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Intense Photoluminescence from Mixed Solutions of C_{70} and Palladium Octaethylporphyrin: A Supramolecular Heavy Atom Effect

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Unusually intense near-infrared (near-IR) photoluminescence has been observed from mixed solutions of C_{70} and palladium octaethylporphyrin (PdOEP). The novel emission has a spectrum similar to C_{70} phosphorescence and an intensity that is ∼20 times greather than that of C_{70} fluorescence. The emitting species is identified as a noncovalently bound, short-lived triplet exciplex of C_{70} with PdOEP. The emission is essentially C_{70} phosphorescence intensified by spin−orbit coupling from the Pd atom in the nearby metalloporphyrin. This supramolecular heavy atom effect increases the C_{70} emissive quantum yield to $\sim 1 \times 10^{-2}$ in degassed hexane solution at room temperature. The radiative rate constant is enhanced by a factor of 10^5, to $\sim 7 \times 10^4$ s^{-1}, which is a value that exceeds the phosphorescence rate constant of PdOEP. Comparative studies in a rigid poly(methyl methacrylate) (PMMA) matrix show that the excited state of the static C_{70}−PdOEP complex decays in ∼150 ns. A Job's plot analysis shows that the complex has a 1:1 stoichiometry. It forms dynamically in solution and is relatively weakly bound, with an estimated equilibrium constant near 100 M^{-1}. Qualitatively similar supramolecular heavy atom effects were also observed for complexes of PdOEP with C_{60} and fullerene derivatives.

Introduction

Covalently linked porphyrin−fullerene molecular complexes have been widely used in studies of photoinduced electron transfer, because of the ability of porphyrins to donate electrons and the ability of fullerenes to accept electrons.[1,2] Weak exciplex emissions were recently reported for several covalently linked porphyrin−fullerene dyads, which displayed weak, red-shifted, and solvent-sensitive emissions that were assigned to a singlet intermediate charge-transfer state.[3−9] Another interesting aspect of porphyrin−fullerene interactions involves the formation of supramolecular complexes. It has been shown that fullerenes and porphyrins are able to form solid- and liquid-phase supramolecular structures stabilized by van der Waals and possibly charge-transfer interactions.[10−13] Recent reports demonstrate that the binding constants of specially designed porphyrin derivatives with fullerenes in solution can range from 10^2 M^{-1} to 10^5 M^{-1};[10,14] significantly higher binding constants (∼10^8 M^{-1}) are evident for porphyrin-based hosts with fullerene guests.[15] Variable-temperature nuclear magnetic resonance (NMR) spectroscopy was previously used to characterize porphyrin−fullerene interactions quantitatively. Complexation is also qualitatively evident from the appearance of red-shifted bands in the ultraviolet−visible (UV−vis) absorption spectra of porphyrin−fullerene mixtures.[10,14−16] However, only a few prior studies have included detailed photophysical studies of noncovalently linked supramolecular porphyrin−fullerene systems.[11,17,18]

Here, we report the discovery of unusual and intense light emission from mixed solutions of C_{70} and palladium octaethylporphyrin (PdOEP). This novel luminescence, which is observed in degassed nonpolar solvents, is spectrally red-shifted and is approximately an order of magnitude more intense than fluorescence from C_{70}. It is also efficiently quenched by dissolved oxygen. Through static and time-resolved studies in different solvents and rigid media, we have assigned the emission to fullerene phosphorescence that has been intensified by the heavy atom effect from the nearby Pd atom in dynamically formed exciplexes. The complex formation process seems well-described by a standard diffusion-limited model. Similar triplet exciplex emission in samples of PdOEP with C_{60} suggests that this photophysical behavior may exist in a range of porphyrin−fullerene mixtures. We note that the photophysical behavior reported here differs substantially from that of the weakly emitting exciplexes formed from a singlet excited state of porphyrin−fullerene dyads.[3−9]

Materials and Methods

1. Materials. Zinc octaethylporphyrin (ZnOEP, 98%) and zinc tetraphenylporphyrin (ZnTPP, 98%), from Aldrich Chemical Co., and C_{70} (99%), from SES Research, were purchased and used without further purification. PdOEP (labeled "∼90% dye content") was obtained from Aldrich Chemical Co. We analyzed this PdOEP for the presence of impurities using high-performance liquid chromatogrpahy (HPLC). This analysis showed that the PdOEP contained only a small amount of low-molecular-weight organic impurities, possibly residual solvents, with optical absorptions of <300 nm. Therefore, the major impurities in the PdOEP stock were spectroscopically inactive and judged unlikely to interfere with photophysical measurements. Optical experiments also revealed traces of free-base octaethylporphyrin at a concentration of <1%. HPLC-grade (Optima) hexane and toluene solvents were obtained from Fisher Scientific.

