Electron Transfer

Integrating Single-Wall Carbon Nanotubes into Donor–Acceptor Nanohybrids**

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Nanoscale carbon materials (i.e., fullerenes and carbon nanotubes) are an attractive platform for applications in optoelectronics and photovoltaics.[1] The presence of extended, delocalized π-electron systems makes these carbon materials very useful for managing charge transfer and charge transport, when combined, for example, with photoexcited electron donors, such as metalloporphyrins.[2,3] This arrangement might lead to novel, highly efficient photoelectrochemical cells for applications such as photochemical water splitting and the reduction of CO_2 to fuels. Despite the interesting properties that single-wall carbon nanotubes (SWNTs) display, there are numerous obstacles in the way of solubilizing SWNTs and integrating SWNTs into fully functional donor–acceptor constructs. Controlled modification of their surface with functional groups, such as chromophores,[4] electron donors,[5] biomolecules,[6] is required to realize their potential in nanotechnology.

In nature, the complex superstructure that is found for many functional architectures is the unique result of self-assembling and self-organizing smaller building blocks.[7] To succeed in fabricating functional systems from simple molecular units the constituent components must be programmed to self-organize into hierarchical structures.

Herein, the systematic immobilization of the octasodium salt of 5,15-bis-[2′,6′-bis{2″,2″-bis(carboxy)ethyl}methyl-4′-*tert*-butylpheny]-10,20-bis(4′-*tert*-butylphenyl)porphyrin (H_2P^{8-})[8] and the related zinc complex (ZnP^{8-})[8]—as oligo-

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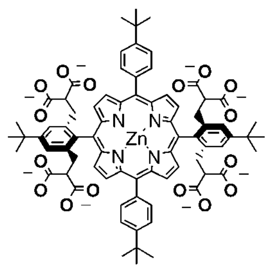
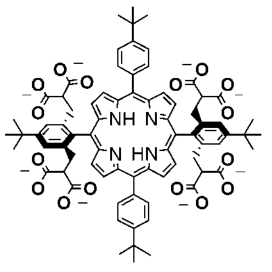
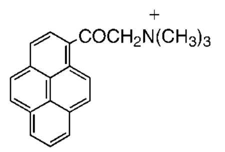


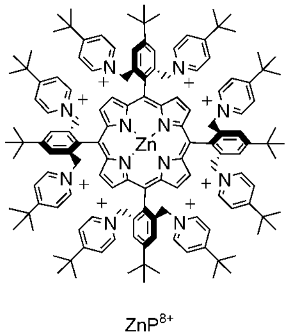
ZnP^{8-}



H_2P^{8-}

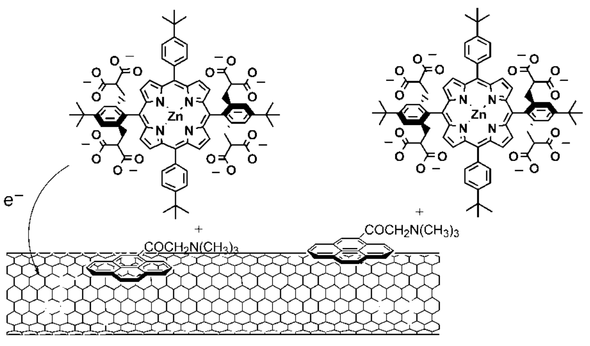


$pyrene^{+}$



ZnP^{8+}

anionic chromophores/electron donors—onto electron-accepting SWNTs is investigated. In particular, van der Waals and electrostatic interactions have been used to favor intermolecular recognition between the SWNT/1-(trimethylammonium acetyl) pyrene (pyrene$^+$), and H_2P^{8-} or ZnP^{8-} units (Scheme 1). Several techniques were employed to determine the photoinduced charge-separation properties in these new SWNT donor–acceptor hybrids.



Scheme 1. Partial structure of SWNT/pyrene$^+$/ZnP^{8-} nanohybrids.

