

## Supporting Information

# Metal-free hydroxyl functionalized quaternary phosphine type hypercrosslinked polymer for cycloaddition of CO<sub>2</sub> and epoxide

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## 1. Experimental Section

### Chemical and Reagents

Glycidyl methacrylate (GMA, 98%), methyltriphenylphosphonium bromide (98%), triphenylphosphine (98%), phloroglucinol (98%), biphenyl (99%), N,N-dimethylformamide (DMF, 99%), tetrabutylammonium bromide (TBAB, 99%), iron(III) chloride anhydrous (98%), dimethoxymethane (FDA, 98%), 1,2-dichloroethane (99.5%), hexane (99.5%), dichloromethane (99.5%), and methanol (MeOH, 99.9%) were purchased from Energy Chemical. 1,2-epoxycyclododecane (95%), epibromohydrin (97%) were obtained from J&K. Tris(dibenzylideneacetone)dipalladium(0) ( $\text{Pd}_2(\text{dba})_3$ , 97%), 2-bromo-4-methylphenol (98%), 2-bromo-4-methoxyphenol (98%) and ethylene glycol (99%) were purchased from Aladdin. Silica gel (200–300 mesh) was bought from Qingdao Haiyang Chemical Plant. All the chemical reagents were employed as received without further purification.

### Synthesis

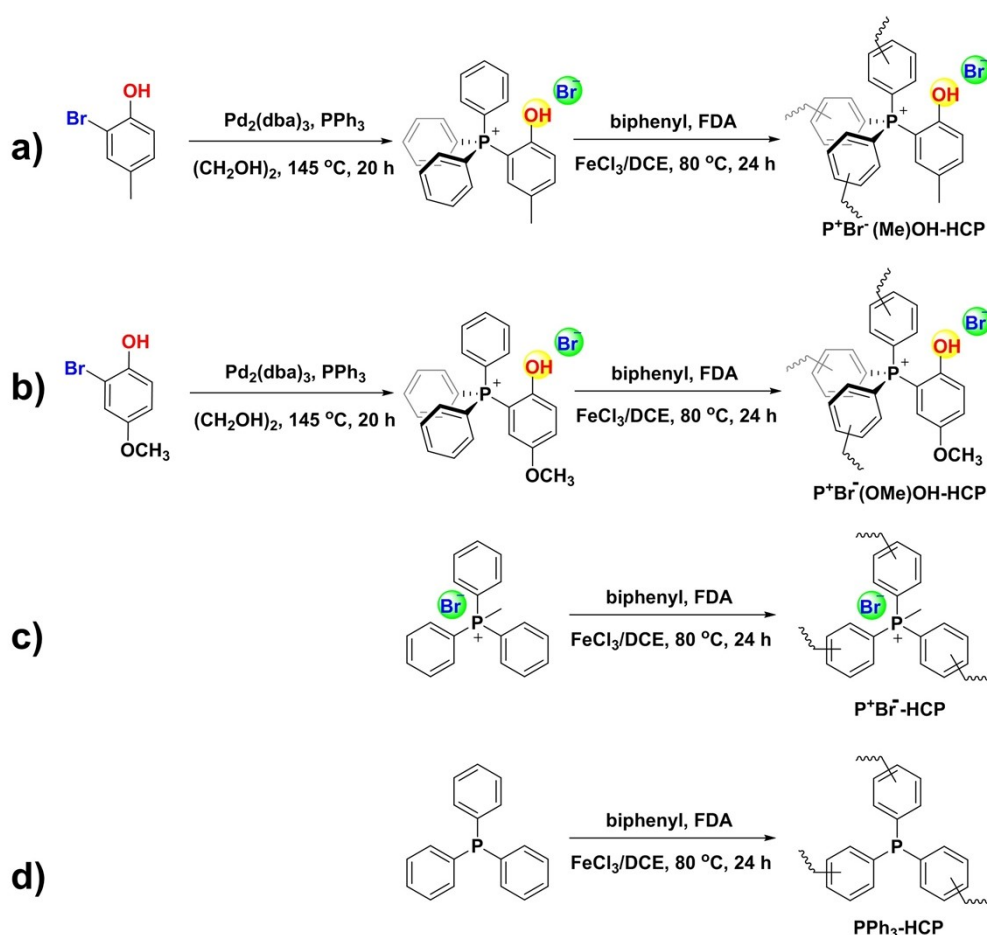


Fig. S1 Schematic illustration for synthesis of various catalysts.

