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Exciplex Mediated Photoinduced Electron Transfer Reactions of Phthalocyanine-Fullerene Dyads

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Evidences of an intramolecular exciplex intermediate in a photoinduced electron transfer (ET) reaction of double-linked free-base and zinc phthalocyanine-C_{60} dyads were found. This was the first time for a dyad with phthalocyanine donor. Excitation of the phthalocyanine moiety of the dyads results in rapid ET from phthalocyanine to fullerene via an exciplex state in both polar and nonpolar solvents. Relaxation of the charge-separated (CS) state $Pc^{\bullet+}$-$C_{60}{}^{\bullet-}$ in a polar solvent occurs directly to the ground state in 30−70 ps. In a nonpolar solvent, roughly 20% of the molecules undergo transition from the CS state to phthalocyanine triplet state $^3Pc^*$-C_{60} before relaxation to the ground state. Formation of the CS state was confirmed with electron spin resonance measurements at low temperature in both polar and nonpolar solvent. Reaction schemes for the photoinduced ET reactions of the dyads were completed with rate constants obtained from the time-resolved absorption and emission measurements and with state energies obtained from the fluorescence, phosphorescence, and voltammetric measurements.

1. Introduction

In photovoltaic devices, such as solar cells, dyad molecules consisting of electron donor and acceptor moieties can be used to perform functions similar to those that reaction centers perform in photosynthesis of green plants. In addition, mimicking of natural photosynthesis requires a light-harvesting unit to capture the energy needed in the electron transfer (ET) reaction. The simplest way to realize this is a dyad molecule where at least one of the two moieties is able to absorb light efficiently. Porphyrin-fullerene dyads have been thoroughly studied for this purpose, and efficient formation of a long-living charge-separated (CS) state has been achieved with many systems.[1–13] Especially recently, there have been studies on replacing porphyrin with phthalocyanine as the electron donor of the dyad with fullerene[14–24] or with other acceptors.[25,26] Phthalocyanines are porphyrin analogues, which absorb light in a wider spectral region compared to porphyrins. This makes phthalocyanines more attractive chromophores in solar energy conversion. In fact, many encouraging results of functioning solar cell prototypes based on phthalocyanine and fullerene have been reported.[27–36]

In addition to appropriate selection of the donor and acceptor, their mutual orientation and distance have been recognized as important factors in dyad design.[11,37–39] Attaching the donor and acceptor with two covalent linkers has provided dyads with well-oriented and fixed structures resulting in efficient ET.[39–42] Typically the ET reaction of such closely arranged dyads occurs via an intramolecular exciplex intermediate.[11,13,39,43–46] We reported earlier the synthesis and characterization of three double-linked phthalocyanine-fullerene dyads for which some indication of an exciplex was observed.[24] Now, two new dyads with better solubility have been synthesized to continue and expand the study of this series of compounds. Because of improved solubility of the compounds, more accurate spectroscopic results were obtained, and the photoinduced reaction schemes were completed. Particularly, evidence of an exciplex state preceding the complete CS state was found in the studies.

2. Materials and Methods

2.1. Compounds. Molecular structures of the studied compounds are presented in Chart 1. To improve the solubility of the previously reported dyad H_2PcF-1,[24] ethyl ester groups of the malonate linkers were replaced by *tert*-butyl esters in dyad **H_2Pc-C_{60}tb**. Some further measurements were carried out also for H_2PcF-1.[24] To stress the similarity of the two studied free-base dyads, H_2PcF-1 is denoted as **H_2Pc-C_{60}ee** in this article. **ZnPc-C_{60}tb** is a Zn complex of **H_2Pc-C_{60}tb**. The synthesis of **H_2Pc-C_{60}ee** and of the corresponding reference compound **H_2Pcee** has been reported earlier.[24]

The solvents and reagents utilized in the synthesis were purchased from Sigma-Aldrich Co. and used without prior purification. The sorbents for column chromatography (Silica 60, Silica 100), TLC plates (aluminum sheet Silica gel 60 F_{254}), and HPTLC plates (glass plate Silica gel 60 F_{254}) were purchased from Merck. The ^{1}H NMR spectra were run on a 300 MHz Varian Mercury spectrometer. High-resolution mass spectra were measured by using a Waters LCT Premier XE ESI-TOF mass spectrometer with either Leucine Enkefalin or sodium iodide solution as a lock mass. The sample solution was continuously introduced into the interface sprayer by a syringe infusion pump at a flow rate of 15 μL min^{-1}. The compounds were first dissolved in chloroform at a concentration of 1 mg mL^{-1}, and 5 μL of these solutions was diluted to 1 mL with 60:40:0.2 toluene:methanol:trifluoroacetic acid solution.

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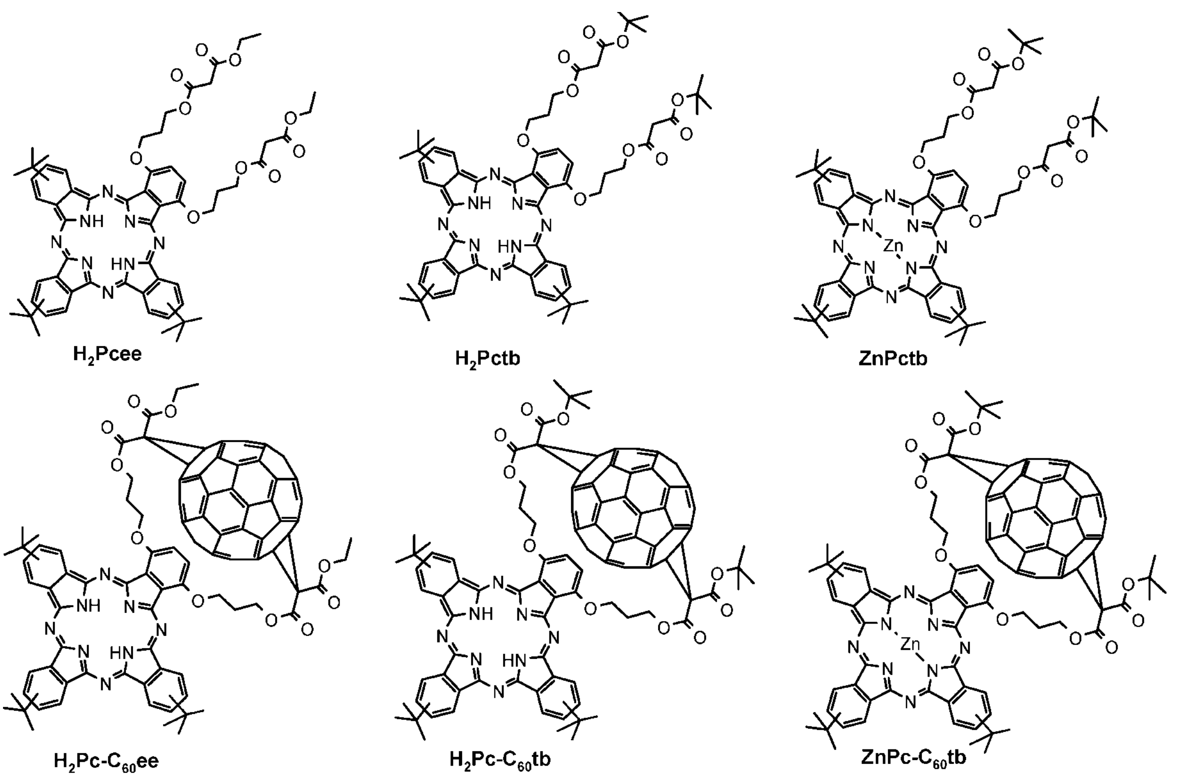
CHART 1: Studied Compounds



1,4-Bis[hydroxypropyloxy]-6(7),10(11),14(15)-tris[tert-butyl] Phthalocyanine. 4-*tert*-Butylphthalonitrile (67 mg, 0.36 mmol), 3,6-dihydroxypropyloxyphthalonitrile (100 mg, 0.36 mmol), and lithium (12 mg, 1.8 mmol) were heated at reflux in 5 mL of 1-pentanol for 5 h under Ar flow. The dark-green solution was cooled down, and the solvent was removed under reduced pressure. The mixture of reaction products was subjected to column chromatography on Silica 100. Gradient elution ($CHCl_3$−$CHCl_3$:EtOH 9:1) yielded a mixture of three products with Rf 0.95, 0.85, and 0.49, respectively (TLC aluminum sheet, in $CHCl_3$:EtOH 18:1). Separation of this mixture on Silica 60 column with gradient elution ($CHCl_3$−$CHCl_3$: EtOH 10:1) yielded three individual fractions: compounds A and B, identified as regioisomers of 2(3),6(7),10(11),14(15)-tetrakis[*tert*-butyl]phthalocyanine, and compound C (18 mg), identified as 1,4-bis[hydroxypropyloxy]-6(7),10(11),14(15)-tris-[*tert*-butyl]phthalocyanine; δ_H ($CDCl_3$/CD_3OD 50/1; Me_4Si) 9.49−6.67 (m, 11 H, phthalo-*H*), 5.02−4.15 (m, 8 H, $OCH_2CH_2CH_2OH$), 1.99−1.67 (m, 31 H, $OCH_2CH_2CH_2OH$, $C(CH_3)_3$), −1.54−1.88 (m, 2 H, N*H*); *m*/*z* (ESI-TOF) 831.4316 (M+H$^+$, $C_{50}H_{54}N_8O_4H$ requires 831.4346).

