Supporting information

Design of halogen-free hyper-crosslinked porous ionic polymers for efficient CO_2 capture and conversion

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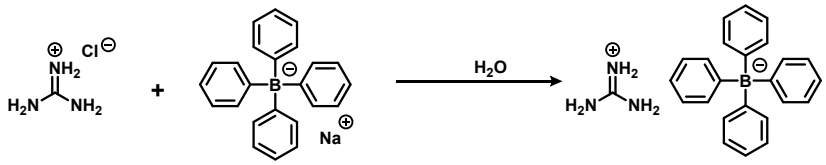
Preparation of [Gua][Bph$_4$]:



Generally, 0.05 mol of [Gua][Cl] and [Na][BPh$_4$] were dissolved in 50 mL of water in a 250 mL beaker, followed by a slow dropwise addition of the aqueous [Na][BPh$_4$] solution to the [Gua][Cl] at room temperature for 24 h. After the reaction, direct filtration and rinsing with large amounts of water to obtain a white solid. The resulting solid was dried under vacuum to obtain the [Gua][BPh$_4$] (yield: 95%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.22 – 7.15 (m, 8H), 6.98 – 6.87 (m, 13H), 6.80 (t, J = 7.2 Hz, 4H) ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.57, 164.08, 163.59, 163.10, 158.31, 136.00, 125.82, 125.79, 125.77, 125.74, 122.00.

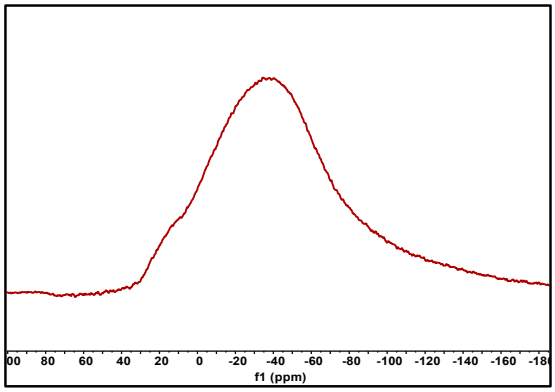


Fig. S1 Solid-state ^{11}B NMR spectrum of Gua-HCPIP-4.

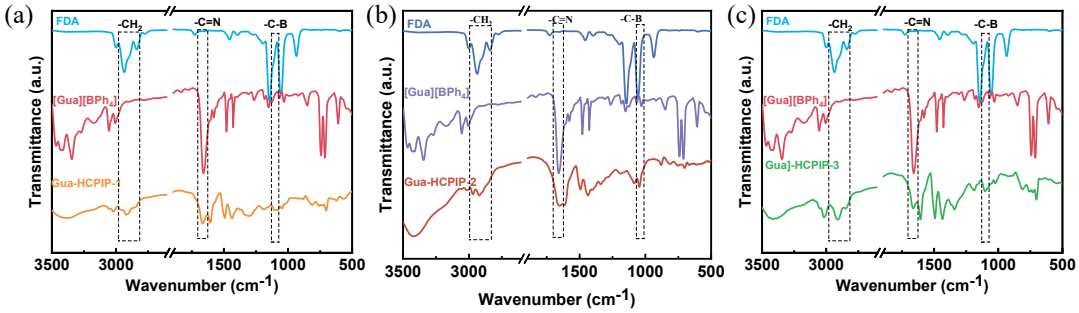


Fig. S2. FT-IR spectra of FDA, [Gua][BPh$_4$] and Gua-HCPIP-x.

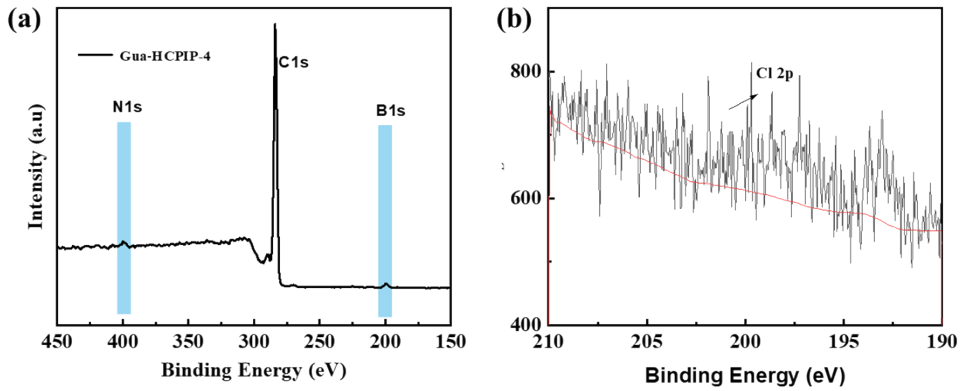


Fig. S3 (a) Survey XPS and (b) high resolution Cl 2p spectra of Gua-HCPIP-4.

