The effects of phenolic hydrogens and methyl substitute groups in organic dyes on their dispersion of multiple-walled carbon nanotubes

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Abstract

Bromocresol green (BCG) and bromophenol blue (BPB) in acidic and basic forms are used as dispersing agents to suspend multiple-walled carbon nanotubes (MWCNTs) into deionized water. The chemical structures of dye molecules are characterised by ultraviolet-visible-near infrared and nuclear magnetic resonance spectroscopies. The presence of MWCNTs in water is evidenced by transmission electron microscopy and Raman spectroscopy. All dyes exhibit critical concentrations in dispersing MWCNTs. This may result from the formation of dye micelles, which induces osmotic pressure on MWCNTs and aids nanotube re-aggregation. The critical values of the basic dyes are lower than their acidic counterparts, which can be ascribed to the stronger hydrophilicity of basic dyes. The critical value of basic BCG is lower than basic BPB and this can be attributed to the effect of methyl substitutes in the former. Basic BCG is superior to basic BPB in stabilizing MWCNTs, which may result from the extra steric hindrance provided by the methyl substitutes.

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1. Introduction

Carbon nanotubes (CNTs) have attracted overwhelming efforts to exploit their applications [1]. Despite the tremendous attempts, the poor solubility of CNTs in liquid media still remains the bottleneck. Noncovalent functionalization of CNTs to promote their solubility is preferable in that the pristine sp^2 hybrid state is preserved [2]. Organic solvents are valuable in solubilization of CNTs [3,4], but inevitably they suffers from poor biocompatibility. Surfactants [5,6,7], polymers [8,9], and DNA [10,11] are potential choices to disperse CNTs into aqueous media, but the difficulty in the subsequent removal of the attached moiety has excluded them from consideration in many applications. In a previous communication, we used organic dyes to disperse CNTs into deionized water and found that using the thin layer chromatography technique dye molecules can easily be exfoliated from CNTs[†]. However, a systematic study on the mechanism of dispersal is still lacking and the work reported here aims to understand how dye molecular constituents, such as phenolic hydrogens, methyl substitutes, and electrical charge, can affect the dispersion of CNTs. We have chosen to use bromocresol green (BCG) and bromophenol blue (BPB) as dispersing agents for a number of reasons. Firstly, Ausman et al. employed various non-ionic organic solvents to disperse CNTs and concluded that the absence of hydrogen donors is crucial to good dispersion [12], but further research is necessary to address the question: whether this rule applies to ionic species, i.e. whether the active hydrogen there also has an important role to play? BCG and BPB can be tailored to produce acidic and basic forms by simply adjusting the pH of deionized water, which makes it quite convenient to study the effect of phenolic hydrogens on CNT dispersion. Secondly, Moore et al. reported that higher molecular

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weight non-ionic surfactants facilitate the improvement of CNT dispersion [13]. Nonetheless, the surfactant structures used are entirely different from each other, with scatters varying from aliphatic to aromatic and N-heterocycles, which makes it complicated to trace the exact reasons. BCG and BPB molecules share a high level of similarity in chemical components, except that BCG bears two extra methyl substitutes in place of hydrogen atoms. Thus, comparisons between acidic and basic pairs of these two dyes can clearly demonstrate the effect of methyl substitutes. Furthermore, deprotonation of acidic forms of BCG and BPB imparts one additional negative charge to the molecule. It is therefore possible to exclude the effect of molecular structural morphology and simply investigate the role of electrostatic forces in the interaction of the dye with CNTs. As such, we propose to use BCG and BPB as model dyes to understand the fundamental mechanisms of dispersing CNTs with organic dyes with the hopes of paving the way towards better dispersion.

2. Experimental

2.1. Materials

Bromocresol green (95 wt. %) and bromophenol blue (95 wt. %) were obtained from Sigma-Aldrich. Multiple-walled carbon nanotube (MWCNT, inner diameter: 5-10nm, outer diameter: 10-20nm, Length: 0.5-200 μ m, purity > 95%) was also a Sigma-Aldrich (US) product.

