

## Organic acids can crosslink poly(ionic liquid)s into mesoporous polyelectrolyte complexest

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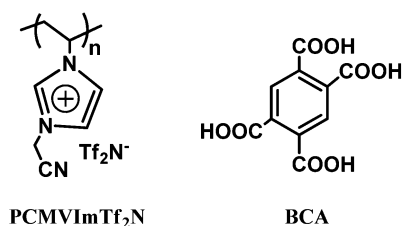
A template-free method was introduced to prepare mesoporous poly(ionic liquid) complexes by employing a variety of multivalent carboxylic acids to electrostatically crosslink imidazolium-based poly(ionic liquid)s in diethyl ether. The as-synthesized porous networks exhibit good structural stability and large specific surface area up to  $290 \text{ m}^2 \text{ g}^{-1}$ . Their performance in dye removal from ethanol was demonstrated to be superior to activated carbon and mesoporous silica.

Polymerized ionic liquids or poly(ionic liquid)s (PILs), which are usually synthesized by polymerization of ionic liquid (IL) monomers, constitute a subclass of polyelectrolytes that combine some IL properties with the common features of polymers.<sup>1–7</sup> As such, PILs hold some unique structural merits and are advantageous in a multitude of materials applications, such as gas separation/absorption, carbon preparation, energy conversion, catalysis, and many more.<sup>8–19</sup> Porous PILs possess increased surface area and can accelerate the interfacial mass and energy exchange, thus are important in some fields, for instance catalysis or fast stimuli-responsive materials.<sup>20–22</sup> In light of this, mesoporous PILs with pore sizes between 2 and 50 nm are promising candidates, as they simultaneously provide adequate mass transfer and large surface area. It has been proven recently that mesoporous PILs absorbed faster and more  $\text{CO}_2$  than their bulk.<sup>23</sup> Very recently, we found that ionic complexation between cationic PILs and deprotonated poly(acrylic acid) could create a micro/mesoporous matrix without using a template, a phenomenon that, to the best of our knowledge, has not been introduced yet in any polyelectrolyte system.<sup>24</sup> In general, mesoporous polyelectrolytes with high surface area are less reported,<sup>12,25–29</sup> and majorly prepared from a hard templating or post-modification method. Taking into

account that the ionic complexation is one of the most fundamental and characteristic properties of polyelectrolyte materials,<sup>30–36</sup> the PIL-based ionic complex architectures are of great scientific curiosity. In addition they may bring in new functional materials to the polyelectrolyte family.

In this communication, we prepared mesoporous polyelectrolyte networks through the ionic complexation between imidazolium-based cationic PILs and organic oligoacids in ammonia-containing diethyl ether. Although this approach is differentiated from the previous one simply by replacing poly(carboxylic acid)s with small organic acids, thus simplifying the synthetic procedure, the incorporation of natural acids is a striking benefit, making the synthesis a step forward towards flexible functionalization, following the framework of green chemistry at the same time.<sup>37</sup>

Scheme 1 illustrates the chemical structures of a PIL poly(3-cyanomethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl)imide) (PCMVImTf<sub>2</sub>N) and a multivalent acid molecule 1,2,4,5-benzenetetracarboxylic acid (BCA), which were employed as a model pair to prepare the mesoporous PIL-based networks. In detail, PIL and BCA mixed at different molar ratios were dissolved in DMSO solvent, forming a homogeneous blend solution. Under this condition BCA molecules stayed in a neutral state, therefore no or only weak ionic complexation occurred at this stage. The blend solution was added dropwise into diethyl ether containing 0.3 wt% of ammonia under sonication conditions. Upon addition the four COOH groups on BCA



**Scheme 1** Chemical structures of the PIL polymer PCMVImTf<sub>2</sub>N and 1,2,4,5-benzenetetracarboxylic acid (BCA).

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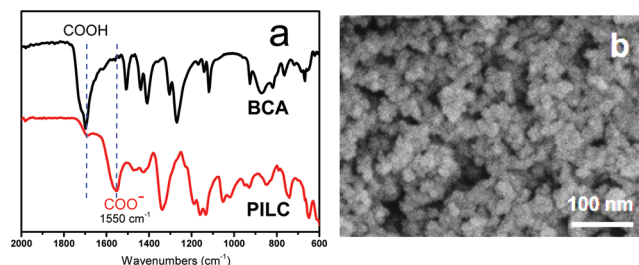


Fig. 1 (a and b) FT-IR and SEM characterization of the PILC product.

molecules were immediately deprotonated by excessive  $\text{NH}_3$  into carboxylate anions ( $\text{COO}^- \text{NH}_4^+$ ), triggering the *in situ* ionic crosslinking of the cationic PIL. This process was facilitated here by homogeneous pre-mixing of both components in DMSO at a molecular level before the precipitation step. Owing to the multi-charge character, a single BCA molecule can effectively crosslink different PIL chains (at least two), producing insoluble networks that were easily collected as precipitates by centrifugation. This material is termed PIL complexes (PILC) with regard to its electrostatic complexation character.