2. Experimental Methods. Experimental setups and instruments that have been described in an earlier report[19] were used

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to measure UV−vis absorption, fluorescence, triplet−triplet absorption kinetics, and transient absorption spectra. A Spex model Fluorolog 3-211 spectrofluorometer that was equipped with a liquid-nitrogen-cooled InGaAs detector was used to measure near-infrared (near-IR) emission spectra.

We used an Oxford Instruments model Optistat-DN cryostat to control the sample temperatures during low-temperature transient absorption measurements. Sample excitation was provided by nanosecond-scale light pulses from a Q-switched Nd:YAG laser (at 532 nm) or from a tunable dye laser. Amplified silicon photodiodes with time constants of 0.70 and 0.12 μs served as the probe detectors.

Results and Discussion

1. Photophysical Properties of C_{70} and PdOEP. It is worthwhile to summarize known photophysical properties and parameters of C_{70} and PdOEP that are relevant to this study. C_{70} is a weak fluorophore: its fluorescence lifetime and quantum yield in toluene are 0.66 ns and 5.7×10^{-4}, respectively.[20,21] The S_1 excited state of C_{70} undergoes quick and efficient intersystem crossing to the T_1 state, with a quantum yield for triplet formation very close to 1.[20,22] The C_{70} triplet state has a long intrinsic lifetime of 24.5 ms at room temperature in a poly(methyl methacrylate) (PMMA) film.[22] However, in a fluid solution, the effective triplet lifetime is greatly shortened by competing decay processes, which include triplet−triplet annihilation, impurity quenching, and self-quenching by ground-state C_{70}. As a result, we observe a C_{70} triplet lifetime in room temperature solution of ∼2 ms, in agreement with a previous report.[23]

Although PdOEP is a well-studied molecule, its photophysical properties have not yet been thoroughly documented. The reported molar absorptivities of PdOEP in benzene at the maxima of its Soret and α-bands are $\epsilon_{395}^{\mathrm{PdOEP}} = 191\,000$ M^{-1} cm^{-1} and $\epsilon_{548}^{\mathrm{PdOEP}} = 58\,900$ M^{-1} cm^{-1}, respectively.[24,25] To determine the absorptivities of PdOEP in toluene and hexane, we began with a reference solution of PdOEP in benzene, then sequentially evaporated, redissolved, and remeasured using toluene, hexane, and then benzene again. In toluene, the extinction spectrum was determined to be essentially the same as that in benzene, whereas in hexane, we found $\epsilon_{392}^{\mathrm{PdOEP}} = 187\,600$ M^{-1} cm^{-1} (Soret band) and $\epsilon_{546}^{\mathrm{PdOEP}} = 75\,500$ M^{-1} cm^{-1} (α-band). In degassed solutions, PdOEP exhibits strong phosphorescence emission and comparatively weak fluorescence. A previous report gives the PdOEP triplet-state lifetime as 0.99 ms and its phosphorescence quantum yield as $\Phi_{\mathrm{Ph}} = 0.2$ in a polystyrene matrix at room temperature.[26] During the course of this work, we measured the PdOEP triplet-state lifetime (τ_{PdOEP}) as 1.53 ms in a degassed PMMA film at room temperature. This value is not greatly different from the previously measured lifetime of 1.9 ms in an *n*-octane matrix at 77 K.[27] Comparison of the properties of PdOEP and ZnOEP shows that the stronger spin−orbit coupling induced by the heavy Pd atom gives PdOEP a shortened triplet lifetime (1.9 ms vs 57 ms at 77 K) and a higher phosphorescence quantum yield.[28] In ambient solution, we observed ZnOEP phosphorescence to be at least a 1000-fold weaker and undetectable with our instrumentation.

