SUPPLEMENTARY MATERIAL

Crystallography

X-ray single crystal diffraction of $[H_4L(H_2O)_2(p\text{-nbz})_4].3H_2O$ 4.

The overall structure of **4** showing the corresponding stoichiometry are presented in Fig. S1.

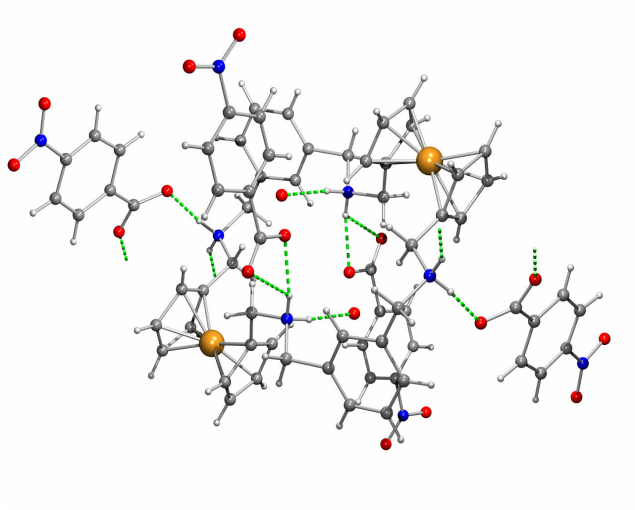

Fig. S1 Structure of the $[H_4L(H_2O)_2(p\text{-nbz})_4]$ **4** showing the overall disposition of the macrocyclic receptor and the anions in the supramolecule in the R:4S ratio.

In $[H_4L(H_2O)_2(p\text{-nbz})_4].3H_2O$, **4**, the detailed analysis of the intermolecular interactions involving the receptor is partially precluded since that hydrogen atoms of the water molecules were not located in the final refinement. On other hand the crystals of **4** are composed of about 50 % of powder and equal amount of crystal, leading to a determination with a high R value. However the $[H_4L(H_2O)_2(p\text{-nbz})_4]$ assembled molecule has a different stoichiometry to the other three structures described above and for comparison proposes is included here. In the crystal structure each macrocyclic receptor interacts with two water molecules and four *p*-nbz^- anions in a centrosymetric arrangement, as shown in Fig. S2. The water molecules form two hydrogen bonds with N–H···O distances of 1.83 Å. The spatial position of the oxygen atom of the water molecule suggests the formation of an additional hydrogen bond with the nitrogen atom N(26). However the N···O distance found of 3.54 Å is slightly long for an O–H···N hydrogen bond. The endocyclic torsion angles of **4**, listed in Table S1, are similar to those found for **1** where the PF_6^- substrate bridges the two linkages of the macrocyclic receptor, suggesting that a similar hydrogen bonding pattern exists. The second proton

attached to the nitrogen atom N(26) is involved in a bifurcated hydrogen bonding arrangement with the two oxygen atoms of the carboxylate group [O(412) and O(413)] from one *p*-nbz^{-} anion. The oxygen atoms O(512) [1-*x*, 1-*y*, 1-*z*] and O(513) [1+*x*, 1+*y*, *z*] of the second crystallographically independent molecules of the substrate, bridge the neighbour receptor molecules leading to the formation of one-dimensional chains running along the base vector [101], see Fig. S2. The corresponding two independent N–H···O distances are 1.78 and 1.89 Å.

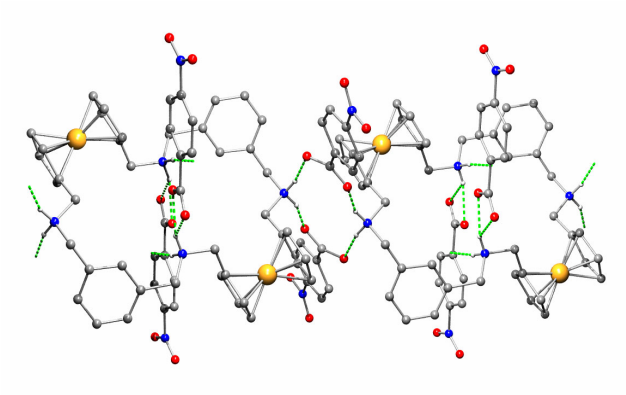

Fig. S2 1-D N–H···O dimensional chains yield by the molecular recognition between **[**$H_4L]^{4+}$ receptor and the *p*-nbz^{-} anions substrates in **4**.

