Increasing surface area and CO_2 uptake of conjugated microporous polymers via a post-knitting method

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The detail synthetic processes of these polymers:

Synthesis of CMP-1: To a solution of 1,3,5-tribromobenzene (1.574 g, 5.0 mmol) and 1,4-phenylenediboronic acid (1.243 g, 7.5 mmol) in DMF (160 mL), $Pd(PhCN)_2Cl_2$ (67 mg, 0.175 mmol) and K_2CO_3 (4.140 g, 30.0 mmol) were added. Then the mixture solution was heated and stirred at 120 °C for 3 days under N_2 atmosphere. Last the reaction was quenched by water, and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C. Last the resulting product was dried in vacuum for 12 h at 120 °C (926 mg, 98% yield).

Synthesis of CMP-2: To a solution of 1,3,5-tribromobenzene (2.235 g, 7.1 mmol) and [1,1'-biphenyl]-4,4'-diyldiboronic acid (2.587 g, 10.7 mmol) in DMF (200 mL), $Pd(PhCN)_2Cl_2$ (134 mg, 0.35 mmol) and K_2CO_3 (5.879 g, 42.6 mmol) were added. Then the mixture solution was heated and stirred at 120 °C for 3 days under N_2 atmosphere. Last the reaction was quenched by water, and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C. Last the resulting product was dried in vacuum for 12 h at 120 °C (2.116 g, 98% yield).

Synthesis of CMP-3: To a solution of 2,4,6-tribromoaniline (2.334 g, 7.1 mmol) and [1,1'-biphenyl]-4,4'-diyldiboronic acid (2.587 g, 10.7 mmol) in DMF (200 mL), $Pd(PhCN)_2Cl_2$ (134 mg, 0.35 mmol) and K_2CO_3 (5.879 g, 42.6 mmol) were added. Then the mixture solution was heated and stirred at 120 °C for 3 days under N_2 atmosphere. Last the reaction was quenched by water, and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C. Last the resulting product was dried in vacuum for 12 h at 120 °C (1.925 g, 85% yield).

Synthesis of CMP-4: To a solution of 3,4',5-tribromobiphenyl (1.950 g, 5.0 mmol) and 1,4-phenylenediboronic acid (1.243 g, 7.5 mmol) in DMF (160 mL), $Pd(PhCN)_2Cl_2$ (67 mg, 0.175 mmol) and K_2CO_3 (4.140 g, 30.0 mmol) were added. Then the mixture solution was heated and stirred at 120 °C for 3 days under N_2 atmosphere. Last the reaction was quenched by water, and the solid product was washed with H_2O, DMF, THF,

EtOH and DCM for several times under refluxing, except for DMF at 100 °C. Last the resulting product was dried in vacuum for 12 h at 120 °C (1.275 g, 97% yield).

Synthesis of **KCMP-F1**: To a solution of CMP-1 (100 mg) and dimethoxymethane (86 mg, 1.1 mmol) in 1,2-dichloroethane (15 mL), dry $FeCl_3$ (1.000 g, 6.2 mmol) was added, the mixture was heated and stirred at 85 °C for 16 h under N_2 atmosphere. Then cooling to room temperature and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C, respectively. Last the resulting product was dried in vacuum for 12 h at 120 °C (129 mg, 126% yield).

Synthesis of **KCMP-F2**: To a solution of CMP-2 (100 mg) and dimethoxymethane (86 mg, 1.1 mmol) in 1,2-dichloroethane (15 mL), dry $FeCl_3$ (1.000 g, 6.2 mmol) was added, the mixture was heated and stirred at 85 °C for 16 h under N_2 atmosphere. Then cooling to room temperature and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C, respectively. Last the resulting product was dried in vacuum for 12 h at 120 °C (131 mg, 128% yield).

