

Electronic supplementary information

**Redefining Friedel-Crafts Porous Polymers: Complex
Architecture from a Multifaceted Linker and
Consequent Engineering into Cation Exchanger**

Yanzhe Shi, Zheng Bian,^{*} Wenbo Lu, Jikuan Qiu,^{*} and Guangshan Zhu^{*}

Table S1. The elemental analyses, C-O/C=O contents and specific surface areas of the POPs

Sample ^a	C ^b wt%	H ^b wt%	Al ^b wt%	Cl ^b wt%	O ^b wt%	Yield ^c	C-O ^d mmol g ⁻¹	C=O ^e mmol g ⁻¹	S _{BET} ^f m ² g ⁻¹
P-BP-25	92.24	4.98	0.29	0.25	1.80	72%	1.0	0.1	0.85
P-BP-50	88.23	4.93	0.19	3.54	4.61	128%	1.9	1.0	589
P-BP-75	84.31	3.14	0.18	2.82	11.77	156%	3.8	3.6	1694
P-BP-100	83.00	3.17	0.33	2.05	12.69	171%	4.2	3.7	1799
P-BP-125	82.89	3.72	0.08	2.72	9.36	169%	3.0	2.9	1717
P-BZ-100	81.38	3.41	0.16	3.90	10.79	150%	3.9	2.8	1222
P-ANT-100	79.53	3.43	0.29	4.13	9.81	161%	3.3	2.8	1301
P-NAP-100	81.26	3.35	0.09	3.46	9.07	165%	2.8	2.8	1302
P-PTP-100	82.16	3.45	0.16	5.23	9.57	155%	4.1	1.9	1806
P-TPB-100	81.35	3.37	0.10	6.86	12.66	150%	5.5	2.4	1887

^aThe letter “P” denotes the polymer. BP, BZ, ANT, NAP, PTP and TPB denote the reaction substrates.

The numbers 25, 50, 75, 100 and 125 denote the reaction temperatures (°C). ^bBy elemental analysis.

^cThe yields of the POPs are calculated based on the starting aromatic substrates only, crosslinkers were not included. ^dBy high resolution XPS O 1s peaks, alcohol species. ^eBy high resolution XPS O 1s peaks, aldehyde/ketone species. ^fBy nitrogen adsorption/desorption isotherms at 77 K.

Table S2. The O content of P-BP-100 samples prepared at different AlCl₃-to-BP molar ratios

BP/AlCl ₃ (mol/mol)	1/1	1/3	1/5
O content (wt%)	5.90	12.69	11.22

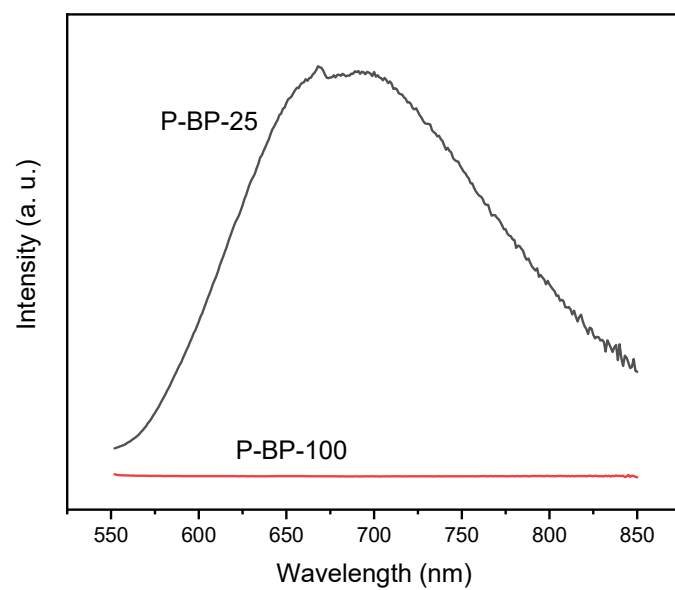


Fig. S1 Emission spectra of P-BP-25 (black) and P-BP-100 (red) in solid. Excitation wavelength, $\lambda_{\text{ex}} = 532$ nm.

