ESI

Nitrogen-rich diaminotriazine-based porous organic polymers for small gas storage and selective uptake

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Preparation of the APOPs

Synthesis of APOP-1

A 50 mL three-necked bottle flask fitted with a condenser and a magnetic stirring bar was charged with B1 (296 mg, 1 mmol), benzaldehyde (424 mg, 4 mmol) and dimethyl sulfoxide (25.0 mL). After degassing by argon bubbling, the mixture was heated to 180 °C for 72 h under an inert atomosphere. After thoroughly washing the obtained powder with MeOH, CH_2Cl_2 and THF, the solids were further Soxhlet extracted using CH_2Cl_2 and THF for 24 h, respectively, and dried under vacuum to afford the final APOP-1 in 66 % yield. Anal. calcd for $C_{26}H_{20}N_{10}$: C, 66.09; H, 4.27; N, 29.64. Found: C, 52.13; H, 4.21; N, 37.75 %.

Synthesis of APOP-1-OH

Similar to the preparation of APOP-1, B1 (296 mg, 1 mmol), 2-hydroxybenzaldehyde (488 mg, 4 mmol) were reacted in dimethyl sulfoxide (25.0 mL) at 180 °C for 72 h to afford APOP-1-OH in 71 % yield. Anal. calcd for $C_{26}H_{20}N_{10}O_2$: C, 61.90; H, 4.00; N, 27.76. Found: C, 55.44; H, 3.88; N, 37.19 %.

Synthesis of APOP-1-ONa

200 mg of APOP-1-OH was dispersed in 5 mL methanol, then 100 mg MeONa dissolved in 10 mL methanol was added to the dispersion and allowed to react for 2 h at room temperature. The dispersion was filtered and washed with methanol.

Synthesis of APOP-1-F

Similar to the preparation of APOP-1, B1 (296 mg, 1 mmol), 4-fluorobenzaldehyde (504 mg, 4 mmol) were reacted in dimethyl sulfoxide (25.0 mL) at 180 °C for 72 h to afford APOP-1-F in 68 % yield. Anal. calcd for $C_{26}H_{18}N_{10}F_2$: C, 61.41; H, 3.57; N, 27.55. Found: C, 50.53; H, 3.84; N, 40.12 %.

Synthesis of APOP-2

Similar to the preparation of APOP-1, B2 (372 mg, 1 mmol), benzaldehyde (424 mg, 4 mmol) were reacted in dimethyl sulfoxide (25.0 mL) at 180 °C for 72 h to afford APOP-2 in 55 % yield. Anal. calcd for $C_{32}H_{24}N_{10}$: C, 70.06; H, 4.41; N, 25.53. Found: C, 41.82; H, 2.91; N, 19.61 %.

Synthesis of APOP-3

Similar to the preparation of APOP-1, B3 (378 mg, 0.5 mmol), benzaldehyde (424 mg, 4 mmol) were reacted in dimethyl sulfoxide (22.5 mL) at 180 °C for 72 h to afford APOP-3 in 38 % yield. Anal. calcd for $C_{65}H_{48}N_{20}$: C, 70.38; H, 4.36; N, 25.25. Found: C, 60.37; H, 3.97; N, 29.55 %.

Synthesis of APOP-4

Similar to the preparation of APOP-1, B4 (438 mg, 0.5 mmol), benzaldehyde (424 mg, 4 mmol) were reacted in dimethyl sulfoxide (22.5 mL) at 180 °C for 72 h to afford APOP-4 in 28 % yield. Anal. calcd for $C_{69}H_{56}N_{20}O_4$: C, 67.41; H, 4.59; N, 22.78. Found: C, 55.02; H, 3.93; N, 25.85 %.

It should be noted that the discrepancies between predicted and actual values are common for porous materials due to the presence of end groups and adsorbed water or the residual solvents.[S1]

Calculation of isosteric heats of adsorption for the APOPs

Virial Equation

A virial-type expression in the following form was used to fit the experimental isotherm data for a given material at different temperatures.[S2]

$$\ln(P) = \ln(N) + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad \text{(I)}$$

Where N is the amount adsorbed at pressure P, T is the temperature, a_i and b_i are temperature independent empirical parameters, and m and n determine the number of terms required to adequately describe the isotherm. The resulting virial coefficients a_0 through a_m can then be used to calculate the isosteric heats of adsorption as function of uptake:

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad \text{(II)}$$

Where R is the universal gas constant (8.314 J K^{-1} mol^{-1})

It follows that the zero-coverage isosteric heats of adsorption is given by

$$Q_{st} = -Ra_0 \qquad \text{(III)}$$

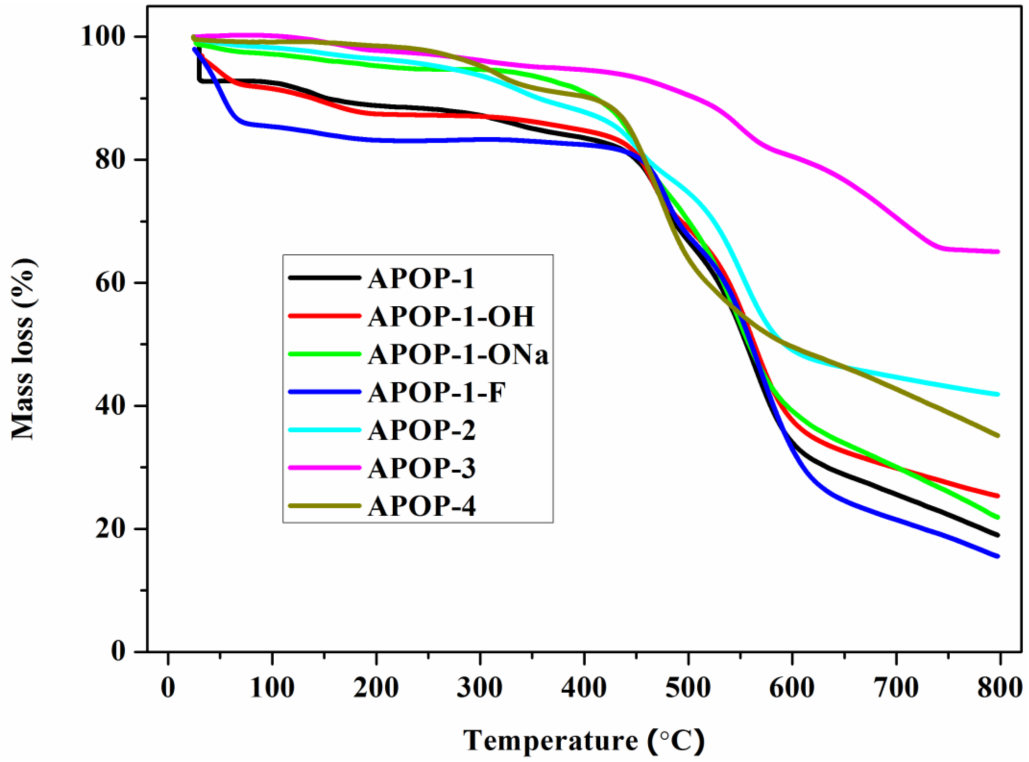

Fig. S1 Thermogravimetric analysis of the APOPs under N_2 atmosphere.

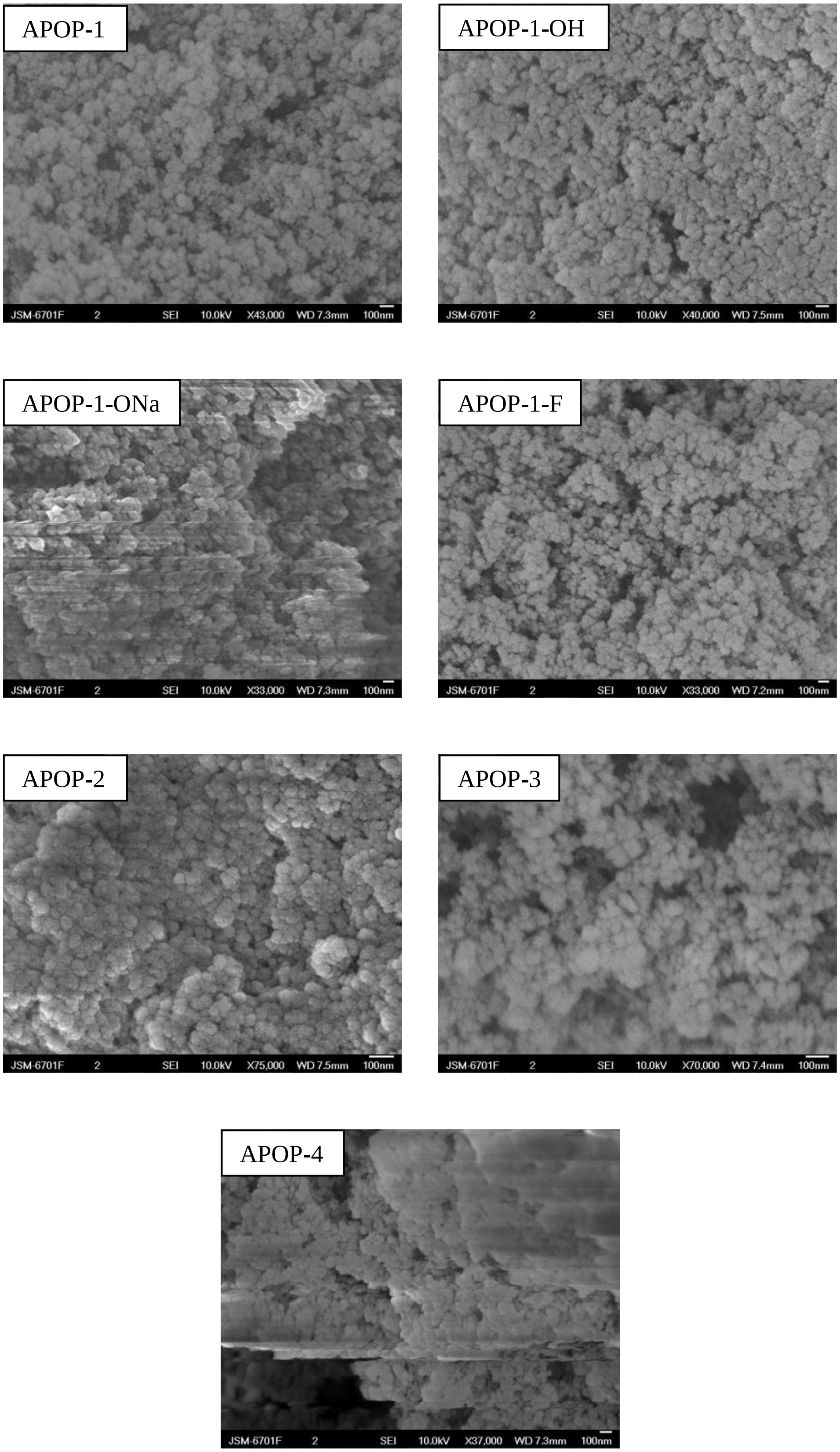

Fig. S2 Scanning Electron Microscopy images of the APOPs.

