Facile Interconversion of Dinuclear Double Helicates and Side-by-Side Species: A Reprogrammable Ligand with Potential Sensor Applications.

Georgios Bokolinis, T. Riis-Johannessen, Lindsay P. Harding, John. C. Jeffery, Neil McLay, Craig R. Rice*.

Electronic Supplementary Information

^{1}H NMR of $[Cu_2(L^1)_2]^{2+}$ + Ba^{2+} (**3**) and $[Cu_2(L^1)_2]^{2+}$ + Na^+ (**2**).

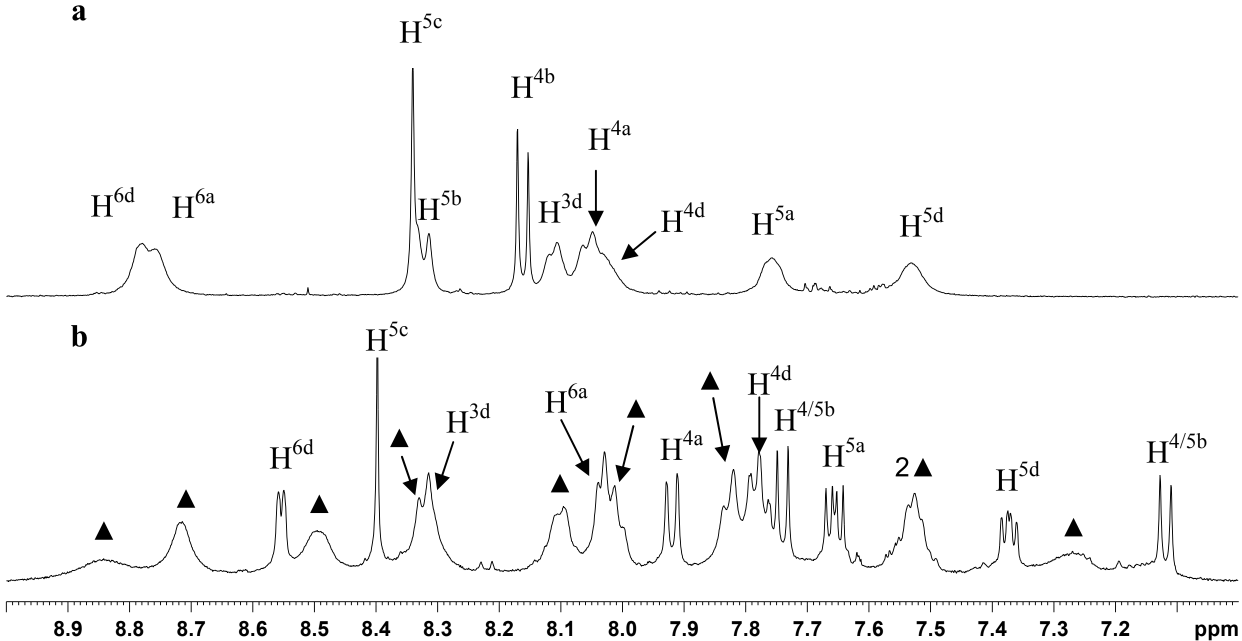
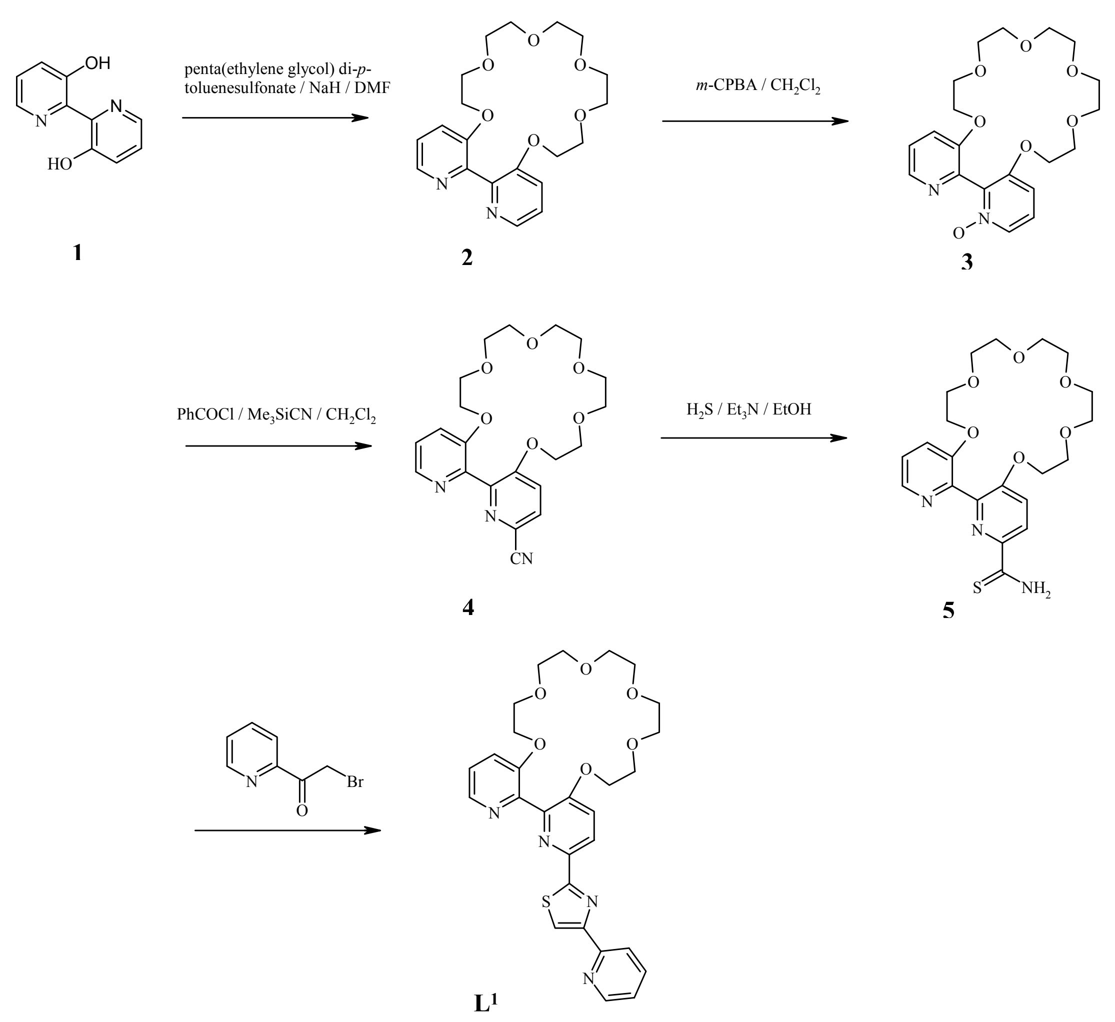


