Host–Guest Systems

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Selective *Endo* and *Exo* Binding of Mono- and Ditopic Ligands to a Rhomboidal Diporphyrin Prism**

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Abstract: *Copper(I) can preferentially form heteroleptic complexes containing two phosphine and two nitrogen donors due to steric factors. This preference was employed to direct the self-assembly of a porphyrin-faced rhomboidal prism having two parallel tetrakis(4-iminopyridyl)porphyrinatozinc(II) faces linked by eight 1,4-bis(diphenylphosphino)-benzene pillars. The coordination preferences of the Cu^{I} ions and geometries of the ligands come together to generate a slipped-cofacial orientation of the porphyrinatozinc(II) faces. This orientation enables selective encapsulation of 3,3′-bipyridine (bipy), which bridges the Zn^{II} ions of the parallel porphyrins, whereas 4,4′-bipy exhibits weaker external coordination to the porphyrin faces. Reaction with 2,2′-bipy, by contrast, results in the displacement of the tetratopic porphyrin ligand and formation of $[\{(2,2'\text{-bipy})Cu^{I}\}_2(\text{diphosphine})_2]$. The differing strengths of interactions of bipyridine isomers with the system allows for a hierarchy to be deciphered, whereby 4,4′-bipy may be displaced by 3,3′-bipy, which in turn is displaced by 2,2′-bipy.*

Metallosupramolecular synthesis has become established as one of the most reliable and versatile methodological pillars of supramolecular chemistry.[1] Much fundamental metallo-supramolecular work has been done by employing homoleptic complexes, which often adopt the geometries of high-symmetry polyhedra.[2] Although homoleptic self-assembly has proven to be a powerful method for producing stable supramolecular architectures, the use of a single ligand type can limit structural diversity. In biological self-assembly processes, several distinct sub-elements may come together to produce low-symmetry structural motifs, which underpin complex biological behavior, for example, catalysis, recognition, and transport.[3] This principle, that the complexity of a self-assembled architecture increases with the number of structurally distinct components that it comprises, can be explored in the context of non-biological supramolecular systems through the preparation of heteroleptic metal–ligand complexes.[4]

Several key steps have already been made in demonstrating that programmed self-assembly in which more than one type of ligand is employed can produce metallosupramolecular architectures with lower symmetries than their homoleptic counterparts.[4a,5] In some cases, the reduced symmetry of these architectures is directly responsible for functional behavior in the self-assembled complex, for example, catalysis,[6] light-harvesting,[7] and tunable molecular recognition.[8] Further work in this area thus promises access to even more complex structures and functions.

The reaction of Cu^{I} with linear ditopic diphosphines (such as 1,4-bis(diphenylphosphino)benzene, **B**) and 2,2′-bipyridine (2,2′-bipy) gives simple heteroleptic dinuclear complexes $[\{(2,2'\text{-bipy})Cu^{I}\}_2\mathbf{B}_2]$ in which the Cu^{I} ions and diphosphine ligands form a hexagonal macrocycle.[9] We envisaged that replacing the 2,2′-bipy subunit with a tetrakis(4-iminopyridyl)porphyrinatozinc(II) ligand (**A**) would produce a $[Cu^{I}{}_8\mathbf{A}_2(\text{diphosphine})_8]$ metallosupramolecular prism, where porphyrin faces (**A**) would be held together by linear diphosphine (**B**) pillars.

Ligands **A** and **B** were chosen to generate heteroleptic $Cu^{I}N_2P_2$ centers: **A** does not form an $Cu^{I}{}_4\mathbf{A}_2$ homoleptic sandwich due to steric clash between the *meso*-phenyl groups,[10] and the steric bulk of the phenyl groups of **B** causes self-assembly to stop at the formation of a dinuclear $[\{(MeCN)_2Cu^{I}\}_2\mathbf{B}_2]$ complex, even in the presence of excess **B**.[5c,e,9a] The hexagonal ring described by the Cu–P and P–P vectors in $[\{(2,2'\text{-bipy})Cu^{I}\}_2\mathbf{B}_2]$ (Supporting Information, Figure S59) and $[\{(MeCN)_2Cu^{I}\}_2\mathbf{B}_2]$[9a] moieties adopts a cyclohexane-chair conformation owing to the tetrahedral geometries of the Cu^{I} centers. This chair conformation was expected to cause slanting of the edges of the prism, generating a rhomboidal cross-section. Thus, a porphyrin-faced rhomboidal prismatic $Cu^{I}{}_8\mathbf{A}_2\mathbf{B}_8$ heteroleptic complex (**1**) was anticipated to form as the thermodynamic product of self-assembly.

