

# Efficient One-Pot Synthesis of Rotaxanes Bearing Electron Donors and [60]Fullerene

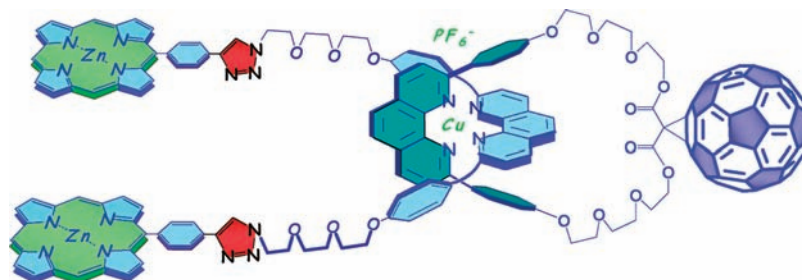
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## ABSTRACT



An easy one-pot procedure to synthesize rotaxanes bearing electron donors and  $C_{60}$  is described. The straightforward strategy, based on copper(I)-templated synthesis and “click” chemistry, proved to be very efficient and versatile, allowing the preparation of porphyrin- and ferrocene-stoppered fullerene–rotaxanes in high yields. As revealed by NMR analysis and computational studies, the highly flexible porphyrin–fullerene rotaxane can assume different conformations, which are most likely driven by attractive interactions between porphyrin and fullerene moieties.

In natural photosynthesis, photoinduced energy and electron-transfer reactions are the key steps in the process that converts sunlight into chemically useful products.<sup>1</sup> In these systems, the noncovalent interactions between electron donor (D) and acceptor (A) moieties create a well-defined energy gradient which drives electron-transfer reactions, generating long-lived charge-separated states.<sup>2</sup> In artificial photosynthesis, much effort has been directed toward understanding these interactions and elucidating the electron-transfer mechanisms.<sup>3</sup> A better understanding of these phenomena is crucial for developing more efficient and inexpensive photovoltaic cells that convert light into electricity.

The design and synthesis of artificial photoactive electron donor–acceptor systems that mimic structures involved in natural photosynthesis require the organization of several components in an elaborate molecular topology. Supramo-

lecular concepts have been introduced into the synthesis of D–A systems to permit the construction of more realistic and more complex models. Controlling the position and interactions of chromophores by means of hydrogen bonds, metal coordination, and  $\pi$ – $\pi$  interactions has led to new possibilities in managing the electron-transfer dynamics in artificial photosynthetic model systems.<sup>4</sup>

Among potentially useful supramolecular systems, interlocked structures, such as rotaxanes and catenanes, are promising architectures for the preparation of noncovalently linked D–A systems. Catenanes are comprised of two or more interlocked rings, while rotaxanes possess a ring

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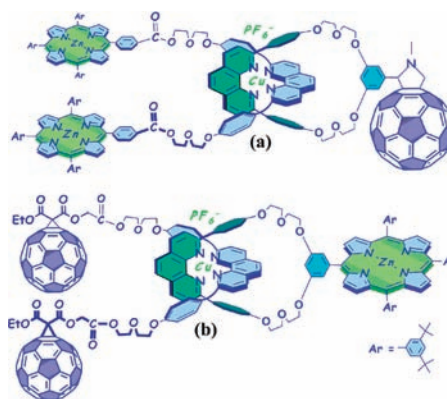
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threaded on a rod bearing bulky substituents at its termini.<sup>5</sup> The interlocked components can undergo submolecular motions by application of external stimuli. For example, in the case of rotaxanes, the ring can be reversibly switched between two different stations on the rod by application of an input such as light, applied voltage, temperature changes, or changes in solvent polarity. Such submolecular motions of the rings in catenanes and rotaxanes have been explored as elegant principles for the construction of molecular machines.

