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Nanorings

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A Dynamic Library of Porphyrinic True Nanorings[**]

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nanorings · porphyrinoids · templates

Control over the shape and size of synthesized molecules has been the driving force for chemists over the last few decades. It has been shown that precisely crafted structural motifs play an essential role in many biological processes. The ringlike arrangement is without doubt a special variant of such well-organized structures, and a controllable synthesis of circularly oriented π systems has been the focus of many synthetic efforts. The elegance of the ringlike arrangement was demonstrated by the discovery of the marvelous organization of porphyrinic chromophores in the light-harvesting antenna (LH2) of the purple bacterium *Rhodopseudomonas acidophila*.[1] The incorporation of the circular form into chemical structures creates several intriguing possibilities that opens up an extraordinary perspective for the exploration of unprecedented electronic structures, electron-transfer phenomena, etc. For example, the search for cylinder-like nano-objects has been the stimulus for generating cyclic *p*-phenylenes (e.g. **1**), which are considered as fundamental for the controlled formation of nanotubes.[2] The extended π systems, when arranged into circular patterns, offer a peculiar conformational mode that enables a directed switching between annulus and cylinder geometries. The origin of such a unique flexibility may result from the mutual rotation of the building blocks, which can be frozen to eventually give diverse geometrical shapes. Evidently, the cyclic π-conjugated nanosized molecular ensembles provide promising features for exploring the intriguing facets of intricate molecular electronic structures, including the migration of excitation energy.[3] The ring-shaped molecules and multimolecular arrays erase difficulties intrinsic to the low symmetry inherent to linear forms. The above representative topics illustrate the large variety of stimuli for the synthetic search for circular nanostructures. The literature concerning cyclic porphyrin arrays shows that efforts have been made to construct structures that resemble and mimic the multichromophoric ensemble in the light-harvesting antenna of the purple bacterium. The pioneering studies on covalently bound, porphyrin-based no-ending structures were reported back in the 1990s by Sanders and co-workers.[4]

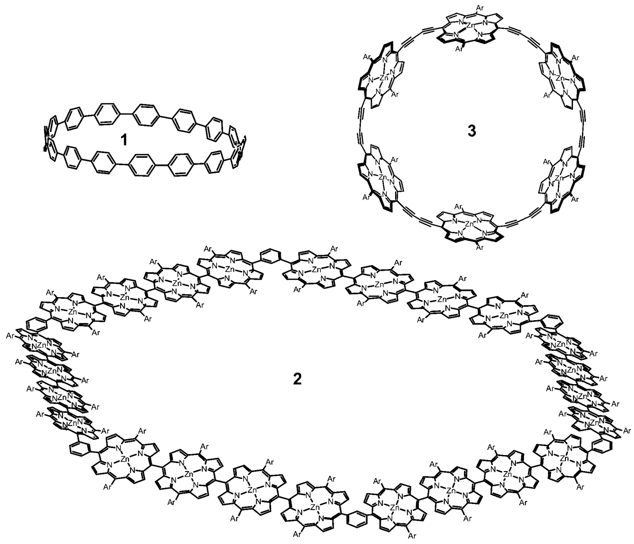

Figure 1. Representative cyclic structures.

The last decade has resulted in remarkable progress being made in the field, as illustrated by the representative examples **1**–**3** in Figure 1. Several fundamentally distinct strategies for creating a ring structure from prearranged porphyrinic (metalloporphyrinic) building blocks are distinguished by the nature of the organizational control over the structure. A templating effect to afford a suitable preorganization has frequently been employed (i.e. to generate **3**).[4] On the other hand, the 24-nanohexagon **2** with a final diagonal distance of 6.5 nm was synthesized starting from directly meso–meso-linked linear units by the dilution approach, which favors intramolecular coupling.[3] The self-assembly approach using covalently linked metallodiporphyrin blocks, utilized by Kobuke and co-workers, also resulted in the formation of nanocylinders, however these cyclic aggregates are constructed by coordination between a central metal ion and the perimeter donor units. The size of the formed molecular belts, determined by the concentration of the porphyrin subunit, reaches a maximum of 22 porphyrins connected in a single circular shape.[5]

In their notably persistent effort, Anderson and co-workers have used a positive templating effect. A palladium-catalyzed reaction of terminal acetylenes of meso-substituted porphyrins, suitably preorganized through coordination to a template, gave 6- (Figure 1, **3**)[6] and 8-nanorings.[7] Such an approach eventually produced a figure-of-eight 12-nanoring with two templates entrapped in the nanoring,

