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Charged Porous organic frameworks bearing heteroatoms with enhanced isosteric

enthalpies of gas adsorption

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Supporting Information



Figure S1. FT-IR spectrum of B-POF under vacuum for different time.



Figure S2. FT-IR spectrum of BP-POF under vacuum for different time.



Figure S3. FT-IR spectrum of P-POF under vacuum for different time.



Figure S4. ³¹P solid state NMR spectra of BP-POF.



Figure S5. ³¹P solid state NMR spectra of P-POF.



Figure S6. SEM images of (left) B-POF, (middle) BP-POF and (right) P-POF.



Figure S7. PXRD patterns of B-POF (black), BP-POF(blue) and P-POF(red).



Figure S8. TGA plots of B-POF (black), BP-POF(blue) and P-POF(red).



Figure S9. H₂ adsorption isotherms of B-POF (circle), BP-POF (square) and P-POF (triangle) at 87 K (solid symbols, adsorption; open symbols, desorption).



Figure S10. CO₂ adsorption isotherms of B-POF (circle), BP-POF (square) and P-POF (triangle) at 295 K (solid symbols, adsorption; open symbols, desorption).



Figure S11. CH₄ adsorption isotherms of B-POF (circle), BP-POF (square) and P-POF (triangle) at 295 K (solid symbols, adsorption; open symbols, desorption).



Figure S12. ¹H NMR spectra of K[B(4-Brpz)₄] in DMSO at room temperature.



Figure S13. ¹H NMR spectra of [P(4-ClPh)₄]Br in DMSO at room temperature.



Figure S14. ¹³C NMR spectra of K[B(4-Brpz)₄] in DMSO at room temperature.



Figure S15. ¹³C NMR spectra of [P(4-ClPh)₄]Br in DMSO at room temperature.