General features of porphyrin−fullerene interactions are well-known.[29−33] A porphyrin−fullerene dyad shows charge transfer (CT) behavior, in which the porphyrin typically serves as an electron donor and the fullerene as an acceptor. In a mixed solution, quenching of fullerene triplet states by porphyrin via an electron transfer mechanism is usually observed. The reported rate constants for such bimolecular quenching approach the theoretical diffusion limit in polar solvents, which suggests a very high probability of quenching.[29,32,33] Another important process is triplet−triplet energy transfer, which commonly occurs between the T_1 states of porphyrin (ca. 15 000 cm^{-1}) and C_{70} (12 600 cm^{-1}).[30,31] ^{3}PdOEP → $^3C_{70}$ energy transfer was clearly evidenced as an increase in the triplet−triplet absorption signal of $^3C_{70}$ after simultaneous excitation of C_{70} and PdOEP at 532 nm. Because of the large absorptivity difference between C_{70} and PdOEP at longer wavelengths, we were able to use 610-nm pulses to selectively excite only the C_{70} component of a binary mixture. In degassed room-temperature solutions, such selective transient absorption measurements revealed no significant energy transfer from $^3C_{70}$ to ^{3}PdOEP.

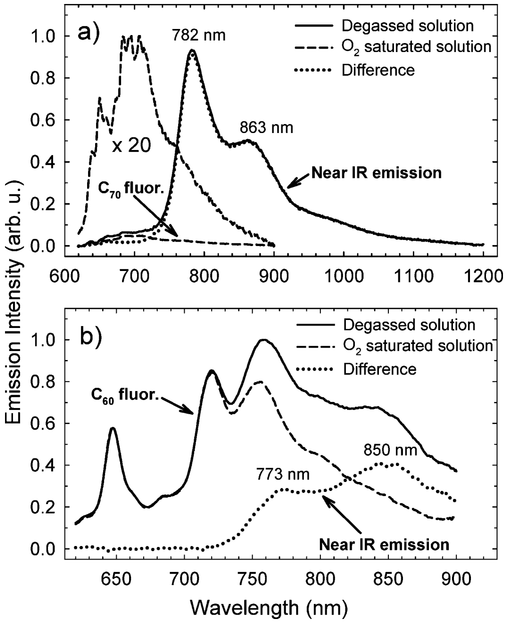

Figure 1. Emission spectra of degassed and air-saturated hexane solutions of (a) 2 μM C_{70} and 8 μM palladium octaethylporphryin (PdOEP) ($\lambda_{\mathrm{exc}} = 600$ nm) and (b) 10 μM C_{60} and 10 μM PdOEP ($\lambda_{\mathrm{exc}} = 595$ nm).

2. Steady-State Absorption and Fluorescence Spectroscopy of Fullerene−PdOEP Solutions. We determined that the new emission was intense only in nonpolar solvents. Figure 1 shows luminescence spectra from binary hexane solutions of PdOEP with C_{60} or C_{70}. In degassed solutions, the spectra contain a superposition of fluorescence plus any new emission. (Phosphorescence from fullerenes is suppressed by the porphyrin.) In oxygenated solutions, by contrast, all emission is quenched, except fluorescence from the short-lived S_1 states. The difference between degassed and oxygen-saturated sample spectra then shows only the new luminescence, which is labeled “Near-IR emission” in the figure. It is remarkable that, in the C_{70}−PdOEP system (Figure 1a), the new emission is ∼20 times as intense as C_{70} fluorescence. This new emission has two distinct maxima, at 782 ± 2 nm and 863 ± 4 nm. For mixtures of C_{60} with PdOEP, the maxima appear at 773 ± 4 nm and 850 ± 6 nm (Figure 1b). Note that the 647-nm peak in Figure 1b is fluorescence from a minor impurity of free-base octaethylporphyrin that is excited by 595-nm radiation. We recorded the excitation spectrum of the new emission from the C_{70}−PdOEP mixture by monitoring intensity at 850 nm while scanning the excitation wavelength between 350 nm and 650 nm. The resulting spectrum reveals superimposed absorption features of C_{70} and PdOEP. This indicates that excited states of both C_{70}

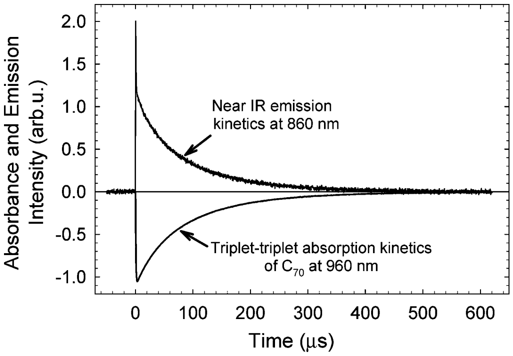

Figure 2. Near-infrared (near-IR) emission at 860 nm and (inverted) induced absorption at 960 nm in a binary mixture of 5 μM C_{70} and 5 μM PdOEP. The sample was dissolved in degassed room-temperature hexane and was excited at 610 nm. The induced absorption signal shows the concentration of T_1 C_{70} in the mixed sample.

and PdOEP lead to formation of the species giving the new near-IR emission.

