Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPLEMENTARY INFORMATION

Tuning the coordination chemistry of cyclotriveratrylene ligand pairs through selective solvophobic aggregation

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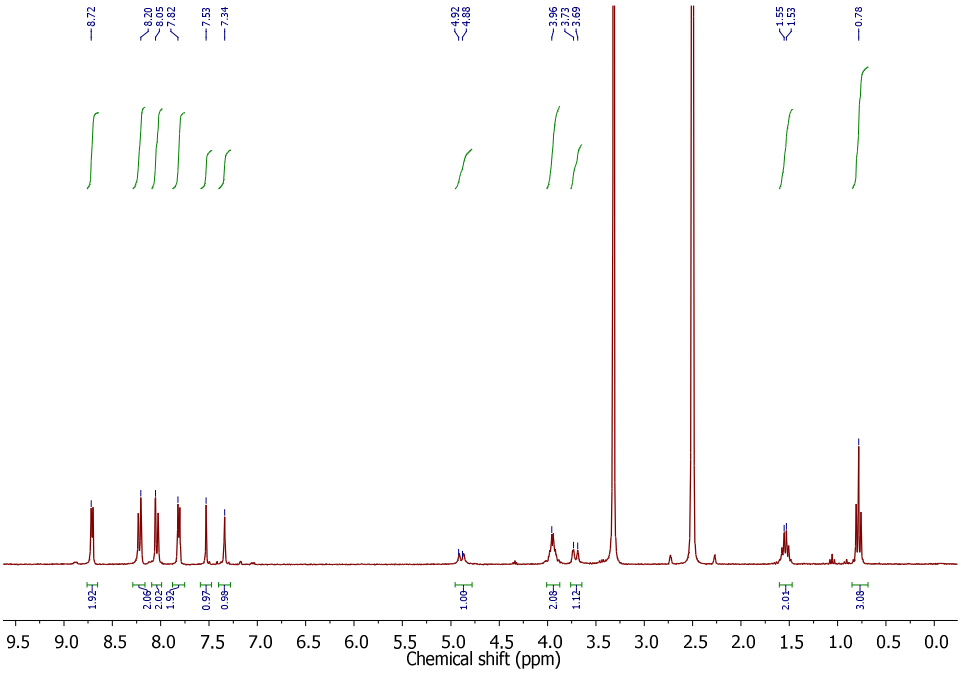