Figure 1. Aromatic regions of the ^{1}H NMR (CD_3CN) spectra of **a**) $[Cu_2(L^1)_2]^{2+}$ + Ba^{2+} (**3**) (295K) and **b**) $[Cu_2(L^1)_2]^{2+}$ + Na^+ (**2**) (243K). The assigned peaks correspond to the side-by-side structure and the helicate species are indicated by ▲.

Synthetic Details



The starting material 2,2'-bipyridine-3,3'-diol **1** was prepared by literature methods[1], as well as 2,2'-bipyridine 20-crown-6 derivative **2**.[2]

Synthesis of 3.

To a solution of **2** (0.70g, 1.80 mmol) in CH_2Cl_2 (20 cm^3) was added 3-chloroperbenzoic acid (50%, 0.50g, 1.45 mmol). The reaction was followed by TLC and on completion, the solvent was removed under vacuum (Care: *N*-oxides are potentially explosive) leaving crude *N*-oxide as thick pale yellow oil. This was then purified by column chromatography (3% MeOH in CH_2Cl_2, Al_2O_3) giving **3** as thick clear oil (0.52g, 71% yield). ^1H NMR (400MHz, $CDCl_3$) δ 8.30 (dd, J = 1.3, 4.6 Hz, 1H), 7.95 (d, J = 6.5 Hz, 1H), 7.34 (dd, J = 8.5, 1.3 Hz, 1H), 7.27 (dd, J = 4.6, 8.5 Hz, 1H), 7.13 (dd, J = 6.5, 8.6 Hz, 1H), 6.91 (d, J = 8.2 Hz, 1H), 4.20 – 3.95 (m, 4H, -CH_2-), 3.75 – 3.45 (m, 16H, -CH_2-). ESI-MS: *m/z* 409 [$M+H^+$], $C_{20}H_{27}N_2O_7$ requires 407.1813 found 407.1811. Elemental Analysis calculated for $C_{20}H_{26}N_2O_7$, C, 59.1; H, 6.4; N, 6.9%. Found: C, 58.7; H, 6.3; N, 6.5%.

Synthesis of 4.

To a refluxing solution of **3** (0.35g, 0.86 mmol) and benzoyl chloride (0.15g, 1.00 mmol) in CH_2Cl_2 (20 cm^3), trimethylsilyl cyanide (0.17g, 1.70 mmol) was added and heating was maintained for 8 hrs. After this time the solution was cooled and extracted with $NaHCO_{3(aq)}$ (3 × 30 cm^3), dried ($MgSO_4$) and the CH_2Cl_2 removed under vacuum. The resulting light yellow oil was then purified by column chromatography (1% MeOH in CH_2Cl_2, Al_2O_3) giving **4** as yellow oil (0.22g, 61% yield). ^{1}H NMR (400MHz, $CDCl_3$) δ 8.37 (dd, *J* = 2.7, 5.9 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.37 (2H, overlapping), 4.33 – 4.10 (m, 4H, -CH_2-), 3.80 – 3.58 (m, 16H, -CH_2-). ESI-MS: *m/z* 416 [M+H^+], $C_{21}H_{26}N_3O_6$ requires 416.1816 found 416.1812. Elemental Analysis calculated for $C_{21}H_{25}N_3O_6$, C, 60.7; H, 6.1; N, 10.1%. Found: C, 60.9; H, 5.8; N, 9.9%.

