Electronic Interplay on Illuminated Aqueous Carbon Nanohorn−Porphyrin Ensembles

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Tetracationic water-soluble porphyrin (H_2P^{4+}) has been immobilized by $\pi-\pi$ stacking interactions onto the skeleton of carbon nanohorns (CNH), without disrupting their π-electronic network. The stable aqueous solution of the CNH−H_2P^{4+} nanoensemble was examined by both electron microscopy and spectroscopic techniques. The efficient fluorescence quenching of the H_2P^{4+} moiety in the CNH−H_2P^{4+} nanoensemble was probed by steady-state as well as time-resolved fluorescence emission spectroscopy, suggesting charge separation from the photoexcited H_2P^{4+} to CNH. In the presence of methyl viologen dication (MV^{2+}) and a hole trap, accumulation of the reduced species of methyl viologen was observed by the photoillumination of CNH−H_2P^{4+}, suggesting that the electron migration from the initially formed charge-separated state takes place. Transient absorption spectroscopy gave further insights on the transient species such as the charge-separated state $(CNH^{\bullet-})-(H_2P^{4+})^{\bullet+}$, which was consumed in the presence of MV^{2+} and hole shifter, leaving the reduced methyl viologen.

Carbon-based nanostructured materials are under extensive investigation in search of their utility toward the realization of novel and innovative hybrids for nanotechnological applications.[1] Electronic interplay between individual components in assembled nanosized hybrids plays major role in defining the functionality of the new material. For example, in the context of photosynthetic biomimetic systems, such aspects include, but are not restricted to, charge-transfer interactions and solubility in physiological media.

Recently, carbon nanohorns (CNH)[2] possessing dahlia-flowerlike morphology have emerged as an intriguing material within the great family of carbon nanotubes (CNT). Three are the critical points that differentiate CNH from CNT: (i) high purity, due to the absence of any metal nanoparticles during the laser ablation production, (ii) heterogeneous surface structure, due to highly strained conical ends, and (iii) aggregation in spherical superstructures, typically ranging between 50 and 100 nm. Moreover, the rough surface structure of CNH aggregates with minimum van der Waals interactions between the superstructures gives rise to better dispersions of CNH in liquid media, as compared to the tightly bundled CNTs, which do not show significant dispersions.

Although covalent attachment of various addends either onto the graphite-like sidewalls of CNH (e.g., via pyrrolidine moieties)[3] or at the conical-shaped tip (e.g., via formation of amides, esters, etc.)[4] leads to significant solubilization and dispersion of the functionalized material, the resulting perturbation of the continuous π-electronic network of CNH is a significant drawback, especially when applications based on nanoelectronics are concerned. Therefore, to overcome drawbacks arising from such issues, supramolecular approaches utilizing noncovalent $\pi-\pi$ stacking interactions between the sidewalls of CNH with aromatic organic materials and/or synergistic electrostatic interactions have been developed.[5]

Considering systems that may mimic natural photosynthesis, nanohybrids consisting of carbon-based materials and porphyrin pigments are particularly promising. The exciting features of porphyrins as light-harvesting antennas that capture visible light and transduce the excitation energy are coupled with the unique structure and electronic properties of CNH, behaving as an electron sink, toward the formation of functional donor−acceptor nanohybrids.

