Supporting Information

Atom-economical Preparation of Polybismaleimide-based Microporous Organic Polymers

Tingting Zhu[a], Qi Yu[a], Lei Ding[a], Tuo Di[a], Tiansheng Zhao[b], Tiesheng Li[c] and Lei Li*[a]

a College of Materials and Fujian Provincial Key Laboratory of Materials Genome, Xiamen University, Xiamen, 361005, P.R. China
b State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, Ningxia University, Yinchuan, 750021, P.R. China
c College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, 450001, P.R. China.

E-mail: lilei@xmu.edu.cn

Tel: +86-592-2186296 Fax: +86-592-2183937

Table S1 Overview of the polymerization conditions.

Samples	BMI monomers			DPS (g)	Polymerization conditions
	BDM (g)	BMP (g)	*m*-PDM (g)		
PBDM-2-280-1	0.300	-	-	0.600	280 °C, 1 h
PBDM-2-280-2	0.300	-	-	0.600	280 °C, 2 h
PBDM-2-280-4	0.300	-	-	0.600	280 °C, 4 h
PBDM-0-280-6	0.300	-	-	-	280 °C, 6 h
PBDM-0.5-280-6	0.300	-	-	0.150	280 °C, 6 h
PBDM-1-280-6	0.300	-	-	0.300	280 °C, 6 h
PBDM-2-280-6	0.300	-	-	0.600	280 °C, 6 h
PBDM-3-280-6	0.300	-	-	0.900	280 °C, 6 h
PBDM-5-280-6	0.300	-	-	1.500	280 °C, 6 h
PBDM-10-280-6	0.300	-	-	3.000	280 °C, 6 h
PBDM-2-240-6	0.300	-	-	0.600	240 °C, 6 h
PBDM-2-340-6	0.300	-	-	0.600	340 °C, 6 h
PBMP-0-280-6	-	0.300	-	-	280 °C, 6 h
PBMP-0.5-280-6	-	0.300	-	0.150	280 °C, 6 h
PBMP-1-280-6	-	0.300	-	0.300	280 °C, 6 h
PBMP-2-280-6	-	0.300	-	0.600	280 °C, 6 h
PBMP-3-280-6	-	0.300	-	0.900	280 °C, 6 h
PBMP-5-280-6	-	0.300	-	1.500	280 °C, 6 h
PBMP-10-280-6	-	0.300	-	3.000	280 °C, 6 h
PBMP-2-240-6	-	0.300	-	0.600	240 °C, 6 h
PBMP-2-340-6	-	0.300	-	0.600	340 °C, 6 h
PPDM-0-280-6	-	-	0.300	-	280 °C, 6 h
PPDM-0.5-280-6	-	-	0.300	0.150	280 °C, 6 h
PPDM-1-280-6	-	-	0.300	0.300	280 °C, 6 h
PPDM-2-280-6	-	-	0.300	0.600	280 °C, 6 h
PPDM-3-280-6	-	-	0.300	0.900	280 °C, 6 h
PPDM-5-280-6	-	-	0.300	1.500	280 °C, 6 h
PPDM-10-280-6	-	-	0.300	3.000	280 °C, 6 h
PPDM-2-240-6	-	-	0.300	0.600	240 °C, 6 h
PPDM-2-340-6	-	-	0.300	0.600	340 °C, 6 h

Table S2 DSC data of pristine BDM and BDM/DPS mixtures.

Samples	T_m[a] (°C)	T_{ei}[b] (°C)	T_p[c] (°C)	ΔH[d] (J/g)
BDM	163	190	237	121.9
BDM-0.5	112	210	254	118.1
BDM-1	113	220	260	115.3
BDM-2	113	227	267	122.0
BDM-3	113	230	270	109.7
BDM-5	112	-	-	-
BDM-10	112	-	-	-

[a] Melting point. [b] Onset temperature for the polymerization reaction. [c] Exothermal peak temperature. [d] Reaction enthalpy. The reaction enthalpy is normalized by the mass of BDM.

Table S3 Elemental analysis of BMOPs.