Synthesis of 5.

To a solution of **4** (0.14g, 0.30 mmol) in ethanol (20 cm^3) triethylamine (2 cm^3) was added. H_2S was then bubbled through this solution until the solution turned yellow, bubbling was continued for a further 2 minutes, and then the flask was stoppered and left overnight. Evaporation of the solvent gave a red/brown residue, which was purified using column chromatography (3% MeOH in CH_2Cl_2, Al_2O_3), giving **5** as a yellow solid (0.11g, 82% yield). ^{1}H NMR (400MHz, $CDCl_3$) δ 9.30 (br s, 1H, -NH_2), 8.74 (d, *J* = 8.8 Hz, 1H), 8.32 (dd, *J* = 1.9, 4.0 Hz, 1H), 7.46 (br s, 1H, -NH_2), 7.40 (d, *J* = 8.8 Hz, 1H), 7.34 (2H, overlapping), 4.35 – 4.18 (m, 2H, -CH_2-), 4.13 – 3.98 (m, 2H, -CH_2-), 3.85 - 3.50 (m, 16H, -CH_2-). ESI-MS: *m/z* 450 [M+H^+], $C_{21}H_{28}N_3O_6S$ requires 450.1693 found 450.1691. Elemental Analysis calculated for $C_{21}H_{27}N_3O_6S$, C, 56.1; H, 6.0; N, 9.3%. Found: C, 55.8; H, 5.8; N, 9.1%.

Synthesis of L^1.

To a solution of **5** (0.10g, 0.22 mmol) in ethanol (25 cm^3) was added 2-(α–bromoacetyl)-pyridine (0.05g, 0.25 mmol) and the reaction was heated at reflux for 3 hrs. After this time the solvent was removed resulting in a white oily solid. Neutralisation by $NaHCO_{3(aq)}$ and extraction into CH_2Cl_2 (3 × 30 cm^3) gave, upon removal of the solvent, crude $\mathbf{L^1}$. Purification, using column chromatography (1% MeOH in CH_2Cl_2, Al_2O_3), gave $\mathbf{L^1}$ as pale brown oil (0.08g, 65%). ^{1}H NMR (400MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.5 Hz, 1H), 8.36 (dd, *J* = 4.3, 1.4Hz, 1H), 8.32 (d, *J* = 8.6 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.07 (s, 1H), 7.78 (ddd, *J* = 1.7, 7.7, 7.7 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 1H), 7.32 (2H, overlapping), 7.22 (dd, *J* = 7.3, 5.3 Hz, 1H) 4.30 – 4.10 (m, 4H, -CH_2-), 3.70 – 3.55 (m, 16H, -CH_2-). ESI-MS: *m/z* 551 [M+H^+], $C_{28}H_{31}N_4O_6S$ requires 551.1958 found 551.1969. Elemental Analysis calculated for $C_{28}H_{30}N_4O_6S$, C, 61.1; H, 5.5; N, 10.2%. Found: C, 60.7; H, 5.2; N, 9.8%.

Synthesis of the complex $[Cu_2(L^1)_2](BPh_4)_2$.

To a suspension of $\mathbf{L^1}$ (0.010g, 0.018 mmol) in acetone (2 cm^3), $Cu(MeCN)_4PF_6$ (0.007g, 0.018 mmol) was added and the solution was stirred until dissolution was complete. To this was added excess NH_4BPh_4 and the solution filtered. Slow diffusion of ethyl acetate gave $[Cu_2(\mathbf{L^1})_2](BPh_4)_2$ as dark red crystals Supplementary Material for Chemical Communications

(41% yield). ESI-MS: *m/z* 1546 [M-$(BPh_4)^-$]. Elemental Analysis calculated for $C_{104}H_{100}N_8B_2Cu_2O_{12}S_2$, C, 66.9; H, 5.4; N, 6.0%. Found C, 66.1; H, 5.6; N, 5.5%.

Synthesis of the complex $[Cu_2(L^1)_2Ba_2](ClO_4)_6$.

To a suspension of $\mathbf{L^1}$ (0.010g, 0.018 mmol) in acetonitrile (2 cm^3), $Cu(MeCN)_4PF_6$ (0.007g, 0.018 mmol) was added and the solution was stirred until dissolution was complete. To this was then added excess $Ba(ClO_4)_2$ and the complex isolated by slow diffusion of ethyl acetate giving yellow crystals of $[Cu_2(\mathbf{L^1})_2Ba_2](ClO_4)_6$ which lost solvent rapidly (45% yield). ESI-MS: *m/z* 949 [M-$2(ClO_4)^-$]. Elemental Analysis calculated for $C_{56}H_{60}N_8Ba_2Cl_6Cu_2O_{36}S_2$, C, 32.0; H, 2.9; N, 5.3%. Found C, 31.6; H, 3.0; N, 4.9%.

References

1 C. Naumann and H. Langhals, *Synthesis*, 1990, 279.

2 J. Rebek, Jr. and R.V. Wattley, *J. Heterocycl. Chem.* 1980, **17**, 749.