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A new designed π conjugated molecule for stable single walled carbon nanotube dispersion in aqueous medium

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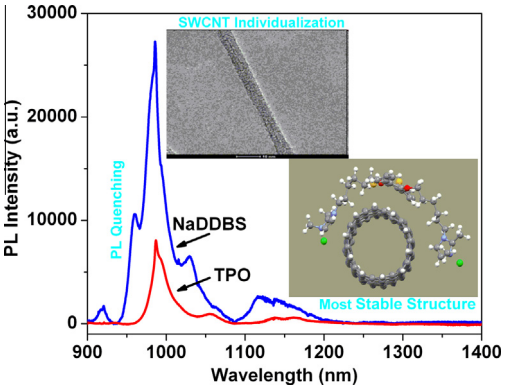
GRAPHICAL ABSTRACT



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ABSTRACT

A molecule with a π conjugated backbone built from aromatic thiophene and dialkoxyphenylene units and substituted imidazolium groups (**TPO**) is designed to obtain ultra-stable single walled carbon nanotube (SWCNT) dispersion in aqueous medium. The proposed mechanism of non-covalent interaction is accompanied by individualization of SWCNT and comprises of dominant nondisruptive π–π and cation–π interaction between them and the **TPO** conjugated oligomer. The individualization of SWCNT and dispersibility and stability of the ultra-stable suspensions were estimated using high resolution transmission electron microscopy, UV–Visible–NIR absorption spectroscopy, Raman spectroscopy, photoluminescence and zeta potential measurement. Nuclear magnetic resonance data provides direct evidence toward possible cation–π interaction.

1. Introduction

The carbon nanotube research, especially involving single walled carbon nanotube (SWCNT), has been considered to be one

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of the exceptional academic areas of study since last two decades. SWCNT has tremendous potential properties to be included as an active material in numerous nanotechnology applications such as field effect transistors, photovoltaic devices, light emitting diodes, biological imaging, sensing and composite technology [1,2]. Many of SWCNT applications are limited to their inherent insolubility in aqueous and common organic solvents what is related to tightly bound rope and bundled structure of SWCNT due to large aspect ratio and strong (0.5 eV/μm) intertube van der Waals attraction. Therefore it is utmost important to devise chemical processing technology to prepare ultra-stable SWCNT dispersion. Covalent chemical functionalization of the SWCNT surface is one of the pathways that have effectively been investigated to prepare stable dispersion [3,4]. However, this process modifies the surface arrangement of sp^2 carbon framework that directly affects their intrinsic physical and electronic properties. Moreover, non-covalent functionalization or no bonding interaction based on weak interaction between carbon π network of SWCNT and commercially available surfactants or chemically designed molecular systems having diverse structural framework are more advantageous means of improving the solubility without impacting the inherent electronic structure and properties of SWCNT [5–7]. The popular category of molecular systems for preparing stable aqueous SWCNT dispersion via non-covalent interaction include ionic and non-ionic surfactants [8–10], neutral molecular container [11,12], polymers [13–15] and biopolymers [16–18], porphyrins [19,20] macrocycles and dendrimers [11,12]. The mechanism of various type of interactions between dispersant and SWCNT depends on the structural aspects of the solubilizer and falls on a broad category such as electrostatic, hydrophobic, hydrogen bond, physical adsorption, van der Walls interaction, π–π stacking, cation–π interactions and polymer wrapping [21].

The above mentioned SWCNT–dispersant nanohybrids are interesting systems for understanding the interactions, solvent effect and doping as well as other fundamental photoinduced properties viz. charger transfer and electron transfer in solution phase. Furthermore depending on the structure and property of the molecules, these nanohybrids are cited to be potentially used in diverse applications including photo-voltaic devices [22] and gas sensing [23].

