Six-Coordinated Zinc Porphyrins for Template-Directed Synthesis of Spiro-Fused Nanorings

Ludovic Favereau,‡ Arjen Cnossen,‡ Julien B. Kelber,‡ Juliane Q. Gong,‡ René M. Oetterli,† Jonathan Cremers,‡ Laura M. Herz,† and Harry L. Anderson‡,†

‡Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, United Kingdom
‡Clarendon Laboratory, Department of Physics, University of Oxford, Oxford OX1 3PU, United Kingdom

Supporting Information

ABSTRACT: Five-coordinate geometry is the standard binding mode of zinc porphyrins with pyridine ligands. Here we show that pseudo-octahedral six-coordinate zinc porphyrin complexes can also be formed in solution, by taking advantage of the chelate effect. UV−vis−NIR titrations indicate that the strength of this second coordination is ca. 6−8 kJ mol⁻¹. We have used the formation of six-coordinate zinc porphyrin complexes to achieve the template-directed synthesis of a 3D π-conjugated spiro-fused array of 11 porphyrin units, covalently connected in a nontrivial topology. Time-resolved fluorescence anisotropy experiments show that electronic excitation delocalizes between the two perpendicular nanorings of this spiro-system within the experimental time-resolution of 270 fs.

The coordination of pyridine ligands to zinc porphyrins has been widely used to explore the principles of cooperative molecular recognition, following pioneering studies by Tabushi and Sanders in the 1980s. The basic ground rule in this field is that a zinc porphyrin can bind one axial ligand, to become five-coordinate, but six-coordinate zinc centers, with two axial pyridine ligands, are never observed in solution (Scheme 1).

Scheme 1. Coordination of Pyridine to a Zinc Porphyrin

Here we demonstrate that zinc porphyrins with two axial ligands can be formed in solution, when the whole system is suitably stabilized by the chelate effect. We also show that six-coordinate zinc centers can be used in the template-directed synthesis of spiro-linked porphyrin nanorings, which exhibit ultrafast energy migration between the two perpendicular fused macrocycles.

Early studies of the interaction of pyridine with zinc porphyrins in solvents such as chloroform, by UV−vis or NMR titration, found that 1:1 complexes are formed, typically with association constants in the range $K_1 \approx 10^3$−10⁴ M⁻¹, whereas 1:2 complexes are not detected ($K_2 \leq 1$ M⁻¹). To the best of our knowledge, six-coordinate zinc porphyrins with two axial pyridine ligands have never previously been detected in solution, although they sometimes occur in crystal structures, and zinc porphyrins with two axial DABCO or pyrazine ligands have been studied in supramolecular tweezer complexes.

We decided to probe the formation of six-coordinate zinc porphyrins, as a potential approach to 3D π-conjugated architectures, by investigating the complexation of a cross-shaped zinc porphyrin pentamer, x-P₅, with a tridentate ligand T₃ (Figure 1). Our idea was that the ability of the central zinc atom of x-P₅ to bind two pyridine ligands would be reflected by the stability of the 1:2 complex, x-P₅·T₃₂. As expected, the UV−vis−NIR titration of x-P₅ with T₃ is sharply biphasic (Figure 1c), showing formation of a strong 1:1 complex x-P₅·T₃, $K_1 = (2.8 \pm 0.4) \times 10^6$ M⁻¹, followed by a weaker 1:2 complex x-P₅·T₃₂, $K_2 = (1.7 \pm 0.3) \times 10^5$ M⁻¹. Under the same conditions, the linear porphyrin trimer with a free-base porphyrin at the center, l-P₃Zn₃H₂Zn (Figure 2), forms a 1:1 complex with T₃ with an association constant of $K_{1l} = (3.3 \pm 0.7) \times 10^5$ M⁻¹. The observation that x-P₅·T₃ binds T₃ about five times more strongly than l-P₃Zn₃H₂Zn demonstrates that there is a significant attractive interaction between the central zinc porphyrin unit of x-P₅ and a second axial pyridine. After correction for statistical factors (see Supporting Information (SI)), the difference in free energies corresponding to the strength of this second axial coordination is 5.8 kJ mol⁻¹ at 298 K, which is comparable to a typical hydrogen-bond. This is about 30% of the free energy of the first axial coordination to the central Zn atom in x-P₅·T₃, which can be estimated as 19.0 kJ mol⁻¹ at 298 K, from the difference in $\Delta G$ of formation of x-P₅·T₃ and l-P₃Zn₃H₂Zn·T₃.

The discovery that the porphyrin pentamer x-P₅ binds two equivalents of T₃ suggested that binding to the hexadentate template T₆ could be used to direct the synthesis of topologically interesting 3D π-conjugated architectures, using chemistry that we developed for the synthesis of simpler nanorings. Palladium-catalyzed oxidative coupling of the deprotected pentamer x-P₅', bearing four terminal alkyne functionalities, with deprotected linear trimer l-P₃Zn₃ in the presence of T₆ gave the spiro-fused porphyrin 11-mer as its

Received: September 26, 2015
Published: November 4, 2015

DOI: 10.1021/jacs.5b10126
J. Am. Chem. Soc. 2015, 137, 14256−14259

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The six-porphyrin nanoring complex $c\cdot P_6 \cdot T_6$ is also formed as a byproduct from coupling of two molecules of $I\cdot P_3_{Zn3}$ bound to $T_6$, however $c\cdot P_6\cdot T_6$ and $s\cdot P_{11}\cdot (T_6)_2$ are readily separated by size-exclusion chromatography. The structure of $s\cdot P_{11}\cdot (T_6)_2$ was confirmed by NMR and mass spectrometry (MALDI-ToF).

