Void and filled supramolecular nanoprisms—notable differences between seemingly identical construction principles†

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Void and filled supramolecular nanoprisms (void: 4900 Å^3) were furnished in quantitative yield utilising the (terpyridine)-Zn^{2+}-(phenanthroline) complex as a dynamic and heteroleptic building motif (HETTAP approach), but only if units serving as panels and pillars in the self-assembly were optimised with regard to their kinetic behaviour.

Metallosupramolecular prisms obtained through self-assembly[1] have been studied not only for their interesting architecture[2] but also for their ability to act as host–guest systems.[3] Using the 2,4,6-trispyridyl-1,3,5-triazine as panels, an assortment of bipyridines as pillars, and palladium(II) ions as coordination corners Fujita *et al*. prepared triangular prisms, which allowed accommodation of exciting π–π stacked pyrenes[3d] or porphyrin dimers[3g] in their cavity. Recently, even nonameric aromatic stacks were realised from interpenetrated coordination cages.[4] As a rule, host–guest interactions in those prisms were designed *via* non-covalent bonding.

Herein, we want to report void and filled nanoprisms conceived on the basis of the HETTAP concept (HETeroleptic Terpyridine And Phenanthroline aggregation).[5] Our concept relies on the formation of heteroleptic pentacoordinated metal centres, such as zinc(II) or copper(I) ions, surrounded by [1,10]-phenanthroline and terpyridine ligands. Due to the heteroleptic arrangement, there exist two seemingly identical strategies for constructing the projected prisms: the first protocol uses a trisphenanthroline as the panel, *e.g*. **TP**, and a bisterpyridine, such as **BT**, as the pillar (Fig. 1a). By contrast, the second method utilises a tristerpyridine as the panel, *e.g*. **TT**, and a bisphenanthroline such as **BP1** as the pillar (Fig. 1b). While both approaches to nanoprisms are thermochemically alike with regard to enthalpic and entropic contributions, as six identical heteroleptic (terpyridine)-Zn^{2+}-(phenanthroline) complex units are formed, we see remarkable differences in their reliability. The present study identifies the disparities of both protocols and analyses reasons why method 2 is much more successful than approach 1.[6]

Ligands used in the present report are depicted in Scheme 1. To assist the heteroleptic self-assembly process conceived on the basis of the HETTAP concept,[5] building blocks **TP**, **BP1** and **BP2** were encoded with the required bulky methylaryl groups in the 2,9-positions of each phenanthroline unit. These prevent association to homoleptic [Zn(phenanthroline)$_2$]$^{2+}$ complexes. While **BP1** and **BP2** have been reported earlier,[5c] ligands **TP** and **TT** were synthesised *via* sequential Sonogashira coupling protocols (ESI†).

It is important to note that method 1 did not reproducibly lead to quantitative formation of the projected prism **P1**. For example, in an attempt to prepare **P1** 3 equivalents of Zn(CF$_3$SO$_3$)$_2$ were added to **TP** in dichloromethane–acetonitrile (8 : 2) followed by heating at 40 °C for 5 minutes. Thereafter, bisterpyridine **BT** in chloroform was added.[7] Although ESI-MS spectra of this solution displayed two weak signals indicative of prism **P1**, *i.e*. at 1173.2 and 1501.9 Da for the 5+ and 4+ charged **P1**, the main set of signals arose from [Zn$_4$(**TP**)$_2$(**BT**)$_2$]$^{n+}$ and [Zn$_2$(**BT**)$_2$]$^{n+}$ attesting incomplete formation of the prism (Fig. S13, ESI†). Moreover, the ^{1}H-NMR spectrum of **P1** provided a set of strongly broadened signals (Fig. S14, ESI†), witnessing that **P1** was formed in equilibrium with other structures. Equally, clean preparation of the analogous copper(I) prism **P2** failed, in spite of the fact that a (terpyridine)-Cu$^+$-(phenanthroline) complex is more stable and kinetically labile than the alike Zn^{2+} complex.[5a,d] Besides, it should be noted that self-assembly along method 1 fails for prism structures independent of size.[6]

