**Answers**

**4.1.** (a) **La** has *five* binding sites for metal cations. The ligand is relative rigid, there are no flexible ether linkages between the N-donor heterocycles, suggesting its ability to form a twisted strand in a helicate assembly might be limited.

(b)



109Ag NMR spectrum would be expected to show six resonances in a 1:4:4:4:4:8 ratio.

(c) To ease strain in the cis conformation, rotation about the central bond of the ligand generates the ‘trans’ form and so result in grids composed of two sets of 2 × 5 ligands. These will have three sets of signals in a 1:2:2 ratio in the 109Ag NMR spectrum.



(d) The symmetry interaction approach is used in these syntheses.

Ligand **Lb** has three possible binding sites for metals cations and so can act as the rungs of a ladder complex that supports three ligand rails (Lr) i.e. M9(Lr)3(Lb)3. The fact that each bipyridyl group will be twisted relative to its neighbours will enable helicates to be formed as these rails (**Lr**) twist around the **Lb** platforms. See *Chem. Eur. J*. 1999, **5**, 113-120.

**4.2.** (a) In the first reaction, two strands of the quaterpyridine ligand wrap themselves around two Cu(I) ions to form a double helicate. This way all donor and acceptor sites are occupied and the Cu(I) tetrahedral coordination geometry is satisfied.

In the second reaction, the same assembly as above would leave two unsatisfied nitrogen donors. However, in the presence of O2 in the air, Cu(I) can be oxidised to Cu(II) allowing the mixed valence helicate to be formed. Cu(II) is d9 and so prefers a distorted octahedral coordination environment due to the Jahn-Teller effect. Both these helicates can twist in a left or right handed manner and so exhibit axial chirality.



(b) In total four different cages are possible. These include a heteroleptic cage: **M3LcLd** and three homoleptic cages: **M3(Lc)2**and two structural isomers of **M3(Ld)2**(see below).



The templation effect of guests with complementary sizes and shapes to the cages could be used to bias the ratio formed. For example, small aromatic guests for **M3(Ld)2** but a bulkier adamantane derivative for **M3(Lc)2**. Medium-sized guests such as CCl4 can be used to favour the heteroleptic cage **M3LcLd**.

(c) The Vernier templates are shown below. Two smaller polypyridyl templates assemble the three tetra-porphyrin nanoring precursors into a figure-of-eight conformation prior to the oxidative covalent coupling reaction.



**4.3.** (a) The self-assembly of a 1D polymeric molecular ribbon is shown below. R and R’ groups block the D/A sites.



The length of the polymer strand aggregates is dependent on the strength of the hydrogen bond interactions. Under relatively non-competitive solvent conditions a stronger association between components will lead to the formation of longer ribbons which may increase the viscosity of the solution. At higher concentrations, cross linking between polymer chains could occur *via* hydrogen bonding or π–π aromatic stacking and so lead to gelation or precipitation of the polymer.

(b) Toluene is a relatively low polarity solvent and so the nature of the aromatic stacking interactions have a significant electrostatic donor–acceptor contribution (note that toluene molecules can even promote this by partitioning themselves between the π–π stacks). This is important because it will ensure that the electron-rich bis-porphyrin unit of one monomer will favour binding to an electron-poor trinitrofluorenone unit of the next to generate an ordered linear supramolecular polymer. This will also hold true in low polarity aprotic solvents such as Et2O and alkanes e.g. hexanes.

However, switching the solvent medium to a protic, polar solvent such as MeOH could trigger more non-discriminatory π–π stacking interactions that instead are driven by the solvophobicity of the aromatic motifs. This could lead to monomers interacting in a non-specific fashion to form polymeric networks with less order (see below) or generate larger non-linear aggregates of monomers with an amorphous structure. Of course, one might anticipate that this compound is insoluble in polar protic solvents and so will simply precipitate from solution!