In the field of artificial photosynthesis, the use of interlocked structures as linkers between electron donor and acceptor moieties has recently been explored. A number of such systems incorporating electron donors and C<sub>60</sub> have been prepared and studied by our group and others.<sup>8,9</sup> In our laboratory,<sup>9</sup> we have used the Cu(I) template synthesis, developed by Sauvage and co-workers,<sup>10</sup> to assemble rotaxanes containing zinc(II)–porphyrins (ZnP) as stoppers and C<sub>60</sub> on the macrocyclic ring (for an example, see Figure 1a).<sup>9a</sup> The alternative configuration, in which ZnP is on the ring and C<sub>60</sub> acts as the stopper, has also been investigated (Figure 1b).<sup>9b</sup> Upon irradiation, these ZnP–C<sub>60</sub>-based Cu(I)–rotaxanes undergo a series of energy- and electron-transfer processes that lead to a charge-separated radical pair (CSRP) state, ZnP<sup>•+</sup>–Cu<sup>+</sup>–C<sub>60</sub><sup>•–</sup>, with lifetimes in the microsecond time domain. In the case of the fullerene-stoppered porphyrin rotaxane, Figure 1b, the CSRP lifetime in THF is 32 μs, the longest lifetime reported to date for an interlocked D–A system in solution at ambient temperatures.

The preparation of these ZnP–C<sub>60</sub> linked Cu(I)–rotaxanes requires a long multistep synthesis. In our previous approach to such materials, classical ester coupling was used for the final “stopping” reaction.<sup>9</sup> As a result, the final product was a complex mixture of interlocked and noninterlocked



**Figure 1.** Examples of structures studied in our previous work:<sup>9</sup> (a) porphyrin-stoppered fullerene–rotaxanes and (b) fullerene-stoppered porphyrin–rotaxanes.

materials. Multiple chromatographic separations were required to afford the pure target rotaxanes, which were isolated in low yields.

Herein, we report an easy and expeditious one-pot procedure to synthesize rotaxanes linked to electron donors and C<sub>60</sub>. In recent contributions to the field of interlocked molecules,<sup>11</sup> we have described efficient protocols that allow the preparation of functionalized macrocycles as well as [2]- and [3]catenanes based on Cu(I)-template synthesis<sup>10</sup> and “click” chemistry.<sup>12</sup> Since Cu(I) can act as both template and catalyst, we have developed a one-pot procedure for the final “stopping” reactions, affording rotaxanes containing electron donor and C<sub>60</sub> moieties in one step with very high yields. The preparations of ferrocene- and porphyrin-stoppered fullerene-rotaxanes are described here to demonstrate the versatility of this protocol.

The building blocks and the synthetic strategy are shown in Scheme 1 (see the Supporting Information for details). First, C<sub>60</sub> was attached to previously prepared phenanthroline macrocycle **1** using the Bingel–Hirsch reaction to afford **2**. Macrocycle **2** (1 equiv) was then dissolved in 2 mL of 7:3 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN (v/v), to which [Cu(CH<sub>3</sub>CN)<sub>4</sub>][PF<sub>6</sub>]<sub>4</sub> (1 equiv) was added as a solid. The solution was stirred for 30 min, and previously reported phenanthroline diazide **3**<sup>11</sup> was added as a solid. The resulting dark brown solution was stirred for 3 h under an inert atmosphere with magnetic stirring to generate pseudo-rotaxane **4**. Alkynylferrocene **5** or alkynylzinc–porphyrin **6**<sup>13</sup> (3 equiv), dissolved in 1 mL of CH<sub>2</sub>Cl<sub>2</sub>, was then added to the brown solution, followed by the addition of sulfonated bathophenanthroline (SBP) (4 equiv), CuI (2 equiv), sodium ascorbate (SA) (4 equiv), and 1,8-