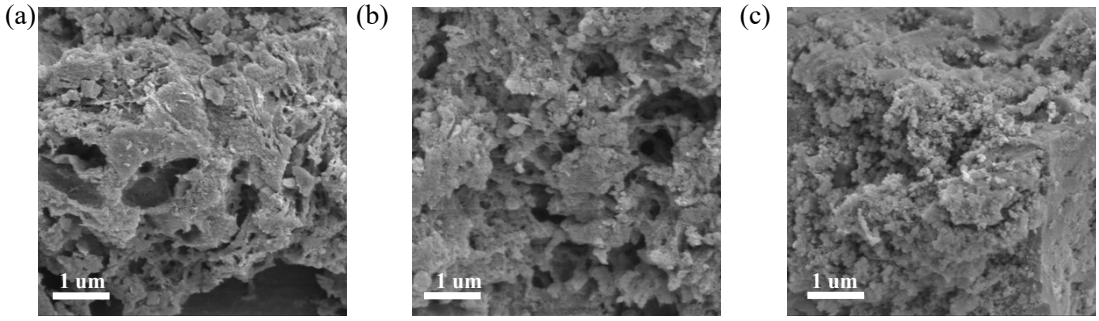


Fig. S4. (a) SEM images of Gua-HCPIP-1, (b)Gua-HCPIP-2, and (c) Gua-HCPIP-3.

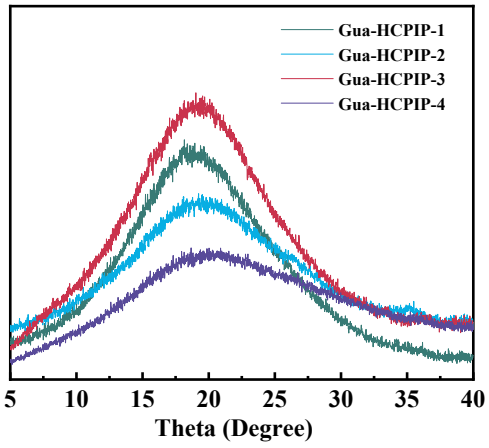


Fig. S5. The XRD patterns of HCPIPs.