In contrast, method 2 led to quantitative formation of nanoprisms **P3** and **P4** without any problems. By following the same self-assembly protocol as for **P1** but now using **TT** as the panel and **BP1** and **BP2** as pillars, **P3** and **P4** were afforded. In both cases, ESI-MS spectra witnessed the clean formation of the prisms. Accordingly, in the ESI-MS spectrum of **P3** the full series of signals, being quite characteristic

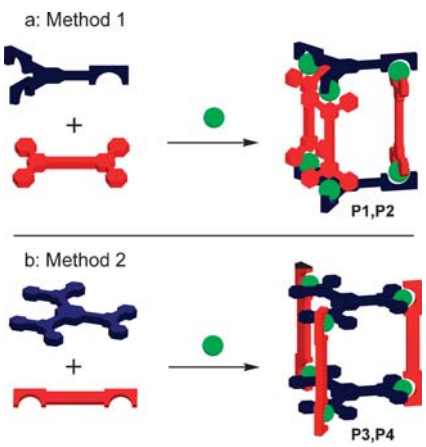

Fig. 1 Pictorial representation of two concepts for the assembly of nanoprisms by the HETTAP approach. **P1** = [Zn$_6$(**TP**)$_2$(**BT**)$_3$]$^{12+}$, **P2** = [Cu$_6$(**TP**)$_2$(**BT**)$_3$]$^{6+}$, **P3** = [Zn$_6$(**TT**)$_2$(**BP1**)$_3$]$^{12+}$, **P4** = [Zn$_6$(**TT**)$_2$(**BP2**)$_3$]$^{12+}$.

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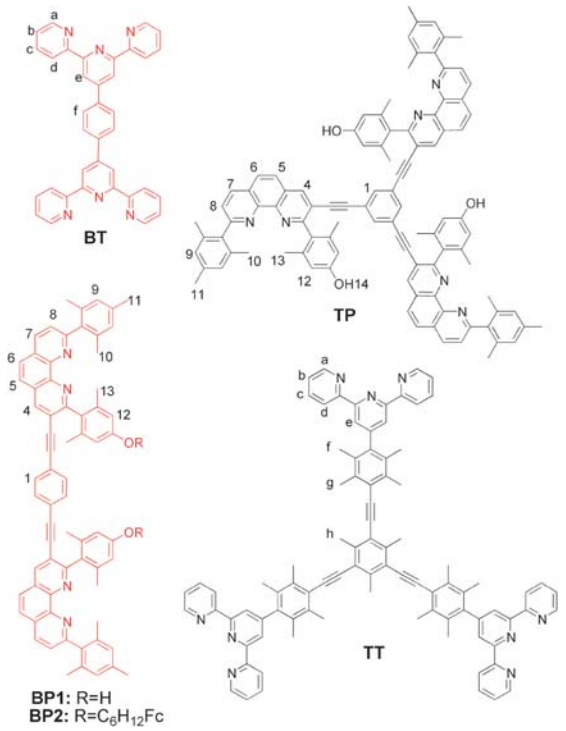

Scheme 1 Ligands used to generate nanoprisms.

because of its charge pattern covering all species from 4+ to 11+, was unequivocally assigned to the nanoprism (Fig. 2). Besides, the isotopic splitting of all charged species matched exactly the theoretical ones (see inset of Fig. 2). The ESI-MS spectrum of **P4** (Fig. S20, S21, ESI†) showed the same characteristic pattern as that of **P3**, again indicative of the nanoprism structure.

The ^{1}H-NMR spectra of **P3** and **P4** (see Fig. 3) displayed only one set of signals, witnessing equally the successful and clean preparation of the prisms. Proton signals from the bisphenanthroline units in **P3** or **P4** were shifted significantly downfield as compared to those of free **BP1**, with shifts being comparable for both prisms. Protons of the phenanthroline 2,9-aryl groups in **BP1**, **BP2** were shifted from 6.60/6.98 ppm in the free ligands to 6.08/6.28 ppm in **P3** and 5.96/6.31 ppm in **P4**. Interestingly, the ^{1}H

