

# Hollow porphyrin prisms: modular formation of permanent, torsionally rigid nanostructures *via* templated olefin metathesis†

Kyoung-Tae Youm, SonBinh T. Nguyen\* and Joseph T. Hupp\*

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**Hollow, hexa-porphyrin prisms of two sizes were template-assembled and covalently locked, *via* cross-olefin metathesis, into permanent, torsionally rigid structures whose active sites (metal sites) can be both accessed and altered in a facile manner.**

Discrete multiporphyrin assemblies have received considerable attention due to their potential in light-harvesting, sensing, molecular transport, and catalysis.<sup>1,2</sup> Ideally, such assemblies should be: (a) easy to construct, (b) persistent and robust, (c) topologically well-defined, (d) hollow (to enable molecular sieving, analyte binding, reactant encapsulation, *etc.*), and (e) highly functional (luminescent, catalytic, *etc.*). Interestingly, while a wide variety of cyclic porphyrin assemblies having one or more of these characteristics exist, few, if any, possess all of them. Two examples from our own labs may serve to illustrate this. The first, a family of  $M_4\text{Por}_4$  “molecular squares” featuring porphyrin edges (Por) and coordinated metal corners (M), are obtainable in high yield by coordinative self-assembly.<sup>3</sup> While suitable for sieving<sup>3d,e,j,i</sup> and sensing,<sup>3c,g</sup> they lack the M-por-M torsional rigidity<sup>3b,e,j,4</sup> and resulting well-defined cavity geometry (ESI†, Fig. S1) needed for strong binding of guests or for highly selective catalysis. A second example comprises porphyrin prisms where replacement of single-porphyrin edges with di-, tri-, or tetra-porphyrin panels enables redundant coordination (directly at porphyrin Zn(II) sites), thereby fixing the overall assemblies and their component panels in well-defined, rigid geometries.<sup>5</sup> Unfortunately, this assembly strategy leaves the porphyrin metal sites blocked and the cavities occupied. Additionally, because the Zn-ligand bonds are weak, the assemblies dissociate in highly polar solvents or at high dilution.

Herein, we demonstrate that templated ring-closing metathesis (tRCM) can be used for the facile preparation of both metallated and metal-free porphyrin prisms possessing all five of the above-mentioned properties, in addition to excellent solubility and chemical stability in high-polarity solvents. We also show that tRCM-prepared assemblies can be demetallated and, if desired, remetallated with the same or other ions, without structural degradation.

Cyclic multiporphyrin assemblies have previously been obtained in high yield *via* a stepwise approach where modular building blocks are organized into the desired shape by a template prior to structure-setting.<sup>6,7</sup> In an elegant example, Anderson and coworkers employed 2,4,6-tris(4-pyridyl)triazine ( $\text{Py}_3\text{T}$ ) as a tem-

plate to assemble three porphyrins into trigonal shapes and then permanently “set” the structure using irreversible Glaser coupling.<sup>7a</sup> Reversible bond formation, referred to as dynamic combinatorial chemistry (DCC), has also been used by Sanders *et al.* to create more flexible disulfide-linked cyclic porphyrin dimers, trimers, and tetramers in the presence of the appropriate templates.<sup>7b,c</sup> Other notable examples deploy the aforementioned tRCM idea to form molecular squares.<sup>6a,b</sup> In each case, however, significant torsional freedom remains in the assembled structure after template removal, potentially reducing its usefulness in applications where structural rigidity is important.

