Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Flow synthesis of hypercrosslinked polymers with additional microporosity that enhance CO_2/N_2 separations

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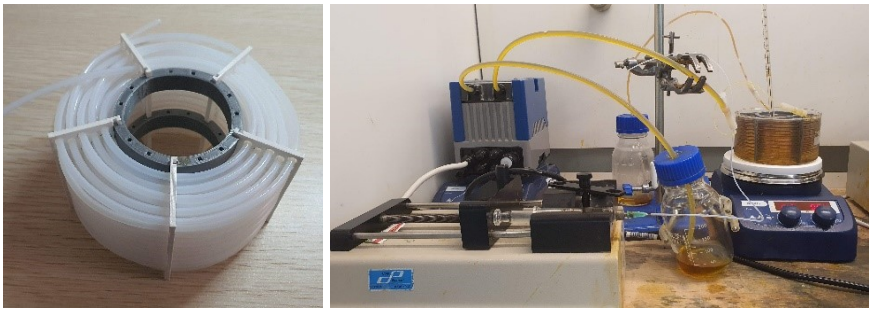

Figure S1 Coiled tubular reactor (Left) and actual set-up (Right)

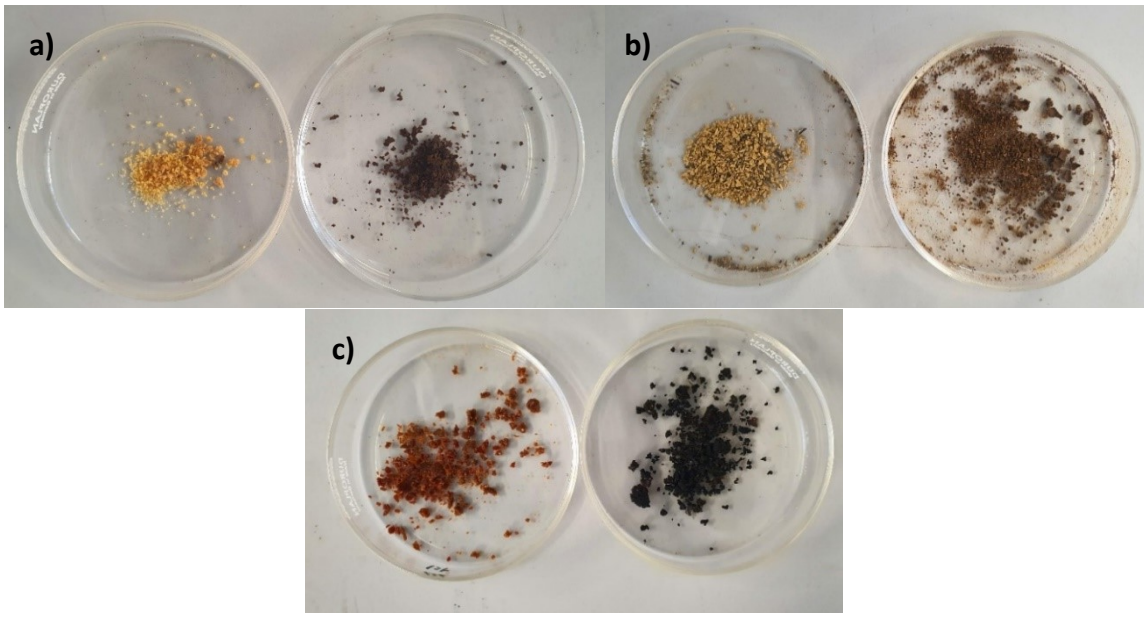

Figure S2 HCPs from the optimal flow-condition (Left) with their batch counterpart (Right): a) p-PS/DCX, b) p-DCX, and c) p-PS/FDA

