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Functionalization of Carbon Nanotubes with Stimuli-Responsive Molecules and Polymers

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Abstract

"Smartly" functionalized carbon nanotubes (CNTs) constitute an actively pursued research topic in the fields of nanomaterials and nanotechnology. The development of highly efficient and selective methodologies for dispersing CNTs in the liquid phase has not only made efficient separation and purification of CNTs possible, but also opened the doors to many fascinating material and biological applications. Very recently, the development of CNT hybrid systems with controlled stimuli-responsiveness has achieved significant breakthroughs. This chapter outlines the state of the art within this vibrant research area, and examples from the most recent literature are selected to demonstrate progress in the preparation of CNT composites, the physical properties of which can be readily switched by various external stimuli (*e.g.*, pH, photoirradiation, solvent, temperature, etc.).

Keywords: carbon nanotubes, chemical functionalization, stimuli-responsiveness, reversibility, nanomaterials, supramolecular chemistry

1. Introduction

Since the first synthesis of carbon nanotubes (CNTs) by Ijima in 1991 [1], CNT-based materials have attracted tremendous interest from both academia and industry. Indeed, CNTs along with other nano-sized carbon materials (*e.g.*, fullerenes and graphenes) have taken the central stage of the present research of nanoscience and nanotechnology, and it is easily foreseeable that research efforts dedicated to these topics will continue to grow in the future [2]. For decades, the extraordinary structural and physical properties of CNTs have promoted extensive investigation aimed at their synthesis, processing, and functionalization, which in turn create

a wide range of applications in electronics [3, 4], optics [5], environment [6], biology, and medicinal science [7, 8].

CNTs are carbon allotropes in a tubular shape with nanoscale diameter (*ca.* 1–2 nm) and high aspect ratio. Generally speaking, CNTs can be classified as single-walled carbon nanotubes (SWNTs), double-walled carbon nanotubes (DWNTs), and multi-walled carbon nanotubes (MWNTs). A SWNT can be viewed as a single layer of graphene sheet rolled up in a cylindrical shape, while the DWNTs and MWNTs are similar carbon nanostructures but made of two or more layers of SWNTs, in which the smaller diameter tube(s) coaxially nested in the larger one(s). The exact structures of SWNTs differ by the ways of rolling the graphene sheet, which can be described using their specific chiral indices (*n,m*) and chiral angles $\theta(n,m)$. As illustrated in **Figure 1**, SWNTs with chiral indices of *m* = 0 or *n* = *m* are achiral and often referred to as *zigzag* and *armchair* tubes, respectively. Other combinations of *n* and *m* define the family of so-called chiral nanotubes. The electronic properties of SWNTs significantly depend on their chiral indices. When $|n-m| = 3q$ where *q* is an integer, the nanotube is metallic or semi-metallic, whereas for all other cases the nanotubes are semiconducting in nature.
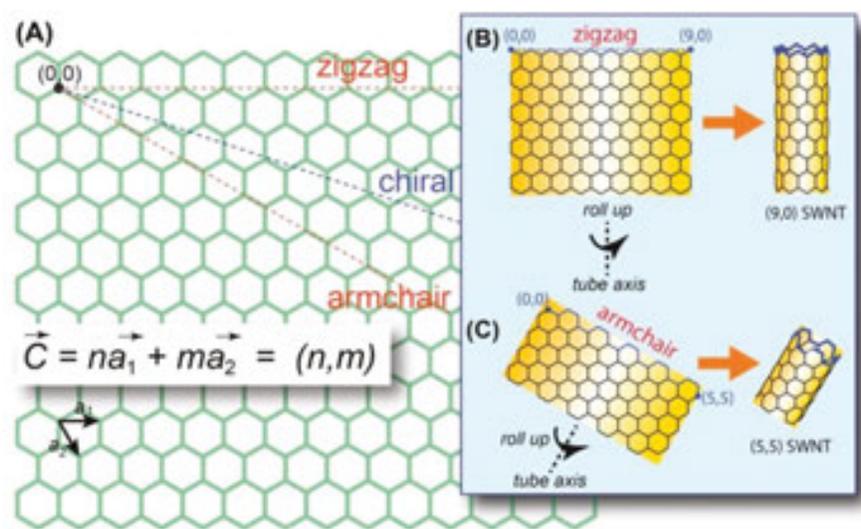

Figure 1. (A)–(C) Illustration of the formation of SWNTs with various chiral indices by rolling graphene sheets.

The synthesis of CNTs can be done in several ways, for example, arc discharge, laser ablation, chemical vapor deposition (CVD), and others [9]. However, all the currently existing processes for CNT production generate mixtures of various CNTs, amorphous carbon, and/or residual metal species. For this reason, post-treatment of as-produced CNT products becomes a critically important and indispensable step toward the application of CNTs [10], since removal of the unwanted impurities can give rise to considerably improved performances for CNT-based electronic and optoelectronic devices, while the purity of CNTs plays a key role in reducing or averting undesired toxicity and side effects in biological and medicinal applications. Another significant technical challenge encountered in the application of CNTs is the extremely low solubility and hence very poor processability of pristine CNTs in common solvents. The very large hydrophobic π-surface of CNTs makes them prone to aggregation

(forming bundles) through π-stacking and van der Waals interactions. Breaking the bundles into individual tubes is an energetically costly process that usually relies on chemical modifications to overcome the strong inter-tube attractions. There are two general approaches for preparation of functionalized CNTs (f-CNTs), namely covalent [11] and non-covalent [12, 13]. The covalent method involves the attachment of certain molecular functionalities to the sidewall and/or the defects/ends of CNTs through covalent bonds. As such, not only very high solubility or dispersity in the solution phase become readily achievable, but new chemical and physical properties can be introduced to the f-CNTs. One significant limitation of the covalent functionalization is that it inevitably converts a number of sp^2 carbons into sp^3 on the sidewall of CNTs, which is an unwanted scenario for applications where the integrity of graphene-type backbone of CNTs must be retained to keep their pristine electronic and mechanical characteristics. In this respect, the non-covalent approach has been deemed as an intrinsically better alternative due to its non-destructive nature.

The generally employed strategy for non-covalent functionalization of CNTs relies on the use of certain dispersing agents (i.e., dispersants) to break CNT bundles. Application of external forces, commonly ultrasonication or mechanical stirring, allows the dispersants to be assembled on the surface of CNTs via non-covalent binding forces (e.g., π-π stacking, CH-π, van der Waals, and charge transfer interactions). As such, CNT bundles could be exfoliated, resulting in individualized (or dispersed) tubes encapsulated or wrapped with dispersants to form stable suspension. Up to now, a vast array of chemical species, ranging from conjugated molecules, synthetic polymers, surfactants, peptides, to biopolymers and DNA molecules, has been demonstrated to show effectiveness at dispersing CNTs in various solvents [10, 12–14]. The scope of this topic is rather broad and encompasses an enormous body of literature. Generally speaking, the purposes of dispersing CNTs are multi-fold and significantly dependent on the requirements of specific applications. For instance, effective exfoliation and dispersion of CNTs in organic solvents allow CNTs to be readily blended with other functional polymers to form new composite materials with enhanced mechanical and electrical properties [13, 15]. Dispersion of CNTs into aqueous media with biocompatible matrices opens the doors to exciting biological and medicinal applications of CNT hybrids [8, 16]. Many initial studies on CNT dispersion were primarily aimed at enhanced dispersity and compatibility with various solvents and matrix materials. As the research moved on, it was observed that certain dispersants exhibited selectivity in binding with CNTs of certain electronic types, diameters, and chirality. The ramification of such behavior was quickly recognized and exploited for various purposes. As mentioned above, as-produced CNTs are structurally heterogeneous and contain significant amounts of impurities. In the past decade, a great deal of research efforts has been dedicated to the purification of CNTs through selective non-covalent functionalization, particularly the studies of sorting SWNTs have been greatly advanced [17, 18]. Very recently, remarkable breakthroughs have also been achieved in the fabrication of high-performance nanodevices using purified CNTs [19–23], which in turn fuels up the development of CNT processing/purification methods featuring excellent efficiency and cost-effectiveness.

In short, the present knowledge and techniques for dispersed CNT systems and subsequent applications have been considerably expanded, thanks to the continued efforts of material chemists on the design and synthesis of novel molecular and macromolecular systems as functional dispersants or agents for CNT modifications. Indeed, the current design of CNT dispersants and development of related processing methods have already surpassed being merely a single-parameter issue of improving dispersity. Rather, the objectives of research have turned out to be more and more diversified and application-oriented. In the following sections, our discussions are firstly focused on a newly emerging topic—reversible dispersion and release of CNTs regulated by rationally designed stimuli-responsive molecular and supramolecular systems—which has attracted rapidly growing attention in recent years. In the second part, the recent progress in polymer-functionalized CNT composites that show controlled responsiveness to one or more environmental stimuli is described.

2. Dispersion and release of CNTs: a microscopic and supramolecular perspective view

Effective dispersion of CNTs requires sufficient energy input (*e.g.*, mechanical stirring, shear mixing, ultrasonication) to disrupt the inter-tube attractions, with the amount of dispersion energy dependent on the length and diameter of CNTs as well as solvent nature and temperature. It has been found that stable dispersion of CNTs could be formed with certain solvents, such as 1,2-dichlorobenzene [24], CS_2 [25], and particular organic amides [26, 27]. For the majority of commonly used solvents, however, the surface of CNTs dispersed in them must be subsequently modified to prevent re-aggregation of CNTs from occurring, and this can be realized by having the CNTs' outer surface adsorbed or encapsulated with solvophilic layers. In this sense, effective CNT dispersants should contain the unit(s) having sufficient affinity for the graphitic surface of CNTs (henceforth referred to as the *graphenophile*). To the graphenophiles various solubilizing groups can be attached, the presence of which dictates the dispersity of the functionalized CNTs in different solvents or matrices.

In the literature, a large array of molecular and macromolecular motifs has been reported to give satisfactory graphenophilic performance. In the category of small molecules, planar structurally rigid polycyclic aromatic hydrocarbons (PAHs) have been known to easily adsorb on the surface of CNTs through a combination of hydrophobic and π-π interactions [28, 29]. Examples of such PAHs include pyrene, naphthalene, and phenathrene, which carry the fused aromatic backbones, mapping out the segmental hexagonal arrangement on the sidewall of CNTs. It is worth noting that since the initial study by Dai and co-workers [30], pyrene has become a popularly employed anchoring group allowing facile assembly of CNT supermolecular constructs imparted with various optoelectronic properties [31–34] and biologic activities [35–38] By the same token, highly π-extended heterocyclic aromatic compounds, such as phorphyrins, [39], phthalocyanines [40], and tetrathiafulvalenes [41, 42], have been found to show strong non-covalent interactions with CNTs, rendering the resulting hybrid systems intriguing photophysical and optoelectronic properties. Besides the small molecule-based systems, π-conjugated polymers have been widely used in CNT dispersion as well [15].

In these conjugated polymers, arene groups are embedded in the repeat units, which collec-tively engender strong binding to CNTs via π-π stacking. Experimental observations and molecular dynamic (MD) simulations have demonstrated that the polymer backbones with a certain degree of flexibility would favor wrapping around the CNTs in different fashions [43, 44]. DNA or RNA molecules can interact with the CNT sidewall via π-π stacking. In particular, single-strand DNA (ssDNA) oligomers and polymers have been extensively explored as SWNT dispersants and the interactions were found to be sequence-dependent [45–51]. Such properties have enabled fascinating applications including precise sorting of SWNTs, DNA sequencing, and chemical sensing applications [52]. Indeed, for many CNT dispersants developed so far, aromatic functional groups (*i.e.*, graphenophiles) are the essential structural components, and the resulting CNT supramolecular assemblies are usually stable and do not dissociate easily. On the other hand, the dispersion of CNTs can be realized by utilizing other types of non-covalent binding forces. For example, the hydrophobic interactions between surfactants and CNTs in water. Typical surfactants such as SDS are known to adsorb on the surface of CNTs with their hydrophobic tails (*e.g.*, alkyl chains), while their hydrophilic cationic or anionic heads directly interact with water molecules. Recent experimental and theoretical modeling studies [53–55] have shown that surfactant molecules can assemble into various arrangements of micellar structures, which effectively encapsulate individual CNTs to form well-dispersed stable suspensions in aqueous media.

