

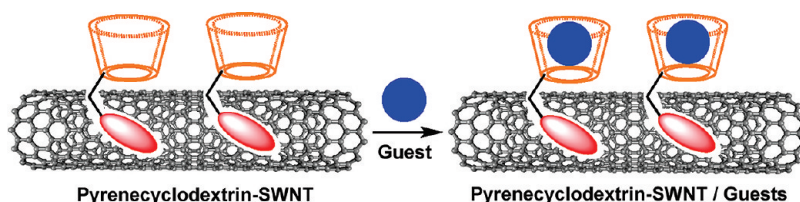
Noncovalent Functionalization of Single-Walled Carbon Nanotubes

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CON SPECTUS



Single-walled carbon nanotubes (SWNTs) have attracted much attention on account of their potential to be transformed into new materials that can be employed to address a wide range of applications. The insolubility of the SWNTs in most solvents and the difficulties of handling these highly intractable carbon nanostructures, however, are restricting their real-life applications at the present time. To improve upon the properties of the SWNTs, low-cost and industrially feasible approaches to their modifications are constantly being sought by chemists and materials scientists. Together, they have shown that noncovalent functionalization of the SWNTs can do much to preserve the desired properties of the SWNTs while remarkably improving their solubilities. This Account describes recent advances in the design, synthesis, and characterization of SWNT hybrids and evaluates applications of these new hybrid materials based on noncovalently functionalized SWNTs. Their solubilization enables the characterization of these hybrids as well as the investigation of the properties of the SWNTs using solution-based techniques. Cognizant of the structural properties of the functional molecules on the SWNTs, we present some of the recent work carried out by ourselves and others under the umbrella of the following three subtopics: (i) aromatic small-molecule-based noncovalent functionalization, (ii) biomacromolecule-based noncovalent functionalization, and (iii) polymer-based noncovalent functionalization. Several examples for the applications of noncovalently functionalized SWNT hybrids in the fabrication of field-effect transistor (FET) devices, chemical sensors, molecular switch tunnel junctions (MSTJs), and photovoltaic devices are highlighted and discussed. The blossoming of new methods for the noncovalent functionalization of the SWNTs promises a new generation of SWNT hybrid-based integrated multifunctional sensors and devices, an outcome which is essential for the development of carbon nanotube chemistry that interfaces with physics, materials, biology, and medical science.

Introduction

Carbon nanotubes (CNTs)¹ are tubular objects with unique structural, mechanical, and electronic properties.² CNTs can be classified, according to their (super)structures, into two types (Figure 1): (i) multiwalled carbon nanotubes³ (MWNTs), which are comprised of multiple layers of concentric cylinders with a spacing of about 0.34 nm between the adjacent layers, and (ii) single-walled carbon nanotubes^{4–6} (SWNTs), which consist of single

layers of graphene sheets seamlessly rolled into cylindrical tubes. The one-dimensional nanometer-scale structure of SWNTs confers on them exceptionally high tensile strength, good thermal conductivity, and excellent resilience. A SWNT is defined by rolling a sheet of two-dimensional graphene into a cylinder along a (n,m) lattice vector (C_n) in the graphene plane, where n and m are integers. Once (n,m) is specified, other structural properties of SWNTs, such as diameter (d) and

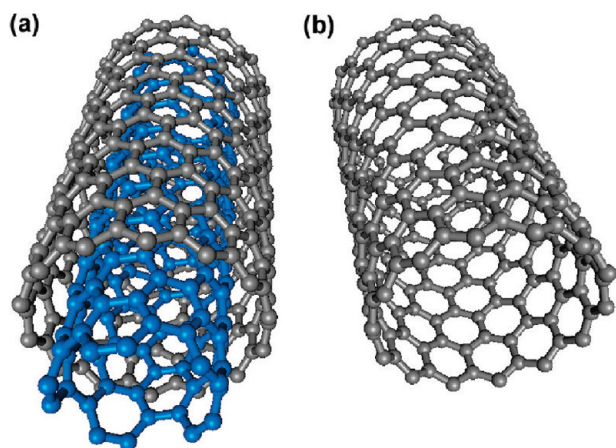


FIGURE 1. (Super)structure representations of (a) a MWNT and (b) a SWNT.

chiral angle (θ), can be determined. Among the large number of possible C_n vectors, there are two inequivalent high-symmetry directions, which have been designated $(n,0)$ and (n,n) and are termed “zig-zag” and “armchair”, respectively.¹ The uniqueness of SWNTs arises from their structures and the inherent subtleties present in them. With the exception of the zig-zag and armchair constitutions, helicity is present in the arrangements of the carbon atoms in hexagonal arrays on their surface honeycomb lattices. This helicity, along with the diameter, introduces significant changes into the electronic states and, hence, provides a unique electronic character for the SWNTs; i.e., SWNTs can be either metallic or semiconducting.^{2,6} Since the discovery^{4,5} of SWNTs in 1993, they have attracted much attention on account of their potential for being transformed into new materials that traverse a wide range of applications.^{7–11} However, the insolubility^{6,7} of SWNTs in most organic solvents and the difficulties of handling these highly intractable carbon nanostructures restrict real-life applications of SWNTs to a considerable extent.

To improve upon the properties of the SWNTs, low-cost and industrially feasible approaches to their modification have been much pursued^{7,8,11–31} vigorously in recent times. These approaches can be simply divided into two categories, i.e., (i) covalent^{7,8,11–14} and (ii) noncovalent^{15–31} functionalizations of the SWNT sidewalls. In the first category, fluorination¹³ of SWNTs has become popular for initial investigations of the covalent functionalization because the SWNT sidewalls are expected to be inert. The fluorine atoms in the fluorinated SWNTs can be substituted by alkyl groups through treatment with alkyl lithium or Grignard reagents. Another convenient method for the covalent functionalization of SWNTs is to convert the SWNT sidewalls to nanotube-bound carboxylic acids upon oxidation.^{11,14} SWNTs, functionalized with carboxylic acid groups, can be modified further with a range of

organic entities by means of amide/ester linkages or carboxylate–ammonium salt ionic interactions. Such functionalized SWNTs can usually be characterized by nuclear magnetic resonance (NMR) and absorption spectroscopies in solution. The covalent functionalization of SWNTs results in a change of carbon hybridization from sp^2 to sp^3 , leading to a possible partial loss of conjugation with consequences for electron-acceptor and/or electron-transport properties.

