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Carbon Nanotubes in Electron Donor—Acceptor Nanocomposites

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ABSTRACT

This Account presents recent advances in the design, synthesis, characterization, and potential applications of new hybrid materials based on carbon nanotube and electron donors. Fast charge separation and slow charge recombination are consistently observed in a variety of composites that contain porphyrin derivatives. The ultimate goal of using these systems to prepare practical photoelectrochemical devices is discussed, and a cell with a monochromatic efficiency of 8.5% conversion of light into current is illustrated.

Introduction

Nanometer-scale structures are the focus of considerable interest because they can be used to test fundamental ideas about the roles of dimensionality and confinement in materials of greatly reduced size.¹ Of the wide range of nanostructures available, carbon nanotubes, in general, and single-wall carbon nanotubes (SWNT), in particular, stand out as unique materials.^{2,3} In fact, the extraordinary electronic, mechanical, and adsorption properties of carbon nanotubes have suggested many possible applica-

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tions.^{4,5} For example, carbon nanotubes are the stiffest materials known to date and exhibit novel electronic properties that bridge those of the bulk and molecules. They also represent a valuable starting point for preparing new nanocomposites.⁵

SWNT are one-dimensional nanowires that can be metallic or semiconducting. They readily accept electrons, which can then be transported under nearly ideal conditions along the axis.⁶ Their electrical conductivity, morphology, and good chemical stability are promising realities for their possible use as truly multifunctional materials where, for instance, the electron or hole transport is associated with mass transport inside the SWNT or along its surface.

One of directions that we have considered in our research is the possibility of using SWNT in the context of photovoltaics, PV, which aims at the conversion of solar energy into electricity. In this sense, a variety of approaches have already been tested that also exploit other carbon systems/allotropes such as fullerenes.⁷ On the other hand, (nano)hybrids based on carbon nanotubes could lead to important breakthroughs.⁸ Traditional PV devices (or solar cell) are made by layers of semiconductor materials with different electronic properties. In the commercial applications, the bulk of the material is silicon. A layer is positively or p-doped, for example, using small quantities of boron. Another thin layer is n-doped, for instance, with phosphorus. Upon photoexcitation, the electron "crosses" the junction between the layers and a current can be generated.

All closed cage carbon structures, including fullerenes and carbon nanotubes, are natural electron acceptors. Proof of this can be obtained mathematically even by qualitative molecular orbital theory;⁹ the same level that readily shows that carbon nanotubes are either semicon-

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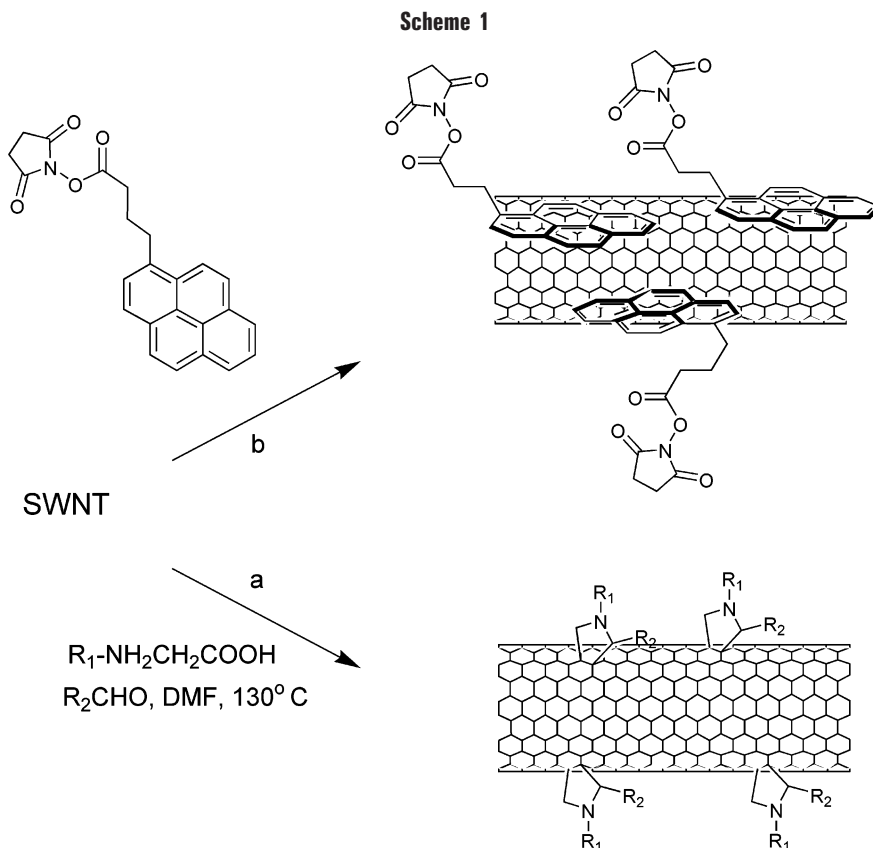
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Francesco Zerbetto graduated in 1982 at the University of Bologna, where he received his Ph.D. in 1986 for work on vibronic coupling in π -electron-conjugated molecules. From 1986 to 1990, he was a Research Associate at the National Research Council of Canada, Ottawa, where he mainly worked on Franck-Condon transitions and atom tunneling. In 1990, he joined the Faculty of Sciences at the University of Bologna, where he is now Professor of Physical Chemistry. His current research interests focus on the computer simulation of the properties and dynamics of large molecular and supramolecular systems that range from fullerenes to nanotubes, to interlocked molecules, and more recently to the interface between inorganic surfaces and organic materials.