2.2. MWCNT/dye dispersion preparation

The pH values of dye solution (0.5 mg dye in 15 cm⁻³ deionized water) were adjusted to 2.0 and 10.0 by the addition of hydrochloric acid and sodium carbonate, respectively. Jenway 370 pH meter (Spectronic Analytical Instruments, UK) was used to measure the pH values. Subsequently, MWCNTs (5.0 mg) were added and the

resulting mixture was then sonicated in QS 10 ultrasonic bath (Ultrawave Ltd. UK) for 1 h. After centrifugation in Espresso (Thermo Electron Corporation, France) at 8,000 g for 10 mins, the supernatant was decanted and characterized.

2.3. Characterization of MWCNT/dye dispersion

Dye/MWCNT dispersion (10 μ l) were dropped on to silicon wafers and put into vacuum desiccators overnight for complete drying. The Raman spectra of deposited samples were then recorded on Renishaw System 2000 microRaman spectrometer (Renishaw, UK). Using glass slides as the substrates and following the above deposition procedure, Transmission electron microscopy (TEM) images were obtained on a Philips CM 200. Ultraviolet-visible-near infrared (UV-Vis-NIR) spectra were recorded on a UV-Vis-NIR scanning spectrophotometer (Cary 5000, Varian Ltd., UK). Quartz cuvette with 10 mm optical path length (CXA-145-055M, Fisher Scientific, UK) was adopted as the solution holder.

2.4. Nuclear magnetic resonance (NMR) spectra

The ^1H -NMR spectra were recorded on a DRX 500 (in deuterium oxide, 99.9%, Cambridge Isotope Lab. Inc.) operating at 500.154MHz. The typical ^1H NMR parameters were as follows: spectral width, 10330.578 Hz, acquisition time, 3.17 s. The number of scans for BCG and BPB are 64 and 512, respectively. The ^1H chemical shifts are given on the δ scale (ppm) and were referenced to internal deuterium oxide (4.80 ppm); coupling constants J are reported in Hertz. The abbreviations s, d, and t were used for singlet, doublet, and triplet, respectively. Basic BCG: 1.97 [1, s], 2.06 [2, s], 7.19 [4, s], 7.21 [8, d, $^3J(\text{H7},\text{H8}):8.0$], 7.27 [3, s], 7.60 [7, t, $^3J(\text{H6},\text{H7}):7.5$, $^3J(\text{H7},\text{H8}):8.0$], 7.74 [6, t, $^3J(\text{H5},\text{H6}):8.0$, $^3J(\text{H6},\text{H7}):9.0$], 8.07 [5, d, $^3J(\text{H5},\text{H6}):8.0$]. Acidic BCG: 2.11 [1, s], 2.18 [2, s], 7.21 [8, d, $^3J(\text{H7},\text{H8}):8.0$], 7.38 [4, s], 7.50 [3, s], 7.62 [7, t, $^3J(\text{H6},\text{H7}):8.5$, $^3J(\text{H7},\text{H8}):8.0$], 7.71 [6, t, $^3J(\text{H5},\text{H6}):8.0$, $^3J(\text{H6},\text{H7}):8.5$],

7.84 [-OH, s], 8.08 [5, d, $^3J(\text{H5},\text{H6}):8.0$]. Basic BPB: 7.05 [5, d, $^3J(\text{H5},\text{H6}):8.5$], 7.62 [1,2,3,4], 7.65 [6, t, $^3J(\text{H5},\text{H6}):8.5$, $^3J(\text{H6},\text{H7}):8.0$], 7.76 [7, t, $^3J(\text{H6},\text{H7}):8.0$, $^3J(\text{H7},\text{H8}):9.0$], 8.06 [8, d, $^3J(\text{H7},\text{H8}):9.0$]. Acidic BPB: 7.17 [5, d, $^3J(\text{H5},\text{H6}):7.6$], 7.18 [-OH, s], 7.55 [6, $^3J(\text{H5},\text{H6}):7.6$], 7.57 [1, 2, 3, 4], 7.60 [7, $^3J(\text{H7},\text{H8}):7.3$], 7.91 [8, d, $J(\text{H7},\text{H8}):7.3$].

