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Quantitative self-assembly of a hetero-bimetallic trinuclear square-shaped macrocycle

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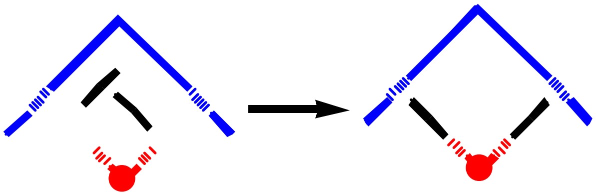
Abstract—A new hetero-bimetallic trinuclear macrocycle has been self-assembled quantitatively, in one step, by means of axial Zn^{II}–N and 90° angular Pt^{II}–N binding, with the metallated angular bisporphyrin, the *cis*-square-planar platinum bistriflate complex and the linear 4,4′-bipyridine, as building block units.

New synthetic strategies focused on metal-ion templates or self-assembly through noncovalent interactions have improved the design and structural knowledge of supramolecules such as macrocycles, catenanes, helicates, cages, ladders, dendrimers and grids.[1] The self-assembled cyclisation of metallated porphyrins containing pendant donor 4-pyridyl analogues,[2] or assisted self-assembly by means of coordinate bonds between basic sites on the porphyrin and metal centres,[3] has been intensively used in recent days.

Molecular squares have been derived from porphyrins before, but the systems in the literature contain only one type of metal ion. We now report the synthesis of a hetero-bimetallic square by the self-assembly of four components. The construction of well-defined structures containing metalloporphyrin fragments is particularly interesting, due to their photochemical properties and their important role in mediating electron and energy transfer. In this letter, we describe the structural characterisation of a four-molecule, square-shaped macrocycle (Scheme 1).



Scheme 1.

The assembly of a square-shaped macrocycle requires the presence of four predesigned 90° angular parts. The metallated bisporphyrin **1** is expected to adopt the 90° conformation as a consequence of the intramolecular hydrogen bonding. The presence of metal ions in the porphyrin cores introduces two new acceptor centres that can be treated with appropriate multidentate donor ligands for construction of the other two angular corners. Finally, the fourth angular corner will be provided by the square-planar platinum complex **2**. In accordance with this idea, the bisporphyrin derivative **1** was prepared by coupling 4-ethoxypyridine-2,6-dicarbonyl dichloride to the corresponding aminoporphyrin followed by metallation with zinc acetate. In our case the angular metallated bisporphyrin **1** was synthesised potentially with three of the four prerequired 90° angular corners and the *cis*-square-planar $dpppPt^{II}(OTf)_2$ **2** (dppp = 1,3-bis(diphenylphosphanyl)propane, OTf = trifluoromethane sulfonate) was used as the fourth 90° angular unit, supplemented by two linear molecules of 4,4′-bipyridine **3**. The metallated bisporphyrin can be axially linked by the ditopic 4,4′-bipyridine ligand as the bridging auxiliary between the metal centre of the porphyrin and the square-planar Pt^{II} complex (Scheme 2).

Although square molecular metalloporphyrins axially connected through bridging ligands have been described during the course of this work,[4] this is the first

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Keywords: Metalloporphyrin; Square supramolecule; Zinc; Platinum.

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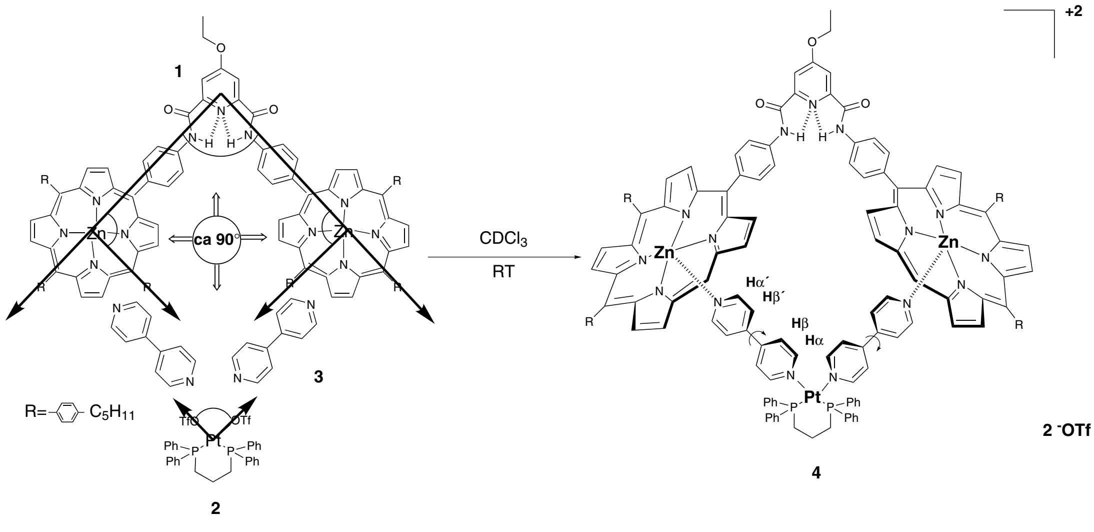