Synthesis of **KCMP-F3**: To a solution of CMP-3 (100 mg) and dimethoxymethane (86 mg, 1.1 mmol) in 1,2-dichloroethane (15 mL), dry $FeCl_3$ (1.000 g, 6.2 mmol) was added, the mixture was heated and stirred at 85 °C for 16 h under N_2 atmosphere. Then cooling to room temperature and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C, respectively. Last the resulting product was dried in vacuum for 12 h at 120 °C (121 mg, 103% yield).

Synthesis of **KCMP-F4**: To a solution of CMP-4 (100 mg) and dimethoxymethane (86 mg, 1.1 mmol) in 1,2-dichloroethane (15 mL), dry $FeCl_3$ (1.000 g, 6.2 mmol) was added, the mixture was heated and stirred at 85 °C for 16 h under N_2 atmosphere. Then cooling to room temperature and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C, respectively. Last the resulting product was dried in vacuum for 12 h at 120 °C (121 mg, 117% yield).

Synthesis of **KCMP-M1**: To a solution of CMP-1 (188 mg) in CH_2Cl_2 (20 mL), dry

$AlCl_3$ (400 mg, 3.0 mmol) was added, the mixture was heated and stirred at 85 °C for 16 h under N_2 atmosphere. Then cooling to room temperature and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C. Last the resulting product was dried in vacuum for 12 h at 120 °C (268 mg, 140% yield).

Synthesis of **KCMP-M2**: To a solution of CMP-2 (303 mg) in CH_2Cl_2 (20 mL), dry $AlCl_3$ (400 mg, 3.0 mmol) was added, the mixture was heated and stirred at 85 °C for 16 h under N_2 atmosphere. Then cooling to room temperature and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C. Last the resulting product was dried in vacuum for 12 h at 120 °C (472 mg, 153% yield).

Synthesis of **KCMP-M3**: To a solution of CMP-3 (326 mg) in CH_2Cl_2 (20 mL), dry $AlCl_3$ (400 mg, 3.0 mmol) was added, the mixture was heated and stirred at 85 °C for 16 h under N_2 atmosphere. Then cooling to room temperature and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C. Last the resulting product was dried in vacuum for 12 h at 120 °C (463 mg, 121% yield).

Synthesis of **KCMP-M4**: To a solution of CMP-4 (264 mg) in CH_2Cl_2 (20 mL), dry $AlCl_3$ (400 mg, 3.0 mmol) was added, the mixture was heated and stirred at 85 °C for 16 h under N_2 atmosphere. Then cooling to room temperature and the solid product was washed with H_2O, DMF, THF, EtOH and DCM for several times under refluxing, except for DMF at 100 °C. Last the resulting product was dried in vacuum for 12 h at 120 °C (377 mg, 139% yield).

The formula for KCMPs yield:

$$Y_{KCMP} = \frac{m_{KCMP}}{m_{CMP}} \times Y_{CMP}$$

In where, Y_{KCMP} is the yield of KCMPs, Y_{CMP} is the yield of the corresponding CMPs, m_{KCMP} is the weight of the dry polymers of KCMPs, and m_{CMP} is the weight of the pristine CMPs.

Table S1 The element content of C, N and H.

Samples	Elements		
	C (wt.%)	H (wt.%)	N (wt.%)
CMP-1	77.7	4.5	-
KCMP-F1	60.0	3.2	-
KCMP-M1	72.0	4.3	-
CMP-2	87.2	4.8	-
KCMP-F2	63.3	4.1	-
KCMP-M2	77.2	4.5	-
CMP-3	81.5	4.9	3.4
KCMP-F3	69.3	3.5	2.6
KCMP-M3	73.0	4.4	2.6
CMP-4	81.2	4.4	-
KCMP-F4	60.0	3.6	-
KCMP-M4	74.6	5.0	-

In addition, the element contents were lower than the theoretical values, and this phenomenon also generated frequently on other amorphous porous polymers (*Macromolecules*, 2011, **44**, 2410–2414). The lower element contents of C and H may be caused by the side reaction, test error and reactant residue.