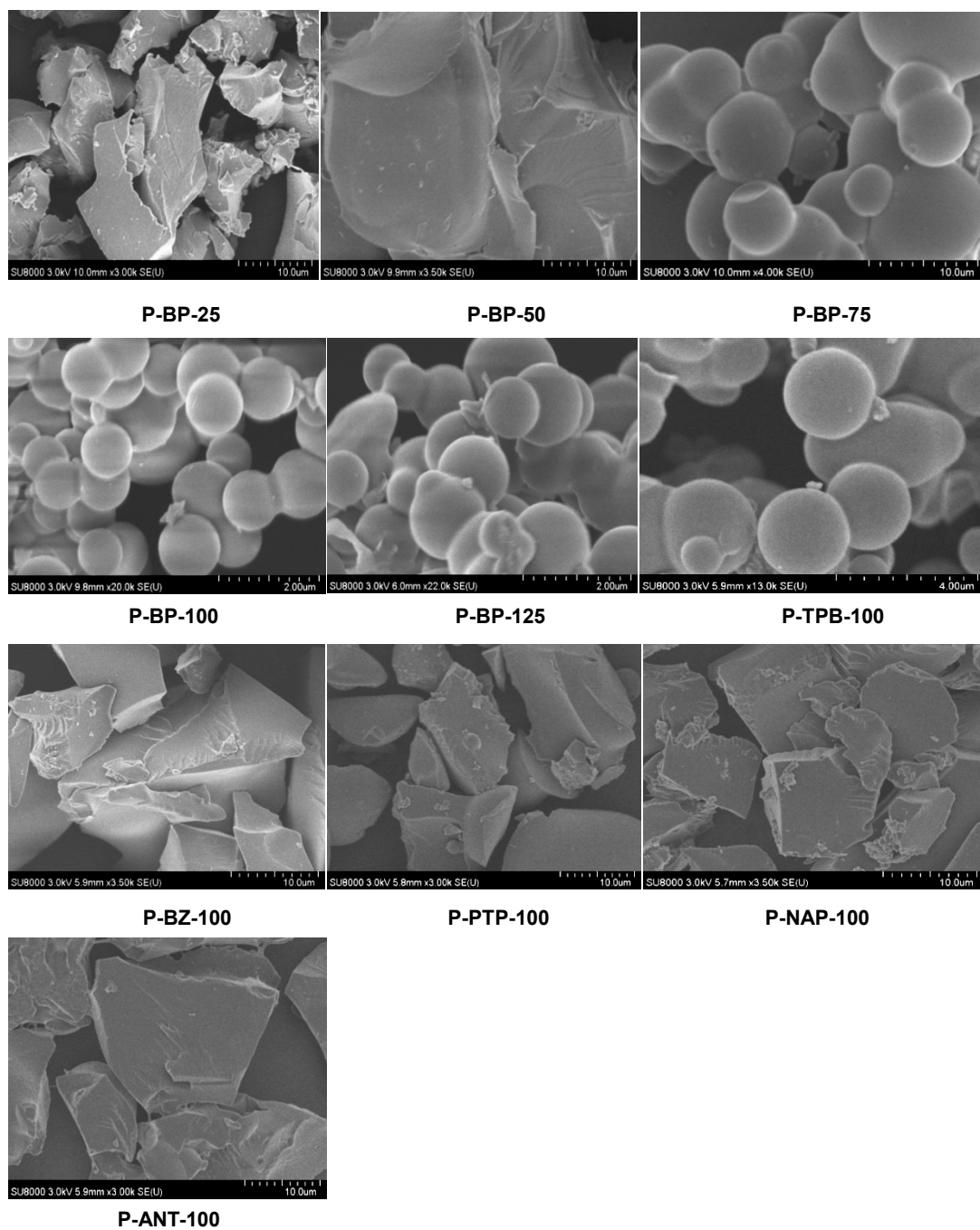


Fig. S2 Scanning electron microscopy images of the POPs

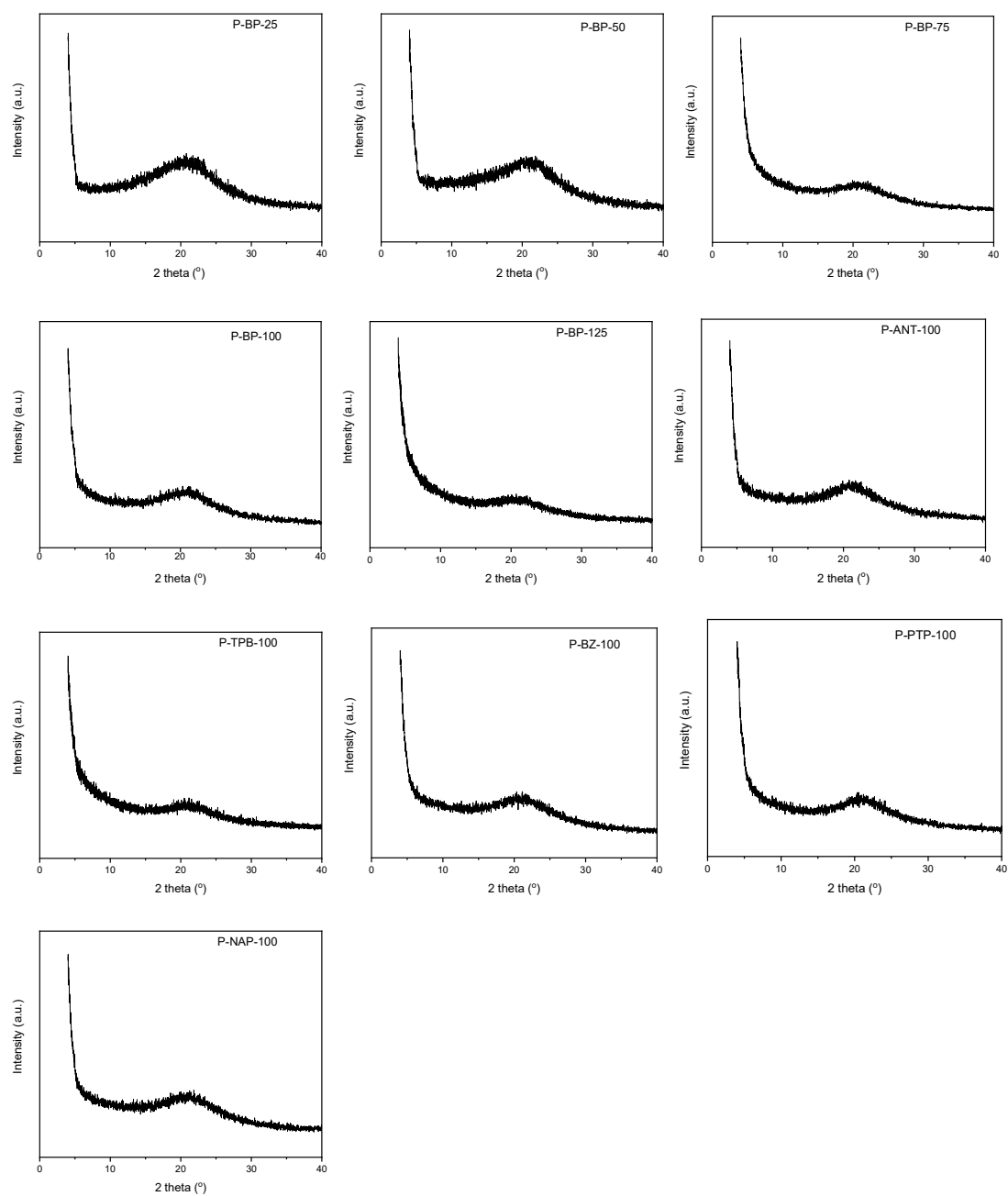


