Metal-directed assembly of a box-like structure

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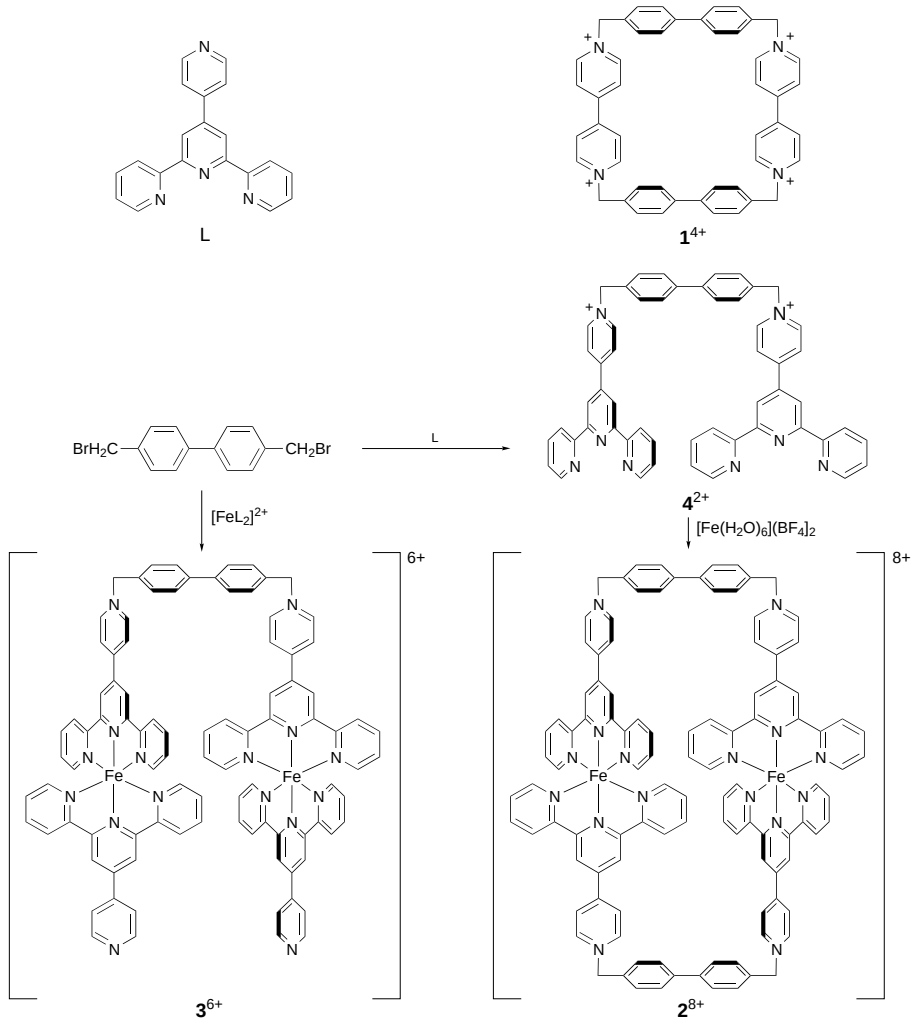
A dinuclear octacationic box is assembled by the reaction of a dicationic bis(2,2′:6′,2″-terpyridine) ligand with iron(II); an {FeL_2} unit [L = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine] acts as an analogue of 4,4′-bipyridine.

Metal-directed self-assembly is a widely used methodology in supramolecular chemistry.[1] In the synthesis of new systems such as helicates, cyclohelicates, boxes, cylinders and grids, *inter alia*, conventional organic substructures are conceptually replaced by metal-containing units. This strategy has been successfully used by Stang and Olenyuk[2] and Lehn and coworkers[3] amongst others[4] for the synthesis of box-like structures. Here, we report the use of the $[FeL_2^{2+}$ unit [L = 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine] as an analogue of 4,4′-bipyridine.

Stoddart and coworkers have reported a range of topologicaly complex structures based upon the molecular box $\mathbf{1}^{4+}$ (Scheme 1).[5] Paradoxically, the key compound $\mathbf{1}^{4+}$ remains elusive and is only obtained in low yield under forcing conditions in the absence of a template,[6] although improved yields are obtained in templated syntheses.[7] We considered the synthesis of $\mathbf{2}^{8+}$ in which the key cyclisation step involved the formation of the 4,4′-bipyridine analogue in a step involving the formation of twelve Fe–N bonds.

Our initial approach to the synthesis of $\mathbf{2}^{8+}$ was a direct analogy to the preparation of $\mathbf{1}^{4+}$ and involved the reaction in acetonitrile of 4,4′-bis(bromomethyl)biphenyl with $[FeL_2][PF_6]_2$,[8] the metallogue of 4,4′-bipyridine. The iron salt was added over 6 h to a boiling solution and heating continued for 72 h to give a dark blue solution which TLC indicated to contain one major blue component. This compound was isolated by chromatography [Kieselgel 60, gradient starting with MeCN:sat. KNO_3 (aq):H_2O (7:1:0.5) and gradually increasing the H_2O content] and identified as $\mathbf{3}[PF6]_6$ (25%).† None of the numerous minor fractions appeared to contain the desired $\mathbf{2}^{8+}$ species. Attempts to prepare $\mathbf{2}^{8+}$ by the reaction of



Scheme 1

$\mathbf{3}^{6+}$ with a second equivalent of 4,4′-bis(bromomethyl)biphenyl in acetonitrile were also unsuccessful.

