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Convergent Synthesis and Photoinduced Processes in Multi-Chromophoric Rotaxanes¹

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Abstract

A series of [2]rotaxane materials, in which [60]fullerene is linked to a macrocycle and ferrocene (Fc) moieties are placed at the termini of a thread, both of which possess a central Cu(I)-1,10-phenanthroline [Cu(phen)₂]⁺ complex, were synthesized by self-assembly using Sauvage metal template methodology. Two types of threads were constructed, one with terminal ester linkages, and a second with terminal 1,2,3-triazole linkages derived from Cu(I)-catalyzed “click” 1,3-cycloaddition reactions. Model compounds lacking the fullerene moiety were prepared in an analogous manner. The ability of the interlocked Fc-[Cu(phen)₂]⁺-C₆₀ hybrids to undergo electron transfer upon photoexcitation was investigated by means of time-resolved fluorescence and transient absorption spectroscopy, using excitation wavelengths directed at the fullerene and [Cu(phen)₂]⁺ subunits. The energies of the electronic excited states and charge separated (CS) states that might be formed upon photoexcitation were determined from spectroscopic and electrochemical data. These studies showed that MLCT excited states of the copper complex in the fullerenerotaxanes were quenched by electron transfer to the fullerene, resulting in charge separated states with oxidized copper and reduced fullerene moieties, (Fc)₂-[Cu(phen)₂]²⁺-C₆₀^{•-}. Even though electron transfer from Fc to the oxidized copper complex is predicted to be exergonic by 0.18 eV, no unequivocal evidence in support of such a process was obtained. The conclusion that Fc plays no role in the photoinduced processes in our systems rests on the lack of enhancement of the lifetime of the charge separated state as measured by decay of C₆₀^{•-} at ~ 1000 nm, since one-electron oxidized Fc is very difficult to detect spectroscopically in the 500–800 nm spectral region.

Introduction

Self-assembly has been an attractive strategy for constructing fascinating and complex supramolecular systems for various purposes.² Various approaches, including hydrogen bonding, Coulombic interactions and metal complexation, have been widely utilized to assemble supramolecular architectures in which organization of the components has been achieved beyond the simple molecular level.³

Supramolecular systems are omnipresent in nature where they perform functions essential to life, such as photosynthesis, vision and respiration. More specifically, light energy

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conversion processes involved in natural photosynthesis is accomplished by means of a suitably organized supramolecular system, in which the proper spatial organization of electron donor (D) and acceptor (A) moieties is achieved through noncovalent interactions. A cascade of vectorial energy and electron transfer processes generate a long-lived charge separated state $D^{\bullet+}-A^{\bullet-}$, thereby transforming the energy of the incident excitation light into redox-related chemical potential.⁴

Recent progress made in molecular recognition and self-assembly processes has allowed the preparation of complex photoactive arrays, in which the D-A moieties are noncovalently linked.⁵ Among the supramolecular concepts applied in constructing artificial photosynthetic systems, metal coordination is a particularly promising approach because in most cases transition metal complexes not only serve as building blocks to assemble the supramolecular system, but also act as electronic relays, facilitating long-range electron and energy transfer processes.⁶

A number of D-A arrays have been prepared in which the active components are linked through metal coordination.⁷ Among the most promising supramolecular architectures are interlocked molecules, specifically rotaxanes and catenanes.^{5k,8} Rotaxanes consist of a ring threaded on a rod, in which the system is held in place by two bulky end groups, while catenanes consist of two or more interlocked rings. Their unique mechanical arrangement, in which constituent groups are located within a set distance without any direct covalent linkage, allows the components to undergo submolecular motions by application of an external stimulus.⁸

Recent developments in the synthesis of rotaxanes and catenanes at NYU have allowed the preparation of new families of organic-inorganic hybrids, where the organic subunits are zinc(II)porphyrins (ZnP) and fullerenes (C_{60}), while the inorganic component is a transition metal complex.⁹ Due to the complementary photophysical properties of ZnP (electron donor) and C_{60} (electron acceptor), photoinduced energy and electron transfer processes can occur between the mechanically linked organic and inorganic subunits.^{7f,9} Addressing light excitation to a given molecular component by choice of excitation wavelength has enabled the assignment of specific roles to each entity in the hybrid structure and allowed the study of the dynamics of the light induced processes.

Our previous studies on porphyrin-fullerene based [2]rotaxanes with polyether linkages,⁹ assembled by the Cu(I) template-directed method pioneered by Sauvage and co-workers,¹⁰ have shown that upon excitation of the porphyrin subunit, a sequence of energy and electron transfer processes takes place through the (1,10-phenanthroline)₂-Cu(I) ($[Cu(phen)_2]^+$) complex used initially for rotaxane preparation. These photoinduced cascade events ultimately yield a long-lived charge separated (CS) state $ZnP^{\bullet+}-Cu(phen)_2^+-C_{60}^{\bullet-}$, which is characterized by oxidized porphyrin and reduced fullerene moieties. Lifetimes of these CS states as high as 32 μ s have been measured in solution at ambient temperatures.^{9b}

A natural extension of this work is to introduce other electron donors into the C_{60} -based rotaxanes, with the ultimate goal of prolonging the lifetime of the charge separated states. Ferrocene (Fc) is a very good electron donor with a low oxidation potential ($E_{1/2} = +0.5$ V vs. SCE),¹¹ and has frequently been used in fullerene-based D-A systems as the ultimate electron donor, to generate long distance charge separated states.¹² It was therefore a logical next step in our research to incorporate Fc into rotaxanes with the expectation that multi-step electron transfer reactions would take place upon electronic excitation at appropriate wavelengths, as in numerous previously studied covalent Fc- C_{60} dyads and triads,^{12a-f} to generate long-distance long-lived charge separated radical pair (CSRP) states.

In the present paper, we describe two convergent synthetic strategies based on the Cu(I)-template approach for the preparation of three D-A rotaxanes possessing C₆₀ and Fc subunits. These target (Fc)₂-Cu(phen)₂]⁺-C₆₀ rotaxanes are shown in Figure 1. Both strategies have proven to be very efficient synthetic tools, affording rotaxanes in very high yields (> 92% in one case). In the present work, the lengths and structure of both the axle and the ring components of the Fc-C₆₀ rotaxanes were altered in order to achieve better understanding of the relationship between molecular topology and interchromophoric separation distance on the rates of forward and back electron transfer processes.

To better understand the photoinduced processes in this new family of rotaxanes, their photophysical properties were compared with those of analogous pseudorotaxane and rotaxane model compounds **4–7** shown in Figure 2, lacking the C₆₀ and/or Fc moieties. These materials were synthesized using similar methodology.

Results and Discussion

1. Synthetic Design

The basic strategy we used to assemble the rotaxanes relied on three steps (see Strategy A, Scheme 1). First, a phenanthroline (phen) based macrocycle was prepared, in which C₆₀ was attached following classical fullerene chemistry. Second, a “threading” reaction of a phen-containing string-like fragment through the C₆₀-macrocycle, promoted by binding to the Cu(I) center,¹⁰ generated a pseudorotaxane precursor. The pseudorotaxane precursor was then subjected to “stoppering reactions” using ferrocene moieties, affording D-A dyads and model systems with rotaxane topologies.

