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Hairpin helicates: a missing link between double-helicates and trefoil knots

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We have prepared a novel ligand in which two qpy metal-binding domains are linked by a polyoxyethylene spacer. The new ligand reacts with copper(II) salts to form dinuclear double helicates with a hairpin structure. The hairpin complex and a model complex have been structurally characterised. The hairpin structure is formed regioselectively as the head-to-tail (HT) stereoisomer. Detailed electrochemical and spectroelectrochemical studies of the complexes are reported.

Introduction

The metal-directed assembly of topologically novel supramolecules is a topic that continues to attract synthetic and theoretical interest.¹⁻⁵ One of the earliest successes in this area was the construction of helical and multiple helical complexes, and synthetic studies of helicates resulted in a broad understanding of the factors that influence metal-directed assembly processes. The vast majority of double helicates have been prepared by self-assembly reactions of two ligand strands with an appropriate number of commensurate metal centres.^{4,5} A number of ligands have been reported which contain multiple and spatially separated metal-binding domains, but these have generally been used for the preparation of higher-doublehelicates.⁶ Rigid⁷ or highly preorganised^{8,9} scaffolds bearing multiple oligopyridine chains have been used for the stereoselective assembly of multiple helicates. A single example has been reported in which two Lehn-type bis(2,2'-bipyridine) ligands have been linked by a polyethyleneoxy spacer and the resultant ligand shown to form a hairpin dicopper(I) complex.9 One of the most spectacular achievements has been the synthesis of molecular trefoil knots using double-helical metal complexes as a synthetic scaffold.¹⁰ Concepts of conventional and topological chirality have played an integral role in the development of strategies for the preparation of topologically novel compounds.

Complexes of stoichiometry [ML₂] with two symmetrical didentate (M four-coordinate pseudotetrahedral) or terdentate ligands (M six-coordinate pseudooctahedral) each have two orthogonal coordination planes defined by the donor atoms of each ligand, exhibit D_{2d} symmetry and are achiral and typified by bis(bipy) and bis(terpy) complexes respectively. Desymmetrising the ligands by substitution such that the two outermost donor atoms of the ligands are no longer chemically equivalent lowers the symmetry to C_2 and the species become chiral.11,12 Conversely, in most cases, symmetrical substitution of the ligand has no effect upon the overall symmetry and, for example, 4'-substituted 2,2':6',2'-terpyridines form achiral D_{2d} [ML₂] complexes. We recently identified a novel situation in which a ditopic ligand containing two terpy domains linked by a flexible spacer gave rise to C_2 symmetrical complexes, even though the linker was attached to the 4'-positions of the terpy (Fig. 1).¹³ In the same way that two mononuclear D_{2d} units may be linked to form the dinuclear double-helical structure that is the key to the trefoil knot the new C_2 unit may be coupled to a D_{2d} unit to give a new type of structure (B) that is conceptually between a double helix (A) and a trefoil knot (C) (Fig. 2, D_2 representations of the structures presented in each case). We use the notation PP or MM to describe the



Fig. 1 The prototype linked system resulting in the formation of C_2 rather than D_{2d} {M(terpy)₂} motifs upon coordination to a single metal centre.



Fig. 2 The relationship between the double helical (A), hairpin (B) and trefoil-knot (C) structures. In each case a single (*PP*) enantiomer has been depicted and for consistency, the trefoil knot is shown in the (coordinated) D_2 rather than the more familiar D_3 form.

chirality at each metal centre; this is strictly redundant in a helical system where the stereodescriptors P and M would suffice, but this usage allows extension to the (non-chiral) PM compound which leads to a macrocycle rather than a trefoil knot upon dual closure. An interesting point is that although each of these structures is chiral, A and B possess Euclidian chirality whilst C is topologically chiral.¹⁴ In this paper, we describe the preparation of hairpin double-helical structure of this type incorporating 2,2':6',2'':6'',2'''.'

Experimental

General

Commercially available chemicals were reagent grade and were used without further purification; 2-(1-oxo-2-pyridinioethyl)pyridine iodide¹⁶ and Ts(OCH₂CH₂)₆OTs¹⁷ were prepared by the literature methods. ¹H and ¹³C NMR spectra were recorded on Bruker 250, 400, 500 or 600 MHz spectrometers and full assignments were made using COSY, ROESY, HMBC and HMQC methods; chemical shifts are defined with TMS = 0 ppm for ¹H and ¹³C spectra and are measured relative to residual CHCl₃ or CHD₂CN. Infrared spectra were recorded

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on Shimadzu FTIR-8400S or Mattson Genesis FTIR spectrophotometers with neat samples on a Golden Gate diamond ATR accessory or in compressed KBr pellet respectively. UV-VIS measurements were performed using a Varian Cary 5000 UV-VIS-NIR photospectrometer; spectra were recorded for $\approx 10^{-5}$ M solutions in CHCl₃ (ligands) or MeCN (coordination compounds). EI mass spectra were recorded on a VG 70 SE or a Kratos MS-50 mass spectrometer and electrospray (ES) mass spectra on a Finnigan MAT LCQ mass spectrometer. Maldi TOF mass spectra were recorded using a PerSeptive Biosystems Voyager-RP or a PerSeptive Biosystems Voyager-DE TM PRO Biospectrometry workstation. The microanalyses were performed with a LECO CHN-900 apparatus.

Preparations

2-Acetyl-6-[3-(4-hydroxyphenyl)-1-oxoprop-3-enyl]pyridine I. A solution of 2,6-diacetylpyridine (1.0 g, 6.1 mmol) and Et₂NH (2 ml) in propanol (20 ml) was heated to reflux. A solution of 4-hydroxybenzaldehye (0.50 g, 4.1 mmol) in propan-1-ol (10 ml) was then added dropwise over a period of an hour. The mixture was heated at reflux for a further 2.5 h and then cooled to room temperature. Solvent and Et₂NH were removed in vacuo. The dark brown, viscous residue was dissolved in the minimum amount of CH₂Cl₂ and components were separated by column chromatography (SiO₂, CH₂Cl₂/MeOH 19/1). The first fraction was unreacted 2,6-diacetylpyridine (0.55 g, 3.4 mmol). The second fraction (intense yellow) was compound I, followed by unreacted 4-hydroxybenzaldehyde. The final fraction was 2,6-bis[3-(4-hydroxyphenyl)-1-oxoprop-3-enyl]pyridine II.18 Analytically pure, yellow I was obtained by recrystallization of I from hot MeOH (yield: 0.41 g, 55% based on 2,6-diacetylpyridine consumed) (Found: C, 71.8; H, 4.9; N, 5.2. Calc. for C₁₆H₁₃NO₃: C, 71.9; H, 4.9; N, 5.2%); mp 198 °C; m/z (Maldi-TOF-MS) 267 [M]⁺; $\delta_{\rm H}$ /ppm (250 MHz, CDCl₃) 8.92 (br, 1H, OH), 8.36 (dd, J 7.8, 1.0 Hz, 1H, H^{C5}), 8.22 (d, J 15.6 Hz, 1H, H^a), 8.22 (dd, J 7.8, 1.0 Hz, 1H, H^{C3}), 8.02 (t, J 7.8 Hz, 1H, H^{C4}), 7.96 (d, J 15.6 Hz, 1H, H^b), 7.64 (d, J 8.3 Hz, 2H, HG), 6.91 (d, J 8.3 Hz, 2H, HG3, 2.87 (s, 3H, HMe); IR $(\tilde{v}_{max}/cm^{-1})$ 3376br, 3200br, 1698s, 1648s, 1594sh, 1582s, 1554vs, 1510vs, 1360s, 1283m, 1270m, 1218s, 1166s, 1047m, 994w, 818w.

