Self-Assembled Porphyrin−C_{60} and Porphycene−C_{60} Complexes via Metal Axial Coordination

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Noncovalently linked electron donor−acceptor complexes consisting of either zinc tetraphenylporphyrin, (TPP)Zn, or zinc octaethylporphycene, (OEPc)Zn, as donor and pyridine appended C_{60}, py∼C_{60}, as acceptor, via axial coordination of zinc, are reported. The UV−visible and ^{1}H NMR spectral studies reveal 1:1 complex formation between the donor and acceptor entities. The determined K values follow the oxidation potential of the employed zinc tetrapyrroles, and the calculated thermodynamic parameters reveal stable complexation. The singlet emission studies show efficient quenching of the investigated zinc tetrapyrrole emission upon axial coordination of pyridine appended C_{60}. Free-energy calculations indicate that the photoinduced electron transfer from the singlet excited zinc tetrapyrrole to C_{60} is exergonic, and the estimated rates of electron transfer are found to be $(2.4 \pm 0.3) \times 10^8$ s^{-1} for the (TPP)Zn−py∼C_{60} complex and $(2.2 \pm 0.3) \times 10^8$ s^{-1} for the (OEPc)Zn−py∼C_{60} complex, respectively.

Introduction

Fullerenes[1] are excellent electron acceptors and potential electron accumulators.[2] The electron accepting properties of fullerenes, in combination with their electronic absorption characteristics extending over most of the visible region,[3] make them attractive candidates as building blocks in artificial light harvesting systems. Accordingly, a number of covalently linked photosensitizer fluorophore and fullerene complexes have been investigated.[4a−j] Such donor−acceptor complexes undergo photoinduced electron transfer (PET) from the excited fluorophore to the fullerene, C_{60}, generating a charge-separated state and/or singlet energy transfer to the fullerene.[4]

During the past few years several noncovalently associated donor−acceptor systems have been studied, both as models for the naturally occurring photosynthetic reaction center and to explore new abiotic systems for light-harvesting.[5] Among the several methods developed to pair the donor−acceptor entities, axial ligation through the central metal ion of the metalloporphyrin by using functionalized acceptor molecules is a commonly used one.[5] Using this approach, recently, electron-transfer reactions between ruthenium tetraphenylporphyrin and C_{60} have been reported.[4k] As part of our continued effort to develop noncovalently bound porphyrinic systems for various photochemical and electrochemical applications, in the present study, we have formed stable self-assembled complexes of zinc tetrapyrrole and C_{60} via the axial ligation method[6] (Figure 1) and report their spectral, electrochemical, and singlet emission behavior.

Toward achieving this, two zinc tetrapyrroles, namely, (*meso*-tetraphenylporphyrinato)zinc, (TPP)Zn, and (octaethylporphycenato)zinc, (OEPc)Zn, have been employed as donors. The latter donor molecule is a structural isomer of zinc porphyrin and is known for its ease of oxidation[8a] and near-IR emission

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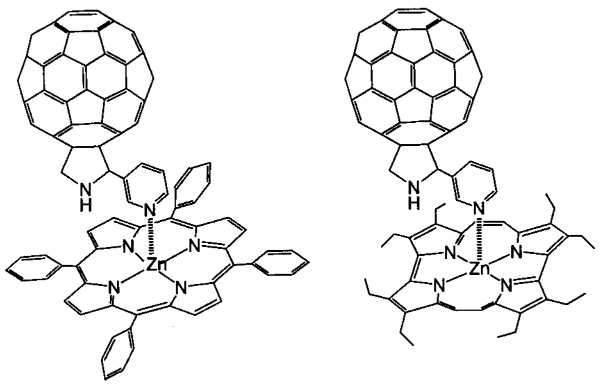

(TPP)Zn-py~C_{60} (OEPc)Zn-py~C_{60}

Figure 1. Structural formulas of the investigated noncovalently linked (TPP)Zn−py∼C_{60} and (OEPc)Zn−py∼C_{60} complexes.

compared to the corresponding porphyrin derivative.[8b] Like zinc porphyrins, zinc porphycene is also known to form pentacoordinated complexes with pyridine ligand.[8c] In the present study, the acceptor C_{60} molecule, abbreviated as py∼C_{60}, is functionalized to bear a pyridine ligand. In this molecule, a *m*-pyridinium bearing pyrrolidine ring is fused to a 6,6 ring junction of C_{60} (Figure 1).