To prepare the rotaxane dyads **1** and **2** shown in Figure 1, we designed an alternative approach based on the Cu(I) template methodology (see Strategy B, Scheme 1). In this approach, the traditional sequence¹⁰ involving threading followed by stoppering (Strategy A, Scheme 1) was inverted. Due to the relative small size of the Fc moiety, we anticipated that a Fc-terminated phen fragment would have no problem threading through the large C₆₀-phen macrocycle precursor. Accordingly, two Fc moieties were first attached to the termini of the phen-containing string-like fragment, which was then threaded through the C₆₀-phen macrocycle using the standard Cu(I) ion template approach.

Fc-C₆₀ rotaxane **3** is a more flexible structure in which the length and size of both the macrocycle and thread components were increased by changing the diethylene glycol spacers used in **1** and **2** to triethylene glycol spacers. Because of the higher flexibility of the linker, we anticipated that the direct stoppering-threading approach, Strategy B, would probably result in low yields of **3**. Instead, we employed an efficient and straightforward method, which combines the virtues of Cu(I) template synthesis¹⁰ with those of “click” 1,3-dipolar cycloaddition CuAAC chemistry,¹³ an approach that has proved to be very effective in our hands for the preparation of highly flexible rotaxanes and catenanes.¹⁴ In this approach, the traditional threading-stoppering sequence of Strategy A was adopted in which the Cu(I) ion acts as both template for self-assembly and catalyst for the final “double-click” reactions between ethynylferrocene and a bis-azido-terminated pseudorotaxane, to which C₆₀ is already attached, affording rotaxane **3** in very high yields.^{14c}

2. Synthesis

The strategy and precursors actually used to prepare rotaxane **1** and **2** are presented in Scheme 2. The route to rotaxane **1** starts with the symmetrical Fc-stoppered thread **10**, which was synthesized in two steps. The ferrocene carboxylic acid **9** was first activated by DIC/DMAP¹⁵ for 10 min at room temperature until a homogenous orange solution was formed. This activated Fc derivative was then coupled with the phen-diol thread **8**.^{10d} The

C₆₀-phen macrocycle **11** was prepared following a published procedure,^{9c,14c} while fulleromacrocycle **14** was made by coupling between phen-diol thread **8** and ethyl malonate chloride **12**, followed by attachment of C₆₀ using a double Bingel-Hirsch reaction.¹⁶ The ¹H NMR spectrum of **14** (see Supporting Information, S. I.), showed broad peaks,^{16a} but nonetheless clearly revealed the absence of the singlet at δ 3.45 ppm assigned to the acidic malonate protons, while the methylene protons of the ester groups appeared at δ 4.50 ppm, in agreement with the structural assignment of **14** as a *bis*-substituted fullerene adduct. MALDI-TOF analysis confirmed the target structure **14**, showing a molecular ion peak at m/z 1485.9 (M + H)⁺. Although this procedure is expected to afford **14** as a mixture of regioisomeric bis-adducts **14**,¹⁶ the material was used directly in the following steps without further purification.

The usual Cu(I) complexation protocol was then carried out directly using macrocycles **11** and **14**, respectively, with thread **10**. The threading process was easily monitored by thin layer chromatography (TLC). For example, in the case of rotaxane **1**, TLC showed a highly fluorescent spot for macrocycle **11** and a yellow spot corresponding to *bis*-Fc thread **10**. Complexation of **11** with [Cu(CH₃CN)₄][PF₆] in 3:1 DCM/MeCN followed by addition of **10** caused disappearance of both these spots, and appearance of a new dark red spot, whose MALDI-TOF mass spectrum corresponded to that of the desired rotaxane **1**, demonstrating that the desired self-assembly process had indeed occurred. The usual workup, followed by chromatographic purification, yielded the target rotaxane **1** in 53% yield. The final product was characterized by ¹H NMR and MALDI-TOF spectral analysis (figures not shown; see S.I.), which left no doubts as to its structure assignment as a rotaxane. These results confirmed that the cavity of fulleromacrocycle **11** was large enough to allowing threading of the *bis*-Fc-terminated phen string **10** through **11** to occur smoothly. Rotaxanes **2** and **4** were prepared in an analogous manner in 23 and 55% yield, respectively.

The synthesis of 1,2,3-triazole-linked rotaxane **3** by the route shown in Scheme 3 was recently reported elsewhere.^{14c} Briefly, threading **16** through macrocycle **17** using the Cu(I) template protocol¹⁰ afforded the fullerene-based pseudorotaxane **18** quantitatively, as revealed by ¹H NMR spectroscopy. Final two “click” stoppering reactions were accomplished using ethynylferrocene following the conditions reported in our previous communication,^{14c} affording rotaxane **3** as a brown amorphous solid in 92% yield. The structure of **3** was confirmed by ¹H NMR and MALDI-TOF analysis.^{14c} Rotaxane model **5** was prepared in an analogous manner in 95% yield.

3. Electrochemistry

The redox properties of rotaxanes **1**, **2** and **3**, model compounds **4**, **5**, **6** and **7**, and the reference compounds shown in Figure 3, namely C₆₀-malonate-derivative **19**,¹³ *bis*-(phen)₂-Cu(I) pseudorotaxane **20**,¹⁷ and unsubstituted Cu(phen)₂⁺-[2]catenate **21**, were studied by differential and cyclic voltammetry experiments in dichloromethane (DCM) and *ortho*-dichlorobenzene (ODCB) as solvents in the presence of tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) or tetra-*n*-butylammonium perchlorate (TBAClO₄) as supporting electrolyte, with ferrocene/ferricenium as internal reference. Table 1 shows the electrochemical data obtained at Clemson and Erlangen, respectively.

As expected, all rotaxanes display the characteristic redox processes associated with Fc, C₆₀ and [Cu(phen)₂]⁺ centers. In the case of rotaxanes **1** and **4**, the Fc group exhibits a single, electrochemically reversible two-electron redox wave around 45 mV, corresponding to oxidation of the two Fc groups in the molecule. These Fc groups possess a higher redox potential than does pristine ferrocene, due to the electron withdrawing effect of the nearby carbonyl group. The [Cu(phen)₂]⁺ complex in **1** and **4** exhibits an one-electron reversible oxidation, which appears in the potential range for this type of derivative.¹⁸ Bis-adduct

rotaxanes **2** and pseudorotaxane **7** present similar reduction waves, but these are cathodically shifted with respect to **1** and **4** due to the saturation of a second double bond on C₆₀, causing a negative shift of the reduction potentials.

For the larger more flexible triazole-linked rotaxanes **3** and **5**, three characteristic oxidation features were discernible in the anodic scan. The first process at 0 V was assigned to the one-electron oxidation of Fc, indicating that the introduction of a triazole ring near the Fc group does not have an appreciable electronic effect on the Fc moiety. The second peak at +0.18 V reflects one-electron oxidation of [Cu(phen)₂]⁺, that is, Cu⁺/Cu²⁺. A third rather broad peak at +1.14 V is tentatively assigned to the Cu²⁺ / Cu³⁺ oxidation (not included in Table 1). In the cathodic scan, only a single one-electron reduction is seen at -2.30 V which correlates with the one-electron Cu⁺/Cu⁰ reduction.

Comparison of the electrochemical data of the rotaxanes with their model compounds, conducted under the same experimental conditions, reveals that the presence of the C₆₀ moiety in the molecule has no noticeable impact on the oxidation and reduction potentials of the other components. These results demonstrate that the various constituents do not electronically couple or strongly interact with each other in the ground state.

4. Steady-State and Time-Resolved Fluorescence Studies

Fluorescence experiments provided initial insights into the photoinduced processes occurring in the new rotaxanes. Figure 4 shows the fluorescence spectra of several rotaxanes as well as those of the corresponding reference compounds, while Table 2 summarizes the spectroscopic data collected for all compounds studied.