Water-suspendable SWNTs were obtained in analogy to previous work, using pyrene$^+$.[9] However, to reduce the amount of free pyrene in solution, the SWNT/pyrene$^+$ complex was allowed to precipitate, and the centrifuged solid was re-suspended in water.

In Figure 1a and b we compare the UV, Vis, and NIR absorption spectra of pyrene$^+$ and SWNT/pyrene$^+$. The absorption spectra of an aqueous SWNT/pyrene$^+$ solution reveal several important features. First, the π–π transitions of pyrene$^+$ are slightly red-shifted (i.e., 1–2 nm) which indicates that electronic communication between the two different ring systems occurs. Second, the overall absorption cross-section increases, particularly in the Vis- and NIR-regions. Third, the characteristic van Hove singularities[2] of SWNTs are discernable in the Vis-NIR region up to around 450 nm, where the π–π* transitions of pyrene$^+$ dominate the spectrum. In fact, a D_2O spectrum of SWNT/pyrene$^+$ verifies that the van Hove singularities extend all the way out to 1500 nm and that they track those seen for a DMF sonicated suspension of SWNT (insert to Figure 1b). Collectively, these observations confirm the presence of both suspended SWNTs and pyrene$^+$ and the notable electronic interactions between them.

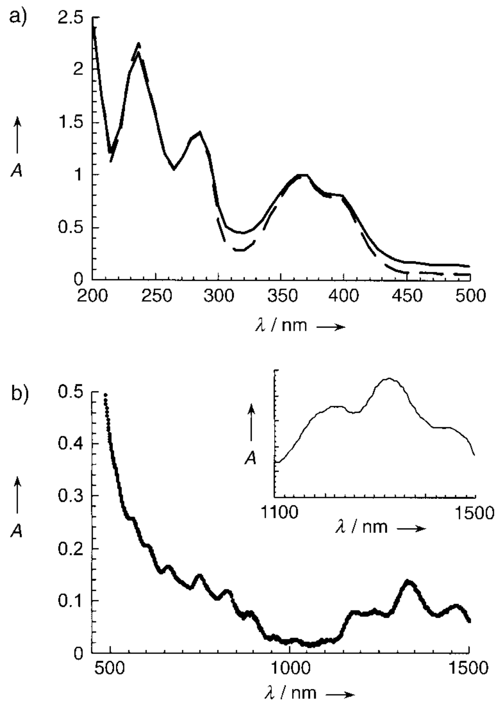


Figure 1. Absorption spectra of pyrene$^+$ (dashed line) and SWNT/pyrene$^+$ (solid line) a) in H_2O at pH 6.5 in the 200–500 nm range and b) in D_2O in the 450–1500 nm range. Insert to Figure b shows the 1100–1500 nm range for a sample of SWNT sonicated in DMF.

Additional proof for SWNT/pyrene$^+$ interactions came from emission experiments, which showed more than 50% quenching of the pyrene$^+$ fluorescence (see Supporting Information).[10]

The trimethylammonium head groups of pyrene were used as electrostatic anchors to bind anionic electron donors, such as water-soluble ZnP^{8-} or H_2P^{8-}.

Initial insight into the formation of SWNT/pyrene$^+$/ZnP^{8-} or SWNT/pyrene$^+$/H_2P^{8-} came from transmission electron microscopy (TEM). Pristine SWNT (as obtained from CNI) was treated with acid to remove the metallic nanoparticles (Figure 2a). Reference images of H_2P^{8-} (or ZnP^{8-}) show dark aggregates at the nanometer level (Figure 2b) while SWNT/pyrene$^+$ reveal bundles of nanotubes with diameters of 25 nm and lengths of several micrometers (Figure 2c). Addition of H_2P^{8-} (or ZnP^{8-}) to the nanotubes results in van der Waals electrostatic interactions between the two components. The corresponding TEM micrographs show darker areas surrounding the nanotubes walls, these areas are H_2P^{8-} (Fig-

