Templated Synthesis

Synthesis of Five-Porphyrin Nanorings by Using Ferrocene and Corannulene Templates

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Abstract: The smallest and most strained member of a family of π-conjugated cyclic porphyrin oligomers was synthesized by using pentapyridyl templates based on ferrocene and corannulene. Both templates are effective for directing the synthesis of the butadiyne-linked cyclic pentamer, despite the fact that the radii of their N5 donor sets are too small by 0.5 Å and 0.9 Å, respectively (from DFT calculations). The five-porphyrin nanoring exhibits a structured absorption spectrum and its fluorescence extends to 1200 nm, reflecting strong π conjugation and Herzberg–Teller vibronic coupling.

Strained π systems, such as picotubes,[1] nanohoops,[2] bowls,[3] cages,[4] and helicences,[5] have attracted increasing attention because of their remarkable electronic structures and properties. Previously, we have investigated the synthesis of butadiyne-linked nanorings consisting of 6–50 porphyrin units.[6] Herein, we present the synthesis of the smallest and most strained macrocycle in this family, the five-porphyrin nanoring c-P5. In this work, we compared the ability of two pentadentate templates to direct the formation of this cyclic pentamer: T5Fc and T5cor, which are based on ferrocene and corannulene cores, respectively (Figure 1, Scheme 1, and Scheme 2).

The design of these templates started with a computational study. Density functional theory (DFT) geometry optimizations using Gaussian09/D.01 at the B3LYP/6-31G* level[7] with Grimme’s D3 dispersion correction[8] indicate that both templates are too small for the cavity of c-P5. The radii of the N5 donor sets (measured to the centroid of the five N atoms) are 7.73 and 7.37 Å for T5Fc and T5cor, respectively. The optimal N5 radius for binding c-P5, computed by multiple methods, is 8.27 ± 0.07 Å.[9] The corannulene core of T5cor

Figure 1. Two orthogonal views of the DFT-calculated geometries of a) c-P5·T5Fc and b) c-P5·T5cor, showing the deviations of the Zn atoms from the mean planes in Å. (B3LYP/6-31G* with D3 dispersion correction; meso-aryl groups and the PO(4-t-Bu)2 were omitted to simplify the calculations.)

Scheme 1. Synthesis of the templates T5Fc and T5cor with overall yields.

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adopts the usual bowl conformation, but upon complexation in c-P5-T5cor, the bowl becomes flatter, thereby extending the radius of the N5 donor set by 0.17 Å to 0.54 Å. All five zinc centers are in the same plane in the ligand-free c-P5 nanoring, whereas they distort into an envelope conformation reminiscent of cyclopentane when c-P5 binds T5Fc and T5cor (Figure 1). The better fit of T5Fc for c-P5, compared with T5cor, is reflected in the deviations from planarity of the Zn5 acceptor set: the root-mean-square deviation from the mean plane is 0.43 Å in c-P5·T5Fc versus 0.67 Å in c-P5·T5cor. Although these calculations demonstrated that the geometries of the templates are not ideal, we decided to test whether they could direct the synthesis of c-P5, and this approach turned out to be successful.

Both templates were prepared through transition-metal-catalyzed C–C/C0 heterocoupling (Scheme 1). The ferrocene-based template T5Fc was synthesized by phosphine-activated palladium-catalyzed aryl–aryl coupling,[10] while T5cor was synthesized from corannulene by iridium-catalyzed borylation,[3a,11] followed by Suzuki coupling. Both templates are effective in directing the palladium-catalyzed oxidative coupling of porphyrin monomer P1 to give the five-porphyrin nanoring in yields of 4.0% for c-P5·T5Fc and 6.1% for c-P5·T5cor (Scheme 2). We also synthesized a version of c-P5 with different solubilizing aryl groups (OC8H17 rather than t-Bu; see the Supporting Information). GPC analysis shows that the main byproducts in these reactions are larger linear and cyclic porphyrin oligomers (see the Supporting Information). The yield of c-P5 is consistently higher when using T5cor rather than T5Fc as the template, for both porphyrin monomers. Addition of excess pyridine quantitatively displaces both templates from their complexes, yielding the template-free nanorings. The template complexes can be regenerated immediately by adding T5Fc or T5cor to a solution of c-P5.

The 1H-NMR spectra of nanoring complexes c-P5·T5Fc and c-P5·T5cor (Figure 2) were fully assigned by using 2D correlation techniques (see the Supporting Information). As expected, the template protons are shielded by the porphyrin ring current; for example the α-pyridine protons are shifted by δH(α(T5) - δH(P1)) = 0.45 ppm in both complexes (see list of δH values in the Supporting Information).