Table S1. Dimensions of the hydrogen bonds in the supramolecular aggregate[$H_4L(H_2O)_2$(*p*-nbz)$_4$].3H_2O **4**

[$H_4L(H_2O)_2$(*p*-nbz)$_4$].3H_2O **4**	H ··A /Å	D ··A /Å	D-H ··A /°
N(17)-H(17A) ··O(513) [1-*x*,-*y*,-*z*]	1.78	2.62(2)	152.2
N(17)-H(17B) ··O(512) [1+*x*,*y*,*z*]	1.89	2.76(2)	161.0
N(26)-H(26A) ··O(412) [1-*x*,-*y*,-*z*]	1.93	2.79(3)	159.0
N(26)-H(26A) ··O(413) [1-*x*,-*y*,-*z*]	2.51	3.18(3)	131.7
N(26)-H(26B) ··O(101) [1-*x*,-*y*,-*z*]	1.83	2.73(3)	172.7

Coloured figures of X-ray structures

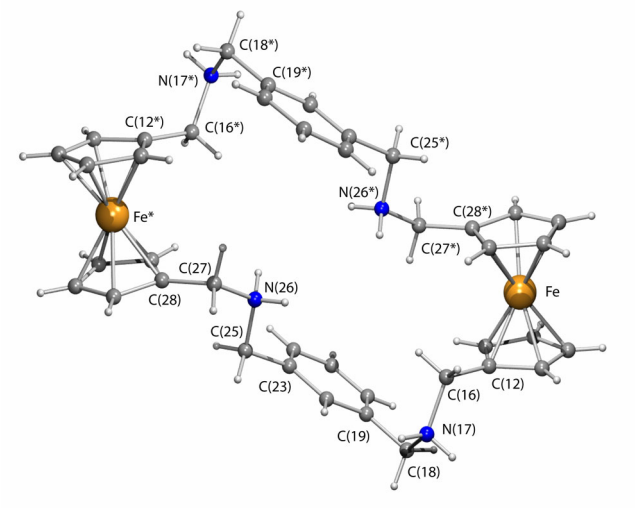

Fig. S3 Molecular structure of the receptor found in **2** showing the labelling scheme adopted for the ferrocenyl spacers. * denotes the symmetry operation: 1-*x*, 1-*y*, 1-*z*.

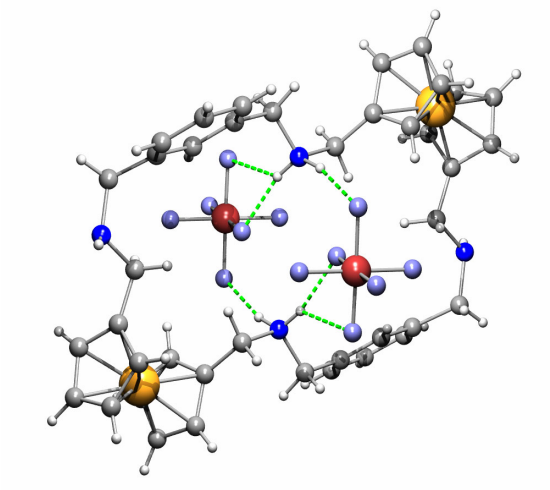

Fig. S4 Structure of the $[H_2L(PF_6)_2]$ **1** showing the overall disposition of the macrocyclic receptor and the anions in the supramolecule in the R:2S ratio.

