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ARTICLE

Dispersion of single-walled carbon nanotubes into aqueous solutions using Poh's cyclotetrachromotropyene (CTCT)

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Paris E. Georghiou,^{a,*} Gopikishore Valluru,^a Celine Schneider,^a Shuai Liang,^b Kathleen Woolridge,^a Karimulla Mulla,^a Alex Adronov^b and Yuming Zhao^{a,*}

Poh's cyclotetrachromotropyene (CTCT), a water-soluble cyclic oligomeric dihydroxynaphthalenedisulfonate, was found to be capable of selectively dispersing single-walled carbon nanotubes (SWCNTs) into the aqueous phase. The resulting supramolecular complexes in the aqueous solutions were characterized by UV-Vis-NIR analysis, while the dried aggregates were examined by Raman spectroscopy and atomic force microscopy (AFM).

Introduction

The diverse properties of single-walled carbon nanotubes (SWCNTs),^{1,2} for example, their potential use in therapeutics^{3,4} and composites⁵ have prompted much research into their separation and dispersion in order to enable the selection and/or enrichment of specific-type SWCNTs from as-prepared mixtures. It is well-known that the strong bundling and aggregation behavior of pristine SWCNTs makes direct processing and application of SWCNTs into the solution phase very challenging. To overcome this barrier, various functionalization methods have been developed.² Among the various methods which have been reported, non-covalent or supramolecular binding of SWCNTs with a suitable dispersant is an appealing approach to overcome solubility difficulties. In 2003,⁶ Richard Smalley and coworkers reported a detailed study on the application of various surfactants toward the dispersion of HiPCO⁷ SWCNTs into water. The surfactants examined⁶ included sodium dodecyl sulfonate (SDS), TREM (sodium alkyl allylsulfosuccinate), SDBS (sodium dodecylbenzenesulfonate), and PSS (the sodium salt of polystyrenesulfonate). Tummala et al.⁸ conducted several studies elaborating upon the use of SDS for dispersing SWCNTs into aqueous solutions. The presence of planar aromatic cyclic structures (e.g. flavin mononucleotide) however has also been presumed to be an essential component for the observed dispersive effectiveness of SWCNTs,⁸ and recently Martín and Guldi et al. used the planar aromatic TCAQ derivatized onto a water-soluble dendron¹⁰ to solubilize SWCNTs in water. A potential dispersant that has two of the features considered to be of importance is the cyclic octasodium salt, "cyclotetrachromotropyene" (**1** or "CTCT"), which was first reported by Poh and coworkers in 1989.¹⁰ As shown in Fig. 1, the CTCT molecule has four naphthyl units linked together through methylene bridges. This π -rich framework was expected to enable strong affinity for the sidewall of SWCNTs. Furthermore, each naphthyl unit is decorated with two water-soluble sulfonate and two hydrophilic hydroxy groups. Considering the amphiphilic nature of CTCT, we envisioned it to be an effective dispersant for SWCNTs in the aqueous phase. We report herein our findings on the dispersion into water of two types of commercially-available SWCNTs, CoMoCAT¹¹ and HiPCO SWCNTs, with the aid of CTCT and the

characterization of the resulting SWCNT-CTCT supramolecular complexes using various analytical methods.

Results and discussion

Poh's group published extensively on the complexation properties of this intriguing water-soluble compound.^{12a-j} We have been interested in the chemistry of chromotropic acid (CTA, **3**) and its disodium salt (DSCTA, **2**) for some time now^{13a-b} and our previously reported results on the chemistry of DSCTA with formaldehyde under the different conditions which we used led to different products.^{13a-b} In the work reported herein, however, CTCT (**1**) as its sodium salt was produced by the reaction, under carefully defined conditions, using 37% w/w formaldehyde solution with DSCTA, of CTA, in a 1:5 ratio in aqueous solution.^{12h}

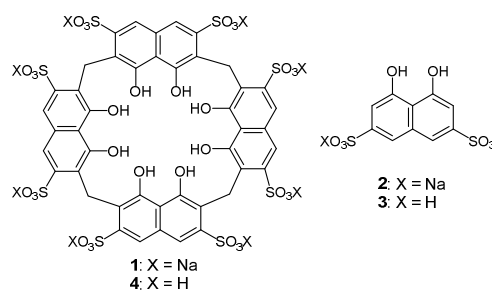


Fig. 1 Molecular structures of compounds 1-4.

