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Five-component trigonal nanoprism with six dynamic corners

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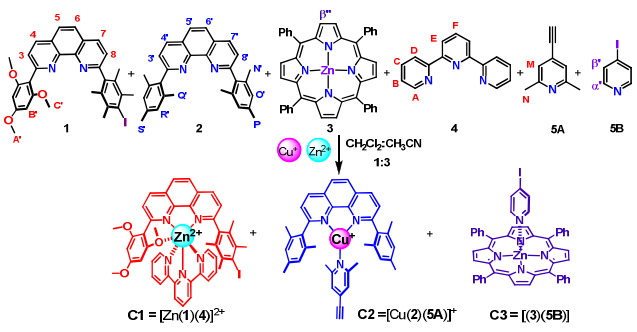
The metallo-supramolecular trigonal prism P is based on five different components and three unlike dynamic coordination motifs: the heteroleptic phenanthroline-terpyridine complex $[Zn(1)(4)]^{2+}$ (HETTAP), the heteroleptic phenanthroline-pyridine complex $[Cu(2)(5A)]^{+}$ (HETPYP-I), and the pyridine → zinc(II)-porphyrin interaction.

Nature combines structurally different components to develop functional three-dimensional assemblies that have inspired chemists to design, synthesise and study artificial heteroleptic assemblies through self-sorting.[1-4] While most of them represent two-dimensional objects, the state-of-art being defined by seven-component assemblies,[5,6] recently Clever[7] and Crowley[8] independently reported on sophisticated 3D heteroleptic coordination cages comprising three different components. Furthermore, Nitschke identified the unprecedented guest(G)-induced transformation of the three-component homometallic $G\subset Fe^{II}_4L_6$ into the four-component heterometallic coordination cage $G\subset Cu^{I}Fe^{II}_2L_4$ after addition of copper(I) ions.[9] As there is a lot of interest to increase the number of components for implementing intricate functions in supramolecular 3D assemblies that go beyond guest complexation, such as demonstrated in multi-component rotors,[10-12] we are inspired to push the limits of 3D multi-component assembly. Increasing the number of components in a dynamic self-assembly process, however, means that also the number of counter-productive interactions is augmented often leading to undesired chemical species.[13] Benefiting from our experience with multi-component self-assembly,[5,6,14] we report herein on the synthesis of a five-component heterometallic supramolecular trigonal prism that encompasses six dynamic cornerstones using three different coordination motifs.

To construct a five-component trigonal prism with three different dynamic coordination motifs requires non-interfering binding algorithms to prevent the formation of alternative 2D and 3D assemblies.[15] For this purpose, we capitalised on the HETTAP (HETeroleptic Terpyridine And Phenanthroline)[16] and HETPYP-I (HETeroleptic PYridine and Phenanthroline-I)[17] algorithms, which are fully orthogonal to each other[18] if properly instructed, as well as on the well-known pyridine → zinc(II) porphyrin (N_{py} → ZnPor) interaction. To avoid any interference between the N_{py} → $[Cu(phen)]^{+}$ (=HETPYP-I)[17] and N_{py} → ZnPor motifs, we selected 2,6-lutidine and pyridine. 2,6-Lutidine has a weak binding to ZnPor (log K = 1.82 in DCM to zinc(II) tetraphenylporphyrin)[19] and thus is not able to compete with the parent pyridine ligand (log K = 3.78) at ZnPor.[19]

To investigate the fidelity of self-sorting, equimolar quantities of ligands **1**–**5**, Cu^{+} and Zn^{2+} in CH_2Cl_2–CH_3CN (1:3) were heated to reflux for 3 h. The selective formation of complexes **C1**, **C2** and **C3**, as verified by ^{1}H–NMR (Figure 1 and Scheme 1) and for **C1** and **C2** by electrospray ionisation mass spectroscopy (ESI–MS), is guided by *maximum site occupancy*[20] and coordination preferences of the metal ions (Figure S52, ESI†).[18,21] Formation of the strong HETTAP complex **C1** = $[Zn(\mathbf{1})(\mathbf{4})]^{2+}$ is due to additional dipole interactions between the –OMe group and Zn^{2+} (log $\beta \cong 14$[18]). The complexes $[Cu(\mathbf{2})(\mathbf{5A})]^{+}$ and **C3** = $[(\mathbf{3})(\mathbf{5B})]$ are formed preferably over $[Cu(\mathbf{2})(\mathbf{5B})]^{+}$ and $[(\mathbf{3})(\mathbf{5A})]$



Scheme 1. Representation of 3–fold completive mixture of complexes **C1**, **C2** and **C3** self-sorted from eight components.

