Supramolecular Triads Formed by Axial Coordination of Fullerene to Covalently Linked Zinc Porphyrin–Ferrocene(s): Design, Syntheses, Electrochemistry, and Photochemistry

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Supramolecular triads have been constructed by using covalently linked zinc porphyrin–ferrocene(s) dyads, self-assembled via axial coordination to either pyridine- or imidazole-appended fulleropyrrolidine. These triads were characterized by optical absorption, computational, and electrochemical methods. The calculated binding constants (*K*) revealed stable complexation and suggested the existence of intermolecular interactions between the ferrocene and fullerene entities. Accordingly, the optimized geometry obtained by ab initio B3LYP/3-21G(*) methods revealed closely spaced ferrocene and fullerene entities in the studied triads. Photoinduced charge-separation and charge-recombination processes were examined in the dyads and triads by means of time-resolved transient absorption and fluorescence lifetime measurements. In the case of zinc porphyrin–ferrocene(s) dyads, upon photoexcitation, efficient ($\Phi_{CS} = 0.98$) to moderate ($\Phi_{CS} = 0.54$) amounts of electron transfer from the ferrocene to the singlet excited zinc porphyrin occurred depending upon the nature of the spacer, resulting in the formation of the Fc⁺–ZnP^{•–} radical pair. Upon formation of the supramolecular triads by axial coordination of fulleropyrrolidines, the initial electron transfer originated either from or to the singlet excited zinc porphyrin, resulting ultimately in the formation of the charge-separated states of Fc⁺–ZnP:C₆₀^{•–} with high quantum efficiency. The calculated ratio of k_{CS}/k_{CR} from the kinetic data was found to be ~100, indicating a moderate amount of charge stabilization in the studied supramolecular triads.

Introduction

Studies on photoinduced electron transfer in molecular and supramolecular donor-acceptor systems have undergone rapid growth in recent years mainly to address the mechanistic details of electron transfer in chemistry and biology, to develop artificial photosynthetic systems for light energy harvesting,^{1–9} and also to develop molecular optoelectronic devices.¹⁰ In the construction of such dyads, fullerenes¹¹ and porphyrins¹² have been utilized as constituents owing to their rich and well-understood redox, optical, and photochemical properties.9,13-14 In contrast with the traditionally used two-dimensional aromatic electron acceptors, fullerenes (C60 and C70) in donor-acceptor dyads accelerate forward electron transfer (k_{CS}) and slow backward electron transfer (k_{CR}) , undoubtedly due to their small reorganization energy in electron-transfer reactions.¹⁵ That is, they form the much desired long-lived charge-separated states. The small reorganization energy of fullerenes predicts that the $k_{\rm CS}$ lies upward along the normal region into the top region of the Marcus curve, and the k_{CR} to lie significantly downward into the inverted region. The small reorganization energy is due to the fullerene's unique structure and symmetry, which are ultimately responsible for its high degree of delocalization and structural rigidity. Consequently, a number of metallotetrapyrrole-fullerene and luminescent transition-metal complexfullerene dyads have been synthesized and studied to probe the

effect of molecular topology and distance and orientation effects of the donor and acceptor entities on the charge separation and recombination processes.⁸

More recently, elegantly designed porphyrin and fullerene bearing molecular and supramolecular triads, tetrads, pentads etc., have also been synthesized and studied.^{8,14,16–18} In some of these supramolecular systems, distinctly separated donor—acceptor radical ion pairs, in succession, are generated upon initial electron transfer by charge migration reactions along the well-tuned redox gradients. Photosynthetic reaction centers, composed of self-assembled donor and acceptor entities, produce long-lived highly energetic charge-separated states with quantum yields close to unity using this mechanism of charge migration.¹⁹ Hence, there is a great need for developing such well-organized molecular/supramolecular systems for harvesting solar energy by means of fast forward electron transfer and slow backward electronic devices.

Building structurally well-defined, self-assembled supramolecular triads or tetrads bearing three or more photo- or redoxactive entities is tedious because of the occurrence of multiple equilibrium reactions and the lower stability in solution of the many utilized self-assembly approaches.^{8,9} Because of this, the most successful models to achieve charge stabilization studied to date have been the covalently linked ones.^{1–9,16,18} However, it is possible to choose a covalently linked dyad or triad and allow it to self-assemble with another donor or acceptor entity with a well-defined binding mechanism. Alternatively, multiple modes of binding could also be used to form structurally welldefined, stable supramolecular systems.^{8,9} In the present study,

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Figure 1. Structure of the donors (1-4) and acceptors (5 and 6) utilized to form supramolecular triads via axial coordination of zinc porphyrin in the present study.

we have employed the former approach of utilizing covalently linked zinc porphyrin—ferrocene(s) dyads to form supramolecular triads by the axial coordination of pyridine or imidazole functionalized fulleropyrrolidines (Figure 1).

As demonstrated in the present study, upon excitation of the donor zinc porphyrin, efficient forward electron transfer to the axially bound C_{60} occurs followed by a hole transfer from the ZnP^{•+} to the ferrocene entity to generate the Fc⁺–ZnP–C₆₀^{•-} charge-separated species. As a consequence of the sequential electron-transfer events, the charge-recombination reaction is slowed to some extent, even though the ferrocene and fullerene entities of the supramolecular triads exhibit some through-space interactions.

Results and Discussion

In the present study, we have utilized three different zinc porphyrin-ferrocene(s) dyads, 2-4 to self-assemble with either pyridine or imidazole-appended fulleropyrrolidine, 5-6. The reference compound 1, zinc tetraphenylporphyrin, is used for control experiments. In compound 2, the zinc porphyrin and ferrocene entities are directly linked via one of the phenyl rings of zinc tetraphenylporphyrin, while in 3, an additional phenyl amide spacer to increase the distance between the two entities is introduced. Compound 4 with two directly linked ferrocene entities is utilized to visualize the effect of a second ferrocence entity on the spectral and photochemical properties. The synthetic details are given in the Experimental Section. The structural integrity of all of the compounds was deduced from ¹H NMR, electrospray ionization (ESI) mass spectrometry in CH₂Cl₂ matrix, optical absorption and emission, and electrochemical methods.