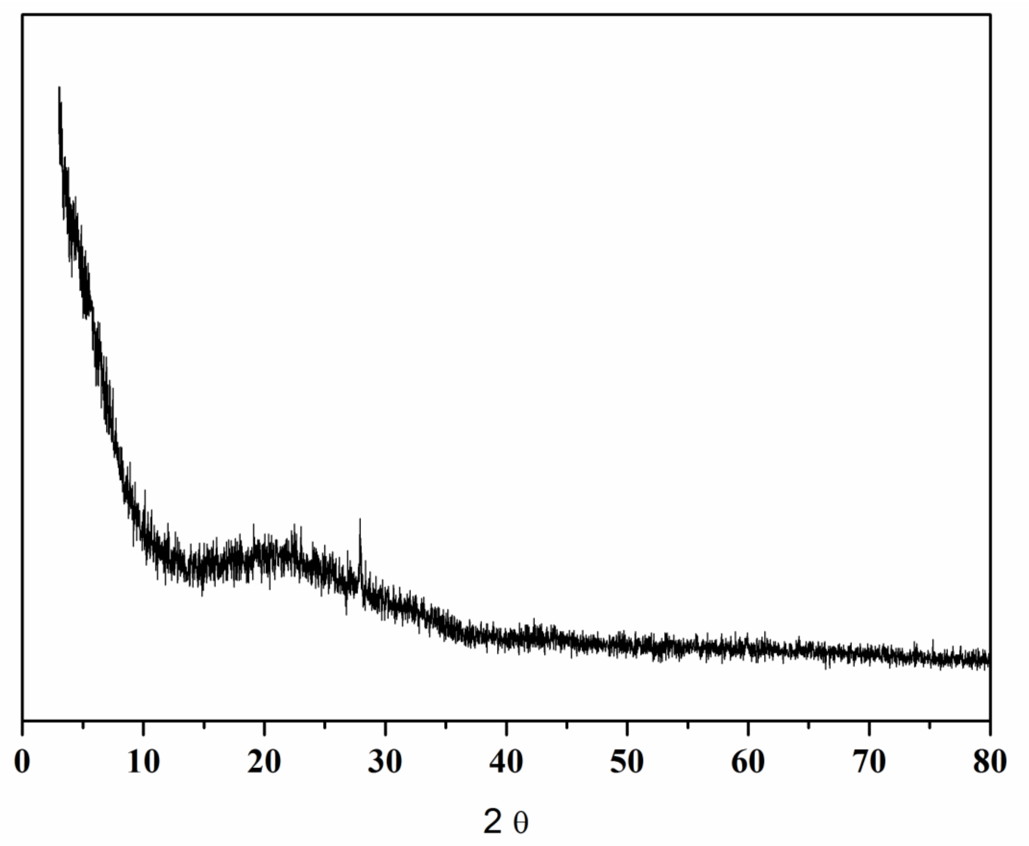

Fig. S3 Powder X-ray diffraction patters of APOP-1 indicate clearly the formation of amorphous porous polymers.

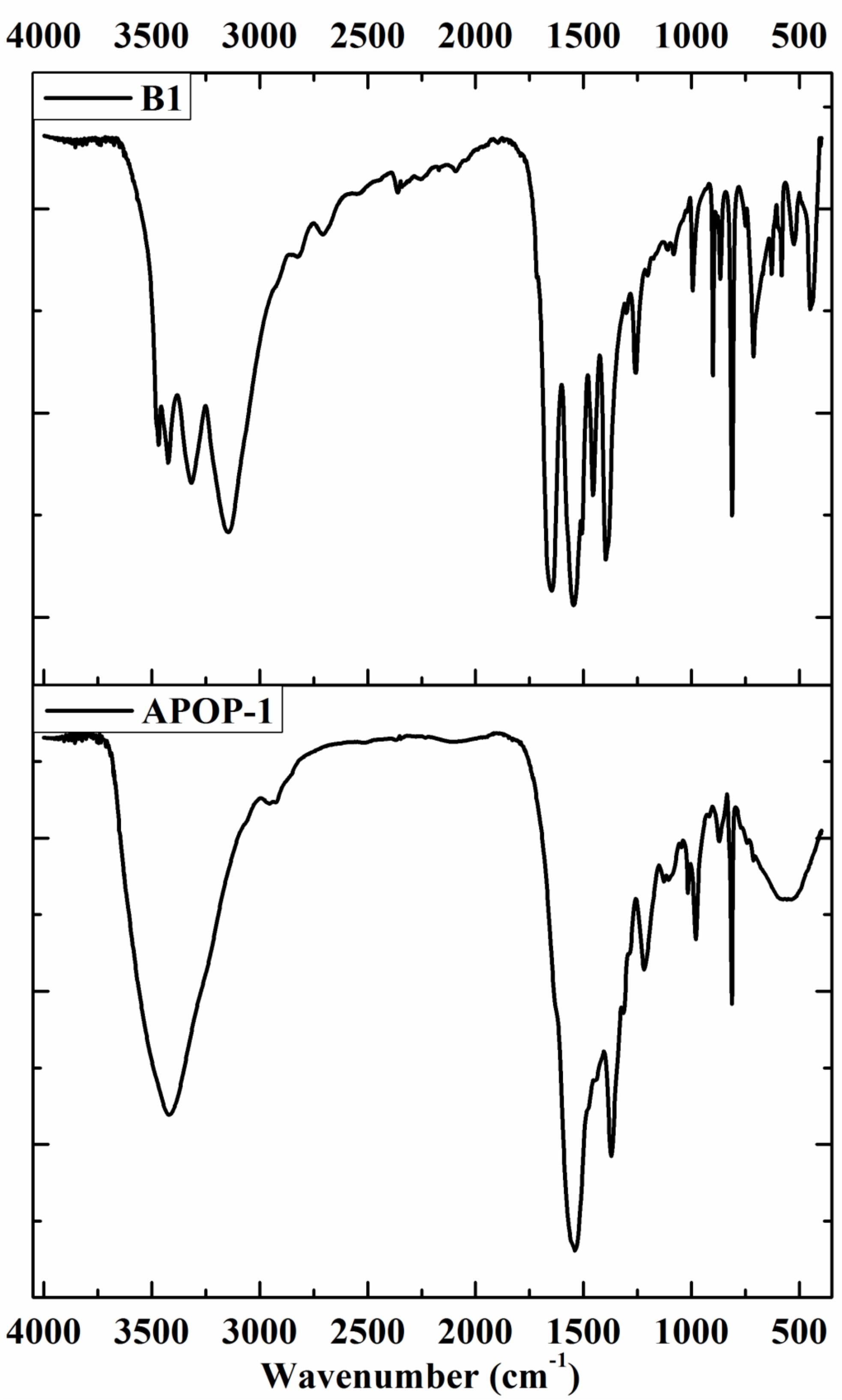

Fig. S4 FTIR spectra of B1 (black) and APOP-1 (black).

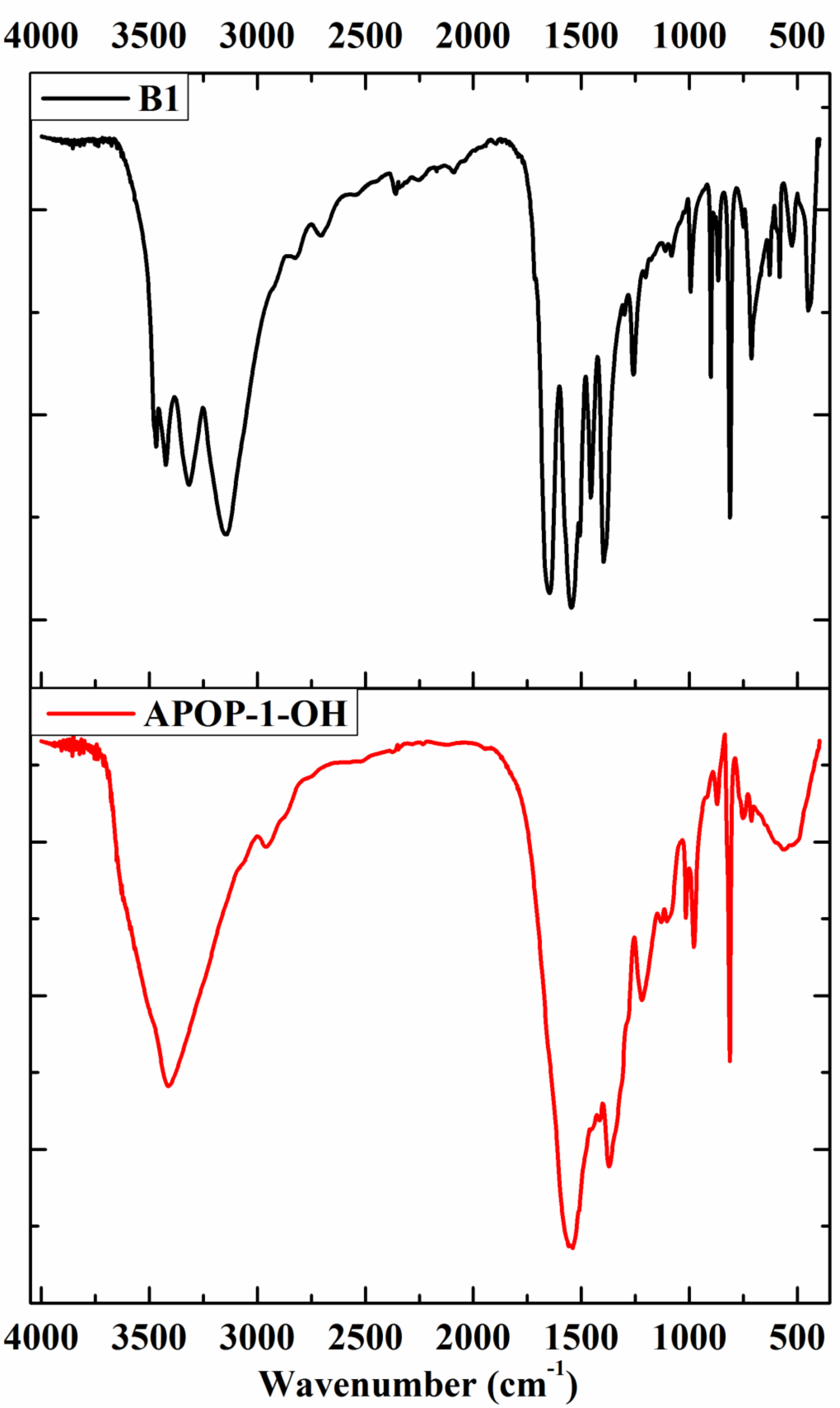

Fig. S5 FTIR spectra of B1 (black) and APOP-1-OH (red).