With the wide range of CNT dispersants studied over the past decade, fundamental under-standing of their non-covalent interactions with CNTs at the molecular and supramolecular levels has been continually developed by state-of-the-art spectroscopic and microscopic analyses as well as high-level theoretical simulations. Knowledge in this field is highly instructive to the design of more sophisticated CNT-dispersing methods that are transferrable to the application of CNT-related materials in science and technology. One topic receiving much attention in the recent research of CNTs is the reversible dispersion and release of CNTs under the control of external stimuli, such as irradiation, chemical reactions, and solvation effects. Basically, to generate stable CNT dispersion in the solution phase, the CNT surface needs to be functionalized or encapsulated with dispersants to a sufficient degree. This in turns makes the dissociation of CNTs from dispersants not an easy task; for instance, many polyar-omatics and π-conjugated polymers are known to irreversibly adsorb onto the surface of CNTs, which makes it extremely difficult to remove them from CNTs by physical means (*e.g.*, solvent rinsing). An efficient approach to release CNTs out of a well-stabilized dispersion is to reverse the attractive forces between the dispersants of CNTs into repulsive interactions, such as the strategy schematically illustrated in **Figure 2**. Generally speaking, a chemical process (*e.g.*, acid-base interactions, redox reactions, and photodegradation) that leads to the reversal of the dispersants from being graphenophilic to graphenophobic would be useful for triggering the release or re-aggregation of CNTs. On the other hand, various supramolecular means (*e.g.*, metal coordination, conformational changes) can also offer sufficient driving forces to induce CNT release. For all the methods perceivable, it is essential for the CNT dispersants to show responsiveness to external inputs one way or another. The following section provides an overview of the recent progress in this field, and the detailed discussion is organized according to the type and mechanism of stimuli-responsiveness.
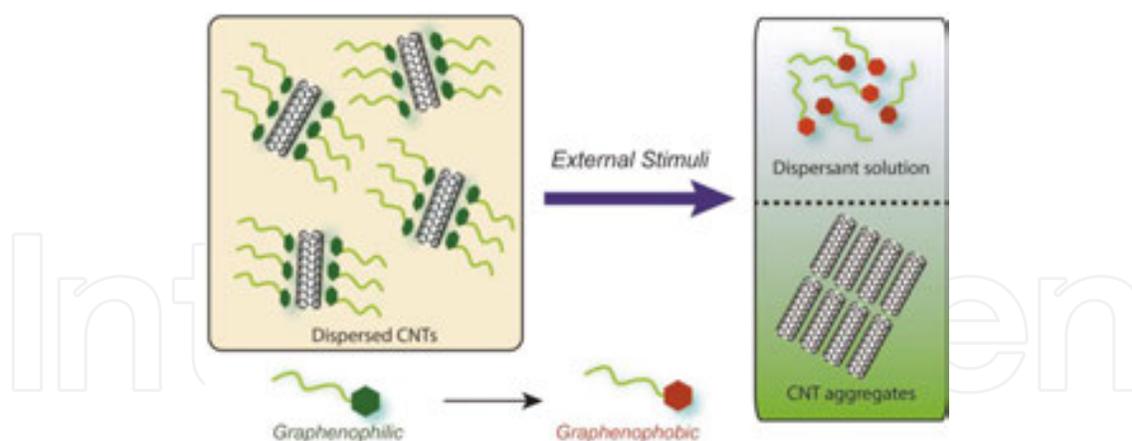
Figure 2. Schematic illustration of release of CNTs by changing the dispersants from being graphenophilic to graphenophobic.

3. Recent advances in reversible dispersion and release of CNTs with stimuli-responsive dispersants

3.1. By acid-base interactions

Acid-base interactions are probably the most straightforward ways to drastically alter the chemical and physical properties, for instance, changing from neutral to cationic/anionic, from organic solubility to water solubility. For this reason, this approach has become the actively pursued one in this field. Das and co-workers [56] recently developed a series of cholesterol-based amino acid carboxylates **1** and dipeptide carboxylates **2** (**Figure 3**) as dispersant for SWNTs as well as for graphene oxide (GO). Herein, the dispersants are amphiphilic, with the structurally rigid, hydrophobic cholesterol unit acting as the graphenophile to interact with the sidewall of SWNTs and the carboxylate-appended tails being hydrophilic. All the dispersants were able to disperse SWNTs in water, forming stable colloidal solutions. Compounds **2** with dipeptide moieties were found to bring about better dispersity than the mono amino acid-containing compounds **1**. Upon lowering the pH of the SWNT-**2c** colloidal suspension by adding 1N HCl, the carboxylate anions were converted into carboxylic acids, which in turn reduced the stability of the colloidal suspension as evidenced by zeta potential analysis. As a consequence of this, SWNTs were found to precipitate out of the aqueous solution. Addition of NaOH to increase the pH of the mixture converted the carboxylic acid groups back to hydrophilic carboxylate anions and re-generated the SWNT dispersion in water. Moreover, the SWNT dispersions engendered using compounds **1**-**2** as dispersants were tested to show cytocompatibility and potential biological applications. Later on, Das and co-workers reported another class of cholesterol-dipeptide amphiphiles **3** (**Figure 3**), which were designed to be highly sensitive and responsive in the pH range of tumorogenic environment (*ca*. pH 5–6) [57]. With these dispersants, SWNTs were well suspended in PBS buffer at pH 8. The SWNT-**3** assemblies could be further loaded with an anticancer drug DOX. At pH 6.0–6.5, precipitation

of SWNTs occurred and concomitantly the drug DOX was released. This performance is useful for specific drug delivery to cancer cells.
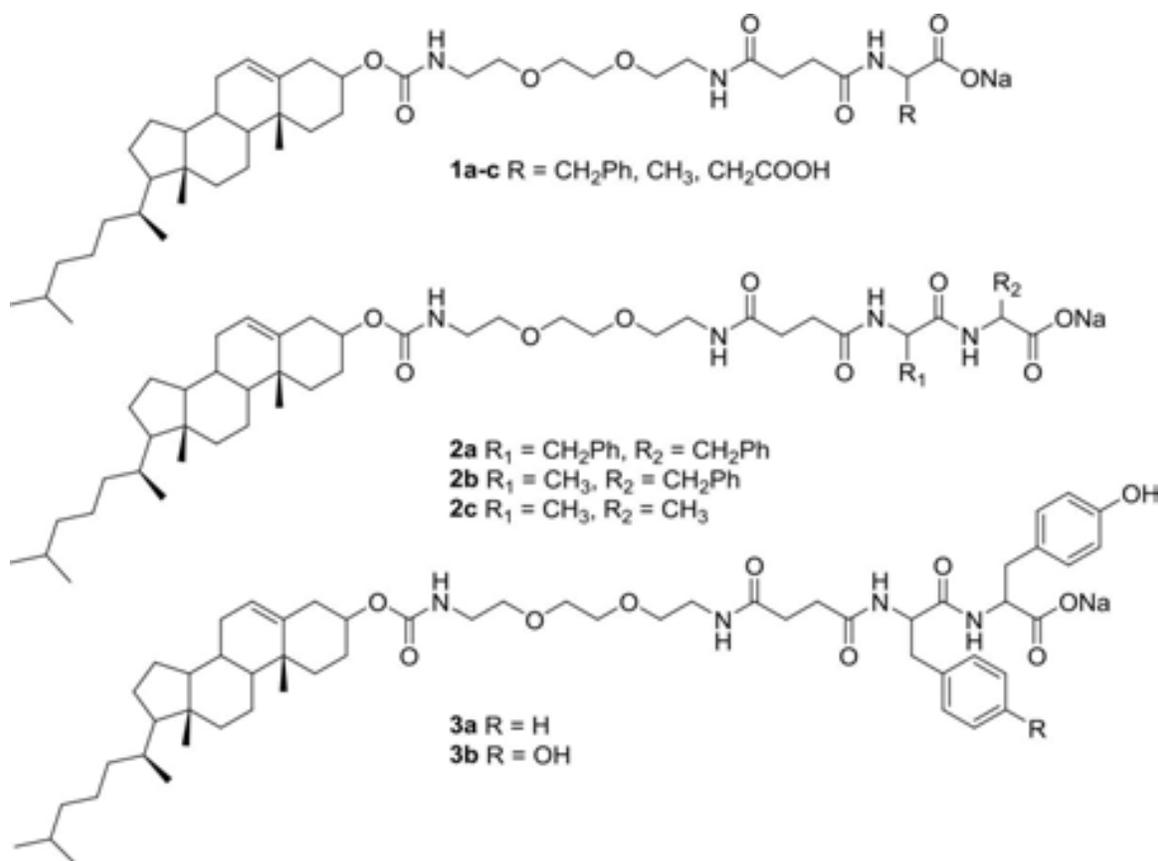

Figure 3. Cholesterol-based carboxylates amphiphiles **1–4** enabling reversible SWNT dispersion in water under pH control.

Based on a similar acid-base exchange concept, Huang and co-workers [58] recently synthesized a pH-responsive pillar[6]arene **4**, the backbone of which was decorated with water-solubilizing carboxylate groups (**Figure 4**). In their work, a pyrene compound **5** was first anchored to the sidewall of MWNTs via π-π stacking. The resulting hybrids were insoluble in water; however, addition of pillar[6]arene **4** to the functionalized MWNTs under sonication resulted in guest-host complexation taking place on the CNT sidewall. Of great interest was that the water solubility of resulting MWNT supramolecular assemblies could be reversibly switched by pH control. Under basic conditions, the carboxylic groups were deprotonated to form carboxylate anions, making the complexed MWNTs water-soluble. Upon acidification, the MWNTs were found to precipitate out of water. This work provided an elegant example of using pH-sensitive guest-host chemistry to achieve reversible dispersion and release of CNTs. Nevertheless, it is worth remarking that this work did not clearly address whether the complexation between **4** and **5** was altered on the CNT sidewall with changing pH, and such an issue may deserve further investigation.
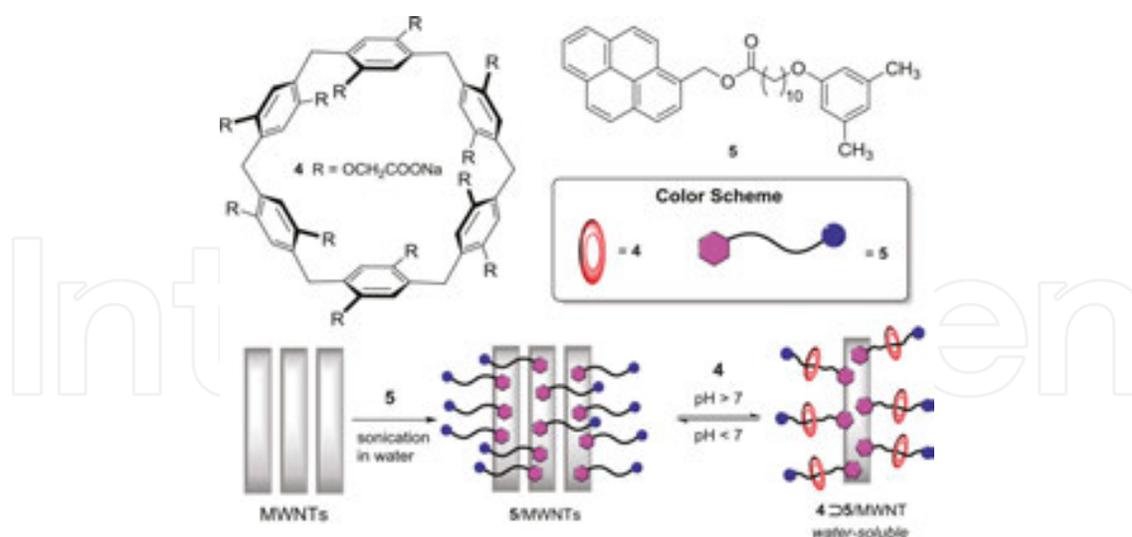
Figure 4. Reversible dispersion and release of MWNTs by pH-sensitive guest-host complexation between pillar[6]arene **4** and pyrene derivative **5**.