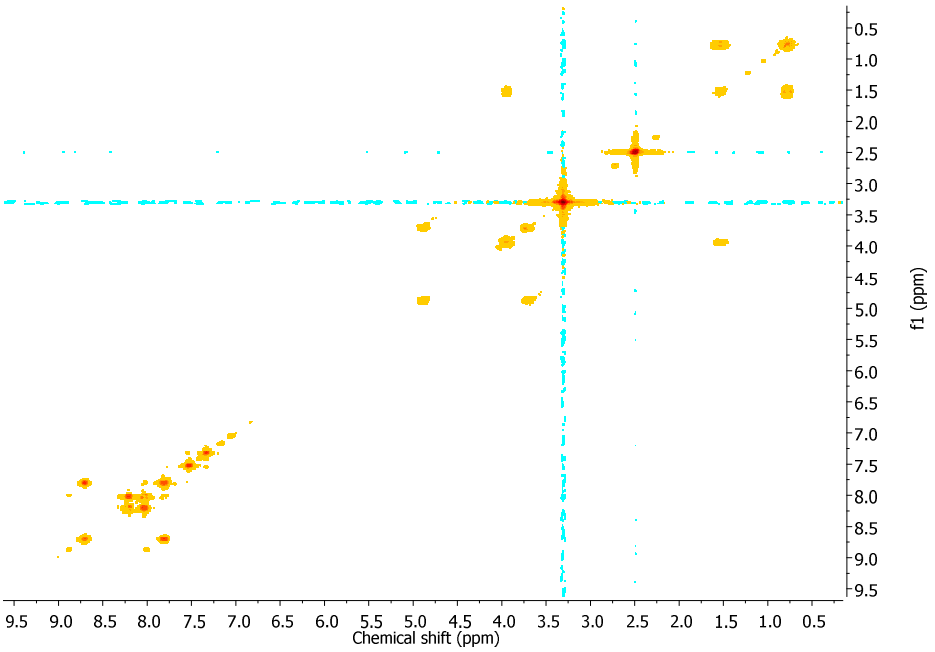
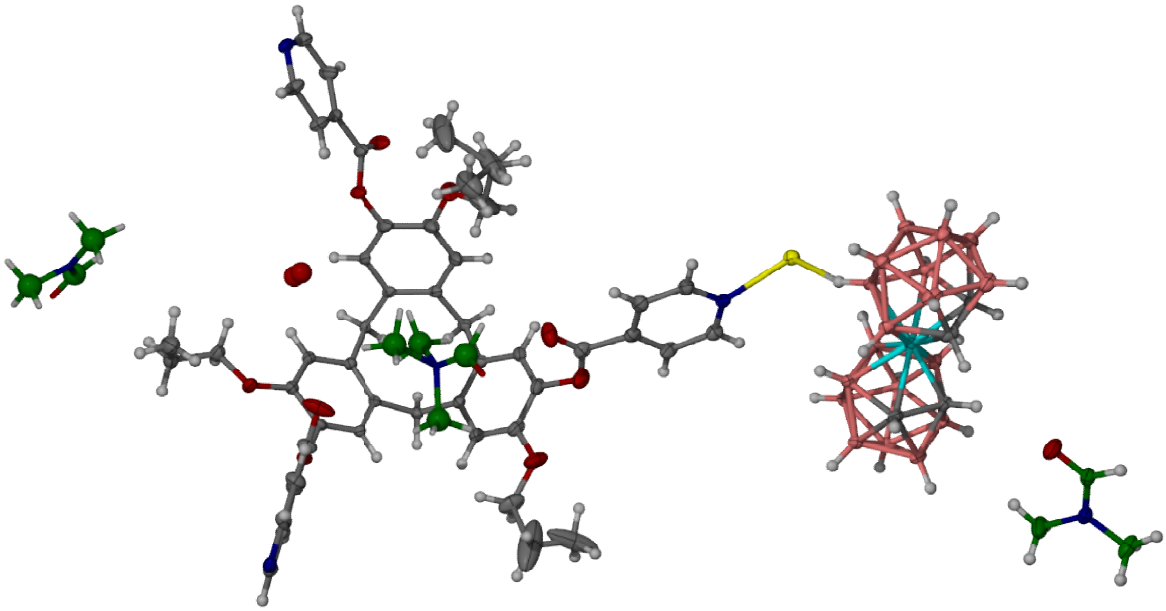
^{1}H NMR and ^{1}H-^{1}H COSY spectra for (±)-2,7,12-Tripropoxy-3,8,13-*tris*(2-quinolylmethyl)-10,15-dihydro-5*H*-tribenzo[*a*,*d*,*g*]cyclononene (L2p) in d_6-DMSO:



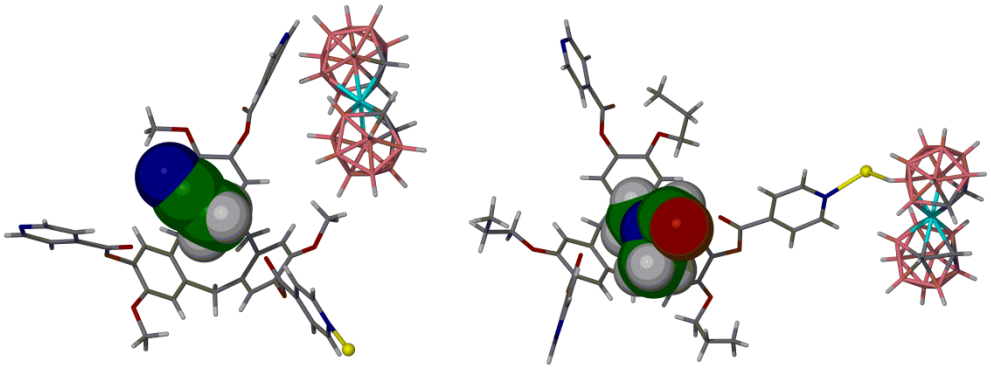


Additional crystallographic information:[1]