The data for fullerene reference compound **2017** and [Cu(phen)₂]⁺ pseudorotaxane **21** will be discussed first. Both **20** and **21** exhibit emission centered at 765 nm, with quantum yields of 3.0×10^{-4} and 4.8×10^{-3} , respectively, and identical fluorescence lifetimes of 2.5 ns in benzonitrile (PhCN). This emission of **21** originates from deactivation of the thermally equilibrated singlet and triplet MLCT excited states of the [Cu(phen)₂]⁺ complex. We note that the fluorescence quantum yield for the more flexible structure **20** is lower than that for the more rigid structure **21**, as expected.

The luminescence properties of rotaxane **1** reflect the interchromophoric interactions in these systems upon photoexcitation. Quenching of the MLCT-type emission band of the [Cu(phen)₂]⁺ moiety is evident (Figure 4A). The luminescence quantum yields and lifetimes of rotaxanes **1** and **2** in benzonitrile, namely $6.8 \times 10^{-6}/40$ ps and $1.2 \times 10^{-5}/77$ ps, respectively, are much lower than those of the model compounds **20**, **21**, and **4**, which indicate that additional photophysical pathways are at work in rotaxanes **1** and **2**. It is important to note that the quantum yields for **1** and **2** are nearly identical to those for pseudorotaxanes **6** (3.8×10^{-5}) and **7** (1.3×10^{-5}). Quenching of the electronically excited [Cu(phen)₂]⁺ moiety in **1** and **2** located 1.70 eV above the ground state is attributed to highly efficient electron transfer to C₆₀ from the lowest MLCT state, to give the energetically lower lying radical ion pair [Cu(phen)₂]²⁺-C₆₀^{•-} located at 1.33 eV, as estimated from the electrochemical data in Table 1.

Turning now to the more flexible triazole-linked structures, excitation of [Cu(phen)₂]⁺-Fc₂ rotaxane **5** at 320 nm produces a rather broad emission band centered at 765 nm (Figure 4B), attributed to luminescence from the MLCT excited state [Cu(phen)₂]⁺. The quantum yield is 6×10^{-4} in DCM or ODCB and 1.6×10^{-3} in PhCN, lower than those measured for **20** and **21** but higher than that measured for [Cu(phen)₂]⁺-C₆₀ pseudorotaxane **6**. Upon 355 nm excitation of C₆₀ in [Cu(phen)₂]⁺-Fc₂ rotaxane **3**, we observe moderate quenching of the C₆₀ emission (Figure 4c). In PhCN, the fluorescence quantum yield is reduced to 2×10^{-4} .

compared to 6×10^{-4} for the C_{60} reference **19**. Considering the fact that energy transfer from the weakly fluorescing C_{60} singlet excited state (1.78 eV) to the $[Cu(phen)_2]^+$ singlet excited state (1.92 eV) is thermodynamically unfavorable, charge transfer is left as the only feasible deactivation pathway for **3** and **5**. This quenching was corroborated by time-resolved fluorescence measurements, as the lifetimes of 0.1 and 1.4 ns determined for rotaxane **3** and reference **19**, respectively, are much lower than those for **20** and **21**. These data should also be compared with those for the pseudorotaxane model **6**, in which the C_{60} fluorescence quantum yield is reduced to 4.0×10^{-4} and 2.3×10^{-5} in DCM and PhCN, respectively. These data are summarized in Table 2.

5. Transient Absorption Studies

Further insight into the formation and decay processes of the photoexcited rotaxanes was obtained by transient absorption studies in PhCN. Excitation of C_{60} reference compound **19** at 387 nm (Figure not shown) populates the fullerene singlet excited state with characteristic absorption maxima at 610 and 920 nm.¹⁹ The latter undergoes quantitative intersystem crossing to the triplet manifold with a characteristic lifetime of 1.4 ns.¹⁹ In the absence of molecular oxygen, the C_{60} triplet excited state ($^3C_{60}^*$) has a lifetime of up to 20 μ s.

Photoexcitation of the $[Cu(phen)_2]^+$ pseudorotaxane reference **20** and catenate **21** at 387 nm in an oxygen free environment generates MLCT excited states. The intermediate singlet MLCT excited state is discernible immediately following the excitation of **20**, for which a transient maximum is seen at 490 nm, which decays with a lifetime of 0.43 ps²⁰ to form the triplet MLCT excited state, which has maxima at 540 and 1000 nm (see Figure 5). Additional minima evolve in the 440 and 700 nm regions, which correspond well with the MLCT absorption and attest to conversion of the ground state into the corresponding MLCT excited state. On the 3 ns time scale of the femtosecond experiments, no appreciable decay of the triplet MLCT excited state is seen. Upon nanosecond excitation of **20** at 355 nm similar characteristics develop, with a lifetime of 886 ns in deaerated PhCN, assigned to the phenanthroline formed by an energy transfer process.²¹

Excitation at 387 nm of $(Fc)_2-[Cu(phen)_2]^+$ rotaxanes **4** and **5**, lacking the C_{60} moiety, generated the MLCT excited states of $[Cu(phen)_2]^+$ with characteristic absorption maxima at 590 nm and a broad absorption centered around 880 nm (see Figure 6 for spectra of rotaxane **5**). Again, the triplet MLCT excited state of **5** is long lived and does not decay appreciably on the time scale of our femtosecond laser experiments (i.e., up to 3 ns). Moreover, on this timescale, Fc does not exert any notable impact on the triplet $[Cu(phen)_2]^+$ MLCT excited state of **5**.

In $(Fc)_2-[Cu(phen)_2]^+-C_{60}$ rotaxane **3**, 387 nm excitation is mainly directed to the C_{60} unit due to its dominant absorption in that spectral region.¹⁹ Instantaneous growth of absorption at 900 nm confirms generation of $^1C_{60}^*$, which decays with accelerated dynamics, attributable to the nearby $[Cu(phen)_2]^+$ subunit (see Figure 7). The average of the first order fits of the time-absorption profiles at various wavelengths gives a value of only 35 ps for the $^1C_{60}^*$ lifetime in **3**, which matches the strongly quenched $^1C_{60}^*$ emission (see above). As the C_{60} singlet excited state decays, new transients evolve with broad absorption in the visible region centered at 590 nm, showing the signature of $[Cu(phen)_2]^{2+}$. At the same time, some new absorption rapidly evolves in the near infrared region with a maximum at 1035 nm, which is the well known fingerprint absorption of the one-electron reduced form of C_{60} , i.e., $C_{60}^{\bullet-}$.¹⁹ Thus, the transient absorption studies confirm the formation by electron transfer of the radical ion pair $(Fc)_2-[Cu(phen)_2]^{2+}-C_{60}^{\bullet-}$, which is stable on the picosecond time scale. Additionally, we see spectroscopic evidence in the visible region for the formation of the singlet MLCT excited state (λ_{max} 490 nm), which is transformed with

lifetimes of 0.43 and 14 ps into the triplet MLCT excited state (λ_{max} 530 nm) and the radical ion pair state (λ_{max} 590 nm), respectively.

