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Stabilization of Charge-Separated States in Phthalocyanine−Fullerene Ensembles through Supramolecular Donor−Acceptor Interactions

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Abstract: A novel ZnPc−C_{60} dyad (**3**), in which two photoactive units are brought together by a phenylenevinylene spacer has been synthesized. The synthetic strategy en route toward **3** involves a Heck reaction to attach 4-vinylbenzaldehyde to a monoiodophthalocyanine precursor, followed by standard cycloaddition of azomethine ylides (generated from the formylPc derivative and *N*-methylglycine) to one of the double bonds of C_{60}. Electrochemical studies reveal that in **3** the ZnPc is about 39 mV more difficult to oxidize than in the corresponding ZnPc reference, which points to appreciable electronic communication between ZnPc and C_{60} in the ground state. In the excited state, photoexcitation leads to the formation of a charge-separated $ZnPc^{•+}−C_{60}^{•−}$ state, for which a lifetime of 130 ns was determined in THF. Hetero-association between complementary Pcs (**1** and **2** or **3** and **2**), which carry different peripheral functionalities (i.e., either electron-donating alkoxy groups or electron-deficient alkylsulfonyl chains) was assessed by different techniques. They provided evidence for donor−acceptor 1:1 complex formation with a stability constant of ca. 10^5 M^{-1} in $CHCl_3$. Interestingly, hetero-association of ZnPc−C_{60} dyad **3** with an electron-deficient PdPc (**2**) allowed the construction of supramolecular triads, in which a substantial stabilization of the radical pair is seen relative to that of the covalently linked dyad ZnPc−C_{60} (**3**).

Introduction

Inspired by the natural photosynthetic systems, which rely on highly organized supramolecular assemblies,[1] donor−acceptor supramolecular systems have stimulated a growing interest in reaction center models and novel materials for photovoltaic applications − owing to their lower synthetic cost and extended charge separation lifetimes.[2]

As in nature, porphyrins are among the pigments most frequently employed as light-harvesting antenna.[3] They efficiently funnel the absorbed energy to an acceptor site, where energy conversion takes place. On the other hand, implementation of fullerenes as three-dimensional electron acceptors holds great promise due to the small reorganization energy in electron-transfer reactions. To this end, fullerenes have exerted noteworthy impact on the improvement of light-induced charge-separation.[4]

Phthalocyanines (Pcs)[5] are synthetic porphyrin analogues that exhibit particularly intense absorption in the red/near-infrared spectral region, where porphyrins fail to exhibit appreciable absorptions. Therefore, Pcs emerge as attractive molecular building blocks for the incorporation into donor−acceptor ensembles,[6] where they function as antennas with both a wider absorbing range of the solar terrestrial spectrum and higher fluorescence quantum yields compared with those of porphyrins.

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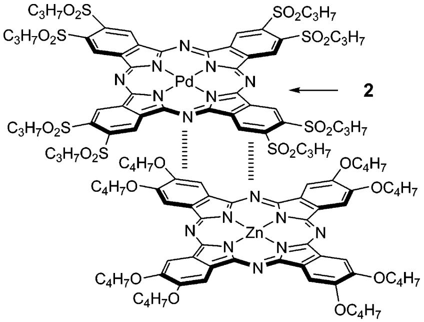

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Figure 1. Donor−acceptor supramolecular complex formed by Pcs **1** and **2**, differently peripherally substituted with donor and acceptor groups, respectively.

Despite the extensive study of supramolecular porphyrin−C_{60} systems,[7] only a few examples of phthalocyanine−C_{60} dyads have been reported, in which the two "active" units are linked by noncovalent interactions.[8]

When, however, focusing on structurally well-defined supramolecular triads or tetrads − formed by three or more photoactive entities − it renders increasingly complex to design suitable molecular building blocks. A simpler approach includes the self-assembly of covalently linked donor−acceptor dyads bearing adequate recognition motifs.

We have recently described a supramolecular assembly of phthalocyanines, which is driven by exceptionally strong donor−acceptor interactions ($K_a = 2 \times 10^7$ M^{-1} in $CHCl_3$) between electron-deficient and electron-rich Pcs (Figure 1) − realized through placing either electron-acceptor alkylsulfonyl groups or electron-donor alkoxy functionalities to the periphery of the macrocycle.[9]

Here, we report on the use of such donor−acceptor supramolecular recognition motif to construct photoactive phthalocyanine−C_{60} ensembles. A leading example, namely, supramolecular donor−acceptor triad **3**/**2**, is depicted in Figure 2. **3**/**2** experiences an appreciable stabilization of the radical ion pair state − formed by photoinduced electron transfer − in comparison to the covalent phthalocyanine−C_{60} analogue reported so far.[10]

Results and Discussion

Synthesis. The novel covalent ZnPc−C_{60} (**3**) was designed to form a stable donor-acceptor complex with a complementary Pc′ (**2**), that is, a Pc substituted with eight electron-accepting propylsulfonyl groups − see Figure 2. The synthesis of **3** was carried out in two steps, starting from the iodophthalocyanine precursor **4**, which was subjected to a Heck reaction with freshly prepared 4-vinylbenzaldehyde in the presence of Et_3N, $Bu_4N^+Br^-$ and a catalytic amount of $Pd(OAc)_2$, yielding 56% of the formylphthalocyanine derivative **5**. A subsequent Prato reaction with C_{60} and sarcosine in refluxing *o*-DCB, followed by purification by column chromatography on silica gel, gave the ZnPc−C_{60} (**3**) in 44% yield (Scheme 1). To eliminate traces of the bis(adduct) (*i.e.*, byproducts), an additional purification by gel permeation chromatography (Bio Beads SX-1) using THF as eluent deemed necessary.