The ionic complexation and the morphology of the as-synthesized PILC material made from PCMVImTf<sub>2</sub>N and BCA were first studied by Fourier transform infrared (FT-IR) spectroscopy and scanning electron microscopy (SEM). In the FT-IR spectra of intact BCA and the PILC in Fig. 1a, the marked absorption peaks at 1700 and 1550  $\text{cm}^{-1}$  were ascribed to the C=O stretching in COOH and  $\text{COO}^-$  groups, respectively. The significant shrinkage of the COOH band and the appearance of an intense  $\text{COO}^-$  band in the PILC product confirmed the deprotonation state of the organic acids.<sup>24</sup> SEM examination (Fig. 1b) visualized that the PILC networks were composed of nanosized particles (25–50 nm) with a distinctive morphology. The secondary structure, the interlinked random nanoparticle packing might provide large transport channels favourable for many practical applications.

The pore characteristics of the PILC product were investigated by nitrogen sorption measurements (Fig. 2a). It presents a type-IV isotherm with a hysteresis loop in a  $P/P_0$  range between 0.7 and 0.9, suggesting that in addition to the features visible in SEM mesopores of 3–10 nm in diameter are the major species (Fig. S2†).<sup>38–40</sup> The specific surface area calculated from the Brunauer–Emmett–Teller (BET) equation and the pore volume

calculated from the Barrett–Joyner–Halenda (BJH) method were 250  $\text{m}^2 \text{g}^{-1}$  and 0.63  $\text{cm}^3 \text{g}^{-1}$ , respectively.<sup>23,40</sup> For such systems these values are in an unusually high range. This illustrates the big difference between our system and the classical polyelectrolyte complexes, which are essentially non-porous as such. Thanks to the strong ionic complexation between PIL and BCA, and appropriate polarizability of the PIL part, these mesopores are mechanically and physicochemically robust and change little under refluxing with some organic solvents, like acetone, THF or ethanol (Fig. S3†). In contrast, the simple physical blend of PIL and BCA is nonporous (Fig. 2a). In this context the pore structure seems to be related to the ionic complexation structures. Indeed, a positive correlation between the specific surface area of PILCs and the degree of ionic complexation (Scheme S2†) was observed in the PILC products (Fig. 2b). Varying the BCA/PIL (represented by COOH/imidazolium) feeding ratio, the complexation and the surface characteristics peak at a COOH/imidazolium molar ratio of 0.85. This value hints that a complete ionic complexation between the imidazolium cations in PILs and the 4 carboxylate anions in BCA for all molecules is sterically impossible (otherwise COOH/imidazolium = 1). The average coordination number is calculated to be 3.4. This is reasonable, because the imidazolium–carboxylate charge pair formed at an earlier stage might introduce spatial hindrance which prevents the later coming BCA molecules from closing their coordination shell along the same polymer chain.

Compared to the common interpolyelectrolyte complex systems,<sup>30–34</sup> introducing multivalent small molecules into the ionic complexation might afford some advantages such as cheap resources, defined geometries, an abundance of candidate choices, and a broad range of added orthogonal chemical functionalities, opening a new avenue to a rich family of mesoporous PILC materials. To demonstrate this potential, several more PILC networks were similarly prepared from PCMVImTf<sub>2</sub>N with different acids. Table 1 summarizes the chemical structure of the acids and the pore properties of the corresponding PILC products. Generally, PILC materials based on the benzene series (entry 1–4, Table 1), citric acid, *trans*-aconitic acid, and even oxalic acid (entry 5–7, Table 1) are all porous rigid solids with specific surface area values ranging from 230 to 290  $\text{m}^2 \text{g}^{-1}$ . The relatively large variation in the pore volume (0.63  $\text{cm}^3 \text{g}^{-1}$  to 1.54  $\text{cm}^3 \text{g}^{-1}$ ) can be attributed to the different chemical structures and charge densities of the acid molecules, and the corresponding varied pore sizes of these PILC systems. In contrast, the monovalent benzoic acid (entry 8, Table 1) produced only a nonporous soft sticky material in a low yield.

As stated before, polyelectrolyte complex systems have been widely investigated so far and have exclusively low surface area and mesoporosity, if not prepared from a template method.<sup>30–34,41,42</sup> A comparison of our system with previous ones highlights two unique features: (1) premixing of the two components at a molecular level prior to carrying out complexation, and (2) the neutralization-triggered *in situ* ionic crosslinking in a poor solvent. Under these conditions, a fast and efficient ionic complexation (min. diffusion for both components) takes place, fixing the non-equilibrium (“frozen

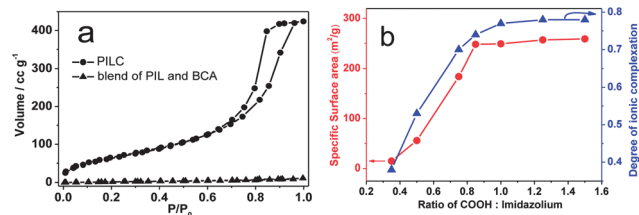
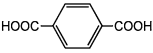
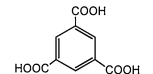
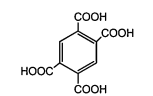
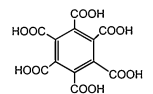
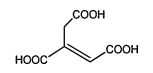
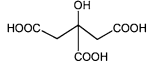
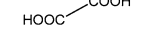
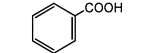


Fig. 2 (a) Nitrogen sorption isotherms of the PILC and the PCMVImTf<sub>2</sub>N–BCA physical blend. (b) Plot of the specific surface area (red) and the degree of ionic complexation (blue) of the PILC products against various COOH/imidazolium molar ratios undertaken in different complexation experiment runs.

