

Non-covalent functionalization through Kentera™: Robust method for irreversibly modifying MWNTs

Abstract:

Functionalization of Carbon Nanotubes (CNTs) has helped in realizing the great potential of carbon nanotechnologies. Zyvex has developed a versatile non-damaging functionalization technology using rigid rod conjugate polymers, poly (aryleneethynylenes) (PAEs) called Kentera™. The interaction between Kentera and CNT is through π stacking, this occurs through the delocalized π electrons present in both CNT and backbone of Kentera polymer. Although π - π interaction is a weaker bond than covalent bonding, the sum of π - π interactions creates a large net-stabilizing energy that results in superior and stable systems. NMR, fluorescence and UV-Vis spectroscopy were used to establish the formation of a strong molecular complex. **The spectroscopic evidence and molecular modeling have shown the interaction between CNT and Kentera is not a simple mixture but forms an *irreversible complex* comparable to covalent bonds.** Molecular mechanics and molecular dynamics have shown the adsorption energies between CNT and Kentera is two times higher when compared to the adsorption energies between CNT. Lastly, Kentera functionalization allows control over the distance between functional groups on the carbon nanotube surface, through variation of the polymer backbone and side chains. The review presented here will highlight all our findings and demonstrates the efficacy of non-covalent functionalization of CNTs.

Introduction

The remarkable properties of carbon nanotubes¹ (CNTs) have proven difficult to harness because of their insolubility in most organic solvents. The strong Van der Waals forces of attraction drive them to exist in large bundles and ropes. To disrupt such Van der Waals forces, covalent and non-covalent functionalization of CNTs² have been highly regarded in recent years. Covalent side wall functionalization can lead to the solubilization of the CNTs, however, by this approach, the CNTs intrinsic properties are changed. On the other hand, non-covalent functionalization retains the intrinsic properties of the CNTs as no chemical bonds are broken or reformed. Non-covalent functionalization can be achieved by polymer wrapping³ and π - π stacking approaches⁴. In the former approach, as the name indicates, a polymer is wrapped around the diameter of a carbon nanotube (CNT), thus preventing the rebundling of the tubes (figure 1). The disadvantages of this approach are that the polymer is very inefficient in wrapping around the small diameter of the CNT and a large quantity of the polymer is required to de-bundle a unit weight of CNT.

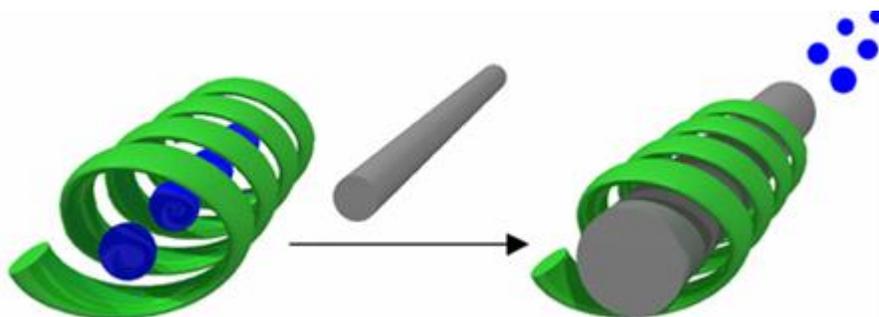


Figure 1: Diagram showing dispersion of CNT by polymer wrapping

In the π - π stacking approach, a short, rigid conjugated polymer, (polyaryleneethynylenes) (PAE), called Kentera™, is used to solubilize CNTs. In contrast to other approaches, the rigid backbone of Kentera cannot wrap around the CNTs. The major interaction between the polymer backbone and the nanotube surface is π - π stacking (Figure 2). The non-covalent approach allows us to control the distance between functional groups on the carbon nanotube surface, through variation of the polymer backbone and side chains. Kentera side chains impart functionality to the otherwise smooth walls of the CNTs. Kentera allows control over the distance, density and placement of functional groups on the carbon nanotube, through variation of the polymer backbone and side chains.

