Design and Studies on Supramolecular Ferrocene–Porphyrin–Fullerene Constructs for Generating Long-Lived Charge Separated States

Francis D'Souza,*,[†] Raghu Chitta,[†] Suresh Gadde,[†] D.-M. Shafiqul Islam,[‡] Amy L. Schumacher,[†] Melvin E. Zandler,[†] Yasuyuki Araki,[‡] and Osamu Ito^{*,‡}

Department of Chemistry, Wichita State University, 1845 Fairmount, Wichita, Kansas 67260-0051, and Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Sendai 980-8577, Japan

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Supramolecular ferrocene-porphyrin-fullerene constructs, in which covalently linked ferrocene-porphyrincrown ether compounds were self-assembled with alkylammonium cation functionalized fullerenes, have been designed to achieve stepwise electron transfer and hole shift to generate long-lived charge separated states. The adopted crown ether-alkylammonium cation binding strategy resulted in stable conjugates as revealed by computational studies performed by the DFT B3LYP/3-21G(*) method in addition to the binding constants obtained from fluorescence quenching studies. The free-energy changes for charge-separation and chargerecombination were varied by the choice of different metal ions in the porphyrin cavity. Free-energy calculations suggested that the light-induced electron-transfer processes from the singlet excited state of porphyrins to be exothermic in all of the investigated supramolecular dyads and triads. Photoinduced charge-separation and charge-recombination processes have been confirmed by the combination of the time-resolved fluorescence and nanosecond transient absorption spectral measurements. In case of the triads, the charge-recombination processes of the radical anion of the fullerene moiety take place in two steps, viz., a direct charge recombination from the porphyrin cation radical and a slower step involving distant charge recombination from the ferrocene cation moiety. The rates of charge recombination for the second route were found to be an order of magnitude slower than the former route, thus fulfilling the condition for charge migration to generate long-lived chargeseparated states in supramolecular systems.

Introduction

Studies on photoinduced electron transfer in molecular and supramolecular donor-acceptor polyads (triads, tetrads, etc.) have undergone rapid growth in recent years mainly to develop artificial photosynthetic systems capable of stabilizing chargeseparated states,¹⁻⁶ which is eventually also useful for the development of molecular optoelectronic devices.^{7,8} In the construction of such polyads, porphyrins and fullerenes have been employed as primary electron donor and acceptor, respectively, whereas ferrocene, carotene, or tetrathiafulvalene has often been utilized as terminal electron donors.^{9,10} In contrast with the traditionally used two-dimensional aromatic electron acceptors, fullerenes in donor-acceptor dyads and polyads accelerate forward electron transfer (k_{CS}) and slow backward electron transfer (k_{CR}) due to their small reorganization energy in electron-transfer reactions.¹¹ This property of fullerenes combined with the adopted electron migration strategy of polyads has resulted in the generation of distinctly separated donor-acceptor radical ion pairs upon initial electron transfer by charge migration reactions along the well-tuned redox gradients.^{12–15} In a few systems, energy funneling antenna molecules have been elegantly connected to the donor-acceptor systems to probe sequential energy/electron-transfer processes, thus mimicking the "antenna-reaction center" functionality of photosynthesis.16

[†] Wichita State University. [‡] Tohoku University.

Although substantial amount of progress in terms of charge stabilization has been accomplished on covalently linked polyads,1-6,9-10 achieving similar results on self-assembled supramolecular polyads has been challenging because of the occurrence of multiple equilibrium processes and the inferior stability of the adopted self-assembly approaches in solution, especially in polar solvents.¹⁰ Recently, we addressed the stability issue by employing multiple modes of binding and formed structurally well-defined, stable supramolecular systems.^{10g} An alternate supramolecular approach was also developed, in which the covalently linked dyads were allowed to self-assemble with either a donor or an acceptor with a well-defined binding mechanism to form the triads.^{10g} In the present study, we have further explored the latter approach where covalently linked ferrocene-porphyrin-crown ether compounds (Fc-MP-crown ether) were self-assembled with alkylammonium cation functionalized fullerenes ($NH_3^+-C_{60}$) (Scheme 1). As demonstrated here, upon excitation of the donor porphyrin, efficient forward electron transfer to the fullerene entity self-assembled via crown ether-alkylammonium cation complexation occurs followed by a hole transfer from the MP^{•+} to the ferrocene entity to generate the final charge-separated states, Fc^+ -MP-crown:NH₃⁺-C₆₀⁻. As a consequence of the sequential electron-transfer events, the charge-recombination reaction is slowed in these supramolecular triads (see Supporting Information).

Results and Discussion

The structures of the newly synthesized compounds are shown in Scheme 1. Porphyrins, 1a-c (MP = H₂P, ZnP, and MgP,

^{*} To whom correspondence should be addressed. E-mail: Francis.DSouza@wichita.edu (F.D); ito@tagen.tohoku.ac.jp (O.I.).

SCHEME 1: Structures of the Crown Ether Appended Porphyrins, Ferrocene–Porphyrins Dyads, and Fullerene Derivatives



respectively) bearing donor, porphyrin, and a 18-crown-6 entity are used as a control for compounds 2a-c possessing a porphyrin covalently linked to a second electron donor, ferrocene, and a 18-crown-6 entity. We have employed free-base, zinc, and magnesium porphyrins because of their different emission and redox properties.¹⁷ The first oxidation potential of these porphyrins generally follows the trend: MgP < ZnP < H₂P. As a result, it has been possible to systematically vary the free-energy change for photoinduced electron transfer in the studied supramolecular dyads and triads. Three derivatives of fullerene functionalized with varying alkyl chain length ammonium cations, **3**–**5**, have been utilized to form the supramolecular complexes via alkylammonium–crown ether complexation.

Optical Absorption Studies. The optical absorption behavior of the porphyrins 1a-c was found to be similar to those of pristine free-base porphyrin, zinc porphyrin, and magnesium porphyrin, respectively. That is, they exhibited an intense Soret band around 425 nm and 2–4 visible bands in the 500–650 nm range depending upon the metal ion in the porphyrin cavity.

No apparent absorption bands in the wavelength region covering 350-700 nm corresponding to the crown ether entities were observed.

The optical absorption spectra in the visible wavelength region of the ferrocene-porphyrin-crown ether systems 2a-c were also found to be similar to the respective 1a-b analogues. However, in each case, the peak maxima exhibited a red-shift of 2-3 nm compared to the corresponding 1a-c derivatives. No new peak corresponding to the appended ferrocene was observed due to the low molar absorptivity of ferrocene compared to the high ϵ values of porphyrin absorption bands in the 380-420 nm region. The binding of functionalized fullerenes, 3, 4, or 5, to ferrocene-porphyrins 2a-c resulted in the formation of the supramolecular triads, which was accompanied by slightly red-shifted absorption bands of porphyrins (Figure 1). A weak band around 700 nm was observed due to the absorption of 3 in this wavelength region. On increasing the concentration of 3, the absorbance near the Soret band increased; compared with such increases, the increment in peak absorbance was small, supporting the supramolecular formation. Under these conditions, it was difficult to isolate any



Figure 1. Absorption spectral changes observed during titration of **2b** (0.15×10^{-5} M) with **3** (4.2×10^{-4} M each addition) in benzonitrile.



Figure 2. DFT B3LYP/3-21G (*) optimized structures of the self-assembled triad, 2b:4 in the (a) closed and (b) extended forms.

weak band corresponding to charge-transfer type interactions between porphyrin and fullerene entities (*wide infra*).