Samples	Experimental (wt %)				Theoretical (wt %)			
	C	H	N	S	C	H	N	S
PBDM-2-280-6	67.59	3.68	7.67	1.30	70.39	3.91	7.82	0.00
PBMP-2-280-6	60.99	3.69	8.64	1.43	63.83	3.55	9.93	0.00
PPDM-2-280-6	60.38	3.67	9.63	1.23	62.63	2.98	10.44	0.00

Table S4 Elemental analysis of DPS and the extracts of the product.

Samples	Experimental (wt %)			Theoretical (wt %)		
	C	H	N	C	H	N
DPS	66.12	4.55	0	66.05	4.58	0
Extract of PBDM-2-280-6	65.70	4.60	0	-	-	-
Extract of PBMP-2-280-6	66.01	4.35	0	-	-	-
Extract of PPDM-2-280-6	66.13	4.52	0	-	-	-

Table S5 Cross-linking degree of BMOPs.

Samples	Degree of cross-linking (%)
PBDM-2-280-6	99.4
PBMP-2-280-6	99.5
PPDM-2-280-6	99.8

Table S6 Gas uptake and the CO_2/N_2 selectivity of BMOPs.

Samples	CO_2 uptake[a] (wt%)		CO_2 selectivity	H_2 uptake[b] (wt%)	CH_4 uptake[c] (mmol g^{-1})
	273 K	298 K	CO_2/N_2	77.3 K	273 K
PBDM-0.5-280-6	6.45	4.06	46.27	-	-
PBDM-1-280-6	11.97	7.60	41.33	-	-
PBDM-2-280-6	13.25	8.31	48.30	1.05	0.64
PBDM-3-280-6	11.62	7.45	52.60	0.93	0.59
PBDM-5-280-6	10.69	6.86	53.54	-	-
PBDM-10-280-6	12.27	8.03	50.56	-	-
PBMP-0.5-280-6	10.00	6.31	55.03	-	-
PBMP-1-280-6	9.80	6.09	56.07	-	-
PBMP-2-280-6	9.89	6.34	50.58	0.67	0.33
PBMP-3-280-6	9.90	6.19	54.09	0.64	0.36
PBMP-5-280-6	9.80	6.58	65.44	-	-
PBMP-10-280-6	10.12	7.03	58.91	-	-
PPDM-0.5-280-6	11.49	7.05	58.45	-	-
PPDM-1-280-6	11.76	7.25	54.80	-	-
PPDM-2-280-6	12.08	7.81	52.11	0.82	0.44
PPDM-3-280-6	12.34	7.91	51.40	0.88	0.45
PPDM-5-280-6	12.06	7.73	56.00	-	-
PPDM-10-280-6	11.43	7.47	56.31	-	-

[a] CO_2 uptake at 1.0 bar. [b] H_2 uptake at 1.13 bar. [c] CH_4 uptake at 1.13 bar.

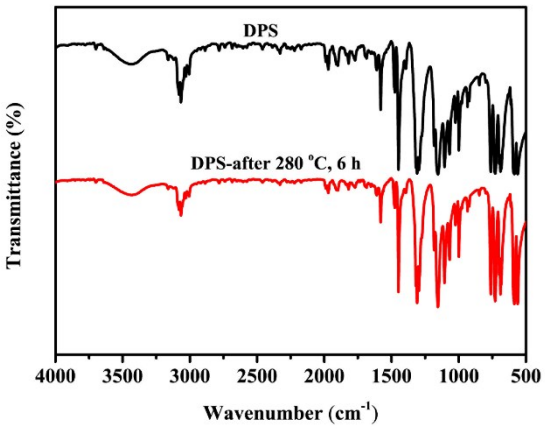

Figure S1. FTIR spectra of DPS before and after heating at 280 °C for 6 h.