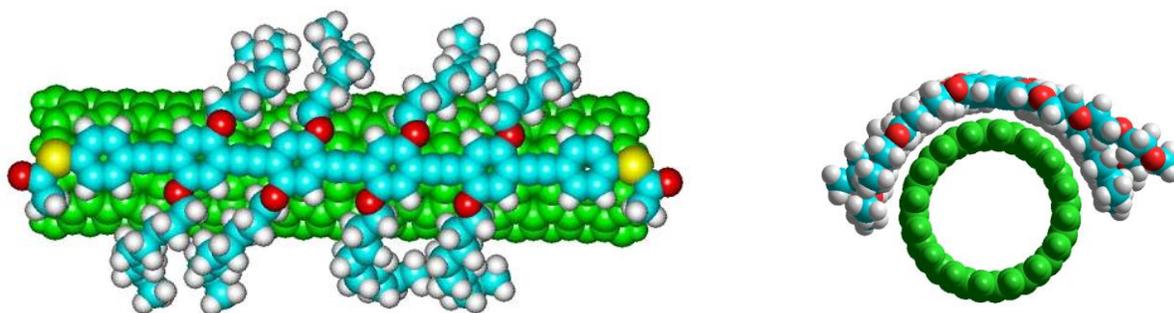


Figure 2: A molecular model of Kentera -SWNT complex, (left) lateral section, (right) cross section

Although π - π interaction is a weaker bond than covalent bonding, the sum of π - π interactions creates a large net-stabilizing energy that results in superior and stable systems. The interactions of such a magnitude are quite common in various systems such as synthetic polymers (aramids, polyphenylenes, polyimide, etc.), DNA, RNA, proteins, and peptides. In supramolecular chemistry, π - π interactions are the result of intermolecular overlapping of π -orbitals in π -conjugated systems. This non-covalent interaction becomes stronger as the number of π -electrons increases. The π - π interactions act strongly on flat polycyclic aromatic hydrocarbons, such as anthracene, triphenylene and coronene (Figure 3) because of the many delocalized π -electrons. To illustrate the power of the π - π interaction in supra-molecular assemblies, two examples are presented: 1) The buckycatcher, depicted shows very high association constant to fullerene in solution, and 2) the molecular tweezers based on bis-anthracene (Figure 3) show strong binding energy to specific aromatic molecules.

