Supplementary Material for Chemical Communications

Supplementary data

Experimental Section

All reagents were used as purchased, except $H_4\mathbf{L^1}$, which was prepared according to the literature procedure.[1] The ^1H and $^{13}C\{^1H\}$ 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] G. Givaja, A. J. Blake, C. Wilson, M. Schröder, and J. B. Love, *Chem. Commun.*, 2003, 2508.

1: A slurry of $H_4\mathbf{L^1}$ (0.400 g, 0.662 mmol) in $CHCl_3$ (25mL) was treated with solid $Zn(OAc)_2.2H_2O$ (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 Et_2O (10 mL) and cooling to –20 ^oC 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. $C_{69}H_{72}N_{12}O_{12}Zn_3$ requires: C, 56.86; H, 4.98; N, 11.53 %; ^1H NMR ($CDCl_3$): δ_H 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, J_{HH} 3.8 Hz, pyrrole), 6.07 (d, 6H, J_{HH} 3.8 Hz, pyrrole), 1.94 (s, 18H, acetate), 1.82 (s, 18H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_c 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^+ - $3Zn(OAc)_2$].

$H_6\mathbf{L^2}$: Solid $Na_2S.9H_2O$ (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 $CHCl_3$ (3 x 15 mL). The volume of the extract was reduced and n-pentane (50 mL) was added, forming 0.113 g, 85% of $H_6\mathbf{L^2}$ as a free-flowing yellow powder. Analysis. Found: C, 75.32; H, 6.12; N, 18.35. $C_{57}H_{54}N_{12}$ requires: C, 75,47; H, 6,00; N, 18.53 %; ^1H NMR (C_6D_6): δ_H 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, J_{HH} 3.6 Hz,

pyrrole), 5.93 (d, 6H, J_{HH} 3.6 Hz, pyrrole), 1.10 (s, 18H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): substantial decomposition to $H_4\mathbf{L^1}$ was observed; ES-MS: m/z 907 (M^+, 100 %).

2: In a similar manner to that for **1**, $H_4\mathbf{L^1}$ (0.200 g, 0.331 mmol) was combined with $Cd(OAc)_2.2H_2O$ (0.180 g, 0.662 mmol) in $CHCl_3$ (15 mL) and stirred at 80 ^oC 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. $C_{46}H_{48}N_8Cd_2O_8.CHCl_3$ requires: C, 47.63; H, 4.17; N, 9.46 %; ^1H NMR ($CDCl_3$): δ_H 12.2 (br.s, 4H, NH), 8.28 (t, 4H, J_{CdH} 30.3 Hz, imine), 7.18 (s, 8H, aryl), 6.84 (d, 4H, J_{HH} 3.8 Hz, pyrrole), 6.23 (d, 4H, J_{HH} 3.8 Hz, pyrrole), 1.94 (s, 12H, acetate), 1.66 (s, 12H, CH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ_c 180.0 (s, C=N), 154.1 (s, C_q), 150.4 (s, CH), 143.6 (s, C_q), 128.6 (s, CH), 127.6 (s, CH), 126.4 (s, CH), 119.6 (s, C_q), 108 (s, CH), 37.4 (s, C_q), 28.7 (s, acetate), 21.2 (s, CH_3); ES-MS: m/z 605 [M^+ - $2Cd(OAc)_2$]; FAB-MS (+ion): m/z 826 (M^+ - 4OAc).

3: In a similar manner to that for **1**, $H_4\mathbf{L^1}$ (0.200 g, 0.331 mmol) was combined with $Zn(BF_4)_2.2H_2O$ (0.158 g, 0.662 mmol) in $CHCl_3$ (15 mL) and stirred at 80 ^oC for 5 h, during which an orange solid precipitated. These solids were collected on a glass frit, washed with $CHCl_3$ (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. $C_{38}H_{36}B_4F_{16}N_8Zn_2$ requires: C, 42.15; H, 3.35; N, 10.35 %; ^1H NMR (CD_3CN): δ_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_3); $^{19}F\{^1H\}$ NMR (CD_3CN): δ_F – 149.8 (s); ESMS (+ve): m/z 605 ($H_4\mathbf{L^1}$, 100 %)

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Calculated global minimum conformations for $H_4\mathbf{L}^1$ and $H_6\mathbf{L}^2$ (MMFF, Spartan'04)