Scheme 2.

square-shaped hetero-bimetallic trinuclear self-assembled structure, based on a mixed selective coordination of the bipyridine, to the metallated zinc porphyrin and the Pt^{II} metal complex.

Here we report the preparation and characterisation of a stable hetero-bimetallic trinuclear macrocycle **4** readily achieved by addition of a stoichiometric amount of dpppPt^{II} bistriflate **2** and 4,4′-bipyridine **3** to a chloroform solution of bisporphyrin **1**.[5] The stoichiometry of the reagents was monitored by NMR. Only one set of signals was observed, corresponding to the complete formation of **4** when the stoichiometry ratio was reached and no free ligands were observed (Fig. 1).

The chelation between the metal centre of the porphyrin and the *cis*-square-planar Pt^{II} complex by the bipyridine unit produced characteristic shifts in the ^{1}H NMR and ^{31}P NMR signals, due to the coordination of 4,4′-bipyridine to both metal centres (Zn^{II} and Pt^{II}) (Fig. 1).

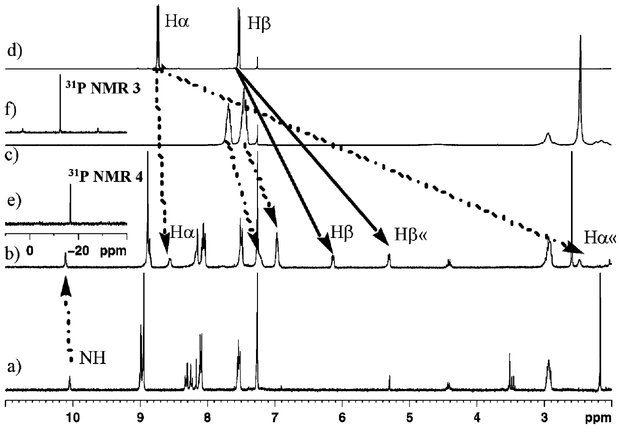

Figure 1. ^{1}H NMR (300 MHz, $CDCl_3$): (a) bisporphyrin **1**; (b) complex **4**; (c) *cis*-square-planar dpppPt^{II} complex **2**; (d) 4-4′ bipyridine **3**. ^{31}P NMR (81 MHz, $CDCl_3$); (e) complex **4**; (f) *cis*-square-planar dpppPt^{II} complex **2**.

The ^{1}H NMR spectrum was found to be relatively simple and consistent with the symmetry of the macrocycle **4**. In the self-assembly process the ditopic 4,4′-bipyridine ligand acts as a donor and the α and β protons show a substantial upfield shift relative to free 4,4′-bipyridine. The main features of the ^{1}H NMR spectrum, which establish the geometry of the complex are, firstly, the axial coordination of the bipyridine ligand with the metalloporphyrin is unequivocally indicated by the large upfield shift of Hα′ and Hβ,β′ resonances due to the ring current effect of the porphyrin. Both porphyrins are magnetically equivalent and give just one set of signals, which are slightly upfield compared to the free ligand **1**; secondly, the 1:2:1 ratio determined by relative integration of the well-resolved signals corresponding to the bisporphyrin ligand **1**, 4,4′ bipyridine **3** and the dpppPt^{II} complex **2**; thirdly, the aromatic resonances of the dpppPt^{II} complex **4** at $\delta = 7.25$ and 6.79 ppm are shifted upfield significantly compared to the free dpppPt^{II} complex **2** at $\delta = 7.74$ and 7.45 ppm.

The doublets of the bipyridine moieties at 8.57, 6.13, 5.30 and 2.47 ppm were assigned to the α, β, β′, α′ protons, respectively, by homonuclear decoupling.

The ^{31}P NMR spectrum of **4** at room temperature, according to the symmetry of the molecule, displays a single resonance at $\delta = -16.31$ ppm with the corresponding platinum satellites $J = 3096$ Hz due to the ^{195}Pt–^{31}P spin–spin coupling. The signal is shifted 5.71 ppm upfield compared to the ^{31}P NMR signal at $\delta = -10.60$ ppm of the bistriflate dpppPt^{II} indicative of the coordination of the nitrogen lone pair to the platinum metal.

