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## Deliberate boxes and accidental wheels

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This report describes systems which combine the structural and reactive motifs of a dinucleating terpyridine-aminomethylpyridine ligand, L, with the coordination preferences and flexibilities of particular divalent metal ions to form a series of closely related box structures in a deliberate fashion. The ligand also produces unprecedented decanickel wheel complexes. Halogen to aromatic hydrogen interactions may be important in stabilising the decanickel wheel structures.

### Introduction

Nature uses metal centres as both structural and reactive units in larger structural arrays.<sup>1-5</sup> For example, the shapes and biological functions of zinc finger proteins and many enzymes result from a combination of the structural features of the ligands and the coordination preferences of metal ions, while the function of the photosynthetic reaction centre is intimately tied to the relative positions of the redox centres and cofactors within the protein scaffold.<sup>6-8</sup> Our goal is to explore how the structural features of ligands and coordination chemistry can be used to control the assembly of polynuclear complexes containing both redox active metal ions and labile metal ions bearing exchangeable ligands.

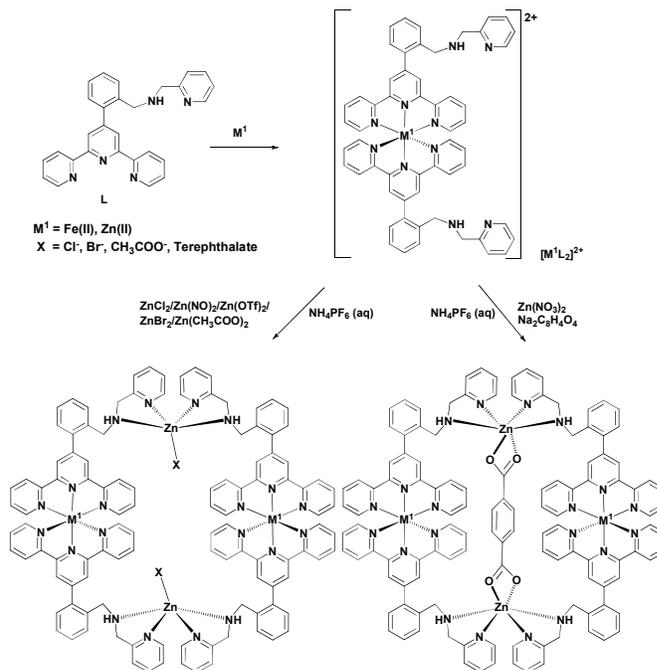
2,2':6',2''-Terpyridine derivatives and their complexes have been extensively studied molecules since the early 20th century, due to their luminescence, spin crossover and redox properties, which have potential uses in charge storage, solar cells and photocatalysis.<sup>9-14</sup> Terpyridines are excellent ligands, providing tridentate metal binding domains with high affinity for many metal ions and limited possibilities for formation of different stereoisomers.<sup>15-20</sup> Thus a terpyridine ligand will bind in a meridional fashion to an octahedral metal ion and, depending on the relative amounts of metal and ligand that are present, a second ligand may bind as well.

In this paper we describe the synthesis of a terpyridine ligand that has an appended bidentate metal-binding domain and subsequent coordination chemistry in which molecular boxes have been prepared in a deliberate fashion.

### Results and discussion

#### Ligand synthesis

The terpyridine-aminomethylpyridine ligand L (Scheme 1), was prepared by reaction of 2-aminomethylpyridine with a brominated terpyridine derivative, following an essentially standard terpyridine synthesis and a subsequent radical bromination reaction. The yields of the bromination reactions were variable, but the crude product mixture could be readily resubmitted to the reaction conditions if the bromination yield was low, and any residual 4'-(2''-toluyl)-2,2':6',2''-terpyridine could be removed in the final chromatographic purification.



**Scheme 1** Ligand L, contains tridentate and bidentate metal ion binding domains which have been used to prepare molecular boxes.

#### Boxes

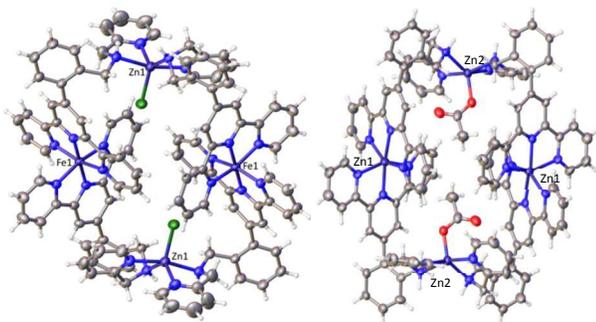
Ligand L contains a tridentate terpyridine binding site which was designed to act either as a structural component through formation of a typical bis-terpyridine complex, or as a site at which to bind a metal ion bearing exchangeable ligands. The 2-aminomethylpyridine binding site allows binding of another metal ion, again carrying exchangeable ligands that could lead to catalytic activity, as shown in Scheme 1.