In the second category, the SWNT sidewalls are functionalized noncovalently by, for example, aromatic compounds, surfactants, and polymers, employing π – π stacking or hydrophobic interactions for the most part.^{15–31} In these approaches, noncovalent modifications of SWNTs can do much to preserve their desired properties, while improving their solubilities quite remarkably. The main focus of this Account is to present recent progress toward the preparation of noncovalently functionalized SWNT composite/hybrid materials and to highlight the emergent properties of these new materials and their applications in the fields of molecular electronics and nanomaterials science. Guided by the structures of the functional molecules on the SWNTs, we will summarize the recent work carried out by ourselves and others under the umbrella of the following three subtopics: (i) aromatic small-molecule-based noncovalent functionalization, (ii) biomacromolecule-based noncovalent functionalization, and (iii) polymer-based noncovalent functionalization.

Aromatic Small-Molecule-Based Noncovalent Functionalization

Aromatic molecules, such as pyrene, porphyrin, and their derivatives, can and do interact with the sidewalls of SWNTs by means of π – π stacking interactions, thus opening up the way for the noncovalent functionalization of SWNTs. Dai and co-workers¹⁵ have reported a general and attractive approach to the noncovalent functionalization of SWNT sidewalls and the subsequent immobilization of biological molecules onto SWNTs with a high degree of control and specificity. They found that the bifunctional molecule, *N*-succinimidyl-1-pyrenebutanoate, is adsorbed (Figure 2) irreversibly onto the hydrophobic surfaces of SWNTs in either *N,N*-dimethylformamide (DMF) or MeOH. The anchored *N*-succinimidyl-1-pyrenebutanoate molecules on the surfaces of the SWNTs are highly resistant to desorption in aqueous solution, a fact which leads to the further functionalization of SWNTs with succinimidyl ester groups that are reactive to nucleophilic substitution by primary and secondary amines of some proteins, such as ferritin, streptavidin, and biotinyl-3,6-dioxaoctanediamine. This technique has enabled the immobilization of a wide

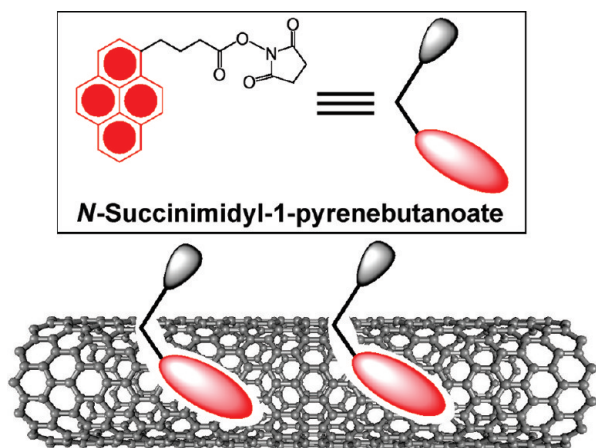


FIGURE 2. Schematic representation of *N*-succinimidyl-1-pyrenebutanoate-decorated SWNT.

range of biomolecules on the SWNT sidewalls with high specificities and efficiencies, an application that may be useful for the development of biosensors.

Guldi and Prato et al.^{8,17,19} have reported that the noncovalent association of SWNTs with pyrene and porphyrin derivatives leads to novel electron donor–acceptor nanohybrids, which, upon photoexcitation, undergo fast electron transfer, followed by the generation of microsecond-lived charge-separated species. In this case, a charged pyrene derivative, 1-(trimethylammonium acetyl) pyrene, (pyrene⁺), was used to solubilize SWNTs through the formation of π – π interactions in aqueous solution. The process induces SWNTs into aqueous solution with solubilities as high as 0.20 mg mL⁻¹. Because the SWNT/pyrene⁺ hybrids are covered with positive charges, they can associate with strong electron donors that carry negative charges by dint of electrostatic interactions. Hence, porphyrin derivatives with negative charges were selected as ideal components for the development of SWNT-based photoelectron-active systems. The porphyrin derivatives formed 1:1 complexes with the charged pyrene⁺, yielding binding constants of the order of 10⁴ M⁻¹. In the SWNT/pyrene⁺/porphyrin hybrid systems, fluorescence and transient absorption investigations in aqueous solution showed a rapid intrahybrid electron transfer (0.2 ± 0.05 ns) from the photoexcited porphyrins to the SWNTs.

An important application of SWNTs and/or their hybrids is the fabrication of SWNT/field-effect transistor (FET) devices. The SWNT/FET devices have been found¹⁰ to be sensitive to numerous analytes. These analytes, attached noncovalently to the surfaces of the SWNTs in the FET devices, can change the SWNT conductivity for at least a couple of different reasons. First, there may be an electron/charge-transfer between the analytes and SWNTs, changing the carrier concentration (n). Second, the analytes may act as a randomly distributed scat-

tering potential, changing the mobility (μ) of the charge carrier. Because conductivity is defined by $G = ne\mu$, where e is the electron charge, transistor measurements of the transfer characteristics in the SWNT/FET devices can distinguish between (i) a change in the carrier concentration and (ii) a change in the mobility of the electrons. Extensive experimentation has established¹⁰ that, in the SWNT/FET devices, changes in n lead to shifts of the threshold voltage, i.e., the voltage where the device turns on for the first time. The binding of electron-accepting molecules (NO₂ and F₄TCNQ) to the SWNTs usually leads to a threshold voltage shift toward positive gate voltages, while the binding of electron-donating molecules (NH₃ and PEI) leads to a shift toward negative gate voltages. In contrast, a change in the mobility μ results in a change in the device transconductance, called the tilt, which is defined as the ratio of the slope of the I_{sd} – V_g curve to its initial slope, where both slopes are measured at zero gate voltage. A decrease in the device mobility can be caused by geometric deformations introduced along the nanotube (i) by the analyte, (ii) by randomly charged scattering centers, or (iii) by changes occurring at the tube–tube interface.

