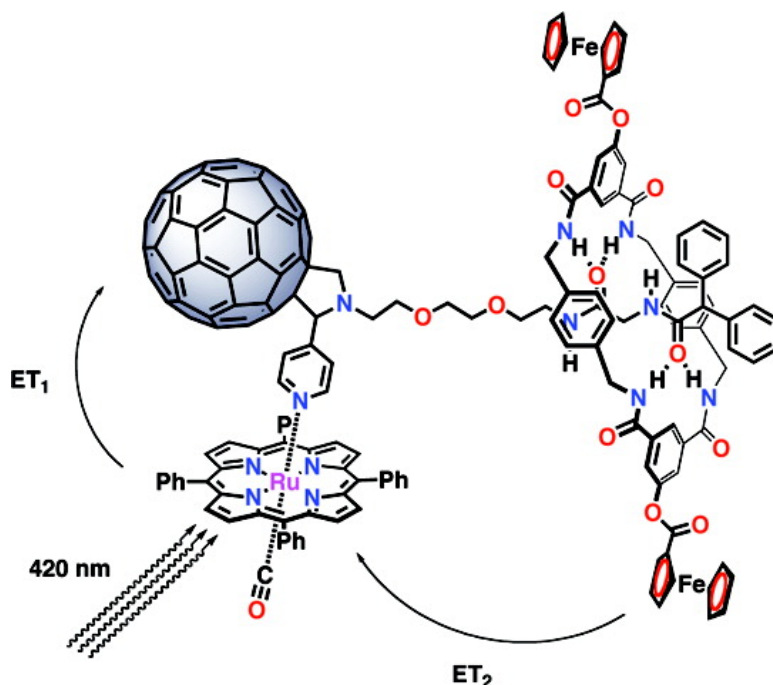


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## Charge Transfer Reactions along a Supramolecular Redox Gradient

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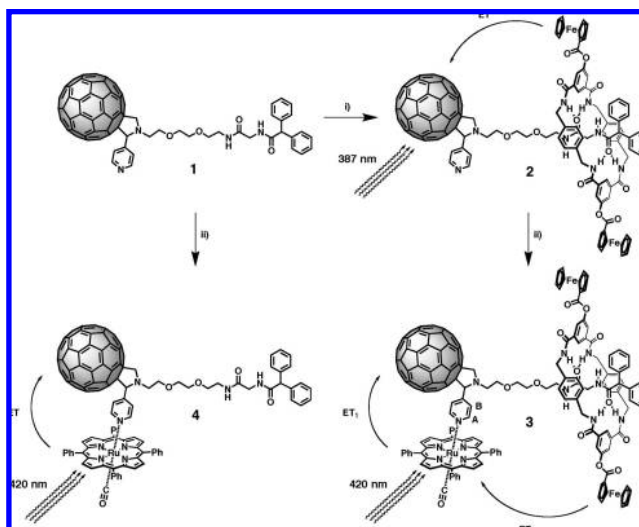
In recent years, the combination of synthetic organic chemistry, supramolecular chemistry, and photophysics has largely improved our understanding of the relation between molecular architecture and photoinduced electron transfer efficiency. Such a multidisciplinary platform is fundamental for attaining novel and efficient photovoltaic materials engineered at the molecular level. An elegant strategy in the development of artificial reaction centers implies the combination of fullerenes as electron accepting species to one or several electron donors, typically metalloporphyrins and/or ferrocene derivatives. A key factor is the structural organization of the electron donating/accepting units, following an electrochemical gradient, which promotes a unidirectional charge transfer cascade. This approach has produced several photoactive systems,<sup>1–3</sup> which successfully (i) harvested visible light energy, (ii) converted it into an electrochemical potential, and (iii) stored it for up to 380 ms—an efficiency similar to that of bacterial photosynthetic reaction centers.<sup>4,5</sup>

Inspired by this encouraging results and by the recent accomplishments on donor–acceptor systems assembled by supramolecular interactions,<sup>6–18</sup> we have designed and prepared triad **3** (Scheme 1), in which three photo/electroactive units are organized along a supramolecular redox gradient. Triad **3** is composed of a fullerene (C<sub>60</sub>) electron-acceptor and two ferrocene (Fc) electron-donors coupled by hydrogen bonds in a rotaxane fashion.<sup>16,17,19</sup> Additionally, **3** presents a ruthenium carbonyl tetraphenylporphyrin (Ru(CO)TPP) coordinated to a pending pyridyl group present between the C<sub>60</sub> and the Fc units. The alignment of the units along a supramolecular electrochemical gradient promotes a unidirectional cascade of two consecutive through-space charge transfer reactions between the three units. This work demonstrates that the redox gradient approach can be also applied to artificial reaction centers with multiple units constructed solely by supramolecular interactions.