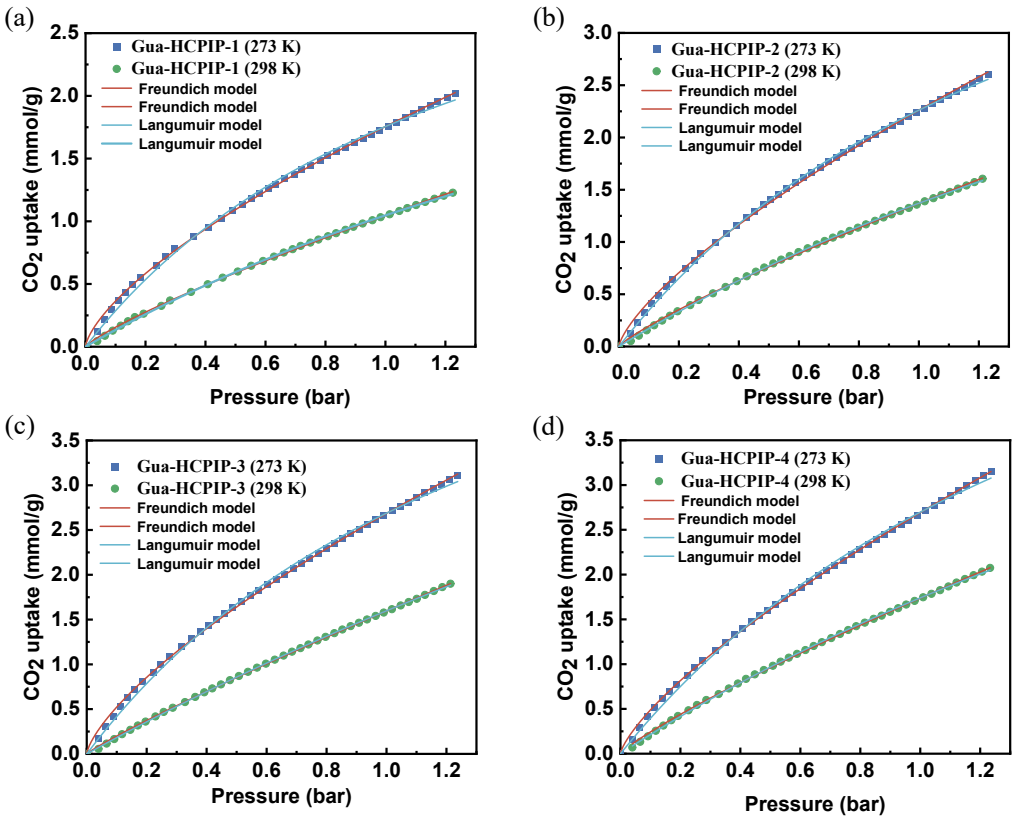


Fig. S6. CO_2 adsorption isotherms for HCPIPs at different temperatures.

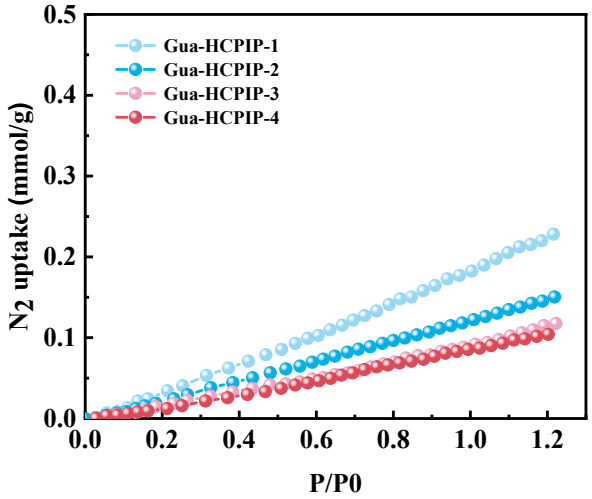


Fig. S7. N_2 adsorption isotherms for HCPIP at 273 K.

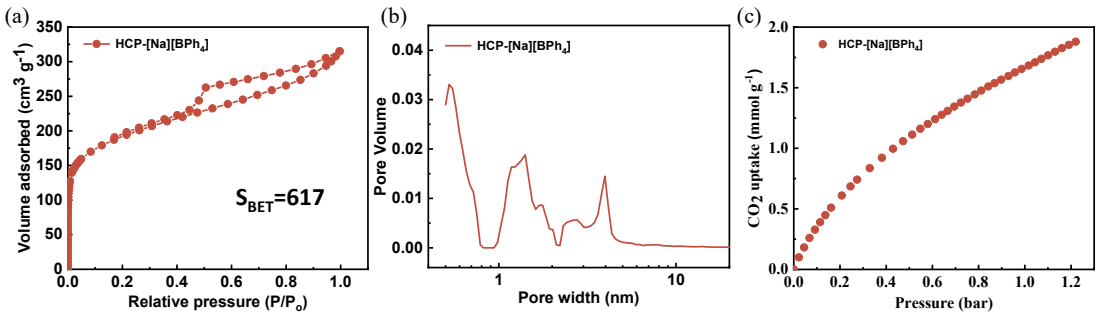


Fig. S8. (a)N_2 adsorption–desorption isotherm and (b) DFT pore distribution of HCP-[Na][BPh_4]; (c)CO_2 adsorption isotherm of HCP -[Na][BPh_4] at 273 K.

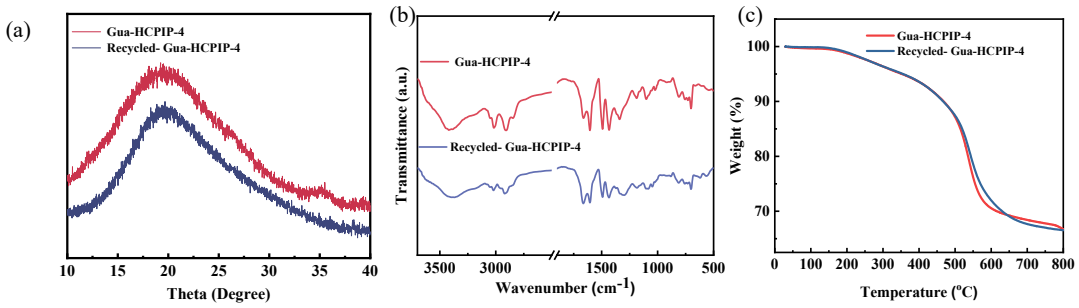


Fig. S9. (a)XRD patterns; (b)FT-IR spectra; and (c) TGA curves of fresh and recycled Gua-HCPIP-4.