Adding a bidentate binding domain to a terpyridine scaffold results in formation of a new class of ligand in which the

denticity and geometric preferences of the metal binding domains may be used to control the outcomes of synthetic reactions.<sup>21-24</sup> Thus a metal ion such as Fe(II), with a strong preference for an octahedral geometry will link two terpyridine units and leave the bidentate site in each of the two ligands free for coordination to other more coordinationally flexible metal ions such as Zn(II). Such metal ions can be coordinated to the aminomethylpyridine ‘tail’ of the ligand, giving either an exposed catalytic site or a means to link two ML<sub>2</sub> units together through an additional metal centre with an incomplete ligand sphere.

The preparation and isolation of the FeL<sub>2</sub> complex is straight forward, as might be expected. Addition of Zn(II) salts to solutions of the FeL<sub>2</sub> complex, in the presence of [PF<sub>6</sub>]<sup>-</sup> ions, resulted in the formation of a [Fe<sub>2</sub>Zn<sub>2</sub>(L)<sub>4</sub>Cl<sub>2</sub>]<sup>6+</sup> box complex (Fig.1).

Given that the coordination chemistry of Zn(II) is notable for its variability in coordination number and geometry, we attempted to prepare similar box complexes in which both kinds of coordination site are occupied by Zn(II) ions. The resulting structure is also shown in Fig.1, and this reveals that acetate ligands can also be bound to the Zn(II) ions in the bidentate sites.

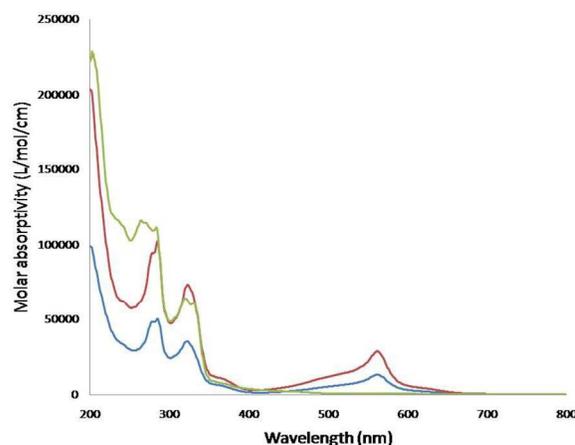


**Fig.1** The [Fe<sub>2</sub>Zn<sub>2</sub>(L)<sub>4</sub>Cl<sub>2</sub>]<sup>6+</sup> (left) and [Zn<sub>4</sub>L<sub>4</sub>(OAc)<sub>2</sub>]<sup>6+</sup> (right) box complexes. The solvent and anions have been omitted for clarity.

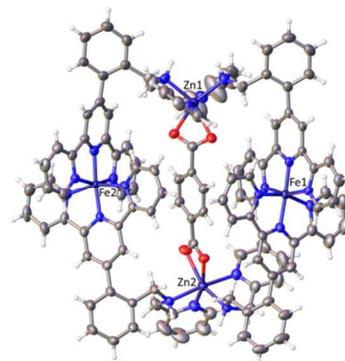
The isolation of the [Zn<sub>4</sub>L<sub>4</sub>(OAc)<sub>2</sub>]<sup>6+</sup> box also enabled us to examine and eliminate the possibility of metal scrambling in the two [Fe<sub>2</sub>Zn<sub>2</sub>(L)<sub>4</sub>X<sub>2</sub>]<sup>6+</sup> mixed metal systems. This possibility was discounted on the basis of the UV-vis measurements and molar absorptivity data (Fig.2). The absorbance at 561 nm can be assigned principally to the Fe(II)-bis(terpyridine) chromophore based on literature precedent.<sup>25,26</sup> Since the [Zn<sub>4</sub>L<sub>4</sub>(OAc)<sub>2</sub>]<sup>6+</sup> box complex is much more weakly coloured ( $\epsilon_{561} = 670 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) than the Fe(II)-containing boxes, and the Fe<sub>2</sub>Zn<sub>2</sub>L<sub>4</sub> complex has a molar absorptivity ( $\epsilon_{561} = 28700 \text{ Lmol}^{-1}\text{cm}^{-1}$ ) slightly larger than twice the extinction coefficient of the FeL<sub>2</sub> complex ( $\epsilon_{561} = 13200 \text{ Lmol}^{-1}\text{cm}^{-1}$ ), there must be little or no scrambling of metal ions either within or between boxes in a sample.

The bis-bidentate bridging ligand terephthalate was also deliberately encapsulated in the middle of the Fe<sub>2</sub>Zn<sub>2</sub>L<sub>4</sub> box to produce the complex where the terephthalate ion (tpt) replaces the Cl<sup>-</sup>/OAc<sup>-</sup> ligands in the coordination sphere of the Zn(II) ions (Fig.3). Collectively, these structures invite speculation that it may be possible to bind and react molecules within these boxes.