Because the new emission is present only in binary solutions of C_{70} and PdOEP, it must result from their interactions. The tendency of porphyrins and fullerenes to form supramolecular assemblies suggests a C_{70}−PdOEP complex as a plausible source of the novel emission. While searching for additional evidence of such complex formation, we closely examined absorption spectra of mixed solutions of C_{70} and PdOEP. It is known that the absorption spectra of porphyrins, particularly their Soret bands, are strongly influenced by a nearby electron acceptor.[3] Ground-state interactions within covalent porphyrin−fullerene dyads are usually recognized from the appearance of red-shifted absorption bands.[3−8] However, our measured absorption spectra of C_{70} with PdOEP in hexane or toluene at various concentrations (up to 100 μM) did not show any noticeable deviations from superimposed spectra of the two isolated components. An earlier report also failed to detect ground-state interactions of noncovalently bound porphyrin with fullerene, even in polar solvents.[32]

3. Time-Resolved Spectroscopy of Near-Infrared (near-IR) Emission in Solutions. Transient absorption and emission kinetics were recorded from a degassed 5.0×10^{-6} M solution of C_{70} and PdOEP in hexane. Figure 2 shows both the transient absorption kinetics of C_{70} measured at its $T_n \leftarrow T_1$ maximum near 960 nm and the near-IR emission kinetics were measured at 860 nm. We note that the intensity of C_{70} delayed fluorescence at this wavelength is negligible (see Figure 1a).[22] The two decay traces in Figure 2 match each other almost exactly for excitation either at 532 or at 610 nm.

4. Time-Resolved Spectroscopy of Near-IR Emission in Polymeric Films. The novel near-IR emission was also observed from a mixture of C_{70} and PdOEP dissolved in a rigid polymeric film, in which there is essentially no diffusional motion. Therefore, the results give a “snapshot” of a dynamic process of reversible complex formation, where, at any time, a small number of C_{70} and PdOEP molecules are located near each other. We prepared a PMMA film that contained high concentrations (~0.5 mM) of porphyrin and fullerene. After degassing, the sample film was excited by laser pulses at 532 nm and the time-resolved emission spectra shown in Figure 3a were recorded. (Dye laser excitation at longer wavelengths was not feasible, because of lower pulse energy and smaller C_{70} absorptivity.) We determined that the emission was represented by three overlaid spectral components with different lifetimes. Two long-lived components with lifetimes of >10 μs correspond to the phosphorescence of isolated PdOEP and the delayed fluorescence of C_{70}. The third, fast-decaying component has a spectrum similar to the near-IR emission observed in the C_{70}−PdOEP solution, although red-shifted and broadened from that shown in Figure 1 by solvent effects. Although our detector with a time constant of 0.70 μs failed to resolve the fast emission component, we were able to partially resolve it using a less-sensitive Si photodetector with a response time of ~0.12 μs. The partially resolved emission trace, measured at 980 nm, is shown in Figure 3b, along with a fit computed as the sum of three exponential decays. The shortest (lifetime of <10 ns) and the longest components (lifetime of >10 μs) obviously result from fast luminescence and/or scattered light, and phosphorescence or delayed fluorescence, respectively. Only the intermediate kinetic component corresponds to the emission of interest; its lifetime is estimated as 150 ± 10 ns. It is likely that the porphyrin−fullerene complexes formed either in PMMA films or in solution assume a variety of geometrical conformations and therefore display a range of spectral and kinetic parameters. Our 150 ns decay value can therefore be considered the average excited-state lifetime of the emitting C_{70}−PdOEP complexes.