The $\alpha$-pyridine protons of the template nearest to the central six-coordinate zinc atom (labeled as $\alpha_{1i}$ in Figure 4) give rise to a sharp doublet at 2.68 ppm. The other three $\alpha$-pyridine protons ($\alpha_{2−4}$) resonate at 2.38−2.40 ppm. The slightly weaker shielding of the central $\alpha$-pyridine protons probably reflects the weaker ring current of the central porphyrin, resulting from its saddle-shaped nonplanar geometry. This explanation is supported by the observation that the singlet from the $\beta$-pyrrole protons of the central nonplanar porphyrin ($\beta_1$) at 9.30 ppm is less deshielded than the $\beta$-pyrrole protons proximate to butadiyne substituents of the other porphyrin units ($\beta_{2−6}$; 9.53−9.58 ppm).

The UV−vis−NIR absorption and fluorescence spectra of $s\cdot P_{11}\cdot (T_6)_2$ are similar to those of $c\cdot P_6\cdot T_6$ (Figure 5), although the absorption and emission bands of $s\cdot P_{11}\cdot (T_6)_2$ are red-shifted by about 20 nm, reflecting the 3D π-conjugation. Time-resolved fluorescence measurements were performed to explore energy migration in the spiro-fused system. The results reveal ultrafast migration of excitation between the two nanorings. Figure 6 shows the fluorescence dynamics of $s\cdot P_{11}\cdot (T_6)_2$ excited at 820 nm, detecting fluorescence at 915 nm polarized parallel ($I_{||}$) or perpendicular ($I_{\perp}$) to the excitation polarization. The time-dependent fluorescence anisotropy, $\gamma = (I_{||} - I_{\perp})/(I_{||} + 2I_{\perp})$, shows no change over 0−20 ps after...
excitation with an average value of $\gamma = 0.03 \pm 0.02$, reflecting the electronic communication between the two nanorings. We use a simple model, based on a subset of dipoles distributed across the two ring planes, which is found to predict a value of $\gamma = 0.025$ for the case of an excited state delocalized over the whole spiro-fused molecule (see SI). The excellent agreement between theoretical and experimental anisotropies demonstrates that the excited state rapidly delocalizes over all 11 porphyrin units within the 270 fs time-resolution of our experiment.

During the course of this work, we also synthesized an analogous spiro-fused nanoring, $s$-Et-P$_{11}$·(T$_6$)$_2$, with eight ethyl substituents on the central porphyrin (Figure 7) because the corresponding cross-pentamer $x$-Et-P$_5$ can be prepared in higher yield than $x$-P$_5$ (see SI). The UV–vis–NIR titration of $x$-Et-P$_5$ with T$_3$ shows similar behavior to titration of $x$-P$_5$, with the distinct formation of a 1:1 complex $x$-Et-P$_5$·T$_3$ and a
1:2 complex sEt-P5·(T3),

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K_s = (4.1 \pm 1.0) \times 10^5 \text{ M}^{-1},
\]

which corresponds to a free energy of 7.9 kJ mol\(^{-1}\) for the second axial coordination at 298 K. The synthesis of spiro-fused nanoring sEt-P11·(T6)\(_2\) was achieved in 23% yield under the same conditions as sP11·(T6)\(_2\). The central α-pyridine proton in sEt-P11·(T6)\(_2\) exhibits a sharp signal at 4.35 ppm; this higher chemical shift, compared to sP11·(T6)\(_2\), probably reflects the greater distortion of the octaethyl-tetraakynyl porphyrin. The photophysical behavior of sEt-P11·(T6) is very similar to that of sP11·(T6)\(_2\) (see SI); it also exhibits ultrafast fluorescence depolarization with an anisotropy of \(\gamma = 0.04 \pm 0.02\).

The template units can be removed from sP11·(T6) and sEt-P11·(T6)\(_2\) by treatment with quinuclidine, as reported previously for c-P6-T6. These displacement tetrations are biphasic (see details in SI), because the first T6 unit to be displaced has a weak six-coordinate zinc interaction, whereas the remaining T6 unit has only five-coordinate zinc interactions. The differences in \(\Delta G\) for binding the first and second T6 units to sP11 and sEt-P11 are 32 ± 3 and 36 ± 3 kJ mol\(^{-1}\), respectively, at 298 K. The first T6 unit binds each spiro-fused porphyrin oligomer about 10\(^6\) times more strongly than the second, illustrating the thermodynamic penalty for formation of a six-coordinate zinc center.

In summary, we have demonstrated that zinc porphyrins can bind two axial pyridine ligands in solution to become six-axial complexes; PL transients and anisotropy dynamics for spiro-nanoring compounds (PDF)

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11. The first binding constant \(K_s\) is too strong to determine accurately from titrations of the type shown in Figure 1c. The value of \(2.8 \times 10^5 M^{-1}\) was determined by titrating s-P5-T3 with pyridine (see SI for details).

14259 DOI: 10.1021/jacs.5b10126
J. Am. Chem. Soc. 2015, 137, 14256–14259