Recently, we fabricated SWNT/FET devices to investigate the electron/charge transfer within the donor–acceptor SWNT hybrids. For example, a SWNT/FET device,²⁸ functionalized noncovalently with a zinc porphyrin derivative, was used (Figure 3) to detect directly a photoinduced electron transfer within the zinc porphyrin derivative–SWNT system. The SWNTs act as the electron donors, and the porphyrin molecules act as the electron acceptors. The photoresponse of the zinc porphyrin-coated SWNT/FET was investigated by its illumination with a light-emitting diode (LED) centered at 420 nm,

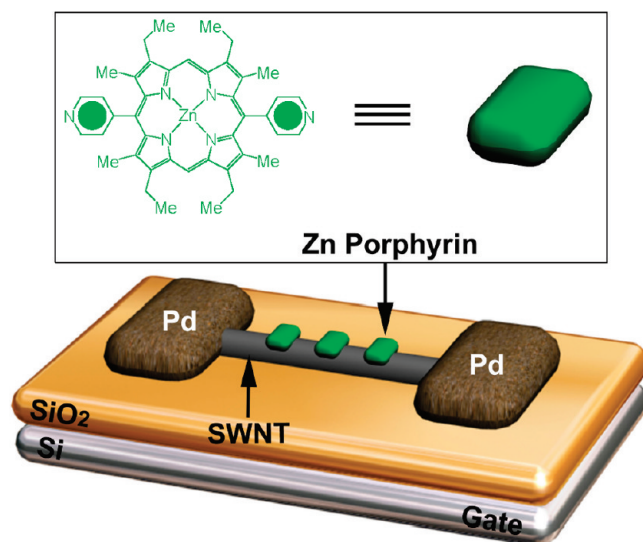


FIGURE 3. Schematic representation of the zinc porphyrin-coated SWNT/FET device employed for transistor measurements.

which approaches the maximum absorption wavelength (416 nm) of the zinc porphyrin Soret band. The response of the device to the light is a shift of the threshold voltage toward positive voltages, indicating hole doping of the SWNTs. The direction of the threshold voltage shift indicates that the process transfers electrons from the SWNTs to the zinc porphyrin, which is quite surprising because porphyrins are usually considered to be electron donors.¹⁷ One explanation for this electron-transfer process is that, upon photoexcitation of the zinc porphyrin, some of the electrons that had been transferred to the SWNT in the ground state are transferred back to the zinc porphyrin molecule in the excited state. The magnitude of the photoinduced electron transfer was found²⁸ to be a function of both the wavelength and the intensity of applied light, with a maximum value of 0.37 electrons per zinc porphyrin for light at 420 nm and 100 W m^{-2} .

The preparation and application of quantum dot/SWNT hybrids have been highly sought after in recent years for the simple reason that these hybrids are well-suited for use in optoelectronic devices. We have prepared²⁹ CdSe–SWNT hybrids (Figure 4) by self-assembling the pyrene-functionalized CdSe (pyrene/CdSe) nanoparticles onto the surfaces of the

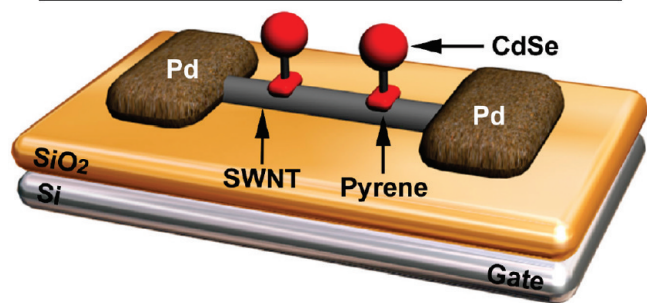
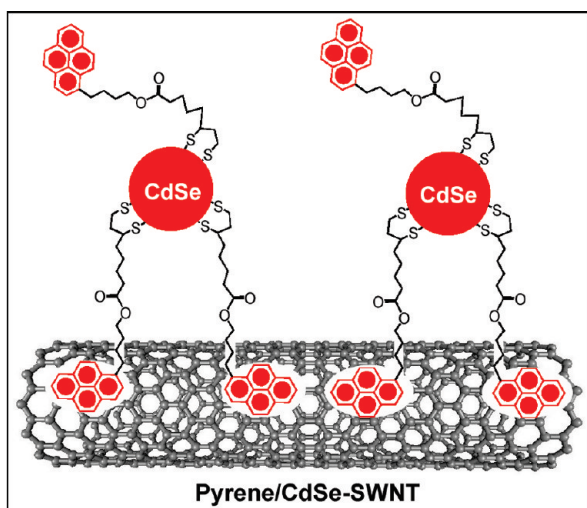


FIGURE 4. Schematic representation of the noncovalent functionalization of SWNT with pyrene/CdSe nanoparticles and a SWNT FET device with a coating of the pyrene/CdSe nanoparticles on top of SWNT.

SWNTs. FET devices have been fabricated using the hybrids to investigate the charge transfer from the pyrene/CdSe nanoparticles to the SWNTs. Fluorescent experiments show that the fluorescence intensity of the pyrene/CdSe nanoparticle solution decreases significantly and the peak blue-shifts about 8 nm on the stepwise addition of a SWNT solution. This fluorescence quenching implies that a charge-transfer process exists in the system. Furthermore, the transfer curve of the pyrene/CdSe–SWNT FET device shifts toward a negative gate voltage by about 2.9 V when the light (40 W m^{-2} intensity and 410 nm wavelength) is switched on. The value of the charge transfer has been determined by the shift of the transistor characteristic of the FET device, giving a maximum value of 2.2 electrons per pyrene/CdSe nanoparticle at the excitation wavelength (λ) of 410 nm and intensity (I) of 40 W m^{-2} . The effective charge transfer from the pyrene/CdSe nanoparticles to the SWNTs in the hybrid shows promise for applications in polymer heterojunction photovoltaic devices and solar cells. Solar cells with such quasi-one-dimensional objects for carrying electrons can have high electron/hole mobility and high absorption for achieving high energy efficiency.

