

Novel Porphyrin-Fullerene Assemblies: from Rotaxanes to Catenanes

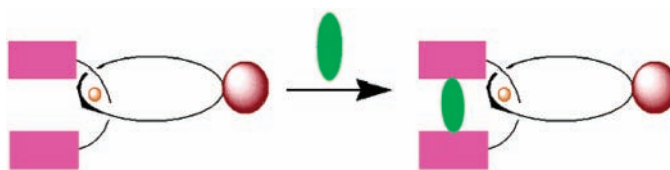
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ABSTRACT



Titration of porphyrin-fullerene rotaxanes with DABCO or 4,4'-bipyridine led to photo- and redoxactive catenanic architectures, which upon photoexcitation undergo a sequence of short-range energy and electron transfer events to give a long-lived charge-separated radical-pair state.

Covalently bonded and self-assembled motifs are widespread organization principles in nature that regulate size, shape, and function down to the nanometer scale. The ability to engineer extended one-, two-, or three-dimensional architectures at the molecular level, by modifying individual chemical building blocks, has sparked a very active field.¹

Mechanically linked nanoscale ensembles such as rotaxanes and catenanes emerged as viable multicomponent model systems to transmit and process solar energy,² in large part due to the close resemblance with the topology in the natural

photosynthetic reaction center.³ In the current paper, we report on the formation of catenanic architectures by complexation of bidentate ligands, namely, DABCO (1,4-diazabicyclo-[2.2.2]octane) and 4,4'-bipyridine (BP), with rotaxanes **1** and **2**. It is well established that DABCO forms very tight complexes with Zn porphyrins (ZnP), with K_a values on the order of 10^5 – 10^8 M⁻¹, depending on the substrate and the solvent.⁴ Such complexation has been frequently used as a means for formation of supramolecular complexes with monomeric porphyrins,⁵ dimeric porphyrin tweezers,⁶ as well as porphyrin-fullerene hybrids.⁷

The procedure for synthesis of rotaxane **1** is depicted in Scheme 1 and discussed in detail elsewhere.⁸ Briefly, compound **3** was synthesized according to literature procedures¹⁰ and then condensed with malonyl dichloride to form the phenanthroline-containing macrocyclic ester **4**, which is then attached to C₆₀ by a Bingel–Hirsch reaction.¹¹ The fullerenomacrocyclic **5** is then complexed, using Cu(I), to a

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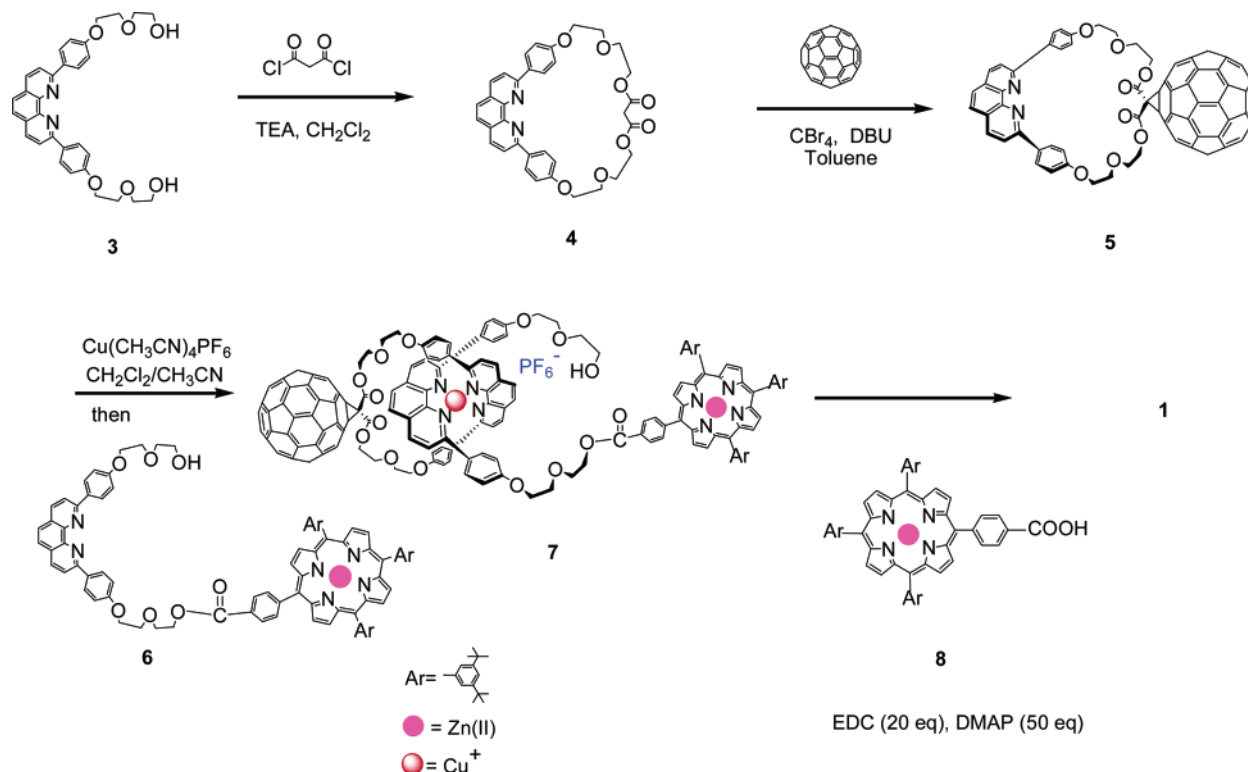
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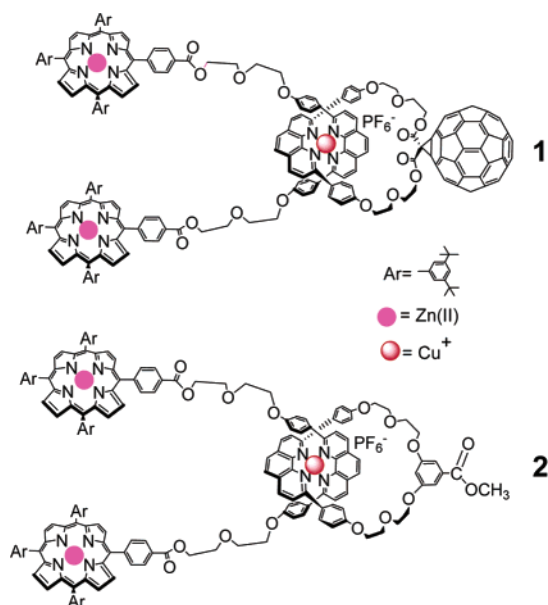
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Scheme 1. Synthesis of Rotaxane **1**