In Poh's original report,¹⁰ CTCT was prepared as a "dark red plastic-like product" which was not unambiguously characterized. In a subsequent paper,^{12h} Poh reported the combustion analysis for the compound consistent with a multi-hydrated form of octasodium CTCT (**1**). Furthermore, after subjecting this compound to a hydrogen ion exchange, they reported only a (-)FAB-MS signal at m/z 1327 corresponding to

a $[M-H]^-$ anion. The very simple ^1H and ^{13}C NMR spectra were also reported; however, the reported data could just as easily be accounted for by other larger cyclic oligomeric products which could be potentially formed between DSCTA and formaldehyde.

In the present work, we prepared the CTCT product by carefully following Poh's 1993 procedure.^{12h} To better characterize the molecular structure of CTCT, the freshly prepared product was subjected to diffusion ^1H NMR analysis^{14,15} in addition to routine spectroscopic characterizations. The diffusion curve (Fig. S1 in the Supplementary Information) shows the shifts observed for the protons of the naphthalene ring $-C_{Naphth}H$ ($\delta = 7.99$ ppm) protons. Based upon this curve, the diffusion coefficient was calculated to be 2.79×10^{-10} m²/s, which corresponds to a "sphere" having a hydrodynamic radius¹⁶ of 7.14 Å. This radius is consistent with a hydrated form of an ellipsoidal CTCT according to our molecular modeling,¹⁷ and it does not match the sizes of any higher-order cyclic oligomers. In further support, after hydrogen ion exchange of our product to the resultant corresponding CTCT octasulfonic acid (4), ion-trap LC/MS analysis run in the negative mode was conducted to reveal the expected molecular ion $[M]^-$ at m/z 1327.8 and the $[M-2H]^{2-}$ at m/z 662.9 (Fig. S2 in the Supplementary Information). Since the molecular structure of CTCT contains a large π -system as well as polar hydroxyl and sulfonate groups, it should have sufficient non-covalent binding potential as a supramolecular host for various π -conjugated molecules. In the meantime, it is also reasonable to hypothesize that CTCT could interact with the surfaces of SWCNTs through π - π interactions.

Dispersions of SWCNTs with CTCT in water were then conducted through a general ultrasonication procedure described as follows: SWCNTs (0.8 mg) and CTCT (0.5 mg) were added in 1.0 mL of deionized water. The mixture was ultrasonicated for 30 min and then subjected to centrifugation for another 30 min. The resulting supernatant was subjected to UV-Vis-NIR spectral analysis. Fig. 2 shows the UV-Vis-NIR spectra of SWCNT suspensions in aqueous CTCT solutions. In Fig. 2A the prominent absorption band centered at ~ 1000 nm⁻¹ is that of the characteristic absorption of (6,5) SWCNTs. As the CoMoCAT sample is known to consist of mainly semiconducting tubes, such as (6,5), (7,5), (7,6), (8,3), and (8,4), tubes, the results shown in Fig. 2A clearly indicate a selectivity for (6,5) chirality by CTCT. In the case of dispersion of HiPCO SWCNTs with CTCT, reasonably resolved absorption bands are observed in the Vis-NIR region as disclosed in Fig. 2B. The bands which emerged in the range of 920 to 1400 nm are due to the semiconducting S_{11} transitions, while the bands from 620 to 920 nm are assigned to metallic M_{11} and semiconducting S_{22} transitions. Overall, the UV-Vis-NIR analysis confirms that CTCT is capable of dispersing SWCNTs in the aqueous phase and the dispersive efficiency is quite satisfactory as evidenced by the significant absorptivity observed in the spectra.