In the solid state, each box shaped assembly is surrounded by PF<sub>6</sub><sup>-</sup> anions. In particular, two of the six PF<sub>6</sub><sup>-</sup> ions are located

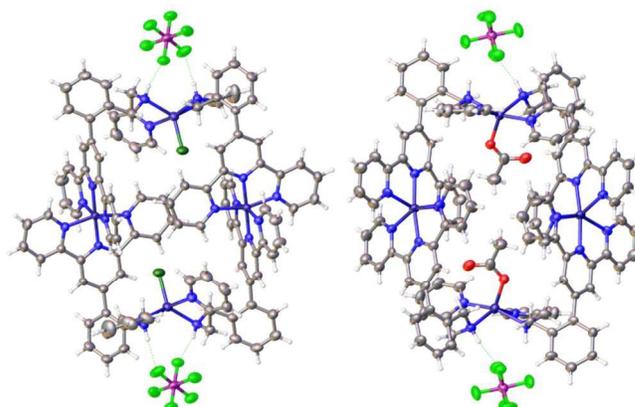


**Fig.2** UV-visible spectra of the [Fe(L)<sub>2</sub>]<sup>2+</sup> (blue) [Fe<sub>2</sub>Zn<sub>2</sub>(L)<sub>4</sub>Cl<sub>2</sub>]<sup>6+</sup> (red) and [Zn<sub>4</sub>(L)<sub>4</sub>(OAc)<sub>2</sub>]<sup>6+</sup> (green) box complexes.



**Fig.3** The [Fe<sub>2</sub>Zn<sub>2</sub>(L)<sub>4</sub>(tpt)]<sup>6+</sup> box complex. The solvent and anions have been omitted for clarity.

immediately above and below the box complexes and have two F···H-N hydrogen bonds to the amine groups of the box (Fig.4). Presumably, the location of these anions helps direct the monodentate ligand on the Zn(II) centre towards the centre of the box structure.

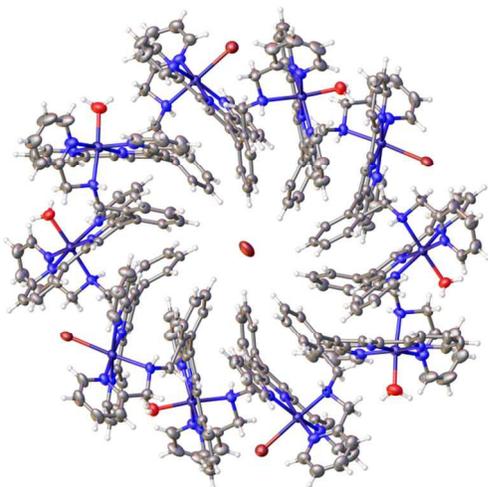


**Fig.4** Hydrogen bonding between PF<sub>6</sub><sup>-</sup> ions above and below the boxes and the coordinated amine groups of the boxes. [Fe<sub>2</sub>Zn<sub>2</sub>(L)<sub>4</sub>Cl<sub>2</sub>]<sup>6+</sup> (left) and [Zn<sub>4</sub>(L)<sub>4</sub>(Ac)<sub>2</sub>]<sup>6+</sup> (right) box complexes. The solvent and spectator anions have been omitted for clarity.

### Wheels

In contrast to the results from Zn(II) complex formation, attempts to prepare Ni(II) complexes of L using NiBr<sub>2</sub> led to isolation of the remarkable decanickel wheel complex [Ni<sub>10</sub>L<sub>10</sub>Br<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>16+</sup>, shown in Fig.5, with a Br<sup>-</sup> ion in its centre. Each six-coordinate Ni(II) ion is bound to the terpyridine moiety of one ligand, the aminomethylpyridine 'tail' of the terpyridine ligand bound to a neighbouring Ni(II) ion, and either a Br<sup>-</sup> ion (on two of the ten Ni(II) ions), a water ligand (on six Ni(II) ions) or a disordered mixture of the two (on two Ni(II) ions). Thus each ligand reaches around to the next Ni(II) ion from the outside of the wheel, with the terpyridine units nearer to the centre of the wheel.

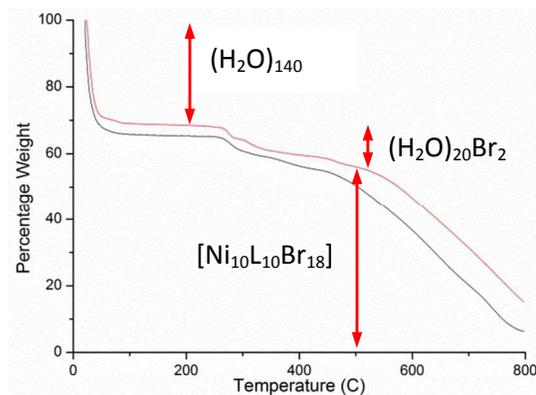
The wheel is approximately circular with an inner cavity diameter measured between the symmetry equivalent hydrogen atoms of 7.696 to 6.016 Å and distances between symmetry equivalent Ni of 18.933 to 20.218 Å. The outer diameter of the ring varies from 29.296 to 26.515 Å and the wheel is 15.349 Å deep. The Ni(II) ions in the wheel are well separated from each other, both in space and through bonds.