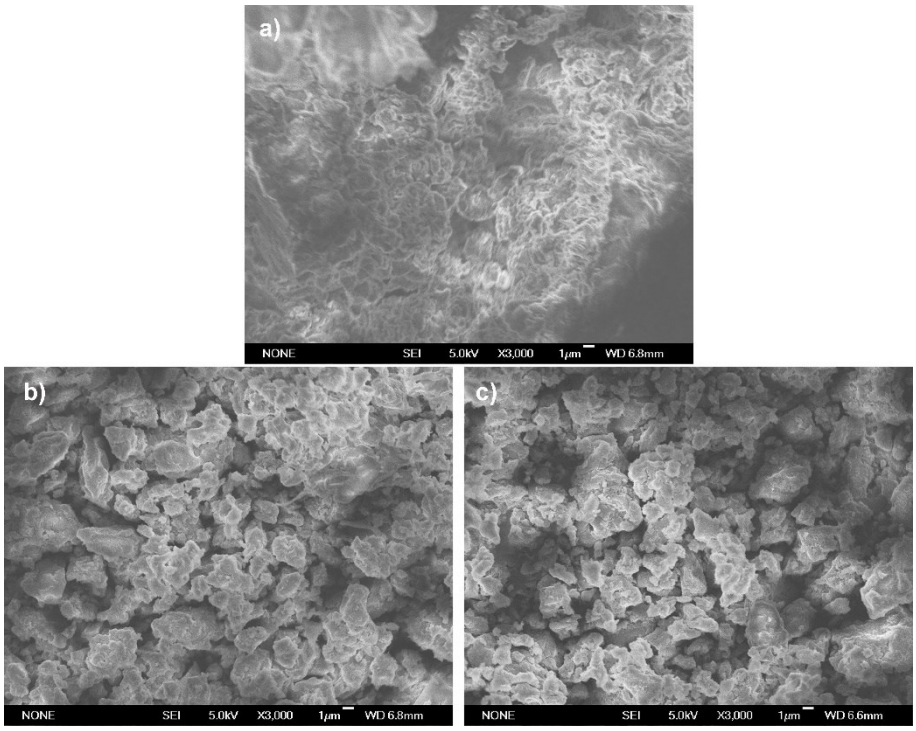

Fig. S1 Scanning electron microscopy (SEM) images: (a) CMP-1, (b) **KCMP-F1** and (c) **KCMP-M1**.