UV–Visible Spectral Studies. The optical absorption spectra in the visible wavelength region of the zinc porphyrin– ferrocene(s) dyads were similar to 1, but the peak maxima revealed a red shift of 2–3 nm. The calculated full width at half maximum values also revealed slight changes, suggesting intramolecular interactions between porphyrin and the appended ferrocene entities. No new peaks corresponding to appended ferrocene were observed due to the low molar absorptivity, ϵ , of ferrocene compared to the high ϵ values of porphyrin absorption bands.²⁰

The binding of C_{60} derivatives, **5** and **6**, to porphyrins 1-4resulting in the formation of the pentacoordinated zinc porphyrin by axial coordination was monitored by optical absorption methods. The formation of pentacoordinated complexes was characterized by red-shifted Soret and visible bands and the appearance of isosbestic points²¹ as shown for porphyrin, 4, binding to fullerene, 5, in o-dichlorobenzene in Figure 2. Job's continuous variation plot also confirmed 1:1 complex formation between the zinc porphyrin-ferrocene(s) and C₆₀-bearing axialcoordinating ligands. Extending the absorption wavelength to 1000 nm revealed the absence of any new charge-transfer bands. The association constants, K, for axial coordination were calculated from the absorption spectral data using the Scatchard method²² (Figure 2 inset) and are listed in Table 1. For comparison purposes, the K values for pyridine binding to the zinc porphyrins are also listed.

It is clear from the data in Table 1 that (i) the *K* values are 2-3 times higher for **5** or **6** binding to zinc porphyrin–ferrocene(s) dyads compared to pristine zinc porphyrin, **1**, (ii) the *K* values are 2-3 times higher for **5** or **6** binding to zinc



Figure 2. UV-vis spectral changes observed during the complexation of 4 (2.36 μ M) and 5 (1.99 μ M each addition) in *o*-dichlorobenzene. The inset figure shows the Scatchard plot of the data analysis monitored at 425 nm.

 TABLE 1: Formation Constants for Axial Coordination of

 Fullerene Ligands to Zinc Porphyrin–Ferrocene(s) Dyads in

 o-Dichlorobenzene at 298 K

compound	pyridine	pyridine-C ₆₀ , 5	imidazole-C _{60,} 6	ref			
1 2 3 4	$\begin{array}{c} 7.8 \times 10^{3} \\ 7.7 \times 10^{3} \\ 5.3 \times 10^{3} \\ 5.8 \times 10^{3} \end{array}$	$\begin{array}{c} 7.2 \times 10^{3} \\ 26.8 \times 10^{3} \\ 20.5 \times 10^{3} \\ 23.4 \times 10^{3} \end{array}$	$\begin{array}{c} 11.6 \times 10^{3} \\ 29.6 \times 10^{3} \\ 22.6 \times 10^{3} \\ 24.6 \times 10^{3} \end{array}$	21d this work this work this work			
a Error = +10%.							

porphyrin-ferrocene(s) dyads compared to pyridine binding to the dyads, (iii) the K values for imidazole $-C_{60}$, 6, binding are larger compared to pyridine $-C_{60}$, 5, and (iv) increasing distance between the porphyrin and ferrocene entities, or increasing the number of ferrocene entities, decreased the binding constants to some extent. The third observation has earlier been attributed to the higher basicity of the imidazole ligand compared to the pyridine ligand. The increased binding ability of zinc porphyrin-ferrocene(s) dyads, 2-4 to C₆₀, 5, or 6 and not to pyridine could be due to (i) a change in the basicity of zinc porphyrin as a result of appended ferrocene entities or (ii) existence of intermolecular interactions between the ferrocene and C₆₀ entities upon axial coordination. The latter effect is more conceivable since pyridine binding to 2-4 did not show such an increased binding ability, and also, by increasing the ferrocene entities in 4, a decrease in the K value was observed. In this regard, the existence of intermolecularly interacting ferrocene-C₆₀ complexes is well known in the literature.²³ To visualize the existence of intermolecular ferrocene-C₆₀ interactions in the self-assembled triads, computational and electrochemical studies were performed and the results are discussed in the forthcoming sections.

Ab initio B3LYP/3-21G(*) Modeling of the Triads. 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.²⁴ Earlier, the B3LYP/3-21G(*) methods were successfully used to predict the geometry and electronic



Figure 3. Ab initio B3LYP/3-21G(*)-optimized geometry of the supramolecular triad formed by 2 and 6.

structure of molecular and self-assembled supramolecular dyads and triads.²⁵ For this, both the zinc porphyrin–ferrocene(s) dyads and functionalized fullerenes were optimized to a stationary point on the Born–Oppenheimer potential-energy surface and allowed to self-assemble via axial coordination. The structure of one of the fully optimized triads involving compounds **2** and **6** is shown in Figure 3. It may be mentioned here that the triads were very flexible and multiple minima were possible. Under these conditions, the optimization process required much experience and considerable computational time to confidently achieve an optimized structure at the B3LYP/3-21G(*) level.

The geometric parameters that are helpful to understand the spectral and photochemical properties (kinetics of charge-separation and charge-recombination), obtained from the B3LYP/ 3-21G(*) optimized structures, are listed in Table 2. The center-to-center distances between the ZnP and coordinated C₆₀ entities were found to range between 10 and 13 Å, while the edge-to-edge distance varied between 4.7 and 9.6 Å, depending upon the nature of the fulleropyrrolidine. The metal-metal distances between Zn and Fe were found to be ~10.7 Å for the directly linked zinc porphyrin-ferrocene(s) dyads and ~16.9 Å for the dyad linked with an additional phenyl amide spacer. Importantly,

 TABLE 2: B3LYP/3-21G(*)-Optimized Distances between the Different Entities of the Investigated Supramolecular Triads

supramolecular complex ^a	center-to distan	o-center ce, Å	edge-to-ede distance, Å				
	ZnP-C ₆₀ ^c	ZnP-Fc ^d	$\overline{ZnP-C_{60}^{e}}$	ZnP-Fc ^e	Fc-C ₆₀ ^e		
1:5 ^b	10.4		4.7				
2:5	9.9	10.7	6.4	4.3	3.7		
4:5	10.3	10.8	6.8	4.3	2.8		
1:6 ^b	12.3		6.9				
2:6	12.1	10.4	9.6	4.3	2.6		
3:6	13.0	16.9	9.6	4.2	3.8		
4:6	13.0	10.5	9.6	4.3	2.8		

^{*a*} See Figure 1 for abbreviations. ^{*b*} From ref 21d. ^{*c*} Zinc center to the center of fullerene sphere. ^{*d*} Zinc center to iron center. ^{*e*} Distance between the closely located porphyrin π system carbon, ferrocene cyclopentadienyl carbon, and/or fullerene sphere carbon (the carbon atoms of spacer units were not considered in estimating the distances).