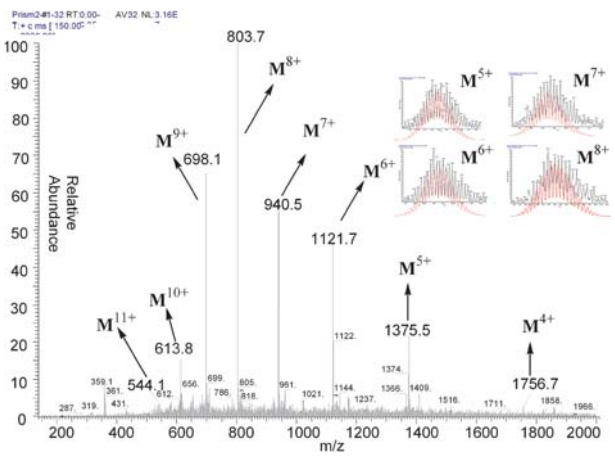

Fig. 2 ESI-MS spectrum of **P3**. The inset shows the experimental (black) and theoretical (red) isotopic distributions, charged from 5+ to 8+.

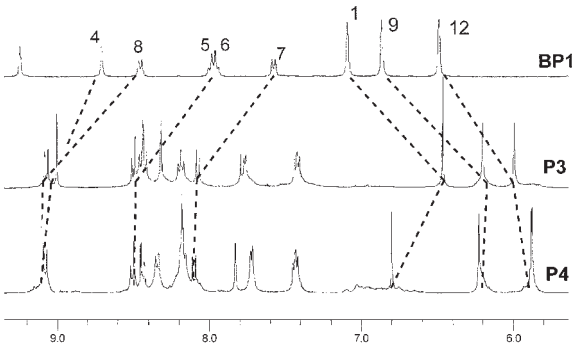

Fig. 3 ^{1}H-NMR spectra of ligand **BP1** and prism **P3** and **P4**.

NMR signal of the central benzene ring in **BP1**, **BP2** was shifted from 7.20 ppm to 6.54 ppm in **P3** ($\Delta\delta$ = 0.66 ppm) but much less in **P4** to 6.88 ppm. The remarkable shift difference is attributed to the different environment of the central **BP1**, **BP2** benzene ring in **P3** and **P4** caused by the ferrocene units (see Fig. 4).

The electronic situation of the ferrocene units in prism **P4** was evaluated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). An earlier report[5c] about ferrocene-filled nanoladders had indicated that the redox potential reflected the average distances of the ferrocene iron atoms held together in the supramolecular framework. The smaller the average distance, *i.e.* 29.5 Å, 18.5 Å and 15.2 Å, the more anodically shifted was the redox potential of the ferrocene units, *i.e.* 0.462, 0.480 and 0.491 V *vs.* DMFc (decamethyl ferrocene). CV and DPV results of **P4** illustrated that the ferrocene units had an oxidation potential of 0.477 V *vs.* DMFc (Fig. S5, ESI†), suggesting an average distance of the six ferrocene iron atoms in prism **P4** of around 22 Å. Evaluation of the average distances of the six ferrocene iron atoms in prism **P4** from a HyperChem® energy minimised structure provided a value of 20.8 Å (Fig. 4), being very close to 22 Å. As the HyperChem® structure of prism **P4** revealed a cavity with a large void of about 4900 Å^3 (calculated from the distances of the Zn^{2+} coordination centres), in principle the inner space should be sufficiently large to accommodate all six ferrocene units inside the prism. However, due to the large pores and flexible hexamethylene linkers the attached redox centres assume the biggest possible distances between the positively charged ferroceniums.

What is the reason for the failure of method 1 and success of method 2 in forming nanoprisms? Why do nanoprisms form quantitatively along pathway 2 but only as a component in an equilibrium in route 1? Based on thermochemical reasoning, there is no obvious difference between the two pathways: both are equivalent with regard to enthalpic (six identical terpyridine-Zn^{2+}-phenanthroline complex units are formed) and overall

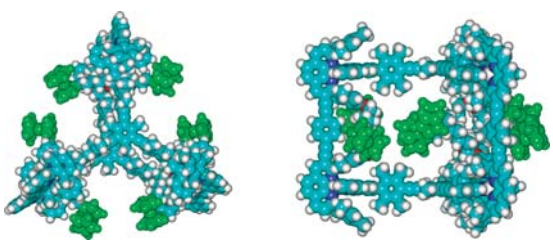

Fig. 4 HyperChem® structure of prism **P4**. The atoms/groups are colour coded for clarity: carbon: cyan; nitrogen: blue; oxygen: red; zinc: *hidden*; ferrocene group: green. Left: top view; right: side view.

