# **Electronic Supplementary Information for**

## Hierarchical meso-macropores poly(ionic liquid) monolith derived from

## single soft template

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### **Experimental details**

#### **Chemicals and Materials**

All chemicals were commercially available and were used as received. 1-allyl-3-vinylimidazolium chloride ([AVIm]Cl,  $\geq$ 99%), 1-allyl-3-vinylimidazolium bromide ([AVIm]Br,  $\geq$ 99%), 1-allyl-3-vinylimidazolium hexafluorophosphate ([AVIm]PF<sub>6</sub>,  $\geq$ 99%) and 1-allyl-3-vinylimidazolium tetrafluoroborate ([AVIm]BF<sub>4</sub>,  $\geq$ 99%) were purchased from Lanzhou Greenchem ILS, LICP, Chinese Academy of Sciences, and used without further purification. The triblock copolymer poly(ethylene oxide)-block-poly(propylene oxide)-block-poly-(ethylene oxide) (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, P123; Mav= 5800) was purchased from Sigma-Aldrich. Ammonium persulfate (APS,  $\geq$ 98%) was purchased from Shanghai Lingfeng Chemical Reagent CO., LTD.

### Synthesis

The hierarchically meso- and macroporous poly(ionic liquid)s monoliths, shorten as HMP, were prepared through soft template method using amphiphilic triblock copolymer P123 as the single soft template. The synthesis was achieved through free radical self-polymerization of 1-allyl-3-vinylimidazolium ionic liquid. In a typical preparation, 3 g P123 was dissolved using 8 g H<sub>2</sub>O in a three-necked flask. Subsequently, 1.7 g ionic liquid monomer [AVIm]Cl was added into above clear homogenous P123 solution with stirring. The three-necked flask was put in water bath with controlled temperature at 25 °C and kept in the bath under vigorous stirring for more than 12 h, in order to form well-dispersed micelles and reach thermal equilibrium. Then, 7 g APS as the initiator was added and stirred for another few hours until achieving a homogeneous and transparent solution. The polymerization process was triggered in the presence of the initiator by heating above 38 °C in water bath under N<sub>2</sub> atmosphere for 24 h. Then the solid was collected by filtration, washed with deionized water three times and dried under vacuum at 50 °C. The template was removed by extracting the as-synthesized material (1.0 g) in 150 mL pure ethanol plus 1.0 mL concentrated aqueous HCl solution (36-38 wt%). The yield of the products was around 75%.

The heteropolyanion loaded hybrid PW@HMP was prepared by immobilizing Keggin-type POM phosphotungstic acid ( $H_3PW_{12}O_{40}$ ) on the mesoporous hierarchically meso- and macroporous poly(ionic liquid)s monoliths through ion-exchange process. The solid HMP materials (0.21 g, 1.25 mmol based on the monomer repeating units) was dispersed in 120 mL water containing pure  $H_3PW_{12}O_{40}$  (1.2 g, 0.42 mmol), followed with

stirred for 72 h at room temperature. The solid was obtained by the consecutive basic operations including filtration, washing and drying. The control hybrid catalyst IL-PW was prepared by pairing the PW anion with IL-cation of [AVIm]Cl. The IL precursor [AVIm]Cl (0.21 g, 1.25 mmol) was dispersed in 120 mL water containing  $H_3PW_{12}O_{40}$  (1.2 g, 0.42 mmol), followed with stirred for 72 h at room temperature. The solid was obtained by the consecutive basic operations including filtration, washing and drying.

#### Characterization

The morphologies and structure of the resultant meso-and macroporous PILs were determined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM measurements were performed by using a Hitachi S4800 electron microscope, and the samples were coated with Au film prior to imaging in order to improve the conductivity. TEM analysis was performed on a JEM-2100 (JEOL) electron microscope operating at 200 kV. Nitrogen sorption isotherms were measured at -196 °C on a BELSORP-MINI volumetric adsorption analyzer, and the samples were outgassed in the degas port of the apparatus at 80°C for 3 h prior to testing. The BET (Brunauer, Emmett, and Teller) specific surface area was calculated using adsorption data acquired at a relative pressure (P/P<sub>0</sub>) range of 0.05–0.22 and the total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution (PSD) curves were calculated from the adsorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) algorithm. The macropore size distribution was detected by using a Poremaster GT-60 mercury inclusion porosimeter. Fourier transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet iS10 FT-IR instrument (KBr disks) ranging from 4000 to 400 cm<sup>-1</sup>. Solid state <sup>13</sup>C and <sup>1</sup>H spin-echo pulse NMR spectra were recorded on a Bruker Avance 400D multinuclear solidstate magnetic resonance spectrometerwith a magnetic field of 9.4 T. The CHN elemental analysis was performed on an elemental analyzer Vario EL cube. Thermogravimetric (TG) analysis was performed with an STA409 instrument in oxygen atmosphere at a heating rate of 10°C min<sup>-1</sup>. The size distribution of the micellar solution was detected by dynamic light scattering (DLS, Microtrac, Zetatrac, USA).