In 2015, Bryce and Lambert [59] synthesized a total of 13 amphiphilic surfactants, the structures of which were made of a pyrene head (hydrophobic) and various hydrophilic tails ending with carboxylate groups. Similar to the design of numerous other CNT dispersants, the pyrene group here was employed to act as a strong graphenophile to irreversibly link the surfactant molecules to the surface of CNTs. The performances of these pyrene-based surfactants in terms of MWNT dispersion in aqueous media were assessed. In particular, the authors examined the pH responsiveness of two of the surfactants **6** and **7** (**Figure 5**) in aqueous NaCl solution, and found that the corresponding MWNT-surfactant complexes could be reversibly dispersed and re-aggregated under basic and acidic conditions. A working mechanism for this acid-base-triggered MWNT dispersion was proposed based on the switching between hydrophobicity and hydrophilicity in different pH environments (see **Figure 5**).
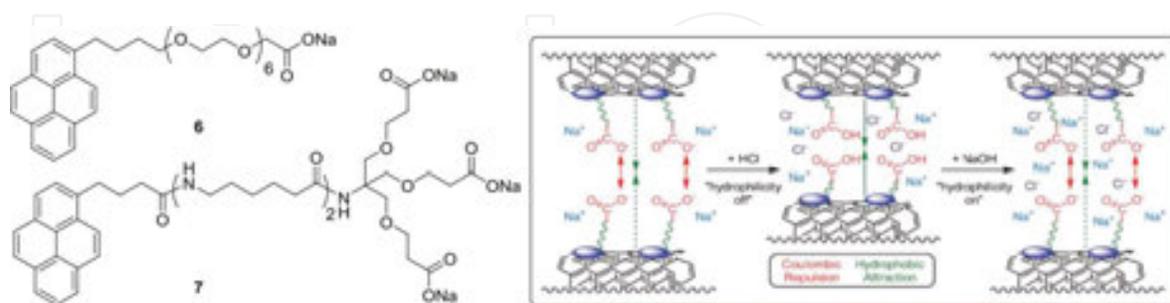

Figure 5. Pyrene-based surfactants **6** and **7** that show pH-responsiveness in dispersing MWNTs. The inset scheme was adopted from reference [59] with permission.

A novel dumbbell-shaped 2-ureido-6[1H]-pyrimidinone (UPy)-based fluorene derivative **8** (**Figure 6**) was recently devised by the Bao group [60] for selective and reversible dispersion of semiconducting SWNTs. In their design, fluorenyl group was chosen as the graphenophile

to promote selectivity for semiconducting SWNTs, while the two UPy terminal groups enabled **8** to self-associate into supramolecular polymers through H-bonding interactions at high concentration. As illustrated in **Figure 6**, the supramolecular polymers of **8** selectively dispersed semiconducting SWNTs allowing for the separation of metallic and semiconducting tubes from as-synthesized SWNTs. Moreover, semiconducting SWNTs could be quantitatively released from the suspension by addition of 1% TFA solution, which induced the disassembly of the supramolecular polymers by breaking the H-bonds within them. Compared with many covalent polymer dispersants, this supramolecular polymer approach offers advantages in terms of releasing dispersant-free SWNTs and easiness in reusing the fluorene-UPy monomer **8**.
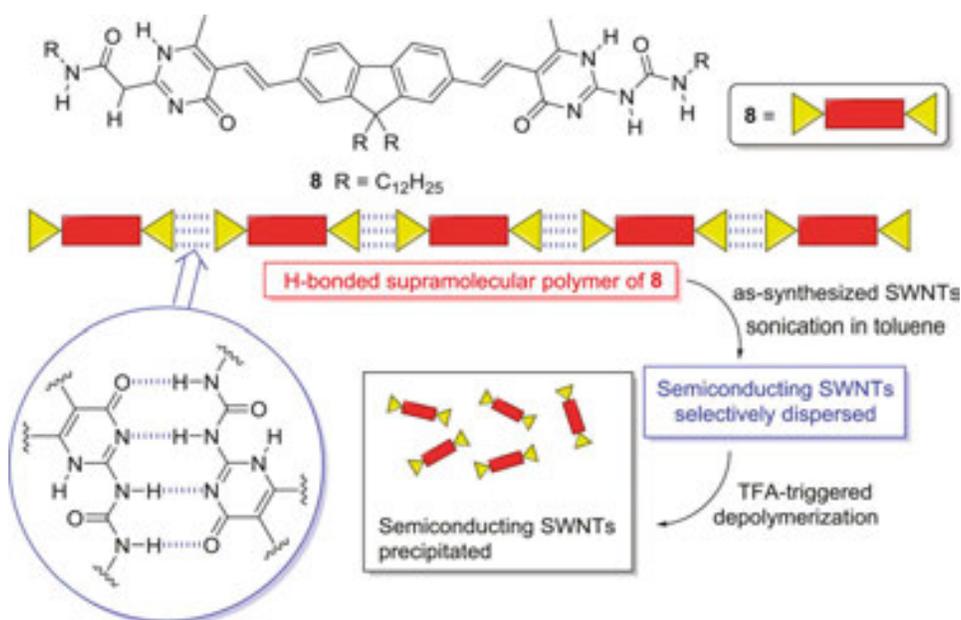

Figure 6. Selective dispersion and quantitative release of semiconducting SWNTs using a pH-sensitive H-bonded supramolecular polymer.

In addition to the above-mentioned rationally designed CNT dispersant systems, some other pH-sensitive molecules and biopolymers have also been reported to induce reversible dispersion/precipitation of CNTs in aqueous media. For example, Sun and co-workers [61] reported that 1-pyreneacetic acid after deprotonation under basic conditions could be noncovalently functionalized on nitric acid-treated as-produced SWNTs to form stable dispersion in water. Upon acidification, 1-pyreneacetic acid was quantitatively removed to yield purified SWNTs. The easy recovery and reuse of dispersants make this method potentially useful for large-scale CNT processing and production. Bhattacharya *et al*. [62] in 2014 reported that the dispersion of SWNTs with *ss*-DNA oligomers was pH-sensitive. At pH 7, the *ss*-DNA oligomers wrapped them around SWNTs to effect debundling and dispersion in water. Under acidic conditions (*e.g.*, at pH 3.5), however, the *ss*-DNA oligomers underwent a reversible structural change leading to unwrapping and precipitation of SWNTs. This method shows the potential in separating metallic and semiconducting SWNTs. Wang and Chen [63] discovered that poly-

L-lysine was capable of dispersing SWNTs in water at pH < 9.7, presumably driven by hydrophobic and cation-π interactions. When the basicity was increased to pH 9.7, poly-L-lysine adopted an α-helix conformation and the ammonium groups were deprotonated into amino, and these changes led to precipitation of SWNTs.

Apart from typical protic acids, CO_2 has been utilized as a form of acid to trigger reversible release of CNTs from corresponding CNT-dispersant assemblies in solution. In 2010, Zhang and co-workers [64] reported the use of N,N-dimethyl-N'-(pyren-1-ylmethyl)acetimidamidinium (PyAH$^+$) as a CO_2-responsive dispersant to control the dispersion and aggregation of SWNTs. The PyAH$^+$ system was functionalized on the surface of SWNTs through π-π stacking and the hydrophilic amidinium group rendered the SWNT-PyAH$^+$ assemblies water soluble. Reversible interconversion between amidinium and amidine could be done by bubbling the solution with CO_2 or argon, and this chemical behavior allowed the water solubility of PyAH$^+$ functionalized SWNTs to be turned on and off by alternated bubbling of CO_2 and argon. Following this strategy, Feng and co-workers [65] in 2013 designed and synthesized a class of functionalized polystyrenes **9** (**Figure 7**) using reversible addition-fragmentation chain transfer (RAFT) polymerization and click reactions. To the backbone of polymers **9** were grafted pyrene and amidine groups. The pyrenes induced binding of the polymers with SWNTs, while the amidine units gave rise to CO_2-sensitivity. With these polymers, reversible dispersion and aggregation of SWNTs were achieved both in water and in a mixed solvent of water and methylene chloride by simply bubbling CO_2 or N_2 into the SWNT/polymer suspension.
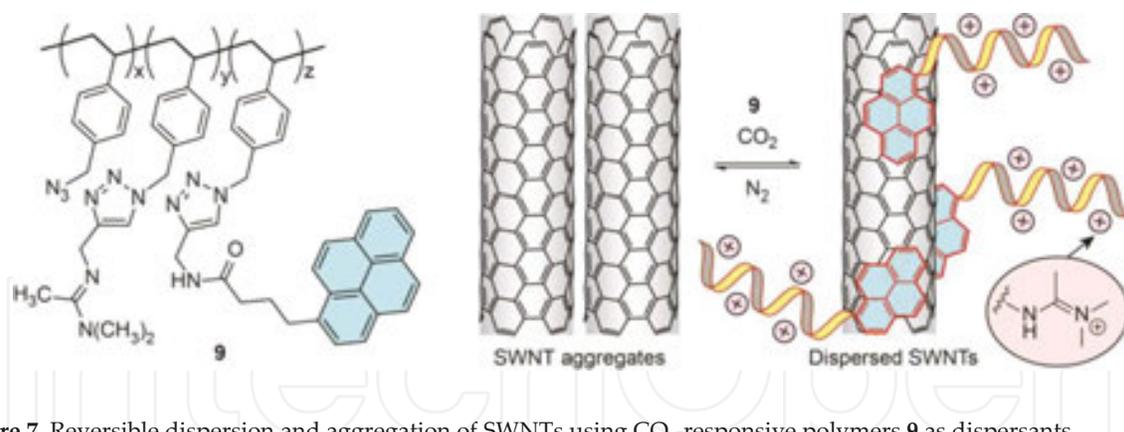

Figure 7. Reversible dispersion and aggregation of SWNTs using CO_2-responsive polymers **9** as dispersants.

3.3. By photoirradiation

Photoirradiation offers an effective way to trigger conformational and bonding changes in molecules, and therefore photo-responsive systems have found wide applications in molecular switches and photochromic devices [66]. In the field of CNT dispersion, photo-responsive dispersant systems have been explored, but not yet to a very large extent.