Computational Studies. To gain insights into the supramolecular geometry and possible existence of intermolecular type interactions, computational studies were performed using density functional methods (DFT) at the B3LYP/3-21G(*) level. The B3LYP/3-21G(*) methods have recently been successfully used to predict the geometry and electronic structure of molecular and self-assembled supramolecular dyads and triads.¹⁸ Here, both the ferrocene-porphyrin-crown ether dyads and functionalized fullerenes were optimized to a stationary point on the Born-Oppenheimer potential energy surface and allowed to selfassemble via crown ether-ammonium cation complexation. Representative structures for the supramolecular triad, 2b:4 are shown in Figure 2 and the structural parameters are given in Table 1. For all of the studied supramolecular dyads and triads, at least two structures were possible, namely, a closed structure and a stretched structure. The closed structures were energetically more stable by about 2-5 kcal/mol; however, the closed structures are not close enough to show the charge-transfer interactions in the absorption spectra. The center-to-center distance between the Fe atom of ferrocene and the zinc atom of zinc porphyrin was ~ 17.1 Å irrespective of the type of structure. However, the center-to-center distances between zinc

 TABLE 1: B3LYP/3-21G(*)-Optimized Distances between

 the Different Entities of the 2b:3–5 Supramolecular Triads

		center-to-center distance, Å						
triads	structure form	Fe-Zn	Zn-C ₆₀	C ₆₀ -Fc				
2b:3	extended closed	17.1 17.1	11.8 5.8	27.2 17.8				
2b:4	extended closed	17.2 17.1	11.7 5.6	27.5 17.5				
2b:5	extended closed	17.2 17.1	11.5 5.7	25.8 17.3				

porphyrin and fullerene, and fullerene and ferrocene were found to depend on the type of structure. For "closed" structures, these distances were ~5.7 and 17.8 Å, respectively, whereas for the "relaxed" structures, these distances were ~11.7 and ~27.0 Å, respectively. That is, there was a significant change in the donor and acceptor distances for these two types of structures. The gas-phase dissociation energy for the alkylammonium cation– crown ether binding, measured as the energy difference between the complex and the sum of the energies of the individual porphyrin and fullerene moieties, calculated by B3LYP/3-21G(*), was found to be ~110 kcal mol⁻¹. Although this small basis set result is sure to be 20–30 kcal/mol too high, this indicates stable complex formation through this binding mechanism.

Electrochemical Studies and Electron-Transfer Driving Forces. Electrochemical studies using the cyclic voltammetric technique were performed to evaluate the redox potentials of the triads and also to evaluate the energetics of electron-transfer reactions. The crown ether appended porphyrins, 1a-c and 2a-c, were titrated with various amounts of functionalized fullerenes, 3-5, to probe the effect of coordination on the redox potentials of the ferrocene, porphyrin, and fullerene entities. Figure 3



Figure 3. Cyclic voltammograms of (a) **2a**, (b) **2b**, and (c) **2c** in the absence (dark lines) and in the presence (blue lines) of **5** in benzonitrile containing 0.1 M (n-C₄H₉)₄NClO₄. The concentrations of porphyrins and fullerene were held at 0.03 mM; scan rate = 100 mV s⁻¹.

shows cyclic voltammograms obtained for compounds $2\mathbf{a}-\mathbf{c}$ in benzonitrile containing 0.1 M *t*-Bu₄NClO₄ (dark lines); the redox potential data are given in Tables 2 and 3. All of the employed porphyrins revealed two one-electron oxidations (MP^{0,++} and MP^{+/2+}) as judged from their peak-to-peak separation, ΔE_{pp} , values and the cathodic-to-anodic peak current ratios. The magnitudes of the $E_{1/2}$ values were found to depend on the metal ion present in the porphyrin cavity, which followed the order: MgP < ZnP < H₂P. In addition, for compounds $2\mathbf{a}-\mathbf{c}$, another reversible redox couple close to 0.0 V vs Fc/Fc⁺

TABLE 2: Electrochemical Redox Potentials (E, V vs Fc/Fc⁺), Energy Levels of the Charge-Separated States (ΔG_{RIP}), and Free-Energy Changes for Charge-Separation (ΔG_{CS}) for the Supramolecular Dyads in Benzonitrile

	$E (MP^{0/\bullet+})$	$E(C_{60}^{0/-})$	$E (MP^{0/\bullet-})$	$-\Delta G_{\mathrm{RIP(P-C)}^{b}}$	$-\Delta G^{\mathrm{S}}_{\mathrm{CS}(\mathrm{P}^*-\mathrm{C})^c}$
compound ^a	/V	/V	/V	/eV	/eV
1a	0.55	_	-1.61	-	-
1a:4	0.54	-1.04	-1.63	1.53	0.37
1b	0.29	—	-1.82	_	
1b:4	0.28	-1.04	-1.83	1.31	0.75
1c	0.15	_	-1.93	—	
1c:4	0.14	-1.04	-1.90	1.18	0.87

^{*a*} See Scheme 1 for structures. ^{*b*} $\Delta G_{\text{RIP}} = E_{\text{ox}} - E_{\text{red}} + \Delta G_{\text{S}}$, where $\Delta G_{\text{S}} = -e^2/(4\pi\epsilon_0\epsilon_R R_{\text{Ct-Ct}})$ and ϵ_0 and ϵ_R refer to vacuum permittivity and dielectric constant of benzonitrile. ^{*c*} $-\Delta G_{\text{CS}} = \Delta E_{0-0} - \Delta G_{\text{RIP}}$, where ΔE_{0-0} is the energy of the lowest excited states (2.07 eV for ¹ZnP*, 2.05 eV for ¹MgP*, 1.95 eV for ¹H₂P*, and 1.72 eV for ¹C₆₀*).

TABLE 3:	Electrochemic	al Redox Potentials	(E, V vs)	Fc/Fc ⁺),	Energy 1	Levels of the	e Charge-Separated	States (ΔG_{RIP}),	
Free-Energ	y Changes for	Charge-Separation	$(\Delta G_{\rm CS})$, a	nd Hole	Shift (Δ	G _{HS}) for 2a-	-c:4 Supramolecula	r Triads in Benz	onitrile

$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		-	-	-				-		
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	compounds ^a	<i>E</i> (MP ^{0/+•}) /V	<i>E</i> (Fc ^{0/•+}) /V	$E(C_{60}^{0/\bullet-})$ /V	<i>E</i> (MP ^{0/•-}) /V	$-\Delta G_{ m RIP(P-C)}{}^{b}$ /eV	$-\Delta G_{ m RIP(F-C)}{}^{b}$ /eV	$-\Delta G_{ m RIP(F-P)}{}^{b}$ /eV	$-\Delta G^{\mathrm{S}}_{\mathrm{CS}(\mathrm{P}^{*}-\mathrm{C})}{}^{c}$ /eV	$-\Delta G_{ m HS(F-P)}$ /eV
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2a	0.55	0.0	-	-1.61	_	_	1.61		_
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2a:4	0.55	-0.01	-1.04	-1.62	1.53	1.05	1.63	0.37	0.48
2b:4 0.31 0.0 -1.04 -1.81 1.30 1.04 1.81 0.77 0.2 2c 0.24 0.0 - -1.91 - - 1.91 2c:4 0.17 -0.01 -1.05 -1.95 1.17 1.06 1.96 0.88 0.1	2b	0.32	0.0	_	-1.79	_	_	1.79		
2c 0.24 0.01.91 1.91 2c:4 0.17 -0.01 -1.05 -1.95 1.17 1.06 1.96 0.88 0.1	2b:4	0.31	0.0	-1.04	-1.81	1.30	1.04	1.81	0.77	0.26
2c:4 0.17 -0.01 -1.05 -1.95 1.17 1.06 1.96 0.88 0.1	2c	0.24	0.0	_	-1.91	-	-	1.91		
	2c:4	0.17	-0.01	-1.05	-1.95	1.17	1.06	1.96	0.88	0.11

^{*a*} See Scheme 1 for structures. ^{*b*} ΔG_{RIP} ; see footnote of Table 2. ^{*c*} ΔG_{CS} ; see footnote of Table 2.



Figure 4. Energy level diagram showing different photochemical events of the investigated supramolecular triads.

corresponding to the covalently linked ferrocene unit was observed. That is, the oxidation potential of the ferrocene unit was easier than the first oxidation potential of any of these porphyrins. During the cathodic potential scan, these porphyrins revealed two one-electron reductions whose potentials followed the trend: MgP > ZnP > H_2P .

The addition of fullerenes **3**–**5** revealed cathodic shifts of the peaks corresponding to the porphyrin unit and not the ferrocene unit (blue traces in Figure 3), and such shifts were more for easily oxidizable MgP. These observations clearly suggest intramolecular type interactions¹⁹ between the porphyrin and fullerene entities in support of the close structure predicted by computational studies. During the cathodic potential scan of the supramolecular complexes, two one-electron reductions corresponding to C₆₀^{0/•-} and C₆₀^{•-/2-} were observed and were independent of the nature of MP. Subsequent reductions at higher negative potentials, depended upon M, involved either the porphyrin (MP^{0/•-} and MP^{•-/2-}) or fullerene entity (C₆₀^{2-/3•-}).