1,4-Bis[tert-butoxymalonateoxypropyloxy]-6(7),10(11),14(15)-tris[tert-butyl]phthalocyanine, H$_2$Pctb. 1,4-Bis[hydroxypropyloxy]-6(7),10(11),14(15)-tris[*tert*-butyl]phthalocyanine (30 mg, 0.036 mmol) and 2-chloro-1-methylpyridinium iodide (40 mg, 0.144 mmol) were dissolved in 10 mL of CH_2Cl_2. Triethylamine (0.04 mL, 0.288 mmol) and *tert*-butylmalonate (0.022 mL, 0.144 mmol) were added, and the reaction mixture was stirred for 18 h. After usual workup, the product was purified by column chromatography on Silica 100 in $CHCl_3$ to yield 27 mg (48%) of 1,4-bis[*tert*-butoxymalonateoxypropyloxy]-6(7),10(11),14(15)-tris[*tert*-butyl]phthalocyanine **H$_2$Pctb**; δ_H ($CDCl_3$/CD_3OD 50/1; Me_4Si) 9.48−6.46 (m, 11 H, phthalo-*H*), 4.86−3.94 (m, 8 H, $OCH_2CH_2CH_2O$), 3.75−3.59 (m, 4 H, $O_2CCH_2CO_2tBu$), 2.01−1.54 (m, 31 H, $OCH_2CH_2CH_2O$, $C(CH_3)_3$), 1.47−1.29 (m, 18 H, $CO_2C(CH_3)_3$), −1.68−2.00 (m, 2 H, N*H*); *m*/*z* (ESI-TOF) 1115.5527 (M+H$^+$, $C_{64}H_{74}N_8O_{10}$ requires 1115.5607).

Dyad H$_2$Pc-C$_{60}$tb. A total of 10 mg (0.036 mmol) of I_2 and 14 mg (0.0198 mmol) of fullerene C_{60} were dissolved in 100 mL of toluene in ultrasound bath. 1,4-Bis[*tert*-butoxymalonateoxypropyloxy]-6(7),10(11),14(15)-tris[*tert*-butyl]phthalocyanine (20 mg, 0.018 mmol) was added, and the solution was stirred under Ar flow, protected from light. After 15 min, a total of 15.2 μL of DBU (16.4 mg, 0.108 mmol) was added, and the reaction mixture was stirred for 2 h at room temperature. The reaction was quenched by adding 2 mL of water, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography on Silica 60 by using $CHCl_3$ as eluent. One main green fraction was collected to yield 26 mg (78%) of the dyad **H$_2$Pc-C$_{60}$tb**; δ_H ($CDCl_3$/CD_3OD 50/1; Me_4Si) 9.54−8.80 (br m, 7 H, phthalo-*H*), 8.39−8.13 (m, 4 H, phthalo-*H*), 5.57−3.81 (br m, 8 H, $OCH_2CH_2CH_2O$), 2.09−1.48 (br m, 31 H, $OCH_2CH_2CH_2OH$, $C(CH_3)_3$), −0.79−1.33 (m, 2 H, N*H*); *m*/*z* (ESI-TOF) 1830.5181 (M$^+$, $C_{124}H_{70}N_8O_{10}$ requires 1830.5215).

Zinc 1,4-bis[tert-butoxymalonateoxypropyloxy]-6(7),10(11),14(15)-tris[tert-butyl]phthalocyanine, ZnPctb. A total of 70 mg (11.87 mmol) of 1,4-bis[hydroxypropyloxy]-6(7),10(11),14(15)-tris[*tert*-butyl]phthalocyanine and 100 mg (mmol) of $Zn(OAc)_2 \cdot 2H_2O$ were heated at reflux in 10 mL of DMF. The completion of the reaction was monitored by absorption spectroscopy. After 18 h, the solution was cooled down, diluted with 30 mL of $CHCl_3$, and poured into 100 mL of water. The organic layer was separated, washed with water (3 × 100 mL), dried with sodium sulfate, and evaporated to yield a green solid of zinc 1,4-bis[hydroxypropyloxy]-6(7),10(11),14(15)-tris[*tert*-butyl]phthalocyanine (60 mg, 86%), which was used in the next step without further purification. 2-Chloro-1-methylpyridinium iodide (71 mg, 0.27 mmol) and zinc 1,4-bis[hydroxypropyloxy]-6(7),10(11),14(15)-tris[*tert*-butyl]phthalocyanine (60 mg, 0.067

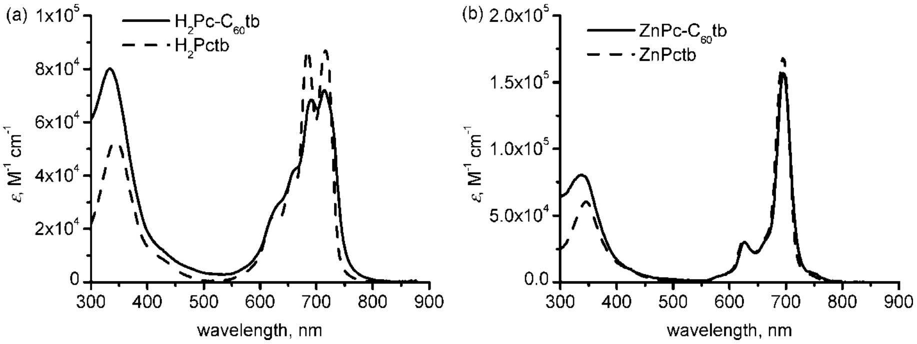


Figure 1. Molar absorptivity spectra of (a) **H_2Pc-C_{60}tb** and **H_2Pctb** and (b) **ZnPc-C_{60}tb** and **ZnPctb** in toluene.

mmol) were dissolved in 20 mL of CH_2Cl_2. Triethylamine (0.075 mL, 0.54 mmol) and *tert*-butylmalonate (0.041 mL, 0.27 mmol) were added, and the reaction mixture was stirred for 4 h. After usual workup, the product was purified by column chromatography on Silica 100 in $CHCl_3$ to yield 23 mg (29%) of zinc 1,4-bis[*tert*-butoxymalonateoxypropyloxy]-6(7),10(11),14(15)-tris[*tert*-butyl]phthalocyanine **ZnPctb**; δ_H ($CDCl_3$/CD_3OD 50/1; Me_4Si) 9.51−8.59 (m, 6 H, phthalo-*H*), 8.30−7.96 (m, 3 H, phthalo-*H*), 7.23−6.34 (m, 2 H, phthalo-*H*), 5.04−3.97 (m, 8 H, $OCH_2CH_2CH_2O$), 3.43−3.12 (m, 4 H, $O_2CCH_2CO_2tBu$), 1.90−1.21 (m, 49 H, $OCH_2CH_2CH_2O$, $CO_2C(CH_3)_3$, $C(CH_3)_3$); *m/z* (ESI-TOF) 1176.4719 (M^+, $C_{64}H_{72}N_8O_{10}Zn$ requires 1176.4663).

Dyad ZnPc-C$_{60}$tb. A solution of 10 mg (0.036 mmol) of I_2, 17 mg (0.0198 mmol) of fullerene C_{60}, and 23 mg (0.019 mmol) of Zn 1,4-bis[*tert*-butoxymalonateoxypropyloxy]-6(7),10(11),14(15)-tris[*tert*-butyl]phthalocyanine in 100 mL of toluene was treated in ultrasound bath for 20 min. The flask was protected from light and flushed with Ar flow, 16.1 μL of DBU (17.3 mg, 0.114 mmol) was added, and the reaction mixture was stirred for 3 h at room temperature. The reaction was quenched by adding 2 mL of water, the solvent was removed under reduced pressure, and the crude product was purified by column chromatography on Silica 60 by using $CHCl_3$ as eluent. One main green fraction was collected to yield 23 mg (63%) of the dyad **ZnPc-C_{60}tb**; δ_H ($CDCl_3$/CD_3OD 50/1; Me_4Si) 9.45−6.82 (br m, 11 H, phthalo-*H*), 5.33−3.86 (br m, 8 H, $OCH_2CH_2CH_2O$), 1.97−1.34 (br m, 31 H, $OCH_2CH_2CH_2OH$, $C(CH_3)_3$); *m/z* (ESI-TOF) 1893.4506 (M+H^+, $C_{124}H_{68}N_8O_{10}Zn$ requires 1893.4429).