In 2008, Zhang and co-workers [67] developed poly(ethylene glycol) **10**, the structure of which contains a photo-reactive terminal moiety of malachite green derivative (PEG-MG). It was

found that SWNTs could be dispersed in water with the aid of **10** under sonication. Upon irradiation of the SWNT-**10** suspension with UV light, the MG moiety underwent a C-C bond cleavage reaction to form PEG-MG$^+$ cation **11**. After standing in air for a few hours, the PEG-MG$^+$ cation was gradually dissociated from SWNTs resulting in the precipitation of SWNTs out of water. This work demonstrated that re-aggregation of non-covalently functionalized SWNTs can be achievable by light control; however, the involvement of an irreversible photo-induced bond breaking step would not make the dispersion/release sequence repeatable in multicycles. Indeed, the authors noted that the dispersion and release of SWNTs could "*only stand one recycle probably because of the fatigue of the photo reaction.*" Kappes and Mayor in 2011 developed a fluorene-based polymer, the structure of which bears photo-cleavable *o*-nitro-benzylether moieties [68]. The presence of fluorene units made the polymer quite selective for dispersing semiconducting SWNTs in toluene. Upon photoirradiation of the resulting suspension for a short period of time, SWNT precipitation was observed as a result of photo-induced depolymerization reactions. This method presents an easy way to selectively disperse SWNTs and cleanly remove the dispersants afterwards. Nevertheless, like the previous method reported by Zhang [67], the use of photo-cleavage reactions hinders multicycle reversibility (**Figure 8**).
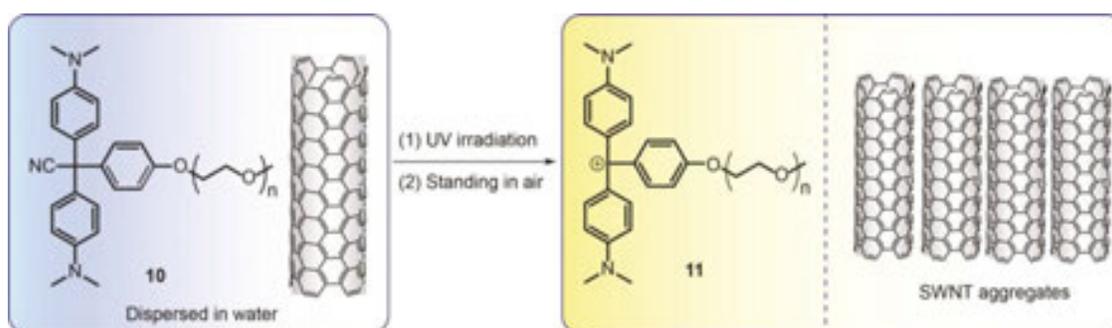

Figure 8. Dispersion and re-aggregation of SWNTs in water by a photo-reactive PEG-MG dispersant 10.

In a very recent report, Feng and co-workers [93] devised a photo-controlled method to achieve reversible dispersion and re-aggregation of SWNTs by means of photoswitchable guest-host chemistry. In their work, a pyrene-attached cyclodextrin **12** was used in combination with an azobenzene-terminated poly(ethylene glycol) **13** as the dispersant system (**Figure 9**). In the *trans* form, azobenzene-PEG **13** readily formed a supramolecular guest-host complex with cyclodextrin **12**, while the pyrene head group of **12** anchored the complex to the sidewall of SWNTs to effect good dispersion in water. Upon photoirradiation with UV light, the azobenzene unit underwent a *trans*-to-*cis* isomerization, which consequently broke the complexation of **12** and **13**. The decomplexation caused precipitation of SWNTs from the aqueous phase. The azobenzene could be further isomerized back to the *trans* form after exposure to sunlight for 24 hours. Sonication for about 10 min then led to the re-formation of SWNT dispersion in water. The authors reported that the dispersion and re-aggregation of SWNTs could be repeated in multicycles under the control of UV and sunlight, which testifies to a very good reversibility.
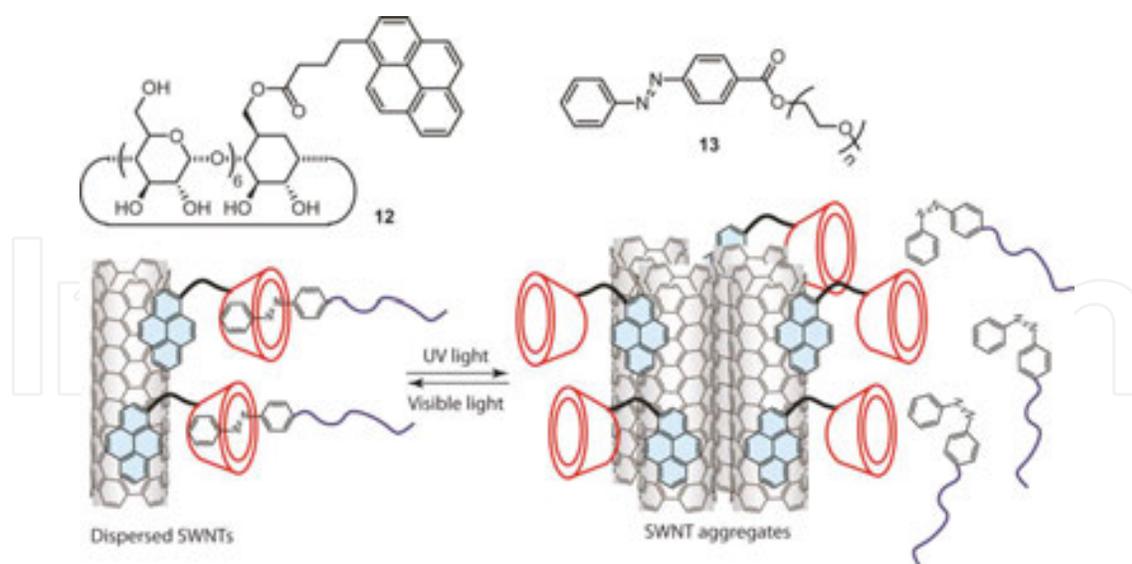
Figure 9. Reversible dispersion and release of SWNTs in water using photo-regulated supramolecular guest-host complexation.

The easy synthesis and controllable photo-switchability of azobenzene have made it a popular building block in the design of photo-responsive CNT dispersants, but one important issue related to it warrants particular attention. It has been noted in some previous studies that when the azobenzene unit is tightly bound to the surface of CNT, the *cis*-to-*trans* photoisomerization behavior may vanish due to the quenching effect of CNTs on the excited state of azobenzene [69, 70]. It was reported that the effect of photoisomerization in combination with other types of controls (*e.g.*, thermal) [71] could effectively remove the dispersants out of the surface of CNTs.

3.3. By redox chemistry

There are many redox-active systems known to undergo facile reversible electron transfers under the controls of either chemical or electrochemical means, and often a reversible redox reaction is associated with a dramatic conformational change in the substrate. Such properties can be utilized to exert control over the dispersion and release of CNTs, if the dispersants are rationally designed to carry certain redox-active units. In 2008, Ikeda and co-workers [72] developed a Cu-based redox-active complex **14** (**Figure 10**) as CNT dispersant. When the oxidation state of **14** was Cu(II), the complex was found to be able to disperse CoMoCAT SWNTs in chloroform. When ascorbic acid was added to the suspension of SWNT/**14**, Cu(II) was reduced into Cu(I) species. Accompanying this reduction, precipitation of SWNTs immediately occurred because the Cu(I) complex did not interact with SWNTs as strongly as the Cu(II) complex did. Re-dispersion of SWNTs could be achieved by bubbling air through the mixture, which converted the Cu(I) back to Cu(II). As such, SWNTs could be reversibly dispersed and released in chloroform by switching the oxidation state of the Cu center in complex **14**.
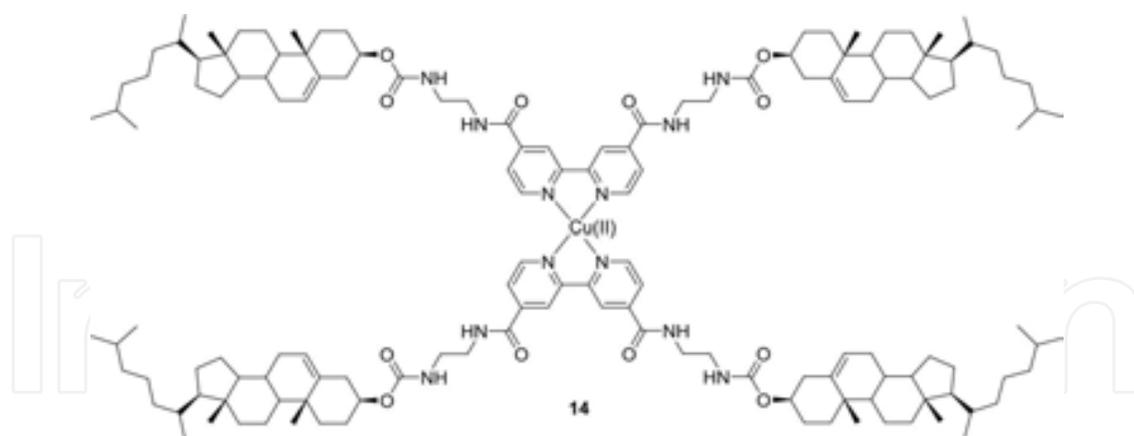
Figure 10. Cu complex **14** developed by Ikeda [72] for reversible dispersion and release SWNTs via redox control.

A class of highly electron-donating organic compounds, namely tetrathiafulvalene vinylo-goues (TTFV), has been investigated by Zhao and co-workers as redox-responsive units to be integrated in redox-regulated "smart" molecular and polymer systems [73]. In general, a TTFV unit can undergo a simultaneous two-electron transfer to form a dication in the presence of a chemical oxidant (*e.g.*, iodine) or under controlled electrochemical conditions. As shown in **Figure 10**, this redox process is reversible and associated with a dramatic conformational change from *pseudo cis* (neutral) to *trans* (dication). Taking advantage of such properties, a series of TTFV-based conjugated polymers **15a-c** was synthesized by the Zhao group [74, 75]. The presence of electron-donating TTFV units here not only enabled redox-control to be readily exerted, but also endowed these polymers with high efficiency in dispersing SWNTs in various organic solvents, such as chloroform, toluene, and THF. The SWNT/**15** suspension in organic solvents was very stable. Upon addition of iodine as oxidant, an immediate color change to dark green was observed, which is indicative of the formation of TTFV dication. Accompanying this oxidation, SWNT precipitation was formed. In this method, excess iodine was needed, which complicated the separation and recovery procedure of the TTFV polymers. The addition of trifluoroacetic acid (TFA) was discovered to be not only very effective in inducing the precipitation of SWNT, but more efficient in recovering the polymers by simple neutralization with base. Herein, the exact effect of acidification on TTFV has not been completely clarified; however, it is believed that TTFV would undergo dramatic conformational changes after protonation, given that tetrathiafuvalene (TTF), the parent structure of TTFV, was known to form cation and radical cation species by protonation [76]. In 2014, Adronov and co-workers [77] prepared a TTFV-fluorene copolymer **16** (**Figure 11**). The inclusion of fluorene in this polymer brought about good selectivity for small-diameter semiconducting SWNTs to be dispersed in organic solvents. Triggered by TFA addition, the selectively dispersed SWNTs were efficiently released from the suspension and collected as dispersant-free pristine nanotubes. The polymer dispersant **16** was easily recovered after neutralization and could be reused in multicycles. This method provides an efficient way to sort nanotubes with specific chiral indices out of as-produced SWNTs.
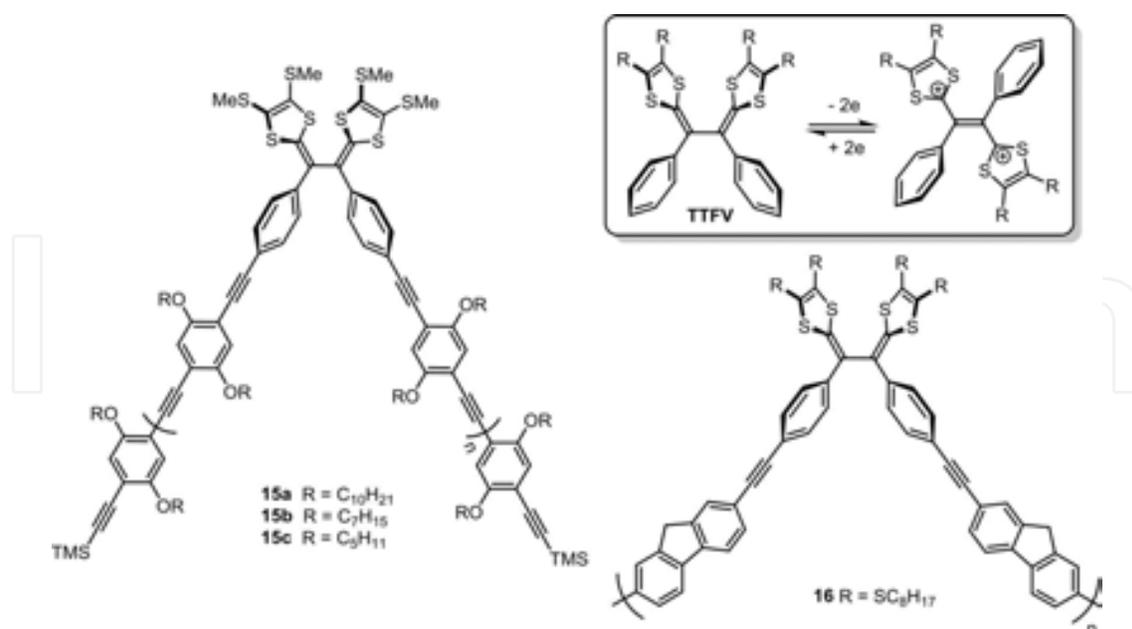
Figure 11. Conjugated polymers **15** and **16** containing redox-active TTFV units as CNT dispersants.

