This is the accepted manuscript made available via CHORUS. The article has been published as:

Quasiphase Transition in a Single File of Water Molecules Encapsulated in (6,5) Carbon Nanotubes Observed by Temperature-Dependent Photoluminescence Spectroscopy

Xuedan Ma, Sofie Cambré, Wim Wenseleers, Stephen K. Doorn, and Han Htoon

Phys. Rev. Lett. 118, 027402 — Published 12 January 2017

DOI: 10.1103/PhysRevLett.118.027402
Molecules confined inside single-walled carbon nanotubes (SWCNTs) behave quite differently from their bulk analogues. In this work we present temperature-dependent (4.2K up to room temperature) photoluminescence (PL) spectra of water-filled and empty single-chirality (6,5) SWCNTs. Superimposed on a linear temperature-dependent PL spectral shift of the empty SWCNTs, an additional step-wise PL spectral shift of the water-filled SWCNTs is observed at ~150 K. With the empty SWCNTs serving as an ideal reference system, we assign this shift to temperature-induced changes occurring in the single-file chain of water molecules encapsulated in the tubes. Our molecular dynamics simulations further support the occurrence of a quasi phase transition of the orientational order of the water dipoles in the single-file chain.

Confinement of molecules determines the properties and functions of many systems in biology, geology, catalysis and nanofluidics,[1] e.g. nanoconfined water plays a vital role in selective single-file water and ion transport through biological membranes[2, 3] and allows for the development of ultraselective nanofluidics applications.[4–9] Single-walled carbon nanotubes[10] (SWCNTs) are an excellent model system to study nanoconfined water due to their close analogy with many natural systems.[11, 12] Additionally, they combine atomically-precise diameters matching the size of various molecules with a one-dimensional character and possess structure-dependent optical properties that are extremely sensitive to the presence of encapsulated molecules, leading to characteristic spectral shifts.[13–17]. In this work, we therefore exploit these optical transitions as ultrasensitive probes for the temperature-dependent behavior of a single file of water molecules encapsulated inside (6,5) SWCNTs. Molecular confinement inside SWCNTs moreover results in new functionalities such as amphoteric doping[18] or photosensitization[19, 20] of the SWCNTs, enhanced stabilities of the encapsulated molecules,[21] and unique molecular order which is only achievable in such quasi-1D nanocavities.[16] Moreover, recent studies[5, 22, 23] have revealed nearly zero friction for confined water transportation and superior water permeability in CNTs, indicating their potential applications in efficient desalination and water purification devices.[24, 25]

Both theoretical calculations[4, 26] and experiments[13–15, 27, 28] have demonstrated that water molecules can spontaneously enter the smooth, hydrophobic channels of SWCNTs. Remarkably, considering that Ising[29] already showed generally that long range (i.e. infinite range) order and thus a strict phase transition cannot exist in a 1D system with short-range interactions, theoretical simulations have predicted highly ordered structures of water confined inside SWCNTs, critically dependent on the tube diameter and chirality, and that additional changes between such structures may still occur.[26, 30, 31] As mathematically such changes cannot be strictly discontinuous, but clearly recognizable as a step (where the actual degree of rounding may still depend strongly on the dimensions of the system), we refer to these as quasi phase transitions. For SWCNTs with diameters d ≥ 0.9 nm, theory has predicted that confined water can transform into low-dimensional ice-nanotubes, either continuously (unlike bulk water) or through a seemingly discontinuous (quasi first-order) transition, with the freezing point being critically dependent on the SWCNT diameter (ranging from 150 K up to 290 K).[26, 31] X-ray diffraction,[32, 33] infrared spectroscopy,[34, 35] neutron scattering[36] and nuclear magnetic resonance[37] studies have demonstrated the existence of such ice-nanotubes. These experiments were however always performed on larger diameter samples with mixed chiralities and diameters (and using techniques unselective for the SWCNT diameter), thus providing only an average view on the water structure and phase transition over the entire diameter range.

Even more intriguing is the behavior of water in the smallest, yet fillable SWCNTs (0.54 nm ≤ d < 0.9 nm) where mutual passage of molecules is excluded and water molecules form one-dimensional single-file chains.[30, 38] Quantum chemical calculations of water confined in these narrow diameters predict the existence of different ferro-electric groundstate conformations, depending on the model used: the water dipoles, all pointing in the same sense, either form an alternating, sizable arrangement with mixed chiralities and diameters (and using techniques unselective for the SWCNT diameter), thus providing only an average view on the water structure and phase transition over the entire diameter range.
FIG. 1. (a) A representative wide-field PL image of DOC-wrapped empty (6,5) SWCNTs obtained at 4.2 K (localized exciton emission). The white circles mark individual SWCNTs. (b) Schematic molecular models of water-filled and empty (6,5) SWCNTs, demonstrating that the tube is just wide enough to fit a single linear chain of water molecules. (color online)

tinguishing liquid from solid phases,[41] a transition in the orientational order of the water molecules cannot be excluded, for which experimental evidence is still lacking.

