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Mechanochemistry

Charged Porous Polymers using a Solid C–O Cross-Coupling Reaction

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Abstract: Herein, we report a green, fast, efficient mechanochemical strategy for charged porous polymers (CPPs). A cationic CPP with basic anions and an anionic CPP with Li^+ cations were fabricated by solid grinding under solvent-free conditions. Compared with solution-based synthesis, mechanochemical grinding can shorten the reaction time from dozens of hours to several minutes (60–90 min) to form polymers possessing a high molecular mass and low polydispersity. During the construction of CPPs, a Pd-catalyzed solid polycondensation based on unactivated organic linkers was introduced. In particular, CPPs with basic phenolic or proline anions showed good activity and stability in SO_2 capture, and Li^+-functionalized CPPs can be post-modified to CPPs with other metal ions by ion exchange, highlighting the tailorable feature of ionic-modified CPPs.

Porous organic materials (POMs) are of huge commercial and scientific interest in separation, catalysis, and sorption applications.[1] In the past decade, various concepts for preparing POMs have been introduced, such as covalent organic frameworks (COFs), conjugated microporous polymers, hyper-cross-linked polymers, porous aromatic frameworks, covalent triazine-based frameworks, polymers of intrinsic microporosity (PIMs), covalent-organic polymers, and porous polymer networks (PPNs).[2] In the family of POMs, charged porous polymers (CPP) are an exception, because the intrinsically charged character of ionic complexation affords some unique applications, such as solid-state conductors, proton conductors and dispersants.[3] Furthermore, post-modification of CPP is accessible through an easy-to-handle ion-exchange process and, in principle, various cations or anions with designable tasks could be attached on the CPP.

Currently, the most popular route to CPP is the polymerization of cation- or anion-functionalized monomers bearing vinyl groups. Thus, most CPPs are based on polyethylene chains or cross-linked polyethylene chains, and hard templates are often required for directing porosity. For example, Wilke et al. synthesized mesoporous poly(ionic liquid)s (150–220 m^2g^{-1}) by polymerization within silica nanoparticles and by etching silica in NaOH.[4] On the other hand, the ionization of existing porous polymers provides an alternative pathway. Using this strategy, Xiao et al.[5a] reported ionic liquid (IL)-functionalized porous polymers formed by performing a quaternization reaction on the porous copolymer-poly(divinylbenzene-pyridine/imidazole) (57–181 m^2g^{-1}), and Zhou et al. synthesized porous ionic adsorbents by the sulfonation of PPNs.[5b] However, this indirect method requires the preparation of a porous polymer scaffold, making the process complicated. Besides the polymers mentioned above, the fabrication of CPPs based on the C–C coupling between a tetraphenylmethane-type knot and a charged monomer has been developed by Thomas et al.[6] Another interesting template-free approach to mesoporous CPPs (up to 330 m^2g^{-1}) with zwitterionic structures was provided recently by the poly(ionic liquid)s group in Germany.[7] The synthesis proceeds by precipitating an organic solution of an imidazolium-based poly(ionic liquid) homopolymer in an ammonia-containing organic solvent. Great progress in the synthesis of CPPs has occurred in the past five years, but the development of a simple, effective, and sustainable reaction for intensively ionized porous polymers is still of great interest.

In this contribution, we demonstrate a solvent-free, fast, and direct synthesis of new CPPs by solid-state polycondensation (Scheme 1). Mechanochemical synthesis (MS) corresponds to the chemical reactivity achieved or promoted by mechanical force and/or instantaneous frictional heating, generally through grinding bulk solid reactants. Since MS inherently avoids the use of a solvent, the solubility of the reactants can be ignored. Recent advances have highlighted MS as a promising tool in organic chemistry and material science.[8] For example, Banerjee et al. recently illustrated a facile MS of interesting COFs based on Schiff base condensation, and the Xiao group developed a template-free method to molecular series by solid-state synthesis.[9] In some cases, MS can enable the formation of C–C and C–X bonds (X = halide) in organic transformations quickly and quantitatively.[9a] From the standpoint of so-called green and sustainable chemistry, the development of solid polymerization for forming CPPs without any solvents, readily usable for scalable synthesis and working rapidly, would be highly attractive. Encouraged by the accessible chemistry of PIMs,[10] CPPs with positive or negative backbones were designed through a dibenzodioxane-forming reaction (C–O bond construction) between highly contorted 5,5,6,6-tetrahydroxy-3,3,3,3-tetramethyl-1,1′-spirobisindane (TTSBI) and fluorine-activated ionic monomers (Scheme 1).

