

Supporting Information for

Selective Band Structure Modulation of Single-Walled Carbon Nanotubes in Ionic Liquids

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1. Materials and sample preparation.

The SWCNT samples was prepared by the electric arc method using Ni/Y as catalysts and purified with previously reported method.¹ The purified SWCNTs was annealed at 800 °C under Ar atmosphere for 4 h before further use. Figure S1 shows the TEM and HRTEM images of the SWCNTs after purification.

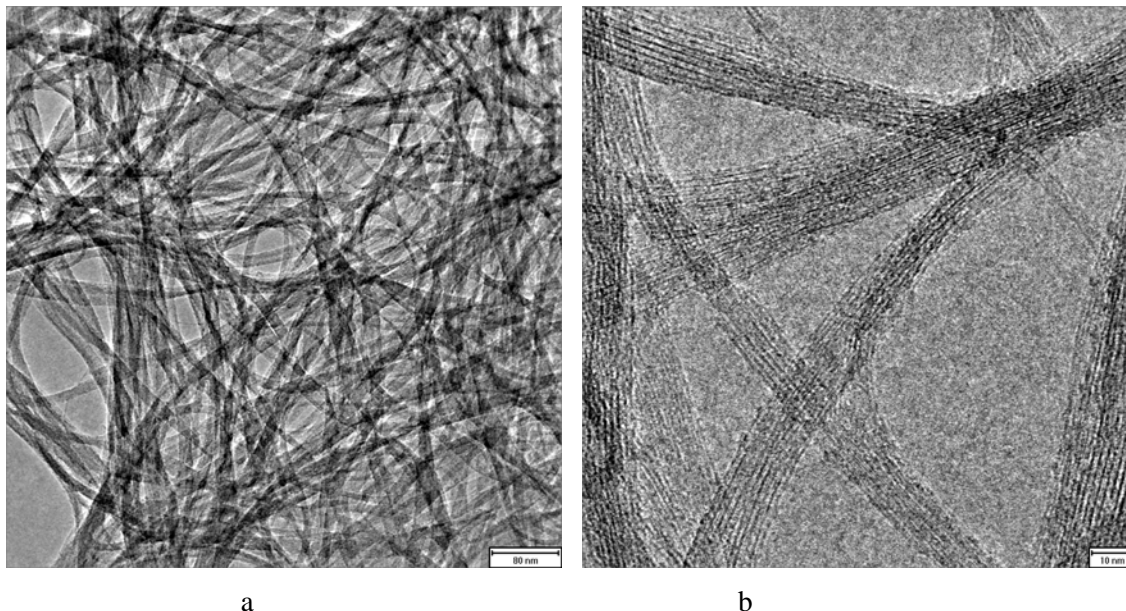


Figure S1. TEM and HRTEM images of the SWCNTs samples after purification. The scale bar is 80nm for (a) and 10nm for (b). The images were taken with a HITACHI H9000 Transmission Electron Microscope operated at 150kV.

The BMIMBF₄ and BMIMPF₆ ionic liquids were obtained from Henan Lihua Pharmaceutical Co Ltd China and used as received. The SDS (sodium dodecyl sulfate), LDS (lithium dodecyl sulfate), PFOA (perfluorooctanoic acid), and PPFOS (potassium perfluorooctanesulfonate) were purchased from Alfa Chemical Ltd. PDS (potassium dodecyl sulfate) was prepared from SDS. Saturated KCl aqueous solution was added into 1wt% SDS solution and the precipitations formed were further washed with saturated KCl aqueous solution. Then the precipitations were dried under vacuum at 30°C for 48 h after washing them thoroughly with deionized water. 12-crown-4 was purchased from Aldrich Chemical Ltd. All other reagents including anhydrous sodium citric acid, tartaric acid, sodium tartrate, octanoic acid, dodecyl acid, sodium stearat, and sodium chloride were all used as received.

The SWCNT suspensions in ionic liquids were prepared by mechanically milling 0.2mg SWCNTs and 10.00g ionic liquids together in the agate for 1h. After surfactants were added into the suspensions, the resultant mixtures were grinded for another hour. The spectra were

collected 1h later.