Maurizio Prato is Professor of Organic Chemistry in the Faculty of Pharmacy at the University of Trieste. He studied chemistry at the University of Padova, where he became Assistant Professor in 1983. He moved to Trieste in 1992 as an Associate Professor and was promoted to Full Professor in 2000. He was Research Associate in 1986–1987 at Yale University, Visiting Scientist in 1992–1993 at the University of California, Santa Barbara, and Professeur Invité at the École Normale Supérieure in Paris, France, in June–July of 2002. His research focuses on the functionalization chemistry of fullerenes and carbon nanotubes for applications in materials science and medicinal chemistry and on the synthesis of biologically active substances.



ducting or metallic. The argument starts from isolated C_2 fragments that are brought together from infinite distance. Each fragment has a π and a π^* orbital. As they are brought together to form the nanotube, the two degenerate sets of π and π^* orbitals mix prevalently between themselves and spread in energy. The low-lying end of the π^* orbitals is very stable and readily accept electrons. The symmetry of these low-lying empty orbitals is the same of rotations and translations, a feature that increases the probability of transport along the tube axis. Although the original example was developed for C_{60} , the authors showed that it also holds for tubular structures.

Carbon nanotubes have the further advantage of their shear size. Upon receiving the charge, the transport along the axis of the nanometers-long carbon structure can contribute to a reduced probability of back transfer to the oxidized donor. Such a transport is largest in metallic nanotubes.²

Several obstacles need to be properly addressed when integrating SWNT into functional hybrids with the ultimate goal of producing new photovoltaic devices. They are the processibility of the nanotubes and the selection of a proper set of donors with the ultimate goals of achieving a very efficient charge separation and very long-lived radical pairs.

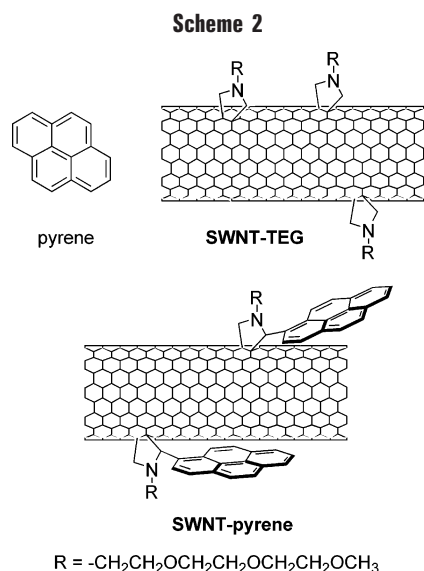
SWNT Processibility

Pristine SWNT are nearly intractable and quite awkward to process. The processibility can be improved following several approaches, including dissolving the tubes in fuming sulfuric acid.¹⁰ In our groups, we have pursued

two general strategies: (i) covalent functionalization¹¹ and (ii) noncovalent functionalization.¹² Both of them can be carried out with molecules or with polymers. Eventually, the two approaches may lead to similar results, but they differ in the degree of involvement of the carbon skeleton in the formation of covalent bonds. Covalent functionalization results in a change of hybridization from sp^2 to sp^3 and in a possible partial loss of conjugation with effects on electron-acceptor and/or electron-transport properties.¹¹