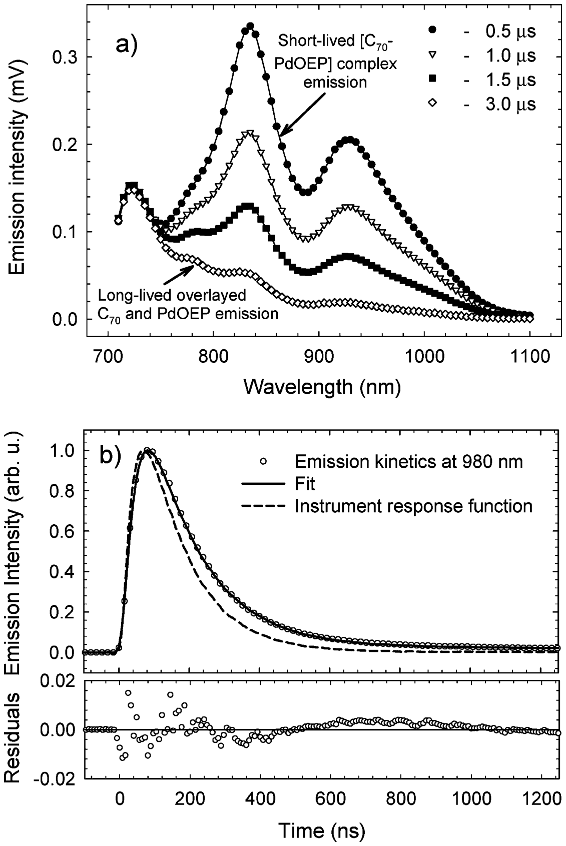

Figure 3. (a) Time-resolved emission spectra of the C_{70}−PdOEP complex in a rigid, degassed poly(methyl methacrylate) (PMMA) matrix (532 nm excitation, 0.70 μs photodetector response); (b) partially resolved 980 nm emission kinetics and kinetic simulation for the C_{70}−PdOEP complex (0.12 μs photodetector response).

We performed cryogenic emission measurements on C_{70} and C_{70}−PdOEP samples in PMMA films to compare the temperature-dependent emission spectra of the complex with C_{70} phosphorescence. We note that low-temperature spectra of C_{70} have been reported earlier.[34,35] Measurement of C_{70} phosphorescence emission at 298 K was hampered by the presence of intense delayed fluorescence (resulting from thermal excitation from T_1 to S_1). Nonetheless, phosphorescence peaks were clearly visible above the long wavelength portion of the fluorescence spectrum, and at 90 K, the thermally induced delayed fluorescence is undetectably weak.[22] As shown in Figure 4a, the C_{70}

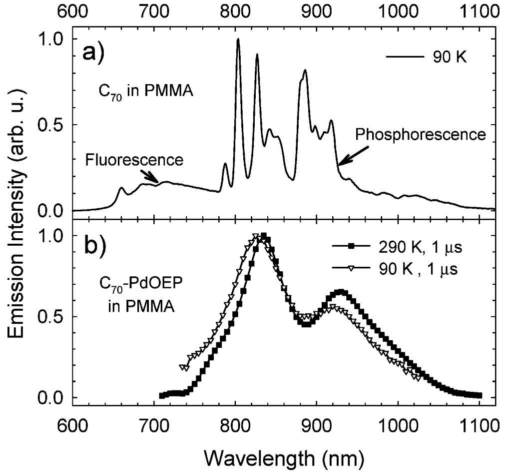

Figure 4. (a) C_{70} fluorescence and phosphorescence spectra in a PMMA film at 90 K; (b) time-resolved emission spectra of the C_{70}–PdOEP complex in a PMMA film at 90 and 290 K (emission intensities have been normalized, and the background component with a decay time of >10 μs has been subtracted).

emission spectrum at 90 K consists of overlaid components from phosphorescence and prompt fluorescence. The C_{70} phosphorescence emission is intensified and sharpened compared to room-temperature phosphorescence. Low-temperature time-resolved near-IR emission spectra of the C_{70}–PdOEP complex in a rigid polymer were recorded in a similar manner, as described previously. Figure 4b shows the short-lived C_{70}–PdOEP complex emission at 290 and 90 K. It is clear that the complex emission appears in the same spectral region as the phosphorescence of pure C_{70}. However, in contrast to C_{70}, emission from the complex does not sharpen or significantly change intensity at low temperatures. This probably reflects inhomogeneous broadening from the diversity of complex conformations. Small spectral shifts to shorter wavelengths at low temperatures were observed for both C_{70} and C_{70}–PdOEP in PMMA; these are likely related to thermally induced changes in the PMMA host.