#### Synthesis of $\text{P}^*\text{Br}^-(\text{Me})\text{OH-HCP}$ (Fig. S1a)

**Step 1  $\text{P}^*\text{Br}^-(\text{Me})\text{OH}$ :** Typically, under the argon atmosphere, 1.07 g 2-bromo-4-methylphenol (5.72 mmol), 2.26 g triphenylphosphine (8.58 mmol), 52.2 mg  $\text{Pd}_2(\text{dba})_3$  (57.2  $\mu\text{mol}$ ), 1.9 mL ethylene glycol were added to the 25 mL Schlenk reaction tube, then the mixture was stirred and heated to 145 °C for 20 h. After cooling and adding with a certain amount of deionized water, the solution was careful extracted with  $\text{CH}_2\text{Cl}_2$ ,

washed with deionized water, dried with anhydrous sodium sulfate, and removed the eluent by rotary evaporation. The (2-hydroxy-5-methylphenyl)triphenylphosphonium bromide (P<sup>+</sup>Br(Me)OH) was purified by column chromatography using CH<sub>2</sub>Cl<sub>2</sub>/MeOH (10/1, v/v) as an eluent to give 88% yield (1.91 g).

(2-hydroxy-5-methylphenyl)triphenylphosphonium bromide: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) = 7.79-7.51 (m, 16H), 7.33 (d, J = 8.7 Hz, 1H), 6.53 (dd, J = 14.9, 2.1 Hz, 1H), 2.11 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) = 160.4, 138.7, 134.5, 134.0, 133.8, 130.0, 119.6, 119.2, 118.8, 101.8, 101.0, 20.6; <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) = 22.04. HRMS (ESI) calcd for C<sub>25</sub>H<sub>22</sub>OP [M-Br]<sup>+</sup> 369.1403, found 369.1397.

**Step 2 P<sup>+</sup>Br(Me)OH-HCP:** Subsequently, under the argon atmosphere, 449 mg as-obtained (2-hydroxy-5-methylphenyl)triphenylphosphonium bromide, 77 mg biphenyl (0.5 mmol), 1.3 g iron(III) chloride anhydrous (8 mmol), 609 mg dimethoxymethane (FDA, 8 mmol), 10 mL 1,2-dichloroethane were added to the 25 mL Schlenk reaction tube, then the mixture was stirred and heated to 80 °C for 24 h, and the solution was cooled to room temperature naturally. After cooling down to room temperature, the solution was filtered and washed with DMF, H<sub>2</sub>O, MeOH, THF, CH<sub>2</sub>Cl<sub>2</sub>, respectively, giving the yellowish-brown crude product. Then, the material was further purified by Soxhlet extractions for 24 h using methanol. After drying in vacuum oven for 24 h at 80 °C, the P<sup>+</sup>Br(Me)OH-HCP material was obtained (0.42 g).

P<sup>+</sup>Br(Me)OH-HCP Elemental analysis: C: 72.76%, H: 5.37%, O: 2.59%, and Br: 1.52 mmol/g.

#### Synthesis of P<sup>+</sup>Br(OMe)OH-HCP (Fig. S1b)

Similarly, P<sup>+</sup>Br(OMe)OH-HCP was synthesized with the same step 1 and step 2 procedure of P<sup>+</sup>Br(Me)OH-HCP and used the 2-bromo-4-methoxyphenol instead, give 61% yield (1.21 g) of (2-hydroxy-5-methoxyphenyl)triphenylphosphonium bromide and 0.29 g of P<sup>+</sup>Br(OMe)OH-HCP.