3. Results and discussion

3.1. Characterisation of dyes

3.1.1. UV-Vis-NIR spectra

The chemical structures of BCG and BPB are shown in Fig. 1, and as displayed, BCG and BPB can exist in both acidic and basic forms.

Figure 1 Chemical structure of BCG and BPB

It was found that as dissolved solutions of BCG and BPB are actually a mixture of acidic and basic forms, which show up as green and purple, respectively. To study the

effect of phenolic hydrogens and methyl substitutes on the dispersion of CNTs, BCG and BPB were converted into their acidic forms by hydrochloride acid and, with the aid of sodium carbonate, the basic forms can be obtained. The solutions of acidic and basic dyes turn out to be yellow and blue, respectively. The UV-Vis-NIR spectra of acidic, basic and as dissolved dye solutions are plotted in Fig. 2.

Figure 2 UV-Vis-NIR spectra of dye solutions: a) BCG, 0.03mg/cm⁻³; b) BPB, 0.02mg/cm⁻³. Inset of a: absorbance at 616 nm and 449 nm. Inset of b: absorbance at 591nm and 434 nm.

When white light passes through a dye solution, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary colour to the wavelengths absorbed. From Fig.2 it can be found that absorption of 600 nm light renders the solution blue, and the absorption of 430 nm light makes it yellow. Fig.2 also illustrates that the acidic and basic form of BCG has an isosbestic point in their spectra, around 510 nm; whereas BPB has an isosbestic point in the vicinity of 490 nm. In addition, Fig.2 demonstrates that when a dye molecule is converted from acidic form to the basic one, the maximum absorption peak shifts to longer wavelength about 160 nm, which can be explained in terms of the conjugation effect. In acidic aqueous solution, the dye molecules ionize to give the monoanionic form (yellow), that further deprotonates on basic condition and yields a dianionic form (blue), as shown in Fig. 1. When the phenolic hydroxyl group becomes deprotonated to yield a phenoxide anion, the conjugation interaction between the lone pair of electrons on the oxygen atom and π electron cloud of the dye molecular skeleton is strengthened, bringing the highest occupied molecular orbital and the lowest unoccupied molecular orbital closer together. The energy required for electron promotion is less, and the wavelength that provides this energy is correspondingly increased. Another striking feature with UV-Vis-NIR is when the dye molecule is converted from the acidic to basic form, the absorbance at the absorption maxima is increased three to fourfold (Fig.2 and its inset). As the dye concentration is kept constant in these experiments, this increase in absorbance can not be ascribed to the increase in numbers of absorbing molecules. A plausible explanation is the

enhancement/extension of molecular conjugation. Besides the bathochromic shift, hyperchromism is another basic characteristic of enhancing/extending conjugation.

3.1.2. NMR spectra

To further elucidate the chemical structure of dye molecules, ^1H NMR analyses were carried out and the chemical shifts and the coupling constants are listed in the experimental section. It is also clear that when a dye molecule exists in its acidic form, a phenolic hydrogen signal can be detected (acidic BCG: δ 7.84 and acidic BPB δ 7.18), whereas in the basic form this signal is absent following deprotonation.

Taken together, the analyses of UV-Vis-NIR and NMR spectra enable us to confirm the chemical structures of dye molecules, which serve as the basis for further investigation on how dye molecular constitution can affect the CNT dispersion.

3.2. Characterisation of CNT dispersions

3.2.1. TEM images

Figure 3 TEM images of the pristine MWCNTs (a, b); the functionalized MWCNTs (c,d) and the HRTEM image (inset to d).

