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Convergent Synthesis and Photophysics of [60]Fullerene/Porphyrin-Based Rotaxanes

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Applications of fullerenes in photoinduced electron-transfer (PET) studies derive from the fact that back electron transfer (BET) is inhibited in donor−acceptor (DA) systems incorporating C_{60}.[1,2] The effect of the introduction of [60]fullerene as an electron acceptor into rotaxanes and catenanes, in which the donor and acceptor moieties are mechanically rather than covalently linked,[3] should enhance our knowledge of the dependence of PET dynamics on molecular topology.
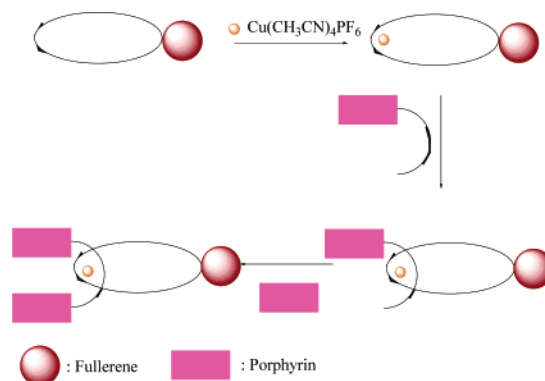
It has been shown by Sauvage and his associates that complexation with transition metals is one of the best methods of accomplishing insertion of a linear thread into a macrocyclic structure.[4,5] In the present study, we have developed routes to Sauvage-type rotaxanes which incorporate noncovalently linked [60]fullerene and porphyrin chromophores around a central Cu(I)−phenanthroline (phen) core.

The general synthetic approach is shown in Scheme 1. First, a macrocyclic structure incorporating a 1,10-phenanthroline moiety appended to [60]fullerene was synthesized. After complexation using Cu(I) cation to a linear phen thread with a zinc tetraarylporphyrin stopper at one end, assembly of the final rotaxane system was achieved by coupling a second porphyrin at the other end of the thread. The rotaxanes were characterized by MALDI-TOF, ¹H NMR, and UV−vis spectra (see Supporting Information).

We designed macrocycles to which a [60]fullerene was appended using standard reactions. Fullerenomacrocycle **2a** was prepared using the Bingel−Hirsch reaction[6] from a macrocyclic precursor. Complexation with Cu(I) was monitored by TLC and MALDI-TOF mass spectrometry. The presence of a 1,10-phen moiety ensures that a linear chain possessing another 1,10-phen will thread through the macrocycle by forming a stable tetrahedral Cu(I) complex. The final step involved EDC/DMAP coupling of the Cu(I) fullerene-containing complex **2b** with the Zn−porphyrin carboxylic acid at room temperature, as illustrated in Scheme 2.

Redox potentials for one-electron oxidation of the porphyrinic subunits ($E_{1/2}$ ZnP/ZnP•⁺ = + 302 mV) and the copper(I) complex ($E_{1/2}$ [Cu(Phen)₂]⁺/[Cu(phen)₂]²⁺ = + 264 mV), in accord with data reported previously for related materials,[7] were determined by cyclic voltammetry in CH_2Cl_2 ($E_{1/2}$ values vs Fc/Fc⁺ internal reference). For rotaxane **1**, the first redox potential at +324 mV involves oxidation of both Zn and Cu centers. Values for the one-electron reduction of the monosubstituted derivative **2** (C_{60}/C_{60}•⁻ = −992 mV) and bis-substituted fullerene derivatives **3** (C_{60}/C_{60}•⁻ = −1110 mV) were also measured (Scheme 3). The electrode potentials for reduction of **2** and **3** are in the range typical of C_{60} mono- and bis-adducts, respectively (see Supporting Information
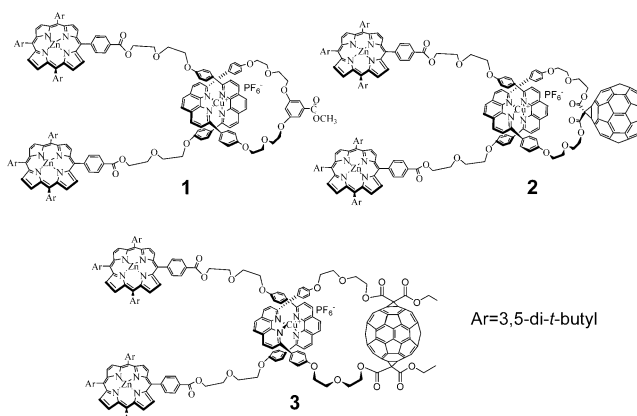
Scheme 1. Synthetic Strategies toward Rotaxanes