To carry out quantitative investigations on the chemical sensors offered by noncovalently functionalized SWNT/FET devices, we have prepared³⁰ a pyrene-modified β -cyclodextrin (pyrenecyclodextrin) derivative and used it to fabricate pyrenecyclodextrin-decorated SWNT/FET devices (Figure 5), which can serve as chemical sensors to detect nonfluorescent organic molecules selectively, on the basis of their molecular recognition by the cyclodextrin torus. In such SWNT/FET devices, the pyrenecyclodextrin derivatives on the surfaces of SWNTs serve as the sensing host. Some organic molecules as the guests being sensed can be immobilized by becoming bound in the cavity of the pyrenecyclodextrin derivative in aqueous solution. In the presence of certain organic molecules, the transistor characteristics of the pyrenecyclodextrin-decorated SWNT/FET device shift toward negative gate voltage, exhibiting the following sequence of sensing abilities for the guest molecules: 1-adamantanol > 2-adamantanol > 1-adamantanecarboxylic acid > sodium deoxycholate > sodium cholate. The results indicate that the electrical conductance of the device is highly sensitive to particular organic molecules and varies significantly with changes in the surface adsorption of these molecules. Satisfyingly, the magnitude of the transistor characteristic movements in the pyrenecyclodextrin–SWNT/FET devices in the presence of the organic molecules depends linearly upon the magnitudes of the complex formation constants (K_s) exhibited by the pyrenecyclodextrin derivative with these molecules. There-

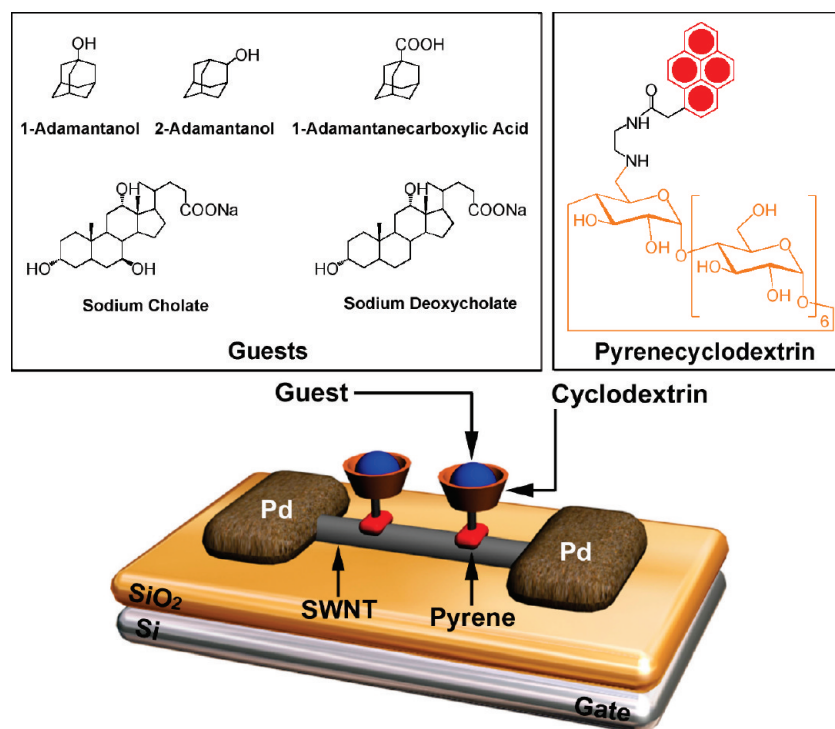


FIGURE 5. Schematic representation of the pyrenecyclodextrin-decorated SWNT/FET device showing how pyrenecyclodextrin-decorated SWNTs interact with guest molecules when they are being sensed in a FET device. The five guest molecules employed were 1-adamantanol, 2-adamantanol, 1-adamantanecarboxylic acid, sodium cholate, and sodium deoxycholate.

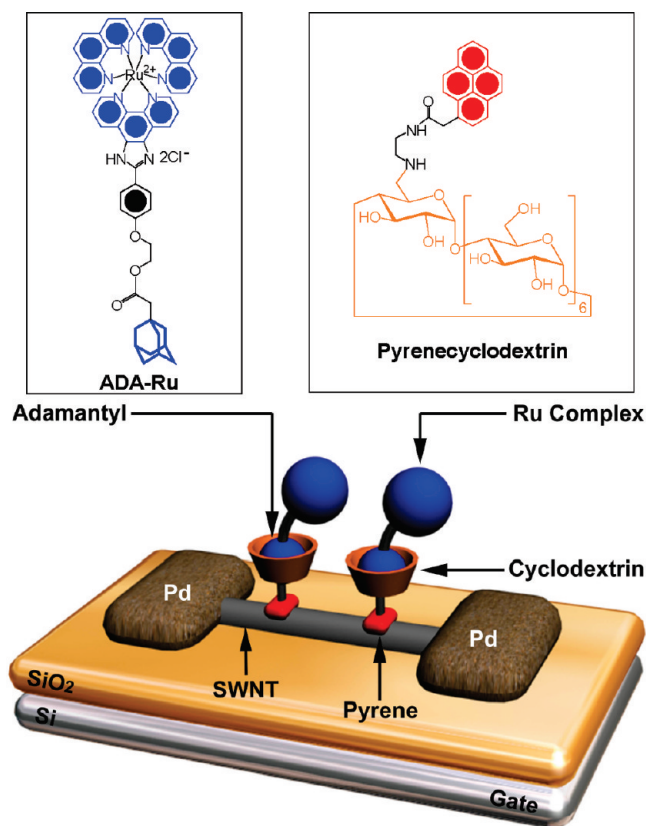


FIGURE 6. Schematic representation of the ADA–Ru complex and pyrenecyclodextrin and how the pyrenecyclodextrin-decorated SWNT hybrids interact with the ADA–Ru complexes when they are being sensed in a FET device.

fore, the pyrenecyclodextrin-decorated SWNT/FET devices serve as chemical sensors to detect organic molecules in aqueous solution, not only selectively but also quantitatively. This technology may lead to new applications in such areas as environmental monitoring, medical diagnostics, and gene-chip technologies.