**Fig.5** [Ni<sub>10</sub>L<sub>10</sub>Br<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>16+</sup> viewed down the a axis. The solvent waters, anions and ligand disorder have been omitted for clarity.

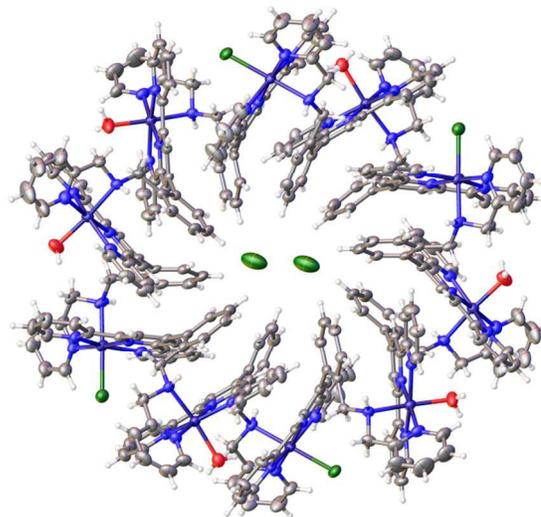
The Br<sup>-</sup> ion that is present inside the wheel cavity appears to be held tightly due to a number of hydrogen bonds and other atomic interactions. Fifteen uncoordinated Br<sup>-</sup> ions are also present in the crystal lattice. The structure of the complex contains approximately 160 water molecules, randomly present in and around the wheels. These water molecules link the wheels in a 3D network by the hydrogen bond interactions between various atoms. Thermogravimetric analysis (Fig.6) is consistent with the presence of ~160 water molecules, as the wheels lose approximately 30% of their mass as they are being heated to 100°C. Samples dried in vacuum rapidly lose their crystallinity when heated through this temperature range, as do samples being heated during attempts to measure melting points.

With NiCl<sub>2</sub>, a similar wheel structure ([Ni<sub>10</sub>L<sub>10</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>16+</sup>) forms (Fig.7). Cl<sup>-</sup> ions occupy all of the Ni(II) coordination sites in which Br<sup>-</sup> ions were found in the first wheel. The remaining six Ni(II) ions have water ligands, as in the Br<sup>-</sup> structure described above.



**Fig.6** Thermogravimetric analyses of the wheel complexes [Ni<sub>10</sub>L<sub>10</sub>Br<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>16+</sup> (red) and [Ni<sub>10</sub>L<sub>10</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>16+</sup> (black).

In the middle of the wheel, the smaller size of the Cl<sup>-</sup> ion means it is disordered over two positions, each with half occupancy. This reduction in size also causes the wheel to become more elliptical, elongating to 7.748 Å along the axis of the Cl<sup>-</sup> ion sites, and compressed to 5.686 Å in the perpendicular direction, with Ni to Ni distances of 18.880 to 20.274 Å and rim to rim distances of 29.886 to 24.551 Å. If even trace amounts of Br<sup>-</sup> ion are present in solution, crystals are isolated in which a Br<sup>-</sup> ion is at the centre of the wheel, while four Cl<sup>-</sup> ions are attached to Ni(II) ions and another 15 are present in the lattice.



**Fig.7** [Ni<sub>10</sub>L<sub>10</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>16+</sup> viewed down the a axis. The solvent waters, anions and ligand disorder have been omitted for clarity. The two Cl<sup>-</sup> ions shown in the centre of the structure have only half occupancy.

The preference for binding Br<sup>-</sup> over Cl<sup>-</sup> in the cavity, seems to be due to the size of the Br<sup>-</sup> ion being the correct size to allow H-bonding with all of the ten hydrogen atoms which point into the cavity from the wheel. The off-centre distribution of the Cl<sup>-</sup> ions over two positions within the wheel maximizes the number and strength of H-bonding interactions that the Cl<sup>-</sup> ion can make with the wheel, given its smaller, and less optimal, size. This in turn leads to a more elliptical shape as the Cl<sup>-</sup> wheel distorts

make these H-bonds stronger. This CH $\cdots$ X tight binding of an appropriately sized central halide by multiple aromatic C-H groups has been exploited in other systems such as the triazolophane macrocycles which have been used as anion sensors.<sup>27</sup>

## Conclusions

A new terpyridine-aminomethylpyridine ligand has been synthesised and yields complexes in which the coordination preferences of the metal ions control the structure of the complex and provide exchangeable sites with the potential for future catalytic function. Reactions with Fe(II) and Zn(II) yield four metal centre boxes with Fe(II) being solely structural and Zn(II) ions offering coordination sites which can be occupied by different ligands without disturbing the structure. The exchangeable ligands point in towards a hydrophobic, aromatic rich environment.

When the Ni(II) ions bind to both sites of the ligand, an unprecedented decanuclear structure is formed. The structure has ten exchangeable sites around the wheel pointing out. A bound Br<sup>-</sup> ion occupies the central position in the wheel in preference to an exchangeable Cl<sup>-</sup> ion.

The F $\cdots$ H-N interactions enhance the stability of the boxes and the Br/Cl $\cdots$ C-H interactions play a significant role in the structures of the wheels.

