Why Single-Walled Carbon Nanotubes Can Be Dispersed in Imidazolium-Based Ionic Liquids

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ABSTRACT Spectroscopic and molecular modeling studies were performed to investigate the underlying dispersion mechanism of single-walled carbon nanotubes (SWCNTs) in imidazolium-based ionic liquids. Both the experimental and the simulation evidence indicate that the ionic liquids interact with SWCNTs through weak van der Waals interaction other than the previous assumed "cation$-\pi$" interaction. Therefore the electronic structure of SWCNTs in the dispersions can be kept intrinsically. The SWCNTs do not significantly influence the local structure of the imidazolium cations, though the local environment of anions adjacent to SWCNTs is somewhat perturbed because of the interfacial effect. The ionic liquids basically keep their overall bulk phase organization. A $\pi-\pi$ interaction-shielding model is proposed to account for the dispersion of SWCNTs in the ionic liquids. The ionic liquids, which possess very high dielectric constants, can effectively shield the strong $\pi-\pi$ stacking interaction among SWCNTs and thus evidently disperse the SWCNTs. The retaining of SWCNTs' intrinsic property and the higher SWCNT content make the ionic liquids ideal media for the study and application of SWCNTs.

KEYWORDS: single-walled carbon nanotubes · imidazolium · ionic liquids · van der Waals interaction · $\pi-\pi$ stacking · Raman spectra · IR

I n recent years, single-walled carbon nanotubes (SWCNTs) have been intensively studied because of their unique structures and remarkable electrical and optical properties.[1-3] However, their processability and application are encumbered by the low solubility in both aqueous and nonaqueous solvents. Thus many methods have been developed to enhance the dispersability of SWCNTs in solvents, including sidewall functionalization,[4,5] polymer and DNA wrapping,[6,7] modification through $\pi-\pi$ stacking with aromatic molecules,[8-10] and addition of surfactants.[11,12] These methods normally can only disperse a very small amount of SWCNTs by the harsh treatments of ultrasonication and chemical reaction. For the large scale application, a much simpler and more efficient method which can disperse the SWCNTs at higher concentration is strongly needed.

Room-temperature ionic liquids are normally organic salts with properties being easily adjusted by changing one of the ions.[13-15] They have attracted much attention as promising green solvents because of their unique physicochemical characters: relatively low viscosity, negligible vapor pressure and effective nonvolatility, thermal stability, increased electrochemical window, and relatively high ionic conductivity.[16-18] Room temperature ionic liquids are good solvents for a lot of inorganic and organic materials as well as polymers.[19-22] They have been widely used as media for chemical reactions and catalysis, liquid−liquid extraction, gas separation, and as solvents in electrochemistry and spectroscopic studies.[23-28]

Recently, it is found that SWCNTs can be easily dispersed in the imidazolium-based room-temperature ionic liquids by mechanical milling, forming a thermally stable gel (bucky gel).[29] The concentration of SWCNTs can be as high as 1 wt %. The bucky gel has many useful applications. They were used to fabricate plastic actuator simply through layer-by-layer casting, in which the effective high surface area of the SWCNT electrode was ensured.[30,31] Homogeneous functionalization of SWCNTs were performed effectively in large quantities in the gel.[32,33] SWCNTs were also finely dispersed in imidazolium ion-containing ionic liquids with different polymerizable functional groups and polymerization of the gel produced a mechanically reinforced, electroconductive, and thermoconductive soft material.[34]

Despite the versatile applications of the bucky gel, there is still no systematic study concerning the interactions between SWCNTs and ionic liquids. The dispersion mechanism for SWCNTs in ionic liquids is still unclear. A possible "cation−π" interaction between the surfaces of SWCNTs and the imidazolium ions was proposed to account for the exfoliation of the heavily en-
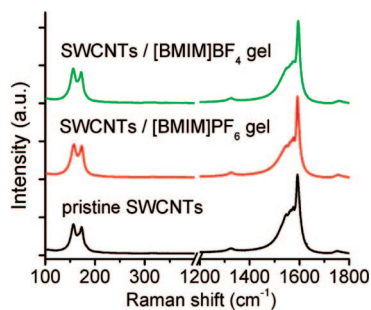
Figure 1. Raman spectra of the pristine SWCNTs and the bucky gels (1 wt % for SWCNTs) upon excitation at 633 nm.

tangled nanotube bundles to much finer bundles.[29,34,35] Yet this hypothesis has not been verified. A molecular level understanding of the interactions between SWCNTs and ionic liquids is required for further study and application of SWCNT-ionic liquid systems.

