Construction of anion-functionalized hypercrosslinked ionic porous polymers for efficient separation of bioactive molecules

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ABSTRACT Porous ionic polymers have demonstrated great potential for high-performance separation by the merits of their unique molecular recognition, but the preparation of anion-functionalized ionic polymers for the separation of bioactive molecules with highly similar structures remains a challenge. Here, through the facile Friedel-Crafts alkylation between benzylimidazole ionic liquids (ILs) and crosslinkers, several anion-functionalized hypercrosslinked ionic porous polymers (HIPs) are reported, which are well decorated with strongly basic carboxylate anions as well as feature tubular morphology and excellent thermal stability. High adsorption capacity (103.6 mg g⁻¹ for tocopherol homologues) and selectivity ($S_{\beta\&\gamma/\alpha}$ 4.26; $S_{\delta/\alpha}$ 3.19) for bioactive compounds with high structural similarity have been realized, superior to those of commercial adsorbents, hypercrosslinked polymer without ILs, and HIPs with common ILs. This study manifests a new synthetic strategy and rational molecular design for functionalized adsorbents, as well as offers new opportunities to enable high-performance separation.

Keywords: anion-functionalization, hypercrosslink, porous ionic polymers, adsorption, tocopherol homologues, phenolic compounds

INTRODUCTION

Porous organic polymers, benefiting from their structural diversity, extremely high porosity, and physicochemical stability, have emerged as a versatile platform for practical applications [1–6]. Precise control of pore structure and pore chemistry promotes the deployment of advanced separation [7–13]. Task-specific functional site is a key factor to enhance the separation efficiency. However, the additional chemical groups decorated onto the pore wall often restrict pore accessibility and lack flexible variability. The utilization of dynamic ionic pairs could weaken the steric-hindrance obstacle and endow the adsorbents with selective interactions with adsorbates [14]. By the merits of unique nanoporous ionic environment, high-performance applications have been developed [14–17]. The past decade has witnessed rapid progress in multiple synthetic methods towards porous ionic polymers [18–21]. The post-modification method provides a facile pathway to introduce ionic sites but suffers from decreased porosity [18]. Templated synthetic strategies

afford well-defined architecture, but inevitably sacrifice templates and rarely construct micropores [19,20]. Hypercrosslinked polymers (HCPs) represent a class of nanoporous materials, featuring extremely high surface areas as well as high chemical and thermal stability, which offer practical and potential applications in the fields of gas sorption and separation, catalysis, and drug delivery [22–26]. Recently, a class of hypercrosslinked ionic porous polymers (HIPs), combining the properties of porous polymers and ionic materials, have been reported, which incorporate ionic liquid (IL)-like ionic sites into the architecture [18,27–31]. With a few exciting recent exceptions, benzylimidazole ILs, in which the imidazolium cation is linked by methylene with phenyl ring, have been employed, the synthesized HIPs afford abundant meso-microporosity and adjustable IL contents [27,30,31].

The rational choice of anions makes for broadened applications [10,32]. Recently, our group reported a kind of mesoporous poly(ionic liquid)s, with long-chain carboxylate ILs, which exhibited a high adsorption capacity of bioactive tocopherol homologues and excellent selectivity [33]. However, the existing HIPs have been almost derived from common ILs with bromine (Br⁻) or chlorine (Cl⁻) anions. Typically, the facile incorporation of functional anions was achieved *via* anion exchange but troubled by the steric hindrance especially for bulky anions. And the research of HIPs was mainly focused on selective carbon dioxide capture and heterogeneous catalysis but has been rarely explored for the separation of bioactive compounds. Therefore, the construction of anion-functionalized HIPs for high-performance separation is of great potential but still challenging.