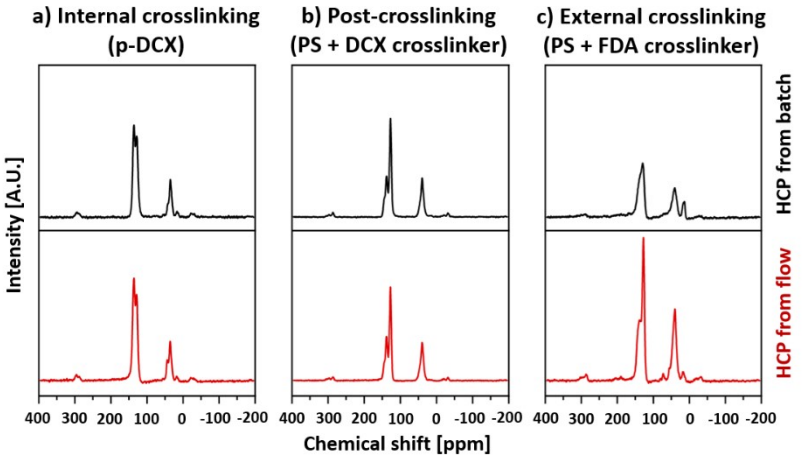

Figure S3 ^{13}C-NMR spectra (Full range from -200 to 400 ppm) of the HCPs

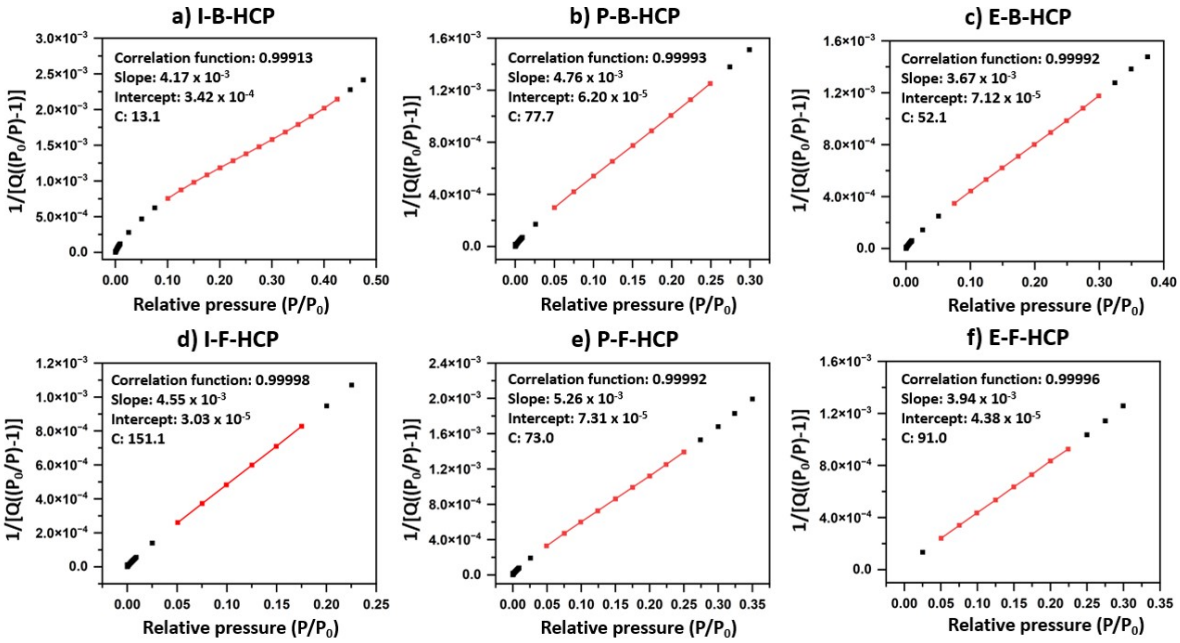

Figure S4 BET plots of six optimal HCP samples of each synthetic approaches (Internal crosslinking, post-crosslinking, and external crosslinking) and synthetic methods (Batch and flow). The fitting region following Rouquerol correction for microporous materials is shown in red dot and line together with correlation function, slope, intercept, and BET constant.