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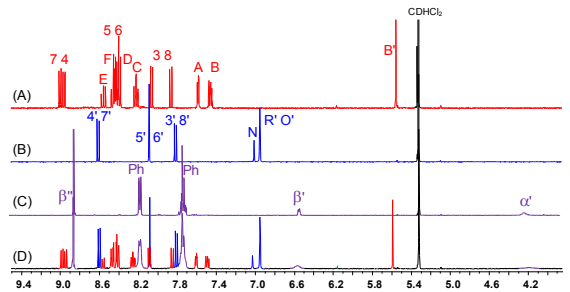


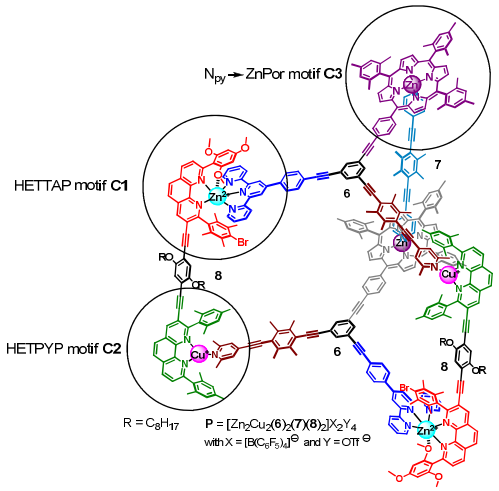
Figure 1. Partial ^{1}H NMR spectra (400 MHz, 298 K, CD_2Cl_2:CD_3CN, v/v, 9:1) for comparison (A) **C1**, (B) **C2**, (C) **C3** and (D) equimolar mixture of **1**, **2**, **3**, **4**, **5A**, **5B**, $[Cu(MeCN)_4]B(C_6F_5)_4$ and $[Zn(OTf)_2]$ = **C**.

(Figure S32, ESI†) because of (i) the sterically inhibited binding of lutidine **5A** to ZnPor and (ii) the strong binding of lutidine **5A** to [Cu(**2**)]$^+$ (log *K* = 4.50 in DCM, ESI†, Figure S54) as compared to that of **5B** to [Cu(**2**)]$^+$ (log *K* = 3.00 in DCM).[18]

After these model studies, we designed the dynamic five-component supramolecular prism **P** (Scheme 2) making use of the three different coordination motifs and molecular modelling (*vide infra*): prism **P** comprises twice (i) the **C1** (HETTAP), (ii) the **C2** (HETPYP-I), and (iii) the **C3** ($N_{py} \rightarrow$ ZnPor) motifs.

As building blocks for **P**, we conceived the trisubstituted panel **6** (Scheme 3A) with its three distinct binding sites, i.e. the ZnPor, terpyridine and 2,6-lutidine terminals. The two pillars **7** and **8** were designed for complexation at the respective corners (**C1**, **C2** and **C3**-type) of ligand **6** (Scheme 3B,C).

For affixing the different coordination terminals to panel **6**, we decided to sequentially connect the terpyridine, ZnPor and 2,6-lutidine units to 1,3,5-tribromobenzene (**9**) by applying a series of Pd-catalysed Sonogashira cross-coupling reactions. Initially, the reaction of trimethylsilylacetylene with 5.0 equiv of **9** in triethylamine afforded the mono-coupled product **10**[22] in 87% yield. Thereafter, the ethynyl-substituted terpyridine **11**[23] and zinc porphyrin **13**[24] were sequentially reacted with dibromo compound **10** by applying standard Sonogashira cross-coupling conditions to yield the ZnPor-terpyridine hybrid **14** in 75% yield (over two steps). Compound **14** was then

