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Universally Dispersible Carbon Nanotubes

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Supporting Information

ABSTRACT: We show that supramolecular chemistry provides a convenient tool to prepare carbone nanotubes (CNTs) that can be dispersed in solvents of any chemical nature, easily recovered and redispersed. Thymine-modified CNTs (CNT-Thy) can be dispersed in solution in the presence of diaminotriazine (DAT) end-functionalized polymers, through supramolecular Thy/DAT association. DAT-polymer chains are selected according to the solvent chemical nature: polystyrene (PS) for hydrophobic/low polarity solvents and a propylene oxide/ethylene oxide copolymer (predominantly propylene oxide based, PPO/PEO) for polar solvents or water. Long-term stable supramolecular CNT dispersions are reversibly aggregated by adding a few droplets of a selective dissociating agent of the Thy/DAT association (DMSO). CNT-Thy, simply recycled by centrifugation or filtration, can be redispersed in another solvent in presence of a suitable soluble DAT-polymer. Dispersion and aggregation can also be switched on and off by choosing a polymer for which a given solvent is close to Θ-conditions, e.g., PS in cyclohexane or PPO/PEO in water.

Stabilizing dispersions of carbon nanotubes (CNTs) is a major challenge since it is a prerequisite to high performance CNT/polymer composites[1] potentially useful in a large field of applications, such as reinforced materials,[2] conductive plastics or adhesives,[3] electronics,[4] and actuators.[5] Because of strong van der Waals forces, CNTs are prone to form entangled bundles[6] and aggregate in solution. In general, dispersion of CNTs involves two stages: first, mechanical disentanglement, usually by sonication, and second, stabilization by adsorbing an organic mediating molecule.[1b,c,7] For instance, because they partly absorb on the CNTs surface through van der Waals hydrophobic forces or $\pi-\pi$-stacking,[1a] block and/or amphiphilic polymers[8] or surfactants[9] can weaken intertube van der Waals interactions and allow steric repulsions between nonadsorbed moieties in good solvents.[8a,9a,10] An alternative way to stabilize CNTs is to chemically modify the CNTs surface either by reacting surface defects (COOH or OH)[11] or by very reactive sp^2 CNT sidewalls;[12] such modified CNTs are dispersible in adequate solvents. Other methods use covalent grafting of polymers either by classical organic reactions or more recently by click reactions.[7a,12a,13] The main disadvantage of these methods is that each modification is specific of the solvent (polar/apolar, hydrophilic/hydrophobic) and requires a particular registration of each newly modified CNTs to environmental administrations.[14] Both stabilization approaches, polymers or surfactants adsorption or polymer grafting, are irreversible, thus limiting recyclability and redispersion possibilities.

A seminal article by Quintana and Prato discloses how to graft Thy units to CNTs and demonstrates that supramolecular chemistry offers a versatile tool to control self-assembly of CNTs.[15a] More rencently, Quintana et al. have shown that supramolecular host/guest interaction between functional polymers and thymine-modified CNTs can be used to prepare CNT-polymer hybrids and to pattern functionalized polymeric surfaces.[15b]

In a different supramolecular chemistry approach, Di Crescenzo et al.[16a] and Llanes-Pallas et al.[16b] used pristine rather than functionalized CNTs and showed that supramolecular polymers carrying the adequate side groups can adsorb (wrap around surface) on CNTs and efficiently stabilize dispersions. As for more classical systems, this approach can work only for good solvents of side groups.