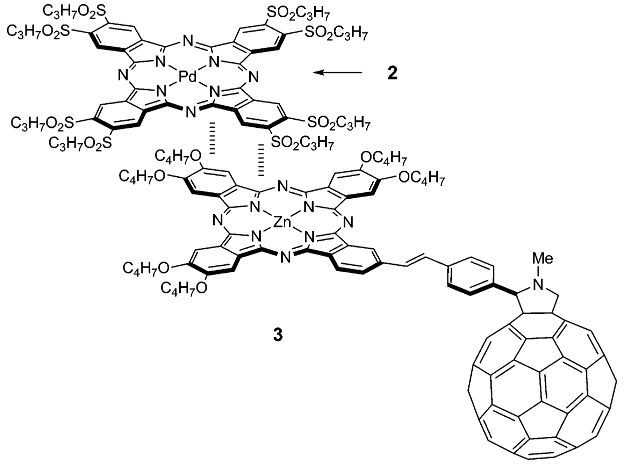

Figure 2. Molecular components and supramolecular donor−acceptor triad **2**/**3**.

On the other hand, the electron-deficient Pd(II)-octakis-(propylsulfonyl)phthalocyanine (**2**) was prepared by refluxing the diiminoisoindoline precursor **7** in a mixture of DMF and *o*-DCB in the presence of $Pd(OAc)_2$ (Scheme 2). Flowing ammonia through a solution of sodium methoxide and phthalonitrile **6** in MeOH gave a mixture of products (substitution of one or two propylsulfonyl substituents by methoxy groups occurs to some extent) from which diiminoisoindoline **7** was isolated in 45% yield.

All new compounds were characterized by MALDI-TOF mass spectrometry, ^1H NMR, UV/Vis and FT-IR spectroscopies. The ^1H NMR spectrum of compound **5** shows the typical broad signals of the alkoxy-substituted phthalocyanines (see Figure S1). This is mainly due to self-aggregation of **5**. In addition, the diagnostic aldehyde singlet at 10.1 ppm is present. On the other hand, the ^1H NMR spectrum of **3** is poorly resolved due to the presence of the C_{60} unit, which produces even higher aggregation at the experimental NMR concentrations (see Figure S2). However, signals assigned to the pyrrolidine ring can be clearly observed between 4.3 and 5.2 ppm, as well as the N−CH_3 resonance at 2.95 ppm.

Concerning mass spectrometry, a peak corresponding to the $[M-C_{60}]^+$ fragment appears in the MALDI-TOF spectrum of **3** together with the molecular ions $[M^+]$ or $[M+H]^+$ as major species.

Figure 3 shows the UV/Vis spectra of **3** and its precursors, namely, the iodoPc **4** and the formylPc **5** in chloroform. The spectrum of **5** reveals a significant splitting of the Q-band as well as a small red shift in comparison with that of the iodo derivative **4**. The splitting is a consequence of the extended

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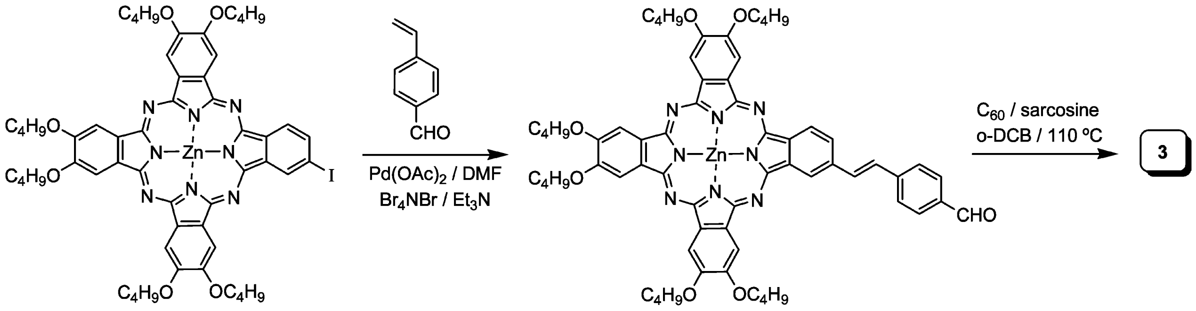
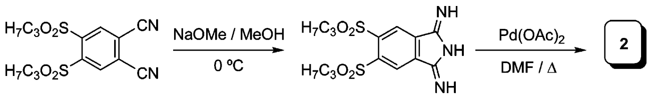
Scheme 1. Synthesis of ZnPc−C_{60} Dyad **3**



4 **5**

Scheme 2. Synthesis of the Electron-Deficient Phthalocyanine **2**



6 **7**

π-conjugation of the macrocycle. Although, the splitting of the Q-band is less significant for **3**, its maximum is still red-shifted by 10 nm compared with that of compound **4**. In addition, a new shoulder appears at 622 nm, indicative of some aggregation. In the UV region, the strong absorptions at 258 and 345 nm are mainly due to C_{60} and to the Soret band of the phthalocyanine. The typical absorption of fulleropyrrolidines can be also observed around 435 nm.

Electrochemical and Photophysical Characterization of the Molecular Components

Electrochemical studies were performed through cyclic voltammetry (CV) and Osteryoung square wave voltammetry (OSWV) measurements. The results gathered for ZnPc−C_{60} (**3**) were compared with those of the symmetrically substituted Zn(II) octabutoxyphthalocyanine (**1**) and 2-phenyl-*N*-methylfulleropyrrolidine (**8**). Data for the electron-deficient Pd(II) octakis(propylsulfonyl)-phthalocyanine (**2**) are also presented. Some representative voltammetric data are shown in Figure 4, while the OSWV peak potentials are summarized in Table 1.

Cyclic voltammograms of compound **2** show − in the anodic scan − a poorly resolved irreversible one-electron oxidation wave at 1.33 V. On the other hand, the first reduction potential of **2** (−176 mV) is substantially below that of the fulleropyrrolidine reference **8** (−914 mV). This result suggests that alkylsulfonylphthalocyanines are not suitable units for the construction of donor−acceptor dyads (i.e., in the combination with electron accepting fullerene derivatives).