It was found that the SWCNTs in the suspensions flocculated after one day. However, the SWCNTs could be re-dispersed in the ionic liquids just by shaking the container gently for 10s with hands.

2. Characterization Methods

Raman measurements were performed under ambient conditions using a 633 nm (1.96 eV) and a 785 nm (1.58 eV) laser in the back-scattering configuration on a Jobin-Yvon HR800 Spectrometer. The absorption spectra were measured using a Lambda 35 UV/VIS Spectrometer.

3. Supporting spectroscopic data

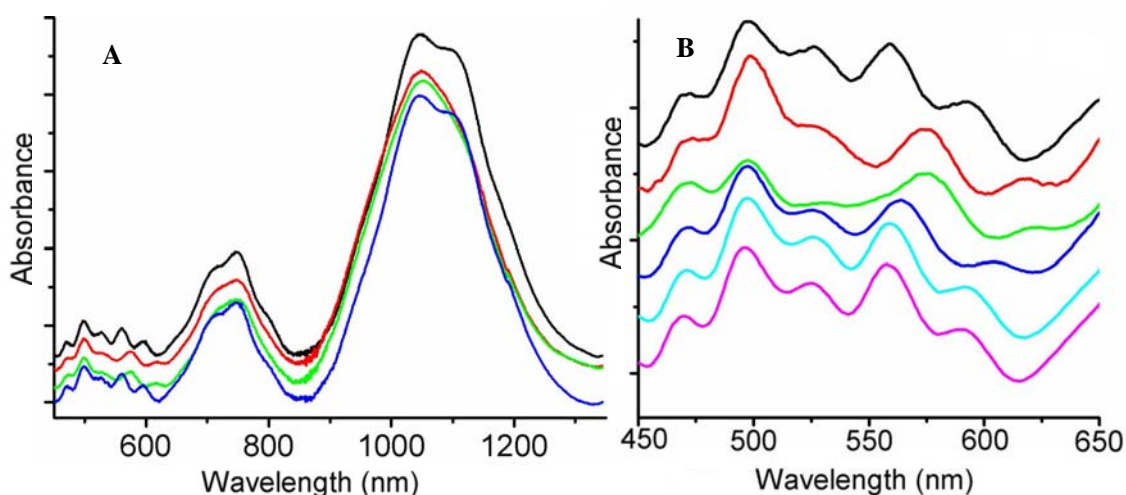


Figure S2. A) The baseline-corrected spectra of Figure 1a. Absorption spectra of SWCNTs suspended in [BMIM]PF₆ and after adding various surfactants, from top to bottom, without any additives (black), with 3.3 mM PFOA (red), 4.7 mM SDS (green), and 5.0 mM PPFOS (blue), respectively. B) Absorption Spectra of SWCNTs suspended in [BMIM]PF₆ and after adding various surfactants, from top to bottom, without any additives (black), 2.5mM PFOA (red), 2.5mM LDS (green), 2.5mM SDS(blue), 8.8mM PDS(cyan), and 5.0mM PPFOS (magenta), respectively. The spectra are baseline-corrected and normalized to the intensity at 470 nm.