2-Acetyl-6-[3-(4-methoxyphenyl)-1-oxoprop-3-enyl]pyridine III. A solution of 2,6-diacetylpyridine (4.77 g, 29.2 mmol) and 4-methoxybenzaldehye (3.55 ml, 3.98 g, 29.2 mmol) were dissolved in propanol (50 ml) and the mixture was heated to 120 °C. Et₂NH (2 ml) was added and the orange solution was heated at reflux for 4 h. During this period, Et_2NH (2 × 2 ml) was added dropwise to the hot mixture. The reaction mixture was cooled to room temperature and the yellow solid that had formed was filtered from the orange solution. Separation of the products by column chromatography was unsuccessful. The crude product was therefore dissolved in hot MeOH; the addition of a small amount of toluene resulted in the preferential recrystallization of 2,6-bis[3-(4-methoxyphenyl)-1oxoprop-3-enyl]pyridine IV (see below). Crystals of IV were separated by filtration. Solvent was removed from the filtrate in vacuo, and the crude yellow product was redissolved in a mixture of CH₂Cl₂ and toluene. This solution was heated, and hexane was slowly added to the hot solution. On cooling to room temperature, III precipitated as a yellow solid (yield: 2.06 g, 25%) (Found: C, 71.69; H, 5.57; N, 4.95. Calc. for C₁₇H₁₅NO₃·0.2H₂O: C, 71.67; H, 5.45; N, 4.92%); m/z (EI-MS) 281 [M]⁺; δ_H/ppm (250 MHz, CDCl₃) 8.36 (dd, J 7.6, 1.0 Hz, 1H, H^{C5}), 8.23 (d, J 16.2 Hz, 1H, H^a), 8.22 (dd, J 7.6, 1.0 Hz, 1H, H^{C3}), 8.02 (t, *J* 7.6 Hz, 1H, H^{C4}), 7.98 (d, *J* 16.2 Hz, 1H, H^b), 7.68 (d, *J* 9.1 Hz, 2H, H^{G2}), 6.97 (d, *J* 9.1 Hz, 2H, H^{G3}), 3.87 (s, 3H, H^{OMe}), 2.87 (s, 3H, H^{Me}); IR (\tilde{v}_{max} /cm⁻¹) 3001w, 1697s, 1666s, 1589s, 1566s, 1512s, 1458m, 1442m, 1420m, 1342m,

1304m, 1250s, 1219m, 1204m, 1180s, 1150m, 1103m, 1034vs, 987vs, 949m, 810vs, 787s, 748m, 725m, 648m.

2-[3-(4-Hydroxyphenyl)-1-oxoprop-3-enyl]-6-[3-(4-methoxyphenyl)-1-oxoprop-3-enyl]pyridine V. The most efficient route to V was the reaction of I with 4-methoxybenzaldehyde (see text). Compound I (6.90 g, 25.8 mmol) and 4-methoxybenzaldehyde (30.0 ml, 33.6 g, 247 mmol) were heated in propanol (100 ml) and Et₂NH (6 ml) at 80 °C. After a few minutes, the reagents had dissolved and the mixture was then heated at reflux for 2.5 h. During this period, further Et_2NH (2 × 4 ml) was added. After cooling the reaction mixture to room temperature, solvent was removed in vacuo and a brown oil resulted. The product and excess reagents were separated by column chromatography $(SiO_2, CH_2Cl_2 : MeOH : Et_2NH 20 : 1 : 0.1)$. The third fraction was collected and V was isolated as an orange powder (yield: 3.6 g, 36%) (Found: C, 71.31; H, 5.22; N, 3.53. Calc. for C₂₄H₁₉NO₄·H₂O: C, 71.45; H, 5.25; N, 3.47%); m/z (EI-MS) 385 [M]⁺; $\delta_{\rm H}$ /ppm (400 MHz, CDCl₃) 9.54 (b, OH), 8.36 (d, J 7.8 Hz, 2H, H^{C3,C5}), 8.32 (overlapping d, J 15.9 Hz, 2H, H^a, H^a'), 8.07 (t, J 7.8 Hz, 1H, H^{C4}), 8.00 (d, J 15.9 Hz, 1H, H^b), 7.99 (d, J 16.2 Hz, 1H, H^b), 7.72 (d, J 8.8 Hz, 2H, H^{G2}), 7.68 (d, J 8.8 Hz, 2H, H^{F2}), 6.98 (d, J 8.8 Hz, 2H, H^{G3}), 6.92 (d, J 8.8 Hz, 2H, H^{F3}), 3.89 (s, 3H, H^{OMe}); δ_C/ppm (150 MHz, CDCl₃) 189 (C=O), 162 (C^{G4}), 159 (C^{F4}), 154 (C^{C2,C6}), 146 (C^{b,b'}), 138 (C^{C4}), 131 (C^{F2,G2}), 128 (C^{F1,G1}), 126 (C^{C3,C5}), 118 (C^{a,a'}), 117 (C^{F3}), 115 (C^{G3}), 57 (C^{Me}); IR (\tilde{v}_{max} /cm⁻¹) 3225w, 2962m, 2824m, 2754m, 2476m, 1651s, 1589vs, 1558vs, 1504vs, 1458s, 1389m, 1342s, 1250vs, 1165vs, 1034vs, 987s, 810vs, 740m, 694m, 663m.