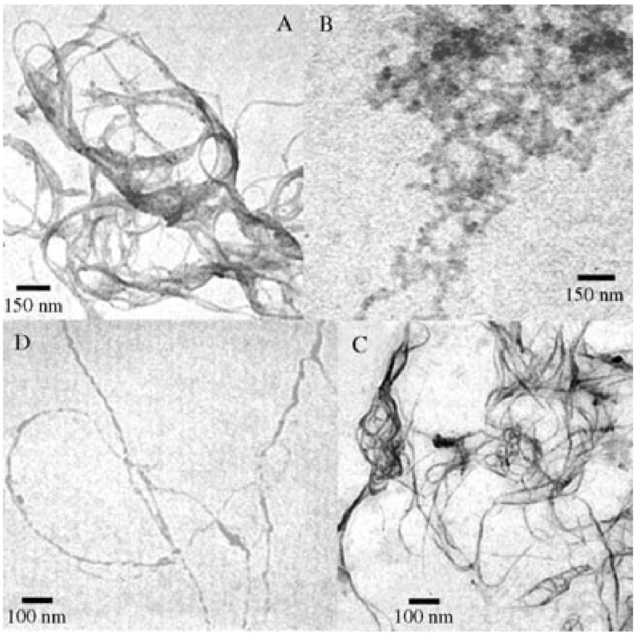


Figure 2. TEM images of a) purified SWNT, b) ZnP^{8-} deposited from an aqueous solution, c) SWNT/pyrene$^+$, d) SWNT/pyrene$^+$/H_2P^{8-}.

ure 2d) or ZnP^{8-}. Therefore, both the successful suspension and debundling in solution of SWNT/pyrene$^+$ and the electrostatic attractive interactions in the SWNT/pyrene$^+$/ZnP^{8-} or SWNT/pyrene$^+$/H_2P^{8-} system have been confirmed by TEM.

Dilute aqueous solution of ZnP^{8-} and H_2P^{8-} ($\approx 10^{-5}$ M) were titrated with variable amounts of SWNT/pyrene$^+$ to form SWNT/pyrene$^+$/ZnP^{8-} or SWNT/pyrene$^+$/H_2P^{8-}, respectively, as monitored by absorption and fluorescence spectroscopy (Figure 3). Relative to the component spectra (i.e., SWNT/pyrene$^+$ and ZnP^{8-}) a number of differences are apparent. For ZnP^{8-}, Soret- and Q-band transitions at 426 nm (Figure 3 a) and 560/600 nm (not shown), respectively, shift incrementally to the red. The Soret-band shows the biggest shifts of around 7 nm. Moreover, the presence of an isosbestic point at 429 nm indicates the transformation of ZnP^{8-} (i.e., starting-point of the titration) into SWNT/pyrene$^+$/ZnP^{8-} (i.e., end-point of the titration). The pyrene π–π transitions in SWNT/pyrene$^+$ are also subjected to changes: Additional red-shifts (2 nm) indicate that SWNT/pyrene$^+$ and ZnP^{8-} interact by virtue of electrostatic interactions.[11]

Excitation of 3.2×10^{-5} M ZnP^{8-} in aqueous solution leads to strong fluorescence emission ($\Phi \approx 0.04$), which maximizes at 612 and 665 nm. The addition of SWNT/pyrene$^+$ to ZnP^{8-} was monitored using 430 nm as the excitation wavelength, which was where the isosbestic point was observed in the absorption spectrum. Under these conditions, competitive light absorption by SWNT/pyrene$^+$ is minimal. When SWNT/pyrene$^+$ is present the fluorescence emission intensity decreased. The decrease is exponential and depends solely on the SWNT/pyrene$^+$ concentration. Inspection of Figure 3 b reveals that simultaneous with the quenching of the ZnP^{8-} emission at 612 nm, a new lower energy emission band develops, centered at 617 nm.[11]