Figure 4. Cyclic voltammograms of (a) 3, (b) 4, and (c) 6 (0.05 mM) in *o*-dichlorobenzene, 0.1 M (TBA)ClO₄. Scan rate = 100 mV/s.

intermolecular-type interactions between the C_{60} and ferrocene units, such as the one shown in Figure 3 for **2:6**, were observed. That is, the edge-to-edge distances between the ferrocene and C_{60} entities were found to range between 2.8 and 3.8 Å (last column in Table 2) and are within the van der Waals interacting distances. As pointed out earlier, such interactions between the ferrocene and C_{60} entities are expected to modulate the photochemical properties; that is, because of the close proximity of these entities, efficient charge recombination of the ferrocene cation and C_{60} anion radical during photochemical electron transfer is expected to occur.

Electrochemical Studies and Electron-Transfer Driving Forces. Electrochemical studies using the cyclic voltammetric technique were performed to visualize the intermolecular interactions and also to evaluate the energetics of electron transfer reactions. Figure 4 shows representative cyclic voltammograms of the newly synthesized zinc porphyrin-ferrocene-(s) dyads, while Table 3 lists their redox potential values. The zinc porphyrin-ferrocene(s) dyads revealed redox peaks corresponding to the zinc porphyrin and the ferrocene entities. On the basis of the peak-to-peak separation, ΔE_{pp} values, and the cathodic-to-anodic peak current ratio, all of the redox processes of compounds 2-4 were found to be electrochemically and chemically reversible.²⁶ However, the peak current corresponding to the oxidation of the ferrocene entity of compound 4 was twice as much as that of the other redox waves corresponding to the presence of two ferrocene entities. Presence of the interacting ferrocene entity on the porphyrin π system caused small shifts in the potential values.

Next, the zinc porphyrin-ferrocene(s) dyads were titrated with various amounts of 5 or 6 to probe the effect of axial coordination on the redox potentials of both the ferrocene and zinc porphyrin entities. Figure 5 shows cyclic voltammograms obtained during the titration of 2 with various amounts of 6 in o-dichlorobenzene, 0.1 M (TBA)ClO₄. Cathodic shifts up to 60 mV corresponding to zinc porphyrin oxidations were observed; however, no significant shift in the redox potentials corresponding to the oxidation of ferrocene was observed. Similar cathodic shifts were also observed when 2 was titrated with 5 under similar solution conditions. The easier oxidation of zinc porphyrin upon axial imidazole coordination suggests that it is a better electron donor in the triads. Additionally, the reduction potentials corresponding to C_{60} reduction of coordinated 6 did not reveal significant changes as compared to the unbound 6(Figure 5 and Table 3). These results suggest that the intermolecular interactions visualized from optical and computational studies either do not appreciably perturb the electronic structure of ferrocene and C₆₀ entities or such effects are within the experimental errors of cyclic voltammetric experiments. The electrochemical HOMO-LUMO energy gap, that is, the difference between the first oxidation potential of the donor, zinc porphyrin, and the first reduction potential of the acceptor, C_{60} , was about 1.40 ± 0.3 V compared with the B3LYP/3-21G(*) value of \sim 1.20 eV. By use of the HOMO-LUMO gap, the

TABLE 3: Electrochemical Half-Wave Redox Potentials (vs Fc/Fc⁺) of the Zinc Porphyrin–Ferrocene(s) and Their Self-Assembled with Functionalized Fulleropyrrolidine Triads in *o*-Dichlorobenzene, 0.1 M (TBA)ClO₄

	potential, V, vs Fc/Fc ⁺									
compound	P ^{+/2+}	P ^{0/+}	Fc ^{0/+}	$C_{60}^{0/-}$	$C_{60}^{-/2-}$	$P^{0/-}$	$C_{60}^{2-/3-}$	P ^{-/2-}	HOMO-LUMO ^a	$\Delta G_{\rm cs}{}^{\circ b}$
1	0.62	0.28				-1.92	_	-2.23		_
1+6 ^c	0.67	0.29		-1.10	-1.49	-1.91	-2.02	-2.19	1.39	-0.52
2	0.61	0.27	0.00	_	—	-1.93	—	-2.25		_
2+6°	0.62	0.21	-0.03	-1.17	-1.56	-1.93	-2.10	-2.27	1.38	-0.53
3	0.66	0.31	0.00			-1.89		-2.21		_
3+5	0.64	0.28	-0.01	-1.14	-1.55	-1.91	-2.06	-2.22	1.42	-0.52
3+6 ^c	0.65	0.27	-0.01	-1.13	-1.52	-1.91	-2.04	-2.23	1.40	-0.51
4	0.61	0.28	0.00			-1.93		-2.25		_
4 +6 ^c	0.61	0.23	-0.12	-1.20	-1.57	-1.94	-2.10	-2.28	1.43	-0.48

^{*a*} HOMO–LUMO is evaluated electrochemically by $P^{0/+}-C_{60}^{0/-}$ in eV. ^{*b*} $\Delta G_{cs}^{\circ} = E_{1/2}(\mathbf{D}^{+}/\mathbf{D}) - E_{1/2}(\mathbf{A}/\mathbf{A}^{-}) - \Delta E_{0-0} + \Delta G_{s}$, where $E_{1/2}(\mathbf{D}^{+}/\mathbf{D})$ is the first one-electron oxidation potential of the donor porphyrin, $E_{1/2}(\mathbf{A}/\mathbf{A}^{-})$ is the first one-electron reduction potential of the C_{60} electron acceptor, ΔE_{0-0} is the energy of the 0–0 transition energy gap between the lowest excited state and the ground state, and ΔG_{s} refers to the solvation energy, calculated by using the "Dielectric Continuum Model" according to the following equation, $\Delta G_{s} = e^{2/4}\pi\epsilon_{0}[(\frac{1}{2}R_{+} + \frac{1}{2}R_{-} - \frac{1}{R_{CC}})(1/\epsilon_{s})$. From Figure 2, values of $R_{+} = 4.8$ Å, $R_{-} = 4.2$ Å, R_{CC} is the center-to-center distance shown in Table 2. ^{*c*} Obtained by addition of 4 eq. of **6** to the zinc porphyrin-ferrocene(s) dyads.