The distortions in the DFT-calculated geometries (Figure 1) are not reflected in the 1H NMR spectra, presumably because there is rapid interconversion between five degenerate envelope conformations for each complex. The symmetry of the ferrocene-based template T5Fc is effectively C5v on the NMR timescale, owing to fast rotation of the isoquinoline substituents and of the phosphine oxide. This symmetry is retained in c-P5·T5Fc, and the rims of the nanoring become non-equivalent, thereby resulting in four β-pyrrole doublets (Figures 2a, 2c and 2d). Spectrum (b) is diffusion-edited to remove overlapping solvent peaks. An impurity signal in spectrum (d) is indicated by *.

**Scheme 2.** Template-directed synthesis of c-P5·T5Fc and c-P5·T5cor.

**Figure 2.** Partial 1H-NMR spectra of a) T5Fc, b) c-P5-T5Fc, c) T5cor, and d) c-P5·T5cor. All spectra were recorded in CD2Cl2, 298 K, 500 MHz. Spectrum (b) is diffusion-edited to remove overlapping solvent peaks. An impurity signal in spectrum (d) is indicated by *.
three (rather than six) signals for the aryl protons. As mentioned above, DFT calculations (Figure 1b) indicate that the \( T_5 \) template is stretched when it binds \( c-P5-T5_{\text{corr}} \), flattening the bowl and reducing the barrier to bowl-to-bowl inversion, but we were unable to test this prediction because the complex is not sufficiently soluble for a low-temperature NMR study.

The NIR absorption spectra of \( c-P5-T5_{\text{Fc}} \), \( c-P5-T5_{\text{corr}} \), and template-free \( c-P5 \) all exhibit sharp finger patterns (Figure 3).

This behavior is similar to that of the six-porphyrin ring \( c-P6 \) whereas larger macrocycles of this type do not have structured Q bands. The absorption spectrum of template-free \( c-P5 \) is similar to those of \( c-P5-T5_{\text{Fc}} \) and \( c-P5-T5_{\text{corr}} \), thus indicating that \( c-P5 \) is shape-persistent and that its conformation is not strongly perturbed by the templates; only a slight broadening arises from the increased flexibility of \( c-P5 \) in the absence of template. The fluorescence spectra of the three compounds extend far into the NIR region (Figure 3), like that of \( c-P6 \). The fluorescence quantum yields, decay times, and radiative rate constants are compared with those of \( c-P6 \) and \( c-P6-T6 \) in Table 1. The low fluorescence quantum yields of all these compounds result from the fact that \( S_1 \)–\( S_0 \) transitions are only weakly allowed in circular \( \pi \) systems. Binding of either \( T5_{\text{Fc}} \) or \( T5_{\text{corr}} \) to \( c-P5 \) reduces the radiative rate and the fluorescence quantum yield. Taken in isolation, the low fluorescence quantum yield of \( c-P5-T5_{\text{Fc}} \) might be viewed as evidence for photoinduced electron transfer involving the redox-active ferrocene core. However, the fact that \( c-P5-T5_{\text{Fc}} \) and \( c-P5-T5_{\text{corr}} \) have similar fluorescence quantum yields implies that this is a consequence of the regular circular geometry of the complexes, which suppresses the symmetry-breaking vibrations required for Herzberg–Teller coupling.

The formation constants \( (K_i) \) of the nanoring–template complexes reflect how well the templates fit the cavity of the five-porphyrin nanoring. The nanoring–template complexes \( c-P5-T5_{\text{Fc}} \) and \( c-P5-T5_{\text{corr}} \) are too stable for their formation constants to be determined by direct titration, so we measured \( K_i \) by displacing the templates with pyridine, giving log \( K_i \) values of 29.3 ± 0.2 and 28.5 ± 0.1 for \( c-P5-T5_{\text{Fc}} \) and \( c-P5-T5_{\text{corr}} \), respectively (see the Supporting Information). The chelate cooperativity of complex formation is quantified by the effective molarity (EM), calculated from the formation constant \( (K_i) \), the statistical factor \( (K_s) \) of the complex, and the corresponding microscopic binding constant \( (K_r) \) for the ligand site (isoquinoline for \( T5_{\text{Fc}} \) and pyridine for \( T5_{\text{corr}} \)). The geometric average of the four effective molarities (EM) of the five-coordinate complex can be calculated from Equation (1).

\[
\text{EM} = \sqrt[4]{\frac{K_r}{K_i K_s}}.
\]

The effective molarities for \( c-P5-T5_{\text{Fc}} \) and \( c-P5-T5_{\text{corr}} \) are 41 ± 9 M and 36 ± 5 M, respectively. While being higher than the values in many supramolecular systems, these effective molarities are lower than those for the corresponding six-porphyrin ring \( c-P6 \), either with a rigid \( T6 \) template (EM = 126 ± 5 M) or with a flexible cyclodextrin-based template (EM = 74 ± 20 M) which reflects the poor size complementarity of \( T5_{\text{Fc}} \) and \( T5_{\text{corr}} \) for \( c-P5 \).