3.4. By temperature control

The control over dispersion and release of CNTs can also be achieved using temperature-sensitive dispersants. For example, Wang and Chen in 2007 investigated the dispersion of SWNTs with temperature-responsive poly(*N*-isopropylacrylamide) [63]. SWNTs dispersed with this polymer were observed to precipitate when heated at a temperature higher than the lower critical solution temperature (LCST), while re-dispersion of SWNTs could be done by cooling and sonication. Later, Theato and Grunlan [78] prepared a pyrene-functionalized poly(*N*-cyclopropylacrylamide) which could disperse SWNTs in water at temperature lower than LCST. When the temperature was increased above LCST, the polymers surrounding the SWNTs underwent a conformational change from coil to a globule-like shape. The authors proposed that such a transformation reduced the steric layer thickness that hinders SWNT aggregation.

Most recently, a family of pyrene-based non-ionic surfactants was synthesized and studied by Bryce and Lambert [79]. Of these compounds, two surfactants **17** and **18** (**Figure 12**) were found to exhibit very good performance in reversible dispersion and aggregation of MWNTs in 0.6 M aqueous NaCl solution. Upon heating the MWNTs dispersion with either of these surfactants at 85 °C for 15 minutes, precipitation of MWNTs was observed. The resulting precipitate was stable for several hours after cooling. With gentle shaking, dispersion of MWNTs was readily attained. The temperature-controlled dispersion and precipitation of MWNTs could be repeatedly executed, testifying to the excellent reversibility of this method. The remarkable performance in terms of reversibility was attributed to two factors: (i) The pyrene group strongly anchored the surfactant molecules to the surface of MWNTs, which prevented the re-

bundling of precipitated MWNTs. (ii) The LCST transition of the surfactants switched the surface of the surfactant-functionalized MWNTs from being hydrophilic to hydrophobic.
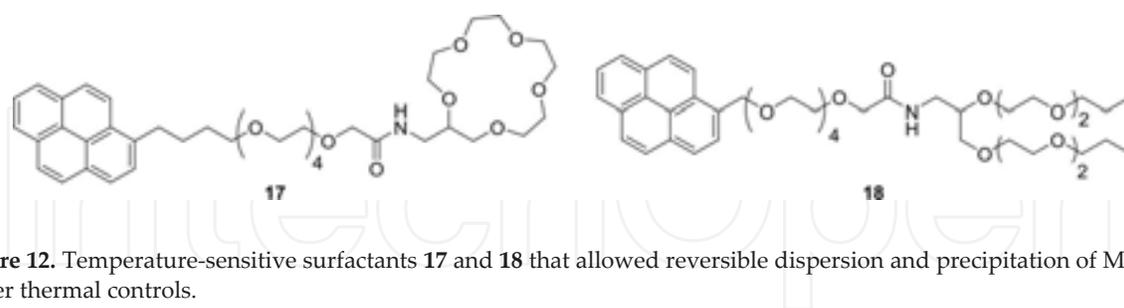

Figure 12. Temperature-sensitive surfactants **17** and **18** that allowed reversible dispersion and precipitation of MWNTs under thermal controls.

3.5. By solvent control

Compared with the aforementioned types of stimuli-responsiveness, the tuning of solvent properties is a much easier way as it neither involves multiple steps of addition and separation of chemical species, nor requires significant energy inputs (*e.g.*, light, heat). In practice, the design of systems with specific solvent-responsiveness at the molecular level is not a trivial task, since solvation is a rather complex issue to be thoroughly understood. Inspired by the type of organic oligomers (*i.e.*, foldamers) [80, 81] that change their conformations in different solvent environments, Moore and Zang in 2010 prepared a 13-mer of olig(*m*-phenylene ethynylene) **19** [82]. In a nonpolar solvent, chloroform, oligomer **19** adopted a flexible non-folded conformation, which allowed it to wrap around SWNTs through π-π stacking, resulting in a stable dispersion of nanotubes. Increasing the solvent polarity by addition of acetonitrile caused the oligomer to self-aggregate into a rigid, helical structure. As a result of this conformational change, the oligomer was unwrapped from the SWNTs, releasing the SWNTs as precipitate (**Figure 13**).
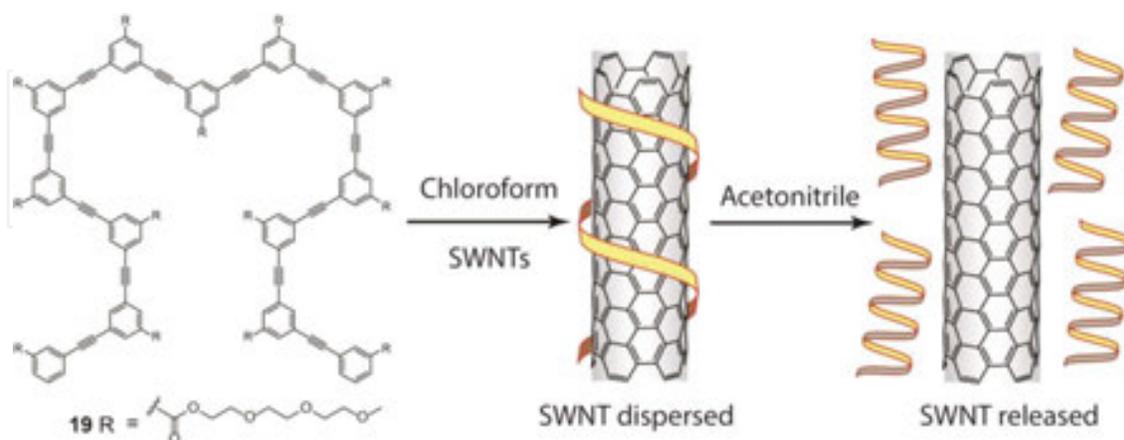

Figure 13. Solvent-controlled wrapping and unwrapping of SWNTs with oligo(*m*-phenylene ethynylene) **19**.

In 2013, Mulla and Zhao [83] reported the synthesis and properties of a series of linear and Z-shaped π-conjugated oligomers with redox-active dithiafulvenyl (DTF) groups attached to the

terminal positions. Some of the oligomers showed very good performance in dispersing SWNTs in organic solvents. Of great interest was a Z-shaped oligomer 20 (**Figure 14**) that showed high efficiency of dispersing SWNTs in chloroform (*ca.* 0.29 mg nanotube/mL). Addition of an equal volume of hexanes to the chloroform suspension resulted in immediate precipitation of SWNTs. The good dispersity and solvent-dependent effect were attributed to the presence of DTF groups, as the parent oligomer without DTF terminal groups was found to give no dispersing effect at all. By the same token, Zhao and co-workers later designed and synthesized poly(phenylene butadiynylene) 21 (**Figure 14**), the backbone of which was click-functionalized with DTF-terminated side chains[84]. This polymer showed a high selectivity in dispersing (6,5), (7,5) and (7,6) semiconducting SWNTs in organic solvents (*e.g.*, toluene, chloroform). Addition of hexanes to the suspension of SWNT-21 in chloroform also led to precipitation of SWNTs. Thermogravimetric analysis (TGA) showed that after addition of hexanes, most of the dispersant 21 had been stripped off the surface of SWNTs and only 7.7% wt of dispersant still remained on the released SWNTs. The solvent-controlled SWNT disper-sity exhibited by the DTF-functionalized π-conjugated oligomers and polymers can be easily applied to large-scale SWNT processing and purification. In the meantime, fundamental studies on the solvent-regulated SWNT-polymer adsorption-desorption equilibrium are warranted to devise better solvent control over efficient and selective SWNT dispersion and release by this method.
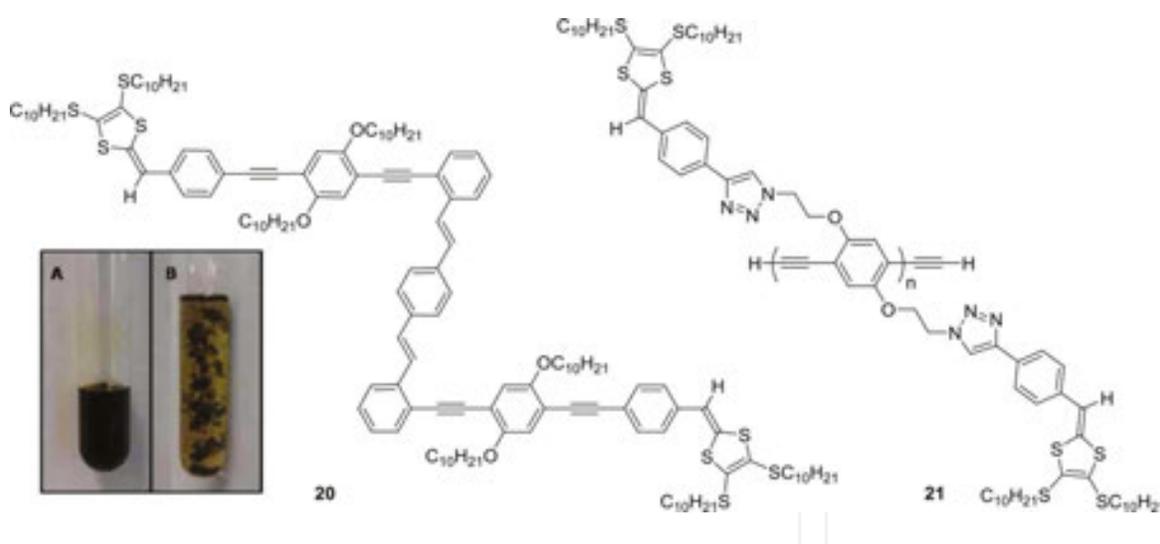

Figure 14. Dithiafulvenyl-functionalized conjugated oligomer 20 and polymer 21. Inset photographic images: (A) SWNTs dispersed in chloroform with 20, (B) SWNTs released after addition of hexanes.