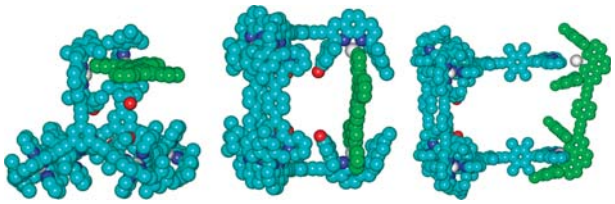

Fig. 5 Illustration of the final step of the self-assembly of **P1** along route 1 (left and middle) and **P3** along route 2 (right). The atoms and the last ligands are colour coded for clarity: carbon: cyan; nitrogen: blue; oxygen: red; zinc: white; last **BT** and **BP1**: green.

entropic contributions. As a consequence, one is apt to assume that route 1, which does not work well, has a kinetic barrier. As there is no kinetic barrier in the generation of simple [2 + 2]-ladders from bisphenanthrolines and bisterpyridines,[5] the most likely reason for a kinetic impediment lies in the last step of the self-assembly process along method 1: herein one needs the last bisterpyridine to clip in sideways against some steric bulk (Fig. 5, left and middle).

Assuming a kinetic barrier in the last step of route 1 and no kinetic barrier for the last step of pathway 2 seems to make sense at first: in approach 2 the binding direction of panel **TT** is pointing outside allowing the third bisphenanthroline to slide on without any steric hindrance (Fig. 5, right). In contrast, self-assembly along method 1 requires an approach of **BT** sideways from the binding direction of the free phenanthroline unit in **TP** as any other approach is sterically impeded by the 2,9-aryl groups. Although the angle between the binding sites of **TP** and **BT** can arrange at anything in between 45 and 135°,[8] this flexibility does not help much for a sideways slip-in motion (Fig. 5).

While the above rationalisation seems to be convincing at first, it can not be maintained after an in-depth evaluation. Control experiments for approach 1 showed that raising the temperature up to 79 °C did not increase the yield. Neither ^{1}H NMR at higher temperature, nor at room temperature (after various times at elevated temperatures) showed any significant changes in the spectra. Such finding clearly argues against a kinetic barrier. Equally, the finding of a templating effect in nanoprisms formed along pathway 1 argues against a kinetic barrier; such effect should not lower a kinetic barrier.[6]

A hypothesis consistent with all findings suggests that oligomeric terpyridine complexes, such as $[Zn_n(\mathbf{BT})_m]^{2n+}$ or $[Zn_n(\mathbf{TT})_m]^{2n+}$, are thermodynamically competitive with the nanoprisms. Along route 1, side products $[Zn_n(\mathbf{BT})_m]^{2n+}$ are able to form because the last step to **P1** is slow. This allows the components to explore the global energy hypersurface for thermochemically competitive structures, such as mononuclear and oligomeric zinc(II) bisterpyridine complexes. In that way, a reasonably high concentration of $[Zn(\mathbf{BT})]^{2+}$ builds up initiating formation of oligomeric complexes. Along pathway 2, oligomeric complexes of **TT** do not arise as the global minimum structure **P3**, **P4** is reached rapidly. Fast formation of the prism structure generates a kinetic barrier of thermodynamic origin. Formation of $[Zn_n(\mathbf{TT})_m]^{2n+}$ complexes by dissociation of the prisms is highly unlikely, as the concentrations of $[Zn(\mathbf{TT})]^{2+}$ and **TT** remain too small.

In conclusion, the novel nanoprisms **P3** and **P4**, *i.e.* $[Zn_6(\mathbf{TT})_2(\mathbf{BP1}_3)]^{12+}$ and ($[Zn_6(\mathbf{TT})_2(\mathbf{BP2}_3)]^{12+}$) were generated quantitatively using a HETTAP guided approach along route 2. Formation of the ferrocene-containing prism **P4** further illustrated the utility of our approach for generating internally functionalised supramolecular structures.