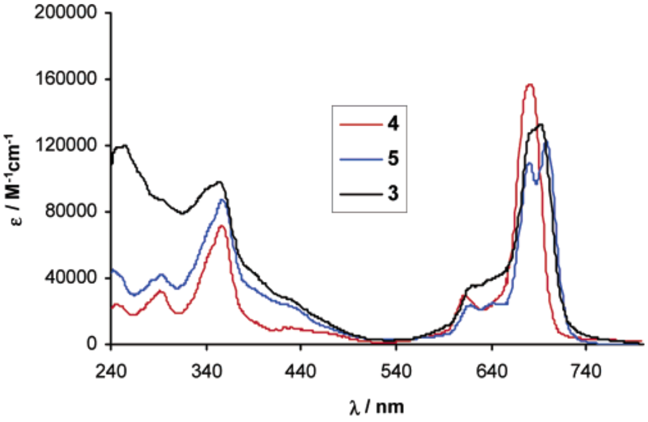


Figure 3. UV−vis spectra of ZnPc−C_{60} **3** and the phthalocyanine precursors **4** and **5** in $CHCl_3$.

Due to aggregation, both alkoxy-substituted phthalocyanines (*i.e.*, **1** and **3**) show poorly resolved voltammograms (Figure 4). The voltammogram of phthalocyanine **1** exhibits two electrochemically irreversible one-electron cathodic waves at −1.446 and −1.648 V and irreversible one-electron anodic waves at 0.194 and 0.960 V. The assignment of the signals in the voltammogram of ZnPc−C_{60} (**3**) was particularly difficult − apart from those observed at −0.911, −1.294 and −1.828 V, which all correspond to fullerene centered reduction processes. In the anodic region, the results refer to the ZnPc oxidation. Moreover, when the first oxidation potentials in **1** and **3** are compared, a 39 mV shift to higher values is seen.

From these studies we conclude that (a) alkoxy-substituted Zn(II)-phthalocyanines are much easier to oxidize than the corresponding alkylsulfonyl Pc analogues and (b) the alkoxy-substituted ZnPc unit becomes more difficult to oxidize when it is covalently connected to a C_{60} unit, indicating an efficient electronic communication between both electroactive units in the ground state.

Additionally, a series of photophysical measurements were performed to characterize photoexcited interactions in **3** (see Table 2). Relative to a ZnPc reference (Zn(II)-octabutoxyphthalocyanine, **1**),[11] the fluorescence quantum yields and fluorescence lifetimes in **3** reveal drastic alterations**.** The quantum yields, for example, are as low as 0.01 (Figure S3) and the lifetimes are around 0.17 ± 0.05 ns. In transient absorption studies, we observed, upon selective photoexcitation of **3**, the ZnPc singlet features. The presence of C_{60} does not affect the singlet excited state formation. C_{60} exerts, however, a notable impact on the singlet lifetime. The singlet−singlet characteristics decay in the presence of the electron accepting C_{60} much faster (i.e., 0.18 ± 0.02 ns) than what is typically seen for the intersystem crossing in **1** (i.e., 2.5 ± 0.02 ns). Important is that in parallel with the singlet decay, features of the radical ion pair develop; that is, the one-electron oxidized ZnPc (i.e., transient maximum around 860 nm and transient bleach around 700 nm, see Figure S4) and the one-electron reduced C_{60} (i.e., transient maximum around 1000 nm,[4c] see Figure S5). The $ZnPc^{\bullet+}-C_{60}^{\bullet-}$ lifetime is 130 ns in THF. This lifetime is already 2 orders of magnitude higher than the one obtained for structurally related covalently linked ZnPc−C_{60} dyads.[5a,10]

Complexation Studies: Ground State

Prior to any binding studies, the susceptibility of **3** to self-associate was evaluated by UV/vis spectroscopy. Importantly,

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[11] Fluorescence quantum yield = 0.3; fluorescence lifetime = 3.1 ± 0.2 ns.

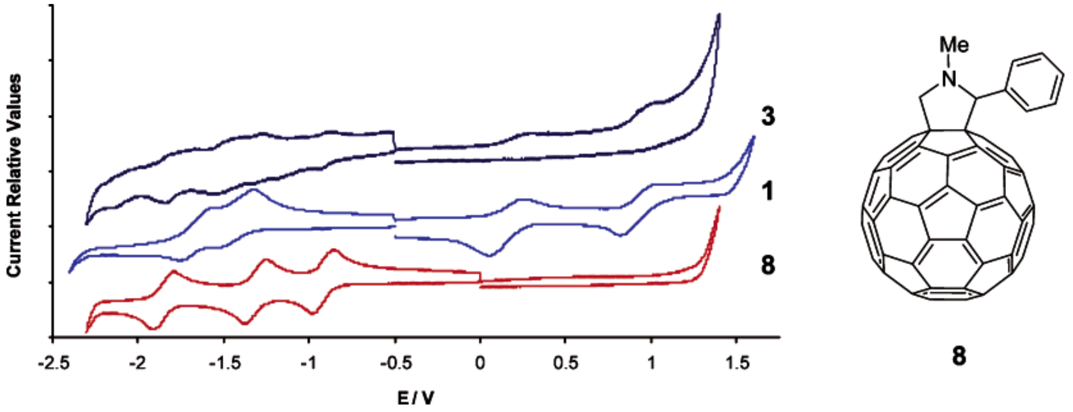

Figure 4. Cyclic voltammograms in *o*-DCB/acetonitrile (4:1) of dyad **3** and their reference compounds **1** and **8**.

Table 1. Redox Potentials (mV) Obtained for the Molecular Components (Dyad **3** and Phthalocyanine **2**) and Their Reference Compounds **1** and **8** Measured by OSWV in *o*-DCB/Acetonitrile (4:1) Solutions at Room Temperature[a]

	E_{red}^1	E_{red}^2	E_{red}^3	E_{red}^4	E_{red}^5	E_{red}^6	E_{ox}^1	E_{ox}^3
3	911	−1073	−1294	−1474	−1828	−2083	233	917
1			−1446	−1648			194	960
2	−176	−355	−749	−1196	−1485		1330	
8	−914		−1317		−1861			

[a] All values are based on the Ag/AgNO$_3$ reference electrode.