4'-(4-Hydroxyphenyl)-4'"-(4-methoxyphenyl)-2,2':6',2":6",2"': 6^{'''},2^{''''}-quinquepyridine VI. Compound V (1.45 g, 3.76 mmol), 2-(1-oxo-2-pyridinioethyl)pyridine iodide (2.61 g, 7.99 mmol) and dry ammonium acetate (10 g, 0.13 mol) were heated to 90 °C in MeOH (12 ml) under argon. Almost all the solids dissolved; 4 drops of freshly distilled CH₃CO₂H were added to the reaction mixture. This was then heated at reflux overnight and a beige precipitate formed. The solution was allowed to cool to 5 °C and the precipitate that formed was collected by filtration. The solid was washed with ice-cold MeOH and dried in vacuo to yield VI (1.07 g, 49%) (Found: C, 75.40; H, 4.89; N, 11.67. Calc. for C38H27N5O2·H2O: C, 75.61; H, 4.84; N, 11.60%); m/z (Maldi-TOF-MS) 587 [M + 2H]⁺; $\delta_{\rm H}$ /ppm (600 MHz, DMSO-d₆) 9.94 (s, 1H, OH), 8.95 (d, J 1.8 Hz, 1H, H^{D3}), 8.93 (d, J 1.7 Hz, 1H, H^{B5}), 8.74 (m, 2H, H^{A6,E6}), 8.71 (m, 2H, H^{C3,C5}), 8.70 (d, J 1.7 Hz, 1H, H^{D3}), 8.67 (m, 3H, HA3, B5, E3), 8.24 (t, J 7.7 Hz, 1H, HC4), 8.02 (td, J 7.6, 1.9 Hz, 2H, H^{E4,A4}), 7.98 (d, 2H, J 8.7 Hz, H^{G2}), 7.89 (d, 2H, J 8.6 Hz, H^{F2}), 7.50 (ddd, J 10.8, 3.6, 1.2 Hz, 2H, H^{A5,E5}), 7.17 (d, 2H, J 8.8 Hz, H^{G3}), 7.01 (d, 2H, J 8.5 Hz, H^{F3}), 3.89 (s, 3H, H^{OMe}); $\delta_{\rm C}$ /ppm (150 MHz, DMSO-d₆) 160.4 (C^{G4}), 159.1 (C^{F4}), 155.4 (C^{B2,C2,D2,B6,C6,D6}), 154.8 (C^{A2,E2}), 149.2 (C^{A6,E6}), 149.1 (C^{B4}), 149.0 (C^{D4}), 138.6 (C^{C4}), 137.4 (C^{A4,E4}), 129.6 (C^{F2}), 128.2 (C^{F3,G2,G3}), 124.4 (CA5,E5), 121.0 (CA3,C3,C5,E3), 117.5 (CB3,B5,D3,D5), 116.2 (CF3), 114.8 (C^{G4}), 56.0 (MeO); IR (\tilde{v}_{max}/cm^{-1}) 3330br, 1574s, 1512vs, 1466m, 1450m, 1381s, 1258vs, 1173s, 1103s, 1103m, 1072m, 1034m, 987m, 887m, 818vs, 787vs, 733vs, 663m.

2-[3-(4-Hydroxyphenyl)-1-oxoprop-3-enyl]-6-(1-oxo-3-phenyl) prop-3-enyl)pyridine VII. Compound I (6.77 g, 25.3 mmol) was suspended in propan-1-ol (100 ml). To this, Et₂NH (30 ml) was added causing the colour to change to red. The suspension was heated to 80 °C and then a solution of benzaldehyde (10.0 ml, 10.5 g, 98.9 mmol) in propan-1-ol (80 ml) was added over a period of 10 min. The resultant solution was heated at reflux overnight during which time its colour changed to brown. After cooling, solvent was removed *in vacuo* to give a brown oil. The mixture was separated by column chromatography (SiO₂, CH₂Cl₂ : MeOH : Et₂NH 20 : 1 : 0.1). Compound **VII** was collected as the second fraction and was isolated as a yellow powder (yield 3.35 g, 37%) (Found: C, 77.44; H, 5.10; N, 3.86; C₂₃H₁₇NO₃ requires C, 77.73; H, 4.82; N, 3.94%); m/z (EI-MS) 355 [M]⁺, 278 [M – Ph]⁺; $\delta_{\rm H}$ /ppm (250 MHz, CDCl₃) 8.50 (m, 4H, H^{C3}, H^{C5}, H^a, H^{a'}), 8.11–7.96 (m, 3H, H^{C4}, H^b, H^{b'}), 7.81–7.73 (m, 2H, H^{F2}), 7.69 (d, J 8.7 Hz, 2H, H^{G2}), 7.49–7.45 (m, 3H, H^{F3}, H^{F4}), 6.91 (d, J 8.5 Hz, 2H, H^{G3}); IR (\tilde{v}_{max} /cm⁻¹) 3356br, 1659s, 1597s, 1558vs, 1504s, 1443m, 1335s, 1281m, 1234s, 1204s, 1165s, 1034vs, 980vs, 810vs, 764m, 741s, 679m.

4'-(4-Hydroxyphenyl)-4"'-phenyl-2,2':6',2":6",2"':6"',2"''-quinquepyridine VIII. Compound VII (2.63 g, 7.40 mmol), 2-(1-oxo-2-pyridinioethyl)pyridine iodide (4.83 g, 14.8 mmol) and ammonium acetate (5.98 g, 77.6 mmol) were dissolved in dry MeOH (40 ml) under argon. An oil bath at 100 °C was used to heat the reaction mixture. A brown solution formed. This was then heated at reflux for 17 h to yield a beige precipitate. After cooling to room temperature, the reaction mixture was filtered. The precipitate was washed with ice-cold MeOH and dried in vacuo. No further purification of VIII was necessary. Yield: 3.64 g (89%) (Found: C, 78.82; H, 4.62; N, 12.52; C₃₇H₂₅N₅O·0.5H₂O requires C, 78.70; H, 4.64; N, 12.40%); m/z (MALDI-TOF MS) 579 $[M + Na + H]^+$, 557 $[M + 2H]^+$; $\delta_{\rm H}$ /ppm (600 MHz, DMSO-d₆) 9.93 (s, 1H, OH), 9.04 (d, J 1.7 Hz, 1H, H^{B5}), 8.98 (d, J 1.9 Hz, 1H, H^{D3}), 8.79-8.70 (m, 6H, H^{C3,C5,A3,A6,E3,E6}), 8.77 (s, 1H, H^{B3}), 8.69 (s, 1H, H^{D5}), 8.27 (t, 1H, J 7.7 Hz, H^{C4}), 8.04 (m, 2H, H^{A4,E4}), 8.02 (m, 2H, H^{F2}), 7.89 (d, J 8.9 Hz, 2H, H^{G2}), 7.64 (t, J 7.4 Hz, 2H, H^{F3}), 7.59 (t, J 7.4 Hz, 1H, HF4), 7.56-7.52 (m, 2H, HA5,E5), 7.00 (d, J 8.8 Hz, 2H, H^{G3}); IR (\tilde{v}_{max} /cm⁻¹) 3186br, 3055m, 1666m, 1605m, 1566s, 1543vs, 1520s, 1474s, 1434m, 1389vs, 1273s, 1219m, 1173m, 1103m, 1072m, 1041m, 995m, 887m, 833m, 818s, 787vs, 764vs, 733s, 694m, 678m, 656m, 640m, 617s.