2.2. Experimental Methods. If not otherwise indicated, all the measurements were done both in polar and nonpolar solvents, that is, in benzonitrile (PhCN) and toluene, respectively. The solvents were of analytical grade and were used without further purification. Absorption spectra were measured with a Shimadzu UV-3600 spectrophotometer. Fluorescence spectra were recorded by using a Fluorolog 3 (SPEX Inc.) fluorimeter and corrected by using a correction spectrum supplied by the manufacturer.

Flash-photolysis method was used to study time-resolved absorption in microsecond time-scale. The experiments were carried out with a modified Luzchem laser flash system (mLFP111 prototype from Luzchem Co.) by using tunable Ti:sapphier laser (pumped by second harmonic of Nd:YAG laser) providing 10 ns pulses at 715 or 400 nm (second harmonic) for excitation. Excitation power density was 4−9 mJ cm^{-2}. A continuous Xe lamp (Oriel Simplesity Arc Source) was used to provide monitoring light, and the signal was recorded with a digitizing oscilloscope (Tektronix, TDS3032B, 300 MHz). The system was controlled with a PC computer. The samples were deoxygenated by nitrogen bubbling for 20 min prior to the measurements, and a nitrogen flow was maintained on the surface of the solution during the measurements. All measurements were carried out at room temperature.

Fluorescence decays of the samples in the nanosecond and subnanosecond time scales were measured by using a time-correlated single photon counting (TCSPC) system (PicoQuant GmBH) consisting of PicoHarp 300 controller and PDL 800-B driver. The samples were excited with the pulsed diode laser head LDH−P-C-405B at 404 nm, and fluorescence decays were measured at the wavelength of maximum emission (715−732 nm). The signals were detected with a micro channel plate photomultiplier tube (Hamamatsu R2809U). The time resolution of the TCSPC measurements was about 60−70 ps (fwhm of the instrument response function).

Pump−probe and up-conversion techniques for time-resolved absorption and fluorescence, respectively, were used to detect the fast processes with a time resolution shorter than 0.2 ps. The instrument and the used data analysis procedure have been described earlier.[43,47]

Differential pulse voltammetry (DPV) was used to estimate the energy of the CS state of the dyads in PhCN as described earlier.[44] Tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) was used as the supporting electrolyte, and the redox potentials were measured by using Ag/AgCl pseudoreference electrode. Ferrocene was used as an internal reference, and the measurements were done in nitrogen flow.

The phosphorescence spectra were measured in 2-methyltetrahydrofuran/ethyl iodide (1:1) at 77 K by using a Cosmo System LVU-200S spectrometer for excitation at 700 nm. A photomultiplier (Hamamatsu R5509−72) was used to detect emission in the near-infrared region. The spectra were measured in a quartz tube (2 mm i.d.) in liquid N_2 dewar.

In the electron spin resonance (ESR) measurements, argon-saturated sample solutions at 123 K were irradiated with a high-pressure mercury lamp (USH-1005D) through a water filter focused on the sample cell in the ESR cavity. The ESR spectra were recorded with a JEOL X-band spectrometer (JES-RE1XE) with a quartz ESR tube (4.5 mm i.d.). The magnitude of the modulation was chosen to optimize the resolution and the signal-to-noise ratio of the observed spectra. The *g* values were calibrated by using a Mn^{2+} marker. PhCN used in the ESR measurements was purified by successive distillation over P_2O_5.[48]

3. Results and Discussion

The steady-state absorption spectrum of **H_2Pc-C_{60}tb** (Figure 1a) is similar to the spectrum reported for **H_2Pc-C_{60}ee** earlier.[24] The spectrum of **ZnPc-C_{60}tb** (Figure 1b) differs from its free-base analogue particularly in the Q-band region: as for other

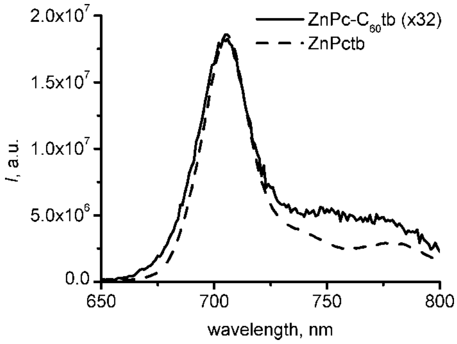


Figure 2. Fluorescence spectra of **ZnPc-C$_{60}$tb** and **ZnPctb** in toluene excited at 625 nm. The spectrum of the dyad has been multiplied for comparison as indicated in the figure.

zinc phthalocyanine compounds, the maximum is a sharp peak compared to the wider double-peak of free-base phthalocyanines.[22,24,49] The difference between Zn and free-base compounds is evident also from the molar absorptivities, which are roughly two times higher at the Q-band maxima for the Zn compounds. The slightly lower molar absorptivities of the dyads compared to the references at the Q bands indicate a weak interaction of the phthalocyanine and fullerene chromophores in the dyads.

Quenching of phthalocyanine emission is very efficient for both dyads. Emission spectra of **ZnPc-C$_{60}$tb** and the corresponding reference in toluene are given in Figure 2, where the spectrum of the dyad has been multiplied by 32 for comparison. Similarly, the emission of **H$_2$Pc-C$_{60}$tb** in toluene is roughly 140 times weaker compared to that of **H$_2$Pctb**. In PhCN, quenching is more efficient for both dyads (1800 times and 340 times for **H$_2$Pc-C$_{60}$tb** and **ZnPc-C$_{60}$tb**, respectively, compared to corresponding references), indicating that ET from phthalocyanine to fullerene may be the cause of the quenching. The exciplex emission typically seen as a distinct band for similar porphyrin-fullerene dyads is not seen as clearly for the phthalocyanine-fullerene dyads. Still, the dyads **H$_2$Pc-C$_{60}$tb** and **ZnPc-C$_{60}$tb** (Figure 2) show stronger emission around 725−800 nm compared to the reference compounds **H$_2$Pctb** and **ZnPctb**, and the emission is more pronounced in toluene than in PhCN. Such a dependence on the solvent polarity is characteristic for exciplex emission.[50] Reasons for the relatively weak exciplex emission of the phthalocyanine-fullerene dyads will be discussed in the context of fluorescence decays in the following section.

3.1. Fluorescence Decay. Time-resolved fluorescence measurements with the up-conversion method were done with photoexcitation of the samples at 420 nm, promoting the phthalocyanine moiety of the dyad to its second excited singlet state. The decay curves were detected at 710 and at 720−730 nm for **ZnPc-C$_{60}$tb** and **H$_2$Pc-C$_{60}$tb**, respectively; that is, emission decays of the phthalocyanine first excited singlet state ^{1}Pc*-C$_{60}$ were monitored (**ZnPc-C$_{60}$tb** in toluene in Figure 3). Also, C$_{60}$ emits around this wavelength region, but because of its considerably lower absorbance at the excitation wavelength and lower fluorescence quantum yield compared to Pc, its contribution to the decay can be neglected.[23] The measurements were repeated with different time scales to determine lifetimes of different components accurately.

For **ZnPc-C$_{60}$tb** in toluene, altogether three decay components were obtained from fitting the results in the two measured time scales. The longest-living component seen in the longer time scale of Figure 3b is weak in amplitude compared to the shorter components and can be ascribed to a small amount of Zn phthalocyanine impurity also based on its long lifetime (too long to be accurate with the measured time scale). In fact, this minor component was detected also in measurements of fluorescence decay with the TCSPC method, and its lifetime of 3 ns corresponds well to the lifetime measured for **ZnPctb** (2.3 ns). Thus, the decay of ^{1}Pc*-C$_{60}$ in the dyad **ZnPc-C$_{60}$tb** is biexponential as was the case for the other dyads of this series of compounds reported earlier.[24] Lifetimes and amplitudes of the two components are presented in Table 1. The faster component has 1.2 times higher amplitude compared to the slower one. In PhCN, the faster component is 1.6 times stronger than the slower component, and the corresponding lifetimes are somewhat shorter than the lifetimes in toluene. Similar decays were detected for **H$_2$Pc-C$_{60}$tb** at 720 and at 730 nm in toluene and PhCN, respectively. As can be seen in Table 1, the fast components have similar lifetimes and relative amplitudes compared to the ones obtained for **ZnPc-C$_{60}$tb**, but in PhCN, the faster component has higher relative intensity compared to that of **ZnPc-C$_{60}$tb**.