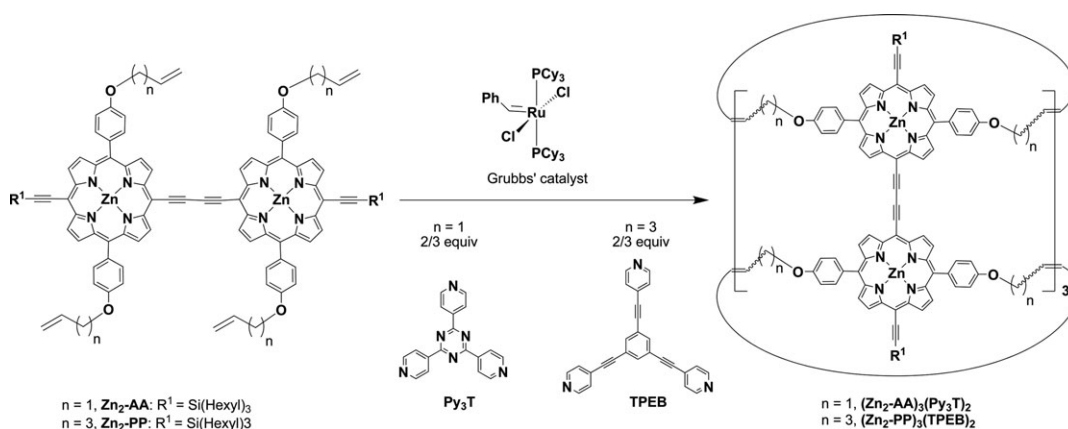
As noted above, we have previously described the reversible assembly of prisms<sup>5</sup> possessing multi-porphyrin panels. Here, we expand upon this strategy to construct torsionally rigid, *permanent* prisms. As proof of principle, we selected panels composed of two Zn(porphyrin) rings fully conjugated through a butadiyne linker (Scheme 1). The judicious use of alkenyloxy and trialkylsilylalkynyl substituents allows these building blocks and their assembled structures to remain fully soluble in solvents such as methylenechloride, toluene, and tetrahydrofuran (THF). As expected, both  $\text{Zn}_2\text{-AA}$  and  $\text{Zn}_2\text{-PP}$  dimers readily bind to Lewis bases such as pyridine and this interaction can be used to pre-organize the panels into assemblies that are ready for tRCM.

Exposing a 3 : 2 molar ratio mixture of  $\text{Zn}_2\text{-AA}$  and  $\text{Py}_3\text{T}$  to Grubbs’ first-generation catalyst<sup>8</sup> in  $\text{CH}_2\text{Cl}_2$  results in the formation of the covalently linked, templated trigonal prism  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$  in high yield (77%) after size-exclusion chromatography.† Similar tRCM of a 3 : 2 molar mixture of  $\text{Zn}_2\text{-PP}$  and tris((4-pyridyl)ethynyl)benzene (TPEB) afforded 76% of the corresponding  $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$  permanent prism. The templates are critical to the formation of the corresponding prisms; only  $(\text{Zn}_2\text{-AA})_2$  or  $(\text{Zn}_2\text{-PP})_2$  (*i.e.*, dimers) form in their absence. In addition, the size of the template must match well that of the corresponding prism; the yield of the covalently stabilized prism  $(\text{Zn}_2\text{-PP})_3$ , for example, is very low when assembled *via* the smaller template,  $\text{Py}_3\text{T}$ .

The identities of  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$  and  $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$  were confirmed by NMR spectroscopy, gel-permeation chromatography (GPC), and MALDI-TOF MS. The  $^1\text{H}$  NMR spectrum of  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$  differs significantly from those for  $\text{Zn}_2\text{-AA}$  and the  $\text{Py}_3\text{T}$  template (ESI†, Fig. S2). While  $\text{Zn}_2\text{-AA}$  exhibits distinct olefinic (6.29(m), 5.64(d), and 5.47(d) ppm) and allylic (4.85(d) ppm) resonances, the olefinic protons of  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$  appear as broad singlets at 6.47 and 6.34 ppm, indicative of both *E* and *Z* conformations. Accordingly, its allyl protons also appear as two discrete singlets at 5.37 and 5.22 ppm. Notably, the chemical shifts of the pyridyl protons of the encapsulated  $\text{Py}_3\text{T}$  template appear at 2.45 and 5.91 ppm, significantly upfield from

Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208-3113, USA. E-mail: stn@northwestern.edu; j-hupp@northwestern.edu; Fax: +1 847-491-7713; Tel: +1 847-467-3347

† Electronic supplementary information (ESI) available: Details of synthesis and spectroscopic data (UV-vis, NMR, GPC, and MALDI-TOF MS). See DOI: 10.1039/b800063h



**Scheme 1** The tRCM syntheses of porphyrinic trigonal prisms. For clarity, template ligands are omitted from the product assembly.

those observed for free  $\text{Py}_3\text{T}$  (8.59 and 8.95 ppm), indicating a strongly shielded environment due to binding of the template within the trigonal prism cavity.<sup>7a,9,10</sup> Similar to that for  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$ , the  $^1\text{H}$  NMR spectrum of  $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$  also shows dramatic changes from those for free  $\text{Zn}_2\text{-PP}$  and TPEB (ESI†, Fig. S2). For example, the olefinic protons (6.00(m), 5.21(d), and 5.12(d) ppm) of free  $\text{Zn}_2\text{-PP}$  disappear and new olefinic protons corresponding to olefin-metathesized  $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$  appear as broad singlets at 5.80 and 5.70 ppm, indicative of a mixture of *E* and *Z* conformers.