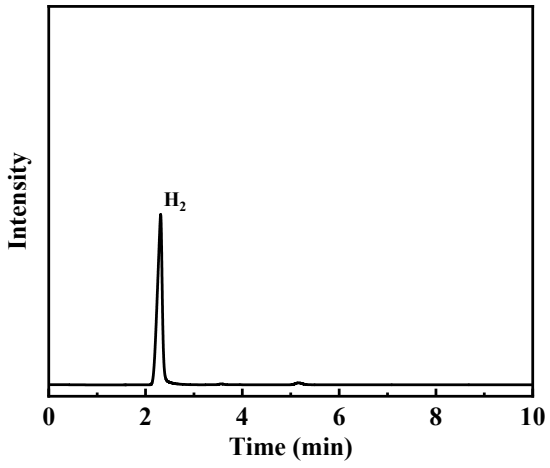
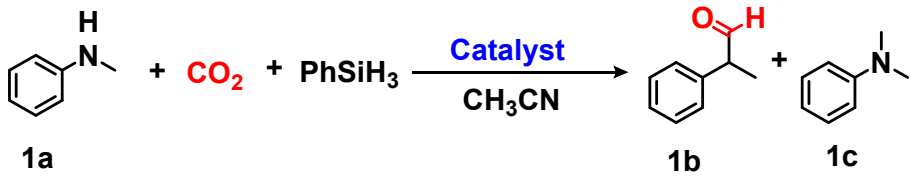


Fig. S10. Gas chromatography chart of reaction exhaust gas.



Scheme S1. N-methylaniline (1a) as a substrate and $PhSiH_3$ as a reducing agent for CO_2 N-formylation in CH_3CN to form the pharmaceutical intermediate N-methylformanilide (1b)

Table S1. Synthesis conditions, and S_{BET} of the HCPIPs.[a]

Sample	FDA/IL	$FeCl_3$ (mmol)	Solvent (mL)	S_{BET} ($m^2\ g^{-1}$)
Gua-HCPIP-1	10	20	20	198
Gua-HCPIP-2	20	20	20	392
Gua-HCPIP-3	30	20	20	551
Gua-HCPIP-4	40	20	20	598

[a]Hyper crosslinking conditions: N_2 protection, 80 °C, 24 h. Solvent: 1,2 dichloroethane

Table S2. Textural parameters of the HCPIP.

Polymers	FDA/ IL	S_{BET} ($m^2\ g^{-1}$)	S_{micro} ($m^2\ g^{-1}$)	S_{meso} ($m^2\ g^{-1}$)	V_{total} ($cm^3\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)	N content (%)	IL content (mmol g^{-1})
Gua-HCPIP-1	10	196	84	112	0.196	0.083	1.50	0.357
Gua-HCPIP-2	20	392	203	189	0.376	0.177	1.35	0.321
Gua-HCPIP-3	30	522	268	254	0.588	0.228	1.21	0.288
Gua-HCPIP-4	40	598	311	287	0.457	0.263	1.02	0.243

Table S3. CO_2 adsorption Langmuir, Freundich parameters isotherms.

Polymers	T(K)	Q_{exp}	Langumuir	Freundich

			q_{mod}	Q_{max}	kl	R^2	q_{mod}	K_f	n	R^2
Gua-HCPIP-1	273.15	2.022	1.968	4.081	0.755	0.997	2.022	1.755	1.462	0.999
	298.15	1.261	1.217	4.376	0.315	0.999	1.237	1.046	1.207	0.999
Gua-HCPIP-2	273.15	2.601	2.556	5.895	0.622	0.999	2.626	2.261	1.383	0.999
	298.15	1.605	1.587	6.195	0.284	0.999	1.605	1.370	1.184	0.999
Gua-HCPIP-3	273.15	3.114	3.041	6.805	0.653	0.998	3.125	2.686	1.406	0.999
	298.15	1.901	1.884	11.752	0.157	0.999	1.900	1.596	1.106	0.999
Gua-HCPIP-4	273.15	3.154	3.078	7.669	0.542	0.998	3.154	1.737	1.171	0.999
	298.15	2.074	2.047	8.599	0.254	0.999	2.074	2.692	1.349	0.999

Table S4. CO_2 adsorption performance of previous materials.