Complex 1p: One propyl group was modelled over two positions and the anisotropic displacement parameters of terminal methyl group constrained to be chemically reasonable. One DMF molecule was modelled as disordered and its bond lengths restrained to be chemically reasonable, the other DMF molecule refined as half occupancy. The two molecules of water were refined at half occupancy. CCDC-988765.

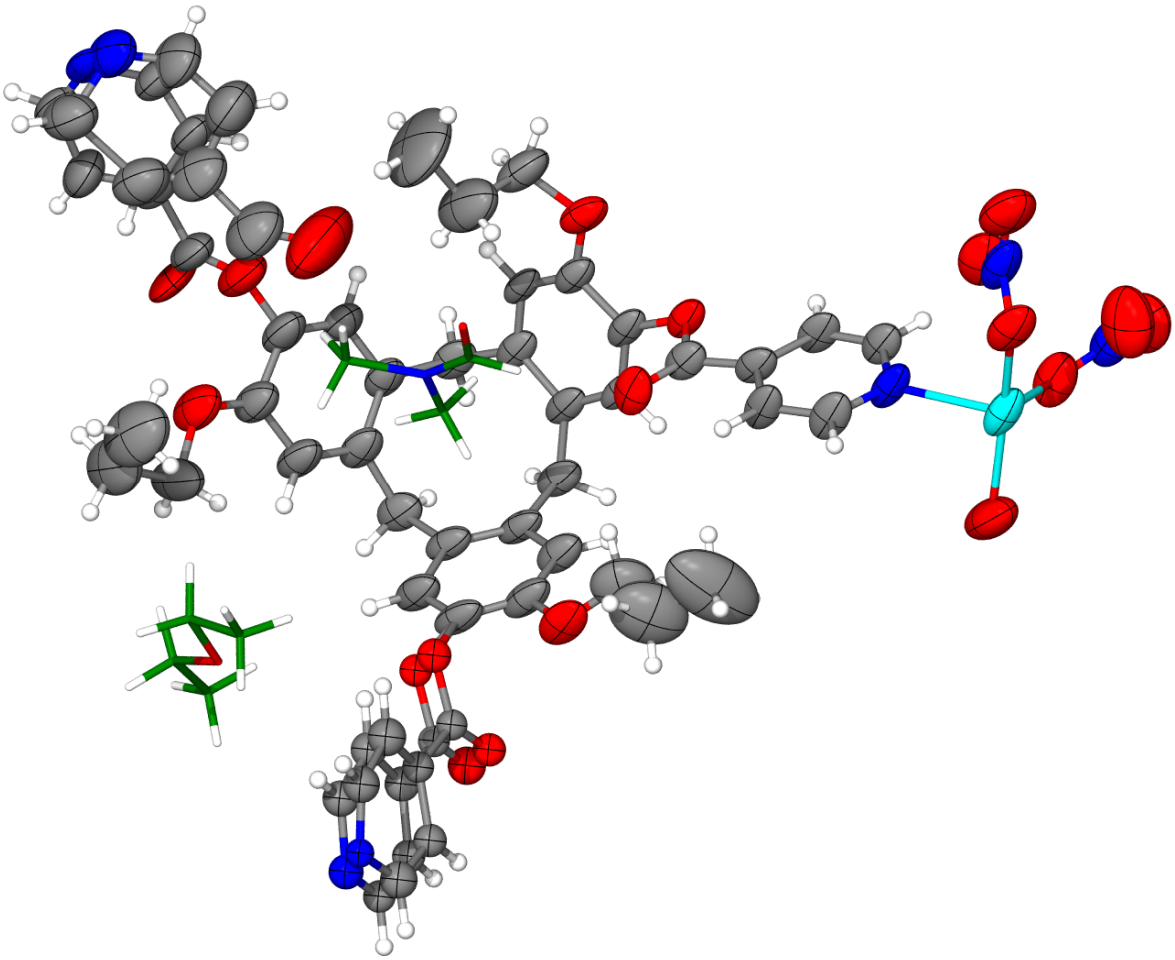


S1. *The asymmetric unit of complex* ***1p****. Atom colours are as follows: yellow (silver), grey (carbon), red (oxygen), blue (nitrogen), pink (boron) and white (hydrogen). All atoms were refined as anisotropic (displacement parameters at 40 %), other than two molecules of DMF and water (displayed as hard spheres). DMF molecules are coloured green for clarity.*

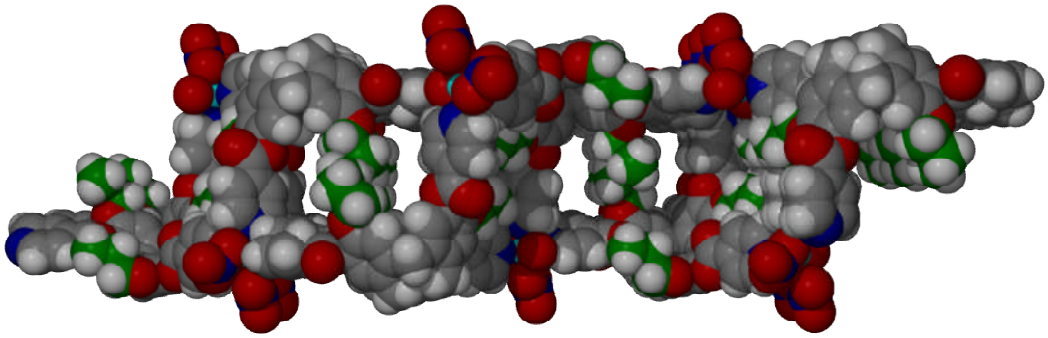


S2. *Analogous solvent host guest behaviour observed in complex* ***1m*** *(left) and* ***2p*** *(right)., with solvents acetonitrile and DMF, respectively. Non-covalently bound solvents shown in green and in space-filling mode.*

Complex 2p: Two of the three pyridyl moieties were modelled as disordered over two positions and bond lengths restrained to be chemically reasonable for pyridyl groups and diethyl-ether. The molecule of diethyl ether was refined as half occupancy, one disordered isonicotinyl was refined as isotropic and the anisotropic displacement parameters were restrained. CCDC-988766.

