Ionic Liquids

Deutsche Ausgabe: DOI: 10.1002/ange.201600419
Internationale Ausgabe: DOI: 10.1002/anie.201600419

Tuning the Hydrophilicity and Hydrophobicity of the Respective Cation and Anion: Reversible Phase Transfer of Ionic Liquids

*Wenhui Yao, Huiyong Wang, Guokai Cui, Zhiyong Li, Anlian Zhu, Suojiang Zhang, and Jianji Wang**

Abstract: *The separation and recycling of catalyst and cocatalyst from the products and solvents are of critical importance. In this work, a class of functionalized ionic liquids (ILs) were designed and synthesized, and by tuning the hydrophilicity and hydrophobicity of cation and anion, respectively, these ILs could reversibly transfer between water and organics triggered upon undergoing a temperature change. From a combination of multiple spectroscopic techniques, it was shown that the driving force behind the transfer was originated from a change in conformation of the PEG chain of the IL upon temperature variation. By utilizing the novel property of this class of ILs, a highly efficient and controllable CuI-catalyzed cycloaddition reaction was achieved wherein the IL was used to entrain, activate, and recycle the catalyst, as well as to control the reaction.*

Phase-transfer processes for two immiscible liquid phases have been widely employed for various applications, such as recycling of catalysts,[1] transfer of nanoparticles from a preparation medium to an application medium,[2] and transport across biological membranes.[3] Indeed, it is more important to develop novel strategies for the use of an external stimulus to induce the reversible phase transfer of a substance. For example, Cole-Hamilton et al.[1a] reported that a rhodium catalyst could move back and forth between aqueous and toluene phases using CO_2 as a trigger, and thus simplifying the process for recycling and reusing the catalyst. Tan et al.[1d] demonstrated a reversible phase transfer of α-cyclodextrin-coated gold nanoparticles between aqueous and toluene phases, and it could be controlled by UV-visible light. Tang et al.[2b] reported a reversible phase transfer of CdTe nanoparticles between aqueous and toluene phases driven by temperature, and Ludwigs et al.[4] found that polythiophenes with a carboxylic acid group could reversibly transfer from the water phase to a mixture of THF and $CHCl_3$ by adjusting the pH value of the solution.

In the last two decades, ionic liquids (ILs) have been found widespread applications in chemical synthesis,[5] materials preparation,[6] biomass dissolution,[7] gas capture,[8] energy production,[9] and separation science[10] because of their unique properties,[11] such as ultralow vapor pressure, wide liquid temperature range, nonflammability, high stability, and tunable structure and property. Many efforts have been made to realize product separation from IL-based solvents by means of pressure,[12] temperature,[13] and CO_2.[14] For example, Leitner et al.[12a] and Cheng et al.[12b] found that a pressure-controlled supercritical CO_2/IL system provides superior advantages in product separation, catalyst recycling, and reuse of the reaction media over traditional organic solvents. Davis et al.[13a] and Wang et al.[13b] reported thermo-driven liquid-solid separation by using an alkane sulfonic acid IL as the solvent for esterification. Phase transfer of block copolymer micelles,[15] nanogels,[16] and carbon nanotubes[17] between H_2O and hydrophobic ILs, triggered by temperature, was also developed. ILs which exhibit phase separation in molecular solvents, depending on temperature, were also reported.[18] However, the separation and recycling of a catalyst and co-catalyst from the products and IL-related solvents still remain a key challenge. Therefore, searching for task-specific ILs for sustainable processes of chemical reactions, product separation, and catalyst and IL recycling is a long-standing topic. Considering the fact that the most interesting feature of ILs is that their structures and properties can be fine-tuned by a judicious variation of the cation and anion, we were interested in the creating of a class of thermo-responsive ILs which can reversibly transfer between water and organic phases to achieve easy separation and recycling of catalyst.