Furthermore, we have employed the pyrenecyclodextrin-decorated SWNT/FET device (Figure 6) as a tunable photosensor³¹ in aqueous solution, to detect a luminescent ruthenium complex as a consequence of its molecular recognition by the pyrenecyclodextrin derivative. The ruthenium complex with an adamantyl tether (ADA–Ru) as the sensing guest can be immobilized as a result of the binding of the adamantyl group inside the cavity of the pyrenecyclodextrin derivative in aqueous solution. It is this molecular recognition event that renders the charge transfer between the ADA–Ru guest and the pyrenecyclodextrin-decorated SWNT hybrids practicable. The experimental results indicate (Figure 7) that the electrical conductance of the pyrenecyclodextrin-decorated SWNT/FET device shows a dramatic change in the absence and presence of the ruthenium complex under light. When the light is on ($I = 40 \text{ W m}^{-2}$ and $\lambda = 280 \text{ nm}$), the transistor characteristic of the pyrenecyclodextrin-decorated SWNT/FET device shifts toward a negative gate voltage by about 1.6 V and its sheet resistance increases rapidly, indicating a charge-transfer pro-

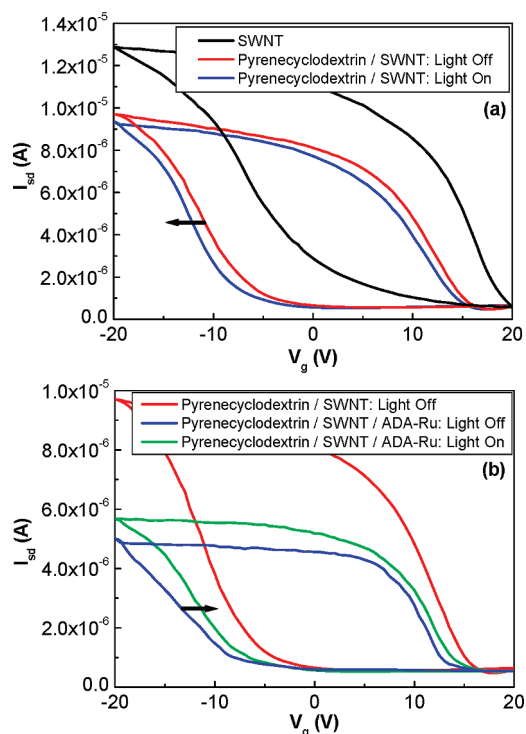


FIGURE 7. (a) I_{sd} - V_g curves of SWNT/FET before (black) and after (red) assembling the pyrenecyclodextrin (1.13 mM) in the dark and the I_{sd} - V_g curve of the pyrenecyclodextrin-SWNT/FET when the light is on (blue), $\lambda = 280$ nm and $I = 40$ W m $^{-2}$. (b) I_{sd} - V_g curves of the pyrenecyclodextrin-SWNT/FET before (red) and after (blue) binding the ADA-Ru complex (2.20 mM) in the dark and the I_{sd} - V_g curve of the ADA-Ru-pyrenecyclodextrin-SWNT/FET when the light is on (green), $\lambda = 490$ nm and $I = 40$ W m $^{-2}$. The arrows in the figure indicate the directions of the I_{sd} - V_g curve shifts.

cess from the pyrenecyclodextrins to the SWNTs. In contrast, the transistor characteristic of the pyrenecyclodextrin-deco-

rated SWNT/FET device in the presence of the ruthenium complex shifts toward a positive gate voltage by about 1.9 V and its sheet resistance decreases slowly when the light is on ($I = 40$ W m $^{-2}$ and $\lambda = 490$ nm), indicating a charge-transfer process from the pyrenecyclodextrin-SWNT hybrids to the ruthenium complex. These photoresponse processes are recoverable after removal of the light. Thus, the pyrenecyclodextrin-decorated SWNT/FET device can indeed serve as a tunable photosensor to detect luminescent molecules. These experimental results raise the prospect of promising applications of SWNT/FET devices in the area of tunable light detection, as in artificial eyes and photovoltaic devices.

Another promising application for SWNT hybrids is the fabrication of SWNT hybrid-based molecular switch tunnel junctions (MSTJs). In our original report,²⁶ we described two-terminal MSTJs that incorporate a semiconducting SWNT as the bottom electrode. The nanotube interacts noncovalently with a monolayer of bistable, nondegenerate [2]catenane tetracations (Figure 8), self-organized by their supporting amphiphilic dimyristoylphosphatidyl anions, which shield the mechanically switchable tetracations from a 2 μ m-wide metallic top electrode. The resulting 0.002 μ m 2 area tunnel junction addresses a nanometer-wide row of ca. 2000 molecules. Active and remnant current-voltage measurements demonstrate that these devices can be switched reconfigurably and cycled repeatedly between high- and low-current states under ambient conditions. These SWNT hybrid-based MSTJs operate just like the previously reported³² silicon-based MSTJs but

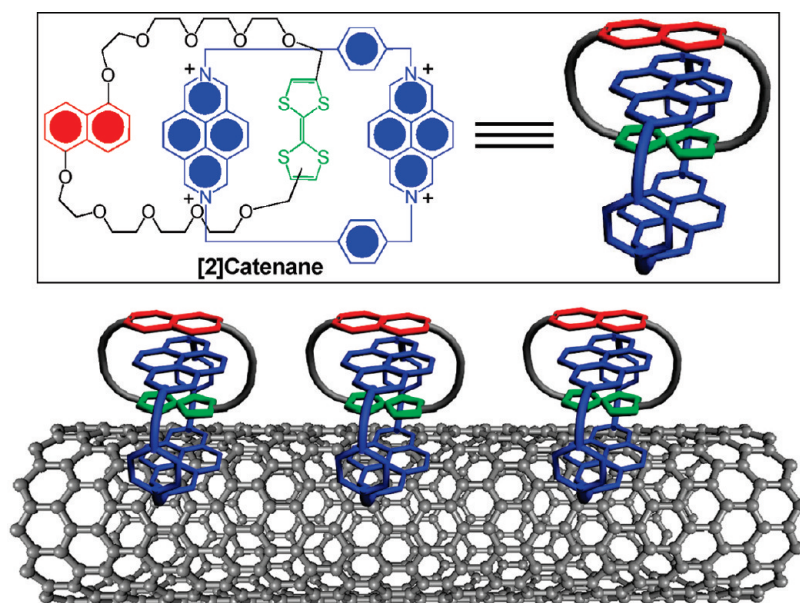


FIGURE 8. Schematic illustration of SWNT MSTJ that gets over the perfect size match between the bistable [2]catenanes (1 nm cubes) and the diameter (1 nm) of the SWNTs, which leads to the [2]catenanes being lined up in rows on the surfaces of SWNTs.