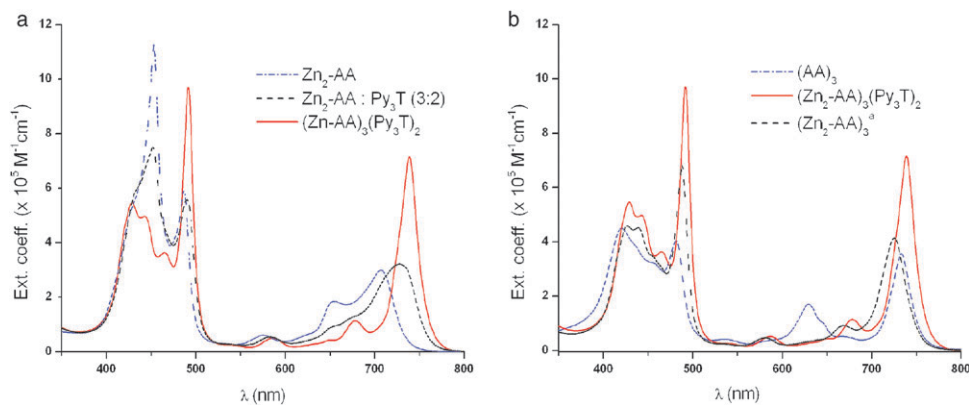
The MALDI-TOF mass spectra (dithranol matrix) of both  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$  and  $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$  exhibited only molecular ion peaks for the zincated prisms, presumably because of removal of the templates during ionization (ESI†, Figs. S5 and S8).<sup>7b,c</sup>

In the gel-permeation chromatograms for purified panels and prisms (ESI†, Fig. S4)—where retention times scale inversely with molecule or assembly size—the prisms appear well before the panels ( $\text{Zn}_2\text{-AA}$  and  $\text{Zn}_2\text{-PP}$ ), with the large-templated prism  $(\text{Zn}_2\text{-PP})_3(\text{TPEB})_2$  eluting first. Comparisons to a previously reported GPC-based size-calibration curve for a family of molecular squares<sup>11</sup> show that the prisms elute in essentially the same time as the largest square examined there: an  $\text{M}_4\text{Por}_4$  assembly comprising of  $\text{Re}(\text{CO})_3\text{Cl}$  corners and dipyriddy-porphyrin edges. While direct comparisons are challenging because of the different assembly shapes, the  $\text{M}_4\text{Por}_4$  square and the current prisms all feature similar cross-sectional

dimensions (albeit, much different depth dimensions). It is also noteworthy that the GPC peak shapes for the prisms are clearly more symmetrical than those for free panels, with the largest prism displaying the most symmetrical shape. All else being equal, a more narrow and symmetrical shape implies a more rigid structure (*i.e.*, less conformational freedom).

Fig. 1 (left panel) compares the electronic absorption spectra for the free panel ( $\text{Zn}_2\text{-AA}$ ), a 3 : 2 molar ratio mixture of  $\text{Zn}_2\text{-AA}$  and  $\text{Py}_3\text{T}$ , and the permanent, covalently linked prism  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$ . Formation of the labile prism from the free panel is marked by intensification of the porphyrin  $\text{B}_y$  band and by narrowing and red-shifting of the  $\text{Q}_y$  band. The narrowing is consistent with dimer panel rigidification and diminution of rotational isomerization.<sup>5,10</sup> The red-shift is consistent with panel planarization and concomitant enhancement of porphyrin–porphyrin electronic coupling, as previously noted by Anderson and co-workers in their studies of “ladder” assemblies of conjugated-porphyrin.<sup>10</sup> Interestingly, tRCM stabilization of the prism results in further Q-band red-shifting and sharpening, implying that the component panels are further planarized and rigidified.

An important consequence of covalently stabilizing cyclic assemblies should be stronger binding of template ligands or other guest molecules, relative to binding by non-permanent structures. While the enthalpy of guest binding should not change (since Zn–N bond strengths are unaffected), pre-organization of the host structure *via* tRCM should considerably lower



**Fig. 1** Left: Electronic absorption spectra of  $\text{Zn}_2\text{-AA}$ ,  $3\text{Zn}_2\text{-AA} \cdot 2\text{Py}_3\text{T}$  (3 : 2 mixture) and covalently linked  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$ . Right: Electronic absorption spectra of covalently linked  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$ , free-base  $(\text{AA})_3$ , and  $(\text{Zn}_2\text{-AA})_3$ . All were examined in  $\text{CH}_2\text{Cl}_2$  as solvent, except  $(\text{AA})_3$ , which was examined in THF.