We initially tried to synthesize a cation-functionalized CPP through ball grinding of TTSBI and an IL monomer (1-methyl-3-(2,3,4,5,6-pentafluoro-benzyl)-imidazoliumhexafluorophosphate: $ImPF_6$) in the presence of K_2CO_3. The resulting mixture was thoroughly washed with water and methanol; however, no polymer product was collected. We reasoned that this outcome was due to the lack of a sufficiently strong electron-withdrawing substituent on the benzene ring and the steric hindrance of the PF_6^- anion. Inspired by palladium (Pd)-mediated carbon-halide bond activation, a catalytic amount of $Pd(acac)_2$ was added into the grinding system.[11] Surprisingly, the inefficient aromatic nucleophilic substitution was distinctly accelerated, resulting in brown solids (labeled as CPP-$ImPF_6$) within 90 min. The CPP-$ImPF_6$ structure was confirmed by ^1H nuclear magnetic resonance (NMR) measurement (see the Supporting

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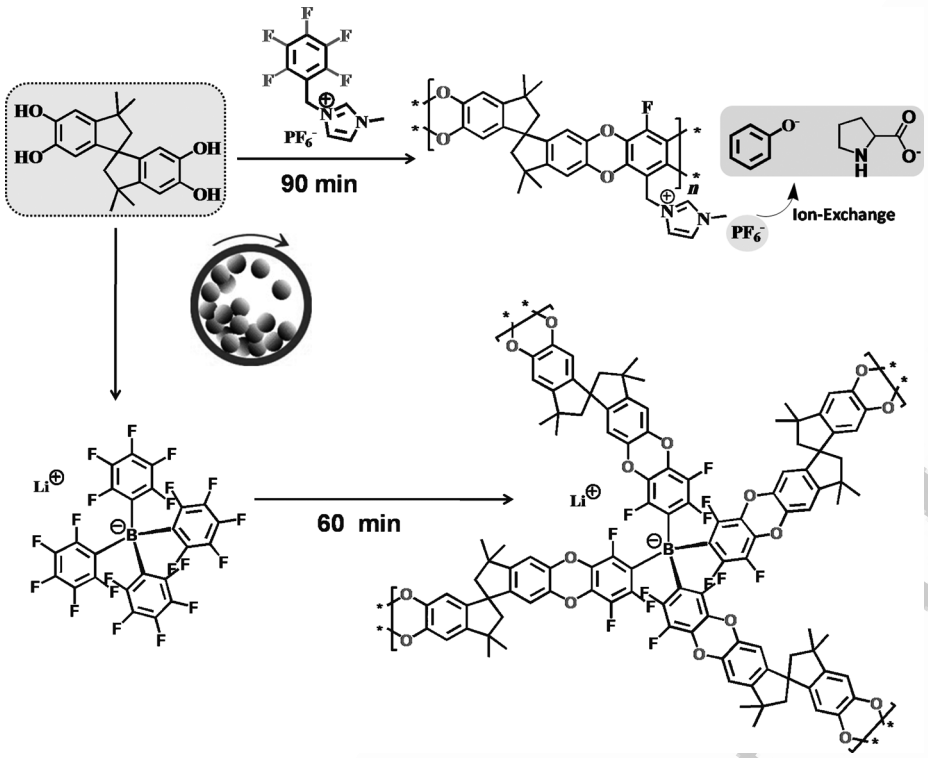

Scheme 1. Synthetic routes to CPPs by ball grinding.