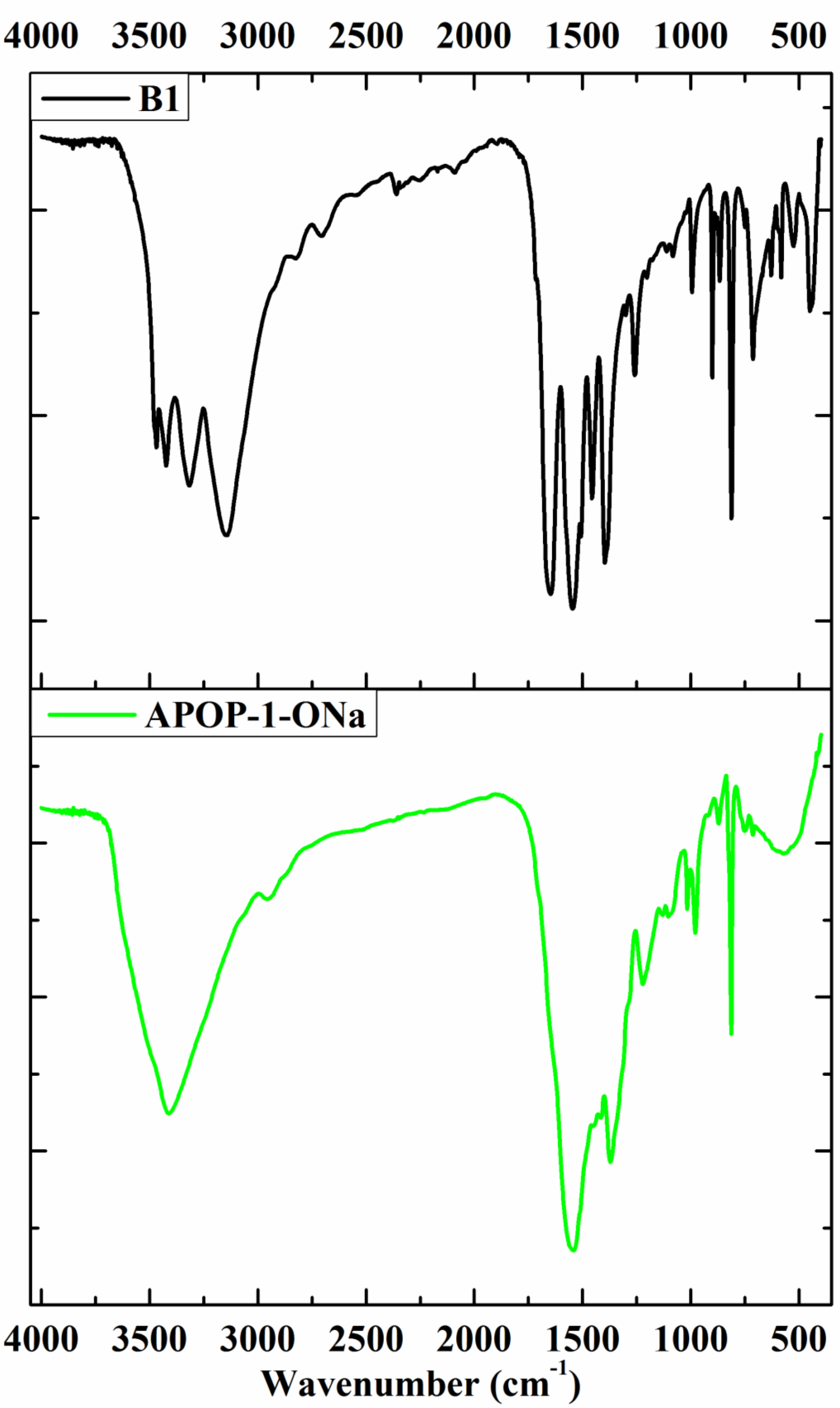

Fig. S6 FTIR spectra of B1 (black) and APOP-1-ONa (green).

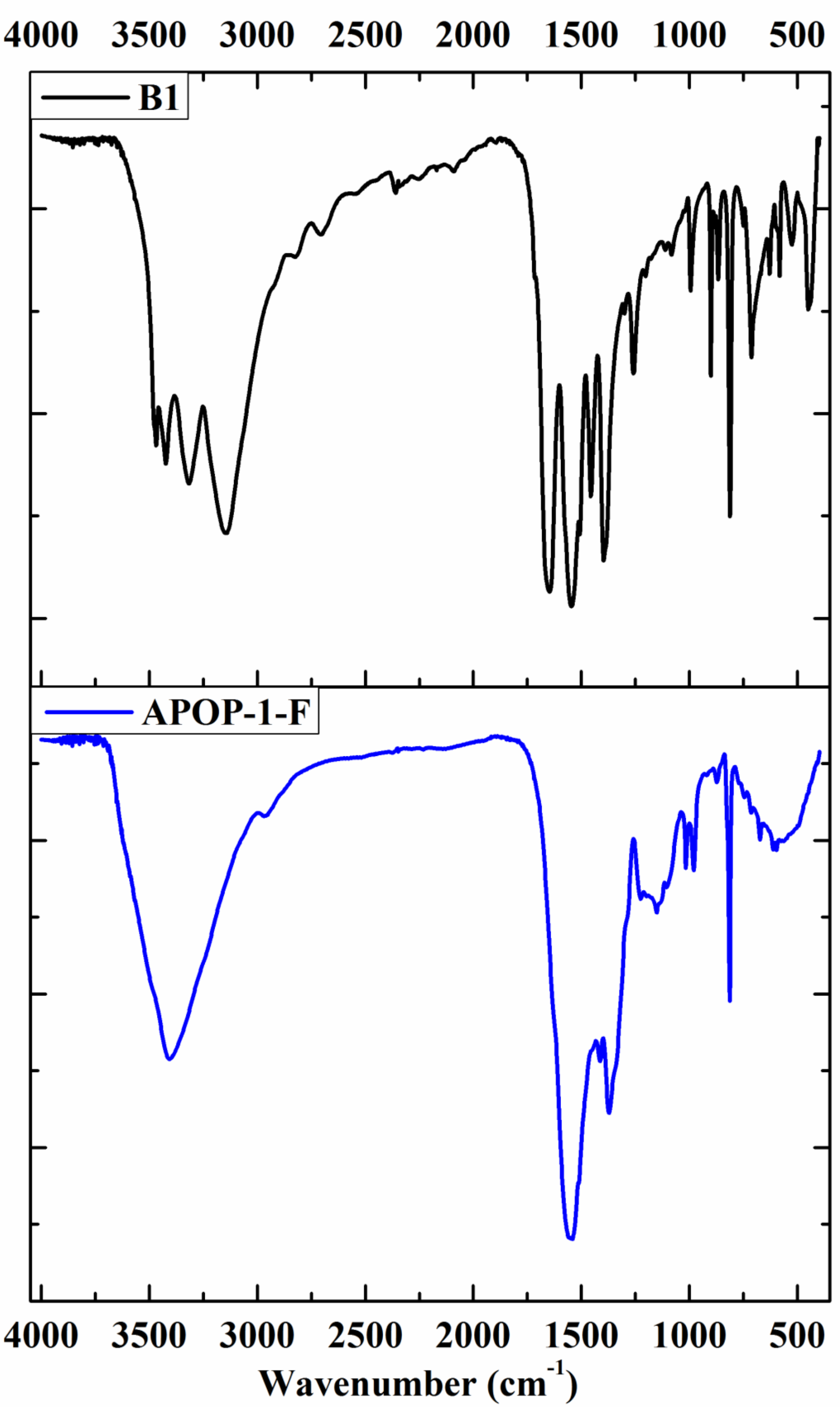

Fig. S7 FTIR spectra of B1 (black) and APOP-1-F (blue).

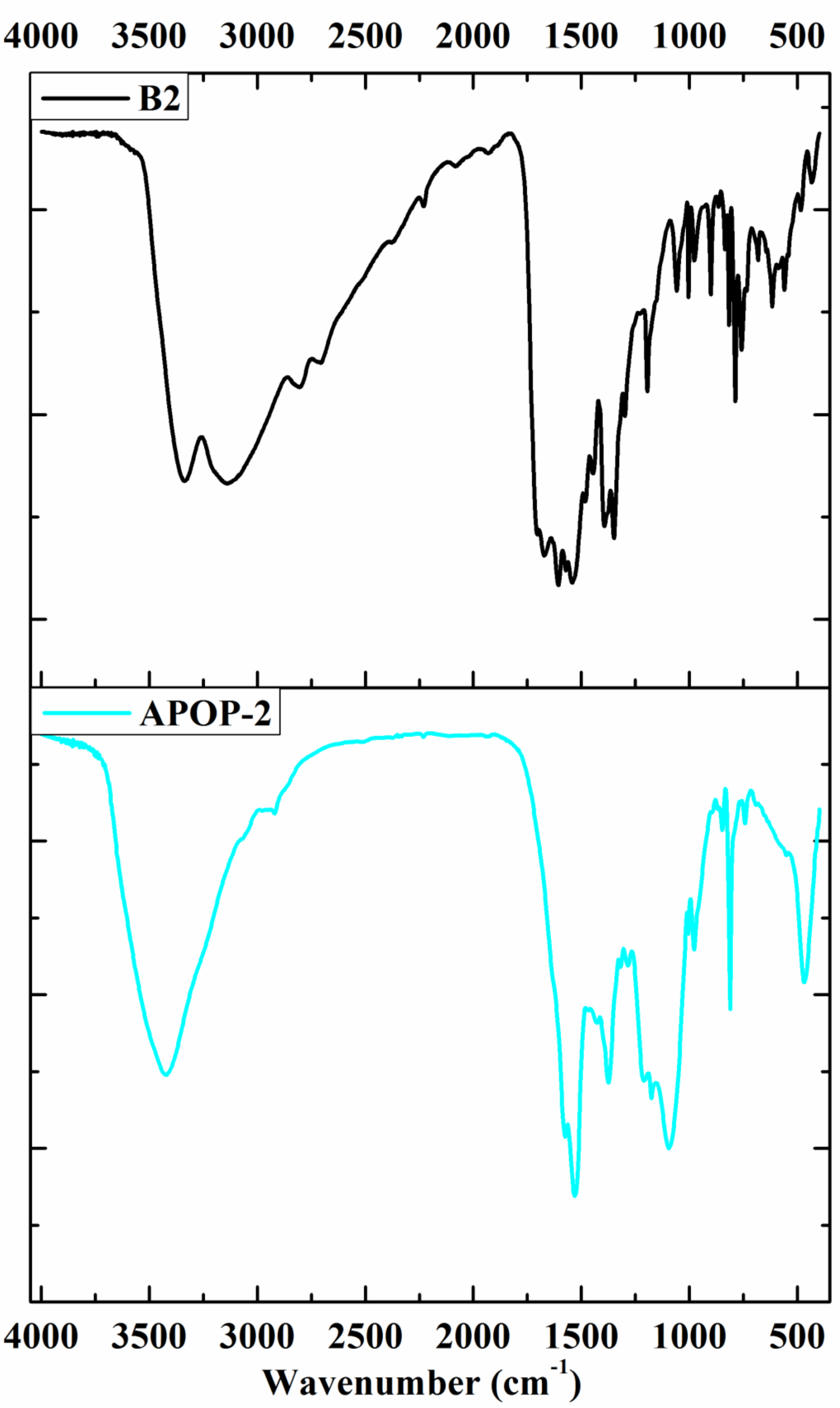

Fig. S8 FTIR spectra of B2 (black) and APOP-2 (cyan).