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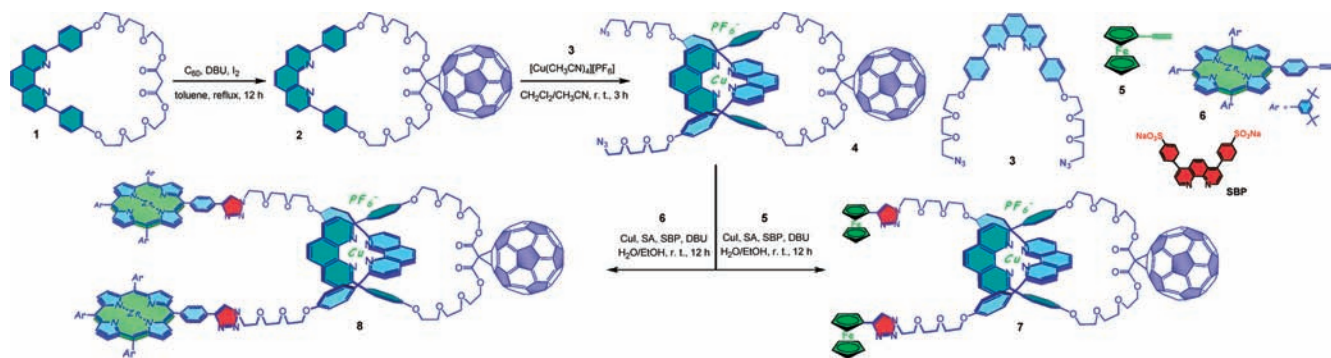
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**Scheme 1.** Building Blocks, Precursors, and Synthetic Strategy Used for the Preparation of Ferrocene- and Porphyrin-Fullerene-Based Rotaxanes<sup>a</sup>

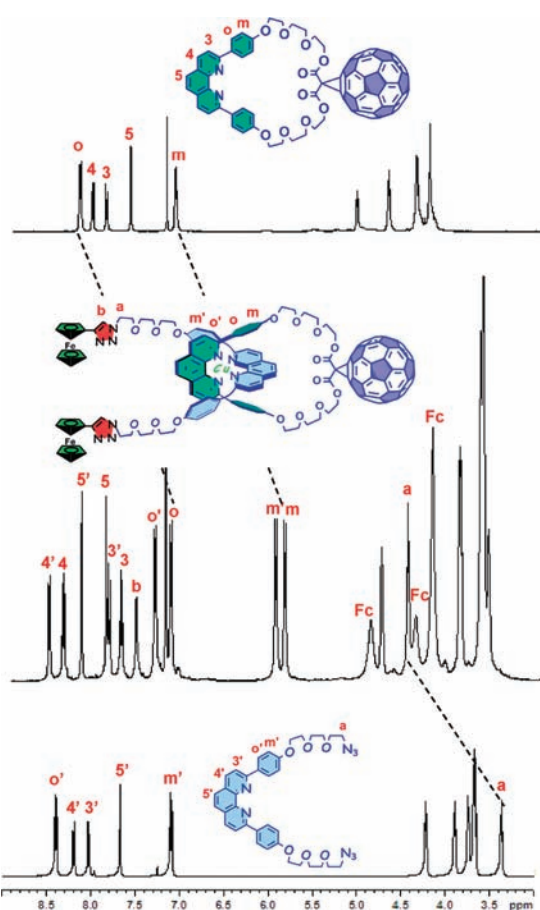


<sup>a</sup> DBU = 1,8-diaza[5.4.0]bicycloundec-7-ene. SA = sodium ascorbate. SBP = sulfonated bathophenanthroline.

diaza[5.4.0]bicycloundec-7-ene (DBU) (2 equiv), all dissolved in 3 mL of an oxygen-free mixture of 1:1 H<sub>2</sub>O/EtOH (v/v), as in our previous study.<sup>11b</sup> The reaction mixture was stirred at room temperature for 12 h under an inert atmosphere. The organic phase was separated, washed with water, and stirred for 2 h with a saturated methanol solution of KPF<sub>6</sub> to effect anion exchange.<sup>14</sup> The solvents were evaporated under reduced pressure, the remaining light brown solid was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the solution was filtered through paper. For rotaxane **7**, final purification was achieved by flash chromatography on silica using CH<sub>2</sub>Cl<sub>2</sub> as the eluent. The first product eluted was unreacted alkynylferrocene. Elution with CH<sub>2</sub>Cl<sub>2</sub>/MeOH (97:3, v/v) afforded target rotaxane **7** as a brown solid in 92% yield.