Vibrational spectroscopy has been widely used to inspect the interactions between molecules and ions because the vibrational modes are susceptive to the local environments.[36–38] In the present study, the dispersion mechanism of SWCNTs in ionic liquids and the related structure change are studied using vibrational spectroscopy and molecular simulation. It is found that the ionic liquid molecules interact with SWCNTs through not the normally assumed cation$-\pi$ interaction but the van der Waals interaction. This means the ionic liquid dispersion offers SWCNTs a chemical environment similar to that of SDS (sodium dodecyl sulfate)-dispersed systems,[2] which is very suitable for the further property study and application of SWCNTs. But the dispersing capacity of ionic liquids is much higher, and the composition of the ionic liquid system is simpler (two components other than three components for SDS system). These characters make imidazolium-based ionic liquids superior as dispersing media for SWCNTs.

RESULTS AND DISCUSSION

Figure 1 shows the resonant Raman spectra of the pristine SWCNTs and the bucky gel (1 wt % of SWCNTs in 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM]PF$_6$) or 1-butyl-3-methyl imidazolium tet-

rafluoroborate ([BMIM]BF$_4$)). The band at 1500~1590 cm^{-1} originates from the tangential vibration of the carbon atoms in the nanotubes and is known as "G band". The band at 100~200 cm^{-1} corresponds to the radial breathing mode (RBM) of the tubes. Resonant Raman spectra have been proved to be sensitive to the changes in both the structural and electronic properties of SWCNTs. According to previous results, charge transfer may take place when SWCNTs interact with electron deficient neutral or positive charged π-electronic molecules through the $\pi-\pi$ and cation$-\pi$ interactions.[39–41] If the cation$-\pi$ interaction does exist between SWCNTs and imidazolium ions, electrons will transfer from SWCNTs to the electron deficient imidazolium ions. Our density functional theory (DFT) calculations also show that if the cation$-\pi$ model takes action, electrons will transfer from SWCNTs to imidazolium ions and the electronic structure of SWCNTs will change correspondingly (see Figure S1 and S2 in Supporting Information). Charge transfer and the electronic structure change can induce changes in the Raman spectra of SWCNTs.[42] Shift and peak shape change of the G band are expected to be observed. Shift and intensity change of the RBM should also be observed because of the change of the resonance conditions.[43–45] However the Raman spectra of the bucky gels in Figure 1 is essentially the same as that of the pristine SWCNTs. These facts demonstrate that the electronic structure of SWCNTs in the bucky gel remains unchanged and there is no charge transfer between
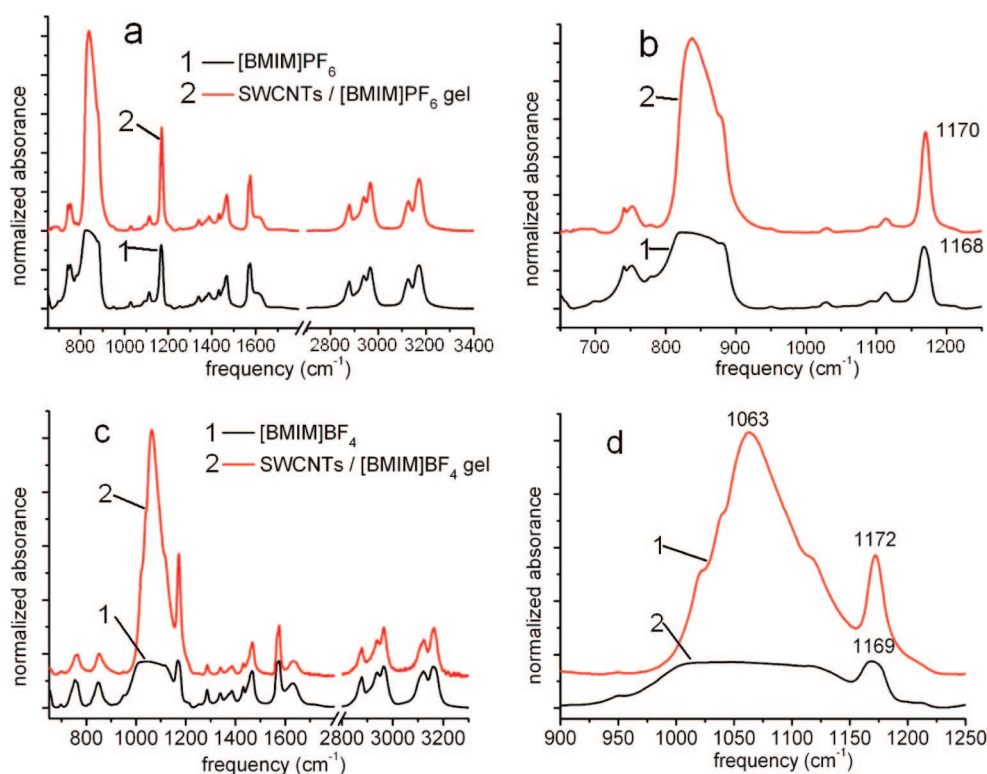

