ACS APPLIED MATERIALS & INTERFACES
Letter
www.acsami.org

Effect of π–π+ Stacking on the Layering of Ionic Liquids Confined to an Amorphous Carbon Surface

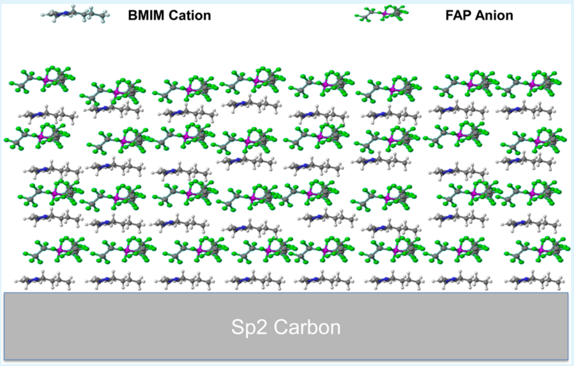
Xiao Gong,[†] Andrew Kozbial,[†] Franck Rose,[‡] and Lei Li*,[†]

[†]Department of Chemical & Petroleum Engineering, Swanson School of Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States

[‡]San Jose Research Center, HGST, A Western Digital Company, 3403 Yerba Buena Road, San Jose, California 95135, United States

Supporting Information

ABSTRACT: In the current paper, AFM studies were conducted on nanometer-thick ionic liquids (ILs) confined to an amorphous carbon (AC) surface, which is critical to the design of the next-generation media lubricant for hard disk drives (HDDs). The results indicated that the existence of the delocalized ring in the cation is critical to layering of ILs. Extended layering was observed only when there is imidazolium ring in the cation. When the imidazolium ring is replaced by an aliphatic moiety, "drop-on-layer" (dewetting) structure was observed. On the basis of the experimental results, we proposed that π–π+ stacking between sp^2 carbon in the AC and the imidazolium cation in the ILs is the key to the extended layering of ILs at the ILs/AC interface.



KEYWORDS: *ionic liquid, π–π+ stacking, layering, media lubricant, amorphous carbon, hard disk drives*

Although room-temperature ionic liquids (RTILs) are salts composed of ions, they are liquids instead of crystalline solids at ambient temperatures. This is because the ions in RTILs are sterically mismatched anions/cations and, as a result, Coulombic attractions are dampened and lattice structure is not formed.[1] When a liquid is confined to a solid surface, the molecular organization of the liquid could be very different from that in the bulk.[1,2] Adjacent to the solid surface, mobile liquid molecules are induced into discrete "solid-like" layers, which could extend to a few molecular diameters from the interface.[2] This liquid ordering, termed "solvation layers", is characterized by an oscillatory molecular density profile and has been observed for many liquids, including simple molecular liquids and polymer melts.[2,3] It is believed that geometric factor (entropy) is critical to the formation of solvation layers, because layering even occurs in the absence of attractive solid–liquid interactions.[2] It has been proposed that the translational entropy available to the liquid molecules under spatial confinement decreases to the point at which it becomes thermodynamically favorable for the molecules to form ordered layering structure.[14] Meanwhile, the strong interfacial solid–liquid attraction, e.g., Coulombic force, promotes the layering structure.[2]

On the basis of the discussion above, it should not be a surprise to find that there are "solid-like" solvation layers of RTILs at RTIL/solid interface. Indeed, several researchers have reported the "solid-like" layering structure of RTILs on solid surfaces.[4−7] What is surprising here is how far the layering structure could extend. Carmichael et al.[4] studied silica-support imidazolium RTIL nanofilms (10−20 nm) with X-ray reflectivity (XRR) and found that, after annealing, the molecular layering is throughout the entire film. In a high-energy XRR study, Mezger et al.[5] found that three bulk RTILs with the tris(pentafluoroethyl)trifluorophosphate (FAP) anion in contact with a charged sapphire substrate show "solid-like" multilayer structure extending at least seven molecular diameters into the bulk liquid. Bovio et al.[6] studied RTIL/mica interface and found that the layering of RTIL molecules could extend to 50 nm above the solid surface. Because all the above-mentioned solid surfaces[4−6] are negatively charged, it is tempting to attribute this unusually thick solvation layers to the strong Coulombic interaction between the solid surface and RTILs. Indeed, Gebbie et al.[7] recently proposed that ionic liquids screen charged solid surfaces through the formation of both bound (Stern) and diffuse electric double layers, where the diffuse double layer comprises effectively dissociated ionic liquid ions and can extend to tens of molecular diameters. The same authors[7] also proposed that the Coulombic force between the charged solid surface and RTILs depends on the detailed structure of RTILs, which explains why the extensive solvation layers were not always observed on the charged surfaces.[8,9] It seems that now the unusually thick solvation layer of RTILs can be reasonably explained by the Coulombic interaction.