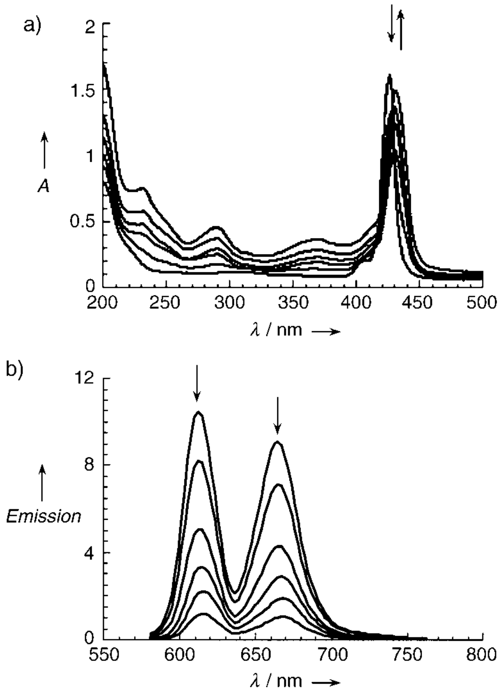


Figure 3. a) Absorption spectra of a dilute aqueous solution of ZnP^{8-} (3.2×10^{-6} M) titrated against SWNT/pyrene$^+$. b) Fluorescence spectra of a dilute aqueous solution of ZnP^{8-} (3.2×10^{-5} M) titrated against SWNT/pyrene$^+$. Excitation wavelength is 430 nm. Arrows indicate changes as the concentration of SWNT/pyrene$^+$ is increased.

In the absence of SWNT/pyrene$^+$, the fluorescence decays of ZnP^{8-} or H_2P^{8-} are fitted by mono-exponential rate laws, for which lifetimes of 2.1 ns and 9.4 ns were determined. Upon adding SWNT/pyrene$^+$ to these solutions, double-exponential fluorescence decays were observed. For example, the ZnP^{8-} fluorescence profiles were now best fitted by lifetimes of 2.1 ± 0.2 ns and 0.2 ± 0.05 ns. The two lifetimes are maintained throughout the titration assay. As the concentration of SWNT/pyrene$^+$ increases, the contribution of the short-lived component increases as well. In such mixtures, intrahybrid SWNT–porphyrin interactions are thought to be responsible for the fast kinetic component and regular porphyrin excited-state deactivations give rise to the slow component. At all concentrations, the pre-exponential factors give rise to a good agreement with the distribution of emitting species, that is, bound, immobilized versus free, non-immobilized ZnP^{8-} or H_2P^{8-}.

Upon addition of acid, the original long-lived fluorescence component is restored, concomitant with the disappearance of the short-lived species. This observation demonstrates that the complex formation is reversible. All these data point to a static quenching event occurring inside well-defined hybrids of SWNT/pyrene$^+$/ZnP^{8-} and SWNT/pyrene$^+$/H_2P^{8-}. The most likely excited-state quenching process involves electron or hole transfer, namely, oxidation of the porphyrin and reduction of the SWNT (see below). Charge transfer in SWNT–ferrocene nanohybrids has been reported recently.[5]

A thermodynamic correlation of the singlet excited states with the radical ion pair states supports our postulate. We estimate the energies of the radical ion pair states from the reduction of SWNT (−0.15 V versus saturated calomel electrode (SCE))[12] and oxidation of ZnP^{8-} (+0.77 V versus SCE)[8] and H_2P^{8-} (+0.94 V versus SCE).[8] The singlet-excited-state energies of ZnP^{8-} and H_2P^{8-} are 2.1 eV and 1.9 eV, respectively. Thus, the driving force for photoinduced electron-transfer reactions is appreciably large with values around 1.0 eV.