Fig. S3 The powder X-ray diffraction patterns of the POPs

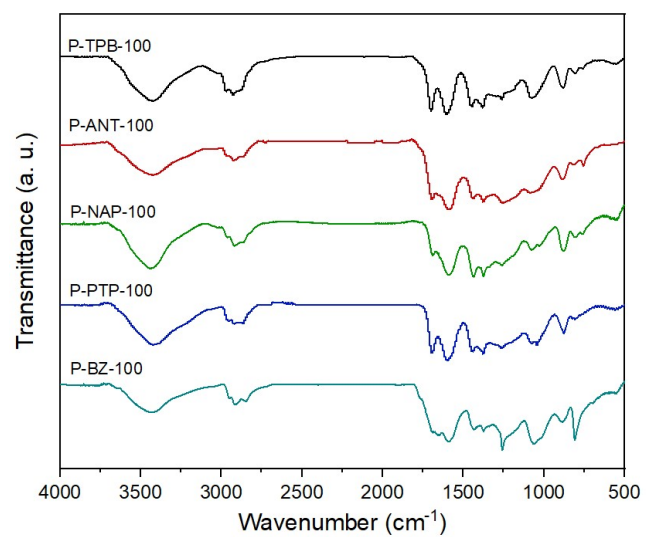


Fig. S4 FTIR spectra of the polymers P-TPB-100, P-ANT-100, P-NAP-100, P-PTP and P-BZ-100.