Received: February 6, 2015
Accepted: March 26, 2015
Published: March 26, 2015

DOI: 10.1021/acsami.5b01140

However, Atkin and Warr[9] found that, on highly ordered pyrolytic graphite (HOPG) surface that has no charge, 1-ethyl-3-methylimidazolium acetate (EMIM ACE) RTIL can form seven solvation layers, whereas the same RTIL has only three solvation layers on mica surface. Because HOPG surface has no charge, Coulombic force cannot be responsible for the extensive solvation layers of EMIM ACE on HOPG. Moreover, the fact that EMIM ACE has significantly thicker solvation layers on HOPG than on mica surface, which is negatively charged, also indicates that there must be other mechanisms. The extensive "solid-like" layering will have dramatic impact on the performance of RTILs confined to graphitic surfaces. For example, in nanofluids, layering of the liquid at the liquid/solid interface is one of the major mechanisms promoting the thermal conductivity.[10] Similarly, layering of RTILs is expected to change their friction and wear performance as media lubricants in hard disk drives.[11] It has also been reported that the solvation layers significantly impact the electrochemical reactions.[12] To date, studies on π−π+ stacking interactions are mainly focused on the interactions of nonheterocycles such as benzene ring, benzene dimmers, and substituents.[13,14] Few studies are focused on π−π+ stacking interactions between the ionic liquids containing heterocycles and carbon surface. From the design viewpoint, it is critical to understand the underlying mechanisms and key governing parameters of the unusually thick solvation layers of RTILs containing heterocycles on carbon surfaces so that the molecular structure of RTILs can be tailored to optimize the performance.

Because of their high thermal stability, RTILs have been proposed[15] to be the material candidate as nanometer-thick media lubricant for heat-assisted magnetic recording (HAMR) in hard disk drives (HDDs), where the lubricant is applied on top of an amorphous carbon (AC) surface with both sp^2 and sp^3 hybridization.[11] The molecular-level structure of RTILs confined to the AC surface is clearly essential to the lubricity of the RTIL nanolubricant in HDDs. However, to date, the understanding on the RTIL/AC interface is very limited. In the current study, we address this issue via an experimental approach by investigating the RTIL nanofilms confined to the AC surface, where the otherwise buried interface can be characterized more easily. Here we report on the direct AFM observation of nanoscale morphological and structural properties of ionic liquid nanofilms confined to an AC surface. AFM topography image shows a "drop-on-layer" structure in the 10 nm MOEDEA FAP/AC sample, whereas the smooth film structure is exhibited in the AFM topography image of 10 nm BMIM FAP/AC. Direct evidence of an extensive layering structure in BMIM FAP/AC is provided by AFM "cross-section" profile. The difference has been attributed to there being π−π+ stacking interactions between BMIM FAP and the AC surface because BMIM has an imidazolium ring, whereas such interaction does not exist at the interface between MOEDEA FAP and the AC because MOEDEA has a nonconjugated ammonium structure. The results indicate that the π−π+ stacking between RTILs and the sp^2 carbon is a key parameter tailoring the molecular-level structure of RTILs confined to a solid substrate. Our work provides the valuable information on the design of RTILs as a nanometer-thick media lubricant in HDD industry.

The two selected RTILs utilized in the current study are 1-butyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (BMIM FAP) and Ethyldimethyl-(2-methoxyethyl) ammonium tris(pentafluoroethyl)trifluorophosphate (MOEDEA FAP) and their chemical structures are shown in Figure 1. The BMIM FAP nanofilms were dip-coated on the solid substrates and the film thickness was determined by ellipsometry,[16] based on the procedure established in our lab previously.[17] It has been well-documented that AFM is powerful in characterizing the "layering" of ILs at the IL-solid interface.[18−21] Here, we also used AFM to investigate the topography of ILs on the AC surface. When 1 nm BMIM FAP is dip-coated on a silicon wafer, although silicon wafer has a negative surface charge,[1] BMIM FAP shows the "drop-on-film" (dewetting) structure as shown in Figure 2a, indicating that the bulk liquid phase (droplets) stays on top of the solvation layers that are not extensive at all.[17] However, when the same 1 nm BMIM FAP is applied on the AC surface, which has no surface charge, a smooth topography that has the same roughness (around 0.2 nm) as the bare AC is observed by AFM (Figure 2b).

