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# A hierarchical porous ionic organic polymer as a new platform for heterogeneous phase transfer catalysis†

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In this work we demonstrate for the first time the construction of a hierarchical porous ionic organic polymer *via* the polymerization of the vinyl-functionalized quaternary phosphonium salt monomer under solvothermal conditions. The resultant polymerized quaternary phosphonium (PQP) salt features a hierarchical porous structure and excellent amphiphilicity. After anion-exchange with peroxotungstate, the afforded  $W_2O_{11}/PQP$  demonstrates excellent performances as a heterogeneous phase-transfer catalyst in the context of epoxidation of olefin and oxidation of dibenzothiophene when using the environmentally benign  $H_2O_2$  as the oxidant, superior to the homogeneous counterparts and other types of phase-transfer catalysts. Our work thereby paves a way to advance hierarchical porous ionic organic polymers as a new type of platform for heterogeneous phase transfer catalysis.

## Introduction

Porous solid catalysts, as represented by zeolites,<sup>1</sup> play an important role in fine chemical and petrochemical industries.<sup>2</sup> It has been of continuous interest from both academia and industry to search for new types of porous materials as heterogeneous catalysts for various organic reactions particularly under environmentally benign conditions.<sup>3</sup> For organic reactions carried out in different immiscible phases especially including water as a green solvent, it has been recognized that phase-transfer catalysts are needed in order to maximize surface contact between substances residing in different immiscible phases thereby accelerating reactions.<sup>4</sup> Silica<sup>5</sup> and polymers<sup>6</sup> functionalized with ionic liquids or polyether<sup>7</sup> have been explored as heterogeneous phase-transfer catalysts; however, ionic liquid functionalized silica prefers to reside in the aqueous phase and usually needs polar solvents to promote the reactions, whereas polymers grafted with ionic liquids have very low surface areas. Therefore, there is still a need to search for new types of heterogeneous phase-transfer catalysts that can efficiently facilitate catalytic reactions in diphasic catalytic systems.

Porous organic polymers (POPs),<sup>8</sup> which feature high surface areas, high water/chemical stability, and functionalizable pore

walls, have recently been explored as a new type of porous material for applications in gas storage,<sup>9</sup> gas separation,<sup>10</sup> catalysis,<sup>11</sup> *etc.*<sup>12</sup> We hypothesize that if an ionic liquid monomer is employed for the construction of POPs, the afforded porous ionic organic polymers can not only overcome the issues of high viscosity and catalyst/product separation for ionic liquids,<sup>13</sup> but also can inherit the advantages of high surface area and high water/chemical stability for POPs as well as exhibit excellent amphiphilicity. In addition, if the hierarchy of pore sizes (*i.e.* existence of both micropores and mesopores) can be achieved, the mass transfer particularly for large sized substrates will be greatly accelerated during the reaction process, as well demonstrated in hierarchical zeolites.<sup>14</sup> Thereby, such kinds of hierarchical porous ionic organic polymers are anticipated to serve as a new type of platform for highly efficient heterogeneous phase transfer catalysis.

In this contribution, we report such a hierarchical porous ionic organic polymer that is based on the vinyl-functionalized quaternary phosphonium salt monomer and after anion-exchange of peroxotungstates demonstrates excellent performances as a heterogeneous phase transfer catalyst in the context of epoxidation of olefin and oxidation of dibenzothiophene.