It is known that the bis(trifluoromethanesulfonyl)imide anion ($[NTf_2]^-$) is a strongly hydrophobic ion,[19] whereas poly(ethylene glycol) (PEG) is hydrophilic and has the ability to dissolve ILs,[20] as well as to coordinate with metallic organic salts[21] and inorganic salts.[22] In this work, a PEG unit was functionalized on both ends with methylimidazolium cations, and then paired with $[NTf_2]^-$ to form PEG-functionalized ILs. By tuning the hydrophilicity of the cation with the molecular weight of PEG against the hydrophobicity of the anion, these ILs can reversibly transfer between water and organic solvents triggered by temperature changes. Through a combination of multiple spectroscopic techniques, the mechanism for the phase transfer of the ILs between water and ethyl acetate (EA) was investigated. In particular, this unique phase behavior of the IL was applied to a CuI-catalyzed alkyne–azide cycloaddition. Thus a highly efficient

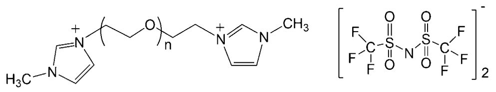
---

[*] W. Yao, Dr. H. Wang, Dr. G. Cui, Z. Li, Dr. A. Zhu, Prof. J. Wang
Henan Key Laboratory of Green Chemistry, Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007 (P.R. China)
E-mail: Jwang@htu.cn
Prof. S. Zhang
Beijing Key Laboratory of Ionic Liquids Clean Process
Institute of Process Engineering, Chinese Academy of Sciences
Beijing 100190 (P.R. China)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: http://dx.doi.org/10.1002/anie.201600419.

process was achieved by using ILs as the entrainer and activator of the catalyst, as well as the controller of the reaction. Additionally, the CuI and IL could be successfully recycled.

A series of functionalized ILs $[PEG_m(mim)_2][NTf_2]_2$ ($m =$ 200, 400, 600, 800, and 1000) were designed and synthesized, and their chemical structures, as shown in Scheme 1, were confirmed by IR and NMR spectroscopy and ESI-MS (see the Supporting Information). The glass transition temperature (T_g) and thermal decomposition temperature (T_d) of these ILs were determined and the results are listed in Table S1 (see the Supporting Information). It was found that all these ILs were liquid at room temperature ($T_g < -46$ °C), and highly stable at temperatures lower than 300 °C. Furthermore, it is clearly indicated that the values of T_g and T_d were not sensitive to the molecular weight of the PEG chain.



Abbreviation	Number of PEG Subunits (n)	PEG Molecular Weight (m)
$[PEG_{1000}(mim)_2][NTf_2]_2$	22	1000
$[PEG_{800}(mim)_2][NTf_2]_2$	17	800
$[PEG_{600}(mim)_2][NTf_2]_2$	12	600
$[PEG_{400}(mim)_2][NTf_2]_2$	9	400
$[PEG_{200}(mim)_2][NTf_2]_2$	4	200

Scheme 1. Structures of the functionalized ILs used in this work.

The phase transfer of $[PEG_m(mim)_2][NTf_2]_2$ was examined for aqueous and EA phases. It was found that $[PEG_{200}(mim)_2][NTf_2]_2$, $[PEG_{400}(mim)_2][NTf_2]_2$, and $[PEG_{600}(mim)_2][NTf_2]_2$ could not undergo reversible phase transfer between water and EA, and they preferred to stay in the EA. This result can be rationalized from the assumption that the hydrophilicity of these cations is not strong enough to compete with hydrophobicity of the anion. It is known that the hydrophilicity of PEGs increases with an increase of their molecular weight.[23] Indeed, it was found that $[PEG_{800}(mim)_2][NTf_2]_2$ and $[PEG_{1000}(mim)_2][NTf_2]_2$ could transfer from water to EA upon heating, and the ILs could almost exclusively transfer from EA to water upon cooling. Thus, reversible phase transfer of these functionalized ILs between water and organics was achieved by tuning the hydrophilicity and hydrophobicity of the cation and anion, respectively.

Here, as a representative example, $[PEG_{1000}(mim)_2][NTf_2]_2$ could move back and forth between water and EA by a change in temperature. When the two immiscible solvents were mixed with the IL in one glass vessel, a thermo-driven reversible phase transfer of the functionalized IL was observed upon heating and cooling (Figure 1). At 20 °C, a yellow solution (aqueous phase) was formed at the bottom of the vessel (Figure 1 a), while a colorless solution (EA phase) formed on the top, thus indicating that the IL was mainly present in the aqueous phase. When the temperature was increased to 50 °C, the lower phase became colorless, while the upper phase became yellow, thus indicating that the IL is present almost exclusively in the EA phase (Figure 1 b).

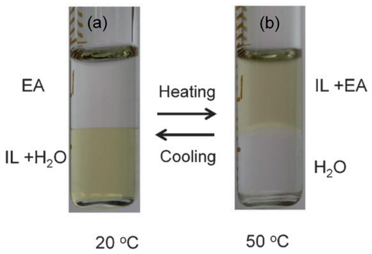


Figure 1. Photographs of the reversible phase transfer of $[PEG_{1000}(mim)_2][NTf_2]_2$ between aqueous and EA phases upon heating and cooling. The IL was originally dispersed in water (15 wt % IL) at 20 °C.

