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Transition of Ionic Liquid [bmim][PF$_6$] from Liquid to High-Melting-Point Crystal When Confined in Multiwalled Carbon Nanotubes

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Room-temperature ionic liquids (ILs) have received much attention in past years due to their importance in a broad range of applications,[1] whereas little is understood about the phase transition of ILs. The main difference between ILs and simple molten salts are that ILs are composed of bulky, asymmetrical ions that can only loosely fit together. Many theoretical and experimental efforts have been made to study the crystallization behavior of ILs.[2−8] Alkyl side chain,[2] hydrogen bonding,[3] thermal history,[4] and the presence of other solvent or impurities[5] were known to affect the phase-transition behavior. However, as for the phase behavior and crystallizablility of ILs, much attention has been paid to the study of these low-melting salts in bulk systems.

Carbon nanotubes (CNTs) are a type of desirable material to encapsulate molecules and form quasi-1D arrays. The effect of nanometer-sized confinement on molecular packing, orientation, translation, rotation, and reactivity has been investigated by a number of researchers.[9] Many substances, including fullerenes, metallofullerenes, metal, metal oxides, biomolecules, inorganic salts, water, organic solvents, and gas molecules have been introduced into the channel of CNTs.[10] Of particular interest is the speculation that matter inside CNTs might exhibit a very different solid−liquid critical point which cannot occur in bulk material. For example, Koga et al.[11] found the existence of a variety of new ice phases inside single-walled CNTs ($d = 1.1 \sim 1.4$ nm), implying a phase transition from liquid water to new ice formulations.

What will happen when ILs are confined in the narrow hollow interior of CNTs? Since many reports revealed that ILs possesses properties of both a solid and a liquid,[12] one may speculate that a transformation of ILs from liquid to solid state will occur if the ILs are present in a confined space. Here we report our study on the behavior of a prototype ILs, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF$_6$], encapsulated in multiwalled carbon nanotubes (MWNTs). It was found that the confinement effect of MWNTs induced the formation of [bmim][PF$_6$] crystals possessing a high melting point (Scheme 1).

The [bmim][PF$_6$] was prepared as before,[13] and its purity was confirmed by NMR. Halka et al.[14] found a slight decrease in surface tension of [bmim][PF$_6$] from 47 mN·m^{-1} to 38 mN·m^{-1} between 280 and 400 K. This value is much below the threshold surface tension of 180 mN·m^{-1} specified by Dujardin et al.[15] for the efficient wetting and filling of CNTs. In this study, a procedure (Supporting Information) including cutting CNTs and incubating at 90 °C under sonication was employed to avoid plugging and to efficiently fill [bmim][PF$_6$] into MWNTs (named as IL@MWNTs for simplicity). To further reduce the viscosity of [bmim][PF$_6$] and facilitate the filling process, a binary mixture of [bmim][PF$_6$] and methanol (v/v = 1:1) was also encapsulated into MWNTs (named as IL/MeOH@MWNTs).

Scheme 1

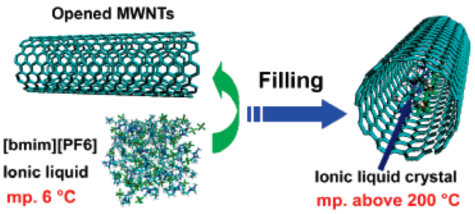

Figure 1 shows the HRTEM images of the opened MWNTs and the filling products. The graphite layer and the empty cavities are clearly seen in the unfilled MWNTs (Figure 1a); however, continuously impregnated tubes are observed in IL@MWNTs and IL/MeOH@MWNTs (Figure 1b and c), indicating the encapsulation of [bmim][PF$_6$] in the hollow interior of MWNTs. Energy dispersive X-ray microanalysis spectra implied the existence of phosphorus, confirming the filling of [bmim][PF$_6$]. Selected area electron diffraction (SAED) pattern (inset of Figure 1) indicated the formation of polymorphous [bmim][PF$_6$] crystals. HRTEM image of a small section of an individual tube of IL@MWNTs sample is also shown in Figure 1d. The contrasting darker area (designated by arrows) clearly seen inside MWNTs should correspond to the crystals of [bmim][PF$_6$].

To further confirm the formation of [bmim][PF$_6$] crystals in the channel of MWNTs, X-ray diffraction (XRD) analysis was performed. Many new peaks appear as a result of the encapsulation of [bmim][PF$_6$] (Supporting Information). Both IL@MWNTs and IL/MeOH@MWNTs show similar diffraction patterns, the diffraction peaks appearing at $2\theta = 18.9°$, 22.9°, 23.8°, 32.1°34.2°, 38.1°, 46.5°, 52.7°, and 58.4° should correspond to the different crystal planes of [bmim][PF$_6$] inside MWNTs.

