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Donor–acceptor nanoensembles of soluble carbon nanotubes†

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Donor–acceptor nanoensembles, prepared *via* electrostatic interactions of single wall carbon nanotubes and porphyrin salts, give rise to photoinduced intra-complex charge separation that lasts tens of microseconds.

Single wall carbon nanotubes, SWNTs, are being considered for many applications, strong support coming from the increased knowledge of their properties.[1,2] The development of SWNT-based photovoltaic hybrids as potent alternatives to inorganic semiconducting materials has, however, drawn much less attention.[3] Here we present the coulomb complex formation of a water-soluble SWNT grafted with poly(sodium 4-styrenesulfonate) (SWNT-PSS, Fig. 1) and an octapyridinium free base porphyrin salt H_2P^{8+} *en route* to versatile donor–acceptor ensembles and the proof for an intra-ensemble charge separation in SWNT-PSS^{n-}/H_2P^{8+} that lives tens of microseconds.

SWNT-PSS, containing 55/45 SWNT/PSS by weight, was prepared by *in situ* free radical polymerization of sodium 4-styrenesulfonate in an aqueous dispersion of pristine HiPco SWNT.[4]

The cyclic voltammetric (CV) curve of a saturated SWNT-PSS^{n-} aqueous solution, obtained in the negative potential region, displays a continuum of diffusion-controlled cathodic currents (Figure S1), with an onset at around −0.15 V *vs.* SCE (Figure S2), which corresponds to the reduction of SWNT-PSS^{n-}.[5] While the cathodic response was reproducible upon repetitive potential scanning up to −1.0 V, oxidation at potentials >0.5 V caused irreversible electrode fouling. Similarly to what was observed for pyrrolidine-functionalised NTs, this behavior is ascribed to the formation of a film on the electrode, through which electron transfer is hindered.

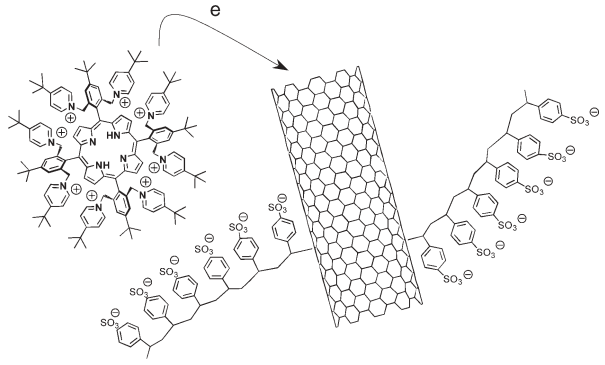

Fig. 1 Partial structure of SWNT-PSS^{n-}/H_2P^{8+} used in this work.

† Electronic supplementary information (ESI) available: experimental data. See http://www.rsc.org/suppdata/cc/b4/b406933a/

First insight into the electrostatic binding of SWNT-PSS^{n-} and H_2P^{8+} came from Transmission Electron Microscopy (TEM). One drop of dilute aqueous solution containing equivalent amounts of SWNT-PSS^{n-} and H_2P^{8+} (0.1%) was cast onto a copper grid (3 mm, 200 mesh) coated with a formvar film. For SWNT-PSS^{n-} thick bundles and ropes were evident, while for SWNT-PSS^{n-}/H_2P^{8+} thinner bundles surrounded by dark areas were observed, most likely deriving from electrostatic interactions (Fig. 2).

The formation of SWNT-PSS^{n-}/H_2P^{8+} was monitored by absorption and fluorescence techniques. A dilute aqueous solution of H_2P^{8+} (3.2×10^{-6} M) was titrated with SWNT-PSS^{n-}. Fig. 3 shows that a clean conversion from H_2P^{8+} to SWNT-PSS^{n-}/H_2P^{8+} is observed through an isosbestic point at 424 nm, with red shift of the Soret- and Q-bands.