Importantly, the reversible phase transfer of this IL was observed for a wide range of IL content (see Table S2).

The transfer was also proven by UV spectrum experiments. It can be seen from Figure 2 that the typical absorbance peak at $\lambda = 211$ nm, which was assigned to the imidazolium ring,[24] became very weak in water when the temperature was increased from 20 to 50 °C. The opposite behavior was observed in EA. It is shown that 99 wt % of the IL preferred to stay in water at 20 °C, but 98 wt % of the IL was transferred from water to EA at 50 °C. The phase transfer of $[PEG_{1000}(mim)_2][NTf_2]_2$ between the aqueous and EA phases could be repeated at least 10 times without significantly altering the intensity and position of the IL peak in UV spectrum. Therefore, this IL can undergo spontaneous, quantitative, and reversible phase transfer between two immiscible phases upon a change in temperature.

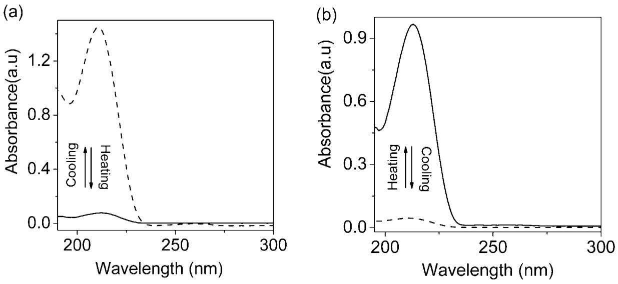


Figure 2. UV-vis spectra of $[PEG_{1000}(mim)_2][NTf_2]_2$ before and after phase transfer between H_2O and EA upon heating (solid, 50 °C) and cooling (dotted, 20 °C) as shown in Figure 1. The IL was originally dispersed in water (15 wt % IL) at 20 °C. a) H_2O. b) EA.

To gain a deeper insight into the phase transfer of the functionalized ILs, the phase behavior of $[PEG_{1000}(mim)_2][NTf_2]_2$ in neat water and EA was investigated at different temperatures by dynamic light scattering (DLS) measurements. Figure 3 shows the DLS size distribution as a function of temperature. It can be seen that with an increase of temperature, a sharp increase in the size of the aggregates was observed in water at 35 °C, which is close to the phase-transition temperature of the mixture (see Table S2). This observation can be ascribed to the formation of IL aggregates in water because of its decreased solubility.[1c] Thus, the solubility of $[PEG_{1000}(mim)_2][NTf_2]_2$ in water decreased with increasing temperature, and this is the typical phase behavior

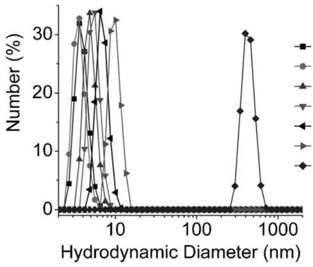


Figure 3. Number-average size distribution of $[PEG_{1000}(mim)_2][NTf_2]_2$ in H_2O (15 wt% IL) observed by DLS as a function of temperature.

of lower critical solution temperature (LCST) systems.[18a] Additionally, no significant change in the DLS size distribution was observed for $[PEG_{1000}(mim)_2][NTf_2]_2$ in EA upon cooling (see Figure S1), which indicates that the change of solubility of the IL in EA was small upon change in temperature. However, this IL could almost exclusively transfer into the water phase upon cooling. Therefore, the transfer of $[PEG_{1000}(mim)_2][NTf_2]_2$ between water and EA is mainly related to the phase behavior of the IL in water.