1,19-Bis[4-(4" - phenyl-2,2':6',2":6",2":6",2":"-quinquepyridin-4'-yl)phenyl]-1,4,7,10,13,16,19-heptaoxanonadecane IX. Dry VIII (319 mg, 0.574 mmol) and dry Cs₂CO₃ (107 g, 0.328 mmol) were suspended in DMF (7 ml) under argon. The brown reaction mixture was heated using an oil bath at 100 °C. A solution of Ts(OCH₂CH₂)₆OTs (169 mg, 0.286 mmol) in DMF (5 ml) was added dropwise over a period of 5 min. The reaction mixture was then heated at 80 °C for 20 h after which time a white precipitate had formed. At this point, a CaCl₂ drying tube was added to the reflux condenser and and the mixture heated at reflux for a further 70 h. During this period, more precipitate formed. The reaction mixture was cooled to room temperature. The solid was separated by filtration, washed with DMF, water, MeOH and Et₂O and finally dried in vacuo. A ¹H NMR spectrum of crude IX indicated that the product was partially protonated. It was therefore treated with dilute aqueous NaOH (pH 11) and extracted with chloroform. The solvent volume was reduced and was then chromatographed $(Al_2O_3, CHCl_3 : Et_2NH 42 : 1)$. Ligand IX was collected as the second fraction and was isolated as a yellow powder (202 mg, 52%) (Found C, 74.93; H, 5.33; N, 10.06; C₈₆H₇₂N₁₀O₇·0.5H₂O requires C, 75.09; H, 5.42; N, 10.18%); m/z (MALDI-TOF MS) 1358 $[M + 2H]^+$; δ_H /ppm (600 MHz, CDCl₃) 8.92 (d, J 1.7 Hz, 2H, H^{B5/D3}), 8.87 (d, J 1.6 Hz, 2H, H^{D3/B5}), 8.73-8.64 (m, 16 H, H^{B3,C3,C5,D5,A3,A6,E3,E6}), 8.00 (t, 2H, J 7.7 Hz, H^{C4}), 7.91–7.81 (m, 12H, H^{F2,A4,E4,G2}), 7.53–7.46 (m, 6H, H^{F3,F4}), 7.34 (ddd, J 7.4, 4.8, 1,1 Hz, 4H, HA5/E5), 7.31 (ddd, J 7.4, 4.7, 1,1 Hz, 4H, HE5/A5), 7.01 (d, J 8.6 Hz, 4H, H^{G3}), 4.19 (t, J 4.8 Hz, 4H, CH₂^f), 3.91 (t, J 4.8 Hz, 4H, CH₂^e), 3.77 (m, 4H, CH₂^d), 3.73 (m, 4H, CH₂^e), 3.69 (m, 8H, $CH_2^{a,b}$); IR (\tilde{v}_{max} /cm⁻¹) 3055m, 2870m, 1605s, 1582vs, 1543vs, 1512vs, 1474s, 1443m, 1420m, 1389vs, 1296m, 1250vs, 1180m, 1111vs, 1072vs, 1041vs, 987s, 941m, 887s, 817vs, 794vs, 764vs, 733vs, 694vs, 663s, 640m, 617vs; UV-VIS (c = 7.37 μ M) λ_{max} /nm (CHCl₃) 257 (ϵ /dm³ mol⁻¹ cm⁻¹ 101 500), 280 (97 600), 307 sh (57 500), 316 sh (46 300).

 $[Cu_2(VI)_2][PF_6]_3$. Ligand VI (19 mg, 32 µmol) and Cu(OAc)_2·H₂O (8.2 mg, 41 µmol) were dissolved in MeOH (3 ml). The brown solution was filtered. After 10 min, a filtered

solution of NH₄PF₆ in MeOH (1 ml) was added to the reaction mixture. The brown precipitate that formed was collected by filtration and was washed with ice-cold MeOH, water, icecold MeOH again, and Et₂O. The product was isolated as a brown powder (19 mg, 34%) (Found C, 49.38; H, 3.29; N, 7.54; C₇₆H₅₄Cu₂F₁₈N₁₀O₄P₃·6H₂O requires C, 49.57; H, 3.61; N, 7.61%); *m/z* (ES MS) 649 [M – L – Cu] ⁺, 433 [M – 3PF₆]³⁺; IR ($\tilde{\nu}_{max}$ /cm⁻¹) 3094br, 1589s, 1543m, 1520m, 1481m, 1458m, 1420m, 1358m, 1242s, 1180s, 1018m, 818vs, 741m, 648m, 617m; UV-VIS (*c* = 111 µM and 11 µM) λ_{max} /nm (MeCN) 226 (*ε*/dm³ mol⁻¹ cm⁻¹ 94 000), 292 (72 000), 317 (66 000), 351 (sh, 51 000), 467 (6400), 581 (2100).

[Cu₂(IX)][PF₆]₃. Ligand IX (21 mg, 15 µmol) and Cu(OAc)₂·H₂O (7.6 mg, 38 µmol) were dissolved in MeOH (3 ml). The mixture was sonicated to give a green solution. A filtered solution of NH₄PF₆ (56 mg, 34 µmol) in MeOH (1 ml) was added to the reaction mixture. A green precipitate formed and this was collected by filtration, was washed with ice-cold MeOH and Et_2O and was dried in vacuo to yield $[Cu_2(IX)][PF_6]_3$ as a brown powder (22 mg, 74%) (Found C, 51.28; H, 3.62; N, 6.75; C₈₆H₇₂Cu₂F_{22.2}N₁₀O₇P_{3.7} requires C, 51.11; H, 3.59; N, 6.93%); m/z (MALDI-TOF MS) 1629, $[M + 2H - 2PF_6]^+$, 1484 $[M + 2H - 3PF_6]^+$; IR (\tilde{v}_{max}/cm^{-1}) 3063br, 2870m, 1597s, 1574m, 1543m, 1520m, 1481m, 1450m, 1412m, 1242s, 1188s, 1111br, 1080m, 1011m, 833vs, 795s, 764s, 741s, 694m, 648m, 617m; UV-VIS ($c = 122 \,\mu\text{M}$ and $12 \,\mu\text{M}$) $\lambda_{\text{max}}/\text{nm}$ (MeCN) 224 (ε/dm³ mol⁻¹ cm⁻¹ 92 000), 289 (79 000), 316 (sh, 64 000), 351 (sh, 40 000), 472 (250), 574 (100).