the entropy of binding. Enhanced binding could be valuable, for example, for improving retention of encapsulated catalysts or for extending host–guest chemistry into higher-polarity solvents. To test the notion of enhanced binding, we compared the abilities of labile and permanent prisms to retain  $\text{Py}_3\text{T}$  when challenged with THF, a competitive ligand for  $\text{Zn}(\text{II})$ . Displacement was monitored by taking advantage of the ability of  $\text{Py}_3\text{T}$ , but not THF, to attenuate the fluorescence of  $\text{Zn}_2\text{-AA}$  when excited at 712 nm (labile assembly) or 723 nm (covalent assembly). For the labile prism, 50% recovery of the full fluorescence emission intensity of  $\text{Zn}_2\text{-AA}$  was observed at  $[\text{THF}] = 0.018 \text{ M}$ . For the covalently stabilized prism, 50% recovery was observed at  $[\text{THF}] = 8.3 \text{ M}$ , *i.e.*, 460× higher.

An additional dividend of covalent stabilization of the prism assemblies should be the ability to remove and/or replace otherwise structurally-crucial  $\text{Zn}(\text{II})$  sites with other metals of interest. We find that the free-base trigonal prism,  $(\text{AA})_3$ , can be readily obtained *via* TFA-demetalation of  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$  in  $\text{CH}_2\text{Cl}_2$  and then purified by size-exclusion chromatography. Interestingly, the analytical GPC peak of purified  $(\text{AA})_3$  appears at about 6.1 min, 0.2 min later than that for  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$  (ESI<sup>†</sup>, Fig. S4), suggesting that the hollow prism is able to distort and sample slightly smaller gel pores than is the more rigid templated structure. Demetalation was confirmed by <sup>1</sup>H NMR spectroscopy (free NH protons at −2.07 ppm; absence of pyridyl (template) protons) and by MALDI-TOF MS (absence of the molecular ion peak for  $(\text{Zn}_2\text{-AA})_3(\text{Py}_3\text{T})_2$  and the presence of a strong signal for  $(\text{AA})_3$  (ESI<sup>†</sup>, Fig. S5)). Fig. 1 (right panel) shows that demetalation introduces additional Q bands, consistent with reductions in porphyrin symmetry upon replacement of  $\text{Zn}(\text{II})$  with protons. Significantly, there were very little changes in the location and breadth of the lowest energy Q band, implying that the porphyrin subunits within each dimeric panel remain coplanar and rigid following prism demetalation. Finally, as detailed in the ESI<sup>†</sup>, the free-base prism  $(\text{AA})_3$  can be easily and completely remetalated with  $\text{Zn}^{2+}$  or  $\text{Co}^{2+}$ .

In conclusion, we have demonstrated that highly conjugated porphyrin dimer panels can be template-assembled into trigonal prisms in solution and permanently “set” into nanoporous assemblies using olefin metathesis. Depending on the lengths of the starting vinyl arms, the assembled structures can be template-adjusted to yield multiporphyrin cavities with various well-defined sizes. Once the structure is “set” by olefin metathesis, the template can be readily removed *via* treatment with Lewis basic ligands, without detriment to the rigid trigonal prism shape. The permanent prisms display much more tenacious guest binding than do their labile counterparts. For the permanent structures, the porphyrin units can be readily demetalated to give the corresponding free-base trigonal prisms, which can be readily remetalated with other functional metals. This strategy lends itself to the preparation of a variety of porphyrinic trigonal prisms possessing tunable metal environments that can be used for molecular recognition, catalysis, or photonic energy transfer. These studies will be reported in due course.

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## Notes and references

† *General tRCM procedure:* Under nitrogen, the dimer panel and template (2 : 3 molar equivalents, ~0.3 mM in dimer) were dissolved together in  $\text{CH}_2\text{Cl}_2$  and allowed to stir for 30 min. A solution of Grubbs’ 1st-generation catalyst (25 mol%) in  $\text{CH}_2\text{Cl}_2$  was then added to this reaction mixture. After stirring at room temperature overnight, the reaction mixture was opened to air and acetone (10 mL) was added. The volatiles were removed from the reaction mixture under reduced pressure using a rotary evaporator. The remaining residue was extracted with  $\text{CH}_2\text{Cl}_2$  and subjected to size-exclusion chromatography (Bio-Rad Bio-Beads S-X1,  $\text{CH}_2\text{Cl}_2$ ) to afford the templated, covalently linked trigonal prisms as a dark solid (>70%).

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