(2-hydroxy-5-methoxyphenyl)triphenylphosphonium bromide: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) = 7.76-7.72 (m, 4H), 7.62-7.56 (m, 12H), 7.14 (dd, J = 9.3, 3.0 Hz, 1H), 6.27 (dd, J = 15.6, 3.1 Hz, 1H), 3.58 (s, 3H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) = 157.4, 152.5, 134.5, 134.0, 133.0, 124.0, 120.6, 119.6, 119.2, 118.8, 118.5, 102.1, 101.4, 55.9; <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, 25 °C) δ (ppm) = 22.23. HRMS (ESI) calcd for C<sub>25</sub>H<sub>22</sub>O<sub>2</sub>P [M-Br]<sup>+</sup> 385.1352, found 385.1371.

P<sup>+</sup>Br(OMe)OH-HCP Elemental analysis: C: 70.45%, H: 5.12%, O: 5.05%, and Br: 1.46 mmol/g.

#### Synthesis of P<sup>+</sup>Br-HCP (Fig. S1c)

Similarly, P<sup>+</sup>Br-HCP was synthesized with the same step 2 procedure of P<sup>+</sup>Br(Me)OH-HCP and used the methyltriphenylphosphonium bromide instead, give 0.98 g of P<sup>+</sup>Br-HCP.

P<sup>+</sup>Br(OMe)OH-HCP Elemental analysis: C: 72.54%, H: 5.43%, O: 5.05%, and Br: 1.42 mmol/g.

#### Synthesis of PPh<sub>3</sub>-HCP (Fig. S1d)

Similarly, PPh<sub>3</sub>-HCP was synthesized with the same step 2 procedure of P<sup>+</sup>Br(Me)OH-HCP and used the triphenylphosphine instead, give 0.29 g of PPh<sub>3</sub>-HCP.

PPh<sub>3</sub>-HCP Elemental analysis: C: 83.36%, H: 6.01%.

## Characterization

The powder X-ray diffraction (XRD) and Elemental analysis (EA) were performed on Bruker D8 Advanced diffractometer and Vario EL cube instrument, respectively. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB 250 X-ray photoelectron system. The nitrogen adsorption and desorption isotherms were obtained with a N<sub>2</sub> Micromeritic ASAP2020M at 77 K, and isotherms of carbon dioxide were collected at 273 K and 298 K. Transmission electron microscopy (TEM) images and scanning transmission electron microscopy (STEM) images were obtained on FEI Tecnai G2 F30 equipped with high-angle annular dark field (HAADF) with an accelerating voltage of 300 kV. Thermogravimetry was carried out in a NETZSCH TG 209 F3 Tarsus instrument under the N<sub>2</sub> atmosphere. Liquid <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR data were collected on a Bruker Varian INOVA500NB spectrometer. The solid-state <sup>13</sup>C and <sup>31</sup>P NMR spectrum was recorded on Bruker AVANCE 400 spectrometer. Gas chromatographic (GC) analysis was performed on a Shimadzu GC2010 equipped with a flame ionization detection.

## Cycloaddition of CO<sub>2</sub> and epoxide

Taking glycidyl methacrylate (GMA) as an example, 2.0 mmol GMA substrate, 1.0 mol% P<sup>+</sup>Br(Me)OH-HCP catalyst, and 0.1 mmol biphenyl (as internal standard) were in turn added to the 10 mL stainless autoclave reactor, then the reaction system was sealed and purged with high-pure CO<sub>2</sub> for three times, followed by adjusted to 1.0 MPa as an initial pressure. Subsequently, the autoclave was put into a preheated oil bath and the mixture was stirred at 80 °C for 24 h. After cooling to 0 °C and slowly venting the excess CO<sub>2</sub>, the reaction mixture was diluted with ethyl acetate and the catalyst was removed by filtration. The filtrate was analyzed by gas chromatography to determine the product yield, and the recycled catalyst was collected, washed, dried, and then directly charged into the next cycle.