Figure 5. Cyclic voltammograms of **2** (0.05 mM) in the presence of (i) 0, (ii) 0.5, (iii) 1.0, (iv) 2, (v) 3, and (vi) 4 equiv of **6** in *o*-dichlorobenzene, 0.1 M (TBA)ClO₄. Scan rate = 100 mV/s. The dashed vertical lines indicate the cathodic potential shift observed for the ZnP^{0/+} redox process upon axial coordination.



Figure 6. Fluorescence spectra of (i) **1**, (ii) **3**, (iii) **2**, and (iv) **4** in *o*-dichlorobenzene ($\lambda_{ex} = 551$ nm). The concentration of all of the species was held at 3.70 μ M.

energy corresponding to the 0–0 transition of the zinc porphyrin, and the solvation energy calculated from the dielectric continuum model,²⁷ the free-energies for charge separation, ΔG_{cs} , were also calculated in Table 3. The calculated ΔG_{cs} values suggest the occurrence of photoinduced electron transfer from the singlet excited zinc porphyrin to the axially bound fullerene.

Fluorescence Emission Studies. The photochemical behavior of the zinc porphyrin-ferrocene(s) dyads was investigated, initially, by using steady-state fluorescence measurements. Figure 6 exhibits the fluorescence spectra of compounds 1-4under the same solution concentrations and when excited at the wavelength of the most intense visible band. Compounds 2 and 4 were found to be almost nonfluorescent (~98% quenching); however, the emission intensity of compound 3 was nearly 50% quenched as compared with that of pristine zinc porphyrin, 1. These results indicate the occurrence of intramolecular events in the zinc porphyrin-ferrocene(s) dyads.

Additional quenching of the zinc porphyrin emission of 3 was observed upon axial coordination of fullerenes, 5 or 6, as

shown in Figure 7. The fluorescence emission bands were quenched over 70% of their original intensity accompanied by a small red shift. The fluorescence quenching data were analyzed by Stern-Volmer plots as shown in the inset of Figure 7. The Stern-Volmer quenching constants, K_{sv}, obtained from the slopes of the linear segments of these plots were in the range of $1.1-3.3 \times 10^4$ M⁻¹, that is, 2–3 orders of magnitude higher than that expected for bimolecular quenching processes involving zinc porphyrin as a fluorophore.^{8g} These results indicate the occurrence of intramolecular quenching processes in the investigated self-assembled supramolecular triads. To further understand the quenching mechanism in the zinc porphyrinferrocene(s) dyads and triads and follow the kinetics of photoinduced processes occurring in these triads, picosecond time-resolved emission as well as nanosecond transient absorption studies was performed.

Time-Resolved Fluorescence Studies. The time-resolved fluorescence spectral features of the zinc porphyrin-ferrocene-(s) dyads tracked that of the steady-state measurements. Figure 8 shows the fluorescence decay time profiles of the investigated dyads along with the reference compound, 1, in o-dichlorobenzene. All of the investigated compounds revealed a monoexponential decay. For compounds 2 and 4, rapid decay was observed and the calculated quantum yield of fluorescence quenching was found to be ~ 0.98 , a result consistent with the steady-state emission results. For compound 3, in which the zinc porphyrin and ferrocene entities were separated by a phenyl amide bond, the quenching was moderate, $\Phi = 0.54$ (Figure 8). These results suggest the occurrence of an excited-state quenching process in the zinc porphyrin-ferrocene(s) dyads. The quenching of zinc porphyrin emission could occur either from energy transfer or an electron-transfer process. In the absence of any appreciable ferrocene absorption in the emission wavelength region of zinc porphyrin, one could eliminate energy transfer as a quenching via the Förster mechanism. The calculated free-energy change, ΔG_{cs}° for electron transfer from the ferrocene entity to the excited zinc porphyrin is found to be weakly exergonic ($\Delta G_{cs}^{\circ} < 0.1 \text{ eV}$). These results suggest the occurrence of excited-state electron transfer in the covalently linked zinc porphyrin-ferrocene(s) dyads.

Additional quenching of the zinc porphyrin-ferrocene dyad, 3, was observed upon axial coordination of fullerene bearing axial ligands, 5 or 6 (Figure 8). By assumption that the quenching is due to electron transfer from the singlet excited porphyrin to the coordinated fullerene, the rates of charge separation ($k_{cs}^{singlet}$) and quantum yields ($\Phi_{cs}^{singlet}$) were evaluated in the usual manner employed for the intramolecular electron-transfer process and the data are given in Table 4. The data in Table 4 suggest the occurrence of efficient electron transfer from the excited zinc porphyrin to the fullerene entity with $\Phi_{cs}^{singlet} = 0.96$. Because of the higher binding constants of 5 and 6 to 3, there was no specific trend in the electrontransfer rates. Further studies involving the nanosecond transient absorption technique were performed to identify the electrontransfer products and monitor the kinetics of charge recombination in the dyads and the self-assembled triads.

Nanosecond Transient Absorption Spectra. The nanosecond transient absorption spectrum of **1** exhibited absorption peaks at 630 and 840 nm corresponding to the triplet state.^{28,29} The transient absorption spectrum of compounds 2-4 revealed a strong band around 500 nm and a weak band at 840 nm corresponding to its triplet state²⁸ (Figure 9). The absorption band of the zinc porphyrin anion radical formed after electron transfer from the ferrocene to the singlet excited zinc porphyrin



Figure 7. Fluorescence spectra of 3 (3.70 μ M) in the presence of various amounts of 6 (3.30 μ M each addition) in *o*-dichlorobenzene ($\lambda_{ex} = 551$ nm). The inset plot shows the Stern–Volmer plots for the fluorescence quenching of 3 by (a) 5 and (b) 6 in *o*-dichlorobenzene.