The functionalized MWCNTs were further characterized with TEM and the images of the pristine nanotubes (Fig.3a and 3b) and the functionalized nanotubes (Fig. 3c and 3d) are shown in Figure 3. As can be seen after functionalization, the bundling size of MWCNTs is reduced and nanotubes are dispersed well. Figure 3d suggests that dye molecules and/or dye molecules aggregates are attached to nanotubes, as indicated by the blue arrows; similar phenomena have been observed with the sodium dodecyl sulfate functionalized nanotubes [14]. Additionally, many circular features with diameter of about 0.6 nm can be observed on nanotube surfaces in the HRTEM image (inset to Fig. 3d), denoted by red arrows. As the kinetic diameter of a benzene ring is

0.585 nm [15], we propose these circular features may be the benzene rings in the dye molecules.

3.2.2. Raman spectra

To further evidence the presence of nanotubes, deposited samples were characterized by Raman spectra, which exhibit two distinct bands in the vicinity of 1350 cm^{-1} and 1590 cm^{-1} (Fig.4).

Figure 4 Raman spectra of dye/MWCNT dispersion. Excitation at 514 nm (green).

These two bands are related to the nanotube's D- and G-mode vibrations, respectively. The D-band is indicative of defects in the nanotube and the G-band is characteristic of the sp^2 hybridized carbon graphite. The Raman spectra also display a weak band at around 2700 cm^{-1} , which can be regarded as the overtone of the D- band and may arise from the two-photon, second-order scattering process that results in the creation of an inelastic phonon. A combination of the abovementioned characteristics of

Raman spectra indicates the existence of nanotubes and consequently the dispersion of nanotubes in water.

As indicated by the blue arrow in Fig. 4, besides the characteristic signals of CNT, an additional Raman band appears at about 1490 cm^{-1} for the acidic BCG/CNT, which may arise from the vibration of dye molecules. Fig. 5 shows the Raman spectra of pure acidic BCG solutions at different concentrations. As observed, two Raman signals are present at 1488 cm^{-1} and 1580 cm^{-1} , respectively. The former one explains the presence of extra Raman peak observed in acidic BCG/CNT. While the energy of the latter band coincides with that of G band vibration of CNT and thus is blurred by this strong band. This explains why the latter band can not be visualized as an individual one in Raman spectrum of dye/CNT dispersion.

Figure 5 Raman spectra of dye solution at various contents. Excitation at 514nm.

3.3. Dispersion of CNTs

The formation of stable and homogenous CNT dispersions is a critical target in the development of practical applications of these materials. Thus, it is of paramount importance to find out to what degree the dispersion of CNTs depends on dye concentration. To evaluate quantitatively the dispersed CNTs, a series of experiments was conducted with fixed initial nanotube concentration (0.33 mg/cm^3) and varying dye concentration ($0 - 1.3 \text{ mg/cm}^3$). The amount of nanotube used was sufficient to ensure undissolved materials. The final supernatant was analyzed by UV-Vis-NIR spectroscopy at 800nm , as at this wavelength, it seems the dye does not interfere with CNT absorption (Fig.2). The absorbance of supernatant is depicted in Fig. 6 as a function of dye concentration.

Figure 6 Absorbance of BPB/CNT and BCG/CNT dispersions at 800nm .

3.3.1. Critical dye concentration phenomena

Aside from the acidic BPB /CNT dispersions, the absorbance of CNT dispersions at 800 nm increases with dye concentration and reaches a maximum, but drops with the