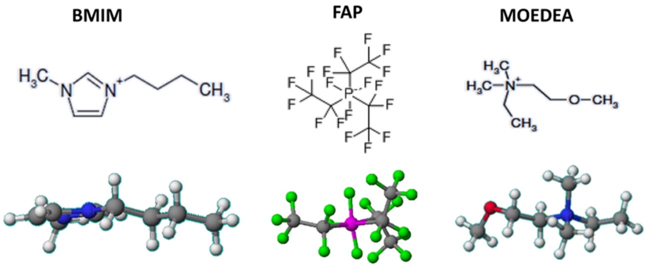


Figure 1. Molecular structure of the anion and cations in the ionic liquids used in this study.

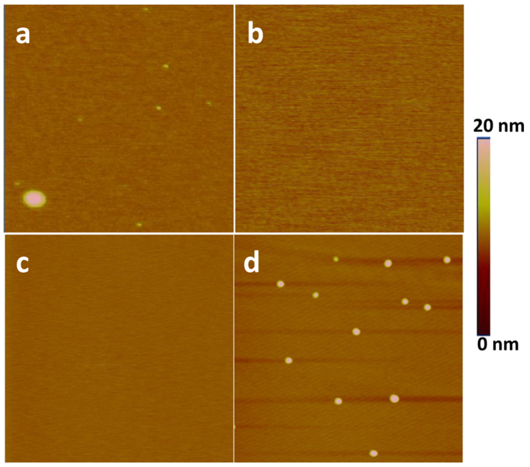


Figure 2. AFM topography of 1 nm BMIM FAP on (a) a silicon wafer and (b) an AC surface. Image is 2 μm × 2 μm. AFM topography of (c) 10 nm BMIM FAP on AC, and (d) 10 nm MOEDEA FAP on AC. Image is 10 μm × 10 μm.

AFM topography images further show that BMIM FAP forms the very uniform film on the AC surface even when the thickness is as high as 10 nm (Figure 2c). Because the monolayer thickness (ML) is estimated to be 0.84 nm for BMIM FAP,[17] the AFM results suggest that the solvation layers of BMIM FAP on the AC surface could extend to 12 MLs. To further test the existence of the extended layering structure of BMIM FAP on the AC surface, we also conducted a "cross-section" AFM experiment. In this experiment, the BMIM FAP/AC sample was punctured gently with a sharp needle and then

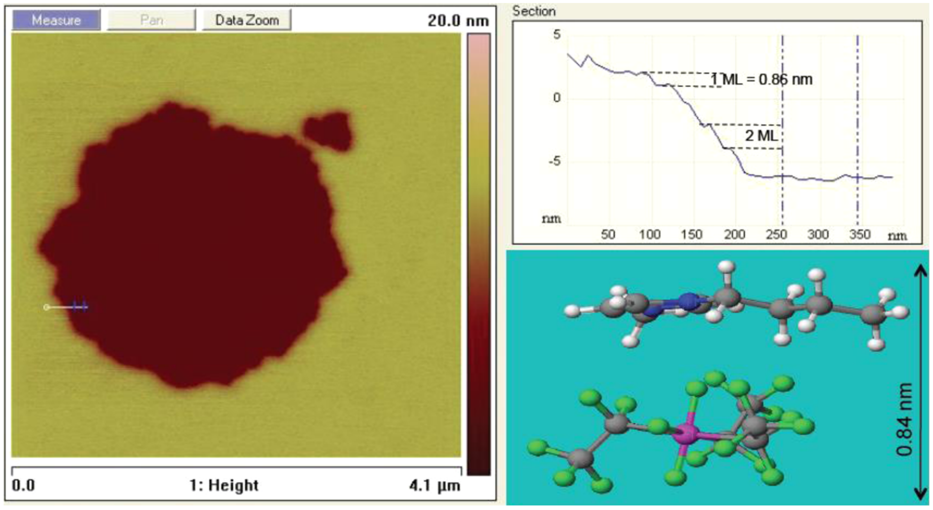


Figure 3. Ten nanometer BMIM FAP on AC with a "hole" and "cross-section" AFM profile of BMIM FAP/AC.