Bonifazi and co-workers [85] in 2011 reported a strategy of solvent-controlled hydrogen bonding interactions to achieve reversible dispersion and release of MWNTs. In their work, H-bonding supramolecular polymers were respectively assembled by complementary H-bonding recognition between di(acetylamino)pyridine-terminated molecules (22 and 23) and uracil-terminated compounds (24–26). The supramolecular polymers were able to strongly interact with MWNTs, yielding stable dispersion in nonpolar solvents. Addition of H-bond

breaking solvents (*e.g.*, MeOH, DMSO) to the MWNT/H-bonding polymer hybrids induced depolymerization and hence released MWNTs from the solution (**Figure 15**).
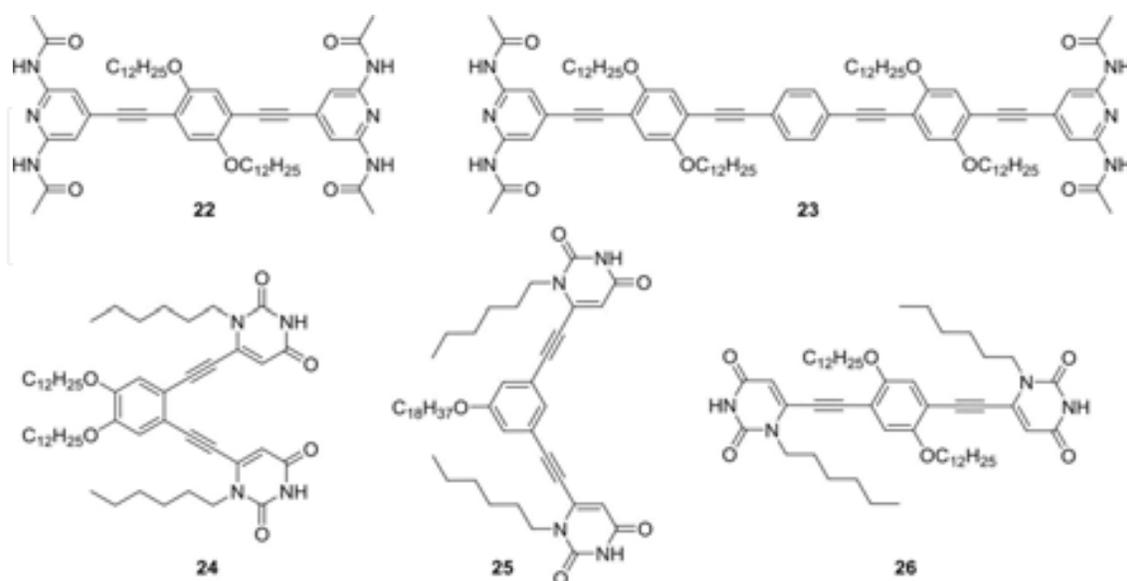

Figure 15. Molecular building blocks **22–26** that formed supramolecular polymers for solvent-controlled dispersion and release of MWNTs.

4. CNT-polymer composites responsive to single or multiple external stimuli

Stimuli-responsive polymers show the intriguing behavior that their shapes, physical, electrical, and optical properties can be significantly changed in response to small variations of environmental conditions, such as pH, temperature, electrical field, ionic strength, solvent, and so on [86, 87]. As such, stimuli-responsive polymers have been widely used as active building blocks to develop advanced nanomaterials and molecular devices. Investigations on functionalization of CNTs, either covalently or non-convalently, with stimuli-responsive polymers have been actively carried out over the past decade. In 2008, Pan and Hong [88] contributed a review article outlining the progress in designing *f*-CNTs that showed responsiveness to a range of external stimuli and potential applications in biosensing. A prominent advantage of synthetic polymers lies in the versatility of structural tuning and modifications to bring about synergistic effects and/or multiple functions in one system. Most recently, there has been a growing effort in developing "smart" polymer materials that are responsive to single or multiple stimuli so as to achieve more sophisticated applications. The following section hence highlights the most recent progress in the design and application of stimuli-responsive CNT-polymer composites.

In 2014, Luo *et al.* prepared CNT composites by mixing MWNTs with shape memory polyurethane (SMPU) through a transfer method [89]. The composites showed good electrical

conductivity and improved hydrophilicity. Of significant interest, the CNT-SMPU composites were found to exhibit dual-stimuli responsive shape memory behavior upon exposure to water and electrical stimulation. The authors proposed that the presence of CNT in the composites facilitated the water diffusion to accelerate shape recovery, while the formation of CNT networks in the composites provided a conductive pathway enabling Joule heat to stimulate the shape recovery. Overall, the incorporation of CNTs in the composites led to enhanced shape memory performance, while the responses to electrical stimulation resulted in much faster shape recovery than water.

In 2012, Yuan and co-workers prepared a copolymer through free radical polymerization of *N*-isopropylacrylamide (NIPAM) and an ionic liquid monomer, 1-ethyl-3-vinylimidazolium bromide (EVImBr) [90]. The NIPAM moieties imparted the copolymer with thermo-sensitivity, while the EVImBr units assisted in the dispersion of CNTs by strong polarization interactions and responded to ionic strength in solution. **Figure 16** schematically illustrates the unique dual stimuli-responsiveness of MWNTs dispersed by this copolymer. Aqueous dispersion of MWNTs with this copolymer was found to retain stability when heated to 60 °C or mixed with excess KBr. Only the combination of heating and KBr addition led to the precipitation of MWNTs. The authors claimed that this method was advantageous in terms of allowing precise and designable control of CNT dispersion over a wide temperature range and at a desired temperature.
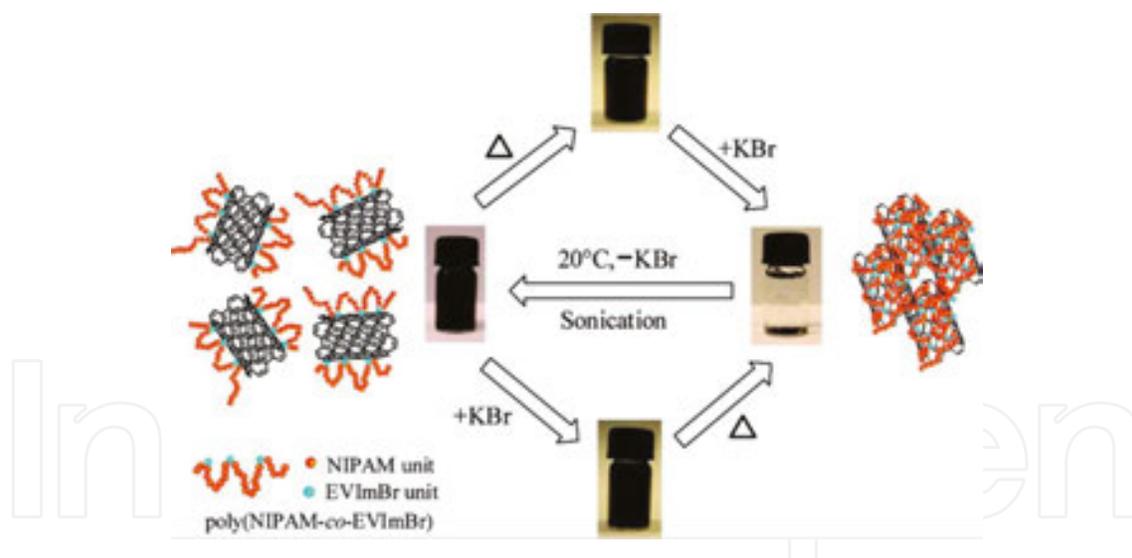

Figure 16. Dispersion and precipitation of MWNTs in aqueous solution of a dual stimuli-responsive copolymer of NI-PAM and EVImBr. Adopted from reference [90] with permission. Copyright 2012 American Chemical Society.

In 2016, Mandal and co-workers used RAFT polymerization to synthesize a type of cationic poly(ionic liquid) **22**, namely poly(triphenyl-4-vinylbenzylphosphonium chloride)s (P[VBTP][Cl]s) (**Figure 17A**) [91]. These polymers showed double responsiveness towards halide ions and temperature (upper critical solution temperature-type) in aqueous solution. The authors reported that one of the polymers with M_n = 40,000 g mol^{-1} could effectively debundle MWNTs in water to form well-dispersed suspension (**Figure 17C**). In response to the addition of NaCl

and temperature, P[VBTP][Cl] **22** acted as a "smart" dispersant to control the dispersion and precipitation of MWNTs in the aqueous phase (see **Figure 17B**).
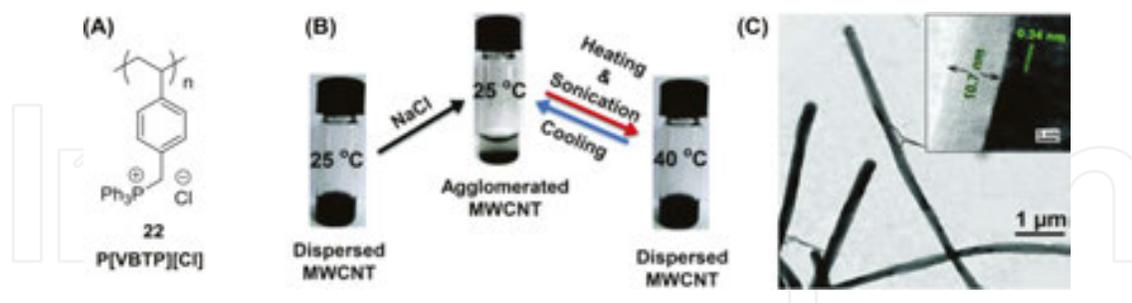

Figure 17. (A) Structure of P[VBTP][Cl] **22**. (B) Photographic images showing the dispersion and precipitation of MWNTs in an aqueous solution of **22** in response to addition of NaCl and temperature. (C) TEM image of MWNTs coated with **22**. Adopted from reference [91] with permission.

Barner-Kowollik and co-workers recently synthesized cyclopentadienyl end-capped poly(*N*-isopropylacrylamide) (PNIPAM-Cp, **23**, **Figure 18**) by RAFT polymerization and Cu-catalyzed alkyne-azide coupling [92]. This polymer was then covalently attached to the sidewall of SWNTs via the Diels-Alder reaction at different temperatures. At low temperature (cooled by an ice bath), stable dispersion of the functionalized SWNTs was attained in water by sonication. As the temperature increased, the polymer chains responded by collapsing onto the CNT surface. As a result, the CNT dispersion became destabilized, leading to the aggregation of the functionalized SWNTs. This work demonstrates that covalent functionalization can be a method of choice to effectively modify/switch the physical properties (*e.g.*, dispersity) of CNT-based nanocomposites.
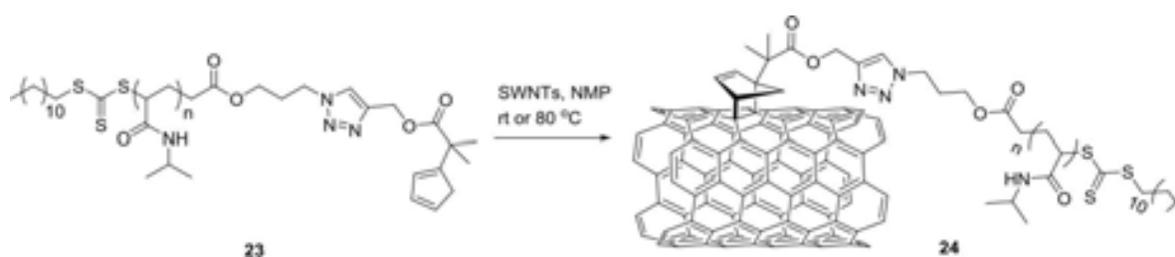

Figure 18. Synthesis of thermo-responsive functionalized SWNTs **24** via the Diels-Alder reaction.