further increase in dye concentration. This means there is a critical dye concentration for the maximization of CNT dispersion. The dye can aid the dispersion of CNTs in water in that the hydrophobic parts of dye molecules can interact with nanotube by π - π stacking, whereas the hydrophilic parts can modulate the CNT-water interfacial properties and stabilize the CNT dispersion. Therefore, its ability in dispersing CNTs relies on how firmly it adsorbs on CNTs and how high this can create an energy barrier against the re-aggregation of CNTs. With an increase in dye concentration, more dye molecules can be adsorbed on the surface of the nanotubes and subsequently provide steric hindrance and electrostatic repulsive force to overcome the attractive van der Waals forces between CNTs. Thus, more individual CNTs can be dispersed in water and the absorbance of CNTs is enhanced. However, when the dye concentration lies beyond the critical value, the dispersion of CNTs deteriorates significantly, and this reduction in absorbance can be explained in light of the theory developed by Asakura and Oosawa [16]. By studying the interactions between two parallel plates immersed in a solution of macromolecules, they suggested that when the distance between two plates is smaller than the diameter of solute molecule, no molecule can enter the space between two plates and consequently a force equivalent to the osmotic pressure of the solution of the macromolecules acts inwards on each plate. They further pointed out that this force is attractive in nature and its value is proportional to the osmotic pressure of the medium and the dimensions of the solute molecules. The dye molecules in CNT dispersions can be free in solution, assembled into micelles, or adsorbed on the nanotube's surface. The distribution of dye molecules between these phases is the competing result of interactions among dye-water molecules, dye-dye molecules and dye molecule-CNT. With the increase in dye concentration over critical value, dye molecules start to form micelles, which induces the osmotic

pressure on CNTs and this attractive force, in turn, results in the re-aggregation of individual CNTs, as shown in Fig. 7.

Figure 7 Effect of dye content on the formation of dye micelles and dispersion of CNTs.

● represents the hydrophilic group in dye molecule.

Only individual CNTs absorb in the UV-Vis-NIR region and bundled CNTs are inactive (as indicated in Fig. 6, pure CNT/water mixture does not exhibit any absorption at 800nm). As a result, the absorbance value reduces. With further increase in dye concentration, both the quantity and dimensions of micelles increase, and a stronger attractive force will be induced, leading to the further reduction of absorbance. These results indicate that it is the amount of dye, rather than the mass ratio of dye/CNT, which governs the dispersion of CNTs. For acidic BPB/CNT dispersions, similar trends can be observed, expect for the presence of a second critical dye concentration, above which the absorbance increases again. This may result from the saturation of dye solutions and will be explained in more detail in section 3.3.

3.3.2. Adsorption of dye molecules on CNTs

The critical dye concentrations for dye/CNT dispersions to obtain the optimum absorbance values are plotted in the inset to Fig. 6, wherein it can be found that the basic form of the dye always exhibits lower critical values than its acidic counterpart. When the dye concentration is below the critical value, dye molecules exist mainly in the equilibrium between adsorption on CNTs to form hybrids and desorption into water to form free molecules. The deprotonation renders the dye molecules more hydrophilic and enhances their interaction with water molecules, causing the equilibrium to move towards free dye molecules. This means that at the same dye concentration, the proportion of free dye molecules in the basic form is higher than that in the acidic form. Thus, the overall dye concentration required to form micelles is decreased when the dye is converted from acidic to basic form.

It is also noteworthy that the critical value of basic BCG is less than half in magnitude of basic BPB. This can be explained in terms of excluded volume effect imposed by methyl substitutes. Organic molecules can adsorb on CNTs by π - π stacking, but this can only occur when two π systems are parallel in orientation and overlap at least partially with each other [17]. There is no doubt that a planar molecule can approach CNTs *via* a face-to-face conformation more easily, which is preferable for π - π interaction between the conjugated aromatic chromophore skeleton and the nanotubes. Owing to the excluded volume effect, the extra methyl substitutes in BCG can somewhat prevent dye molecules from approaching the CNT surface and achieving a good position to induce the π - π interaction with CNTs. This actually increases the proportion of free dye molecule in solution and consequently lowers the overall

critical concentration value. For acidic BCG and BPB, the effect of methyl substitutes is not obvious and the difference in critical values is insignificant. As mentioned above, in contrast to basic dye, the hydrophobicity of their acidic counterparts is increased and thus the affinity between dye molecule and CNT is boosted. A combination of these facts suggests the hydrophobicity of dye molecule is the predominant parameter here in controlling dye adsorption on CNTs, which blurs the excluded volume effect caused by methyl substitutes.