Scheme 1 shows typical examples of each approach at the molecular level. In path **a**, azomethine ylide cycloadditions to the double bonds of SWNT, both at the tips and the sidewalls, lead to the formation of pyrrolidine rings.¹³ Functional groups are present at both nitrogen and carbon atoms, and substituted pyrrolidine rings are obtained. Multiple additions generate very soluble functionalized systems with, for example, triethylene glycol side chains, SWNT–TEG. These systems, however, show a loss of the characteristic absorption bands in the near-infrared region that are typical of semiconducting SWNT.^{13a,b}

In path **b**, a polycyclic aromatic derivative, such as pyrene, interacts with the surface of SWNT;^{12,14a} other van der Waals interactions have been proposed for similar purposes.^{14b} Qualitatively, one can assess the size of the interactions between a single pyrene and a nanotube starting from the estimated binding energy of a pyrene dimer which, depending upon the level of calculation, is 11–13 kcal mol⁻¹.^{15a} Although this value is likely to overestimate the experimental one,^{15a} it can serve as a



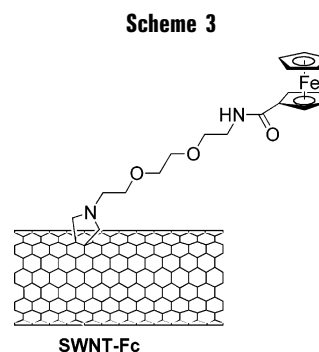
reference. In general, when aromatic molecules form π stacks, they do not overlap perfectly because of the existence of local charges that displace the two platelets with respect to each other. Adsorption of a pyrene molecule on a graphitic structure, however, can take advantage of the extended sheet structure, and it is expected that the binding energy is somewhat larger. In turn, however, the nanotube curvature may decrease the overlap and make it as low as that of naphthalene, which has an experimental binding energy for the dimer of $\sim 4 \text{ kcal mol}^{-1}$.^{15b} Even in this extreme case, at room temperature, only one molecule in a thousand is not residing on the nanotube surface.

The interaction with pyrene molecules partially exfoliates the SWNT bundles and brings individual tubes into solution. This chemical approach does not form any covalent bonds but only π - π interactions and perturbs weakly the nanotube conjugated system. Pyrene derivatives with a large variety of functional groups can be easily prepared so that the approach is very general and easy to exploit.

Processible SWNT Have Tunable Photophysics

The combination of SWNT with electron-donor groups is an innovative concept in the context of PV systems.⁸ Pyrene is a natural candidate because it can adsorb on the nanotube surface, which, in turn, should result at least in the unbundling of the tubes. Pyrene is also known to be a good electron donor upon photoexcitation. Following Scheme 2, pyrene was covalently linked to the all-carbon network.^{13a}

To assess the photophysics of SWNT-pyrene, in a first assay, its emission was compared with that of a solution containing SWNT-TEG and pyrene in about the same ratio. Upon visible light excitation, the emission of the SWNT-pyrene nanohybrid is significantly quenched ($\Phi = 0.056$) relative to the reference system ($\Phi = 0.72$). The fluorescence lifetimes also differ substantially, with values of 8.7 and 124 ns, respectively. The large difference in fluorescence lifetimes proves the existence of an



efficient intramolecular quenching process in SWNT-pyrene. From a detailed spectroscopic characterization of fluorescence and transient absorption spectroscopy, it was concluded that the rapid intramolecular excited-state deactivation involves the transfer of energy from the photoexcited pyrene to SWNT.^{13a} Unfortunately, the anticipated electron transfer, i.e., formation of $\text{SWNT}^{\cdot-}$ -pyrene⁺, is inhibited by the strongly anodic oxidation potential of pyrene.

Proof of Concept for Possible PV Applications

While in the formation of the SWNT-pyrene hybrids the photophysics of pyrene is modified, the lack of a charge separation process leads to the consideration of the less anodic ferrocene, Fc, moiety as a donor. Following Scheme 3, Fc was linked covalently to SWNT.

