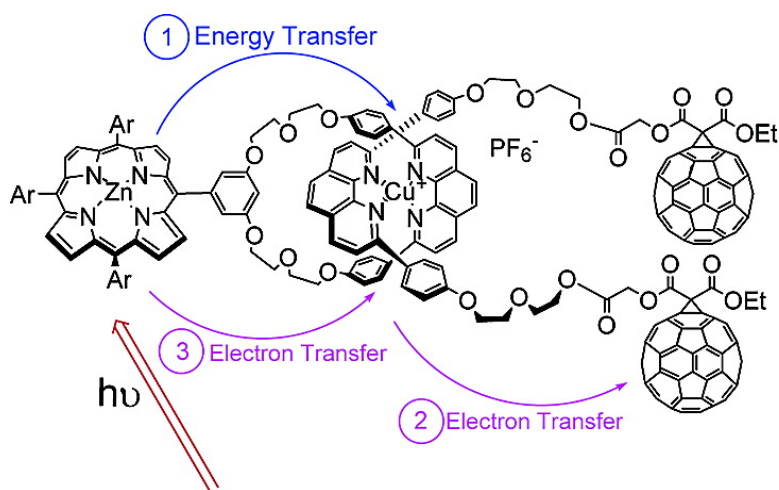


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[60]Fullerene-Stopped Porphyrinorotaxanes: Pronounced Elongation of Charge-Separated-State Lifetimes

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We recently reported the synthesis and photophysical properties of Sauvage-type rotaxanes that incorporate noncovalently linked zinc porphyrin (ZnP) and [60]fullerene chromophores around a central Cu(I)–phenanthroline (phen) core.¹ In the first-generation materials, the fullerene was appended to the macrocycle and two ZnPs were positioned as stoppers on the phen-containing thread. Photoexcitation of these materials induced a series of rapid intramolecular energy transfer (EnT) and electron transfer (ET) processes mediated by the [Cu(phen)₂]⁺ core along an energy gradient, resulting in a relatively long-lived charge-separated radical pair (CSRPs), with the positive charge (hole) localized on the ZnP moiety and the negative charge on the fullerene. Since back-electron transfer (BET) must occur over long distances, ~2 nm, and is in the Marcus inverted region for systems of this type,² the CSRPs lifetimes were relatively long, 0.5–1.2 μs in CH₂Cl₂ at ambient temperatures. We now report on rotaxanes in which the location of the ZnP and C₆₀ moieties is reversed, such that ZnP is appended to the macrocycle and the fullerenes act as stoppers on the thread around the central [Cu(phen)₂]⁺ core. This change in topology results in substantially longer CSRPs lifetimes, greater than analogous covalently linked ZnP–C₆₀ systems,³ and comparable to those for some multicomponent systems, such as ZnP–H₂P–C₆₀.⁴

Previously, Armaroli et al. reported on a rotaxane with a [Cu(phen)₂]⁺ core and two methanofullerene stoppers in which a diyne linker connects the fullerenes to the phen moiety.⁵ It was proposed that energy transfer takes place from the fullerene to the Cu(I) complex, followed by ET from the ³MLCT* state to C₆₀, but the CSRPs state was not detected and its lifetime was not determined.

Our general synthetic approach is illustrated for rotaxane **3** in Scheme 1. First, a macrocyclic structure incorporating a 1,10-phenanthroline moiety appended to a porphyrin moiety was synthesized.⁶ Formation of a Cu(I) tetrahedral complex between the macrocycle and a linear phen thread with hydroxyl functionalities at both ends was monitored by TLC and MALDI-TOF mass spectrometry. The final step involved acid-activated coupling to a C₆₀ carboxylic acid synthon **4**⁷ at room temperature.

Rotaxanes **1–3** were characterized by MALDI-TOF, ¹H NMR, and UV–vis spectra (see Supporting Information). By changing the nature of the linkage between the ZnP and Cu(I)–phen moiety in the macrocyclic precursors to rotaxanes **2** and **3**, the distance between the centers of positive and negative charge in the final CSRPs state could be altered while keeping the thermodynamic driving force for BET essentially fixed. Thus, from electrochemical data, –Δ*G*^o values for BET for **2** and **3** are 1.34 and 1.33 eV, respectively. Rotaxanes **2** and **3** undergo several reversible oxidation