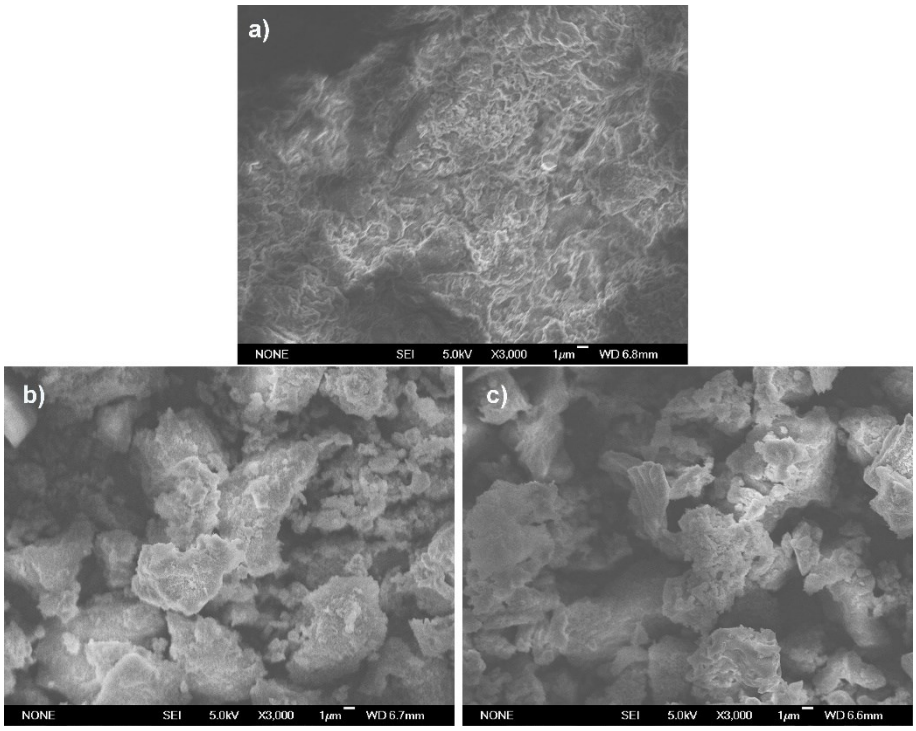

Fig. S2 SEM images: (a) CMP-2, (b) **KCMP-F2** and (c) **KCMP-M2**.

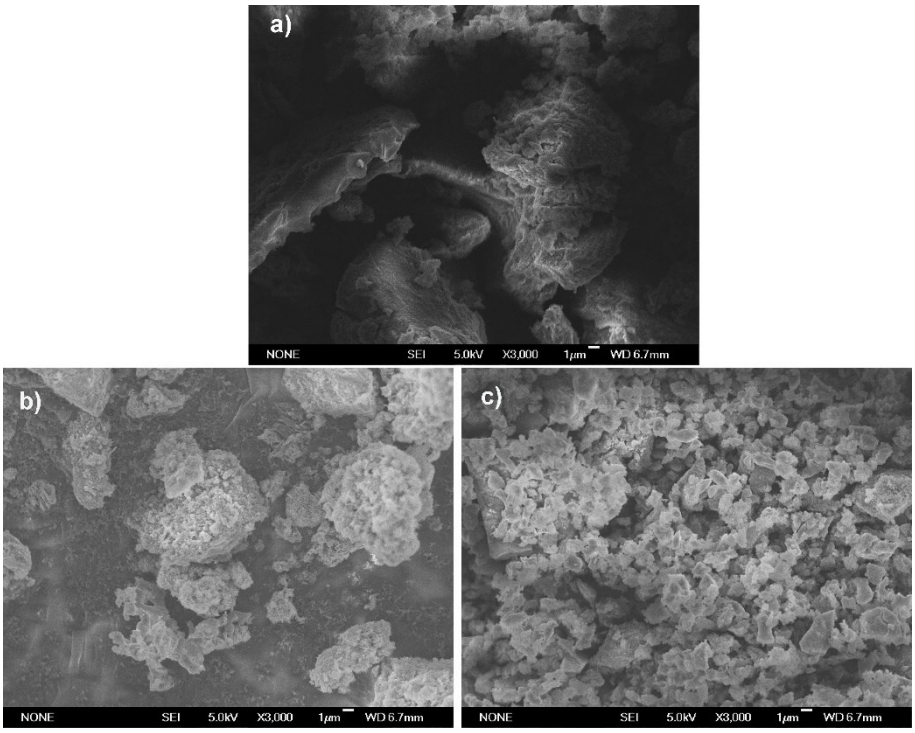

Fig. S3 SEM images: (a) CMP-3, (b) **KCMP-F3** and (c) **KCMP-M3**.