Prism **1** was initially synthesized as the bis(quinuclidine) host–guest complex $[\mathbf{Q}_2\subset\mathbf{1}]$ (where **Q** = quinuclidine) by subcomponent self-assembly[11] of 5,10,15,20-tetrakis(4-aminophenyl)porphyrinatozinc(II) (Zn-TAPP), diphosphine **B**, 2-formylpyridine, and quinuclidine with tetrakis(acetonitrile)copper(I) bis(trifluoromethylsulfonyl)imide $[Cu(MeCN)_4]NTf_2$ in DMF (Scheme 1). Quinuclidine serves as an axial ligand for coordination to the porphyrinatozinc(II) subcomponent during self-assembly. Prism **1** formed in low

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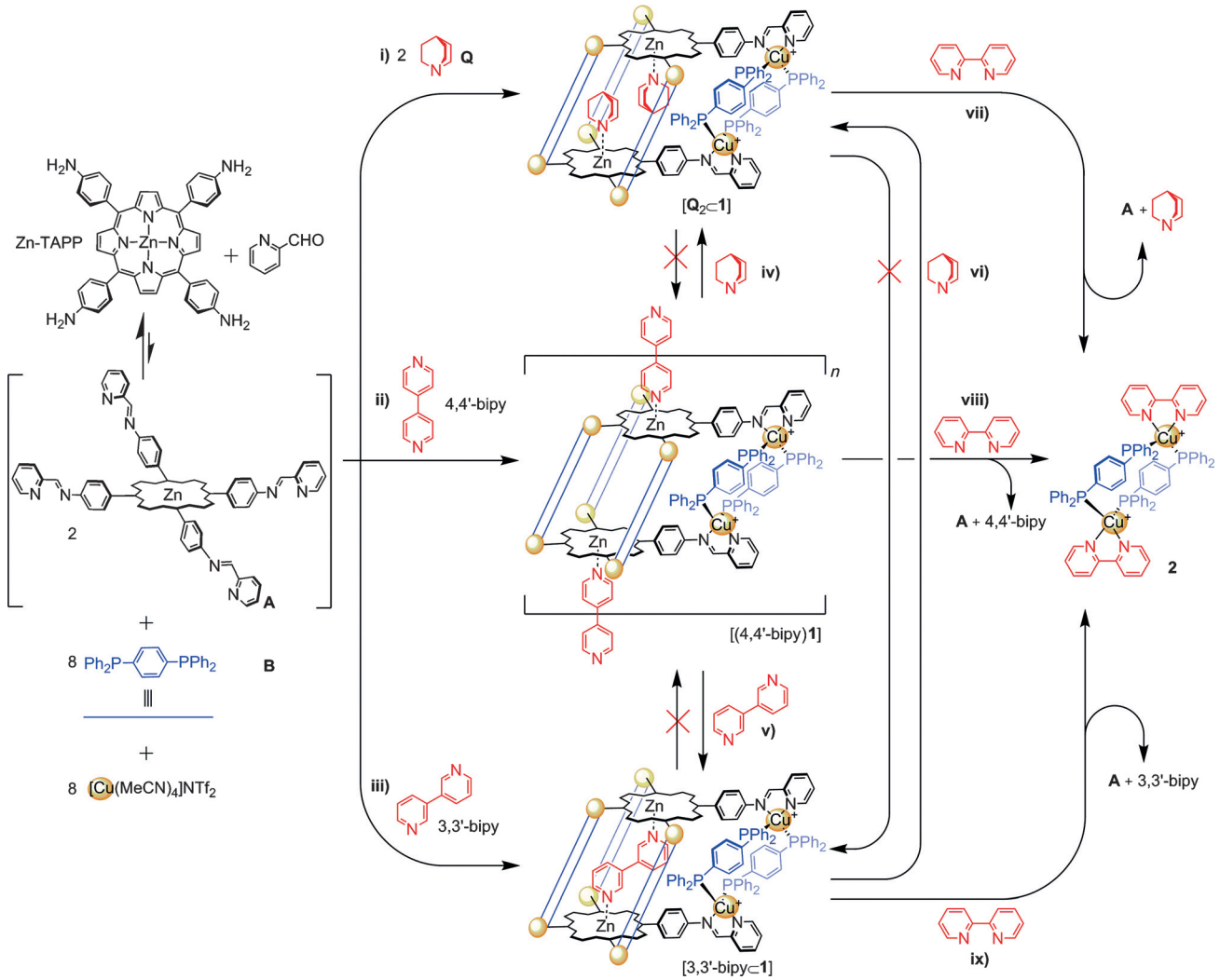

