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Exciplex Intermediates in Photoinduced Electron Transfer of Porphyrin−Fullerene Dyads

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Abstract: The photoinduced electron transfer in differently linked zinc porphyrin−fullerene dyads and their free-base porphyrin analogues was studied in polar and nonpolar solvents with femto- to nanosecond absorption and emission spectroscopies. A new intermediate state, different from the locally excited (LE) chromophores and the complete charge-separated (CCS) state, was observed. It was identified as an exciplex. The exciplex preceded the CCS state in polar benzonitrile and the excited singlet state of fullerene in nonpolar toluene. The behavior of the dyads was modeled by using a common kinetic scheme involving equilibria between the exciplex and LE chromophores. The scheme is suitable for all the studied porphyrin−fullerene compounds. The rates of reaction steps depended on the type of linkage between the moieties. The scheme and Marcus theory were applied to calculate electronic couplings for sequential reactions, and consistent results were obtained.

1. Introduction

During the past decade, porphyrin−fullerene donor−acceptor (DA) systems have gained great attention, and a vast variety of porphyrin−fullerene dyads, triads, and more complex systems have been synthesized and studied.[1,2] They have shown promising results, e.g., in molecular device applications for efficient conversion of light to electrostatic energy.[3,4,5] In addition, they are considered to be good modeling systems to mimic natural photosynthesis.[6−8] Similarly to chlorophyll-based natural reaction centers, the electron transfer (ET) reaction of porphyrin−fullerene DA compounds is characterized by a relatively low reorganization energy, which is important for a fast charge separation (CS).[9,10]

However, the results of the studies show that the excitation relaxation is a complex process for these porphyrin−fullerene systems. The desired ET was reported for a series of DA dyads.[6−9,11] This primary charge separation can be extended by construction of triad and more complex systems,[8,9,12,13] thus confirming that complete charge separation (CCS) takes place in the primary DA pair. Typically, the porphyrin chromophores serve as a light antenna of the dyads. However, the fullerene excited singlet state, which may relax to the CS state, was observed under certain conditions.[6,7,13] On the contrary, the final formation of the CS state was not detected for a series of free-base and zinc porphyrin−fullerene dyads in nonpolar solvents.[7,12,13] At the same time, in nonpolar solvents and in solid films, an infrared emission was observed for dyads characterized by a close proximity of the donor and acceptor.[10,14,15] The emission was attributed to an emissive CS state, and was

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(1) Imahori, H.; Sakata, Y. *Adv. Mater.* **1997**, *9*, 537−546.
(2) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445−2457.
(3) Tkachenko, N. T.; Vuorimaa, E.; Kesti, T.; Alekseev, A. S.; Tauber, A. Y.; Hynninen, P. H.; Lemmetyinen, H. *J. Phys. Chem. B* **2000**, *104*, 6371−6379.
(4) Imahori, H.; Ozawa, S.; Ushida, K.; Takahashi, M.; Azuma, T.; Ajavakom, A.; Akiyama, T.; Hasegawa, M.; Taniguchi, S.; Okada, T.; Sakata, Y. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 485−502.
(5) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 100−110.
(6) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771−11782.
(7) Kuciauskas, D.; Lin, S.; Seely, G. R.; Moore, A. L.; Moore, T. A.; Gust, D.; Drovetskaya, T.; Reed, C. A.; Boyd, P. D. W. *J. Phys. Chem.* **1996**, *100*, 15926−15932.
(8) Kuciauskas, D.; Liddell, P. A.; Lin, S.; Johnson, T. E.; Weghorn, S. J.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1999**, *121*, 8604−8614.
(9) Imahori, H.; Tamaki, K.; Guldi, D. M.; Luo, C.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 2607−2617.
(10) Imahori, H.; Tkachenko, N. V.; Vehmanen, V.; Tamaki, K.; Lemmetyinen, H.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 1750−1756.
(11) Schuster, D. I.; Cheng, P.; Wilson, S. R.; Prokhorenko, V.; Katterie, M.; Holzwarth, A. R.; Braslavsky, S. E.; Klihm, G.; Williams, R. M.; Luo, C. *J. Am. Chem. Soc.* **1999**, *121*, 11599−11600.
(12) Luo, C.; Guldi, D. M.; Imahori, H.; Tamaki, K.; Sakata, Y. *J. Am. Chem. Soc.* **2000**, *122*, 6535−6551.
(13) Liddell, P.; Kuciauskas, D.; Sumida, J.; Nash, B.; Nguyen, D.; Moore, A.; Moore, T.; Gust, D. *J. Am. Chem. Soc.* **1997**, *119*, 1400−1405.
(14) Tkachenko, N. V.; Guenther, C.; Imahori, H.; Tamaki, K.; Sakata, Y.; Fukuzumi, S.; Lemmetyinen, H. *Chem. Phys. Lett.* **2000**, *326*, 344−350.
(15) Vehmanen, V.; Tkachenko, N. V.; Imahori, H.; Fukuzumi, S.; Lemmetyinen, H. *Spectrochim. Acta A* **2001**, *57*, 2229−2244.

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observed for both free-base and zinc complexes of porphyrin and fullerene.

Despite these diversities in phenomena, the ET reactions of the porphyrin−fullerene dyads are usually discussed considering three intermediate states, namely, the locally excited (LE) porphyrin and fullerene states, and the CS state. This ignores the tendency of porphyrin and fullerene to interact with each other in the ground and especially in the excited states. The former can be illustrated by an ability to form mixed crystals with sandwich-like structures.[16,17] The latter is confirmed by the CT emission,[10,14,15] which can occur at relatively high electronic couplings only. This kind of phenomenon is usually referred to as an exciplex, meaning that two separate chromophores form in the excited state a common molecular orbital, which exists only as an excited state. The newly formed state may result in an essential electron density redistribution. In such a case, it can be qualified as a CS state. It is also called a "contact ion pair" state to emphasize that the system can proceed to a complete charge-separated state, in which the chromophores are again separated from each other but hold an extra charge, being a cation and anion radical.[18−22] This type of behavior was observed for phytochlorin−fullerene dyads,[23,24] where the exciplex was the key intermediate preceding the CCS state.

An important property that complicates the photochemistry of the porphyrin−fullerene systems is that the excited-state energies of fullerene and porphyrin are close to each other.[2,25,26] An obvious result of this situation is an efficient energy transfer from the excited singlet state of porphyrin to that of fullerene, which can compete with the electron transfer and even be more efficient than the ET in nonpolar solvents.[7,12] A less obvious result is the formation of an exciplex. Both chromophores, porphyrin and fullerene, hold extended conjugated π-electron subsystems, which can interact efficiently with each other. When the distance between the donor and acceptor is short, as in mixed crystals or in some covalently linked dyads,[6] the interaction can already be seen from the ground-state absorption: a new absorption band is formed in the near-infrared region.[10,15] However, the intensity of the band is low, roughly a thousand times lower than that of the Soret band. The ground-state complex can be excited directly to the excited CT state.[27−30] Alternatively, one of the chromophores can be excited selectively, and the resulting LE state is transformed to an exciplex.[31−33] In the latter case, the chromophores may not form a ground-state complex, although they must be close enough to form an exciplex, and the formation of the exciplex cannot be predicted from the absorption spectrum of the dyad. An indication of the exciplex is a new emission band, which, however, may not be detected if the exciplex relaxes quickly to the CCS state. Then, to clarify the mechanism of the photoinduced ET reaction, a detailed analysis of the transient absorption and emission properties of the dyads is required.

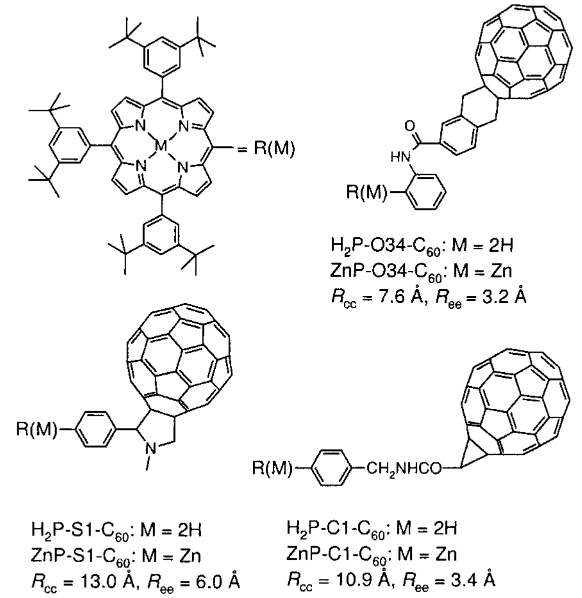

Figure 1. Molecular structures of porphyrin−fullerene donor−acceptor dyads studied. The study of the P−S1−C_{60} and P−C1−C_{60} dyads is reported in this paper. The P−O34−C_{60} dyads were studied earlier[10,15] and are included for comparison. The porphyrin part, denoted by *R*(M), is common for all the dyads. The porphyrin−fullerene center-to-center (R_{cc}) and edge-to-edge (R_{ee}) distances are given for each dyad.

The exciplex has been reported to be a precoursor of the CCS state of covalently linked phytochlorin−fullerene dyads.[23,24] The structural similarities between the phytochlorin−fullerene and porphyrin−fullerene compounds are a good reason to study whether the mechanism could be generalized to include the charge-transfer reactions of the latter compounds as well.