Herein, we prepared several new anion-functionalized HIPs endowed with carboxylate ILs featuring strong hydrogen-bonding basicity and great biocompatibility, *via* a direct Friedel-Crafts alkylation reaction between the benzylimidazole IL monomers and crosslinkers. These prepared anion-functionalized HIPs exhibit abundant meso-microporosity and tunable IL contents, as well as feature tubular morphology and excellent thermal stability. For bioactive tocopherol homologues and phenolic compounds with highly similar structures, high-performance adsorptive separation has been achieved by the anion-functionalized HIPs, in comparison to commercial adsorbents, HCP without ILs, and HIPs with common ILs. And recycling tests for the adsorption tocopherol homologues verify the good reusability for anion-functionalized HIPs.

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EXPERIMENTAL SECTION

Synthesis of 1-benzyl-3-methylimidazolium-based ILs

The ILs synthesized in this work were 1-benzyl-3-methylimidazolium bromide ([BzMIm][Br]), 1-benzyl-3-methylimidazolium acetate ([BzMIm][CH₃COO]), 1-benzyl-3-methylimidazolium caproate ([BzMIm][C₅H₁₁COO]) and 1-benzyl-3-methylimidazolium laurate ([BzMIm][C₁₁H₂₃COO]) (Fig. S1). As shown in Fig. S2, [BzMIm][Br] was prepared by the quaternisation reaction of equimolar 1-methylimidazole and benzyl bromide in ethanol at 333 K for 24 h. For the preparation of [BzMIm][CH₃COO], [BzMIm][C₅H₁₁COO], and [BzMIm][C₁₁H₂₃COO], [BzMIm][Br] aqueous solution was passed through a strongly basic anion-exchange resin (Dowex MonoSphere 550A UPW; OH type) to get [BzMIm][OH] and then mixed with equimolar amounts of the corresponding fatty acids including acetic acid, *n*-hexanoic acid and lauric acid at room temperature for 24 h [34–37]. All the obtained ILs were dried by a vacuum freeze dryer for 24 h after most solvents were removed by a rotary evaporator at 333 K. The chemical structure and purity of ILs were evaluated by a ¹H nuclear magnetic resonance (NMR) spectrum (see the Supplementary information).

Synthesis of IL-based HCPs

Several IL-based HCPs were synthesized *via* the Friedel-Crafts alkylation reaction with the ratio of ILs:α,α'-dibromo-*p*-xylene (DBX):ferric chloride (FeCl₃) = 1:2:4 (mol:mol:mol). The reaction was carried out with FeCl₃ as a catalyst and 1,2-dichloroethane (DCE) as a solvent in nitrogen atmosphere at 353 K for 24 h. Afterwards, the solid products were filtered and washed with ethanol and water until the solution became colorless. Then the filtered solid products were dried in a vacuum oven at 333 K for 24 h. The obtained HCPs were named HIP-[BzMIm][Br], HIP-[BzMIm][CH₃COO], HIP-[BzMIm][C₅H₁₁COO] and HIP-[BzMIm][C₁₁H₂₃COO]. For comparison, HCP without ILs was also prepared only using DBX, following a similar procedure.

Batch adsorption experiments

The batch adsorption experiments were implemented as follows. For tocopherol homologues, 20 mL of *n*-heptane solution was prepared with 1.41 mg mL⁻¹ α-tocopherol, 1.40 mg mL⁻¹ β- and

γ-tocopherol and 0.56 mg mL⁻¹ δ-tocopherol in a conical flask. For organic phenolic compounds, the *n*-heptane solution contained 1.06 mg mL⁻¹ phenol, 1.13 mg mL⁻¹ *p*-cresol and 1.22 mg mL⁻¹ 2,6-dimethylphenol. Then HCPs (0.1 g) were added and shaken at 160 r min⁻¹ and 298 K for 24 h. After achieving adsorption equilibrium, the filtered solution was analyzed by high-performance liquid chromatography (HPLC). The detailed analytical condition of HPLC and calculation can be seen in the Supplementary information.

Furthermore, batch adsorption experiments using 2.3 g of HIP-[BzMIm][C₅H₁₁COO] were also carried out to evaluate practical separation performance. After achieving adsorption equilibrium, the filtered solution was analyzed using HPLC. The adsorbent was regenerated, and adsorbed tocopherols were collected with ethanol at 45°C. The corresponding results were summarized in Table S1.