The energy levels of the charge-separated states (ΔG_{RIP}) were evaluated using the Weller-type approach²⁰ utilizing the redox potentials, center-to-center distance, and dielectric constant of the solvent as listed in Tables 2 and 3. By comparing these energy levels of the charge-separated states with the energy levels of the excited states, the driving forces ($\Delta G_{\rm CS}$) were evaluated. The generation of MP^{•+}-crown:NH₃⁺-C₆₀^{•-} and Fc-MP^{•+}-crown:NH₃⁺-C₆₀^{•-} were exothermic via the singlet excited states of any of the porphyrins or the fullerene in benzonitrile and followed the trend MgP > ZnP > H₂P. A hole shift from MP^{•+} to Fc was found to be feasible for all the supramolecular triads. On the basis of these calculations, an energy diagram for Fc-MP-crown:NH₃⁺-C₆₀ can be depicted as shown in Figure 4.

Fluorescence Emission Studies. The photochemical behavior of the ferrocene-porphyrins dyads was investigated, initially by using steady-state fluorescence measurements. The emission behavior of the crown ether appended porphyrins was found to be similar to that of porphyrins with two emission bands in the visible-near-IR regions. The fluorescence intensities of 2a-c were found to be quenched compared with those of the crown-ether appended porphyrins, 1a-c. These results indicate the occurrence of intramolecular events in the ferrocene-porphyrin dyads.

Additional quenching of the porphyrin emission was observed upon complexation of fullerenes 3-5 to the crown ether appended porphyrins. Representative emission changes of 2con increasing addition of 5 are shown in Figure 5. By using the



Figure 5. Fluorescence spectral changes observed on increasing addition of fullerene **5** (2.0 μ M each addition) to a solution of porphyrincrown ether, **2c** in benzonitrile. $\lambda_{ex} = 420$ nm. (Inset) Benesi– Hildebrand plot at 620 nm constructed for measuring the binding constant; I_0 (fluorescence intensity in the absence of **5**), and ΔI (changes of fluorescence intensity on addition of **5**).

TABLE 4: Formation Constants (K) Calculated from the Benesi–Hildebrand Plots of the Fluorescence Data for the Bound Porphyrin–Fullerene Conjugates in Benzonitrile at 25 °C

	<i>K</i> , N	K, M ⁻¹ Fullerene derivative							
Porphyrin	3	4	5						
1a	6.4×10^{4}	1.7×10^{3}	5.9×10^{3}						
1b	1.9×10^{5}	2.5×10^{4}	3.2×10^{3}						
1c	7.1×10^{4}	1.8×10^4	2.5×10^{3}						
2a	8.0×10^4	1.5×10^{4}	5.3×10^{3}						
2b	1.7×10^{5}	2.5×10^{4}	6.7×10^{3}						
2c	2.8×10^4	1.0×10^{4}	1.9×10^{3}						

emission data, the binding constants (*K*) for the formation of self-assembled dyads and triads were obtained by constructing Benesi-Hildebrand plots.²¹ (Figure 5, inset), and the data are listed in Table 4. The magnitude of the binding constants varied from 10^3-10^5 M⁻¹ and revealed stable self-assembly process in polar benzonitrile. The binding of **3** was found to be higher than that of either of **4** and **5**.

Further picosecond time-resolved emission measurements were performed to study the kinetics and mechanism of quenching in these supramolecular triads.

Picosecond Time-Resolved Emission Studies. The timeresolved emission spectra of the self-assembled conjugates tracked those of steady-state spectra. Figure 6 shows the emission decay profiles of the crown ether appended porphyrins, **1a**, in the absence and presence of fullerene, **3**. The appended crown ether moieties had little influence on the lifetime of porphyrins in 1a-c. In the presence of **3**, fast fluorescence decays were observed that could be curve-fitted to a biexponential function involving a major short lifetime and a minor longer lifetime, as listed in Table 5. It was difficult to assign



Figure 6. Fluorescence decays at 650 nm range of (i) porphyrin, **1a** (0.02 mM), (ii) **1a** (0.02 mM) in the presence of fullerene **3** (0.15 mM), (iii) ferrocene-porphyrin, **2a** (0.02 mM), and (iv) **2a** (0.03 mM) in the presence of fullerene **3** (0.15 mM) in benzonitrile; $\lambda_{ex} = 400$ nm.

TABLE 5: Fluorescence Lifetime ($\tau_{F,dvad}$),
Charge-Separation Rate Constant (k^{S}_{CS}) , Charge-Separation
Quantum Yield (Φ^{S}_{CS}), Charge-Recombination Rate
Constant (k_{CR}), and Lifetime of the Radical Ion Pair (τ_{RIP})
for the Investigated Porphyrin–Fullerene Conjugates in
Benzonitrile

porphyrin	fullerene	$ au_{ m F,dyad}$ /ps (%)	$\frac{k^{\mathrm{S}}\mathrm{CS}^{a}}{\mathrm{S}^{-1}}$	$\Phi^{S}_{CS}{}^{a}$	$k_{\rm CR} / {\rm s}^{-1}$	$ au_{ m RIP}$ /ns
1 a		9510 (100) ^b	-	_	-	_
1a	3	1350 (65)	6.4×10^{8}	0.86	1.3×10^{7}	80
	4	2350 (55)	3.2×10^{8}	0.75	7.1×10^{6}	140
	5	2640 (45)	2.7×10^{8}	0.71	1.4×10^{7}	70
1b	-	1950 (100) ^b	_	_	_	_
1b	3	250 (60)	3.5×10^{9}	0.88	6.7×10^{6}	150
	4	830 (50)	7.0×10^{8}	0.58	5.6×10^{6}	178
	5	1025 (45)	4.6×10^8	0.48	9.6×10^{6}	104
1c		6520 (100) ^b	_	_	_	_
1c	3	420 (60)	2.2×10^{9}	0.92	1.2×10^{7}	80
	4	390 (55)	2.4×10^{9}	0.93	5.1×10^{6}	200
	5	490 (50)	1.9×10^9	0.92	7.2×10^7	15

 $^{a}k^{S}_{CS} = (1/\tau_{F,dyad}) - (1/\tau_{F,ref}), \Phi^{S}_{CS} = [(1/\tau_{F,dyad}) - (1/\tau_{F,ref})]/(1/\tau_{F,dyad})$ for **1**. $^{b}\tau_{F,ref.}$

these two decays either to the "closed-extended" structures or to the alkylammonium-crown ether "bound-unbound" fractions. Because the fluorescence quenching is due to charge separation from the singlet excited porphyrin to the complexed fullerene,^{15a} the rates (k^{S}_{CS}) and quantum yields (Φ^{S}_{CS}) of charge separation were evaluated for both closed (or bound) and extended (or unbound) forms in the usual manner and the data are given in Table 5. For **1a**-**b**, the k^{S}_{CS} values are on the order of 10⁸ s⁻¹, whereas the k^{S}_{CS} values are on the order of 10⁹ s⁻¹ for **1c**.

As shown in Figure 6 for representative 2a, the fluorescence time profiles of the ferrocene-porphyrin dyads 2a-c showed quick decays compared with the time profiles of the references compounds 1a-c in benzonitrile. Here also, the decay could be fitted to a biexponential fitting curve. The evaluated fluorescence lifetimes are summarized in Table 6. These results suggest the occurrence of an excited-state quenching process of MP by Fc in the ferrocene-porphyrin dyads.²² The quenching process of the porphyrin emission could occur either from energy-transfer or electron-transfer processes. In the absence of any appreciable ferrocene absorption in the emission wavelength region of porphyrins, one could eliminate energy transfer as a quenching via the Förster mechanism. The calculated free-

TABLE 6: Fluorescence Lifetime ($\tau_{F,triad}$),^{*a*} Charge-Separation Rate Constant (k^{S}_{CS}), Charge-Separation Quantum Yield (Φ^{S}_{CS}), Charge-Recombination Rate Constant (k_{CR}), and Lifetime of the Radical Ion Pair (τ_{RIP}) for the Investigated Porphyrin–Fullerene Conjugates in Benzonitrile