In addition, we performed temperature-dependent FTIR measurements for the mixture of $[PEG_{1000}(mim)_2][NTf_2]_2$ and D_2O (60 wt% IL) between 25 and 52 °C (Figure 4). Here, D_2O was used instead of H_2O as the solvent to eliminate the overlap of the broad O−H stretching of H_2O with the C(4,5)−H and C(2)−H stretching of the imidazolium ring in the 3700–3000 cm^{-1} range. For the pure IL at 25 °C, it was shown that the peaks at 3153 and 3114 cm^{-1} could be assigned to C(4,5)−H and C(2)−H stretching, respectively, of the imidazolium ring, while those at 2871 and 1093 cm^{-1} could be assigned to C−H stretching of the PEG chain with a helical conformation and C-O-C stretching of the PEG chain, respectively (see Figure S2).[25] When mixed with D_2O at 25 °C, the original peak at 2871 cm^{-1} for the pure IL was shifted to 2882 cm^{-1} and a new peak was observed at 2918 cm^{-1}, which was assigned to C−H stretching for the PEG chain having a random-coil conformation resulted from the formation of water molecules having well-ordered structures around the hydrophobic segments (CH_2CH_2) of the PEG chain.[25e] In addition, it was found that once the temperature was increased from 25 to 52 °C, the change in stretching vibrations of C(4,5)−H, C(2)−H, and C-O-C was very small (see Figure S2). However, the ratio of the IR absorbance at 2918 cm^{-1} to that at 2882 cm^{-1}, A_{2918}/A_{2882}, showed an obvious decrease with the increase of temperature, thus indicating that the relative proportion of the random-coil conformation of the PEG chain decreased. This change led to the loss of ordered water around the CH_2CH_2 groups of the PEG chain with increasing temperature (see Figure S3),[25f] and thus phase transition of the IL from water to EA. To study the isotopic effect, we performed temperature-dependent FTIR measurements for the mixture of $[PEG_{1000}(mim)_2][NTf_2]_2$ and H_2O (60 wt% IL) in the same range of temperature, and a similar temperature dependence was observed (see Figures S4–S6).

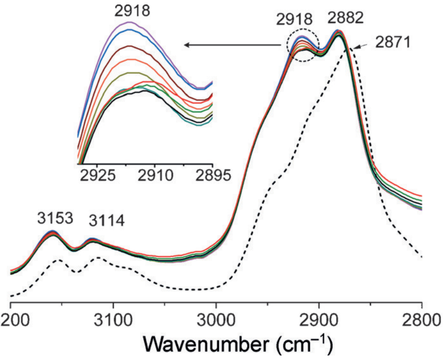


Figure 4. Temperature-dependent FTIR spectra of $[PEG_{1000}(mim)_2][NTf_2]_2$ in D_2O (60 wt% IL) during heating from 25 to 52 °C compared with pure IL at 25 °C.

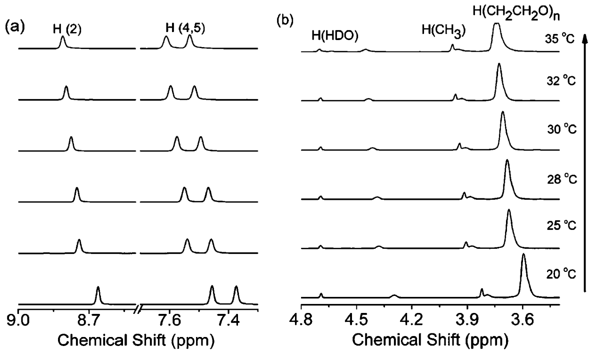


Figure 5. Temperature-dependent ^1H NMR spectra of $[PEG_{1000}(mim)_2][NTf_2]_2$ in D_2O (15 wt% IL).

To further elucidate the mechanism of the thermo-responsive behavior of the ILs, temperature-dependent ^1H NMR spectroscopy was used to understand the phase behavior of $[PEG_{1000}(mim)_2][NTf_2]_2$ in D_2O at a given concentration of 15 wt% IL (Figure 5). For the aqueous IL at 20 °C, the typical peaks at $\delta = 8.67$, 7.45, and 7.35 ppm could be assigned to C(2)−H and C(4,5)−H of the imidazolium ring, while the peaks at $\delta = 3.82$ and 3.59 ppm could be assigned to hydrogen atoms of CH_3 and $(CH_2CH_2O)_n$ of the PEG chain, respectively. Here, the chemical shifts were reported with reference to residual water resonance at $\delta = 4.69$ ppm. It is clearly indicated that with the increase of temperature all the typical proton peaks of the IL were shifted downfield, and suggests that the interactions between (CH_2CH_2) segments of the PEG chain and water decreased while those between the cation and anion of the IL increased.[26] As temperature was increased from 20 to 32 °C, the typical peaks remain sharp, thus indicating the high solubility of the IL in water.[26b] However, when the temperature was increased to 35 °C, the change in the peak intensities of C(2)−H and C(4,5)−H was small (Figure 5 a), but the peaks corresponding to the PEG chain began to broaden and their intensities were significantly decreased (Figure 5 b). This change probably also results from the conformation change of the PEG chain, thus leading to the loss of ordered water around them as the temperature increases.[26c] Unlike the characteristics in water, the peaks of the IL in EA showed almost no change in the temperature range investigated, which indicates that the interactions between the IL and EA are not sensitive to the change of temperature (see Figure S7). These results are consistent with the FTIR analysis.