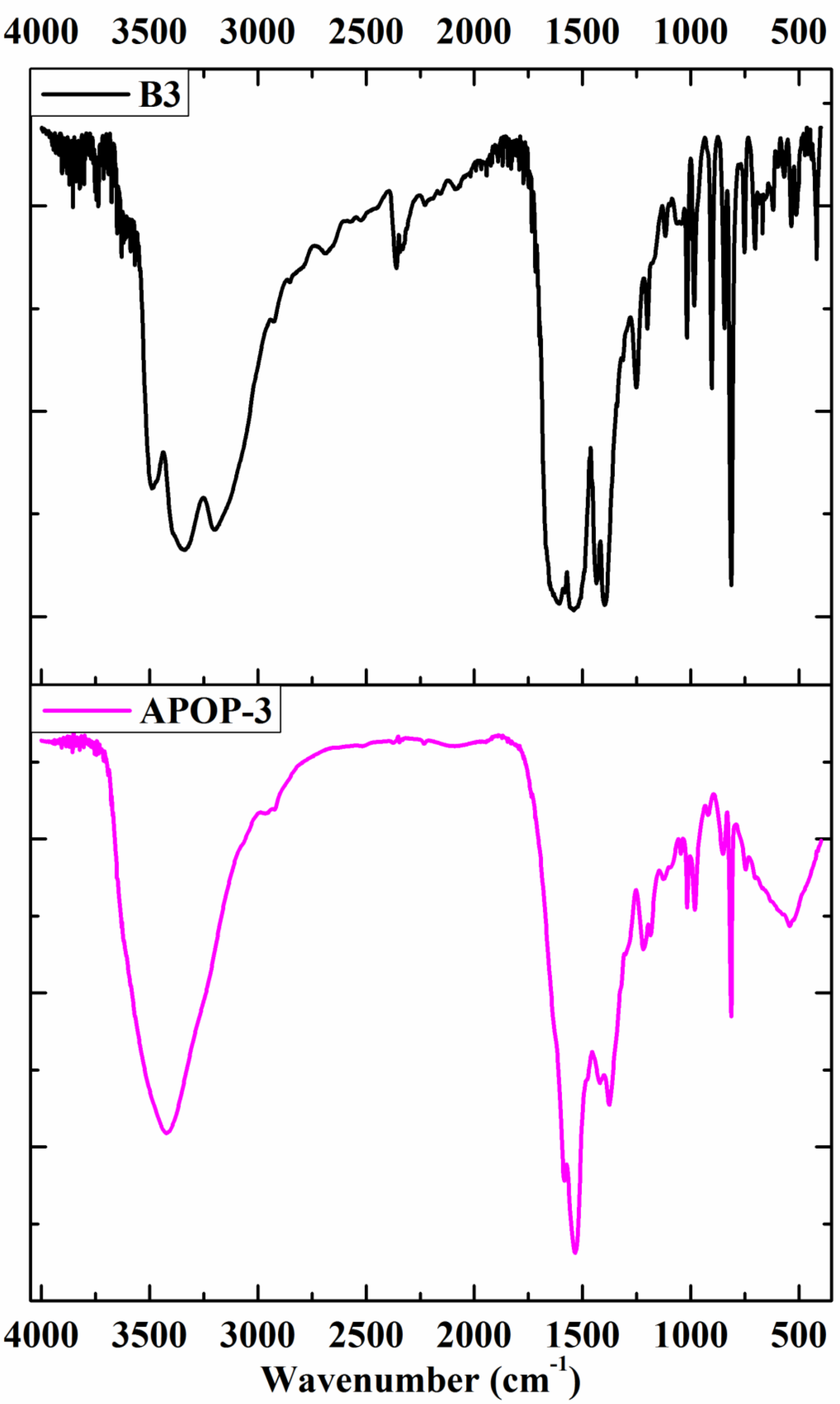

Fig. S9 FTIR spectra of B3 (black) and APOP-3 (magenta).

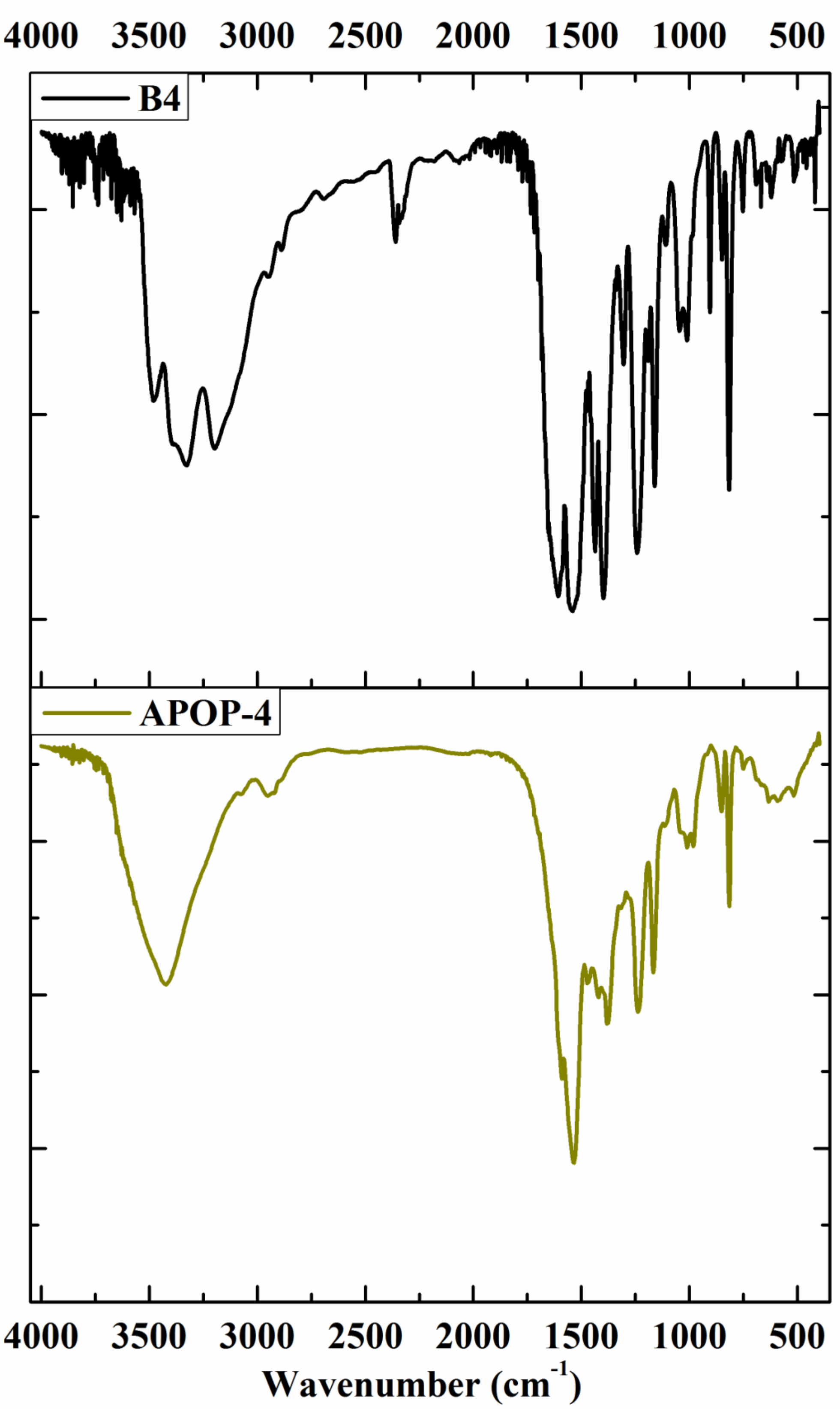

Fig. S10 FTIR spectra of B4 (black) and APOP-4 (dark yellow).

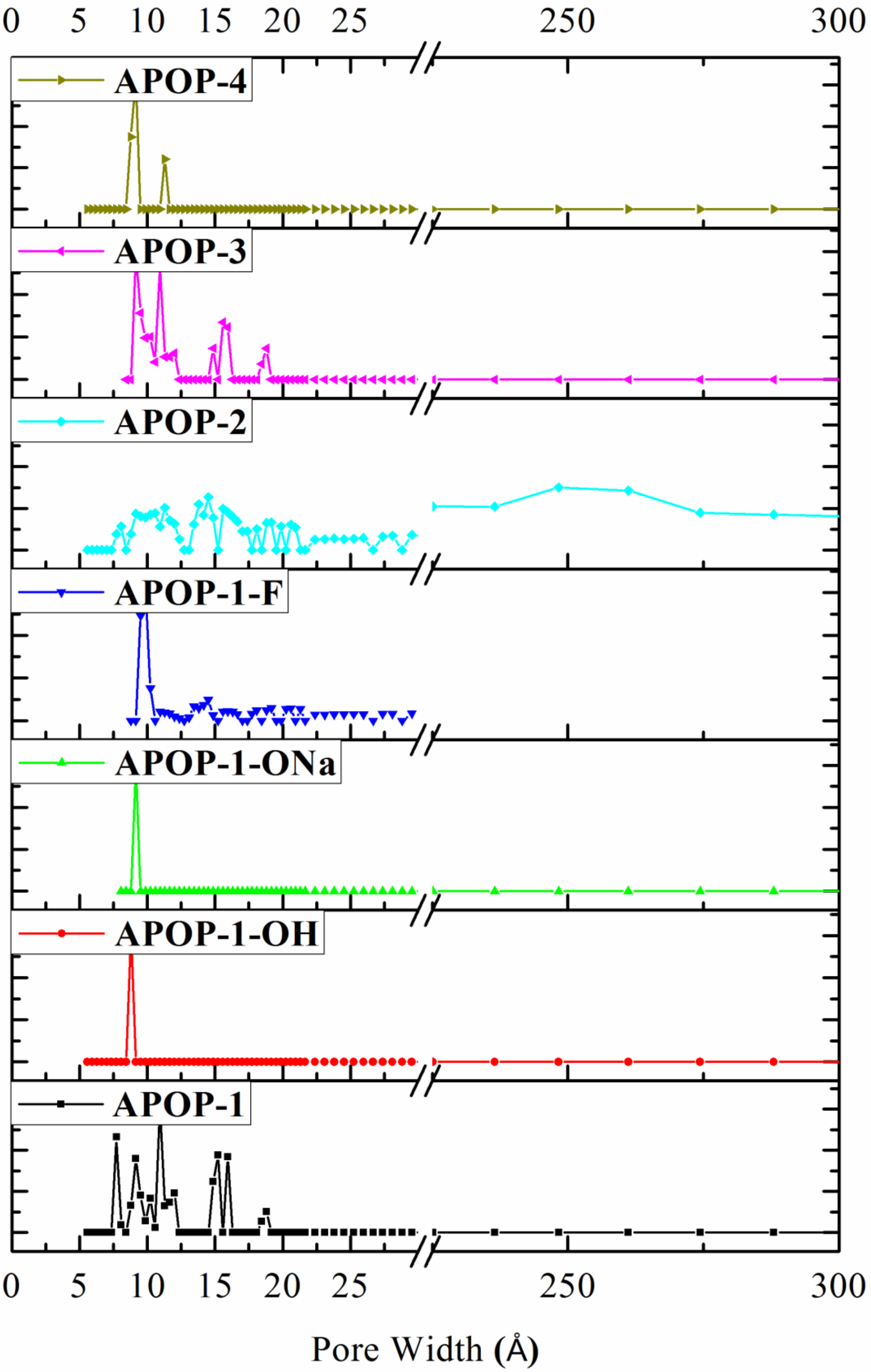

Fig. S11 The size distribution of APOP-1 (black), APOP-1-OH (red), APOP-1-ONa (green), APOP-1-F (blue), APOP-2 (cyan), APOP-3 (magenta) and APOP-4 (dark yellow).