In complementary nanosecond experiments, excitation of triazole-linked (Fc)₂-[Cu(phen)₂]⁺-C₆₀ rotaxane **3** at 355 nm in PhCN leads to the same radical ion pair spectral features characteristic of C₆₀^{•−} and [Cu(phen)₂]²⁺ (figure not shown). A multiwavelength analysis for decay of the transient absorption revealed two major decay components for (Fc)₂-[Cu(phen)₂]²⁺-C₆₀^{•−}, a short lived oxygen concentration-independent component and a long lived oxygen concentration-dependent component. We believe that the short-lived component – decay time 15 ns – corresponds to charge recombination to afford the singlet ground state. Independent confirmation for this conclusion come from a freshly prepared sample of pseudorotaxane **6,17** which lacks the Fc units, whose radical ion pair state decays with a lifetime of 15 ns. A possible rationale for the second component whose lifetime is 121 ns emerges upon consideration of the driving force of −0.16 eV for a charge shift reaction, i.e., movement of the positive charge from the [Cu(phen)₂]²⁺ complex to Fc to give (Fc)₂^{•+}-[Cu(phen)₂]⁺-C₆₀^{•−}. We estimate the energies of the two charge-separated states as 1.20 and 1.04 eV, respectively, based on our electrochemical data (Table 1).²² Once again, the low extinction coefficient of one-electron oxidized Fc even at its maximum absorption of 680 nm¹² renders this spectroscopic identification uncertain, however plausible. Direct charge transfer from Fc to C₆₀ is not likely due to the large donor-acceptor separation, close to 2 nm. We anticipated that the lifetime of the long distance radical ion pair state of **3**, (Fc)₂^{•+}-[Cu(phen)₂]⁺-C₆₀^{•−}, would be at least 1 μs, as seen in the covalent systems described previously in which such a charge transfer step was invoked.¹² This was not observed in our experiments.^{23,24} To shed further light on this issue, experiments were carried out at different oxygen concentrations, that is, oxygen saturated, air saturated and argon saturated. It is noteworthy that the short-lived component of 15 ns remains constant throughout these measurements, while the lifetime of the longer-lived component varies between 121 ns and 7.7 μs. The resemblance of the latter response to quenching of C₆₀ triplet excited states by molecular oxygen¹⁹ forces us to conclude that the longer-lived component is in fact the triplet excited state C₆₀ rather than the (Fc)₂^{•+}-[Cu(phen)₂]⁺-C₆₀^{•−} radical ion pair state. Nevertheless, we cannot absolutely rule out the possible generation of (Fc)₂^{•+}-[Cu(phen)₂]⁺-C₆₀^{•−} provided that its lifetime is as low as 121 ns. On the basis of the driving forces for charge recombination (−1.2 eV) and charge shift (−0.16 eV), along with a reorganization energy of around 0.8 eV, it is clear that the former process (i.e., charge recombination) is in the Marcus inverted region, while the latter (i.e., charge shift) is in the normal region of the Marcus parabola. Correspondingly, we estimate – assuming similar electronic couplings – that the charge shift reaction is three orders of magnitude slower than charge recombination. In other words, the efficiency of the charge shift is estimated to be at most 0.001 %.

Similarly, in studies of **1** (Figure 8) and **2** (Figure 9), we note that instead of the slow intersystem crossing dynamics, the singlet-singlet absorption of C₆₀ (i.e., at 900 and 920 nm) decays in the presence of [Cu(phen)₂]⁺ complex with accelerated dynamics, along with the enhanced decay of the rapidly formed (i.e., 0.43 ps) triplet MLCT excited state (i.e., at 540 nm). There is a close resemblance of the dynamics noted in **1** (lifetimes 33 and 9 ps) and **2** (48 and 15 ps) with those in **3** (35 and 14 ps). In all three cases, new transients are seen in the visible range, which match those of the one-electron oxidized [Cu(phen)₂]²⁺ at 590 nm, and, in the near-infrared, the one-electron reduced C₆₀^{•−} at 1035 nm. Thus, the spectroscopic features of the observed transients confirm the formation of a radical ion pair state, which is stable on the femtosecond and picosecond time scales.

We examined the charge-recombination dynamics for first generation C₆₀-(Fc)₂ rotaxanes **1** and **2** on the nanosecond time scale using 6 ns laser pulse excitation at 355 nm. In this

context, the spectral fingerprints of the radical ion pair state, $\text{Fc}_2\text{-}[\text{Cu}(\text{phen})_2]^{2+}\text{-C}_{60}^{\bullet-}$ are seen immediately after the ns laser pulse, indicating these states are the ultimate product of the charge transfer process.¹⁹ The lifetime of the CS states of both **1** and **2** is 16 ns, determined by the decay of the fingerprint absorption for $\text{C}_{60}^{\bullet-}$ at 1035 nm. Quite interestingly, these values of 16 ns exactly match the lifetimes determined for pseudorotaxane reference compounds **6** and **7** lacking Fc moieties as well as the lifetime of 15 ns determined for the triazole-linked rotaxane **3**. The small molar extinction coefficient of the ferricenium ion at 800 nm unfortunately precludes direct detection of the formation and decay of $\text{Fc}^{\bullet+}$.¹² The quite short lifetime of the charge separated states in these rotaxanes, on the order of 16 ns, argues against the proposal that $\text{Fc}_2^{\bullet+}\text{-}[\text{Cu}(\text{phen})_2]^+\text{-C}_{60}^{\bullet-}$ charge separated radical ion pair are formed in rotaxanes **1**, **2** and **3**, contrary to the claim in the recent paper of Ito and coworkers on Al(III)porphyrin- C_{60} -Fc triads.²³ In addition to the short-lived components in these systems a longer lived component is observed, whose lifetime depends strongly on the oxygen concentration. Thus, lifetimes of 126 ns and 115 ns are observed for **1** and **2**, respectively, in oxygen-saturated PhCN, with much longer lifetimes observed in oxygen-free solutions. While these values could be considered to be upper limits for the lifetimes of $(\text{Fc})^{\bullet+}\text{-}[\text{Cu}(\text{phen})_2]^+\text{-C}_{60}^{\bullet-}$ radical ion pair states in **1** and **2**, we believe they are more likely due to C_{60} triplet excited states, as discussed earlier.