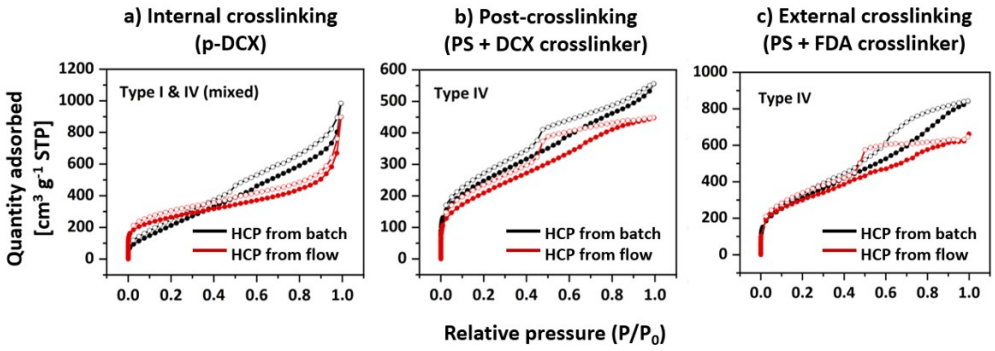

Figure S5 N_2 sorption at 77 K of HCP products. Adsorption isotherm is shown as filled dot marker. Desorption isotherm is shown as empty dot marker.

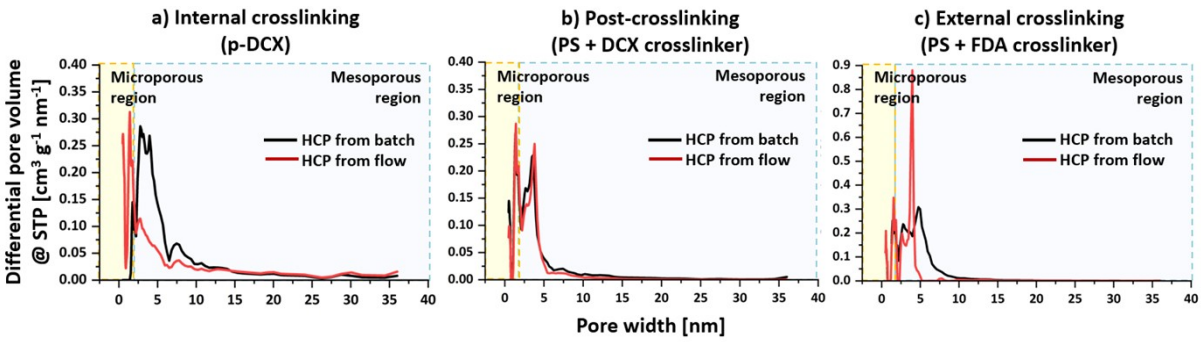

Figure S6 Pore size distribution from 0 – 40 nm pore width of flow-produced HCPs and their batch equivalents

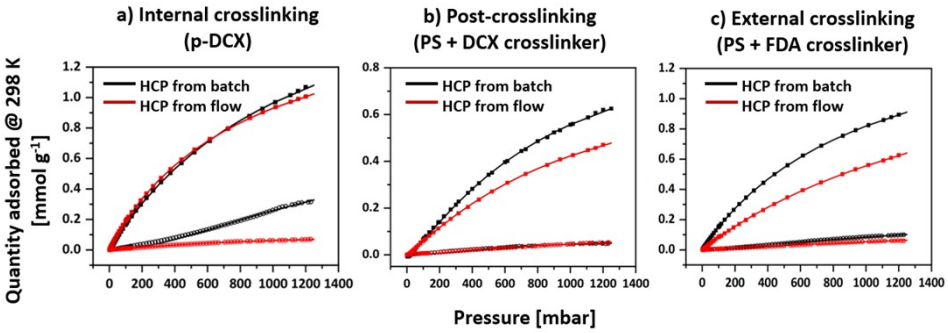

Figure S7 CO_2 uptake isotherms at 298 K. Experimental data is presented as marker points. IAST curve fitting is shown as solid lines. CO_2 adsorption is shown as filled square marker. N_2 adsorption is shown as empty circle marker.