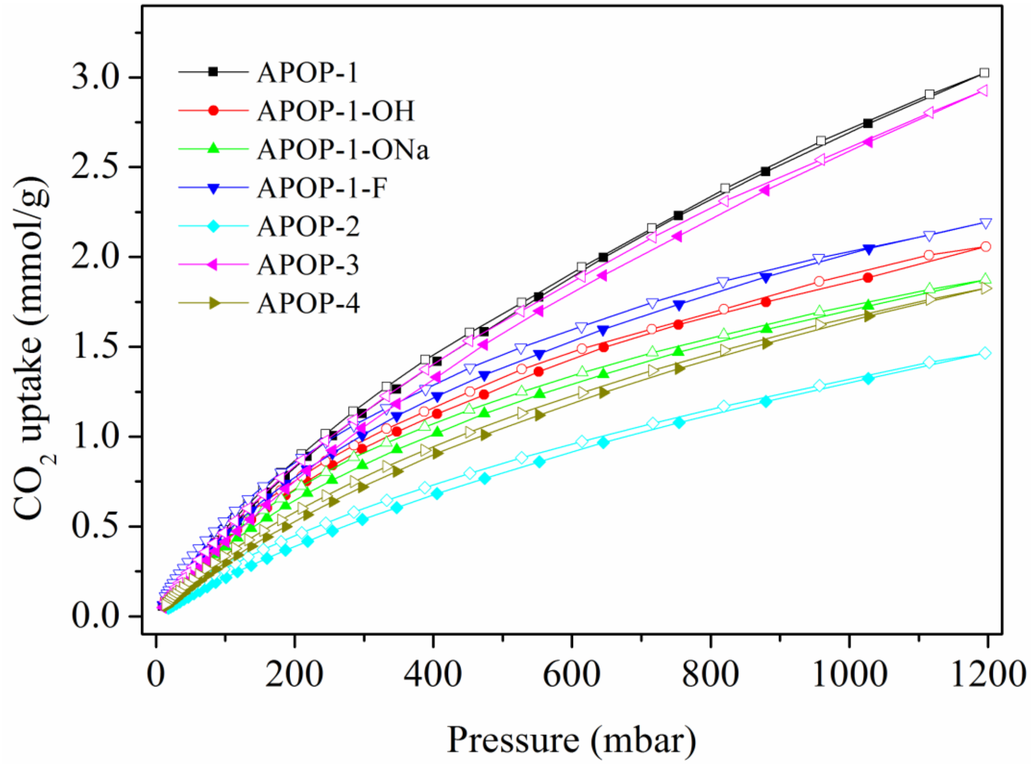

Fig. S12 CO_2 sorption isotherms of the APOPs at 298 K.

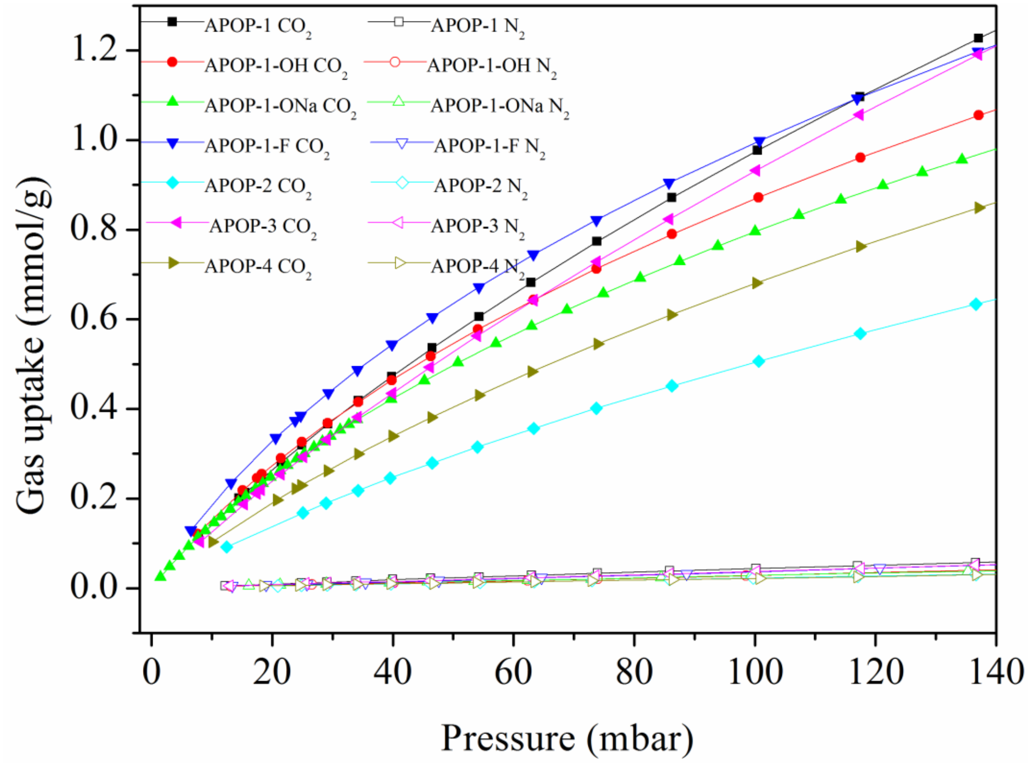

Fig. S13 CO_2 and N_2 adsorption isotherms at 273 K for the APOPs at a low-pressure range.

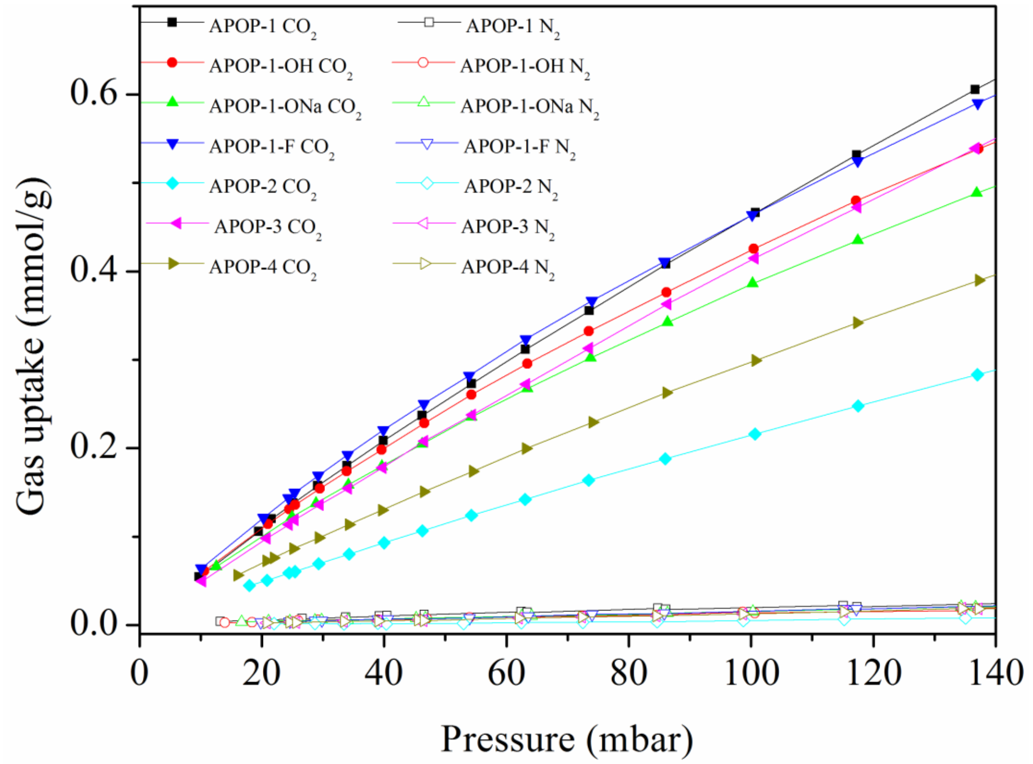

Fig. S14 CO_2 and N_2 adsorption isotherms at 298 K for the APOPs at a low-pressure range.

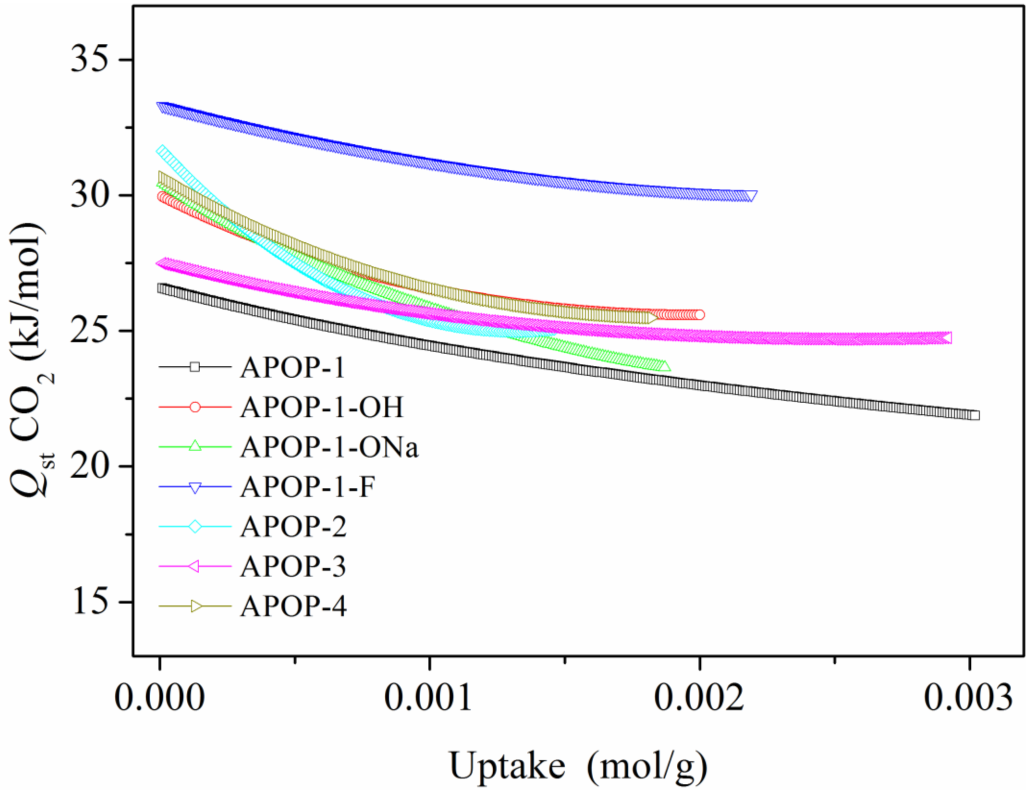

Fig. S15 Calculated Q_{st} for the APOPs as a function of the uptake of CO_2.