TABLE 4: Fluorescence Lifetimes (τ_f), Charge-Separation Rate Constants (k_{CS})^{*a*}, and Charge-Separation Quantum Yields (Φ_{CS}) for Zinc Porphyrin–Ferrocene(s) Dyads and Triads Formed by Axial Coordination of Fulleropyrrolidines in *o*-Dichlorobenzene

			ZnP*-Fc		$ZnP*-C_{60}$			
$compound^b$	$\tau_{\rm F}/{\rm ps}~({\rm fra}~\%)$		$k_{\rm CS}, {\rm s}^{-1}$	$\Phi_{\rm CS}$	$k_{\rm CS}, {\rm s}^{-1}$	$\Phi_{\mathrm{CS}^{t}}$	$k_{\rm CR}, {\rm s}^{-1}$	
1	1920 (100%)							
2	40 (100%)		2.5×10^{10}	0.98				
3	890 (100%)		6.0×10^{8}	0.54				
4	35 (100%)		$2.8 imes 10^{10}$	0.98				
2:5 ^c	40 (100%)		2.5×10^{10}	0.98			2.6×10^{8}	
2:6 ^c	40 (100%)		2.5×10^{10}	0.98			1.7×10^{8}	
3:5 ^c	80 (31%)	890 (69%)	6.0×10^{8}	0.54	1.2×10^{10}	0.96	1.3×10^{8}	
3:6 ^c	80 (68%)	890 (32%)	6.0×10^{8}	0.54	1.2×10^{10}	0.96	1.2×10^{8}	
4:5 ^c	35 (100%)		$2.8 imes 10^{10}$	0.98				
4:5 ^c	35 (100%)		$2.8 imes 10^{10}$	0.98				

 ${}^{a}k_{\text{CS}}^{\text{singlet}} = (1/\tau_{\text{f}})_{\text{sample}} - (1/\tau_{\text{f}})_{\text{ref}}, \Phi_{\text{cs}}^{\text{singlet}} = [(1/\tau_{\text{f}})_{\text{sample}} - (1/\tau_{\text{f}})_{\text{ref}}]/(1/\tau_{\text{f}})_{\text{sample}}.$ For biexponential fitting, τ_{f} from the initial decay component was employed. b For abbreviations, see Figure 1. c [porphyrin] = 0.05 mM; [fullerene] = 0.50 mM.



Figure 8. Fluorescence decay profiles of **1** (0.05 mM), **3** (0.05 mM), and **3** (0.05 mM) + **6** (0.50 mM) in argon-saturated *o*-dichlorobenzene. Absorbances were matched at the excitation wavelength of 532 nm.

is expected to occur at 600 nm but was apparently masked by the strong absorption bands of the triplet state of the zinc porphyrin. In addition, we could not observe a new band corresponding to the formation of ferrocenium cation because of its low molar absorptivity ($\epsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}$ at 800 nm).^{16e}

Upon formation of the supramolecular triads by the axial



Figure 9. Transient absorption spectra of **2** (0.1 mM) in *o*-dichlorobenzene at $2 \ \mu s$ (\bullet), and $20 \ \mu s$ (\odot) after the 532-nm laser irradiation. The inset is the time profile for the peak at 880 nm.

coordination of **3** with either **5** or **6**, the transient absorption spectra clearly showed the formation of radical ion pairs. A strong absorption peak at 1010 nm characteristic of the anion radical of fulleropyrrolidine was observed for both of the studied triads (Figure 10). In addition, the zinc porphyrin cation radical was also observed at 460 nm. No new peak corresponding to



Figure 10. (a) Nanosecond transient absorption spectra of 3:6 (0.1:0.5 mM) in *o*-dichlorobenzene at 8 ns (\bullet) and 220 ns (\bigcirc) after the 565-nm laser irradiation. Parts b and c, respectively, show the absorption time profiles monitored at 1010 and 460 nm.

the formation of ferrocenium cation, as a result of charge migration from the ferrocene entity to the zinc porphyrin cation radical, was observed for reasons discussed earlier.

The rate of charge recombination, k_{CR} , monitored at 1010 nm was found to be $1.2 \times 10^8 \text{ s}^{-1}$ for the triad **3:5** (: represents an axial coordinate bond) and $1.3 \times 10^8 \text{ s}^{-1}$ for the triad **3:6**. Similar values for k_{CR} were obtained when the decay was monitored at 460 nm corresponding to the zinc porphyrin cation radical. By use of k_{CS} and k_{CR} thus calculated, the ratio k_{CS}/k_{CR} was evaluated as a measure of the extent of charge stabilization in the photoinduced electron-transfer process and was found to be ~100. This k_{CS}/k_{CR} ratio, reported earlier for a self-assembled zinc porphyrin–C₆₀ dyad without ferrocene, **1:6**, was ~2.³⁰ These results clearly demonstrate charge stabilization in the studied supramolecular triads as a result of sequential electron transfer from the ferrocene entity to the zinc porphyrin cation radical.

Energy Level Diagram and Charge Stabilization. The energy levels in *o*-dichlorobenzene, which are expected to be of significance for photoinduced electron transfer in the studied supramolecular triads, are taken from the data in Tables 3 and 4 and are illustrated in Figure 11.

The steady-state and the time-resolved emission and transient absorption studies have revealed the occurrence of electron transfer from the singlet excited zinc porphyrin of 3 to the coordinated C_{60} of 5 or 6 resulting in the formation of Fc- $\text{ZnP}^{\bullet+}:C_{60}^{\bullet-}$. The measured rate constant ($k_{\text{ET}} = 1.2 \times 10^{10} \text{ s}^{-1}$) and the quantum yield ($\Phi_{CS} = 0.96$) indicate efficient formation of Fc–ZnP^{•+}: $C_{60}^{\bullet-}$ upon excitation of the zinc porphyrin entity in the self-assembled triads. The fluorescence results also indicate that the photoinduced electron transfer occurs from the ferrocene to the singlet excited zinc porphyrin in 3 to produce Fc⁺-ZnP^{•-}. However, the electron transfer from the ferrocene to the zinc porphyrin is relatively slower ($k_{\rm ET} = 6.0 \times 10^8 \, {\rm s}^{-1}$) than electron transfer from singlet-excited zinc porphyrin to C_{60} . Thus, the deactivation pathway to generate Fc⁺-ZnP^{•-}:C₆₀ in the triad is negligible. Moreover, formation of Fc⁺-ZnP-C₆₀• from Fc⁺–ZnP^{•–}:C₆₀ is energetically highly favorable ($-\Delta G^{\circ}$ = 0.76 eV), that is, any Fc^+ -ZnP^{•-}:C₆₀ formed will undergo a rapid charge migration to yield Fc⁺–ZnP:C₆₀^{•–}, although it was not possible to obtain the rate of this reaction from the time resolution of the utilized nanosecond transient spectroscopic technique.



Figure 11. Energy-level diagram showing the different photochemical events of the supramolecular triad composed of ferrocene, zinc porphyrin, and fullerene entities.