the topography of the created "hole" was characterized by AFM. As shown in Figure 3, along the inner wall of the "hole", well-defined steps are clearly visible, indicating the extended layering structure. The step height is either one ML or two MLs, matching the estimated ML thickness very well. The ML thickness is estimated to be 0.84 nm for BMIM FAP[17] and AFM results showed that ML step height is 0.85 nm. The "cross-section" AFM topography analysis confirms that there is extended layering of BMIM FAP confined to the AC surface.

To investigate the possible effect of π−π+ stacking between ILs and the AC surface, we tested another RTIL, MOEDEA FAP, on the AC surface. Compared to BMIM FAP, MOEDEA FAP has the same anion but different cation. The imidazolium ring in BMIM is replaced by a nonconjugated ammonium in MOEDEA (See Figure 1). Interestingly, as shown in Figure 2d, a "drop-on-film" structure is clearly detected in the AFM topography image of 10 nm MOEDEA FAP/AC, indicating that the number of solvation layers formed is significantly less than BMIM FAP/AC. AFM results suggest that there are π−π+ stacking between BMIM FAP and AC surface because BMIM has aromatic imidazolium rings, whereas such interaction does not exist between MOEDEA FAP and the AC surface because MOEDEA only has aliphatic ammonium cations.

In the previous report[9] showing the extensive solvation layers of RTILs on HOPG, the RTIL used, 1-ethyl-3-methylimidazolium acetate (EMIM ACE), has different anion but also contains imidazolium ring in the cation. Our results are consistent with ref 9 and both studies suggest that there are unusually thick solvation layers of RTILs on sp^2 carbon surfaces even when there is no interfacial Coulombic force. It has also been reported that single-walled carbon nanotubes form "bulky gels" when they are mixed with imidazolium-containing RTILs and it was proposed that the π−π+stacking between the imidazolium ring and the sp^2 carbon in the nanotubes initiates the ordered long-range packing of RTIL molecules.[22]

In the imidazolium cation, the positive charge is delocalized (π+).[23] When the imidazolium cation is in contact with the solid surface containing sp^2 carbon (π electron), e.g., HOPG and amorphous carbon (has ~70% sp^2 carbon), π−π+ interaction could occur at the interface. The π−π+ interaction originates from both electrostatic and nonelectrostatic interaction and the exact nature is still a matter of investigation.[23] However, previous studies[23,24] suggested that if the π−π+ interaction occurs between sp^2 π electron and the imidazolium ring, the imidazolium ring could take a parallel orientation to the solid substrate, e.g., π−π+ stacking, because the imidazolium ring is a delocalized π system. As a result, RTIL cations form a highly ordered "lamella-like" structure on the solid surface. In other words, the solid surface serves as a template to orient the imidazolium ring in an ordered parallel geometry, which does not exist in the bulk liquid. This parallel geometry initiates the extensive solvation layers and the Coulombic force between anions and cations of RTILs could further promote the growth of the lamella-like structure. It needs to be pointed out that, on the basis of this mechanism, the Coulombic force between the solid surface and RTILs is not necessary for the formation of the extensive solvation layers, as indicated in our data here and in the previous report.[9] To further confirm the π−π+ stacking effect, we dip-coated three more ILs, 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (EMIM FAP), 1-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate (HMIM FAP), and 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (DMPIIm), respectively, on the AC surface (10 nm films). AFM results showed they all form uniform films on the AC surface, indicating extended layering structure, just like BMIM FAP (see Figure S1 in the Supporting Information). It has been reported that the alkyl chain length of the ionic liquid cation affects the properties and structure of the IL films.[25] These three ILs all contain imidazolium in the cation; but have different substitute structure. Therefore, the results support the hypothesis that π−π+ stacking is the key to extended layering of ILs. This proposed mechanism is schematically shown in Figure 4. Clearly, the formation of the "solid-like" layering will impact the friction and wear performance of nanometer-thick RTILs dramatically as the media lubricant in HDDs. Our results suggest that π−π+ stacking is a critical design parameter in the development of the next-generation media lubricants for HAMR in HDDs.