Inspired by these results and by physics of colloidal stabilization, we address the question of efficient stabilization. Here, we propose a method to achieve universal, reversible, and controllable CNTs dispersions by using supramolecular chemistry through host/guest association. Molecules acting as hosts were grafted onto the CNT surface. Linear polymer chains of different chemical composition containing a complementary guest group at one end were synthesized. Thanks to the host/guest interaction, the polymer chains attach onto the CNTs by their end functional group. Thus, a layer of polymer is formed on the surface of the CNTs and ensures steric stabilization of dispersions in good solvents of the polymer (Figure 1A). Using polymers with one functional end, rather than polymers bearing multiple functional units, is essential to avoid bridging by polymers and CNTs aggregation at high concentrations.[15b] Adding a selective host/guest dissociating additive breaks the supramolecular interaction. While the guest-polymer chains remain in solution, the CNT-host aggregates can be separated by centrifugation or filtration (Figure 1B). CNT-host can be subsequently redispersed in another solvent using adequate guest-polymers (Figure 1C). As a consequence, such CNTs-host/guest-polymer systems are universal since good dispersions can be achieved in any solvent by appropriate choice of guest-polymer chains. Figure 1D illustrates how aggregation/dispersion can be controlled by changing temperature. Indeed, in a bad solvent, polymer chains collapse, so steric stabilization is no longer effective and CNTs

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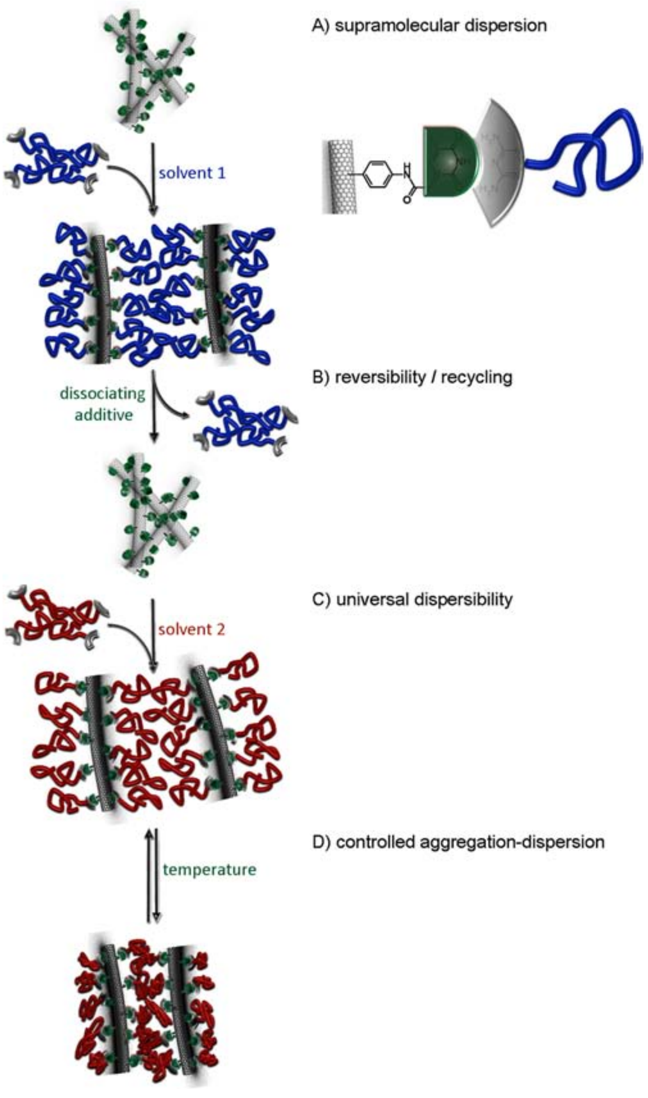


Figure 1. Universal, reversible, and controllable CNT dispersions through supramolecular chemistry.

aggregate. By changing the temperature, the solvent quality can be improved and CNTs redispersed.