○ : Fullerene ▮ : Porphyrin

Scheme 2. Synthesis of Rotaxane **2**

1) Cu(CH₃CN)₄PF₆ CH₂Cl₂/CH₃CN 2)

EDC (20 eq), DMAP(50 eq)

Ar= M= Zn
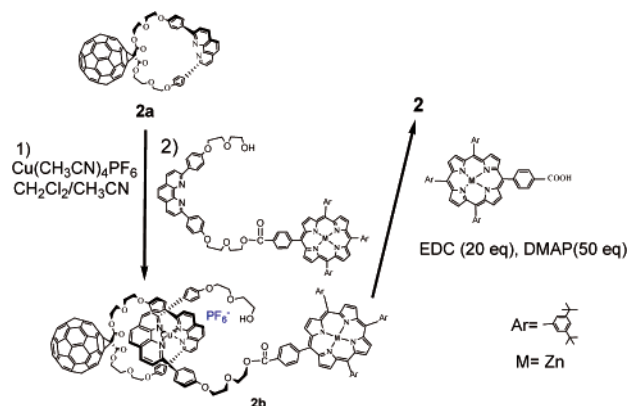
Scheme 3. Rotaxanes

Ar=3,5-di-*t*-butyl

for details). No evidence of electronic interaction between the electroactive units in the ground state was observed by electrochemistry.

† New York University.
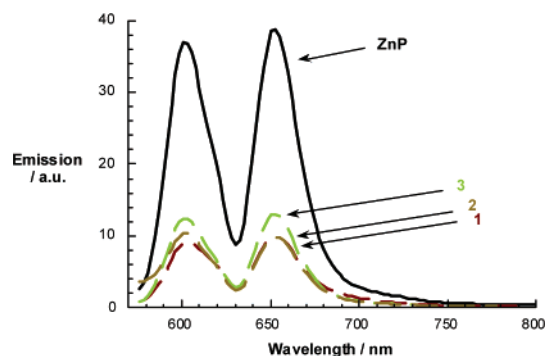‡ University of Notre Dame.
§ Clemson University.

Figure 1. Fluorescence spectra of ZnP, **3**, **2**, and **1** in dichloromethane with matching absorption (OD = 0.5) at the 550 nm excitation wavelength.
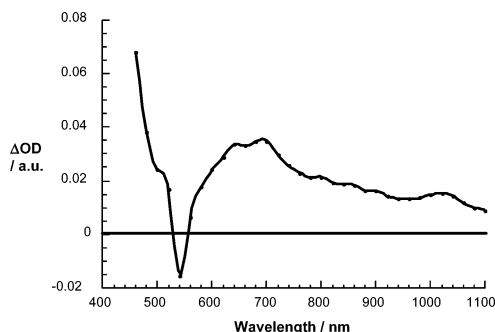

Figure 2. Differential absorption spectrum (visible and near-infrared) obtained upon nanosecond flash photolysis (532 nm) of ~1.0 × 10⁻⁵ M solutions of **2**.

