Porous Liquids

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Transforming Porous Organic Cages into Porous Ionic Liquids via a Supramolecular Complexation Strategy

*Kecheng Jie, Nicole Onishi, Jennifer A. Schott, Ilja Popovs, De-en Jiang, Shannon Mahurin, and Sheng Dai**

Abstract: *Porous liquids are a type of porous materials that engineer permanent porosity into unique flowing liquids, exhibiting promising functionalities for a variety of applications. Here a Type I porous liquid is synthesized by transforming porous organic cages into porous ionic liquids via a supramolecular complexation strategy. Simple physical mixing of 18-crown-6 with task-specific anionic porous organic cages affords a porous ionic liquid with anionic porous organic cages as the anionic parts and 18-crown-6/potassium ion complexes as the cationic parts. In contrast, mixing of 15-crown-5 and anionic porous organic cages in a 2:1 ratio gives only solids, while the addition of excess 15-crown-5 affords a Type II porous liquid. The permanent porosity in the cage-based porous liquids has been also confirmed by molecular simulation, positron (e^+) annihilation lifetime spectroscopy, and enhanced gas sorption capacity compared with pure crown ethers.*

The concept of porous liquids, that is, liquids with permanent porosity, has attracted more and more attention since it was proposed by James et al. in 2007.[1] By combining the properties of porous solids and fluids, porous liquids may show promising applications in shape- and size-selective sorption or catalytic behavior, loading and delivering gaseous guests in a flowing system, and so on.[2] Generally, porous liquids can be classified into three types: Type I is a neat liquid composed of fluid hosts with empty cavities, while Type II and Type III are essentially dissolved empty hosts and homogeneously dispersed framework materials in sterically hindered solvents, respectively.[1–3] Because of the difficulty of preparing them, the porous liquid concept was not realized until 2015, seven years after it was proposed.[3a] To date, reports of porous liquids are limited, and most of them are made from porous organic cages,[2] porous carbons,[3e] zeolites,[3f] and metal–organic frameworks.[3g,h] Thus, a current breakthrough in the development of porous liquids still relies on the preparation or the synthesis. In 2015, James and Cooper et al. reported the first example of a Type II porous liquid in which a tetrahedral porous organic cage functionalized with six crown ether substituents was dissolved into the sterically hindered solvent 15-crown-5.[2a] Furthermore, a more easy-to-prepare Type II porous liquid was obtained by dissolving scrambled porous organic cages into a size-excluded solvent, hexachloropropene (PCP). These two porous liquids show enhanced gas uptake compared with pure solvents. However, both of them have some inherent shortcomings for practical applications. For the crown-ether porous liquid, a practical scale-up issue is the six-step cage synthesis with an overall low yield (3.1–6.5%). Also, pore volume is limited by the high content of 15-crown-5 as both solvent and functional group. For the scrambled-cage porous liquid, the volatility of PCP cannot be neglected for applications in pressure or temperature swing schemes.

To overcome these issues, direct liquefaction of porous cage solids might be an ideal solution. In the initial attempt, James et al. found that functionalization of alkyl chains onto imine cages could afford cages with low-melting neat liquid phases.[2c] However, a clear risk is that the ends of long alkyl chains would be able to pass through the cage windows to occupy the central cavities and so remove the porosity. Another potential solution is to use the porous ionic liquids concept. A typical ionic liquid is a low-melting-point salt (melting point below 100 °C) with low vapor pressure, composed of a large asymmetric organic cation and an inorganic or organic anion.[4] If the cationic or anionic part of an ionic liquid is replaced by an ionic molecule with an inherent cavity and a counterion too large to enter the cavity, a porous ionic liquid may be obtained.