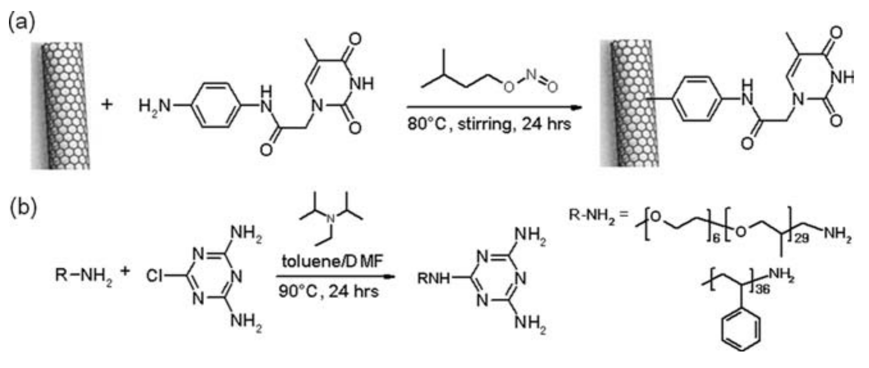
The host/guest system used in this study is Thy and 2,6-diamino-1,3,5-triazine (DAT) that associate through three parallel H-bonds. Since Thy/DAT complementary association is much stronger than either Thy-Thy or DAT-DAT self-association, CNTs grafted with Thy (CNT-Thy) will exclusively interact with DAT-ended polymer chains (Figure 1A).[17] Purified CNTs (pristine, CNTp) were grafted in water with a Thy derivative of 1,4-phenylenediamine in presence of isoamylnitrite (Scheme 1a).[18] Grafting of phenyleneamine-Thy was monitored by UV/vis spectroscopy by following the K-band of Thy at 280 nm. CNT-Thy were analyzed by TGA, Raman, and infrared spectroscopies. Grafting was estimated to be 1 Thy group per 50 carbon atoms (See Supporting Information, SI). Two low molecular weight polymers were used: poly(propylene oxide-ethylene oxide) (29/6 monomers, PPO/PEO-DAT, M_w(PPO/PEO) = 2000 g/mol) and polystyrene (PS-DAT, M_w(PS) = 3600 g/mol). PPO/PEO-DAT was synthesized from a commercial monoamine PPO/PEO-NH_2 according to a procedure described elsewhere.[19] Polystyrene oligomer PS-Br was synthesized by atom-transfer radical polymerization (ATRP), converted to amine derivative PS-NH_2,[20] and grafted with DAT unit according to the same reaction as for PPO/PEO-NH_2 (Scheme 1b). Syntheses and characterizations of DAT-polymer chains are given in SI.

To evidence that supramolecular Thy/DAT interaction favors stable dispersions of CNTs in solvents of any chemical nature (Figure 1), we prepared by sonication (150W, 30 min) solutions of 0.05 wt % CNT-Thy and 0.1 wt % DAT-polymer in solvents of increasing polarity: cyclohexane, toluene, chloroform, acetone, and water (Figure 2b). PS-DAT was used in apolar solvents and PPO/PEO-DAT in polar solvents and water.

For comparison, the same solutions were prepared with CNTp alone (Figure 2a) and CNT-Thy alone (see Figure S14). All solutions were allowed to stand 24 h and observed by optical microscopy (Figure 2a,b). Particle size analysis was performed with ImageJ. CNTs were considered as dispersed when detected aggregates represent ≤1% of the total analyzed surface with a mean projected area particle size <5 μm. Furthermore, particle size distributions (PSD) revealed a median diameter <2 μm and mode diameter comprised between 1 and 2 μm (see SI).

CNT surface consists of sp^2 hybridized carbon planes and is mostly apolar and hydrophobic. CNTp used in this study have been purified by a sulphuric acid treatment and present carboxylic acid functionalities on the surface.[21] Nevertheless, their surface was neither hydrophobic/hydrophilic or apolar/polar enough to ensure good dispersions in any studied solvent (Figure 2a). Even for chloroform and acetone where CNTp seemed "macroscopically" dispersed, large aggregates were observed by optical microscopy (Figure 2a). All pure CNT-Thy

Scheme 1. (a) Chemical Grafting of Thymine Derivatives on Purified CNTs and (b) DAT End-Functionalization of Polymer Chains