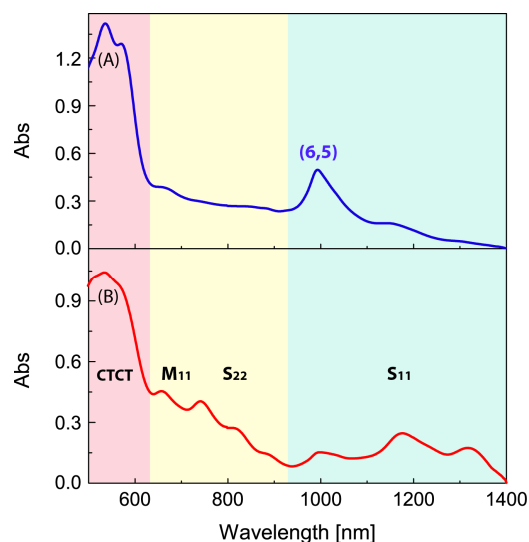


Fig. 2 UV-Vis-NIR spectra: (A) CoMoCAT and (B) HiPCO nanotubes dispersed by CTCT in aqueous solutions.

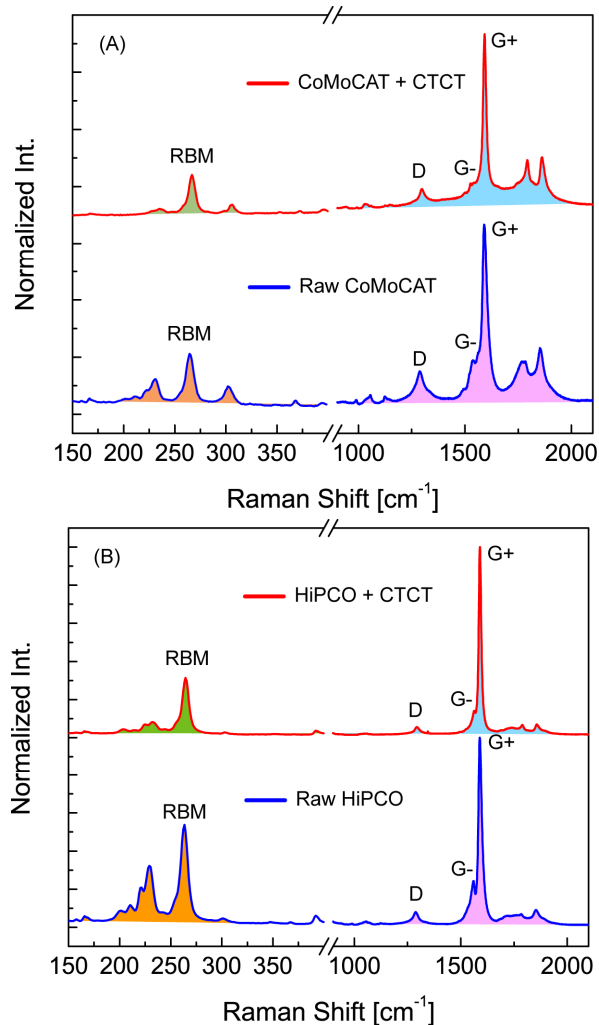


Fig. 3 Raman spectra comparing the SWCNTs before and after being dispersed with CTCT in water. (A) CoMoCAT nanotubes, (B) HiPCO nanotubes. Excitation wavelength: 785 nm.

To confirm the UV-Vis-NIR observations, the CTCT-SWCNT suspensions were then examined using Raman spectroscopy.¹⁸ Fig. 3 shows the Raman spectra of CoMoCAT and HiPCO SWCNTs before and after dispersed with CTCT. As shown in Fig. 3A, the CoMoCAT nanotubes dispersed with CTCT show a much weaker D-band than the raw sample, indicating that the dispersion results in better-quality tubes. It is also worth noting that the metallic G⁻ band is considerably reduced after dispersion, which suggests that CTCT is selective for semiconducting tubes. In the radial breathing mode (RBM) region,¹⁹ three major bands are observed at 231, 266 and 302 cm⁻¹ for the raw CoMoCAT sample, corresponding to nanotubes with different diameters. After dispersion, only the band at 266 cm⁻¹ remains, significantly, whereas the other two bands diminish substantially. The Raman data clearly shows that CTCT is selective towards nanotubes with certain diameters. It has been known that the RBM frequency is inversely proportional to the diameter of a nanotube as described by the equation: $\omega = 223.5/d + 12.5$, where ω is the RBM frequency in cm⁻¹ and d is the nanotube diameter in nm. The CoMoCAT nanotubes selectively dispersed by CTCT are estimated to have an average diameter of 0.88 nm. Similar results can be seen in the dispersion of HiPCO nanotubes (see Fig. 3B). In the RBM region, the raw HiPCO nanotubes give a number of bands at 201, 210, 220, 229, and 266 cm⁻¹. After dispersion, only the band at 266 cm⁻¹ appears to be the major one, while the others diminish considerably.