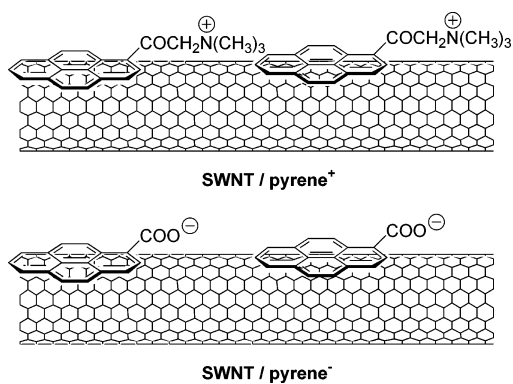
The spectroscopic and kinetic analyses of the photophysical properties of the system were interpreted in terms of intramolecular charge separation.^{13c} The moderate absorption extinction coefficients of ferrocene limits the initial photoexcitation to SWNT. In this new hybrid, the charge separation dynamics, which is the formation of $\text{SWNT}^{\cdot-}$ -Fc⁺, is very fast ($k_{\text{CS}} = 3.6 \times 10^9 \text{ s}^{-1}$), whereas the charge recombination is very slow. The analysis of the decay component of $\text{SWNT}^{\cdot-}$ -Fc⁺ throughout the 400–700-nm region yields a lifetime of $1.11 \pm 0.1 \mu\text{s}$. Because the correct identification of the $\text{SWNT}^{\cdot-}$ -Fc⁺ product was deemed to be critical, additional pulse radiolytic (i.e., time-resolved) and bulk electrolytic (i.e., steady-state) experiments were carried out to establish characteristic fingerprints of $\text{SWNT}^{\cdot-}$. All techniques gave similar broad absorptions in the visible range and confirmed the formation of the reduced $\text{SWNT}^{\cdot-}$. Fc⁺ formation was also confirmed by absorptions in the 300-nm range.

Supramolecular Donor–Acceptor SWNT Nanohybrids

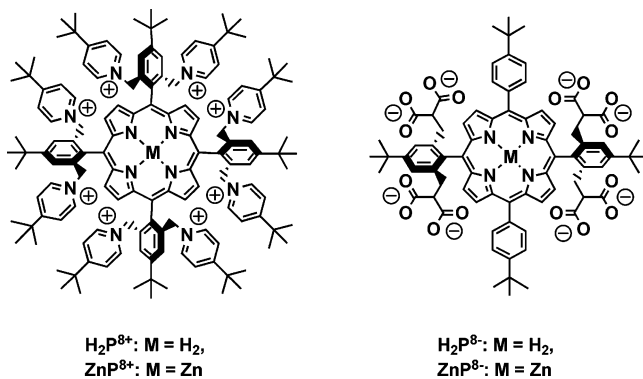
Although the covalent approach is very versatile, the supramolecular approach is practically simpler. Van der Waals and Coulombic interactions lead to the formation of supramolecular assemblies, where the donor and acceptor are in contact.

Charged pyrene derivatives are used to solubilize the SWNT through the formation of π - π interactions. SWNT were treated with 1-(trimethylammonium acetyl) pyrene (pyrene⁺) in water. The process brings the carbon wires

Scheme 4



Scheme 5



into solution (Scheme 4) with solubilities as high as 0.20 mg/mL.¹⁹ The formation and strength of the π - π interaction is reflected in the instantaneous (<1 ps) deactivation of the singlet excited state of pyrene.

The vis–NIR spectrum of the SWNT/pyrene⁺ in D₂O is reported in Figure 1. The typical absorptions of HiPCO SWNT are easily discernible, with the classical transitions between van Hove singularities of both metallic (bands centered at around 400–600 nm) and semiconducting (bands centered at 600–900 and 1200–1500 nm) nanotubes.¹⁶

The SWNT/pyrene⁺ are now covered with positive charges. They can be electrostatically associated to strong electron donors that carry negative charges. Porphyrins and phthalocyanines are both strongly absorbing and can be made water-soluble. Scheme 5 shows H₂P⁸⁻, ZnP⁸⁻, H₂P⁸⁺, and ZnP⁸⁺ that were selected as ideal components for the development of SWNT-based photoelectron active systems.

The supramolecular association was followed by absorption spectroscopy. Red shifts of the porphyrin-centered transitions together with the occurrence of isosbestic points attested to the clean formation of SWNT/pyrene⁺/ZnP⁸⁻ or SWNT/pyrene⁺/H₂P⁸⁻ complexes. H₂P⁸⁻, ZnP⁸⁻, H₂P⁸⁺, and ZnP⁸⁺ form 1:1 complexes with the charged pyrene⁺ (or pyrene⁻). The binding constants are typically on the order of 10⁴ M⁻¹.¹⁶ The SWNT/pyrene⁺/ZnP⁸⁻ or SWNT/pyrene⁺/H₂P⁸⁻ association is reversible as was confirmed by the addition of acid, which led to the restoring of the strongly fluorescent excited states of porphyrin.