Information). Interestingly, the CPP-ImPF$_6$ sample can be totally dissolved in some organic solvents, such as *N*,*N*-dimethylformamide (DMF). Further analysis by gel-permeation chromatography (GPC) illustrated the moderate molar mass of CPP-ImPF$_6$ (number-average molar mass, $M_n = 14\,200$ g mol^{-1}; weight-average molar mass, $M_w = 14\,900$ g mol^{-1}), and the corresponding polydispersity (M_w/M_n) was calculated as 1.05 (Table 1). The

Table 1. Characterization of CPP-ImPF$_6$ and Li-CPP.[a]

Sample	$M_n/10^3$ [g mol^{-1}]	$M_w/10^3$ [g mol^{-1}]	M_w/M_n	S_{BET} [m^2 g^{-1}]
CPP-ImPF$_6$	14.2	14.9	1.05	87
Li-CPP	40.2	54.0	1.34	210

[a] Molecular mass from gel-permeation chromatography test based on polystyrene standards, BET surface area from N_2 sorption measurement at 77 K. M_n: number-average molar mass, M_w: weight-average molar mass.

macromolecular character of CPP-ImPF$_6$ revealed the successful polycondensation by solid grinding. Nitrogen sorption measurement (77 K) of CPP-ImPF$_6$ showed a BET surface area of 87 m^{2}g^{-1} (Figure 1 a). Compared with PIM-1, the introduction of an ionic unit seemed to lower the porosity, and we consider that the increased polymer–polymer Coulombic interactions would cause some collapse of the microporosity.[10] However, the ionic structure indeed affords a good opportunity for post-modification and, in principle, various anions could be attached by a simple ion-exchange method.

Currently, the efficient and reversible capture of acid gases is highly desirable and is of critical importance for environmental protection.[12] CPPs with phenolic CPP-ImPhO or proline anions (CPP-ImPro) were subsequently prepared by acid-base neutralizations between phenol or proline and CPP-ImOH, which was obtained by exchanging the anion of CPP-ImPF$_6$ within 0.5 M NaOH (Figure 1 b). Then those polymer products with basic anions were tested for SO_2 capture under atmospheric pressure.[12b] The SO_2 capture by CPP-ImPhO proceeded rapidly and reached an equilibrium state in 20 min (Figure 1 c). A total of 154 mg of SO_2 was thus adsorbed per gram of CPP-ImPhO adsorbent (2.40 mmol g^{-1}), a relatively high capacity because the CPP-ImPhO actually possessed only low porosity (S_{BET} = 23 m^{2}g^{-1}, Figure S1 in the Supporting Information). Ideally, SO_2 adsorbents should be recoverable, and the endothermic regeneration step under mild conditions is highly welcome, as it avoids excessive energy use.[12] To test its reusability, the CPP-ImPhO adsorbent previously used for SO_2 adsorption was heated in a vacuum at 80 °C for 2 h. The adsorbent was then used again for SO_2 adsorption. Those adsorption/desorption cycles were repeated ten times without significant loss in adsorption capacity (Figure 1 d).

The polymer with an amino acid anion (CPP-ImPro) was also investigated for SO_2 capture. It was found that the SO_2 absorption capacity of CPP-ImPro could reach 24.6 wt% (3.84 mmol g^{-1}), higher than the value achieved by CPP-ImPhO (Figure 1 e). The existence of two basic sites in CPP-ImPro (carboxylic anion and amine) might lead to this increased capacity, because a controlled SO_2 absorption with CPP-ImPF$_6$ only led to a low capacity of 3.0 wt% (0.47 mmol g^{-1}).[13] The sorption behavior of CPP-ImPro may combine the physisorption and chemisorption. The Fourier transform infrared spectroscopy (FTIR) spectrum of CPP-ImPro before and after reaction with SO_2 is shown in Figure 1 f. There are two important features in the spectrum. First, new sorption bands in the [CPP-ImPro]-SO_2 adduct at 1318 cm^{-1} and 971 cm^{-1} give evidence for the sulfate S=O/S–O stretch, as a result of the absorption of SO_2. Second, a new band around 1670 cm^{-1} appears and can be assigned to the new COOH moiety formed by proton migration, in agreement with previous observations during SO_2/CO_2 capture by ILs (Figure 1 g).[13] The high basicity of the proline anion in CPP-ImPro might be considered the main factor in SO_2 capture.