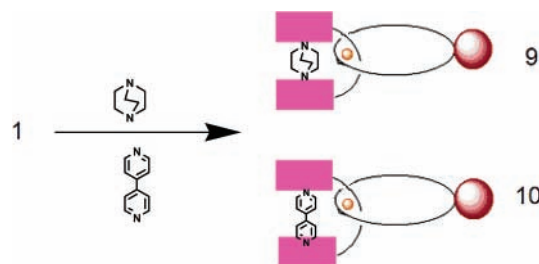
thread containing a second phenanthroline moiety with a zinc porphyrin stopper at one end, to give the tetrahedral complex **7**. Attachment of the porphyrin carboxylic acid **8** at the other end of the thread affords the target rotaxane **1**. Model rotaxane **2** was described previously.⁸ The rotaxanes were fully characterized spectroscopically.^{8,9}



Molecular modeling of fullerenorotaxane **1** and model rotaxane **2** suggests that the two ZnPs constitute a molecular scaffold that should exhibit excellent binding features toward

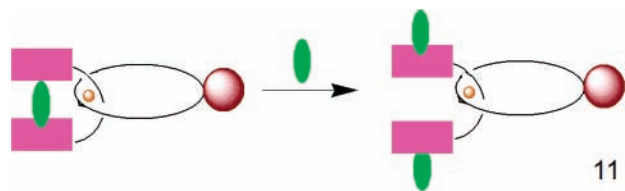
a variety of guest molecules. In this context, selective complexation of the free nitrogen lone pairs in bidentate ligands such as DABCO or BP to the axial d_{z^2} orbitals of ZnP opens pathways to novel molecular catenanic architectures such as **9** and **10** (see Scheme 2). Spectroscopic

Scheme 2. Formation of the 1:1 Sandwich Complexes



techniques were employed to follow binding of DABCO and BP to the bis-ZnP scaffold in rotaxanes **1** and **2**. NMR studies show that when the rotaxanes were mixed with DABCO in a 1:1 ratio, the predicted sandwich complex was formed. The chemical shift of the DABCO protons appears in the complex at -4.55 ppm, in sharp contrast with the value of 2.76 ppm for the free ligand in CDCl_3 . This strong shielding effect of the porphyrin tweezers is in agreement with literature data on related structures.⁴ When more DABCO was added to the solution, the peak at $\delta -4.55$ ppm steadily decreased and a new peak at 0.08 ppm appeared, signaling transformation of the complex from a 1:1 sandwich

Scheme 3. Conversion of 1:1 to 2:1 Supramolecular Complexes



complex to a 2:1 monoligated complex with DABCO on the outside (see Scheme 3). This type of shielding effect of DABCO bound to Zn porphyrins is also well documented.⁴