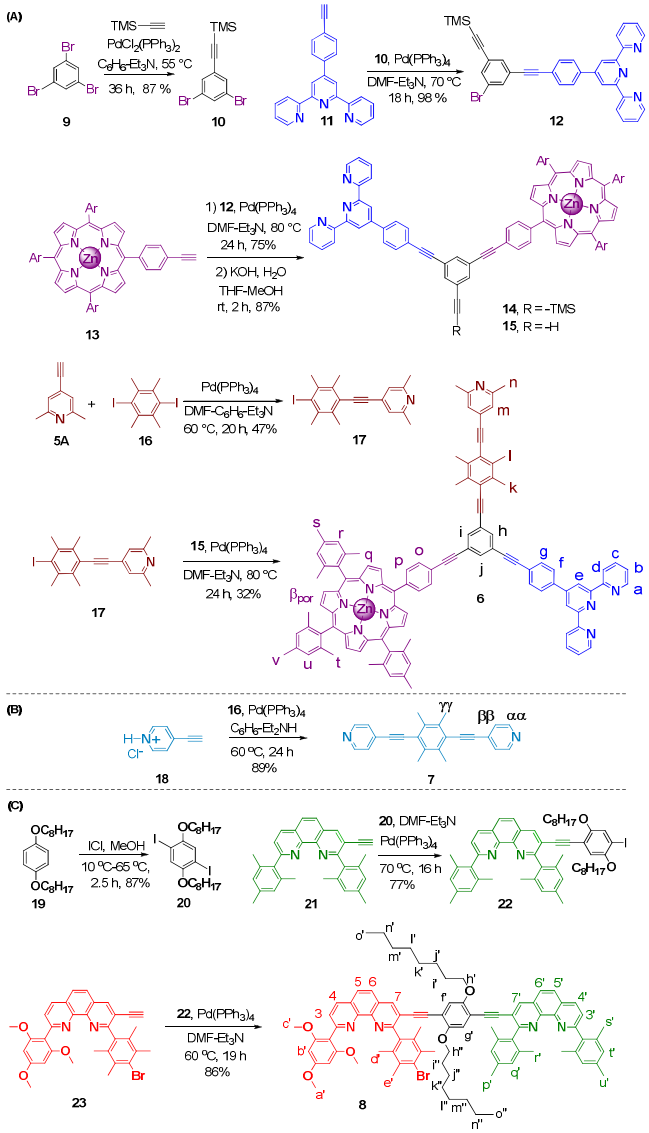


Scheme 2. Five-component nanoprism **P**.

deprotected under aqueous basic conditions in THF / MeOH to furnish compound **15** in good yield.

Synthesis of 2,6-lutidine segment **17** was accomplished by treating 4-ethynyl-2,6-dimethylpyridine (**5A**)[25] with 5.0 equiv of **16**[26] in presence of Pd(0) as a catalyst in a mixture of DMF, benzene and triethylamine. Finally, the terminal alkyne **15** was reacted with 4.0 equiv of aryl iodide **17** in DMF and triethylamine at 80 °C affording the desired panel **6** in 32% yield (Scheme 3A). Synthesis of the bipyridine pillar **7**[27] was achieved in 89% yield by treating 4-ethynylpyridine hydrochloride and **16** under optimised reaction conditions (Scheme 3B).

The synthesis of pillar **8** was completed in three steps. Arene **19**[28] was subjected to iodination by reaction with iodine monochloride in MeOH to furnish compound **20**.[28] Afterwards, phenanthroline **21**[29] was cross-coupled with **20** in presence of Pd(0) as a catalyst to yield **22**, which was reacted with



Scheme 3. (A) Synthesis of tris-substituted ligand **6**, (B) synthesis of ligands **7** and (C) ligands **8**.

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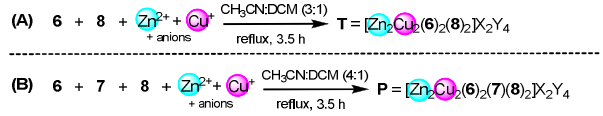
phenanthroline **23**[30] in DMF and triethylamine at 60 °C furnishing pillar **8** in 86% yield (Scheme 3C).

At first, we prepared tweezer **T** = $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2]X_2Y_4$ (X = $B(C_6F_5)_4$; Y = OTf), which represents prism **P** = $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})_2]X_2Y_4$ without pillar **7** between the two zinc porphyrin sites (Scheme 4A). Ligands **6**, **8**, $Zn(OTf)_2$ and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ were thus refluxed for 3.5 h in CH_3CN/DCM (v/v, 3:1) furnishing **T** in 95% yield.



