3.47 Å, respectively. In contrast, for the N3/N4 bpy unit, only the ring containing N3 is involved in significant π -stacking. The interaction occurs with the N3ⁱⁱ ring across an inversion centre with the distance between least squares planes through the pyridine rings being 3.46 Å. The π stacked interactions therefore operate in orthogonal directions to produce a network that is reinforced by hydrogen bonding between carboxylates and carboxylic acids. Every CO₂⁻ or CO₂H group is involved, as well as the water molecules, resulting in a rigid network (Fig. 13).



Fig. 13 Crystal packing in $4[Cu(H_22)(H2)]$ - $3H_2O$ involves extensive π -stacking and hydrogen bonding in orthogonal directions.

Performance of DSCs

Prior to our recent communication concerning the efficient performances of DSCs with carboxylate-derivatized $[CuL_2]^+$ complexes in which $L = H_24$, 7, H_28 and 9 (Scheme 3),⁵ reports of photosensitization by copper(I) dyes were surprisingly few.²⁸⁻³⁰ Here, we describe a comparison of the performances of DSCs using the copper(I) dyes H_22 , H_24 and H_26 . Each is functionalized with carboxylic acids, and is therefore expected to bind to TiO₂. We have also constructed DSCs using 3 as the dye in order to assess the binding capabilities of the furan functionality.



Scheme 3 Ligands previously incorporated into copper(1)-based solar cells in addition to $\rm H_24.^5$

The characteristics of these DSCs and of the standard dye N719 were measured using our modified scanning electrochemical microscope system and are given in Table 1.

Like $[Cu(H_24)_2]^+$,⁵ complexes $[Cu(H_22)_2]^+$ and $[Cu(H_26)_2]^+$ bind strongly to TiO₂ nanoparticles, giving good dye-modified surfaces. To the best of our knowledge, no dyes bearing furan functionalities as the anchoring group have previously been reported. After being immersed in a CHCl₃ solution of $[Cu(3)_2][PF_6]$ for several hours, the TiO₂ nanoparticles on the conducting glass slides were coloured indicating chemisorption of the dye. The UV-VIS spectrum exhibited an MLCT band at 494 nm consistent with the solution spectrum of the complex (Table 1). Although this is consistent with $[Cu(3)_2]^+$ binding to TiO₂ nanoparticles through the furan *O*-donors, we cannot rule out the possibility of oxidation of the furan functionalities to carboxylic acids.

The lower performance of the DSCs constructed with H_26 compared with H_24 is a combination of the lower absorptivity of the complex and lower adsorption on the oxide surface.

Conclusions

In this paper, we have described systematic approaches to 6,6'disubstituted-2,2'-bipyridine ligands bearing carboxylic acid substituents at the 4,4'- or 5,5'-positions. Copper(1) complexes with these ligands have been prepared and a preliminary assessment of their utilisation as dye-sensitizers in copper-based DSCs has been made.

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