5. Dynamics of C_{70}–PdOEP Complex Formation. The experiments described previously give important insights into the nature of the complex formation. We have identified ${}^3C_{70}$ as the precursor of the emitting complex, because its characteristic near-IR emission is induced by exciting the C_{70} component in degassed solutions. ${}^3C_{70}$ can be formed directly by C_{70} optical excitation or indirectly and less efficiently by energy transfer from ^{3}PdOEP. This explains the appearance of both C_{70} and PdOEP absorption features in the complex's excitation spectrum. We observed similar emission spectra in solid matrixes and liquid solutions.

The short-lived emission signal in the film and long-emission kinetics in solution, which match the ${}^3C_{70}$ decay, suggest dynamic complex formation in solution from excited C_{70} molecules. Indeed, we know that ${}^3C_{70}$ can be quenched in solution by diffusional encounters with porphyrin molecules. Although some ground-state C_{70}–PdOEP complexes may always be present in mixed solutions, absorption spectroscopy suggests that their concentration must be very low. The near-IR emission trace shown in Figure 2 contains two kinetic components: a short unresolved spike at the time of excitation, followed by a long decay that matches that of ${}^3C_{70}$. We interpret the kinetic match between ${}^3C_{70}$ concentration and complex emission as indicating that the complex decays much more rapidly than it is formed through bimolecular encounters that occur on the time scale of 10^{-5} s, under our experimental conditions. The short decay component, which contains only a small fraction of the total luminescence, may result from the emission of C_{70}–PdOEP complexes that are already present when the sample is excited, as well as from C_{70} fluorescence.

In modeling the photophysics of this system at low excitation intensities and relatively high porphyrin concentrations, one may disregard minor second-order processes such as triplet–triplet annihilation, relative to interactions between C_{70} and PdOEP. The general kinetic scheme when only C_{70} is optically excited can then be written as

$$C_{70} \underset{k_T^{C_{70}}}{\overset{k_{exc}}{\rightleftharpoons}} {}^3C_{70}$$

$${}^3C_{70} + \text{PdOEP} \underset{k_{diss}}{\overset{k_{diff}}{\rightleftharpoons}} X^*$$

$$X^* \xrightarrow{k_r + k_{nr}} C_{70} + \text{PdOEP} \qquad (1)$$

where X* and ${}^3C_{70}$ represent the excited complex and triplet state C_{70}, respectively; $k_T^{C_{70}}$ is the first-order decay constant of ${}^3C_{70}$ in solution; k_{diff} is the bimolecular rate constant for diffusional encounters; k_{diss} is the constant for dissociation of the excited complex into ${}^3C_{70}$ and PdOEP; and $k_r + k_{nr}$ is the sum of the radiative (k_r) and nonradiative (k_{nr}) first-order decay constants of the excited complex. Using the near-IR emission intensity as a measure of the concentration of X*, we can construct a Job's plot to determine the complex's stoichiometry. Although a 1:1 ratio of C_{70} to PdOEP has been anticipated in eq 1, a Job's plot should confirm or refute this assumption. To construct the plot, we measured the near-IR emission intensity for a series of samples with different proportions of the two components but equal total concentrations of 10 μM. Each sample was freeze–pump–thaw-degassed before its steady-state emission spectrum was measured. The dependence of the complex emission intensity on the sample composition is shown in Figure 5a. Using the aforementioned kinetic scheme and the steady-state approximation, one finds that the emitting complex concentration [X*] obeys the following relation:

$$[X^*] \propto \frac{[C_{70}][\text{PdOEP}]}{k_T^{C_{70}} + k_{diff}P[\text{PdOEP}]} \qquad (2)$$

where P is the probability of excited complex deactivation, expressed as

$$P = \frac{k_r + k_{nr}}{k_r + k_{nr} + k_{diss}}$$

and the term $(k_T^{C_{70}} + k_{diff}P[\text{PdOEP}])^{-1}$ is the triplet-state lifetime of C_{70}, as measured independently. Thus, we must normalize the emission intensity signal to the ${}^3C_{70}$ lifetime to construct a corrected Job's plot representation that properly reveals the complex's stoichiometry. Figure 5b is a plot of the measured C_{70} triplet state decay constant versus sample composition, and Figure 5c shows the corrected Job's plot data. The symmetric form of Figure 5c plot, with a maximum at 5 μM, confirms that the excited complex between C_{70} and PdOEP is indeed formed in a 1:1 molecular ratio. The shape of the Job's plot, which is smoothly parabolic rather than triangular, indicates that the equilibrium constant for complex formation falls below ~10^6 M^{-1} but does not provide a precise value.