Crystal structure determinations

Data were collected on an Enraf Nonius Kappa CCD instrument; data reduction, solution and refinement used the progammes COLLECT¹⁹, SIR92²⁰ and CRYSTALS.²¹

Crystal data for III. C₁₇H₁₅NO₃, M = 281.31, monoclinic, space group $P2_1/c$, a = 12.394(7), b = 4.032(4), c = 28.900(16)Å, $\beta = 90.73(4)^\circ$, U = 1444.3(17)Å³, Z = 4, $D_c = 1.294$ Mg m⁻³, μ (Mo-K_a) = 0.089 mm⁻¹, T = 293 K, 2494 reflections collected on an Enraf Nonius Kappa CCD instrument. Refinement of 1877 reflections (191 parameters) with $I > 1.0\sigma(I)$ converged at final R1 = 0.0725, wR2 = 0.0579, gof = 1.06.

Crystal data for $[Cu_2(VI)_2][PF_6]_3 \cdot 1.5Me_2CO.$ $C_{80.50}H_{63}Cu_2$ - $F_{18}N_{10}O_{5.50}P_3$, M = 1820.43, triclinic, space group PI, a = 11.709(1), b = 17.378(3), c = 19.3791(9) Å, a = 92.837(7), $\beta = 92.355(6)$, $\gamma = 98.49(1)^\circ$, U = 3890.5(7) Å³, Z = 2, $D_c = 1.554$ Mg m⁻³, μ (Mo-K_a) = 0.712 mm⁻¹, T = 173 K, 28493 reflections collected on an Enraf Nonius Kappa CCD instrument. Refinement of 15370 reflections (1288 parameters) with $I > 3.0\sigma(I)$ converged at final R1 = 0.0618, wR2 = 0.0674, gof = 1.14.

Crystal data for [**Cu**₂(**IX**)][**PF**₆]₃**·**2**·5Me**₂**CO.** C_{93.5}**H**₈₇**Cu**₂**·** F₁₈**N**₁₀**O**_{9.50}**P**₃, M = 1481.18, triclinic, space group $P\overline{1}$, a = 15.6921(2), b = 16.0207(2), c = 21.2804(3) Å, a = 103.9732(7), $\beta = 102.0324(8)$, $\gamma = 109.0858(7)^{\circ}$, U = 4659.0(1) Å³, Z = 2, $D_c = 1.472$ Mg m⁻³, μ (Mo-K_a) = 0.607 mm⁻¹, T = 173 K, 21247 reflections collected on an Enraf Nonius Kappa CCD instrument. Refinement of 12623 reflections (1355 parameters) with $I > 3.0\sigma(I)$ converged at final R1 = 0.0588, wR2 = 0.0514, gof = 1.16.

CCDC reference numbers 241100, 259911 and 259912. See http://www.rsc.org/suppdata/dt/b5/b500209e/ for crystallographic data in CIF or other electronic format.

Electrochemistry

The voltammetric experiments (cyclic and differential pulse) were measured with a BAS 100 B/W electrochemical workstation and a three-electrode cell, consisting of a silver wire as a pseudo-reference, a glassy carbon disk as the working and a platinum wire as counter electrode. After gaining a full set of voltammograms, ferrocene was added in order to determine the exact position of the signals within the potential window. Tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆, 0.1 M) acted as the electrolyte. All solutions were degassed thoroughly for at least 15 min with argon; an inert gas blanket was maintained over the solution during the measurements. All potentials given in this paper refer to the ferrocene–ferrocenium redox couple at 0 V. The spectroelectrochemistry was measured with a three-electrode configuration in a 1 mm cuvette with platinum mesh as working electrode and counter electrode and a silver wire as pseudo-reference electrode. The instrument used for recording the spectra was an Agilent 8453 diode array spectrophotometer.

Results and discussion

Ligand syntheses

Our strategy was to prepare an asymmetrically-substituted 2,2':6',2":6",2":6",2"''-quinquepyridine (qpy) in which a hydroxyphenyl substituent was subsequently to be used as a nucleophile in a reaction with a bis-electrophile to yield the desired bisqpy ligand. Our initial synthetic targets were the asymmetric 2,2':6',2":6",2"':6"',2"''-quinquepyridine (qpy) ligands VI and VIII. Compound VI was attractive as, in principle, it would allow us to complete the conceptual relationship between double helix, hairpin and trefoil knot by deprotection of the methyl group and a second coupling reaction. Standard Kröhnke methodology¹⁶ was chosen for the final assembly of the ligands, but the initial requirement was a route to the asymmetrical bis-enones V and VII. Two strategies for compound V were explored and these are summarised in Scheme 1. The reaction of 2,6-diacetylpyridine with either 4-hydroxybenzaldehyde or 4-methoxybenzaldehyde (in 1 : 1 molar ratio or with the 2,6-diacetylpyridine in excess) in propanol in the presence of Et₂NH yielded mixtures of the enones I or III and the bis-enones II or IV. The mono- and bisenones were readily separated by column chromatography. The



Scheme 1 Synthetic routes to compounds I-V; showing the ring labelling used.

mono-enones are particularly easy to detect by IR spectroscopy as they exhibit two C=O stretching modes; one is characteristic of an aryl ketone at $\approx 1698 \text{ cm}^{-1}$ and the other is assigned to the enone and is shifted 30–40 cm⁻¹ to lower energy. Reaction of I with an excess of 4-methoxybenzaldehyde in propanol at reflux in the presence of Et₂NH gave the bis(enone) V in 36% yield. Compound V could be separated by column chromatography. The alternative route to V by reaction of III with 4-hydroxybenzaldehyde yielded mixtures which were relatively difficult to separate by chromatography. These conversions are summarised in Scheme 1, which also presents the nomenclature used to distinguish the various aromatic rings.

In a Kröhnke reaction, the bis(enone) V reacted smoothly with 2-(1-oxo-2-pyridinioethyl)pyridine iodide (Scheme 2) and ammonium acetate in methanol at 90 °C to give the asymmetrical qpy ligand VI in 49% yield. The ligand was characterized by ¹H and ¹³C NMR spectroscopies and mass spectrometry. In the Maldi-TOF mass spectrum, the highest mass peak at m/z 587 corresponded to $[M + 2H]^+$. The ¹H and ¹³C NMR spectra were fully assigned (see Experimental section) using a combination of COSY, ROESY, HMBC and HSQC technqiues. We discuss the coordination behaviour of ligand **III** later in the paper.



Scheme 2 Synthetic route to ligand VI showing the ring labelling used.

Ligand VI contains a single qpy domain, and has a 'labelled' head and tail which give us the opportunity to investigate prefences for head-to-head or 'head-to-tail' binding upon the formation of dinuclear helicates.²² These preferences will be crucial in determining the nature of hairpin helicates with linked qpy domains.