RESULTS AND DISCUSSION

Fig. 1 displays the synthetic route for anion-functionalized HIPs. Imidazolium cation featuring phenyl group has been chosen to participate in the Friedel-Crafts reaction with the crosslinker DBX in the presence of FeCl₃ and DCE as the catalyst and solvent, respectively. The formed methylene bridges between the crosslinker and benzene ring in ILs can hypercrosslink ionic sites into the polymer skeleton. Meanwhile, the methylene bridges between the crosslinkers can further promote the construction of porous ionic network. The rational selection for the kinds of anions and adequate IL contents possesses the potential to accomplish high-performance separation for organic compounds with highly similar structures.

Synthesis and characterization of HIPs

In this work, several anion-functionalized HIPs derived from carboxylate ILs were successfully fabricated. For exploring the effect of carbon number of carboxylate anions, [BzMIm][CH₃COO], [BzMIm][C₅H₁₁COO] and [BzMIm][C₁₁H₂₃COO] with different carboxylate anions were employed to construct hypercrosslinked networks, respectively. The molar ratio of ILs and the crosslinker DBX was chosen to be 2:1 for further study. Their chemical compositions were detected by element analysis, which verifies the successful introduction of carboxylate ILs, and

Figure 1 Synthesis route of HIPs by Friedel-Crafts alkylation.

the calculated contents of ILs in HIPs range from 0.44 to 0.81 mmol g⁻¹. To investigate the pore structure of the HIPs, the N₂ adsorption/desorption isotherms were collected at 77 K. The detailed textural parameters were summarized in Table 1, Fig. 2 and Fig. S3. As depicted in Fig. 2, anion-functionalized HIPs show typical type I isotherms with a faint type IV character. The isotherms exhibit a rapid uptake at a low relative pressure, reflecting all the samples demonstrate abundant microporosities with micropore sizes mainly ranging from 0.59 to 2.00 nm. And there is a slightly increased uptake at high relative pressures ($P/P_0 > 0.9$), indicating of the coexistence of micropores and a small number of mesopores. In contrast to

others, HIP-[BzMIm][C₅H₁₁COO] derived from ILs with a medium carbon number of carboxylate anions affords the highest IL content of 0.81 mmol g⁻¹, the surface area (calculated by Brunauer-Emmett-Teller (BET) equation, referred as S_{BET}) is 323 m² g⁻¹, the total pore volume (V_{total}) is 0.281 cm³ g⁻¹, and the mesopore size (D_{BJH}) is 5.36 nm; for microporosity (<2 nm), the micropore surface area (S_{micro}) is 149 m² g⁻¹, and pore volume (V_{micro}) is 0.075 cm³ g⁻¹, affording 26.7% of V_{total} value, the median micropore size (D_{HK}) is 0.51 nm. HIP-[BzMIm]-[CH₃COO] and HIP-[BzMIm][C₁₁H₂₃COO] with lower IL contents of 0.55 and 0.44 mmol g⁻¹ exhibit more abundant microporosity, higher S_{BET} (512 and 516 m² g⁻¹) and V_{total} (0.328

Table 1 Textural parameters of HCPs

Sample	S_{BET}^a (m ² g ⁻¹)	S_{micro}^b (m ² g ⁻¹)	V_{micro}^b (cm ³ g ⁻¹)	V_{total}^c (cm ³ g ⁻¹)	$V_{\text{micro}}/V_{\text{total}}$ (%)	$V_{\text{meso}}/V_{\text{micro}}$	D_{DJH}^d (nm)	D_{HK}^e (nm)	IL content ^f (mmol g ⁻¹)
HCP	843	436	0.224	0.730	30.7	2.26	5.92	0.48	0
HIP-[BzMIm][Br]	494	354	0.181	0.302	59.9	0.67	4.06	0.44	0.43
HIP-[BzMIm][CH ₃ COO]	512	359	0.183	0.328	55.8	0.79	4.51	0.45	0.55
HIP-[BzMIm][C ₅ H ₁₁ COO]	323	149	0.075	0.281	26.7	2.75	5.36	0.51	0.81
HIP-[BzMIm][C ₁₁ H ₂₃ COO]	516	362	0.185	0.340	54.4	0.84	4.85	0.44	0.44
HIP-[BzMIm][C ₅ H ₁₁ COO] (1:4) ^g	855	390	0.168	1.151	14.6	5.85	10.7	0.52	0.40
HIP-[BzMIm][C ₅ H ₁₁ COO] (1:1) ^g	65	47	0.021	0.035	60.0	0.67	5.71	0.60	1.02