## Results and discussion

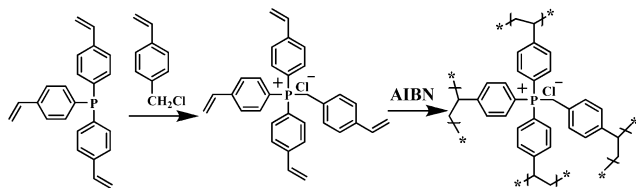
### Synthesis and characterization of PQP salt

As shown in Scheme 1, the vinyl-functionalized quaternary phosphonium salt monomer [VP-IL, (4-vinyl-benzyl)-tris-(4-vinyl-phenyl)-phosphonium chloride] was first synthesized from vinyl-functionalized triphenylphosphorous and 4-vinyl-benzyl chloride. Under solvothermal conditions in

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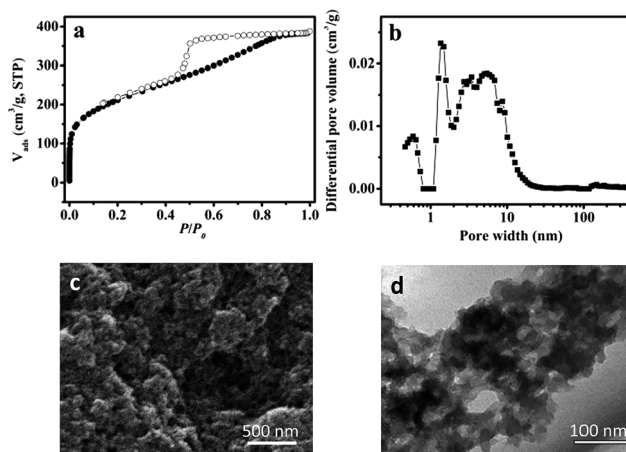


Scheme 1 Synthesis procedure of PQP salt.

dimethylformamide (DMF) at 100 °C, the polymerization of the VP-IL monomers in the presence of AIBN (azobisisobutyronitrile) afforded the porous ionic organic polymer of polymerized quaternary phosphonium (PQP) salt as a white solid.

$^{13}\text{C}$  solid-state NMR spectra of the PQP salt (Fig. 1a and Fig. S1†) show a new peak at 41.6 ppm assignable to the polymerized vinyl groups from the VP-IL monomers (Fig. S2b†).<sup>14a</sup> In addition, the  $^{31}\text{P}$  MAS NMR spectrum (Fig. 1b) reveals just one signal at 20.5 ppm and the chemical shift is similar to that observed in the monomer (Fig. S2c†), suggesting the robustness of the quaternary phosphonium salt structure during the solvothermal polymerization process. The powder X-ray diffraction (PXRD) pattern (Fig. S3†) shows a broad peak in the range of 10 to 35°, indicating the amorphous nature of the PQP salt.

$\text{N}_2$  sorption isotherms collected at 77 K reveal that the PQP salt possesses a BET surface area of 758  $\text{m}^2 \text{g}^{-1}$  and a total pore volume of 0.59  $\text{cm}^3 \text{g}^{-1}$ . It is noteworthy that the PQP salt exhibits a sorption behavior of type I plus type IV (Fig. 2a), suggesting its hierarchical porous structure comprised of both micropores and mesopores. The adsorption at low pressure ( $P/P_0 < 0.01$ ) is due to the filling of micropores, while the hysteresis loops at higher relative pressure ( $P/P_0 = 0.4\text{--}0.9$ ) is assigned to the presence of mesoporosity in the sample. Pore size distribution analysis based on the nonlocal density functional theory method (NLDFT) reveals that pore sizes of the PQP salt are distributed at 0.6, 1.4, 3.3, and 5.6 nm (Fig. 2b). The SEM (Fig. 2c) and TEM (Fig. 2d) images further confirm the presence of hierarchical porosity in the PQP salt. Thermogravimetric analysis conducted in a  $\text{N}_2$  atmosphere (Fig. S4†) shows that the