We decided upon the use of a polyoxyethylene spacer to link the two qpy domains, partly because of the successful use of such spacers in the synthesis of catenanes and knots,1,2 and partly because we hoped to use a "caesium effect" to maximise the yield in the coupling reaction.²³ We also decided that the most successful approach would be to work with ligands in which a simple phenyl rather than a 4-methoxyphenyl group acted as the desymmetrising spectator, to avoid ether exchange reactions. The strategy for the assembly of the new ligand **IX** with a phenyl spectator in the 4"-position is shown in Scheme 3. The reaction of compound I (Scheme 1) with benzaldehyde in the presence of Et₂NH in propanol at reflux gave, after chromatographic workup, the asymmetric bis(enone) VII in moderate yield. Compound VII was converted into the asymmetrical qpy ligand VIII using standard Krönke methodology. The ligand was isolated in 89% yield and was characterized by spectroscopic and mass spectrometric techniques, the ¹H NMR spectrum being assigned by COSY and ROESY methods. Following the reaction of VIII with Cs₂CO₃ in DMF at 100 °C to generate the phenoxide, the two qpy domains were linked by reaction with Ts(OCH₂CH₂)₆OTs in DMF at reflux for 90 h. Ligand IX was obtained as a pale yellow solid in moderate yield,



Scheme 3 Synthetic route to ligand IX; ring labelling as used in the Experimental section.

and was characterized by spectroscopic and mass spectrometric techniques. The highest mass peak in the MALDI-TOF mass spectrum at m/z 1358 was assigned to $[M + H]^+$.

One of the principal difficulties we encountered in this work was in distinguishing the asymmetric species from mixtures of symmetric compounds. For example, the ¹H NMR spectum of **VIII** is essentially a superposition of the two symmetrical compounds 4',4"'-diphenyl-2,2':6',2":6",2"''-quinquepyridine and 4',4"-bis(4-hydroxyphenyl)-2,2':6',2": 6"',2"'':6"'',2"''-quinquepyridine. Similarly, the asymmetric bisenones are almost indistinguishable from mixtures of the symmetrical components and the mono-enones to mixtures of 2,6-diacetylpyridine and the bisenone. Unambiguous proof of the structure of the mono-enones came from a crystal structure of **III**.

Crystal structure of compound III

Several crystals of III suitable for X-ray crystallography grew fortuitously from a hexane/ethyl acetate/diethylamine solvent mixture during attempts to purify the crude material by column chromatography. The molecular structure of III is shown in Fig. 3, and selected bond distances and angles are given in the figure caption. All intramolecular bond lengths and angles are typical, and as expected from the ¹H NMR spectrum (${}^{3}J_{HH} =$ 16.2 Hz), the alkene has an E stereochemistry. With the exception of the hydrogen atoms of the two methyl groups, all the atoms in a molecule of **III** are close to being coplanar; the angle between the least squares planes of the pyridine and aryl rings is 9.1°. The molecules form a herring-bone assembly along the b-axis. Along the c-axis, molecules are assembled in stacks, each molecule being off-set with respect to the next; van der Waals interactions operate between aromatic rings with closest pyridine-pyridine contacts being 3.43 Å, and aryl-aryl contacts of 3.65 Å.



Fig. 3 The molecular structure of III. Important bond lengths and angles: C(1)-O(1) = 1.206(3), C(1)-C(3) = 1.483(4), C(3)-N(1) = 1.337(3), N(1)-C(7) = 1.336(3), C(7)-C(8) = 1.491(4), C(8)-O(2) = 1.217(3), C(8)-C(9) = 1.464(3), C(9)-C(10) = 1.323(3), C(10)-C(11) = 1.451(3), C(14)-O(3) = 1.363(3), O(3)-C(17) = 1.421(3) Å; O(1)-C(1)-C(2) = 121.9(3), O(1)-C(1)-C(3) = 120.1(3), C(2)-C(1)-C(3) = 118.0(3), C(3)-N(1)-C(7) = 117.9(2), C(7)-C(8)-O(2) = 119.6(2), O(2)-C(8)-C(9) = 122.4(2), C(7)-C(8)-C(9) = 118.0(2), C(8)-C(9)-C(10) = 121.3(2), C(9)-C(10)-C(11) = 127.6(2), $C(14)-O(3)-C(17) = 117.3(2)^{\circ}$.

Complex formation and characterisation

Two qpy ligands present a total of ten nitrogen donor atoms. Each qpy ligand strand is expected to be partitioned into a 2,2':6',2"-terpyridine-like terdentate and a 2,2'-bipyridinelike bidentate domain giving, in the absence of participation by donor solvent molecules, compatibility with 4-, 5- or 6coordinate metal centres. Dicopper double helicates of qpy ligands are known that have two copper(I), one copper(I) and one copper(II) and two copper(II) centres.²⁵⁻²⁸ The latter two coordination modes have been structurally characterised; in the mixed oxidation state complex the total of ten nitrogen donors satisfies the total coordination requirement of the fourcoordinate copper(I) and six-coordinate copper(II) centres and a [4 + 6] helicate is formed. In the case of the dicopper(II) compound, one metal is in a six-coordinate $\{Cu(terpy)_2\}$ environment whilst the other is coordinated to four nitrogens from the two qpy strands and additional solvent or counter-ion donors.

Ligand VI reacted readily with copper(II) acetate in methanol and the mixed oxidation state complex $[Cu_2(VI)_2][PF_6]_3$ was isolated as the hexafluorophosphate salt in 34% yield. The brown colour suggested reduction of Cu(II) had taken place; the formation of the mixed Cu(I)/Cu(II) complex was supported by elemental analysis and mass spectrometric data. The electrospray MS showed an envelope at 433 with component peaks at 0.33 mass unit separation; the envelope of peaks was collectively assigned to $[M - 3PF_6]^{3+}$ and the isotopomer distribution corresonded to that simluated for a dicopper species. A broadened and shifted, but very poorly resolved ¹H NMR spectrum (600 MHz in CD₃CN) exhibited signals in a shift range δ +25 to +6 ppm, indicative of a paramagnetic species. No attempt was made to further assign this spectrum. A crystal structure determination of the complex was undertaken and provided confirmation of a mixed valence copper complex. Brown, X-ray quality crystals of [Cu₂(VI)₂][PF₆]₃·1.5Me₂CO were grown by diffusion of Et₂O into an acetone solution of the complex. In the cation $[Cu_2(VI)_2]^{3+}$, the two ligands form a double helical arrangement embracing two copper centres. Cations with both PP and MM chirality are present in the lattice. The five pyridine rings in each ligand are partitioned into bipyand terpy-coordination domains. The copper(II) centre is in a distorted octahedral environment, while the copper(I), is in a distorted tetrahedral environment. The Cu ··· Cu separation is 3.94 Å, too long to be considered a bonding interaction. Two views of the dicopper cation are given in Fig. 4. The cation suffers from several disorders. In one of the methoxy groups,



(b)