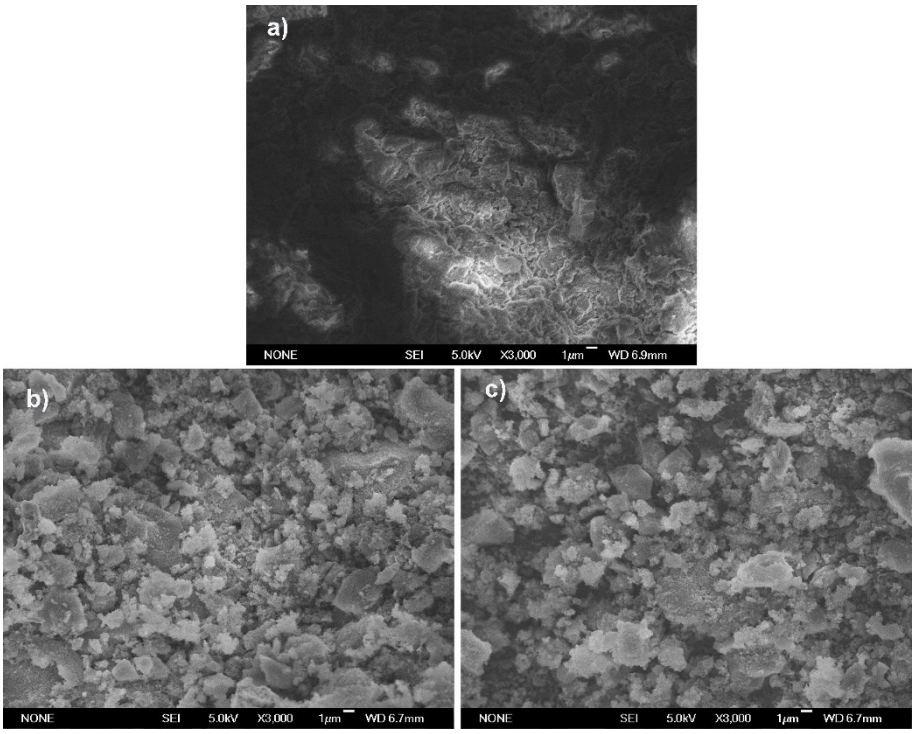

Fig. S4 SEM images: (a) CMP-4, (b) **KCMP-F4** and (c) **KCMP-M4**.

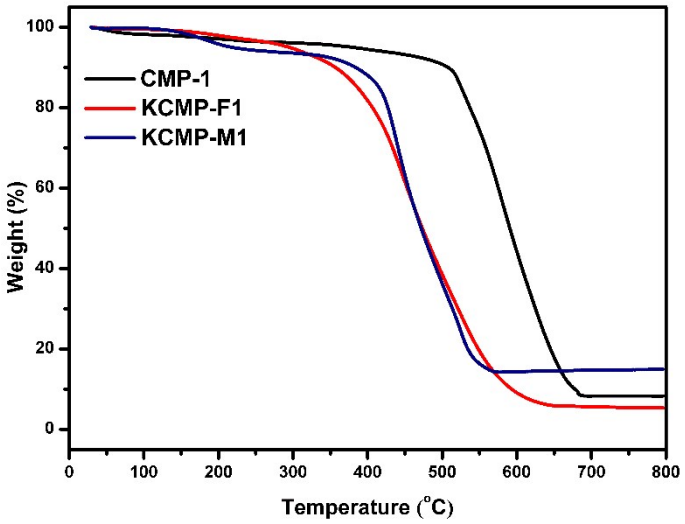

Fig. S5 Thermogravimetric analysis (TGA) of CMP-1, **KCMP-F1** and **KCMP-M1**.

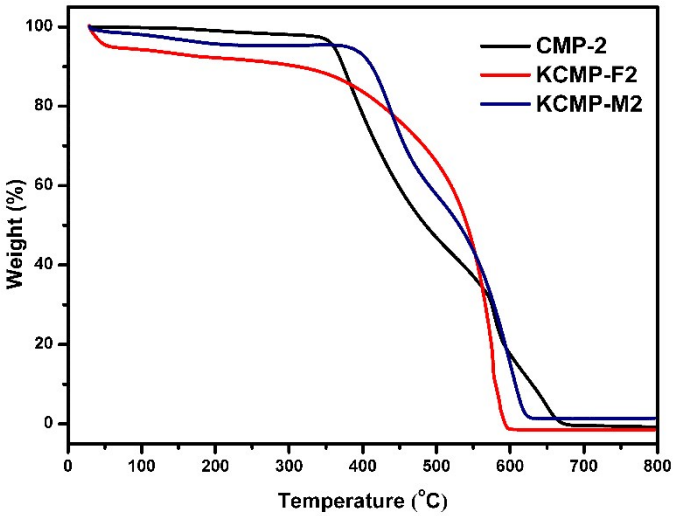

Fig. S6 TGA of CMP-2, **KCMP-F2** and **KCMP-M2**.

