## **Supporting Information**

## **Pitch-Based Hyper-cross-linked Polymers with High**

## **Performance for Gas Adsorption**

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| Samples | Petroleum | Coal tar  | Coal tar  | Coal tar  | AlCl <sub>3</sub> /g |
|---------|-----------|-----------|-----------|-----------|----------------------|
|         | pitch/g   | pitch-1/g | pitch-2/g | pitch-3/g |                      |
| PHCP-1  | 0.3091    | -         | -         | -         | 1.2364               |
| PHCP-2  | 0.3091    | -         | -         | -         | 1.5455               |
| PHCP-3  | 0.3091    | -         | -         | -         | 1.8546               |
| PHCP-4  | 0.3091    | -         | -         | -         | 2.4728               |
| PHCP-5  | 0.3091    | -         | -         | -         | 2.7819               |
| C1HCP-1 | -         | 0.3091    | -         | -         | 1.2364               |
| C1HCP-2 | -         | 0.3091    | -         | -         | 1.5455               |
| C1HCP-3 | -         | 0.3091    | -         | -         | 1.8546               |
| C1HCP-4 | -         | 0.3091    | -         | -         | 2.4728               |
| C1HCP-5 | -         | 0.3091    | -         | -         | 2.7819               |
| C2HCP-1 | -         | -         | 0.3091    | -         | 1.2364               |
| C2HCP-2 | -         | -         | 0.3091    | -         | 1.5455               |
| C2HCP-3 | -         | -         | 0.3091    | -         | 1.8546               |
| C2HCP-4 | -         | -         | 0.3091    | -         | 2.4728               |
| C2HCP-5 | -         | -         | 0.3091    | -         | 2.7819               |
| C3HCP-1 | -         | -         | -         | 0.3091    | 1.2364               |
| C3HCP-2 | -         | -         | -         | 0.3091    | 1.5455               |
| C3HCP-3 | -         | -         | -         | 0.3091    | 1.8546               |
| C3HCP-4 | -         | -         | -         | 0.3091    | 2.4728               |
| C3HCP-5 | -         | -         | -         | 0.3091    | 2.7819               |

## Table S1. The formula of pitch and AlCl<sub>3</sub> in each experiment.<sup>a</sup>

<sup>a</sup> In all experiments, the fixed amount of CHCl<sub>3</sub> is 10 ml.



Figure S1. The FT-IR spectra of the PHCP-1, PHCP-2, PHCP-4 and PHCP-5.



Figure S2. The FT-IR spectra of C1HCP-1, C1HCP-2, C1HCP-4 and C1HCP-5.



Figure S3. The FT-IR spectra of C2HCP-1, C2HCP-2, C2HCP-4 and C2HCP-5.



Figure S4. The FT-IR spectra of C3HCP-1, C3HCP-2, C3HCP-4 and C3HCP-5.



**Figure S5.** Solid state <sup>13</sup>C cross-polarization nuclear magic-angle spinning (CP/MAS) NMR spectra of PLP, CTP1, CTP2 and CTP3. Asterisks denote spinning sidebands.



Figure S6. EDS results of the PLP (a), PHCP-3 (b), CTP2 (c), C2HCP-3 (d), CTP3 (e) and C3HCP-3 (f).

| Samples | C/wt% | H/wt% | S/wt% |
|---------|-------|-------|-------|
| РНСР-3  | 69.27 | 3.68  | 1.00  |
| C1HCP-3 | 74.42 | 4.21  | 0.21  |
| C2HCP-3 | 49.36 | 4.29  | 0.36  |
| СЗНСР-З | 69.40 | 3.97  | 0.88  |

**Table S2.** Elemental analysis of pitch-based HCPs.



Figure S7. C 1s (a) and Cl 2p (b) XPS spectra of C1HCP-3.



Figure S8. C 1s (a) and Cl 2p (b) XPS spectra of C2HCP-3.



Figure S9. C 1s (a) and Cl 2p (b) XPS spectra of C3HCP-3.