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which has recently been highlighted.[8,9] In their recent remarkable studies, Anderson and co-workers mastered their method.[10] Consequently, they were in a position to elaborate their method to a very elegant synthesis of sizeable nanorings, including a record-breaking structure which encompasses 24 porphyrins in a 10 nm diameter cycle. These nanorings are generated by a Vernier-templating self-organization of hexa- or octadentate templating units (**4** and **5**, Figure 2) that efficiently preorganize the covalently linked hexamer **6** or octamer **7**, which after straightforward Glaser–Hay coupling form the known 12-nanoring, and the novel 16-, 18-, and 24-nanorings (Figure 3).[10] Such an approach provides a promising method to create a variable library of nanorings. Impressively, the reaction can be steered to the required diameter simply by choosing the appropriate template and set of oligomeric substrates (Figure 3). Thus, the combination of **4** and **7** (Figure 3, Path A) results in the formation of a mixture of still-templated structures that, after removal of the inner unit (the template), gives 16- and 24-nanorings. The alternative approach (**5** + **6**; Figure 3, Path B) eventually produces a mixture of 12-, 18-, and 24-nanorings, thus illustrating a combinatorial approach. The removal of the templates is reversible. Thus, the conformational flexibility that is characteristic of the 24-nanoring can be impeded by a reinsertion of the templates. Impressively, the 24-nanoring (c-P24-Zn) may acquire two fundamental conformational limits, corresponding to the idealized annulus and cylinder geometries. The remarkable switching between the annulus and cylinder geometries can be controlled by appropriate choice of the zinc(II) axial ligand: the coordination of didentate DABCO (1,4-diazabicyclo[2.2.2]octane) creates a dimeric structure, whereas two annuli are coplanarized by linking them with 24 DABCO bridges. A similar behavior was observed for the 12-nanoring.[11]

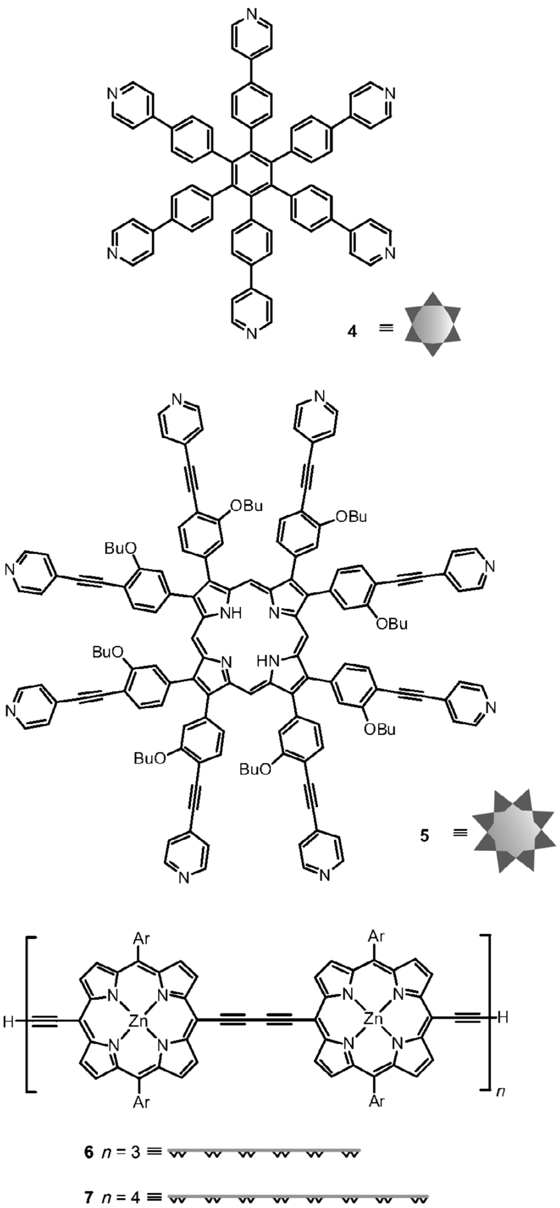

Figure 2. Templates utilized in the formation of nanorings.