Scheme 1. Self-assembly of C_4-symmetric tetrakis(bidentate) ligand **A**, 2-formylpyridine, 1,4-bis(diphenylphosphino)benzene **B**, and [Cu(MeCN)$_4$]NTf$_2$ with quinuclidine (**Q**) and the three bipyridine isomers (2,2′, 3,3′, and 4,4′) in DMF to form prisms i) [$\mathbf{Q}_2\subset\mathbf{1}$] (77%), ii) [(4,4′-bipy)**1**] (60%), and iii) [3,3′-bipy⊂**1**] (64%). Transformations between these complexes are also shown (iv–ix), which were monitored by ^{1}H NMR spectroscopy (Supporting Information, Section 4). The blue lines and orange spheres represent 1,4-bis(diphenylphosphino)benzene and Cu^I, respectively.

yield in its absence, which is presumably due to coordination of 2-formylpyridine to Zn-TAPP.

NMR and ESI-MS spectra of [$\mathbf{Q}_2\subset\mathbf{1}$] (Supporting Information, Figures S1–S14) were consistent with our proposed composition and structure. The ^{1}H NMR spectrum of [$\mathbf{Q}_2\subset\mathbf{1}$] in CD$_3$CN was complicated but displayed features consistent with the formation of a 2:1 quinuclidine/**1** complex (Figure 1) as the predominant species in solution. Co-diffusion of quinuclidine and **1** as a single entity by ^{1}H DOSY NMR spectroscopy (Supporting Information, Figure S7), as well as upfield shifting of the quinuclidine proton signals (confirmed by ^{1}H–^{1}H COSY; Supporting Information, Figures S1–S6) are both diagnostic of quinuclidine coordination to the porphyrinatozinc(II) moiety under slow exchange on the NMR timescale,[12] supporting the persistence of [$\mathbf{Q}_2\subset\mathbf{1}$] in solution. At low temperature, an additional set of ^{1}H NMR signals for bound quinuclidine, accounting for around about 15% of the

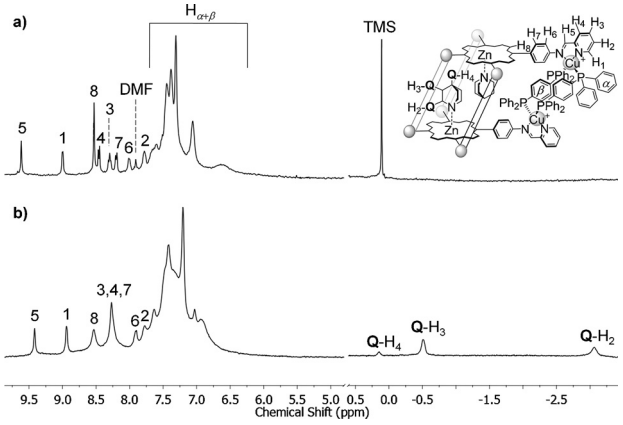

Figure 1. Partial ^{1}H NMR spectra (500 MHz, 298 K) of heteroleptic diporphyrin prism [$\mathbf{Q}_2\subset\mathbf{1}$] in a) [D$_8$]THF and b) CD$_3$CN (see the Supporting Information, Section 1.1 for more details).

host–guest species present, could be identified; we infer these peaks to arise from a 1:1 quinuclidine/**1** complex [**Q**⊂**1**]. Encapsulation of quinuclidine by **1** was further supported by studies on a monoporphyrinic analogue, which displayed fast-exchange binding behavior with quinuclidine at 298 K in CD_3CN (Supporting Information, Section 1.1).