Recent advances in chiral sorting of carbon nanotubes,[42–44] combined with the extreme sensitivity (and chiral selectivity[45]) of optical spectroscopy for the filling of SWCNTs with various molecules,[13–16] provides an ideal platform for studying the thermodynamic properties of single files of water molecules confined in SWCNTs with a well-defined, small diameter. In this Letter, we report temperature-dependent photoluminescence (PL) spectroscopy of empty and water-filled sorted, single-chirality (6,5) SWCNTs. Superimposed on the linear shift of the emission energy of the empty SWCNTs, the PL of the water-filled SWCNTs shifts significantly at about 150K, which is attributed to a change of the dipole orientations of the encapsulated water molecules. MD calculations indeed show that qualitative changes in orientational order should occur within the measured temperature range.

For the temperature-dependent PL experiments, a home-built confocal laser microscope was used (see also Supporting Material (SM)[46]). Samples were prepared as follows: An aqueous dispersion of HiPco SWCNTs was prepared using sodium deoxycholate (DOC, 1%wt/V) as surfactant by gentle magnetic stirring for 3 weeks. Sonication was avoided to prevent structural damage to the SWCNTs.[13, 47] From this suspension, (6,5) SWCNTs were extracted by a two-step aqueous two-phase procedure.[43, 44] The resulting chirality-sorted nanotube suspension was first diazyized to 1%wt/V DOC, as surfactant by gentle magnetic stirring for 3 weeks. Sonication was avoided to prevent structural damage to the SWCNTs.[13, 47] From this suspension, (6,5) SWCNTs were extracted by a two-step aqueous two-phase procedure.[43, 44] The resulting chirality-sorted nanotube suspension was first diazyized to 1%wt/V DOC, using a stirred ultrafiltration cell, and subsequently density gradient ultracentrifugation was used to separate the empty and water-filled (6,5) SWCNTs.[48, 49] Similar to previous work[13–16, 48, 49] a combination of optical absorption, resonant Raman and PL-excitation spectroscopy was used to assign the composition of each of the fractions, see SM[46] indicating that the amount of filled SWCNTs are negligible in the empty fraction (< 3.7%), while in the PL spectra of the filled fraction a small contribution of empty SWCNTs can be observed, with an amplitude of ~ 20% of the total PL intensity. For temperature-dependent optical experiments, SWCNTs were drop-cast on quartz substrates, dried and mounted in a Microstat He2 cryostat (Oxford Instruments). The sample holder was in thermal contact with the heat exchanger and temperature sensor to allow for efficient temperature control. To avoid influences from intertube interactions such as energy transfer[50] and intertube exciton tunneling[51] on the PL spectra, the concentration of the SWCNTs in the films was kept sufficiently low. A continuous-wave Ti:Sapphire laser operating at 822nm was used to excite the (6,5) SWCNTs at their E_{11} phonon sidebands. For the wide-field imaging, the laser was expanded to a semi-homogeneous spot of ~60 x 60µm and the excitation power was kept below 100W/cm^2 in order to avoid any thermal effects. A 300mm spectrograph equipped with a liquid-nitrogen-cooled InGaAs array detector was used to record the PL spectra and images.

Figure 1(a) shows a representative wide-field PL image of DOC-wrapped empty (6,5) SWCNTs acquired at 4.2K. Each white circle highlights an individual SWCNT. For each sample and at each temperature, a minimum of 10 PL spectra were collected at different positions using the wide-field imaging method. Note that the so-obtained PL spectra are not from single tubes, but instead represent an ensemble average over a small area, effectively collecting PL signals from ~ 25 individual SWCNTs per
FIG. 3. (a) Mean PL peak positions ($E_{11}$) and standard errors of the mean for the empty (red, open circles) and water-filled (blue, filled circles) SWCNTs measured at different temperatures. The mean values and standard errors of the mean were determined from wide-field PL spectra measured for 3 different samples, with at least 10 different positions for each sample at each temperature. The values of the empty SWCNTs are fitted linearly (magenta). (b) $\Delta E_{11} = E_{11}(T) - E_{11}(4.2K)$ for empty and water-filled SWCNTs. The values of the empty SWCNTs are fitted linearly (magenta). (c) Energy difference for water-filled and empty SWCNTs ($|E_{11}^f - E_{11}^E|$) as a function of temperature. (color online)

