Supporting Information

Ionic Polymer with Cooperative CO_2 Adsorption and Catalytic Sites for Efficient CO_2 Cycloaddition

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Experimental section

1. Materials and methods

2,4,6-Tris(dimethylaminomethyl)phenol (95%) was purchased from Shanghai Macklin Biochemical Technology Co., Ltd. 1,3,5-Tris(bromomethyl)benzene (>97%) was obtained from Shanghai Adamas Reagent Co., Ltd. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 97%), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 99%), 1,1,3,3-tetramethylguanidine (TMG, 98%), and epoxide compounds (98%) were supplied by Shanghai Energy Chemical Reagent Co., Ltd. Ethyl acetate (>99%) was procured from Chengdu Jinshan Chemical Reagent Co., Ltd. High-purity carbon dioxide (CO_2, 99.999%) and nitrogen (N_2, 99.999%) were provided by Guizhou Sanhe Gas Technology Co., Ltd. All chemicals were used as received.

Surface morphology and pore structure were characterized using scanning electron microscopy (SEM, Quanta FEG 650) and transmission electron microscopy (TEM, FEI G2 F20), respectively. Crystal structure was determined by X-ray diffraction (XRD, D8 Advanced). FTIR spectra were collected on a Nicolet 50 spectrometer; conventional spectra were recorded using the KBr pellet method in the range of 400-4000 cm^{-1}, and in-situ IR spectra were acquired on the same instrument. Specific surface area (BET) and pore volume were determined from N_2 adsorption-desorption isotherms measured on a BSD-PM analyzer. Thermal stability was evaluated using thermogravimetric analysis (TGA, TG 209 F1 Libra) under N_2 atmosphere at a heating rate of 10 $^{o}C/min$. Surface elemental composition was analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha Plus). Cyclic carbonate yields were determined using a Shimadzu GC-2014 gas chromatograph.

2. Preparation of materials

Synthesis of ionic polymers (IPs): A 50 mL single-neck flask was charged with 2,4,6-tris(dimethylaminomethyl)phenol (265 mg, 1.0 mmol) and ethyl acetate (10 mL), and the mixture was stirred until complete dissolution. Separately, 1,3,5-tris(bromomethyl)benzene (367 mg, 1.0 mmol) was dissolved in ethyl acetate (10 mL) and added dropwise over 5 min. The reaction mixture was stirred at 30 ^{o}C for 24 h. The resulting white solid was collected by centrifugation, washed three times with ethyl acetate, and dried under vacuum at 70 °C to afford the ionic polymers.

Preparation of IPs@[BaseH][TAPhO]: The synthesized IPs (1.0 mmol equivalent) were dispersed in ethyl acetate (10 mL) and pre-stirred for 10 min. DBU (337 mg, 2.0 mmol) was dissolved in ethyl acetate (10 mL) and added dropwise to the dispersion. The mixture was stirred at 30 °C for 24 h. The solid product was isolated by centrifugation, washed three times with ethyl acetate, and dried under vacuum at 70 °C for 12 h to yield IPs@[DBUH][TAPhO]. Using an equimolar amount of DBN or TMG in place of DBU under otherwise identical conditions afforded IPs@[DBNH][TAPhO] and IPs@[TMGH][TAPhO], respectively.

Synthesis of [DBUH][TAPhO]: TAPhOH and DBU were mixed in a 1:1 molar ratio in a dry 50 mL flask and stirred under solvent-free conditions at 30 °C for 24 h. The crude product was washed three times with ethyl acetate, and the resulting viscous liquid was dried under vacuum at 60 °C for 24 h to yield [DBUH][TAPhO] as a pale yellow ionic liquid.

3. CO_2 conversion

Catalytic performance was evaluated using allyl glycidyl ether (AGE) as a model substrate under co-catalyst- and solvent-free conditions. AGE (5 mmol) and catalyst (50 mg) were added to a 100 mL glass reaction tube. The tube was connected to a CO_2 balloon and stirred at 70 °C for 6 h. After the reaction, the mixture was cooled to room temperature, and the product was extracted with ethyl acetate and quantified by gas chromatography (Shimadzu GC-2014).