To this end, we prepared a kind of porous ionic liquid based on ionic porous organic cages via a supramolecular complexation strategy (Scheme 1).■■ok here?■■ Specifically, simple physical mixing of dicyclohexano-18-crown-6 (18-C-6) with an anionic porous organic cage afforded a porous ionic liquid with anionic porous organic cages as the anionic parts and 18-C-6/potassium ion complexes as the cationic parts. The state-of-the-art design of the strategy relied on several points: 1) Ion exchange of the alkali metal cations of the anionic imine cages with large organic cations may afford ionic liquid cages. However, the anionic imine cages will decompose in water (Supporting Information, Figure S7), an inevitable solvent for ion exchange. 2) Reduction of imine cages to water-stable amine cages will lead to the loss of permanent cavities.[5] 3) Previous reports have shown that the complexes between crown ethers and alkali metal cations (increasing steric hindrance) can act as the cationic

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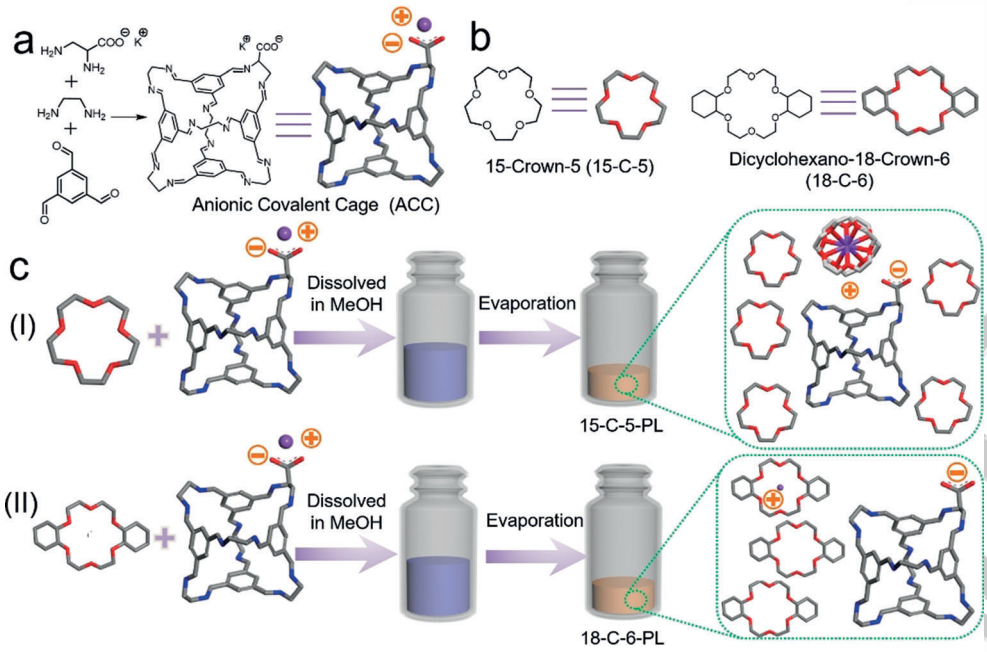

Scheme 1. a) Synthetic procedure and chemical structure of anionic covalent cage (ACC). b) Chemical structures of 15-crown-5 and dicyclohexano-18-crown-6. c) Rrepresentation of synthetic procedures for the crown ether-ACC porous liquids.

parts of ionic liquids.[6] In contrast, mixing of 15-crown-5 (15-C-5) and anionic porous organic cages in a 2:1 ratio gave only solids, while the addition of excess 15-C-5 afforded a Type II porous liquid in which the 15-C-5/cage complex was dissolved in 15-C-5. The permanent porosity in the cage-based porous liquids was confirmed by molecular simulation, positron (e^+) annihilation lifetime spectroscopy (PALS), and enhanced gas sorption capacity compared with pure crown ethers.

In synthesizing a porous ionic liquid of this type, ionic liquid formation through supramolecular complexation between crown ethers and ionic organic salts should first be verified. Specifically, we demonstrated the formation of ionic liquids using crown ethers and a potassium carboxylate group-appended diamine (KCDA), a ligand for the synthesis of an imine-based anionic covalent cage (ACC). Crown ethers including dicyclohexano-18-crown-6 (18-C-6) and 15-crown-5 (15-C-5) were chosen for their ability to complex with K^+ ions to form large cations, respectively. As anticipated, viscous liquids formed upon simple mixing of 15-C-5 or 18-C-6 with KCDA in a 2:1 or 1:1 ratio at room temperature (Supporting Information, Figure S1), confirming the formation of ionic liquids.[6] Meanwhile, thermogravimetric analysis (TGA) curves showed that the thermal stability of 18-C-6/KCDA complexes was higher than that of pure 18-C-6, while the thermal stabilities of 15-C-5/KCDA and 15-C-5 were similar (Supporting Information, Figures S2, S3). This may be due to the higher binding strength between 18-C-6 and K^+ than between 15-C-5 and K^+. These results thus offer the potential for the synthesis of porous ionic liquids using the complexation between 18-C-6 and K^+ with relatively lower volatility.