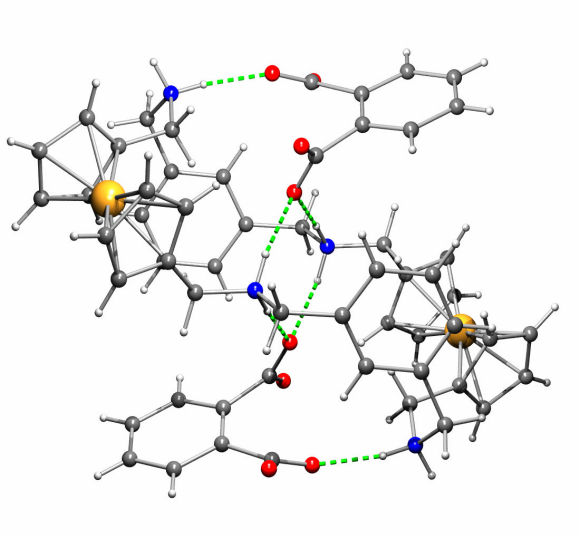

Fig. S5 Structure of the $[H_4L(ph)_2]$ **2** showing the overall disposition of the macrocyclic receptor and the anions in the supramolecule in the R:2S ratio.

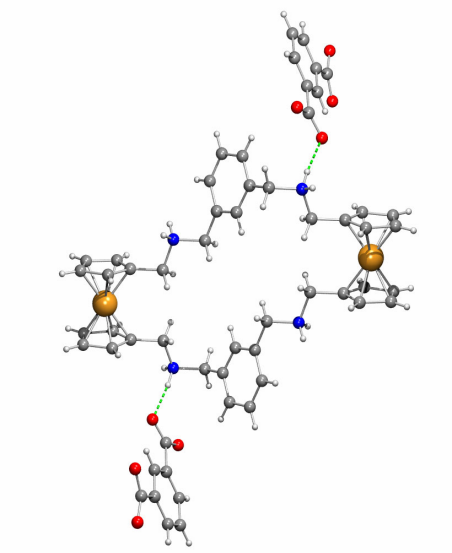

Fig. S6 Structure of the $[H_4L(iph)_2]$ **3** showing the overall disposition of the macrocyclic receptor and the anions in the supramolecule in the R:2S ratio.

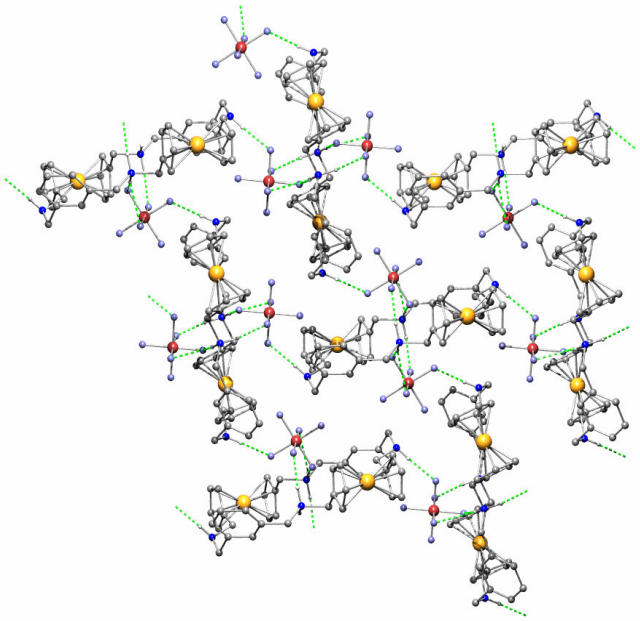

Fig. S7 Crystal packing diagram of **1** showing the network of N–H···F hydrogen bonds.