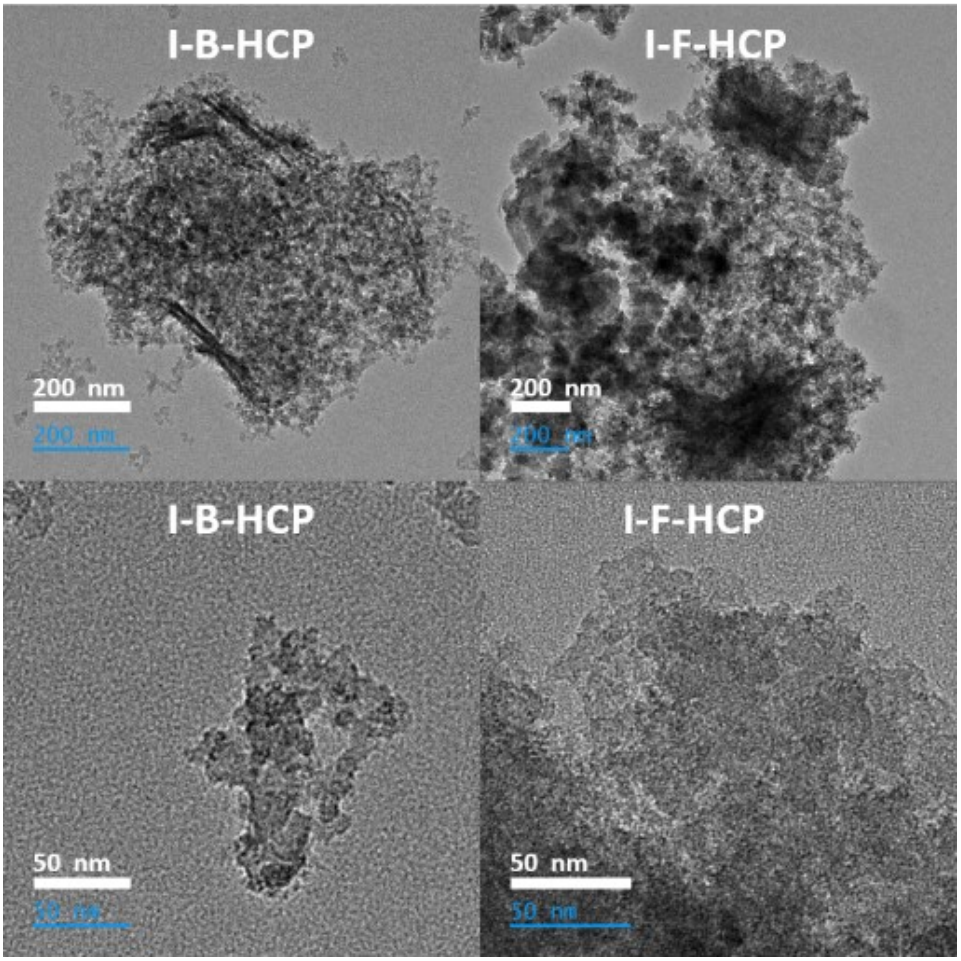

Figure S8 TEM images of I-B-HCP and I-F-HCP

Table S1 Operating parameters of batch production and correspond product yields

Crosslinking approach	Substrate conc.[% w/v]	Substrate: $FeCl_3$: Crosslinker	Temp. [K] [24]	Reaction time [day] [41]	Yield [%]	BET SA [$m^2 g^{-1}$]	Sample names
Internal crosslinking	1.923	1:1:0 (mol)	373	24	64.42	686.356	-
	2.884	1:1:0 (mol)	373	24	58.50	964.309	I-B-HCP
Post-crosslinking	0.385	1:1:1 (wt)	353	24	155.38	903.183	P-B-HCP
External crosslinking	0.762	1:5:5 (wt)	353	24	156.63	1161.864	E-B-HCP