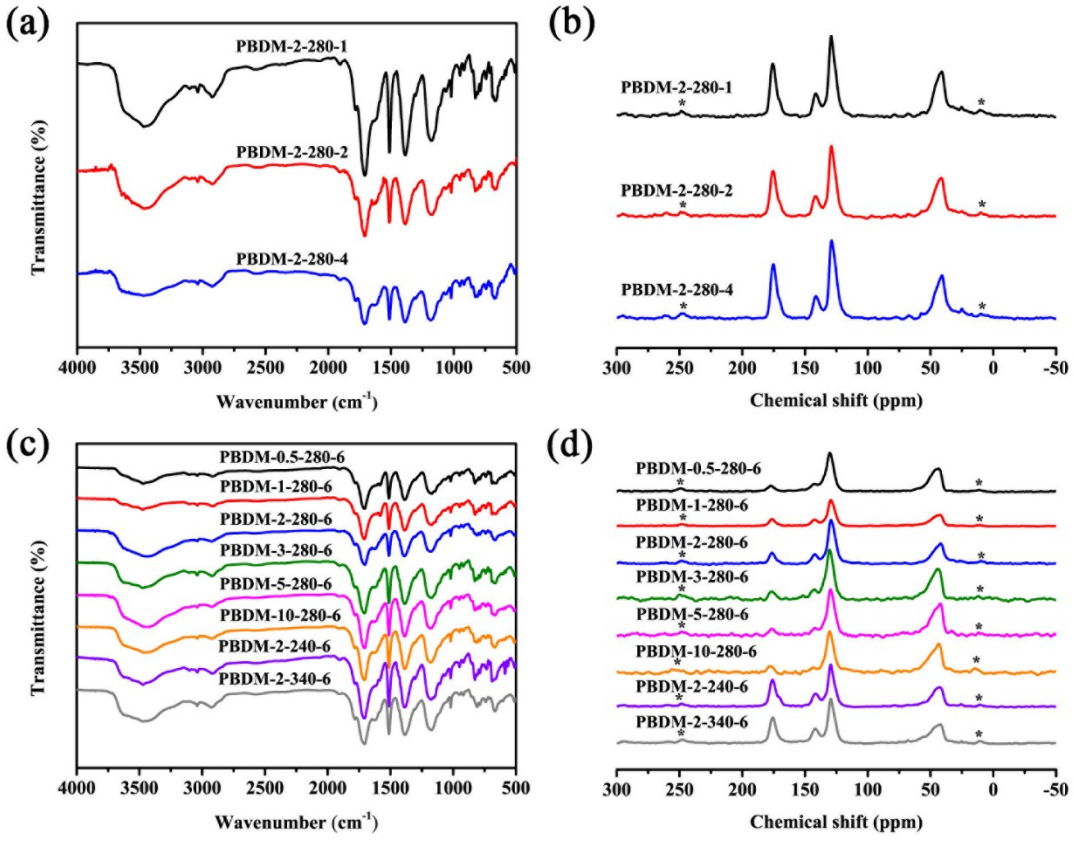

Figure S2. (a), (c) FTIR spectra of PBDMs. (b), (d) Solid state ^{13}C cross-polarization nuclear magic-angle spinning (CP/MAS) NMR spectra of PBDMs. Asterisks denote the spinning sidebands.

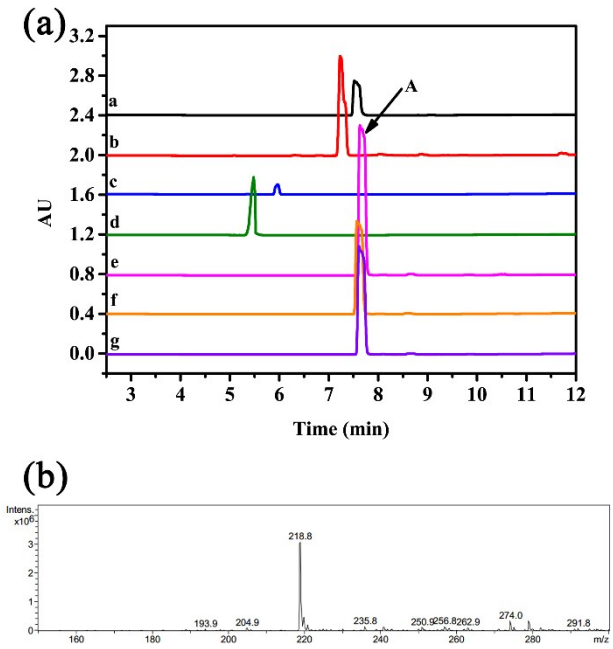

Figure S3. (a) UPLC chromatogram of samples (a: DPS; b: BDM; c: BMP; d: PDM; e: solution after extraction of PBDM-2-280-6; f: solution after extraction of PBMP-2-280-6; g: solution after extraction of PPDM-2-280-6). (b) ESI-MS spectrum of A, indicating the signal of DPS.