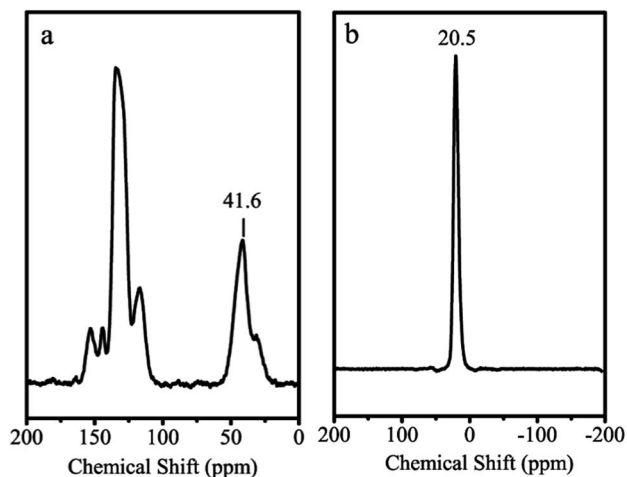
Fig. 2 (a)  $\text{N}_2$  sorption isotherms, (b) pore size distributions, (c) SEM, and (d) TEM images of the PQP salt.

decomposition of the PQP salt starts from 400 °C, indicating its good thermal stability. Its high chemical stability has been revealed by the fact that the PQP salt can retain its porous framework structure after the treatments in strong acidic solution (10 M HCl), as evidenced by the negligible drop in the surface area (Fig. S5 and Table S1†).

The amphiphilicity of the PQP salt has been indicated from the photographs (Fig. S6†) of water, ethanol, hexane, or DMF droplets on its surface, all of which exhibit excellent wettability. Liquid adsorption tests (Fig. S7†) show that the PQP salt can uptake as high as 5.4 g/g water and 4.2 g/g hexane, further confirming its amphiphilic feature, which is very important for phase transfer catalysts.<sup>15</sup>

### Synthesis and characterization of PQP salt based phase transfer catalyst

To evaluate the performances of the PQP salt as a phase transfer catalyst, olefin epoxidation and dibenzothiophene oxidation using the environmentally benign oxidant of  $\text{H}_2\text{O}_2$  (ref. 16) were chosen as model reactions considering their importance and significance for the production of fine chemicals and desulfurization of fuels.<sup>17</sup> Given that both hydrophobic and hydrophilic substrates are involved as the reactants, phase transfer catalysts are favorable for enhancing the performances of these two types of reactions. To prepare PQP salt as a phase transfer catalyst, peroxotungstate anions, which have been proven to be highly active and highly selective for reactions involving  $\text{H}_2\text{O}_2$ , were chosen for anion-exchange into the PQP salt in this work to demonstrate the “proof-of-concept”; but in principle, various types of catalytically active anions can be introduced into the PQP salt. The anion in the PQP salt was first exchanged from  $\text{Cl}^-$  to  $\text{PF}_6^-$  and then to peroxotungstate to afford the phase transfer catalyst of  $\text{W}_2\text{O}_{11}/\text{PQP}$ .<sup>16,17</sup> Fig. S8† shows IR spectra of PQP salt,  $\text{W}_2\text{O}_{11}/\text{PQP}$ , and potassium peroxotungstate ( $\text{K}_2\text{W}_2\text{O}_{11}$ ). Compared with PQP salt, the  $\text{W}_2\text{O}_{11}/\text{PQP}$  displays three additional bands around 570, 729, and 870  $\text{cm}^{-1}$ , which are associated with the characteristic bands of  $\text{W}_2\text{O}_{11}^{2-}$ .<sup>18</sup> XPS

Fig. 1 (a)  $^{13}\text{C}$  and (b)  $^{31}\text{P}$  MAS NMR spectra of PQP salt.

spectroscopy analysis shows that the  $W_2O_{11}/PQP$  and the potassium peroxotungstate have almost the same binding energy values of W 4f (Fig. S9†). These results confirm the successful incorporation of peroxotungstate *via* the anion exchange process. ICP-OES results reveal a W loading of 7.4 wt% in the  $W_2O_{11}/PQP$  (theoretical value is about 12.5 wt% for complete exchange). The  $W_2O_{11}/PQP$  also exhibits hierarchical porosity (a BET surface area of  $520\text{ m}^2\text{ g}^{-1}$ , a pore volume of  $0.41\text{ cm}^3\text{ g}^{-1}$ , and pore size distribution at 0.6–1.4, and 2.8–5.4 nm, Fig. S10†) and amphiphilic feature (adsorption capacity for water and hexane is 4.3 and 3.5 g/g, respectively, Fig. S11 and S12†). The performances of  $W_2O_{11}/PQP$  as the phase transfer catalyst were then evaluated in the context of the aforementioned two types of reactions.