The ZnP transitions in the visible region for **1** and **2** are identical, with the Soret band at 423 nm and Q-bands at 550 and 590 nm. A typical titration complexation experiment is illustrated in Figure 1 for addition of 4,4'-bipyridine (in

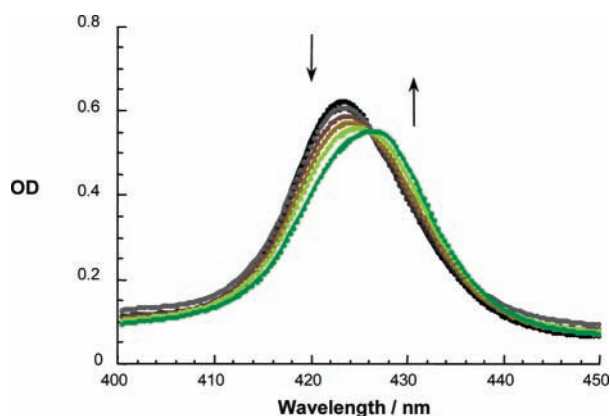


Figure 1. Absorption spectra of rotaxane **1** (0.9×10^{-6} M) in dichloromethane with various equivalents of BP (4.6×10^{-7} to 1.5×10^{-5} M) to form catenane **10**.

concentrations ranging from 4.6×10^{-7} to 1.5×10^{-5} M) to rotaxane **1** (1.0×10^{-6} M in CH_2Cl_2). In line with an earlier observation,⁴ formation of a 1:1 complex, i.e., one bidentate ligand per rotaxane, was confirmed by the bathochromic shift of 3 nm observed for both the Soret- and Q-band transitions, from 423 to 426 nm and from 550 to 553 nm, respectively. Such a shift is associated with binding of a single DABCO or BP moiety to the two ZnP binding sites of the rotaxane. The presence of an isosbestic point at 425 nm testifies to a clean rotaxane-catenane transformation. In contrast, complexation of two ligands per rotaxane should result in larger bathochromic shifts, on the order of 8–10 nm, as seen for axial coordination of various nitrogen bases with Zn porphyrins.⁷ Considering that micromolar rotaxane

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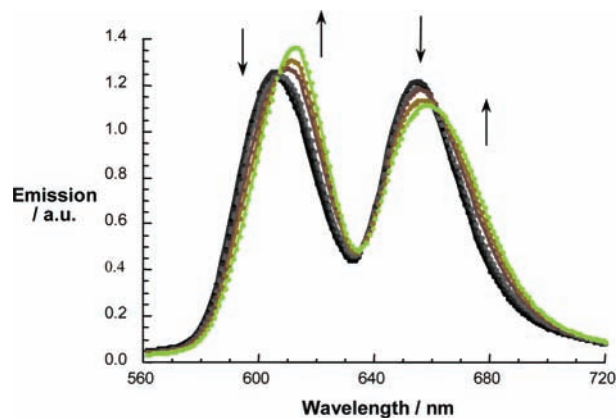


Figure 2. Fluorescence spectra of rotaxane **1** (0.9×10^{-6} M) in dichloromethane with various equivalents of BP (4.6×10^{-7} to 1.5×10^{-5} M) to form catenane **10**; the excitation wavelength is 425 nm, which is the isosbestic point.

concentrations were employed in these experiments, inter-rotaxane complexation is unlikely to occur.

Analyzing the ground-state absorption shifts within the framework of the Benesi–Hildebrand equation¹² led to association constants K_a of $2.0 \pm 0.5 \times 10^5$ and $1.8 \pm 0.5 \times 10^5 \text{ M}^{-1}$ for complexation of rotaxane **1** with DABCO and BP, respectively. Nearly identical values were determined for model rotaxane **2**: $2.0 \pm 0.5 \times 10^5 \text{ M}^{-1}$ (DABCO) and $1.7 \pm 0.5 \times 10^5 \text{ M}^{-1}$ (BP). For a 2:1 DABCO–rotaxane complex such as **11**, notably smaller association constants, on the order of 10^4 M^{-1} would be expected.^{4b}

Steady-state and time-resolved fluorescence experiments were also used to visualize the transformation of rotaxane **1** to catenanes **9** and **10**. Analogous experiments were performed with rotaxane **2**. It should first be noted that the fluorescence of the porphyrin moiety in rotaxanes **1** and **2** is reduced relative to Zn tetraphenylporphine, the ZnP reference. This quenching is due to rapid intramolecular energy transfer to the $[\text{Cu}(\text{phen})_2]^+$ building block; fluorescence quantum yields for **1** and **2** are reduced to 0.01 ± 0.001 .⁸ Titration of the bis-ZnP scaffold with DABCO or BP, using the concentrations cited in Figure 1, was accompanied by changes in the fluorescence spectra. Three key observations can be deduced from Figure 2. First, in accord with the shifts seen in the ground-state spectra, the fluorescence spectra also feature a progressive red shift. Second, three clean isosbestic points are observed at 606, 636, and 660 nm. Third, the quenched ZnP fluorescence exhibits a slight reactivation of <10% upon increasing the ligand