## Experimental

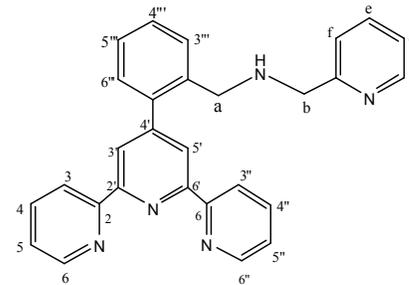
### Synthesis

**4'-(2'''-(Toluy)l)-2,2':6',2''-terpyridine** 2-Acetylpyridine (2.4 g, 20 mmol) was added to a solution of potassium *t*-butoxide (3.36 g, 30 mmol) in freshly distilled dry THF (160 mL) and the resultant creamy yellow suspension was treated with *o*-tolualdehyde (1.2 g, 10 mmol) and the mixture was stirred overnight at room temperature under nitrogen. A solution of dry ammonium acetate (15.8 g) in 2:1 ethanol:acetic acid (190 mL) was then added and the clear brown mixture obtained was heated at reflux for 5 hours. The resulting orange-yellow reaction mixture was cooled to room temperature and treated with ice (500 g) and water (2 L) to give a yellow precipitate. The precipitate was collected by filtration. Recrystallisation from ethanol gave pure 4'-(2'''-(toluyl)-2,2':6',2''-terpyridine as pale yellow crystals. Yield: 2.5 g (68%); m.p. 146-152°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.72 (d, 2H, H<sub>6,6''</sub>), 8.71 (d, 2H, H<sub>3,3''</sub>), 8.49 (s, 2H, H<sub>3',5'</sub>), 7.90 (t, 2H, H<sub>4,4''</sub>), 7.30-7.36 (m, 6H, H<sub>5,5''</sub>, toluyl), 2.38 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>): 156.5, 155.6, 152.2, 149.4, 139.9, 137.1, 135.4, 130.7, 129.7, 128.5, 126.2, 124.1, 121.9, 121.6, 20.7 (CH<sub>3</sub>); ESI-MS *m/z*: [M+H]<sup>+</sup> 324.13.

**4'-(2'''-(Bromomethyl)phenyl)-2,2':6',2''-terpyridine** 4'-(2'''-Toluy)l)-2,2':6',2''-terpyridine (2.0 g, 6.1 mmol) and purified N-bromosuccinimide (1.2 g, 6.5 mmol) were added to a dry three-necked round bottom flask while flushing with N<sub>2</sub>. Freshly distilled CCl<sub>4</sub> (150 mL) was also transferred to the three-necked flask while flushing under N<sub>2</sub>. The solution was irradiated with a tungsten lamp for about 5 hours after adding a catalytic amount of dibenzoyl peroxide (0.002 g). The mixture was heated to 25°C for 12 hours under N<sub>2</sub>. The reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated under vacuum to give the crude brominated product, 4'-(2'''-(bromomethyl)phenyl)-2,2':6',2''-terpyridine as a yellow oil, which was used directly because of its tendency to decompose. Yield= 2.2 g (90%); <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  = 8.72 (d,2H), 8.71 (d, 2H), 8.58(s,2H), 7.91 (t,2H), 7.58 (d,1H), 7.58 (d,1H), 7.35-7.44(m,5H), 4.45 (s, 2H, CH<sub>2</sub>Br); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 156.2, 155.8, 150.5, 149.5, 140.1, 137.3, 135.3, 131.2, 130.4, 129.2,

129.0, 124.2, 121.8, 121.7, 31.8 (CH<sub>2</sub>Br); ESI-MS: *m/z* [M+H]<sup>+</sup> 402.0612.

**4'-(2'''-(2-pyridylmethyl)aminomethyl)phenyl)-2,2':6',2''-terpyridine (L)** (2-Aminomethyl)pyridine (0.53 g, 4.9 mmol) was dissolved in dry CH<sub>3</sub>CN (100 mL), with stirring, followed by the addition of K<sub>2</sub>CO<sub>3</sub> (0.68 g, 4.9 mmol). The mixture was stirred for 10 mins at 35°C. 4'-(2'''-



(Bromomethyl)phenyl)-2,2':6',2''-terpyridine (2.0 g, 4.9 mmol) was added to the stirring solution. The resulting mixture was heated to 50°C for 4 days under a reflux condenser, filtered and the filtrate was taken to dryness under vacuum. The residual oil was a crude product containing L, unreacted amine and 4'-(2'''-(toluyl)-2,2':6',2''-terpyridine. Yield (crude): 2.0 g (95%).