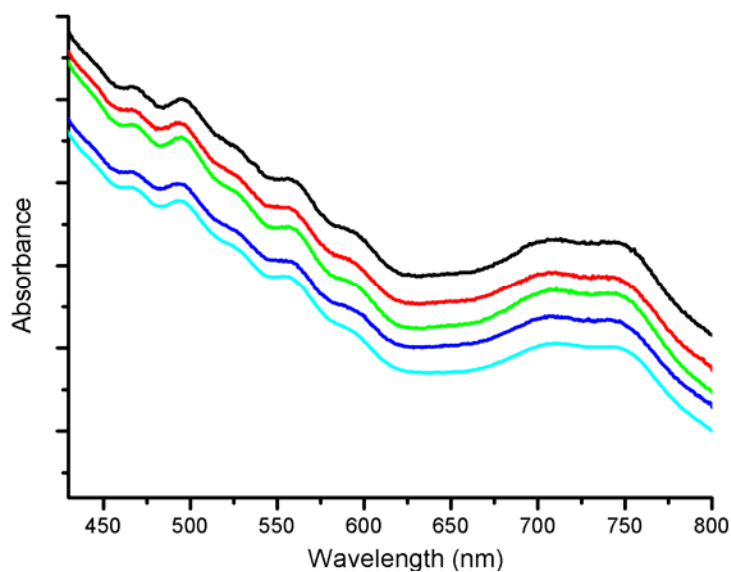


Figure S3. Absorption spectra of SWCNTs suspended in [BMIM]PF₆ after adding 0.0025 M PPFOS (red), 0.013 M PPFOS (green), 0.025M PPFOS (blue), 0.043 M PDS(cyan), respectively. The black profile is the spectrum of SWCNTs in [BMIM]PF₆ without any additives.

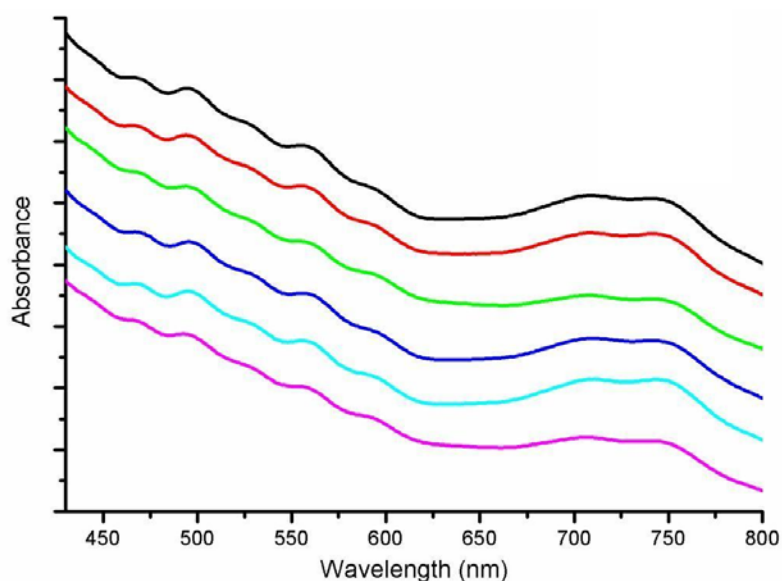


Figure S4. Absorption spectra of SWCNTs suspended in [BMIM]BF₄ after adding 0.016 M PFOA (red), 0.025 M LDS (green), 0.024 M LDS SDS (blue), 0.013 M PPFOS (cyan), and 0.012 M CaDS (magenta), respectively. The black profile is the spectrum of SWCNTs in [BMIM]BF₄ without any additives.