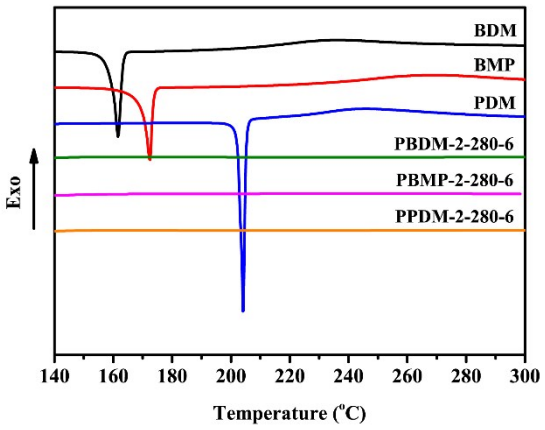

Figure S4. DSC curves of BMI monomers and BMOPs.

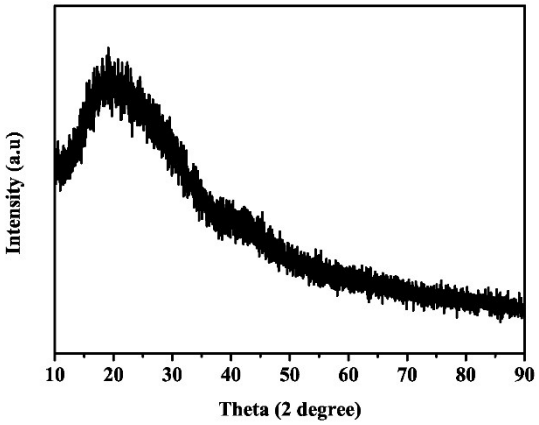

Figure S5. X-ray diffraction spectrum of PBDM-2-280-6.

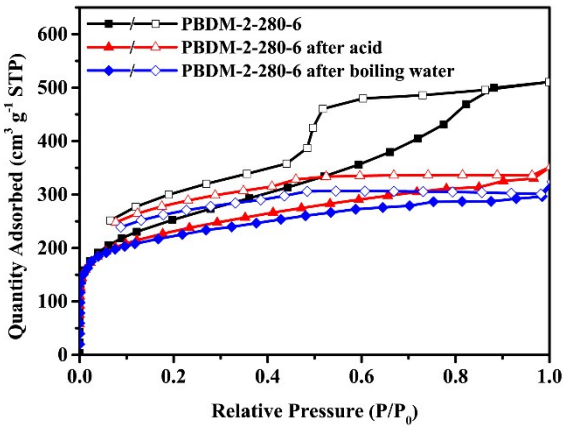

Figure S6. Nitrogen adsorption-desorption isotherms for PBDM-2-280-6 before and after being immersed in 1 M HCl and boiling water for 12 h.

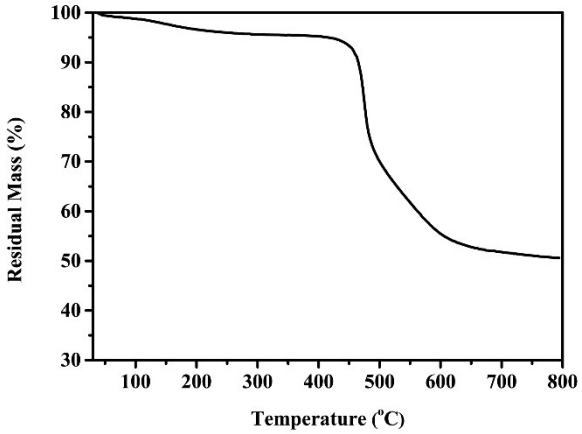

Figure S7. TGA curve of PBDM-2-280-6.