Explanation for the two decay components can be an equilibrium between ^{1}Pc*-C$_{60}$ and the intramolecular exciplex (Pc-C$_{60}$)*, which is a highly probable intermediate in this class of compounds as proved for the phytochlorin- and porphyrin-fullerene dyads studied previously.[11,13,39,43–46] For the porphyrin-fullerene dyads, the exciplex shows characteristic emission in steady-state measurements, especially in nonpolar solvents. Guldi et al. have reported on charge-transfer (CT) emission also for a Zn phthalocyanine-fullerene dyad.[23] The steady-state exciplex or CT emission detected for the double-linked phthalocyanine-fullerene compounds studied here is considerably weaker than that of similar porphyrin-fullerene dyads.[39] The reason for this may be that the CS state is formed rather rapidly in the double-linked phthalocyanine-fullerene dyads even in nonpolar medium, quenching the exciplex emission efficiently. For the porphyrin-fullerene dyads measured in toluene, the singlet excited state of porphyrin and the exciplex had lifetimes in the order of 0.1 ps and 1 ns, respectively.[39] Because of the very different lifetimes of the two emitting states, the steady-state emission spectrum showed weak traces of the porphyrin singlet excited state emission and a relatively strong exciplex emission band. For the phthalocyanine-fullerene dyads, the singlet excited state and the exciplex have lifetimes of the same order of magnitude (see Table 1). The relatively short lifetimes of both states are consistent with the weak steady-state emission.

Another reason for not seeing the clear exciplex emission can be the overlapping of the fluorescence spectra of ^{1}Pc*-C$_{60}$ and (Pc-C$_{60}$)*. The exciplex state energy is expected to be slightly lower than that of the locally excited singlet states ^{1}Pc*-C$_{60}$ and Pc-^{1}C$_{60}$*. Energies, E_{ps}, of ^{1}Pc*-C$_{60}$ (Table 2) and Pc-^{1}C$_{60}$* (1.75 eV for pristine C$_{60}$ in toluene)[51] are close to each other, and therefore, the exciplex energy may also have a value corresponding to 720−730 nm. However, a distinctive feature of the exciplex is a gradual shift of electron density, which results in a relatively large Stokes shift of the emission maximum. This shift can be quantitatively expressed by the solvent reorganization energy λ_s[39]

$$\nu^{\mathrm{a}}_{\max} - \nu^{\mathrm{e}}_{\max} = \frac{2\lambda_{\mathrm{s}}}{h} \tag{1}$$

where $\nu^{\mathrm{a}}_{\max}$ and $\nu^{\mathrm{e}}_{\max}$ are the maxima of the CT absorption and exciplex emission and h is the Planck constant. On the basis of earlier studies on the double-linked porphyrin-fullerene dyads, one can estimate that $\lambda_s \approx 0.1$ eV,[39] which results in the exciplex emission maximum being at roughly 800 nm, if one assumes that the CT absorption overlaps with the phthalocyanine Q-band

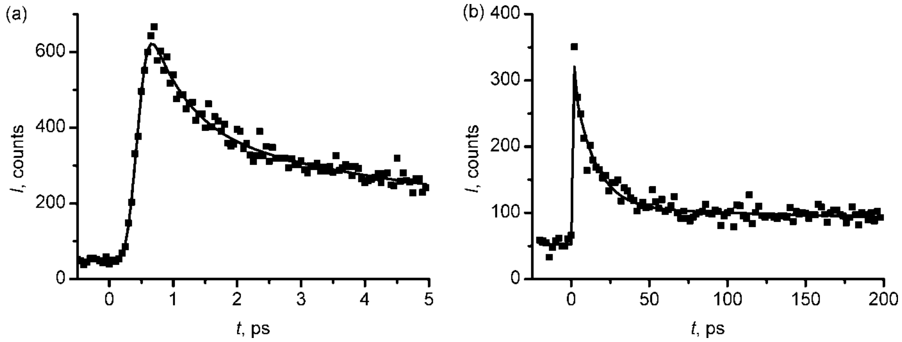


Figure 3. Fluorescence decay of **ZnPc-C_{60}tb** in toluene in (a) 5 ps and (b) 200 ps time scales.

TABLE 1: Lifetimes τ and Amplitudes a of the Fast Decay Components Obtained from the Fitted Up-Conversion Results

solvent	τ_1 (ps)	a_1	τ_2 (ps)	a_2
		H_2Pc-C_{60}tb		
toluene	0.28 ± 0.10	732 ± 7	6.0 ± 1.1	552 ± 2
PhCN	0.41 ± 0.08	792 ± 5	4.8 ± 1.0	351 ± 2
		ZnPc-C_{60}tb		
toluene	0.6 ± 0.2	413 ± 4	9 ± 4	341 ± 2
PhCN	0.44 ± 0.13	609 ± 5	4.7 ± 1.2	375 ± 2

around 720 nm. Thus, the emission decay monitored at 710−720 nm is mainly the emission of ^{1}Pc*-C_{60}, and the contribution of the (Pc-C_{60})* emission is largely negligible.

Further evidence of the exciplex intermediate was obtained in up-conversion measurements of **H_2Pc-C_{60}tb** in toluene at 740 nm, that is, at the red shoulder of the Pc emission band, where the (Pc-C_{60})* emission may overlap with that of ^{1}Pc*-C_{60}. A different time profile of the fluorescence decay was detected at this wavelength compared to the decay at 720 nm (Figure 4). The two decays can be fitted together, leading to lifetimes of 0.3 and 5.9 ps. As can be seen in Figure 4, the relative amplitudes of the two components are different at the two wavelengths: at 740 nm, the faster component is clearly weaker. This supports the idea of ^{1}Pc*-C_{60} and (Pc-C_{60})* emissions overlapping at 740 nm; that is, at 720 nm, the major emitting species is ^{1}Pc*-C_{60}, but at 740 nm, (Pc-C_{60})* contributes significantly to the emission.

An alternative cause of the biexponential emission decay is the existence of two dyad conformations with different distances between the donor and acceptor, resulting in two rate constants for the ET reaction from ^{1}Pc*-C_{60} to $Pc^{\bullet+}$-$C_{60}^{\bullet-}$. However, this alternative is not supported by the wavelength-dependent fluorescence decay discussed above: if the reason for the two decay components were two different conformations, the ratio of the component amplitudes should be the same at all wavelengths, because a similar emission spectrum is expected for different conformers. Further evidence that rules out this alternative explanation of the biexponential decay was obtained from the pump−probe results as will be discussed in the following section.

3.2. Transient Absorption. ***Pump−Probe.*** Formation of the CS state was seen clearly in both polar and nonpolar solvent for both dyads in the pump−probe measurements (Figure 5 for **ZnPc-C_{60}tb** in toluene as an example), where the samples were excited at 420 nm. The decay component spectra of Figure 5 consist of amplitudes of the components obtained in global exponential fitting of the transient absorption decay curves at different wavelengths. Thus, the number of the components should represent the number of transients in the reaction. In this case, there are two components indicating formation of the radical ion pair or the CS state $Pc^{\bullet+}$-$C_{60}^{\bullet-}$ from the first excited singlet state ^{1}Pc*-C_{60} and decay of $Pc^{\bullet+}$-$C_{60}^{\bullet-}$. The CS state can be identified in the NIR region of the spectrum, where characteristic absorption band of phthalocyanine cation appears around 850 nm. The band is broadened compared to the band of the free radical cation of phthalocyanine[52] because of the interaction of the phthalocyanine cation with the fullerene anion in the dyad.[23,24] As reported earlier for doubly linked porphyrin-fullerene dyads[39] and for the other phthalocyanine-fullerene dyads of this series of compounds,[24] the formation of the doubly linked C_{60} anion gives rise to absorption in a broad spectral range, 900−1100 nm, instead of the well-defined band of pristine C_{60} anion at 1060 nm.[53] Absorption changes similar to those of **ZnPc-C_{60}tb** were detected for **H_2Pc-C_{60}tb**, but the phthalocyanine cation band was seen around 900 nm, as expected on the basis of previously reported free-base phthalocyanine compounds.[23,24]

The second excited singlet state of phthalocyanine (the initially generated excited state in the experiment) could not be observed in the measurement because of its extremely fast decay to the first excited singlet state. Furthermore, the exciplex state (Pc-C_{60})* was not resolved in the global fitting of the pump−probe results. Two fast components were seen in the decay of ^{1}Pc*-C_{60} emission (up-conversion measurements) indicating an equilibrium between ^{1}Pc*-C_{60} and (Pc-C_{60})*. Both of these components should be seen in pump−probe, too, but adding a third exponent to the global fitting does not improve the fit quality of the pump−probe measurements. However, if the NIR region of the spectrum is fitted separately, using triexponential fitting for **H_2Pc-C_{60}tb** in both toluene and PhCN (Figure 6) enhances the sigma value of the fit by 10% compared to that of the biexponential fitting. Adding the third exponent reveals two fast components with lifetimes (0.65 and 4.7 ps in PhCN) in excellent agreement with the lifetimes obtained from up-conversion measurements (0.41 and 4.8 ps). Thus, also the pump−probe measurements provide strong proof of an intermediate state in the ET reaction path from ^{1}Pc*-C_{60} to $Pc^{\bullet+}$-$C_{60}^{\bullet-}$, that is, an exciplex (Pc-C_{60})*.