a) **b)**

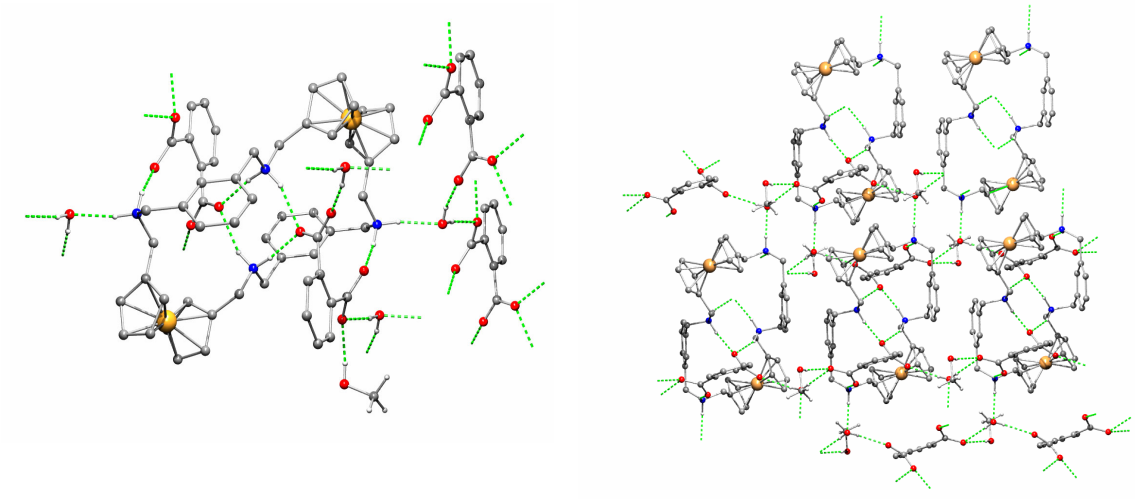

Fig. S8 Crystal packing diagram of **2: a)** entire binding of **[**$H_4L]^{4+}$ receptor *via* N–H···O hydrogen bonds to the surrounding methanol, water solvent molecules and anions substrates; **b)** a view of 2-D hydrogen bonding network.

a) **b)**

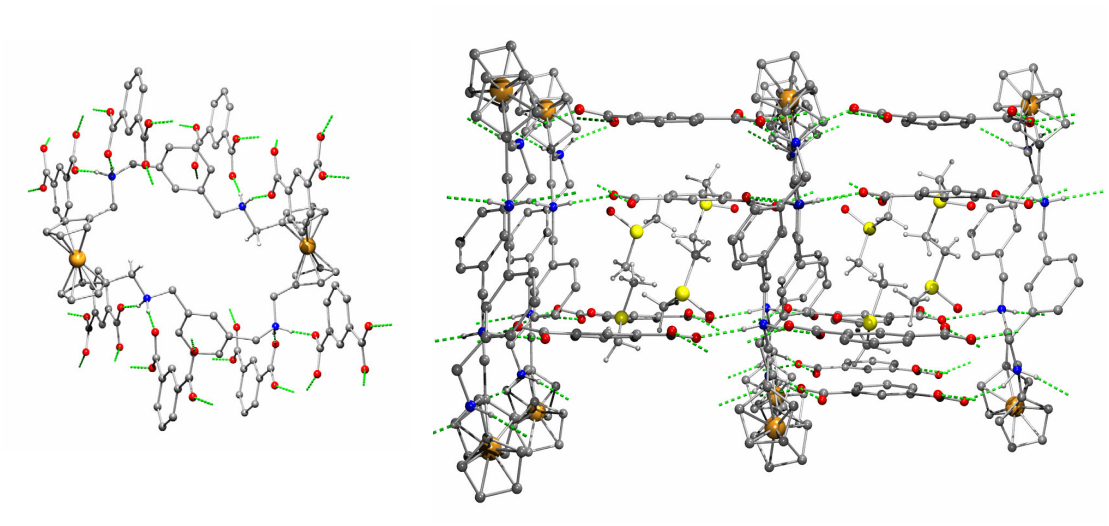

Fig. S9 Crystal packing diagram of **3: a)** a view shows the binding of **[**$H_4L]^{4+}$ to the eight neighbouring iph^{2-} anions by hydrogen bonding interactions; **b)** a view of 3-D hydrogen bonding network forming open channels, which are fulfilled with DMSO solvent molecules.