In conclusion, nanoscale morphological and structural properties of two nanometer-thick RTILs, BMIM FAP and MOEDEA FAP, on the AC surface were characterized by ellipsometry and AFM. AFM topography images showed a "drop-on-layer" structure on the MOEDEA FAP/AC sample. However, smooth topography was observed for the BMIM

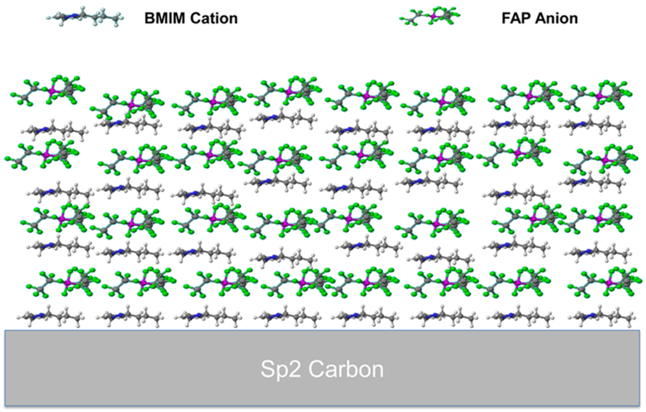


Figure 4. Proposed "lamella-like" structure of solvation layers in BMIM FAP on the sp^2 carbon surface.

FAP/AC sample, where "cross-section" AFM profile analysis confirmed that there is an extensive layering structure in BMIM FAP/AC. The difference between BMIM FAP and MOEDEA FAP has been attributed to there being $\pi-\pi+$ stacking between BMIM FAP and the AC surface because BMIM has an aromatic imidazolium ring, although such interaction does not exist between MOEDEA FAP and the AC surface because MOEDEA has a nonconjugated ammonium. Our results highlight the importance of the $\pi-\pi+$ stacking in determining the molecular-level structure of RTILs confined to the AC surface and provide the valuable information for the future design of RTILs as media lubricants for HAMR in HDD industry.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details including materials, fabrication of AC films, deposition of ionic liquid nanofilms on AC, and characterization of RTIL nanofilms. AFM images of EMIM FAP, HMIM FAP, and DMPIIm on AC surface, respectively. This material is available free of charge via the Internet at http://pubs.acs.org/.

AUTHOR INFORMATION

Corresponding Author

*E-mail: lel55@pitt.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully thank the Advanced Storage Technology Consortium (ASTC) for the financial support. X.G. acknowledges the financial support by the National Natural Science Foundation of China (21104069).

REFERENCES

(1) Hayes, R.; Warr, G. G.; Atkin, R. At the Interface: Solvation and Designing Ionic Liquids. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1709–1723.

(2) Israelachvili, J. N. *Intermolecular and Surface Forces*, revised third ed.; Academic Press: New York, 2011.

(3) Granick, S. Motions and Relaxations of Confined Liquids. *Science* **1991**, *253*, 1374–9.

(4) Carmichael, A. J.; Hardacre, C.; Holbrey, J. D.; Nieuwenhuyzen, M.; Seddon, K. R. Molecular Layering and Local Order in Thin Films of 1-alkyl-3-methylimidazolium Ionic Liquids using X-ray Reflectivity. *Mol. Phys.* **2001**, *99*, 795–800.

(5) Mezger, M.; Schröder, H.; Reichert, H.; Schramm, S.; Okasinski, J. S.; Schöder, S.; Honkimäki, V.; Deutsch, M.; Ocko, B. M.; Ralston, J. Molecular Layering of Fluorinated Ionic Liquids at a Charged Sapphire (0001) Surface. *Science* **2008**, *322*, 424–428.

(6) Bovio, S.; Podesta, A.; Lenardi, C.; Milani, P. Evidence of Extended Solidlike Layering in [BMIM][NTf2] Ionic Liquid Thin Films at Room-Temperature. *J. Phys. Chem. B* **2009**, *113*, 6600–6603.

(7) Gebbie, M. A.; Valtiner, M.; Banquy, X.; Fox, E. T.; Henderson, W. A.; Israelachvili, J. N. Ionic Liquids Behave as Dilute Electrolyte Solutions. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 9674–9679.

(8) Deyko, A.; Cremer, T.; Rietzler, F.; Perkin, S.; Crowhurst, L.; Welton, T.; Steinruck, H. P.; Maier, F. Interfacial Behavior of Thin Ionic Liquid Films on Mica. *J. Phys. Chem. C* **2013**, *117*, 5101–5111.