#### **Catalysis assess**

The catalytic performances were assessed in the epoxidation of the probe substrate *cis*-cyclooctene with aqueous  $H_2O_2$  as oxidant and methanol as solvent. In a typical run, cis-cyclooctene (5 mmol), methanol (1 mL) and catalyst (8.4 µmol based on the PW anion) were stirred in a flask at 60 °C for several minutes, and then 30 wt% aqueous  $H_2O_2$  was added drop by drop. The reaction was continued for 4 h with heating at reflux. After reaction, the internal standard *n*-heptanol was added and the resulting mixture was diluted with methanol. The organic phase was collected and analyzed by gas chromatography (Agilent 7890B) equipped with a flame ionization detector and a capillary column (HP-5,  $30m \times 0.25mm \times 0.25\mu m$ ). Conversion (based on  $H_2O_2$ ) = (mmol cis-cyclooctene converted)/(mmol initial  $H_2O_2$ ) ×100%; selectivity of epoxide= (mmol epoxide)/(mmol cis-cyclooctene converted) ×100%. During catalyst reusability assessment, the catalyst was separated by filtration, washed with ethanol three times, dried in a vacuum at 80 °C for 6 h, and then reused in next run.

| Entry | С     | Ν     | Н    | S    | C/N       |  |
|-------|-------|-------|------|------|-----------|--|
|       | (%)   | (%)   | (%)  | (%)  | (mol/mol) |  |
| 1     | 36.32 | 10.65 | 5.05 | 9.20 | 3.98      |  |
| 2     | 37.50 | 10.85 | 4.83 | 9.82 | 4.04      |  |
| 3     | 36.88 | 7.12  | 5.43 | 7.12 | 6.04      |  |
| 4     | 56.31 | 16.42 | 6.51 | -    | 4.00      |  |

Table S1. The elemental analysis data of selected samples.<sup>[a]</sup>

[a]Synthesis conditions: the samples entry 1-3 are polymerized firstly at 38 °C for 10 h then at 50 °C for 14 h, with the initial weight amounts of *x* g P123, 1.7 g [AVIm]Cl, 8 g H<sub>2</sub>O and 7 g APS; *x*= 0 for entry 1, *x*= 3 for entry 2, and *x*= 3 for entry 3 but without removing the template; entry 4 is the result for the ionic liquid monomer [AVIm]Cl. According to the elemental analysis of this Table, it can be calculated that about 39.6% of Cl<sup>-</sup> over HMP(3) sample was anion-exchanged with SO<sub>4</sub><sup>2-</sup>. The calculation was based on the equation of *p*= (W<sub>S</sub>%/M<sub>S</sub>/e<sub>S</sub>)/(W<sub>N</sub>%/M<sub>N</sub>/n<sub>N</sub>), in which *p*: the proportion of anion exchanged with sulphate counter-ion; W<sub>S</sub>%: the weight percentage of S atom obtained from the elemental analysis result; M<sub>S</sub>: atomic weight of S; e<sub>S</sub>: the valence of SO<sub>4</sub><sup>2-</sup>; W<sub>N</sub>%: the weight percentage of N atom obtained from the elemental analysis result; M<sub>S</sub>: atomic weight of N; *n*<sub>N</sub>: the quantity of N in each repeat unit of the MPIL that is 2 in this work. The calculation assumes that the counter anions were Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>, and the cation was the repeat unit of the MPIL.