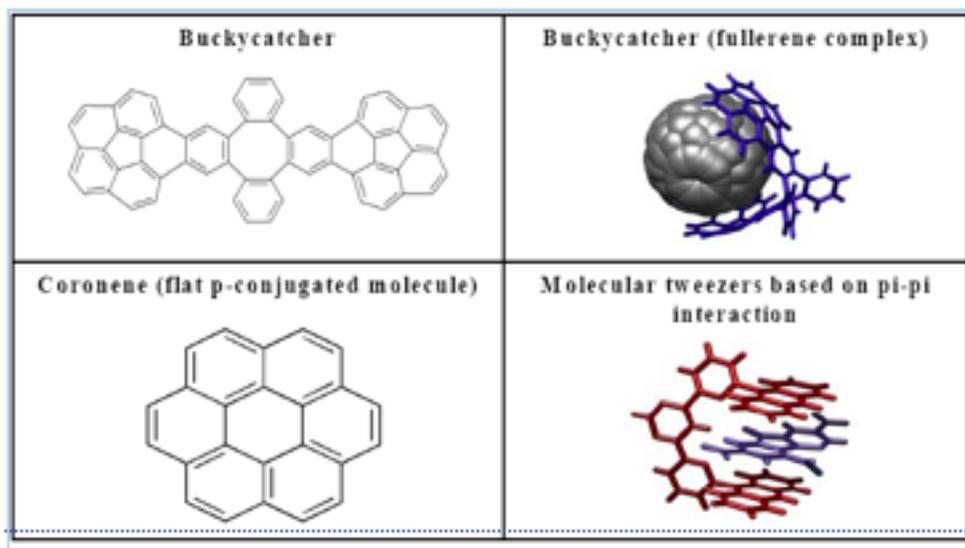


Figure 3: Pi-Pi Interactions in supramolecular assemblies

SWNTs have structures that exhibit greater order and simplicity when compared to the MWNTs. The structural simplicity of SWNTs allowed them to be studied with a greater degree of accuracy through both experimental and theoretical investigations. The high polydispersity of MWNTs possess great challenges in creating models for studying the π - π interactions with Kentera. In order to simplify our investigations, ZyveX chose to understand the interactions of Kentera with SWNTs. Furthermore, availability of published data on the interaction SWNTs with small polyaromatic and polymers makes it easy to make some logical conclusions. By analogy and extrapolation we expect the deductions made on SWNTs representative of MWNTs as well. The next few paragraphs describe some of our seminal findings on the π - π interactions between SWNT and Kentera.

Kentera CNTs Not a Simple Mixture: Rather a Molecular Complex with Strong Adsorption

Chen et al. at ZyveX have shown formation of stable and irreversibly bound complexes between the Kentera and the SWNTs in CHCl_3 , using NMR (Nuclear Magnetic Spectroscopy), UV-Vis (Ultra violet spectroscopy) and molecular modeling studies. SWNTs (the results are consistent with SWNT or MWNTs) were solubilized in CHCl_3 by mixing with Kentera along with vigorous shaking and/or bath-sonication. The minimum mass ratio of Kentera:SWNT that is needed to solubilize the SWNT is about 0.4, and the solubility is about 4.0 mg/mL. In an effort to keep the experimental variables as low as possible, high purity SWNTs produced from HiPco process were used. In 1999 Richard E. Smalley and his co-workers⁹ developed a high-pressure carbon monoxide method called HiPco for the synthesis of carbon nanotubes. With the HiPco method the thinnest single-walled carbon nanotubes of very high quality, few structural defects, and high intrinsic selectivity were achieved.¹⁰

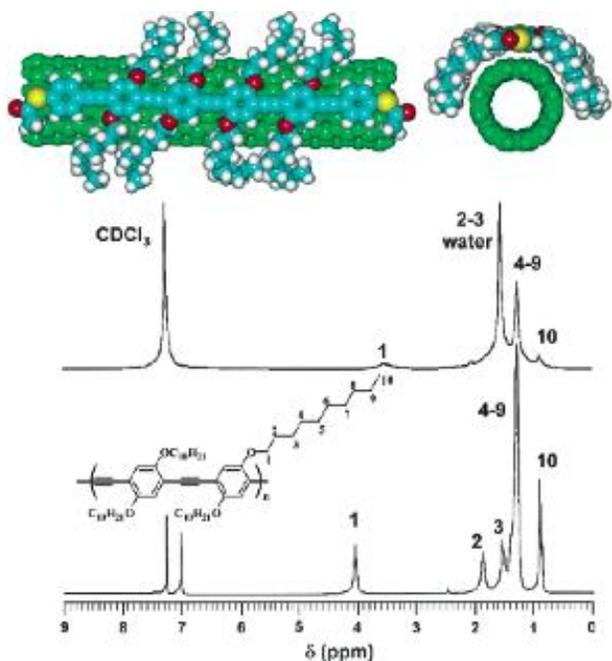


Figure 4: A molecular model of SWNT(6,6) Kentera complex (top) and 1H NMR spectra (300 MHz, CDCl₃) of Kentera (bottom) and SWNT-Kentera complex (middle).