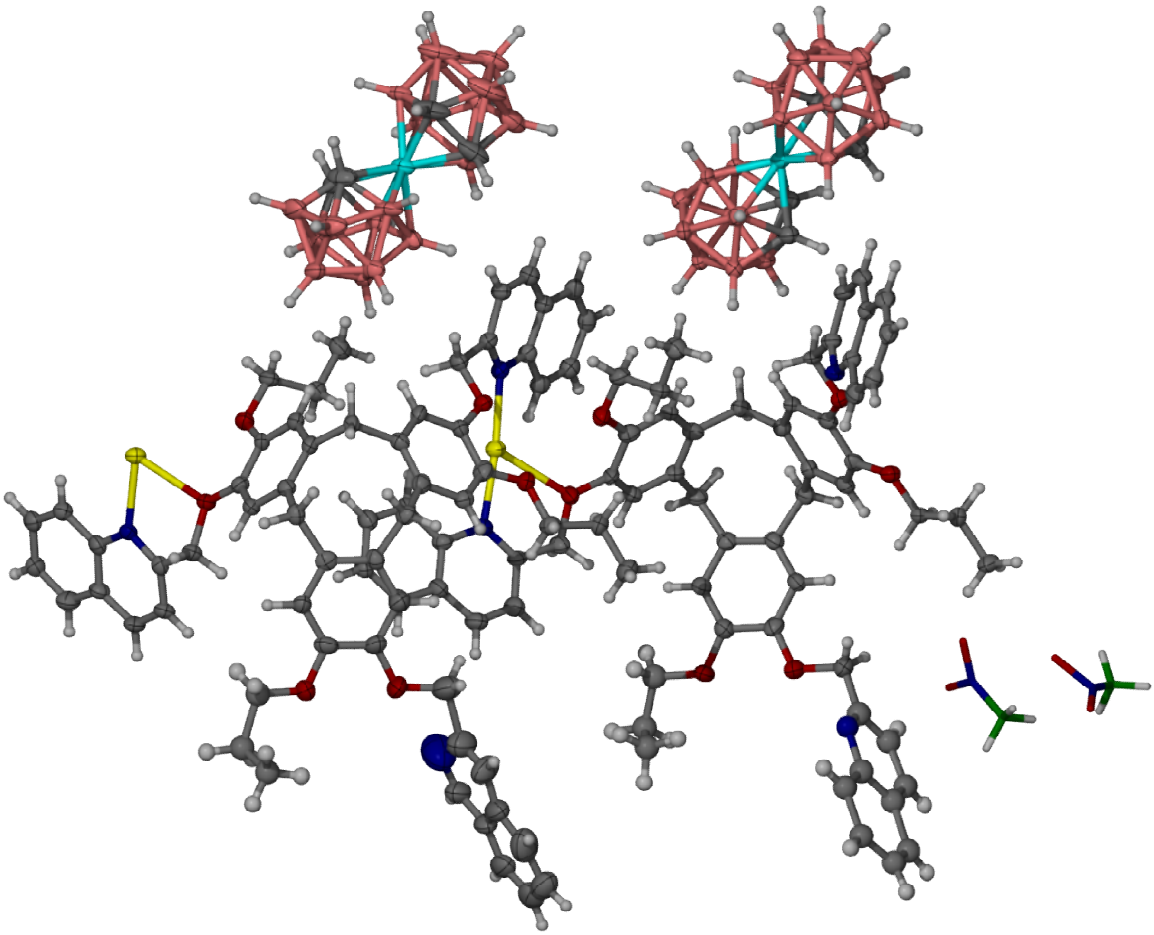


S3. *The asymmetric unit of complex* ***2p****. Atom colours are as follows: turquoise (cadmium), grey (carbon), red (oxygen), blue (nitrogen) and white (hydrogen). All atoms were refined as anisotropic (displacement parameters at 40 %), other than a molecule of DMF and diethyl ether (displayed as hard spheres). DMF and diethyl ether molecules are coloured green for clarity.*

