Porphyrrin−Polyyne [3]− and [5]Rotaxanes

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Supporting Information

ABSTRACT: Porphyrrin−polyyne [3]− and [5]rotaxanes have been synthesized by condensing aldehyde−rotaxanes with pyrrole or dipyrromethane. The crystal structure of a [3]rotaxane shows that the macrocycles adopt compact conformations, holding the hexaynes near the porphyrin core, and that the phenanthroline units form intermolecular π-stacked dimers in the solid. Fluorescence spectra reveal singlet excited-state energy transfer from the threaded hexayne to the porphyrin, from the phenanthroline to the porphyrin, and from the phenanthroline to the hexayne.

Macrocycles consisting entirely of sp-hybridized carbon are intriguing synthetic targets.1−3 Cyclocarbons have been studied in the gas phase,1−3,4 but they have not yet been isolated or characterized in solution, despite attempts by Diederich, Tobe, Rees, and co-workers.1−3 Advances in active metal template synthesis5 provide access to an expanding diversity of interlocked molecules, including threaded polynes,6−11 and it has been found that linear chains of sp-hybridized carbon atoms (both polynes and cumulenes) can be stabilized by threading them through macrocycles to form rotaxanes.11−13 As part of a project directed toward the synthesis of cyclocarbon catenanes, we are exploring strategies for positioning several polyyne rotaxane units around a central molecular hub, so that the polynes can then be linked together to form a threaded cyclocarbon. Here, we present the first step in this endeavor: the synthesis of a [5]rotaxane in which four hexaynes are positioned around a porphyrin core. While the primary motivation for this work was to explore approaches to cyclocarbon catenanes, this study also provides insights into the interactions between the singlet excited states of polyne and porphyrin chromophores.

The initial target of this work was the porphyrin [5]rotaxane P5Ra shown in Figure 1. All attempts at the synthesis of this [5]rotaxane failed, presumably as a consequence of the steric bulk of the four [2]rotaxane substituents. However, we successfully synthesized the analogous porphyrin [5]rotaxane P5Rb with p-phenylene spacers at the meso-positions and the corresponding porphyrin [3]rotaxanes P3Ra and P3Rb (Scheme 1). Here, we present the synthesis of these rotaxanes and an analysis of their fluorescence behavior, together with the crystal structure of a porphyrin [3]rotaxane P3Ra. This structure shows that the macrocycles adopt compact conformations due to the predominantly gauche geometries of the O−CH2CH2−O links, which increases the effective steric bulk of the rotaxane substituents and explains why the [5]rotaxane P5Ra could not be synthesized.

Our synthetic approach starts with the macrocyclic aldehyde Ma (Scheme 1).14−15 Active metal template Cadiot−Chodkiewicz coupling7,11 of supertrityl triyne TrC6H and bromotriyne TrC6Br [where Tr is tri(3,5-di-tert-butylphenyl)methyl16] in the presence of the copper(I) complex of Ma gave the [2]rotaxane aldehyde 2Ra in 58% yield. A wide variety of conditions were tested for the reaction of 2Ra with pyrrole in attempts to prepare P5Ra, but they all failed to give even a trace of this target [5]rotaxane, whereas control reactions of aldehyde Ma produced porphyrin PM4a in good yield. In contrast, reaction of the rotaxane aldehyde 2Ra with dipyrromethane gave the porphyrin [3]rotaxane P3Ra in 62% yield. These results

Figure 1. Structure of target [5]rotaxane P5Ra.

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imply that formation of \( P5Ra \) is blocked by the steric bulk of the rotaxane units, so we investigated the analogous compounds derived from macrocycle \( Mb \), which has a \( p \)-phenylene spacer between the aldehyde functionality and the macrocycle. Increasing the distance between the bulky rotaxane unit and the porphyrin hub made it possible to synthesize \( [5] \)rotaxane \( P5Rb \) (10% yield isolated).