Accordingly, we adopted an alternative strategy in which the iron is incorporated into the metallocycle in the final step. The reaction of L with 4,4′-bis(bromomethyl)biphenyl proceeded smoothly in acetonitrile to give $\mathbf{4}^{2+}$ which was isolated as its hexafluorophosphate salt in 62% yield (Scheme 1).‡ The subsequent cyclisation was performed under high dilution conditions (6×10^{-5} mol dm^{-3} in each component) by the addition of 1 equiv. of iron(II) tetrafluoroborate to 1 equiv. of $\mathbf{3}[PF_6]_2$ in 1 : 1 methanol–acetonitrile solution (Scheme 1). Finally, the deep blue solution was treated with an excess of NH_4PF_6 and the blue solid collected by filtration. Fractional recrystallisation yielded $\mathbf{2}[PF_6]_8$ as deep blue microcrystals in 35% yield.§ Chromatographic analysis and separation indicated that a series of higher oligomers with varying metal : ligand stoichiometries were formed.

The ^{1}H NMR spectrum of a solution of $\mathbf{2}[PF_6]_8$ in CD_3CN is surprisingly simple§ and fully confirms the structural proposal with a single chemical and magnetic 2,2′ : 6′,2″-terpyridine environment and a single AB pattern for the biphenylene unit. The primary characterisation relied upon electrospray mass spectrometry which exhibited a series of ions corresponding to the species $\{\mathbf{2}(PF_6)_n\}^{(8-n)+}$ indicating the formation of the dinuclear species rather than a higher oligomer. This was further confirmed by the preparation of the tetraphenylborate analogue by metathesis with $NaBPh_4$; the electrospray mass spectrum revealed the expected peaks assigned to $\{\mathbf{2}(BPh_4)_n\}^{(8-n)+}$. Attempts to obtain X-ray quality crystals have failed and even the very small crystals that we have obtained are extremely prone to solvent loss.

To date we have been unable to obtain NMR evidence for the inclusion of electron rich aromatic guest molecules into the cavity of $\mathbf{2}^{8+}$ although modelling studies indicate that such interactions are reasonable. We note that the compound is obtained in a highly solvated form containing significant numbers of acetone, methanol or water molecules which may be removed under high vacuum to yield material with somewhat different solubility characteristics. We are currently studying the introduction of such guest molecules.

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Notes and References

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† $\mathbf{3}[PF_6]_6$: ^{1}H NMR (250 MHz, CD_3CN): δ 9.32 (4 H, s, H^{3b}), 9.26 (4 H, s, H^{3D}), 9.20 (4 H, d, J 6.8 Hz, H^{3M}), 9.03 (4 H, d, J 6.4 Hz, H^{3N}), 8.91 (4 H, d, J 6.8 Hz, H^{2M}), 8.65 (8 H, m, H^{3A}), 8.24 (4 H, d, J 5.9 Hz, H^{2N}, 7.94 (8 H, m, H^{4A}), 7.93, 7.77 (4 H, d, J 8.3 Hz, H^{Y}), 7.15 (16 H, m, $H^{5A,6A}$), 6.00 (4 H, s, CH_2). ESMS (calc.): *m/z* 255.9 (255.4, $[M - 6PF_6]^{6+}$); 455.5 (455.6, $[M - 4PF_6]^{4+}$).

‡ $\mathbf{4}[PF_6]_2$: ^{1}H NMR (250 MHz, CD_3CN): δ 8.91 (4 H, d, J 6.8 Hz, H^{6A}), 8.88 (4 H, s, H^{3B}), 8.73 (8 H, m, $H^{3M,2M/3A}$), 8.50 (8 H, d, J 6.8 Hz, $H^{2M/3A}$), 8.01 (4 H, ddd, J 7.8, 2 Hz, H^{4A}, 7.80 (4 H, d, J 8.8 Hz, H^{Y}), 7.59 (4 H, d, J 8.3 Hz, H^{Y}), 7.55 (4 H, m, H^{5A}), 5.83 (4 H, s, CH_2). LD TOF-MS (calc.): *m/z* 947 (945, $[M - PF_6]^+$), 799 (800, $[M - 2PF_6]^+$). Mp 195–196 °C.

§ $\mathbf{2}[PF_6]_8$: ^{1}H NMR (250 MHz, CD_3CN): δ 9.22 (8 H, s, H^{3B}), 9.17 (4 H, d, J 6.9 Hz, H^{3M}), 9.81 (8 H, d, J 6.4 Hz, H^{2M}), 8.55 (8 H, d, J 8.3 Hz, H^{3A}), 7.78 (24 H, m, $H4_{A,Y}$), 7.00 (16 H, m, $H^{5A,6A}$), 5.97 (8 H, s, CH_2). ESMS (calc.): *m/z* 265.6 (265.5, $[M - 7PF_6]^{7+}$), 334.0 (333.9, $[M - 6PF_6]^{6+}$), 429.6 (429.7, $[M - 5PF_6]^{5+}$), 573.3 (573.4 $[M - 4PF_6]^{4+}$), 812.5 (812.8, $[M - 3PF_6]^{3+}$), 1291.9 (1291.7, $[M - 2PF_6]^{2+}$). $\mathbf{2}[BPh_4]_8$: *m/z* 1175.5 (1176.0, $[M - 6PF_6]^{2+}$), 1334.9 (1335.7, $[M - 5PF_6]^{2+}$), 1494.7 (1495.3, $[M - 4PF_6]^{2+}$), 1656.0 (1654.9, $[M - 3PF_6]^{2+}$), 1814.0 (1814.5, $[M - 2PF_6]^{2+}$).

Throughout, the notation used is: A, terminal tpy ring; B, central tpy ring with free 4-pyridyl; D, central tpy ring with quaternised 4-pyridyl; M, quaternised 4-pyridyl ring; N, free 4-pyridyl ring; Y, biphenyl spacer.

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