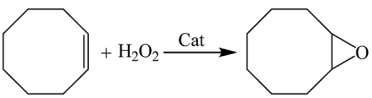
### Evaluation of catalytic performances

Table 1 presents catalytic data in the epoxidation of cyclooctene with equivalent  $H_2O_2$  as the oxidant and water as the green solvent over various catalysts containing the same amount of the  $W_2O_{11}^{2-}$ . Notably, the soluble hydrophilic  $K_2W_2O_{11}$  and amphiphilic  $[PPh_3Bn]_2[W_2O_{11}]$  catalysts exhibit relatively low activities (4.5% and 11.2%, entries 1 and 2 in Table 1). The insoluble hydrophobic porous polymer framework (polydivinylbenzene, PDVB) containing  $W_2O_{11}^{2-}$  species ( $W_2O_{11}/PDVB$ ) and insoluble amphiphilic nonporous ionic polymer

anchored with  $W_2O_{11}^{2-}$  anions ( $W_2O_{11}/NP$ ) also exhibit poor activities, giving the conversion of cyclooctene at 8.7% and 24.6%, respectively (entries 3 and 4 in Table 1). In contrast, the  $W_2O_{11}/PQP$  is highly active for this reaction, affording the conversion as high as 71.1% (entry 5 in Table 1). It is worth mentioning that the given PQP is inactive for this reaction, and much higher activity observed for the  $W_2O_{11}/PQP$  than that for the soluble  $K_2W_2O_{11}$  and  $[PPh_3Bn]_2[W_2O_{11}]$  as well as the insoluble  $W_2O_{11}/PDVB$  and  $W_2O_{11}/NP$  should be attributed to the combined contributions from the amphiphilic nature and the high porosity of the sample (Fig. S13†). It is known that the excellent amphiphilicity is helpful for the miscibility of both the hydrophilic and hydrophobic reactants,<sup>4</sup> and the high porosity is favorable for the adsorption of reactants thus to concentrate them in the pores.<sup>19</sup> Therefore,  $W_2O_{11}/PQP$  featuring these two advantages can enrich with the reactant in its pores and facilitate the miscibility of them to the nearby active sites thereby promoting the overall reaction. This has been supported by that the concentration of  $H_2O_2$  enriched in the catalyst is about ten times of that in the solution, and about 90% of cyclooctene in the system can be adsorbed by the catalyst (Fig. S14†). Such a kind of local enrichment in the amphiphilic porous structure thus results in a significant increase of catalytic activities in the epoxidation of cyclooctene with  $H_2O_2$  for the  $W_2O_{11}/PQP$  catalyst, compared with the soluble  $K_2W_2O_{11}$  and  $[PPh_3Bn]_2[W_2O_{11}]$  catalysts. Moreover, a higher yield of cyclooctene oxide (95.3%) can be obtained using 1.5 equiv. of 30%  $H_2O_2$  (entry 9 in Table 1). The  $W_2O_{11}/PQP$  can retain its catalytic activity after 5 recycles (entry 10 in Table 1 and Table S2†). Hot filtration was performed when the reaction proceeded at 4 h (the conversion of cyclooctene was given at 49.1%). W species in the filtrate were undetectable as verified by ICP-OES analysis (<10 ppb), and the epoxidation reaction was completely quenched after separating the catalyst, highlighting its heterogeneous nature. The above results also underscore the advantages of  $W_2O_{11}/PQP$  for environmentally friendly olefin epoxidation compared with conventional catalysts.