A better estimate of the formation equilibrium constant can be obtained by measuring the lifetime of the excited complex. Although the dynamic nature of the complex formation prevents

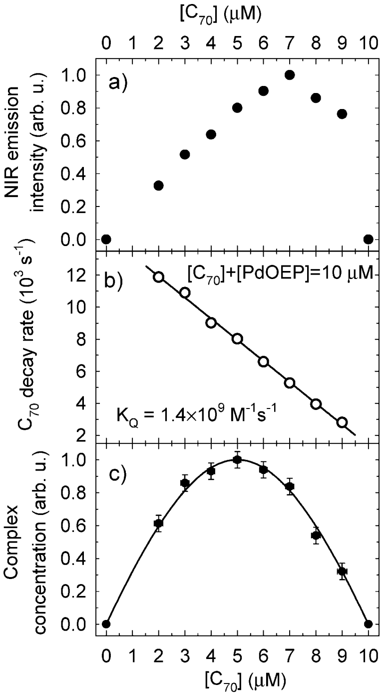

Figure 5. Job's plot analysis for mixed hexane solutions of C_{70} and PdOEP with the sum of concentrations fixed at 10 μM: (a) measured near-IR emission intensity versus concentration of C_{70}, (b) variation of $^3C_{70}$ decay rate versus composition of the mixed solutions, and (c) deduced normalized concentration of C_{70}−PdOEP complex versus C_{70} concentration in the mixed solutions, determined by correcting the data in panel a for the $^3C_{70}$ decay rate variation shown in panel b.

such measurements in solution, we observed a lifetime of ∼150 ns for the complex in a PMMA host. Because the dielectric properties of PMMA (dielectric constant ≈ 3, refractive index = 1.49) are similar to those of our nonpolar solvents (listed below), we will assume that the lifetime value found in PMMA is not very different in our fluid solvents. With this assumption, one can identify the excited complex lifetime as $(k_r + k_{nr})^{-1}$ in our kinetic model. The 150 ns value can then be used with the $^3C_{70}$ quenching probabilities listed in Table 1 to evaluate the following expression:

$$K_{eq} = \frac{k_{diff}}{k_{diss}} = \frac{k_{diff}}{k_r + k_{nr}}\left(\frac{P}{1-P}\right) \qquad (3)$$

In this way, we deduce complex formation constants of $\sim 2 \times 10^2$ M^{-1} in hexane and $\sim 6 \times 10^2$ M^{-1} in toluene. These values seem plausible in comparison with related data from previous reports. In particular, the estimated equilibrium constants are several times smaller than those observed for specifically designed porphyrin conjugates.[10] Note that the deduced equilibrium constants describe complex formation in the electronically excited state. Using eq 2, one can estimate the average dissociation lifetime of C_{70}−PdOEP complexes to be on the order of 10^{-8} s, or substantially longer than the lifetime of an unbound encounter complex.

6. Photophysical Characteristics of the $^3C_{70}$−PdOEP Exciplex. Similarly to previous studies of ZnOEP−fullerene interactions in solution,[32,33] we observed efficient quenching of $^3C_{70}$ by PdOEP. By measuring the $^3C_{70}$ lifetime at different PdOEP concentrations, we determined quenching rate constants of $(1.4 \pm 0.1) \times 10^9$ M^{-1} s^{-1} in hexane and $(2.8 \pm 0.3) \times 10^9$ M^{-1} s^{-1} in toluene (see Figure 5b).

Using previously established values of the C_{70} fluorescence quantum yield as a reference, we can estimate the quantum yield of emission for the complex. Steady-state fluorescence spectra of air-saturated and degassed binary solutions of C_{70} (2 μM) and PdOEP (8 μM) in hexane or toluene were recorded while selectively exciting the C_{70} solute with light near 600 nm (see Figure 1). To minimize experimental errors, background emission from an 8 μM PdOEP air-saturated solution was measured separately and then subtracted. Near-IR emission quantum yields were then computed as $\Phi_{fl} \times (S_{NIR}/S_{fl})$, where S represents the integrated emission signal from the complex or the C_{70} reference sample (with matched absorbances), and Φ_{fl} is the fluorescence quantum yield of C_{70}. As listed in Table 1, along with other photophysical parameters, we determined the complex's emissive quantum yield to be $\sim 9 \times 10^{-4}$ in toluene and $\sim 1 \times 10^{-2}$ in hexane.