A triexponential fitting can be used also for **ZnPc-C_{60}tb** in the NIR region, and the lifetimes obtained for the fast components are in good agreement with the up-conversion results. However, adding the third exponent does not improve the quality of the fit as much as it does for **H_2Pc-C_{60}tb**. This is probably because the signal in the NIR region was weaker for **ZnPc-C_{60}tb** because of lower concentration of the dyad. It should be noted that the up-conversion measurements give more accurate results than the pump−probe method, because in the up-conversion, it is possible to follow distinctively the decay of a specific state, that is, ^{1}Pc*-C_{60}. In the up-conversion measurements, the biexponential decay of ^{1}Pc*-C_{60} was clearly

TABLE 2: Rate Constants, k, and State Energies, E, of the ET Reaction[a]

solvent	E_{ps} (eV)	k_{psx}/k_{xps} (10^9 s^{-1})	E_x (eV)	k_{xcs} (10^9 s^{-1})	E_{cs} (eV)	k_{csg} (10^9 s^{-1})	E_{pt} (eV)
				H$_2$Pc-C$_{60}$ee			
toluene	1.72	[b]	[b]	[b]		0.1−0.8[c]	1.32[d]
PhCN	1.70	900/320	1.67	110	1.22	12	
				H$_2$Pc-C$_{60}$tb			
toluene	1.72	2110/1350	1.71	280		0.1−0.8[c]	1.32[b]
PhCN	1.70	1800/620	1.67	290	1.24	14	
				ZnPc-C$_{60}$tb			
toluene	1.77	960/620	1.76	190		0.8	1.29[d]
PhCN	1.77	1620/770	1.75	310	1.16	33	

[a] Subscript notations: ps, phthalocyanine first excited singlet state; x, exciplex; cs, CS state; g, ground state; and pt, phthalocyanine triplet state. For example, k_{psx} is the rate constant for transition from the phthalocyanine first excited singlet state to the exciplex. [b] Could not be determined accurately because of poor solubility of **H$_2$Pc-C$_{60}$ee** in toluene. [c] Could not be determined accurately because the process falls in the time gap of the two transient absorption measurement systems used in this study. [d] Measured in 2-methyltetrahydrofuran/ethyl iodide (1:1).

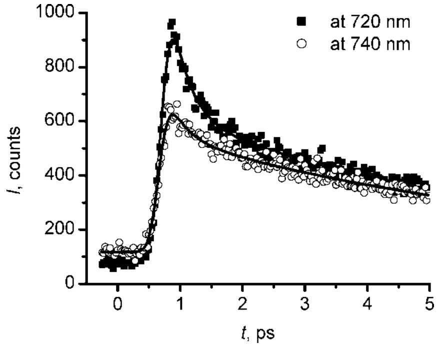


Figure 4. Fluorescence decay of **H$_2$Pc-C$_{60}$tb** in toluene at 720 nm and at 740 nm.

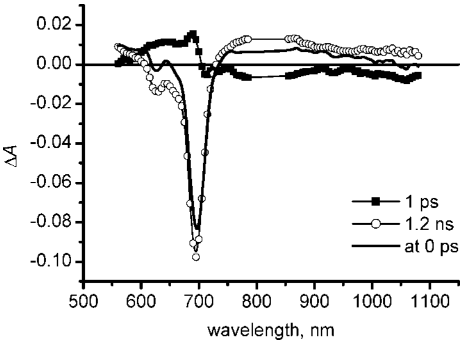


Figure 5. Absorption decay component spectra and calculated time-resolved spectrum at 0 delay time for **ZnPc-C$_{60}$tb** in toluene.

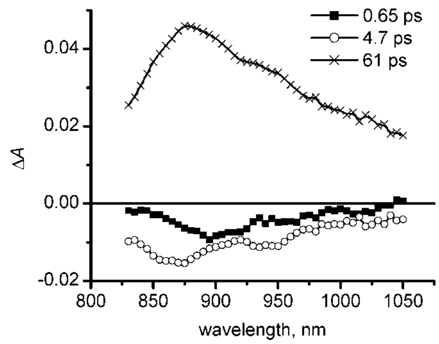


Figure 6. Absorption decay component spectra obtained from separate 3-exponential fitting of the NIR region for **H$_2$Pc-C$_{60}$tb** in PhCN.

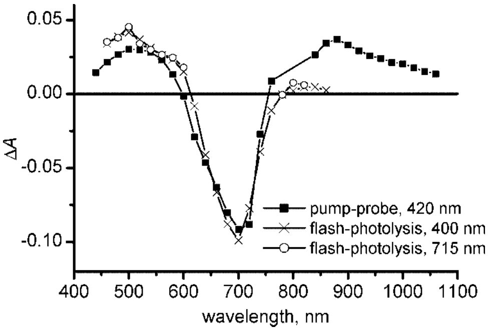


Figure 7. Comparison of the final decay component spectra from pump−probe and flash-photolysis measurements of **H$_2$Pc-C$_{60}$tb** in toluene. The excitation wavelengths of each measurement are given in the figure. The flash-photolysis spectra have been multiplied for comparison by 6 and by 12 with excitation at 400 and 715 nm, respectively. Because of scattering, it was not possible to measure flash-photolysis in the range 620−760 nm when exciting at 715 nm.

seen also for **ZnPc-C$_{60}$tb** even though it is not that evident from the pump−probe measurements.

As was mentioned above, the pump−probe results give evidence that supports the exciplex intermediate over the alternative explanation of the biexponential emission decay, that is, the existence of two conformers of the dyad. If there were two conformers with different distances between the phthalocyanine and fullerene moieties, we should see biexponential formation of the CS state absorption in the NIR wavelength range with equal ratio of the amplitudes of the two fast components (0.65 and 4.7 ps in Figure 6) at all wavelengths. As can be seen in Figure 6, the ratio of amplitudes is different at different wavelengths, indicating that the components correspond to the formation of two different intermediate states following $^1\mathrm{Pc}^*$-C_{60}, that is, first the exciplex $(\mathrm{Pc}\text{-}\mathrm{C}_{60})^*$ and finally the CS state $\mathrm{Pc}^{\bullet+}$-$\mathrm{C}_{60}^{\bullet-}$.

Flash-Photolysis. Flash-photolysis measurements were carried out with two excitation wavelengths: at 715 nm, only the phthalocyanine chromophore of the molecule absorbs, but at 400 nm, fullerene also has significant absorption. Time-resolved spectra of the reference samples showed that for both **H$_2$Pcee** and **ZnPctb**, the triplet excited state has a broad absorption band around 500 nm and very weak or no absorption at all above 800 nm, as has been reported for free-base and Zn phthalocyanines in the literature.[23,52]

The aim of the flash-photolysis measurements was to resolve the longer-living components seen for the samples in toluene in pump−probe, that is, to determine the accurate lifetime of the CS state in toluene. An estimation of the CS state lifetime from the pump−probe results was 2.5 ns for **H$_2$Pc-C$_{60}$tb** and 1.2 ns for **ZnPc-C$_{60}$tb**. Such fast components were not seen in the flash-photolysis measurements, because the lifetime of the CS state in toluene seems to fall in the time gap of the two instruments.[54]

However, clearly, another transition occurs after charge separation in toluene because a longer-living transient state is

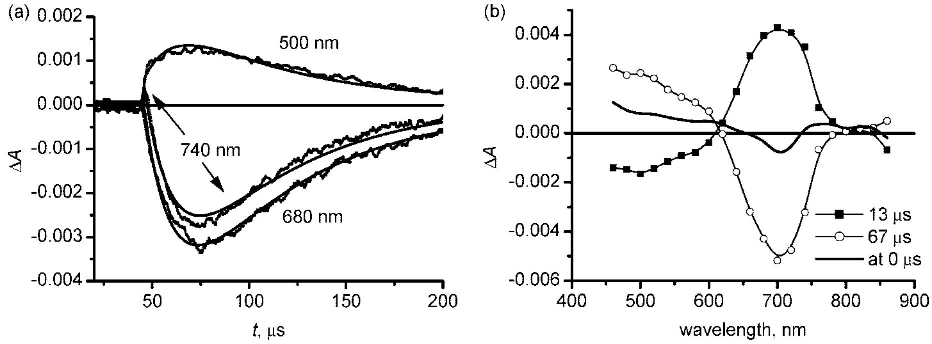


Figure 8. Flash-photolysis measurements of **H_2Pc-C_{60}tb** in PhCN with excitation at 400 nm. (a) Transient absorption decay curves and biexponential global fitting at selected wavelengths. (b) Decay component spectra and calculated time-resolved spectrum at 0 delay time.