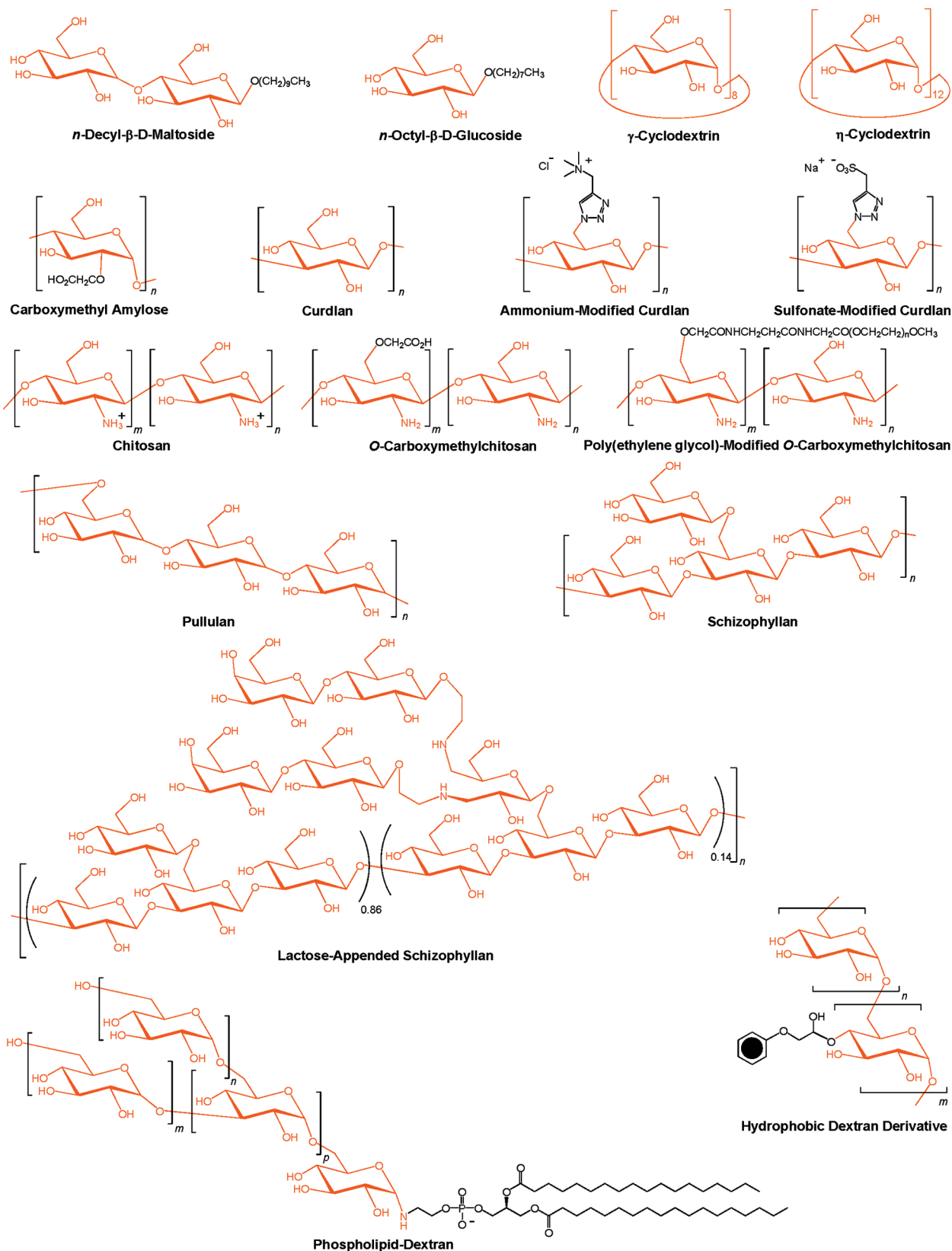


FIGURE 9. Chemical structures of *n*-decyl- β -D-maltoside, *n*-octyl- β -D-glucoside, γ -cyclodextrin, η -cyclodextrin, carboxymethyl amylose, curdlan, ammonium-modified curdlan, sulfonate-modified curdlan, chitosan, O-carboxymethylchitosan, poly(ethylene glycol)-modified O-carboxymethylchitosan, pullulan, schizophyllan, lactose-appended schizophyllan, phospholipid-dextran, and a hydrophobic dextran derivative for the noncovalent functionalization of the SWNTs.

quite differently from similar devices incorporating bottom metal electrodes.

Biomacromolecule-Based Noncovalent Functionalization

The solubilization of SWNTs associated noncovalently with biomacromolecules in both aqueous and organic solutions has been investigated recently at some considerable length.^{15,16,18,22,33–42} The biomacromolecules employed in the noncovalent functionalization of SWNTs include simple saccharides and polysaccharides,^{15,18,22,33–42} proteins,¹⁵ enzymes, DNA, etc. In this section, we will focus our discussion exclusively on the saccharide- and polysaccharide-functionalized SWNTs.

Our earliest experiments demonstrated²² that, although SWNTs are not soluble in an aqueous solution of starch, they are soluble in an aqueous solution of the starch–iodine complex. These observations suggest that iodine pre-organizes the backbone of the amylose in starch into a helical geometry and makes its hydrophobic cavity accessible to a single SWNT or bundles thereof. The formation of such starch-wrapped SWNT complexes is driven by simultaneous enthalpic and entropic gains that result from creating favorable van der Waals interactions and from expelling the many small iodine molecules located inside the helix out into the solvent by a “pea-shooting” type of mechanism. This result leads to a simple protocol for the purification of SWNTs, under ambient conditions, using the readily available starch–iodine complex. The reversible solubilization of starch-wrapped SWNTs in water has been further investigated by the action of enzymatic hydrolysis, using the commercially available amyloglucosidase from *Rhizopus* mold. Addition of this enzyme to an aqueous solution of starch-wrapped SWNTs results in the precipitation of all of the SWNTs within 10 min, as indicated by light-scattering measurements and also by changes that are clearly visible to the naked eye. This reversible water solubilization of SWNTs in aqueous solution using starch could provide a cheap and easy way to produce integrated biological nanotube devices.