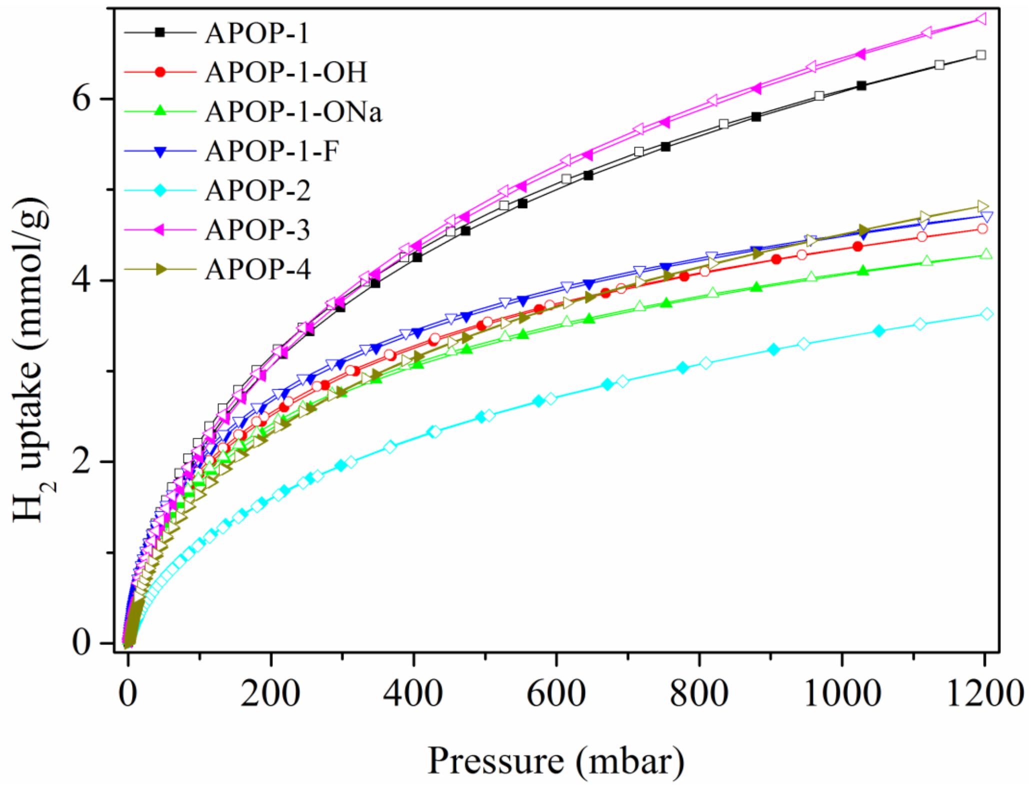

Fig. S16 H_2 sorption isotherms of the APOPs at 87 K.

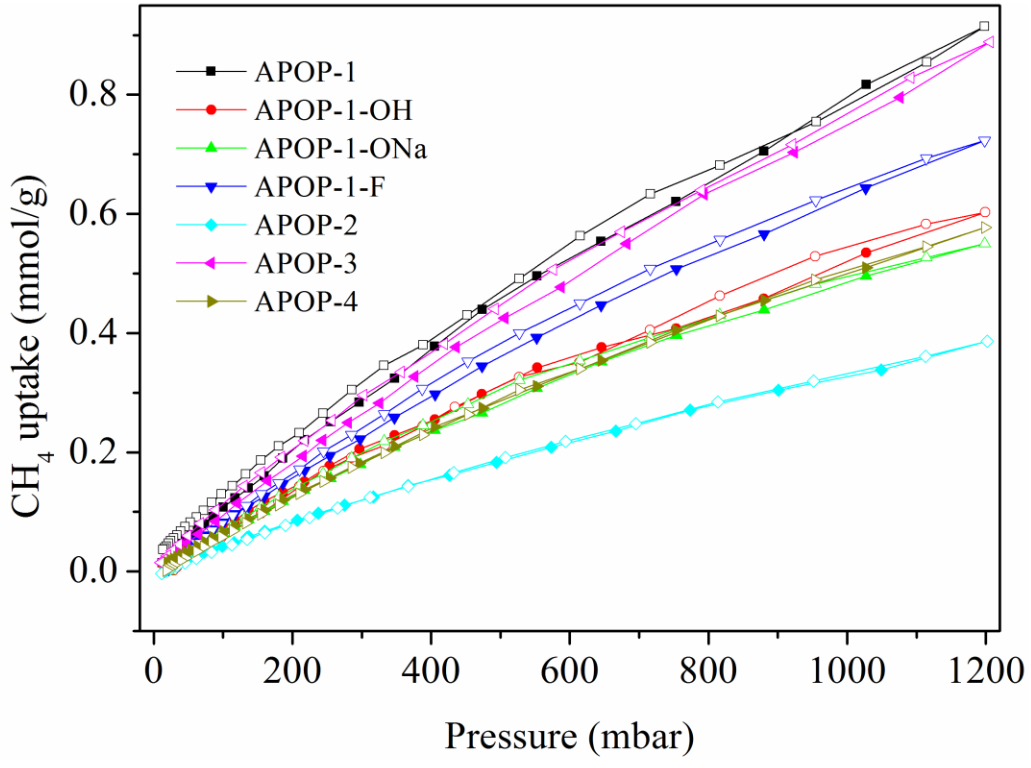

Fig. S17 CH_4 sorption isotherms of the APOPs at 298 K.

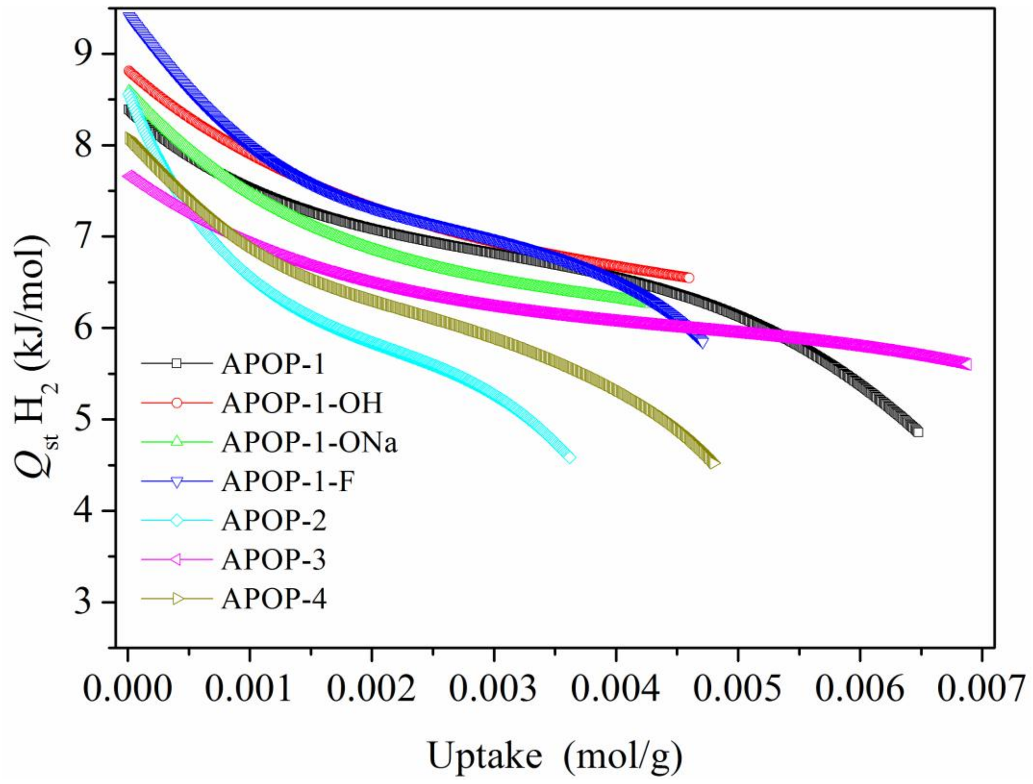

Fig. S18 Calculated Q_{st} for the APOPs as a function of the uptake of H_2.

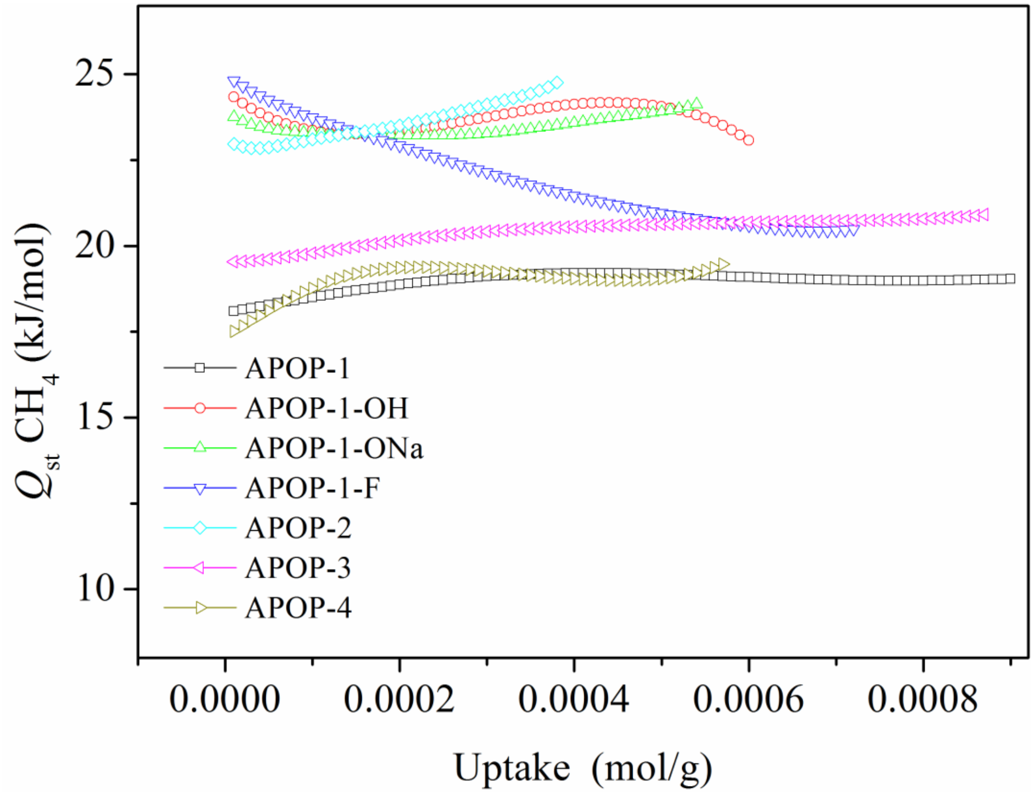

Fig. S19 Calculated Q_{st} for the APOPs as a function of the uptake of CH_4.