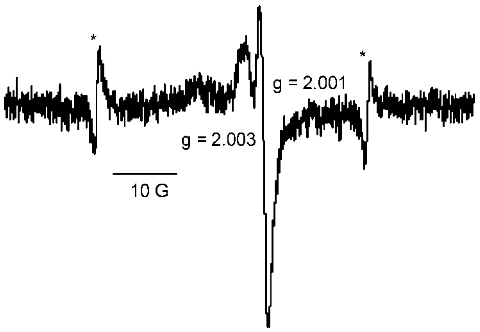


Figure 9. ESR spectrum of 0.2 mM **H_2Pc-C_{60}ee** in toluene photo-irradiated with a high-pressure mercury lamp, measured at 123 K. The asterisk denotes the signal from the Mn^{2+} marker.

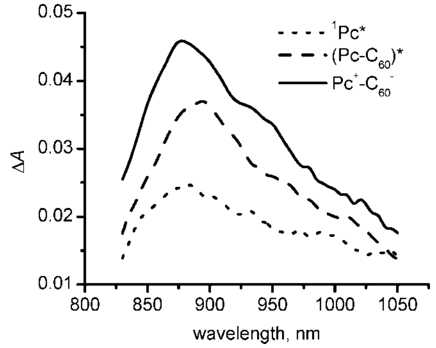
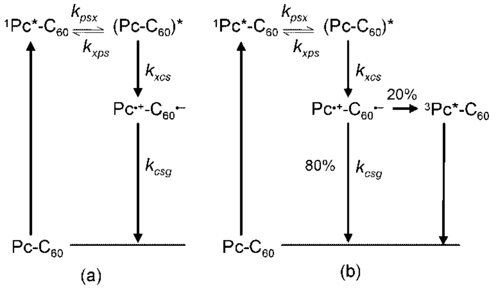


Figure 10. Calculated transient absorption spectra of the states involved in the ET reaction for **H_2Pc-C_{60}tb** in PhCN.

SCHEME 1: ET Reaction Schemes of Photoinduced Pc-C_{60} Dyads (a) in PhCN and (b) in Toluene



resolved for both dyads in the flash-photolysis measurements. The spectra obtained for the dyads are similar to the triplet state spectra detected for the corresponding references, and as seen for **H_2Pc-C_{60}tb** in Figure 7, they differ from the spectra of the CS state measured with pump−probe. Thus, it seems that ^{3}Pc*-C_{60} is formed from $Pc^{•+}$-$C_{60}^{•-}$ for both dyads in toluene. Previously, Guldi et al. have observed phthalocyanine triplet state formation from the CS state in high yield for phthalocyanine-fullerene dyads in nonpolar solvents.[23] By comparing the signal intensities at 500 nm, it can be estimated that relative to the reference phthalocyanine compounds **H_2Pcee** and **ZnPctb**, the phthalocyanine triplet state is formed 4.5 and 6.1 times less efficiently in the **H_2Pc-C_{60}tb** and **ZnPc-C_{60}tb** dyads, respectively. This indicates that for the double-linked dyads, the main pathway of BET is directly to the ground state, and only 15−20% of the molecules relax via ^{3}Pc*-C_{60}.

On the basis of the results of the pump−probe measurements, no signal was expected for the dyad samples in PhCN, because the CS state was seen to relax in less than 100 ps, and no longer-living components were detected. In fact, this was the case when the samples were excited at 715 nm. However, a clear signal was recorded for both **H_2Pc-C_{60}tb** and **ZnPc-C_{60}tb** in PhCN when exciting at 400 nm (see Figure 8 for **H_2Pc-C_{60}tb**). This signal seems to arise from the excited fullerene chromophores and was not seen in the pump−probe measurements because the excitation was at 420 nm, where fullerene does not absorb as much as at 400 nm.[55]

Figure 8a presents three transient absorption decay curves at selected wavelengths and the biexponential global fit of the data. In the decay component spectra of Figure 8b, the amplitudes of the two components of the fitting are plotted at each measured wavelength. The absorption curve at 500 nm clearly shows a slow increase of absorption after the excitation. Corresponding to this, the decay component spectrum of 13 µs shows formation (negative amplitude) of a wide band around 500 nm. Simultaneously, at 740 nm, the initial absorption decays and in the decay component spectrum of 13 µs, this is seen as positive amplitude. These changes can be ascribed to the formation of ^{3}Pc*-C_{60} and decay of Pc-$^3C_{60}$*, that is, intramolecular triplet−triplet energy transfer occurring after excitation to Pc-$^1C_{60}$*. Intersystem crossing from Pc-$^1C_{60}$* to Pc-$^3C_{60}$* is too fast for the instrument and was not resolved in the measurements. Bleaching of the phthalocyanine Q-band seen in the absorption time profile at 680 nm and in the decay component spectra around 700 nm is slow compared to the bleaching associated with triplet formation in the reference compound **H_2Pcee**. Also, this confirms that the formation of ^{3}Pc*-C_{60} occurs via Pc-$^3C_{60}$*. It is rather surprising that Pc-$^3C_{60}$* can be seen for the dyad, because for similar porphyrin-fullerene dyads, efficient ET from $^1C_{60}$* has been observed.[39] Because the slow intersystem crossing can be detected, the competing ET process via Pc-$^1C_{60}$* has to be very inefficient.

It is not possible to assign the exact absorption maximum of Pc-$^3C_{60}$* from the decay component spectra because its decay overlaps with the bleaching of the phthalocyanine Q-band occurring simultaneously and because the differential absorption of ^{3}Pc*-C_{60} is much higher that that of Pc-$^3C_{60}$*. In principle, the calculated time-resolved spectrum at 0 delay plotted in Figure 8b should represent absorption of Pc-$^3C_{60}$*, because it is the first detectable state. Even though this spectrum is quite weak, it shows absorption around 750 nm, in agreement with $^3C_{60}$* absorption reported for pristine C_{60} (720−750 nm).[52,56] The triplet−triplet energy transfer from fullerene to phthalocyanine was seen also for **ZnPc-C_{60}tb**.

3.3. ESR. The formation of the CS state $Pc^{\bullet+}$-$C_{60}^{\bullet-}$ was also confirmed by ESR measurements of **H_2Pc-C_{60}ee** in both PhCN and toluene (5×10^{-4} and 2×10^{-4} mol dm^{-3}, respectively) at low temperature. The resulting spectrum obtained under photoirradiation of **H_2Pc-C_{60}ee** in toluene at 123 K is shown in Figure 9. The ESR spectrum consists of two characteristic signal peaks, one of which is attributable to fullerene radical anion derivative ($g = 2.001$)[57] and the other to phthalocyanine radical cation ($g = 2.003$).[58] This proves that the ET reaction takes place also in nonpolar solvent as was seen in the transient absorption measurements. The rather weak ESR intensity in Figure 10 is consistent with the short CS lifetime at room temperature (vide supra), which may become longer at 123 K. Upon cutting off the light, the ESR signal disappeared. The decay rate was too fast to be determined at 123 K with our ESR equipment, and the ESR signal was only observed under the steady-state photoirradiation conditions. A similar spectrum was obtained for the dyad in PhCN.