L was purified by alumina column chromatography. Initial elution with DCM removed any unreacted 4'-(2'''-(toluyl)-2,2':6',2''-terpyridine. L was eluted with a 0.5% MeOH:DCM mixture. The eluate was taken to dryness and pure L was collected as a pale yellow fine powder. Yield 1.2 g (60%); m.p. 125-127°C; Elemental analysis: Found (%): C 78.34, H 5.61, N 16.61, Calcd. C<sub>28</sub>H<sub>23</sub>N<sub>5</sub> (%): C 78.44, H 5.42, N 16.34; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.68 (d, J=8, 2H, H<sub>3,3''</sub>), 8.65 (d, J=4, 2H, H<sub>6,6''</sub>), 8.54 (s, 2H, H<sub>3',5'</sub>), 8.34 (d, J=5, 1H, H<sub>c</sub>), 7.86 (td, 2H, H<sub>4,4''</sub>), 7.65 (d, J=8, 1H, H<sub>3''</sub>), 7.42-7.38 (m, 4H, H<sub>5''</sub>, 6''', 4'', e), 7.34 (td, 2H, H<sub>5,5''</sub>), 7.23 (d, J=8, 1H, H<sub>f</sub>), 6.98 (t, J=5, 1H, H<sub>d</sub>), 3.85 (d, 4H, H<sub>a,b</sub>); <sup>13</sup>C NMR (500MHz) 158.3, 156.1 (2C), 155.3 (2C), 150.9, 149.2 (2C), 149.0, 139.9, 136.8 (2C), 136.3, 135.9, 129.9-129.8 (2C), 128.7, 127.5, 123.8 (2C), 122.3, 121.9, 121.6 (2C), 121.3 (2C), 53.9, 50.5; IR (KBr, cm<sup>-1</sup>) 3140 m, 3055 m, 2925 m, 2854 m, 1585 s, 1567 ssh, 1541 msh, 1466 s, 1393 w, 1335 m, 1264 m, 1131 w, 992 m, 907 w, 851 m, 762 s, 652 w, 627 m, 508 w, 467 w; ESI-MS: *m/z* [M+H]<sup>+</sup> 430.202, [M+2H<sup>2+</sup>] 215.605, [2M+H<sup>+</sup>] 859.396.

**[FeL<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>·4H<sub>2</sub>O** FeCl<sub>2</sub>·2H<sub>2</sub>O (0.05 g, 0.025 mmol) in methanol was added to a solution of L (0.02 g, 0.05 mmol) in methanol to give a purple solution, immediately. The solution was heated for 1 h while stirring and then cooled to room temperature, followed by addition of few drops of a concentrated methanolic solution of ammonium hexafluoridophosphate. An excess of cold water was also added to enhance the precipitation of complex. The purple complex was collected from the aqueous solution following centrifugation, washed with ether:methanol (2:1) solution, and dried under a N<sub>2</sub> stream. Yield 0.030 g, 75%; m.p. 255-260°C; Elemental analysis Found (%): C 52.41, H 4.13, N 10.61, Calcd. C<sub>56</sub>H<sub>46</sub>N<sub>10</sub>Fe<sub>2</sub>F<sub>12</sub>·4H<sub>2</sub>O (%): C 52.63, H 4.26, N 10.97. <sup>13</sup>C NMR (CD<sub>3</sub>CN)  $\delta$ : 160.0, 157.8, 153.2, 149.8, 148.9, 138.8, 137.5, 132.1, 131.1, 130.9, 130.4, 129.7, 127.4, 124.4, 124.0, 123.3, 122.8, 51.7, 49.7; IR (KBr, cm<sup>-1</sup>) 3635 s, 3064 w, 1608 m, 1573 w, 1613 m, 1545 w, 1469 m, 1423 w, 1365 m, 1288 s, 1163 w, 1056 w, 1028 w, 1000 s, 830 vs, 790 w, 754 m, 654 w, 558 s, 497 w, 458 w; ESI-MS (CH<sub>3</sub>CN): *m/z* [Fe+2L]<sup>2+</sup> 457.1623, [Fe+2L+PF<sub>6</sub>+H]<sup>2+</sup> 530.1483, [Fe+2L]<sup>2+</sup> 305.1106; UV-vis (CH<sub>3</sub>CN):  $\lambda_{\max}$  ( $\epsilon$ ) = 275 (45800), 287 (47900), 322 (34200), 561 (13200) nm (Lmol<sup>-1</sup>cm<sup>-1</sup>).

**[Fe<sub>2</sub>Zn<sub>2</sub>L<sub>4</sub>Cl<sub>2</sub>](PF<sub>6</sub>)<sub>6</sub>·4H<sub>2</sub>O** FeCl<sub>2</sub>·2H<sub>2</sub>O (0.05 g, 0.025 mmol) in methanol (1 mL) was added to L (0.02 g, 0.05 mmol) in chloroform (1 mL) to give a purple solution. The resulting purple solution was treated with an excess of ZnCl<sub>2</sub>·2H<sub>2</sub>O in methanol. The mixture was heated for 1 h with stirring and then