Nuclear Magnetic Spectroscopy studies

The 1H NMR spectrum supports a strong π - π interaction between Kentera and the nanotube. The CH₂ group (C) shows a significant up-field shift (δ 3.51) and broadening as compared to that of free Kentera (δ 4.05). In addition, the phenylene protons (δ 7.3), clearly evident in free Kentera are too broad to be detected in the complex. These observations are consistent with theoretical evidence for the existence of large diamagnetic ring currents in carbon nanotubes.⁵ No substantial shifts are observed for the other CH₂ groups, indicating that, *although the polymer backbone interacts strongly with the nanotube surface, the side chain (C3- C10) of Kentera is relatively free in solution.* It is interesting to note that the Kentera side chains **do not** interact with CNTs, therefore are available for interacting with the matrix into which the functionalized CNTs are dispersed. Setting up of a thermoset resin typically involves use of chemical agents called curing agents that help in cross-linking the resin matrix. Zyvex uses complementary functionalities on the Kentera side chains that aid CNTs in locking into the matrix during the setting-up of thermoset resins. In addition no free Kentera can be detected in Kentera-SWNT solution, in contrast PmPV-wrapped SWNTs solutions show a significant amount of free PmPV,³ which demonstrate a better interaction between Kentera and SWNT.

Fluorescence and UV-Vis spectroscopy

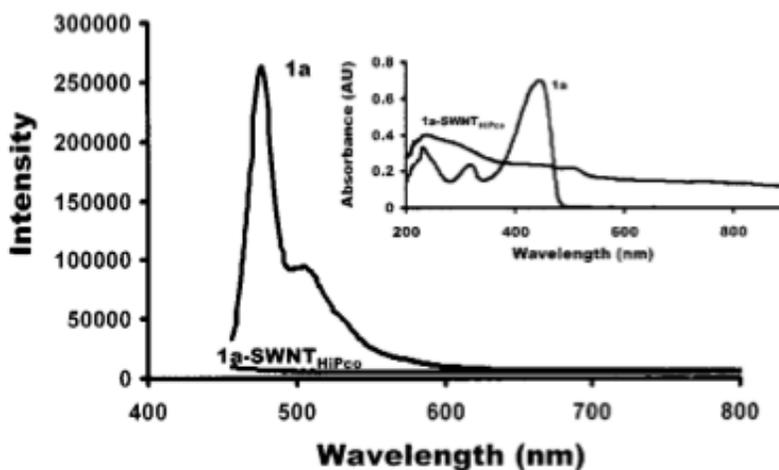


Figure 5: Room-temperature solution-phase (CHCl₃) fluorescence spectra (excitation wavelength: 400 nm) and UV-visible spectra (inset) of Kentera (1a) and Kentera-SWNTs complex.

The optical spectroscopy supports a significant π - π interaction between the polymer and the nanotube (Figure 5). The strong fluorescence of Kentera (1a) is efficiently quenched in Kentera-SWNT complex. The quenching likely arises from efficient energy transfer between Kentera and SWNTs, rather than the disruption of π -conjugation caused by a conformational change. Energy transfer quenching between molecules and for molecules on graphitic carbon and metal surfaces is well known.⁶⁻⁸ The lowest absorption band for Kentera in the Kentera-SWNTs thin film does not shift significantly from that in the free (1a) thin film, indicating that the π -conjugation of Kentera is largely unchanged. In the polymer wrapped the nanotube, one would expect a blue shift of Kentera's lowest energy absorption band because of interruption of the π -conjugation. The thin film visible and near-IR spectroscopy of Kentera-SWNT is very similar to those of pristine SWNT, indicating that the electronic structures of SWNTs are basically intact after polymer complexation.