3.4. Differential Pulse Voltammetry (DPV). The first reduction and oxidation potential of fullerene and phthalocyanine, respectively, were determined with the DPV measurements of the dyads in PhCN (see Supporting Information Figure S1). Ignoring the Coulombic interactions, the CS state energies of the dyads, E_{cs}, can be determined from the difference between these potentials. The calculated E_{cs} values (Table 2) are in agreement with the values reported earlier for the compounds in this series of phthalocyanine-fullerene dyads.[24]

3.5. Phosphorescence. The phosphorescence measurements were carried out to determine whether the triplet state energies of the phthalocyanines, E_{pt}, were lower than the CS state energies, that is, whether the transition from $Pc^{\bullet+}$-$C_{60}^{\bullet-}$ to ^{3}Pc*-C_{60}, seen in the transient absorption measurements in toluene, was energetically favorable. It can be seen from the phosphorescence spectra of the reference compounds (Supporting Information Figure S2) that E_{pt} is exactly the same (940 nm = 1.32 eV) for **H_2Pctb** and **H_2Pcee** and slightly lower for **ZnPctb** (960 nm = 1.29 eV), agreeing with previously reported values for phthalocyanines.[23,26,59] Compared to the CS state energies of the dyads (Table 2), the triplet states lay 0.08−0.13 eV higher. However, the CS state energies were determined in PhCN, and it is expected that the CS state rests slightly higher in nonpolar toluene, decreasing the difference between $Pc^{\bullet+}$-$C_{60}^{\bullet-}$ and ^{3}Pc*-C_{60}. By taking this into account, the transition from $Pc^{\bullet+}$-$C_{60}^{\bullet-}$ to ^{3}Pc*-C_{60} is quite reasonable for all three dyads in nonpolar solvent. No phosphorescence signal could be detected for the dyads, as was expected by taking into account that the majority of the molecules do not reach the triplet state but relax directly to the ground state from the CS state. Furthermore, by comparing the determined energy of ^{3}Pc* to the reported energy of $^3C_{60}$*,[60] the triplet−triplet energy transfer reaction seen in PhCN after excitation of fullerene is energetically favorable.

4. Conclusions

By considering the equilibrium between ^{1}Pc*-C_{60} and (Pc-C_{60})*, it is possible to calculate the intrinsic rate constants k_{psx}, k_{xps}, and k_{xcs} (Scheme 1) from the experimental lifetimes (τ_1, τ_2) and amplitudes (a_1, a_2) of the up-conversion measurements as[12,61]

$$\begin{aligned} k_{psx} &= \frac{r\lambda_1 + \lambda_2}{-r - 1} \\ k_{xcs} &= \lambda_1 \lambda_2 k_{psx}^{-1} \\ k_{xps} &= -\lambda_1 - \lambda_2 - k_{psx} - k_{xcs} \end{aligned} \qquad (2)$$

where $r = a_1/a_2$, $\lambda_1 = -1/\tau_1$, and $\lambda_2 = -1/\tau_2$. The calculated rate constants are given in Table 2. Furthermore, by knowing the rate constants of the equilibrium, it is possible to estimate the energy difference of the two states in equilibrium as

$$\Delta E_{psx} = k_B T \ln\left(\frac{k_{psx}}{k_{xps}}\right) \qquad (3)$$

and from this, the exciplex state energy, E_x, can be determined (Table 2).

Because of the equilibrium, there is no time delay at which point the calculated transient absorption spectrum would represent the absorption spectrum of the exciplex purely. However, an expression for calculating the exciplex spectrum by starting from the reaction rate constants determined above has been derived earlier for similar schemes concerning porphyrin- and phytochlorin-fullerene dyads.[12,61] The real exciplex absorption, A_x, can be calculated from absorption of ^{1}Pc*-C_{60}, A_{ps},[62] by using the amplitudes ΔA_1 and ΔA_2 of the first two components of the fitting as

$$A_x = \frac{1}{c_3}[A_{ps} c_3 - \Delta A_1 (c_2 + c_3) + \Delta A_2 (c_1 - c_3)] \qquad (4)$$

where

$$\begin{aligned} c_1 &= \frac{(k_s - k_{xps} - k_{xcs} + k_{psx})}{2k_s} \\ c_2 &= \frac{(k_s + k_{xps} + k_{xcs} - k_{psx})}{2k_s} \\ c_3 &= \frac{k_{psx}}{k_s} \\ k_s &= [(k_{psx} + k_{xcs} + k_{xps})^2 - 4k_{psx}k_{xcs}]^{1/2} \end{aligned} \qquad (5)$$

Transient absorption spectrum of the exciplex in Figure 10 has been calculated with eq 4. Because the very rapid internal conversion from the second excited singlet state to ^{1}Pc*-C_{60} was not resolved in the measurements, the calculated time-resolved spectrum at 0 delay time is the spectrum of ^{1}Pc*-C_{60}. The spectrum of the last component of the fitting can be attributed as the spectrum of the CS state. The spectral similarity of the exciplex and the CS state is in good agreement with the reports of exciplex and CS state spectra of porphyrin- and phytochlorin-fullerene dyads.[39,61]

Scheme 1a,b can be concluded from the experimental results summarized above, and the same schemes apply to both **H_2Pc-C_{60}tb** and **ZnPc-C_{60}tb**, with only minor differences in the exact energy levels and lifetimes of the states. After starting the reaction by excitation of phthalocyanine to ^{1}Pc*-C_{60}, the dyads undergo rapid ET to yield $Pc^{\bullet+}$-$C_{60}^{\bullet-}$ via an intramolecular exciplex (Pc-C_{60})*. In polar solvent, BET occurs in less than 100 ps, returning the molecule to its ground state. In nonpolar solvent, the main relaxation pathway of the CS state is directly to the ground state, but roughly 20% of the molecules relax via ^{3}Pc*-C_{60}. On the other hand, exciting the fullerene moiety of the dyads did not result in ET but in intersystem crossing from Pc-$^1C_{60}$* to Pc-$^3C_{60}$*, followed by intramolecular triplet−triplet energy transfer to ^{3}Pc*-C_{60}, and finally relaxation to the ground state.

Energies and rate constants associated with Scheme 1a,b are given in Table 2. The schemes are now otherwise complete, but to determine the accurate rate constant for BET in toluene, equipment with appropriate measuring time range needs to be used.

Acknowledgment. The authors are grateful to the National Technology Agency of Finland and Finnish Academy for financial support.

Supporting Information Available: Differential pulse voltammograms of **H_2Pc-C_{60}tb** and **ZnPc-C_{60}tb** in PhCN and phosphorescence spectra of **H_2Pcee**, **H_2Pctb**, and **ZnPctb** in 2-methyltetrahydrofuran/ethyl iodide (1:1). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Imahori, H.; Hagiwara, K.; Aoki, M.; Akiyama, T.; Taniguchi, S.; Okada, T.; Shirakawa, M.; Sakata, Y. *J. Am. Chem. Soc.* **1996**, *118*, 11771–11782.

(2) 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.

(3) Dietel, E.; Hirsch, A.; Zhou, J.; Rieker, A. *J. Chem. Soc., Perkin Trans. 2* **1998**, *6*, 1357–1364.

(4) Yamada, K.; Imahori, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y. *Chem. Lett.* **1999**, *895*, 896.

(5) Imahori, H.; Sakata, Y. *Eur. J. Org. Chem.* **1999**, 2445–2457.

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

(7) Fukuzumi, S.; Imahori, H.; Yamada, H.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O.; Guldi, D. M. *J. Am. Chem. Soc.* **2001**, *123*, 2571–2575.

(8) 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.

(9) D'Souza, F.; Gadde, S.; Zandler, M. E.; Arkady, K.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. A* **2002**, *106*, 12393–12404.

(10) D'Souza, F.; Deviprasad, G. R.; Zandler, M. E.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O. *J. Phys. Chem. B* **2002**, *106*, 4952–4962.

(11) Imahori, H.; Tkachenko, N. V.; Vehmanen, V.; Tamaki, K.; Lemmetyinen, H.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 1750–1756.

(12) Kesti, T. J.; Tkachenko, N. V.; Vehmanen, V.; Yamada, H.; Imahori, H.; Fukuzumi, S.; Lemmetyinen, H. *J. Am. Chem. Soc.* **2002**, *124*, 8067–8077.

(13) Tkachenko, N. V.; Lemmetyinen, H.; Sonoda, J.; Ohkubo, K.; Sato, T.; Imahori, H.; Fukuzumi, S. *J. Phys. Chem. A* **2003**, *107*, 8834–8844.

(14) Linssen, T. G.; Dürr, K.; Hanack, M.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1995**, *103*, 104.

(15) Sastre, Á.; Gouloumis, A.; Vázquez, P.; Torres, T.; Doan, V.; Schwartz, B. J.; Wudl, F.; Echegoyen, L.; Rivera, J. *Org. Lett.* **1999**, *1*, 1807–1810.

(16) Zhu, P.; Wang, P.; Qiu, W.; Liu, Y.; Ye, C.; Fang, G.; Song, Y. *Appl. Phys. Lett.* **2001**, *78*, 1319–1321.