Experimental Section

Chemicals. Buckminsterfullerene, C_{60} (+99.95%), was from Bucky-USA (Bellaire, TX). 1,2-Dichlorobenzene in a sure seal bottle, glycine, 3-pyridinecarboxaldehyde, benzaldehyde, and tetrabutylammonium perchlorate, (TBA)ClO_4, were from Aldrich Chemicals (Milwaukee, WI). All chemicals were used as received. Syntheses of (TPP)Zn and (OEPc)Zn were performed according to the literature procedure.[7,8a]

Synthesis of 2-(*m*-Pyridyl)-3,4-fulleropyrrolidine, py∼C_{60}. The title compound was synthesized according to the general procedure of fulleropyrrolidine synthesis developed by Prato and co-workers.[9] For this, a mixture of C_{60} (100 mg), glycine (31 mg), and 3-pyridinecarboxaldehyde (68 μL) in toluene (60 mL) was refluxed for 12 h. At the end, the solvent was removed under reduced pressure. The crude product was dissolved in toluene and purified over a silica gel column using 1:1 ethyl acetate and toluene as eluent (yield = 22%). The compound was recrystallized in CS_2 and methanol (1:1 v/v) solvent mixture. FAB mass (*m/e*): calcd, 840.8; found, 841.1. ^{1}H NMR in $CS_2/CDCl_3$ (1:1 v/v) (δ, ppm): 5.80, 5.13, 4.88 (s, d, d, 3H, pyrrolidine-H), 8.59, 7.38, 8.19, 9.05 (d, q, d, s, 4H, pyridine-H). λ_{max} in 1,2-dichlorobenzene: 310.0 and 430.2 nm.

Synthesis of 2-Phenylfulleropyrrolidine, ph∼C_{60}. This was synthesized by using a procedure similar to that adopted for py∼C_{60}. To a solution of C_{60} (100 mg) in toluene (60 mL) were added glycine (31 mg) and benzaldehyde (75 μL). The combined solution was refluxed for 12 h. At the end, the solvent was evaporated under reduced pressure. The solid was adsorbed on silica gel and purified over a silica gel column by using ethyl acetate and toluene (1:1 v/v) as eluent (yield = 25%). The compound was recrystallized in CS_2 and methanol (1:1 v/v) solvent mixture. FAB mass (*m/e*): calcd, 839.7; found, 840.0. ^{1}H NMR in $CS_2/CDCl_3$ (1:1 v/v) (δ, ppm): 7.88, 7.80 (d, 2H, phenyl-H), 7.51, 7.35 (m, 3H, phenyl-H), 5.83 (s, 1H, pyrrolidine-H), 5.18 (d, 1H, pyrrolidine-H), 4.82 (d, 1H, pyrrolidine-H). λ_{max} in 1,2-dichlorobenzene: 327.5 and 432 nm. The synthesized py∼C_{60} and ph∼C_{60} derivatives were found soluble in most of the nonpolar organic solvents.

Instrumentation. The UV−visible spectral measurements were carried out with a Shimadzu model 1600 UV−visible spectrophotometer. The fluorescence was monitored by using a Spex Fluorolog spectrometer. A right angle detection method was used. The ^{1}H NMR studies were carried out on a Varian 400 MHz spectrometer. Tetramethylsilane (TMS) was used as an internal standard. Cyclic voltammograms were obtained by using a conventional three-electrode system on an EG&G model 263A potentiostat. A platinum or a glassy carbon disk electrode was used as the working electrode. A platinum wire served as the counter electrode. An Ag/AgCl electrode, separated from the test solution by a fritted supporting electrolyte/solvent bridge, was used as the reference electrode. The potentials were referenced to an internal ferrocene/ferrocenium redox couple. All the solutions were purged prior to spectral and electrochemical measurements using argon gas.