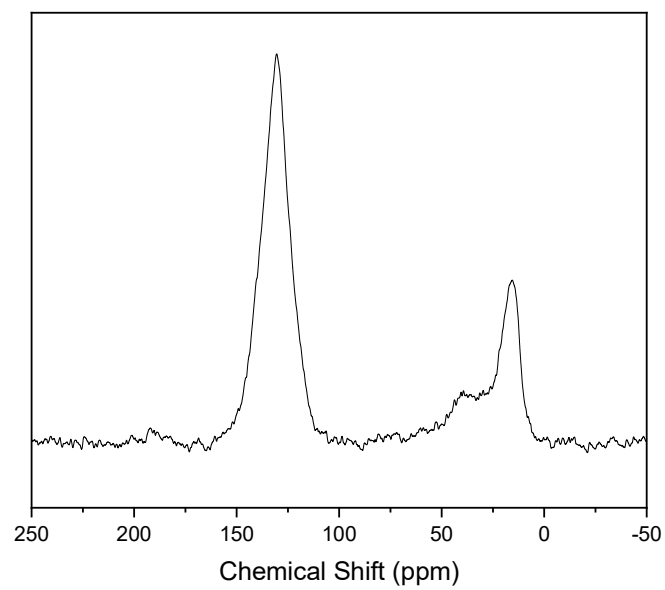


Fig. S5 Solid-state ^{13}C CP/MAS NMR spectrum of the polymer P-TOL-100

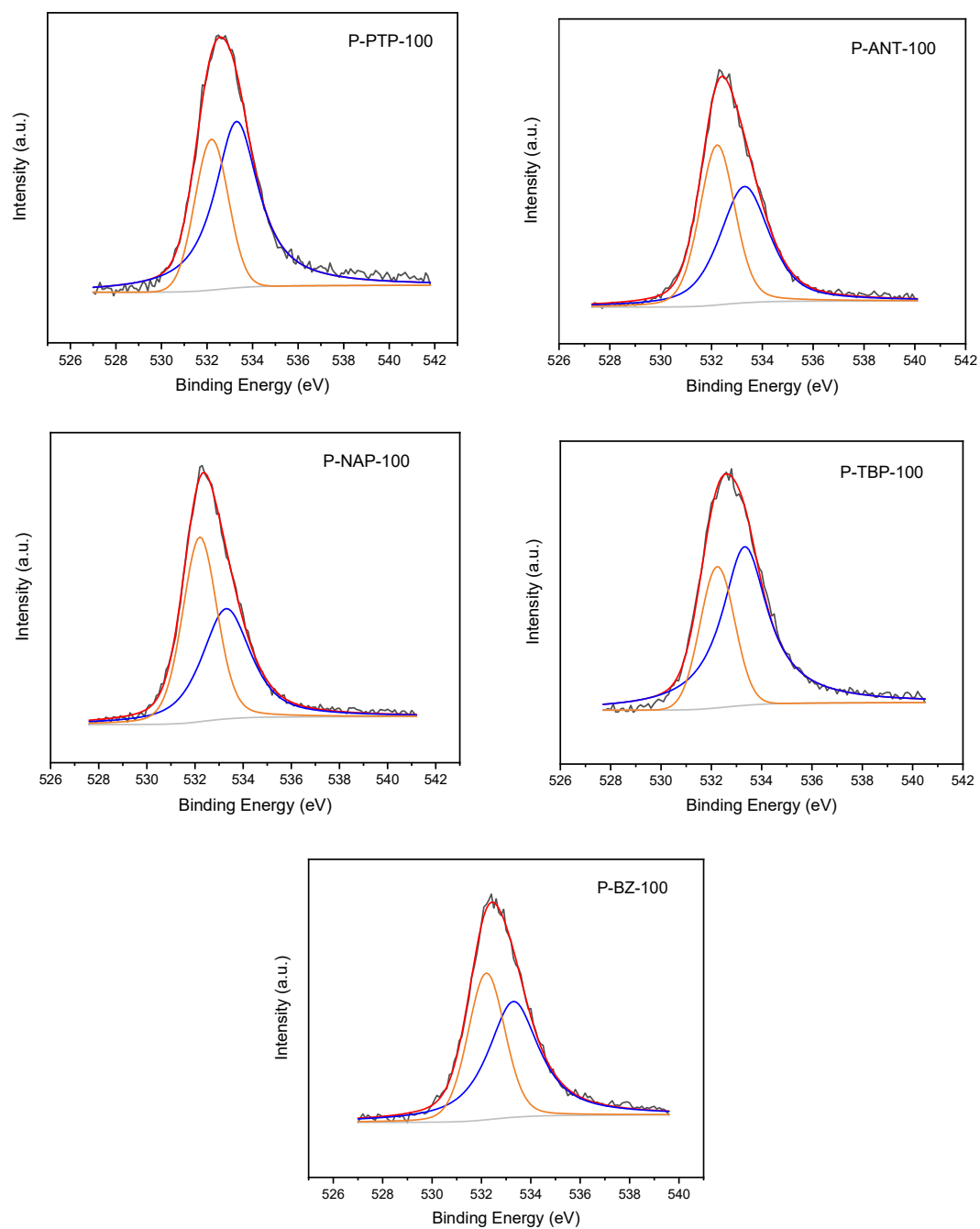
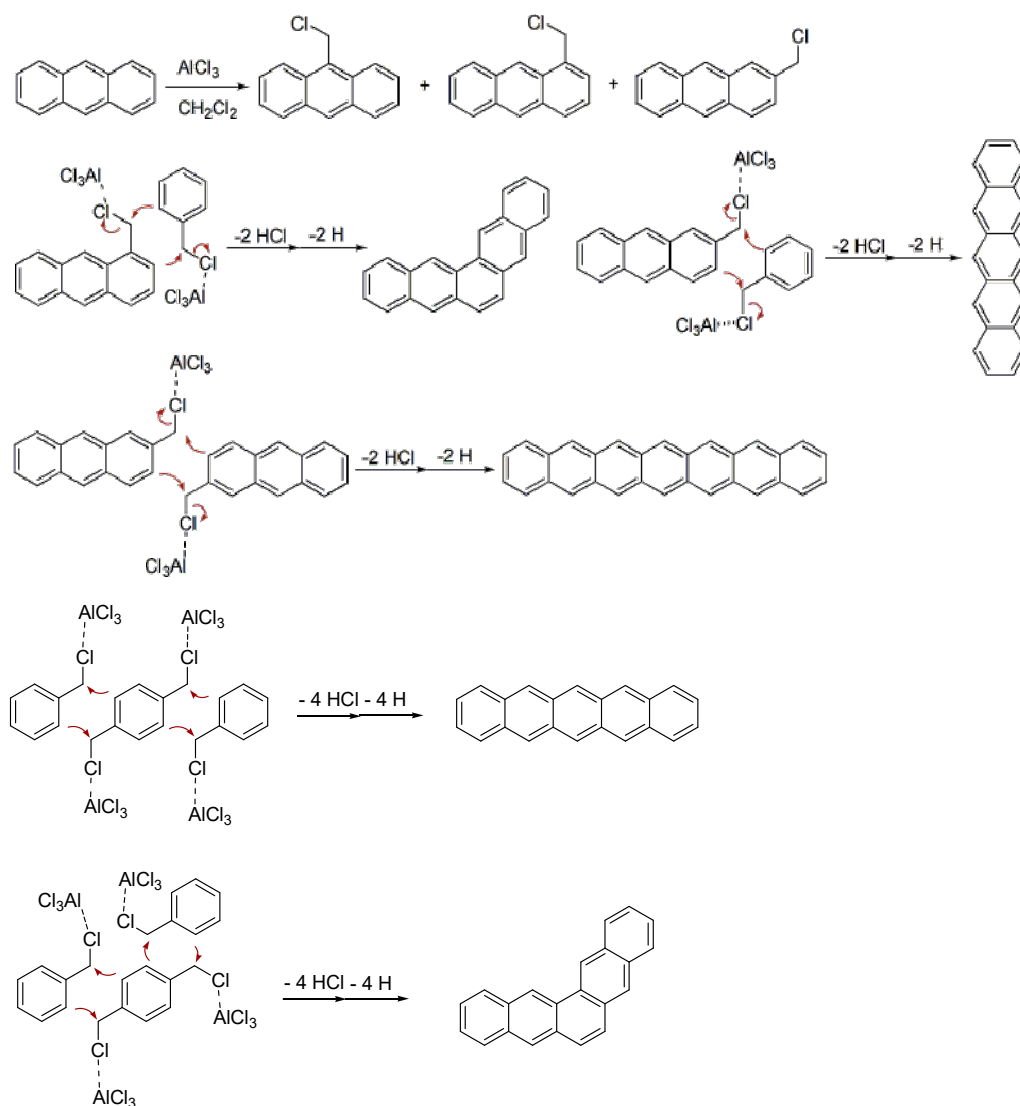


Fig. S6 The XPS O 1s peaks of the POPs and the peak differentiation imitating analyses



Scheme S1 The postulated deep aromatization based on Friedel-Crafts alkylation under the activation of AlCl_3 (Taking benzene as the model substrate).