Figure 2. Room temperature IR spectra of [BMIM]PF$_6$ (a, b) and [BMIM]BF$_4$ (c, d) and the corresponding bucky gels (1 wt % for SWCNTs). Panels b and d are the magnifications of panels a and b, respectively.
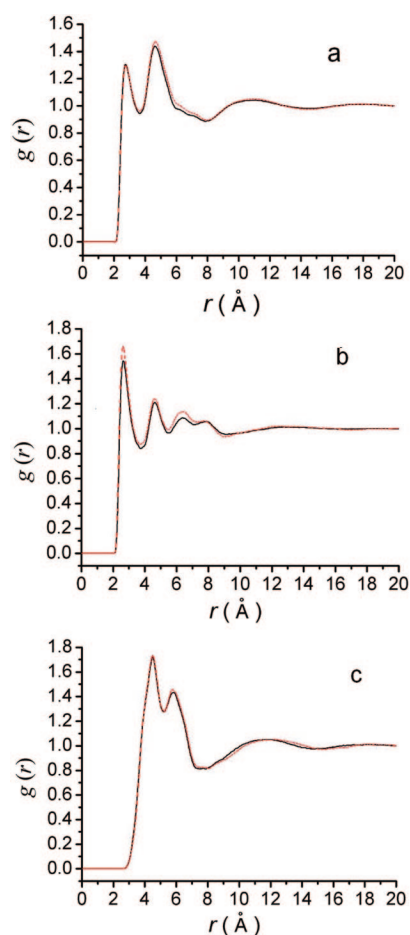
Figure 3. Radial distribution functions $g(r)$ of fluorin atom relative to hydrogen atom in the butyl group (a), hydrogen atom in the imidazolium ring (b), and nitrogen atom (c) in the pure ionic liquid (black line) and bucky gel (red line), respectively.

SWCNTs and BMIM$^+$ cations thus no cation$-\pi$ interaction exists. The interactions between them are very weak.

Infrared spectra of [BMIM]PF$_6$/[BMIM]BF$_4$ and their bucky gels are presented in Figure 2. The spectra have been normalized with respect to the C$-$H band at 2800$\sim$3000 cm^{-1}, making the relationship among the spectra readily apparent. Because SWCNTs do not support a static dipole moment, a relatively weak dynamic dipole moment is responsible for the observation of infrared-active modes of SWCNTs. Thus the characteristic IR absorption peaks of SWCNTs are very weak. The observed spectra of the gels come from only the ionic liquids. The bands at 3011$\sim$3082 cm^{-1} region in Figure 2 are assigned to C$-$H stretching vibration mode of the imidazolium ring. The unresolved CH$_3$$-$N stretching vibration, CH$_2$$-$N stretching vibration, and ring in plane asymmetric stretching appear at 1170 and 1570 cm^{-1}.[21] The frequencies of the ring C$-$H stretching vibration, C$-$N stretching vibration, and ring in plane asymmetric stretching are sensitive to the electronic density of the imidazolium ring.[46] It can be seen from Figure 2 that no change of the vibration modes related

to the imidazolium ring is observed, except the 1168 or 1169 cm^{-1} features shift to higher frequency by 2$-$3 cm^{-1}. This indicates that the electron configuration of imidazolium ring is basically retained upon gelation, which is in good accordance with the Raman results. According to previous study, multiple hydrogen bonds may form between the alkyl C$-$H and ring C$-$H of BMIM$^+$ and PF$_6$$^-$/BF$_4$$^-$ anions.[14] The alkyl C$-$H and ring C$-$H stretching modes provide useful spectroscopic probes for the study of hydrogen bond interactions in ionic liquids.[47] Since no changes in alkyl C$-$H and ring C$-$H stretching modes were observed, the hydrogen bond interactions for the ionic liquids in the bucky gel is similar to that in the bulk phase. However, it should be emphasized that the asymmetric stretching vibrations of PF$_6$$^-$ ($\sim$840 cm^{-1}) and BF$_4$$^-$ ($\sim$1050 cm^{-1}) become remarkably sharper and stronger in the bucky gels. These results suggest that the addition of SWCNTs does not significantly perturb the local structure of the imidazolium cations, while the local environment of the anions may be changed in the gels.