Portous organic materialsSurr (H) Uptake (m ³ g ⁻¹)H, Uptake (m ³ g ⁻¹)Queuk (m ³ g ⁻¹)Ref.B-POF515103.38.546.032.413.822.4This work This workP-POF629102.87.848.435.213.321.4This workP-POF223100.07.943.527.713.621.5This workPAF-156001864.64615.61814.01COF-1023620"1363.9"28.522HCP-1164655.3"27.54FCTF-1662104.6"35-55BILP-1172"21.28.0"11428.6"3413.26BILP-31306"2358.0"11428.6"3413.26PMOP-1806"65.718.5"17.7"11.07PMOP-255937.6"18.9"15.2"11.47PMOP-1806"37.6"18.9"15.211.17PMOP-182.725"90.3"115.4-"37.6"5.0423.2016.61812.211.17PMOP-182.725"90.3"115.4-"37.6"5.0423.20"16.6"2									
B+POF 515 013.3 8.5 46.0 32.3 13.8 22.4 This work P-POF 629 102.8 7.8 48.4 35.2 13.3 21.4 This work BP-POF 223 100.0 7.9 43.5 27.7 13.6 21.5 This work BP-POF 2360 7.36 4.6 4.6 16.6 18.0 14.0 1 COF-102 3620 "136 3.9 "28.5 - - 3 2 HCP-1 1646 - - 104.6 "37.5 - - 5 BILP-1 1172 "212.8 7.9 "95.7 26.5 "32.2 16.3 5 BILP-3 1306 "22.8 7.9 "95.7 26.5 "32.2 16.3 5 BILP-3 1306 "24.5 8.0 "114 28.6 "34.6 15.2 6 PMOP-2 55.9 10.17-"212.3 <td< th=""><th>Porous organic materials</th><th>SBET</th><th>H₂ Uptake</th><th>Q_{stH2}</th><th>CO₂ Uptake</th><th>Q_{stCO2}</th><th>CH₄ Uptake</th><th>Q_{stCH4}</th><th>Ref.</th></td<>	Porous organic materials	SBET	H ₂ Uptake	Q _{stH2}	CO ₂ Uptake	Q _{stCO2}	CH₄ Uptake	Q _{stCH4}	Ref.
B-POF515103.38.546.032.313.822.4This workP-POF629102.87.843.527.713.621.4This workPAF-156001864.64615.618.614.01COF-10236207363.972.52HCP-116463872.54CTF-1746-5.372.545BILP-31172712.87.979.726.532.216.35BILP-41172721.2.87.979.726.532.216.35BILP-51366725.518.571.716.666BILP-61261724.68.2108.428.478.413.26PMOP-180665.518.571.771.077PMOP-255.977.818.915.271.17PCTF 1.779.2235701.7~212.3-73.6~50.423.7310.8~15.72.187PMOP-14482.7279.3~115.4-73.712.511.4712.513.311PCTF 1.779.223570.3~115.4-73.6~50.42.37.510.8~15.71.111POfvarbacic CPO-122.073.673.6~50.42.7.510.8~15.17.			(cm³ g-1)	(kJ mol ⁻¹)	(cm ³ g ⁻¹)	(kJ mol ⁻¹)	(cm ³ g ⁻¹)	(kJ mol-1)	
P-POF629102.87.848.435.213.321.4This workBP-POF23.3100.07.943.535.213.621.5This workPAF-156001864.64615.618.614.01COF-1023620~13.63.9~28.523HCP-1164638.0~27.533CTF-166210.473.555-5-14.033-5-14.035-44514.014	B-POF	515	103.3	8.5	46.0	32.3	13.8	22.4	This work
<table-container>BP-POF23310.007.943.527.713.621.5This workPAF-156001864.64615.6181.401COF-1023620-13628.523HCP-1164-74.03872.54CTF-1662-104.6735-55BILP-11172712.872.532.216.36BILP-313062358.0'11428.6'34.013.26BILP-41261746.08.2'10828.4'38.013.26PMOP-180665.518.9'17.7'11.07PMOP-255941.5-73.025.3014.6-23.6'8CTF-DCRT500'73.6'.13.8'8.9'13.8'.13.8''11PMOP-1-448.72'90.3~'11.5-'73.6'.13.8'.13.8'.1'''10.8'.15.7''10.8'.15.7''10.8'.15.7''10.8'.15.7'N4CMP-1-5592.426'90.3~'11.5-'73.6'.1.13.8'.13.8'.13.8'.13.8'.1</table-container>	P-POF	629	102.8	7.8	48.4	35.2	13.3	21.4	This work
PAF-156001864.64.64.615.6181.4.01COF-1023620"1363.9"28.522HCP-11646-Sa"28.5"2.513CTF-174655.3"27.555BILP-1112"21.87.995.726.5"32.216.355BILP-31306"23.58.0"14.428.6"34.416.666BILP-4126.1"246.28.0"14.228.4"34.416.666BILP-5126.1"245.210.1"15.216.63.813.2771.47PMOP-180616.518.514.614.63.677711.47PMOP-19.23510.1.7-21.3-14.57.015.210.47711.47711.47711.47711.477711.47711.47711.477711.47711.477711.47711.47711.47711.47711.47711.47711.47711.47711.4711.4711.	BP-POF	223	100.0	7.9	43.5	27.7	13.6	21.5	This work