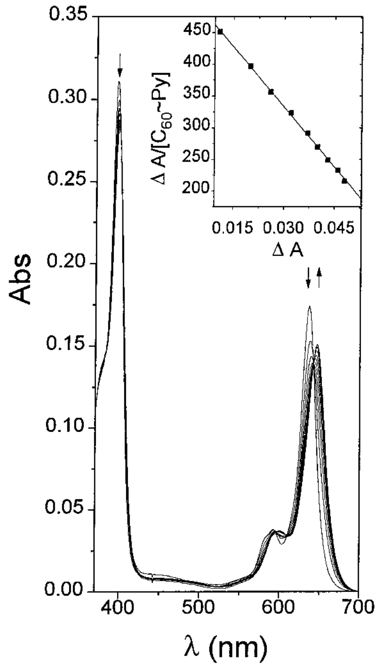

Figure 2. UV−visible spectral changes observed during the complexation of (OEPc)Zn by py∼C_{60} in 1,2-dichlorobenzene. The inset figure shows the Scatchard plot of the change of absorbance at 636 nm.

Results and Discussion

Addition of py∼C_{60} to a solution of (TPP)Zn in 1,2-dichlorobenzene revealed spectral changes characteristic of pentacoordinated zinc porphyrin; i.e., it exhibited red-shifted Soret and visible absorption bands with the appearance of isosbestic points.[6] The formation of pentacoordinated (OEPc)-Zn−py∼C_{60} was characterized by diminished Soret band intensity, red-shifted visible bands, and appearance of isosbestic points (Figure 2). Control experiments performed by using pyridine as axial ligand to (OEPc)Zn also revealed similar spectral changes. A Job's plot for the method of continuous variation confirmed 1:1 complex formation between (OEPc)-Zn and py∼C_{60}. To confirm that the pyridine unit of py∼C_{60} is involved in coordination and not the pyrrolidine nitrogen, a control experiment involving 2-phenylfulleropyrrolidine, i.e., the compound bearing a phenyl ring instead of pyridine, was performed. No spectral changes were observed during the titration of 2-phenylfulleropyrrolidine with either (TPP)Zn or (OEPc)Zn indicating the absence of coordination through the pyrrolidine nitrogen. ^{1}H NMR studies performed in CS_2/DMSO-d_6 (80:20 v/v) also revealed zinc tetrapyrrole−py∼C_{60} formation. That is, in the limit of complete complexation, the pyridine protons experienced a shielding of 1 to 4 ppm, in agreement with the axial coordination of the pyridine unit.[6c] The pyrrolidine ring protons also experienced a shielding effect but to a lesser extent (<1 ppm).

The formation constant, *K*, for zinc tetrapyrrole−C_{60} conjugates was obtained from the absorption spectral data by using

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Table 1. Formation Constant, *K*, and the Thermodynamic Parameters for Zinc Tetrapyrrole−C_{60} Complexes in 1,2-Dichlorobenzene

	$E_{1/2}$, V vs Fc/Fc$^+$ [a]						
donor	first oxdn	second oxdn	axial ligand	K,[b] M^{-1}	ΔG,[b] kJ/mol	ΔH, kJ/mol	ΔS, kJ/mol
(TPP)Zn	0.28	0.62	py∼C_{60}	7337	−22.06	−26.08	−12.31
			py	7749	−22.12	−27.31	−17.14
(OEPc)Zn	0.16	0.33	py∼C_{60}	9412	−22.68	−35.68	−43.60
			py	10323	−22.91	−38.11	−50.97

[a] In 0.1 M (TBA)ClO_4 1,2-dichlorobenzene. [b] At 298.15 K.