Fig. 4 (a) Structure of the *P*-enantiomer of the cation in $[Cu_2(VI)_2][PF_6]_3 \cdot 1.5Me_2CO$ with selected atom labelling. (b) View of the cation looking down the Cu–Cu axis showing the helical array of the two ligands. Selected bond lengths and angles: $Cu(1)-N(4) = 2.037(3), Cu(1)-N(5) = 1.986(3), Cu(1)-N(9) = 2.011(3), Cu(1)-N(10) = 2.011(3), Cu(2)-N(1) = 2.186(3), Cu(2)-N(2) = 1.963(3), Cu(2)-N(3) = 2.357(3), Cu(2)-N(6) = 2.104(3), Cu(2)-N(2) = 1.932(3), Cu(2)-N(8) = 2.243(3) Å; N(4)-Cu(1)-N(5) = 81.4(1), N(4)-Cu(1)-N(9) = 133.9(1), N(5)-Cu(1)-N(10) = 123.6(1), N(4)-Cu(1)-N(10) = 109.8(1), N(5)-Cu(1)-N(10) = 134.7(1), N(9)-Cu(1)-N(10) = 80.7(1), N(1)-Cu(2)-N(2) = 77.9(1), N(2)-Cu(2)-N(3) = 75.7(1), N(3)-Cu(2)-N(6) = 83.0(1), N(1)-Cu(2)-N(7) = 78.7(1), N(1)-Cu(2)-N(7) = 107.7(1), N(6)-Cu(2)-N(7) = 78.7(1), N(1)-Cu(2)-N(8) = 83.6(1), N(2)-Cu(2)-N(8) = 102.7(1), N(3)-Cu(2)-N(8) = 76.9(1), N(1)-Cu(2)-N(6) = 104.4(1), N(2)-Cu(2)-N(6) = 101.9(1)^{\circ}.$

there are two methyl positions (C130 and C180) with 71.5 and 28.5% occupancies respectively; the major occupancy (C130) is shown in Fig. 4. Each of the C_6 rings in the 4-hydroxyphenyl substituents is disordered over two positions, each with a 50% occupancy. The two phenyl rings of the 4-methoxyphenyl substituents are mutually staggered and there are weak van der Waals interactions between them (closest distance between C atoms is 3.90 Å). A number of features are of interest in this structure. Firstly, the introduction of the substituents has remarkably little effect on the gross structural features of the helicates as shown by a comparison with the analogous mixed oxidation state helicates with 2,2':6',2":6",2":6",2""-quinquepyridine 2,2':6',2":6",2"':6"',2"''-quinquepyridine (Cu · · · Cu, 3.957 Å)²⁸ although the helical pitch, as measured through the torsion angles between bipy and terpy domains varies slightly.

Although the substituents do not greatly change the basic helical structure, they exert a remarkable degree of regiospecificity. Although we cannot comment on the solution equilibria, the solid state crystal contains only the head-to-tail (HT) regioisomer in which each metal centre is coordinated to the B ring of one ligand strand and the D ring of the other. Although the substituents are similar in size, the hydroxyphenyl residue can become involved in classical hydrogen bonding, but although the two hydroxy groups are on the same side, as seen in Fig. 4b, the O \cdots O distance of 6.1 Å precludes intramolecular hydrogen bonding. However, extensive hydrogen bonding with the counterions and solvent is apparent with HO \cdots X (X = F, acetone O) distances in the range 2.816–2.900 Å.

The hairpin ligand IX reacted with copper(II) acetate in methanol to give a green solution from which a green solid was precipitated by the addition of NH_4PF_6 . After washing

with ice-cold MeOH, H₂O and Et₂O, the colour darkened and $[Cu_2(IX)][PF_6]_3$ was isolated as a brown powder in 74% yield. The colour change indicates that initially a dicopper(II) species is formed, that is readily reduced to a mixed-valence species. This same scenario is observed when copper(II) reacts with the parent qpy ligand.^{24,25} The elemental analysis of the product indicated that the bulk sample was a mixture of Cu(II)Cu(II) and Cu(II)Cu(I) species (see Experimental section). In the MALDI-TOF mass spectrum, the highest mass envelopes at m/z 1629 and 1484 were assigned to the ions $[M + 2H - 2PF_6]^+$ and $[M + 2H - 3PF_6]^+$; the isotope patterns observed matched those simulated. The ¹H NMR spectrum of the complex exhibited broad signals over the range δ +25 to +3.5 ppm. Although the spectrum could not be fully assigned, the lowest field signals can be attributed with some confidence to protons closest to the paramagnetic metal centres, while signals at δ 3.9, 3.8, 3.6 and 3.5 were assigned to CH_2 protons within the polyether chain which is spatially remote from the metal centres.

Single crystals of [Cu₂(IX)][PF₆]₃·2.5Me₂CO were grown by diffusion of Et₂O vapour into an acetone solution of the complex. The $[Cu_2(IX)]^{3+}$ cation is chiral and the unit cell contains both PP and MM enantiomers related by an inversion centre. Fig. 5a shows the structure of the *PP*-enantiomer. The two qpy coordination domains of ligand IX form a helical assembly around the two copper centres (Fig. 5b). As in the structure of [Cu₂(VI)₂]³⁺, each qpy ligand strand is partitioned into a bipy- and terpy-subunit, providing appropriate coordination environments for a copper(I) centre (distorted tetrahedral Cu(2), Σ N–Cu–N angles = 664.3°) and a copper(II) centre (distorted octahedrals). The terpy unit of one ligand strand consists of rings C, D and E (see Scheme 3) while that of the second strand is made up of rings A, B and C. The two bipy domains are made up of rings A and B of strand 1 and rings D and E of strand 2. The polyether chain forms a hairpin conformation, but the extent to which this preorganises the two qpy strands for helicate formation must be viewed with caution (see below). The two Cu centres are non-bonded and the separation (4.0 Å) is very similar to that in $[Cu_2(qpy)_2][PF_6]_3^{24,25}$ (3.96 Å) and $[Cu_2(VI)_2][PF_6]_3$ (see above). In the hairpin complex, as in $[Cu_2(VI)_2][PF_6]_3$ there is the possibility of forming head-to-head (HH) and head-to-tail (HT). Once again, in the solid state, a remarkable regioselectivity is observed and only the HT stereoisomer is observed. There is extensive interstrand π -stacking within the double helix with most significant interactions between D pyridine rings of each strand and between the aryl rings G (Scheme 3 for numbering and Fig. 5b).

We had originally speculated about the possibility of binding Group 1 metals to the polyoxyethylene spacer which might act as a pseudo-crown ether. However, as the space-filling representation in Fig. 5c shows, the binding cavity is more apparent than real. The role of the caesium carbonate in the synthesis remains speculative, although the yields were significantly and reproducably higher than when potassium or sodium carbonate were used as base.

Electrochemistry and spectroelectrochemistry

Even though the structural properties of the hairpin complex closely resembled those of the model complexes with simple qpy ligands, we hoped that the electrochemical properties might give an insight into the dynamic properties. In particular, we hoped that rearrangements involving ligand dissociation would be retarded through the linking of the two qpy domains.