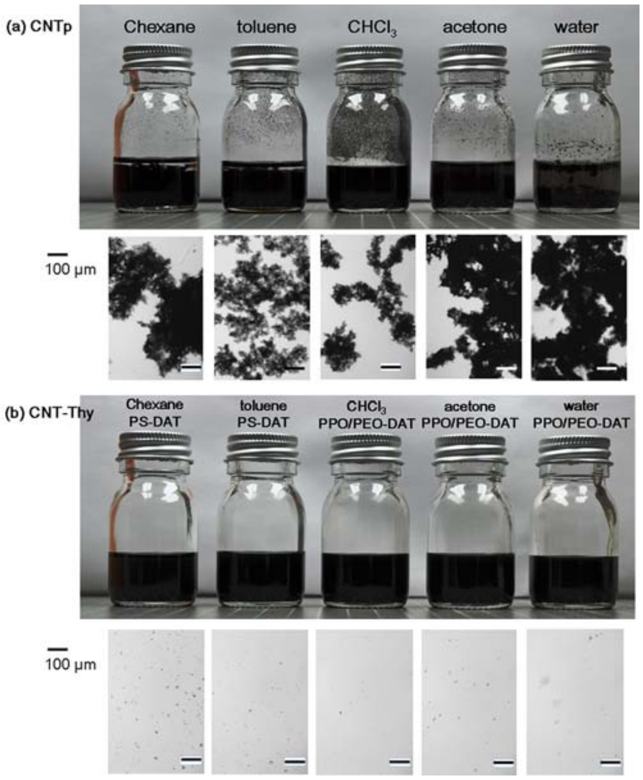


Figure 2. 0.05 wt % CNTs solutions in cyclohexane (at 40 °C), toluene, chloroform, acetone, and water and corresponding optical microscopy: (a) purified CNTp and (b) Thy-grafted CNT-Thy/DAT-polymer (PS or PPO/PEO).

solutions were also aggregated. Contrariwise, in all DAT-polymer solutions, CNT-Thy were dispersed since large aggregates were no longer observed by optical microscopy (Figure 2b). Furthermore, in organic solvents, these dispersions were stable over a few months. To confirm that dispersions are driven by the Thy/DAT supramolecular interaction,[15b,16] test solutions in toluene of (i) CNT-Thy, (ii) CNTp/DAT-polymer (PS or PPO/PEO), and (iii) CNT-Thy/H_2N-polymer were prepared according to the same protocol. All test solutions showed large aggregates, indicating that polymer (PS or PPO/PEO) derivatives were not good dispersants for CNTp or CNT-Thy (see Figure S15).

Thus, Thy/DAT association allows universal dispersions of CNTs in a large variety of solvents. Since Thy/DAT interaction consists of three parallel hydrogen bonds (Figure 1A), this supramolecular interaction can be broken by adding a competitive molecule, i.e., a dissociating additive. CNT dispersions can then be destabilized, and the CNTs recovered by filtration or centrifugation (figure 1B).

Water, polar, and/or protic solvents, such as DMSO or alcohols, are H-bond competitors that can break H-bonded supramolecular associations.[16,22] Indeed, adding two droplets of DMSO to a stable dispersion of CNT-Thy/DAT-PS in toluene led to a complete aggregation of CNT-Thy within 20 min (Figure 3a,b). Aggregation by Thy/DAT disruption allowed CNT-Thy recovery from the DAT-PS solution by centrifugation. By using a solution of 0.1 wt % DAT-PPO/PEO in acetone, it was possible to redisperse the recovered CNT-Thy (Figures 1C and 3c). In contrast to DMSO, a dispersion stable for at least 24 h could be obtained in water with 1 wt % DAT-PPO/PEO (Figure 2b). Differences in solubility of Thy and DAT in DMSO and water could explain these results: the more Thy and DAT are soluble, the faster and complete is the dissociative effect of the solvent.

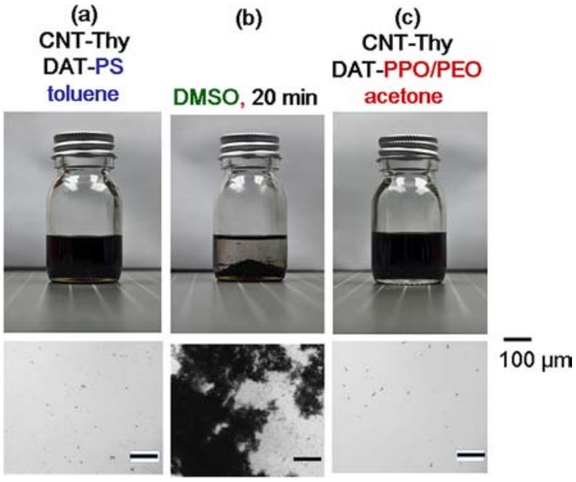


Figure 3. Universal dispersion and recycling of CNT-Thy: (a) 0.05 wt % CNT-Thy/0.1 wt % DAT-PS in toluene; (b) CNT-Thy aggregation triggered by two drops of DMSO; and (c) redispersion in a solution of 0.1 wt % PPO/PEO-DAT in acetone.