Conclusions

Based on these findings, we propose the energy level diagram and decay pathways shown in Figure 10 for rotaxanes **1**, **2** and **3** upon excitation of either the $[\text{Cu}(\text{phen})_2]^+$ or C_{60} moieties. In all three cases, excitation at 387 nm leads to electron transfer to give the charge separated state $(\text{Fc})_2\text{-}[\text{Cu}(\text{phen})_2]^{2+}\text{-C}_{60}^{\bullet-}$, with an oxidized $[\text{Cu}(\text{phen})_2]^{2+}$ and a reduced C_{60} . This charge separated state has lifetime of 15–16 ns in benzonitrile, virtually identical to model compounds lacking ferrocene moieties. Thus, charge shift from the Fc moiety to the $[\text{Cu}(\text{phen})_2]^{2+}$ to generate the long-distance $^+(\text{Fc})_2\text{-}[\text{Cu}(\text{phen})_2]^+\text{-C}_{60}^{\bullet-}$ charge separated states does not appear to take place in these rotaxanes. This conclusion is based mainly on the lack of elongation of the CS state lifetime on introducing Fc moieties into the system, despite the fact that such a charge shift process is predicted to be exergonic by 0.18 eV. It certainly would be advantageous to be able to follow the formation and decay of $\text{Fc}^{\bullet+}$ moieties to absolutely confirm this conclusion, but thus far this has not proved possible. These findings are in contrast to previous reports on the photophysics of covalently linked donor-acceptor triads and related Fc-ZnP- H_2P - C_{60} tetrads in which the CS lifetime is significantly elongated by introducing Fc groups, an effect attributed to a charge shift from the $\text{ZnP}^{\bullet+}$ to the Fc moieties,¹² as well as the recent report on an Al(III)- C_{60} -Fc triad mentioned earlier.²³ In rotaxanes **1**, **2** and **3**, ET from Fc to the oxidized $[\text{Cu}(\text{phen})_2]^{2+}$ complex to generate the analogous long-distance CSRP state $^+(\text{Fc})_2\text{-}[\text{Cu}(\text{phen})_2]^+\text{-C}_{60}^{\bullet-}$ does not appear to be competitive with charge recombination from $(\text{Fc})_2\text{-}[\text{Cu}(\text{phen})_2]^{2+}\text{-C}_{60}^{\bullet-}$ to regenerate the rotaxane ground state. This could be due to the increased dimensions of the rotaxanes, in which the center-to-center distance between the Fc stoppers and $[\text{Cu}(\text{phen})_2]^+$ cores is 1.0 nm in rotaxane **1** and further increases to 1.8–1.9 nm in the case of rotaxane **3**, both in extended conformations. For the covalent systems,¹² linkage is provided by an amide group and the Fc-ZnP distance is also much shorter. However, it is worthy of note that in triazole-linked rotaxanes analogous to **3** with ZnP stoppers in place of Fc and identical dimensions, photoinduced electron transfer does take place to give the long-lived long distance charge separated radical pair state $(\text{ZnP})_2^{\bullet+}\text{-}[\text{Cu}(\text{phen})_2]^+\text{-C}_{60}^{\bullet-}$. Details of this investigation will be reported shortly.²⁴ Obviously, in rotaxane systems with similar dimensions electronic coupling between ZnP and the oxidized $[\text{Cu}(\text{phen})_2]^{2+}$ complex is much better than coupling between Fc and the same Cu^{2+} complex.

Experimental Section

1. General Information and Materials

NMR spectra were obtained on either a Bruker AVANCE 400 (400 MHz) or an AVANCE 500 (500 MHz) spectrometer using deuterated solvents as the lock. The spectra were collected at 25 °C and chemical shifts (δ , ppm) were referenced to residual solvent peak (^1H , CDCl_3 at 7.26 ppm; ^{13}C at 77.2 ppm). In the assignments, the chemical shift (in ppm) is given first, followed, in brackets, by multiplicity (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad), the value of the coupling constants in Hz if applicable, the number of protons implied and finally the assignment. In the ^1H NMR assignment (δ), H_o and H_m refer to the hydrogen atoms at the *ortho* and *meta* positions, respectively, of the phenyl ring attached to the phenanthroline ring system, whose hydrogen atoms are numbered $\text{H}_{3,8}$, $\text{H}_{4,7}$, $\text{H}_{5,6}$, respectively. Ar and Cp are used as abbreviations for aromatic and cyclopentadienyl rings, respectively. Mass spectra were obtained on an Agilent 1100 Series Capillary LCMSD Trap XCT Spectrometer in positive or negative-ion mode and ThermoFinnigan PolarisQ ion-trap GCMS Spectrometer. MALDI-TOF mass spectra were recorded in a Bruker OmniFLEX MALDI-TOF MS Spectrometer. This instrument was operated at an accelerating potential of 20 kV in linear mode. The mass spectra represent an average over 256 consecutive laser shots. The mass scale was calibrated using the matrix peaks and the calibration software available from Bruker OmniFLEX. Mentioned m/z values correspond to monoisotopic masses. The compound solutions (10^{-3} mol/L) were prepared in THF. Matrix compound was purchased from Aldrich and used without further purification. The matrix, α -cyano-4-hydroxy-cinnamic acid (CCA), was dissolved (10 g/L) in a solvent mixture composed of water/acetonitrile/trifluoroacetic acid (25/75/1, v/v). Two microliters of compound solution were mixed with 10 μL of matrix solution. The final solution was deposited onto the sample target and allowed to dry in air. All chemicals were purchased from Sigma-Aldrich and Alfa Aesar and used without further purification. For moisture sensitive reactions, solvents were freshly distilled. Methylene chloride (DCM), toluene (PhMe) and acetonitrile (CH_3CN) were dried over calcium hydride while tetrahydrofuran (THF) was dried using sodium/benzophenone. Anhydrous dimethylformamide (DMF) was used as received. All syntheses were carried out using Schlenk line techniques. Moisture sensitive liquids were transferred by canula or syringe. The progress of the reactions was monitored by thin-layer chromatography (TLC) whenever possible. TLC was performed using precoated glass plates (Silica gel 60, 0.25 mm thickness) containing a 254 nm fluorescent indicator. Column chromatography was carried out using Merck Silica gel 60 (0.063–0.200 mm). Compounds **8**, **10d**, **11**, **9**, **14c**, **15**, **10d**, **16**, **14c** and **17**, **14c** were synthesized following literature procedures.

2. Electrochemical Studies

The solution electrochemistry of compounds **1–7** and reference systems **19**, **20** and **21** was investigated by Cyclic Voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV). The solutions were prepared at concentrations between 0.1–0.5 mM in deoxygenated methylene dichloride (CH_2Cl_2) or *o*-dichlorobenzene (*o*-DCB), and containing tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) (0.1 M) or tetra-*n*-butylammonium perchlorate (TBAClO₄) as supporting electrolytes, respectively. A glassy carbon electrode (3 mm diameter) was used as the working electrode, a platinum mesh as the counter, and an Ag/AgNO₃ (CH_3CN) as reference electrode. Ferrocene was added as an internal reference and all values are reported vs ferrocene. For derivatives **1**, **2**, **4**, and **6** (see Figures 1 and 2) decamethylferrocene was added as an internal reference and it was referenced against ferrocene. The redox potentials are summarized in Table 1.

All electrochemical measurements were performed with a BAS 100 W electrochemical analyzer (Bioanalytical systems) or an E.G.C. Princeton Applied Research model 263A potentiostat/galvanostat.

3. Photophysical Studies

Femtosecond transient absorption studies were performed with 387 and 420 nm laser pulses (1 kHz, 150 fs pulse width) from an amplified Ti:Sapphire laser system (Model CPA 2101, Clark-MXR Inc.). Nanosecond Laser Flash Photolysis experiments were performed with 355 or 532 nm laser pulses from a Quanta-Ray CDR Nd:YAG system (6 ns pulse width) in front face excitation geometry. Fluorescence lifetimes were measured by using a Fluorolog (Horiba Jobin Yvon). Steady-state fluorescence measurements were performed by using a Fluoromax 3 (Horiba Jobin Yvon). The experiments were performed at room temperature.

4. Synthesis

Thread compound 10—1,3-dicycloisopropylcarbodiimide (DIC) (0.150 g, 1.20 mmol) was added to a suspension of *p*-ferrocenyl benzoic acid **9** (0.320 g, 1.05 mmol), 4-dimethylaminopyridine (DMAP) (0.050 g, 0.41 mmol) in dry CH₂Cl₂ (10 mL) at room temperature. The suspension turned into orange solution quickly. After 15 min, phen-diol **12** (0.270 g, 0.50 mmol) was added to the orange solution as a solid and the mixture was stirred for 16 h. The precipitated N,N'-dicycloisopropylcarboureia was removed by filtration and the filtrate was subject to column chromatography (SiO₂) using CH₂Cl₂/CH₃OH (98:2, v/v) to afford **10** as a orange powder in 82% yield (0.46 g). ¹H NMR (CDCl₃), δ ppm: 8.44 (d, *J* = 8.8 Hz, 4H, H₀); 8.24 (d, *J* = 8.5 Hz, 2H, H₄ and H₇); 8.07 (d, *J* = 8.5 Hz, 2H, H₃ and H₈); 7.96 (d, *J* = 8.3 Hz, 4H, ferrocene *orto* Ar-H); 7.73 (s, 2H, H₅ and H₆); 7.46 (d, *J* = 8.3 Hz, 4H, ferrocene *meta* Ar-H); 7.22 (d, *J* = 8.8 Hz, 4H, H_m); 4.65 (t, *J* = 4.9 Hz, 4H, Ar-COO-CH₂); 4.52 (t, *J* = 4.9 Hz, 4H, CH₂-O-phenanthroline); 4.30-3.90 (m, 26H, O-CH₂-CH₂-O and Cp-H); MALDI-TOF: *m/z* found 1116.94 [M+H]⁺, calculated 1116.27 for C₆₆H₅₆N₂O₈Fe₂.