Using IPs@[DBUH][TAPhO] as the catalyst, reaction conditions including temperature, time, and catalyst loading were systematically optimized. Catalyst versatility and recyclability were also investigated. After each cycle, the catalyst was washed thoroughly with ethyl acetate, dried, and reused under the following conditions: epichlorohydrin (ECH, 5 mmol), IPs@[DBUH][TAPhO] (50 mg), CO_2 (1 bar), 70 °C, 12 h.

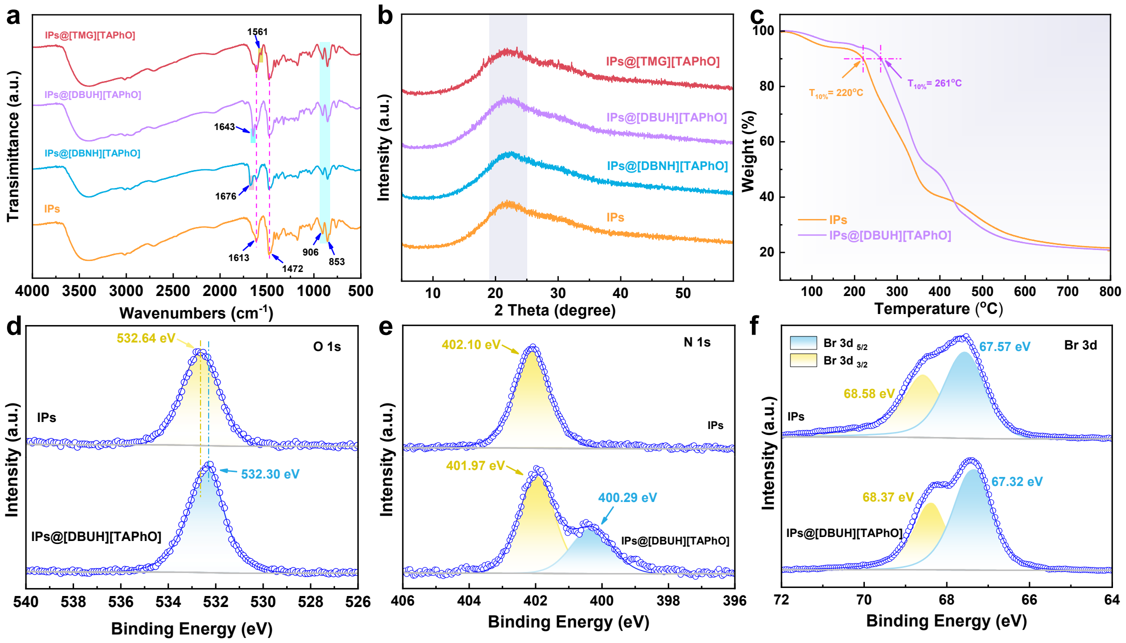

Fig. S1 (a) FTIR spectra, (b) XRD patterns, and (c) TGA curves of the prepared materials. XPS analysis: (d) N 1 s, (e) O 1s, (f) Br 3d spectra.

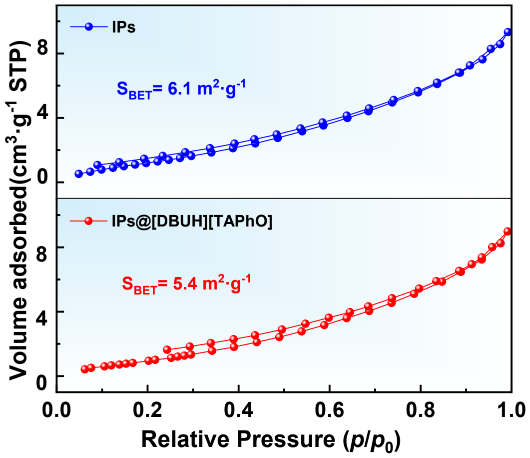

Fig. S2 N_2 adsorption-desorption isotherms and IPs and IPs@[DBUH][TAPhO].