Table 2. Selected Photophysical Properties of **1** and **3** in Toluene

compound	fluorescence quantum yield Φ	fluorescence lifetime τ (ns)	singlet–singlet lifetime τ (ns)	radical ion pair lifetime τ (ns)
1	0.3	3.1 ± 0.02	2.5 ± 0.02	
3	0.01	0.17 ± 0.05	0.18 ± 0.02	130 (THF)

Table 3. Selected Photophysical Properties of the Supramolecular Ensembles **1**/**2** and **3**/**2** in Toluene

ensemble	binding constant, K× 10^5 M^{-1}	fluorescence quantum yield Φ	fluorescence lifetime τ (ns)	singlet–singlet lifetime τ (ns)	radical ion pair lifetime τ (ns)
1/**2**	1.5 ± 0.5		0.19 ± 0.1	not determined	
3/**2**	2.9 ± 1.0	0.002	0.25 ± 0.5	0.17 ± 0.02	475 (THF)

the lack of significant changes in the absorption spectra (i.e., in the 10^{-5}−10^{-6} M range) infers only minute degrees of aggregation.

Insight into the spontaneous supramolecular organization of **3** in the presence of **2** to form a noncovalent PdPd/ZnPc−C$_{60}$ triad (**3**/**2**) came from titration experiments.[5,12] As a control, complexation between **1** and **2** was also studied.[13] In particular, diluted toluene solutions of **1** or **3** were titrated with variable amounts of **2** and changes were routinely monitored by absorption and fluorescence spectroscopy. In absorption spectroscopy, a decrease in the intensity of the 679 or 692 nm maxima (assigned to the butoxy-ZnPc (i.e., **1** and **3**)) and a concomitant increase of maxima at 620 or 630 nm (assigned to the heterodimers formed with **2**) are observed upon complexation (Figure 5). Important are the observations of isosbestic points around 686 nm. These points of equal absorbances attest to clear transformations of **1** or **3** (i.e., beginning-point of the titration) into the **1**/**2** or **3**/**2** supramolecular emsembles (i.e., end-point of the titration).

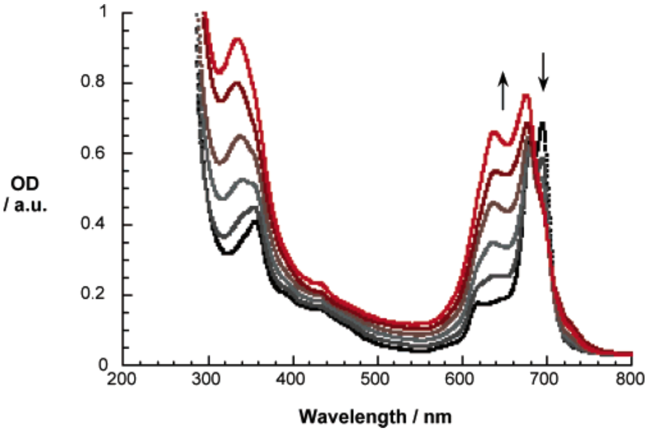

Figure 5. Absorption spectra of a diluted toluene solution of ZnPc−C$_{60}$ dyad **3** (5.3×10^{-6} M) upon adding variable concentrations of PdPc **2**.

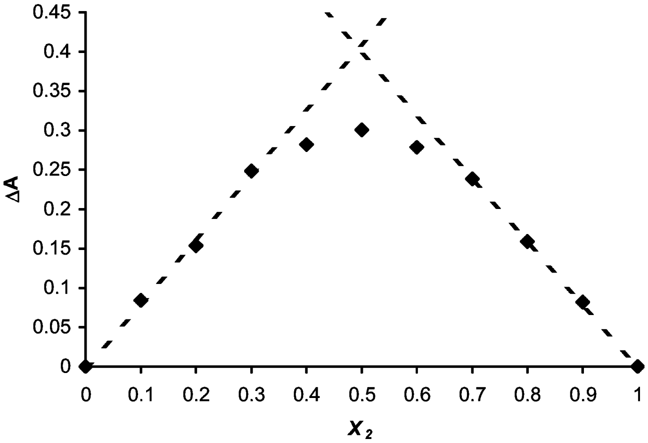

Figure 6. Graphical representation of the equimolar Job diagram for the 1:1 complex between dyad **3** and PdPc **2** in CHCl$_3$.

Next, the Job plot method[14] was used to ascertain the 1:1 stoichiometry of **3**/**2** and **1**/**2** (Figure 6). Additionally, equimolar experiments were analyzed numerically to assess the association constant.[15] A fairly high value of 4.5×10^5 M^{-1} in CHCl$_3$ was estimated for the association constant of the **3**/**2** complex.[16]

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(13) Although more structural information about the supramolecular complexes could be achieved from NMR experiments, unfortunately, the ^{1}H NMR signals were not sufficiently resolved at the relatively high NMR concentrations to obtain any accurate results (see ^{1}H NMR spectrum of compound **3** in the Supporting Information).

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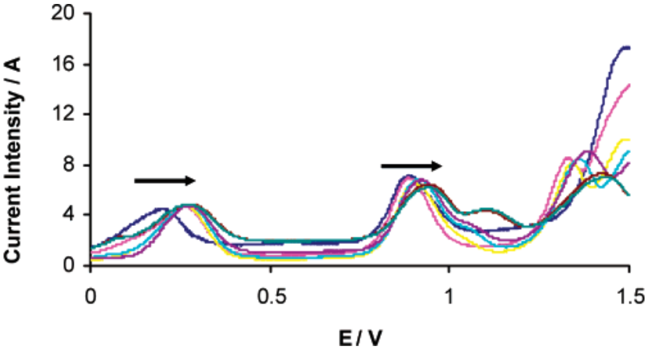

Figure 7. Anodic square wave voltammograms for the titration of ZnPc **1** with increasing amounts of PdPc **2** in *o*-DCB/acetonitrile (4:1).