Fluorescence spectroscopy helps to shed light onto the intramolecular events following the initial photoexcitation. Upon 555 nm excitation of the ZnP chromophores, moderate quenching was noted for reference rotaxane **1** ($\Phi = 0.01$ as compared to 0.04 for zinc tetraphenylporphine, ZnTPP; see Figure 1). The fluorescence lifetime for **1** was 1.0 ns as compared to 3.2 ns for ZnTPP. Involvement of a charge-transfer process can be ruled out on thermodynamic grounds,[8] leaving exothermic energy transfer as the likely quenching pathway. When the $[Cu(phen)_2]^+$ is excited at 460 nm (where $[Cu(phen)_2]^+$ absorption is maximal and ZnP absorption is minimal), quenching of the MLCT luminescence ($\Phi = 3 \times 10^{-4}$) is observed, with a lifetime of 5.2 ns (in both aerated and deaerated solution). This quenching produces the long-lived ZnP triplet state (1.53 eV) in nearly quantitative yield from the $[Cu(phen)_2]^+$ MLCT state (1.91 eV). The characteristic triplet−triplet absorption features of ZnP were detected by transient absorption spectroscopy following 532 nm laser excitation (see Figure S5).[9]

The ZnP data do not change for fullerenorotaxanes **2** and **3**, suggesting that the same kind of ZnP/$[Cu(phen)_2]^+$ interactions occur as in **1**. In contrast to **1**, the $[Cu(phen)_2]^+$ luminescence of **2** and **3** is nearly absent, with $\Phi < 5.0 \times 10^{-5}$. An illustration is given in Figure S4. The MLCT luminescence lifetime is reduced to 0.50 and 0.56 ns, respectively. This strongly suggests that, once the excited-state energy reaches the $[Cu(phen)_2]^+$ center, either transduced from ZnP or directly deposited, the presence of C_{60} accelerates the MLCT decay kinetics by activating an intramolecular ET pathway.

Spectroscopic proof for the ET mechanism came from transient absorption measurements, following 532 nm laser excitation. It can be seen from Figure 2 that the transient absorption spectra recorded for **2** after the completion of the laser pulse do not resemble those of the ZnP triplet state seen after excitation of **1**. The transient

spectrum for **2** reveals broad bands in the 600−800 nm range, which match those of the one-electron oxidized ZnP radical cations ($ZnP^{\bullet+}$).[10] At longer wavelengths, absorption characteristic of C_{60} radical anions ($C_{60}^{\bullet-}$) is seen, with maxima at 1040 nm (**2**) and 1020 nm (**3**).[11] This confirms formation of the long-distance $(ZnP^{\bullet+})_2-[Cu(phen)_2]^+-C_{60}^{\bullet-}$ charge-separated radical pair (CSRP), perhaps in equilibrium with $(ZnP)_2-[Cu(phen)_2]^{2+}-C_{60}^{\bullet-}$. Decay of the $ZnP^{\bullet+}$ and the $C_{60}^{\bullet-}$ transients obeys a clean unimolecular rate law, corresponding to radical-pair lifetimes of 0.49 μs for **2** and 1.17 μs for **3**. In line with previous observations of $ZnP^{\bullet+}/C_{60}^{\bullet-}$ CSRP lifetimes in related systems,[10] this stabilizing trend indicates that charge recombination occurs deep in the Marcus-inverted region, because $-\Delta G_{CR}°$ is 0.1 eV more exothermic for **3** than for **2** (1.4 eV vs 1.5 eV).[12]

In summary, a convergent synthesis of fullerene−porphyrin rotaxanes using Sauvage's methodology has been realized, using a basic set of readily prepared starting materials. The topology of these systems prevents close approach of the porphyrin and fullerene moieties, confirmed by molecular modeling, so that intramolecular electronic interactions following excitation must take place through the $[Cu(phen)_2]^+$ complex. A sequence of energy- and electron-transfer processes along an energy gradient ultimately gives the $(ZnP^{\bullet+})_2-[Cu(phen)_2]^+-C_{60}^{\bullet-}$ CSRP, detected spectroscopically, whose lifetime is on the order of microseconds. This is considerably longer than the CSRP lifetime of 180 ns observed by Ito for a $P-C_{60}$ rotaxane loosely held together by hydrogen bonds.[13] The enhancement in CSRP lifetime for **2** and **3** is consistent with the significant difference in topology in these supramolecular systems.

Supporting Information Available: Electrochemical data, transient absorption spectra, and experimental preparations of **1**, **2**, and **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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