After confirming the possibility of synthesizing ionic liquids via supramolecular complexation, we further synthesized an imine-based ACC compound with KCDA as one of the starting materials. In the synthetic procedure, KCDA was used to partially substitute for ethylenediamine, thus affording an ACC modified with an anionic carboxylate group and K^+ as the cation (referred to as KACC). Various techniques were used to characterize the KACC compound. Fourier transform-infrared spectroscopy (FTIR) clearly shows a peak at 1689 cm^{-1}, which is typical for an antisymmetric stretching vibration band of the carboxylate groups (Figure 1 a). The ^1H nuclear magnetic resonance (NMR) spectrum of KACC was quite similar to that of the analogous neutral cage CC1.[7] A minor difference was that the KACC spectrum had a small triplet peak at 3.88 ppm, which should correspond to the proton close to the carboxylate groups (−CH−CO_2K; Supporting Information, Figure S4). ^1H COSY NMR spectrum of KACC shows a clear ^3J vicinal coupling signal between the protons on −CH−CO_2K and its adjacent CH_2 protons (Supporting Information, Figure S5), revealing the presence of CH and CH_2 groups on the carboxylate bearing part of KACC. The ^{13}C NMR spectrum of KACC revealed a peak at 24.07 ppm, a typical signal for the carbon on carboxylate groups (Supporting Information, Figure S6). These results confirmed the successful synthesis of an imine cage compound bearing carboxylate groups. Moreover, the

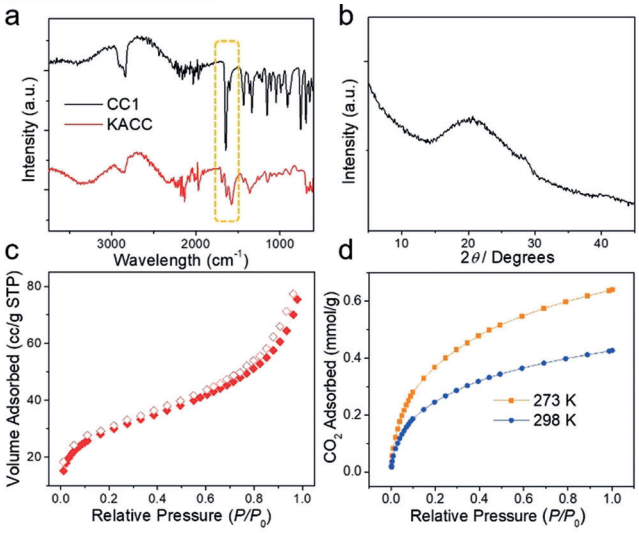

Figure 1. Characterizations of KACC: a) FTIR spectra; b) PXRD pattern; c) N_2 sorption isotherm at 77 K; d) CO_2 adsorption isotherm at 273 K and 298 K.

integral of the protons on −CH−CO_2K calculated from the ^{1}H NMR spectrum is around one, indicating that KACC bears only one carboxylate group on average. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed to further evaluate the numbers of carboxylate groups in a single KACC molecule. The ESI-MS spectrum of KACC revealed a clear peak at m/z 835.4171, corresponding to KACC bearing only one carboxylate group (Supporting Information, Figure S7). No other peaks of KACC bearing more carboxylate groups could be found. All these results indicated that KACC had been successfully prepared and that it bore only one carboxylate group on a single ACC molecule.

Quite different from the as-synthesized neutral cage CC1 with high crystallinity,[7] powder X-ray diffraction (PXRD) experiments showed that KACC is amorphous, perhaps as a result of the significant loss of symmetry in the carboxylate group-modified ACC molecule. N_2 sorption experiments were then performed to evaluate the porosity of KACC. Previous studies have shown that the as-synthesized neutral cage CC1 is barely porous (BET surface area = 24 $m^2 g^{-1}$) because of the dense window-to-body packing mode.[7] However, as-synthesized KACC showed a moderate BET surface area of 108 $m^2 g^{-1}$ (Figure 1c). We assumed that the amorphous nature of KACC facilitated it achieving a moderate surface area owing to the random placement of KACC molecules. Meanwhile, KACC also showed a moderate CO_2 adsorption capacity with 0.62 mmol g^{-1} at 273 K and 1 bar and 0.41 mmol g^{-1} at 298 K and 1 bar (Figure 1d).