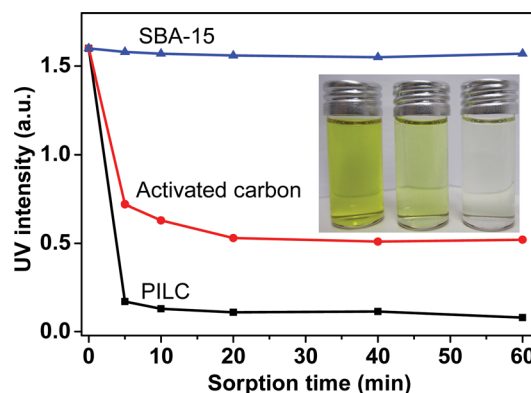


**Table 1** Specific surface area (from the BET equation) and pore volume (from the BJH method) of the PILC materials prepared from PCMVImTf<sub>2</sub>N and various acids

| Entry | Acids   | Specific surface area (m <sup>2</sup> g <sup>-1</sup> ) | Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) |
|-------|---|---|--|
| 1     |  | 263   | 1.54   |
| 2     |  | 277   | 0.77   |
| 3     |  | 249   | 0.63   |
| 4     |  | 233   | 0.83   |
| 5     |  | 255   | 1.23   |
| 6     |  | 233   | 1.11   |
| 7     |  | 290   | 1.35   |
| 8     |  | <10   | 0.01   |

state" due to the insolubility) polymer chain conformation into a porous state.<sup>24,43,44</sup> A supportive proof is that the same PILCs (entry 1–7 in Table 1) were nonporous when prepared by dropping their mixture solution into water, ethanol, acetone or tetrahydrofuran, simply because these solvents can dissolve or heavily solubilize the PILs or the organic acids.

Being highly dipolar, polarizable, and in a mesoporous state, the PILC materials are expected to find potential applications in heterogeneous catalysis, absorption, separation, purification, etc.<sup>45,46</sup> This can be illustrated here by using PILCs as absorbents for the efficient removal of organic dye molecules from organic solvents (note that this is a more difficult problem as compared to the removal of dyes from water). Such a function is frequently required for organic solvents recycling. Currently, approaches such as solvent resistant nanofiltration (SRNF) are investigated for this purpose because the traditional means like thermal distillation is too energy-demanding.<sup>47,48</sup> Fig. 3 shows the performance of the PILC material ( $S_{\text{BET}} \sim 250 \text{ m}^2 \text{ g}^{-1}$ , entry 3 in Table 1), activated carbon ( $S_{\text{BET}} \sim 800 \text{ m}^2 \text{ g}^{-1}$ ) and mesoporous silica ( $S_{\text{BET}} \sim 400 \text{ m}^2 \text{ g}^{-1}$ ) in absorbing methyl orange (MO) under a default set of conditions from ethanol. When the mesoporous PILC was used, the UV absorption intensity of MO molecules decreased by 90% and 95% after 5 and 60 minutes, respectively. In contrast, under the same conditions after 5 minutes only 70% decrease in the absorption intensity was observed by activated carbon and only 2% by mesoporous silica. We also tested anion exchange resins (Fig. S4†), and the absorbing process is much slower compared to the PILC. Hence, PILC's superior efficiency in capturing dye molecules



**Fig. 3** UV absorption ( $\lambda \sim 435 \text{ nm}$ ) of methyl orange solution (0.02 M in ethanol) after being treated with 10 mg of PILC (black line), activated carbon (red line), and SBA-15 (blue line), respectively. The inset is a photograph of the methyl orange solution after 1 h treatment with SBA-15, activated carbon, and PILC from left to right.

seems to stem from a judicious combination of its polarity, mesopores, charge character as well as its fine dispersibility in ethanol. All of these enable a shortened diffusion distance and a strong interaction with MO molecules.

In conclusion, mesoporous poly(ionic liquid) complex networks with specific surface area up to  $290 \text{ m}^2 \text{ g}^{-1}$ , large pore volume, and stable pore structures were prepared by employing electrostatic interaction between an imidazolium-based PIL and multivalent organic acids. This unique template-free strategy is exceptionally simple in operation and was shown to be generally valid for a variety of other multivalent carboxylic acids, including many natural acid molecules. As an applicative example, the mesoporous PILC products were tested and showed an enhanced dye absorption performance in ethanol, making them promising candidates for impurity removal even from organic solvents.

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