Since our report²² on the preparation of the amylose-wrapped SWNT hybrids, a whole host of different saccharides and polysaccharides (Figure 9), such as *n*-decyl- β -D-maltoside,³³ *n*-octyl- β -D-glucoside,³³ γ -cyclodextrin,³⁴ η -cyclodextrin,³⁵ carboxymethyl amylose,¹⁶ curdlan,^{36–38} ammonium-modified curdlan,^{38,39} sulfonate-modified curdlan,³⁸ chitosan,⁴⁰ *O*-carboxymethylchitosan,⁴⁰ poly(ethylene glycol)-modified *O*-carboxymethylchitosan,⁴⁰ pul-lulan,¹⁶ schizophyllan,^{36,37} lactose-appended schizophyllan,⁴¹ phospholipid–dextran,⁴² and a hydrophobic dextran

derivative,¹⁸ have been used to effect the noncovalent functionalization of SWNTs. The research has been aided and abetted by the fact that (i) such saccharides and polysaccharides have almost no light absorption in UV–vis wavelength region, so that the SWNT hybrids can be characterized by photochemical experiments, and (ii) the saccharide- and polysaccharide-coated SWNT hybrids are usually biocompatible and may be applicable for many medicinal purposes. For example, Shinkai and co-workers^{36,37} have reported that schizophyllan and curdlan are capable of wrapping not only SWNTs cut to 1–2 mm length but also as-grown SWNTs, reflecting the strong helix-forming nature of the β -1,3-glucan main chains.

Polymer-Based Noncovalent Functionalization

Polymers,^{21,23–25,43–49} especially conjugated polymers,^{21,23–25,43–45,47,49} have been shown to serve as excellent wrapping materials for the noncovalent functionalization of SWNTs as a result of π – π stacking and van der Waals interactions between the conjugated polymers and the surfaces of SWNTs. Because there has been a great deal of research work reported recently focusing on the preparation of noncovalently polymer-functionalized SWNTs using similar approaches,^{43–49} we will summarize our original investigations^{21,23–25} relating to the preparations of conjugated polymer-wrapped SWNTs in this section. We have prepared some organic-soluble conjugated polymers/dendrimers (Figure 10), e.g., poly(*m*-phenylenevinylene)-co-(2,5-dioctoxy-*p*-phenylene)vinylene (PmPV),²¹ poly(2,6-pyridinenevinylene)-co-(2,5-dioctoxy-*p*-phenylene)vinylene (PPyPV),²³ poly-(5-alkoxy-*m*-phenylenevinylene)-co-(2,5-dioctoxy-*p*-phenylene)vinylene (PAmPV),²⁵ and stilbene-like dendrimers,²⁴ to investigate their noncovalent functionalization for SWNTs.

Unlike polysaccharides, PmPV behaves as a photonic material with distinctive photophysical properties. Curran and co-workers⁵⁰ have reported the preparation of a PmPV/MWNT composite and found that the introduction of MWNTs can increase the electrical conductivity of the PmPV polymer by up to 8 orders of magnitude. The SWNTs have high aspect ratios, making them ideal candidates for bridging across electrodes for charge-transport measurements. We have prepared^{21,23} PmPV/SWNT hybrids and obtained some useful results from two key experiments, which indicate that the PmPV polymer is in intimate electrical contact with SWNTs and that the polymer wraps itself around bundles of the SWNTs, rather than around individual tubes, which then aggregate to form ropes. The two experiments relate to (i) the photoconductivity

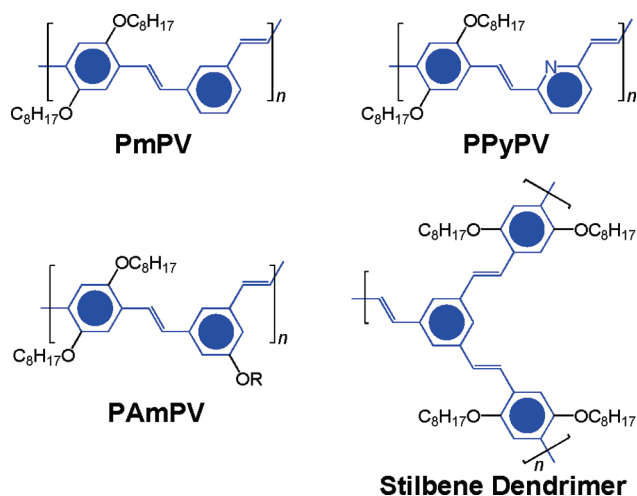


FIGURE 10. Structural formulas of PmPV, PPyPV, PAmPV, and stilbene-like dendrimer employed in the preparation of the SWNT hybrids.

response of a single polymer-wrapped SWNT bundle and (ii) some two-photon fluorescence measurements of single PmPV/SWNT bundles, which correlate with structural measurements obtained by atomic force microscopy. Control experiments on unwrapped SWNT devices exhibit no optically modulated response, and only PmPV-wrapped SWNTs show on/off differences for negatively and positively biased junctions. The magnitude of the change in current is similar and corresponds to ca. 15–20% of the total current. Thus, the current passing through the PmPV/SWNT device is photo-amplified for a positive applied bias but is photorectified for a negative one. This feature is an intrinsic property of PmPV-wrapped SWNTs and is not reversed by changing the connections to the two electrodes. The wavelength dependence of the optically gated conductivity in PmPV-wrapped SWNT ropes was recorded from 375 to 805 nm in 5–10 nm measurements. The absolute value of the wavelength dependence of the illumination on the current response, along with the polymer absorption

spectrum, suggests a correlation between the polymer absorption spectrum and the wavelength of the photomodulated conductivity of these devices.

On the basis of the available experiment results, we have modified²⁵ the PmPV polymer and prepared and characterized a variety of PmPV derivatives functionalized in synthetically accessible C-5 position of the meta-disubstituted phenylene ring, affording PAmPV derivatives. The PAmPV derivatives have also been found to solubilize SWNT bundles in organic solvents by wrapping themselves around the bundles. Interestingly, the PAmPV derivatives, which bear tethers or rings, can form pseudo rotaxanes with rings and threads, respectively. Wrapping of these functionalized PAmPV polymers around SWNTs results in the grafting of pseudo rotaxanes along the walls of the SWNTs in a periodic fashion (Figure 11). Thus, the noncovalent functionalization of the SWNT bundles with these conducting polymers that have the capacity to form pseudo rotaxanes represents the operation of supramolecular phenomena at three different levels of superstructure, viz., (i) the aggregation of SWNTs into bundles, (ii) the wrapping of SWNT bundles by the polymers, and (iii) the formation, through the side arms attached to the polymers, of threaded complexes. The results hold out the prospect of being able to construct arrays of molecular switches and actuators.