To further verify whether there is any special influence of SWCNTs on the structure of ionic liquids, we compared the IR spectra of the bucky gel with the mixtures of ionic liquids and many other materials including as prepared silica spheres, spectrum pure graphite, activated carbon, APS-3, and zeolite (see Figure S3 in Supporting Information). These spectra are very similar to those of the bucky gel. No changes of the vibration modes related to the imidazolium ring is observed except the 1168 cm^{-1} feature shifts to higher frequency than that of bulk ionic liquid by 2 cm^{-1}, while PF$_6$ asymmetric stretching mode becomes sharper and stronger. These materials differ dramatically in the surface structure and property from each other, thus changes in the infrared spectra do not result from the special interaction between SWCNTs and ionic liquids, which is different from those of other materials used. This fact provides further evidence that there is no cation$-\pi$ interaction between SWCNTs and ionic liquids.

To make insight into the structure of bucky gel more deeply, molecular dynamics (MD) simulation was performed on SWCNT-[BMIM]BF$_4$ system. Figure 3 shows the radial distribution function $g(r)$ of many sites in the ionic liquid molecule. If there is any change in the structure of the ionic liquids, the relative positions between certain atom pairs change accordingly, which will be reflected by $g(r)$. It is noticeable that the radial distribution functions for both the bucky gel and pure [BMIM]BF$_4$ are very similar, which suggests that the overall organization of the ionic liquids is relatively unperturbed when SWCNTs were added. This may be ascribed to the strong long-range electrostatic interaction between the cations and anions in the ionic liquids. It is unfavorable in energy if the overall structure of ionic liquids changes a lot. Figure 4 shows the radical distribution functions of the nitrogen atoms, the fluorine at-
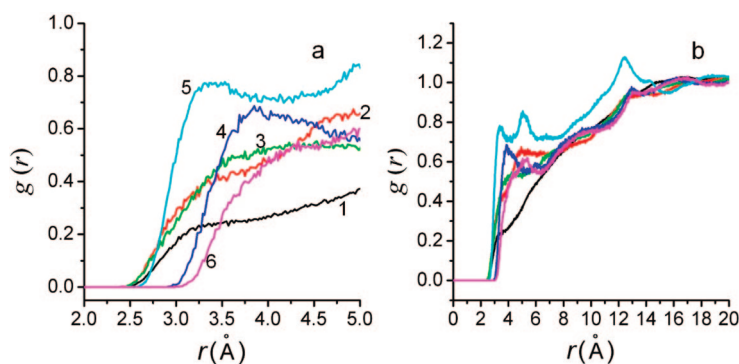
Figure 4. (a) Radial distribution functions of the hydrogen atom in the butyl group (1), hydrogen atom in the methyl group (2), hydrogen atom in the imidazolium ring (3), carbon atom in the imidazolium ring (4), fluorine atom (5) and nitrogen atom (6), respectively. The reference is SWCNT surface. Panel b is the result at extended distance range.
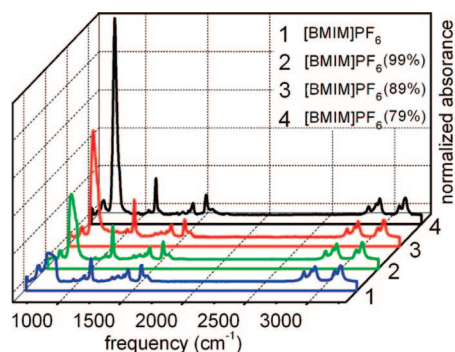

Figure 5. Room temperature IR spectra of the SWCNT-[BMIM]PF$_6$ bucky gels with different composition.

