

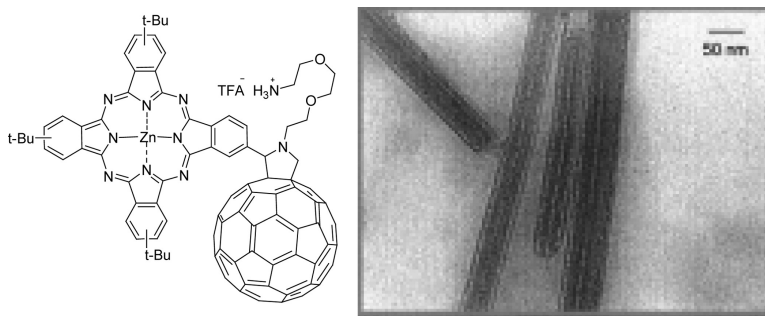
Communication

**Nanoscale Organization of a Phthalocyanine–Fullerene System:
 Remarkable Stabilization of Charges in Photoactive 1-D Nanotubules**

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Nanoscale Organization of a Phthalocyanine–Fullerene System: Remarkable Stabilization of Charges in Photoactive 1-D Nanotubules

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The construction of precisely defined molecular materials,^{1,2} designed to perform specific functions such as electrical conductivity, requires the incorporation of functional building blocks and a control of the supramolecular assembly process.

Phthalocyanines (Pcs),³ one of the best known synthetic porphyrin analogues, are highly versatile and stable chromophores with unique physicochemical properties that make them, alone or in combination with many other electro- and photoactive moieties,⁴ ideal building blocks for the construction of molecular materials having special electronic and optical properties. In general, the design of Pcs linked to strong acceptor moieties appears particularly promising. We have recently described the preparation of strongly coupled ZnPc–C₆₀ dyads⁵ in which long-lived and highly emissive charge-separated states are formed.⁶

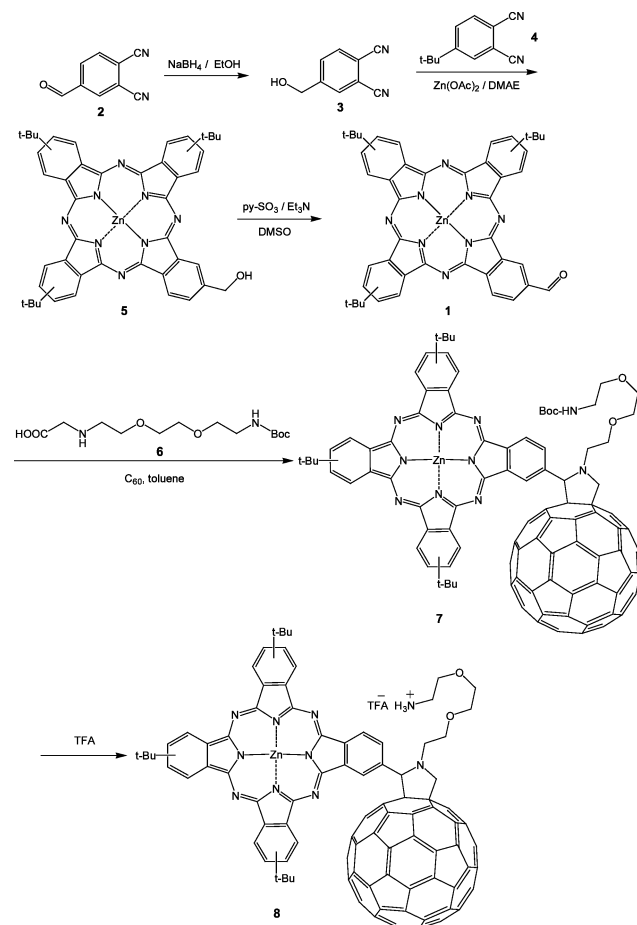
Additionally, owing to their extended flat hydrophobic aromatic surface, phthalocyanine molecules can interact with each other by attractive π – π stacking interactions,^{3a,7} leading to aggregation both in solution and in the solid state. However, the formation of long-range ordered Pc aggregates based on the mutual noncovalent recognition⁸ of Pcs is a challenging task and requires the introduction of additional structural features within the Pc ring.