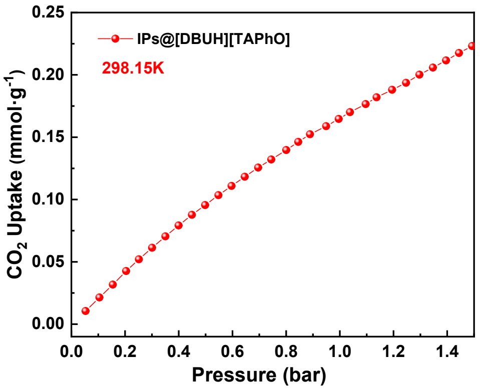

Fig. S3 CO$_2$ adsorption isotherm of IPs@[DBUH][TAPhO] at 298.15 K.

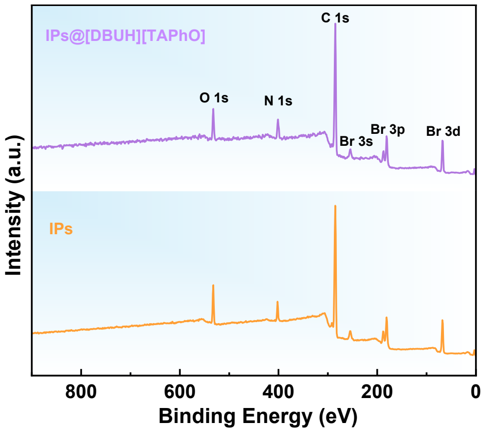

Fig S4. XPS survey spectrum.

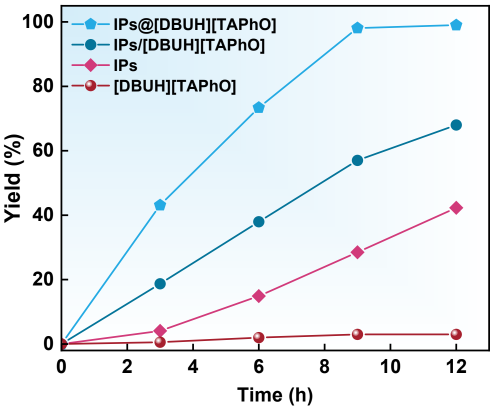

Fig. S5 Kinetic curves of various catalysts.

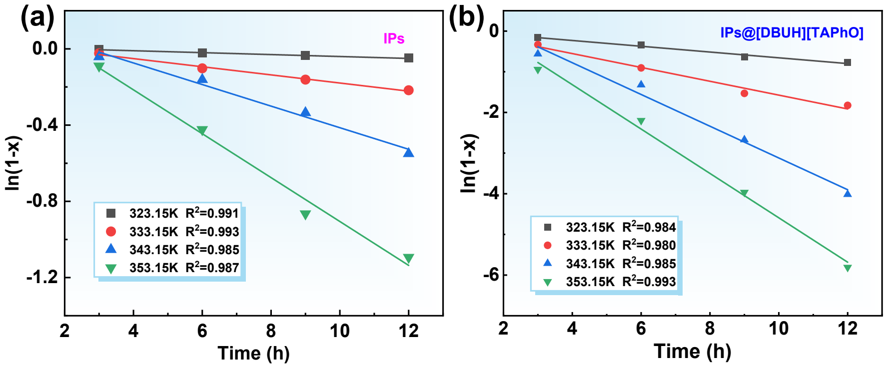

Fig. S6 First-order kinetic plots ln(1-x) versus time at different temperatures (a) IPs, (b) IPs@[DBUH][TAPhO].

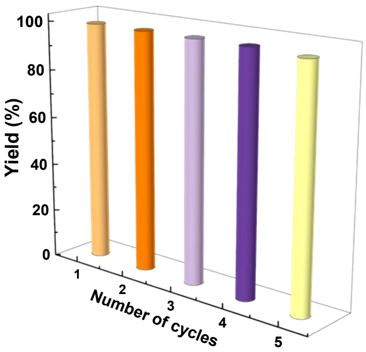

Fig. S7 Reusability of IPs@[DBUH][TAPhO].