To further evaluate  $W_2O_{11}/PQP$  as a heterogeneous phase transfer catalyst, we investigated its performances in the context of oxidation of dibenzothiophene (DBT), which is an important reaction for removal of sulfur compounds from fuels to satisfy the new environmental legislations.<sup>20</sup> Given the difficulty in reducing refractory DBT and its derivatives to an ultra-low level using the conventional hydrodesulfurization method,<sup>21</sup> the selective catalytic oxidation of the DBT into the corresponding sulfone is one of the most promising ultra-deep desulfurization processes, where the additives such as acetonitrile and ionic liquids are necessary.<sup>22</sup> However, the addition of these additives may result in a change in the properties of the fuel, and this can be avoided when a phase transfer catalyst is employed without the need for any additives as recently demonstrated in a homogeneous catalyst system.<sup>23</sup> Table 2 presents the catalytic data in the oxidation of DBT with  $H_2O_2$  as the oxidant over various catalysts. It is observed that the  $W_2O_{11}/PQP$  is very active for the selective oxidation of DBT to sulfone (model S contained oil: 2500 ppm in *n*-octane) with  $H_2O_2$  at 30 °C without any additives, giving the conversion higher than 99.8% and

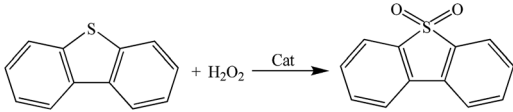
**Table 1** Catalytic data in epoxidation of cyclooctene with  $H_2O_2$  using water as a solvent over various catalysts<sup>a</sup>



Entry	Catalyst	Catalyst state	Time (h)	Conv. (%)	Select. (%)
1 <sup>b</sup>	$K_2W_2O_{11}$	Soluble	12	4.5	>99.0
2 <sup>c</sup>	$[PPh_3Bn]_2[W_2O_{11}]$	Soluble	12	11.2	>99.0
3 <sup>d</sup>	$W_2O_{11}/PDVB$	Insoluble	12	8.7	>99.0
4 <sup>e</sup>	$W_2O_{11}/NP$	Insoluble	12	24.6	>99.0
5 <sup>f</sup>	$W_2O_{11}/PQP$	Insoluble	12	71.1	>99.0
6 <sup>g</sup>	PQP	Insoluble	24	<1.0	—
7	$W_2O_{11}/PQP$	Insoluble	24	79.3	>99.0
8 <sup>h</sup>	$W_2O_{11}/PQP$	Insoluble	24	76.4	>99.0
9 <sup>i</sup>	$W_2O_{11}/PQP$	Insoluble	24	75.9	>99.0
10 <sup>j</sup>	$W_2O_{11}/PQP$	Insoluble	12	96.7	98.6

<sup>a</sup> Reaction conditions: cyclooctene (110 mg, 1.0 mmol),  $H_2O_2$  (30% aq., 1.0 mmol, 113 mg), water as a solvent (4.0 mL), 50 °C, 12–24 h, and in the presence of various catalysts with the same amount of W species. The conversions and selectivity were determined by GC. <sup>b</sup>  $K_2W_2O_{11}$  was synthesized from potassium tungstate and  $H_2O_2$  [ref. 18] (6.6 mg). <sup>c</sup>  $[PPh_3Bn]_2[W_2O_{11}]$  was synthesized from an anion-exchange of benzyl-trisphenylphosphonium chloride with  $K_2W_2O_{11}$  solution [ref. 18] (12.5 mg). <sup>d</sup>  $W_2O_{11}/PDVB$  was synthesized from copolymerization of divinylbenzene (DVB) and (4-vinyl-benzyl)-tris-(4-vinyl-phenyl)-phosphonium chloride at a molar ratio of 3.0, followed by the anion-exchange of  $W_2O_{11}^{2-}$  (90 mg). <sup>e</sup>  $W_2O_{11}/NP$  was synthesized from polymerization of triphenyl(4-vinylbenzyl)phosphonium chloride, followed by the anion-exchange of  $W_2O_{11}^{2-}$  (65 mg). <sup>f</sup> 50 mg. <sup>g</sup> 50 mg. <sup>h</sup> Reuse. <sup>i</sup> Recycles for 5 times. <sup>j</sup> 1.5 equiv. of  $H_2O_2$  (170 mg).