COF-1021660'136'.9.'.2.8.51.'.2.HCP-11640'.2'.3.'.3.'.2'.2'.3.'.3.'.3.CTF-176.0'.2'.3 <td>PAF-1</td> <td>5600</td> <td>186</td> <td>4.6</td> <td>46</td> <td>15.6</td> <td>18</td> <td>14.0</td> <td>1</td>	PAF-1	5600	186	4.6	46	15.6	18	14.0	1
HCP-116468*23.53(1bar 298)-(1bar 298)-(1bar 298)4FCT-166255.3?27.55BILP-11170?21.87.9~95.726.5~32.216.36BILP-31305~225.510.428.6~34.415.66BILP-61261?2468.2~10828.4~38.813.26PMOP-186.065.518.57.7.711.17PMOP-259.975.818.915.21.1.17PMOP-159.9101.7~21.2.3-41.5~7.3025.3014.6~23.61.2.18PMOP-179.235101.7~21.2.311.071.2.18PMOP-179.235101.7~21.3-1.0.21.0.21.0.21.0.21.0.2PMOP-129.201.0.2 <td>COF-102</td> <td>3620</td> <td>~136</td> <td>3.9</td> <td>~28.5</td> <td>-</td> <td>-</td> <td>-</td> <td>2</td>	COF-102	3620	~136	3.9	~28.5	-	-	-	2
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CTF-174655.377.54FCT-1662104.073555BILP-11172721.87.995.726.532.216.35BILP-313062358.0'114.028.6'34.016.66BILP-6126.172468.2'108.028.4'38.013.26PMOP-180665.518.517.7'11.07PMOP-2559655.014.62.8'12.0'11.07PCTF 1-779-22.5'101.7~21.3-41.57.025.3014.6~23.62.82.8'13.0'12.0'11.07PCTF 1-779-22.5'101.7~21.337.844.28.92.2'13.0'14.0 <td></td> <td></td> <td></td> <td></td> <td>(1 bar 298 K)</td> <td></td> <td></td> <td></td> <td></td>					(1 bar 298 K)				
FCT-1662···104.6~35··5BILP-11172~212.87.9~95.726.5~32.216.35BILP-31306~212.88.0~11428.6~34.016.66BILP-61261~2468.2~108.028.4~38.013.26PMOP-1806~57.818.9~17.7~11.07PMOP-259.9~101.7~21.23-41.5~73.025.3014.6~23.6.28CTF-DCBT79.235~101.7~21.23-1.5<73.0	CTF-1	746	-	-	55.3	~27.5	-	-	4
BILP-11172'212.8'7.9'95.726.5'32.216.35BILP-31366'2358.0'11428.6'34.016.66BILP-61261'2468.2'10828.4'38.013.26PMOP-1806-2'65.518.9'17.7'11.07PMOP-2559'57.818.9'15.2'11.07PCTF 1-779.235'101.7-'21.3-4.57.3025.3014.6-23.62.89CTF-DCBT'59.0'101.7-'21.3-13.2'10.2'10.2'10.21PCTF 1-7'9.235'101.7-'21.3-'11.2'10.2'10.2'10.2'10.2CTF-DCBT'59.0'10.1-'21.3-'15.7'10.2'10.2'10.2'10.2'10.2PCTF 1-7'90.3-'11.54''27.5'10.2 <t< td=""><td>FCTF-1</td><td>662</td><td>-</td><td>-</td><td>104.6</td><td>~35</td><td></td><td></td><td>5</td></t<>	FCTF-1	662	-	-	104.6	~35			5
BILP-3 BILP-31306'2358.0'11428.6'3416.66BILP-6'264'8.2'080'28.4'38.0'1.26PMOP-1806-'65.518.5'1.7.7'1.17PMOP-2559'57.818.9'1.62.0'1.17PCTF 1-779-235'101.7-'21.2.3-1.4'1.5-'3.02.5-30.1.4e-'3.62.2.89CTF-DGT500'1.7.'21.2.3-'1.8'1.8''1.8''1.8''1.8''1.8'BDPCMP-1.4'82.725'90.3-'11.5.4'1.6'1.7''2.3''1.8''1.8''1.8''1.8''1.8'PDCMP-1.5'90.3-'11.5.4'90.3-'11.5.4''1.8''1	BILP-1	1172	~212.8	7.9	~95.7	26.5	~32.2	16.3	5
BILP-61261'2468.2'10828.4'3813.26PMOP-180665.518.5'17.7'117PMOP-2559'57.818.9'15.2'11.07PCTF 1-779.235'101.7^212.3-14.57.3025.3014.62.3.6-8CTF-DCBT50037.844.28.922.899BDPCMP-1-4828.75'90.3~115.4-(73.6 * .15.9)'10.8~15.710.8~15.710.8~15.710.8~15.710.8~15.710.8~15.710.8~15.711.8BDPCMP-1-5592.1426'73.6*7.50.423.27.3'10.8~15.710.8~15.711.811.8Polycarbazole CPOP-122.00'32.6-'45.9~81.125.35.112.112.1Polycarbazole CPOP-122.00'32.613.7'48.227.414.112.112.112.112.112.112.112.113.112.113.112.113.112.113.112.113.113.112.113.114	BILP-3	1306	~235	8.0	~114	28.6	~34	16.6	6