We report herein the study of four porphyrin−fullerene dyads: ZnP−S1−C_{60}, H_2P−S1−C_{60}, ZnP−C1−C_{60},[34] and H_2P−C1−C_{60} (Figure 1). Their properties are compared to those of ZnP−O34−C_{60} and H_2P−O34−C_{60}, for which the charge-transfer emission has been studied earlier.[10,15] These dyads are involved in this study for comparison and elucidation of the role of the exciplex in the ET photodynamics. The P−S1−C_{60} and P−C1−C_{60} dyads have a moderate donor−acceptor center-to-center distance (roughly 1 nm), which is short enough to promote CCS but long enough to make the electronic coupling between the porphyrin and fullerene moieties weak. The exciplex interaction for these dyads was considered to be less probable and the exciplex emission less intense than for the

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(16) Boyd, P. D. W.; Hodgson, M. C.; Richard, C. E. F.; Oliver, A. G.; Chaker, L.; Brothers, P. J.; Bolskar, R. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 10487−10495.

(17) Olmstead, M. M.; Costa, D. A.; Maitra, K.; Noll, B. C.; Phillips, S. L.; Calcar, P. M. V.; Balch, A. L. *J. Am. Chem. Soc.* **1999**, *121*, 7090−7097.

(18) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794−3796.

(19) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068−2080.

(20) Gould, I. R.; Mueller, L. J.; Farid, S. *Z. Phys. Chem.* **1991**, *170*, 143−157.

(21) Gould, I. R.; Farid, S. *J. Phys. Chem.* **1992**, *96*, 7635−7640.

(22) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522−528.

(23) Tkachenko, N. V.; Rantala, L.; Tauber, A. Y.; Helaja, J.; Hynninen, P. H.; Lemmetyinen, H. *J. Am. Chem. Soc.* **1999**, *121*, 9378−9387.

(24) Vehmanen, V.; Tkachenko, N. V.; Tauber, A. Y.; Hynninen, P. H.; Lemmetyinen, H. *Chem. Phys. Lett.* **2001**, *345*, 213-218.

(25) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461.

(26) Tsue, H.; Imahori, H.; Kaneda, T.; Tanaka, Y.; Okada, T.; Tamaki, K.; Sakata, Y. *J. Am. Chem. Soc.* **2000**, *122*, 2279−2288.

(27) Hubig, S. M.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 2926−2935.

(28) Hubig, S. M.; Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 3842−3851.

(29) Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1999**, *121*, 1688−1694.

(30) Rosokha, S. V.; Kochi, J. K. *J. Am. Chem. Soc.* **2001**, *123*, 8985−8999.

(31) Palmans, J. P.; Swinnen, A. M.; Desie, G.; Van der Auweraer, M.; Vandendriessche, J.; De Schryver, F. C.; Mataga, N. *J. Photochem.* **1985**, *28*, 419−431.

(32) Van der Auweraer, M.; Grabowski, Z. R.; Rettig, W. *J. Phys. Chem.* **1991**, *95*, 2083−2092.

(33) Jeoung, S. C.; Eom, H. S.; Kim, D.; Cho, D. W.; Yoon, M. *J. Phys. Chem. A* **1997**, *101*, 5412−5417.

(34) Tamaki, K.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Shimomura, A.; Okada, T.; Sakata, Y. *Chem. Lett.* **1999**, 227−228.

P$-$O34$-$C$_{60}$ dyads, as the emission yield is proportional to the square of the electronic coupling matrix element.[19,35] However, an emission component, which can be attributed to exciplex, was resolved for the P$-$S1$-$C$_{60}$ dyads in toluene with time-resolved emission spectroscopy.

Porphyrin and fullerene have been observed to form exciplexes with many compounds. For example, fullerene forms exciplexes with aromatic amines,[36,37] and porphyrin forms exciplexes with anthraquinone,[38] polynucleotides,[33] and naphthalene.[39] However, this is the first study devoted to detailed investigation of the exciplex photodynamics and its impact on electron-transfer properties of porphyrin$-$fullerene dyads.

2. Results and Discussion

The P$-$S1$-$C$_{60}$ and P$-$C1$-$C$_{60}$ dyads were studied in two solvents: toluene and benzonitrile. In all cases, the absorption spectra of the dyads are well presented as a sum of the spectra of two chromophores, porphyrin and fullerene. This indicates that there are no observable ground-state interactions between the chromophores. In contrast, for ZnP$-$O34$-$C$_{60}$[6,10] and H$_2$P$-$O34$-$C$_{60}$,[15] significant ground-state interactions were previously observed.

For all the dyads, the fluorescence of the porphyrin moiety is strongly quenched. In benzonitrile, the remaining emission spectra of the dyads resemble that of the corresponding reference porphyrin, and contribution from the fullerene emission is weak (Figure S1 in the Supporting Information). In toluene, the fullerene emission is relatively strong, except for that of H$_2$P$-$C1$-$C$_{60}$. This indicates that there is an intramolecular energy transfer from porphyrin to fullerene. The results of the steady-state emission measurements were similar to those of previously studied porphyrin$-$fullerene dyads.[7,12]

The ultimate goal of this study was to investigate the dynamics of the photoinduced ET. This was accomplished by using three methods: femto- to picosecond pump$-$probe transient absorption spectroscopy, femto- to picosecond emission up-conversion, and pico- to nanosecond time-correlated single-photon counting (TCSPC). In the femtosecond experiments, the excitation wavelength was 410$-$420 nm. Therefore, the second excited singlet state of porphyrin, P^{2S}C, was formed right after the excitation pulse (width typically 50 fs). For some zinc porphyrins, the internal conversion of the second excited state to the first can be relatively slow, up to a picosecond.[40] The slow internal conversion was observed for ZnP$-$C1$-$C$_{60}$, as will be noted later, but otherwise the conversion was not resolved in time, and the first observed state was the first excited singlet state of the porphyrin chromophore, P^{1S}C. In TCSPC experiments, the excitation wavelength was adjusted in the range 580$-$605 nm to the nearest absorption band of the porphyrin moiety, thus creating mainly locally excited porphyrin, P^{1S}C.

2.1. P$-$S1$-$C60. 2.1.1. ZnP$-$S1$-$C$_{60}$ in Benzonitrile.

The population of the porphyrin locally excited state, P^{1S}C, can be monitored by measuring the emission decay profile at the wavelength of maximum porphyrin fluorescence, e.g. 605 nm. The emission decay was dominated by a 2 ps component (Figure 2a). For dyads similar to ZnP$-$S1$-$C$_{60}$, the excited singlet state usually undergoes ET. The charge-separated state was also observed in the present case, as can be seen from the spectrum of the longest lived component (130 ps, Figure 2c), which has pronounced bands at 620 and 1020 nm usually attributed to the porphyrin radical cation and the fullerene radical anion, respectively.[7,6,41−47] However, the 12 ps component in Figure

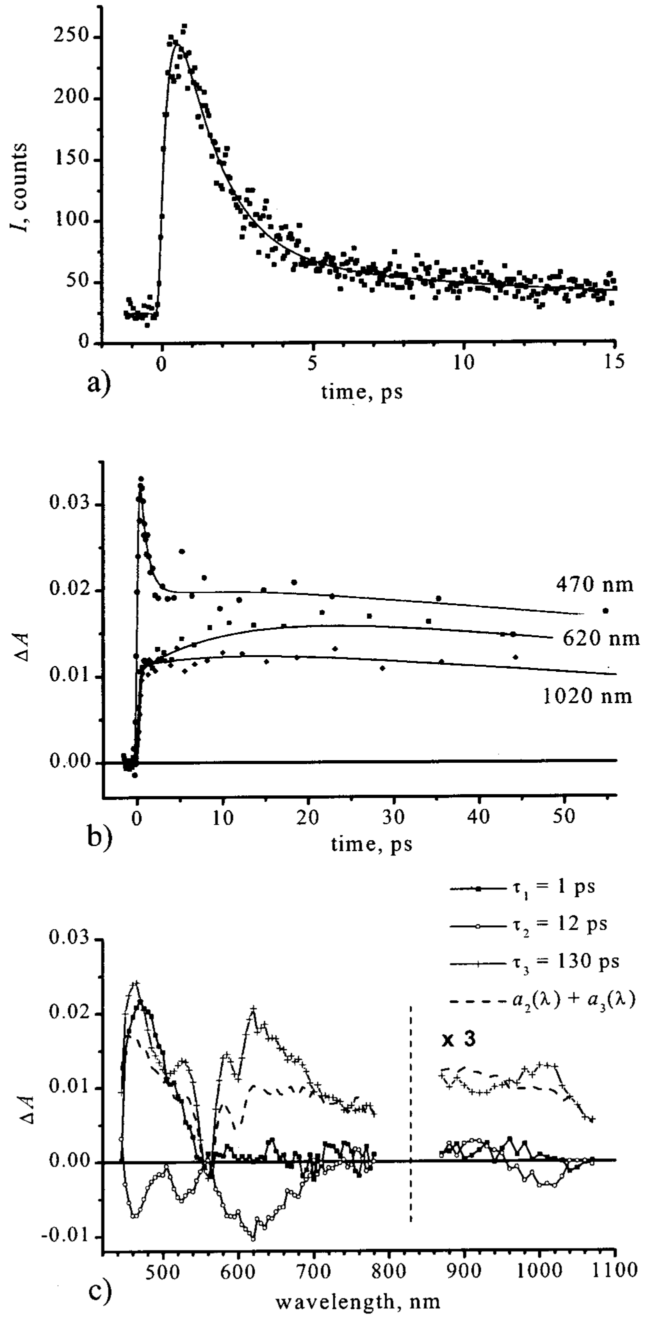

Figure 2. Time-resolved spectroscopy for ZnP$-$S1$-$C$_{60}$ in benzonitrile: (a) fluorescence up-conversion at 605 nm (15 ps time scale), (b) transient absorption decays at 470, 620, and 1020 nm (50 ps), and (c) transient absorption component spectra together with the spectrum of the exciplex (dashed line) obtained by adding the 12 and 130 ps components.