To evaluate the intermolecular interactions between ZnPc (**1**) and PdPc (**2**) in the ground state, cyclic voltammograms and OSWVs of different mixtures of the two components were recorded and carefully compared with those of the individual compounds. The overlap of reduction peaks in the cathodic scan rendered it, however, difficult − if not impossible − to draw any meaningful conclusions about the aggregation. In the anodic region, the waves do not overlap and, therefore, a proper assignment of the peaks was possible. Figure 7 shows the oxidation square wave voltammograms for the titration experiment of ZnPc **1** with PdPc **2**.

In these experiments, the concentration of **1** was kept constant (*i.e.,* at 1 mM in *o*-dichlorobenzene/acetonitrile (4:1)) and increasing quantities of **2** were added. A notable shift of the first oxidation wave to higher values was observed, when as little as 0.33 mM of **2** were present. Up to 1.33 mM of **2**, the potentials continued to increase. Beyond 1.33 mM of **2**, the oxidation potentials remained, however, nearly constant. Such shifts to higher potential values were also observed for the second oxidation of ZnPc, but in this case a linear relationship evolved. In addition, a new band appears at ca. 1.070 V, when, for example, one equivalent of PdPc **2** is present. A likely rationale implies formation of a new aggregate. Again, this new peak exhibited a shift to higher potentials. Finally, an anodic peak appeared at the expected potential (1.33 V), which shifted to higher values along the experiment. The three processes become with increasing concentration of **2** more and more irreversible. In conclusion, the electrochemical experiments have further demonstrated the donor−acceptor nature of the intermolecular interactions, which govern the heteroassociation between complementary phthalocyanines **1** and **2**, featuring electron-rich and electron-deficient substituents, respectively.

Complexation Studies − Excited State

Prior to the addition of the electron-deficient **2**, photoexcitation of **1** in toluene led to a strong fluorescence, which maximizes at 704 nm. When, however, variable concentrations of **2** were added, the fluorescence emission intensity decreased exponentially. The decrease of fluorescence, as shown in Figure 8, depends exclusively on the concentration of **2** and was successfully used to determine the association constant for the **1**/**2** complex as 1.5 ± 0.5 × 10^5 M^{-1}.[17]

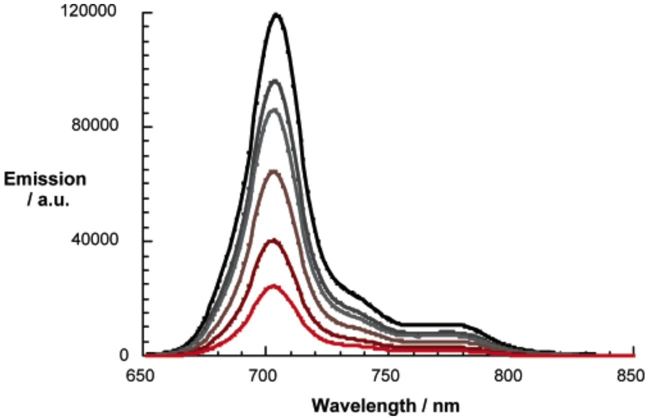

Figure 8. Fluorescence spectra of a dilute toluene solution of ZnPc **1** (5.3 × 10^{-6} M) upon adding of PdPc **2**. Excitation wavelength is 686 nm.

In time-resolved fluorescence measurements, the decay of just the ZnPc fluorescence (*i.e.,* in **1**) is well fitted by a monoexponential rate law. From our fitting procedures a lifetime of 2.5 ns was determined in oxygenated toluene. When adding **2** to these solutions, double-exponential fluorescence decays were observed. For example, the 704 nm fluorescence profiles were best fitted by lifetimes of 2.4 ± 0.2 ns and 0.19 ± 0.1 ns (not shown). The two lifetimes are maintained throughout the titration assay, with an increasing contribution of the short-lived component − as the concentration of **2** increases. In such mixtures − **1**/**2** −, intraensemble interactions are likely to be responsible for one kinetic component (*i.e.,* the fast one) and regular ZnPc excited-state deactivations gives rise to the other component (*i.e.,* the slow one).

Different are the fluorescence assays where **3** was tested in the presence of variable concentrations of **2**. An obvious difference is the already low ZnPc fluorescence quantum yield (0.01), due to the intraconjugate electron-transfer deactivation (vide supra). Despite the quenching, an additional decrease is seen during the gradual formation of **3**/**2** − see Figure S7. Concomitant with the decrease is a slight blue shift of the emission maximum. Implicit is here that the two phthalocyanine building blocks, namely, the electron deficient **2** and the electron reach ZnPc unit of **3** are subject to strong excitonic couplings. In the final stage of the fluorescence titration, which correlates quantitatively to **3**/**2**, the fluorescence approaches a minimal value of 0.002. The association constant of complex **3**/**2** was 2.9 ± 1.0 × 10^5 M^{-1}. Parallel with the steady-state measurements, we noted that the fluorescence lifetime of **3** with a value of 0.25 ± 0.5 ns is also decreased.[18]

Next, we like to focus on the transient absorption changes that were monitored when associating **1** with **2**. Applying the 700−900 nm marker, we see in nanosecond flash photolysis with different mixtures of **1** and **2** (*i.e.,* see above titration experiments) differential absorption changes that are essentially identical to those seen for the ZnPc triplet excited state. Apparently, similar to the singlet excited states (i.e., **2**: 1.79 eV versus **1**: 1.76 eV) the PdPc triplet excited state is higher than that of ZnPc (1.23 eV). Thus, **1** constitutes an energetic

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(15) Klausen, K. S. *Anal. Chim. Acta* **1969**, *44*, 377.