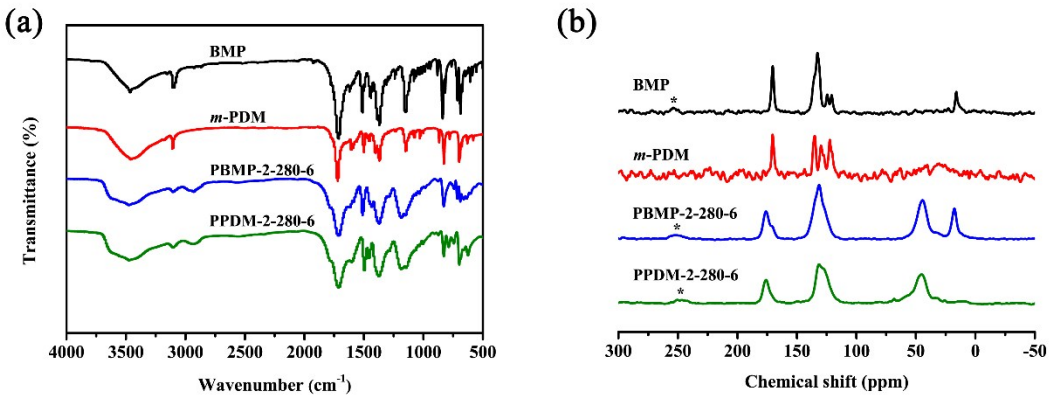

Figure S8. (a) FTIR spectra of BMP, m-PDM, PBDM-2-280-6 and PPDM-2-280-6. (b) Solid state ^{13}C cross-polarization nuclear magic-angle spinning (CP/MAS) NMR spectra of BMP, *m*-PDM, PBDM-2-280-6 and PPDM-2-280-6. Asterisks denote the spinning sidebands.

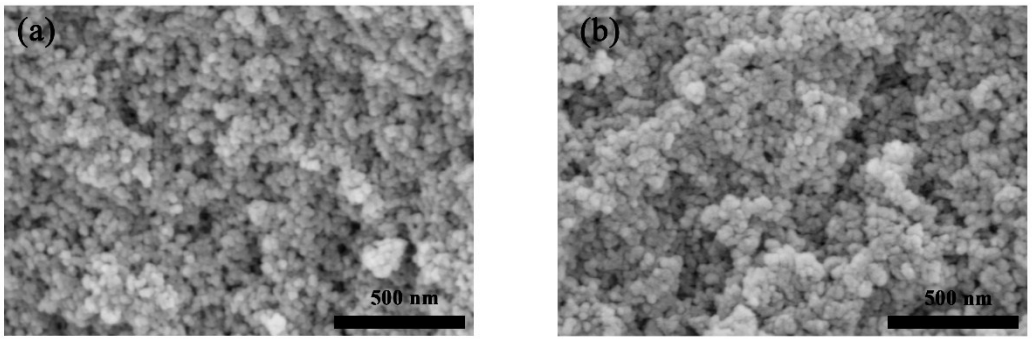

Figure S9. SEM images of PBMP-2-280-6 and PPDM-2-280-6.

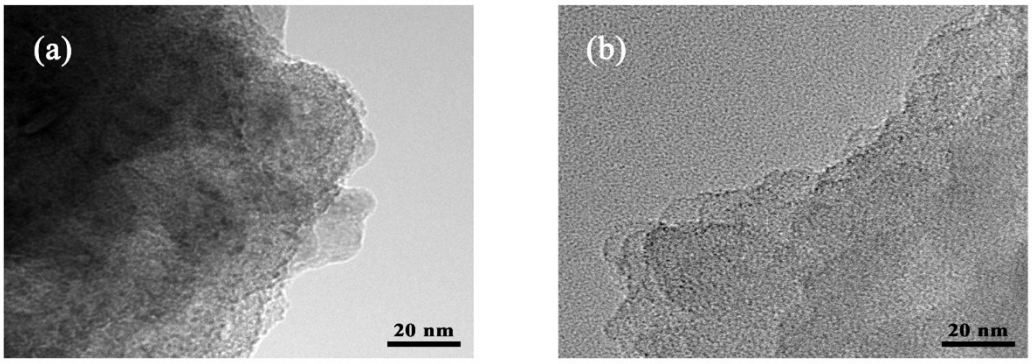

Figure S10. TEM images of PBMP-2-280-6 and PPDM-2-280-6.