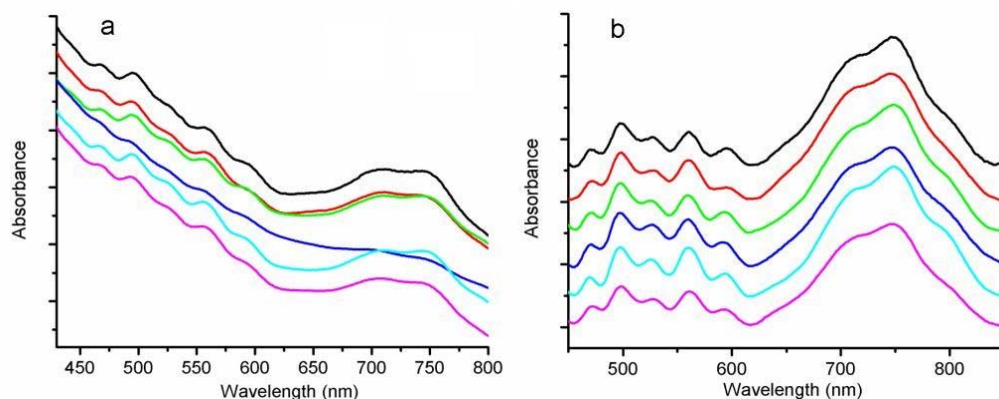


Figure S5. Absorption spectra before (a) and after baseline correlation (b) for SWCNTs suspended in [BMIM]PF₆ after adding 0.011 M NaCl (red), 0.028 M octanoic acid (green), 0.0045 M sodium stearat (blue), 0.0059 M sodium tartrate (cyan), and 0.0066 M dodecyl acid (magenta), respectively. The black profile is the spectrum of SWCNTs in [BMIM]PF₆ without any additives. (b) has been normalized to the intensity at 470 nm.

4. Detailed discussion about the Raman data.

The resonance Raman spectra is sensitive to the SWCNTs' electronic transition energy. When the electronic transition energy changes, the resonance Raman profile will change accordingly. For metallic SWCNTs whose E_{11} is in resonance with 1.96 eV excitation, their RBM bands appear at $\sim 173 \text{ cm}^{-1}$. For large diameter semiconducting SWCNTs whose E_{33} is in resonance with 1.96 eV excitation, their RBM bands appear at $\sim 156 \text{ cm}^{-1}$. The RBM bands of both kinds of SWCNTs become weaker when PFOA was added because they are out of resonance. This indicates the shift of their electronic transition energy. For the small diameter semiconducting SWCNTs whose E_{33} is in resonance with 1.96 eV excitation, their RBM bands appear at $\sim 166 \text{ cm}^{-1}$. It is still in the same resonance condition as before when PFOA was added. They do not diminish their RBM intensity. When using a 1.58 eV laser, the Raman signal mainly comes from the metallic SWCNTs in our sample. (Figure S6) Upon addition of PFOA, the metallic SWCNTs lost their RBM band intensity. The above results indicates that the PFOA selectively interact with metallic and large diameter semiconducting SWCNTs.

The overall G band ($\sim 1590 \text{ cm}^{-1}$ in Figure 1e and Figure S6) intensity change little with the increase of the PFOA concentration. The G band intensity at $\sim 1590 \text{ cm}^{-1}$ shows an upshift by $\sim 1 \text{ cm}^{-1}$ (1.96 eV) and $\sim 3 \text{ cm}^{-1}$ (1.58 eV), due to C-C bond strengthening of the positive charged SWCNTs. The broad peak at $\sim 1550 \text{ cm}^{-1}$ is the Breit-Wigner-Fano (BWF) mode of

the metallic SWCNTs. According to previous study, the BWF mode results from the phonon coupling to the continuum electronic states near the Fermi level. In our case, the high energy electrons transfer from SWCNTs to the cations, leaving positive charges in the nanotube. This leads to a shift of the Fermi level for metallic SWCNTs. The phonon coupling to the continuum electronic states near the Fermi level is lessened. A diminishment of BWF mode feature is observed with the increase of the PFOA concentration.

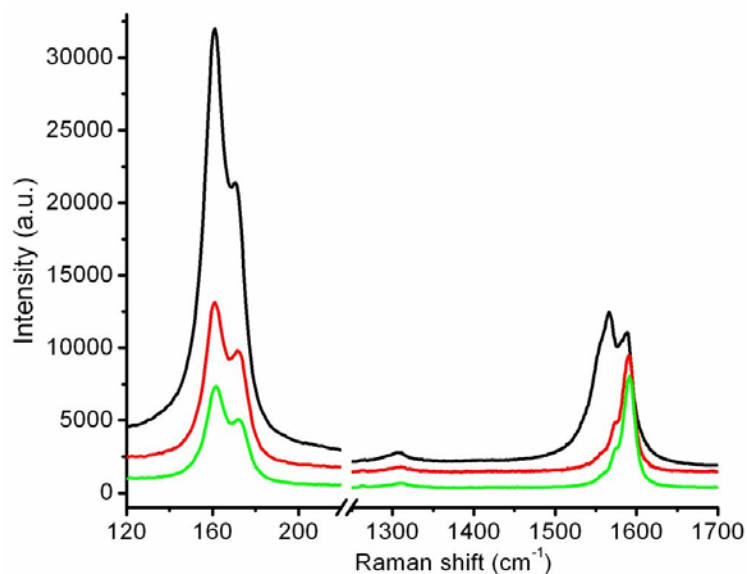


Figure S6. Raman spectra ($E_{\text{laser}} = 1.58$ eV), from top to bottom, upon addition of 0.0(black), 1.6 (red) and 3.3 (green) mM PFOA, respectively.

