Supplementary Material for Chemical Communications
This journal is © The Royal Society of Chemistry 2005

Supplementary data

Experimental Section
All reagents were used as purchased, except H₄L¹, which was prepared according to the literature procedure.¹ The ¹H and ¹³C{¹H} NMR spectra were recorded using a Bruker DPX-300 spectrometer operating at 300.13 and 75.47 MHz, respectively; residual protio-solvent served as an internal reference for the former. Elemental analysis was carried out by Mr. Stephen Bowyer of the London Metropolitan University. Electrospray mass spectra were recorded using a Micromass LCT spectrometer, +ve ion FAB mass spectra were recorded by the EPSRC National service at Swansea University. IR and UV/vis spectra were recorded using Nicolet 210 FT-IR and Perkin-Elmer Lambda 5 UV/Vis instruments, respectively. Conformer global minimum calculations were carried out using a MMFF molecular mechanics model within SPARTAN’04.


1: A slurry of H₄L¹ (0.400 g, 0.662 mmol) in CHCl₃ (25mL) was treated with solid Zn(OAc)₂.2H₂O (0.290 g, 1.324 mmol) and the resulting mixture heated to reflux for 5 h; the solids dissolved forming a deep red solution in ca. 30 min. The addition of Et₂O (10 mL) and cooling to –20 °C caused the deposition of 0.427 g, 44% of 1 as bright yellow crystals that were isolated by suction filtration. Analysis. Found: C, 56.82; H, 4.75; N, 11.56. C₆₉H₇₂N₁₂O₁₂Zn₃ requires: C, 56.86; H, 4.98; N, 11.53 %; ¹H NMR (CDCl₃): δH 11.8 (br.s, 6H, NH), 8.43 (s, 6H, imine), 7.38 (m, 6H, aryl), 7.28 (m, 6H, aryl), 6.93 (d, 6H, JHH 3.8 Hz, pyrrole), 6.07 (d, 6H, JHH 3.8 Hz, pyrrole), 1.94 (s, 18H, acetate), 1.82 (s, 18H, CH₃); ¹³C{¹H} NMR (CDCl₃): δC 179.4 (s), 151.4 (s), 151.1 (s), 141.5 (s), 127.8 (s), 127.5 (s), 126.9 (s), 117.8 (s), 110.4 (s), 38.0 (s), 27.8 (s), 27.2 (s); ES-MS: m/z 907 [M+ - 3Zn(OAc)₂].

H₆L₂: Solid Na₂S.9H₂O (0.141 g, 0.587 mmol) was added to a suspension of 1 (0.214 g, 0.147 mmol) in MeOH (15 mL). The resulting yellow, flocculent slurry was stirred at room temperature for 30 min, after which the solvent was removed under vacuum and the solid residues extracted with CHCl₃ (3 x 15 mL). The volume of the extract was reduced and n-pentane (50 mL) was added, forming 0.113 g, 85% of H₆L₂ as a free-flowing yellow powder. Analysis. Found: C, 75.32; H, 6.12; N, 18.35. C₅₇H₅₄N₁₂ requires: C, 75.47; H, 6.00; N, 18.53 %; ¹H NMR (CD₆D₆): δH 9.11 (br.s, 6H, NH), 8.07 (s, 6H, imine), 7.10 (m, 6H, aryl), 7.00 (m, 6H, aryl), 6.34 (d, 6H, JHH 3.6 Hz,
Supplementary Material for Chemical Communications
This journal is © The Royal Society of Chemistry 2005

pyrrole), 5.93 (d, 6H, J_{HH} 3.6 Hz, pyrrole), 1.10 (s, 18H, CH\textsubscript{3}); \textsuperscript{13}C{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}): substantial
decomposition to H\textsubscript{4}L\textsuperscript{1} was observed; ES-MS: m/z 907 (M\textsuperscript{+}, 100 %).

2: In a similar manner to that for 1, H\textsubscript{4}L\textsuperscript{1} (0.200 g, 0.331 mmol) was combined with
Cd(OAc)\textsubscript{2}.2H\textsubscript{2}O (0.180 g, 0.662 mmol) in CHCl\textsubscript{3} (15 mL) and stirred at 80 °C for 8 h, to yield
0.275 g, 72% of 2 as orange crystals. Analysis. Found: C, 47.23; H, 3.81; N, 9.08.
C\textsubscript{46}H\textsubscript{48}N\textsubscript{8}Cd\textsubscript{2}O\textsubscript{8}.CHCl\textsubscript{3} requires: C, 47.63; H, 4.17; N, 9.46 %; \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \delta\textsubscript{H} 12.2 (br.s, 4H, NH), 8.28 (t, 4H, J\textsubscript{CdH} 30.3 Hz, imine), 7.18 (s, 8H, aryl), 6.84 (d, 4H, J\textsubscript{HH} 3.8 Hz, pyrrole), 6.23 (d, 4H, J\textsubscript{HH} 3.8 Hz, pyrrole), 1.94 (s, 12H, acetate), 1.66 (s, 12H, CH\textsubscript{3}); \textsuperscript{13}C{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}): \delta\textsubscript{c} 180.0 (s, C\textsubscript{=N}), 154.1 (s, C\textsubscript{q}), 150.4 (s, CH), 143.6 (s, C\textsubscript{q}), 128.6 (s, CH), 127.6 (s, CH), 126.4 (s, CH), 119.6 (s, C\textsubscript{q}), 108 (s, CH), 37.4 (s, C\textsubscript{q}), 28.7 (s, acetate), 21.2 (s, CH\textsubscript{3}); ES-MS: m/z 605 [M\textsuperscript{+} - 2Cd(OAc)\textsubscript{2}]; FAB-MS (+ion): m/z 826 (M\textsuperscript{+} - 4OAc).

3: In a similar manner to that for 1, H\textsubscript{4}L\textsuperscript{1} (0.200 g, 0.331 mmol) was combined with
Zn(BF\textsubscript{4})\textsubscript{2}.2H\textsubscript{2}O (0.158 g, 0.662 mmol) in CHCl\textsubscript{3} (15 mL) and stirred at 80 °C for 5 h, during which
an orange solid precipitated. These solids were collected on a glass frit, washed with CHCl\textsubscript{3} (3 x 20 mL) and dried under vacuum, yielding 0.310 g, 87 % of 3 as an orange powder. Analysis. Found: C, 42.33; H, 3.27; N, 10.28. C\textsubscript{38}H\textsubscript{36}B\textsubscript{4}F\textsubscript{16}N\textsubscript{8}Zn\textsubscript{2} requires: C, 42.15; H, 3.35; N, 10.35 %; \textsuperscript{1}H NMR (CD\textsubscript{3}CN): \delta\textsubscript{H} 10.7 (br.s, 4H, NH), 8.50 (s, 4H, imine), 7.51 (m, 4H, aryl), 7.29 (m, 4H, aryl), 7.08 (br.d, 4H, J 3.0 Hz, pyrrole), 6.41 (d, 4H, J 4.0 Hz, pyrrole), 1.97 (br.s, 12H, meso-CH\textsubscript{3}); \textsuperscript{19}F{\textsuperscript{1}H} NMR (CD\textsubscript{3}CN): \delta\textsubscript{F} – 149.8 (s); ESMS (+ve): m/z 605 (H\textsubscript{4}L\textsuperscript{1}, 100 %)
Calculated global minimum conformations for $H_4L^1$ and $H_6L^2$ (MMFF, Spartan’04)