Clearer, higher-resolution NMR spectra of **1** were obtained by dissolving [$\mathbf{Q}_2$⊂**1**] in [D_8]THF. This solvent was able to displace the quinuclidine guests[13] to give well-resolved ^{1}H NMR (Figure 1), ^{1}H–^{1}H COSY and NOESY spectra (Supporting Information, Figures S13 and S14), which simplified complete assignment of the proton environments of the tetrakis(4-iminopyridyl)porphyrinatozinc(II) moiety. Unfortunately, we were unable to obtain single crystals of **1** or [$\mathbf{Q}_2$⊂**1**] of sufficient quality to perform X-ray diffraction analysis.

The anticipated rhomboidal prismatic structure of **1**, featuring parallel-offset porphyrin faces, led us to postulate that **1** might selectively encapsulate 3,3′-bipy through ditopic axial coordination to the porphyrinatozinc(II) centers. Furthermore, ditopic guest binding within **1** would conformationally rigidify the complex, assisting with crystallization. MM3 molecular modeling of the complex indicated good geometric complementarity between **1** and 3,3′-bipy. Indeed, synthesis of the prism in the presence of 3,3′-bipy afforded the 1:1 complex [3,3′-bipy⊂**1**] (Scheme 1). The ^{1}H NMR spectrum of [3,3′-bipy⊂**1**] was similar to that of [$\mathbf{Q}_2$⊂**1**] (Supporting Information, Figures S56 and S57). Crucially, the signals for 3,3′-bipy were observed upfield from their normal chemical-shift values (Supporting Information, Figures S25 and S26), which is diagnostic of the proposed ditopic binding of 3,3′-bipy within **1** under slow exchange.[14] ESI-MS showed signals corresponding to [3,3′-bipy⊂**1**] (Supporting Information, Figures S32 and S33).

Unambiguous confirmation of the solid-state structure of [3,3′-bipy⊂**1**] was obtained by single-crystal X-ray diffraction (Figure 2 a). The eight distorted tetrahedral Cu^I centers form the expected rhomboidal prism, with two tetrakis(bidentate) porphyrinatozinc(II) ligands forming the upper and lower faces (Cu–Cu separations of 14.4–15.5 Å) and two diphosphine ligands lying along each of the four vertical edges (Cu–Cu separations of 8.2 Å). As observed for similar dinuclear heteroleptic Cu^I complexes,[9] all of the $Cu_2\mathbf{B}_2$ subunits of [3,3′-bipy⊂**1**] adopt a chair configuration (Supporting Information, Figure S59), which brings about the unusual slipped-cofacial configuration of the porphyrinatozinc(II) faces of the cage (Zn-to-Zn offset distance of 4.7 Å). The 3,3′-bipy perfectly bridges the gap between the zinc atoms of the porphyrinatozinc(II) subunits. Of the 32 phenyl rings attached to the phosphorus donor atoms, four are positioned within the shielding cones of the aromatic ring currents of the porphyrins (Figure 2 a, shown in yellow). Further evidence that a similar configuration is adopted in solution is given by the upfield ^{1}H chemical shift values observed for some phenyl ring signals in the region of 3.0 to 7.0 ppm for [3,3′-bipy⊂**1**] at 243 K (Supporting Information, Figure S25).