It is very difficult to obtain stable [bmim][PF$_6$] crystals by cooling, as the solidification often results in glass formation.[6,16] Recently, Choudhury et al.[6] employed an in situ cryocrystallization method to avoid glass formation of [bmim][PF$_6$] and collected crystal data at −80 °C. The authors also mentioned that even under very low temperature the effect of thermal history and the presence of impurities must be considered for the XRD studies. In our case, due to the existence of MWNTs, a detailed investigation of the IL crystal structure inside the tube is difficult. However, we recorded XRD at ambient temperature, and the reproducibility of patterns is very good after several repeated measurements, indicating that the IL crystal formed inside MWNTs is more stable than in the bulk system. This is further proven by differential scanning calorimetry (DSC) analysis (Figure 2). The melting point of pure [bmim][PF$_6$] is ∼6 °C. For the filled materials, the onset of endothermic peaks in DSC curves of both IL@MWNTs and IL/MeOH@MWNTs appear above 200 °C (Figure 2c and d). This means that the [bmim][PF$_6$] crystal formed inside the MWNTs possesses an unexpected high thermal stability. Two sharp fusion peaks at 221 and 266 °C

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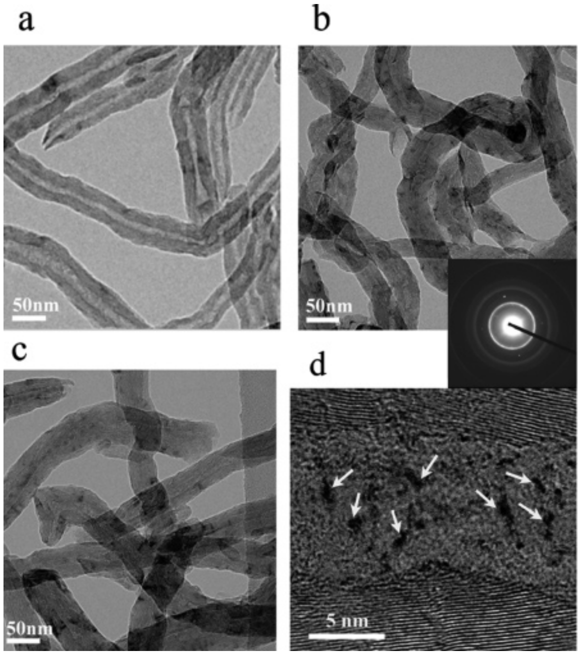

Figure 1. TEM images of opened MWNTs (a), IL@MWNTs (b), IL/MeOH@MWNTs (c), and HRTEM image of a small section of an individual tube of IL@MWNTs (d). (Inset) Electron diffraction of a selected area of an individual nanotube filled with [bmim][PF$_6$].

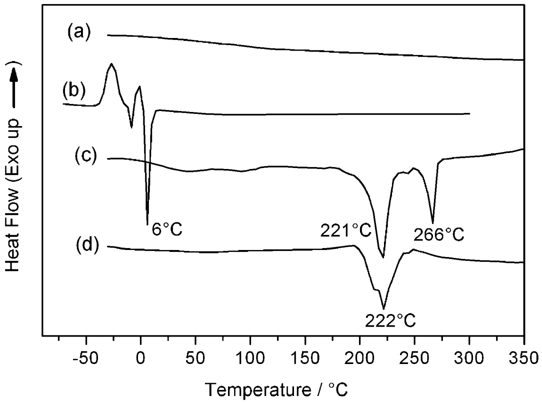

Figure 2. DSC heating curves for MWNTs (a), [bmim][PF$_6$] (b), IL@MWNTs (c), and IL/MeOH@MWNTs (d) at a scan rate of 10 °C/min.

are observed in the DSC curve of IL@MWNTs (Figure 2c), indicating the coexistence of two polymorphous crystals of the solid [bmim][PF$_6$]. They are probably corresponding to the two rotational isomers of [bmim] cation.[2c] To the contrary, due to the influence of methanol on the conformation of [bmim],[5,6] only one fusion peak at 222 °C was detected for IL/MeOH@MWNTs (Figure 2d).

The structure of ILs results from a balance between long-range electrostatic forces and geometric factors. Various studies have been made to elucidate the role of weak interactions, such as H-bonding, $\pi-\pi$ stacking, Van der Waals forces, and electrostatic forces in ILs.[12] CNTs offer atomically thin channels within a restricted diameter range, and their internal van der Waals surfaces will regulate the growth behavior of encapsulated crystals in a precise fashion.[17] It is speculated that the confinement of MWNTs changes some geometric factors of the encapsulated [bmim][PF$_6$], leading to the enhancement of weak interactions and the high stability of as-formed crystals.[18] Golovanov et al.[19] reported an unexpectedly high melting point (mp 210 °C) of 1-methyl-3-propylimidazolium SiF$_6$ IL, resulting from the presence of extremely short C−H···F contacts in the crystal. In our case, the high pressure and electric charge density inside MWNTs should significantly shorten the intermolecular spacing as compared to the unconfined state, which will be especially strong for charge-assisted hydrogen bonds,[3b] forming multiple stable hydrogen bond networks, in which the short C−H···F contacts can be generated. In addition, our previous work on the thermal stability of inner grafted functional groups inside CNTs also manifested the narrow channel of CNTs to be a protective cage for the encapsulated materials.[20]

In summary, we demonstrated for the first time the crystallization behavior of IL inside MWNTs. It was found that [bmim][PF$_6$] undergoes a fully different phase transition and crystal formation when confined in MWNTs, resulting in the formation of a stable, polymorphous crystal possessing a melting point of above 200 °C. Our results not only provide a good addition to the development of new types of CNT-based composites, but they also are helpful for the understanding of phase transitions of dimensionally confined environments and the related phenomena within the nanoscale confines.

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Supporting Information Available: Experimental details, characterizations, and XRD patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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