5. Effect of the crown ether.

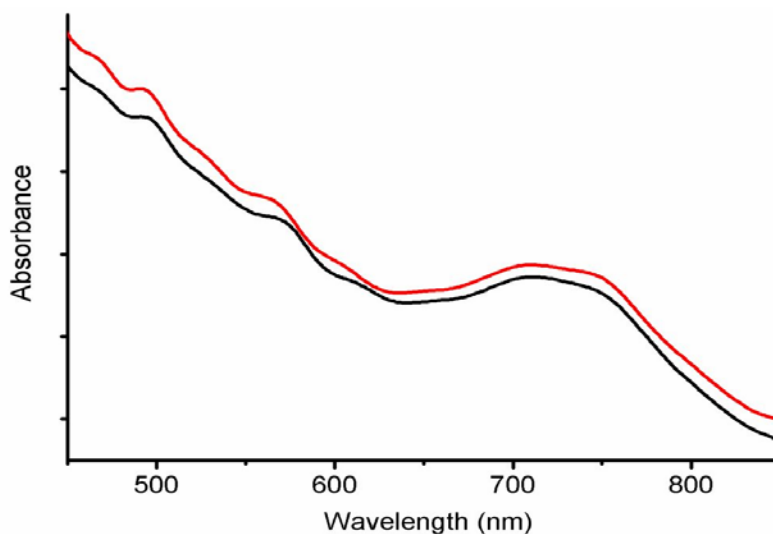


Figure S7. Absorption spectra of SWCNTs together with 2.5mM LDS suspended in [BMIM]PF₆ before (black) and after (red) adding 1.0 wt% 12-crown-4.

Upon the addition of 1.0 wt% 12-crown-4, the E_{33} transitions of the large-diameter semiconducting SWCNTs tend to recover. The metallic E_{11} peaks did not revert to their initial intensities upon the addition of 1.0 wt% crown ether. This indicates that the metallic SWCNT has priority over the semiconducting SWCNT when interacting with the surfactant. Crown ether has absorption band in the near-infrared region, which makes it is unable to find out the change of E_{22} peaks for the large-diameter semiconducting SWCNTs.

6. Explanation on the change of the absorption spectra.

We performed local-density approximation calculation to investigate the change in the band structures and absorption spectra of SWCNTs after the modification by anionic surfactant. Due to the modification, electrons should transfer from the SWCNTs to the surfactants, thus resulted in the positive charging of SWCNTs.

Figure S8 shows the band structures and densities of the states of (10, 10) and (19, 0) SWCNTs with different amount of positive charges. It can be clearly seen that shift of the Fermi energy and the band structure occur as a result of charge transfer. When increasing the amount of positive charges on SWCNT, the Fermi energy and the band structure are further shifted. The high energy electrons in the vicinity of Fermi level are more easily affected than the lower energy electrons. The first van Hove singularity of the valence band will firstly become an empty state, followed by the second van Hove singularity. The absorption bands arise from the optical transitions between corresponding pairs of singularities. Since the

electrons have been exhausted, there are no electrons taking part in the optical transitions, thus the corresponding absorption bands will disappear.