a) BET surface area evaluated from N₂ adsorption isotherms at relative pressures (P/P_0) from 0.05 to 0.30. b) Micropore surface area and volume estimated by the t-plot method. c) Total pore volume at $P/P_0 = 0.990$. d) Average mesopore size calculated by BJH adsorption equation for P/P_0 from 0.1 to 0.990. e) Median micropore size calculated using Horvath-Kawazoe (HK) equation for P/P_0 from 0.1 to the lowest value. f) The IL contents on the HIPs determined from the element analysis. g) HIP-[BzMIm][C₅H₁₁COO] prepared by the reaction of IL with DBX at ratios of 1:1 and 1:4, respectively; others prepared by the reaction of ILs with DBX at the ratios of 1:2.

Figure 2 N₂ adsorption/desorption isotherms (a, c) and pore size distributions (b, d) of HCPs.

and $0.340 \text{ cm}^3 \text{ g}^{-1}$), as well as higher S_{micro} (359 and $362 \text{ m}^2 \text{ g}^{-1}$) and V_{micro} (0.183 and $0.185 \text{ cm}^3 \text{ g}^{-1}$, accounting for 55.8% and 54.4% of V_{total} value), the D_{BJH} values are 4.51 and 4.85 nm, respectively, the D_{HK} values are 0.45 and 0.44 nm, respectively. HIP-[BzMIm][Br], with the IL content of 0.43 mmol g^{-1} , exhibits similar textural parameters with HIP-[BzMIm][CH₃COO] and HIP-[BzMIm][C₁₁H₂₃COO]. Its S_{BET} and V_{total} values reach $494 \text{ m}^2 \text{ g}^{-1}$ and $0.302 \text{ cm}^3 \text{ g}^{-1}$. According to the above results, it can be concluded that the carbon number of carboxylate anions and the kind of anions have few effects on the pore structure, whereas the IL content in HIPs is the key factor, which will be further explored in detail. Besides, the pure crosslinker DBX was polymerized for comparison, and the resultant polymer is denoted as HCP, which also displays a type I and type IV mixed isotherm along with the highest surface area and pore volume (S_{BET} : $843 \text{ m}^2 \text{ g}^{-1}$, V_{total} : $0.730 \text{ cm}^3 \text{ g}^{-1}$).

To explore the effect of IL content on the pore structure, HIPs with [BzMIm][C₅H₁₁COO] were synthesized with different ratios of ILs and DBX including 1:1, 1:2 and 1:4. The content of ILs in the resulted polymer increases with the increased initial ratio of IL to crosslinker. Because of the easy self-aggregation of IL moiety, the higher IL content, the lower surface area and pore volume. As depicted in Fig. 2c, d, the three HIPs present remarkably different N₂ sorption isotherms. HIP-[BzMIm]-[C₅H₁₁COO] (1:4) (1:4 denotes the molar ratio of ILs and DBX) with the lowest IL content of 0.40 mmol g^{-1} presents a sharper and higher uptake at a low P/P_0 (<0.03) than others, indicative of more abundant microporosity. Meanwhile, it displays an increased uptake at P/P_0 ranging from 0.4 to 0.8 and a sharp rise at high P/P_0 (>0.8), implying the existence of mesopores and macropores (Fig. 2d). Its S_{BET} and V_{total} values are up to $855 \text{ m}^2 \text{ g}^{-1}$ and $1.151 \text{ cm}^3 \text{ g}^{-1}$. In a striking contrast, HIP-[BzMIm][C₅H₁₁COO] (1:1) possesses the highest IL content of

1.02 mmol g^{-1} , while its S_{BET} and V_{total} values are low to $65 \text{ m}^2 \text{ g}^{-1}$ and $0.035 \text{ cm}^3 \text{ g}^{-1}$. These results manifest that excessive IL content could make the materials non-porous. Proper molar ratio of ILs and DBX can achieve the “trade-off” for the ionic nature and pore structure, which is important for adsorptive separation application.