Nanosecond transient absorption spectra of either of the triads **3:5** or **3:6** exhibited the characteristic peak of $C_{60}^{\bullet-}$ at 1010 nm, although the transient spectral signature of $ZnP^{\bullet+}$ was relatively difficult to observe because of the triplet absorption peaks buildup of ZnP and C_{60} at longer time scales and the expected rapid disappearance of $ZnP^{\bullet+}$ as a result of sequential electron transfer. Considering a low ϵ for Fc⁺, one would expect the transient absorption spectrum of Fc⁺–ZnP:C₆₀^{\bullet-} to look more like that of Fc–ZnP^{\bullet+}:C₆₀^{\bullet-}. In this regard, the transient spectrum recorded at 8 ns in Figure 8 is not very different from that reported earlier for covalently linked Fc⁺–ZnP:C₆₀^{\bullet-} species of the triad.^{16e}

Another intriguing question we would like to address in the present study is the formation of the energetically favorable $Fc^+-ZnP:C_{60}$ ^{•-} from $Fc^+-ZnP^{\bullet-}:C_{60}$ in the case of triads formed by nonfluorescent 2 coordinated to either 5 or 6. As pointed out earlier, photoexcitation of either 2 or 4 generates $Fc^{\bullet+}-ZnP^{\bullet-}$ exclusively with almost unit quantum efficiency of charge separation because of the short spacer between the



Figure 12. (a) Nanosecond transient absorption spectra of 2:6 (0.1:0.4 mM) in *o*-dichlorobenzene at 8 ns (\bullet) and 220 ns (\bigcirc) after the 565-nm laser irradiation. Parts b and c, respectively, show the absorption time profiles at 460 and 1010 nm.

two entities. Optical absorption studies have shown that both 2 and 4 bind 5 and 6 to form stable supramolecular triads. Steadystate fluorescence studies showed additional quenching of the already quenched (~98%) ZnP fluorescence in 2 or 4 upon coordination of 5 or 6 (data not shown). Figure 12 shows the transient absorption spectrum of the triad 2:6 under solution conditions similar to those used in Figure 10 for the supramolecular triad 3:6. Similar spectral features were observed for 2:5. The transient absorption spectral features of 2:5 and 2:6 are very similar to those seen in Figure 10 for 3:6, especially the strong absorption at 1010 nm corresponding to the formation of $C_{60}^{\bullet-}$. The k_{CR} values calculated from the decay of this band were found to be very similar to those obtained for 3:5 or 3:6 (Table 4). These results clearly suggest formation of Fc⁺–ZnP– C_{60} • as the ultimate product before the occurrence of charge recombination, irrespective of the initial path of photoinduced electron transfer, that is, via $Fc^+-ZnP^{\bullet-}:C_{60}$ (in case of 2:5, **2:6**, **4:5**, and **4:6** triads) or $Fc-ZnP^{\bullet+}:C_{60}^{\bullet-}$ (in the case of the 3:5 and 3:6 triads).

The calculated ratio of k_{CS}/k_{CR} from the kinetic data was found to be ~ 100 for the supramolecular triads composed of ferrocene, zinc porphyrin, and fullerene, indicating a moderate amount of charge stabilization, although the low-lying charge-separated states for all of the triads were generated with the highest quantum yields (close to unity). The calculated lifetime for the charge-separated state of Fc^+ –ZnP– $C_{60}^{\bullet-}$ was around 10 ns, which is 100 times smaller than that reported earlier for covalently linked ferrocene-zinc porphyrin-C₆₀ triads.^{16e} One reason for this observation could be the overall geometry of the supramolecular triads as shown in Figure 3 for the supramolecular triad 2:6 and from Table 2 where presence of the intermolecular type interactions between the ferrocene and C_{60} entities was visualized. Because of the spatially close disposition of the terminal charge bearers in the present type of triads, relatively rapid charge recombination occurs. Importantly, the present study demonstrates utilization of the selfassembled supramolecular approach to build triads bearing donor and acceptor entities with a redox gradient and demonstrates the occurrence of sequential electron transfer ultimately resulting in the formation of long-lived charge-separated states.

Experimental Section

Chemicals. Buckminsterfullerene, C_{60} (+99.95%) was from SES Research (Houston, TX). *o*-Dichlorobenzene in a sure-seal bottle, sarcosine, pyrrole, and benzaldehydes were from Aldrich Chemicals (Milwaukee, WI). Tetra-*n*-butylammonium perchlorate, (TBA)ClO₄, was from Fluka Chemicals. All chemicals were used as received. Syntheses and purification of **1**, **5**, and **6** were carried out according to the literature procedure.^{21d,e}

4-Ferrocenylbenzonitrile. Ferrocene (3.80 g, 20.4 mmol) was dissolved in concentrated sulfuric acid (25 mL) and stirred for 2 h. The solution was then poured into ice cold water (100 mL). A solution of sodium nitrite (0.91 g, 13.2 mmol) in 5 mL of ice cold water was added dropwise to a stirred solution of 4-aminobenzonitrile (1.42 g, 12.0 mmol) in 1:1 water/ concentrated HCl (25 mL) and stirred for 30 min at 0 °C. Copper powder (1.0 g) was added to the ferrocenium solution, and the diazonium salt solution was added dropwise. The reaction mixture was then stirred overnight. Ascorbic acid (5.0 g) was added, and the organic layer was extracted with methylene chloride and dried over sodium sulfate. The compound was purified over silica gel column using CH₂Cl₂/hexanes (60:40 v/v) as the eluent. Yield 1.36 g; ¹H NMR (CDCl₃), δ ppm, 7.53 (m, 4H), 4.69 (t, 2H), 4.42 (t, 2H), 4.04 (s, 5H); ¹³C NMR $(CDCl_3), \delta$ 145.8, 132.3, 126.4, 119.5, 109.0, 82.6, 70.4, 70.1, 67.1; ESI mass in CH₂Cl₂ calcd., 287.1; found, 287.3.

4-Ferrocenylnitrobenzene. To the 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 with further CH₂Cl₂. The crude compound purified on silica gel by using CH₂Cl₂/ hexanes (40:60). Yield (25%); ESI mass in CH₂Cl₂ calcd., 307.58; found, 307.12; ¹H NMR in CDCl₃, δ ppm, 8.14 and 7.56 (d,d, 4H, C₆H₄), 4.74 and 4.48 (d, d, 4H, C₅H₄), 4.05 (s, 5H, C₅H₅).