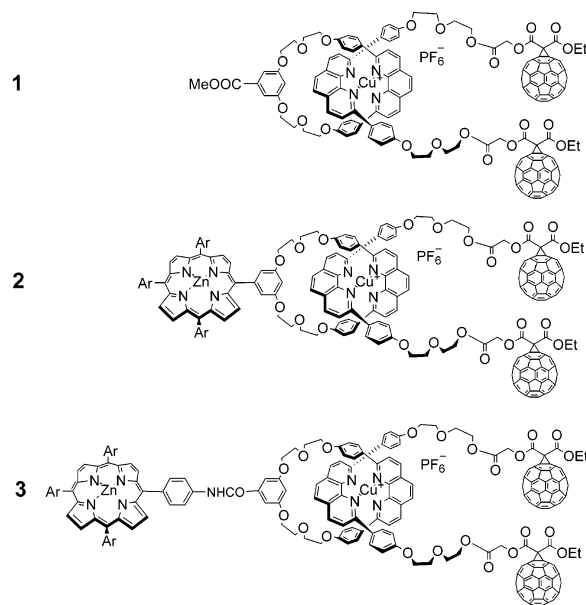
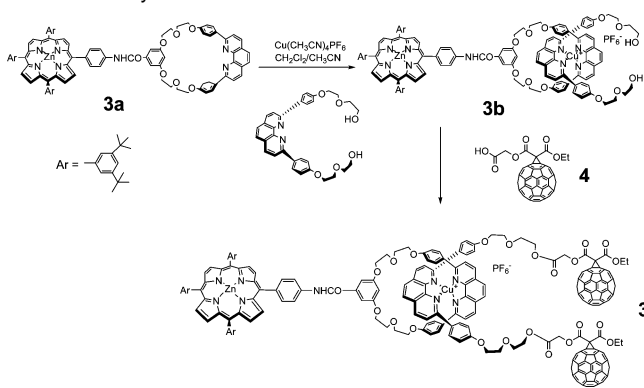


Figure 1. New fullerene-stoppered rotaxanes.

Scheme 1. Synthesis of Rotaxane **3**



and reduction processes (see Supporting Information for details). Redox potentials in CH₂Cl₂ vs Fc/Fc⁺ for one-electron oxidation of a reference Cu(I) complex (*E*_{1/2} [Cu(phen)₂]^{+/0}/[Cu(phen)₂]²⁺ = +264 mV) and for porphyrinic subunits (*E*_{1/2} ZnP/ZnP^{•+} = +302 mV) were reported previously.¹ For rotaxanes **2** and **3**, the first oxidation wave, at +299 and +263 mV, respectively, clearly corresponds to a two-electron process (both Zn and Cu centers are oxidized at the same potential). The resonance donor (+R) effect of the phenylamido group in **3** is responsible for the difference between the half-wave potentials in these derivatives. Rotaxanes **2** and **3** display only three reduction peaks, indicating that both fullerene moieties are reduced simultaneously. Values for the one-

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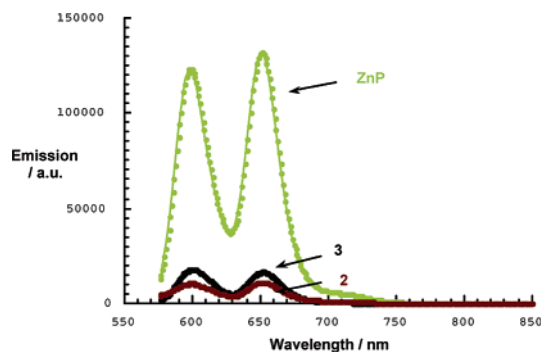


Figure 2. Fluorescence spectra of ZnP, **3**, and **2** in dichloromethane with matching absorption (OD = 0.5) at the 550 nm excitation wavelength.

electron reduction of **2** and **3**, $C_{60}/C_{60}^{\bullet-}$, -1044 mV for **2** and -1065 mV for **3**, are in the range typical of C_{60} monoadducts.⁸

For model rotaxane **1**, excitation of the $[Cu(phen)_2]^+$ complex at 460 nm results in ET, as shown by quenching of MLCT* luminescence and appearance of a transient absorption band at 1040 nm characteristic of C_{60} radical anions ($C_{60}^{\bullet-}$). From the decay of this absorption, the CS state lifetimes for **1** are 310 and 730 ns in CH_2Cl_2 and THF, respectively. The inverse dependence on solvent polarity shows that BET is occurring in the Marcus inverted region.² The fluorescence decays of ZnP-rotaxanes **2** and **3** are monoexponential, with lifetimes of 0.22 and 0.44 ns, respectively. These are sharply reduced relative to the lifetime of 3.2 ns for ZnP itself and are essentially identical to those of synthetic precursors lacking the fullerene. Indeed, the lifetime of **2** is identical to that of Sauvage-type porphyrin-bearing [2]-catenanes.⁹ These data indicate that energy transfer (EnT) is occurring from $^1ZnP^*$ in **2** and **3** to the $[Cu(phen)_2]^+$ MLCT* luminescence, as in the porphyrinocatenanes,⁹ and that electron transfer (ET) directly from $^1ZnP^*$ to C_{60} does not take place. The slightly shorter $^1ZnP^*$ lifetime of **2** and its synthetic precursor is attributed to two factors: (1) the reduced separation of the ZnP and $[Cu(phen)_2]^+$ moieties in **2** vs **3**, and (2) differences in topology, since the porphyrin and “western” phen planes in **2** are essentially coplanar, whereas in **3** they are nearly perpendicular.¹⁰ The $[Cu(phen)_2]^+$ MLCT* luminescence in **2** and **3** is barely observable, with $\Phi < 5.0 \times 10^{-5}$, due to intramolecular ET to the fullerene. Thus, the MLCT* lifetime is reduced from 58 ns in the reference system to 0.58 ns and 0.59 ns in **2** and **3**, respectively.

