

Dispersion of carbon nanotubes using an azobenzene derivative

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Aqueous dispersions of carbon nanotubes (CNTs) were obtained by noncovalent adsorption of an azobenzene derivative carrying polyglycerol dendritic structures. UV/Vis absorption spectra and photoluminescence maps were recorded to confirm successful nanotube debundling and suspension.

Comparison to dispersion of nanotubes using sodium dodecyl sulfate (SDS) revealed shifts of the nanotube E_{22} excitation peaks from 28 to 67 meV as well as shifts from 21 to 37 meV of the E_{11} emission peaks.

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1 Introduction Due to their electronic structure carbon nanotubes (CNTs) are very sensitive to their dielectric environment. Functionalization of CNTs as means to alter their optical and transport properties has been demonstrated to open up a series of potential applications in the fabrication of optoelectronic devices [1–3].

The attachment of molecules to the surface can be used as a way to disperse and individualize nanotubes. As CNTs form bundles and thus quench their photoluminescence, functionalization allows suppressing this effect and therefore makes nanotube luminescence observable in the first place.

Noncovalent functionalization of CNTs is believed to be a method that only induces little perturbations to their electronic structure, as the tubes' extended π -network remains intact. Additionally, as no heating or acidic treatment is necessary, damage to the tubes remains minimal. Thus, much effort has been put into exploring noncovalent functionalization [4] with amphiphiles bearing alkyl chains [5, 6] aromatic compounds based on pyrene [7–9], porphyrin [1], perylene [10], as well as wrapping by polymers [11].

Recently, it was shown that the properties of CNTs can be tuned by functionalizing them with porphyrin molecules. Under illumination with UV light a charge transfer between the tubes and the porphyrin can be triggered, thus inducing temporary changes in the electronic transport through the tubes [1].

Switchable molecules as a way of tuning the electronic properties of CNTs recently became the subject of scientific investigation. Molecular switches are molecules possessing two or more (meta-)stable configurations. When excited (optically, chemically, *etc.*), the molecules undergo electronic and/or conformational changes.

The attachment of conformational molecular switches based on azobenzene compounds to individual, immobilized (dried) nanotubes was reported. Zhou et al. used a small difference in the electric dipole moment of *trans*- and *cis*-azobenzene to alter the I/I_0 -characteristics of a nanotube-based field effect transistor (CNT-FET) [2]. They observed that illumination with visible light changed the transistors threshold voltage. In a similar experiment, Simmons et al. used UV light to manipulate the transistors I/I_0 -characteristics [3].

A different approach of controlling the electronic properties of a CNT is using the conformational switch as the linker between tubes and adjacent functional groups. In this way, the distance between the nanotube and functional unit can be varied, thus, altering the magnitude of their interaction (see Figs. 3a, b). The switching is done by irradiating the sample with light of a specific wavelength. Moreover, by noncovalently functionalizing the nanotube, the tubes' electronic properties only experience small perturbations, since – unlike the covalent approach – this method does not involve the creation of additional defects to the nanotube sidewall.

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Nano-electronic devices such as FETs based on switch-functionalized nanotubes are sensitive to changes in the state of the adsorbed molecules and can thus serve as light detection systems. As the wavelength that can be detected depends upon the absorption properties of the switch molecule and not the chirality of the nanotube, there is no need for chirality sorting.

The overlap of the pyrene and azobenzene absorption spectra can be tuned by exchanging the attached functional group. Exchanging the OH for a CN group hinders the switching. Since the peaks at 450 nm are significantly less pronounced, the inset shows a part of the spectrum magnified by a factor of 15.

Until now, molecular switches were only adsorbed on immobilized nanotubes. The nanotube devices were pre-assembled and functionalized afterward. Obtaining switch-functionalized CNTs in solution, however, gives a more homogeneous coverage of the nanotube surface. As luminescence is no longer quenched, PL and PLE experiments can be used to investigate the compounds. Also it would allow the production of larger quantities and thus open a door toward applications while making the system easier to deploy. After functionalization, selection of certain chiralities could be obtained by different methods like density gradient centrifugation [12] or exploiting the selectivity of the interaction between aromatic moieties and nanotubes of a certain chirality [6, 13].

In this work, we report a dispersion agent for CNTs based on azobenzene, paving the way toward development of switching dispersion agents in the liquid phase. We investigated pyrene-azobenzene-PG (PAPG), an azobenzene molecule with walter-solubilizing polyglycerol dendrons on one end. The molecule additionally contains a pyrene head group that serves as a noncovalent anchor to the CNT.