Recently, the supramolecular association of porphyrins as well as polymers with carbon nanotubes, resulting in highly dispersed hybrids in organic solvents, has been demonstrated.[6,7] In this framework, seeing the advantages of keeping intact the skeleton of CNH, which is without disrupting its continuous π-electronic network by any covalent attachment of organic units, we explore the immobilization of a water-soluble tetracationic water-soluble porphyrin H_2P^{4+} {5,10,15,20-tetrakis-(1-methyl-4-pyridinio) porphine tetra-(*p*-toluenesulfonate)}; Frontier Scientific, Inc.) onto the CNH skeleton (Chart 1). The focus of the current work is the association of a photoredox-active pigment with CNH, aiming to develop novel donor−acceptor CNH-based hybrids
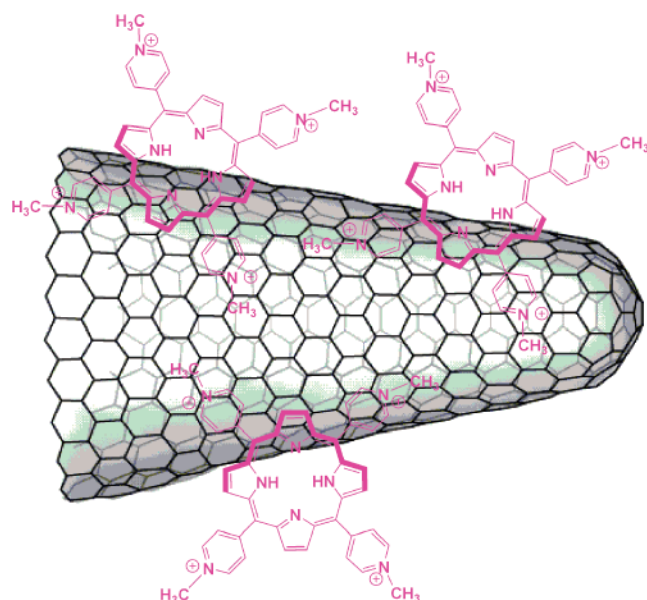
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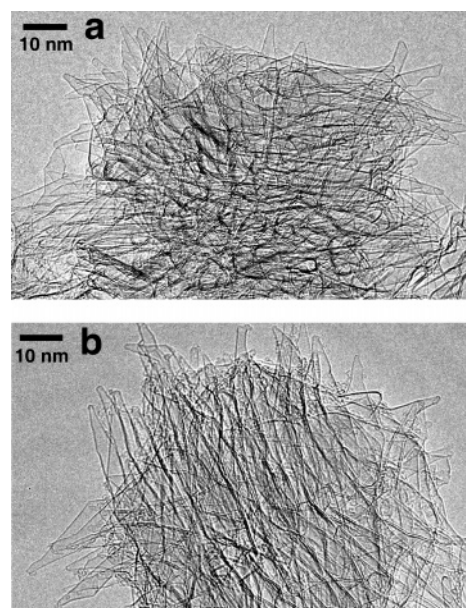§ NEC Corporation.
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CHART 1. Schematic Representation of CNH−H_2P^{4+} Nanoensemble

Figure 1. Representative HR-TEM image of (a) pristine CNH and (b) CNH−H_2P^{4+} nanoensemble.

for managing electronic interactions in environmentally friendly aqueous media.

The CNH used in this study was produced by CO_2 laser ablation of graphite in the absence of any metal catalyst under an inert Ar atmosphere (760 Torr) at room temperature, with a purity >90%. The realization of the water-soluble CNH−H_2P^{4+} hybrid was achieved upon mild sonication for 3 min of 5 mg of CNH in an aqueous solution (10 mL) of H_2P^{4+} (10^{-5} M). The resulting ink-like solution was vigorously stirred for 20 h. After that period, CNH−H_2P^{4+} hybrid was obtained as a black powder after centrifugation and decantation of the aqueous supernatant that contains unbound H_2P^{4+}. The aqueous CNH−H_2P^{4+} was filtered through a PTFE 0.2 mm and the residue was washed with water. Finally, CNH−H_2P^{4+} was re-dissolved in pure water and the resultant solution was found to be stable for months.

The formation of CNH−H_2P^{4+} hybrid was investigated by complementary microscopy and spectroscopic methods. In Figure 1, high-resolution TEM image of CNH−H_2P^{4+} hybrid is shown at high magnification, comparing with that of pristine CNH. Notably, the characteristic morphology and nanostructure of CNH are highly retained upon immobilization of H_2P^{4+}, suggesting that the stacking of H_2P^{4+} onto CNH does not alter the dahlia-flowerlike aggregation of CNH. The typical diameter of the aggregated superstructure as 70−80 nm is retained upon addition of H_2P^{4+}. Although aggregation of H_2P^{4+} onto CNH is not apparent only from TEM images, highly solubilization of CNHs into aqueous solution suggests that the surface of CNHs is covered by H_2P^{4+} as already reported with carbon nanotubes.[6g]

Steady-state electronic absorption spectroscopy was used to follow the formation of the CNH−H_2P^{4+} hybrid, by monitoring the characteristic Soret and Q-bands of the porphyrin. In Figure 2a, absorption spectra of free H_2P^{4+} and CNH−H_2P^{4+} ensemble are compared. Important points observed in the spectrum of CNH−H_2P^{4+} include the continuous absorbance from the NIR to the UV region due to the presence of nanohorns as well as the broadening and red shift of the Soret and Q-absorption bands at 421 and 515 nm and 586 nm, respectively, although the exact comparison at the same H_2P^{4+} concentration was impossible. These findings not only manifest the efficient formation of

CNH−H_2P^{4+} but also most importantly give evidence for electronic communication in the ground state between the two components within the nanoensemble.