After successful preparation of KACC solids, we pursued transforming KACC solids into ionic liquids via supramolecular complexation of 18-C-6 or 15-C-5 with K^+ ions. However, simple mixing of 15-C-5 with KACC in a 2:1 ratio led to the formation of only solids rather than liquids (Supporting Information, Figure S8). When the 15-C-5:KACC ratio was increased to 7:1, KACC was finally transformed to a viscous liquid (referred to as 15-C-5-PL, Figure 2b). In contrast, evaporation of a methanol solution of 18-C-6:KACC, with a ratio as low as 3:1 to completely remove methanol, afforded a viscous yellow liquid at room temperature (referred to as 18-C-6-PL, Figure 2a). It is particularly notable that both KACC and 18-C-6 were solids at room temperature, but a physical mixture of the two became a liquid. To characterize the two cage liquids, differential scanning calorimetry (DSC) was first carried out. The glass transition point of 18-C-6-PL was demonstrated to be around −30 °C, and the melting point of 18-C-6 around 50 °C (Figure 2c). However, for 15-C-5-PL, two peaks related to the melting points, one at −37 °C and another at −30 °C, were found in the DSC spectrum (Figure 2d). Compared with the melting point of pure 15-C-5, we concluded that the peak at −37 °C can be regarded as the melting point of the extra 15-C-5 in 15-C-5-PL, and −30 °C was the melting point of the 15-C-5/KACC complex. These results indicate that 18-C-6-PL is an ionic liquid at room temperature, whereas 15-C-5-PL is a solution in which 15-C-5/KACC complex is dissolved in 15-C-5. TGA was then performed to verify the thermostability of the two liquids. As can be seen from the Supporting Information, Figure S10, 18-C-6-PL starts to decompose at over 200 °C, about 45 °C higher than 18-C-6, indicating the higher thermal stability of 18-C-6-PL compared with 18-C-6. This result may stem from the high binding strength between 18-C-6 and K^+. For 15-C-5-PL, the weight loss began at around 100 °C, which is almost the same as for 15-C-5 but much lower than for 18-C-6-PL (Supporting Information, Figure S11). The low thermal stability of 15-C-5-PL is probably due to the lower boiling point of 15-C-5, as well as the lower affinity between 15-C-5 and K^+ compared with 18-C-6 and K^+.

To obtain atomistic insight into the structures of the porous liquids, classical molecular simulations were carried out. We found that the cages remain empty upon the addition of crown ethers, with cavity diameters of 4.4 and 4.6 Å for 15-C-5-PL and 18-C-6-PL, respectively (Figure 3a). The pore size in 15-C-5-PL is slightly smaller because 15-C-5 can partially enter the cage more easily than the bulkier 18-C-6. This is confirmed by the radial distribution functions of 15-C-5 and 18-C-6 around the geometric center of ACC, where

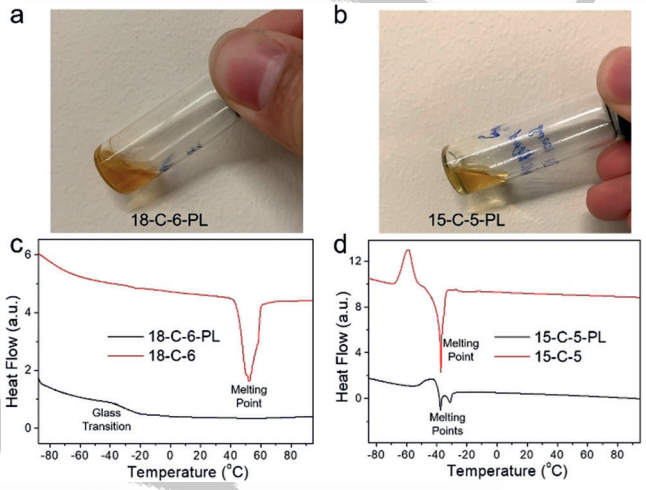

Figure 2. Photographs of a) 18-C-6-PL and b) 15-C-5-PL; DSC curves of c) 18-C-6-PL and d) 15-C-5-PL.