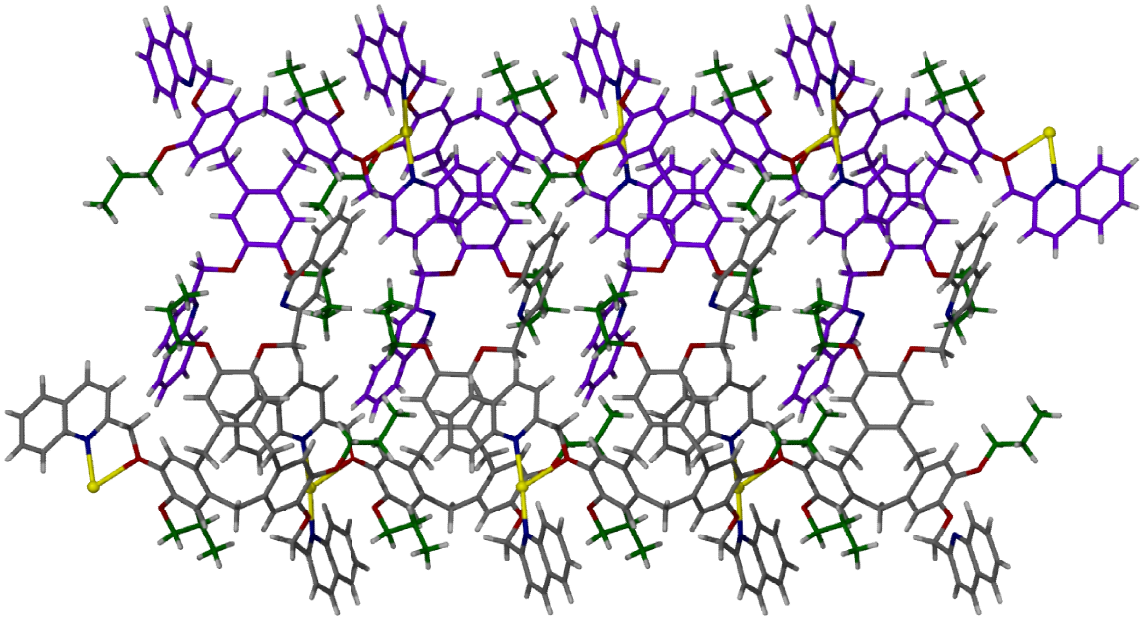


S4. *Highlighting the propyl aggregation in a single 2D sheet of complex* ***2p****. All atoms shown in space-filling mode and propyl moieties shown in green for clarity.*

Complex 3p: Crystals were small, weakly diffracting and twinned. The twin law was applied (TWIN 100 0-10 00-1) and the BASF refined to ca. 0.20. One quinolyl arm, two propyl moieties and both nitromethane solvent molecules were refined isotropically. One of the two nitromethane solvent molecules was refined at half occupancy, one with group Uiso. Nitromethane solvent were subjected to bond restraints to be chemically reasonable. CCDC-988767