Similar to the transfer between water and EA, the transfer of $[PEG_{1000}(mim)_2][NTf_2]_2$ between water and other organic solvents was also studied. It was shown that the other hydrophobic esters and alcohols were also effective organic solvents. For example, we found that $[PEG_{1000}(mim)_2][NTf_2]_2$ could transfer from water to hexyl alcohol after stirring for 5 minutes at 50 °C, and the IL could transfer back to water upon cooling to 20 °C.

The copper-catalyzed Huisgen 1,3-dipolar cycloaddition reaction of organic azides and terminal alkynes, also known as a click reaction, has become one of the most important reactions for the preparation of 1,2,3-triazoles. Although CuX (X = Br, I, etc) is an active catalyst for the reaction, it usually has to be used together with a nitrogen-containing ligand, which is difficult to recycle.[27] In addition, the complicated product separation by chromatography on silica gel also remains a problem.[28] Herein, our functionalized ILs were used as the entrainer and activator of CuI, because of the coordination property of PEG with metallic salts, to catalyze the reaction in EA at 50 °C. Then the IL + CuI were separated from the reaction system and transferred spontaneously to the water phase upon cooling to 20 °C (see the Experimental Section in the Supporting Information). As a representative example, the product 1-benzyl-4-phenyl-1,2,3-triazole remained in EA and was obtained through rotary evaporation under reduced pressure, and was identified by ^1H NMR spectroscopy (see Figure S8). The yield was 95 %. Then, IL + CuI could be conveniently transferred back to EA through heating. Once new substrates were added in the organic phase, the same reaction took place again. In addition, it is feasible to use this strategy to quench the catalytic reaction at will by removal of IL + CuI from EA upon cooling. Such an interesting result indicates that this unique property of the IL could be used to control reactions. Figure 6 shows such a reaction and separation process in the preparation of 1-benzyl-4-phenyl-1,2,3-triazole, as well as the recovery and recycling of the IL + catalyst, all of which is quite difficult to do in conventional chemical processes. It was found that after five recycles, the leaching of the IL and CuI was about 7–9 % and 3 %, as determined by ^1H NMR spectroscopy and flame atomic absorption spectrometry, respectively. The yield of the isolated product became 81 % at this time. In addition, it was found that the reaction did not work under similar experimental conditions without $[PEG_{1000}(mim)_2][NTf_2]_2$, and the yield was only 5 %. Obviously, the PEG-functionalized ILs reported here could be used as the entrainer and activator of the catalyst as well as the controller of the reaction.

To extend the scope with respect to the substrates, other terminal alkynes containing hydrophilic groups, such as 1-ethynyl-1-cyclohexanol, 2-phenyl-3-butyn-2-ol, propiolic acid, and 5-hexyn-1-ol, were used to react with benzyl azide in a Huisgen 1,3-dipolar cycloaddition reaction. The products were confirmed by ^1H NMR spectroscopy (see Figures S9–S12), and the yields of the isolated products were 88–94 %.

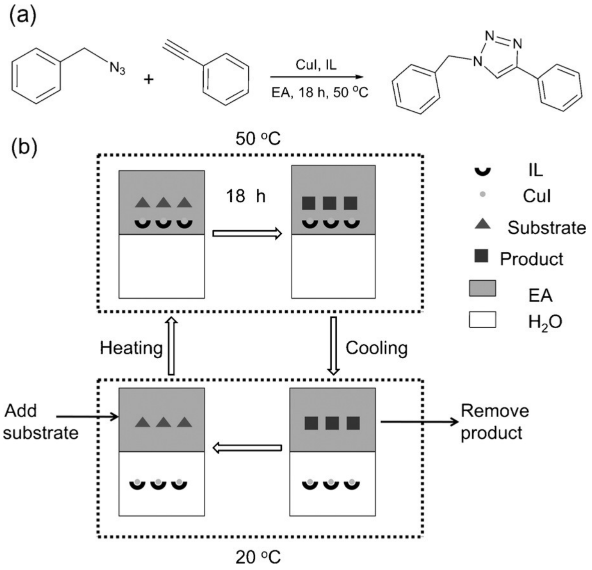


Figure 6. a) Reaction between benzyl azide and phenyl acetylene catalyzed by CuI in the presence of $[PEG_{1000}(mim)_2][NTf_2]_2$. b) The reaction and separation procedures for (a).