Relatively few recognition motifs have been employed for the construction of nanosized supramolecular architectures based on Pcs. Among them are the introduction of adequate peripheral substituents to promote a mesomorphic behavior,⁹ the cation complexation of crowned-phthalocyanines,¹⁰ and the use of hydrogen-bonding¹¹ and metal–ligand¹² interactions to self-assemble phthalocyanine molecules forming either discrete supramolecular structures or infinite ill-defined aggregates.

In this connection, we have described recently the first Pc supramolecular assembly, driven by strong donor–acceptor interactions between Zn(II)– and Ni(II)–phthalocyanine rings that possess alkoxy and alkylsulfonyl substituents at the periphery, respectively, which has allowed the construction of donor–acceptor Pc–nanoaggregates.¹³

In this communication, we describe the synthesis, nanoscale organization, and photophysical properties of a novel Pc–C₆₀ system **8**. Interestingly, unique electron-transfer benefits stem from the tertiary organization of **8** into perfectly ordered one-dimensional (1-D) ZnPc–C₆₀ nanotubules (NTs). When dissolving **8** or its precursor **7** homogeneously, for example, in nonpolar solvents, fast charge recombination occurs (i.e., ns), whereas in polar solvents, utilizing the amphiphilic structure of **8**, aggregates form which lead to very long charge-separated states (i.e., ms).

Scheme 1. Synthesis of Pc–C₆₀ System 8



The synthesis of formylphthalocyanine **1** was carried out starting from 4-formylphthalonitrile (**2**)⁵ in a three-step sequence (Scheme 1).

The reduction of the formyl group in **2** was performed with an excess of NaBH₄, thus affording 4-hydroxymethylphthalonitrile (**3**) in almost quantitative yield. The statistical crossover condensation of **3**¹⁴ with 4-*tert*-butylphthalonitrile (**4**) in the presence of Zn(OAc)₂ in refluxing *N,N*-dimethylaminoethanol (DMAE) afforded tri-*tert*-butyl-hydroxymethylphthalocyanine (**5**) in 22% yield, after isolation from the statistical mixture of phthalocyanines by column chromatography on silica gel. Further oxidation of **5** to the Pc–aldehyde **1**⁵ was carried out by treatment with an excess of the SO₃–pyridine complex and triethylamine in dry DMSO at 50 °C to afford **1** in 84% yield. Compound **1** was much easier to obtain

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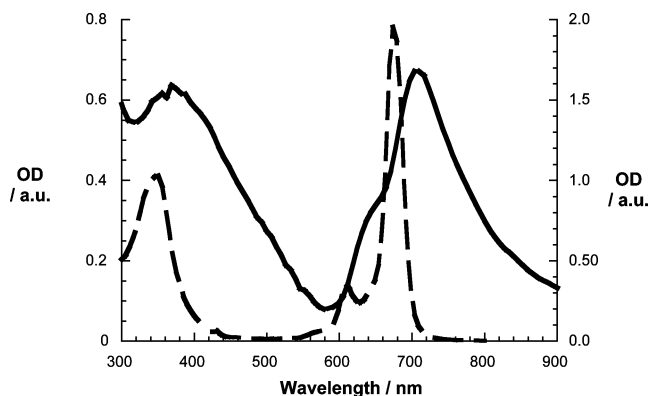


Figure 1. Ground-state absorption spectra of ZnPc–C₆₀ **7** (dashed spectrum) in THF and ZnPc–C₆₀ NT (salt **8**) (solid spectrum) in H₂O.

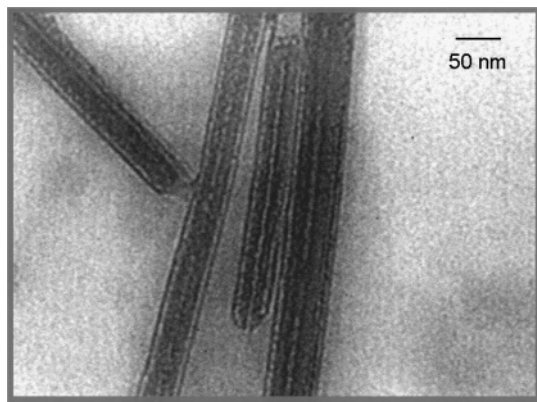


Figure 2. Nanotubules formed in water solution deposited on a TEM grid.

by this method than by the alternative ozonolysis procedure of the corresponding vinyl Pc described previously by us.⁵ The structures of all compounds were fully supported by their analytical and spectroscopic data. The UV–vis spectrum of **5** presents a sharp Q-band at 678 nm, whereas the MS-MALDI-TOF spectrum shows the molecular ion peak at m/z 776–778 as multiprotonated isotopic pattern without relevant fragmentations.