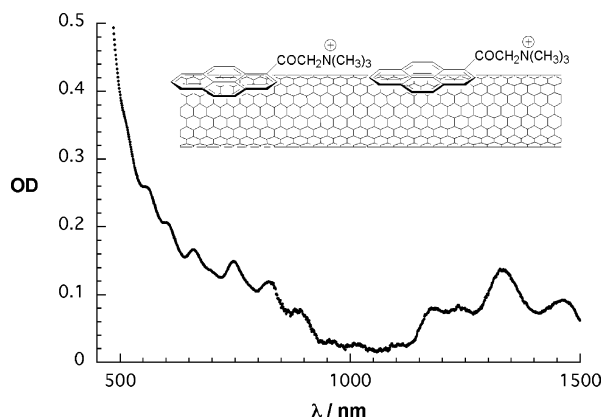


FIGURE 1. Absorption spectrum of SWNT/pyrene⁺ in D₂O.

Photoexcitation in SWNT/Pyrene/Porphyrin Hybrids

For ZnP⁸⁻, the fluorescence quantum yield is 0.04 and the lifetime is 2.1 ± 0.2 ns, and for H₂P⁸⁻, the fluorescence quantum yield is 0.11 and the lifetime is 9.4 ± 0.5 ns. In the composite systems, fluorescence and transient absorption studies in solutions showed rapid intrahybrid electron transfer (0.2 ± 0.05 ns).¹⁷ The electron-transfer evolves from the photoexcited porphyrins, excited-state energies around 2.0 eV, to SWNT and creates exothermically long-lived radical ion pairs. The driving force for photoinduced electron-transfer reactions is appreciably large with values around 1.0 eV. The differential absorption changes of the SWNT/pyrene⁺/ZnP⁸⁻ or SWNT/pyrene⁺/H₂P⁸⁻ assemblies are governed by broad absorptions in the visible between 600 and 800 nm because of ZnP⁸⁻- or H₂P⁸⁻-centered redox products. After the initial excitation, the spectroscopic features of the oxidized donors tend to disappear with time. This reflects the return of the radical ion-pair state to the ground electronic state. Through the analysis of several wavelengths under unimolecular conditions, it was possible to obtain a lifetime for the newly formed ion-pair state of 0.4 ± 0.05 μs.

Multiwall Nanotubes (MWNT)

MWNT are slightly easier to process than SWNT, because they are less prone to form tight bundles. Because of the large number of concentric cylindrical graphitic tubes, MWNT should be even more suitable for achieving charge transfer and charge transport. MWNT interact similarly to SWNT with pyrene⁺ and produce stable, dark solutions.¹⁸ Transmission electron microscopy (TEM) photographs of these solutions, deposited on a grid, show that MWNT exist as individuals with diameters ranging from 20 to 30 nm (Figure 2).

The electrostatically driven supramolecular organization of the hybrids with ZnP⁸⁻ creates photoactive assemblies, similar to SWNT/pyrene⁺/ZnP⁸⁻. Photoexcitation gives rise to charge-separated species with lifetimes of the order of microseconds (5.8 ± 0.2 μs). The better delocalization of electrons in MWNT, relative to SWNT, is most likely the reason for longer lifetimes. Percolation

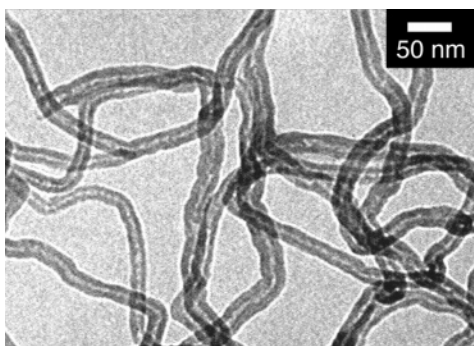
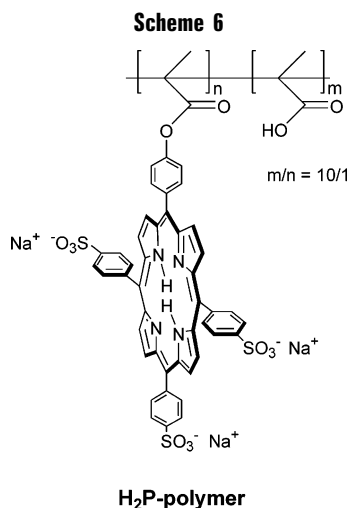


FIGURE 2. TEM photograph of MWNT/pyrene⁺, obtained from an aqueous solution.



of the charge inside the concentric wires decelerates the decay dynamics of the charge recombination.