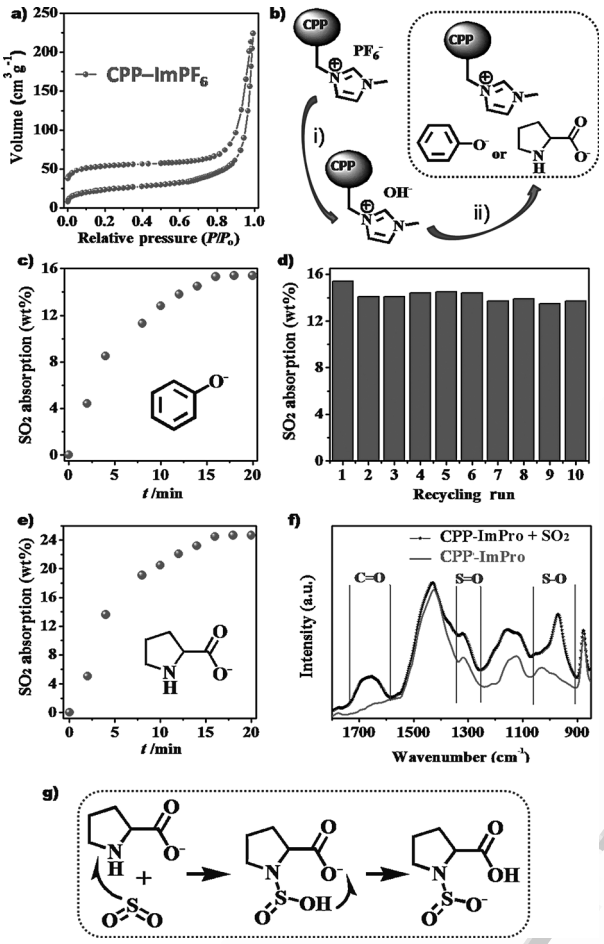

Figure 1. a) N_2 sorption isotherm of CPP-ImPF_6 sample at 77 K. b) The synthetic pathway to CPPs with basic anions. c) SO_2 absorption by CPP-PhO at 25 °C. d) The recyclability of CPP-PhO in SO_2 capture. e) SO_2 absorption by CPP-Pro at 25 °C. f) FTIR spectra of CPP-Pro before and after SO_2 capture. g) A suggested mechanism of SO_2 capture by CPP-Pro.

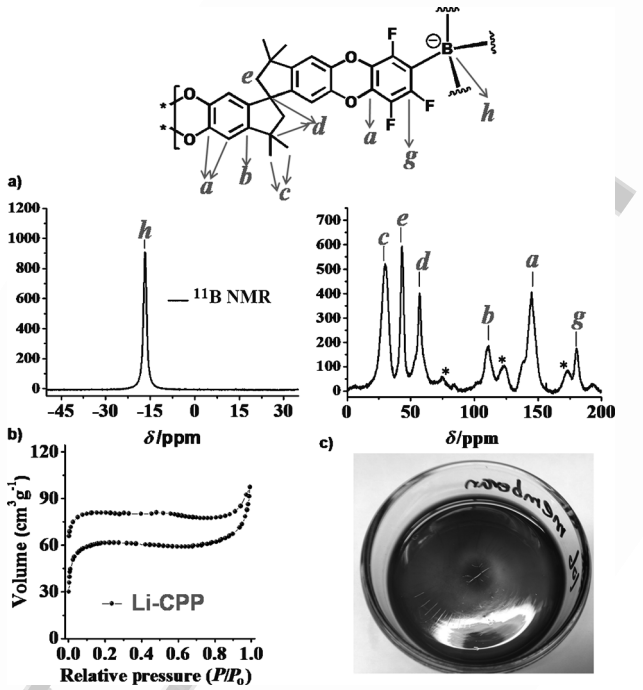

Figure 2. a) ^{11}B and ^{13}C CP/MAS solid-state nuclear magnetic resonance of Li-CPP sample. b) N_2 sorption isotherm of Li-CPP at 77 K. c) A film of Li-CPP on a glass dish.