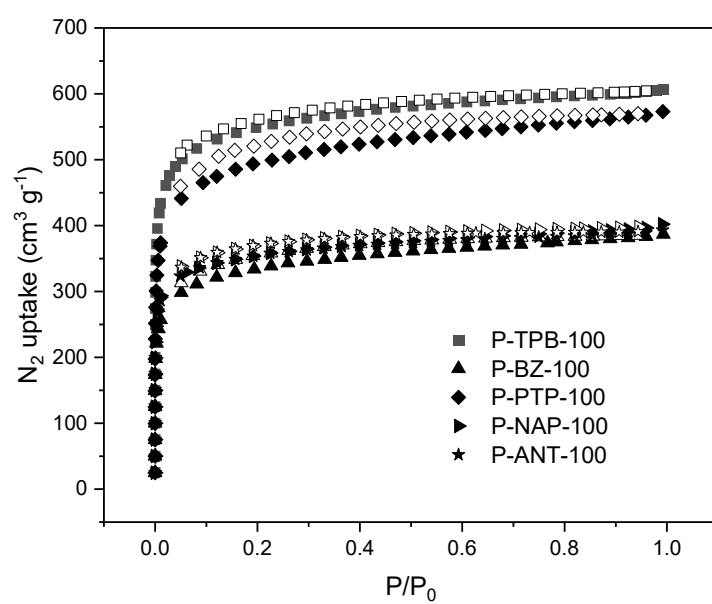


Fig. S7 The nitrogen adsorption (solid) and desorption (hollow) isotherms of the POPs at 77 K