7. Origin of Near-IR Emission. The C_{70}−PdOEP exciplex emits in the same spectral region as C_{70} phosphorescence (in hexane and toluene), and its formation occurs from the C_{70} triplet state. We suggest that the complex's near-IR emission is essentially spin-forbidden $T_1 \rightarrow S_0$ phosphorescence of C_{70} that has been intensified and perturbed by the close proximity of a Pd atom in the exciplex. This may be considered to be a form of external heavy atom effect,[35,36] but enhanced by the charge transfer and van der Waals interactions responsible for binding the fullerene and PdOEP.[16]

To verify the role of the heavy Pd atom, we performed a set of similar experiments with the metalloporphyrins ZnOEP and ZnTPP, which have electronic structures similar to PdOEP and show similar interactions with fullerenes,[29,33] but have much weaker spin−orbit coupling, because of the lower atomic number of zinc. We found that these zinc metalloporphyrins did not exhibit any noticeable phosphorescence by themselves and also did not lead to near-IR emission in mixed solutions with C_{70}.

Near-IR emission intensity was determined to be very sensitive to solvent polarity. Charge transfer is the major pathway for deactivation of $^3C_{70}$ by PdOEP and ia strongly dependent on the solvent polarity.[32,33] More-polar or more-polarizable media stabilize the charge-separated state, thus competing kinetically against exciplex emission and decreasing the quantum yield. This trend was clearly observed in our data: the complex emission was strongest in the least-polar solvent, *n*-hexane (dielectric constant = 1.89, refractive index = 1.375),

TABLE 1: Photophysical Parameters of the Emissive C_{70}−PdOEP Complex in Toluene and Hexane

property	Value	
	toluene	hexane
diffusion constant at 25 °C,[28] k_{diff}	1.1×10^{10} M^{-1} s^{-1}	2.1×10^{10} M^{-1} s^{-1}
$^3C_{70}$ quenching rate constant by PdOEP, k_Q	$(2.8 \pm 0.3) \times 10^9$ M^{-1} s^{-1}	$(1.4 \pm 0.1) \times 10^9$ M^{-1} s^{-1}
probability of quenching $^3C_{70}$ per collision, k_Q/k_{diff}	0.26	0.07
near-IR emission quantum yield, Φ_{NIR}	$(9 \pm 3) \times 10^{-4}$	$(1.0 \pm 0.1) \times 10^{-2}$
excited-state lifetime of the complex, τ	∼150 ns[a]	∼150 ns[a]
radiative rate constant of the complex, Φ_{NIR}/τ	$\sim 6 \times 10^3$ s^{-1} [a]	$\sim 7 \times 10^4$ s^{-1} [a]

[a] Assuming that the decay rate of the complex in PMMA is the same as that in solution.

weaker in toluene (dielectric constant = 2.44, refractive index = 1.496), and undetectable in polar solvents in which charge-transfer processes are dominant.

The near-IR emission of C_{70}−PdOEP complex has certain similarities to the previously reported cases of near-IR emission in covalently linked porphyrin−fullerene dyads.[3,5−7] Those emissions were weak and displayed short lifetimes of a few nanoseconds, in sharp contrast with the strong and relatively long-lived C_{70}−PdOEP phosphorescence signal uncovered in the present study.

Conclusions

New and unusually intense near-infrared (near-IR) emission has been discovered from noncovalently bound complexes of palladium octaethylporphyrin (PdOEP) with fullerenes. The effect was clearly observed for the two most abundant fullerenes, C_{60} and C_{70}, in different nonpolar media. Similar but weaker emission was also observed for [5,6]-$C_{60}O$.[37] We suggest that the observed emission is phosphorescence of C_{70} that is intensified and perturbed by proximity to the heavy atom Pd in the complex. As a result of this supramolecular heavy atom effect in hexane, the radiative rate constant of $^3C_{70}$ is increased by a factor of at least 10^5. In polar environments, charge-transfer interactions effectively deactivate the excited state and prevent the strong emission. Because near-IR emission is expected to be dependent on environment and the perturbing heavy atom, it may be useful to study the influence of these parameters, to maximize the emission intensity. The supramolecular heavy atom effect described here reveals short-lived dynamic exciplexes that are otherwise invisible and may serve as an aid to better understanding of the photophysical processes in a variety of porphyrin−fullerene systems.

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