We have also investigated²⁴ the interactions between stilbene-like dendrimers and the SWNTs. The stilbene-like dendrimers, which may be regarded as hyperbranched analogues of PmPV, possess two-dimensional shapes and contain well-defined pockets. A molecular-modeling investigation has suggested that only single (10,10)-SWNTs can fit inside these pockets. We have found that these hyperbranched polymers are more efficient at breaking up SWNT bundles. Introducing

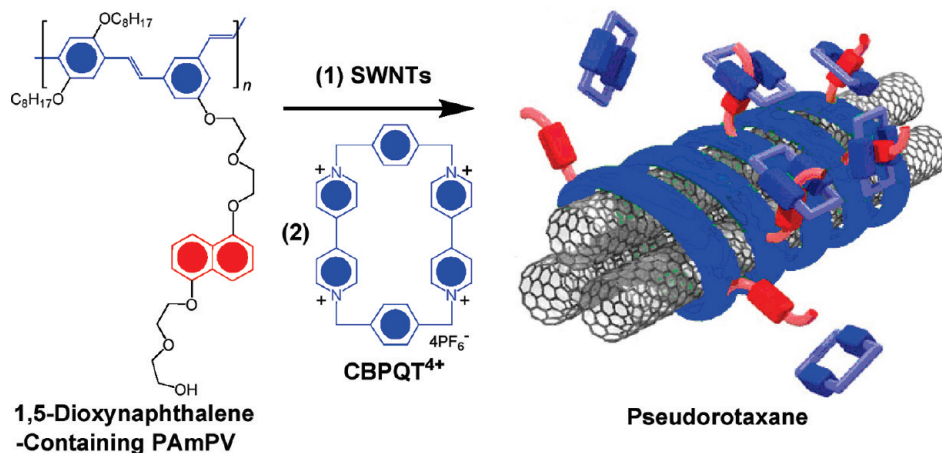


FIGURE 11. Schematic representation of the formation of the pseudo rotaxanes, wherein the side arms of the 1,5-dioxynaphthalene-containing PAmPV-decorated SWNT hybrids associate with cyclobis(paraquat-*p*-phenylene) (CBPQT⁴⁺) rings.

a certain degree of branching into the PmPV polymer makes it more rigid and less efficient when it comes to wrapping the SWNT bundles, and thus, more polymeric material is required to achieve a sufficient coverage for SWNT dispersion and solubilization. However, the pockets provided by the hyperbranched polymer offer a better fit for SWNTs. The outcome is that more single strands of the SWNTs were observed on a mica wafer by atomic force microscopy than in the case when the PmPV polymer was used.²¹

Conclusions

Functionalized CNTs have been playing an increasingly central role in the research, development, and application of nanotube-based nanomaterials and systems. In this Account, we have described briefly recent progress in the preparation, characterization, and application of these new hybrid materials based on noncovalently functionalized SWNTs by reflecting selectively upon three subtopics: aromatic small-molecule-based noncovalent functionalization, biomacromolecule-based noncovalent functionalization, and polymer-based noncovalent functionalization. The solubility of SWNTs modified by the noncovalent functionalization offers excellent opportunities, not only in the characterization and understanding of the SWNTs in solution but also in their use in various nanomaterials and devices. Thus, several examples for the application of noncovalently functionalized SWNT hybrids to the fabrication of FET devices, chemical sensors, MSTJs, and photovoltaic devices are highlighted. The methodologies for noncovalent functionalization of SWNTs, carried out by ourselves and others, promise a new generation of SWNT hybrid-based integrated multifunctional sensors and devices. The investigation of these and other integrated devices is essential for the development of CNT chemistry which interfaces with physics, materials, biology, and medical science. For further development of this demanding area of research, comparative investigations on single or individual SWNTs before and after noncovalent functionalization are necessary. In this manner, the dependence of reactivity upon electronic structures of SWNTs and the effect of noncovalent functionalization on the electrical and mechanical properties of SWNTs can be determined and monitored in solution and in devices.

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BIOGRAPHICAL INFORMATION

Yan-Li Zhao was born in Chifeng, People's Republic of China, in 1978. He received his B.Sc. degree in chemistry from Nankai University in 2000 and his Ph.D. degree in physical chemistry from the same university in 2005 under the supervision of Professor Yu Liu. He joined Professor Fraser Stoddart's research group at University of California, Los Angeles (UCLA) as a postdoctoral scholar in October 2005. At UCLA, he has conducted research in the broad areas of organic chemistry and nanoelectronics, with emphasis on noncovalent functionalization and device fabrication in the domains of single-walled carbon nanotubes, mechanically interlocked molecule-based nanomaterials, and biocompatible mechanized nanoparticles for drug delivery.

Fraser Stoddart was born in Edinburgh, Scotland, in 1942. He received his B.Sc. (1964), Ph.D. (1966), and D.Sc. (1980) degrees from Edinburgh University. In 1967, he went to Queen's University (Canada) as a National Research Council Postdoctoral Fellow and then, in 1970, to Sheffield University as an Imperial Chemical Industries (ICI) Research Fellow, before joining the academic staff there as a Lecturer in Chemistry. After spending a sabbatical (1978–1981) at the ICI Corporate Laboratory in Runcorn, he returned to a Readership at Sheffield in 1982. In 1990, he took up the Chair of Organic Chemistry at Birmingham University and was Head of the School of Chemistry there (1993–1997) before moving to UCLA as the Saul Winstein Professor of Chemistry in 1997. He was the Director of the CNSI from 2002 to 2007 and during that time held the Kavli Chair in NanoSystems Sciences. He joined the faculty at Northwestern University as a Board of Trustees Professor of Chemistry in January 2008. His research interests are focused on transporting well-established concepts in biology from the life sciences into materials and medicinal chemistry.

FOOTNOTES

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