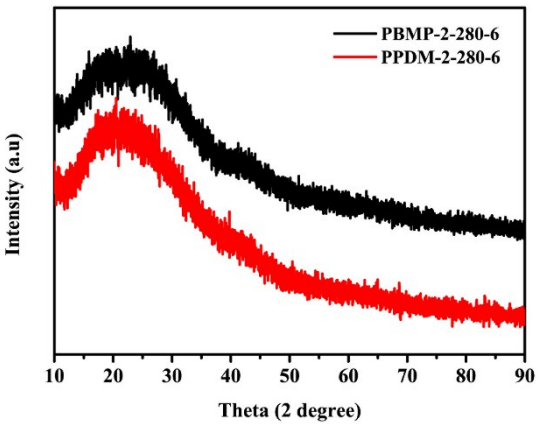

Figure S11. X-ray diffraction spectra of PBMP-2-280-6 and PPDM-2-280-6.

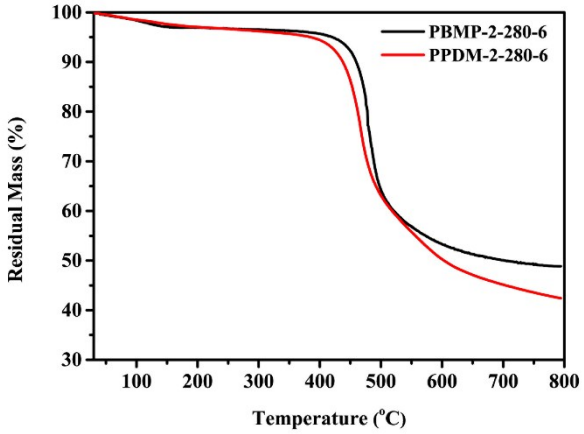

Figure S12. TGA curves of PBMP-2-280-6 and PPDM-2-280-6.

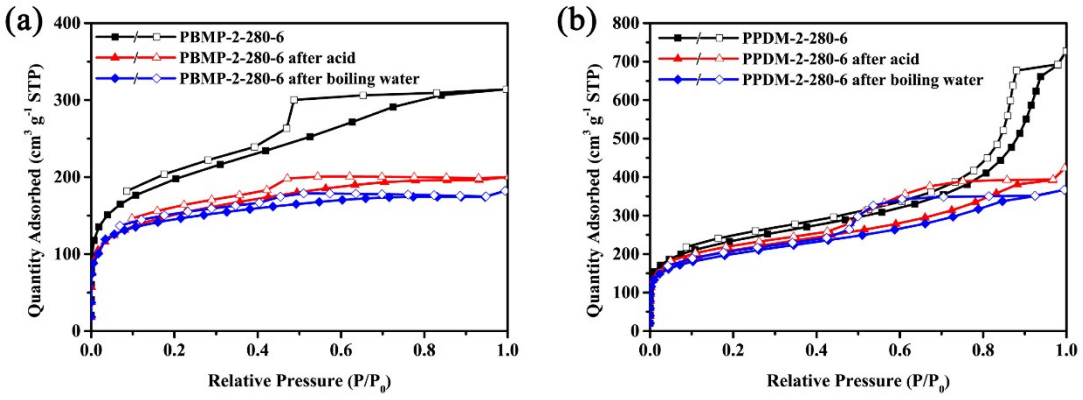

Figure S13. Nitrogen adsorption-desorption isotherms for PBMP-2-280-6 (a) and PPDM-2-280-6 (b) before and after being immersed in 1 M HCl and boiling water for 12 h.

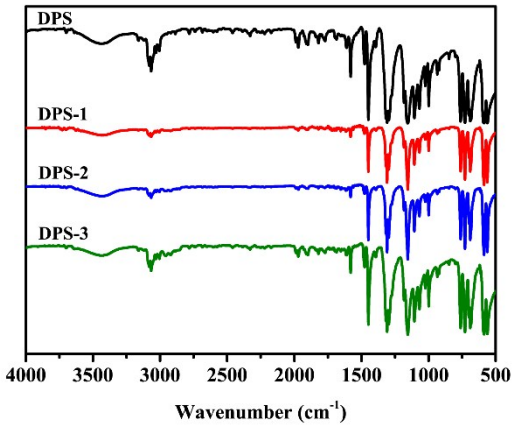

Figure S14. FTIR spectra of DPS and DPS-s (s represents the number of cycles).