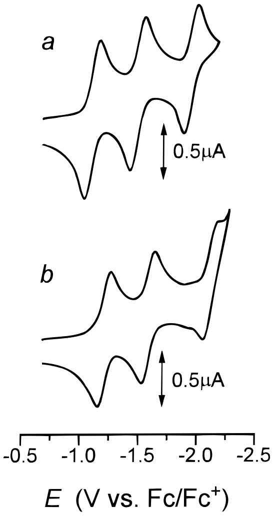

Figure 3. Cyclic voltammogram of (a) C_{60} and (b) py∼C_{60} in 0.1 M (TBA)ClO_4 1,2-dichlorobenzene. Scan rate = 100 mV/s.

Scatchard method.[10] Table 1 lists the *K* values along with the thermodynamic parameters evaluated from van't Hoff plots of ln *K* vs T^{-1}. The thermodynamic parameters for pyridine binding and the oxidation potentials of the donor zinc tetrapyrroles (vide infra) are also listed in Table 1 for comparison purposes. In agreement with the formal oxidation potential of the donor, the *K* value for (OEPc)Zn−py∼C_{60} formation is found to be slightly higher than that for (TPP)Zn−py∼C_{60} formation. The calculated thermodynamic parameters also follow a similar trend (Table 1).

Cyclic voltammetric studies have been performed in order to obtain the redox potentials of the donor and acceptor entities and also to visualize the existence of any electronic interactions between the donor, zinc tetrapyrrole, and acceptor, C_{60}, within the donor−acceptor self-assembled complex. In 0.1 M (TBA)ClO_4 1,2-dichlorobenzene, both (TPP)Zn and (OEPc)Zn exhibit two one-electron oxidations corresponding to the formation of π-cation radical and dication species respectively (Table 1). The first oxidation process of (OEPc)Zn is easier by 120 mV than the first oxidation of (TPP)Zn.

Figure 3 shows the cyclic voltammograms of C_{60} and py∼C_{60}. C_{60} was studied under similar solution conditions for comparison purposes. The first three reversible reductions of py∼C_{60} in 0.1 M (TBA)ClO_4 1,2-dichlorobenzene are located at $E_{1/2} = -1.22$, -1.59, and -2.12 V vs Fc/Fc$^+$, respectively. These values compare with the $E_{1/2} = -1.10$, -1.49, and -1.95 V vs Fc/Fc$^+$, respectively, for C_{60}. Depending upon the redox state, a negative shift of 100 to 170 mV is observed for py∼C_{60} redox couple as compared to the respective C_{60} redox couple. These observations are in agreement with the earlier reported for the other C_{60} pyrrolidine derivatives[9b] and also for the bisalkylated C_{60} derivatives.[11] It is observed that addition of either (TPP)Zn or (OEPc)Zn (up to 10 mM) to a solution of py∼C_{60} (0.5 mM) does not change appreciably the redox potentials of the voltammograms corresponding to C_{60} reduction. This indicates the absence of interactions between the porphyrin π-system and the C_{60} macrocycle within the complex. A CPK model revealed a 4−5 Å separation between the zinc tetrapyrrole and the C_{60} unit in the coordinated complex.

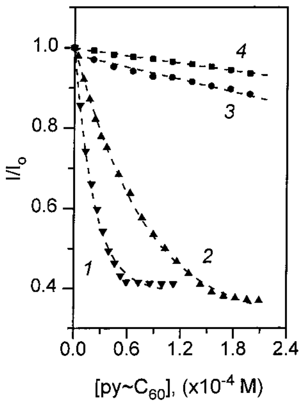

Figure 4. Steady-state fluorescence titrations of (OEPc)Zn (20 μM), $\lambda_{ex} = 600$ nm and $\lambda_{em} = 646$ nm (curve 1), and (TPP)Zn (20 μM), $\lambda_{ex} = 554$ nm and $\lambda_{em} = 646$ nm (curve 2), in deareated 1,2-dichlorobenzene. Curves 3 and 4 show the changes in the fluorescence intensity of (TPP)Zn during the titration of 2-phenylfulleropyrrolidine and pyridine.