The electrochemical properties of complex $[Cu_2(IX)][PF_6]_3$ and its non-linked analogue $[Cu_2(VI)_2][PF_6]_3$ were measured, and were found to very closely resemble those of $[Cu_2(qpy)_2][PF_6]_3$.^{24,25} Two peaks associated with metal-centred processes were observed for both compounds at moderate potentials (-0.44 V, 0.13 V for $[Cu_2(VI)_2][PF_6]_3$ and -0.43 V, 0.16 V for $[Cu_2(IX)][PF_6]_3$ (determined by differential pulse



Fig. 5 (a) Structure of the PP-enantiomer of the cation in $[Cu_2(IX)][PF_6]_3 \cdot 2.5Me_2CO$ with selected atom labelling. (b) View of the cation looking down the Cu-Cu axis showing the helical assembly of the two ligand strands. Selected bond lengths and angles: Cu(1)-N(1) =2.117(3), Cu(1)-N(2) = 1.950(3), Cu(1)-N(3) = 2.240(3), Cu(1)-N6 = 0.0002.027(3), Cu(2)-N(5) = 2.006(3), Cu(2)-N(9) = 2.035(3), Cu(2)-N(10 = 2.001(3) Å; N(1)-Cu(1)-N(2) = 79.3(1), N(2)-Cu(1)-N(3) = 77.1(1), N(1)-Cu(1)-N(6) = 103.6(1), N(2)-Cu(1)-N(6) = 96.0(1), N(3)-Cu(1)-N(6) = 96.0(1), N(3)-N(6) = 96.0(1), N(6) = 96.0(N(6) = 84.9(1), N(1)-Cu(1)-N(7) = 99.3(1), N(3)-Cu(1)-N(7) =104.8(1), N(6)-Cu(1)-N(7) = 78.3(1), N(1)-Cu(1)-N(8) = 80.7(1), N(2)-Cu(1)-N(8) = 110.5(1), N(3)-Cu(1)-N(8) = 102.1(1), N(7)-Cu(1)-N(8) = 75.2(1), N(4)-Cu(2)-N(5) = 81.4(1), N(4)-Cu(2)-N(9) = 81.4(1), N(4)-Cu(2)130.0(1), N(5)-Cu(2)-N(9) = 114.1(1), N(4)-Cu(2)-N(10) = 119.8(1), $N(5)-Cu(2)-N(10) = 137.1(1), N(9)-Cu(2)-N(10) = 81.9(1)^{\circ}.$ (c) A space-filling representation of the hairpin complex showing that the polyoxyethylene linker is tightly folded and has no crown-like metal-binding cavity.

voltammetry, potentials quoted *versus* Fc/Fc⁺), indicating that all three redox states (Cu(I)Cu(I), Cu(I)Cu(II) and Cu(II)Cu(II) are readily accessible. As in $[Cu_2(qpy)_2][PF_6]_3$,^{24,25} both metalcentred processes for $[Cu_2(VI)_2][PF_6]_3$ are reversible. In contrast, the metal-centred processes for $[Cu_2(IX)][PF_6]_3$ are irreversible at a scan rate of 100 mV s⁻¹. At slower scan rates, the redox processes of $[Cu_2(IX)][PF_6]_3$ become more reversible, with a smaller difference between anodic and cathodic waves in the cyclic voltammogram (Fig. 6). A higher reversibility at lower scan rates is in contrast to most irreversible processes, in which the redox process competes with chemical reactions of the reduced or oxidised state of the compound. Therefore, it is proposed that the complex is chemically stable in all redox states, but that the electron-transfer processes, commencing from the



Fig. 6 Cyclic voltammograms for $[Cu_2(IX)][PF_6]_3$ with a scan speed of 100 mV s⁻¹ (dotted line) and 50 mV s⁻¹ (dashed line) measured in acetonitrile.

fully reduced state, Cu(1)Cu(1), are particularly slow. The reason for this behaviour is unknown, but we speculate that the reduced flexibility of the bridged ligand in $[Cu_2(IX)][PF_6]_3$ makes it more difficult for the complex to adjust its structure to accommodate a change in oxidation state: *i.e.* the ligand is more pre-organised. This gives rise to a higher reorganisation energy on changing redox state, leading to slower electron transfer rates.²⁹ In order to examine the stability of the complexes in different oxidation states, spectroelectrochemical experiments were performed. For $[Cu_2(VI)_2][PF_6]_3$ and $[Cu_2(IX)][PF_6]_3$, the development of UV-VIS absorption spectra was measured with applied negative potentials or applied positive potentials in order to generate the Cu(1)Cu(1) and Cu(II)Cu(II) states, respectively. The results are presented in Fig. 7.



Fig. 7 Evolution of UV-VIS absorption spectra under applied potentials for $[Cu_2(VI)_2][PF_6]_3$ and $[Cu_2(IX)][PF_6]_3$ (A: $[Cu_2(VI)_2][PF_6]_3$, oxidative conditions; B: $[Cu_2(VI)_2][PF_6]_3$, reductive conditions; C: $[Cu_2(IX)][PF_6]_3$, oxidative conditions; D: $[Cu_2(IX)][PF_6]_3$, reductive conditions). The applied potentials were chosen 200 mV more positive and more negative, respectively, than the according redox potentials.

The major features of the spectra in Fig. 7 between 400 and 750 nm are due to a MLCT transitions of the copper(I) species of the two complexes. Oxidation to copper(II) quenches these absorptions for both complexes (Fig. 6, A and C). Upon rereduction of copper(II) to copper(I) restores the original features of the spectra with an absorption maximum at 475 nm and a shoulder at longer wavelengths (around 600 nm). The overlaid spectra of complexes [Cu₂(**VI**)₂][PF₆]₃ and [Cu₂(**IX**)][PF₆]₃ and 429 and 720 nm for [Cu₂(**VI**)₂][PF₆]₃. The latter values closely resemble the results reported previously for [Cu₂(qpy)₂][PF₆]₃.

The reversibility of the spectroelectrochemistry indicates that despite the irreversible behaviour seen in the voltammetric experiments, $[Cu_2(IX)][PF_6]_3$ is stable in all oxidation states, supporting the conclusion that the electron transfer rates are slow due to demanding re-organisation processes.

Conclusions

We have prepared a novel ligand in which two qpy metalbinding domains are linked by a polyoxyethylene spacer. The new ligand reacts with copper(II) salts to form dinuclear double helicates with a hairpin structure. The hairpin structure is formed regioselectively as the HT stereoisomer. Ligand **IX** is sterically more demanding than **VI**, and this results in a significantly slower geometrical reorganisation within the dinuclear complex leading to sluggish electron transfer rates upon switching of redox states. In future work, we will extend these studies to the preparation of qpy-based trefoil knots.

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