Formylphthalocyanine **1** was condensed in toluene at reflux with N-functionalized glycine **6** to afford the expected fulleropyrrolidine ZnPc–C₆₀ **7**, which was characterized by NMR and IR and whose purity was confirmed by direct-phase HPLC (see Supporting Information). The amino group in **7** was deprotected by reaction with excess of trifluoroacetic acid (TFA) to afford the ammonium salt **8**. Due to the presence of the positively charged end groups, this latter compound could be dispersed in aqueous solutions. Figure 1 compares the ground-state spectrum of an aqueous ZnPc–C₆₀ **8** with that of monomeric ZnPc–C₆₀ **7** in THF. In line with the tight π -stacking of the ZnPc and C₆₀ moieties, the absorption spectrum of such dispersions is characterized by substantial broadening, which is further augmented by light scattering of the aggregated species. Important also are the red-shifts of the 350 and 690 nm maxima to 375 and 710 nm, respectively.

To study the aggregation properties, amphiphilic ZnPc–C₆₀ salt **8** was dispersed in water, and the resulting mixture was sonicated in an ultrasonic bath. The insoluble material was removed by centrifugation at 3000 rpm, and one drop of the solution was transferred to a TEM copper grid, coated with Formvar film. Long, extremely well-organized nanorods were consistently observed throughout the grid—Figure 2 (see also Figure S1 in Supporting Information). Although atomic resolution was not possible, the nanotubules reported here are formed by many other substructures,

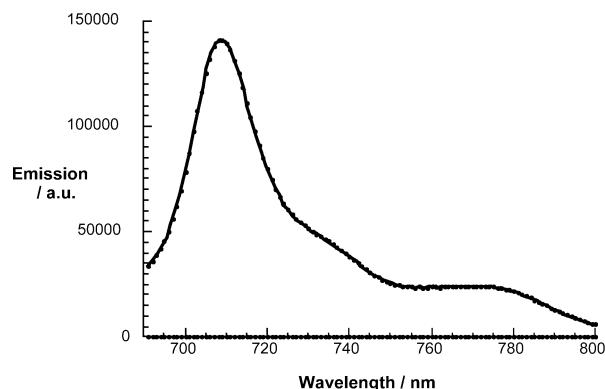


Figure 3. Steady-state fluorescence spectra of ZnPc–C₆₀ NTs (lower line) in H₂O and ZnPc reference (upper line) in THF at room temperature with matching absorption at the 375 nm excitation wavelength (i.e., OD_{375nm} = 0.2).

namely, other nanorods. These long shapes are reminiscent of those observed for a similar donor–acceptor array, where a smaller porphyrin macrocycle was attached to C₆₀ instead of to the phthalocyanine macrocycle.¹⁵ Obviously, phthalocyanines and fullerenes are strong elements of order in this system, and self-organization occurs through intermolecular forces.

Despite the strong fluorescence that the phthalocyanine chromophore exhibits in the ZnPc reference ($\Phi = 0.3$) and in the ZnPc–C₆₀ **7** ($\Phi \approx 0.005$), we determined a fluorescence quantum yield for a ZnPc–C₆₀ NT dispersion of $<10^{-5}$ at 375 or 710 nm excitation. Figure 3 illustrates the comparison of ZnPc fluorescence in the ZnPc reference and in the ZnPc–C₆₀ NTs. Implicit in the near quantitative fluorescence quenching is an ultrafast electron-transfer activation—once the phthalocyanine chromophore is photoexcited—to the electron-accepting C₆₀ core.

Next, we complemented the steady-state fluorescence experiments with time-resolved measurements. In particular, the long-lived ZnPc fluorescence, for which we determined a lifetime of 3.1 ± 0.2 ns in the reference, emerges also as a sensitive probe for such studies. However, we could not detect any appreciable fluorescence signal for the NTs made from amphiphilic **8**, because the electron-transfer deactivation of the ZnPc singlet excited-state occurs on a time scale much faster than our instrumental time resolution. In fact, with the help of the fluorescence quantum yields (i.e., ZnPc reference and ZnPc–C₆₀ NT) and the fluorescence lifetime (i.e., ZnPc reference) we extrapolated a rate constant of electron transfer of about 10^{12} s⁻¹.