oms, the hydrogen atoms in the butyl groups, and the hydrogen atoms in the imidazolium rings around the surfaces of the SWCNTs. It can be seen that the fluorine atoms and the hydrogen atoms of the alkyl groups are much closer to the SWCNTs than the nitrogen atoms and carbon atoms of the imidazolium rings. This indicates that the SWCNTs are surrounded by the polar parts and nonpolar parts of the [BMIM]BF$_4$ molecules simultaneously. This also suggests that no cation−π interaction exists between SWCNTs and the imidazolium rings. The BF$_4^-$ anions of the [BMIM]BF$_4$ molecules near the SWCNT walls have different environment compared to the bulk molecules. Therefore their IR spectra change a lot in the bucky gel because the vibrational modes of ions are very sensitive to their local environments.[36−38] The percentage of anions near the nanotube walls increases with the increase of the

SWCNT content. Accordingly the asymmetric stretching vibration band of the anions should change a lot along with the increase of SWCNT content. Our IR data validate this point. Figure 5 shows the IR spectra of SWCNT/ionic liquids mixtures with different content of SWCNTs. It can be seen that the vibrational modes of the imidazolium cations do not change essentially as a function of the amount of [BMIM]PF$_6$. However, the PF$_6$ asymmetric stretching band becomes sharper and stronger with the decrease of [BMIM]PF$_6$ content.

From all previous, we have shown that there is no special interaction (such as π−cation interaction) between SWCNTs and ionic liquids. Then what is the driving force that disperses SWCNTs in ionic liquids? Let us start with the reason why SWCNTs are difficult to be dispersed by ordinary solvents. In a SWCNT bundle, the SWCNTs adhere tightly to each other due to strong π−π stacking interactions, making it very difficult to disperse the SWCNTs by ordinary solvents. The π−π stacking is proposed as an electrostatic interaction in which the π orbitals on adjacent molecules orient to maximize the opposing σ−π attractive interactions and minimize the opposing π−π repulsive interactions.[48,49] When SWCNTs are ground with ionic liquids, the shear force detaches the SWCNTs from the bundles. Once the SWCNTs are detached, they are immediately surrounded by ionic liquids. It is well-known that the dielectric constants of the ionic liquids are normally very large. Therefore, the strong π−π interaction between SWCNTs is shielded by the ionic liquids, eventually preventing the detached SWCNTs from rebundling. Meanwhile, the high surface energy of the isolated SWCNTs is effectively appeased since they are enveloped by ionic liquid molecules *via* van der Waals force (see Figure S4 in Supporting Information). This should be the reason why ionic liquids can disperse SWCNTs more efficiently than ordinary solvents. The dispersing process is shown in Scheme 1.

SDS[2] and DNA[6] have been widely used to disperse SWCNTs in aqueous solution. These dispersions can be used for further property study and characterization of
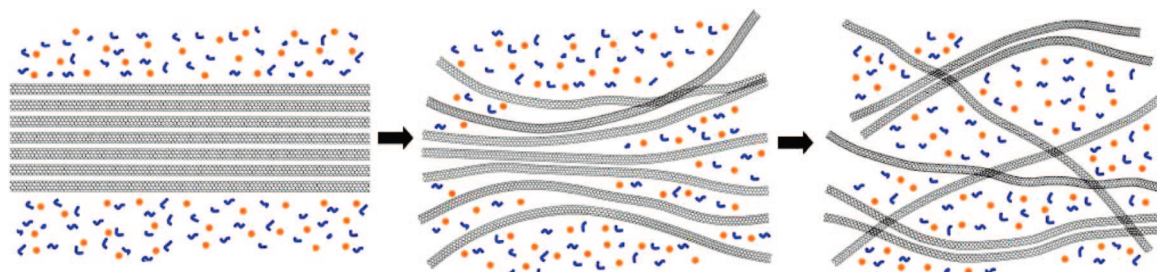
Scheme 1. Schematic representation of the dispersion process for SWCNTs in ionic liquids. The cartoon was not drawn to scale.

SWCNTs. It is already known that the ionic liquids can disperse a higher concentration of SWCNTs than SDS or DNA assisted methods.[29] And the treatment process for dispersing SWCNTs in ionic liquids is very simple. We now have verified that the interaction between SWCNTs and ionic liquids is also a weak van der Waals force, just like that between SWCNTs and SDS molecules[2] or DNA.[6] This hints that the chemical environment of SWCNTs in ionic liquids is also similar to those of SDS- and DNA-containing systems. Therefore, the ionic liquid system is a better choice to disperse SWCNTs for further study on the property of SWCNTs (see an example in Figure S5 in Supporting Information).