Compound 13—The diol **8** (1.08 g, 2.0 mmol) was dissolved in dry (50 mL) CH₂Cl₂. The solution was cooled to 0°C in an ice bath, then Et₃N (1.0 mL) and DMAP (0.005 g, 0.041 mmol) were added. The subsequent addition of ethyl malonyl chloride **12** (0.60 g, 4 mmol) was made by syringe dropwise. The solution was then allowed to stir at 0°C for 3h, and then at rt for 12 h. TLC indicated that the reaction had proceeded to completion. The reaction mixture was extracted with HCl (5%) and then saturated NaHCO₃ solutions. The organic layer was washed with water (150 mL), dried over MgSO₄, filtered through paper and concentrated under reduced pressure. The resulting oil residue was subjected to column chromatography (SiO₂) using CH₂Cl₂/CH₃OH (98:2, v/v) to afford **13** as a yellow oil in 85% yield (1.30 g). ¹H NMR (CDCl₃), δ ppm: 8.43 (d, *J* = 8.8 Hz, 4H, H₀); 8.25 (d, *J* = 8.5 Hz, 2H, H₄ and H₇); 8.05 (d, *J* = 8.5 Hz, 2H, H₃ and H₈); 7.73 (s, 2H, H₅ and H₆); 7.08 (d, *J* = 8.8 Hz, 4H, H_m); 4.38 (t, 4H, COO-CH₂-CH₃); 4.25 (t, *J* = 4.9 Hz, 4H, CH₂-O-phenanthroline); 4.20-3.80 (m, 12H, O-CH₂-CH₂-O); 3.45 (s, 4H, O=C-CH₂-C=O); 1.25 (s, 6H, O-CH₂-CH₃). LCMS: *m/z* found 769.1 [M+H]⁺, calculated 768.3 for C₄₂H₄₄N₂O₁₂.

Macrocycle 14—Phen di-malonate **13** (0.153 g, 0.20 mmol), C₆₀ (0.144 g, 0.2 mmol) and I₂ (0.107 g, 0.42 mmol) were dissolved in dry chlorobenzene (80 mL) under N₂ atmosphere. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.180 g, 0.177 mL, 1.20 mmol) was added to the above solution and the solution was stirred at rt for 10 h. The crude product was concentrated under reduced pressure and purified by column chromatography (SiO₂) using toluene/CH₃OH (97:3, v/v) to afford **14** as a brown solid in 23% yield (0.065 g). ¹H NMR (CDCl₃), δ ppm: 8.45 (br, *J* = 8.8 Hz, 4H, H₀); 8.22 (br, *J* = 8.5 Hz, 2H, H₄ and H₇); 8.05 (br, *J* = 8.5 Hz, 2H, H₃ and H₈); 7.70 (s, 2H, H₅ and H₆); 7.10 (br, *J* = 8.8 Hz, 4H, H_m);

4.7–4.0 (br, 8H, O–CH₂–CH₂–O); 3.80 (br, 4H, O–CH₂–CH₃); 1.30 (br, 6H, O–CH₂–CH₃). MALDI-TOF: found 1485.9 [M+H]⁺, calculated 1484.2 for C₁₀₂H₄₀N₂O₁₂.

Rotaxane 1—Fulleromacrocycle **11** (0.013 g, 0.01 mmol) and [Cu(CH₃CN)₄][PF₆] (0.0038 g, 0.01 mmol) were placed in a round bottomed flask under N₂ atmosphere. A mixture composed of CH₂Cl₂ and CH₃CN (3 mL, 3:1) was added by syringe. The solution was stirred at room temperature under N₂ atmosphere for 30 min. Ferrocene thread **10** (0.0113 g, 0.01 mmol) in dry CH₂Cl₂ (1 mL) was added dropwise by syringe. The mixture was then stirred for another 2 h at room temperature. The solvent was removed under reduced pressure, followed by column chromatography (SiO₂) using CH₂Cl₂/CH₃OH (97:3, v/v) as eluent to yield the desired rotaxane **1** as a brown solid in 53% yield (0.014 g). ¹H NMR (CDCl₃), δ ppm: 8.56 (d, *J* = 8.6 Hz, 2H, H₄' and H₇'); 8.40 (d, *J* = 8.6 Hz, 2H, H₄ and H₇); 8.21 (s, 2H, H₅' and H₆'); 7.99 (d, *J* = 8.3 Hz, 4H, ferrocene *orto* Ar–H); 7.90 (s, 2H, H₅ and H₆); 7.89 (d, *J* = 8.6 Hz, 2H, H₃' and H₈'); 7.75 (d, *J* = 8.6 Hz, 2H, H₃ and H₈); 7.46 (d, *J* = 8.3 Hz, 4H, ferrocene *meta* Ar–H); 7.60 (d, *J* = 8.8 Hz, 4H, H₀'); 7.37 (d, *J* = 8.8 Hz, 4H, H₀); 6.03 (d, *J* = 8.8 Hz, 4H, H_m'); 5.90 (d, *J* = 8.8 Hz, 4H, H_m); 4.94 (br, 2H, Cp–H); 4.40 (br, 2H, Cp–H); 4.25 (br, 5H, Cp–H); 4.00–3.50 (m, 32H, O–CH₂–CH₂–O). MALDI-TOF: *m/z* found 2505.29 [M – PF₆]⁺, calculated, 2650.23 for C₁₆₁H₈₆N₄O₁₆Fe₂CuPF₆.

Rotaxane 2—This rotaxane was prepared from thread **10** and macrocycle **14** following the same procedure described for rotaxane **1**. Brown solid, 23% yield (0.007 g). ¹H NMR (CDCl₃), δ ppm: 8.59 (br, *J* = 8.6 Hz, 2H, H₄' and H₇'); 8.43 (br, *J* = 8.6 Hz, 2H, H₄ and H₇); 8.24 (br, 2H, H₅' and H₆'); 7.96 (br, *J* = 8.3 Hz, 4H, ferrocene *orto* Ar–H); 7.91 (br, 2H, H₅ and H₆); 7.88 (br, *J* = 8.6 Hz, 2H, H₃' and H₈'); 7.75 (br, *J* = 8.6 Hz, 2H, H₃ and H₈); 7.46 (br, *J* = 8.3 Hz, 4H, ferrocene *meta* Ar–H); 7.60 (br, *J* = 8.8 Hz, 4H, H₀'); 7.37 (br, *J* = 8.8 Hz, 4H, H₀); 6.03 (br, *J* = 8.8 Hz, 4H, H_m'); 5.90 (br, *J* = 8.8 Hz, 4H, H_m); 4.94 (br, 2H, Cp–H); 4.40 (br, 2H, Cp–H); 4.25 (br, 5H, Cp–H); 4.00–3.50 (br, 32H, O–CH₂–CH₂–O) 3.30 (br, 4H, O–CH₂–CH₃); 1.30 (br, 6H, O–CH₂–CH₃). MALDI-TOF: *m/z* found 2880 [M – PF₆]⁺, calculated, 3025.14 for C₁₆₈H₉₆N₄O₂₀Fe₂CuPF₆.

