We recently reported the synthesis and photophysical properties of Sauvage-type rotaxanes that incorporate noncovalently linked zinc porphyrin \((\text{ZnP})\) and \([60]\) fullerene chromophores around a central \(\text{Cu(phen)}_2\) core.\(^1\) In the first-generation materials, the fullerene was appended to the macrocycle and two \(\text{ZnP}\) 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 \([\text{Cu(phen)}_2\] core along an energy gradient, resulting in a relatively long-lived charge-separated radical pair (CSRP), 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, \(\sim 2 \text{ nm}\), and is in the Marcus inverted region for systems of this type,\(^2\) the CSRP lifetimes were relatively long, \(0.5-1.2 \mu\text{s}\) in \(\text{CH}_2\text{Cl}_2\) at ambient temperatures. We now report on rotaxanes in which the location of the \(\text{ZnP}\) and \(\text{C}_{60}\) moieties is reversed, such that \(\text{ZnP}\) is appended to the macrocycle and the fullerenes act as stoppers on the thread around the central \([\text{Cu(phen)}_2\] core. This change in topology results in substantially longer CSRP lifetimes, greater than analogous covalently linked \(\text{ZnP} - \text{C}_{60}\) systems,\(^3\) and comparable to those for some multicomponent systems, such as \(\text{ZnP} - \text{H}_2 \text{P} - \text{C}_{60}\).\(^4\)

Previously, Armaroli et al. reported on a rotaxane with a \([\text{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 \(\text{Cu(I)}\) complex, followed by ET from the \(3\text{MLCT}\) state to \(\text{C}_{60}\), but the CSRP 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 \(\text{Cu(I)}\) 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 \(\text{C}_{60}\) carboxylic acid synthon \(^7\) at room temperature.

Rotaxanes 1-3 were characterized by MALDI-TOF, \(^1\)H NMR, and \(\text{UV}\) - \(\text{vis}\) spectra (see Supporting Information). By changing the nature of the linkage between the \(\text{ZnP}\) and \(\text{Cu(I)}\) -phen moiety in the macrocyclic precursors to rotaxanes 2 and 3, the distance between the centers of positive and negative charge in the final CSRP state could be altered while keeping the thermodynamic driving force for BET essentially fixed. Thus, from electrochemical data, \(-\Delta G^\circ\) values for BET for 2 and 3 are 1.34 and 1.33 eV, respectively. Rotaxanes 2 and 3 undergo several reversible oxidation and reduction processes (see Supporting Information for details). Redox potentials in \(\text{CH}_2\text{Cl}_2\) vs \(\text{Fe/Fe}^+\) for one-electron oxidation of a reference \(\text{Cu(I)}\) complex \((E_{1/2}[\text{Cu(phen)}]^{3+/2+}) = +264 \text{ mV}\) and for porphyrinic subunits \((E_{1/2} \text{ZnP/ZnP}^{2+} = +302 \text{ mV})\) 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 \(\text{Zn}\) and \(\text{Cu}\) 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-electron
electron reduction of ZnP, \( \text{ZnP}^- \), and \( \text{C}_6\text{O}_6 \) with lifetimes of 0.22 and 0.44 ns, respectively. These data indicate that exponential, with lifetimes of 0.22 and 0.44 ns, respectively.

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 \( \text{C}_6\text{O}_6 \) radical anions (\( \text{C}_6\text{O}_6^- \)). From the decay of this absorption, the CS state lifetimes for 1 are 310 and 730 ns in CH$_2$Cl$_2$ and THF, respectively. The inverse dependence on solvent polarity shows that BET is occurring in the Marcus inverted region.

The fluorescence decays of ZnP–rotaxanes 2 and 3 are monoeponential, 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. These data indicate that energy transfer (ET) is occurring from ZnP$^+$ to 2 and 3 to the [Cu(phen)$_2$]$^+$ MLCT state, as in the porphyrinocatenanes, and that electron transfer (ET) directly from ZnP to \( \text{C}_6\text{O}_6 \) does not take place. The slightly shorter ZnP$^+$ 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. 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$^+$), as well as the \( \text{C}_6\text{O}_6^- \) band at 1040 nm (see Supporting Information). This confirms generation of the long-distance (ZnP$^+$)[Cu(phen)$_2$]$^+$–(C$_6$O$_6$)$^+$ charge-separated radical pair (CSRP) state. Since this state is nearly isoenergetic with ZnP–[Cu(phen)$_2$]$^+$–(C$_6$O$_6$)$^+$, according to electrochemical data, the two species may be in equilibrium. The decay of both the ZnP$^+$ and the \( \text{C}_6\text{O}_6^- \) transient absorptions obeys a first-order kinetics, corresponding to CSRP lifetimes in CH$_2$Cl$_2$ of 0.73 \( \mu \)s for 2 and 29 \( \mu \)s for 3. In THF, these increase to 0.89 and 32 \( \mu \)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 temperatures 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 \( \text{C}_6\text{O}_6^- \). In these linear triads, the free base porphyrin acts as an ET relay between the terminal ZnP and \( \text{C}_6\text{O}_6^- \) moieties.

A relatively small increase in the distance between the ZnP and \( \text{C}_6\text{O}_6^- \) moieties in 3 compared to 2 results in a 40-fold increase in

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**References**

10. We are grateful to a referee for valuable suggestions on this issue.

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