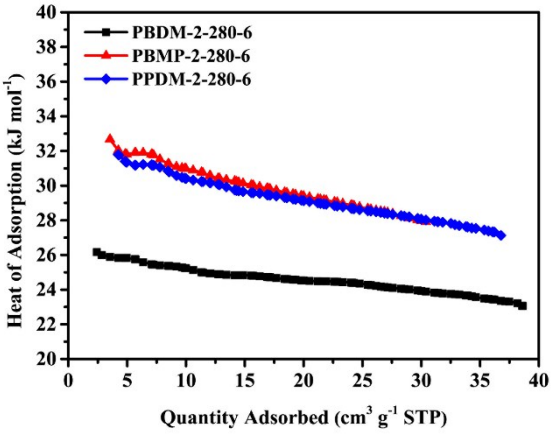

Figure S15. Isosteric heat of adsorption for PBDM-2-280-6, PBMP-2-280-6 and PPDM-2-280-6 determined from CO_2 adsorption isotherms at 273 K and 298 K.

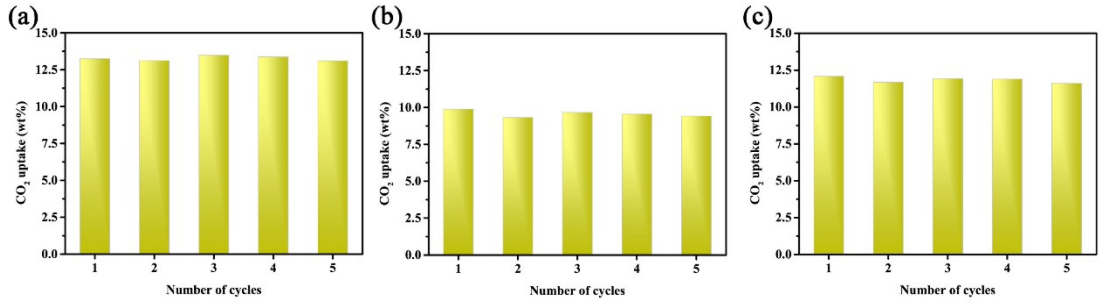

Figure S16. CO_2 adsorption capacity for recycled PBDM-2-280-6 (a), PBMP-2-280-6 (b) and PPDM-2-280-6 (c) at 273 K, 1.0 bar.