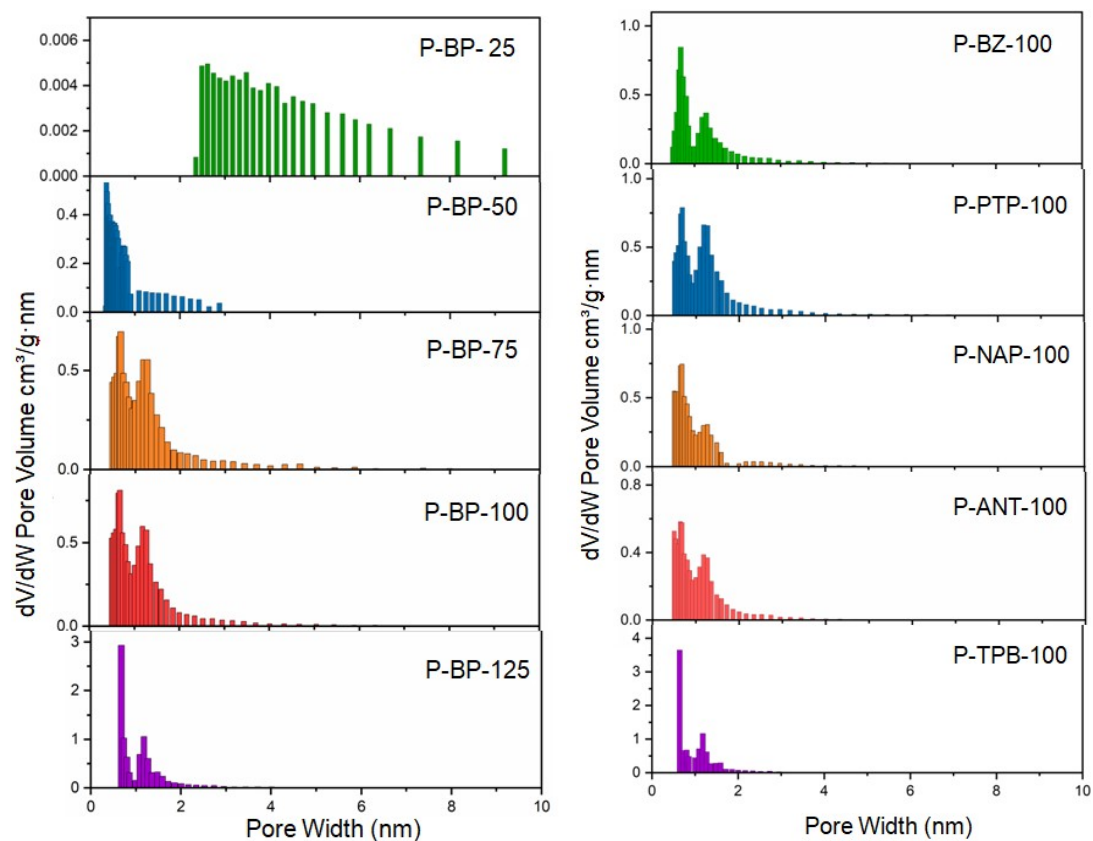


Fig. S8 The pore size distribution of the POPs

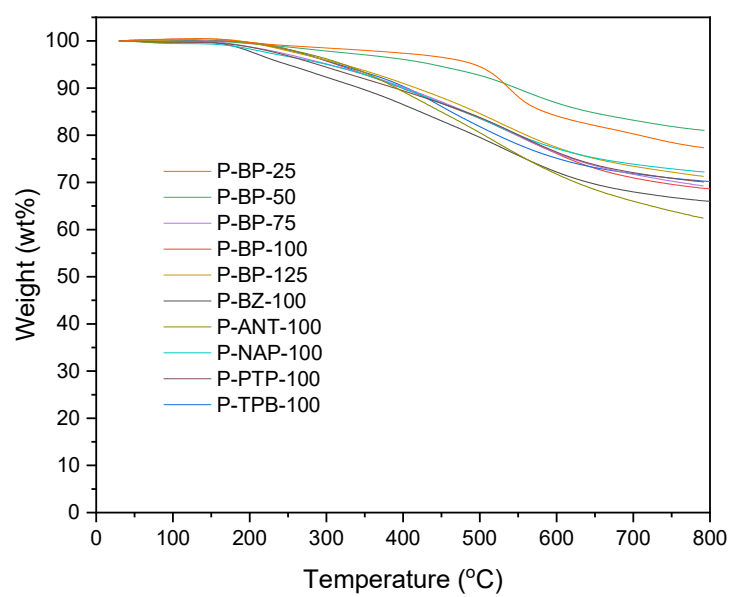


Fig. S9 Thermo-gravimetric curves of the POPs under nitrogen atmosphere

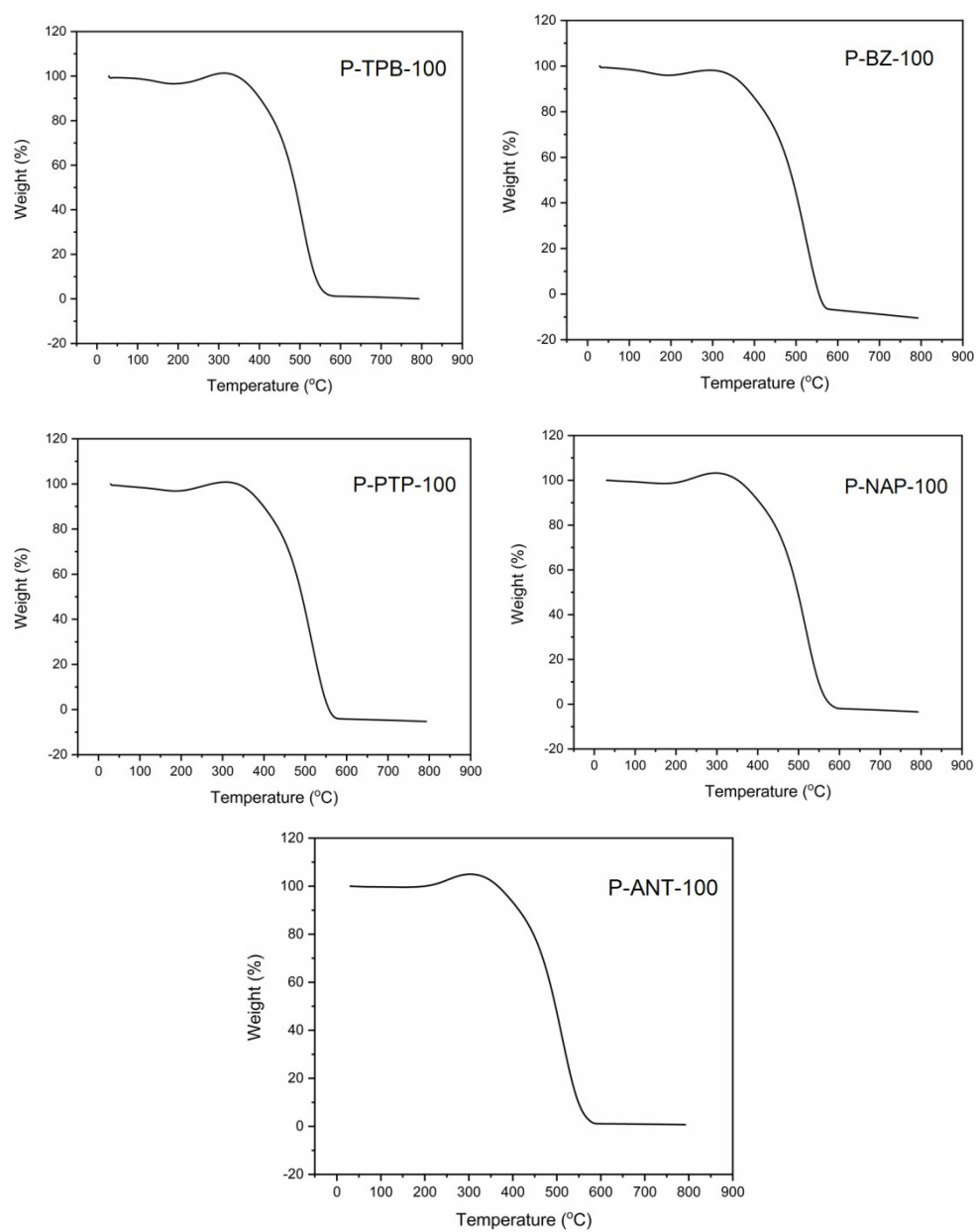


Fig. S10 The TG curves of the POPs under air atmosphere.