(9) Atkin, R.; Warr, G. G. Structure in Confined Room-Temperature Ionic Liquids. *J. Phys. Chem. C* **2007**, *111*, 5162–5168.

(10) Keblinski, P.; Phillpot, S. R.; Choi, S. U. S.; Eastman, J. A. Mechanisms of Heat Flow in Suspensions of Nano-Sized Particles (Nanofluids). *Int. J. Heat Mass Transfer* **2002**, *45*, 855–863.

(11) Kasai, P. H. Carbon Overcoat: Structure and Bonding of Z-DOL. *Tribol. Lett.* **2002**, *13*, 155–166.

(12) Endres, F.; Höfft, O.; Borisenko, N.; Gasparotto, L. H.; Prowald, A.; Al-Salman, R.; Carstens, T.; Atkin, R.; Bund, A.; El Abedin, S. Z. Do Solvation Layers of Ionic Liquids Influence Electrochemical Reactions? *Phys. Chem. Chem. Phys.* **2010**, *12*, 1724–1732.

(13) Li, P.; Zhao, C.; Smith, M. D.; Shimizu, K. D. Comprehensive Experimental Study of N-Heterocyclic pi-Stacking Interactions of Neutral and Cationic Pyridines. *J. Org. Chem.* **2013**, *78*, 5303–5313.

(14) Smith, T.; Slipchenko, L. V.; Gordon, M. S. Modeling Pi-Pi Interactions with the Effective Fragment Potential Method: The Benzene Dimer and Substituents. *J. Phys. Chem. A* **2008**, *112*, 5286–5294.

(15) Li, H.; Wood, R. J.; Rutland, M. W.; Atkin, R. An Ionic Liquid Lubricant Enables Superlubricity to Be "Switched On" In Situ using an Electrical Potential. *Chem. Commun.* **2014**, *50*, 4368–4370.

(16) Wang, Y. J.; Sun, J. N.; Li, L. What Is the Role of the Interfacial Interaction in the Slow Relaxation of Nanometer-Thick Polymer Melts on a Solid Surface? *Langmuir* **2012**, *28*, 6151–6156.

(17) Gong, X.; Frankert, S.; Wang, Y.; Li, L. Thickness-dependent molecular arrangement and topography of ultrathin ionic liquid films on a silica surface. *Chem. Commun.* **2013**, *49*, 7803–7805.

(18) Liu, Y. D.; Zhang, Y.; Wu, G. Z.; Hu, J. Coexistence of liquid and solid phases of Bmim-PF6 ionic liquid on mica surfaces at room temperature. *J. Am. Chem. Soc.* **2006**, *128*, 7456–7457.

(19) Bovio, S.; Podesta, A.; Lenardi, C.; Milani, P. Evidence of Extended Solidlike Layering in [Bmim][NTf2] Ionic Liquid Thin Films at Room-Temperature. *J. Phys. Chem. B* **2009**, *113*, 6600–6603.

(20) Yokota, Y.; Harada, T.; Fukui, K. I. Direct observation of layered structures at ionic liquid/solid interfaces by using frequency-modulation atomic force microscopy. *Chem. Commun.* **2010**, *46*, 8627–8629.

(21) Hayes, R.; Warr, G. G.; Atkin, R. At the interface: solvation and designing ionic liquids. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1709–1723.

(22) Fukushima, T.; Kosaka, A.; Ishimura, Y.; Yamamoto, T.; Takigawa, T.; Ishii, N.; Aida, T. Molecular Ordering of Organic Molten Salts Triggered by Single-Walled Carbon Nanotubes. *Science* **2003**, *300*, 2072–2074.

(23) Ma, J. C.; Dougherty, D. A. The Cation-π Interaction. *Chem. Rev.* **1997**, *97*, 1303–1324.

(24) Singh, R.; Monk, J.; Hung, F. R. A Computational Study of the Behavior of the Ionic Liquid [BMIM+][PF6−] Confined Inside Multiwalled Carbon Nanotubes. *J. Phys. Chem. C* **2010**, *114*, 15478–15485.

(25) Smith, A. M.; Lovelock, K. R. J.; Perkin, S. Monolayer and bilayer structures in ionic liquids and their mixtures confined to nano-films. *Faraday Discuss.* **2013**, *167*, 279–292.