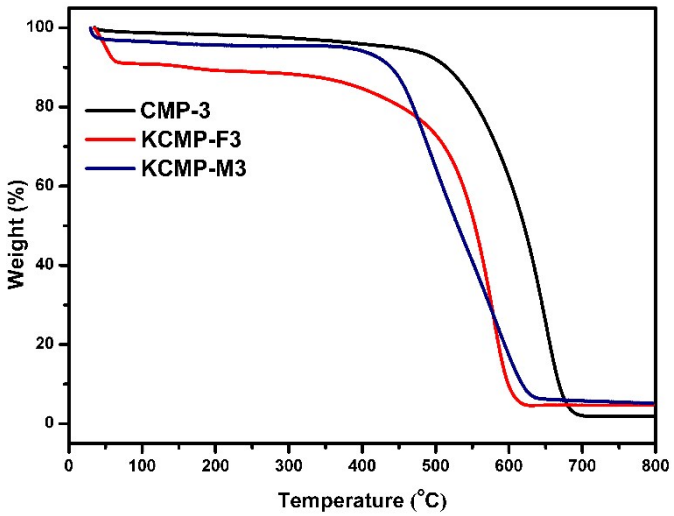

Fig. S7 TGA of CMP-3, **KCMP-F3** and **KCMP-M3**.

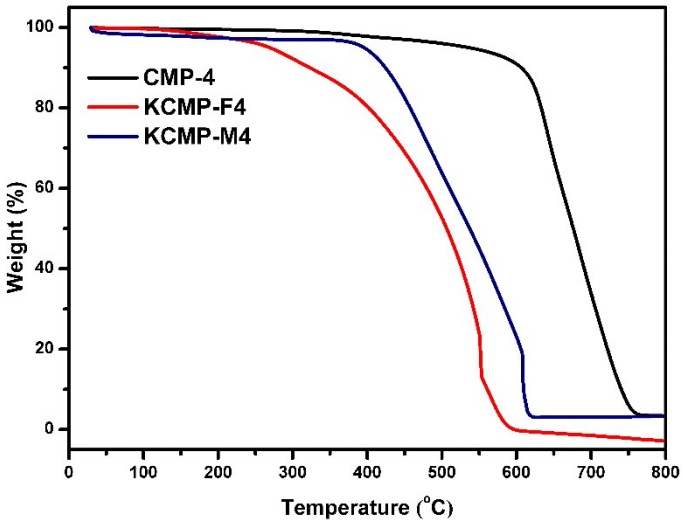

Fig. S8 TGA of CMP-4, **KCMP-F4** and **KCMP-M4**.

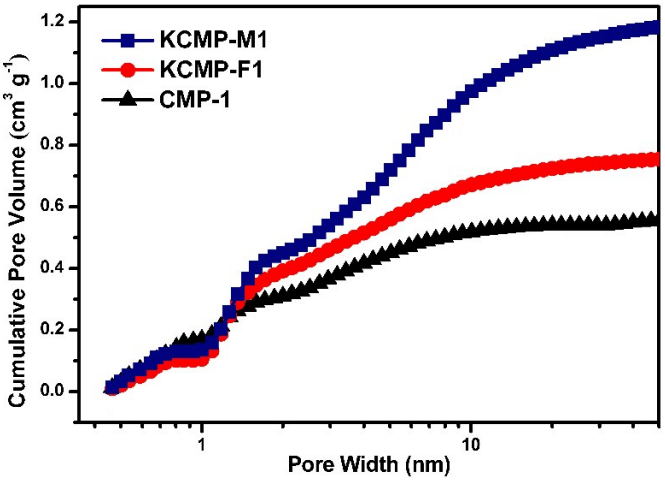

Fig. S9 Cumulative pore volume distributions of CMP-1, **KCMP-F1** and **KCMP-M1**.