4-Ferrocenylaniline.^{31a} A mixture of granulated tin (1.0 g) and 4-ferrocenylnitrobenzene (0.7 g, 2.28 mmol) in 1:1 HCl and ethanol was stirred and refluxed for 2 h. The resulting solution was then cooled to room temperature and neutralized with 40% aqueous NaOH. The solution was extracted with dichloromethane and purified on silica gel. Yield (80%); ESI mass in CH₂Cl₂ calcd., 277.84; found, 277.18; ¹H NMR in DMSO, δ ppm, 7.25 and 6.67 (d,d, 4H, C₆H₄), 4.61 and 4.22 (d,d, 4H, C₅H₄), 3.99 (s, 5H, C₅ H₅), 3.35 (s, 2H, NH₂).

4-Ferrocenylbenzaldehyde. To a solution of 4-ferrocenylbenzonitrile (1.31 g, 4.77 mmol) dissolved in dry toluene (50 mL) and purged with argon for 15 min, DIBAL (4.6 mL, 1.0 M in CH₂Cl₂) was added dropwise. The solution was then stirred for 2 h. Then methanol (8 mL) was added, and the mixture was stirred further for another 10 min. A solution of concentrated sulfuric acid/water (1:3; 40 mL) was added, and the organic layer was extracted with methylene chloride and dried over sodium sulfate. The product was purified over a silica gel column using CH₂Cl₂/hexanes (80:20 v/v) as eluent. Yield 0.80 g; ¹H NMR (CDCl₃), δ ppm, 9.97 (s, 1H), 7.79 (d, 2H), 7.59 (d, 2H), 4.74 (t, 2H), 4.43 (t, 2H), 4.05 (s, 5H); ¹³C NMR (CDCl₃), δ 191.8, 147.5, 134.2, 130.1, 126.3, 83.0, 70.1, 67.3; ESI mass in CH₂Cl₂ calcd., 289.8; found, 290.5.

4-Ferrocenyl-5-phenyldipyrromethane.^{31b} To pyrrole (3.88 mL, 56.0 mmol), ferrocenylbenzaldehyde was added (400 mg, 1.4 mmol) and purged with argon for 15 min. Then TFA (10 μ L) was added and stirred for 15 min. The reaction was quenched with NaOH (50 mL, 0.1 M), 100 mL of CH₂Cl₂ was added, and the organic layer was extracted over sodium sulfate. Excess pyrrole was distilled off by vacuum distillation at room temperature, and the compound was purified over silica gel flash column using CH₂Cl₂/cyclohexane (80:20 v/v) as eluent. Yield 0.35 g; ¹H NMR (CDCl₃), δ ppm, 7.85 (br s, 2H), 7.40 (d, 2H), 7.10 (d, 2H), 6.66 (m, 2H), 6.15 (m, 2H), 5.92 (m, 2H), 5.40 (s, 1H), 4.59 (t, 2H), 4.28 (t, 2H), 4.02 (s, 5H); ¹³C NMR (CDCl₃), δ 139.9, 138.2, 132.8, 128.6, 126.6, 117.4, 108.7, 107.5, 85.4, 69.8, 69.1, 66.8, 43.9; ESI mass in CH₂Cl₂ calcd., 405.8; found, 406.3.

5,15-Diphenyl-10,20-bis(4-ferrocenylphenyl)porphyrin. A solution of 4-ferrocenyl-5-phenyldipyrromethane (100 mg, 0.25 mmol) dissolved in 200 mL of dry methylene chloride was purged with argon for 15 min. Then benzaldehyde (25 μ L, 0.25 mmol) and BF₃O(Et)₂ (31 μ L, 0.25 mmol) were added, and the mixture was stirred for 2 h. *p*-Chloranil (90 mg, 0.37 mmol) was then added, and the reaction mixture was stirred overnight. The solvent was evaporated under vacuum and the compound was purified over silica gel column using CHCl₃/hexanes (30:70 v/v) as eluent. Yield 55 mg; ¹H NMR (CDCl₃), δ ppm, 8.88 (m, 8H), 8.16 (m, 8H), 7.78 (m, 10H), 4.89 (s, 4H), 4.45 (s, 4H), 4.21 (s, 10H), -2.73 (br s, 2H); UV-vis in CHCl₃, λ_{max} nm, 420, 451, 518, 557, 650, 592; ESI mass in CH₂Cl₂ calcd., 982.0; found, 982.8.

5,10,15-Triphenyl-20-(4-ferrocenylphenyl)porphyrin. To a solution of 4-ferrocenyl-benzaldehyde (2.0 g, 6.9 mmol) and benzaldehyde (2.1 mL, 20.7 mmol) dissolved in 300 mL of propionic acid, pyrrole (1.9 mL, 27.6 mmol) was added, and the resulting mixture was refluxed for 5 h. The propionic acid was then distilled off, and the compound was purified over basic alumina using CHCl₃/hexanes (30:70 v/v) as eluent. Yield 0.35 g; ¹H NMR (CDCl₃), δ ppm, 8.91 (m, 8H), 8.18 (m, 8H), 7.81

(m, 11H), 4.91 (s, 2H), 4.47 (s, 2H), 4.23 (s, 5H), -2.72 (br s, 2H); UV–vis in CHCl₃, λ_{max} nm, 419, 449, 517, 554, 592, 650; ESI mass in CH₂Cl₂ calcd., 798.0; found, 798.6.

5,10,15-Triphenyl-20-(4-ferrocenylphenyl)porphyrinatozinc(II) (2). To a solution of 5,10,15-triphenyl-20-(4-ferrocenylphenyl)porphyrin (60 mg, 0.08 mmol) dissolved in CHCl₃ (100 mL) was added a solution of zinc acetate (82 mg, 0.38 mmol) dissolved in MeOH (30 mL), and the solution was stirred for 1 h. The solution was then washed with water and dried over sodium sulfate. The product was purified over a silica gel column using CHCl₃/hexanes (30:70 v/v) as eluent. Yield 65 mg; ¹H NMR (CDCl₃), δ ppm, 9.01 (m, 8H), 8.19 (m, 8H), 7.81 (m, 11H), 4.93 (s, 2H), 4.48 (s, 2H), 4.25 (s, 5H); UV– vis in CHCl₃, λ_{max} nm, 425, 551, 591; ESI mass in CH₂Cl₂ calcd., 859.7; found, 860.3.