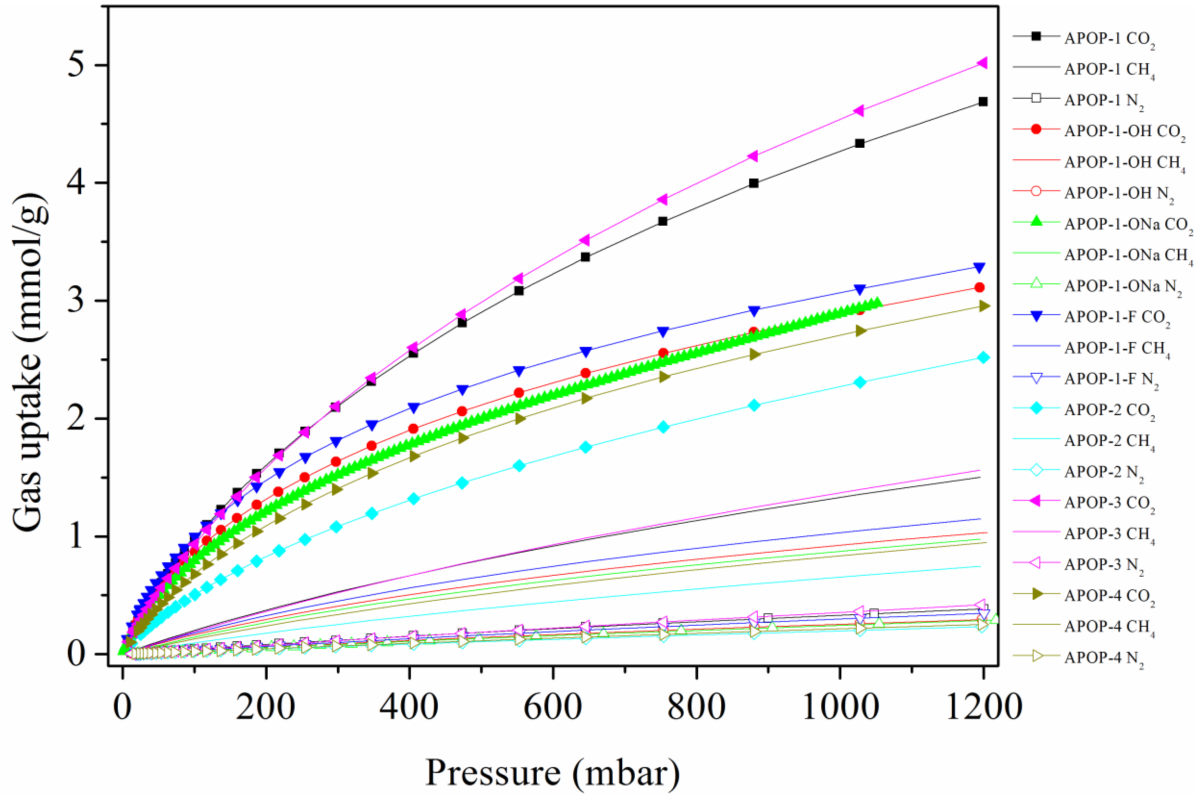

Fig. S20 CO_2, CH_4 and N_2 adsorption isotherms of the APOPs at 273 K.

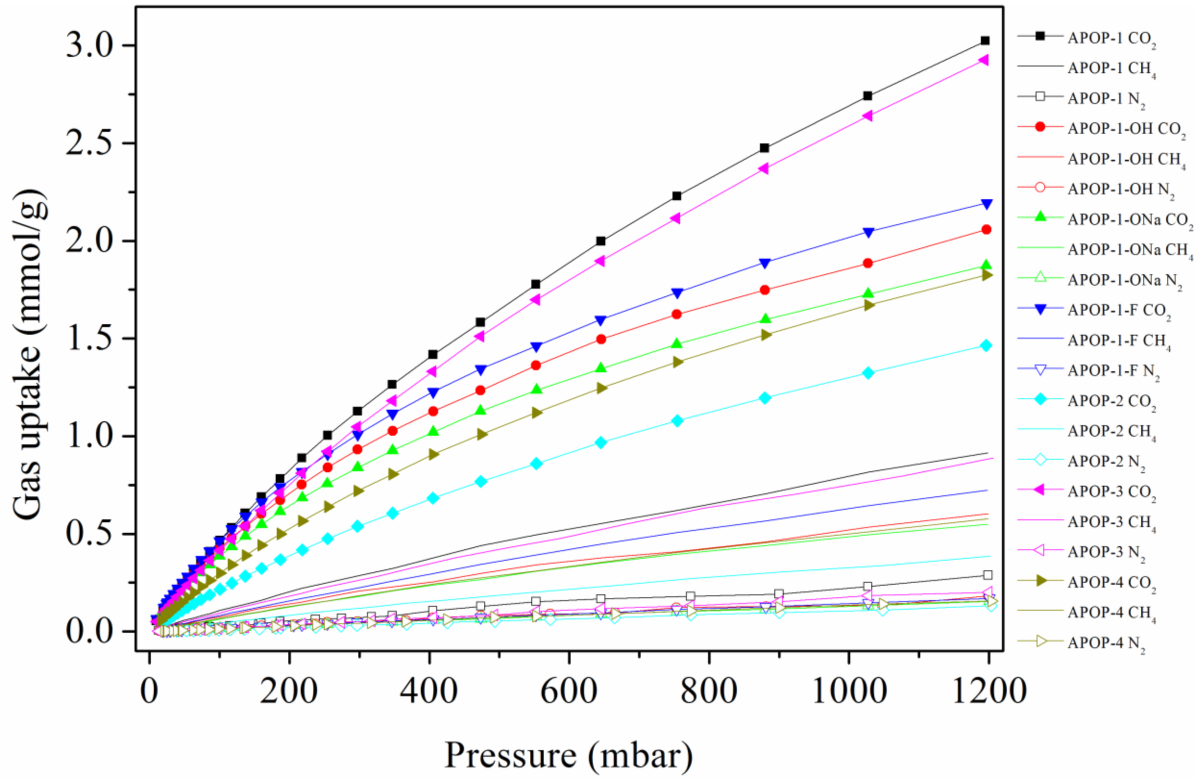

Fig. S21 CO_2, CH_4 and N_2 adsorption isotherms of the APOPs at 298 K.

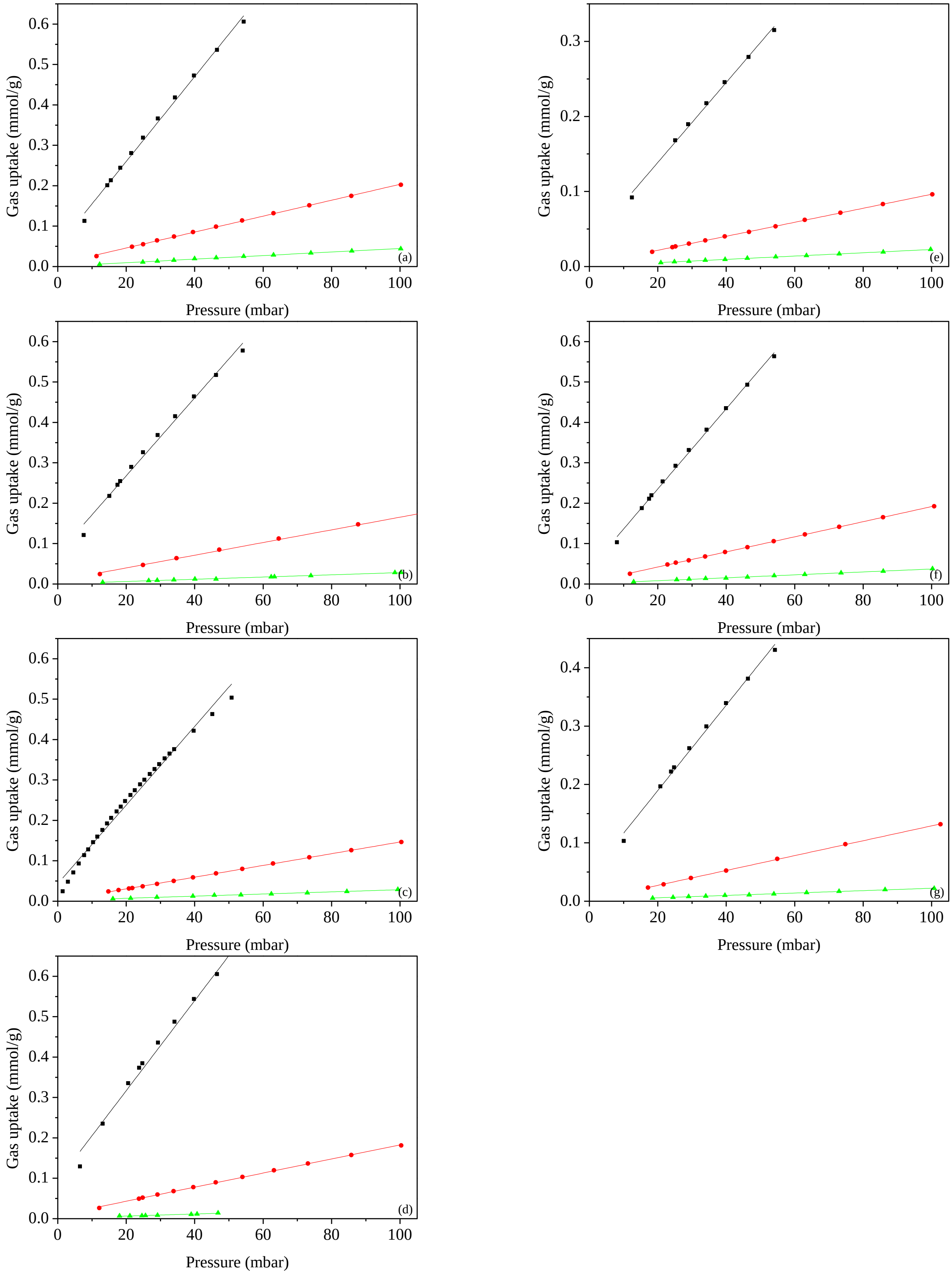

Fig. S22 The initial slope of the adsorption isotherms of CO_2 (black), CH_4 (red), and N_2 (Green) at 273 K: APOP-1(a), APOP-1-OH (b), APOP-1-ONa (c), APOP-1-F (d), APOP-2 (e), APOP-3 (f), and APOP-4 (g).