(17) Guldi, D. M.; Ramey, J.; Martinez-Diaz, M. V.; de la Escosura, A.; Torres, T.; Da Ros, T.; Prato, M. *Chem. Commun.* **2002**, *67*, 2774–2775.

(18) D'Souza, F.; Ito, O. *Coord. Chem. Rev.* **2005**, *249*, 1410–1422.

(19) Chen, Y.; El-Khouly, M. E.; Sasaki, M.; Araki, Y.; Ito, O. *Org. Lett.* **2005**, *7*, 1613–1616.

(20) Ballesteros, B.; de la Torre, G.; Torres, T.; Hug, G. L.; Rahman, G. M. A.; Guldi, D. M. *Tetrahedron* **2006**, *62*, 2097–2101.

(21) de la Escosura, A.; Martinez-Diaz, M. V.; Guldi, D. M.; Torres, T. *J. Am. Chem. Soc.* **2006**, *128*, 4112–4118.

(22) Gouloumis, A.; Liu, S.-G.; Sastre, Á.; Vázquez, P.; Echegoyen, L.; Torres, T. *Chem. Eur. J.* **2000**, *6*, 3600–3607.

(23) Guldi, D. M.; Zilbermann, I.; Gouloumis, A.; Vázquez, P.; Torres, T. *J. Phys. Chem. B* **2004**, *108*, 18485–18494.

(24) Isosomppi, M.; Tkachenko, N. V.; Efimov, A.; Vahasalo, H.; Jukola, J.; Vainiotalo, P.; Lemmetyinen, H. *Chem. Phys. Lett.* **2006**, *430*, 36–40.

(25) Liu, S.-G.; Liu, Y.-Q.; Xu, Y.; Jiang, X.-Z.; Zhu, D.-B. *Tetrahedron Lett.* **1998**, *39*, 4271–4274.

(26) Fukuzumi, S.; Ohkubo, K.; Ortiz, J.,.; Gutiérrez, A. M.; Fernández-Lázaro, F.; Sastre-Santos, Á. *Chem. Commun.* **2005**, 3814–3816.

(27) Murata, K.; Ito, S.; Takahashi, K.; Hoffman, B. M. *Appl. Phys. Lett.* **1996**, *68*, 427–429.

(28) Peumans, P.; Forrest, S. R. *Appl. Phys. Lett.* **2001**, *79*, 126–128.

(29) Gebeyehu, D.; Maennig, B.; Drechsel, J.; Leo, K.; Pfeiffer, M. *Sol. Energy Mater. Sol. Cells* **2003**, *79*, 81–92.

(30) Koeppe, R.; Sariciftci, N. S.; Troshin, P. A.; Lyubovskaya, R. N. *Appl. Phys. Lett.* **2005**, *87*, 2441021−3.

(31) Drechsel, J.; Männig, B.; Kozlowski, F.; Pfeiffer, M.; Leo, K.; Hoppe, H. *Appl. Phys. Lett.* **2005**, *86*, 244102/1−3.

(32) Suemori, K.; Miyata, T.; Yokoyama, M.; Hiramoto, M. *Appl. Phys. Lett.* **2005**, 063509/1−3.

(33) Loi, M. A.; Denk, P.; Hoppe, H.; Neugebauer, H.; Meissner, D.; Winder, C.; Brabec, C. J.; Sariciftci, N. S.; Gouloumis, A.; Vazquez, P.; Torres, T. *Synth. Met.* **2003**, *137*, 1491–1492.

(34) Neugebauer, H.; Loi, M. A.; Winder, C.; Sariciftci, N. S.; Cerullo, G.; Gouloumis, A.; Vazquez, P.; Torres, T. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 201–209.

(35) Hong, Z. R.; Maennig, B.; Lessmann, R.; Pfeiffer, M.; Leo, K. *Appl. Phys. Lett.* **2007**, *90*, 203505/1−3.

(36) Janssen, A. G. F.; Riedl, T.; Hamwi, S.; Johannes, H.-H.; Kowalsky, W. *Appl. Phys. Lett.* **2007**, *91*, 073519/1−3.

(37) Frey, W.; Klann, R.; Laermer, F.; Elsaesser, T.; Baumann, E.; Futscher, M.; Staab, H. A. *Chem. Phys. Lett.* **1992**, *190*, 567–573.

(38) Häberle, T.; Hirsch, J.; Pöllinger, F.; Heitele, H.; Michel-Beyerle, M. E.; Anders, C.; Döhling, A.; Krieger, C.; Ruckemann, A.; Staab, H. A. *J. Phys. Chem.* **1996**, *100*, 18269–18274.

(39) Chukharev, V.; Tkachenko, N. V.; Efimov, A.; Guldi, D. M.; Hirsch, A.; Scheloske, M.; Lemmetyinen, H. *J. Phys. Chem. B* **2004**, *108*, 16377–16385.

(40) Dietel, E.; Hirsch, A.; Eichhorn, E.; Rieker, A.; Hackbarth, S.; Roder, B. *Chem. Commun.* **1998**, 1981–1982.

(41) Schuster, D. I.; Cheng, P.; Wilson, S. R.; Prokhorenko, V.; Katterle, M.; Holzwarth, A. R.; Braslavsky, S. E.; Klihm, G.; Williams, R. M.; Luo, C. *J. Am. Chem. Soc* **1999**, *121*, 11599–11600.

(42) Schuster, D. I.; Cheng, P.; Jarowski, P. D.; Guldi, D. M.; Luo, C.; Echegoyen, L.; Pyo, S.; Holzwarth, A. R.; Braslavsky, S. E.; Williams, R. M.; Klihm, G. *J. Am. Chem. Soc.* **2004**, *126*, 7257–7270.

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

(44) Isosomppi, M.; Tkachenko, N. V.; Efimov, A.; Lemmetyinen, H. *J. Phys. Chem. A* **2005**, *109*, 4881–4890.

(45) Chukharev, V.; Tkachenko, N. V.; Efimov, A.; Lemmetyinen, H. *Chem. Phys. Lett.* **2005**, *411*, 501–505.

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

(47) Vehmanen, V.; Tkachenko, N. V.; Imahori, H.; Fukuzumi, S.; Lemmetyinen, H. *Spectrochim. Acta A* **2001**, *57*, 2229–2244.

(48) Armarego, W. L. F.; Chai, C. L. L. *Purification of Laboratory Chemicals*, 5th ed.; Butterworth-Heiemann: Oxford, 2003.

(49) Kameyama, K.; Satake, A.; Kobuke, Y. *Tetrahedron Lett.* **2004**, *45*, 7617–7620.

(50) Mattes, S. L.; Farid, S. *Science* **1984**, *226*, 917–921.

(51) Vail, S. A.; Schuster, D. I.; Guldi, D. M.; Isosomppi, M.; Tkachenko, N.; Lemmetyinen, H.; Palkar, A.; Echegoyen, L.; Chen, X.; Zhang, J. Z. H. *J. Phys. Chem. B* **2006**, *110*, 14155–14166.

(52) Nojiri, T.; Alam, M. M.; Konami, H.; Watanabe, A.; Ito, O. *J. Phys. Chem. A* **1997**, *101*, 7943–7947.

(53) Greaney, M. A.; Gorum, S. M. *J. Phys. Chem.* **1991**, *95*, 7142–7144.

(54) Up to 1.2 ns with pump−probe and from 10 ns with flash-photolysis.

(55) For example, comparing absorption spectra of ZnPc-C 60 tb and ZnPctb shows that absorption due to fullerene is 3.5 times higher at 400 nm than at 420 nm.

(56) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; McCauley, J. P.; Smith III, A. B.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075–6078.

(57) Fukuzumi, S.; Ohkubo, K.; Imahori, H.; Shao, J.; Ou, Z.; Zheng, G.; Chen, Y.; Pandey, R. K.; Fujitsuka, M.; Ito, O.; Kadish, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 10676–10683.

(58) Fu, Y.; Fu, G.; Lever, A. B. P. *Inorg. Chem.* **1994**, *33*, 1038–1044.

(59) Vincett, P. S.; Voigt, E. M.; Rieckhoff, K. E. *J. Chem. Phys.* **1971**, *55*, 4131–4140.

(60) Zeng, Y.; Biczok, L.; Linschitz, H. *J. Phys. Chem.* **1992**, *96*, 5237–5239.

(61) Vehmanen, V.; Tkachenko, N. V.; Efimov, A.; Damlin, P.; Ivaska, A.; Lemmetyinen, H. *J. Phys. Chem. A* **2002**, *106*, 8029–8038.

(62) A_{ps} is given by the spectrum at 0 delay time.

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