## 2. Supplementary Figures and Tables

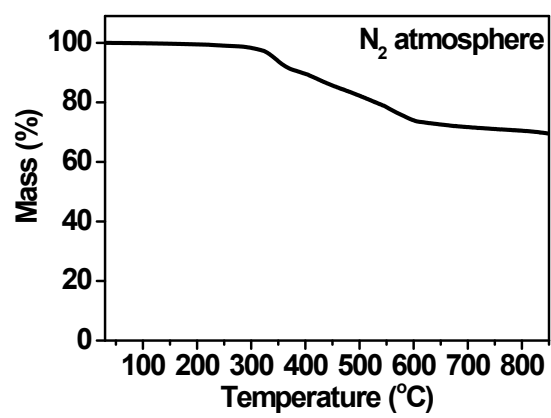


Fig. S2 Thermogravimetry curve of P+Br(Me)OH-HCP under the N<sub>2</sub> atmosphere.

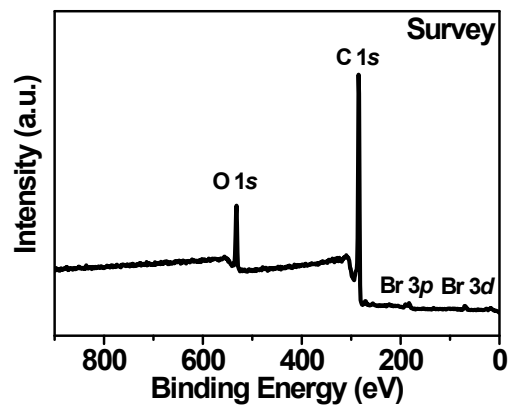


Fig. S3 Survey XPS spectrum of P<sup>+</sup>Br(Me)OH-HCP.

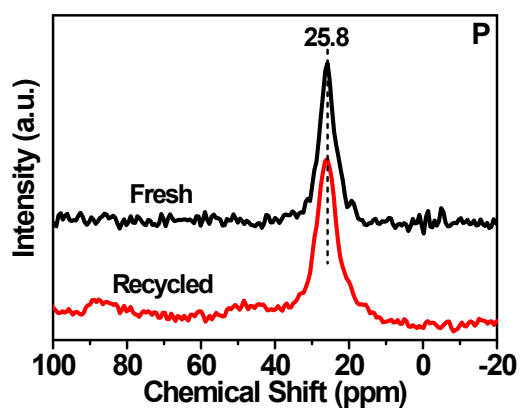


Fig. S4 Solid-state  $^{31}\text{P}$  NMR spectrum of the fresh and recycled  $\text{P}^+\text{Br}(\text{Me})\text{OH-HCP}$ .