In our case, the E_{33} absorption bands of the large diameter semi-conducting SWCNTs do not diminish but red shift to lower energy. This indicates that the electron states of the third van Hove singularity in the valence band are not empty. The shift of the absorption bands should be attributed to the charge transfer induced perturbation on the SWCNT. The high energy electrons near the Fermi level have a screening effect on the electrons in the third van Hove singularity. The screening effect is reduced after charge transfer, since the high energy electrons have been exhausted. The empty of previous occupied electron states has a net bonding contribution to the SWCNT. Additionally, we observe a geometry relaxation and a slight decrease in the C-C bond length upon charge transfer. For example, the C-C bond length decreases by 0.001 Å after charge transfer for the (19, 0) (0.0197 e per carbon atom). The above reasons may lead to the red shift of the E_{33} absorption band.

For the small diameter semi-conducting SWCNT, no charge transfer occurs due to its large band gap. Its band structure is maintained, thus no change in its absorption band is observed.

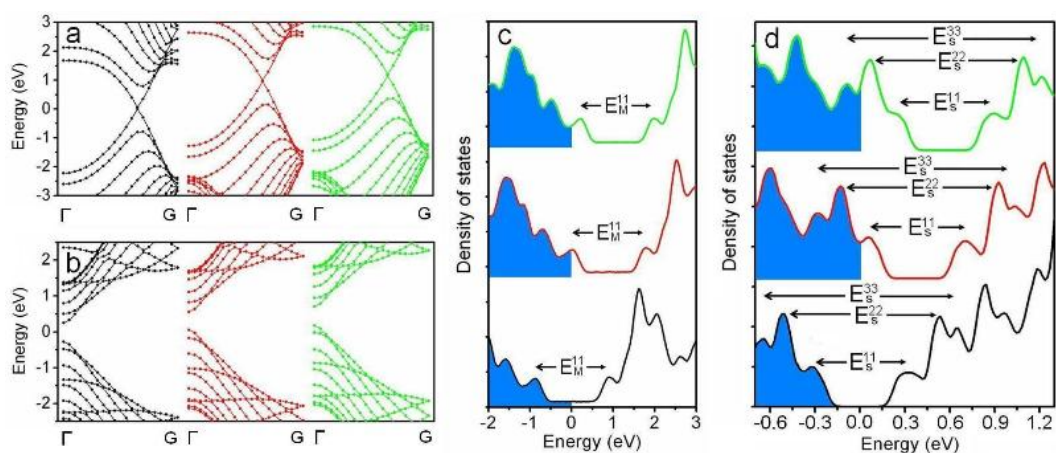


Figure S8. Band structure (a) and density of states (c) of (10, 10) SWCNT with different amount of positive charges: 0 (black), 0.0250 e per carbon atom (red) and 0.0375 e per carbon atom. Band structure (b) and density of states (d) of (19, 0) SWCNT with different amount of positive charges: 0 (black), 0.0132 e per carbon atom (red) and 0.0197 e per carbon atom.

7. Comparison between the SWCNTs suspended in [BMIM]PF₆ and those in water

The dispersing ability of ionic liquids is obviously much higher than that of the aqueous

media. Even with the help of some surfactants such as PFOA and PPFOS, SWCNT samples still could not be effectively dispersed in aqueous solution at various concentrations. It is well known that SDS can disperse SWCNTs in aqueous solution. However, usually the SWCNT samples cannot be dispersed thoroughly even under strong sonication and a centrifugation procedure is needed to remove the insoluble residues. Therefore, it is impossible to prepare an aqueous SDS suspension of SWCNTs with fixed concentration by weighing certain amount of SWCNT samples. Whereas in [BMIM]PF₆, the SWCNTs can be completely dispersed at a concentration as high as 1 wt% (> 10 g/L) simply by mechanical milling. And the addition of surfactants to [BMIM]PF₆ does not show any obvious influence on the dispersion of SWCNTs. This indicates that [BMIM]PF₆ is a very good solvent for the spectroscopic study of SWCNTs.