| Entry           | Solvent   | Ionic liquid     |            | $T_1$ | $T_2$ | $S_{BET}^{[b]}$ | $V^{[c]}$    | $D_{av}^{[d]}$ |
|-----------------|-----------|------------------|------------|-------|-------|-----------------|--------------|----------------|
|                 | $H_2O(g)$ | Anion            | Amount (g) | (°C)  | (°C)  | $(m^{2}/g)$     | $(cm^{3}/g)$ | (nm)           |
| 1               | 8         | Cl-              | 0.5        | 38    | 50    | 21              | 0.21         | 39.9           |
| 2               | 8         | Cl <sup>-</sup>  | 0.8        | 38    | 50    | 90              | 0.45         | 19.7           |
| 3               | 8         | Cl-              | 1.0        | 38    | 50    | 135             | 0.64         | 19.0           |
| 4               | 8         | Cl-              | 2.5        | 38    | 50    | 103             | 0.77         | 29.6           |
| 5               | 5         | Cl-              | 1.7        | 38    | 50    | 122             | 0.62         | 20.6           |
| 6               | 8         | Cl-              | 1.7        | 38    | 50    | 144             | 0.94         | 26.0           |
| 7               | 10        | Cl <sup>-</sup>  | 1.7        | 38    | 50    | 131             | 0.58         | 17.8           |
| 8               | 20        | Cl <sup>-</sup>  | 1.7        | 38    | 50    | 107             | 0.76         | 28.3           |
| 9               | 8         | Cl-              | 1.7        | 38    | 38    | 151             | 1.02         | 27.0           |
| 10              | 8         | Cl <sup>-</sup>  | 1.7        | 45    | 45    | 132             | 0.69         | 20.8           |
| 11              | 8         | Cl-              | 1.7        | 50    | 50    | 119             | 0.75         | 25.3           |
| 12              | 8         | Cl-              | 1.7        | 55    | 55    | 124             | 0.59         | 18.8           |
| 13              | 8         | Cl-              | 1.7        | 60    | 60    | 117             | 0.97         | 33.1           |
| 14              | 8         | Cl-              | 1.7        | 38    | 45    | 137             | 0.92         | 26.7           |
| 15              | 8         | Cl-              | 1.7        | 38    | 55    | 144             | 0.87         | 24.1           |
| 16              | 8         | Cl-              | 1.7        | 38    | 60    | 130             | 0.96         | 29.2           |
| 17 <sup>e</sup> | 8         | Br <sup>-</sup>  | 1.7        | 38    | 50    | 63              | 0.35         | 21.8           |
| 18 <sup>e</sup> | 8         | BF₄ <sup>−</sup> | 17         | 38    | 50    | 32              | 0.17         | 21.8           |

Table S2.Textural properties of HMP materials synthesized under different conditions.<sup>[a]</sup>

[a] Synthesis conditions: P123 (3g), APS (7 g). [b] BET surface area. [c] Total pore volume. [d] Average pore diameter. [e] The influence of the counter anions on the pore formation has been previously reported in some references (H. P. Lin, C. P. Kao, C. Y. Mou, S. B. Liu, *J. Phys. Chem. B*, 2000, **104**, 7885-7894; S. Che, S. Lim, M. Kaneda, H. Yoshitake, O.Terasaki and T. Tatsumi, *J. Am. Chem. Soc.*, 2002, **124**, 13962–13963). In this work, the influence of the counter anions of the IL precursor was also studied and the results indicate that the counter anions significantly affect the pore formation. The reason can be assigned to the different counter anions will affect the interaction between IL precursor (I<sup>+</sup>) and the template (S<sup>0</sup>) through S<sup>0</sup>H<sup>+</sup>X<sup>-</sup>I<sup>+</sup> mode, which is crucial for the pore formation process. For example, the size of Br is larger than Cl<sup>-</sup>, thus may decrease the S<sup>0</sup>H<sup>+</sup>X<sup>-</sup>I<sup>+</sup> interaction, which ultimately results in a relative smaller surface area and pore volume (Entry 17, Table S2). At same synthetic conditions, the sample synthesized using BF<sub>4</sub><sup>-</sup> with larger size than Br<sup>-</sup> presented further smaller surface area and pore volume (Entry 18, Table S2). Moreover, the S<sup>0</sup>H<sup>+</sup>X<sup>-</sup>I<sup>+</sup> interaction will be further decreased when the counter anion was changed to be PF<sub>6</sub><sup>-</sup>, causing no solid product during the synthetic process. The above results and analysis suggest that the counter anions significantly affect the pore formation process and it seems that the smaller size of the counter anion, the larger surface area and pore volume can be obtained.



Figure S1. FTIR spectra of (a) IL precursor, (b) HMP(3), (c)HMP(3) without removing the template and (d) HMP(0).