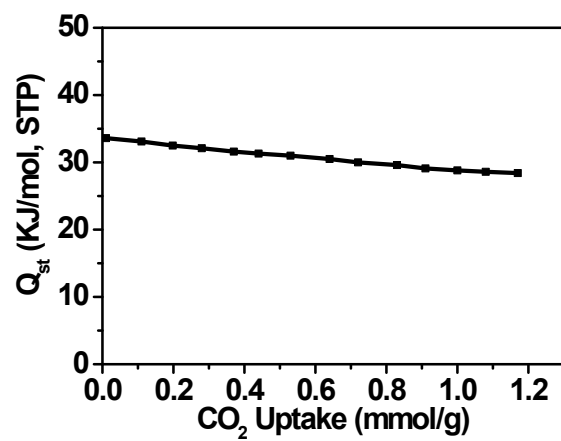
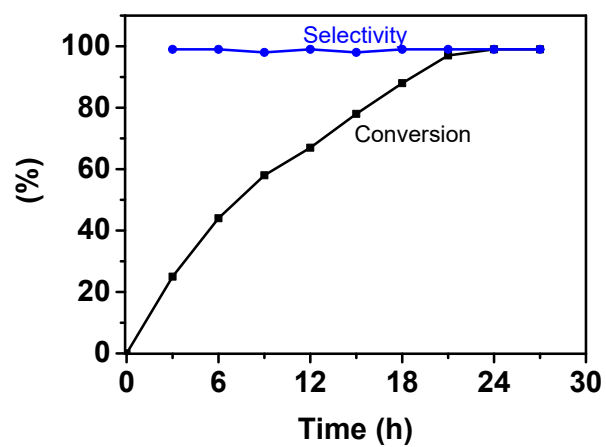
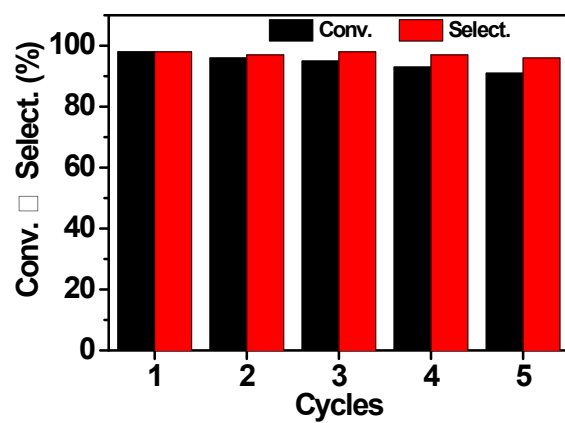


Fig. S5 Isosteric heat of  $CO_2$  adsorption of the P<sup>+</sup>Br(Me)OH-HCP.





**Fig. S6** Kinetic curves of the P<sup>+</sup>Br(Me)OH-HCP for the cycloaddition of CO<sub>2</sub> with GMA. Reaction conditions: substrate (2.0 mmol), catalyst (1.0 mol%), initial CO<sub>2</sub> pressure 1.0 MPa, 80 °C.



**Fig. S7** Catalytic reusability of the P<sup>+</sup>Br(Me)OH-HCP for the cycloaddition of CO<sub>2</sub> with GMA. Reaction conditions: substrate (2.0 mmol), catalyst (1.0 mol%), diluted CO<sub>2</sub> (15 % CO<sub>2</sub> in N<sub>2</sub>, v/v), initial CO<sub>2</sub> pressure 3.0 MPa, 80 °C, 36

h.

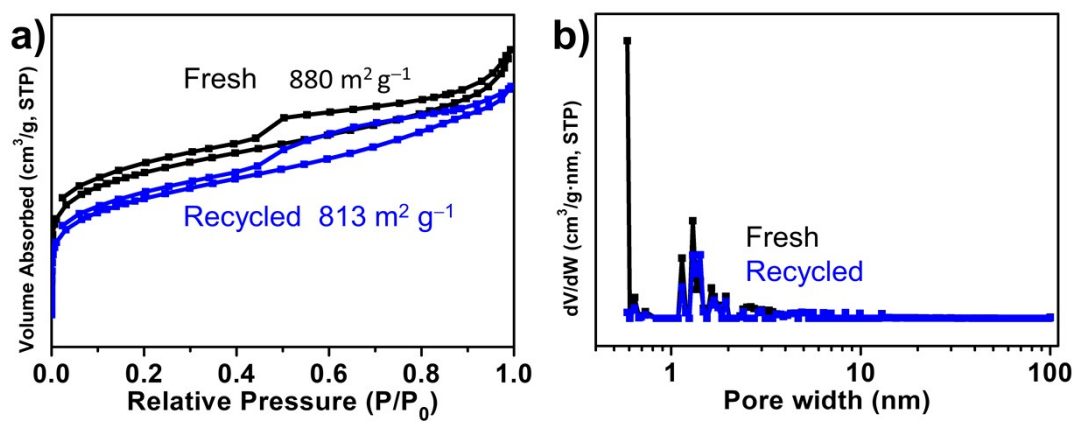
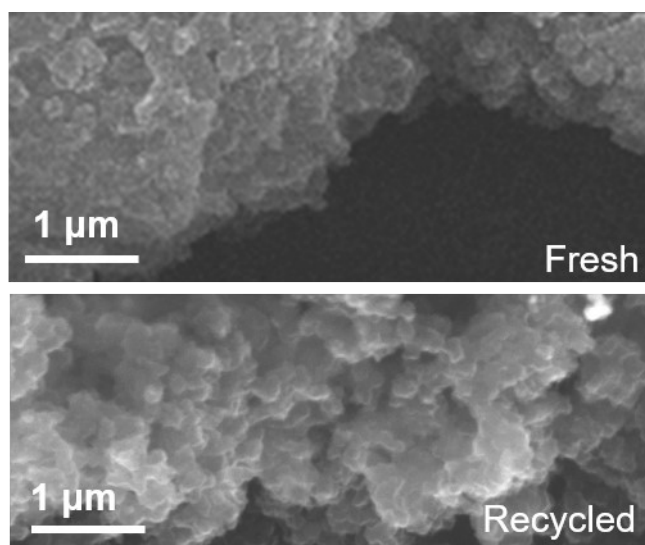