Further insight of the electronic interplay between CNH and H_2P^{4+}, in the excited states, is derived from fluorescence emission studies. Thus, in steady-state measurements of aqueous solutions of free H_2P^{4+} and CNH−H_2P^{4+} nanohybrids, the strong fluorescence intensity of the unbound H_2P^{4+} (712 and 665 nm) was suppressed in the CNH−H_2P^{4+} nanohybrid by the presence of CNH (Figure 2b). The fluorescence quenching is attributed to the efficient immobilization of the H_2P^{4+} onto CNH. Additional quantitative electronic interplay on the photoexcited CNH−H_2P^{4+} nanohybrid could be evaluated by time-resolved fluorescence spectroscopy (Figure 2c). In this context, the fluorescence emission decay of CNH−H_2P^{4+} was found to proceed faster than the one observed on the free H_2P^{4+}. By the biexponential fitting of the fluorescence decay of CNH−H_2P^{4+} the fluorescence lifetimes (τ_f) were evaluated to be 615 ps (66%) and 2700 ps (34%), which are considerably shorter than the one of the free H_2P^{4+} (4700 ps (100%)). From such efficient fluorescence quenching it is presumed that the porphyrin is mostly adsorbed strongly onto CNH's. By comparing the τ_f value of CNH−H_2P^{4+} with the τ_{f0} of free H_2P^{4+}, the quenching rate-constant (k_q) and quantum yield (Φ_q) of the excited singlet-state of CNH−H_2P^{4+} were calculated as 1.4×10^9 s^{-1} and 0.86, respectively. The latter values are in good agreement with the steady-state fluorescence intensity quenching. Compared with carbon nanotubes,[6l] these k_q and Φ_q values in the CNH−H_2P^{4+} nanohybrid are slightly higher, suggesting that H_2P^{4+} is mostly adsorbed within the empty space between each carbon nanohorn rather than at the end cone of the carbon nanohorn.

To shed light and follow the photoinduced processes within the CNH−H_2P^{4+} nanohybrids, further experiments were conducted, with the aid of an electron mediator, such as methyl viologen dication (MV^{2+}) and a hole-shifter, such as 1-benzyl-1,4-dihydro-nicotinamide (BNAH).[8] Thus, upon addition of MV^{2+} and BNAH to nanohybrid CNH−H_2P^{4+}, accumulation of $MV^{\bullet+}$ was observed by the repeated 532-nm laser excitation of the CNH−H_2P^{4+}, as shown in Figure 3. At a first insight, the $MV^{\bullet+}$ was generated by accepting electron from the electron-rich species initially generated directly by photoexcitation of
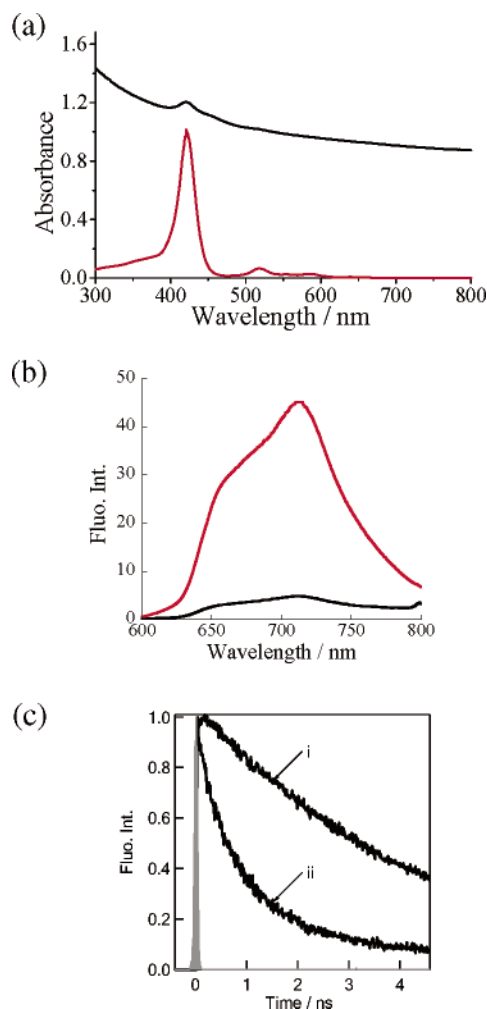
Figure 2. (a) Steady-state absorption spectra of CNH−H$_2$P^{4+} nano-hybrid (black) and free H$_2$P^{4+} porphyrin (red); concentration of the H$_2$P^{4+} in CNH−H$_2$P^{4+} nanohybrid is unclear. (b) Fluorescence spectra of aqueous solutions of CNH−H$_2$P^{4+} (black) and H$_2$P^{4+} (red); λ_{ex} = 420 nm. (c) Fluorescence decays of CNH−H$_2$P^{4+} (ii) and H$_2$P^{4+} (i) at 700 nm, as observed by the 400-nm laser excitation.
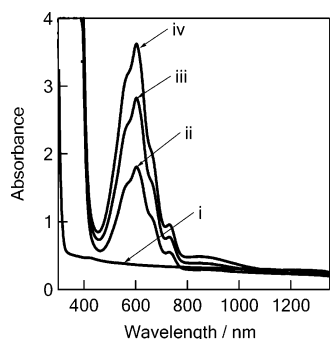
Figure 3. Steady-state absorption spectral changes of an Ar-saturated aqueous solution of CNH−H$_2$P^{4+} after the repeated irradiation of 532-nm laser light (ca. 3 mJ/pulse) in the presence of 1 mM of MV^{2+} and added concentrations of BNAH (i) 0 mM, (ii) 1 mM, (iii) 2 mM, and (iv) 3 mM, respectively. Each of the maximal absorbance is depicted after several times of laser light irradiation.