Negatively Charged Pyrenes

The use of π – π interactions can be extended to a series of negatively charged pyrene derivatives (pyrene[−]) such as 1-pyrenecarboxylic acid (Scheme 4).¹⁹ Important here is the balance between the hydrophobic pyrene core and the hydrophilic ionic functionality. The objective is the optimization of (i) exfoliation/association of SWNT and (ii) water solubility. Solubilities of SWNT/pyrene[−] are about 0.20 mg/mL. SWNT/pyrene[−] hybrids were tested to bind ZnP⁸⁺ or H₂P⁸⁺ (Scheme 5) and found to behave similarly to the previous systems.

Polymer-Based Systems

Alternative and complementary both to the covalent functionalization and the supramolecular approaches is the association of SWNT with linear polymers. For example, SWNT are solubilized through polymer wrapping with redox-inert poly(methylmethacrylate) or PMMA. Upon functionalization of PMMA with H₂P, novel donor–acceptor nanohybrids were obtained. The hydrophilic character of the sulfonate groups (see Scheme 6)²⁰ drives the porphyrin chromophores at or close to the interface with water.

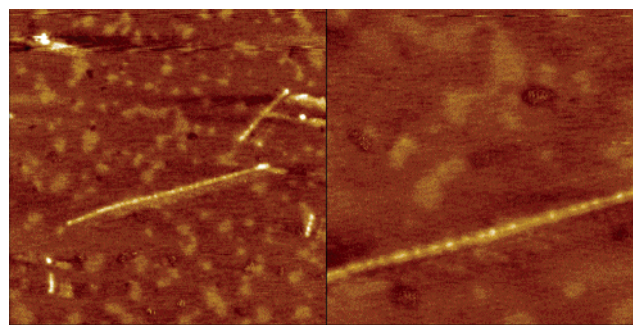


FIGURE 3. AFM photograph showing an isolated SWNT/H₂P–polymer nanohybrid; scan size is 750 × 750 nm (left image) and 300 × 300 nm (right image).

Other functionalities such as in 5-(4-hydroxyphenyl)-10,15,20-tris(phenyl)porphyrin lead to chromophoric immobilization deep inside the PMMA matrix.

Microscopic proof of the interaction of SWNT and H₂P–polymer came from TEM and atomic force microscopy (AFM). Typical TEM and AFM images illustrate that for SWNT/H₂P–polymer individual SWNT are given in Figure 3. We found that this is a rather general behavior and confirms that H₂P–polymer assists the formation of isolated individual SWNT from bundled ropes.

A similar conclusion was derived from absorption spectroscopy. The fingerprints of SWNT and H₂P–polymer interactions are discernible throughout the UV, vis, and NIR part of the solar spectrum and consist of (i) the broader and weaker absorbing Soret bands and (ii) Q bands that are bathochromic shifted at 515, 550, 592, and 648 nm.

The H₂P–polymer has a fluorescence quantum yield of 0.14 and a fluorescence lifetime of 10 ± 1 ns. In the SWNT/H₂P–polymer hybrid, the intrahybrid charge separation is 0.8 ± 0.4 ns. The radical pair features are stable, with a lifetime of 2.1 ± 0.1 μs in deoxygenated DMF solutions.

Covalently Linked Polymers

Water-soluble SWNT grafted with poly(sodium 4-styrenesulfonate) (SWNT–PSS^{n−}) was used to form an electrostatic complex with H₂P⁸⁺ (Scheme 7).²¹ In SWNT–PSS^{n−}, the number of functional groups is significantly reduced relative to what was estimated for the SWNT–Fc nanohybrids discussed above. Several analytical techniques were used to evaluate a SWNT/PSS^{n−} ratio of 55:45.²² Absorption spectra showed that the electronic fine structure of the SWNT is maintained throughout the NIR, but the oscillator strengths are markedly reduced with respect to those of pristine SWNT. The formation of the SWNT–PSS^{n−}/H₂P⁸⁺ complex was followed by absorption and fluorescence spectroscopy, complemented with TEM microscopy. In the complex, photoexcitation of the porphyrin chromophore is followed by a rapid and efficient intrahybrid charge separation event (0.3 ns), for which we detected a radical ion-pair state. The charge separation is governed by a large $-\Delta G_{CS}$ of 0.81 eV. Under anaerobic