Table S2 Operating parameters of flow production and correspond product yields

Internal crosslinking approach

DCX conc. [% w/v]	DCX:$FeCl_3$ (molar ratio)	Temp. [K]	Flow rate [mL min^{-1}]	Residence time [min]	Yield [%]	BET SA [$m^2 g^{-1}$]	Sample names
0.962	1:1	343	1.94	15	Unreacted	N.A.	-
0.962	1:1	343	1.46	20	3.59	N.A.	-
1.923	1:1	343	2.94	10	Unreacted	N.A.	-
1.923	1:1	343	2.26	13	12.19	542.197	-
1.923	1:1	343	1.94	15	Clogged	N.A.	-
2.884	1:1	343	9.40	3	Unreacted	N.A.	-
2.884	1:1	343	5.40	5	7.24	950.130	I-F-HCP
2.884	1:1	343	4.14	7	Clogged	N.A.	-
0.673	1:2	343	9.40	3	17.83	702.780	-

Post-crosslinking approach

PS conc. [%w/v]	PS:$FeCl_3$: DCX (weight ratio)	Temp. [K]	Flow rate [mL min^{-1}]	Residence time [min]	Yield [%]	BET SA [$m^2 g^{-1}$]	Sample names

0.385	1:1:1	343	4.14	7	Unreacted	N.A.	-
0.385	1:1:1	343	2.94	10	126.72	815.900	P-F-HCP
0.385	1:1:1	343	2.26	13	133.51	771.330	-
0.385	1:1:1	343	1.94	15	Clogged	N.A.	-
0.577	1:1:1	343	9.40	3	Clogged	N.A.	-
0.385	1:2:2	343	9.40	3	119.15	N.A.	-
0.385	1:2:2	343	5.40	5	Clogged	N.A.	-

External crosslinking approach							
PS conc. [%w/v]	**PS:$FeCl_3$: FDA (weight ratio)**	**Temp. [K]**	**Flow rate [mL min^{-1}]**	**Residence time [min]**	**Yield [%]**	**BET SA [$m^2 g^{-1}$]**	**Sample names**
0.762	1:5:5	343	2.94	10	85.30	711.388	-
0.762	1:5:5	343	2.26	13	103.70	893.733	-
0.762	1:5:5	343	1.94	15	114.30	1091.656	E-F-HCP
0.762	1:5:5	343	1.74	17	98.01	647.282	-
0.762	1:5:5	343	1.46	20	94.51	377.181	-
0.962	1:1:1	343	2.94	10	Unreacted	N.A.	-
0.962	1:3:3	343	2.94	10	69.48	28.542	-
0.962	1:5:5	343	2.94	10	102.47	534.331	-
0. 577	1:5:5	323	2.94	10	Unreacted	N.A.	-
0. 577	1:5:5	333	2.94	10	97.65	214.311	-
0. 577	1:5:5	343	2.94	10	99.17	671.391	-
0.385	1:5:5	343	2.94	10	80.65	296.193	-
0. 577	1:5:5	343	2.94	10	99.17	671.391	-
0.762	1:5:5	343	2.94	10	110.74	605.777	-
0.962	1:5:5	343	2.94	10	102.47	534.331	-

Table S3 Micropore volumes, and STY of flow-produced external crosslinked HCPs from different synthesis parameters

Residence time [min]	**DFT micropore volume [$cm^3 g^{-1}$]**	**Space-time-yield [mg mL^{-1} day^{-1}]**
10	0.042150	964.514
13	0.083919	897.427
15	0.292950	691.573
17	0.198340	652.577
20	0.101110	526.243

PS:$FeCl_3$:FDA (weight ratio)	DFT micropore volume [$cm^3\ g^{-1}$]	Space-time-yield [mg mL^{-1} day^{-1}]
1:1:1	N.A.	N.A.
1:3:3	0.006543	981.166
1:5:5	0.104223	1447.037
Temperature [K]	**DFT micropore volume [$cm^3\ g^{-1}$]**	**Space-time-yield [mg mL^{-1} day^{-1}]**
323	N.A.	N.A.
333	0.058939	828.693
343	0.108909	841.592
PS concentration [% w/v]	**DFT micropore volume [$cm^3\ g^{-1}$]**	**Space-time-yield [mg mL^{-1} day^{-1}]**
0.40	0.079204	457.185
0.60	0.108909	841.592
0.80	0.115116	1252.172
1.00	0.104223	1447.037