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(35) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078−3086.
(36) Rath, M. C.; Pal, H.; Mukherjee, T. *J. Phys. Chem. A* **1999**, *103*, 4993−5002.
(37) Seshadri, R.; Rao, C. N.; Pal, H.; Mukherjee, T.; Mittal, J. P. *Chem. Phys. Lett.* **1993**, *205*, 395−398.
(38) Kamioka, K.; Cormier, R. A.; Lutton, T. W.; Connolly, J. S. *J. Am. Chem. Soc.* **1992**, *114*, 4414−4415.
(39) Pispisa, B.; Venanzi, M.; Palleshi, A.; Zanotti, G. *J. Photochem. Photobiol. A* **1997**, *105*, 225−233.
(40) Akimoto, S.; Yamazaki, T.; Yamazaki, I.; Osuka, A. *Chem. Phys. Lett.* **1999**, *309*, 177−182.
(41) Greaney, M. A.; Gorum, S. M. *J. Phys. Chem.* **1991**, *95*, 7142−7144.
(42) Sun, Y.; Drovetskaya, T.; Bolskar, R. D.; Bau, R.; Boyd, P. D. W.; Reed, C. A. *J. Org. Chem.* **1997**, *62*, 3642−3649.

2c and the corresponding time profiles at 620 and 1020 nm in Figure 2b show that the formation of the CS state is much slower (12 ps) than the decay of $P^{1S}C$ (2 ps). A fast process (lifetime roughly 1 ps) can also be seen in the transient absorption, but it is not related to the CS state. It only shows some recovery of the absorption band at 480 nm.

The transient absorption spectrum between 2 (relaxation of the $P^{1S}C$ state) and 12 ps (formation of the P^+C^-state) is shown by the dashed line in Figure 2c. The spectrum has characteristic features of the porphyrin excited state, such as a bleached Q-band at 560 nm, and thus cannot be attributed to the fullerene locally excited state, PC^{1S}. In conclusion, there are three intermediate states in the relaxation of the photoexcited dyad. Two of them can be identified as the excited singlet porphyrin, $P^{1S}C$, and the CCS state, P^+C^-. The third one is a new state, which will be denoted as (PC)*. The relaxation chain can be presented schematically as

$$PC \xrightarrow{h\nu} P^{1S}C \xrightarrow{k_{px}} (PC)^* \xrightarrow{k_{xi}} P^+C^- \xrightarrow{k_{ig}} PC \qquad (1)$$

where the rate constants of the reactions are[48] $k_{px} \approx 5 \times 10^{11}$ s^{-1}, $k_{xi} \approx 8 \times 10^{10}$ s^{-1}, and $k_{ig} \approx 7.7 \times 10^9$ s^{-1}.

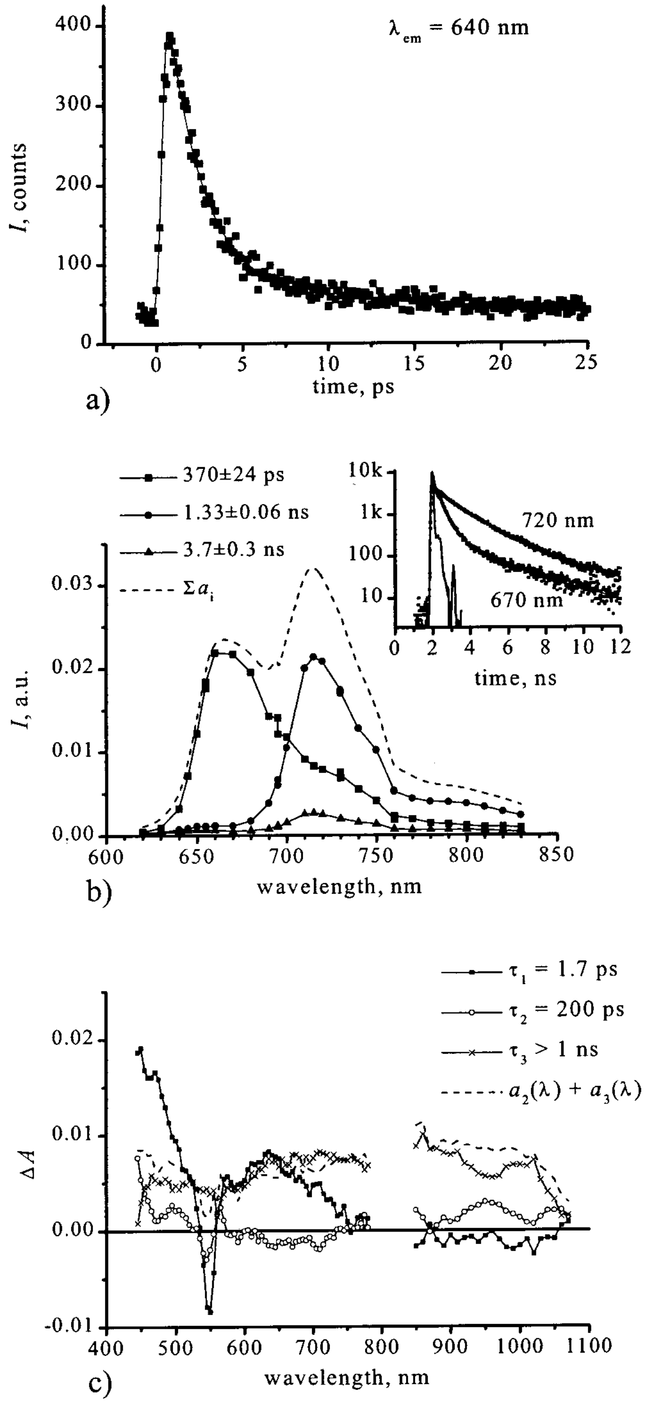

Figure 3. Time-resolved spectroscopy for ZnP−S1−C_{60} in toluene: (a) fluorescence up-conversion at 640 nm (25 ps time scale) and (b) emission decay-associated spectra (DAS) and exciplex spectrum (Σa_i, sum of all shown components, dashed line). An additional component ($\lambda_{max} \approx 650$ nm), whose lifetime was shorter than the time resolution ($\tau < 20$ ps), was omitted from the figure. The inset shows the time profiles of the decays at 670 and 720 nm. (c) Transient absorption component spectra together with the spectrum of the exciplex (dashed line).

2.1.2. ZnP−S1−C_{60} in Toluene. For ZnP−S1−C_{60} in toluene, the pump−probe measurements yielded three transient components with lifetimes of 1.7 ps, 200 ps, and >1 ns (Figure 3c). There was no evidence of the ET in toluene, since no formation of the porphyrin cation band was observed in the 600−700 nm region. The up-conversion emission measurements show that the fluorescence of the porphyrin chromophore has a lifetime close to 2 ps (Figure 3a). Therefore, the first component in transient absorption can be identified as the relaxation of the $P^{1S}C$ state. The longest lived component in transient absorption has a broad nonstructured spectrum typical for the fullerene excited singlet state. The formation of the PC^{1S} state is also well confirmed by the emission spectroscopy studies. The steady-state emission spectrum of the sample correlates with that of the fullerene reference compound. The time-resolved emission spectroscopy (TCSPC method) yields a component with a spectrum similar to that of fullerene (Figure 3b). The lifetime of the component is 1.3 ns, which agrees with the lifetime of the unquenched excited singlet state of the fullerene chromophore.[49−51] However, there is a subnanosecond component in the emission (Figure 3b). The component has a maximum at 655 nm, and its lifetime is 370 ps. Its presence is quite evident from the time-resolved measurements, as illustrated by the decay profiles in the inset of Figure 3b. The component cannot be attributed to the emission of the porphyrin chromophore, which has a double-peaked spectrum with maxima at 605 and 645 nm. Moreover, its emission maximum is blue shifted too much to be attributed to the fullerene chromophore. Evidently, there is an intermediate state between the porphyrin and fullerene excited singlet states.

A charge-transfer emission, or an exciplex, was observed for ZnP−O34−C_{60} in nonpolar solvents, e.g. toluene.[10] The maxi-

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(43) Fukuzumi, S.; Nakanishi, I.; Maruta, J.; Yorisue, T.; Suenobu, T.; Itoh, S.; Arakawa, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 6673−6680.

(44) Nojiri, T.; Watanabe, A.; Ito, O. *J. Phys. Chem. A* **1998**, *102*, 5215−5219.

(45) Kadish, K. M.; Gao, X.; Caemelbecke, E. V.; Hirasaka, T.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem. A* **1998**, *102*, 3898−3906.

(46) Luo, C.; Fujitsuka, M.; Huang, C.-H.; Ito, O. *J. Phys. Chem. A* **1998**, *102*, 8716−8721.

(47) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **1998**, *120*, 8060−8068.

(48) The two letters in the subsripts of the rate constant symbols denote the initial and final states of the transition, respectively. The different states are the ground state (g), the excited singlet states of porphyrin (p) and fullerene (c), exciplex (x), complete charge-separated state (i), and excited triplet state of fullerene (T).