When SWNT-PSS^{n-} was added to H_2P^{8+}, the fluorescence also underwent several key changes. Fig. 4 summarizes the steady-state fluorescence with 424 nm excitation. Firstly, the fluorescence intensities decrease exponentially and converge to a final plateau value. This trend is exemplified in the I/I_0 *versus* SWNT-PSS^{n-} concentration relationship, shown in the insert to Fig. 4. The

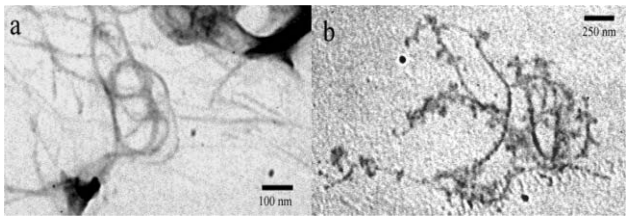

Fig. 2 TEM photos of (a) SWNT-PSS^{n-} and (b) SWNT-PSS^{n-}/H_2P^{8+}.

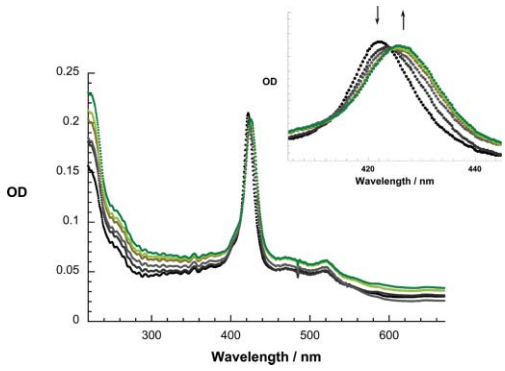

Fig. 3 Absorption spectra of a dilute aqueous solution of H_2P^{8+} (3.2×10^{-6} M) upon adding SWNT-PSS^{n-}. The inset zooms in on the 400–450 nm Soret-band region of H_2P^{8+}.

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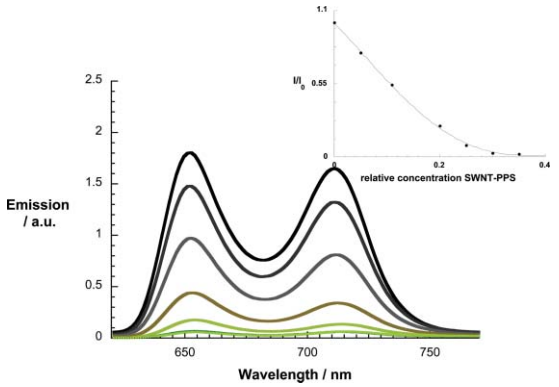

Fig. 4 Fluorescence spectra of a dilute aqueous solution of H_2P^{8+} (3.2×10^{-6} M) upon adding of SWNT-PSS^{n-}—complementary to Fig. 3. Excitation is 424 nm. Insert: I/I_0 *versus* SWNT-PSS^{n-} relationship.

decrease in H_2P^{8+} fluorescence with SWNT-PSS^{n-} is as large as 30 times. Secondly, the intensity of the fluorescence peaks at 651 and 711 nm shift progressively to the red with final maxima at 654 and 715 nm. This trend mirrors the changes in the ground state absorption spectra. Thirdly, the H_2P^{8+} fluorescence lifetime (*i.e.,* 10.2 ns), which in the absence of SWNT-PSS^{n-} is best fitted by a mono-exponential rate law, is replaced by a bi-exponential decay. In the presence of SWNT-PSS^{n-} a long- (10.2 ns) and a short-lived component (0.3 ns) are observed. The long-lived component relates to free H_2P^{8+} that is not associated with any SWNT-PSS^{n-}, while the short-lived component is attributed to the deactivation within the SWNT-PSS^{n-}/H_2P^{8+} nanoensemble. Finally, analyzing the pre-exponential factors of the two lifetime components, the long-lived one dominates only in the low SWNT-PSS^{n-} concentration regime and, ultimately, disappears in the plateau region.[6]