Scheme 7

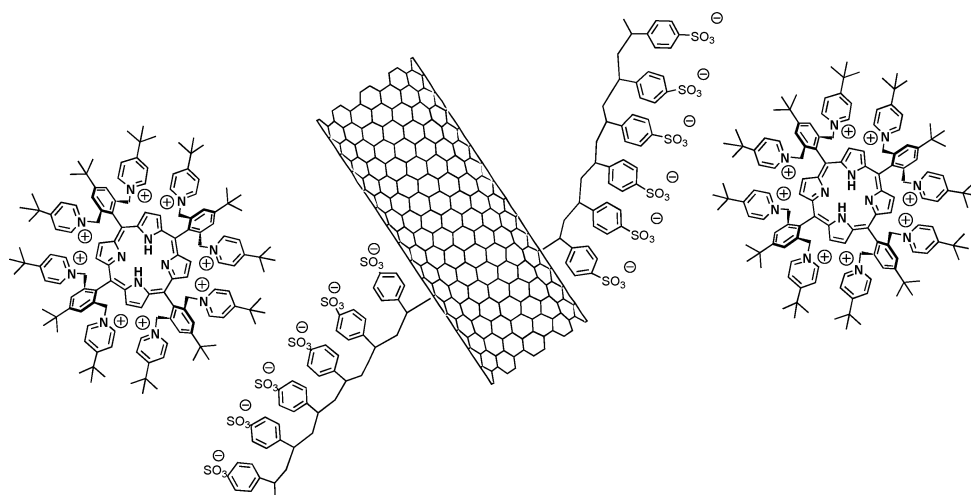


Table 1. Summary of the Lifetimes for the Generation of the Charge Separation and Charge Recombination of the Systems Discussed in This Account

	charge separation (ns)	charge recombination (μ s)
SWNT–pyrene	not observed	not observed
SWNT–Fc	3.6	1.11 ± 0.1
SWNT/pyrene ⁺	not observed	not observed
SWNT/pyrene ⁺ /ZnP ⁸⁻	0.2 ± 0.05	0.4 ± 0.05
MWNT/pyrene ⁺ /ZnP ⁸⁻	0.2 ± 0.02	5.8 ± 0.2
SWNT/H ₂ P–polymer	0.8 ± 0.4	2.1 ± 0.1
SWNT–PSS/H ₂ P ⁸⁺	0.3 ± 0.05	14 ± 0.5

conditions, a lifetime of 14 μ s was observed for the newly formed ion pair. This is the longest reported for the system discussed in this Account.

Summary of the Critical Photophysical Properties

Table 1 summarizes the two critical photophysical properties of the new nanotube/donor systems. In general, they all show a fast charge separation and a slow charge recombination. The longest-lived systems are found for SWNT–PSS/H₂P⁸⁺, although, as a rule, the combination of nanotubes covered with charged pyrene derivatives and having porphyrin derivatives as donors consistently results in lifetimes that are in the microsecond domain. This feature indicates the suitability and more importantly the versatility of these hybrids for real PV applications.

Toward Practical Devices

The favorable features that result from the combination of SWNT with porphyrin systems (SWNT/pyrene⁺/ZnP⁸⁻, SWNT/H₂P–polymer, and SWNT–PSSⁿ⁻/H₂P⁸⁺) hold a promise for the construction of photoactive surfaces. Using a layer-by-layer assembly technique, we have demonstrated that the successful incorporation of SWNT hybrids into semitransparent ITO electrodes leads to photoactive electrodes.²³ It was thought that the systematic and molecularly controlled integration of SWNT with

the extensive absorptions of porphyrin systems into nanostructured photoelectrochemical devices would lead to an efficient use of the solar light spectrum.

Mechanistic studies that probed different composition, different scavengers, different electrochemical bias, etc. illustrated the nature of the photocurrent generation. In analogy to the work in condensed media, rapid and efficient charge separation processes from the photoexcited porphyrin to SWNT afforded long-lived electron–hole separation. The primary light absorbers are the porphyrins. Pyrene⁺, originally exploited for the processing of SWNT, is useful also as a spacer that decreases the probability of electron–hole recombination, once the electron has reached the nanotube. In fact, the presence of a pyrene layer on the nanotube surface separates the donor and acceptor by at least 6 Å. The current generation process is achieved via the redox gradient from SWNT⁻ to ITO_{conduction band}, which draws the electrons in a thermodynamically allowed transfer to the ITO conduction band. The entire process is illustrated in Figure 4. The oxidized porphyrins are converted to their ground state through the reduction via ascorbic acid, which serves as a sacrificial electron donor.