5. Conclusions and perspectives

The literature survey discussed above has demonstrated that stimuli-responsive molecular and macromolecular systems can be successfully applied to attain reversible dispersity of CNTs in solutions as well as sensitive changes in other physical properties. Each type of the external stimuli aforementioned exhibits certain advantages and offers promising opportunities for the preparation of "intelligent" nanohybrids with improved properties and enhanced

performance than conventional CNT-based materials. On the other hand, significant challenges are still present, which require continued research efforts to address both the fundamental and practical aspects. For the systems based on chemical or photochemical stimuli, controllability and tenability of the reversibility of the chemical and supramolecular reactions involved are the key issues to investigate. Besides the currently used methods (*e.g.*, acid/base, photoisomerism, redox, hydrogen bonding), new design concepts and ideas can be developed from related stimuli-responsive molecular and biological systems already established in other fields. For methods relying on relatively simple physical inputs (*e.g.*, temperature, solvent polarity), molecular modeling studies are of great value for gaining in-depth mechanistic understanding and more reliable and predictive theoretical models for the design of task-specific and better performing stimuli-responsive CNT-based systems. In this light, recent advances in molecular dynamic (MD) simulations of various CNT systems have paved a way for achieving this goal. Overall, the major drivers of technological advancements in CNTs are their wide-ranging applications, while new research thrusts are expected to emerge from synergistic efforts by the theoretical, synthetic, materials, and engineering communities.

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References

[1]   Iijima S. Helical Microtubules of Graphitic Carbon. Nature. 1991;354(6348):56–8.

[2]   Zhang Q, Huang J-Q, Qian W-Z, Zhang Y-Y, Wei F. The Road for Nanomaterials Industry: A Review of Carbon Nanotube Production, Post-Treatment, and Bulk Applications for Composites and Energy Storage. Small. 2013;9(8):1237–65.

[3]   Park S, Vosguerichian M, Bao Z. A Review of Fabrication and Applications of Carbon Nanotube Film-based Flexible Electronics. Nanoscale. 2013;5(5):1727–52.

[4]   Sgobba V, Guldi DM. Carbon Nanotubes-Electronic/Electrochemical Properties and Application for Nanoelectronics and Photonics. Chem Soc Rev. 2009;38(1):165–84.

[5]   Avouris P, Freitag M, Perebeinos V. Carbon-Nanotube Photonics and Optoelectronics. Nat Photon. 2008;2(6):341–50.

[6]   Liu X, Wang M, Zhang S, Pan B. Application Potential of Carbon Nanotubes in Water Treatment: A Review. J Environ Sci. 2013;25(7):1263–80.

[7]   Heister E, Brunner EW, Dieckmann GR, Jurewicz I, Dalton AB. Are Carbon Nanotubes a Natural Solution? Applications in Biology and Medicine. ACS Appl Mater Interf. 2013;5(6):1870–91.

[8]   Prato M, Kostarelos K, Bianco A. Functionalized Carbon Nanotubes in Drug Design and Discovery. Acc Chem Res. 2008;41(1):60–8.

[9]   Prasek J, Drbohlavova J, Chomoucka J, Hubalek J, Jasek O, Adam V, et al. Methods for Carbon Nanotubes Synthesis-Review. J Mater Chem. 2011;21(40):15872–84.

[10] Karousis N, Tagmatarchis N, Tasis D. Current Progress on the Chemical Modification of Carbon Nanotubes. Chem Commun. 2010;110(9):5366–97.

[11] Dyke CA, Tour JM. Covalent Functionalization of Single-Walled Carbon Nanotubes for Materials Applications. J Phys Chem A. 2004;108(51):11151–9.

[12] Di Crescenzo A, Ettorre V, Fontana A. Non-covalent and Reversible Functionalization of Carbon Nanotubes. Beilstein J Nanotechnol. 2014;5:1675–90.

[13] Bilalis P, Katsigiannopoulos D, Avgeropoulos A, Sakellariou G. Non-covalent Functionalization of Carbon Nanotubes with Polymers. RSC Adv. 2014;4(6):2911–34.

[14] Zhao Y-L, Stoddart JF. Noncovalent Functionalization of Single-Walled Carbon Nanotubes. Acc Chem Res. 2009;42(8):1161–71.

[15] Samanta SK, Fritsch M, Scherf U, Gomulya W, Bisri SZ, Loi MA. Conjugated Polymer-Assisted Dispersion of Single-Wall Carbon Nanotubes: The Power of Polymer Wrapping. Acc Chem Res. 2014;47(8):2446–56.

[16] Kharissova OV, Kharisov BI, de Casas Ortiz EG. Dispersion of Carbon Nanotubes in Water and Non-aqueous Solvents. RSC Adv. 2013;3(47):24812–52.

[17] Yang H, Bezugly V, Kunstmann J, Filoramo A, Cuniberti G. Diameter-Selective Dispersion of Carbon Nanotubes via Polymers: A Competition between Adsorption and Bundling. ACS Nano. 2015;9(9):9012–9.

[18] Hersam MC. Progress Towards Monodisperse Single-walled Carbon Nanotubes. Nat Nanotechnol. 2008;3(7):387–94.

[19] Sun D-m, Timmermans MY, Tian Y, Nasibulin AG, Kauppinen EI, Kishimoto S, et al. Flexible High-Performance Carbon Nanotube Integrated Circuits. Nat Nanotechnol. 2011;6(3):156–61.

[20] Yun D-J, Jeong YJ, Ra H, Kim J-M, An TK, Seol M, et al. Fabrication of High-Performance Composite Electrodes Composed of Multiwalled Carbon Nanotubes and Glycerol-doped Poly(3,4-ethylenedioxythiophene):Polystyrene Sulfonate for Use in Organic Devices. J Mater Chem C. 2015;3(28):7325–35.

[21] Wang F, Kozawa D, Miyauchi Y, Hiraoka K, Mouri S, Ohno Y, et al. Considerably Improved Photovoltaic Performance of Carbon Nanotube-based Solar Cells Using Metal Oxide Layers. Nat Commun. 2015;6.

[22] Jung Y, Li X, Rajan NK, Taylor AD, Reed MA. Record High Efficiency Single-Walled Carbon Nanotube/Silicon p–n Junction Solar Cells. Nano Lett. 2013;13(1):95–9.

[23] Hata K, Futaba DN, Mizuno K, Namai T, Yumura M, Iijima S. Water-Assisted Highly Efficient Synthesis of Impurity-Free Single-Walled Carbon Nanotubes. Science. 2004;306(5700):1362–4.

[24] Bahr JL, Mickelson ET, Bronikowski MJ, Smalley RE, Tour JM. Dissolution of Small Diameter Single-Wall Carbon Nanotubes in Organic Solvents? Chem Commun. 2001(2):193–4.

[25] Zhou B, Lin Y, Li H, Huang W, Connell JW, Allard LF, et al. Absorptivity of Functionalized Single-Walled Carbon Nanotubes in Solution. J Phys Chem B. 2003;107(49): 13588–92.

[26] Landi BJ, Ruf HJ, Worman JJ, Raffaelle RP. Effects of Alkyl Amide Solvents on the Dispersion of Single-Wall Carbon Nanotubes. J Phys Chem B. 2004;108(44):17089–95.

[27] Krupke R, Hennrich F, Hampe O, Kappes MM. Near-Infrared Absorbance of Single-Walled Carbon Nanotubes Dispersed in Dimethylformamide. J Phys Chem B. 2003;107(24):5667–9.

[28] Kah M, Zhang X, Jonker MTO, Hofmann T. Measuring and Modeling Adsorption of PAHs to Carbon Nanotubes Over a Six Order of Magnitude Wide Concentration Range. Environ SciTechnol. 2011;45(14):6011–7.

[29] Yang K, Xing B. Adsorption of Organic Compounds by Carbon Nanomaterials in Aqueous Phase: Polanyi Theory and Its Application. Chem Rev. 2010;110(10):5989–6008.

[30] Chen RJ, Zhang Y, Wang D, Dai H. Noncovalent Sidewall Functionalization of Single-Walled Carbon Nanotubes for Protein Immobilization. J Am Chem Soc. 2001;123(16): 3838–9.

[31] Maligaspe E, Sandanayaka ASD, Hasobe T, Ito O, D'Souza F. Sensitive Efficiency of Photoinduced Electron Transfer to Band Gaps of Semiconductive Single-Walled Carbon Nanotubes with Supramolecularly Attached Zinc Porphyrin Bearing Pyrene Glues. J Am Chem Soc. 2010;132(23):8158–64.

[32] Perez EM, Illescas BM, Herranz MA, Martin N. Supramolecular Chemistry of π-Extended Analogues of TTF and Carbon Nanostructures. New J Chem. 2009;33(2):228–34.

[33] Bottari G, de la Torre G, Torres T. Phthalocyanine–Nanocarbon Ensembles: From Discrete Molecular and Supramolecular Systems to Hybrid Nanomaterials. Acc Chem Res. 2015;48(4):900–10.

[34] Bartelmess J, Frasconi M, Balakrishnan PB, Signorelli A, Echegoyen L, Pellegrino T, et al. Non-covalent Functionalization of Carbon Nano-Onions with Pyrene-BODIPY Dyads for Biological Imaging. RSC Adv. 2015;5(62):50253–8.

[35] Hong G, Diao S, Antaris AL, Dai H. Carbon Nanomaterials for Biological Imaging and Nanomedicinal Therapy. Chem Rev. 2015;115(19):10816–906.

[36] Sudibya HG, Ma J, Dong X, Ng S, Li L-J, Liu X-W, et al. Interfacing Glycosylated Carbon-Nanotube-Network Devices with Living Cells to Detect Dynamic Secretion of Biomolecules. Angew Chem Int Ed. 2009;48(15):2723–6.

[37] Li C, Mezzenga R. Functionalization of Multiwalled Carbon Nanotubes and Their pH-Responsive Hydrogels with Amyloid Fibrils. Langmuir. 2012;28(27):10142–6.

[38] Ogoshi T, Takashima Y, Yamaguchi H, Harada A. Chemically-Responsive Sol–Gel Transition of Supramolecular Single-Walled Carbon Nanotubes (SWNTs) Hydrogel Made by Hybrids of SWNTs and Cyclodextrins. J Am Chem Soc. 2007;129(16):4878–9.

[39] Zhong Q, Diev VV, Roberts ST, Antunez PD, Brutchey RL, Bradforth SE, et al. Fused Porphyrin–Single-Walled Carbon Nanotube Hybrids: Efficient Formation and Photophysical Characterization. ACS Nano. 2013;7(4):3466–75.

[40] Wang Y, Hu N, Zhou Z, Xu D, Wang Z, Yang Z, et al. Single-walled Carbon Nanotube/Cobalt Phthalocyanine Derivative Hybrid Material: Preparation, Characterization and Its Gas Sensing Properties. J Mater Chem. 2011;21(11):3779–87.

[41] Romero-Nieto C, García R, Herranz MÁ, Ehli C, Ruppert M, Hirsch A, et al. Tetrathiafulvalene-Based Nanotweezers—Noncovalent Binding of Carbon Nanotubes in Aqueous Media with Charge Transfer Implications. J Am Chem Soc. 2012;134(22):9183–92.

[42] Ehli C, Guldi DM, Angeles Herranz M, Martin N, Campidelli S, Prato M. Pyrene-Tetrathiafulvalene Supramolecular Assembly with Different Types of Carbon Nanotubes. J Mater Chem. 2008;18(13):1498–503.

[43] Didenko VV, Moore VC, Baskin DS, Smalley RE. Visualization of Individual Single-Walled Carbon Nanotubes by Fluorescent Polymer Wrapping. Nano Lett. 2005;5(8):1563–7.

[44] Von Bargen CD, MacDermaid CM, Lee O-S, Deria P, Therien MJ, Saven JG. Origins of the Helical Wrapping of Phenyleneethynylene Polymers about Single-Walled Carbon Nanotubes. J Phys Chem B. 2013;117(42):12953–65.

[45] Xiao Z, Wang X, Xu X, Zhang H, Li Y, Wang Y. Base- and Structure-Dependent DNA Dinucleotide–Carbon Nanotube Interactions: Molecular Dynamics Simulations and Thermodynamic Analysis. J Phys Chem C. 2011;115(44):21546–58.