(49) Fujitsuka, M.; Ito, O.; Yamashiro, T.; Aso, Y.; Otsubo, T. *J. Phys. Chem. A* **2000**, *104*, 4876−4881.

(50) Imahori, H.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 325−332.

(51) Palit, D. K.; Sapre, A. V.; Mittal, J. P.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *195*, 1−6.

mum of the emission was at 810 nm, thus the exciplex was much lower in energy than the excited singlet fullerene, PC^{1S} (1.75 eV[50]). In the case of ZnP−S1−C_{60}, the exciplex energy is somewhat higher than that of the PC^{1S}state, since the new emission maximum is at a shorter wavelength than that of the fullerene.

Assuming a linear reaction chain

$$PC \xrightarrow{h\nu} P^{1S}C \xrightarrow{k_{px}} (PC)^* \xrightarrow{k_{xc}} PC^{1S} \xrightarrow{k_{cT}} PC^{1T} \qquad (2)$$

one can obtain the following reaction rate constants:[48] $k_{px} \approx 5 \times 10^{11}\ s^{-1}$, $k_{xc} \approx 2.7 \times 10^{9}\ s^{-1}$, and $k_{cT} \approx 7.5 \times 10^{8}\ s^{-1}$. The emission spectrum of the exciplex, i.e. the emission spectrum after the decay of the $P^{1S}C$ state, 2 ps, and before the formation of the PC^{1S} state, 370 ps, can be obtained as a sum of the decay-associated spectra (DAS),[52] and it is shown by the dashed line in Figure 3b. The calculated spectrum has two maxima and a shoulder in the red region. The spectrum can be used to calculate the principal energetics parameters of the exciplex by using a procedure similar to that described previously,[10,14,15,19] as discussed later.

The intermediate lifetime obtained from the transient absorption measurements was 200 ps (Figure 3c). However, the value is inaccurate, because the contribution of the corresponding component is rather weak over the measured wavelength range (450−1060 nm). This lifetime should correspond to the rather accurate lifetime of 370 ps obtained from TCSPC measurements (Figure 3b). According to Scheme 2, the transient absorption spectrum of the exciplex can be obtained as the sum of the spectra of the two long-lived components.[52] The calculated spectrum is presented by the dashed line in Figure 3c. It can be compared to the spectrum of the new intermediate state observed for the dyad in benzonitrile (Figure 2c, dashed line), and a good correlation between them can be observed.

In conclusion, in both solvents, the primary excited singlet state of porphyrin, $P^{1S}C$, decays to an intramolecular exciplex, $P^{1S}C \rightarrow (PC)^*$, in 2 ps. In benzonitrile, the exciplex relaxes to the CCS state in 12 ps. In toluene, the exciplex is relatively long-lived (370 ps), and its emission efficiency is comparable to that of the locally excited fullerene. The exciplex relaxes to the excited singlet state of fullerene.

2.1.3. H_2P−S1−C_{60} in Toluene and Benzonitrile. H_2P−S1−C_{60} demonstrated similar emission properties in toluene (Figure S2) as the corresponding zinc porphyrin dyad, ZnP−S1−C_{60} (Figure 3b). The lifetimes were 30 ps, 230 ps, and 1.4 ns for the LE porphyrin, exciplex, and LE fullerene, respectively. The pump−probe experiments confirmed the decay of the LE porphyrin in 30 ps and the decay of the fullerene excited singlet state at a longer delay time. However, no component with a lifetime close to 230 ps was detected in the transient absorption measurements. This is probably due to relatively small changes in the transient absorption between the LE porphyrin and the exciplex.

In benzonitrile, the fluorescence lifetime of the porphyrin chromophore is 27 ps, which correlates well with the formation time constant (24 ps) of the CCS, obtained from the time-resolved transient absorption measurements. The CCS state decayed in 900 ps. No direct evidence of a transient between the $P^{1S}C$ and CCS states was found.

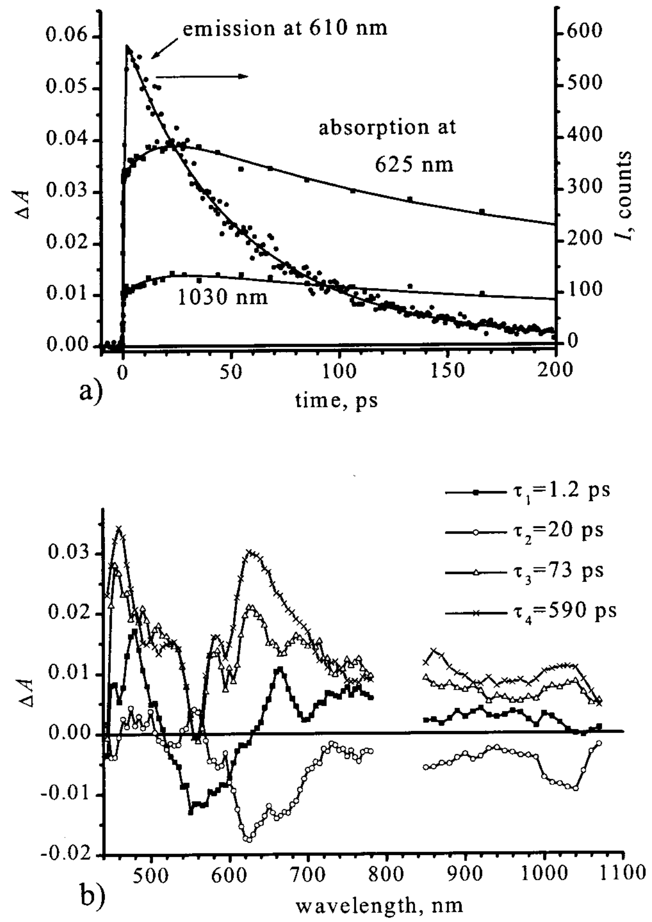

Figure 4. Time-resolved spectroscopy of ZnP−C1−C_{60} in benzonitrile: (a) fluorescence decay at 610 nm and transient absorption curves at 625 and 1030 nm and (b) transient absorption component spectra obtained after 4-exponential fit (the fit global σ value was 0.0008).

2.2. P−C1−C60. 2.2.1. ZnP−C1−C_{60} and H_2P−C1−C_{60} in Benzonitrile. For ZnP−C1−C_{60} and H_2P−C1−C_{60}, the pump−probe experiments revealed four intermediate states, as the data measured in the 460−1060 nm range could not be fitted successfully with less than four components. The fitting results for ZnP−C1−C_{60} are presented in Figure 4b. The fastest component represents the $P^{2S}C \rightarrow P^{1S}C$ transition. This was confirmed by up-conversion measurements at 600 nm, where a formation of the porphyrin fluorescence (i.e. the first excited singlet state) is observed with a time constant of 1 ps. A relatively slow internal conversion is in agreement with the results reported previously in the literature.[40]

The second component in the transient absorption spectra indicates the formation of the bands at around 625 and 1030 nm (Figure 4a), which are usually attributed to the porphyrin cation and fullerene anion radicals, respectively.[7,6,41−47] The corresponding time constant is 20 ps for ZnP−C1−C_{60}, as indicated in Figure 4b. The third and fourth components correspond to the recovery of the bands at 625 and 1030 nm with lifetimes of 73 and 590 ps, respectively. The emission measurements at 610 nm (the fluorescence maximum of the porphyrin chromophore) show that the excited singlet state of porphyrin does not relax with a time constant of 20 ps (Figure 4a), as could be expected from the transient absorption data.

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[52] The method to calculate the real emission or absorption spectra of the intermediate states is shown in the Supporting Information.

Table 1. Rate Constants, Exciplex Energies (E_x), and Free Energies ($-\Delta G_{px}$ and $-\Delta G_{xc}$)[a]

		rate constants, 10^9 s^{-1}				energies, eV		
compd	solvent	k_{px} (k_{xp})	k_{xi}	k_{xc} (k_{cx})	k_{ig}	E_x	$-\Delta G_{px}$	$-\Delta G_{xc}$
ZnP−S1−C_{60}	benzonitrile	530	83		7.7			
	toluene	480		2.9		1.89		
H_2P−S1−C_{60}	benzonitrile	37			1.1			
	toluene							
ZnP−C1−C_{60}	benzonitrile	24 (6.1)	20		1.7	2.05	0.036	
	toluene			0.3 (0.4)		1.74		−0.007
H_2P−C1−C_{60}	benzonitrile	7.6 (11)	7		0.5	1.92	−0.01	
	toluene			0.6 (0.1)				

[a] The subscripts refer to the initial and final states of the transition, respectively: p = $P^{1S}C$, x = (PC)*, c = PC^{1S}, i = P^+C^-, g = PC.

A careful analysis of the emission decay curves revealed that a biexponential fitting gives a better approximation, and the resulting lifetimes match those obtained from the transient absorption measurements. In the case of ZnP−C1−C_{60}, the lifetimes are 25 and 65 ps with relative amplitudes 23% and 77%, respectively. The goodness of fit was $\chi^2 = 1.05$, whereas a monoexponential fitting gave a lifetime of 55 ps and $\chi^2 = 1.15$, in accordance with an earlier report.[34]

The biexponential decay of the porphyrin fluorescence could be accounted for by assuming that the dyad exists in two distinct conformers. The relative proportions of the conformers would be given by the relative intensities of the two components in the emission decay, i.e. 23 and 77% in the case of ZnP−C1−C_{60}. Thus, after the relaxation of the porphyrin singlet states, both conformers should be in some intermediate (e.g. CS) state. The decays of these states should yield two additional decay components, which should be distinguishable as the relative population of the minor conformer is as high as 23%. However, only one component was observed: 590 ps. Therefore, the two-conformer model cannot adequately describe our experimental data.