**Figure S10.** X-ray diffractions spectra of PHCP-2, C1HCP-2, C2HCP-2 and C3HCP-2.



**Figure S11.** HR-TEM images of PHCP-3 (a), C1HCP-3 (b), C2HCP-3 (c) and C3HCP-3 (d). Scale bar: 5 nm.

|                | S <sub>BET</sub> <sup>a</sup> | S <sub>Micro</sub> b | $M_{PV}^{c}$    | PV <sup>d</sup> |
|----------------|-------------------------------|----------------------|-----------------|-----------------|
| Sample         | $(m^2 g^{-1})$                | $(m^2 g^{-1})$       | $(cm^3 g^{-1})$ | $(cm^3 g^{-1})$ |
| PHCP-1         | 1119                          | 810                  | 0.48            | 0.68            |
| PHCP-2         | 1197                          | 816                  | 0.51            | 0.74            |
| PHCP-4         | 1063                          | 765                  | 0.46            | 0.67            |
| PHCP-5         | 1108                          | 776                  | 0.48            | 0.69            |
| C1HCP-1        | 752                           | 570                  | 0.33            | 0.42            |
| C1HCP-2        | 845                           | 689                  | 0.37            | 0.48            |
| C1HCP-4        | 751                           | 495                  | 0.32            | 0.46            |
| C1HCP-5        | 629                           | 415                  | 0.27            | 0.43            |
| <b>C2HCP-1</b> | 587                           | 475                  | 0.26            | 0.32            |
| <b>C2HCP-2</b> | 621                           | 497                  | 0.27            | 0.36            |
| <b>C2HCP-4</b> | 848                           | 621                  | 0.37            | 0.51            |
| <b>C2HCP-5</b> | 788                           | 579                  | 0.34            | 0.45            |
| C3HCP-1        | 345                           | 273                  | 0.15            | 0.21            |
| С3НСР-2        | 493                           | 369                  | 0.21            | 0.31            |
| C3HCP-4        | 434                           | 325                  | 0.19            | 0.30            |
| C3HCP-5        | 375                           | 311                  | 0.16            | 0.22            |

Table S3. Surface areas and pore properties of pitch-based HCPs.

<sup>a</sup> Surface area calculated from the nitrogen adsorption isotherms at 77.3 K using the BET equation. <sup>b</sup> Micropore surface area calculated from the nitrogen adsorption isotherms at 77.3 K using the t-plot equation. <sup>c</sup> Micropore volume calculated from the nitrogen isotherm at  $P/P_0 = 0.15$ , 77.3 K using the t-plot equation. <sup>d</sup> Pore volume calculated from the nitrogen isotherm at  $P/P_0 = 0.99$ , 77.3 K.



**Figure S12.** Nitrogen adsorption-desorption isotherms for PHCP-1 before and after being immersed and stirred in 1 M NaOH (blue) and 1 M HCl (red) for 24 h, respectively.



**Figure S13.** Nitrogen adsorption-desorption isotherms for C1HCP-5 before and after being immersed and stirred in 1 M NaOH (blue) and 1 M HCl (red) for 24 h, respectively.



**Figure S14.** Nitrogen adsorption-desorption isotherms for C2HCP-5 before and after being immersed and stirred in 1 M NaOH (blue) and 1 M HCl (red) for 24 h, respectively.



**Figure S15.** Adsorption (filled) and desorption (empty) isotherms of  $CO_2$  at 273 K for PHCP-1, PHCP-2, PHCP-4 and PHCP-5.



**Figure S16.** Adsorption (filled) and desorption (empty) isotherms of  $CO_2$  at 273 K for C1HCP-1, C1HCP-2, C1HCP-4 and C1HCP-5.



**Figure S17.** Adsorption (filled) and desorption (empty) isotherms of  $CO_2$  at 273 K for C2HCP-1, C2HCP-2, C2HCP-4 and C2HCP-5.



**Figure S18.** Adsorption (filled) and desorption (empty) isotherms of  $CO_2$  at 273 K for C3HCP-1, C3HCP-2, C3HCP-4 and C3HCP-5.



Figure S19. CO<sub>2</sub> adsorption capacity for recycled PHCP-3 at 273 K, 1.0 bar.



Figure S20. CO<sub>2</sub> adsorption capacity for recycled C1HCP-2 at 273 K, 1.0 bar.



Figure S21. CO<sub>2</sub> adsorption capacity for recycled C2HCP-2 at 273 K, 1.0 bar.



Figure S22. CO<sub>2</sub> adsorption capacity for recycled C3HCP-2 at 273 K, 1.0 bar.



Figure S23. Nitrogen adsorption/desorption isotherms for activated carbon.