cooled to room temperature, followed by addition of few drops of saturated ammonium hexafluoridophosphate in methanol. An excess of cold water was added to enhance the precipitation of complex. The complex was collected by centrifugation, washed with an ether:methanol (2:1) solution, and dried under a stream of N<sub>2</sub>. X-ray quality single crystals (fragile purple plates) were formed by slow evaporation of an acetonitrile solution. Yield 0.056 g, 60%. M.P. > 280 °C. UV-vis (CH<sub>3</sub>CN): λ<sub>max</sub> (ε) = 275 (88900), 287 (95800), 322 (73200), 561 (28700), nm (Lmol<sup>-1</sup>cm<sup>-1</sup>). Elemental analysis found (%): C 44.71, H 3.40, N 9.40. Calcd. for C<sub>112</sub>H<sub>92</sub>N<sub>20</sub>Zn<sub>2</sub>Fe<sub>2</sub>Cl<sub>2</sub>P<sub>6</sub>F<sub>36</sub>·5H<sub>2</sub>O (%): C 44.97, H 3.44, N 9.36. IR (KBr, cm<sup>-1</sup>) 3340 s, 2368 w, 1844 w, 1611 m, 1535 w, 1468 w, 1368 w, 1040 w, 794 s, 626 w, 558 m, 497 w, 458 w.

**[Zn<sub>4</sub>L<sub>4</sub>(OAc)<sub>2</sub>](PF<sub>6</sub>)<sub>6</sub>·2CH<sub>3</sub>CN** A methanolic solution of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.01 g, 0.046 mmol) was mixed with a methanolic solution of L (0.010 g, 0.023 mmol), resulting in a pale yellow solution. The solution was then treated with a concentrated methanolic solution of ammonium hexafluoridophosphate. Later addition of an excess of cold water resulted in formation of a white precipitate. The precipitate was collected following centrifugation, and washed with methanol and ether. Vapour diffusion of diisopropyl ether into an acetonitrile solution of the white precipitate produced colourless blocks of X-ray quality crystals within two days. Yield 0.012 g, 63%; m.p. 245 - 248 °C; Elemental analysis: Found (%): C 46.17, H 3.34, N 9.37, Calcd. C<sub>116</sub>H<sub>98</sub>N<sub>20</sub>Zn<sub>4</sub>O<sub>4</sub>P<sub>6</sub>F<sub>36</sub>·2H<sub>2</sub>O (%): C 46.40, H 3.42, N 9.34; <sup>1</sup>H NMR (DMSO) δ = 8.86 (d, 2H), 8.83 (d, 2H), 8.69 (d, 3H), 8.23 (d, 3H), 7.85 (s, 1H), 7.67 (t, 2H), 7.54-7.46 (m, 5H), 7.17 (d, 1H), 6.98 (t, 1H), 3.80 (s, 2H), 3.76 (s, 2H); IR (KBr, cm<sup>-1</sup>) 3675 w, 3340 s, 2542 w, 1866 w, 1603 s, 1575 w, 1549 w, 1478 s, 1419 w, 1371 w, 1325 w, 1248 m, 794 s, 764 w, 739 w, 658 w, 559 s, 469 w; UV-vis (CH<sub>3</sub>CN): λ<sub>max</sub> (ε) = 275 (111200), 287 (96800), 322 (63400), 561 (670) nm (Lmol<sup>-1</sup>cm<sup>-1</sup>).

**[Fe<sub>2</sub>Zn<sub>2</sub>L<sub>4</sub>C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>](PF<sub>6</sub>)<sub>6</sub> (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (9 mg, 0.035 mmol) in methanol (1 mL) and L (30 mg, 0.070 mmol) in chloroform (1 mL) were mixed, producing a purple solution. Excess sodium terephthalate (70 mg) in water (5 mL) was added. After stirring for 30 min, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (20 mg, 0.070 mmol) in methanol (1 mL) was added. The mixture was heated at reflux for 8 hrs and then cooled to room temperature. A few drops of saturated ammonium hexafluoridophosphate in methanol and cold water (20 mL) were used to precipitate the complex. The precipitate was collected by centrifugation, washed with an ether:methanol (2:1) solution, and dried under a stream of N<sub>2</sub>. X-ray quality single crystals (square purple plates) were formed by slow diffusion of ethyl acetate into an acetonitrile solution over a period of 3 weeks. Yield 0.056 g, 60%. M.P. >280 °C. UV-vis (CH<sub>3</sub>CN): λ<sub>max</sub> (ε) = 275 (88300), 287 (94830), 322 (71800), 561 (24720) nm (Lmol<sup>-1</sup>cm<sup>-1</sup>). IR (neat, cm<sup>-1</sup>) 3340 s, 2368 w, 1844 w, 1698 w, 1557 s, 1551 m, 1504 w, 1381 w, 1020 w, 823 s, 789 s, 653 w, 556 m, 447 w. Elemental analysis: found (%): C 47.42, H 3.72, N 8.89. calcd for C<sub>112</sub>H<sub>92</sub>N<sub>20</sub>Fe<sub>2</sub>Zn<sub>2</sub>C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>P<sub>6</sub>F<sub>36</sub>·3H<sub>2</sub>O (%): C 47.28, H 3.37, N 9.19.**