Another interpretation for the biexponential decay of the porphyrin fluorescence is that the porphyrin LE state is in equilibrium with some other state. The other state could be a CS state, since the formation of the state is associated with the formation of the bands at 625 and 1030 nm. However, the decay of the transient absorption is clearly biexponential (73 and 590 ps), meaning that there are two transient states formed after $P^{1S}C$. Therefore, it is reasonable to assign the longest lived state, 590 ps, to the CCS state. The intermediate state between the porphyrin LE and CCS states is the exciplex, (PC)*, whose spectrum is rather similar to that of the CCS state as discussed later. Thus, the kinetic scheme for ZnP−C1−C_{60} and H_2P−C1−C_{60} in benzonitrile can be presented as

$$\mathrm{PC} \xrightarrow{h\nu} \mathrm{P^{1S}C} \underset{k_{xp}}{\overset{k_{px}}{\rightleftharpoons}} \mathrm{(PC)^*} \xrightarrow{k_{xi}} \mathrm{P^+C^-} \xrightarrow{k_{ig}} \mathrm{PC} \tag{3}$$

The time profile of the porphyrin emission is determined by three intrinsic rate constants: k_{px}, k_{xp}, and k_{xi}.[48] The experimentally obtained parameters are the two emission decay time constants, τ_1 and τ_2, and the ratio of the preexponential factors, $r = a_1/a_2$. Therefore, assuming that the initially populated state is the first excited singlet state of porphyrin, i.e., $[P^{1S}C] = 1$ and $[(PC)^*] = 0$ at $t = 0$, the intrinsic rate constants can be calculated. As shown in the Supporting Information, the intrinsic rate constants are

$$k_{px} = \frac{r\lambda_1 + \lambda_2}{-r - 1}$$

$$k_{xi} = \lambda_1 \lambda_2 k_{px}$$

and

$$k_{xp} = -\lambda_1 - \lambda_2 - k_{px} - k_{xi} \tag{4}$$

where $\lambda_1 = -1/\tau_1$ and $\lambda_2 = -1/\tau_2$. The calculated rate constants are presented in Table 1, and can be used to model the time-profiles of the populations of the intermediate states. The results of the modeling are shown in Figure 5. The population of $P^{1S}C$ is directly proportional to the emission intensity in Figure 4a.

The calculated rate constants for the equilibrium ($P^{1S}C \rightleftharpoons (PC)^*$) allow one to estimate the energy difference between the two states: $\Delta E = k_B T \ln(k_{px}/k_{xp})$. Since the energy of the LE porphyrin is known, the corresponding energy of the exciplex can be calculated. The results are presented in Table 1.

The principal behavior of the free-base dyad, H_2P−C1−C_{60}, was very similar to that of ZnP−C1−C_{60}. The corresponding experimental data are collected in the Supporting Information (Figure S3). The fitted lifetimes were 32 ps, 300 ps, and > 2 ns from the transient absorption measurements and 30 (25% relative amplitude) and 450 ps (75%) from the porphyrin emission decays. The calculated intrinsic rate constants and the exciplex energy are presented in Table 1.

2.2.2. ZnP−C1−C_{60} and H_2P−C1−C_{60} in Toluene. For ZnP−C1−C_{60} in toluene, three components were observed in the transient absorption measurements (Figure 6b), but the longest living component was not time-resolved.[53] The shortest lived component, 1.3 ps, corresponds to the internal conversion $P^{2S}C \rightarrow P^{1S}C$. The second component, 65 ps, is mainly associated with the decay of the signal at 480 nm and has a minor influence on the transient spectra at the red and infrared parts of the spectrum. The decay of the emission measured by the up-conversion method at wavelengths specific for porphyrin is monoexponential with a lifetime very close to 65 ps, in accordance with ref 34. This lifetime can be resolved by using the TCSPC method. The emission DAS measured with this method are shown in Figure 6a. There are two DAS with the

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(53) The relaxation process was not completed in 1 ns (the instrument time scale). This is indicated by the third component with $\tau_3 > 1$ ns.

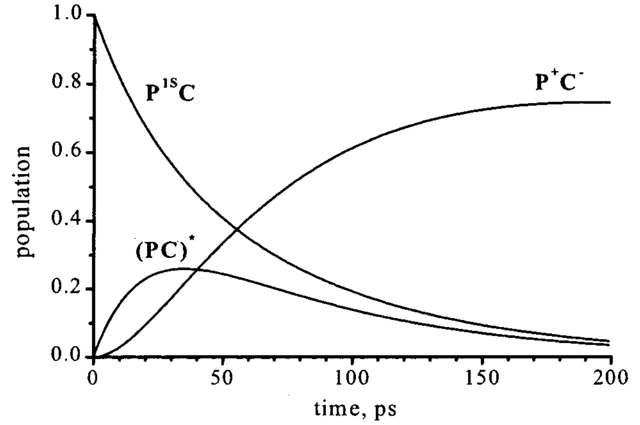

Figure 5. Populations of the transient states of ZnP−C1−C_{60} in benzonitrile calculated by using the model of eq 3.

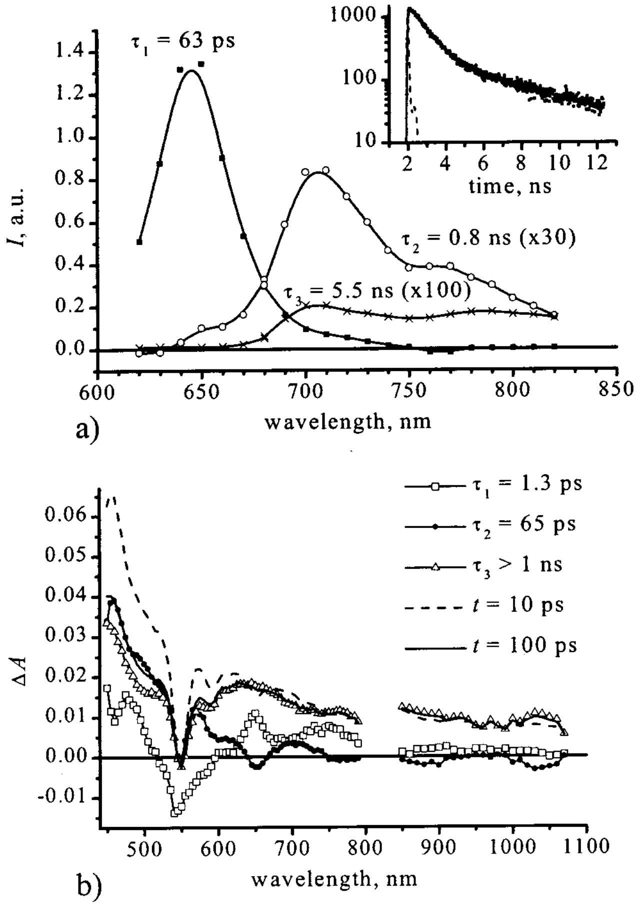

Figure 6. Time-resolved spectroscopy of ZnP−C1−C_{60} in toluene: (a) emission DAS obtained for 3-exponential fit (global $\chi^2 = 1.2$) and emission decay at 780 nm (see inset) fitted by using the biexponential model (lifetimes are 0.81 ± 0.05 and 5.4 ± 0.5 ns, $\chi^2 = 0.96$) and (b) transient absorption component spectra obtained after 3-exponential fit (the fit goodness $\sigma = 0.0011$) and time-resolved spectra at 10 (dashed line) and 100 ps delay time (solid line).

lifetimes of 0.8 and 5.5 ns in addition to the short-lived component (65 ps). Both spectra have maxima at 710 nm, and could be attributed to the emission of the LE fullerene. However, neither of the lifetimes matches the lifetime expected for fullerene decaying via intersystem crossing, 1.3 ns. While the shorter lifetime, 0.8 ns, could be attributed to a quenched PC^{1S}-state, the longer one, 5.5 ns, can hardly be explained in the frame of a linear reaction chain. The explanation can be found if the fullerene excited state is in equilibrium with some other state. Thus, the kinetic scheme for ZnP−C1−C_{60} in toluene can be drawn as in eq 5, where $k_{pc} = 1/65\ \text{ps} \approx 1.5 \times 10^{10}\ \text{s}^{-1}$.

$$\begin{tikzcd}
PC \arrow[r, squiggly, "h\nu"] & P^{1S}C \arrow[r, "k_{pc}"] & PC^{1S} \arrow[r, shift left, "k_{cx}"] \arrow[d, "k_{cT}"'] & (PC)^{*}, \arrow[l, shift left, "k_{xc}"] \\
 & & PC^{1T} &
\end{tikzcd}$$
(5)

The exciplex plays the role of a reservoir that allows a long emission lifetime for the excited singlet state of fullerene.