As shown in the above FTIR spectra, all these samples as well as the IL precursor exhibited a very broad and strong band at 3000-2850 cm<sup>-1</sup> attributable to stretching vibrations of the C-H group. The samples of HMP(3), HMP(3) without removing the template and HMP(0) all presented several featured bands for imidazole, in which the bands around 1650 and 1560 cm<sup>-1</sup> were indicative of the imidazole ring skeleton, 1460 cm<sup>-1</sup> was the deformation vibration from imidazole ring C-H bond and 1210-1220 cm<sup>-1</sup> was the imidazole ring C-H bond plane bending vibration. The observation of these bands evidences the existence of the imidazolium-IL moiety in the polymeric framework. The bands around 3065 and 957 cm<sup>-1</sup> attributable to the unsaturated C-H vibrations were clearly observed on the spectrum of IL precursor (curve a) but disappeared on the spectra of HMP(3), HMP(3) without removing the template and HMP(0), suggesting the consuming of the olefinic bond (*Chem. Comm., 2014,* **50**, 11957-11960). Therefore, the polymerization can be recognized as complete. The vibration of C=C is not adopted as one judgment due to the overlapping of this band with the vibration of C=N that complicated the IR spectra.

By comparing curve b and c of the IR spectra, no significant variation can be observed mainly due to that the template only produced C-H and C-O vibrations that were usually overlapped with the C-H and C-N vibration over imidazolium-IL moiety. Therefore, it is difficult to identify the remove of template from the variation of the IR spectra. In this work, the removal of the template was identified by the elemental analysis (Table S1) through comparing the C and N content before and after template removal. The template P123, EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> containes the elements of C, H and O but is lack of N. The template-containing sample contained much high C content, index of the existence of the template. After template removal, the C content decreased and the molar ratio of C to N was similar to the IL precursor, suggesting the (almost) complete removal of template.

Besides the similar major featured bands of imidazolium-IL moiety, there indeed existed some slight difference between the spectrum d and b (Figure S1) though we had repeated several times. However, the exact reason is unclear presently. It may be the drastic variation in pore structure of these two samples that influences the secondary polymeric structure and ultimately leads to the slight difference.



Figure S2. <sup>1</sup>H NMR (left) and <sup>13</sup>C NMR (right) spectra of (a) HMP(0) and (b) HMP(3).

In the <sup>1</sup>H NMR spectrum, the broad multi-signals ranging from 1.0 to 1.5 ppm were assigned to the backbone protons on the methine that is not adjacent next to the nitrogen atom. The signal at 3.5 ppm on the spectrum of HMP(3) was ascribed from the methine  $[-CH_2-CH(N)-CH_2-]$  that is close to the nitrogen atom, which was almost invisible in HMP(0). The  $[-CH_2CN]$  methylene protons appeared at 5.5 ppm. The above analysis is according to the reference *Chem. Mater.*, 2013, **25**, 3003-3010. The chemical shift peak of the solid state <sup>13</sup>C NMR spectrum for HMP (0) and HMP(3) around 35-37 ppm corresponded to the CH moiety and peaks around 55 ppm to the methylene units linking the imidazolium ring. The strong overlapping peak at around 125 ppm was ascribed to the C4 and C5 atoms in imidazolate ring. The C2 atom in the same imidazolate ring was reflected by the single at 137 ppm (*Green chem.*, 2013, **15**, 1584-1589). The signal at 68 ppm of HMP(3) was assigned to traces of ethylene oxide organic residues from the P123 (*Dalton Trans.*, 2013, **42**, 13381-13389).



Figure S3. (A) TG and (B) DSC curves of HMP(3) and HMP(0).



Figure S4. The macropore size distribution curves detected by mercury inclusion porosimetry of HMP(x) series materials synthesized with the initial composition containing P123 (x g), [AVIm]Cl (1.7 g), H<sub>2</sub>O (8 g) and APS (7 g).



Figure S5. Size distributions of micelles in the micellar solutions containing 8 g H<sub>2</sub>O and (a) 3 g P123; (b) 3 g P123+1.7 g IL; (c) 3 g P123+0.5 g IL; (d) 3 g P123+0.8 g IL; (e) 3 g P123+1 g IL; (f) 3 g P123+2.5 g IL; (g) 0.5 g P123+1.7 g IL; (h) 1 g P123+1.7 g IL; (i) 2 g P123+1.7 g IL; (j) 4 g P123+1.7 g IL.