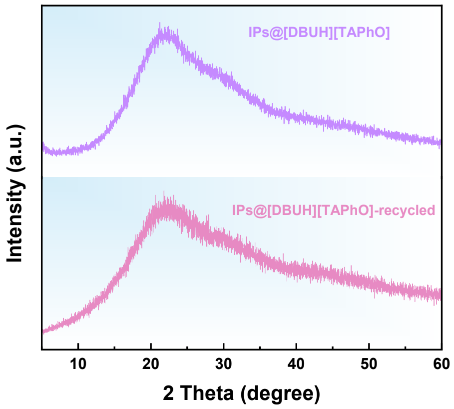

Fig. S8 XRD pattern before and after cycling.

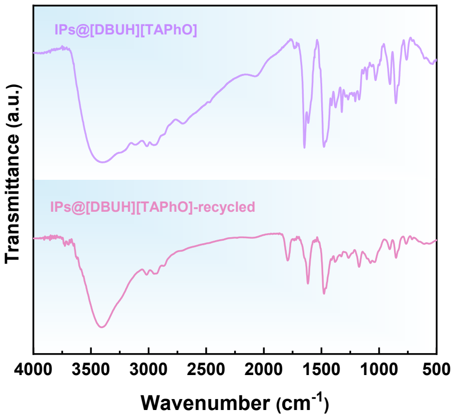

Fig. S9 FTIR spectra before and after cycling.

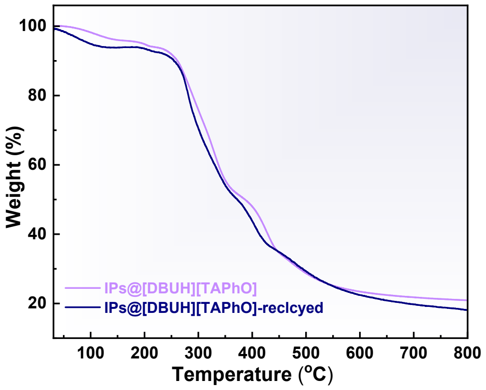

Fig. S10 FTIR spectra before and after cycling.

Table S1. Comparison of the catalytic activity of various catalysts for the cycloaddition of epichlorohydrin (ECH) and CO_2

Entry	Catalyst	Cat. usage	T(°C)/p(bar)/t(h)	Co-catalyst	Yield(%)	Ref.
1	Zn-Salen-IP	2.16 wt%	110/10/8	/	99	1
2	Co (salen) -HPiP	10.8 wt%	100/10/9	/	97.2	2
3	HPIL-$ZnBr_2$	13.6 wt%	70/10/3	/	94	3
4	CD@KI	4.1wt%	80/1/34	/	74	4
5	TZ-AP	2.16 wt%	90/5/6	/	95.8	5
6	PIL@NENPs	2.16 wt%	110/10/8	/	91	6
7	MCTF-10	10.8 wt%	80/1/24	/	90	7
8	Py-HCP-Br	12.5 wt%	120/20/8	/	99	8
9	PIL-DVB-IV	15.7 wt%	110/20/6	/	95	9
10	PTA-2-DBX	13 wt%	100/1/12	/	99	10
11	FcIP-2Br	8.2 wt%	80/1/20	/	92.2	11
12	VIPOP-3	4.9 wt%	80/1/24	/	94	12
13	PIL-2	5.4 wt%	100/10/6	/	97	13
14	PIP-urea	0.3 mol %	100/10/5	/	97	14
15	MA-PDA IL@COF	8.6 wt%	70/1/14	/	99	15
16	NSAC-(1:1)550	5.4 wt%	120/10/8	20mg TBAB	90	16
17	2,3-DhaTph	0.2 mol%	110/1/12	0.5 mol% TBAB	88	17
18	CTP-1-NH_2/TBAB	2.16 wt%	40/1/36	2 mol% TBAB	93	18
19	BPO_4@BCN-800	1.1wt%	80/1/36	1.0 mmol KI	99	19
20	POM@ImTD COF	10.8 wt%	80/1/24	5.4 mol% TBAB	99	20
21	Zn-N-C-800	5 wt%	80/10/6	0.1 mmol TBAB	99	21
22	IPs@[DBUH][TAPhO].	9.8 wt%	70/1/12	/	99	This work

TBAB: tetrabutylammonium bromide. TBAI: Tetrabutylammonium iodide

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