Table 2 Catalytic data in oxidation of dibenzothiophene with H<sub>2</sub>O<sub>2</sub> over various catalysts<sup>a</sup>



Entry	Catalyst	Time (h)	Conv. (%)	Select. (%)	Residual sulfur (ppm)
1 <sup>b</sup>	K <sub>2</sub> W <sub>2</sub> O <sub>11</sub>	8	5.1	>99.0	2373
2 <sup>c</sup>	[PPh <sub>3</sub> Bn] <sub>2</sub> [W <sub>2</sub> O <sub>11</sub> ]	8	33.2	>99.0	1670
3 <sup>d</sup>	W <sub>2</sub> O <sub>11</sub> /PQP	8	>99.8	>99.0	<5
4	W <sub>2</sub> O <sub>11</sub> /PQP	2	69.4	>99.0	765
5	W <sub>2</sub> O <sub>11</sub> /PQP	4	96.9	>99.0	78
6	W <sub>2</sub> O <sub>11</sub> /PQP	6	99.2	>99.0	20
7 <sup>e</sup>	W <sub>2</sub> O <sub>11</sub> /PQP	8	>99.8	>99.0	<5
8 <sup>f</sup>	W <sub>2</sub> O <sub>11</sub> /PQP	8	>99.8	>99.0	<5

<sup>a</sup> Reaction conditions: dibenzothiophene (25 mg, 0.136 mmol), *n*-octane (10 g), H<sub>2</sub>O<sub>2</sub> (30% aq., 0.68 mmol, 77 mg), 30 °C, and in the presence of various catalysts with the same amount of W species. Conversion and selectivity were determined by GC. <sup>b</sup> 0.5 mg. <sup>c</sup> 0.9 mg. <sup>d</sup> 3.4 mg. <sup>e</sup> Reuse. <sup>f</sup> Recycles for 5 times.

selectivity higher than 99.0%. It is notable that the product can be easily separated due to the insolubility of sulfone in *n*-octane. In addition, the W<sub>2</sub>O<sub>11</sub>/PQP can also be fully recycled without the loss of any activity (Table S4<sup>†</sup>). These results therefore suggest the potential of W<sub>2</sub>O<sub>11</sub>/PQP as a green heterogeneous phase transfer catalyst for the removal of sulfur in the fuels.

## Conclusions

In summary, we have demonstrated for the first time the preparation of a hierarchical porous ionic organic polymer that is based upon the vinyl-functionalized quaternary phosphonium salt monomer. The resultant polymerized quaternary phosphonium (PQP) salt can be readily anion exchanged with peroxotungstate to afford W<sub>2</sub>O<sub>11</sub>/PQP, which demonstrates excellent performances as a heterogeneous phase transfer catalyst to catalyze the epoxidation of olefin and oxidation of dibenzothiophene due to the combined contributions of excellent amphiphilicity, hierarchical porous structure, and highly accessible active sites of W<sub>2</sub>O<sub>11</sub><sup>2-</sup>. Our work therefore not only advances porous ionic organic polymers as a new type of heterogeneous phase transfer catalyst, but also provides a new perspective for the design of highly efficient and robust heterogeneous catalysts for phase transfer catalysis. On-going work in our laboratories includes the investigation of the hierarchical porous ionic organic polymers for other types of phase-transfer reactions and the design of new POP-based catalysts for heterogeneous catalysis.

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