The photochemical behavior of the zinc tetrapyrrole−C_{60} conjugates has been investigated by using steady-state singlet emission measurements. The results are shown in Figure 4. It is observed that the addition of either phenyl-appended C_{60}, ph∼C_{60}, or pyridine to a deareated 1,2-dichlorobenzene solution of either (TPP)Zn or (OEPc)Zn does not change appreciably the emission intensity (curves 3 and 4). In contrast, the fluorescence emission of both (TPP)Zn and (OEPc)Zn decreased drastically on increased addition of py∼C_{60}. At the limit of complete complexation, the fluorescence quantum yields were nearly 60% smaller than that of the uncoordinated zinc tetrapyrroles or the pyridine-coordinated zinc tetrapyrrole complexes (curves 1 and 2).

The above results demonstrate excited-state quenching of zinc tetrapyrroles upon complexation of py∼C_{60}. The free-energy calculations[12] performed for the electron transfer (ΔG_{ET}) from the donor, singlet excited zinc tetrapyrrole, to the acceptor, py∼C_{60}, according to eq 1 is found to be exergonic for both

$$\Delta G_{ET} = E_{1/2}(\mathrm{ox}) - E_{1/2}(\mathrm{red}) - E_{0-0} \qquad (1)$$

(TPP)Zn−py∼C_{60} (∼−0.48 eV) and (OEPc)Zn−py∼C_{60} (∼−0.60 eV) complexes, where $E_{1/2}$(ox) and $E_{1/2}$(red) are the potentials for one-electron oxidation of the donor and acceptor, respectively, and E_{0-0} is the singlet state energy of the donor molecule. These results suggests that the observed singlet quenching is a consequence of electron transfer, similar to that

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reported for several covalently linked porphyrin−C_{60} molecules.[4] Additionally, energy transfer could also contribute to the deactivation of the excited zinc tetrapyrrole.[4f] In the present study, we have neglected the contributions from energy transfer since the absorption of fullerenes in the emission wavelength region of the employed zinc tetrapyrroles is found to be almost zero. In addition, the excitation spectra recorded by fixing the wavelength of the emission monochromator to λ_{em} of the zinc tetrapyrrole revealed no traces of C_{60} absorption, indicating absence of energy transfer from the C_{60} moiety to the excited zinc tetrapyrrole or such processes are less efficient.

An estimate of the rates of electron transfer has been performed on the basis of the fluorescence lifetime and quantum yields using the expression[13]

$$k_{ET} = k_P\phi_{ET}/(1 - \phi_{ET}) \qquad (2)$$

where k_P is the decay rate constant of the donor zinc tetrapyrrole in the absence of quenching ligand and ϕ_{ET} is the fluorescence quantum yield of the electron donor in the presence of the acceptor. Monoexponential decay rates, k_P, of 4.16×10^8 s^{-1} for (TPP)Zn[14] and 3.13×10^8 s^{-1} for (OEPc)Zn[8c] were utilized. The estimated rates of electron transfer from the singlet excited zinc tetrapyrrole to the complexed C_{60} are found to be $(2.4 \pm 0.3) \times 10^8$ s^{-1} for the (TPP)Zn−py∼C_{60} complex and $(2.2 \pm 0.3) \times 10^8$ s^{-1} for the (OEPc)Zn−py∼C_{60} complex, respectively. These rates indicate the occurrence of efficient electron transfer from the singlet excited zinc tetrapyrroles to the axially ligated C_{60} molecule.

In summary, the present investigation demonstrates formation of self-assembled porphyrin−C_{60} and porphycene−C_{60} complexes via the axial ligation method. The UV−visible and ^{1}H NMR studies reveal 1:1 stoichiometric ratio between the donor−acceptor pair. The determined *K* values follow the oxidation potential of the zinc tetrapyrrole, and the calculated thermodynamic parameters reveal stable complexation. The singlet emission studies show efficient quenching of the excited zinc tetrapyrrole upon axial ligation of C_{60} bearing pyridine. On the basis of the free-energy calculations, the fluorescence quenching has been assigned to the occurrence of PET from the excited donor, zinc tetrapyrrole, to the axially positioned C_{60}. The estimated rates of electron transfer indicate efficient electron transfer from the donor, singlet excited zinc tetrapyrrole, to the C_{60} acceptor molecule.

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