The morphological structure is worth investigating for further applications. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images indicate that HIPs and HCP possess different morphologies on the micro-meter level (Fig. 3a, d, Figs S4 and S5). HCP exhibits an amorphous morphology composed of irregular particles. HIP-[BzMIm][Br] presents aggregations of large particles. Differently, HIP-[BzMIm][C₅H₁₁COO] exists mainly as nanotubes with a mean exterior diameter of 200 nm, which is also displayed in the TEM images. The tubular morphology is probably attributed to the self-assembly behavior of carboxylate ILs in the polymerization process. For HIP-[BzMIm][C₅H₁₁COO] (1:1) with a higher IL content, the hollow nanotubes present a larger mean exterior diameter of $1.92 \mu\text{m}$. Such well-developed structure promotes substrate diffusion and adsorption, as well as provides new ideas for the design and synthesis of ionic porous adsorbents. Rational design of the tubular HIPs could also provide new opportunities of porous nanotube materials with promising application [38–41]. XRD patterns of HCP and HIP-[BzMIm][C₅H₁₁COO] show that these polymers all possess amorphous structure (Fig. S6). Moreover, Fourier transform infrared (FTIR) spectroscopy was collected to identify the chemical composition (Fig. 3c). Compared with HCP, the absorption peaks of HIPs at 1150 cm^{-1} are assigned to substituted N3 in imidazolium-based ILs, the peaks ranging from 1570 to 1670 cm^{-1} represent the characteristic peaks of the imidazole ring skeleton [33]. As shown in Fig. S7, the solid

Figure 3 SEM image (a) and TEM image (b) of HIP-[BzMIm][C₅H₁₁COO]; the comparison of FTIR (c) and TGA curves (d) at N₂ atmosphere for HIPs and HCP.

state ^{13}C NMR spectrum also provides evidence for the successful introduction of IL moiety. The thermogravimetric analysis (TGA) results indicate that HIPs afford excellent thermal stability—the temperature for 10% weight loss under the N_2 atmosphere is higher than 550 K (Fig. 3d), which is beneficial to practical applications.

Selective separation of tocopherol homologues

The efficient purification of bioactive compounds is the key step to achieve their high value. Tocopherols are the main compositions of natural vitamin E, and their antioxidative capacity makes tocopherols be free radical scavengers and important for human health and food supplement industry [42,43]. Among the tocopherol homologues, α -tocopherol possesses the highest biological activity, but always coexisting with β -, γ -, and δ -tocopherols. These tocopherol homologues possess high structural similarity, all of which contain a chromanol head and an alkyl side chain with slight differences in the number and position of methyl groups on the chromanol head (Fig. S8) [44]. Therefore, the separation of α -tocopherol is of great significance but challenging. The difference in their hydrogen-bonding acidities, which decrease as δ -tocopherol > β - and γ -tocopherol > α -tocopherol, provides the possibility for the selective separation of α -tocopherol from the homologues [45,46]. Many progresses on ILs and deep eutectic solvents (DESs) capable of achieving efficient separation of tocopherols have been made, but there are still difficulties in the subsequent separation pro-

cess, which requires much energy consumption [37,47–53]. It is necessary to design high-efficiency adsorbents to improve this difficult purification process.