Triad **3** was prepared in two steps from thread **1**. The macrocycle with the two Fc electron donors was clipped following a modification of Leigh's protocol,<sup>16</sup> yielding rotaxane **2** (Supporting Information, Figure S1–S4). Addition of Ru(CO)TPP to **2**, resulted in red shifts of the Soret- (2 nm) and Q-bands (3 nm) in absorption measurements, and in upfield shifts of the pyridyl signals A (7.1 ppm) and B (2.2 ppm) (see lettering in Scheme 1) in NMR measurements, which is consistent with previous observations,<sup>15,18,20,21</sup> providing conclusive evidence for the formation of triad **3**.

The photophysical behavior of the different components and their combination was investigated in detail by time-resolved absorption measurements in dichloromethane. Photoexcitation of **1** at 387 nm reveals the formation of the C<sub>60</sub> singlet excited-state with the

Scheme 1. Preparation of **3** and **4**<sup>a</sup>



<sup>a</sup> (i) 5-Ferroceneacetoxisophtaloyl chloride (12 equiv), *p*-xylylenediamine (12 equiv), NEt<sub>3</sub> (24 equiv), CHCl<sub>3</sub> high dilution conditions, 17%; (ii) Ru(CO)TPP (1 equiv) CH<sub>2</sub>Cl<sub>2</sub>.

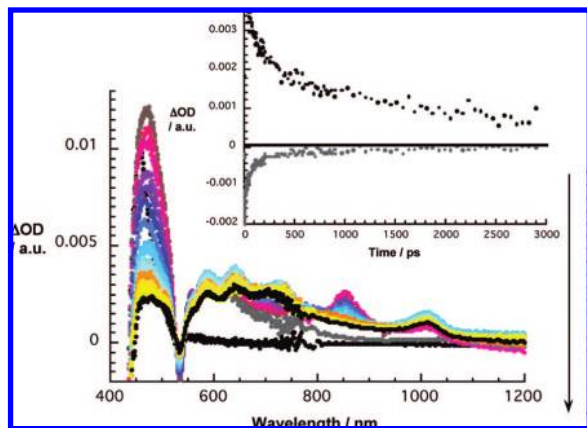
characteristic transition around 880 nm, which transforms into the triplet excited state ( $6.6 \times 10^8 \text{ s}^{-1}$ ) (not shown). An additional feature of the C<sub>60</sub> singlet excited-state is a fluorescence spectrum in the 700–800 nm range with an overall quantum yield of  $6.0 \times 10^{-4}$ . In **2**, a quenching of the C<sub>60</sub>-centered fluorescence is observed ( $2.1 \times 10^{-4}$ ), together with a fast deactivation of the C<sub>60</sub> singlet excited-state that leads to a radical ion pair state (C<sub>60</sub><sup>•−</sup>–Fc<sup>•+</sup>) formation, as illustrated by the fingerprint of the one-electron reduced C<sub>60</sub> at 1010 nm,<sup>22</sup> for which a lifetime of 26 ns ( $3.8 \times 10^7 \text{ s}^{-1}$ ) was determined.

Similar experiments were carried out with **1** coordinated to Ru(CO)TPP in dichloromethane that yield the reference dyad **4** (Figure S6). Femtosecond excitation (420 nm) of **4** generates the fingerprint absorption of the Ru(CO)TPP radical cation (i.e., 400–800 nm with maxima at 470, 510, 565, 585, 645, and 715 nm), in good agreement with the spectrum of the Ru(CO)TPP radical cation generated electrochemically (maxima at 460, 565, 580, 640, and 715 nm and shoulders at around 510 and 560 nm) (Figure S7).<sup>23</sup> At the same time, the C<sub>60</sub> radical-anion develops ( $1.4 \times 10^{10} \text{ s}^{-1}$ ) predominantly in the near-infrared part with a maximum at 1010 nm, providing evidence for the formation of C<sub>60</sub><sup>•−</sup>–Ru(CO)TPP<sup>•+</sup>. Such radical ion pair state decays after 2200 ps to regenerate the singlet ground state.