Biological receptors often employ different modes of binding (for example, *endo*/*exo*) to recognize a range of chemical species in complex natural systems.[15] Reinhoudt et al. highlighted that in the domain of synthetic receptors, this type of multi-mode recognition is rare and worthy of further study.[15b] Given that previously reported porphyrin boxes display a preference for aligned porphyrin faces,[16] we investigated how **1** would respond to 4,4′-bipyridine: would the host distort to accommodate *endo* guest binding, or do the geometric preferences of the box allow only *exo* binding? Thus, **1** was prepared in the presence of 4,4′-bipy (1 equiv) to give a product [(4,4′-bipy)**1**] with similar aromatic ^{1}H NMR features as [3,3′-bipy⊂**1**] and [$\mathbf{Q}_2$⊂**1**]; however, no peaks attributable to 4,4′-bipy (bound or free) were observed. Titration of excess 4,4′-bipy into [(4,4′-bipy)**1**] resulted in significantly broadened signals for the excess 4,4′-bipy which were shifted slightly upfield from the chemical shift values of free 4,4′-bipy, suggesting a relatively weak interaction with host **1** in CD_3CN (Supporting Information, Figures S72 and S73). Continued addition of 4,4′-bipy gave chemical shift values increasingly similar to those of free 4,4′-bipy, consistent with an interaction with **1** in intermediate exchange.

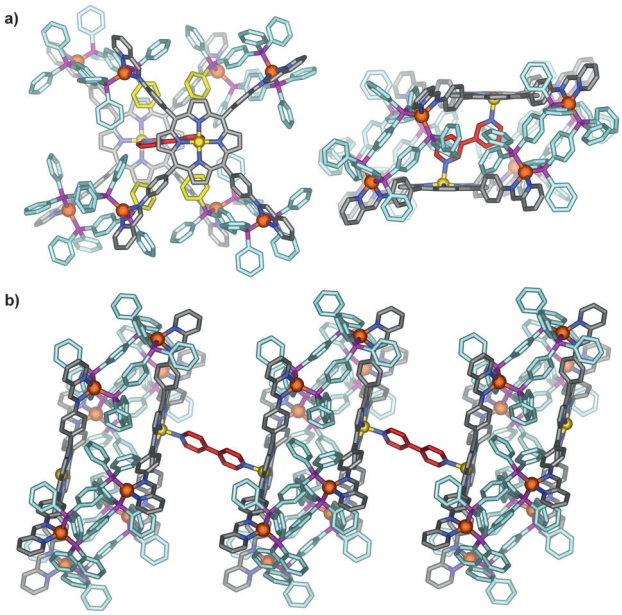

Figure 2. a) Top and side views of the crystal structure of [3,3′-bipy⊂**1**]8 NTf_2.[17] The phenyl groups pointing inside the capsule are shown in yellow in the top view. b) Crystal structure of the 1D-coordination polymer [(4,4′-bipy)**1**]8 OTf[17] showing three units of **1**. Counterions, solvent, disorder, and hydrogen atoms are omitted for clarity. N blue, P purple, Cu orange, Zn yellow; the carbon atoms of the porphyrins, bipyridines, and 1,4-bis(diphenylphosphino)benzene are colored gray, red, and cyan, respectively.

Single-crystal X-ray analysis of [(4,4′-bipy)**1**] revealed **1** to crystallize with 4,4′-bipy to give a 1D-coordination polymer in the solid state (Figure 2 b), which is consistent with the weak external-face-binding observed in solution. As observed for [3,3′-bipy⊂**1**], [(4,4′-bipy)**1**] crystallizes with inversion symmetry such that one half of the prism is crystallographically unique and the structure of **1** in both complexes is similar. The plane-to-plane distance between the two porphyrin subunits within a single prism is 8.05 Å. We infer that the Zn-to-Zn offset in **1** coupled to this short inter-porphyrin separation prevents 4,4′-bipy (nitrogen-to-nitrogen distance 7.06 Å)

binding inside **1** in an intramolecular fashion. Rather, 4,4′-bipy binds intermolecularly, connecting neighboring prisms with a Zn-to-Zn separation of 11.3 Å.

The different modes of binding of 3,3′-bipy and 4,4′-bipy to prism **1** contrast strongly. The binding of 3,3′-bipy is unusual in the context of 3D porphyrin-based host–guest complexes since both covalent and non-covalent diporphyrin cages reported previously show a strong preference for aligned porphyrin faces with minimal lateral displacement,[10,16,18] which precludes the binding of lower-symmetry guests, such as 3,3′-bipy, in favor of more symmetric guests (for example, 4,4′-bipy).