The formation of the macrocycle **4** was also monitored by following the typical red shift of the visible Q bands of the bisporphyrin, where changes were observed from 548.8 and 587.6 nm to 563.8 and 604.4 nm (Fig. 2a and b). The Q band exhibited a sharp saturation at

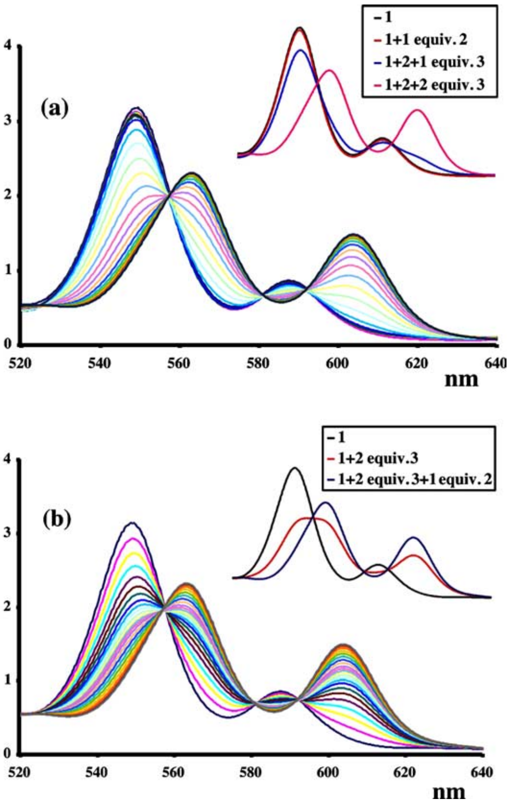

Figure 2. (a) UV–vis titration of **1** (6.5×10^{-5} M) with 2 equiv of bipyridine **3** in the presence of 1 equiv of dpppPt^{II} **2**; (b) titration of **1** (6.5×10^{-5} M) with 1 equiv of dpppPt^{II} **2** in the presence of 2 equiv of bipyridine **3**.

the stoichiometric ratio 1:2 for the species **1** and **3** if the titration was performed in the presence of 1 equiv of the dpppPt^{II} complex **2** (Fig. 2a), or at the stoichiometric ratio 1:1 for the bisporphyrin **1** and dpppPt^{II} **2** species if the titration is carried out in the presence of 2 equiv of the bipyridine **3** (Fig. 2b).

Since we can predict that binding constants are significantly higher if cyclisation takes place, due to the cooperativity effects, compared to those obtained if cyclisation does not occur,[6] simple UV–vis experiments were performed to determine the binding strength between bisporphyrin **1** and the bipyridine **3** in the presence of 1 equiv of dpppPt^{II} complex **2**. The titration plots were analysed by fitting the experimental points to a 1:2 binding isotherm to determine the binding constant.[7] The binding constant between the bipyridine nitrogen and the Zn centre, was measured directly by titrating 4,4′-bipyridine into a solution of a monomeric zinc porphyrin ($K = 5\times10^3\ \mathrm{M}^{-1}$). The constant between **1** and **3** was largely improved ($K \sim 10^8\ \mathrm{M}^{-2}$) when the titration was performed in the presence of the dpppPt^{II} complex **2**, supporting that the macrocycle **4** was formed.

More evidence of this complexation was obtained from the ^{1}H NMR titration, where we observed the formation of the macrocycle **4** from the first addition of dpppPt^{II} to a solution of bisporphyrin/bipyridine (1:2). Both ^{1}H NMR and UV–vis spectra confirmed that the two molecules of bipyridine are tightly bound to both the Zn–porphyrin and the platinum complex.

Further experiments to show the presence of the macrocycle **4** by (ESI-MS) failed,[8] the electrospray mass spectrum just exhibiting free ligands. The highest detected species at $m/z = 1982.8903$ (calcd $m/z = 1982.8475$) corresponded to the protonated bisporphyrin ligand. The molecular ion was in perfect concordance with the calculated isotopic distribution.

In summary, this study demonstrates an effective assembly process of different frameworks with specific topologies, and the resulting cavity is suitable for molecular recognition of appropriately shaped molecules through hydrogen bonding or π–π interactions. The kinetic lability of the Zn–pyridine interactions can be exploited in the construction of more complex structures and studies along these lines are currently in progress.

Acknowledgements

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