Molecular modeling:

In our preliminary work, the design of the Kentera polymer was aided by computational analysis on the energetic of Kentera polymer binding to SWNTs, compared to the binding of SWNTs to themselves. SWNTs are round, cylindrical structures made of a single graphite sheet, and their structure and physical properties vary according to how the graphite sheet is rolled. Structure of SWNTs is described by integers n and m (in parenthesis) called chirality. The integers referred to as chiral vectors n and m determine the "twist" of the nanotube.¹¹ Although, SWNTs with specific chirality were used; in an effort to keep the narrative simple, the chirality of the SWNTs has been deliberately omitted. Molecular Mechanics Modeling was done using MM+ force-field and geometry optimization of SWNT-SWNT and SWNT-Kentera systems on 1 nm length (unpublished results). A continuum model determined the energy of adsorption for the SWNT-SWNT system. Calorimetric measurements have shown that for every nanometer overlap between two SWNT tubes, the binding energy is 950 meV. Zyvex calculations showed that the energy of interaction for every nanometer

overlaps of SWNT-SWNT system is about 970 meV (Figure 6), similar to published results. These comparisons indicate the model we chose is comparable to the experimental values hence the results obtained from the model should closely reflect the experiments.

We further calculated that the energy of adsorption of a Kentera-SWNT system is 2-6 times greater than SWNT-SWNT interactions (Figure 6), suggesting that the binding of Kentera to SWNTs is sufficiently strong enough to de-bundle the Nanotubes by overcoming their attraction for one another. As can be seen from Figure 6, the adsorption energy between SWNT-SWNT is 0.97eV/nm that between Kentera and CNT is in the range of 1.81 – 5.84 eV/nm. Net lowering of the total energy (enthalpy) due to the interaction of the Kentera and CNTs is the driving force for the formation of an irreversible complex between the CNT and Kentera. We expect the irreversible complex to be stable under the processing conditions of our resin products containing Kentera functionalized CNT that do not typically exceed 200 C.

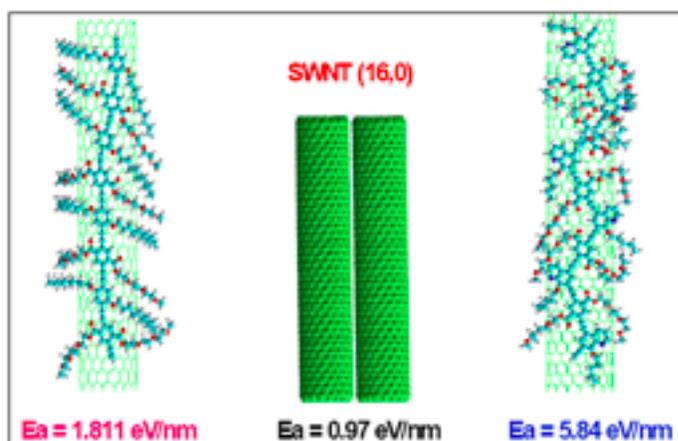


Figure 6: Adsorption energies of CNT-CNT and CNT-Kentera

Conclusion:

In closing, the above paragraphs convincingly demonstrate that Kentera forms an **irreversible complex** with CNTs. The Kentera, through π stacking, irreversibly modifies the surface of the CNTs by imparting required functionalities to otherwise smooth walled CNTs. Adsorption between CNTs and Kentera is very strong (5.84 eV/nm) such that during the process of dispersing functionalized CNTs into the resins it is highly unlikely that the Kentera will separate from the CNTs. Kentera functionalized CNTs not only help in de-bundling of CNTs but also aid the CNTs dispersal into the resins. Kentera functionalization creates a physical barrier between the CNTs and hence prevents the re-bundling. Kentera treatment compatibilizes the surface energies of CNTs with that of resin matrix, thereby helping the dispersion of the CNTs. Surface modification of the CNTs by Kentera renders unique chemical characteristics to CNTs which are distinct when compared to pristine CNTs. For all practical purposes CNTs functionalized through Kentera can be considered equivalent to the covalently functionalized CNTs. Kentera functionalization allows control over the distance, density and placement of functional groups on the CNT surface that to this date has proven difficult to achieve in the covalent

functionalization approach.

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