For rotaxane **8**, final purification was achieved by column chromatography on silica, using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (gradient from 0 to 3%, v/v) as the eluent. The first material eluted was unreacted alkynylporphyrin **6**, while the second (purple solid, 20% yield) fraction was the noninterlocked bis-porphyrin dumbbell compound (MALDI-TOF *m/z* 2752, [M + H]<sup>+</sup>). The third eluted material was target rotaxane **8**, isolated as a purple solid in 75% yield. The lower yield obtained for **8** compared to that of **7** is rationalized in terms of the size difference between alkynylferrocene **5** and alkynylporphyrin **6**. Steric effects in the final 1,3-dipolar cycloaddition reaction should be greater for formation of **8** vs **7**, in which case the reaction to give **8** is expected to be slower. As a consequence, it is not surprising that the pseudorotaxane precursor **4** may be more susceptible to unthreading<sup>10</sup> during the final rotaxane assembly, accounting for the lower yield observed for **8** vs **7**.

Both rotaxanes were fully characterized by standard spectroscopic techniques. The <sup>1</sup>H NMR spectrum of **7** (Figure 2) shows the expected upfield shift for the phenyl protons of the phenanthroline fragments entwined around the Cu(I) center.<sup>10</sup> The methylene groups adjacent to the triazole rings appear at 4.52 ppm, while the protons on the triazole rings appear at 7.60 ppm. The ferrocene protons are observed at 4.95, 4.45, and 4.25 ppm.<sup>15</sup>



**Figure 2.** Partial <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>, 300 K) of macrocycle **2**, Cu(I) rotaxane **7**, and thread **3**.

MALDI-TOF results (*m/z* 2576 [M – PF<sub>6</sub>]<sup>+</sup>) are in agreement with the structure of rotaxane **7** shown in Scheme 1.<sup>16</sup> The <sup>1</sup>H NMR spectrum of rotaxane **8** is more complex (see the Supporting Information), suggesting that it is

(14) Both Cu(I)-rotaxanes have been isolated as PF<sub>6</sub><sup>−</sup> salts.

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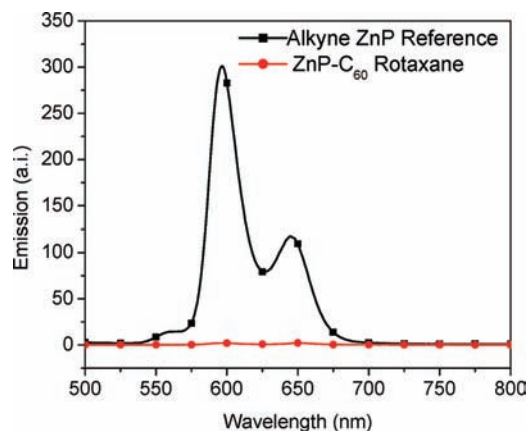
(16) Since both rotaxanes bear a positive charge (Cu<sup>+</sup>), the ionization process in MALDI experiments occurs with loss of a counterion PF<sub>6</sub><sup>−</sup>.



conformationally flexible due to attractive interactions between ZnP and C<sub>60</sub> moieties as well as the high flexibility of the polyoxoethylene linkers (see below).