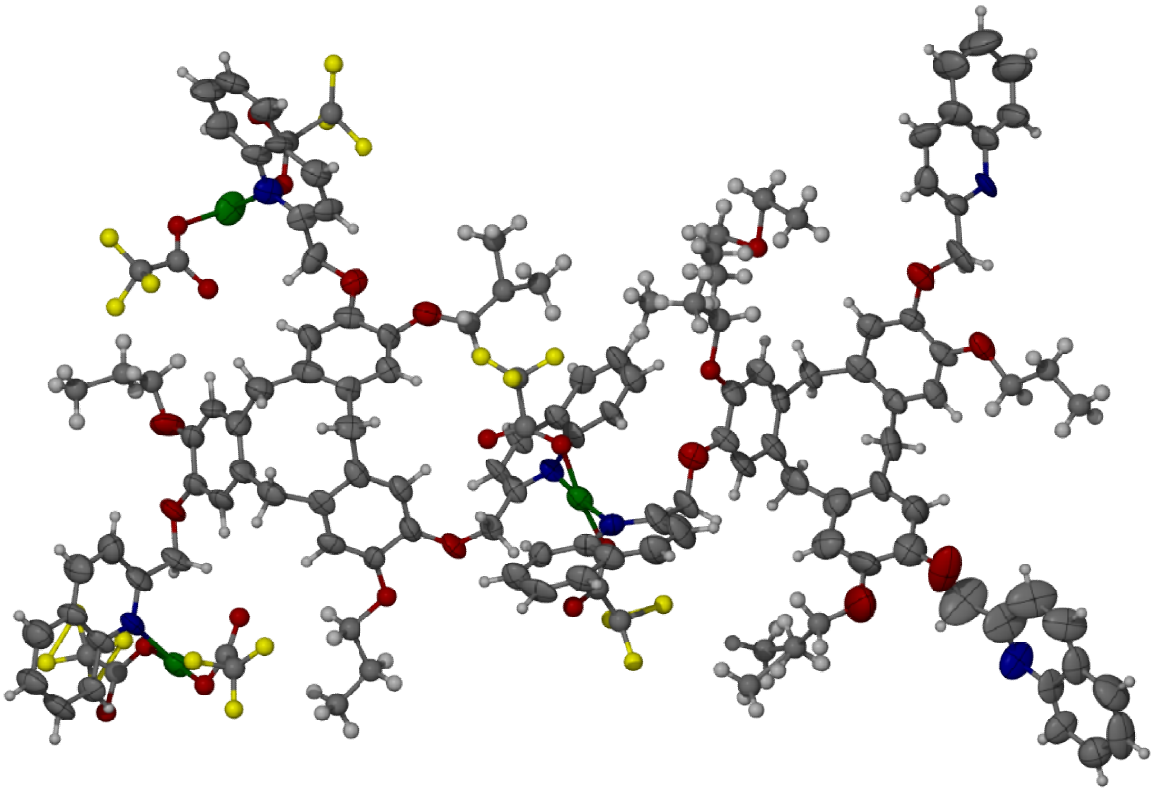


S5. *The asymmetric unit of complex* ***3p****. Atom colours are as follows: yellow (silver), turquoise (cobalt), grey (carbon), red (oxygen), blue (nitrogen), magenta (boron) and white (hydrogen). All atoms were refined as anisotropic (displacement parameters at 40 %), other than the two moles of nitromethane (coloured green for clarity), alongside two propyl moieties and a quinalyl group (displayed as hard spheres).*

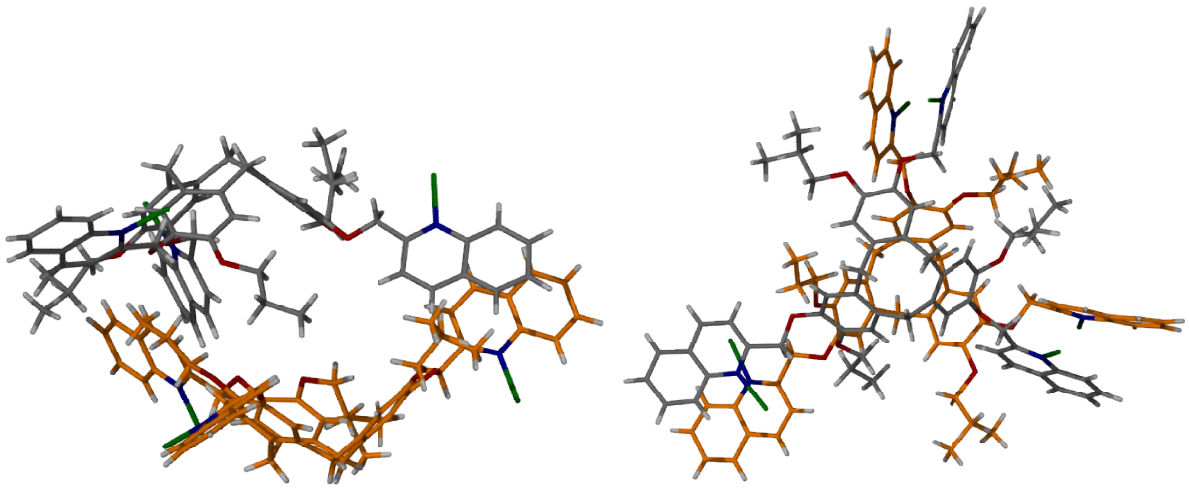


S6. *Aggregation of individual 1D polymers in complex* ***3p****, through aromatic interactions and hydrophobic aggregation. Individual 1D polymers are coloured grey and purple respectively and nitromethane solvent and complex anions have been omitted for clarity.*