[46] Gao H, Kong Y. Simulation of DNA-Nanotube Interactions. Annu Rev Mater Res. 2004;34(1):123–50.

[47] Kato Y, Inoue A, Niidome Y, Nakashima N. Thermodynamics on Soluble Carbon Nanotubes: How Do DNA Molecules Replace Surfactants on Carbon Nanotubes? Sci Rep. 2012;2:733.

[48] Landry MP, Vuković L, Kruss S, Bisker G, Landry AM, Islam S, et al. Comparative Dynamics and Sequence Dependence of DNA and RNA Binding to Single Walled Carbon Nanotubes. J Phys Chem C. 2015;119(18):10048–58.

[49] Manohar S, Tang T, Jagota A. Structure of Homopolymer DNA−CNT Hybrids†. J Phys Chem C. 2007;111(48):17835–45.

[50] Karachevtsev MV, Karachevtsev VA. Peculiarities of Homooligonucleotides Wrapping Around Carbon Nanotubes: Molecular Dynamics Modeling. J Phys Chem B. 2011;115(29):9271–9.

[51] Johnson RR, Johnson ATC, Klein ML. Probing the Structure of DNA−Carbon Nanotube Hybrids with Molecular Dynamics. Nano Lett. 2008;8(1):69–75.

[52] Zhang S, Wang X, Li T, Liu L, Wu H-C, Luo M, et al. Sensitive Detection of a Modified Base in Single-Stranded DNA by a Single-Walled Carbon Nanotube. Langmuir. 2015;31(36):10094–9.

[53] Sohrabi B, Poorgholami-Bejarpasi N, Nayeri N. Dispersion of Carbon Nanotubes Using Mixed Surfactants: Experimental and Molecular Dynamics Simulation Studies. J Phys Chem B. 2014;118(11):3094–103.

[54] Uddin NM, Capaldi FM, Farouk B. Molecular Dynamics Simulations of Carbon Nanotube Dispersions in Water: Effects of Nanotube Length, Diameter, Chirality and Surfactant Structures. Comput Mater Sci. 2012;53(1):133–44.

[55] Tummala NR, Morrow BH, Resasco DE, Striolo A. Stabilization of Aqueous Carbon Nanotube Dispersions Using Surfactants: Insights from Molecular Dynamics Simulations. ACS Nano. 2010;4(12):7193–204.

[56] Dutta S, Kar T, Brahmachari S, Das PK. pH-responsive Reversible Dispersion of Biocompatible SWNT/Graphene-Amphiphile Hybrids. J Mater Chem. 2012;22(14):6623–31.

[57] Ghosh M, Brahmachari S, Das PK. pH-Responsive Single Walled Carbon Nanotube Dispersion for Target Specific Release of Doxorubicin to Cancer Cells. Macromol Biosci. 2014;14(12):1795–806.

[58] Yu G, Xue M, Zhang Z, Li J, Han C, Huang F. A Water-Soluble Pillar[6]arene: Synthesis, Host–Guest Chemistry, and Its Application in Dispersion of Multiwalled Carbon Nanotubes in Water. J Am Chem Soc. 2012;134(32):13248–51.

[59] Welsh DJ, O'Driscoll LJ, Bailey SWD, Visontai D, Howes K, Frampton H, et al. Key Role of the Linker in Pyrene-Linker-Carboxylate Surfactants for the Efficient Aqueous Dispersion of Multiwalled Carbon Nanotubes. RSC Adv. 2015;5(115):95360–8.

[60] Pochorovski I, Wang H, Feldblyum JI, Zhang X, Antaris AL, Bao Z. H-Bonded Supramolecular Polymer for the Selective Dispersion and Subsequent Release of Large-Diameter Semiconducting Single-Walled Carbon Nanotubes. J Am Chem Soc. 2015;137(13):4328–31.

[61] Lu F, Wang X, Meziani MJ, Cao L, Tian L, Bloodgood MA, et al. Effective Purification of Single-Walled Carbon Nanotubes with Reversible Noncovalent Functionalization. Langmuir. 2010;26(10):7561–4.

[62] Maji B, Samanta SK, Bhattacharya S. Role of pH Controlled DNA Secondary Structures in the Reversible Dispersion/Precipitation and Separation of Metallic and Semiconducting Single-Walled Carbon Nanotubes. Nanoscale. 2014;6(7):3721–30.

[63] Wang D, Chen L. Temperature and pH-Responsive Single-Walled Carbon Nanotube Dispersions. Nano Lett. 2007;7(6):1480–4.

[64] Ding Y, Chen S, Xu H, Wang Z, Zhang X, Ngo TH, et al. Reversible Dispersion of Single-Walled Carbon Nanotubes Based on a CO_2-Responsive Dispersant. Langmuir. 2010;26(22):16667–71.

[65] Guo Z, Feng Y, He S, Qu M, Chen H, Liu H, et al. CO_2-Responsive "Smart" Single-Walled Carbon Nanotubes. Adv Mater. 2013;25(4):584–90.

[66] Natali M, Giordani S. Molecular Switches as Photocontrollable "Smart" Receptors. Chem Soc Rev. 2012;41(10):4010–29.

[67] Chen S, Jiang Y, Wang Z, Zhang X, Dai L, Smet M. Light-Controlled Single-Walled Carbon Nanotube Dispersions in Aqueous Solution. Langmuir. 2008;24(17):9233–6.

[68] Lemasson F, Tittmann J, Hennrich F, Sturzl N, Malik S, Kappes MM, et al. Debundling, Selection and Release of SWNTs Using Fluorene-based Photocleavable Polymers. Chem Commun. 2011;47(26):7428–30.

[69] Imin P, Imit M, Adronov A. Supramolecular Functionalization of Single-Walled Carbon Nanotubes (SWNTs) with a Photoisomerizable Conjugated Polymer. Macromolecules. 2012;45(12):5045–50.

[70] Maggini L, Marangoni T, Georges B, Malicka JM, Yoosaf K, Minoia A, et al. Azobenzene-based Supramolecular Polymers for Processing MWCNTs. Nanoscale. 2013;5(2):634–45.

[71] Umeyama T, Kawabata K, Tezuka N, Matano Y, Miyato Y, Matsushige K, et al. Dispersion of Carbon Nanotubes by Photo- and Thermal-responsive Polymers Containing Azobenzene Unit in the Backbone. Chem Commun. 2010;46(32):5969–71.

[72] Nobusawa K, Ikeda A, Kikuchi J-i, Kawano S-i, Fujita N, Shinkai S. Reversible Solubilization and Precipitation of Carbon Nanotubes through Oxidation–Reduction Reactions of a Solubilizing Agent. Angew Chem Int Ed. 2008;47(24):4577–80.

[73] Zhao Y, Chen G, Mulla K, Mahmud I, Liang S, Dongare P, et al. Tetrathiafulvalene Vinylogues as Versatile Building Blocks for New Organic Materials. Pure Appl Chem. 2012;84(4):1005–25.

[74] Liang S, Chen G, Zhao Y. Conformationally Switchable TTFV-Phenylacetylene Polymers: Synthesis, Properties, and Supramolecular Interactions with Single-Walled Carbon Nanotubes. J Mater Chem C. 2013;1(35):5477–90.

[75] Liang S, Chen G, Peddle J, Zhao Y. Reversible Dispersion and Releasing of Single-Walled Carbon Nanotubes by a Stimuli-responsive TTFV-Phenylacetylene Polymer. Chem Commun. 2012;48(25):3100–2.

[76] Adeel SM, Li Q, Nafady A, Zhao C, Siriwardana AI, Bond AM, et al. A Systematic Study of the Variation of Tetrathiafulvalene (TTF), TTF^+ and TTF^{2+} Reaction Pathways with Water in the Presence and Absence of Light. RSC Adv. 2014;4(91):49789–95.

[77] Liang S, Zhao Y, Adronov A. Selective and Reversible Noncovalent Functionalization of Single-Walled Carbon Nanotubes by a pH-Responsive Vinylogous Tetrathiafulvalene–Fluorene Copolymer. J Am Chem Soc. 2014;136(3):970–7.

[78] Etika KC, Jochum FD, Theato P, Grunlan JC. Temperature Controlled Dispersion of Carbon Nanotubes in Water with Pyrene-Functionalized Poly(N-cyclopropylacrylamide). J Am Chem Soc. 2009;131(38):13598–9.

[79] O'Driscoll LJ, Welsh DJ, Bailey SWD, Visontai D, Frampton H, Bryce MR, et al. Reversible Thermal Switching of Aqueous Dispersibility of Multiwalled Carbon Nanotubes. Chem-Eur J. 2015;21(10):3891–4.

[80] Hill DJ, Mio MJ, Prince RB, Hughes TS, Moore JS. A Field Guide to Foldamers. Chem Rev. 2001;101(12):3893–4012.

[81] Guichard G, Huc I. Synthetic Foldamers. Chem Commun. 2011;47(21):5933–41.

[82] Zhang Z, Che Y, Smaldone RA, Xu M, Bunes BR, Moore JS, et al. Reversible Dispersion and Release of Carbon Nanotubes Using Foldable Oligomers. J Am Chem Soc. 2010;132(40):14113–7.

[83] Mulla K, Zhao Y. When Dithiafulvenyl Functionalized π-Conjugated Oligomers Meet Fullerenes and Single-Walled Carbon Nanotubes. J Mater Chem C. 2013;1(33):5116–27.

[84] Mulla K, Liang S, Shaik H, Younes EA, Adronov A, Zhao Y. Dithiafulvenyl-grafted Phenylene Ethynylene Polymers as Selective and Reversible Dispersants for Single-Walled Carbon Nanotubes. Chem Commun. 2015;51(1):149–52.

[85] Llanes-Pallas A, Yoosaf K, Traboulsi H, Mohanraj J, Seldrum T, Dumont J, et al. Modular Engineering of H-Bonded Supramolecular Polymers for Reversible Functionalization of Carbon Nanotubes. J Am Chem Soc. 2011;133(39):15412–24.

[86] Schattling P, Jochum FD, Theato P. Multi-Stimuli Responsive Polymers – The All-in-One Talents. Polym Chem. 2014;5(1):25–36.

[87] Stuart MAC, Huck WTS, Genzer J, Muller M, Ober C, Stamm M, et al. Emerging Applications of Stimuli-Responsive Polymer Materials. Nat Mater. 2010;9(2):101–13.

[88] Hong CY, Pang CY. Functionalized Carbon Nanotubes Responsive to Environmental Stimuli. J Mater Chem. 2008;18(16):1831–6.

[89] Luo H, Li Z, Yi G, Zu X, Wang H, Huang H, et al. Multi-Stimuli Responsive Carbon Nanotube–Shape Memory Polymeric Composites. Mater Lett. 2014;137:385–8.

[90] Soll S, Antonietti M, Yuan J. Double Stimuli-Responsive Copolymer Stabilizers for Multiwalled Carbon Nanotubes. ACS Macro Lett. 2012;1(1):84–7.

[91] Biswas Y, Maji T, Dule M, Mandal TK. Tunable Doubly Responsive UCST-Type Phosphonium Poly(ionic liquid): A Thermosensitive Dispersant for Carbon Nanotubes. Polym Chem. 2016;7(4):867–77.

[92] Zydziak N, Hubner C, Bruns M, Vogt AP, Barner-Kowollik C. Modular Ambient Temperature Functionalization of Carbon Nanotubes with Stimuli-Responsive Polymer Strands. Polym Chem. 2013;4(5):1525–37.

[93] Guo Z, Feng Y, Zhu D, He S, Liu H, Shi X, et al. Light-Switchable Single-Walled Carbon Nanotubes Based on Host–Guest Chemistry. Adv Funct Mater. 2013;23(40):5010–8.