Scheme 4. (A) Synthesis of four-component tweezer **T** and (B) five-component supramolecular nanoprism **P**. Anions: X = $B(C_6F_5)_4$; Y = OTf.

After evaporation of the solvents, tweezer **T** was analysed by ^1H, ^1H–^1H COSY NMR, UV-vis and ESI–MS spectroscopy. The diagnostic ^1H NMR signals of terpyridine protons a-H, b-H and c-H of **6** are shifted from δ = 8.73, 7.39 and 7.92 ppm to δ = 7.66, 7.52 and 8.32 ppm, respectively, together with an upfield shift of proton b'-H of ligand **8** from δ = 6.25 to 5.60 ppm crisply confirming the formation of HETTAP complex (Figure 2B and ESI†, Figures S36 and S37).[31] The ESI–MS of the final reaction mixture exhibits peaks at 1576.2 and 1231.3 Da that correspond to $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{8})_2]^{6+}$ with two or one counter anion(s), respectively (ESI†, Figure S53). The experimental isotopic splitting pattern of the peak at 1231.3 Da is in good agreement with the theoretical isotopic splitting.

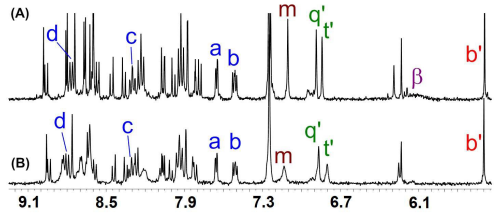


Figure 2. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2:CD_3CN, v/v, 9:1, 298 K) for comparison: (A) prism **P**. (B) tweezer **T**.

Although formation of tweezer **T** as a subpart of prism **P** was not fully completive, we decided to implement it into the one-pot synthesis of **P** (Scheme 4B), expecting that the prism would profit from cooperative effects. Indeed, a titration (ESI†, Figure S57) revealed a strong binding of **7** to tweezer **T** (log K = 9.29 ± 0.04). All components (**6**, **7**, **8**, $[Cu(CH_3CN)_4]B(C_6F_5)_4$ and $Zn(OTf)_2$ were thus mixed in a 2:1:2:2:2 ratio and refluxed for 3.5 h (4:1, v/v, CH_3CN/DCM). After evaporation of the solvents, the resultant mixture was analysed by ^1H, ^1H-^1H COSY, diffusion-ordered (DOSY) NMR and ESI–MS spectroscopy. The presence of all three complexation motifs **C1-C3** in the metallo-supramolecular nanoprism was confirmed on the basis of ^1H–NMR spectroscopy (Table 1, ESI†, Figures S38, S39). For instance, (i) the characteristic downfield shifts of terpyridine protons b-H, c-H and d-H (ligand **6**) from δ = 7.39, 7.92 and 8.69 to 7.53, 8.32 and 8.78 ppm, and the upfield shift of a-H from δ = 8.73 to 7.67 ppm together with proton b'-H of ligand **8** being upfield shifted from δ = 6.25 to 5.61 ppm collectively corroborate the formation of the HETTAP corner, (ii) the slight downfield shifts of mesityl protons q'-H and t'-H of ligand **8** from δ = 6.97 and 6.95 to 6.90 and 6.86 ppm reveal the formation of the HETPYP-I corner, and (iii) the broad singlets at δ = 6.14 (ββ-H) and 3.65 ppm (αα-H) suggest sandwich type complexation of ligand **7** between two ZnPor units of two panels **6** (Scheme 2).

In the UV-vis spectrum of **P** (in DCM), the Soret band is situated at 428 nm, which confirms the presence of **C3**-type complexation units (ESI†, Figure S55).[32] As the Soret band of **C3** shows a shoulder when the complex is partially dissociated, the shoulder-free absorption band of **P** at 428 nm indicates a fully closed prism structure (ESI†, Figure S55). In addition ^1H-^1H COSY and diffusion-ordered spectroscopy (DOSY) NMR corroborate the formation of the intact trigonal prism with a single diffusion coefficient of $D = 3.1 \times 10^{-10}$ m^2 s^{-1} ($r \sim 17.1$ Å, ESI†, Figure S40). Without any further purification the resultant greenish-purple solution was then characterised by ESI–MS spectroscopy. The ESI-MS data of the mixture exhibit signals at 1298.3 and 1403.8 Da denoting $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})_2(OTf)]^{5+}$ and $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})_2\,B(C_6F_5)_4]^{5+}$, respectively, providing strong evidence for the formation of nanoprism **P** (Figure 3), while other signals (e.g. at 1231.2 Da) are derived from fragmentation of **P**.