Furthermore, $[PEG_{1000}(mim)_2][NTf_2]_2$ and CuI were successfully recycled through temperature-mediated reversible phase transfer.

In conclusion, by tuning the hydrophilicity and hydrophobicity of the cation and anion, respectively, we have designed and prepared a class of functionalized ILs which exhibit reversible phase transfer between water and organics triggered by temperature changes. From temperature-dependent FTIR, ^1H NMR spectroscopy and DLS measurements, it was found that the driving force for the transfer originated from the change in conformation of the PEG chain with temperature. Furthermore, a highly efficient and controllable CuI-catalyzed alkyne–azide cycloaddition reaction was achieved in EA at 50 °C by using the IL as the entrainer and activator of the catalyst as well as the controller of the reaction. The CuI + IL could be successfully recycled by changing the temperature. To the best of our knowledge, this is the first example of functionalized ILs being used to entrain, activate and recycle the catalyst, and to control the reaction. The strategy developed in this work opens the door to achieving highly efficient separation and recycling of catalyst systems from products and solvents. In addition, this completely new mode for phase transfer could have potential applications in a wide range of fields such as advanced materials preparation, separation science, and nanotechnology.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 21273062, 21133009).

Keywords: homogeneous catalysis · hydrophobic effect · ionic liquids · phase transfer · thermoresponse

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 7934–7938
Angew. Chem. **2016**, *128*, 8066–8070

[1] a) S. L. Desset, D. J. Cole-Hamilton, *Angew. Chem. Int. Ed.* **2009**, *48*, 1472–1474; *Angew. Chem.* **2009**, *121*, 1500–1502; b) G. Liu, J. Wang, *Angew. Chem. Int. Ed.* **2010**, *49*, 4425–4429; *Angew. Chem.* **2010**, *122*, 4527–4531; c) Y. Yang, B. Zhang, Y. Wang, L. Yue, W. Li, L. Wu, *J. Am. Chem. Soc.* **2013**, *135*, 14500–14503; d) L. Peng, M. You, C. Wu, D. Han, I. Öçsoy, T. Chen, Z. Chen, W. Tan, *ACS Nano* **2014**, *8*, 2555–2561.

[2] a) J. Yang, J. Y. Lee, J. Y. Ying, *Chem. Soc. Rev.* **2011**, *40*, 1672–1696; b) B. Qin, Z. Zhao, R. Song, S. Shanbhag, Z. Tang, *Angew. Chem. Int. Ed.* **2008**, *47*, 9875–9878; *Angew. Chem.* **2008**, *120*, 10023–10026; c) D. Dorokhin, N. Tomczak, M. Han, D. N. Reinhoudt, A. H. Velders, G. J. Vancso, *ACS Nano* **2009**, *3*, 661–667; d) A. Stocco, M. Chanana, G. Su, P. Gernoch, B. P. Binks, D. Wang, *Angew. Chem. Int. Ed.* **2012**, *51*, 9647–9651; *Angew. Chem.* **2012**, *124*, 9785–9789.

[3] a) E. P. Holowka, V. Z. Sun, D. T. Kamei, T. J. Deming, *Nat. Mater.* **2007**, *6*, 52–57; b) N. Sakai, S. Matile, *J. Am. Chem. Soc.* **2003**, *125*, 14348–14356.

[4] T. V. Richter, C. Bühler, S. Ludwigs, *J. Am. Chem. Soc.* **2012**, *134*, 43–46.

[5] a) J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508–3576; b) N. Liu, C. Liu, Z. Jin, *Green Chem.* **2012**, *14*, 592–597; c) V. I. Pârvulescu, C. Hardacre, *Chem. Rev.* **2007**, *107*, 2615–2665.