To characterize the supramolecular interactions between CTCT and SWCNTs in the solid state, suspensions of SWCNTs were drop-cast on freshly cleaved mica surface for atomic force microscopic (AFM) analysis. Fig. 4 shows the 3-D AFM images of the supramolecular self-assemblies of CTCT and CoMoCAT SWNTs on surface. The AFM results clearly that CTCT and nanotubes strongly aggregate together to exhibit somewhat “worm-like” morphologies. Cross-section analysis (Fig. S3 in the Supplementary Information) shows that the heights of these aggregates are in the range of *ca.* 10 to 20 nm, which likely correspond to bundles of nanotubes encapsulated by CTCT molecules.

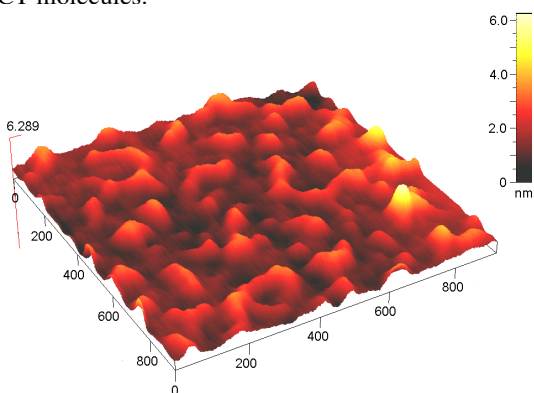


Fig. 4 3-D AFM image showing the supramolecular assemblies of CTCT and CoMoCAT SWNT drop-cast onto mica. The sample surface was rinsed by water and methanol prior to measurement (measurements are in nm).

To further understand the interactions between CTCT and SWCNTs at the molecular level, molecular modeling studies were conducted. In our work, complexes of CTCT and SWCNTs were simulated by the molecular mechanics (MM) method using the MMFF force field implemented in Spartan'10 software. Fig. 5 illustrates a possible mode in which CTCT molecules could interact with representative SWCNTs. In this representation, the CTCT molecules are shown in a “cone”-shaped conformation in which the naphthyl groups are bound to the SWCNTs via intimate π -stacking, with the sulfonate groups on the opposite sides which can become hydrated with the water molecules but also with neighboring similarly CTCT-bound SWCNTs. The modeling results are consistent with the AFM analysis in that nanotubes still remain in small bundles when dispersed in the aqueous phase. Indeed, this bundling phenomenon prevented us from acquiring reasonable photoluminescence-excitation (PLE) mapping data, which would be very useful in characterizing the chirality distribution of the dispersed nanotubes.

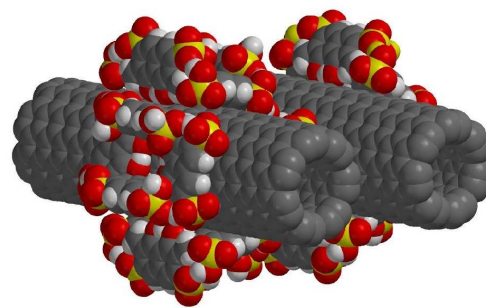


Fig. 5 Spartan'10-generated molecular modeling (MMFF) showing a putative mode of binding between CTCT molecules and two SWCNTs. Water molecules are not shown for simplicity.

Conclusions

In summary, CTCT which was characterized additionally in aqueous solution by diffusion ¹H NMR spectroscopy was found to show significant selectivity in dispersing CoMoCAT and HiPCO SWCNTs in water, although this dispersion appears to in fact comprise small bundles of SWNTs rather than individual tubes. Our finding discloses a new approach to process and/or enrich SWCNTs in the aqueous phase, and we expect it to be useful in the applications of nanoelectronic and nanobiological systems.

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Notes and references

- Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, Canada, A1B 3X7
- Department of Chemistry, McMaster University, Hamilton, ON, Canada, L8S 4M1
parisg@mun.ca or yuming@mun.ca

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† Electronic Supplementary Information (ESI) available: General experimental conditions, ¹H NMR and MS. See DOI: xxxxxxxx.

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Graphical Abstract

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