		$ au_{ m F,triad}$	k ^s cs	7 0 J	k _{CR1}	$k_{\rm CR2}^{c}$	$ au_{ m RIP1}$	$ au_{ ext{RIP2}}{}^{c}$
porphyrin	fullerene	/ps (%)	/s ⁻¹ ^b	Φ^{s}_{CS}	$/s^{-1}$	/s ⁻¹	/ns	/ns
2a	_	980 (85)	$(2.0 \times 10^8)^b$	0.18				
2a	3	320 (78)	2.1×10^{9}	0.67	1.6×10^{7}	2.6×10^{5}	60	3910
2a	4	730 (75)	4.0×10^{8}	0.30	6.7×10^{6}	1.0×10^{6}	150	910
2a	5	826 (73)	2.4×10^{8}	0.20	1.7×10^{7}	6.3×10^{5}	60	1590
2b	-	910 (85)	$(2.0 \times 10^8)^b$	0.18				
2b	3	130 (76)	6.5×10^{9}	0.86	1.0×10^{7}	1.6×10^{5}	100	6210
2b	4	440 (73)	1.2×10^{9}	0.52	9.4×10^{6}	2.8×10^{5}	110	3570
2b	5	600 (70)	5.6×10^{8}	0.34	1.5×10^{7}	1.6×10^{5}	70	6140
2c	-	1240 (55)	$(2.0 \times 10^8)^b$	0.18			—	
2c	3	90 (60)	1.1×10^{10}	0.99	7.0×10^{6}	1.4×10^{5}	140	7140
2c	4	240 (55)	3.3×10^{9}	0.80	8.0×10^{6}	1.5×10^{5}	130	6490
2c	5	350 (45)	2.1×10^{9}	0.72	6.5×10^{7}	1.5×10^{5}	15	6580

^{*a*} The singlet excited lifetimes (τ_0) of free-base porphyrin (**1a**), zinc porphyrin (**1b**), and magnesium porphyrin (**1c**) were found to be 9.6, 1.9, and 5.6 ns, respectively. ^{*b*} $k_{CS}^S = (1/\tau_{F,triad}) - (1/\tau_{F,2a-c}), \Phi^S_{CS} = [(1/\tau_{F,triad}) - (1/\tau_{F,2a-c})]/(1/\tau_{F,triad}))$ for **2**. ^{*c*} k_{CR2} and Φ_{CR2} (see Figure 4).

energy change, $\Delta G_{\rm CS}$ for electron transfer from the ferrocene entity to the excited porphyrin is found to be slightly exothermic ($\Delta G_{\rm CS} = -0.1 \text{ eV}$). These results indicate the occurrence of excited-state charge-separation in the covalently linked ferrocene-porphyrin dyads, generating Fc⁺-MP^{•-}. The $k^{\rm S}_{\rm CS}$ values were evaluated to be $2.0 \times 10^8 \text{ s}^{-1}$. Earlier, similar results were obtained for covalently linked ferrocene-porphyrin dyads held by different covalent connectivity.^{12c}

Addition of 3 equiv of fullerene derivatives was performed to ensure complete complexation of the porphyrins (2a-c) with the fullerenes. Additional fluorescence quenching of MP of the ferrocene-porphyrin(s) dyads, 2a-c, was observed upon complexation of fullerene, 3. Similar observations were made for complexation of 2a-c dyads with the fullerenes 4 and 5. The porphyrin emission decay in the triads could be fitted satisfactorily to a biexponential decay curve; the lifetimes (τ_f) are summarized in Table 6. On the basis of the observations that the time-resolved fluorescence spectra did not show the appearance of the transient fluorescence peak of the C_{60} moiety after the decay of the fluorescence of the porphyrin moiety, the quenched lifetimes of porphyrins were predominantly ascribed to charge-separation within both structural forms of the supramolecular triads. Since the quenching is due to charge separation from the singlet excited porphyrin to the complexed fullerene,^{15a} the k^{S}_{CS} and Φ^{S}_{CS} values were evaluated as given in Table 6. Generally, the k^{S}_{CS} values were found to be higher for the triads in the order of 10^9 s^{-1} , with the slowest rate of $\sim 5 \times 10^8 \text{ s}^{-1}$ for 2a:4 and 2b:5 and the fastest rate of 1×10^{10} s^{-1} for 2c:3, respectively. Thus, for Fc-MP:NH₃⁺-C₆₀ supramolecular triads, the charge-separation (CS1) generating Fc- MP^{+} -crown: NH_3^{+} - C_{60}^{-} is predominant compared to the charge-separation (CS2) generating Fc⁺-MP^{•-}.

The data in Tables 5 and 6 indicate that the $k_{\rm CS}$ values follow the order: $H_2P < ZnP < MgP$, that is, they depend on the magnitude of the $-\Delta G_{\rm CS}$ values. The $\Phi_{\rm CS}$ values follow the same order: $H_2P < ZnP < MgP$ for both the dyads and triads. Among the fullerene derivatives, **3**–**5**, the $k_{\rm CS}$ followed the trend **3** > **4** ~ **5**. The higher $k_{\rm CS}$ values obtained for fullerene, **3** agreed well with the higher *K* values evaluated earlier.

Further studies involving the nanosecond transient absorption technique were performed to identify the electron-transfer products and monitor the kinetics of charge recombination in the dyads and the self-assembled triads.

Nanosecond Transient Absorption Studies. The nanosecond transient absorption spectrum of 1a-c exhibited absorption peaks at 630 and 800-840 nm corresponding to the triplet states.



Figure 7. Nanosecond transient absorption spectra of (a) the crown ether appended porphyrin (**1a**, 0.04 mM) in the presence of fullero-pyrrolidine (**5**, 0.07 mM) and (b) porphyrin (**2a**, 0.1 mM) in the presence of fulleropyrrolidine (**5**, 0.15 mM) in benzonitrile after 532-nm laser irradiation. (Inset) Absorption time profile at 1020 nm band.

Fullerenes 3-5 showed a band at 720 nm corresponding to their excited triplet states.

Nanosecond transient spectra recorded after 532-nm laser irradiation of ferrocene–porphyrins, 2a-c showed weak absorption peaks in the 800–840 nm region corresponding to the excited triplet states of porphyrins.^{15a} The absorption bands of the porphyrin anion radicals formed after charge separation from the ferrocene to the singlet excited porphyrins are expected to appear at 600–640 nm; however, such absorption was not observed, probably due to the occurrence of quick charge-recombination of Fc⁺–MP^{•–}.

The transient absorption spectra for the studied self-assembled free-base porphyrin—fullerene dyad (**1a:5**) are shown in Figure 7a. In the spectra, in addition to the peaks corresponding to the triplet excited states of porphyrin and fullerene at 700 and 800 nm, respectively, peaks around 640 nm corresponding to the formation of porphyrin cation radical was also observed. Furthermore, peak at 1020 nm corresponding to the formation

of fulleropyrrolidine anion radical was observed. These spectral features clearly support that the charge separation occurred from the singlet excited porphyrin to fullerene.^{15a} The rates of charge recombination $k_{\rm CR}$ for MP^{•+}-crown:NH₃⁺-C₆₀^{•-} were evaluated from the decay of the 1020 nm band, which obeyed the first-order kinetics. The $k_{\rm CR}$ values were found to be about $1 \times 10^7 \text{ s}^{-1}$ with a slowest rate of $0.6 \times 10^7 \text{ s}^{-1}$ for **1b:4** and a fastest rate of $7 \times 10^7 \text{ s}^{-1}$ for **1c:5**, as listed in Table 5. The nondecaying part after 200 ns has been attributed to the tail of the absorption of the triplet excited states of zinc porphyrin and fullerene because the peak at 1020 nm completely disappeared after about 1000 ns.

The transient absorption spectra for the studied self-assembled ferrocene-free base porphyrin-fullerene triads (2a:5) are shown in Figure 7b. Upon formation of the supramolecular triad by the complexation of 2a with 5, the transient absorption spectra showed a peak at 1020 nm corresponding to the formation of fulleropyrrolidine anion radical. On the other hand, no new peak corresponding to the formation of the porphyrin cation radical appeared at 640 nm. Although formation of ferrocenium cation was not observed for reasons of weak absorbance, disappearance of the porphyrin cation radical supports the hole migration from the zinc porphyrin cation radical to the ferrocene entity. Interestingly, unlike the spectrum of the dyad shown in Figure 7a, the C₆₀^{•-} peak at 1020 nm survived beyond 800 ns, indicating the formation of a prolonged charge-separated state. The transient absorption spectra for the other studied selfassembled ferrocene-porphyrin-fullerene triads yielded similar results.