Taking into account the fact that the intramolecular energy transfer, $P^{1S}C \rightarrow PC^{1S}$, is much faster than the reactions involved in the equilibrium, the second part of the scheme, $PC^{1T} \leftarrow PC^{1S} \rightleftharpoons (PC)^*$, can be analyzed separately. The initial populations are $[PC^{1S}] = 1$ and $[(PC)^*] = [PC^{1T}] = 0$. The biexponential decay of the fullerene emission (see inset in Figure 6a) yields two lifetimes and the ratio of the preexponential factors. These values can be used to calculate the intrinsic rates, k_{xc}, k_{cx}, and k_{cT} using equations similar to (4), but because of the difference in the scheme, the ratio r must be calculated as $r = a_2/a_1$. The intersystem crossing rate constant for fullerene obtained by this method is $k_{cT} = 7 \times 10^8\ \text{s}^{-1}$, which is in agreement with the actually measured value ($7 \times 10^8\ \text{s}^{-1}$).[49−51] This strongly supports the applicability of Scheme 5 and gives an additional argument against the two-conformer model. The equilibrium rate constants and the calculated energy of the exciplex are given in Table 1.

The general behavior of the free-base dyad, H_2P−C1−C_{60}, is similar to that of the zinc dyad (Figure S4). However, the fitted time constants are rather close to each other, e.g. the porphyrin emission lifetime is 0.61 ns (measured at 650 nm) and the fullerene emission decays biexponentially with the lifetimes of 0.89 and 2.3 ns (measured at 800 nm). In addition, the fluorescence spectrum of free-base porphyrin overlaps with that of fullerene. Therefore, quantitative estimation of the intrinsic rates is unreliable for H_2P−C1−C_{60} in toluene.

2.3. Generalized Kinetic Scheme. The kinetic schemes used for the modeling of the photodynamics are apparently different for the P−S1−C_{60} and P−C1−C_{60} dyads in different solvents, because the relative rates of the individual reaction steps vary from case to case. However, the schemes have common intermediate states ($P^{1S}C$, PC^{1S}, $(PC)^*$, and P^+C^-),[54] and a general scheme presenting all the reactions between the states can be drawn (Figure 7).[55] A similar kinetic model was used to analyze the photodynamics of phytochlorin−fullerene dyads.[23,24]

The main difference between the present scheme and those used previously to analyze the photodynamics of the porphyrin−fullerene dyads[56] is the existence of the exciplex, $(PC)^*$. Formally, the scheme can be reduced to the ones used previously by combining the exciplex and CCS states. From the practical point of view, this may happen when the formation rate of the exciplex is much slower than the rate of its decay, e.g. the

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(54) In the frame of this study, only the primary reactions of the excited state relaxation are studied. This is limited by the time scale of roughly 1 ns, and does not cover the possible reactions involving triplet states.

(55) The scheme presents the reaction chains only, and does not intend to indicate the relative energies of the intermediate states, which may vary significantly from dyad to dyad and from solvent to solvent. The energies are dicussed later in the paper.

(56) See for example references 1, 2, 6−8, and 12.

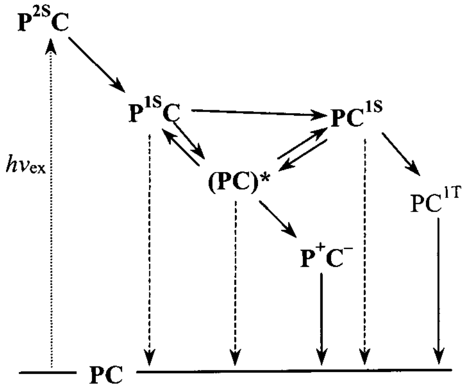

Figure 7. Generalized kinetic scheme describing the photophysical processes in porphyrin−fullerene dyads. Transitions which may result in photon emission are shown by the dotted arrows. The energy levels are not drawn to scale.[55] The states shown are the ground state (PC), locally excited porphyrin ($P^{2S}C$ and $P^{1S}C$) and fullerene (PC^{1S}), exciplex ((PC)*), complete charge-separated state (P^+C^-), and fullerene triplet state (PC^{1T}).

reactions $P^{1S}C \rightarrow (PC)^*$ and $PC^{1S} \rightarrow (PC)^*$ are much slower than the reaction $(PC)^* \rightarrow P^+C^-$, or if the formation rate of the CCS is much slower than the rate of its decay. Then, only exciplex (the latter case) or CCS state (the former case) is observable. However, in the case of P−S1−C_{60} and P−C1−C_{60} dyads, both the exciplex and CCS state should be taken into account and can be resolved experimentally. Application of the kinetic model shown in Figure 7 is crucial for the interpretation of the transient absorption and emission data. It also allows a comparison of the behavior of different dyads and a collection of new information on the nature of the exciplex and CCS states.

2.4. Nature of the Exciplex and Its Impact on Intramolecular ET Reactions. The series ZnP−O34−C_{60}, ZnP−S1−C_{60}, and ZnP−C1−C_{60} forms an ideal basis for comparing the influence of the molecular geometry on the principal ET parameters and for discussing the nature and the role of the exciplex in intramolecular ET interactions. The charge-transfer emission was previously observed for ZnP−O34−C_{60} and H_2P−O34−C_{60} dyads.[10,15] Their steady-state emission spectra were analyzed in the frame of the semiclassical Marcus electron-transfer theory to obtain principal energetics parameters: the outer-sphere and internal reorganization energies (λ_s and λ_v, respectively), the reaction free energy (ΔG°), and the DA vibrational frequency (ν_v). The same procedure can be applied to ZnP−S1−C_{60} in toluene, by fitting the calculated exciplex spectrum shown in Figure 3b according to the equation[19,35]

$$I(\nu) = A \sum_{i=0}^{\infty} e^{-S}\frac{S^i}{i!}\exp\left[-\frac{(\Delta G^\circ + \lambda_s + ih\nu_v + h\nu)^2}{4\lambda_s k_B T}\right] \quad (6)$$

where $A = n((n^2+2)/3)^2(16\pi^2/3)\tilde{\nu}^3[4\pi^3/h^2\lambda_s k_B T]^{1/2}M^2$, $S = \lambda_v/(h\nu_v)$ is the electronic-vibrational coupling, n is the refractive index of the medium, $h\nu$ is the energy of the emitted photon, and M is the electronic transition dipole moment. The energetics parameters and the measured rate constants are linked by the semiclassical Marcus electron-transfer theory[57,19,58] (see also the Supporting Information)

$$k_{et} = \frac{2\pi}{\hbar} V^2 \frac{1}{[4\pi\lambda_s k_B T]^{1/2}} \sum_{i=0}^{\infty} e^{-S}\frac{S^i}{i!}\exp\left[-\frac{(\Delta G^\circ + \lambda_s + ih\nu_v + h\nu)^2}{4\lambda_s k_B T}\right] \quad (7)$$

which can be used to evaluate the electronic couplings V associated with the different reaction steps. The calculated results can be visualized with use of Franck−Condon plots, where the reaction coordinate is scaled to adopt the correct value of the reorganization energy (see the Supporting Information). Further insight can be gained by comparing the differential absorption spectra of the exciplexes with those of the LE and CCS states.

The transient spectra can be calculated on the basis of the proposed kinetic scheme and the experimental results, as shown in the Supporting Information. The results for ZnP−S1−C_{60} and ZnP−C1−C_{60} in benzonitrile are presented in Figure 8. Although the transient absorption spectra of $P^{1S}C$ states are reasonably alike and so are those of the CCS states, the spectra of the exciplexes are very different (Figure 8). In the cases of ZnP−C1−C_{60} and ZnP−O34−C_{60},[59] the spectrum of the (PC)* state resembles that of CCS. For ZnP−S1−C_{60}, the spectrum of (PC)* is rather similar to that of $P^{1S}C$ except for a strong absorption recovery in the 450−550 nm region.

The rigid structure of the P−S1−C_{60} dyads prevents any formation of a contact ion pair. Thus, the origin of the exciplex should be in the interplay of the LE states of porphyrin and fullerene. The linkage between the donor and the acceptor is an aromatic phenyl ring, which, in principle, could mediate through-bond interaction of porphyrin and fullerene electronic subsystems. This may involve the formation of a common molecular orbital with a relatively small total shift of the electron density. This type of interaction may result in a minor change in the reaction coordinates and, thus, in a small reorganization energy.

Unlike in the cases of ZnP−O34−C_{60} and H_2P−O34−C_{60}, the exciplex emission cannot be extracted from the steady-state spectra of ZnP−S1−C_{60}. However, if the reaction chain $P^{1S}C \rightarrow (PC)^* \rightarrow PC^{1S}$ is assumed, the emission spectrum of the exciplex can be calculated in toluene as a sum of all the shown components in the emission DAS (Figure 3). The exciplex emission corresponds to the minor relaxation channel $(PC)^* \rightarrow PC$. The spectrum fit (eq 6 and Figure S5) gives the following values: $-\Delta G^\circ = 1.89 \pm 0.01$ eV, $\lambda_s = 0.04 \pm 0.005$ eV, $\lambda_v = 0.13 \pm 0.01$ eV, and $h\nu_v = 0.13 \pm 0.01$ eV.[60] Thus, the exciplex is 1.89 eV higher in energy than the ground state. The energies of the excited singlet states of porphyrin and fullerene are 2.07 and 1.75 eV, respectively. Accordingly, the free energy changes of the reactions $P^{1S}C \rightarrow (PC)^*$ and $(PC)^* \rightarrow PC^{1S}$ are 0.18 and 0.14 eV, respectively.

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(57) Moser, C. C.; Keske, J. M.; Warncke, K.; Farid, R. S.; Dutton, P. L. *Nature* **1992**, *355*, 796−802.