CNH−H$_2$P^{4+}. As such first events, the charge-separation of the CNH−H$_2$P^{4+} nanohybrid generating (CNH$^{\bullet-}$)−(H$_2$P^{4+})$^{\bullet+}$ can be considered from the fluorescence lifetime shortening. Then, from the CNH$^{\bullet-}$, excess electron may migrate to MV^{2+}, generating MV$^{\bullet+}$. Importantly, the MV$^{\bullet+}$ concentration tends to increase with increasing the BNAH concentration, which

indicates that the charge recombination between (CNH$^{\bullet-}$)− vs (H$_2$P^{4+})$^{\bullet+}$ and (CNH$^{\bullet-}$)−(H$_2$P^{4+})$^{\bullet+}$ vs MV$^{\bullet+}$ may be suppressed by the presence of an irreversible hole trapper BNAH. From the observed maximal Abs(MV$^{\bullet+}$) at 620 nm, the maximal MV$^{\bullet+}$ concentration after repeated 532-nm laser light irradiations was evaluated to be 0.24 mM, which corresponds to the conversion of 24% of the added MV^{2+}. When 355-nm was employed, instead of the 532-nm laser light as an excitation source, the maximal MV$^{\bullet+}$ concentration was as low as 0.02 mM, counting for a conversion of only 2%. Notably, the higher efficiency obtained by the 532-nm light is important when considering novel applications of the current nanohybrid, for example, to solar light harvesting system for mimicking photosynthesis. When the aqueous solution without CNH was irradiated with 532-nm laser light, the accumulation of MV$^{\bullet+}$ concentration was negligible (<0.002 mM), when similar concentrations of H$_2$P^{4+}, MV^{2+} and BNAH were employed (see Supporting Information).

Eventually, to obtain direct support to the above scenarios as well as to monitor the intermediate generated species, transient absorption spectra were measured following 532-nm laser light pulse irradiation of the H$_2$P^{4+} moiety of the CNH−H$_2$P^{4+} nanohybrids. Upon the nanosecond photoexcitation of CNH−H$_2$P^{4+}, the characteristic triplet−triplet transition of H$_2$P^{4+} is completely absent, suggesting that the singlet excited state of H$_2$P^{4+}, which is a precursor of the triplet state, was quenched by CNH as observed in the fluorescence quenching experiments. Evidently, transient absorption bands in the wide region from VIS to NIR were observed, as shown in Figure 4a, in which the absorption maxima appeared near 400 and 550 nm can be attributed to the (H$_2$P^{4+})$^{\bullet+}$,[9] while the absorptions of the triplet state of H$_2$P^{4+} may be overlapped (see Supporting Information). In addition, broad bands appearing in the NIR region may be ascribed to electrons trapped within nanohorns, (CNH$^{\bullet-}$), similar to cases identified in higher fullerene radical anions.[10] Thus, the formation of a charge-separation state (CNH$^{\bullet-}$)−(H$_2$P^{4+})$^{\bullet+}$ in the nanohybrid was suggested by the transient bands. The depletion observed near 1100 nm is due to scattering of the YAG laser light by the dispersed particles. The decay rates of the transient absorption bands can be attributed to charge recombination, after the formation of charge-separation state (CNH$^{\bullet-}$)−(H$_2$P^{4+})$^{\bullet+}$. Analysis of the decay time profiles of these transient bands aids to calculate the rate of charge recombination (k_{CR}) process, to be 1.5×10^7 s^{-1} in water. The inverse of k_{CR} value corresponds to the lifetime of (CNH$^{\bullet-}$)−(H$_2$P^{4+})$^{\bullet+}$ nanohybrid, which is thus calculated to be 67 ns.