In conclusion, templates based on ferrocene and corannulene can be used to direct the synthesis of the five-porphyrin nanoring \( c-P5 \) which has a diameter of 2.1 nm. The corannulene-based template gives a higher yield of \( c-P5 \), despite being too small and having a lower affinity for \( c-P5 \). The lack of correlation between the size of the template and its ability to direct the formation of \( c-P5 \) may indicate that the transition state for template-directed coupling is smaller than the final product. The five-porphyrin nanoring exhibits highly structured absorption and fluorescence spectra and a low radiative rate, thus indicating that emission is strongly suppressed due to the high rotational symmetry of the lowest excited state, with the majority of the fluorescence arising from dynamic symmetry breaking through Herzberg–Teller coupling. This work demonstrates that perfect size complementarity is not essential in template-directed synthesis, and it illustrates how templates can be used to synthesize strained \( \pi \)-conjugated macrocycles.

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**Table 1**: Fluorescence quantum yields \( \Phi \), fluorescence decay times \( \tau \), and radiative rate constants \( k_r \).

| Compound     | \( \Phi \) [%] | \( \tau \) [ns] | \( k_r \) [ns\(^{-1}\)] |
|--------------|---------------|----------------|--------------------------|
| \( c-P5 \)   | 3.1%          | 0.45           | 0.067                    |
| \( c-P5-T5_{\text{Fc}} \) | 0.89%        | 0.42           | 0.021                    |
| \( c-P5-T5_{\text{corr}} \) | 0.61%        | 0.37           | 0.016                    |
| \( c-P6 \)   | 1.5%          | 0.49           | 0.031                    |
| \( c-P6-T6 \) | 0.42%        | 0.25           | 0.017                    |

[a] Solvent: toluene with 1% pyridine, 298 K. [b] Quantum yields measured as described in Ref. [13] using linear porphyrin hexamer \( L-P6 \) as a standard (\( \Phi_L = 28\% \)). [c] \( k_r = \Phi_L / \Phi \). [d] Data for \( c-P6 \) and \( c-P6-T6 \) from Ref. [13].
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[12] The mean crystallographic pyridine to zinc porphyrin N–Zn bond length is 2.16 ± 0.03 Å and the mean displacement of the Zn atom from the plane of the porphyrin is 0.24 ± 0.06 Å.[6b] Three methods can be used to estimate the optimal template N5 radius for binding e-P5: Method A starts from the geometry of the template-free 5-porphyrin nanoring e-P5 from DFT calculations. The mean distance between the centroid of four N atoms in each porphyrin unit and the centroid of all 20 N atoms is 10.61 Å, giving an optimal template N5 radius of 10.61 – 0.24 = 8.21 Å. Method B considers the 5-porphyrin nanoring as a perfect circle; the circumference of the circle can be calculated from the distance between the centers of the two porphyrin units in a linear porphyrin dimer (13.51 Å, from P. N. Taylor, J. Huuskonen, G. Rumbles, R. T. Aplin, E. Williams, H. L. Anderson, Chem. Commun. 1998, 909–910). The radius of a perfectly circular template-free 5-porphyrin nanoring is calculated as 10.75 Å, giving the optimal template N5 radius as 10.75 – 0.24 = 8.51 Å. Method C starts from the crystallographic geometry of the 6-porphyrin nanoring/template complex e-P6,[6b] this structure has an average N–Zn centroid distance of 12.18 Å, but this nanoring is slightly distorted because T6 is too small by a factor of 2.5%. Thus the ideal Zn-centroid distance of a 5-porphyrin nanoring/template complex is (5/6) x 12.18/0.975 = 10.41 Å, and the optimal template N5 radius is 10.41 – 2.16 = 8.25 Å.
DFT (B3LYP/6-31G*) calculations predict that the strain energy in c-P$_5$ is 121 kJ mol$^{-1}$ (see the Supporting Information). This strain is similar to that calculated for a 2.8 nm [20]-cycloparaphenylene (119 kJ mol$^{-1}$). By contrast, [15]-cycloparaphenylene, which has a similar diameter to c-P$_5$ (2.1 nm), has a strain energy of 164 kJ mol$^{-1}$; Y. Segawa, H. Omachi, K. Itami, Org. Lett. 2010, 12, 2262–2265. This difference reflects the greater flexibility of butadiynes and porphyrins compared to para-phenylene units. For comparison, the strain in [5]-cycloparaphenylene is calculated to be 490 kJ mol$^{-1}$; T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki, S. Yamago, J. Am. Chem. Soc. 2011, 133, 8354–8361.

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