(16) The same experiment was carried out for the reference donor−acceptor ensemble **1**/**2**, obtaining similar results. The 1:1 stoichiometry of **1**/**2** and **3**/**2** was also confirmed by mass spectrometry. The spectra recorded from a 1:1 mixture of the two components of each complex display peaks at $m/z = 2618$ and 3351, respectively.

(17) Closer inspection of Figure 8 reveals that simultaneous with the quenching of the ZnPc **1** emission at 704 nm, a new lower-energy emission develops, which is centered at 702 nm.

(18) However, given the margin of error, it was very difficult to analyze the decays of the **3**/**2** ensemble. Still a double-exponential fitting provides the best results.

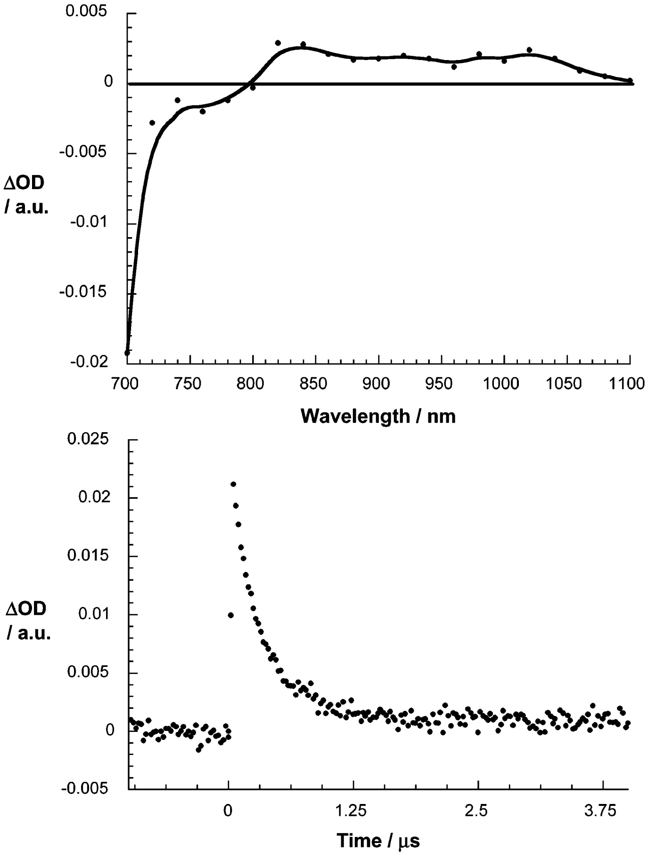

Figure 9. Nanosecond differential transient absorption spectrum following excitation of the **3**/**2** complex at 532 nm in nitrogen-saturated toluene solution: time delay is 75 ns. Shown are the radical ion pair features (upper spectrum) and the time absorption profile at 1000 nm (lower spectrum).

trap − both for the singlet and the triplet manifolds − in the **1**/**2** ensemble. Notably, the triplet quantum yields in **1** and **1**/**2** are nearly identical, confirming the photosensitization of **1**.[19]

Finally, we probed the **3**/**2** ensemble. In picosecond experiments we noted first the formation of the ZnPc singlet excited state, which subsequently transforms (*i.e.,* 0.17 ± 0.02 ns) into the ZnPc$^{\bullet +}$−$C_{60}$$^{\bullet -}$ radical ion pair state.[20] Again, we employed the ZnPc radical cation ion fingerprint − see Figure S8 − to confirm this process and to derive the underlying dynamics. On the picosecond time scale no appreciable changes are recorded that would indicate any decay of the radical ion pair state or any charge shift reaction. According to the oxidation potentials of phthalocyanines **1** and **2** (vide supra), a charge shift reaction to form the one-electron oxidized PdPc **2**, would be under thermodynamic consideration energetically unfavorable. In fact, Figure 9 shows that also the nanosecond transient spectrum indicates the fingerprints of the one-electron oxidized ZnPc and the one-electron reduced C_{60}. However, relative to **3**, the radical ion pair lifetime in the **3**/**2** ensemble is appreciable longer, with 475 ns. Beneficial for retarding the charge recombination is the electronic coupling of the two phthalocyanines by donor−acceptor interactions. This is expected to help in delocalizing the radical cationic charge over the ZnPc and the PdPc moieties. In fact, spectroscopic evidence for this conclusion stems from the analysis of the 700 to 800 nm region, which matches the bleaching of the broad ground-state features of the **3**/**2** complex.

Conclusions

In summary, a photosynthetic reaction center model has been constructed in which donor and acceptor phthalocyanines act as (i) primary light-harvesting chromophores and (ii) relay station to funnel the visible light absorption toward the acceptor C_{60} unit. Heteroassociation between complementary Pcs, peripherally substituted either with electron-rich or electron-deficient substituents, produced a substantial stabilization of the radical ion pair formed by exothermic electron transfer between the electron-donor ZnPc and electron-acceptor C_{60} units in the covalent ZnPc−C_{60} dyad **3**.

Currently, we are applying our strategy to the formation of supramolecular tetrads, in which additional electroactive components (such as ferrocene, Ru(II)tris(bipy) complexes, etc.) are incorporated by, for instance, covalent grafting to the electron-deficient phthalocyanine units.

Experimental Section

Most of the solvents employed in this work were purchased from SDS (http://www.sds.tm.fr). DMF and toluene solvents were dried over molecular sieves (3 and 4 Å, respectively), previously activated by microwaves, and stored under argon before use. Chemicals were purchased from Aldrich Chemical Co., Acros Organics, or Fluka Chemie and used as received without further purification. The C_{60} derivative **8** was synthesized, accordingly with the literature, by a Prato reaction of C_{60} with benzaldehyde in the presence of sarcosine.[21] The monitoring of the reactions was carried out by thin-layer chromatography (TLC), employing aluminum sheets precoated with silica gel 60 F_{254} (Merck). The purification and isolation of most of the products was performed by flash column chromatography using silica gel Merck-60 (230−400 mesh, 0.040−0.063 mm).