When Ru(CO)TPP was coordinated to **2** in dichloromethane to afford triad **3**, a trend was observed that differs from that seen for

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**Figure 1.** Differential absorption spectra (visible and near-infrared) obtained upon femtosecond flash photolysis (420 nm–150 nJ) of **3** in  $\text{CH}_2\text{Cl}_2$  with several time delays between 0 and 167 ps at room temperature. Arrow illustrates the time evolution. (Insert) Time-absorption profile at 480 nm (black) and 532 nm (gray), reflecting the charge separation and charge shift dynamics.

**4.** Initially, **3** presented similar charge transfer features to those of **4** (Figure 1), including electron transfer ( $1.8 \times 10^{10} \text{ s}^{-1}$ ) from the photoexcited  $\text{Ru}(\text{CO})\text{TPP}$  to the  $\text{C}_{60}$  to give the  $\text{C}_{60}^{\bullet-}-\text{Ru}(\text{CO})\text{TPP}^{\bullet+}$  radical pair. However, in the case of **3**, the ground-state recovery is in competition with a charge shift that yields the  $\text{C}_{60}^{\bullet-}-\text{Fc}^{\bullet+}$  radical pair. This process is illustrated by the 1010 and 630 nm absorptions, related to the spectral attributes of the one-electron reduced  $\text{C}_{60}$  and the one-electron oxidized  $\text{Fc}$ , respectively.<sup>22</sup> Such a charge transfer reaction is corroborated kinetically. As a matter of fact, the lifetime of the  $\text{C}_{60}^{\bullet-}-\text{Ru}(\text{CO})\text{TPP}^{\bullet+}$  radical pair of **3** (895 ps) is  $\sim 2.5$  times shorter than that observed for **4** (2200 ps), which shows an accelerated decay as a consequence of the charge transfer shift reaction that promotes the formation of the  $\text{C}_{60}^{\bullet-}-\text{Fc}^{\bullet+}$  radical-pair. Additionally, the charge shift elongates the lifetime of  $\text{C}_{60}^{\bullet-}$ , as observed by a major  $\text{C}_{60}^{\bullet-}$  component that remains persistent on the 3.0 ns time scale (see inset to Figure 1). The lifetime of the final charge transfer product on **3** is much longer than that of **4**, exceeding the 3.0 ns time window of our apparatus, which is again consistent with the formation of the  $\text{C}_{60}^{\bullet-}-\text{Fc}^{\bullet+}$  radical-pair.

In conclusion, we have prepared a triad by a combination of hydrogen bonding and metal coordination that were employed to organize the different units along a supramolecular redox gradient. The excitation of the central  $\text{Ru}(\text{CO})\text{TPP}$  unit results in the transfer of an electron from  $\text{Ru}(\text{CO})\text{TPP}$  to  $\text{C}_{60}$ , followed by a charge shift to yield  $\text{C}_{60}^{\bullet-}-\text{Fc}^{\bullet+}$ , as demonstrated by a systematic study based on time-resolved absorption measurements. This work illustrates that the redox gradient approach can also be applied to the construction of supramolecular donor–acceptor systems, opening the door to the preparation and investigation of supramolecular

polyads with donor–acceptor geometries that could not be otherwise accessed by covalent chemistry.

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**Supporting Information Available:** Characterization of **2** and **3**. Differential absorption spectra and time absorption profile of **4**. Spectroelectrochemistry of methyl 5-ferroceneacetoxysphthalate and  $\text{Ru}(\text{CO})\text{TPP}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (22) The absorption coefficient of the one-electron oxidized ferrocene at 630 nm is very weak (Figure S5).
- (23) It should be noted that in this spectral range (i.e., 400–900 nm) even the relative intensities are a good match between the photolytically and spectroelectrochemically generated species.

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