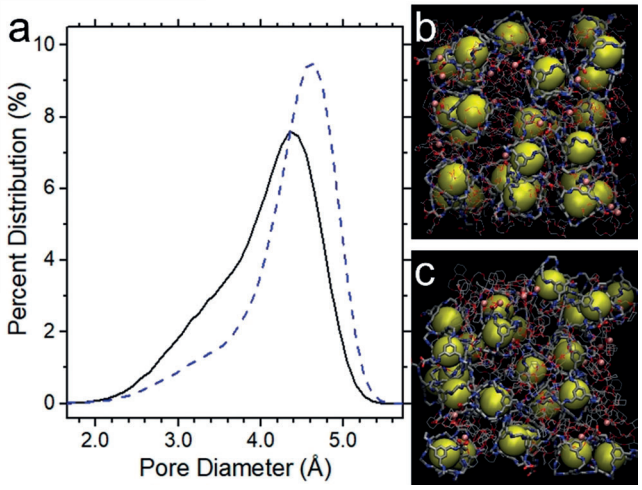

Figure 3. a) Cavity size distribution of simulated 15-C-5-PL (solid black) and 18-C-6-PL (dashed blue). Snapshots of equilibrated b) 15-C-5-PL and c) 18-C-6-PL simulation boxes with cavities shown as yellow spheres (hydrogens omitted for clarity).

there is a significantly larger amount of 15-C-5 than 18-C-6 in the range close to the cage (Supporting Information, Figure S15). Still, 15-C-5-PL and 18-C-6-PL maintain large enough permanent cavities (yellow spheres in Figure 3b and c) to absorb small molecules like CO_2 and N_2.

PALS experiments were carried out to confirm the empty cavities in the porous liquid. The *ortho*-positronium (*o*-Ps) lifetime of 15-C-5-PL is shown to be 0.436 ns, while that of 18-C-6-PL is 0.468 ns (Supporting Information, Figures S12, S13). According to these parameters, an average pore size can be calculated as 0.4022 nm for 15-C-5-PL, whereas the average pore size of 18-C-6-PL is determined to be 0.4661 nm; these sizes are very similar to the molecular simulation results. This finding indicates the existence of abundant micropores in both 18-C-6-PL and 15-C-5-PL; that is, the microporous anionic cages are still empty in the liquid phase.

To further demonstrate the empty cavities of the cages in the two porous liquids, the CO_2 sorption capacities of these specific samples were measured by an intelligent gravimetric analyzer. The 18-C-6 and KACC solids were also chosen as contrasts for CO_2 sorption, while 15-C-5 was excluded because of its low density and relatively high volatility. However, the CO_2 adsorption capacity in 18-C-6 was so low that it was below the detection limit of the instrument. Compared with 18-C-6 with limited CO_2 adsorption ability, the CO_2 uptake capacities of both 15-C-5-PL and 18-C-6-PL are significantly enhanced (Figure 4). At a pressure of 10 bar, the CO_2 adsorption capacities of 15-C-5-PL and 18-C-6-PL are 0.375 mmol g^{-1} and 0.429 mmol g^{-1}, respectively. The higher CO_2 adsorption in 18-C-6-PL can be ascribed to the higher concentration of KACC in 18-C-6-PL, which offers more pore volume for CO_2. Meanwhile, the adsorption capacities in both 15-C-5-PL and 18-C-6-PL are significantly lower than in the KACC solids (1.062 mmol g^{-1}). This result is partly attributable to the greater pore volume that existed in both the intrinsic and extrinsic forms of KACC solids, while the extrinsic porosity that can bind CO_2 did not exist in the two porous liquids. Also, the KACC concentration of the two porous liquids was much lower than that of the pure KACC solids. Moreover, both porous liquids, as well as the KACC solids, exhibit hysteresis loops (Figure 4). This result indicates that the adsorbed CO_2 can be restored during the desorption process because of the permanent porosity and suggests a potential application of two porous liquids in gas storage. N_2 adsorption experiments at room temperature were also performed as contrasts. However, the N_2 adsorption capacities in both porous liquids were too low to detect (Supporting Information, Figure S14). In this regard, the two porous liquids may have potential application as a separation media for the selective separation of CO_2 and N_2.