In contrast, 2,2′-bipy cannot bind to the Zn^{II} centers of **1**, as do 4,4′-bipy and 3,3′-bipy, due to steric constraints. Instead, it competes with the iminopyridyl ligands, resulting in disassembly of prism **1** and reconstitution into the dinuclear [{(2,2′-bipy)Cu^{I}}$_2$**B**$_2$] complex **2**.

Since prism **1** displays characteristically different responses to the aforementioned isomers of bipy, we sought to map this behavior as a network of chemical transformations. This network (Scheme 1 iv–ix; Supporting Information, Section 4, Figures S61–S71) allows us to trace the thermodynamic preferences of the system. NMR competition experiments were performed, whereby a second guest was titrated into a solution of the each of the pre-formed host–guest complexes. Addition of **Q** (2 equiv) to [(4,4′-bipy)**1**] in CD_3CN produced a spectrum characteristic of [**Q**$_2$⊂**1**] (Supporting Information, Figures S61 and S62). In contrast, titration of 4,4′-bipy (8 equiv) did not result in any significant changes to the spectrum of [**Q**$_2$⊂**1**] (Supporting Information, Figure S63). We infer the higher basicity of **Q** and its complete encapsulation within the cavity of host **1** to render its interaction more favorable than that of 4,4′-bipy. Similarly, treatment of [(4,4′-bipy)**1**] with 3,3′-bipy (1 equiv) in CD_3CN at 243 K produced a spectrum characteristic of [3,3′-bipy⊂**1**] (Supporting Information, Figure S64), whereas titration of 4,4′-bipy (1 equiv) into [3,3′-bipy⊂**1**] did not cause any significant ^{1}H NMR changes (Supporting Information, Figure S65). It is interesting to note that the titration of ditopic 3,3′-bipy did not displace the monotopic **Q** ligands even after 24 h at 298 K followed by 323 K for 1 h (Supporting Information, Figures S66 and S67), whereas the converse addition of **Q** to [3,3′-bipy⊂**1**] resulted in the displacement of 3,3′-bipy, as evidenced by NMR spectroscopy (Supporting Information, Figure S68). We infer this unexpected preference for a monotopic ligand over a ditopic ligand to be due to the steric strain engendered by the eclipsing of the *ortho* protons of 3,3′-bipy in [3,3′-bipy⊂**1**] as a result of its nearly coplanar conformation (Figure 2a); no such torsional strain applies to the quinuclidine complex. Treatment of [**Q**$_2$⊂**1**], [3,3′-bipy⊂**1**], or [(4,4′-bipy)**1**] with 2,2′-bipy (1 equiv per Cu^{I}) resulted in the formation of dinuclear complex **2** and the liberation of **A** (Scheme 1 vii–ix; Supporting Information, Section 4, Figures S69–S71).

The guest-binding ability of **1** relies on coordination to the porphyrinic Zn^{II} centers. Titrating planar aromatics of different degrees of electron richness and sizes into a solution of [(4,4′-bipy)**1**] did not result in host–guest encapsulation, indicating that this system is selective for coordinating guest molecules (for more details, see the Supporting Information, Section 7 and Figure S75). The other coordinating ligands DABCO, triethylamine, quinoline, isoquinoline, quinine, and quinidine did not exhibit well-defined binding, which is presumably due to steric clashes with the host or geometric constraints (Supporting Information, Figures S76–S79).

In conclusion, a simple one-pot synthesis of a heteroleptic rhomboidal diporphyrin prism has been demonstrated using mixed tetratopic iminopyridyl and ditopic phosphine ligands with copper(I). This heteroleptic approach provides access to an unusual slipped-cofacial porphyrin–porphyrin geometry, which resulted in dual *endo* and *exo* binding modes in response to 3,3′-bipy and 4,4′-bipy, contrary to the binding preferences of other porphyrin-based hosts.[10,16,18] Complete transformation of prism **1** into a simpler dinuclear complex occurred upon treatment with 2,2′-bipy. Studies to expand the generality of this heteroleptic self-assembly methodology towards the formation of cages with different multitopic pyridylimine and phosphine ligands are currently underway.

Keywords: heteroleptic complexes · host–guest systems · N ligands · porphyrin assemblies · self-assembly

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