Melting points were determined on a Büchi apparatus and are uncorrected. Infrared spectra were recorded on a Bruker (FT-IR) spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker AC-200 (200 MHz) and AC-300 (300 MHz). UV/vis spectra were recorded on a Perkin-Elmer 8453 and a spectrophotometer. The mass spectra were determined on a REFLEX (MALDI-TOF) and a VG AutoSpec spectrometers.

Cyclic voltametry (CV) and Osteryoung square wave voltammetry (OSWC) were performed on an Autolab-PGSTAT30 electrochemical analyzer with a three-electrode configuration in *o*-DCB/acetonitrile (4:1) solutions containing the substrate (typically about 1 mmol/dm^3) and the supporting electrolyte (tetrabutylammonium perchlorate). A glassy carbon (Ø 3 mm) disk serves as the working electrode, a platinium wire (Ø 1 mm) and a commercial Ag/$AgNO_3$ electrode being the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. Solutions were stirred and deoxygenated by bubbling argon for a few minutes prior to each measurement. The scan rate was 100 mV/s. Experimental uncertainty on all measured potentials reported in this paper are estimated at less than 5 mV.

Picosecond laser flash photolysis experiments were carried out with 532-nm laser pulses from a mode-locked, Q-switched Quantel YG-501 DP Nd:YAG laser system (18 ps pulse width, 2−3 mJ/pulse). Nanosecond laser flash photolysis experiments were performed with laser pulses from a Quanta-Ray CDR Nd:YAG system (532 nm, 6 ns pulse width) in a front face excitation geometry.

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(19) Although the intra-ensemble transduction of the excited-state energy must occur in the singlet excited states, our picosecond analysis was unsuccessful to confirm this. Our failure is mainly due to the similar singlet excited-state features of the two phthalocyanine building blocks.

(20) Our picosecond analysis was unsuccessful to resolve the transduction of energy.

(21) Wei, X.; Yao, S.; Yin, G.; Suo, Z.; Xu, Z.; Wang, P.; Zhang, W.; Chen, P.; Zhang, Y.; Li, Z.; Niu, Y. *Fullerene, nanotubes carbon nanostructures* **2002**, *10*, 137.

Fluorescence lifetimes were measured with a Laser Strobe Fluorescence Lifetime spectrometer (Photon Technology International) with 337-nm laser pulses from a nitrogen laser fiber-coupled to a lens-based T-formal sample compartment equipped with a stroboscopic detector. Details of the Laser Strobe systems are described on the manufactures web site, http://www.pti-nj.com.

Emission spectra were recorded with a SLM 8100 spectrofluorometer. The experiments were performed at room temperature. Each spectrum was an average of at least five individual scans, and the appropriate corrections were applied whenever necessary.

Synthetic Procedures: Formylphthalocyanine 5. A solution of iodophthalocyanine **4**[22] (75 mg, 0.066 mmol), 4-vinylbenzaldehyde[23] (10 μL, 0.073 mmol), $Et_2{}^iPrN$ (0.1 mL), tetra-*n*-butylammonium bromide (25 mg, 0.077 mmol), and $Pd(OAc)_2$ (1.5 mg, 0.0066 mmol) in anhydrous DMF (2 mL) was heated at 80 °C for 12 h under argon atmosphere. The solvent was evaporated, and the solid residue was triturated with methanol/water (3:1), filtered, and purified by column chromatography (SiO_2, hexane/dioxane 3:1, $R_f = 0.19$) to yield **5** (55 mg, 73%) as a dark-green solid: mp > 250 °C; ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 9.96$ (s, 1H, CHO), 7.8 (m, 8H, arom H), 7.3 (m, 7H, 5 arom H, 2 vinyl H), 4.0 (m, 8H, OCH_2), 3.7 (m, 2H, OCH_2), 3.5 (m, 2H, OCH_2), 1.9 (m, 12H, CH_2), 1.6 (m, 12H, CH_2), 1.1 (m, 18H, CH_3); IR (KBr): $\bar{\nu} = 3446$ (ArC−H), 2957, 2930, 2870 (CH), 1697 (HC=O), 1595 (C=C), 1278 (ArO−C), 1095, 1047, 858 cm^{-1}; UV/vis ($CHCl_3$): λ_{max} (log ϵ) = 298 (4.63), 300 (4.86), 354 (4.70), 614 (4.36), 692 nm (5.1); MALDI-TOF MS: $m/z = 1138$ [M^+]. Elem. anal. (%) calculated for $C_{65}H_{70}N_8O_7Zn{\cdot}H_2O$ (1158.71): C, 67.38; H, 6.26; N, 9.67. Found: C, 67.54; H, 6.41; N, 9.43.

Pc−C_{60} Dyad 3. To a well-stirred mixture of C_{60} (56 mg, 0.078 mmol) and sarcosine (2.3 mg, 0.026 mmol) in *o*-DCB (10 mL) at 60 °C was added a solution of phthalocyanine **5** in 5 mL of *o*-DCB and the solution heated to 110 °C for a further 8 h. After removal of the solvent, column chromatography was performed, eluting C_{60} with toluene and compound **3** with toluene/THF 20:1 ($R_f = 0.18$). Further purification by a Bio-Beads column allowed obtaining compound **1** as a dark-green solid: mp > 250 °C; ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.9{-}6.5$ (m, 13 arom H and 2 vinyl H), 5.1 (m, 2H, pyrrolidine H), 4.4 (m, 1H, pyrrolidine H), 3.7 (m, 12H, OCH_2), 2.96 (s, 3H, NCH_3), 1.8−1.5 (2 × m, 24H, CH_2), 1.1 (m, 18H, CH_3); IR (KBr): $\bar{\nu} = 3443$ (ArC−H), 2956, 2925, 2870 (CH), 1605 (C=C), 1494, 1458 (C−N), 1278 (ArO−C), 1097, 1047, 859 cm^{-1}; UV/vis ($CHCl_3$): λ_{max} (log ϵ) = 257 (5.07), 357 (4.99), 435 (4.39), 622 (4.55), 694 nm (5.12); MALDI-TOF MS: $m/z = 1886$ [M^+], 1166 [$M - C_{60}$]$^+$. Elem. anal. (%) calculated for $C_{127}H_{75}N_9O_6Zn{\cdot}4H_2O$ (1960.49): C, 77.81; H, 4.27; N, 6.43. Found: C, 77.29; H, 4.37; N, 6.48.