To calculate the rate of charge recombination, the decay of the fulleropyrrolidine anion radical peak at 1020 nm was monitored. The charge recombination process occurred in two steps, namely a relatively fast process and a relatively slow process. The rates of charge recombination calculated from the fast decaying component (k_{CR1} for Fc-MP^{•+}-crown:NH₃⁺- $C_{60}^{\bullet-}$ in Table 6) were found to be close to the k_{CR} values for the dyad systems, MP⁺⁺-crown:NH₃⁺-C₆₀⁺⁻ (1a-c:3-5 in Table 5). These observations suggest that the k_{CR1} corresponds to the charge-recombination process occurring before the hole shift from MP^{•+} to Fc. On the other hand, slow decay at 1020 nm can be ascribed to the distant charge-recombination process between the ferrocinium cation and fulleropyrrolidine anion radical species in Fc⁺-MP-crown:NH₃⁺-C₆₀^{•-}. The rate of charge recombination, k_{CR2} for the slow process was found to be 2 or 3 orders of magnitude smaller than the k_{CR1} in Table 6 or k_{CR} of the dyads in Table 5. The longest lifetime of Fc⁺-MP-crown:NH₃⁺-C₆₀^{•-} was found for **2c**:**3** about 7 μ s, which is longer than that observed for 1c:3 by a factor of about 100 times. As pointed earlier, this effect could be easily rationalized to the increased distance between the opposite charges, that is, from about 17 Å for the dyads to 27 Å for the triads.

By using the $k_{\rm CS}$ and $k_{\rm CR}$ thus evaluated, the ratios $k_{\rm CS}/k_{\rm CR}$ were evaluated as a measure of the extent of charge stabilization in the photoinduced electron-transfer process. These values were found to be 100–150 for $k_{\rm CS}/k_{\rm CR1}$ and 1000–10 000 for $k_{\rm CS}/k_{\rm CR2}$ clearly demonstrating charge stabilization in the supramolecular triads.

A comparison between the results reported earlier for the covalently linked triad bearing same $Fc-ZnP-C_{60}$ entities^{12c} to the supramolecular triads of the present study is important. Unlike the present supramolecular triads, a single step charge recombination was observed for the covalently linked $Fc-ZnP-C_{60}$ triad^{12c} where the rate for the exothermic hole-shift (HS) process was evaluated to be > 10⁹ s⁻¹.^{12c} Thus, the dual phases

of the charge-recombination process are quite characteristic of supramolecular systems, which suggests that the k_{CR1} is comparable to k_{HS} . Indeed, the k_{CR1} values in the present supramolecular systems are greater than that of covalently bonded dyad (ZnP-C₆₀; 700 ns in PhCN).^{11c} Although the molecular flexibility of the supramolecular systems appears to accelerate the charge-recombination, substantial charge-stabilization has been indeed achieved by the adopted supramolecular strategy.

In the case of covalently linked triad, the $Fc^+-ZnP-C_{60}^{\bullet-}$ was insensitive to O_2 because of the distant doublet-doublet spin character. This was in contrast to the $ZnP^{\bullet+}-C_{60}^{\bullet-}$ of the covalently linked dyad that was quenched by O_2 because of the triplet spin character.^{12c} In the present supramolecular dyads, acceleration of the decay of the radical ion pair was observed in a similar way to the covalently linked dyads. For the supramolecular triads, further quick decay of $Fc-MP^{\bullet+}$ -crown: $NH_3^+-C_{60}^{\bullet-}$ was observed in the presence of O_2 as expected from the covalently linked case. However, the slow decay part of Fc^+-MP -crown: $NH_4^+-C_{60}^{\bullet-}$ was also quenched by O_2 probably because of the occurrence of different phenomenon in solution such as flexibly linked "close" forms of the structures.

Summary. A series of supramolecular triads composed of ferrocene, porphyrin, and fullerene were designed, synthesized, and studied using various physicochemical techniques. The adopted crown ether-alkylammonium cation complexation binding strategy resulted in well-defined stable triads. The freeenergy changes for charge-separation and charge-recombination were varied by varying the metal ion in the porphyrin cavity. The charge-separation processes were monitored by steady-state and time-resolved emission studies. The rate of charge-separation was found to depend on the associated free-energy changes. The rates of charge-recombination monitored by nanosecond transient absorption spectral studies were found to follow two routes, namely, direct charge-recombination from the initial charge-separated state, $Fc-ZnP^{\bullet+}-C_{60}^{\bullet-}$ and charge-recombination from the charge migrated state, $Fc^+-ZnP-C_{60}^{\bullet-}$. The k_{CR} values for the latter route were found to be 1-2 orders of magnitude slower than the former route, thus fulfilling the condition of charge migration to generate long-lived chargeseparated states.

Experimental Section

Chemicals. Buckminsterfullerene, C_{60} (+99.95%) was from SES Research, (Houston, TX). All the reagents were from Aldrich Chemicals (Milwaukee, WI) whereas the bulk solvents utilized in the syntheses were from Fischer Chemicals. Tetrabutylammonium perchloride, *n*-Bu₄NClO₄, used in electrochemical studies was from Fluka Chemicals. Synthesis of **4** is given elsewhere.^{19b}

Synthesis of Benzo-[18-crown-6] Functionalized Ferrocenyl Porphyrins: 5-(4-Methoxycarbonylphenyl)dipyrromethane (1). This compound was prepared according to the general procedure outlined for the synthesis of dipyrromethanes by Lindsey et al.²³ To pyrrole (68 mL, 0.98 mol), methyl 4-formyl benzoate (4 g, 0.024 mol) was added and purged with argon for 15 min. Then trifluoroacetic acid (190 μ L, 0.0024 mmol) was added and stirred at room temperature for 15 min. The mixture was diluted with CH₂Cl₂, and the reaction was quenched with NaOH (100 mL, 0.1 M), and the organic layer was extracted over Na₂SO₄. Excess pyrrole was distilled through vacuum at room temperature, and the compound was purified by flash column chromatography on silica gel using hexanes: ethyl acetate (60:40 v/v) as eluent. Evaporation of the solvent yielded pale-yellow solid. Yield: 2 g (30%).

¹H NMR (CHCl₃-*d*): δ (in ppm): 8.05–7.90 (m, 4H, pyrrole *NH* and phenyl *H*), 7.28 (d, 2H, phenyl *H*), 6.75–6.65 (m, 2H, pyrrole *H*), 6.18–6.12 (m, 2H, pyrrole *H*), 5.92–5.87 (m, 2H, pyrrole *H*), 5.54 (s, 1H, –CH–), 3.90 (s, 3H, –COOCH₃).

H₂-5,15-Di(*p*-methoxycarbonylphenyl)-10,20- -di(*p*-tolyl)porphyrin (2). This compound is prepared according to Luo et al.²⁴ A solution of 1 (1.6 g, 5.71 mmol) was added to *p*-tolualdehyde (675 μ L, 5.71 mmol) in CHCl₃, and the reaction mixture was stirred under argon for 1 h. Then BF₃•O(Et)₂ (724 μ L, 5.71 mmol) was added, and the reaction mixture was stirred in the dark for 2 h. p-Chloranil (2.11 g, 8.57 mmol) was added to the reddish-black reaction mixture, and the resultant mixture was stirred for 18 h. Triethylamine (2.4 mL, 17.25 mmol) was added, and the reaction mixture was stirred for 1 h and then concentrated. Column chromatography on silica gel using chloroform as eluent gave a mixture of five porphyrins including the titled compound. Subsequent column chromatography of this fraction on silica gel using toluene:CHCl₃ (70:30 v/v) as eluent yielded the titled compound as the third band. Evaporation of the solvent yielded the desired compound as a purple solid. Yield: 208 mg (5%).

¹H NMR (CHCl₃-*d*): δ (in ppm): 8.82 (dd, 8H, β -pyrrole *H*), 8.42 (d, 4H, phenyl *H*), 8.25 (d, 4H, phenyl *H*), 8.10 (d, 4H, phenyl *H*), 7.58 (d, 4H, phenyl *H*), 4.12 (s, 6H, -COOCH₃), 2.7 (s, 6H, -CH₃), -2.80 (s, br, 2H, -NH).