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Notes and references

1 M. Schmittel and V. Kalsani, *Top. Curr. Chem.*, 2005, **245**, 1–53.
2 (*a*) C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner and A. F. Williams, *J. Am. Chem. Soc.*, 1993, **115**, 8197–8206; (*b*) C. J. Kuehl, T. Yamamoto, S. R. Seidel and P. J. Stang, *Org. Lett.*, 2002, **4**, 913–915; (*c*) B. Manimaran, P. Thanasekaran, T. Rajendran, R.-T. Liao, Y.-H. Liu, G.-H. Lee, S.-M. Peng, S. Rajagopal and K.-L. Lu, *Inorg. Chem.*, 2003, **42**, 4795–4597; (*d*) C.-Y. Su, Y.-P. Cai, C.-L. Chen, M. D. Smith, W. Kaim and H.-C. zur Loye, *J. Am. Chem. Soc.*, 2003, **125**, 8595–8613; (*e*) Y. K. Kryschenko, S. R. Seidel, D. C. Muddiman, A. I. Nepomuceno and P. J. Stang, *J. Am. Chem. Soc.*, 2003, **125**, 9647–9652; (*f*) D. Kim, J. H. Paek, M.-J. Jun, J. Y. Lee, S. O. Kang and J. Ko, *Inorg. Chem.*, 2005, **44**, 7886–7894; (*g*) Z.-M. Liu, Y. Liu, S.-R. Zheng, Z.-Q. Yu, M. Pan and C.-Y. Su, *Inorg. Chem.*, 2007, **46**, 5814–5816.
3 (*a*) N. Fujita, K. Biradha, M. Fujita, S. Sakamoto and K. Yamaguchi, *Angew. Chem., Int. Ed.*, 2001, **40**, 1718–1721; (*b*) J. D. Crowley, A. J. Goshe and B. Bosnich, *Chem. Commun.*, 2003, 2824–2825; (*c*) K. Kumazawa, K. Biradha, T. Kusukawa, T. Okano and M. Fujita, *Angew. Chem., Int. Ed.*, 2003, **42**, 3909–3913; (*d*) M. Yoshizawa, J. Nakagawa, K. Kumazawa, M. Nagao, M. Kawano, T. Ozeki and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 1810–1813; (*e*) P. Govindaswamy, D. Linder, J. Lacour, G. Süss-Fink and B. Therrien, *Chem. Commun.*, 2006, 4691–4693; (*f*) S. Tashiro, M. Kobayashi and M. Fujita, *J. Am. Chem. Soc.*, 2006, **128**, 9280–9281; (*g*) K. Ono, M. Yoshizawa, T. Kato, K. Watanabe and M. Fujita, *Angew. Chem., Int. Ed.*, 2007, **46**, 1803–1806; (*h*) K. Ono, M. Yoshizawa, T. Kato and M. Fujita, *Chem. Commun.*, 2008, 2328–2330.
4 Y. Yamauchi, M. Yoshizawa and M. Fujita, *J. Am. Chem. Soc.*, 2008, **130**, 5832–5833.
5 HETTAP: this strategy makes use of steric and electronic effects originating from bulky aryl substituents at the bisimine coordination sites to control the coordination equilibrium both kinetically and thermodynamically. The steric stoppers at coordination sites (2, 9 positions) of phenanthroline prevent any competitive homoleptic combination with itself, therefore leading to just hetero combinations; (*a*) M. Schmittel, V. Kalsani, R. S. K. Kishore, J. W. Bats and H. Cölfen, *J. Am. Chem. Soc.*, 2005, **127**, 11544–11545; (*b*) M. Schmittel, V. Kalsani, P. Mal and J. W. Bats, *Inorg. Chem.*, 2006, **45**, 6370–6377; (*c*) M. Schmittel, B. He, V. Kalsani and J. W. Bats, *Org. Biomol. Chem.*, 2007, **5**, 2395–2403; (*d*) M. Schmittel and P. Mal, *Chem. Commun.*, 2008, 960–962.
6 M. Schmittel, B. He and P. Mal, *Org. Lett.*, 2008, **10**, 2513–2516.
7 This protocol helps to suppress the formation of terpy-Zn(II)-terpy complexes after addition of tristerpyridine ligand **BT**.
8 S. Bonnet, J.-P. Collin and J.-P. Sauvage, *Inorg. Chem.*, 2007, **46**, 10520–10533.