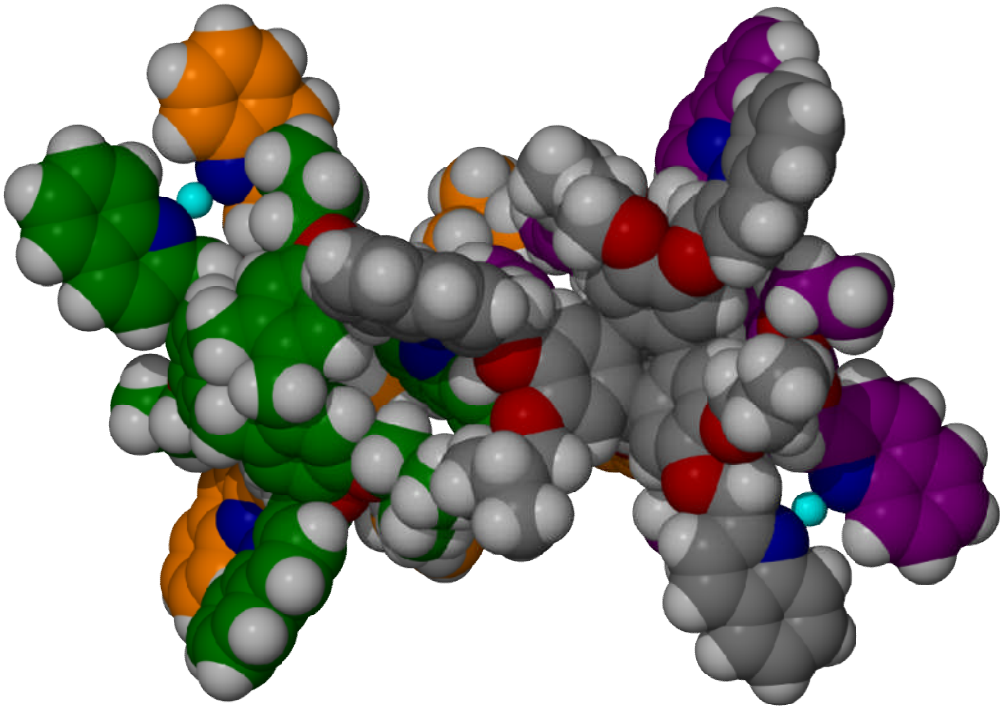
Complex 4p: Crystals were very weakly diffracting and data was observed to only θ = 20˚. Propyl groups, $CF_3CO_2^-$ anions and solvent ether were refined isotropically. Two CF_3 groups and three CH_3 groups of propyl chains were modelled as disordered and the ether was refined at half occupancy. Two C positions of one $CF_3CO_2^-$ anion were refined with a group displacement parameter, and numerous C-C and C-F bond lengths within $CF_3CO_2^-$ anions, propyl groups and the ether were restrained to be chemically reasonable. The structure contained significant void space and residual electron density that could not be meaningfully modelled; hence the SQUEEZE routine of PLATON was employed.[1] CCDC-955888.



S7. *The asymmetric unit of* $[Pd_6(\mathbf{L2p})_4(CF_3CO_2)_{12}]\cdot n$*(diethyl ether), complex* ***4p****, comprising half the overall complex. Atom colours are as follows: green (palladium), grey (carbon), red (oxygen), blue (nitrogen), yellow (fluorine) and white (hydrogen). All atoms were refined as anisotropic (displacement parameters at 40 %), other than disordered* $CF_3CO_2^-$ *anions and propyl groups, alongside the molecule of diethyl ether and hydrogen atoms (all shown as hard spheres).*



S8. *Views of the head-to-head arrangement of* ***L2p*** *ligands between neighbouring* ***4p*** *complexes. Only one* ***L2p*** *ligand of each complex shown and in different colours for clarity.*



S9. *Complex* ***4p****, shown in space-filling mode and with each of the four* ***L2p*** *ligands depicted in a different colour for clarity. Anions and solvents have been omitted.*

References:

1. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112; L. J. Barbour, *Supramol. Chem*., 2001, **1**, 189; A. Spek and P. Van der Sluis, *Acta. Crystallogr., Sect. A*, 1990, **46**, 194; A. Spek, *Acta Crystallogr., Sect. D*, 2009, **65**, 148.