H₂-5,15-Di(*p*-carboxyphenyl)-10,20-di(*p*-tolyl)porphyrin (3):^{12b} A suspension of 2 (200 mg, 0.264 mmol) in THF:ethanol (1:1) was taken in a 250 mL round-bottom flask and potassium hydroxide (1.5 g, 0.027 mol) dissolved in water (12 mL) was added to it. The reaction mixture was refluxed for 8 h. After cooling, the solvent was evaporated, the residue was diluted with water (100 mL) and then filtered. The desired compound was obtained as the dipotassium salt. The aqueous suspension of porphyrin dipotassium salt was acidified with concentrated HCl (pH 2) and then filtered. The titled compound was obtained as a purple powder and used without any further purifications. Yield: 85 mg (44%).

¹H NMR (DMSO-*d*): δ (in ppm): 8.8 (dd, 8H, β-pyrrole *H*), 8.38 (d, 8H, phenyl *H*), 8.18–8.10 (d, 4H, phenyl *H*), 7.65–7.55 (d, 4H, phenyl *H*), 2.55 (s, 6H, -CH₃), -2.40-2.95 (s, br, 2H, -NH).

4-Ferrocenylnitrobenzene (4).²⁵ To ferrocene (3.80 g, 20.4 mmol), 25 mL of sulfuric acid was added, and the resulting deep-blue solution was stirred at room temperature for 2 h. The solution was then poured into ice-cold water (100 mL) and allowed to reach room temperature. A solution of sodium nitrite (0.91 g, 13.2 mmol) in 5 mL water at 0 °C was added dropwise to a stirred solution of 4-nitroaniline (1.66 g, 12.0 mmol) in 1:1 water/HCl (10 mL) kept at 0 °C by an ice/water bath. The above mixture was stirred for 30 min to ensure full diazotization. Copper powder (1.0 g) was added to the ferrocenium solution, and the diazonium solution was added dropwise with vigorous solution. After 24 h of stirring at room temperature, ascorbic acid (5 g) was added to reduce any remaining ferrocenium to ferrocene. Dichloromethane was added, and the organic layer was separated. The aqueous layer was extracted further with CH₂Cl₂. The crude compound purified on silica gel by using CH₂Cl₂/hexanes (40:60 v/v). Yield: 925 mg (25%).

ESI mass (in CH₂Cl₂): calcd., 307.58; found, 307.12. ¹H NMR (CHCl₃-*d*): δ (in ppm): 8.14 (d, 2H, phenyl *H*), 7.56 (d, 2H, phenyl *H*), 4.74 (t, 2H, C₅H₄), 4.48 (t, 2H, C₅H₄), 4.05 (s, 5H, C₅H₅).

4-Ferrocenylaniline (5).²⁵ A mixture of granulated tin (170 mg, 1.43 mmol) was added to a solution of **4** (162 mg, 2.28 mmol) in 1:1 HCl:ethanol and refluxed for 2 h. The resulting solution was then cooled to room temperature and neutralized with 40% aqueous NaOH. The compound was washed with dichloromethane and water and the organic layer was collected and dried over anhydrous Na₂SO₄. Evaporation of the organic layer yielded an orange oil which, upon refrigeration, gave the desired compound as orange crystals. Yield: 112 mg (78%).

ESI mass (in CH₂Cl₂): calcd., 277.84; found, 277.18. ¹H NMR (DMSO-*d*): δ (in ppm): 7.20 (d, 2H, phenyl H), 6.52 (d, 2H, phenyl H), 5.02 (s, br, 2H, $-NH_2$), 4.58 (t, 2H, C₅H₄), 4.22 (t, 2H, C₅H₄), 3.98 (s, 5H, C₅ H₅).

H₂-5-{4-[2-(4-benzo-[18-crown-6])amido]phenyl}-15-{4-[2-(4-ferrocenylphenyl) amido]phenyl]-10,20-di(p-tolyl)porphyrin (6, Compound 2a in Scheme 1). 3 (78 mg, 0.11 mmol) was taken in dry toluene (20 mL), thionyl chloride (160.5 μ L, 2.2 mmol) and pyridine (160 μ L) were added, and the reaction mixture was refluxed under argon for 3 h. After cooling, the solvent was evaporated and the resultant green compound was redissolved in dry toluene (20 mL). Then, pyridine (516 μ L) was added followed by 5 (30.5 mg, 0.11 mmol) and 4'-amino benzo-[18-crown-6] (36 mg, 0.11 mmol). The reaction mixture was allowed to stir at room temperature under argon for 12 h. The solvent was evaporated and the crude compound was purified by column chromatography on basic alumina using hexanes:CHCl₃ (20:80 v/v). Evaporation of the second fraction yielded the desired compound as a purple solid. Yield: 44 mg (30%).

ESI mass (in CH₂Cl₂): calcd., 1299.32; found, [M⁺] 1299.7 (100%). ¹H NMR (CDCl₃-*d*): δ (in ppm): 8.92–8.70 (m, 8H, β-pyrrole H), 8.35–8.10 (m, 8H, phenyl H), 8.05 (d, 4H, phenyl H), 7.70 (d, 2H, phenyl H), 7.60–7.45 (m, 6H, phenyl H), 7.28–7.25 (m, 1H, benzocrown phenyl H), 7.10–7.05 (m, 1H, benzocrown phenyl H), 6.88 (d, 1H, benzocrown phenyl H), 4.65 (t, 2H, C₅H₄), 4.32 (t, 2H, C₅H₄), 4.28–4.22 (m, 2H, crownethylene H), 4.20–4.12 (m, 2H, crownethylene H), 4.05 (s, 5H, C₅H₅), 3.98–3.90 (m, 4H, crownethylene H), 3.80–3.65 (m, 12H, crownethylene H), 2.65 (s, 6H, –CH₃), –2.78 (s, br, 2H, –NH).

H₂-5-(*p*-methoxycarbonylphenyl)-10,15,20- tri(*p*-tolyl)porphyrin (7). Methyl 4-formylbenzoate (6 g, 0.037 mol) was dissolved in propionic acid (1000 mL) and pyrrole (10.3 mL, 9.92 g, 0.15 mol) was added followed by *p*-tolualdehyde (13 mL, 0.111 mol). The mixture was refluxed for 3 h. The propionic acid was removed under reduced pressure and the compound was purified by column chromatography on basic alumina using hexanes:CHCl₃ (70:30 v/v) as eluent. Evaporation of the solvent yielded the desired compound as a purple solid. Yield: 1.7 g (6%).

¹H NMR (CHCl₃-*d*): δ (in ppm): 8.92–8.72 (m, 8H, β-pyrrole *H*), 8.45 (d, 2H, phenyl *H*), 8.30 (d, 2H, phenyl *H*), 8.10 (d, 6H, phenyl *H*), 7.55 (d, 6H, phenyl *H*), 4.12 (s, 3H, -COOCH₃), 2.7 (s, 9H, -CH₃), -2.78 (s, br, 2H, -NH).

H₂-5-(*p*-carboxyphenyl)-10,15,20-tri(*p*-tolyl)porphyrin (8): A mixture of 7 (840 mg, 1.18 mmol) in THF (60 mL) and potassium hydroxide (4.62 g, 0.082 mol) in water (20 mL) was refluxed for 20 h. After cooling, the reaction mixture was diluted with CH₂Cl₂, acidified with concentrated HCl, and extracted. The organic layer was washed with saturated NaHCO₃ solution and dried over anhydrous Na₂SO₄. The solvent was evaporated, and the compound was purified by column chromatography on silicagel using CHCl₃:methanol (95:5 v/v) as eluent. Yield: 700 mg (85%). ¹H NMR (CHCl₃-*d*): δ (in ppm): 8.88–8.72 (m, 8H, β -pyrrole *H*), 8.60–8.48 (m, 2H, phenyl *H*), 8.38–8.35 (d, 2H, phenyl *H*), 8.10 (d, 6H, phenyl *H*), 7.58 (d, 6H, phenyl *H*), 2.72 (s, 9H, -CH₃), -2.78 (s, br, 2H, -NH).