5,15-Diphenyl-10,20-bis(4-ferrocenylphenyl)porphyrinatozinc(II) (4). To a solution of 5,15-diphenyl-10,20-bis(4ferrocenylphenyl)porphyrin (55 mg, 0.06 mmol) dissolved in CHCl₃ was added a solution of zinc acetate (61 mg, 0.30 mmol) dissolved in MeOH (30 mL), and the solution was stirred for 1 h. The solution was then washed with water and dried over sodium sulfate. The compound was purified over a silica gel column using CHCl₃/hexanes (30:70 v/v) as eluent. Yield 58 mg; ¹H NMR (CDCl₃), δ ppm, 9.01 (m, 8H), 8.20 (m, 8H), 7.81 (m, 10H), 4.93 (s, 4H), 4.48 (s, 4H), 4.25 (s, 10H); UV– vis in CHCl₃, λ_{max} nm, 425, 552, 591; ESI mass in CH₂Cl₂ calcd., 1045.0; found, 1044.2.

5,10,15-Triphenyl-20-[4-(methoxycarbonyl)phenyl]porphyrin. To a solution of propionic acid (350 mL) containing methyl-4-formyl benzoate (2.96 g, 18.0 mmol) was added benzaldehyde (5.5 mL, 54.1 mmol) and pyrrole (5.0 mL, 72.2 mmol), and the mixture was refluxed for 3 h. The solvent was distilled off, and the product was purified over basic alumina column using CHCl₃/hexanes (30:70 v/v) as eluent. Yield 600 mg; ¹H NMR (CDCl₃), δ ppm, 8.83 (m, 8H), 8.45 (d, 2H), 8.31 (d, 2H), 8.22 (m, 6H), 7.76 (m, 9H), 4.12 (s, 3H), -2.78 (s br, 2H); UV-vis in CHCl₃, λ_{max} nm, 418, 515, 549, 590, 648; ESI mass in CH₂Cl₂ calcd., 672.2; found, 672.9.

5,10,15-Triphenyl-20-[4-(carboxy)phenyl]porphyrin. To a solution of 5,10,15-triphenyl-20-[4-(methoxycarbonyl)phenyl]-porphyrin (100 mg, 0.1 mmol) dissolved in 2-propanol (50 mL) was added a solution of KOH (560 mg) dissolved in water (10 mL), and the mixture was refluxed for 6 h. The solution was acidified with concentrated HCl and extracted with chloroform. The organic layer was washed with saturated aqueous sodium bicarbonate solution and dried over sodium sulfate. The product was purified over silica gel column using CHCl₃/MeOH (90:10 v/v) as eluent. Yield 40 mg; ¹H NMR (CDCl₃), δ ppm, 8.84 (m, 8H), 8.51 (d, 2H), 8.35 (d, 2H), 8.23 (m, 6H), 7.77 (m, 9H), -2.78 (s br, 2H); UV-vis in CHCl₃, λ_{max} nm, 418, 514, 551, 592, 650; ESI mass in CH₂Cl₂ calcd., 658.3; found, 659.1.

5,10,15-Triphenyl-20-[4'-(amidophenylferrocene)phenyl]porphyrin. To a solution of 5,10,15-triphenyl-20-[4-(carboxy)phenyl]porphyrin (40 mg, 0.06 mmol) dissolved in dry toluene (10 mL) after purging with argon for 15 min was added pyridine (750 μ L) and thionyl chloride (89 μ L, 1.2 mmol), and the mixture was refluxed under argon for 3 h. The solution was then evaporated, and the residue was redissolved in toluene (10 mL) and pyridine (250 μ L). Then 4-ferrocenylaniline (17 mg, 0.06 mmol) was added, and the solution was stirred overnight under argon. The compound was purified over silica gel column using CHCl₃/hexanes (40:60 v/v) as eluent. Yield 25 mg; ¹H NMR (CDCl₃), δ ppm, 8.85 (m, 8H), 8.37 (d, 2H), 8.28 (d, 2H), 8.22 (m, 6H), 7.76 (m, 9H), 4.69 (t, 2H), 4.34 (t, 2H), 4.09 (s, 5H), -2.77 (br s, 2H); UV–vis in CHCl₃, λ_{max} nm, 422, 516, 551, 592, 648; ESI mass in CH₂Cl₂ calcd., 917.8; found, 918.3.

5,10,15-Triphenyl-20-[4'-(amidophenylferrocene)phenyl]porphyrinatozinc (3).^{16e} To a solution of 5,10,15-triphenyl-20-[4'-(amidophenylferrocene)phenyl]porphyrin (25 mg, 0.03 mmol) dissolved in CHCl₃ (50 mL) was added zinc acetate (30 mg, 0.14 mmol) dissolved in MeOH (20 mL), and the solution was stirred for 1 h. The solution was then washed with water and dried over anhydrous sodium sulfate. The compound was purified over silica gel column using CHCl₃/hexanes (40:60 v/v) as eluent. Yield 95%; ¹H NMR (CDCl₃), δ ppm, 8.96 (m, 8H), 8.24 (m, 8H), 7.76 (m, 11H), 4.70 (s, 2H), 4.36 (s, 2H), 4.10 (s, 5H); UV-vis in CHCl₃, λ_{max} nm, 423, 551, 594; ESI mass in CH₂Cl₂ calcd., 978.8; found, 979.3.

Instrumentation. The UV-vis spectral measurements were carried out with a Shimadzu Model 1600 UV-vis spectrophotometer. The fluorescence emission was monitored by using a Spex Fluorolog- τ spectrometer. A right-angle detection method was used. The ¹H NMR studies were carried out on a Varian 300 or 400 MHz spectrometers. Tetramethylsilane (TMS) was used as an internal standard. Cyclic voltammograms were recorded on a EG&G Model 263A potentiostat using a threeelectrode system. A platinum button or glassy carbon electrode was used as the working electrode. A platinum wire served as the counter electrode, and a Ag wire (Ag/Ag^+) was used as the reference electrode. A ferrocene/ferrocenium redox couple was used as an internal standard. All the solutions were purged prior to electrochemical and spectral measurements using argon gas. The computational calculations were performed by ab initio B3LYP/3-21G(*) methods with the Gaussian 98²⁴ software package on high-speed computers. The ESI-mass spectral analyses of the newly synthesized compounds were performed by using a Fennigan LCQ-Deca mass spectrometer. For this, the compounds (about 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) and a streak scope (Hamamatsu Photonics). The details of the experimental setup are described elsewhere.³² Nanosecond transient absorption spectra in the NIR region were measured by means of laser-flash photolysis; 532-nm light from a Nd:YAG laser was used as the exciting source, and a Geavalanche-photodiode module was used for detecting the monitoring light from a pulsed Xe lamp as described in our previous report.²⁰

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