CONCLUSION

Raman and IR measurements on the mixtures of ionic liquids and SWCNTs as well as many other materials and the DFT calculation all unambiguously show that no strong interaction such as cation-π interaction exists between SWCNTs and imidazolium ions. Molecular simulation results further provide strong evidence for this conclusion together with the general image about the structure of ionic liquids and SWCNTs in the dispersions. The overall organization of ionic liquids is not remarkably altered by SWCNTs. However, the shielding effect of ionic liquids on the $\pi-\pi$ stacking interaction among SWCNTs takes the key role in dispersing the SWCNTs. The ionic liquids interact with SWCNTs through weak van der Waals interaction. This indicates that ionic liquids are ideal dispersing solvents for SWCNTs with no obvious influence on the electronic structure and property of SWCNTs. Using ionic liquids as dispersing media may help us acquaint more interesting chemical and physical behaviors and properties of SWCNTs.

METHODS

Materials. The SWCNT samples were prepared by arc discharge using Ni/Y as catalysts[50] and purified by reflux in hydrochloric acid. The diameter of SWCNTs was revealed from the TEM images and Raman spectroscopy to be 1.4 ± 0.3 nm, and the length of the tube is $1-2$ μm. [BMIM]PF_6 and [BMIM]BF_4 were purchased from Henan Lihua Pharmaceutical Co. Ltd., China, and used as received. The uniform silica spheres were prepared by the Stöber method.[51] The diameters of the silica spheres are ~400 nm. APS-3 meso-porous material was purchased from Changchun Jilin University High-Tech. Co. Ltd., China. Spectrum pure graphite, activated carbon, and zeolite were obtained from J&K Chemical Ltd. The ionic liquids were grounded with SWCNTs, SiO_2 spheres, spectrum pure carbon, zeolite, and APS-3, respectively, with an agate mortar for ~30 min. For the SWCNT/ionic liquids system, we observed similar phase separation behavior as reported in ref 29. Phase separation behavior was observed with decreasing the amount of SWCNTs (<1 wt % for SWCNTs). Centrifuging the SWCNTs−ionic liquid mixture could accelerate the phase-separation process. The upper phase was colorless bulk ionic liquids. The lower phase was the black bucky gel. Along with the increase of the amount of SWCNTs, the SWCNT-ionic liquid mixture got viscous and finally became a plastic solid when the amount of SWCNTs was 21%. Further increasing the amount of SWCNTs led to the formation of a black powdery solid.

Characterization. FTIR spectra were taken using a Nic-Plan microscope attached to a Nicolet system Magna-IR 750 IR spectrometer ($650-4000$ cm^{-1}) equipped with a liquid nitrogen-cooled MCT detector. The spectral resolution is 2 cm^{-1} and 1000 scans were performed for each sample. Raman measurement was performed under ambient conditions using a helium−neon laser (633 nm, 1.96 eV excitation) in the back-scattering configuration on a Jobin-Yvon HR800 spectrometer (1800 g/mm, monochromator) equipped with an air-cooled CCD detector.

Theoretical Methods. The bulk ionic liquids and SWCNT-ionic liquid dispersions were modeled using full atom molecular dynamics simulations in NPT ensemble using the universal force field, subjected to periodic boundary conditions in all three directions. The ionic liquid bulk phase consisted of 240 pairs of BMIM$^+$ cations and BF$_4^-$ anions in a 42.4 Å $\times$ 42.4 Å $\times$ 42.4 Å unit cell with the density of 1180 kg/m^3. The initial configuration of the SWCNT−ionic liquid system consists of an uncapped armchair (7,7) carbon nanotube (3.00 nm long) and the ionic liquid phase which includes 216 pairs of ions. Van der Waals and long-range electrostatic interactions were treated using the Ewald method. Our MD simulations were performed at the temperature of 298 K and pressure of 1 bar. Andersen temperature coupling and pressure coupling were used for the temperature and pressure control. A simulation time of 1.0 ns was carried out to relax the system into equilibrium at a time step of 1 fs. After that, a simulation time of 100 ps was performed for property analysis.

Supporting Information Available: DFT calculation method and results, IR spectra of the mixtures of [BMIM]PF_6 and various materials, illustration of the interface between SWCNT and [BMIM]BF_4 resulted from MD simulation, and typical absorption spectrum of SWCNTs/ [BMIM]PF_6 solution. This material is available free of charge *via* the Internet at http://pubs.acs.org.

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