(58) Jortner, J.; Bixon, M. *J. Chem. Phys.* **1988**, *88*, 167−170.

(59) Following the discussion above, the spectrum previously attributed to the CT state[6] should be treated as the exciplex spectrum.

(60) A "wavy" shape of the exciplex emission receives a good interpretation in terms of eq 6. A small value of the reorganization energy ($2\lambda_s k_B T < (h\nu_v)^2$) makes the transitions to different vibrational levels ($ih\nu_v$) spectrally resolved, the distance between the emission maxima being determined by $h\nu_v$.

The reorganization energies of the excited states ($P^{1S}C$ and PC^{1S}) relative to the ground state can be assumed to be small based on the small Stokes shifts of the corresponding reference compounds.[61] Therefore, the reorganization energies for the reactions (PC)* → PC, $P^{1S}C$ → (PC)*, and (PC)* → PC^{1S} must be the same, i.e., $\lambda_s = 0.04$ eV. Naturally, one can expect also the DA vibration frequency ν_v and the internal reorganization energy λ_v to be the same for these reactions. Thus, using eq 7 and the corresponding rates and energies, the electronic couplings can be estimated to be $V_{px} \approx 4$ meV (30 cm^{-1}) and $V_{xc} \approx 0.3$ meV (2.5 cm^{-1}) for the formation of the exciplex and for its relaxation to PC^{1S}, respectively. The calculated values are quite reasonable.[26,62,63] The fact that $V_{px} > V_{xc}$ indicates that the exciplex resembles more $P^{1S}C$ than PC^{1S}. This conclusion is in accord with the result that the transient absorption spectrum of the exciplex is very similar to that of the porphyrin LE singlet state (compare the solid line spectra in Figure 8, parts a and b, respectively).

From the Franck–Condon plot (Figure 9), the relaxation pathway of the exciplex is evident for ZnP–S1–C_{60} in toluene: (PC)* → PC^{1S}. The potential barrier for this path is almost the same as that for the formation of the exciplex, $P^{1S}C$ → (PC)*. However, the electronic coupling is lower (see above), and hence the rate is slower, for the relaxation of the exciplex than for its formation.

Only for the P–O34–C_{60} dyads were charge-transfer absorption bands in the 700–800 nm range observed, indicating ground-state interaction.[10,15] According to ^{1}H NMR measurements and molecular mechanics calculations, ZnP–O34–C_{60} exists mainly in a conformation where the fullerene moiety is folded onto the porphyrin ring.[6] It is therefore reasonable to qualify the exciplex as a contact ion pair.

For ZnP–O34–C_{60} studied previously in nonpolar benzene,[6,10] the emission fit gave the following:[10] $-\Delta G° = 1.66$ eV, $\lambda_s = 0.13$ eV, $\lambda_v = 0.1$ eV, and $h\nu_v = 0.13$ eV. The rate of the decay of the exciplex, (PC)* → PC, was $k_{xg} = 3 \times 10^9$ s^{-1}.[6] Thus, the electronic coupling calculated from eq 7 is $V_{xg} = 0.60$ eV (5000 cm^{-1}). This is clearly too large a value. The applied theory can be used to calculate the electronic coupling only in the diabatic case when $V < h\nu_v$. The electronic coupling for the same transition was estimated previously from the CT absorption corresponding to the transition PC → (PC)*. The result was $V_{gx} = 0.03$ eV (270 cm^{-1}).[10]

An explanation for the inconsistency in the two electronic coupling values can be that the decay rate of the exciplex, 3×10^9 s^{-1}, was assigned to a wrong transition. The situation can be discussed by using the energy plots in Figure 9. The excitation of the dyads populates the porphyrin LE state, $P^{1S}C$, which yields the exciplex, (PC)*,[64] at energy 1.66 eV.[10] There is no evident way for the relaxation of the exciplex to occur. The small reorganization energy associated with the (PC)* state (relative to PC) results in a high potential barrier for the radiationless relaxation to the ground state. This is illustrated by Figure 9, where the crossing point of the potentials for the ground state and exciplex does not fit to the scale. Unlike in the case of the P–S1–C_{60} dyads, the exciplex cannot relax to the fullerene LE state, because the energy of the exciplex is lower than that of the LE fullerene. However, the experimentally determined lifetime of the state is relatively short, 300 ps, and an attempt to attribute it to the radiationless relaxation of the exciplex to the ground state results in an unreasonably high value of the electronic coupling. A solution to the problem can be found if both exciplex and CCS state are present in the reaction

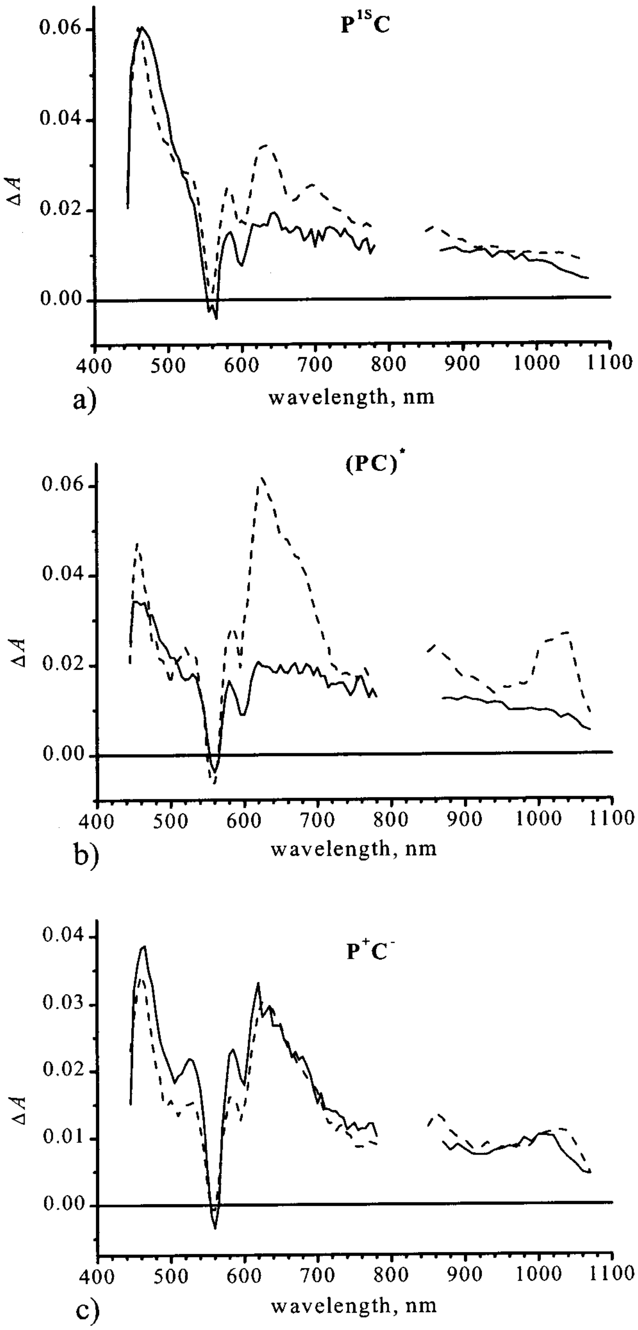

Figure 8. Transient spectra of the (a) LE porphyrin, $P^{1S}C$, (b) exciplex, (PC)*, and (c) CCS state, P^+C^-, of ZnP–S1–C_{60} (solid line) and ZnP–C1–C_{60} (dashed line) in benzonitrile. The spectra were calculated according to the kinetic schemes proposed for each compound; see text for details.

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(61) Assuming the Stokes shift to be 5 nm (for a band at 650 nm) the reorganization energy can be estimated to be 0.03 eV. This is probably the limit when one can neglect the reaction coordinate change for the excited states.

(62) Katz, N. E.; Mecklenburb, S. L.; Graff, D. K.; Chen, P.; Meyer, T. J. *J. Phys. Chem.* **1994**, *98*, 8959–8961.

(63) Williams, R. M.; Koeberg, M.; Lawson, J. M.; An, Y.; Rubin, Y.; Paddon-Row: M. N.; Verhoeven, J. W. *J. Org. Chem.* **1996**, *61*, 5055–5062.

(64) Although the potential barriers for the transitions $P^{1S}C$ → (PC)* and $P^{1S}C$ → P^+C^- are almost equal (Figure 9), the respective electronic coupling matrix elements V_{px} and V_{pi} are not. Because the charge shift is much greater for the CCS than for the exciplex, the overlap of the $P^{1S}C$ wave function $\Psi_{P^{1S}C}$ must be greater with $\Psi_{(PC)^*}$ than with $\Psi_{P^+C^-}$, and $V_{px} > V_{pi}$. Therefore (eq 7), the transition to the exciplex dominates over direct charge transfer.