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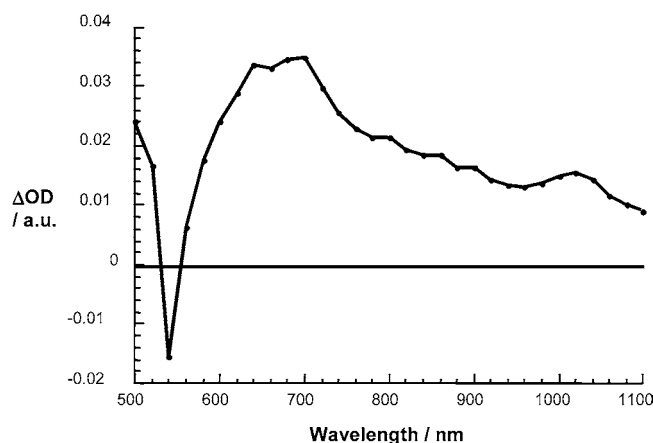


Figure 3. Differential absorption spectrum (visible and near-infrared) obtained upon nanosecond flash photolysis (532 nm) of $\sim 1.0 \times 10^{-5}$ M catenane **10** in deoxygenated dichloromethane solutions.

concentration. Parallel experiments with the ZnP reference in dichloromethane gave rise to similar effects. We conclude that the spectral changes observed for complexation of the bidentate ligands with **1** and **2** result from a change in the ZnP coordination sphere, from a square-planar geometry in weak solvent-coordinated complexes to pyramidal complexes with DABCO and BP.¹³ The complexation can be reversed by the addition of dilute HCl, which ties up the nitrogen lone pair electrons on the ligands.

In complementary transient absorption studies, we probed the origin of the ZnP fluorescence quenching and identification of products. Pumping light into the ZnP ground state in **1**, **9**, and **10** with short 532 nm laser pulses leads to the population of the ZnP singlet excited state, $^1\text{ZnP}^*$ (2.1 eV).¹⁴ In **1**, **9**, and **10**, the lifetime of this intermediate state (~ 1.0 ns) is shorter than in the ZnP reference (3.2 ns), since the lowest vibrational state of the singlet excited-state undergoes efficient energy transfer to yield the photoexcited $[\text{Cu}(\text{phen})_2]^+$ MLCT state (1.9 eV). From the latter, an exothermic electron-transfer relay follows, generating the final long-distance $(\text{ZnP}^+)_2\text{-}[\text{Cu}(\text{phen})_2]^+\text{-C}_{60}^{\bullet-}$ charge-separated radical-pair (CSR) state (1.3 eV), which may be in equilibrium

(13) Parallel fluorescence lifetime measurements afforded virtually indistinguishable values for the **1–3** series.

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with the intermediate $(\text{ZnP})_2\text{-}[\text{Cu}(\text{phen})_2]^{2+}\text{-C}_{60}^{\bullet-}$ state (also ~ 1.3 eV).⁸ Spectral characteristics of the CSR state (see Figure 3) feature transient absorption in the visible and near-infrared with characteristic maxima at ~ 650 nm for ZnP^+ ¹⁵ and 1040 nm for $\text{C}_{60}^{\bullet-}$,¹⁶ respectively, similar to those found in related ZnP- C_{60} dyads.^{17,18} The decay of the $\text{ZnP}^+/\text{C}_{60}^{\bullet-}$ radical ion pair transient absorption for **1**, **9**, and **10** showed clean first-order kinetic behavior. Interestingly, the radical ion pair lifetimes (500 ± 50 ns) are nearly identical for **1**, **9**, and **10**, which can be rationalized on the basis of a preorganized structure for rotaxanes **1** and **2** that provides a molecular scaffold for binding of DABCO and BP without inducing significant structural changes. This result is quite different from a system in which two ZnP moieties surround a fullerene in a linear geometry, where bridging between the two ZnP groups using DABCO results in a drastic change in the conformation and photophysical properties of the system.¹⁹

In summary, we have demonstrated that novel catenanic supramolecular architectures can be prepared from fullerene-rotaxanes incorporating bis-Zn-porphyrin molecular tweezers, and that photoexcitation results in the formation of relatively long-lived charge-separated states. Such systems, when incorporated into membranes or assembled on metallic surfaces, have potential applications in solar energy conversion and in photovoltaic devices.⁹

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Supporting Information Available: Experimental procedure for synthesis of intermediates **4–6** and NMR spectral assignments, as well as NMR spectra for complexation of DABCO and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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