Figure S6. TEM images of the micellar solutions containing 8 g H<sub>2</sub>O and (A) 3 g P123, (B) 3 g P123+1.7 g IL.

#### The understanding of the formation mechanism of the hierarchical meso-macroporous structure:

Figure S5 gave the size distributions of micelles in the micellar solutions with different P123 and IL concentrations. The micellar solution of P123 showed a relative narrow size distribution ranging from 15 to 33 nm centered at 23 nm (curve a). After the addition of IL in above solution, similar size distribution was observed, suggesting that the micelles changed slightly before and after addition of IL, which was further confirmed by the TEM images (Figure S5). Moreover, similar size distribution curves were observed over the micellar solutions with with different P123 and IL concentrations (curves c-j), indicating that the concentrations of the ILs and P123 only slightly influence the micelle state in the micellar solutions before polymerization. The pore size distributions of the mesoporosity of the final materials were similar to the size distributions of micelles in the initial meclellar solution, reflecting close relationship between the micelle states of P123 with the meso-structure of the final materials. No aggregations of micelles located in macroporous scales were observed in the initial micellar solutions before and after addition of ILs, revealing that the macroporous structure of the final materials may not be directly caused by the template effect of P123 micelles. The above results and analysis indicate that the micelle state was related to the meso-structure of final materials but the concentrations of the ILs and P123 did not directly determine the ultimate overall porosity. There should be some reassembly process occurred during the polymerization step that affected the final pore structure. Different concentrations of ILs and P123 will cause different reassembly process, thus producing the variation of the pore structure. The formation of macroporous structure can be recognized as the packing of the small particles. During the synthesis, macroporous structure can be preserved when the fusion of the particles occurred through a macro-scale to form a monolithic macro-morphology. Such phenomenon has been observed over various syntheses of mesoporous silica (Chem. Eur. J., 2009, 15, 6748-6757; Chem. Commun., 2009, 3627-3629) or periodic mesoporous organosilica materials (J. Mater. Chem. B, 2013, 1, 1738-1748). In the synthesis of silicate materials, the fusion was derived from the condensation of the surface silanol groups (Chem. Eur. J., 2009, 15, 6748-6757; Microporous Mesoporous Mater., 1999, 27, 273-285). Here, the fusion of the particles of the mesoprous poly(ionic liquid) can be assigned to reaction of the surface free radicals and the intertwine of polymeric framework. Briefly, the mesoporosity is templated by the P123 micelles while the macroporous structure is suggested to be caused by the particles packing and fusion process.



Figure S7. Nitrogen adsorption/desorption isotherms (left) and pore size distribution (right) of (a) HMP(0), (b) HMP(0.5), (c) HMP(1), (d) HMP(2), (e) HMP(3) and (f) HMP(4).



Figure S8. Nitrogen adsorption/desorption isotherms (left) and pore size distribution (right) of the HMPs polymerized firstly at 38 °C for 10 h then at 50 °C for 14 h, with the mass amounts of raw materials in initial compositions being 3 g P123, y g [AVIm]Cl, 8 g H<sub>2</sub>O and 7 g APS. (a) y=0.5, (b) y=0.8, (c) y=1 and (d) y=2.5.



Figure S9. Nitrogen adsorption/desorption isotherms (left) and pore size distribution (right) of the HMPs polymerized firstly at 38 °C for 10 h then at 50 °C for 14 h, with the mass amounts of raw materials in initial compositions being 3 g P123,1.7 g [AVIm]Cl, z g H<sub>2</sub>O and 7 g APS. (a) z= 5, (b) z= 10 and (c) z= 20.



Figure S10. Nitrogen adsorption/desorption isotherms (left) and pore size distribution (right) of the HMPs, with the mass amounts of raw materials in initial compositions being 3 g P123, 1.7 g [AVIm]Cl, 8 g H<sub>2</sub>O and 7 g APS. The samples (a-e) are prepared by polymerizing at (a) 38 °C, (b) 45 °C, (c) 50 °C, (d) 55 °C and (e) 60 °C for 24 h; the samples (f-h) are prepared by polymerizing at 38°C for 10 h then at (f) 45 °C, (g) 55 °C and (h) 60 °C for 14 h.