Recently imidazolium based room temperature ionic liquids (RTILS) were observed to be a new class of non-covalently interacting efficient green dispersants in the library of SWCNT solubilizing agents [24–26]. Considering the extensive use of the highly conjugated aromatic molecules as well as ionic surfactants for non-covalent functionalization of SWCNTs in the literature, we strategized here a synthetic design of a new conjugated π-system with cationic imidazolium groups ((1,4-bis(thiophen-2-yl)-2,5-bis(6-chlorohexyloxy) benzene bis (2,3-dimethyl-1H-imidazol-3-ium) chloride) (**TPO)** to disperse SWCNT in aqueous medium. Fig. 1 presents the schematic chemical structure of **TPO**. We have already demonstrated that the combination of thienylene and dialkoxyphenylene fragments leads to a highly conjugated planar molecule due to non-covalent S···O interactions and strong hybridization of π fragment molecular orbitals [27].

In the present study, we characterize and investigate the factors responsible for stability of the **TPO** assisted SWCNT aqueous dispersion. The unchanged clarity and color of the dispersion along with measured zeta potential over period of time support the enhanced stability of the SWCNT/**TPO** nanohybrid. The stability of the dispersion is directly correlated with the strong non-covalent interactions between SWCNT and **TPO**. The mechanism of complex formation between SWCNT and **TPO** is proposed on the basis of various interactions observed from combined experimental optical and microscopic study and molecular dynamics simulation (MDS). To gain better insight into the mechanistic

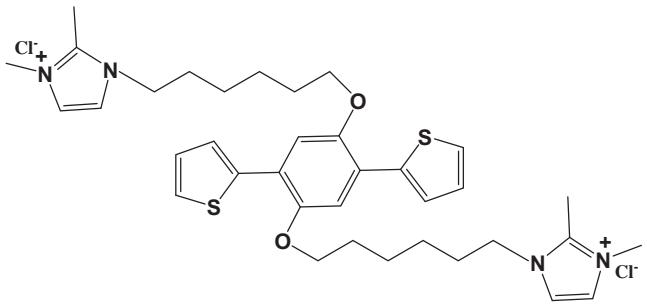

Fig. 1. Schematic chemical structure of **TPO**.

interactions, the optical and microscopic data of the SWCNT/**TPO** nanohybrid is further compared with those of prepared common surfactant sodium dodecylbenzenesulfonate (NaDDBS) assisted SWCNT dispersion keeping all the experimental parameters identical. The resulting stable SWCNT/**TPO** nanohybrid in aqueous solutions could be scaled up, expected to show enhanced optical absorption and electrical conductivity due to non-covalent interactions and it can effectively be used for biological labeling, photovoltaic and sensing application. Chemical methodologies for synthesis and characterization of TPO are explained in Section 1 of supplementary materials.

2. Experimental section

2.1. Preparation of SWCNT/*TPO* dispersion

TPO assisted SWCNT aqueous dispersions were obtained as follow:

First, to investigate the time dependence of sonication, four samples of a 1.0 mL D_2O solution containing 2 mg of **TPO** and 0.5 mg of SWCNT were sonicated for 30, 60, 120 and 240 min using an ultrasonic bath and then centrifuged at 20,000 g for 60 min. A second set of samples was prepared to investigate the dependence of **TPO** concentration. A number of solutions were prepared using a fixed SWCNT concentration of 0.5 mg/mL and varying the concentration of **TPO** from 0.25 to 5.0 mg/mL. Each solution was bath sonicated for 60 min and centrifuged at 20,000 g for 60 min. The last set of samples was prepared by varying the SWCNT concentration from 0.0 to 1.0 mg/mL with a constant concentration of **TPO** at 3.0 mg/mL. The resultant dispersions were sonicated and ultracentrifuged in the same way as above. For comparison, a SWCNT dispersion containing the commercially available sodium dodecyl benzene sulfonate (NaDDBS) surfactant was prepared as described elsewhere [28].

2.2. Characterization techniques

2.2.1. Transmission electron microscopy (TEM)

High resolution transmission electron microscopic measurements of the dispersed samples were performed using FEI TECNAI F30 electron microscope (200 kV acceleration voltage). The samples for the TEM measurement were prepared by casting few drops of dispersion on the perforated holey carbon grid and allowed to dry off the solvent.

2.2.2. Photophysical measurements

Ground state UV–Vis–NIR optical absorption spectral measurements were performed using a Shimadzu UV-3600 spectrophotometer. Photoluminescence (PL) spectra in the range of 900–1400 nm were recorded using single mode of T64000 monochromator (Horiba) equipped with liquid nitrogen cooled