[6] a) H. Itoh, K. Naka, Y. Chujo, *J. Am. Chem. Soc.* **2004**, *126*, 3026–3027; b) H. J. Ryu, L. Sanchez, H. A. Keul, A. Raj, M. R. Bockstaller, *Angew. Chem. Int. Ed.* **2008**, *47*, 7639–7643; *Angew. Chem.* **2008**, *120*, 7751–7755; c) T. Y. Kim, W. J. Kim, S. H. Hong, J. E. Kim, K. S. Suh, *Angew. Chem. Int. Ed.* **2009**, *48*, 3806–3809; *Angew. Chem.* **2009**, *121*, 3864–3867; d) P. Zhang, T. Wu, B. Han, *Adv. Mater.* **2014**, *26*, 6810–6827.

[7] a) H. Wang, G. Gurau, R. D. Rogers, *Chem. Soc. Rev.* **2012**, *41*, 1519–1537; b) A. K. Ressmann, P. Gaertner, K. Bica, *Green Chem.* **2011**, *13*, 1442–1447; c) K. Fujita, D. R. MacFarlane, M. Forsyth, *Chem. Commun.* **2005**, 4804–4806.

[8] a) G. Cui, J. Zheng, X. Luo, W. Lin, F. Ding, H. Li, C. Wang, *Angew. Chem. Int. Ed.* **2013**, *52*, 10620–10624; *Angew. Chem.* **2013**, *125*, 10814–10818; b) B. E. Gurkan, J. C. de la Fuente, E. M. Mindrup, L. E. Ficke, B. F. Goodrich, E. A. Price, W. F. Schneider, J. F. Brennecke, *J. Am. Chem. Soc.* **2010**, *132*, 2116–2117.

[9] S. Zhang, J. Sun, X. Zhang, J. Xin, Q. Miao, J. Wang, *Chem. Soc. Rev.* **2014**, *43*, 7838–7869.

[10] a) T. Vander Hoogerstraete, S. Wellens, K. Verachtert, K. Binnemans, *Green Chem.* **2013**, *15*, 919–927; b) Z. Li, X. Liu, Y. Pei, J. Wang, M. He, *Green Chem.* **2012**, *14*, 2941–2950; c) I. Khimji, K. Doan, K. Bruggeman, P. Huang, J. Liu, *Chem. Commun.* **2013**, *49*, 4537–4539; d) X. Han, D. W. Armstrong, *Chem. Res.* **2007**, *40*, 1079–1086; e) S. H. Ha, N. L. Mai, Y. M. Koo, *Process Biochem.* **2010**, *45*, 1899–1903.

[11] a) R. Giernoth, *Angew. Chem. Int. Ed.* **2010**, *49*, 2834–2839; *Angew. Chem.* **2010**, *122*, 2896–2901; b) N. V. Plechkova, K. R. Seddon, *Chem. Soc. Rev.* **2008**, *37*, 123–150; c) P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789; *Angew. Chem.* **2000**, *112*, 3926–3945; d) J. F. Huang, H. Luo, C. Liang, I. Sun, G. A. Baker, S. Dai, *J. Am. Chem. Soc.* **2005**, *127*, 12784–12785; e) J. L. Anderson, R. Ding, A. Ellern, D. W. Armstong, *J. Am. Chem. Soc.* **2005**, *127*, 593–604; f) T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206–237; g) D. L. Gin, R. D. Noble, *Science* **2011**, *332*, 674–676; h) A. Abate, A. Petrozza, V. Roiati, S. Guarnera, H. Snaith, F. Matteucci, G. Lanzani, P. Metrangolo, G. Resnati, *Org. Electron.* **2012**, *13*, 2474–2478.

[12] a) M. Solinas, A. Pfaltz, P. G. Cozzi, W. Leitner, *J. Am. Chem. Soc.* **2004**, *126*, 16142–16147; b) J. Cheng, G. Zhang, J. Du, L. Tang, J. Xu, J. Li, *J. Mater. Chem.* **2011**, *21*, 3485–3494.

[13] a) A. C. Cole, J. L. Jensen, I. Ntai, K. L. T. Tran, K. J. Weaver, D. C. Forbes, J. H. Davis, *J. Am. Chem. Soc.* **2002**, *124*, 5962–5963; b) Y. Leng, J. Wang, D. Zhu, X. Ren, H. Ge, L. Shen, *Angew. Chem. Int. Ed.* **2009**, *48*, 168–171; *Angew. Chem.* **2009**, *121*, 174–177; c) H. Zhi, C. Lu, Q. Zhang, J. Luo, *Chem. Commun.* **2009**, 2878–2880.

[14] D. Xiong, G. Cui, J. Wang, H. Wang, Z. Li, K. Yao, S. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 7265–7269; *Angew. Chem.* **2015**, *127*, 7373–7377.