Rotaxane 314c—In the reaction flask, macrocycle **17** (0.060 g, 0.0425 mmol) was dissolved in 5 mL of degassed CH₂Cl₂/CH₃CN (7:3, v/v) to which [Cu(CH₃CN)₄][PF₆] (0.016 g, 0.0425 mmol) was added under N₂ atmosphere. The dark orange solution was stirred for 30 min at rt. The diazidophenanthroline ligand **16** (0.029 g, 0.0425 mmol) was then added as a solid to the flask and the deep red solution was stirred under N₂ at rt for 3 h to afford precursor **18**. Meanwhile, CuI (0.017 g, 0.089 mmol), sodium ascorbate (0.07 g, 0.353 mmol) and sulfonated bathophenanthroline (0.100 g, 0.17 mmol) were added to 5 mL of a degassed and solvent mixture composed of H₂O/EtOH (1:1, v/v) under N₂ atmosphere. The suspension was heated to reflux for 2 min, cooled to rt and added by syringe to the flask containing **18**. Finally, ethynyl ferrocene (0.026 g, 0.127 mmol, added as a solid) and DBU (0.019 g, 19 μL, 0.127 mmol) were added and the red mixture was stirred under N₂ for 12 h at rt. The crude mixture was neutralized by adding 2 mL of 10% HCl aqueous solution and extracted with CH₂Cl₂ (3 × 50 mL). The organic phase was washed with water (3 × 50 mL), concentrated to a volume of 10 mL and then stirred for 2 h with saturated MeOH solution of KPF₆ to effect the anion exchange. The solvents were evaporated under reduced pressure, and the remaining insoluble light brown solid was extracted with CH₂Cl₂ (3 × 100 mL) and then filtered through paper. The solvent was evaporated under reduced pressure, and the crude product was purified by flash chromatography (SiO₂) first using CH₂Cl₂ to elute unreacted ethynyl ferrocene and then CH₂Cl₂/CH₃OH (97:3, v/v) to afford rotaxane **3** as brown solid in 92% yield (0.025 g). ¹H NMR (CDCl₃), δ ppm: 8.56 (d, *J* = 8.6 Hz, 2H, H₄' and H₇'); 8.40 (d, *J* = 8.6 Hz, 2H, H₄ and H₇); 8.21 (s, 2H, H₅' and H₆'); 7.93 (s, 2H, H₅

and H₆); 7.89 (d, $J = 8.6$ Hz, 2H, H₃' and H₈'); 7.75 (d, $J = 8.6$ Hz, 2H, H₃ and H₈); 7.75 (s, 2H, H-triazole ring); 7.60 (d, $J = 8.8$ Hz, 4H, H_o'); 7.37 (d, $J = 8.8$ Hz, 4H, H_o); 6.03 (d, $J = 8.8$ Hz, 4H, H_m'); 5.90 (d, $J = 8.8$ Hz, 4H, H_m); 4.94 (br, 2H, Cp-H); 4.82 (br, 4H, O-CH₂-CH₂-OOC); 4.52 (m, 4H, CH₂-triazole ring); 4.40 (br, 2H, Cp-H); 4.25 (br, 5H, Cp-H); 4.00-3.50 (m, 36H, O-CH₂-CH₂-O). MALDI-TOF: m/z found 2577.36 [M - PF₆]⁺, calculated, 2722 for C₁₅₉H₉₈N₁₀O₁₆Fe₂CuPF₆.

Rotaxane model 4—This rotaxane was prepared from thread **10** and a phen-based methyl-benzoate ester macrocycle, which was prepared in accordance to our previous works^{14b,c}, following the same procedure described for rotaxane **1**. Red solid, 66% yield (0.013 g). ¹H NMR (CDCl₃), δ ppm: 8.53 (d, $J = 8.6$ Hz, 2H, H₄' and H₇'); 8.46 (d, $J = 8.6$ Hz, 2H, H₄ and H₇); 8.20 (s, 2H, H₅' and H₆'); 7.96 (d, $J = 8.3$ Hz, 4H, ferrocene *orto* Ar-H); 7.93 (s, 2H, H₅ and H₆); 7.89 (d, $J = 8.6$ Hz, 2H, H₃' and H₈'); 7.77 (d, $J = 8.6$ Hz, 2H, H₃ and H₈); 7.41 (d, $J = 8.3$ Hz, 4H, ferrocene *meta* Ar-H); 7.60 (d, $J = 8.8$ Hz, 4H, H_o'); 7.37 (d, $J = 8.8$ Hz, 4H, H_o); 6.96 (d, 2H, ester-containing *orto* Ar-H); 6.66 (d, 1H, ester-containing *para* Ar-H); 6.03 (d, $J = 8.8$ Hz, 4H, H_m'); 5.90 (d, $J = 8.8$ Hz, 4H, H_m); 4.94 (br, 2H, Cp-H); 4.40 (br, 2H, Cp-H); 4.25 (br, 5H, Cp-H); 4.00-3.50 (m, 35H, O-CH₂-CH₂-O and COOCH₃). MALDI-TOF: m/z found 1851.18 [M - PF₆]⁺, calculated 1996.45 for C₁₀₆H₉₂N₄O₁₆CuFe₂PF₆.

Rotaxane model 5—This rotaxane was prepared from thread **16** and a phen-based methyl-benzoate ester macrocycle, which was prepared in accordance to our previous works^{14b,c}, following the same procedure described for rotaxane **3**. Red solid, 94% yield (0.019 g). ¹H NMR (CDCl₃), δ ppm: 8.63 (d, $J = 8.6$ Hz, 2H, H₄' and H₇'); 8.48 (d, $J = 8.6$ Hz, 2H, H₄ and H₇); 8.26 (s, 2H, H₅' and H₆'); 7.85 (s, 2H, H₅ and H₆); 7.81 (d, $J = 8.6$ Hz, 2H, H₃' and H₈); 7.78 (s, 2H, H-triazole ring); 7.75 (d, $J = 8.6$ Hz, 2H, H₃ and H₈); 7.60 (d, $J = 8.8$ Hz, 4H, H_o'); 7.37 (d, $J = 8.8$ Hz, 4H, H_o); 6.90 (d, 2H, ester-containing *orto* Ar-H); 6.62 (d, 1H, ester-containing *meta* Ar-H); 6.09 (d, $J = 8.8$ Hz, 4H, H_m'); 5.90 (d, $J = 8.8$ Hz, 4H, H_m); 4.94 (br, 2H, Cp-H); 4.52 (m, 4H, CH₂-triazole); 4.40 (br, 2H, Cp-H); 4.25 (br, 5H, Cp-H); 4.00-3.50 (m, 47H, O-CH₂-CH₂-O and COOCH₃). MALDI-TOF: m/z found 1937.18 [M - PF₆]⁺, calculated 2082.45 for C₁₀₅H₁₀₆N₁₀O₁₆CuFe₂PF₆.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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20. In benzonitrile, two processes were detected. We are not sure about the nature of the second process. However, the most probable explanation to us seems to be a conformational rearrangement of the phenanthroline ligand, due to the oxidation of Cu(I) to Cu(II).
21. A longer lived minor component with a lifetime of 7.9 μ s is also detected.
22. Implementation of the solvent correction term to adjust for the energy of solvation by benzonitrile is expected to minimally affect these energy values.
23. In a recent study of an Al(III)P-C₆₀-Fc triad, electron transfer from Fc to the oxidized porphyrin was invoked, even though the lifetime of the charge-separated state of the triad was lower, not higher, than that of the corresponding dyad. See: Poddutoori PK, Sandanayaka ASD, Hasobe T, Ito O, van der Est V. *J. Phys. Chem. B.* 2010 doi: 10.1021/jp911937d.
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Figure 1.