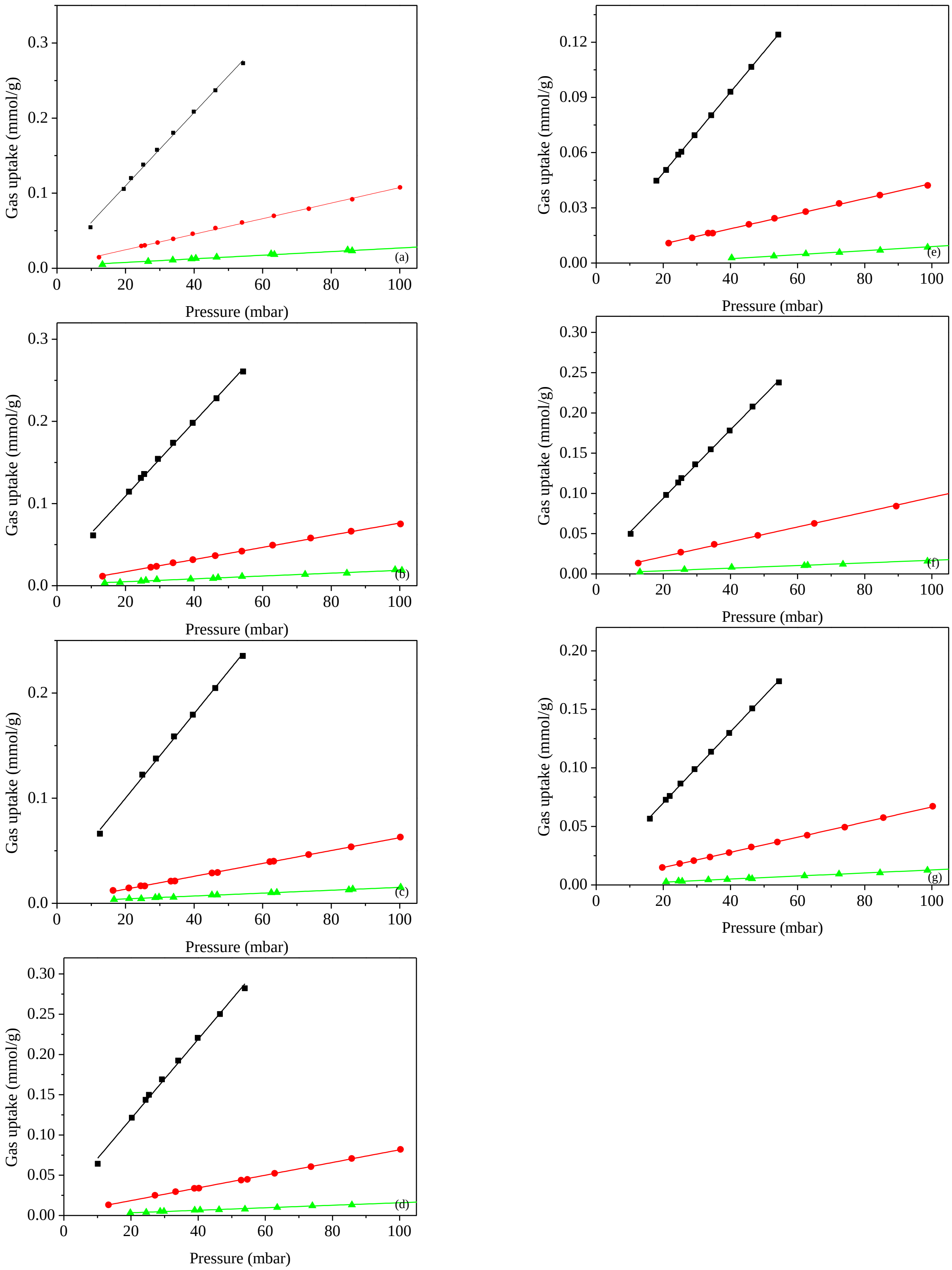

Fig. S23 The initial slope of the adsorption isotherms of CO_2 (black), CH_4 (red), and N_2 (Green) at 298 K: APOP-1(a), APOP-1-OH (b), APOP-1-ONa (c), APOP-1-F (d), APOP-2 (e), APOP-3 (f), and APOP-4 (g).

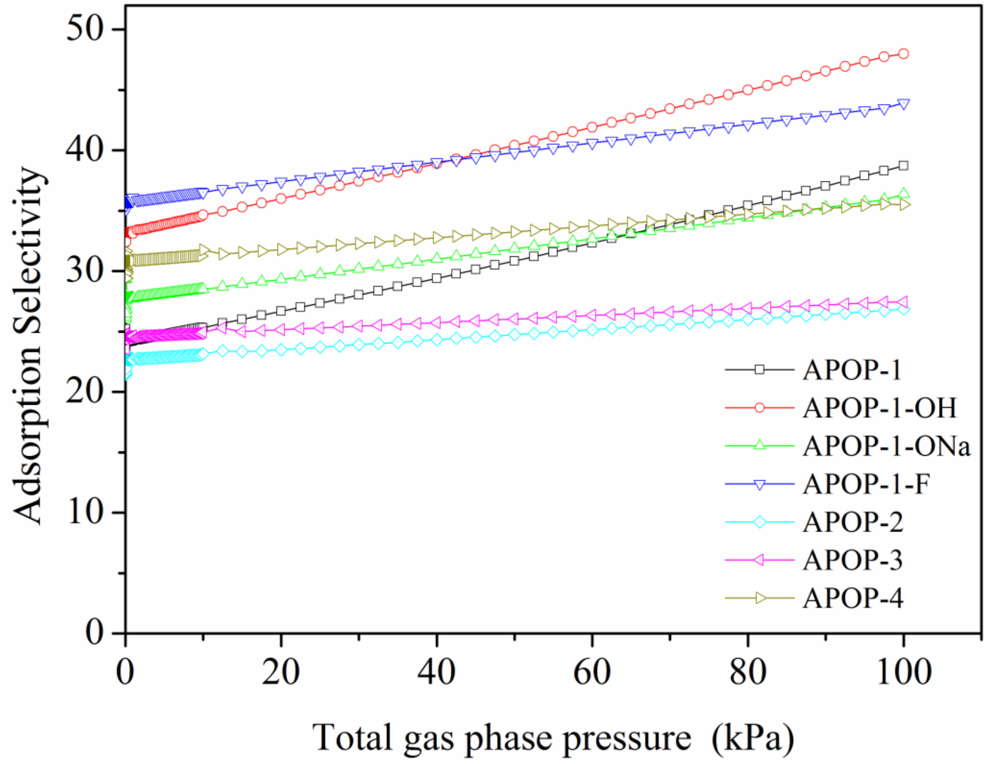

Fig. S24 IAST predicted 15% CO_2 over 85% N_2 adsorption selectivities for the APOPs at 273 K.

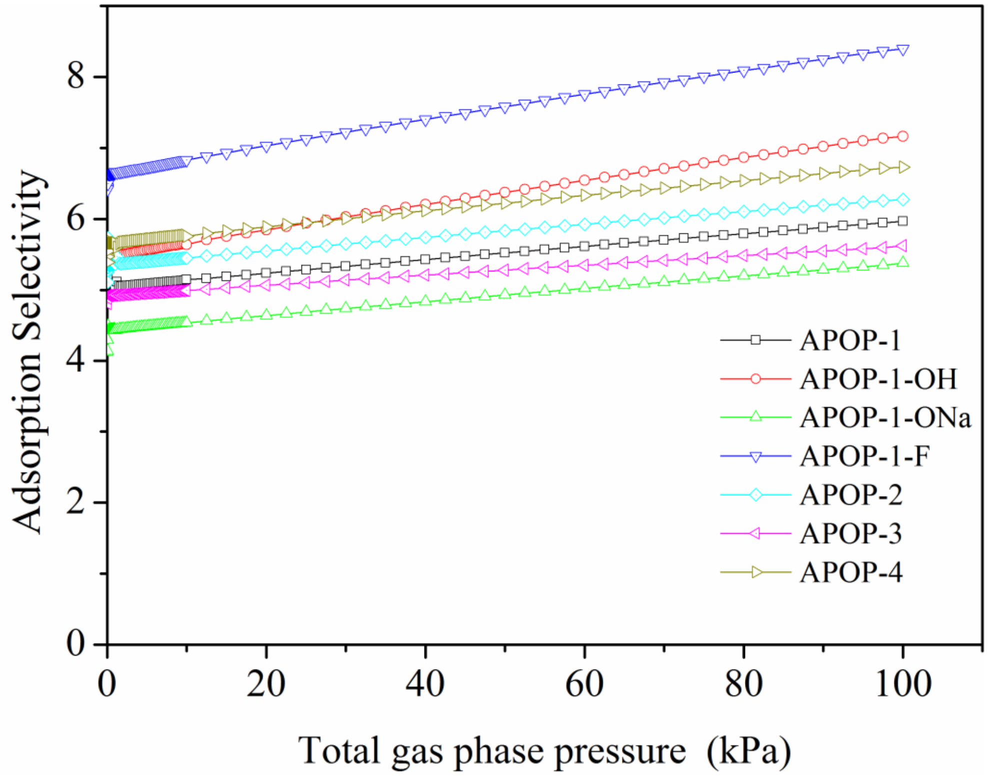

Fig. S25 IAST predicted 15% CO_2 over 85% CH_4 adsorption selectivities for the APOPs at 273 K.

Table S1. Summary of CO_2 uptake capacities at 273 K of the chemical functionalized POPs at low pressure.

Porous materials	S_{BET} (m^2/g)	CO_2 uptake at 0.15 bar (mmol/g)	CO_2 uptake at 1.0 bar (mmol/g)	Q_{st} (kJ/mol)	Polar sites	Ref.
APOP-1	1298	1.31	4.26	26.6	aminal	This work
APOP-1-OH	875	1.11	2.89	30.0	aminal	This work
APOP-1-ONa	760	1.02	2.89	30.6	aminal	This work
APOP-1-F	724	1.26	3.07	33.3	aminal	This work
APOP-2	906	0.68	2.27	31.7	aminal	This work
APOP-3	1402	1.27	4.54	27.5	aminal	This work
APOP-4	833	0.90	2.70	30.7	aminal	This work
TFM-1	738	0.55	1.73	27.8	*s*-triazine	S3
P6M	947	0.63	4.17	-	*s*-triazine	S4
CE-1	960	0.85	2.52	39.7	*s*-triazine	S5
Ni-Por-1	1711	-	3.13	-	porphyrin	S6
Fe-POP-1	875	1.49	4.30	-	porphyrin	S7
CPOP-1	2220	1.22	4.82	27	carbazole	S8
Th-1	726	0.90	2.89	27	thiophene	S9
BILP-1	1172	1.63	4.27	26.7	benzimidazole	S10
BILP-4	1306	1.99	5.34	28.7	benzimidazole	S11
PECONF-3	851	1.43	3.49	26	DAB	S12
HCP 4	1642	-	3.91	21.6	-	S13
MOP-C	1237	1.34	3.86	33.7	triazole	S14
Tet4	1917	-	3.03	-	alkyne	S15
POF1B	917	1.78	4.09	-	-OH	S16
BINOL-4	1015	1.33	3.96	29.8	-OH	S17
PPN-6-SO_3Li	1186	2.02	4.20	35.7	-SO_3Li	S18
PAF-1-450	1191	1.47	4.46	31.6	carbonization	S19
PPN-6-CH_2DETA	555	4.06	5.27	56	-CH_2DETA	S20
PAF-1	5600	0.3	2.05	15.6	-	S21
PAF-3	2932	0.58	3.47	19.2	-	S21
COF-102	3620	-	1.56	-	-	S22
COF-103	3530	-	1.70	-	-	S22

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