Last, upon addition of MV^{2+} and BNAH, most of the transient bands disappeared leaving the 620-nm band of MV$^{\bullet+}$ as shown in Figure 4b. The latter comes to support our interpretation that the transient absorption bands were overlapped bands of (CNH$^{\bullet-}$)−(H$_2$P^{4+})$^{\bullet+}$. From the rise of MV$^{\bullet+}$, the intermolecular electron migration rate from CNH$^{\bullet-}$ in the nanohybrid to MV^{2+} in solution can be evaluated to be 5.0×10^9 M^{-1} s^{-1}, a value which is close to the diffusion controlled limit, because of collisions between the freely diffusing MV^{2+} in solution with the fixed nanohybrid.

In summary, stable water-soluble CNH−H$_2$P^{4+} nanohybrids were realized, in which the porphyrin is immobilized onto the CNH skeleton via π−π stacking interactions. Absorption and fluorescence spectroscopic studies verified not only the forma-tion of the CNH−H$_2$P^{4+} nanohybrids but also the electronic interplay between the aqueous porphyrin H$_2$P^{4+} and CNHs. Photoinduced charge-separation processes within the illuminated

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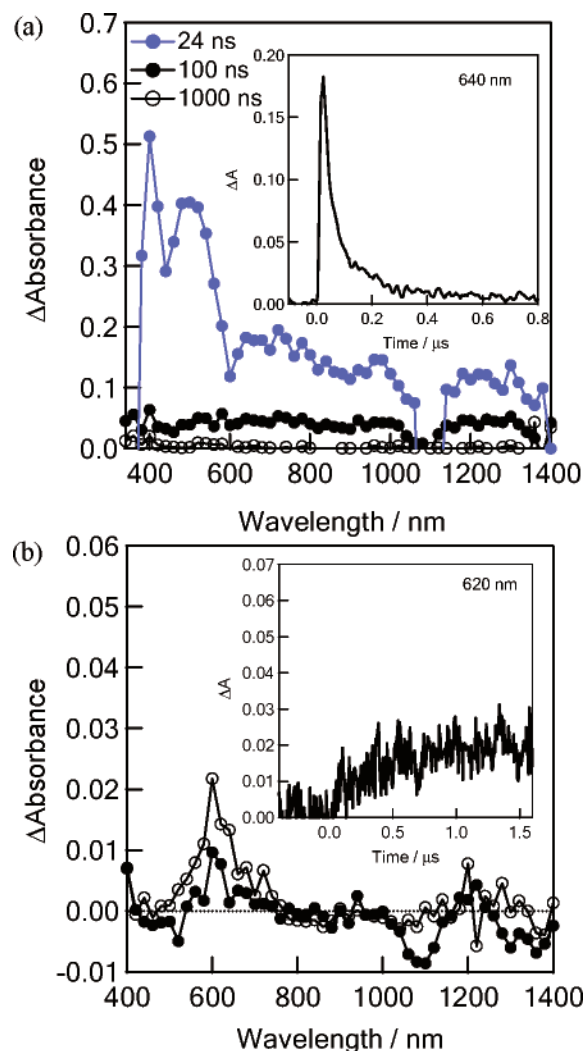
Figure 4. (a) Nanosecond transient absorption spectra of CNH−H$_2$P^{4+} observed by 532 nm laser light (ca. 3 mJ/pulse) irradiation in H$_2$O. (b) Nanosecond transient absorption spectra of CNH−H$_2$P^{4+}, in the presence of MV^{2+} (3 mM) and BNAH (3 mM). Inset: Time profiles.

CNH−H$_2$P^{4+} nanohybrids, namely oxidation of the porphyrin and reduction of the nanohorns, were monitored by transient absorption spectroscopy, while with the aid of an electron mediator and a hole shift agent the charge-separated state of (CNH$^{•−}$)−(H$_2$P^{4+})$^{•+}$ was probed by the accumulation of the electron rich mediator, which can be useful for solar energy conversion systems.

Supporting Information Available: Steady-state absorption spectra observed by 532-nm laser light irradiation of H$_2$P^{4+} in the presence of MV^{2+} and BNAH and transient spectrum of H$_2$P^{4+}. This material is available free of charge via the Internet at http://pubs.acs.org.

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