2 Experimental details

2.1 Materials Azobenzene is a bistable aromatic molecule consisting of two phenyl rings connected by two nitrogen atoms. When illuminated with UV light, the molecule undergoes a conformational change from a *trans*- into a *cis*-configuration. Absorption measurements can be taken to monitor the isomerization process (see Fig. 1). This switching behavior can be used to influence the properties of CNTs in different ways.

Pyrene is an aromatic compound that shows strong absorption features below 350 nm and serves as a non-covalent linker to the nanotubes. The spectral overlap between pyrene and the azobenzene moiety can be tuned by changing the functional group attached to the azobenzene.

In this preliminary study, polyglycerol was used as functional group as there is no spectral overlap with the azobenzene absorption and it shows no emission. At the same time the polyglycerol makes the molecule amphiphilic, thus allowing solubility in polar solvents like water.

For these experiments we used HiPCO CNTs from Unidym (lot no. SP0295).

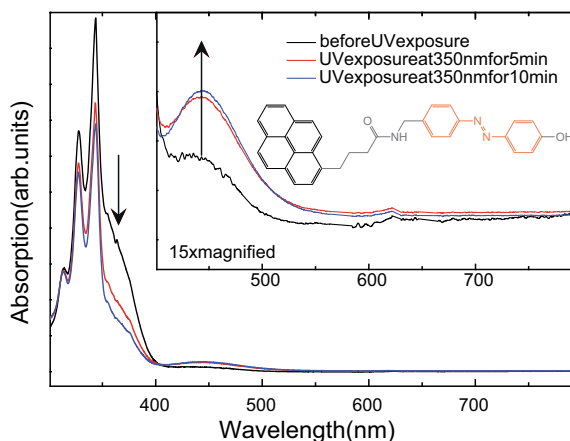


Figure 1 (online colour at: www.pss-b.com) Absorption measurements of an azobenzene molecule similar to PAPG, with a hydroxy group replacing the dendrons. Pyrene exhibits distinctive peaks below 400 nm. The absorption features of azobenzene are seen as a shoulder of the pyrene spectrum around 350 nm, as well as at 450 nm. UV exposure at a wavelength of 350 nm causes the compound to undergo a conformational change from the stable *trans*-form into the meta stable *cis*-form [14]. Both configurations exhibit different absorption spectra as can be seen.

2.2 Sample preparation

CNT-sodium dodecyl sulfate (SDS) CNTs were solubilized in water at a concentration of 0.1 g/L using 1% w/v of SDS. The sample was then sonicated for 30 min at a power of 140 W and afterward centrifuged twice at $3420 \times g$ for 30 min at room temperature. The supernatant was used for the experiments.

PAPG1 A solution of PAPG in methanol was prepared at a concentration of 1 g/L.

Different ratios of both samples (CNT-SDS and PAPG1) and additional water were combined under sonication (see Table 1).

CNT-PAPG To obtain a sample containing no SDS, CNTs were dispersed in water at a concentration of 0.1 g/L using a tip sonicator at a power of 200 W. This sample was then combined with the PAPG1 solution and further sonicated.

The resulting solution was left to sonicate for 1 h and then centrifuged at $3420 \times g$ for 30 min at room temperature.

Table 1 Ratios of solvents and surfactants.

label	ratio	
	water:methanol	SDS:PyrAzoPG
CNT-SDS	1:0	1:0
ratio 20:1	2:1	20:1
ratio 10:1	2:1	10:1
ratio 5:1	1:2	5:1
CNT-PAPG	5:1 (10:1, 20:1, 40:1, 80:1)	0:1

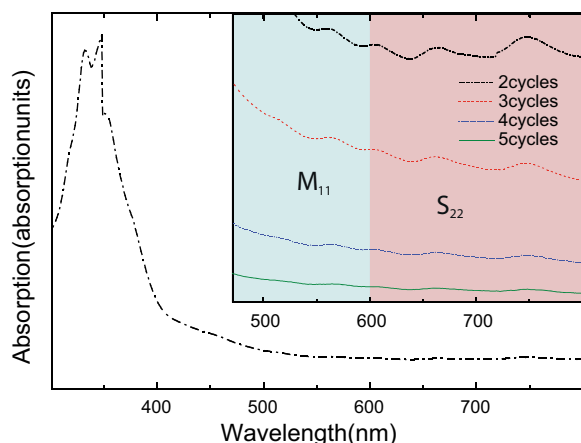


Figure 2 (online colour at: www.pss-b.com) Absorption measurements of CNT-PAPG. The graph shows the pyrene absorption features around 350 nm as well as two shoulders resulting from the azobenzene on the low energy side. The inset shows a magnification of the long wavelength part of the spectrum and contains additional data from different centrifugation cycles of the dispersion. All samples show the characteristic nanotube absorption features.