H₂-5-{4-[2-(4-benzo-[18-crown-6])amido]phenyl}-10,15,-20-tri(*p*-tolyl)porphyrin (9, compound 1a in Scheme 1). A solution of 8 (500 mg, 0.71 mmol), SOCl₂ (521 μ L, 7.15 mmol) and pyridine (1 mL) in dry toluene (50 mL) was refluxed under argon for 3 h. After cooling, the solvent was evaporated and the resultant green mixture was redissolved in dry toluene (40 mL). Then, pyridine (1 mL) was added followed by 4'-amino benzo-[18-crown-6] (470 mg, 1.43 mmol). The reaction mixture was allowed to stir at room temperature under argon for 12 h. The solvent was evaporated, and the crude compound was purified by column chromatography on silica gel using hexanes: CHCl₃ (40:60 v/v). Evaporation of the solvent yielded the desired compound as a purple solid. Yield: 500 mg (70%).

ESI mass (in CH₂Cl₂): calcd., 1010.2; found, [M⁺] 1010.5 (100%). ¹H NMR (CDCl₃-*d*): δ (in ppm): 8.90–8.70 (m, 8H, β -pyrrole H), 8.22 (m, 2H, phenyl H), 8.18–8.10 (d, 2H, phenyl H), 8.02 (d, 6H, phenyl H), 7.54 (s, 1H, benzocrown phenyl H), 6.98 (d, 1H, benzocrown phenyl H), 6.75 (d, 1H, benzocrown phenyl H), 4.18–4.12 (m, 2H, crownethylene H), 4.06–4.02 (m, 2H, crownethylene H), 3.88–3.76 (m, 4H, crownethylene H), 3.75–3.55 (m, 12H, crownethylene H), 2.60 (s, 9H, –CH₃), –2.78 (s, br, 2H, –NH).

5-{4-[2-(4-benzo-[18-crown-6])amido]phenyl}-15-{4-[2-(4-ferrocenylphenyl)amido]-phenyl]-10,20-di(*p***-tolyl)porphyrinato zinc (II) (10, Compound 2b in Scheme 1). The freebase porphyrin 6 (10 mg, 0.008 mmol) was dissolved in CHCl₃ (10 mL), a saturated solution of zinc acetate in methanol was added to the solution, and the resulting mixture was refluxed for 2 h. The course of the reaction was monitored by absorption spectroscopy. At the end, the reaction mixture was washed with water and dried over anhydrous Na₂SO₄. Chromatography on basic alumina column by using hexanes:CHCl₃ (20:80 v/v) gave the title compound. Yield: 10 mg (90%).**

ESI mass (in CH₂Cl₂): calcd., 1362.69; found, [M⁺] 1362.3 (100%). ¹H NMR (CDCl₃-d): δ (in ppm): 8.98–8.82 (m, 8H, β-pyrrole H), 8.38–8.15 (m, 8H, phenyl H), 8.10 (m, 4H, phenyl H), 7.72 (d, 2H, phenyl H), 7.60–7.48 (m, 6H, phenyl H), 7.22– 7.16 (m, 1H, benzocrownphenyl H), 7.12–7.05 (m, 1H, benzocrownphenyl H), 6.80 (d, 1H, benzocrownphenyl H), 4.68 (t, 2H, C₅H₄), 4.32 (t, 2H, C₅H₄), 4.08 (s, 5H, C₅H₅), 4.0–3.86 (m, 2H, crownethylene H), 3.85–3.72 (m, 2H, crownethylene H), 3.70–3.52 (m, 2H, crownethylene H), 3.48–3.08 (m, 14H, crownethylene H), 2.72 (s, 6H, –CH₃).

5-{4-[2-(4-benzo-[18-crown-6])amido]phenyl}-15-{4-[2-(4ferrocenylphenyl)amido]-phenyl]-10,20-di(p-tolyl)porphyrinato magnesium (II) (11, Compound 2c in Scheme 1). This was prepared according to a general procedure developed by Lindsey and Woodford²⁶ for Mg porphyrin synthesis. A sample of 6 (10 mg, 0.008 mmol) was dissolved in 10 mL of CH_2Cl_2 . Then triethylamine (0.022 mL, 15.6 mg, 0.15 mmol) was added followed by MgBr₂•O(Et)₂ (20 mg, 0.08 mmol). The mixture was stirred for 20 min at room temperature. The course of the reaction was monitored by absorption spectroscopy. The mixture was diluted with 20 mL of CH₂Cl₂, washed with 5% NaHCO₃, and dried over anhydrous Na₂SO₄, and the filtrate was evaporated. Chromatography on basic alumina column with CHCl₃ as eluent yielded residual 6. Elution with CHCl₃:methanol (98:2 v/v) yielded a greenish-purple fraction of the desired compound. Yield: 8 mg (80%).

ESI mass (in CH₂Cl₂): calcd., 1321.61; found, [M⁺] 1321.3 (100%). ¹H NMR (CDCl₃-*d*): δ (in ppm): 8.95–8.58 (m, 8H, β -pyrrole H), 8.32–7.80 (m, 12H, phenyl H), 7.60–7.40 (m, 8H, phenyl *H*), 7.10–6.75 (s, br, 2H, benzocrown phenyl *H*), 6.38–6.22 (m, 1H, benzocrown phenyl *H*), 4.65–4.55 (t, 2H, C₅H₄), 4.30–4.22 (t, 2H, C₅H₄), 4.02 (s, 5H, C₅H₅), 3.65–3.60 (m, 2H, crownethylene *H*), 2.85–2.80 (m, br, 2H, crownethylene *H*), 2.78–2.62 (s, 6H, –CH₃), 2.38–2.30 (m, 4H, crownethylene *H*), 2.25–1.78 (m, 8H, crownethylene *H*), 1.68–1.52 (m, 4H, crownethylene *H*).

5-{**4-**[**2-**(**4-benzo-**[**18-crown-6**])**amido**]**pheny**]**-10,15,20-tri-**(*p*-**toly**]**)porphyrinato zinc (II) (12, Compound 1b in Scheme 1).** This compound was prepared from porphyrin **9** (10 mg, 0.01 mmol) according to the procedure outlined above for **10**. Chromatography on basic alumina column by using hexanes: CHCl₃ (40:60 v/v) gave the title compound. Yield: 10 mg (90%).

ESI mass (in CH₂Cl₂): calcd., 1073.58; found, [M⁺] 1073.4 (100%). ¹H NMR (CDCl₃-*d*): δ (in ppm): 8.95–8.62 (m, 8H, β -pyrrole *H*), 8.42–8.32 (m, 1H, phenyl *H*), 8.05–7.82 (m, 7H, phenyl *H*), 7.80–7.65 (m, 2H, phenyl *H*), 7.58–7.35 (m, 6H, phenyl *H*), 6.95 (s, br, 1H, benzocrownphenyl *H*), 6.82–6.75 (s, br, 1H, benzocrown phenyl *H*), 6.30–6.22 (m, 1H, benzocrown phenyl *H*), 3.20–3.05 (m, 2H, crownethylene *H*), 2.80–2.72 (m, 2H, crownethylene *H*), 2.65 (s, 9H, –CH₃), 2.40–2.02 (m, 9H, crownethylene *H*), 1.95–1.75 (m, 6H, crownethylene *H*), 0.85 (s, br, 1H, crownethylene *H*).

5-{4-[2-(4-benzo-[18-crown-6])amido]phenyl}-10,15,20-tri-(*p*-tolyl)porphyrinato magnesium (II) (13, Compound 1c in Scheme 1). This compound was prepared from porphyrin 9 (10 mg, 0.001 mmol) according to the procedure outlined above for 11. Chromatography on basic alumina column with CHCl₃ as eluent yielded residual 9. Elution with CHCl₃:methanol (98:2 v/v) yielded a greenish-purple fraction of the desired compound. Yield: 8 mg (80%).

ESI mass (in CH₂Cl₂): calcd., 1032.49; found, [M⁺] 1032.5 (100%). ¹H NMR (CDCl₃-*d*): δ (in ppm): 8.92–8.58 (m, 8H, β -pyrrole H), 8.35–8.22 (m, 1H, phenyl H), 8.12–7.90 (m, 7H, phenyl *H*), 7.70–7.42 (m, 8H, phenyl H), 7.05 (s, br, 1H, benzocrownphenyl *H*), 6.82 (s, br, 1H, benzocrown phenyl *H*), 6.25 (m, 1H, benzocrown phenyl *H*), 2.85–2.75 (m, 2H, crownethylene *H*), 2.65 (s, 9H, –CH₃), 2.60–2.50 (m, 2H, crownethylene *H*), 2.25–2.05 (m, 2H, crownethylene *H*), 1.98– 1.62 (m, 8H, crownethylene *H*), 1.58–1.30 (m, 4H, crownethylene *H*), 0.10 (s, br, 2H, crownethylene *H*).