Throughout the entire temperature range, the $E_{11}$ energy of the water-filled SWCNTs is always smaller than that of the empty SWCNTs, which has previously been attributed to an increased dielectric screening for the water-filled SWCNTs.[13, 15, 48] Note also that the empty and water-filled SWCNT $E_{11}$ energies observed for the film samples at room temperature are in excellent agreement with those reported for aqueous suspensions,[15] proving that the SWCNTs remain well isolated from each other and from the substrate, and that the water remains encapsulated in the SWCNTs even under high vacuum conditions (possibly due to the thick solid surfactant layer in which the SWCNTs are embedded). Also the larger standard error of $E_{11}$ due to tube-to-tube variations observed for the water-filled SWCNTs compared to that of the empty tubes is in excellent agreement with the internal-water-induced inhomogeneous spectral broadening observed in previous single-nanotube experiments.[15]

To illustrate the temperature-induced shifts of the $E_{11}$ peak positions observed for empty and water-filled SWCNTs, Figure 3(b) presents the relative emission shifts using the value of $E_{11}$ obtained at 4.2K as the reference, i.e. $\Delta E_{11} = E_{11}(T) - E_{11}(4.2K) \approx E_{11}(T) - E_{11}(0K)$. The $E_{11}$ peak position of the empty SWCNTs blue-shifts linearly with increasing temperature at a slope of $9.7 \pm 1.7 \times 10^{-3}$ meV, resulting in an overall shift of only 2.8meV over the entire temperature range (4.2 - 296K).

These temperature-dependent PL shifts can be ascribed to two competing effects. First of all, softening of the strong coupling between band-edge states and the lowest energy optical phonon modes results in a red-shift of $E_{11}$ for all SWCNT chiralities at increasing temperatures[52–54] (observed for strain-free suspended tubes[52]; note that this shift is opposite from what we observe). Additionally, previous studies demonstrated that due to the mismatch of thermal expansion coefficients of SWCNTs and their host matrices, the emission energy can either blue or red shift depending on the chirality,[52, 54–58] and in fact, this strain-induced shift dominates in surfactant-coated SWCNTs.[54, 55, 57] Following a similar procedure as defined previously in the literature for SWCNTs embedded in surfactants or polymers,[54, 55, 57] a uniaxial strain component of $(0.044 \pm 0.004) \times 10^{-3}$ %/K is exerted by the external host environment on the empty SWCNTs (see SM[46]).

Superimposed on the linear temperature-dependent PL shifts observed for the empty SWCNTs (Fig. 3(b)), an additional step-wise PL-shift is observed for the water-filled SWCNTs centered at ~ 150K. Such a change has previously been observed in FTIR measurements for larger-diameter mixed-chirality SWCNTs embedded in films,[58] and was postulated to arise either from adsorption/desorption of molecules on the external SWCNT surface or from a phase transition of water inside the SWCNTs. However, the results remained inconclusive on the true origin.
In this work, however, the empty SWCNTs can serve as an ideal reference system, allowing us to assign this change in slope for the water-filled SWCNTs to temperature-induced changes occurring in the chain of water molecules encapsulated inside the (6,5) SWCNTs. Subtracting the data of the empty SWCNTs from those of the water-filled SWCNTs (denoted as $|E_{11}^F - E_{11}^E|$) allows us to exclude the effect of the external host matrix (i.e., the surfactant layer). Therefore, $|E_{11}^F - E_{11}^E|$ represents the sole effect of the encapsulated water molecules on the electronic transition energies of SWCNTs, which clearly defines a sudden transition centered at $\sim 150\text{K}$.

The change of $E_{11}$ observed at $\sim 150\text{K}$ is a sizeable fraction of the maximal difference in $E_{11}$ between empty and water-filled SWCNTs, and more than two times larger than the strain-induced shift observed for the empty SWCNTs imposed by the external environment over the entire temperature range. Therefore, it is unlikely that the additional PL shift of the water-filled SWCNTs at $\sim 150\text{K}$ is mediated through strain from the encapsulated molecules (note that the diameter of the (6,5) SWCNTs is sufficiently large to provide more than enough space for the single file water molecules[30], see also Fig. 1). Theoretical calculations[59] and experimental studies[16, 59] have suggested that optical transition energies of SWCNTs are extremely sensitive to both the effective size and orientation of the molecular dipoles encapsulated in or adsorbed on SWCNTs (larger effect for dipoles oriented perpendicular to the tube axis[59]). Therefore, a significant change in the orientation of the water dipoles most likely lies at the origin of the observed spectral shift.