Fig. S8 N<sub>2</sub>-sorption isotherms measured at 77 K of the fresh and recycled P<sup>+</sup>Br(Me)OH-HCP.



**Fig. S9** SEM image of the fresh and recycled P<sup>+</sup>Br(Me)OH-HCP.

**Table S1** Activity comparison in the propylene oxide to propylene carbonate conversion reaction

Catalyst	Additive (mol%)	Solvent	T (°C)	CO <sub>2</sub> (MPa)	t (h)	Yield (%)	Ref.
P <sup>+</sup> Br <sup>-</sup> (Me)OH-HCP	- <sup>a</sup>	-	80	1.0	24	99	This work
IM-iPHP-2	-	-	80	0.1	48	96	Chem. Eng. J., 2020, 381, 122765
ILA@U6N	-	-	80	1.2	4	94	ChemSusChem, 2019, 12,1033–104
SYSU-Zn@IL2	-	-	80	1.0	12	99	ACS Sustain. Chem. Eng., 2018, 6, 1074–1082
PDBA-Cl-SCD	-	-	90	0.1	6	99	J. Mater. Chem. A, 2017, 5, 25594–25600
TBB-Bpy-a	-	-	90	1.0	12	99	ACS Appl. Mater. Interfaces, 2017, 9, 7209–7216
P(DMAEMA-EtOH)Br	-	-	110	2.0	3	96	Green Chem., 2019, 21, 2352–2361
Mg-por/pho@POP	-	-	140	3.0	1	78	ACS Sustain. Chem. Eng., 2017, 5, 4523–4528
Py-Zn@MA	-	-	150	2.0	6	96	Chem. Asian J., 2017, 12, 1095–1103
POM3-IM	-	EtOH	120	1.0	8	96	Chem. Commun., 2015, 51, 12076–12079.
HIP-Br-2	ZnBr <sub>2</sub>	DMF	25	0.1	96	99	Green Chem., 2017, 19, 2675–2686
SH4-Al(Cl)	[C <sub>1</sub> C <sub>6</sub> Im][HCO <sub>3</sub> ]	-	25	1.0	24	99	Green Chem.,2020, 22,4509–4515
Cu-MOF	TBAB	-	25	0.1	48	96	J. Am. Chem. Soc., 2016, 138, 2142–2145
Cu/POP-Bpy	TBAB	-	29	0.1	48	99	ChemSusChem, 2017, 10, 1186–1192
PMO-CPF-20	TBAI	-	90	2.0	6	99	Chem. Eng. J., 2021, 418, 129360

<sup>a</sup> Not added additive or solvent.