Synthesis of Fullerene Derivatives: *N*-Boc-(2-amino)ethylamine (14). This compound was prepared according to Muller et al.^{27a} Di-*tert*-butyl bicarbonate (6.53 g, 0.03 mol) dissolved in 100 mL of dry CHCl₃ was added to a solution of ethylenediamine (20 mL, 0.3 mol) in 300 mL of CHCl₃ during 2.5 h with stirring and cooling in an ice bath. The reaction mixture was stirred for additional 24 h at room temperature and was then washed with water, extracted with CHCl₃, and dried over anhydrous Na₂SO₄. Evaporation of the organic layer yielded the desired compound as a pale-yellow oil. Yield: 5.2 g (11%).

¹H NMR (CHCl₃-*d*): δ (in ppm): 5.28 (s, br, 1H, -NH), 3.25-3.08 (m, 2H, CH₂), 2.8 (t, 2H, CH₂), 1.65-1.40 (m, 9H, Boc-H).

Benzyl-*N***-[2-(***N***-Boc)aminoethyl]glycinate (15).** This compound was prepared according to Kordatos et al.^{27b} A solution of benzyl 2-bromo acetate (1.53 g, 1.1 mL, 6.67 mmol) dissolved in 30 mL of 1,4-dioxane was added to a solution of **14** (3.2 g, 0.02 mol) in 20 mL of 1,4-dioxane at 0 °C over a period of 1

h, and the reaction mixture was stirred overnight. The solvent was evaporated under reduced pressure, and the residue was dissolved in water and extracted with ethyl acetate. The organic extract was dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude compound was purified by column chromatography on silicagel using petroleum ether:ethyl acetate (40:60 to 20:80 v/v). Evaporation of the solvent yielded the desired compound as a pale-yellow oil. Yield: 1.9 g (73%).

¹H NMR (CHCl₃-*d*): δ (in ppm): 7.45–7.40 (m, 5H, phenyl *H*), 5.18 (s, 2H, CH₂), 5.04 (s, br, 1H, NH), 3.45 (s, 2H, benzyl CH₂), 3.25–3.15 (m, 2H, CH₂), 2.74 (t, 2H, CH₂), 1.65 (s, br, 1H, NH), 1.45 (s, 9H, Boc-H).

N-[2-(*N*-Boc)aminoethyl]glycine (16). To a methanolic solution of 15 (1.55 g, 5 mmol) was added 100 mg of % Pd/C, and the mixture was stirred under a hydrogen atmosphere for 24 h. The catalyst was removed by filtration on Celite, and the solvent was evaporated. The residue was triturated in diethyl ether to give the desired compound as a white solid. Yield: 500 mg (46%).

¹H NMR (D₂O): δ (in ppm): 3.52 (s, 2H, CH₂), 3.45 (t, 2H, CH₂), 3.18 (t, 2H, CH₂), 1.45 (s, 9H, Boc-H).

N-[2-(*N*-Boc)aminoethyl]-2-phenyl-3,4-fulleropyrrolidine (17). To a 200 mg (0.28 mmol) of C₆₀ in toluene (200 mL), 122 mg (0.56 mmol) of 16 and benzaldehyde (140.4 μ L) were added and the mixture was refluxed for 2 h. After cooling to room temperature, the solvent was evaporated under reduced pressure. The crude compound was purified on silica gel by flash column chromatography using toluene:ethyl acetate (98:2 v/v) as eluent. Evaporation of the solvent yielded the desired compound as a brown solid. Yield: 123 mg (45%).

¹H NMR [CDCl₃:CS₂ 1:1 (v/v)]: δ (in ppm): 7.84–7.74 (m, 2H, phenyl *H*), 7.46–7.32 (m, 3H, phenyl *H*), 5.22–5.05 (m, 3H, NH & CH₂), 4.2 (d, 1H, pyrrolidine *H*), 3.78–3.58 (m, 2H, pyrrolidine *H*), 3.45–3.30 (m, 1H, CH₂), 2.78–2.65 (m, 1H, CH₂), 1.52 (s, 9H, Boc-H).

To a dichloromethane solution of **17** (123 mg, 0.13 mmol), 3 mL of trifluoroacetic acid was added, and the mixture was stirred for 3 h at room temperature. The solvent and excess acid was removed under reduced pressure. The compound was washed with CH_2Cl_2 in order to remove the unreacted starting material. Evaporation of CH_2Cl_2 followed by drying yielded the compound **18** (compound **3** in Scheme 1) as a brown solid. Yield: 85 mg (68%).

ESI mass (in $CH_2Cl_2+CH_3OH$)): calcd., 883.26 (without CF_3COO^-); found, $[M^+]$ 883.2 (100%).

N-methyl 2-(4-(2-(*N*-Boc)-amino) ethoxy phenyl) 3,4fulleropyrrolidine, 19 (Compound 5 in Scheme 1). To a 100 mg (0.138 mmol) of C₆₀ in toluene, 109 mg (0.414 mmol) of 4-(2-Boc- amino) ethoxy benzaldehyde^{27c} and 31 mg (0.345 mmol) of sarcosine was added and refluxed for 4 h. The solvent was evaporated under vacuum, and purified on silica gel using toluene and ethyl acetate [7:3]. Yield 50%. Next, to dichloromethane solution of *N*-Boc, protected 19 (70 mg, in 5 mL), trifluroacetic acid (3 mL), and *m*-cresol (50 μ L) were added and stirred for 3 h. The solvent and acid were removed under vacuum and solid product was washed with toluene for several times to get desired compound 19 (Yield 95%).

¹H NMR (CD₃OD): δ 7.71, 6.95 (d, d, 4H, phenyl), 4.98, 4.82, 4.22 (d, s, d, 3H, pyrolidine-H), 4.0, 3.51 (d, m, $-(CH_2)_2-$), 2.78 (N $-CH_3$), ESI mass in CH₂Cl₂ calcd: 913; found: 913.3. UV-vis (MeOH, nm) 204, 254.5 nm.

Instrumentation. The UV-visible spectral measurements were carried out with a Shimadzu Model 1600 UV-visible

spectrophotometer. The steady-state fluorescence emission was monitored by using a Spex Fluorolog-tau spectrometer. A right angle detection method was used. The ¹H NMR studies were carried out either on a Varian 400 MHz or Varian 300 MHz spectrometers. Tetramethylsilane (TMS) was used as an internal standard. Cyclic voltammograms were recorded on a EG&G Model 263A potentiostat using a three electrode system in benzonitrile containing 0.1 M *n*-Bu₄NClO₄ as the supporting electrolyte. A platinum button or glassy carbon electrode was used as the working electrode. A platinum wire served as the counter electrode and a Ag/AgCl was used as the reference electrode. Ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as an internal standard. All the solutions were purged prior to spectral measurements using argon gas.

The computational calculations were performed by the DFT B3LYP/3-21G(*) method with the GAUSSIAN-03 software package²⁸ on various PCs. The ESI-Mass spectral analyses of the self-assembled complexes were performed by using a Fennigan LCQ-Deca mass spectrometer. The starting compounds and the triads (about 0.1 mM concentration) were prepared in CH₂Cl₂, freshly distilled over calcium hydride.

Time-Resolved Emission and Transient Absorption Measurements. The picosecond time-resolved fluorescence spectra were measured using an argon-ion pumped Ti:sapphire laser (Tsunami; pulse width = 2 ps) and a streak scope (Hamamatsu Photonics; response time = 10 ps). The details of the experimental setup are described elsewhere.²⁹ Nanosecond transient absorption measurements were carried out using the SHG (532 nm) of an Nd:YAG laser (Spectra Physics, Quanta-Ray GCR-130, fwhm 6 ns) as excitation source. For the transient absorption spectra in the near-IR region (600–1600 nm), the monitoring light from a pulsed Xe lamp was detected with a Ge-avalanche photodiode (Hamamatsu Photonics, B2834).²⁹

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Supporting Information Available: Diagram of hole transfer/electron transfer. This material is available free of charge via the Internet at http://pubs.acs.org.

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