4,5-Dipropylsulfonyldiiminoisoindoline 7. A stirred solution of sodium (160 mg, 7 mmol) in methanol (120 mL) was cooled to 0 °C in an ice−water bath. 4,5-Dipropylsulfonylphthalonitrile **6**[24] (3 g, 8.8 mmol) was then added, and ammonia was bubbled through the reaction mixture. After 20 min, the solution color became yellow, and TLC ($CHCl_2$/methanol, 9:1) showed that there was no unreacted starting material. The solvent was then evaporated and subjected to column chromatography on silica gel ($CHCl_2$/methanol, 9:1, $R_f = 0.37$); 1.42 g (45%) of compound **7** was isolated as a yellow solid: mp = 128−130 °C dec; ^1H NMR (methanol-d_4, 200 MHz, 25 °C, TMS): $\delta = 8.68$ (s, 2H, arom H), 3.64 (t, $J = 7.04$ Hz, 4H, SO_2CH_2), 1.8 (m, 4H, CH_2), 1.1 (t, $J = 7.52$ Hz, 6H, CH_3); ^{13}C NMR (methanol-d_4, 300 MHz, 25 °C, TMS): $\delta = 143.9$, 142.7, 127.6, 108.4, 57.5, 23.3, 14.2; IR (KBr): $\bar{\nu} = 3305$ (NH), 2926, 2857 (CH), 1678, 1634 (C=N), 1300, 1185, 1145 (SO_2), 1101, 655, 588 cm^{-1}; MS (EI) m/z (%): 357 (29) [M^+], 251 (23) [$M - C_3H_7SO_2$]$^+$, 144 (51) [$M - 2 \times C_3H_7SO_2$]$^+$. Elem. anal. (%) calculated for $C_{14}H_{19}N_3S_2O_4$ (357.44): C, 47.04; H, 5.36; N, 11.76; S, 17.94. Found: C, 46.88; H, 5.10; N, 11.95; S, 17.88.

Pd(II)−Octakis(propylsulfonyl)phthalocyanine 2. A DMF/*o*-DCB (1:1, 2 mL) solution of diiminoisoindoline **7** (157 mg, 0.45 mmol) and $Pd(OAc)_2$ (105 mg, 0.45 mmol) was heated at 140 °C for 12 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue triturated with methanol/water (3:1). The crude was purified by column chromatography (SiO_2, $CHCl_3$/THF, 40:1) to give compound **2** as a dark-green solid. Yield: 52 mg, 32%; $R_f = 0.39$; mp >250 °C; ^1H NMR ($CDCl_3$, 300 MHz, 25 °C, TMS): $\delta = 10.3$ (br s, 8H, arom H), 4.1 (m, 16H, SO_2CH_2), 2.2 (m, 16H, CH_2), 1.2 (m, 24H, CH_3); IR (KBr): $\bar{\nu} = 3441$ (ArC−H), 2968, 2933, 2879 (CH), 1646 (C=C), 1293, 1146, 1087 cm^{-1} (SO_2); UV/vis ($CHCl_3$): λ_{max} (log ϵ) = 257 (4.81), 281 (4.74), 347 (4.84), 601 (4.63), 639 (4.6), 665 nm (5.36); MALDI-TOF MS: $m/z = 1465$ [$M + H$]$^+$, 1464 [M^+]. Elem. anal. (%) calculated for $C_{56}H_{64}N_8S_8O_{16}Pd{\cdot}2H_2O$ (1504.09): C, 44.72; H, 4.56; N, 7.45; S, 17.05. Found: C, 44.29; H, 4.72; N, 7.09; S, 17.18.

UV/Vis Dilution Studies. A stock 1.5×10^{-5} M solution of compound **3** in chloroform was prepared in a volumetric flask (2 mL). An aliquot of the stock solution (1 mL) was transferred to a dry vial using a microanalytical syringe and was diluted with solvent (1 mL). This solution was then used as the stock in the preparation of a third dilution. This procedure was repeated to give a total of five different concentrations. Finally, the spectra of each of these solutions were registered.

UV/Vis Titrations. Stock 1.5 μM solutions of ZnPc derivatives **1** or **3** were prepared in chloroform, and then used as solvent for the preparation of a stock (76.6 or 67.3 μM, respectively) solution of compound **2**. This procedure ensures a constant concentration of **1** and **3** throughout the titration. The titration was performed by adding the required volumes of the solution of phthalocyanine **2** to 2 mL of the solution of ZnPc derivative **1** or **3**. The Q-band absorption was monitored as a function of the concentration of **2**.

UV/Vis Job Plot of Dyad 3 with Phthalocyanine 2. Two 8.97 μM stock solutions of derivatives **2** and **3** in chloroform were prepared in a volumetric flask (10 mL). Afterward, nine solutions with molar fractions of component **2** going from 0.1 to 0.9 were prepared in 2-mL volumetric flasks by diluting the required amounts of the stocks. $A_{exp} - A_o$ (ΔA) values were calculated according to the following equation:

$$A_o = \epsilon_{\mathbf{2}} x C_o + \epsilon_{\mathbf{3}}(1 - x)C_o$$

where x is the molar fraction of the titrating agent (**2**) and C_o the total concentration of the solutions. The plotting of ΔA as a function of x can be used to draw a curve that is useful to know the stoichiometry of the complex as well as to estimate the association constant.

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Note Added after ASAP Publication: In the version published on the Internet March 8, 2006, the paragraph explaining that Supporting Information is available was missing. It is present in the version published March 10, 2006, and in the print version.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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