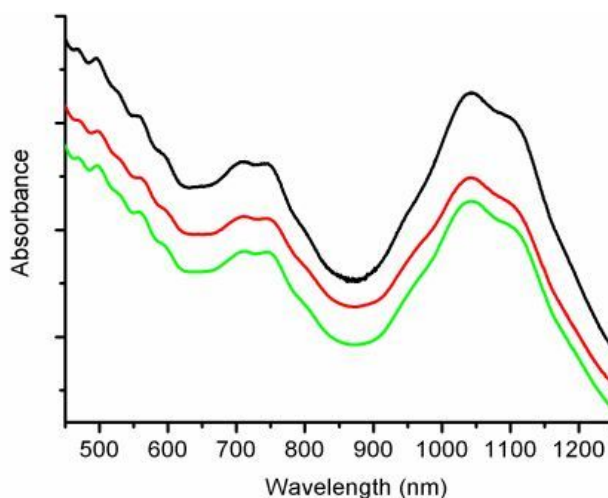


Figure S9. Absorption spectra of SWCNTs suspended in pure [BMIM]PF₆ (black), 34.7 mM LDS aqueous solution (red), and 34.7 mM SDS aqueous solution (green). The spectra have been scaled for clear comparison.

Figure S9 shows the absorption spectra of SWCNTs suspended in 34.7 mM LDS and 34.7 mM (1 wt %) SDS aqueous solutions as well as SWCNTs in [BMIM]PF₆. The three spectra are very similar in their profiles. The absorption bands in the three spectra appear at almost the same positions, which is in agreement with the results reported by Takanori Fukushima et al.² Because both the ionic liquids and the anionic surfactants in water interact with SWCNTs through weak van der Waals interaction,³ then the electronic structures of SWCNTs in both cases can be kept intrinsically and therefore the absorption spectra are similar. It must be pointed out that in [BMIM]PF₆ media, even the concentrations of SDS and LDS are only

several mM, which is only 10 percent of our tested concentration in aqueous media, the absorption bands of SWCNTs still change obviously. This shows the big difference between the interactions of SWCNTs with anionic surfactants in water and those in ionic liquids.

Previous study by Strano et al. found that the transition energy of the SWCNTs red-shifted slightly to lower energy when decreasing the concentration of the anionic surfactant in water below its critical micellar concentration.⁴ This is due to an increase in micropolarity at the nanotube surface with the decrease of the concentration of the anionic surfactant.^{4,5} The transition energy shift shows no nanotube diameter or type selectivity, since the change of micropolarity influences all kinds of nanotubes in the same way. The spectral profiles of all tubes are largely preserved with only slight shift in their peak positions.

In [BMIM]PF₆, the change of the electronic structure of SWCNT upon the addition of surfactant is different from that in the aqueous solution. The change of the spectra is ascribed to the charge transfer between the cations of the surfactants and certain kinds of SWCNTs. The surfactant selectively interacts with the SWCNTs in a much stronger way. Only metallic and large diameter semi-conducting SWCNTs interact with the surfactants. For the semi-conducting SWCNTs with a small diameter, no charge transfer occurs, thus their spectral profiles remain unchanged. For metallic and large diameter semi-conducting SWCNTs, the electrons near the Fermi have been exhausted after interacting with the surfactants. Since there are no electrons taking part in the optical transitions, the corresponding absorption bands disappear. The optical transitions far away from the Fermi level do not lose their spectral profiles but red-shift when increasing the concentration of surfactants, which is just in an opposite trend to that in the aqueous solution⁴.

Reference:

- (1) Li, H.; Guan L.; Shi, Z.; Gu, Z. *Solid State Communications* **2004**, *132*, 219-224.
- (2) Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Takigawa, T.; Ishii, N.; Aida, T. *Science* **2003**, *300*, 2072-2074.
- (3) Wang, J.; Chu, H.; Li, Y. *ACS Nano*, **2008**, *2*, 2540-2546.
- (4) Strano, M. S.; Miller, M. K.; Allen, M. J.; Moore, V. C.; O'Connell, M. J.; Kittrell, C.; Hauge, R. H.; Smalley, R. E. *J. Nanosci. Nanotechnol.* **2003**, *3*, 81-86.
- (5) Moore, V. C.; Strano, M. S.; Haroz, E. H. ; Hauge, R. H.; Smalley, R. E. *Nano Lett.* **2003**, *3*, 1379-1382.