PMOP-1806 </td <td>BILP-6</td> <td>1261</td> <td>~246</td> <td>8.2</td> <td>~108</td> <td>28.4</td> <td>~38</td> <td>13.2</td> <td>6</td>	BILP-6	1261	~246	8.2	~108	28.4	~38	13.2	6
PMOP-2559***18.9**15.2**17PCTF 1-779-2235*101.7~212.3-41.5-73.025-3014.6-23.6-88CTF-DCBT50037.844.28.922.899BDPCMP-1-4482-725*0.3~115.423-27.3*10.8~15.7-1010BDPCMP-1-5592-1426(77.3 K, 1.13 bar)(73.5 K, 1.13 bar)(73.5 K, 1.13 bar)-12Polycarbazole CPOP-12220*322.6-137.027.012Polycarbazole CPOP-12220*32.6-137.027.012Polycarbazole CPOP-122.0*32.62012Polycarbazole CPOP-122.0*32.62012Polycarbazole CPOP-159.142620-1212Polycarbazole CMDF512.1018f10.22012141414CMP 0-5512.01367.571015151614 <td< td=""><td>PMOP-1</td><td>806</td><td>-</td><td>-</td><td>~65.5</td><td>18.5</td><td>~17.7</td><td>~11</td><td>7</td></td<>	PMOP-1	806	-	-	~65.5	18.5	~17.7	~11	7
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CTF-DCBT 500 - - 37.8 44.2 8.9 22.8 9 BDPCMP-1-4 482-725 90.3~115.4 - ~37.6~50.4 23-27.3 ~10.8~15.7 - 1 N4CMP-1-5 592-1426 - - ~73.6~50.4 25.5-35.1 ~10.8~15.7 - 1 Polycarbazole CPOP-1 2200 ~322.6 - - 7 25.5-35.1 - - 12 Polycarbazole CPOP-1 2200 ~322.6 - - - 29 - - 13 P-THIDT - - - - - 13 - - 13 P-GNF 672 ~10.9 6.6 ~38.2 29.8 ~13.3 22.7 14 GNP-0 512-1018 67-155 70 - 28.7 16.1 24.1 14 JUC-27-10 3305-4889 217-245 563-6.88 58.85 15.94-23.17 23-27 15.69-15.96 1	PCTF 1-7	79-2235	~101.7-~212.3	-	41.5-73.0	25-30	14.6-23.6	-	8
BDPCMP-1-4 482-725 $^{90.3 \times 115.4}$ $^{-0.5}$ $^{37.6 \times 50.4}$ $^{23.27.3}$ $^{10.8 \times 15.7}$ $^{10.8}$ <th< td=""><td>CTF-DCBT</td><td>500</td><td>-</td><td>-</td><td>37.8</td><td>44.2</td><td>8.9</td><td>22.8</td><td>9</td></th<>	CTF-DCBT	500	-	-	37.8	44.2	8.9	22.8	9
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$					(1 bar 298 K)		(1 bar 298 K)		
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Polycarbazole CPOP-1 2220 "322.6 - 137.0 27 - - 12 P-THIDT - - - - 13 P-DTBDT - - - 13 preGNF 672 "102.9 6.6 "38.2 29.8 "13.3 22.7 14 GNF-1 679 "116.6 7.7 "48.2 28.7 "16.1 24.1 15 JUC-27-10 305-4889 217-245 5.63-6.88 58-85 15.94-23.17 23-27 15.69-15.96 16 Carbazole-based CMPs 540-917 "108.6~192.5 - ~43.9~65.6 27.1-30.8 "14.6~22.6 - 17 Starbazole-based CMPs 547-63 "107.4~13.9.5 - ~55.1~73.9 27.4-33.5 "16.8~19.3 - - - Starbazole-based MOPs 654-763 "107.4~13.9.5 - ~55.1~73.9 27.4-33.5 "16.8~19.3 - - - CPN1-Br - -	N4CMP-1-5	592-1426	-	-	~45.9-~81.1	25.5-35.1	-	-	11
P-THIDT 92 13 P-DTBDT 13 pre-GNF 672 102.9 6.6 38.2 29.8 13.3 2.7 14 GNF-1 679 116.6 7.7 48.2 28.7 16.1 24.1 14 JUC-27-10 3305-488 67-155 10 - - - - 15 Carbazole-based CMPs 540-917 108.6~192.5 - 43.9~65.6 27.1-30.8 14.6~22.6 - 16 Carbazole-based MOPs 654-763 107.4~139.5 - - - - - 17 Storingio-based MOPs 654-763 107.4~139.5 - - - - - 18 CPN1-Br - 107.4~139.5 - - - - - - 18 CPN1-Br - </td <td>Polycarbazole CPOP-1</td> <td>2220</td> <td>~322.6</td> <td>-</td> <td>137.0</td> <td>27</td> <td>-</td> <td>-</td> <td>12</td>	Polycarbazole CPOP-1	2220	~322.6	-	137.0	27	-	-	12