3.3.3. Stabilization of dye/CNT dispersions

As Fig. 6 displays, at the same dye concentration, the absorbance of basic BCG/CNT dispersion is always higher than basic BPB one. As the absorbance is proportional to the amount of individual CNTs present in water, this suggests that basic BCG is more effective than basic BPB in dispersing nanotubes and this can be ascribed to the presence of methyl substitutes in BCG. Once adsorbed on CNTs, these groups can create extra steric hindrance between CNTs and impede nanotube aggregation. A similar trend can also be observed when comparing acidic BCG and acidic BPB dispersions, although, the situation here becomes a bit complicated and the difference in absorbance values can not be solely ascribed to the quantity of CNTs present in water. It was found that for acidic dyes when the initial dye content is over a certain value, 0.2 mg/cm^{-3} for BCG and 0.4 mg/cm^{-3} for BPB, pure dye solutions exhibit 'absorbance' values, as shown diagrammatically in Fig. 8, which can be explained in terms of light scattering effect. At high dye concentrations, the water becomes saturated with dye molecules and no more dye can be dissolved. As a result, parts of dye exist as small particles in solutions and the solutions show up somewhat turbid instead of being completely transparent. When incident light travels through the dye

solution in UV-Vis-NIR measurements, part of the light is scattered by suspended particles, leading to the presence of absorbance values. It should be pointed out that basic dyes at all the concentrations studied in this work and acidic dyes at lower concentration ($<0.2 \text{ mg/cm}^{-3}$) do not experience light scattering as the absorbance values are all present as zero (see Fig. 8). Thus, this insolubility issue does not affect the validity of previous discussions and, as a matter of fact, this different dissolving behaviour reflects the level of the interaction between dye and water molecules. In basic dye molecules, the presence of the phenoxide ion enhances its interaction with the strongly polar water molecule, resulting in improved solubility. This is in agreement with the above discussion that basic dyes are superior to acidic dyes with respect to hydrophilicity. Fig. 8 also displays that the acidic BCG starts to scatter light at lower concentrations (around 0.2 mg/cm^{-3}) in contrast to the acidic BPB (around 0.4 mg/cm^{-3}), which may be associated with the presence of methyl substitutes in BCG, which increases its dissimilarity with water molecules. In accordance with ‘like dissolves like’ principle [18], the dye becomes less soluble in water.

Figure 8 Absorbance of dye solution against dye concentration at 800nm

It is also worth noting that when dye concentrations are lower than critical values (Fig. 6), eliminating the effect of scattering light, basic dyes are superior to acidic dyes with respect to dispersing CNTs. This is because the basic dye carries an extra negative charge and thus can impart an extra negative charge to the surface of the dispersed CNTs, facilitating the improvement of electronic repulsive forces between CNTs and stabilizing the CNT dispersion.

4. Conclusions

Noncovalent functionalization of MWCNTs with organic dyes is a simple and economical approach to disperse and stabilize nanotubes in aqueous media. The data suggest an optimum dye concentration for dispersion, which is proposed to be a competing result between adsorption of dye molecules on nanotube surfaces and formation of micelles in water. This critical value is largely related with the balanced point between hydrophilicity and hydrophobicity of dye molecule and its molecular architecture as well. The deprotonation of phenolic hydroxyl group increases the molecular hydrophilicity and boosts its interaction with water molecules, lowering the critical value. Once adsorbed on nanotube, methyl groups occupy more space and hamper further adsorption of dye molecules, resulting in lower critical value. With respect to the stabilization, dye molecules bearing methyl groups are preferable, which is likely due to the extra steric hindrance that methyl substitutes can provide. At low dye concentrations, basic dyes are superior to their acidic counterparts as the former bear an extra electric charge and can provide better electrostatic repulsion between nanotubes, which benefits the stabilization of nanotube dispersion. We

believe this general picture is applicable to other dye/nanotube systems, and we also hope this study can further the understanding on the interactions between dye molecule and nanotube in aqueous media, and leads to a better dispersion of nanotube.