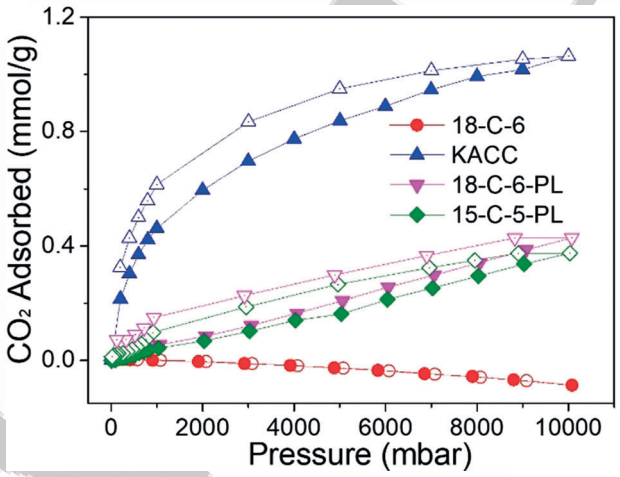

Figure 4. CO_2 adsorption (solid symbol)–desorption (open symbol) isotherms of 18-C-6, KACC, 18-C-6-PL, and 15-C-5-PL collected below 10 bar at 298 K.

In summary, porous liquids based on anionic covalent cages and crown ethers via a supramolecular complexation strategy were successfully developed as a proof-of-concept. Specifically, simple physical mixing of 18-C-6 with task-specific KACC afforded a Type I porous ionic liquid with anionic porous organic cages as the anionic parts and 18-crown-6/potassium ion complexes as the cationic parts. In contrast, mixing of 15-crown-5 and anionic porous organic cages in a 2:1 ratio produced only solids, while the addition of excess 15-C-5 afforded a Type II porous liquid in which the 15-C-5/KACC complex was dissolved in 15-C-5. Compared with previously reported Type II cage-based porous liquids and 15-C-5-PL, 18-C-6-PL as a porous ionic liquid has some remarkable advantages. For example, the thermal stability of 18-C-6-PL was enhanced as a result of the high binding strength between 18-C-6 and K^+ as well as the high boiling point of 18-C-6. This presents the possibility for the use of porous liquids in pressure or temperature swing schemes. Since the cage/crown ether ratio was the highest in the cage-based porous liquid systems, the permanent pore volume in 18-C-6-PL was the largest, enabling it to adsorb and store more gas. Considering the potential universality of this supramolecular strategy for making porous ionic liquids, future work will attempt to achieve the synthesis of porous ionic liquids using other anionic porous molecules with larger pores or even anionic porous framework nanoparticles.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: crown ethers · ionic liquids · microporous materials · porous liquids · porous organic cages

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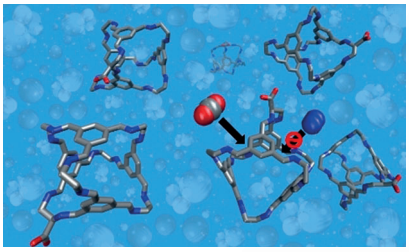

A Type I porous liquid is synthesized by transforming porous organic cages into porous ionic liquids via a supramolecular complexation strategy. Simple physical mixing of 18-crown-6 with an anionic porous organic cage affords a porous ionic liquid with anionic porous organic cages as the anionic parts and 18-crown-6/potassium ion complexes as the cationic parts.

Poröse Flüssigkeiten

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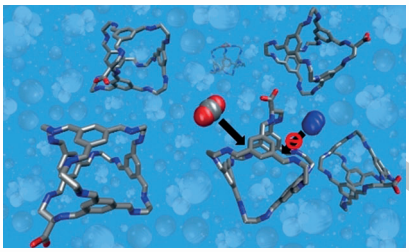

Eine poröse Flüssigkeit vom Typ I wird synthetisiert, indem poröse organische Käfige über eine supramolekulare Komplexierungsstrategie in poröse ionische Flüssigkeiten umgewandelt werden. Die einfache physikalische Mischung von [18]Krone-6 mit einem anionischen porösen organischen Käfig ergibt eine poröse ionische Flüssigkeit mit anionischen porösen organischen Käfigen als anionische und [18]Krone-6/Kaliumionen-Komplexen als kationische Komponente.

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