New family of fullerene/ferrocenyl (Fc)₂-Cu(phen)₂⁺-C₆₀ rotaxanes. The size and structure of the macrocycle and the thread have been varied in order to study the correlation between interchromophoric distance and electron transfer dynamics.

Figure 2.
Rotaxane and pseudorotaxane model compounds used for photophysical studies.

Figure 3.

Reference compounds: malonate-C₆₀ **19**, (phenanthroline)₂-Cu(I) pseudorotaxane complex **20** and unsubstituted Cu(phen)₂⁺-[2]catenate **21**.

Figure 4.

Fluorescence spectra at room temperature in benzonitrile. (A): rotaxanes **1** and **2**, and (phenanthroline)₂-Cu(I) complex **20** using solutions having the same optical density (0.25) at the excitation wavelength of 320 nm. (B): rotaxanes **3**, **5**, and model [2]catenate **21** using solutions having the same optical density (0.15) at the 320 nm excitation wavelength. (C): rotaxane **3** and C₆₀-reference **19** using solutions having optical density 0.4 at the 355 nm excitation wavelength.

Figure 5.

Left: differential absorption spectra (i.e., visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of $[Cu(phen)_2]^+$ pseudorotaxane **20** in benzonitrile with time delays between 0 and 10 ps at room temperature (see figure legend/arrow for details of time progression). Right: time-absorption profiles at 475 and 550 nm of the spectra on the left reflecting the excited state dynamics.

Figure 6.

Left: differential absorption spectra (i.e., visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of $(Fc)_2-[Cu(phen)_2]^+$ rotaxane **5** in benzonitrile with time delays between 0 and 200 ps at room temperature (see figure legend/arrow for details of time progression). Right: time-absorption profiles at 600 nm of the spectra on the left reflecting the excited state dynamics.

Figure 7.

Left: differential absorption spectra (i.e., visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of **3** in benzonitrile with different time delays between 0 and 100 ps at room temperature (see figure legend/arrow for details of the time progression). Right: time-absorption profiles at 480, 590, 900, and 1040 nm of the spectra on the left reflecting the charge-separation dynamics.

Figure 8.

Left: differential absorption spectra (i.e., visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of rotaxane **1** in benzonitrile with different time delays between 0 and 200 ps at room temperature (see figure legend/arrow for details of time progression). Right: time-absorption profiles at 480, 590, 900, and 1040 nm of the spectra on the left reflecting the charge-separation dynamics.

Figure 9.

Left: differential absorption spectra (i.e., visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of **2** in benzonitrile with different time delays between 0 and 200 ps at room temperature (see figure legend/arrow for details of time progression). Right: time-absorption profiles at 550 and 915 nm of the spectra on the left reflecting the charge-separation dynamics.

Figure 10. Schematic energy level diagram and photophysical decay pathways for rotaxanes **1**, **2** and **3** upon excitation at 387 or 460 nm.

Strategy A – Threading followed by stoppering reaction **Strategy B** – Stoppering followed by threading reaction **Scheme 1.**

Representation of the two approaches used to assembly rotaxanes in this work.

Scheme 2.

Synthetic strategy and precursors used to prepare ferrocene-stoppered fullerorotaxane **1** and **2**.

a) DIC/DMAP, CH₂Cl₂, rt, 16 h, 82% yield; b) [Cu(CH₃CN)₄][PF₆], CH₂Cl₂/CH₃CN, rt, 2 h, 53% yield for **1** and 23% for **2**; c) DMAP, Et₃N, CH₂Cl₂, 0°C for 3 h and then rt for 12 h, 85% yield; d) I₂, C₆₀, DBU, chlorobenzene, rt, 23% yield.

Scheme 3.

Synthetic strategy and precursors used to prepare the ferrocene-stoppered fullerorotaxane **3**.
 a) i) TsCl , Et_3N , CH_2Cl_2 , $0\text{ }^\circ\text{C}$ for 4 h and rt for 20 h, 75% yield; ii) NaN_3 , DMF, $80\text{ }^\circ\text{C}$, 24 h, 93% yield; b) $[\text{Cu}(\text{CH}_3\text{CN})_4][\text{PF}_6]$, $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$, rt, 3 h, quantitative; c) CuI , SA, SBP, DBU, $\text{H}_2\text{O}/\text{EtOH}$, rt, 12 h, 92% yield.

Table 1

Electrochemical oxidation and reduction potentials.^a

Compound	Oxidation		Reduction		
	Fc/Fc ⁺	Cu ⁺ /Cu ²⁺	C ₆₀ /C ₆₀ ^{•−}		Cu ⁺ /Cu ⁰
			E ⁰ −	E ¹ −/2−	E ² −/3−
1^b	+0.048	+0.24	−1.02	−1.42	−1.84
2^b	+0.052	+0.25	−1.11	−1.49	−1.92
3^c	0	+0.16	−1.04	−1.42	−1.90
4^b	+0.040	+0.24	---	---	---
5^b	0	+0.18	---	---	−2.30
6^b	---	+0.16	−1.01	−1.42	−1.85
7^c	---	+0.25	−1.11	−1.49	−1.92
19^b	---	---	−0.99	−1.36	−1.84
20^c	---	+0.16	---	---	−2.30
21^c	---	+0.16	---	---	−2.30

^a All values (V) are relative to the Fc/Fc⁺ internal reference.

^b In dichloromethane and 0.1 M TBAPF₆ (Clemson University).

^c In *o*-dichlorobenzene and 0.1 M TBAClO₄ (University of Erlangen).

Table 2

Fluorescence parameters and charge separated state lifetimes at 298 K in air-equilibrated solutions.

Compound	Excited State	λ_{max} (nm)	τ_{lum} (ns)	Φ_{F}	τ_{CR} (ns)
1 ^a	Fe*Cu ⁺ -C ₆₀	765	0.04	6.8×10^{-6}	16
2 ^a	Fe*Cu ⁺ -C ₆₀	765	0.08	1.2×10^{-5}	16
3 ^a	Fe-Cu ⁺ -C ₆₀ *	700	0.10	2.0×10^{-4}	15
5 ^a	Fe*Cu ⁺	765	2.0	1.6×10^{-3}	---
7 ^a	*Cu ⁺ -C ₆₀	765	---	1.3×10^{-5}	16
19 ^b	¹ C ₆₀ *	920	1.4	6.0×10^{-4}	---
	³ C ₆₀ *	700 ^c	2.0×10^4	---	---
20 ^d	MLCT ¹	765	5.2	3×10^{-4}	---
21 ^a	MLCT	765	2.5	4.8×10^{-3}	---

^aIn benzonitrile.

^bIn ortho-dichlorobenzene.

^cFrom reference 19.

^dFrom reference 9a.

λ_{max} = maxima emission; τ_{lum} = fluorescence lifetime; Φ_{F} = fluorescence quantum yield; τ_{CR} = lifetime of the charge separated state.