**[Ni<sub>10</sub>L<sub>10</sub>Br<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>][Br<sub>16</sub>·68H<sub>2</sub>O]** NiBr<sub>2</sub>·3H<sub>2</sub>O (0.008 g, 0.029 mmol) in water (10 mL) was added to L (0.006 g, 0.014 mmol) in methanol:chloroform (4:1, 5 mL), and the resulting solution was heated at reflux for 30 min. The volume of the yellow green solution of the complex was reduced to 1 mL by rotavap. The solution was filtered, and slow evaporation resulted in the formation of pale green X-ray quality crystals (blocks) over a period of 3 weeks. Yield 0.009 g, 90 %. IR (KBr, cm<sup>-1</sup>) 3645 w, 3190 s, 1605 s, 1550 w, 1470 m, 1417 w, 1302 w, 1247 m,

1162 w, 1055 w, 1016 s, 890 w, 772 s, 645 w, 598 w, 548 w, 516 w, 499 w, 481 w, 465 w. Elemental analysis: found (%): C 43.91, H 4.86, N 9.18%. Calcd. for C<sub>280</sub>H<sub>230</sub>N<sub>50</sub>Ni<sub>10</sub>Br<sub>20</sub>·68H<sub>2</sub>O (7705.19) (%): C 43.65, H 4.80, N 9.09.

#### X-ray Crystallography

X-Ray data were collected on an Oxford-Agilent Supernova instrument with a focused microsource Cu Kα [λ = 1.5405 Å] radiation and an ATLAS CCD area detector. CCDC 1039222, 1011648, 1011574, 1011644 and 1011645 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

The [Fe<sub>2</sub>Zn<sub>2</sub>L<sub>4</sub>(tpt)]<sup>6+</sup> [Ni<sub>10</sub>L<sub>10</sub>Br<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>+</sup> and [Ni<sub>10</sub>L<sub>10</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>] structures contained significant amounts of disordered solvent molecules. This was handled systematically for the two wheel structures. First, a phase solution was found and the structure of interest was determined and refined anisotropically for all non-hydrogen atoms. Hydrogen atoms were calculated as riding atoms with thermal parameters dependant on the riding atom for all carbon atoms. For all non-carbon atoms with hydrogens except for solvent molecules, the hydrogens were located in the electron difference map, and allowed to refine at a fixed distance from the heteroatom, with a thermal parameter dependant on the riding atom. Solvent water atoms and counterions were inserted into the model as isolated, isotropic atoms where there was sufficient electron density, sufficiently distant from other solvent waters/counterions, and their occupancies were allowed to refine. This used about 60 water molecules of some occupancy in the asymmetric unit of [Ni<sub>10</sub>L<sub>10</sub>Br<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>16+</sup> and [Ni<sub>10</sub>L<sub>10</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>6</sub>]<sup>16+</sup>. Estimates of these numbers were included in the formula used for the final absorption correction, but not in the final atom count. Counterions were distinguished from solvent waters by the electron density, and were refined anisotropically. No attempt was made to model co-occupancy of a partial counterion with a solvent water. Once a stable refinement had been achieved, water molecules with an occupancy of less than one were deleted from the model and the OLEX2 solvent mask was used to correct for these poorly refined water molecules and the additional, highly disordered regions occupied by solvent water which had not been modelled. The remaining water molecules were refined as isotropic oxygen atoms, without hydrogens, due to the lack of electron density to indicate the position of the hydrogen atoms for most of the solvent waters. The total number of waters from the model and electrons corrected for in the mask (180 waters) approximately agrees with the results from TGA experiments (>160 waters)

[Zn<sub>4</sub>L<sub>4</sub>(Ac)<sub>2</sub>]<sup>6+</sup> was solved and refined with the complex of interest, three well-ordered PF<sub>6</sub> anions and one acetonitrile solvent molecule in the asymmetric unit as above. A solvent mask was used to remove a small, but poorly order void in the model (187 Å<sup>3</sup>)

[Fe<sub>2</sub>Zn<sub>2</sub>L<sub>4</sub>(tpt)]<sup>6+</sup> was solved and refined with the complex of interest, four well-ordered PF<sub>6</sub> anions and one acetonitrile solvent molecule in the asymmetric unit as above. The final PF<sub>6</sub> anion and a single nitrate anion were poorly ordered, with the PF<sub>6</sub> anion being rotationally disordered about the phosphorous atom, occupying at least two closely spaced sites. The nitrate anion is involved in hydrogen bonding to the nitrogen atoms coordinated to the zinc atoms, and is disordered over two sites. This was modelled as disordered over two equal occupancy sites, with isotropic thermal parameters fixed at the value of the central phosphorous atom. The OLEX2 solvent

mask was used to correct for the remaining unidentified solvent molecules as above.  $[\text{Fe}_2\text{Zn}_2\text{L}_4\text{Cl}_2]^{6+}$  was solved and refined with the complex of interest, three independent PF<sub>6</sub> anions, two half occupancy water molecules and two partial occupancy ethyl acetate molecules (0.2 and 0.3 occupancy) in the asymmetric unit. No mask was required for this structure.

### Notes and references

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## Deliberate boxes and accidental wheels

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Box structures containing four ligands and four metal ions (two of each of two kinds) and labile ligands that point into the box cavity have been prepared – as well as decanickel wheels.