Anionic CPPs with different metal counter-ions are of great interest, for instance: Li-activated CMP displayed a high H_2 sorption uptake, and an Mn^{2+}-containing microporous polymer is catalytically active in the aerobic oxidation of styrene with isobutyraldehyde as a radical initiator.[14,6a] Our efficient synthesis of CPPs by ball grinding was also investigated for preparing anionic organic networks based on the chemistry of PIMs. The synthetic route to Li-CPP involves C–O cross-coupling between TTSBI and commercially available lithium tetrakis(2,3,4,5,6-pentfluorophenyl)borate (Li[$B(C_6F_5)_4$]). The reactants were mechanically milled for 60 min, and no solvent was introduced in the process. The molecular structure of Li-CPP was assessed with ^{13}C CP/MAS solid-state NMR (Figure 2).The presence of primary sp^3 carbon, secondary sp^3 carbon, and quaternary sp^3 carbon from the spirobisindane ring was confirmed by peaks at 30.1, 43.6, and 57.0 ppm. The signals at 110.9 and 145.1 ppm were ascribed to the carbon atoms of the aromatic ring in the indane, and the peak at 180.0 ppm corresponded to the aromatic carbon next to a fluorine atom. Also, the ^{11}B NMR spectrum of Li-CPP showed just one intensive signal (−16.8 ppm) for the anionic borate. It is interesting that this Li-CPP polymer can be dissolved in DMF solvent, and a dark red film was cast on the glass dish after solvent evaporation. Unfortunately, the film was so brittle that we could not obtain a freestanding membrane at the current stage.

Further GPC measurement of Li-CPP illustrated its high molecular weight ($M_w = 54\,000\ g\,mol^{-1}$, $M_n = 40\,200\ g\,mol^{-1}$) with a narrow polydispersity of 1.34 (Table 1). The N_2 sorption measurement of Li-CPP showed a primary uptake at a low relative pressure and reached a plateau at relative pressures from approximately 0.1 to 0.8, a typical isothermal for microporous material (Figure 2b). The BET specific surface area of Li-CPP was 210 $m^2 g^{-1}$. Moreover, the Li-CPP polymer could be easily converted to the Na-CPP form ($S_{BET} = 190\ m^2 g^{-1}$) by stirring the polymer in 1 M NaCl for 24 h, monitored by inductively coupled plasma mass spectrometry. Therefore, the cation-exchange feature of this polymer may enable the feasible introduction of various metal ions, endowing those polymers with different capabilities.

In summary, cationic or anionic CPPs with high molecular weight and low polydispersity can easily be fabricated by ball grinding through a C–O cross-coupling process. It is important that the cationic CPPs with basic anions demonstrated good performance in SO_2 capture under atmospheric pressure. Meanwhile, soluble metal-CPPs could be easily cast as films, expanding the currently organic-dominated library of PIMs available for making membranes. Our strategy once again highlights MS in the synthesis of polymers by allowing solvent-free preparation and a fast reaction at room temperature.

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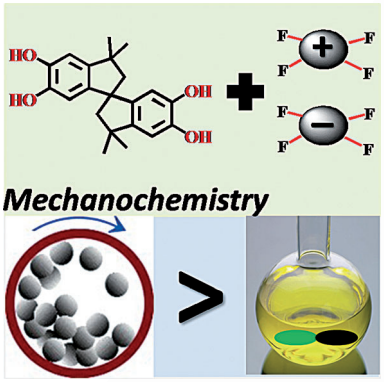
COMMUNICATION

A versatile and clean mechanochemical strategy has been developed for the dibenzodioxane-forming reaction toward charged porous polymers. Charged polymers with cationic or anionic skeletons were synthesized in a fast (60–90 min) and solvent-free manner. The intrinsically charged character makes these polymers ideal matrices for introducing various cations or anions with specific tasks (e.g., basic anions for SO_2 capture or metal ions).



Mechanochemistry

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