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References

- [1] Harris PJF. Carbon nanotube science. Cambridge: Cambridge university press; 2009.
- [2] Zhao Y, Stoddart JF. Noncovalent functionalization of single-walled carbon nanotubes. *Acc Chem Res* 2009; 42(8):1161-71.
- [3] Ganter MJ, Landi BJ, Worman JJ, Schauerman CM, Cress CD, Raffaele RP. Variation of single wall carbon nanotube dispersion properties with alkyl amide and halogenated aromatic solvents. *Mater Chem Phys* 2009; 116(1):235-41.
- [4] 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(2):193-4.
- [5] White B, Banerjee S, O'Brien S, Turro NJ, Herman IP. Zeta-potential measurements of surfactant-wrapped individual single-walled carbon nanotubes. *J Phys Chem C* 2007; 111(37):13684-90.

- [6] Bergin SD, Nicolosi V, Cathcart H, Lotya M, Rickard D, Su Z, et al. Large populations of individual nanotubes in surfactant-based dispersions without the need for ultracentrifugation. *J Phys Chem C* 2008; 112(4): 972-7.
- [7] Matarredona O, Rhoads H, Li Z, Harwell JH, Balzano L, Resasco DE. Dispersion of single-walled carbon nanotube in aqueous solutions of the anionic surfactant NaDDBS. *J Phys Chem B* 2003; 107(48): 13357-67.
- [8] Lee JH, Paik U, Choi J, Kim KK, Yoon SM, Lee J, et al. Dispersion stability of single-walled carbon nanotubes using nafion in bisolvent. *J Phys Chem C* 2007; 111(6):2477-83.
- [9] Hasan T, Tan SV, Rozhin AG, Milne WI, Ferrari AC. Stabilization and "debundling" of single-wall carbon nanotube dispersions in N-methyl-2-pyrrolidone (NMP) by polyvinylpyrrolidone (PVP). *J Phys Chem C* 2007; 111(34): 12594-602.
- [10] Tu X, Manohar S, Jagota A, Zheng M. DNA sequence motifs for structure-specific recognition and separation of carbon nanotubes. *Nature* 2009; 460(7252):250-3.
- [11] Khripin CY, Manohar S, Zheng M, Jagota A. Measurement of electrostatic properties of DNA-carbon nanotube hybrids by capillary electrophoresis. *J Phys Chem C* 2009; 113(31):13616-21.
- [12] Ausman KD, Piner R, Lourie O, Ruopff RS. Organic solvent dispersions of single-walled carbon nanotubes: toward solution of pristine nanotubes. *J Phys Chem B* 2000; 104(38):8911-15.
- [13] Moore VC, Strano MS, Haroz EH, Hauge RH, Smalley RE, Schmidt J, et al. Individually suspended single-walled carbon nanotube in various surfactants. *Nano Lett* 2003; 3 (10): 1379-82.

- [14] Geng HZ, Lee DS, Kim KK, Han GH, Park HK, Lee YH. Absorption spectroscopy of surfactant-dispersed carbon nanotube film: modulation of electronic structures. *Chem Phys Lett* 2008; 455(4-6): 275-8.
- [15] Liu JX, Dong M, Sun ZL, Qin ZF, Wang JG. Sorption of benzene in CoAlPO₄-5 molecular sieves. *Adsorption* 2004;10(3):205-10.
- [16] Asakura S, Oosawa F. On interaction between two bodies immersed in a solution of macromolecules. *J Chem Phys* 1954; 22(7): 1255-56.
- [17] Glowka ML, Martynowski D, Kozłowska K. Stacking of six-membered aromatic rings in crystals. *J Mol Struct* 1999; 474(1-3): 81-9.
- [18] Williamson KJ. *Macroscale and microscale organic experiments*. 2nd ed. Lexington: D. C. Heath. 1994: 40.

Figure captions

Figure 1 Chemical structure of BCG and BPB

Figure 2 UV-Vis-NIR spectra of dye solutions: a) BCG, $0.03\text{mg}/\text{cm}^{-3}$; b) BPB, $0.02\text{mg}/\text{cm}^{-3}$. Inset a: absorbance at 616 nm and 449 nm. Inset b : absorbance at 591nm and 434 nm.

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