The residuum was replenished with water at a ratio of 1:1 and sonicated again for 1 h. Afterward it was centrifuged as before. This process was repeated several times and the supernatants after the different centrifugation cycles were analyzed (this corresponds to the different water:methanol ratios in Table 1).

2.3 Equipment We used a Bandelin SonoPlus HD 2070 with a maximum power of 200 W. The samples were centrifuged using a Hettig Mikro 220R centrifuge with a 1195-A rotor. FFT-Absorption spectra were recorded with a Scinco S-3100 UV-Vis Spectrophotometer with a tungsten-deuterium lamp providing excitation from 190 to 1100 nm. PLE measurements were taken using a Fluorlog-3 Spectrofluometer by Horiba Jobin Yvon. The excitation was provided by a xenon lamp with a range of 240–1000 nm, the signals were recorded using a nitrogen cooled InGaAs detector with a range of 800–1600 nm.

3 Results and discussion We investigated the dispersions of CNTs in water using PAPG. UV/Vis absorption measurements in Fig. 2 show the characteristic nanotube

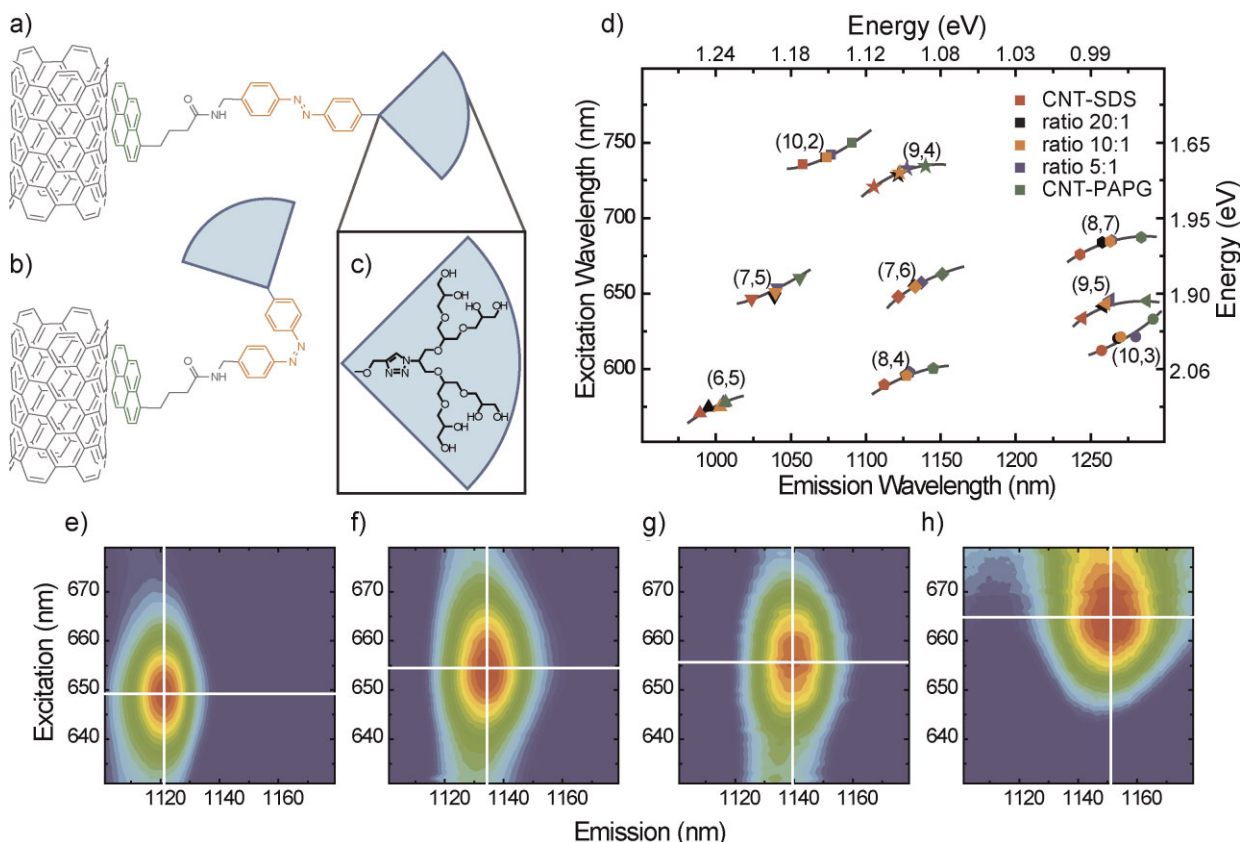


Figure 3 (online colour at: www.pss-b.com) An azobenzene based switch can be used to shift the distance between a CNT and an adjacent functionality. When the azobenzene is in the *trans*-form (a), the distance is comparatively larger than in the *cis*-case (b). The polyglycerol dendron we used as a first approach to such a system are shown in (c). Substituting SDS for this PAPG compound leads to a significant red shift in the PLE signals of CNTs in emission as well as in excitation (d). The actual measurements are shown on the (7,6)-tube for the CNT-SDS sample (e), the ratio (SDS:PAPG) 20:1 (f), ratio 10:1 (g), and CNT-PAPG samples (h). The shift is clearly visible. Chiralities were assigned by comparing with of Bachilo et al. [15].

features, the E_{11} transitions of the metallic tubes – denoted M_{11} – as well as the E_{22} transitions of the semiconducting tubes (S_{22}). This implies the presence of nanotubes in the solutions. To see whether the samples contain individual nanotubes or bundles, photoluminescence excitation measurements were taken (see Fig. 3h). Since in nanotube bundles the luminescence is quenched by the metallic nanotubes, the PLE measurements confirm the existence of individual nanotubes (or at least very small bundles of semiconducting tubes) in the sample.