Spectroscopic proof for the proposed ET mechanism came from transient absorption measurements following 532 nm laser excitation. The transient spectra for **2** and **3** reveal broad bands in the 600–800 nm range, which match those of the one-electron oxidized ZnP radical cations ($ZnP^{\bullet+}$),² as well as the ($C_{60}^{\bullet-}$) band at 1040 nm (see Supporting Information).¹¹ This confirms generation of the long-distance ($ZnP^{\bullet+}$)– $[Cu(phen)_2]^+$ –(C_{60}) $_2^{\bullet-}$ charge-separated radical pair (CSRP) state. Since this state is nearly isoenergetic with ZnP – $[Cu(phen)_2]^{2+}$ –(C_{60}) $_2^{\bullet-}$, according to electrochemical data, the two species may be in equilibrium. The decay of both the $ZnP^{\bullet+}$ and the $C_{60}^{\bullet-}$ transient absorptions obey clean first-order kinetics, corresponding to CSRP lifetimes in CH_2Cl_2 of 0.73 μ s for **2** and 29 μ s for **3**. In THF, these increase to 0.89 and 32 μ s, respectively. The values for **3**, to the best of our knowledge, are the longest CSRP lifetimes measured to date for simple porphyrin–fullerene systems in solution at ambient temperatures³ and are comparable to those of linear arrays in which a ZnP moiety is linked to a free base porphyrin, which in turn is linked to C_{60} .⁴ In these linear triads, the free base porphyrin acts as an ET relay between the terminal ZnP and C_{60} moieties.⁴

A relatively small increase in the distance between the ZnP and C_{60} moieties in **3** compared to **2** results in a 40-fold increase in

CSRP lifetime, despite the fact that the driving force for BET is similar for the two rotaxanes. We believe that a diminished electron coupling element between the centers of positive and negative charge is responsible for slower electron tunneling in **3**, since BET in these rotaxanes must necessarily occur through the intervening bonds, i.e., through-space mechanisms are excluded by the rotaxane topology. An equally intriguing rationalization invokes distinctly different energy gaps between the distant $[ZnP^{\bullet+}$ – $[Cu(phen)_2]^+$ –(C_{60}) $_2^{\bullet-}$] and the adjacent $[ZnP$ – $[Cu(phen)_2]^{2+}$ –(C_{60}) $_2^{\bullet-}$] CSRP states. Due to the nature of the ZnP linker, this energy gap is substantially reduced in **3** relative to **2**, which would delay BET in **3** by a stepwise electron hopping mechanism. The conformational difference in these two rotaxanes discussed above may also play an important role. Regardless of these considerations, the long CSRP lifetimes for **2** and **3** and their solvent dependency leave no doubt that BET is positioned deep in the Marcus inverted region, in line with observations made for many other types of ZnP/ C_{60} hybrids.²

In summary, in these novel fullerene-stoppered porphyrinrotaxanes, where close approach of the ZnP and C_{60} moieties is excluded, intramolecular electronic interactions following photoexcitation must take place through the $[Cu(I)phen_2]^+$ complex. A sequence of short-range EnT and ET processes leads to the ($ZnP^{\bullet+}$)– $[Cu(phen)_2]^+$ –(C_{60}) $_2^{\bullet-}$ CSRP state, with a lifetime as long as 32 μ s in solution at room temperature. The dependence of BET rate on the distance between the $ZnP^{\bullet+}$ and $C_{60}^{\bullet-}$ moieties and on molecular conformation suggests that further structural modifications will lead to even longer CSRP lifetimes. Since the $[Cu(phen)_2]^+$ moiety relays the electronic interaction between ZnP and C_{60} , much as in Sauvage’s purely porphyrinic architectures,¹² the effect of removing the metal center on the photophysical dynamics in these systems should be profound. This is currently under investigation.

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Supporting Information Available: Electrochemical data, transient absorption spectra, UV/vis absorption spectrum and general procedures for preparations of **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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