In this work, anion-functionalized HIPs, with dual characteristics of porous polymers and carboxylate ILs, afford efficient adsorptive separation of tocopherol homologues. The batch experiments with tocopherols were executed to explore the separation performance for the HCPs. As shown in Fig. 4a, all the anion-functionalized HIPs (HIP-[BzMIm][$\text{C}_n\text{H}_{2n+1}\text{COO}$], $n = 1, 5, 11$) demonstrate high tocopherol adsorption capacities (95.5–109.5 mg g^{-1}). HIP-[BzMIm][CH_3COO] possesses the highest tocopherol adsorption capacity reaching 109.5 mg g^{-1} at 25°C, which is significantly higher than that of HIP-[BzMIm]-[Br] with common anion Br^- and similar structure parameters (83.2 mg g^{-1}). HCP without ILs affords the highest specific surface area and total pore volume (S_{BET} : 843 $\text{m}^2 \text{g}^{-1}$, V_{total} : 0.730 $\text{cm}^3 \text{g}^{-1}$), as well as accounts for higher $V_{\text{micro}}/V_{\text{total}}$ (30.7%) than that of better-performing HIP-[BzMIm][$\text{C}_5\text{H}_{11}\text{COO}$] (103.6 mg g^{-1} for tocopherols, S_{BET} : 323 $\text{m}^2 \text{g}^{-1}$, V_{total} : 0.281 $\text{cm}^3 \text{g}^{-1}$, $V_{\text{micro}}/V_{\text{total}}$: 26.7%), but the lowest tocopherol adsorption capacity (68.8 mg g^{-1}). It can be explained that the introduction of ionic sites is the key factor for enhancing the separation performance: ILs and tocopherols serve as hydrogen-bonding receptors and donors, respectively; IL moieties being embedded in the highly crosslinked network can improve the adsorption capacity by hydrogen-bonding interaction between ILs and tocopherols; and more strongly basic carboxylate ILs

Figure 4 Adsorption capacity (a) and selectivity (b) of tocopherol homologues by different adsorbents at 298 K. Adsorbents: A, Amberlite XAD-4; B, Amberlite 717; C, HCP; D, HIP-[BzMIm][Br]; E, HIP-[BzMIm][CH₃COO]; F, HIP-[BzMIm][C₅H₁₁COO]; G, HIP-[BzMIm][C₁₁H₂₃COO]. (c) Adsorption capacity and selectivity of tocopherol homologues by HIP-[BzMIm][C₅H₁₁COO] with different IL contents at 298 K. (d) Five cycles of tocopherol homologues adsorption for HIP-[BzMIm][C₅H₁₁COO] at 298 K.

have a more pronounced effect on the enhanced adsorption of tocopherols than common anions [34,38,52–55]. Besides, the tocopherol adsorption capacity of HIP-[BzMIm][CH₃COO] surpasses those of commercial resins including Amberlite XAD-4 (63.2 mg g⁻¹) and Amberlite 717 (97.5 mg g⁻¹).

The selectivity is the important evaluation criteria to efficient separation of α -tocopherol from tocopherol homologues. As displayed in Fig. 4b, HIPs have excellent separation performance for tocopherol homologues. The best-performing HIP-[BzMIm][C₅H₁₁COO] possesses high selectivity of β/γ -tocopherol to α -tocopherol ($S_{\beta/\gamma/\alpha}$) reaching 4.26 and the selectivity of δ -tocopherol to α -tocopherol ($S_{\delta/\alpha}$) up to 3.19. In distinct contrast, HCP without ILs has a low selectivity with only 1.63 and 1.08 for $S_{\beta/\gamma/\alpha}$ and $S_{\delta/\alpha}$, respectively. That is, tocopherol homologues possess highly similar structures but subtle difference in acidity, and for carboxylate-based HIPs, the efficient separation of α -tocopherol arises from the introduction of adequate carboxylate ILs featuring the unique recognition for α -tocopherol with the lowest acidity among tocopherol homologues [37,51–54]. Although the two commercial resins have good tocopherol adsorption capacity, their $S_{\beta/\gamma/\alpha}$ and $S_{\delta/\alpha}$ values are only close to 1, which means that they are unable to recognize the subtle difference of acidity among tocopherol homologues.