It is remarkable that a cell containing a single stack of SWNT/pyrene⁺/ZnP⁸⁻, namely, a single layer of SWNT/pyrene⁺ and a single layer of ZnP⁸⁻ leads to monochromatic incident-photon-to-photocurrent efficiency, IPCE, of up to 4.2%.²³ Multilayered cells, on the other hand, give a power conversion efficiency of up to 8.5%.²³ To evaluate the performance of SWNT/pyrene⁺/ZnP⁸⁻ and compare it with reference systems, the electron accepting SWNTs were replaced with a suitably charged functionalized fullerene. In the corresponding fullerene cells, namely, PDDAⁿ⁺/C₆₀⁹⁻/ZnP⁸⁺, only moderate IPCE values of 0.15% were observed.²⁴ This result highlights the role of the SWNT acceptor unit in the composite, referred to as C₆₀, an electron acceptor par excellence. As expected, in the absence of any electron acceptor, neither SWNT nor fullerene, the efficiencies for PSSⁿ⁻/ZnP⁸⁺ cells drop dramatically to 0.08%.

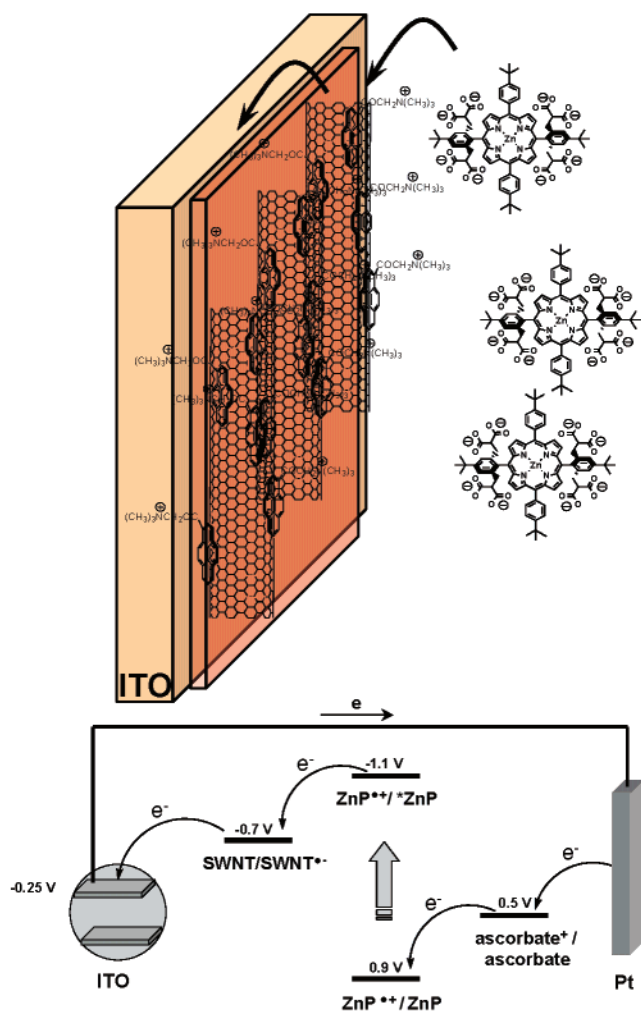


FIGURE 4. Schematic illustration of photocurrent generation in ITO electrodes covered with a single SWNT/pyrene⁺/ZnP⁸⁻ stack.

Conclusions and Outlook

Covalent and supramolecular functionalizations are the basic synthetic techniques to make SWNT easier to manipulate and soluble in many solvents, including water, so that they can be used for (self-)assembling with electron donors. The combination of SWNT with donors leads to a new generation of donor–acceptor nanohybrids, which, upon illumination, give a fast charge separation and a slow charge recombination. The lifetimes of the charge-separated species are so long that these systems appear excellent candidates for the fabrication of photovoltaic devices with the layer-by-layer assembly technique. The strategy illustrated in the last section of this Account is not optimized and has ample of room for potential improvement. While other systems may presently show higher efficiency, the approach offers high flexibility with the formation of long-lived charge separated species under a wide variety of conditions and can be considered complementary to the techniques already existing. We believe that the initial results are so promising that further research in this field to obtain practical conversion of light energy into electricity is not only justified but also desirable.

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