In parallel sets of experiments, interactions of SWNT/pyrene$^+$ with zinc 5,10,15,20-tetrakis-(2′,6′-bis(*N*-methylene-(4″-*tert*-butylpyridinium))-4′-*tert*-butylphenyl) porphyrin octabromide (ZnP^{8+})[8] were tested. Owing to repulsive electrostatic interactions in these similarly charged systems, the absorption spectra (see Supporting Information) remain—throughout the titrations—virtually as the superimpositions of the component spectra. The lack of mutually interacting systems was also confirmed in fluorescence experiments (see Supporting Information). Only a maximum of 10% quenching is noted, relative to >95% quenching in the oppositely charged systems, that is, SWNT/pyrene$^+$/ZnP^{8-}. In fact, the moderate quenching was due to competitive pyrene$^+$/ZnP^{8+} light absorption.[13]

Potential pyrene$^+$ interactions with ZnP^{8-} or H_2P^{8-} were tested in another assay. In this experiment changes in the Soret- and Q-bands mirror those noted when SWNT/pyrene$^+$ was present (not shown). However, the magnitude of the red shifts is with 3 nm notably smaller than the 7 nm red shifts in SWNT/pyrene$^+$/ZnP^{8-}. This result verifies the presence of electrostatically driven couplings between pyrene$^+$ and ZnP^{8-} or H_2P^{8-}. Apparently, SWNTs augment the electronic perturbations of the π-system of the porphyrin. A moderate fluorescence quenching of less than 15% rules out energy or electron-transfer deactivation of the photoexcited porphyrins. A thermodynamic evaluation leads to the same conclusion, that is, both processes would be highly endothermic. Singlet–singlet energy transfer would be uphill by about 0.5 eV and the driving force for charge separation would be 0.2 ± 0.1 eV.

In complementary transient-absorption studies we monitored the fate of the porphyrin fluorescence quenching and carried out the identification of the photo products. Pumping light into the ZnP^{8-} or H_2P^{8-} ground state with short 532 nm laser pulses (i.e., ps or ns) led to the population of their singlet excited states. The long-lived and molecular-oxygen-sensitive triplet spectra of, for example, ZnP^{8-} or H_2P^{8-} reveal, besides bleaching in the Soret- and Q-band region, characteristic triplet maxima around 800 nm (i.e., ZnP^{8-}: 840 nm; H_2P^{8-}: 780 nm).[14]

In contrast, the changes in the differential absorption spectra of the SWNT/pyrene$^+$/ZnP^{8-} or SWNT/pyrene$^+$/H_2P^{8-} ensembles are dominated by broad absorptions in the 600–800 nm region, which indicate the presence of ZnP^{8-} or H_2P^{8-} based redox products. Figure 4 shows the spectral changes seen in the case of SWNT/pyrene$^+$/ZnP^{8-}. At increasing times after excitation, the features of the oxidized ZnP^{8-} unit diminish in the 600–800 nm region, reflecting the return of the charge-separated state to the ground electronic state. The lifetime of the newly formed ion pair state—as derived by analyzing several wavelengths under unimolecular conditions—is 0.4 μs.

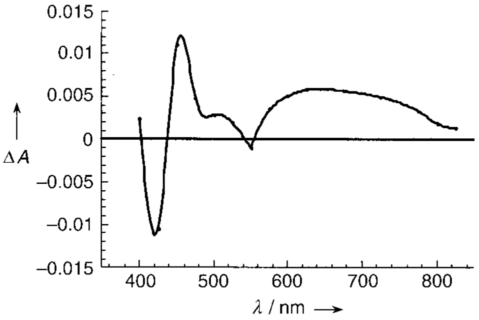


Figure 4. Differential absorption spectrum (Vis and NIR) obtained upon nanosecond flash photolysis (532 nm) of SWNT/pyrene$^+$/ZnP^{8-} in nitrogen-saturated solutions with a time delay of 100 ns.

In summary, the transient absorption data, like the static and time-resolved fluorescence data, show that SWNTs serve as the electron-acceptor component in donor–acceptor materials, just as fullerenes have been found to be the electron acceptors in related research. Intra-ensemble electron transfer from the photoexcited porphyrins (i.e., ZnP^{8-} or H_2P^{8-}) to SWNT creates long-lived radical ion pairs. This result, taken together with the light harvesting features of the used porphyrins, suggests that our approach towards versatile nanohybrids opens the way to novel chemical and light driven systems.

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