* DFT micropore volume data was obtained from the cumulative pore volume of the pore size up to 2 nm

Table S4 Surface area, volume, and specific area of batch and flow reactors

Reactor types	Reactor surface area [m^2]	Reactor volume [m^3]	Reactor specific areas [$m^2\ m^{-3}$]
Batch: 250mL three neck round bottle *	0.0101	1.340×10^{-4}	75
Flow: Helical coil reactor	0.1520	2.988×10^{-5}	5087

* Assumed the sphere shape bottle of 8 cm diameter is half filled

Table S5 Reynolds numbers from the synthesis of externally crosslinked HCPs in flow reactor at different residence times

Residence time [min]	Volumetric flow rate [mL min^{-1}]	Feed flow velocity [m s^{-1}]	Reynolds number*
10	2.94	0.02499	98.14
13	2.26	0.01921	75.44
15	1.94	0.01649	64.76
17	1.74	0.01479	58.08
20	1.46	0.01241	48.73

* $Re = \frac{\rho V D}{\mu} = \frac{\rho F D}{\mu A_{cross}}$ where $\rho\ [kg\ m^{-3}]$ is fluid density; $V\ [m\ s^{-1}]$ is fluid velocity; $D\ [mm]$ is tube inner diameter; $\mu\ [mPa \cdot s]$ is fluid dynamic viscosity; $F\ [mL\ min^{-1}]$ is fluid volumetric flow rate; and $A_{cross}\ [mm^2]$ is cross-sectional area of the tube

** DCE thermodynamic properties at 343 K are $\mu = 0.476\ mPa \cdot s$ and $\rho = 1183\ kg\ m^{-3}$

*** $D = 1.58\ mm$, thus $A_{cross} = 1.96\ mm^2$

Table S6 Single site Langmuir-Freundlich parameters of HCPs for CO_2/N_2 selectivity calculation

Samples	CO_2				N_2			
	q	k	n	R^2	q	k	n	R^2
I-B-HCP	2.08438	8.45 x 10^{-4}	1.00271	0.99984	0.69661	1.69 x 10^{-6}	1.84764	0.99632
I-F-HCP	1.78092	1.44 x 10^{-3}	0.96006	0.99999	0.13976	5.43 x 10^{-4}	1.05481	0.99868
P-B-HCP	1.00444	1.99 x 10^{-4}	1.26554	0.99906	0.05773	2.72 x 10^{-6}	2.03761	0.98983
P-F-HCP	0.87939	4.03 x 10^{-4}	1.12066	0.99984	0.09412	2.50 x 10^{-5}	1.52846	0.99668
E-B-HCP	1.68105	1.07 x 10^{-3}	0.98250	0.99999	0.20433	3.33 x 10^{-5}	1.44437	0.99944
E-F-HCP	1.70057	5.57 x 10^{-4}	0.98019	0.99997	0.15265	9.61 x 10^{-5}	1.24803	0.99895

Estimation of Reynolds number in batch reactor

The Reynolds number in our batch reactor (250 mL three neck round bottom flask) was estimated using an equation for a propeller turbine mixer tank[42] in which the propeller is equivalent to the stirrer bar in our work. The thermodynamic properties of feed fluid mixture were assumed as pure DCE at 343 K since the concentration of feed was considerably low. The equation is shown as follows:

$$Re = ND^2\frac{\rho}{\mu}$$

$N\ [rps]$ is rotational speed of the stirrer bar, which was set to 250 rpm or 4.167 rps

$D\ [m]$ is diameter of the stirrer bar, which was 0.025 m

$\mu\ [mPa \cdot s]$ is fluid dynamic viscosity, which is 0.476 mPa s

$\rho\ [kg\ m^{-3}]$ is fluid density, which is 1183 kg m^{-3}

After substituting with values, we got the solution of Re = 6524.