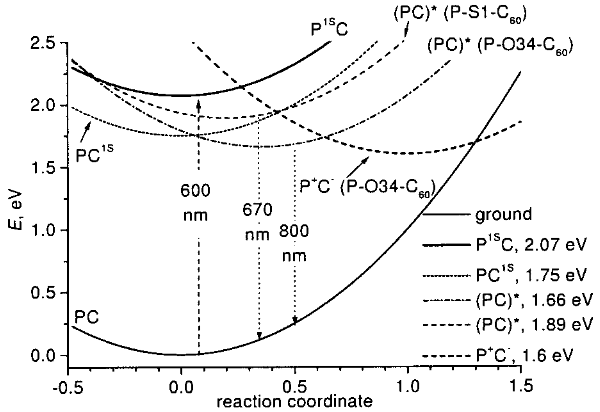

Figure 9. Potential energy profiles of the ground, LE, exciplex, and CCS states of ZnP$-$S1$-$C$_{60}$ and ZnP$-$O34$-$C$_{60}$ in toluene. See text for explanations. Note that the P$^+$C$^-$ state only applies to ZnP$-$O34$-$C$_{60}$.

scheme. The potential profile of the hypothetical CCS state is shown by the dotted line in Figure 9. The energy of the CCS state (1.6 eV)[65] roughly equals the energy of the exciplex, but is characterized by a greater shift in the reaction coordinate. Thus, it can provide a two-step relaxation channel: (PC)* → P$^+$C$^-$ → PC. Apparently, the rate-determining step in this case is (PC)* → P$^+$C$^-$.

In ZnP$-$C1$-$C$_{60}$, the bridge between the fullerene and the phenyl ring attached to the porphyrin macrocycle consists of five single bonds (Figure 1), which cannot mediate electronic coupling of the donor and acceptor effectively. Therefore, the formation of the exciplex and the following CCS state should take place through the space. It is reasonable to suggest that the ET takes place first to a rather high lying level characterized by a small nuclear rearrangement (small reorganization energy), whereas the final CCS state is characterized by a complete charge stabilization and, thus, by a relatively high reorganization energy.

For ZnP$-$C1$-$C$_{60}$, only the energy of the exciplex can be evaluated based on the experimental data, because the emission spectrum of the exciplex could not be obtained from the steady-state or time-resolved spectra. In toluene, the energy of the (PC)* state is only ~0.01 eV below that of PC^{1S} based on the intrinsic rate constants k_{cx} and k_{xc} associated with the equilibrium of Scheme 5. Assuming the reaction coordinate for the exciplex to be similar to that of ZnP$-$O34$-$C$_{60}$, a potential curve for ZnP$-$C1$-$C$_{60}$ can be drawn as presented in Figure 10a. Qualitatively, this figure fits well to the proposed kinetic model with an equilibrium between the exciplex and the LE fullerene (Scheme 5).

In benzonitrile, the energy of the exciplex for ZnP$-$C1$-$C$_{60}$ was estimated to be 2.05 eV based on the intrinsic rate constants k_{px} and k_{xp} (Scheme 3), and the reaction coordinate was assumed to be the same as in toluene. Reasonable energy profiles for ZnP$-$C1$-$C$_{60}$ in benzonitrile resemble those presented in Figure 10b. To draw the figure, the energy of the CCS state was determined to be 1.33 eV based on cyclic voltammetry data, and the reaction coordinate (reorganization energy) was chosen to satisfy the kinetic model. As a result, the exciplex ((PC)* in Figure 10b) reduces the potential barrier between the LE (P^{1S}C) and CCS (P$^+$C$^-$) states.

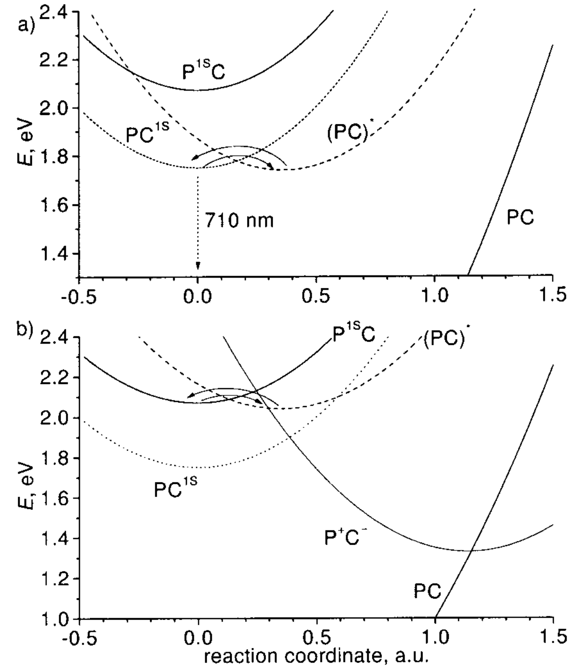

Figure 10. Potential energy profiles of the ground, LE, exciplex, and CCS states of ZnP$-$C1$-$C$_{60}$ in toluene (a) and benzonitrile (b). See text for explanations.

In summary, the linker of the P$-$S1$-$C$_{60}$ dyads has an influence on the ET properties of the dyad, whereas for the P$-$O34$-$C$_{60}$ and P$-$C1$-$C$_{60}$ dyads, the exciplex and CCS states are formed through space. In contrast to the P$-$S1$-$C$_{60}$ dyads, the ET of the P$-$C1$-$C$_{60}$ and P$-$O34$-$C$_{60}$ dyads can be discussed in terms of degree of the charge transfer,[66,67] rather than taking into consideration the electronic wave functions of the donor and acceptor.

A clear drawback of the Franck$-$Condon plots in Figures 9 and 10 is that in the case of the multistep reactions, a 1D reaction coordinate may not work,[68] and a more complex approach is required. In addition, the placement of the potential minima of the ground and LE states at the same reaction coordinate (at 0 in our case) may be inaccurate.[61]

3. Conclusions

The ET cabability of the porphyrin$-$fullerene dyads is well-established today, and recently a charge-transfer emission has been reported for a series of dyads. The present study shows that the emission occurs from a state that can be characterized as an exciplex. Furthermore, the exciplex can undergo complete charge separation, manifesting itself as a distinct intermediate state between the locally excited and complete CS states. The appearance of the exciplex depends on the DA distance, type

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(65) Oxidation potentials are measured in polar solvents and are not directly available in nonpolar solvents. In benzonitrile, the energy level of the CCS state of ZnP$-$O34$-$C$_{60}$ was determined to be 1.43 eV relative to the ground state on the basis of electrochemical data. On one hand, the energy should be higher in a nonpolar solvent. On the other hand, it should be less than the energy level of the exciplex. The value 1.6 eV was chosen arbitrarily to meet these criteria.

(66) Matyushov, D. V.; Voth, G. A. *J. Phys. Chem. A* **2000**, *104*, 6470$-$6484.
(67) Matyushov, D. V.; Voth, G. A. *J. Phys. Chem. A* **2000**, *104*, 6485$-$6494.
(68) Gayathri, N.; Bagchi, B. *J. Phys. Chem. A* **1999**, *103*, 8496$-$8504.
(69) Higashida, S.; Imahori, H.; Kaneda, T.; Sakata, Y. *Chem. Lett.* **1998**, 605.
(70) Hammel, D.; Kautz, C.; Müllen, K. *Chem. Ber.* **1990**, *123*, 1353.
(71) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798.
(72) Wang, Y.; Schuster, D. I.; Wilson, S. R.; Welch, C. J. *J. Org. Chem.* **1996**, *61*, 5198.
(73) Imahori, H.; Tamaki, K.; Araki, Y.; Hasobe, T.; Ito, O.; Shimomura, A.; Kundu, S.; Okada, T.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2002**, *106*, 2803$-$2814.

of linker, and solvent. A common kinetic scheme, accounting for the LE chromophores, the exciplex, and CCS states, can be presented to analyze the ET properties of the dyads. The scheme can be used to estimate the energetics parameters of the exciplex and to construct a consistent model for the dynamics of the photoinduced ET of the porphyrin−fullerene dyads characterized by short and moderate DA separation distances.

4. Experimental Section

The studied compounds are presented in Figure 1. The synthesis and NMR characterization of P−S1−C_{60} and P−C1−C_{60} dyads are described in the Supporting Information.[34,69−73]

The instruments for steady-state and time-resolved optical spectroscopic studies are described elsewhere.[23] The fast processes were monitored by using the fluorescence up-conversion and pump−probe transient absorption techniques with time resolutions of about 100 fs.[23] The samples were excited at 415 nm, which corresponds to the absorption of the second excited singlet state of porphyrin. The fluorescence up-conversion measurements provided the lifetimes of porphyrin singlet state in the different dyads. The time-resolved transient absorption spectra were measured for all compounds in three wavelength regions (440−660, 560−780, and 850−1070 nm). Typically, 50−60 spectra at different time delays were recorded. The results were combined and fitted globally to decay-associated spectra (DAS), which can be used to reconstruct the sample transient absorption with a compensated probe pulse dispersion. The differential transient absorbance at wavelength λ and time t is given by $\Delta A(\lambda,t) = \sum A_i(\lambda)\exp(-t/\tau_i)$, where A_i and τ_i are the amplitudes and lifetimes of the DAS components. With use of this procedure, a time resolution of roughly 0.1 ps can be achieved. Since the longest delay time was 1 ns, the fitted lifetimes longer than 1 ns are inaccurate and can be treated as tentative values only.

In the nanosecond time range, the time-resolved fluorescence was measured by using the time-correlated single-photon counting (TCSPC) technique with a time resolution of about 100 ps. The excitation wavelength was 590 nm, which corresponds to the porphyrin Q-band. With a global analysis of the TCSPC emission decay data, the spectra and lifetimes of different emitting species can be distinguished. This method was particularly useful for nonpolar solutions, where fullerene emission was significant. For the fitting model, a minimum number of exponents necessary to achieve a satisfactory weighted mean square deviation value was used.

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Supporting Information Available: Synthesis and NMR characterization of the compounds, emission and transient absorption spectra, spectral fits, and derivation of intrinsic rate constants, and spectra of intermediate states (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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