Fluorescence experiments support this hypothesis. In our previous studies of less flexible ZnP–C<sub>60</sub> rotaxanes,<sup>9</sup> in which both macrocycle and thread were prepared using diethylene glycol “arms” (Figure 1), steady-state fluorescence analysis showed modest quenching of the ZnP singlet excited state. The fluorescence lifetime for the porphyrin-stoppered rotaxane in Figure 1a was 1.0 ns, compared to 3.2 ns for a model ZnP system. This relatively inefficient quenching is not at all typical of covalently linked porphyrin–fullerene hybrid molecules,<sup>17</sup> for which lifetimes are typically 0.1 ns or less. This suggests that fluorescence quenching in the first-generation rotaxanes (Figure 1) does not involve direct interaction between the <sup>1</sup>ZnP\* and C<sub>60</sub> moieties.<sup>9</sup> Further investigation revealed that the (phen)<sub>2</sub>Cu(I) complex quenches the ZnP fluorescence (by energy transfer) and that the intramolecular electronic interactions between ZnP–C<sub>60</sub> take place via the (phen)<sub>2</sub>Cu(I) complex.<sup>9d</sup>

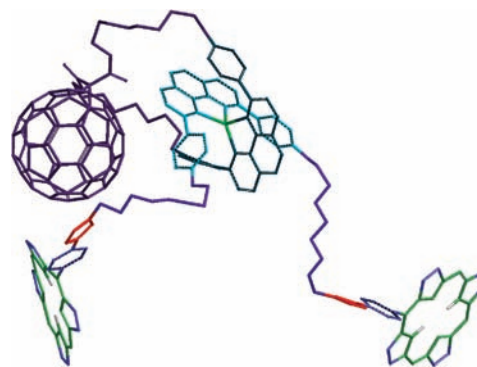
The steady-state fluorescence spectrum of rotaxane **8** in dichloromethane (DCM) (Figure 3) reveals unexpectedly strong quenching of the porphyrin fluorescence compared to that of reference porphyrin **6**. Time resolved fluorescence experiments with **8** in DCM indicate two different decay components, with lifetimes of 0.42 and 1.94 ns.



**Figure 3.** Fluorescence spectra of alkyne zinc porphyrin **6** and ZnP–C<sub>60</sub> rotaxane **8** in CH<sub>2</sub>Cl<sub>2</sub> with matching absorption (OD = 0.20) at the 424 nm excitation wavelength.

The fluorescence lifetime should be directly related to the distance between the chromophores. Indeed, the 3D structure of the lowest energy conformation of free-base rotaxane **8**, computed using PM3 minimization, is folded as shown in Figure 4. C<sub>60</sub> and the (phen)<sub>2</sub>Cu(I) complex are much closer to one of the two porphyrins and at a considerable distance

from the second one, in accord with the biexponential fluorescence decay. The edge-to-edge distances between the two porphyrins and the C<sub>60</sub> moiety are approximately 4.0 and 24.0 Å. Interestingly, for an analogous rotaxane lacking the C<sub>60</sub> moiety, computations show that the extended structure with porphyrins close to each other is the most stable (see the Supporting Information), presumably due to  $\pi$ – $\pi$  interactions between the ZnP moieties.



**Figure 4.** Molecular model of free-base rotaxane **8**. Energy was minimized with 3,5-di-*tert*-butylphenyl groups in the meso positions of each porphyrin, which were later removed for clarity, along with most hydrogen atoms.

In conclusion, we report a straightforward and versatile method to prepare electron donor–fullerene rotaxanes in high yields. This approach is very promising for the synthesis of more elaborate C<sub>60</sub>-containing interlocked structures, such as [2]- and [3]catenanes. The quenching of the ZnP fluorescence in C<sub>60</sub>–rotaxane **8** was much stronger than expected, indicating that the ZnP, C<sub>60</sub>, and (phen)<sub>2</sub>Cu(I) complex are in closer proximity than expected on the basis of the extended structure. Time-resolved fluorescence experiments revealed two decay components, consistent with a structure in which one of the ZnP groups is close to both the C<sub>60</sub> moiety and the (phen)<sub>2</sub>Cu(I) complex, while the second one is at a much greater distance. Support for such a low energy folded conformation was obtained computationally. A complete and detailed investigation of the photophysical properties of the rotaxanes reported in this paper is in progress.

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**Supporting Information Available:** Experimental details for the preparation and spectral characterization of all products and their precursors. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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