The PLE maps revealed redshifts in the nanotubes luminescence peaks ranging from about 28 to 67 meV of the E_{22} excitation peaks and 21 to 37 meV of the E_{11} emission peaks compared to samples prepared with SDS (see Fig. 3d). We conducted further measurements on samples containing both SDS and PAPG as cosurfactants¹. We found that the luminescence peaks of the intermediate samples (using both surfactants), do not lie on a straight line connecting the peaks of the CNT-SDS and CNT-PAPG samples, but rather on a curve. Depending on the nanotube, this curve can either be convex or concave. This non-rigid shift indicates that the influence of the PAPG on the nanotubes is not only due to a change in the refractive index of the solvent. Not only the magnitude of the shifts, but also the curvature of the peak trajectory depends upon the type of tube: this observation suggests that each (n,m) tube interacts with the compound differently. We also found that CNT-PAPG samples of different centrifugation cycles possessed different optical density and thus nanotube abundance. The PLE peak positions however remain constant.

We investigated the switching of the PAPG compound under UV irradiation. We found that the compound was not able to change conformations. There are several issues this can be attributed to. For one, replacing the functional group can lead to significant changes in the overlap of the absorption spectra of pyrene and azobenzene. A large overlap allows efficient energy transfer from the azobenzene to the pyrene and thus fast deexcitation that hinders the switching process. As the azobenzene absorption peak positions can be tuned by the selection of the functional group, this effect will be overcome by modifying the attached functionality.

On the other hand, recent investigations of solvent effects on the isomerization of azobenzene suggest that, in polar solvents, the isomerization process is strongly altered [16]. Hence, depending on the functional group connected to the azobenzene moiety as well as the polarity of the solvent, the switching dynamics may be hindered.

When comparing the PL intensities in nanotubes solubilized using only SDS or only PAPG, it becomes apparent, that the relative intensities in the CNT-PAPG samples show much less fluctuation compared to the SDS sample.

4 Conclusions In conclusion, we found that PAPG is a viable surfactant for CNTs. We were successful in dispersing and individualizing CNTs. The relative intensities of the luminescence signals originating from different (n,m) nanotubes suggest that PAPG and SDS have different selectivities toward CNTs. When comparing PLE peak positions for CNT-SDS, CNT-PAPG, and the intermediate samples, we observed a non-rigid shift indicating that this effect can be attributed to an influence of the surfactant and not the surrounding medium. This is further supported since between CNT-PAPG with different ratios of water:methanol, the peak positions for any specific (n,m) nanotube do not differ.

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¹ See Table 1 for the SDS to PAPG ratios.