The formation of circular structures is still a synthetically demanding challenge. Evidently the most limiting obstacle remaining is a “friendly” access to the nanomaterial necessary for a wider investigation. The dynamic library approach reported by Anderson and co-workers opens up a new chapter that makes available a rational route for the formation of nanorings composed of porphyrinoids. Of course, several difficulties (solubility, separation etc.) still remain, but at this stage it requires some essential synthetic developments that would make the nanorings accessible for the multidisciplinary exploration. In the future, several ambitious goals can be envisaged. For example, the possibility of knotting linear oligomers, as mentioned by Anderson and co-workers, will require nanorings even larger than the 24-nanoring structures if the building block is based on a porphyrinoid. The study of electron transfer in such systems is still in its infancy, and access to different-sized molecules is expected to deliver a correlation between the size of the nanoring and the molecular shape, including different conformations for a given size of the cyclic structures. In our opinion, coordination chemistry will provide the freedom to control the molecular or material properties. Thus, the insertion of different, in particular transition-metal ions, will be instrumental in determining the overall features in terms of the function of the metal ion and/or porphyrin oxidation states, affinity to a given donor atom, or preference for the coordination of one or two axial ligands. In fact, a single nanoring may also afford a specific coordination environment that acts as a poly-heterometallic, but still monomolecular, system, whereas a subtle control of the electronic structure, including the magnetic properties seems to be readily accessible.

From our perspective, the reported structure of (c-P24-Zn)$_2$(DABCO)$_{24}$, with two 24-planarized nanorings linked by 24 bridges, has a water-wheel architecture and brings an incentive for extending such nanostructures into the third dimension.

We have visualized the three-dimensional cylinders as molecular containers with the general formula (c-P24-M)$_2$-(c-P24-M*)$_n$(L)$_{24(n+1),}$ exemplified here for $n = 1$ (Figure 4),

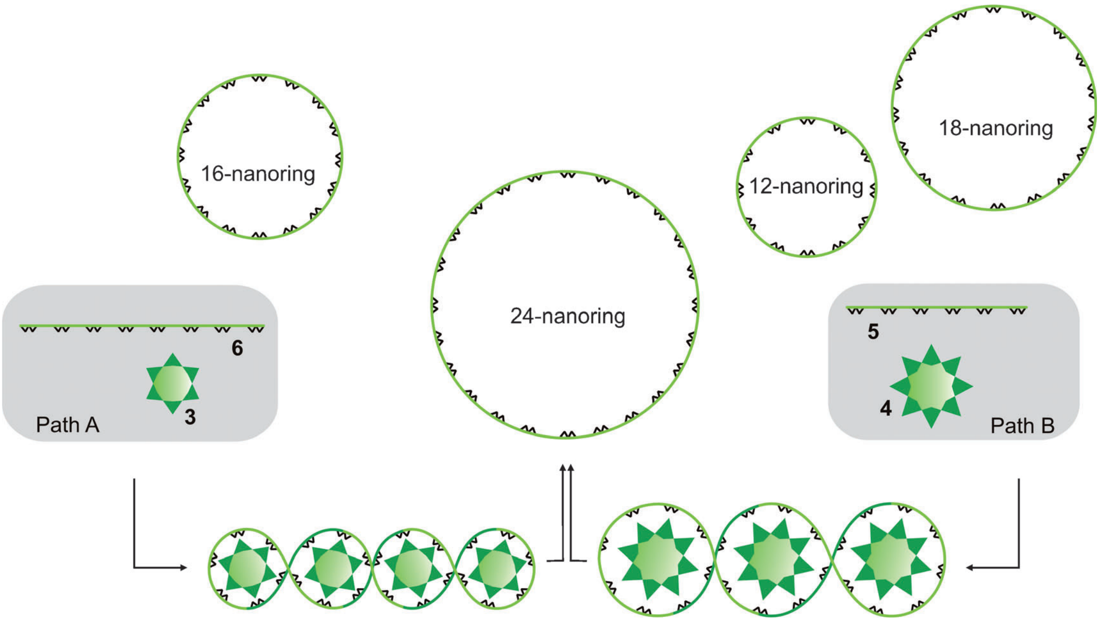

Figure 3. Templated synthesis of nanorings (schematic representations are explained in Figure 2).

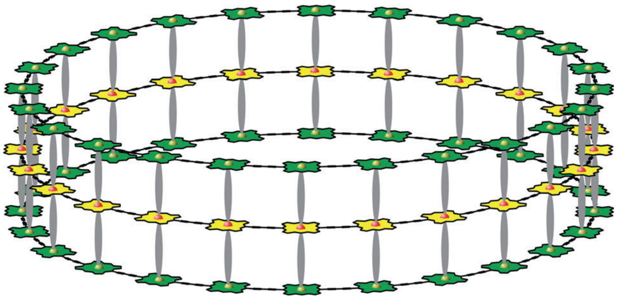

Figure 4. A concept of a three-decker tower constructed from the Anderson rings.

where L is a bridging ligand and M and M* have specific preferences for five and six coordination (i.e. zinc(II) and iron(II) respectively). The chemistry of porphyrinic nanorings offers the potential for extensive exploration. It remains to be seen how the most fundamental factors such as the nature of the porphyrinoid and/or the coordinated metals can control the unprecedented properties of materials encompassing the Anderson rings.

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