Anion-functionalized ILs contribute to highly efficient separation performance. Considering that HIP-[BzMIm][C₅H₁₁COO] exhibits the best separation selectivity for tocopherol homologues, HIP-[BzMIm][C₅H₁₁COO], prepared by the reaction of [BzMIm][C₅H₁₁COO] with DBX at ratios of 1:4 and 1:1, was also put into the batch experiments. As presented in Fig. 4c, HIP-[BzMIm][C₅H₁₁COO] (1:4) with a low IL content (0.40 mmol g⁻¹) but the largest S_{BET} (855 m² g⁻¹) and V_{total} (1.151 cm³ g⁻¹) possesses the highest adsorption capacity (175.6 mg g⁻¹). That is, adsorption performance of tocopherols is cooperatively affected by porosity and functional sites. Besides, HIP-[BzMIm][C₅H₁₁COO] (1:1) (S_{BET} : 65 m² g⁻¹), a nearly non-porous material with the highest IL content (1.02 mmol g⁻¹), also exhibits a high adsorption capacity (140.4 mg g⁻¹). The possible explanation is that the high content of strongly basic carboxylate IL moiety in the polymers will lead to high capacity benefiting from the strong hydrogen-bonding interaction with the acid tocopherols; meanwhile, the swelling behavior could also make for adsorption. And all the three samples exhibit high selectivity. In conclusion, rational choice for the ratio of IL and

DBX is the key to achieve high-performance adsorptive separation. In addition, HIP-[BzMIm][C₅H₁₁COO] shows excellent recycling performance. After five recycling tests, the adsorption capacity almost remains unchanged (Fig. 4d). Besides, the batch adsorption experiment with 2.3 g of HIP-[BzMIm][C₅H₁₁COO] was conducted to evaluate the practical separation ability. The results shown in Table S1 prove that HIPs achieve the efficient separation and concentration of tocopherol homologues. After adsorption equilibrium, α -tocopherol is concentrated in the liquid phase, and the percentage is obviously improved from 41.84% to 68.44%; meanwhile, β -/ γ -tocopherol and δ -tocopherol are concentrated in the adsorbent. Moreover, the regeneration and collection are achieved by conducting elution with ethanol.

Moreover, FTIR and solid state ¹³C NMR spectra were also collected after adsorption. As depicted in Fig. S8, after adsorption, HIP-[BzMIm][C₅H₁₁COO] presents the similar structure with the pristine sample, indicating well-preserved structural integrity during the batch experiments. The new peaks at 2924 and 2867 cm⁻¹ in FTIR results as well as the peaks at 21 ppm in the solid state ¹³C NMR spectrum belong to the adsorbed tocopherols. To further confirm the effect of hydrogen-bonding interaction, a control experiment was carried out. After the addition of 2 wt% acetic acid into the separation systems, the tocopherol adsorption capacity for HIP-[BzMIm][C₅H₁₁COO] decreases from 103.6 to 25.2 mg g⁻¹, $S_{\beta/\gamma/\alpha}$ and $S_{\delta/\alpha}$ also decrease from 4.26 and 3.19 to 1.30 and 1.13, respectively. These results clarify that the extra hydrogen-bonding donor acetic acid can destroy the hydrogen bonds between HIPs and tocopherols, leading to reduced performance.

Selective separation of organic phenolic compounds

Phenol, *p*-cresol and 2,6-dimethylphenol with highly similar structures but difference in hydrogen-bonding acidity (Fig. S7) are important raw materials for pharmaceutical intermediates, and the efficient separation of these phenolic compounds is significant but still difficult.