Due to electrostatic attraction between the positively charged H_2P^{8+} and the polyanionic SWNT-PSS^{n-}, stable SWNT-PSS^{n-}/H_2P^{8+} ensembles are formed. The synopsis of the emission studies is a rapid singlet excited state deactivation *via* an intra-ensemble electron transfer. A thermodynamic correlation of the H_2P^{8+} singlet excited state (1.9 eV) with the radical ion pair state (1.09 eV: E_{red} (SWNT-PSS^{n-}) = −0.15 V; E_{ox} (H_2P^{8+}) = +0.94 V *vs.* SCE[7]) further supports our postulate: charge separation is governed by a large $-\Delta G_{CS}$ of 0.81 eV.

To corroborate that the electron transfer effects seen in SWNT-PSS^{n-}/H_2P^{8+} are due to the presence of the SWNTs we also probed H_2P^{8+} with a commercial sample of PSS^{n-}—see Figures S3 and S4. The absorption spectra still give rise to the trend summarized above for SWNT-PSS^{n-}. However, no notable quenching was found in steady-state and time-resolved fluorescence experiments. This proves the electrostatically driven association of H_2P^{8+} with the negatively charged -SO_3^- head groups in either SWNT-PSS^{n-} or PSS^{n-}, but the lack of redox-activity of PSS^{n-} alone prevents electron transfer deactivation of the fluorescence.

Spectroscopic evidence in support of a successful electron transfer quenching came from transient absorption measurements, following 532 nm laser excitation. The excitation wavelength guarantees the exclusive population of the H_2P^{8+} singlet excited states, which intersystem crosses with a time constant of 10 ns to the triplet manifold. The long-lived and molecular oxygen sensitive triplet spectrum is shown in Fig. 5. Besides bleaching in the Soret- and Q-band region, the most important characteristic is the triplet maximum at 775 nm.[8] The differential absorption changes of the SWNT-PSS^{n-}/H_2P^{8+} ensemble, on the other hand, are governed by broad absorptions in the 550–800 nm range, indicating a H_2P^{8+} centered redox product.[8] The reduced form of SWNT-PSS^{n-} has a

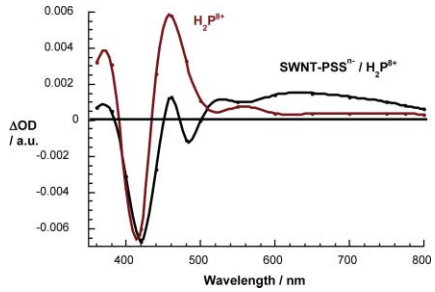

Fig. 5 Differential absorption spectrum (visible and near-infrared) obtained upon nanosecond flash photolysis (532 nm) of $\sim 1.2 \times 10^{-5}$ M solutions of H_2P^{8+} (red spectrum) and of SWNT-PSS^{n-}/H_2P^{8+} (black spectrum) in nitrogen saturated solutions with a time delay of 100 ns.

broad maximum at 450 nm[9] that is masked by the strong changes associated with the redox chemistry of H_2P^{8+}.

Under anaerobic conditions, the lifetime of 14 μs observed for the newly formed ion pair is remarkably long. The effect that molecular oxygen exerts on the lifetime of the ion pair state absorption is interesting. The lack of notable changes in the 550–800 nm region confirms that the H_2P^{8+} redox product must be the π-radical cation.[10] The transient absorption around 460 nm, on the other hand, shows decays that depend linearly on the oxygen concentration. This speaks for features of a reduced species (*i.e.,* SWNT-PSS^{n-}).

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9 The Soret-band bleaching tracks nicely the red-shift seen for SWNT-PSS^{n-}/H_2P^{8+} relative to H_2P^{8+}.
10 The H_2P^{8+} π-radical anion, which also exhibits characteristic absorption changes in this spectral range, would be oxygen sensitive.