The MM^+-minimised **P** (Figure 4) shows a slightly distorted prism structure because the pillars **7** and **8** have a different length so that both panels **6** are slightly tilted against each other: the Cu^+(HETPHEN)-Zn^{2+}(HETTAP) distance is 1.77/1.79 nm, the Zn_{ZnPor}-Zn_{ZnPor} distance is 2.05 nm (ESI†, Figure S41).

Table 1. Comparison of selected ^1H NMR chemical shifts (CD_2Cl_2:CD_3CN = 9:1, 400 MHz, 298 K) of model complexes **C1**, **C2** and **C3** with prism **P**. **C** = **C1**+**C2**+**C3**. For complete data see ESI†.

Unit	Terpyridine-H		Dimesityl Phen-H		Trimethoxyphenyl-Phen-H			λ_{max} /nm[a]	Pyridine α'/αα β'/ββ	
	A/a	B/b	O'/t'	R'/q'	B'/b'	7	4			
C1	7.67	7.55	–	–	5.61	9.00	8.96	–	–	–
C2	–	–	6.95	6.95	–	–	–	–	–	–
C3	–	–	–	–	–	–	–	427	4.25	6.55
6/8	8.73[b]	7.39[b]	6.95[c]	6.97[c]	6.25[c]	8.46[c]	8.27[c]	421[b]	–	–
C	7.62	7.49	6.96	6.96	5.58	8.96	8.94	426	4.20	6.58
T	7.66	7.52	6.80	6.87	5.60	8.96	8.94	421	–	–
P	7.67	7.53	6.86	6.90	5.61	9.00	8.98	428	3.65	6.14

[a] Absorption maximum of Soret band. [b] Ligand **6**. [c] Ligand **8**.

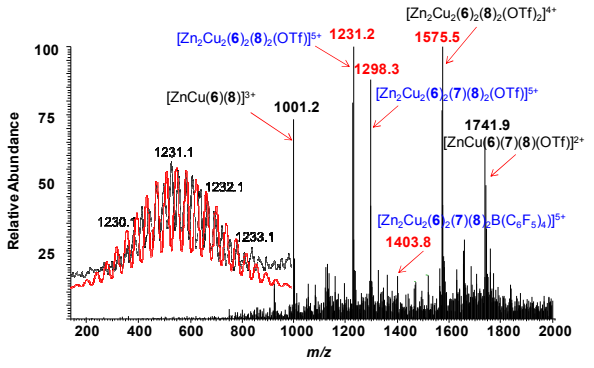


Figure 3. ESI-MS spectra of **P** = $[Zn_2Cu_2(\mathbf{6})_2(\mathbf{7})(\mathbf{8})_2](B(C_6F_5)_4)_2(OTf)_4$ in DCM:CH_3CN = 9:1.

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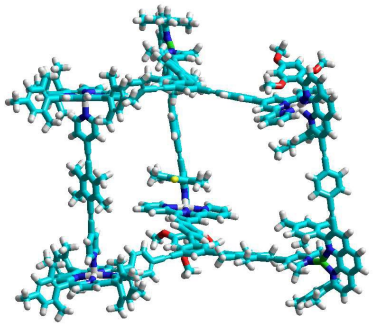

Figure 4. MM^{+} minimised structure of **P**.

In conclusion, we have blended three orthogonal binding motifs, i.e. HETTAP (**C1**-type), HETPYP-I (**C2**-type) and py→ZnPor (**C3**-type) complexation to build the dynamic heterometallic ($M_2M'_2L_2L'_2L''$) nanoprism **P**. This five-component assembly adds a new facet to the large family of trigonal two-component (M_2L_3),[33] (M_3L_2),[34] (M_6L_2)[35] or (M_6L_3),[36] three-component ($M_3L_2L'_6$)[37] or ($M_6L_2L'_3$)[38] and four-component ($M_6L_3L'_2L''$)[39] prisms.[40] To the best of our knowledge, the assembly **P** is the first five-component heterometallic supramolecular nanoprism with three different dynamic corners. Such heteroleptic structures should allow tailoring of smart compartments for selective reactions and extractions.[41]

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