[15] Y. He, T. P. Lodge, *J. Am. Chem. Soc.* **2006**, *128*, 12666–12667.

[16] T. Ueki, S. Sawamura, Y. Nakamura, Y. Kitazawa, H. Kokubo, M. Watanabe, *Langmuir* **2013**, *29*, 13661–13665.

[17] Y. Wang, W. Leng, Y. Gao, J. Guo, *ACS Appl. Mater. Interfaces* **2014**, *6*, 4143–4148.

[18] a) K. Fukumoto, H. Ohno, *Angew. Chem. Int. Ed.* **2007**, *46*, 1852–1855; *Angew. Chem.* **2007**, *119*, 1884–1887; b) A. M. Scurto, S. N. V. K. Aki, J. F. Brennecke, *J. Am. Chem. Soc.* **2002**, *124*, 10276–10277; c) A. Arce, M. J. Earle, S. P. Katdare, H. Rodriguez, K. R. Seddon, *Chem. Commun.* **2006**, 2548–2550.

[19] M. G. Freire, L. M. N. B. F. Santos, A. M. Fernandes, J. A. P. Coutinho, I. M. Marrucho, *Fluid Phase Equilib.* **2007**, *261*, 449–454.

[20] a) E. E. Fenn, D. E. Moilanen, N. E. Levinger, M. D. Fayer, *J. Am. Chem. Soc.* **2009**, *131*, 5530–5539; b) X. Li, M. Hou, Z. Zhang, B. Han, G. Yang, X. Wang, L. Zou, *Green Chem.* **2008**, *10*, 879–884; c) B. E. Gurkan, T. R. Gohndrone, M. J. McCready, J. F. Brennecke, *Phys. Chem. Chem. Phys.* **2013**, *15*, 7796–7811.

[21] a) J. Ren, L. Wu, B. Li, *Ind. Eng. Chem. Res.* **2013**, *52*, 8565–8570; b) Z. Yang, D. Jiang, X. Zhu, C. Tian, S. Brown, C. Do-Thanh, L. He, S. Dai, *Green Chem.* **2014**, *16*, 253–258; c) A. Liu, R. Ma, C. Song, Z. Yang, A. Yu, Y. Cai, L. He, Y. Zhao, B. Yu, Q. Song, *Angew. Chem. Int. Ed.* **2012**, *51*, 11306–11310; *Angew. Chem.* **2012**, *124*, 11468–11472.

[22] L. C. Branco, J. N. Rosa, J. J. M. Ramos, C. A. M. Afonso, *Chem. Eur. J.* **2002**, *8*, 3671–3677.

[23] J. F. Lutz, *Adv. Mater.* **2011**, *23*, 2237–2243.

[24] L. Ropel, L. S. Belvèze, S. N. V. K. Aki, M. A. Stadtherr, J. F. Brennecke, *Green Chem.* **2005**, *7*, 83–90.

[25] a) A. Wulf, K. Fumino, R. Ludwig, *J. Phys. Chem. A* **2010**, *114*, 685–686; b) I. Rey, P. Johansson, J. Lindgren, J. C. Lassèguss, J. Grondia, L. Servant, *J. Phys. Chem. A* **1998**, *102*, 3249–3258; c) M. Babucci, A. Akçay, V. Balci, A. Uzun, *Langmuir* **2015**, *31*, 9163–9176; d) P. Schmidt, J. Dybal, M. Trchová, *Vib. Spectrosc.* **2006**, *42*, 278–283; e) E. C. Cho, J. Lee, K. Cho, *Macromolecules* **2003**, *36*, 9929–9934; f) M. Gemmei-Ide, T. Miyashita, S. Kagaya, H. Kitano, *Langmuir* **2015**, *31*, 10881–10887.

[26] a) D. Chandler, *Nature* **2005**, *437*, 640–647; b) D. Li, G. L. Jones, J. R. Dunlap, F. Hua, B. Zhao, *Langmuir* **2006**, *22*, 3344–3351; c) J. F. Lutz, K. Weichenhan, Ö. Akdemir, A. Hoth, *Macromolecules* **2007**, *40*, 2503–2508.

[27] M. Teyssot, A. Chevry, M. Traïkia, M. El-Ghozzi, D. Avignant, A. Gautier, *Chem. Eur. J.* **2009**, *15*, 6322–6326.

[28] C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.* **2002**, *67*, 3057–3064.

Received: January 14, 2016
Revised: March 29, 2016