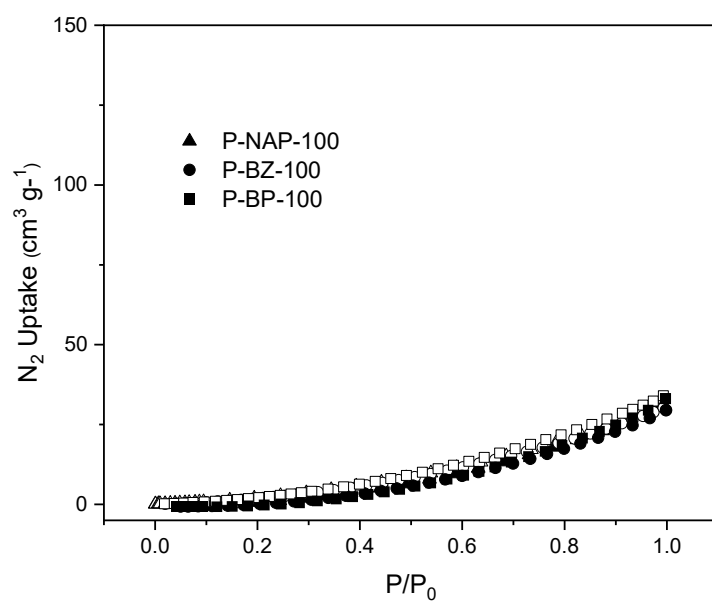


Fig. S11 The nitrogen adsorption (solid) and desorption (hollow) isotherm of P-BP-100-[O], P-BZ-100-[O] and P-NAP-100-[O] at 77 K

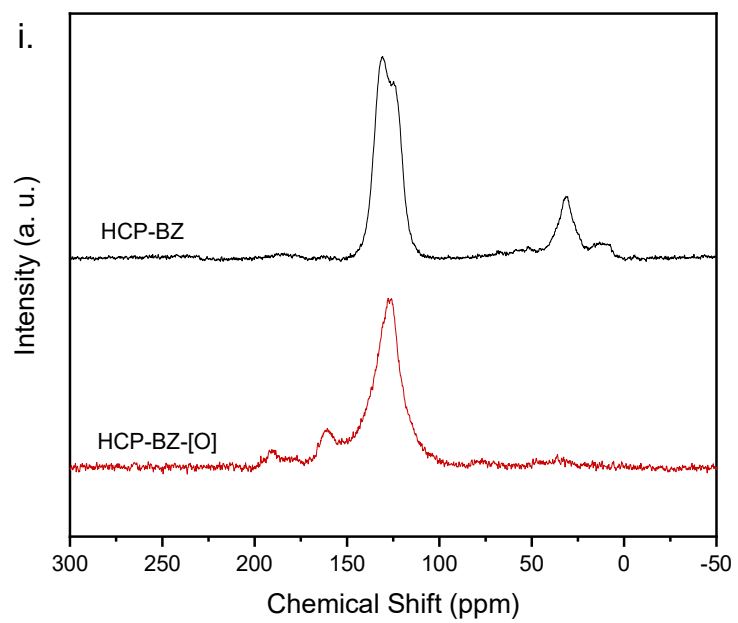


Fig. S12 Solid-state ^{13}C CP/MAS NMR spectra of HCP-BZ and HCP-BZ-[O]

The cost accounting of the oxidized products

The feedstock costs of P-BZ-100-[O], P-NAP-100-[O] and P-BP-100-[O] are evaluated according to the current prices of bulk commodities (benzene, \$1007 per ton; naphthalene, \$1048 per ton; biphenyl, \$2317 per ton; anhydrous AlCl_3 , \$772 per ton; CH_2Cl_2 , \$346 per ton; 31 wt% conc. HCl, \$35 per ton). It takes about 0.8 Kg of biphenyl/benzene/naphthalene, 2.13 Kg of AlCl_3 , 10 Kg of CH_2Cl_2 , and 10 Kg of conc. HCl to prepare one kg of P-BP-100-[O]/P-NAP-100-[O]/P-BZ-100-[O]. So the feedstock costs of P-BP-100-[O], P-NAP-100-[O] and P-BZ-100-[O] are about \$7.3 per Kg, \$6.3 per Kg and \$6.3 per Kg, respectively.