Figure S11. Nitrogen adsorption/desorption isotherms (left) and pore size distribution (right) of the HMPs polymerized firstly at 38 °C for 10 h then at 50 °C for 14 h, with the mass amounts of raw materials in initial compositions being 3 g P123, 1.7 g [AVIm]X, 8 g H<sub>2</sub>O and 7 g APS. (a) X: Br and (b) X: BF<sub>4</sub><sup>-</sup>.



Figure S12. Nitrogen sorption isotherms (left) and pore size distribution (right) of PW@HMPs and IL-PW samples.



Figure S13.Thermogravimetric (TG) analysis results of PW@HMPs and IL-PW samples. The different percentage of residual weight at 700 °C of the various materials depends on the variation of loading amount of the PW. The reason can be assigned to the pore structure variation of these materials.



Figure S14. FTIR spectrum of (a) PW@HMP(0.5); (b) PW@HMP(1); (c) PW@HMP(2); (d) PW@HMP(3). All the PW@HMP(x) samples exhibited the featured bands for imidazole, in which the bands around 1650 and 1560 cm<sup>-1</sup> were indicative of the imidazole ring skeleton, 1460 cm<sup>-1</sup> was the vibration from imidazole ring C-H or N-H bond and 1210-1220 cm<sup>-1</sup> was the imidazole ring C-H bond plane bending vibration, evidencing the existence of the imidazolium-IL moiety in the catalyst framework. The spectra also presented the vibration bands characteristic of the Keggin anion locating at 1082, 984, 889, and 816 cm<sup>-1</sup>, corresponding to vibrations v(P-O<sub>a</sub>), v(W=O<sub>t</sub>), v(W-O<sub>b</sub>-W), and v(W-O<sub>c</sub>-W), respectively. The observation in FTIR spectra provides additional evidence for the successful immobilization of PW species.



Figure S15. Reaction results of PW@HMP(3)-catalyzed epoxidation of cis-cyclooctene using different molar ratios of cis-cyclooctene to  $H_2O_2$  ( $n_{cyc}/n_{H2O_2}$ ). Reaction conditions: catalyst (0.03 g), cis-cyclooctene (5 mmol), 30 wt%  $H_2O_2$  (4 mmol, 4.5 mmol, or 5 mmol), methanol (1 mL, solvent), 60 °C, 4 h. The conversion is calculated based on  $H_2O_2$ .



Figure S16. Catalytic reusability of PW@HMP(3) in catalyzing the epoxidation of cis-cyclooctene with  $H_2O_2$ . Reaction conditions: catalyst (0.05 g), cis-cyclooctene (5 mmol), 30 wt%  $H_2O_2$  (4 mmol), methanol (1 mL, solvent), 60 °C, 4 h. The conversion is calculated based on  $H_2O_2$ .



Figure S17. FTIR spectra of (a) reused PW@HMP(3) from the third recycling run and (b) fresh PW@HMP(3).



Figure S18. Nitrogen sorption isotherm with mesopore size distribution (inset) of reused PW@HMP(3) sample. from the third recycling run.



Figure S19. SEM images (A, B) and TEM images (C, D) of the reused PW@HMP(3) sample from the third recycling run.

Details of the description and discussion on the characterizations for the reused PW@HMP(3) sample (Figure S17-19):

The reused PW@HMP(3) sample showed similar IR spectrum to the fresh one (Figure S17). Both the fresh and reused sample exhibited the featured bands for imidazole. The bands around 1650 and 1560 cm<sup>-1</sup> were indicative of the imidazole ring skeleton, 1460 cm<sup>-1</sup> was the vibration from imidazole ring C-H or N-H bond and 1210-1220 cm<sup>-1</sup> was the imidazole ring C-H bond plane bending vibration, which evidences the existence of the imidazolium-IL moiety in the catalyst framework. The spectra also presented the vibration bands characteristic of the Keggin anion located at 1082, 984, 889, and 816 cm<sup>-1</sup>, corresponding to vibrations v(P-O<sub>a</sub>), v(W=O<sub>t</sub>), v(W-O<sub>b</sub>-W), and v(W-O<sub>c</sub>-W), respectively. The above IR observations indicate that the polymeric framework and the PW species were preserved on the reused sample. Nitrogen sorption analysis (Figure S18) showed that the reused sample also gave the type IV isotherm with similar hysteresis loop as the fresh one, indicating the retaining of the specific porous structure on the reused sample, which is confirmed by the SEM and TEM images (Figure S19). In general, the reused catalyst preserves the compositional and porous structural properties, which accounts for the observation that the catalyst can be catalytically reused several times.