Transient absorption measurements confirmed that the product of the ultrafast excited-state deactivation is indeed the radical ion pair, ZnPc^{•+}–C₆₀^{•-}. Spectroscopic evidence for the electron-transfer product came from the features—see Figure 4—developing immediately with the conclusion of the laser pulse (i.e., 18 ps or 6 ns). In the far-visible region, the observed maximum at 850 nm corresponds to the one-electron oxidized π -radical cation of ZnPc (i.e., ZnPc^{•+}), while in the near-infrared region the 1010 nm maximum resembles the signature of the one-electron reduced form of C₆₀ (i.e., C₆₀^{•-}).^{6c}

An additional feature of the new transient is bleaching in a region which is dominated by the broadened, ground-state absorption—see Figure 1. It is important that both spectral attributes, namely ZnPc^{•+} and C₆₀^{•-}, are persistent on the pico-, nano-, and micro-second time scale. It is only in the millisecond regime that ZnPc^{•+} and C₆₀^{•-} start to decay slowly. Time-absorption profiles—depicted as an insert to Figure 4—illustrate that ZnPc^{•+}–C₆₀^{•-} decay via a single step. The charge recombination dynamics within the ZnPc–C₆₀ NTs were determined accurately by fitting the decays

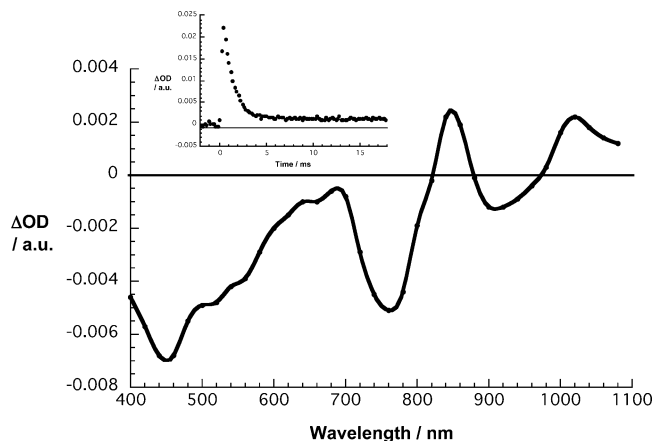


Figure 4. Differential absorption spectra obtained upon nanosecond flash photolysis (337 nm) of $\sim 5.0 \times 10^{-5}$ M (based on monomer) of ZnPc-C₆₀ NT in nitrogen saturated aqueous dispersion with a time delay of 100 ns – indicating the radical pair features of the donor–acceptor ensemble. (Insert) Radical pair decay at 1050 nm.

of both fingerprints to a monoexponential rate law which yielded a lifetime of 1.4 ms.¹⁶

In conclusion, induction of self-organization between ZnPc and C₆₀ moieties in an amphiphilic ZnPc-C₆₀ salt **8**, which occurs predominantly through intermolecular forces, results in uniformly nanostructured 1-D nanotubules. Their photoreactivity, in terms of ultrafast charge separation (i.e., $\sim 10^{12}$ s⁻¹) and ultraslow charge recombination (i.e., $\sim 10^3$ s⁻¹), is remarkable. In addition, the observed ZnPc⁺-C₆₀⁻ lifetime of 1.4 ms implies, relative to that of the monomeric ZnPc-C₆₀ **7** ($\tau \approx 3$ ns), an impressive stabilization of 6 orders of magnitude. The charge separation lifetime found in ZnPc-C₆₀ NTs reaches into a time domain typically found in thin solid films of donor–acceptor composites. Equally important to the unique self-organization is the fact that charge recombination dynamics in the ZnPc-C₆₀ couple are deeply located in the Marcus inverted region where the rate constants for electron transfer decrease with increasing driving force.^{6c}

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Supporting Information Available: Synthesis and spectroscopic characterization of compounds **1**, **7**, and **8**; preparation of the samples of the amphiphilic ZnPc-C₆₀ salt **8** for TEM microscopy; and measurement conditions for photophysical study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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