Inspired by this peculiar experimental observation, and furthermore motivated by the fact that theoretical calculations have predicted qualitatively different ground state structures for 1D water chains in nanochannels[14, 30, 38–40], it seemed plausible that quasi phase transitions might occur between such differently ordered water structures. To assess whether significant changes in dipole orientations indeed occur in the relevant temperature range, we performed molecular dynamics (MD) simulations of a single-file chain of water molecules in a (6,5) SWCNT as a function of temperature, using the CHARMM force field[60] combined with realistic partial atomic charges for the water molecules (see SM[46]). Figure 4 presents the angular distribution of water dipole moments relative to the SWCNT axis, for a few selected temperatures (see also Figs. S7-S8 in the SM[46]). At low temperature, the water molecules form a traditional hydrogen-bonded chain with ferro-electrically ordered water dipoles pointing at angles of $\theta \sim 31^\circ$ with the SWCNT axis (dipole moment components parallel to the tube axis all aligned in the same sense; perpendicular components aligned in alternating senses, see also Fig. S9 in the SM[46]). Around $\sim 70\text{K}$, dipole orientations parallel to the tube axis ($\theta \sim 0^\circ$) start to dominate, corresponding to the occurrence of bifurcated hydrogen bonds (i.e., hydrogen bond from a single oxygen atom distributed over both hydrogen atoms of a single neighboring water molecule). For $T > 200\text{K}$ also angles of $90^\circ$ start to occur frequently, allowing the dipole moments to flip their orientation completely, and destroying the ferro-electric order. The MD calculations thus indicate three different regimes (hence two transitions): classical hydrogen-bonded, predominantly bifurcated hydrogen-bonded and disordered chains. The direction of the experimentally observed shift is both in line with the much larger effective total dipole moment (albeit along the SWCNT axis) of the ferroelectrically-ordered chains (both classical and bifurcated hydrogen-bonds) with respect to a disordered chain (Fig. S8b in the SM[46]), and with the increased angle of the dipoles with the SWCNT axis for the classical hydrogen-bonded chain with respect to the predominantly bifurcated state. Thus, the MD calculations support the interpretation that changes in the dipole orientation are at the basis of the observed change in transition energy of the SWCNTs, but further, more extended theory is certainly desired to identify the exact nature of this quasi phase transition.

In conclusion, our experimental results provide new insights in the phase behavior of water molecules confined to a single file inside SWCNTs and demonstrate the need for more advanced theories to explain the origin of the experimentally observed transition. With the electronic transition energies of SWCNTs acting as very sensitive sensors for the encapsulated molecules, PL spectroscopy opens new perspectives to investigate the temperature-dependent behavior of confined molecules. SWCNTs present a close analogy with many natural nanopore systems and thus can serve as general model systems for understanding the behavior of water molecules in more
complex natural systems.[11, 12] The superior ion/water molecule permeability of carbon nanotubes has enabled their applications in highly efficient purification and desalination devices[5–7, 9, 22–25] and the study of ultrafast proton transport through one-dimensional molecular arrays.[2, 3, 8] Our finding of confined water phase transition in SWCNTs is essential to understand and achieve the fundamental limits of carbon nanotube nanofluidics devices.

This work was supported in part by the LANL LDRD program and was performed in part at the Center for Integrated Nanotechnologies, a U.S. Department of Energy, Office of Science User Facility. S.C. and W.W. acknowledge the financial support from the Fund for Scientific Research Flanders, Belgium (FWO; projects G040011N, G021112N, 1513513N and 1512716N), which also granted S.C. a postdoctoral fellowship and a mobility grant for visiting LANL. Funding from the Hercules Foundation (grant AUHA/13006) and the European Research Council under Horizon 2020 / ERC starting Grant Agreement no. 679841 is gratefully acknowledged.

* These authors contributed equally; corresponding authors: xuedan.ma@anl.gov; sofie.cambre@uantwerpen.be


[44] N. K. Subbainay, A. N. G. Parra-Vasquez, S. Cambré,


[46] Spectroscopic sample characterization, all temperature-dependent PL spectra and more details on the MD simulations can be found in the Supporting Material, which includes Refs. [61-71].


[68] @HyperChem(TM) Professional 7, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA.