To sum up, dispersibility and recycling of CNTs can be controlled by supramolecular chemistry: CNT-Thy are universally dispersed by adapting DAT-polymer nature to the desired dispersing solvent and recycled by using a selective dissociating additive of the supramolecular association. In addition, some CNT-Thy dispersions can be controlled by temperature (Figure 1D) since, in Θ-solvents, DAT-polymer chains can swell or collapse.

For instance, cyclohexane is a Θ-solvent of PS with an upper critical solution transition of 36 °C, and water is a Θ-solvent of PPO/PEO with a lower critical solution temperature of 18 °C for the used PPO/PEO-DAT (see SI). 0.05 wt % CNT-Thy/0.1 wt % DAT-PS in cyclohexane gave stable dispersions at 50 °C. When cooled in an ice bath for 10 min, almost complete aggregation was observed. Heating and stirring the aggregated solution at 50 °C for 10 min restored a stable dispersion (Figure 4a). 0.05 wt % CNT-Thy/1 wt % DAT-PPO/PEO in

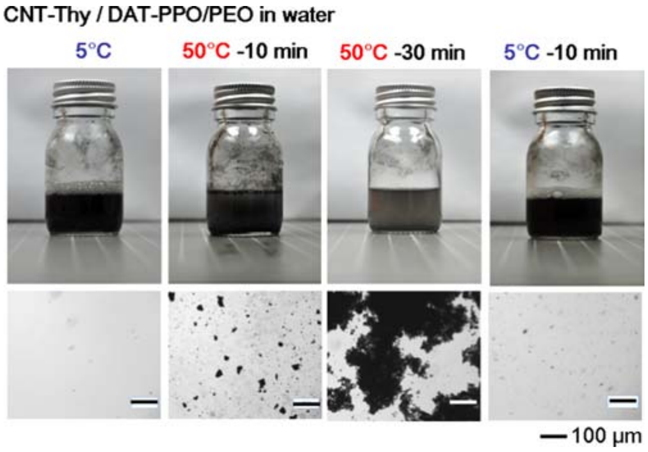


Figure 4. Aggregation and redispersion 0.05 wt % of CNT-Thy/1 wt % DAT-PPO/PEO in water (from left to right): stable dispersion at 5 °C, aggregation at 50 °C in 20 min, and redispersion at 5 °C under stirring.

water gave stable dispersions at 5 °C. When heated at 50 °C, aggregation occurred after 2 min and was complete within 10 min. Cooling and stirring the aggregated solution in an ice bath for 10 min restored a stable dispersion (Figure 4b and Figure S11 for PSD analysis). These temperature cycles were repeated three times and led to the same aggregation/dispersion process.

In summary, we have demonstrated that supramolecular chemistry is a convenient way to control stable dispersions of CNTs in any type of solvent. Thymine-grafted CNTs can be stabilized thanks to a host/guest association using any DAT-end-grafted polymer chains soluble in a given solvent. Steric repulsions between polymer chains ensure dispersions stability. Moreover, we have shown that CNT supramolecular dispersions can be destabilized by adding a dissociating additive selective of the host/guest association. In this manner, Thy-grafted CNTs are recycled and can be redispersed in another solvent in presence of DAT-end-polymer chains soluble in that solvent. To conclude, such CNT-Thy/DAT-polymer complexes are universally dispersible and recyclable. In addition, possibility of reversible switch on and off dispersion/aggregation by heating or cooling the solution offers desirable opportunities. This concept could be applied to other particles that are difficult to disperse and stabilize in solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ NOTE ADDED AFTER ASAP PUBLICATION

Scheme 1 has been updated. The revised version was re-posted on November 30, 2012.