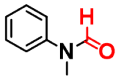
Sample	CO_2 uptake (mmol g^{-1}) (273 K, 1bar)	CO_2/N_2 selectivity		Ref.
		Method	(273 K, 1 bar)	
Gua-HCPIP-4	2.72	IAST	332	This work
PIPs-6	2.35	IAST	256	[1]
COP-222	1.08	-	-	[2]
ILs-$POF_{0.5}$	2.14	-	-	[3]
PAF-167	1.68	IAST	49.7	[4]
PCP-Cl	2.31	IAST	48	[5]

HPILs-Cl-1	3.25	IAST	44	[6]
SCHPP-3	1.32	-	-	[7]
PDI-HIP-1	2.11	-	-	[8]
PTPIM-IL	2.69	-	-	[9]
HIP-Br-His	2.90	IAST	53	[10]
HBIM(2)@QA	2.97	-	-	[11]
HPMBr0.5	1.83	-	-	[12]
[HBIM- 2]Br- DCX (3)	1.80	-	-	[13]
Al-HIP-3	2.10	-	-	[14]
IHCP-2	2.87	IAST	24.5	[15]

Table S5. Comparison of catalysts for CO_2 N-formylation reaction

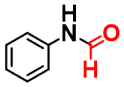
Sample	Solvent	Temperature (°C) / Time (h)	Pressure (bar)	Yeild (%)	Ref.
ZIF-90-C	CH_3CN	50/24	1	87	[16]
$Zn(OAc)_2$/phen	CH_3CN	25/72	5	92	[17]
Pd/Bi-ZnOx	CH_3CN	30/24	5	29.6	[18]
$(C_5H_7N_2)_5[CuW_{12}O_{40}]$	CH_3CN	25/24	1	94	[19]
$[Fe(acac)_2]+pp_3$	THF	25/18	1	45	[20]
$[Ph_3PMe]CO_3Me$	THF	70/16	1	72	[20]

NSC1	DMF	50/24	1	77	[21]
43# ILHCP	-	35/16	5	99	[22]
TB-G/H-COF	CH_3CN	80/7	1	97	[23]
Gua-HCPIP-4	CH3CN	80/24	3	94	This work



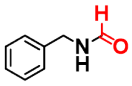
1b

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.53 (s, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.32 (d, J = 7.4 Hz, 2H), 7.25 (t, J = 7.4 Hz, 1H), 3.21 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.48, 142.53, 129.86, 126.04, 121.93, 31.43.



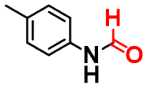
2b

^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 8.88 – 8.29 (m, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 7.9 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.99, 160.06, 138.73, 129.84, 129.31, 124.06, 119.63, 117.99.



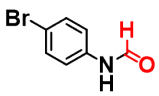
3b

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.52 (s, 1H), 8.15 (s, 1H), 7.41 – 7.19 (m, 5H), 4.31 (d, J = 6.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.40, 161.50, 139.46, 128.81, 127.77, 127.35, 45.01, 41.18.



4b

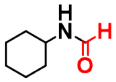
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.12 (s, 1H), 8.25 (s, 1H), 7.49 (d, J = 8.2 Hz, 2H), 7.11 (t, J = 7.1 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.92, 159.79, 136.26, 136.23, 133.17, 132.98, 130.24, 129.67, 119.56, 118.15, 20.90, 20.76.



5b

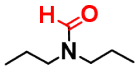
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.29 (d, J = 46.1 Hz, 1H), 8.89 – 8.22 (m, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.97, 160.23,

138.32, 138.05, 132.59, 132.15, 121.54, 119.79, 115.64.



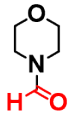
6b

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (s, 1H), 3.68 – 3.53 (m, 1H), 1.81 – 1.46 (m, 4H), 1.19 (dt, J = 42.6, 12.1 Hz, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.32, 50.67, 46.51, 34.64, 32.75, 25.61, 24.81.



7b

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.77 (s, 1H), 2.98 – 2.83 (m, 4H), 1.23 (dh, J = 14.9, 7.4 Hz, 4H), 0.57 (td, J = 7.5, 2.5 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.00, 48.43, 43.22, 21.80, 20.59, 11.58, 11.08.



8b

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.02 (s, 1H), 3.58 (t, J = 4.9 Hz, 2H), 3.53 (t, J = 5.0 Hz, 2H), 3.39 (q, J = 5.6 Hz, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.36, 67.18, 66.21, 45.54.

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