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pre-GNF 672 ~102.9 6.6 ~38.2 29.8 ~13.3 22.7 14 GNF-1 679 ~116.6 7.7 ~48.2 28.7 ~16.1 24.1 14 CMP 0-5 512-1018 67-155 ~10 - - - - 15 JUC-Z7-10 3305-4889 217-245 5.63-6.88 58-85 15.94-23.17 23.27 15.69-15.96 16 Carbazole-based CMPs 540-917 ~108.6~192.5 - ~43.9~65.6 27.1-30.8 ~14.6~22.6 - 17 Isoindigo-based MOPs 654-763 ~107.4~139.5 - ~55.1~73.9 27.4-33.5 ~16.8~19.3 - 18 CPN-1-Br - - - - - - - - 19 cCTFs 744-1247 - - - 50.4~67.7 43.49 - - 19	P-DTBDT								13
GNF-1 679 ~116.6 7.7 ~48.2 28.7 ~16.1 24.1 14 CMP 0-5 512-1018 67-155 ~10 - - - - 15 JUC-27-10 3305-4889 217-245 5.63-6.88 58-85 15.94-23.17 23-27 15.69-15.96 16 Carbazole-based CMPs 540-917 ~108.6~192.5 - ~43.9~65.6 27.1-30.8 ~14.6~22.6 - 17 Isoindigo-based MOPs 654-763 ~107.4~139.5 - - - 75.1~73.9 27.4-33.5 ~16.8~19.3 - 18 CPN-1-Br - - - - - - 19 cCTFs 744-1247 - - ~50.4~67.7 43.49 - - 20	pre-GNF	672	~102.9	6.6	~38.2	29.8	~13.3	22.7	14
CMP 0-5 512-1018 67-155 ~10 - - - - 15 JUC-27-10 3305-4889 217-245 5.63-6.88 58-85 15.94-23.17 23-27 15.69-15.96 16 Carbazole-based CMPs 540-917 ~108.6~192.5 - ~43.9~65.6 27.1-30.8 ~14.6~22.6 - 17 Isoindigo-based MOPs 654-763 ~107.4~139.5 - ~55.1~73.9 27.4-33.5 ~16.8~19.3 - 18 CPN-1-Br - - - ~55.8 31.0 - - 19 cCTFs 744-1247 - - ~50.4~67.7 43.49 - - 20	GNF-1	679	~116.6	7.7	~48.2	28.7	~16.1	24.1	14
JUC-27-10 3305-4889 217-245 5.63-6.88 58-85 15.94-23.17 23-27 15.69-15.96 16 Carbazole-based CMPs 540-917 "108.6~192.5" - "43.9~65.6" 27.1-30.8 "14.6~22.6" - 17 Isoindigo-based MOPs 654-763 "107.4~139.5" - "55.1~73.9" 27.4-33.5 "16.8~19.3" - 18 CPN-1-Br - - 55.8 31.0 - - 19 cCTFs 744-1247 - - "50.4~67.7 43-49 - - 20	CMP 0-5	512-1018	67-155	~10	-	-	-	-	15
Carbazole-based CMPs 540-917 ~108.6~~192.5 - ~43.9~65.6 27.1-30.8 ~14.6~~22.6 - 17 Isoindigo-based MOPs 654-763 ~107.4~~139.5 - ~55.1~~73.9 27.4-33.5 ~16.8~~19.3 - 18 CPN-1-Br - - ~55.8 31.0 - 19 cCTFs 744-1247 - ~50.4~~67.7 43.49 - 20	JUC-Z7-10	3305-4889	217-245	5.63-6.88	58-85	15.94-23.17	23-27	15.69-15.96	16
(77.3 K, 1.13 bar) Isoindigo-based MOPs 654-763 ~107.4~139.5 - ~55.1~73.9 27.4-33.5 ~16.8~19.3 - 18 (77.3 K, 1.13 bar) - - 755.8 31.0 - 19 CPN-1-Br - - ~50.4~67.7 43-49 - 20	Carbazole-based CMPs	540-917	~108.6-~192.5	-	~43.9-~65.6	27.1-30.8	~14.6-~22.6	-	17
Isoindigo-based MOPs 654-763 ~107.4~139.5 - ~55.1~73.9 27.4-33.5 ~16.8~19.3 - 18 CPN-1-Br - - ~55.8 31.0 - - 19 cCTFs 744-1247 - - ~50.4~67.7 43-49 - - 20			(77.3 K, 1.13 bar)						
(77.3 K, 1.13 bar) CPN-1-Br - - ~55.8 31.0 - - 19 cCTFs 744-1247 - - ~50.4~67.7 43-49 - 20	Isoindigo-based MOPs	654-763	~107.4-~139.5	-	~55.1-~73.9	27.4-33.5	~16.8-~19.3	-	18
CPN-1-Br - ~55.8 31.0 - - 19 cCTFs 744-1247 - - ~50.4~67.7 43-49 - 20	-		(77.3 K, 1.13 bar)						
cCTFs 744-1247 ~50.4~67.7 43-49 20	CPN-1-Br		-	-	~55.8	31.0	-	-	19
	cCTFs	744-1247	-	-	~50.4-~67.7	43-49	-	-	20

Table S1 Comparison of BET surface area, CO₂, CH₄, H₂ sorption capabilities, and isosteric enthalpies for B-POF, BP-POF and P-POF with other porous organic materials.

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