As depicted in Fig. 5, HIPs have remarkably higher adsorption capacity of phenolic compounds than that of HCP. The adsorption capacity in HIP-[BzMIm][C₅H₁₁COO] is 264.0 mg g⁻¹, which is 2.9 times that of HCP (91.2 mg g⁻¹). And these carboxylate-based HIPs possess higher capacities (230.5–264.0 mg g⁻¹) than HIP-[BzMIm][Br] (195.8 mg g⁻¹). The selectivities of phenol to 2,6-dimethylphenol ($S_{\text{phenol/2,6-dim}}$)

Figure 5 Adsorption capacity and selectivity of phenolic compounds by different adsorbents (a) and HIP-[BzMIm][C₅H₁₁COO] with different IL contents (b) at 298 K. Adsorbents: A, HCP; B, HIP-[BzMIm][Br]; C, HIP-[BzMIm][CH₃COO]; D, HIP-[BzMIm][C₅H₁₁COO]; E, HIP-[BzMIm][C₁₁H₂₃COO].

and *p*-cresol to 2,6-dimethylphenol ($S_{p\text{-cresol}/2,6\text{-dim}}$) are 4.28 and 3.63 for HIP-[BzMIm][Br], respectively, which obviously exceed those of HCP ($S_{\text{phenol}/2,6\text{-dim}}$: 1.77, $S_{p\text{-cresol}/2,6\text{-dim}}$: 2.87). When the common anion [Br][−] is replaced by [C₅H₁₁COO][−], $S_{p\text{-cresol}/2,6\text{-dim}}$ and $S_{\text{phenol}/2,6\text{-dim}}$ are further improved in HIP-[BzMIm][C₅H₁₁COO], which reach 5.62 and 4.87, respectively. Therefore, the inclusion of adequate functional anions is the efficient strategy to achieve high-performance separation. Besides, the content of ILs can also affect the separation performance of phenolic compounds (Fig. 5b). The increased IL content gives rise to enhanced selectivity with high capacity.

CONCLUSIONS

In summary, we have demonstrated an easy and straightforward route for the preparation of anion-functionalized HIPs. Carboxylate ILs have been successfully introduced into the hypercrosslinked framework *via* direct Friedel-Crafts alkylation between the benzylimidazole ILs and crosslinkers. These anion-functionalized HIPs exhibit abundant meso-microporosity and adequate IL moieties. The tubular morphology and excellent thermal stability make HIPs more useful for practical application. High adsorption capacity (103.6 mg g^{−1} for tocopherols) and excellent selectivity ($S_{\beta\delta\gamma/\alpha}$: 4.26; $S_{\delta/\alpha}$: 3.19) for tocopherol homologues with highly similar structures have been realized by anion-functionalized HIPs, in comparison to commercial adsorbents, HCP without ILs and HIPs with common ILs. Good reusability is demonstrated by the recycling tests of adsorption for tocopherol homologues. High-performance adsorptive separation has also been accomplished for phenolic compounds. Well-developed pore structures collaborated with strongly basic ILs promote excellent adsorptive separation with unique molecular recognition for important organic compounds. This work can inspire the design of new porous ionic materials for advanced separation *via* the rational molecular design and the inclusion of functional sites.

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Author contributions Xing H, Suo X and Huang Y proposed the idea; Suo X and Huang Y designed the samples and performed the experiments; Li Z and Pan H did the measurements; Suo X and Huang Y wrote the paper with support from Xing H and Cui X. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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阴离子功能化超交联离子多孔聚合物的构建及生物活性物质高效分离

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摘要 多孔离子聚合物由于其独特的分子识别能力在高效分离中表现出巨大的潜力, 但制备阴离子功能化离子聚合物用于结构高度相似生物活性物质分离仍然具有挑战。本文通过苄基咪唑离子液体与交联剂发生简易的Friedel-Crafts烷基化反应, 报道了一类具有强碱羧酸阴离子功能化、管状形貌和高热稳定性的超交联离子多孔聚合物(HIPs)。实现了对结构高度相似的生物活性化合物的高容量(生育酚同系物: 103.6 mg g⁻¹)和高选择性($S_{\beta\>\gamma/\alpha}$, 4.26; $S_{\delta/\alpha}$, 3.19)吸附分离, 其性能优于商业吸附剂、不含离子液体的超交联聚合物和含常规离子液体的HIPs。本研究展示了功能化吸附剂新的合成策略和合理的分子设计, 为实现高效分离提供了新的机会。