The porphyrin \([3]\) and \([5]\)rotaxanes, and reference porphyrins, were fully characterized as their zinc complexes \( \text{Zn}−\text{P3Ra}, \text{Zn}−\text{P3Rb}, \text{Zn}−\text{P5Rb}, \text{Zn}−\text{PM2a}, \text{Zn}−\text{PM4a}, \text{Zn}−\text{PM2b}, \) and \( \text{Zn}−\text{PM4b} \) (see the Supporting Information). Crystals of \( \text{Zn}−\text{P3Ra} \) were grown by diffusion of methanol vapor into a solution in chloroform and analyzed by single-crystal X-ray diffraction. The crystal structure has two molecules of
meso-simplified reference porphyrin derivatives (Zn of the porphyrin Soret band at around 415 nm. This perturbation to the electronic structure of the component Zn polyynes.9,11,16,18 contacts with the polyyne chains held close to the porphyrin units. Thus, all four fluorescence quantum yield, measured on excitation (EET) from the polyyne to the porphyrin and from the phenanthroline macrocycle to the porphyrin as summarized in Table 1 (see the SI for full details).

The comparison of macrocycle → porphyrin EET efficiencies in the presence and absence of polyyne show that the polyyne acts as a sink for singlet excited state energy from the phenanthroline macrocycle, even though it does not quench the porphyrin.18 The excited-state energy of the macrocycle is split between the porphyrin and the polyyne. The higher efficiency of polyyne → porphyrin EET in [3]rotaxane Zn–P3Ra, compared with Zn–P3Rb and Zn–P5Rb, reflects the shorter polyyne–porphyrin distance. The polyyne → porphyrin EET must be very rapid to compete with intersystem crossing (τ ≈ 0.5 ns).18 Furthermore, the S1 of the polyyne is a dark state with negligible oscillator strength; therefore, Förster-type energy transfer is expected to be very inefficient, implying that the observed EET occurs via a Dexter mechanism.

In conclusion, we have prepared a series of porphyrin–polyyne [3]- and [5]rotaxanes that comprise multiple chromophores in a unique interlocked architecture. An analysis

Figure 2. Projection of the structure of the [3]rotaxane Zn–P3Ra from X-ray crystallography. This figure only shows one of the two molecules in the asymmetric unit.

Table 1. Energy-Transfer Efficiencies φEET

| compd   | φEET (macrocycle → porphyrin) | φEET (polyyne → porphyrin) |
|---------|-----------------------------|-----------------------------|
| Zn–PM2a | 0.67 ± 0.08                 | 0.16 ± 0.02                 |
| Zn–P3Ra | 0.32 ± 0.03                 | 0.11 ± 0.01                 |
| Zn–PM2b | 0.88 ± 0.11                 | 0.10 ± 0.03                 |
| Zn–P3Rb | 0.22 ± 0.03                 | 0.09 ± 0.02                 |
| Zn–PM4b | 0.68 ± 0.06                 |                             |
| Zn–P5Rb | 0.25 ± 0.02                 |                             |

Figure 3. (a) Absorption spectra (continuous line) and excitation spectra (dashed line) of Zn–P3Ra (red) and Zn–PM2a (blue); the spectral intensities are normalized to 1.0 at the Q-band, and the excitation spectra are recorded for emission at 639 nm (porphyrin Q-band). Solvent: CH2Cl2. (b) Jablonski diagram showing the energy-transfer processes.
of the absorption, fluorescence, and excitation spectra of the rotaxanes reveals three types of energy-transfer processes (a) from the phenanthroline macrocycle to the porphyrin, (b) from the phenanthroline macrocycle to the polyyne, and (c) from the polyyne to the porphyrin. This work paves the way for a template-directed synthesis of polycatenane cyclon[\textit{n}]carbons.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03528.

Details of synthetic procedures and characterization data, analysis of absorption, fluorescence and excitation spectra, and crystallographic analysis (PDF)

Crystallographic data for \textit{P}3\textit{Ra} (CIF)

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Notes

The authors declare no competing financial interest.

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(19) Single Crystal Data: \textit{C}301H348N8O17Zn, \textit{M} = 4415.49, monoclinic, \(a = 31.7209(5)\text{Å}, b = 19.3373(2)\text{Å}, c = 50.4748(7)\text{Å}, \beta = 96.0619(14)\text{°}, \Delta = 30787.9(7)\text{Å}, data/restraints/parameters: 52640/18794/5933, \text{R}_{\text{int}} = 6.99\%, \text{final} R_{1} = 12.36\%, wR_{2} = 31.63\% (I > 2\sigma(I)), \Delta R_{\text{max}} = -0.78, +0.88 e\text{Å}{\textsuperscript{-3.}} Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1519120); copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

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