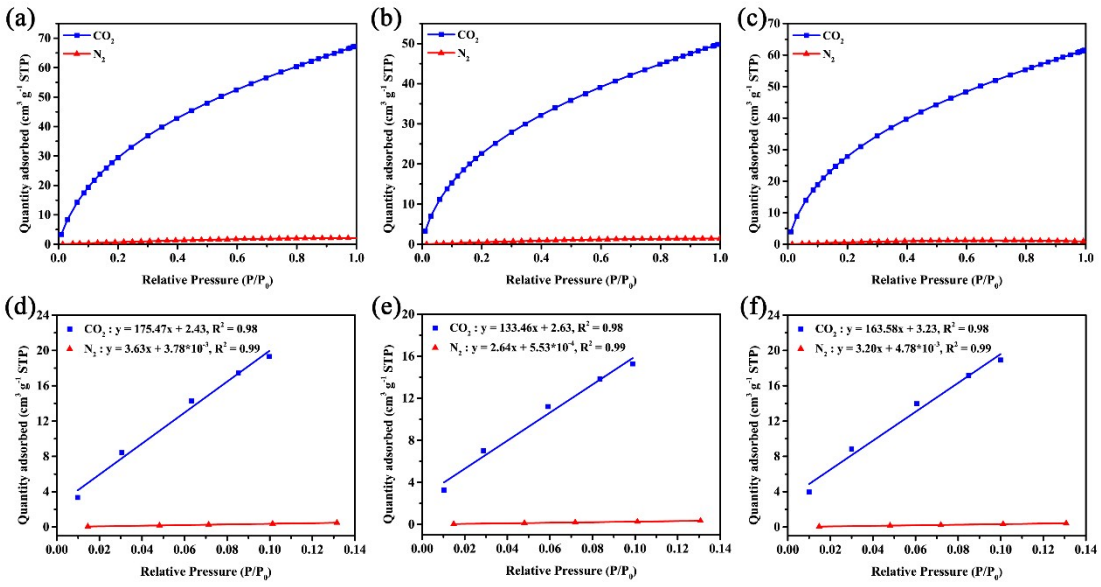

Figure S17. Adsorption isotherms of CO_2 and N_2 at 273 K for PBDM-2-280-6 (a), PBMP-2-280-6 (b) and PPDM-2-280-6 (c). Adsorption selectivity of CO_2 over N_2 for PBDM-2-280-6 (d), PBMP-2-280-6 (e) and PPDM-2-280-6 (f) derived from the initial slope method at 273 K.

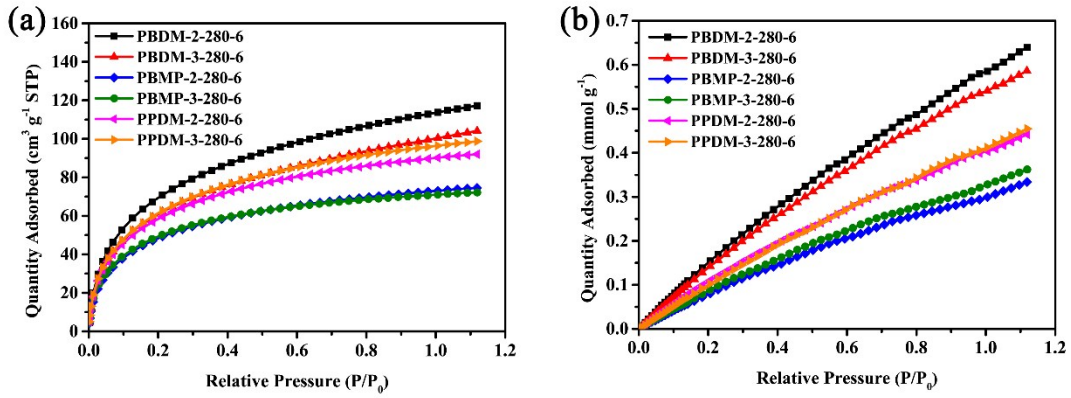

Figure S18. H_2 adsorption isotherms at 77.3 K (a) and CH_4 adsorption isotherms at 273 K (b) for PBDM-2-280-6, PBDM-3-280-6, PBMP-2-280-6, PBMP-3-280-6, PPDM-2-280-6 and PPDM-3-280-6.

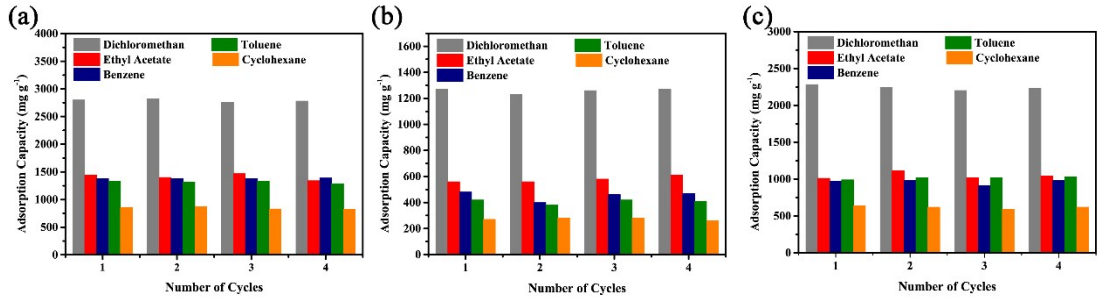

Figure S19. VOCs adsorption capacities for recycled PBDM-2-280-6 (a), PBMP-2-280-6 (b) and PPDM-2-280-6 (c) at 298 K and relative saturation pressure.