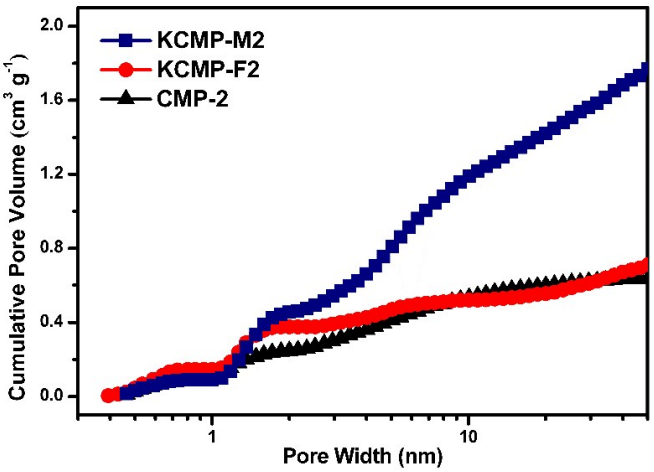

Fig. S10 Cumulative pore volume distributions of CMP-2, **KCMP-F2** and **KCMP-M2**.

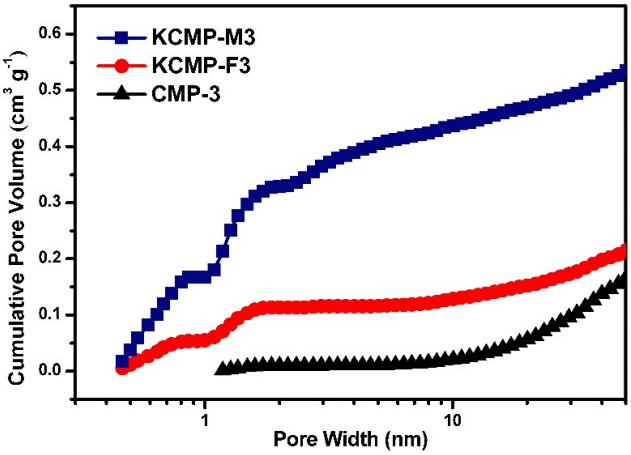

Fig. S11 Cumulative pore volume distributions of CMP-3, **KCMP-F3** and **KCMP-M3**.

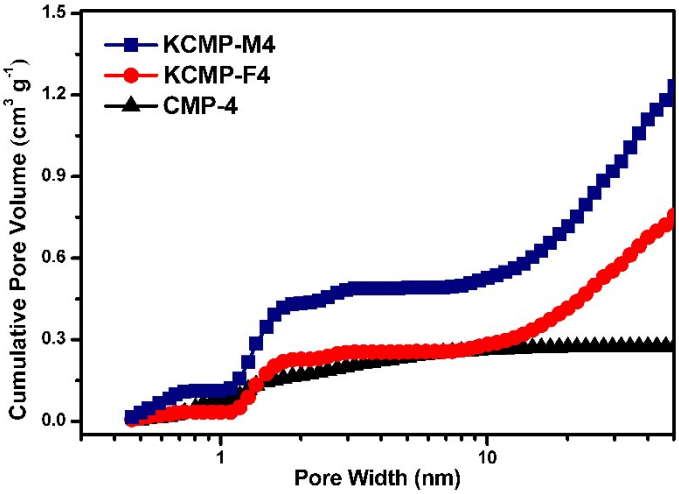

Fig. S12 Cumulative pore volume distributions of CMP-4, **KCMP-F4** and **KCMP-M4**.

Calculations of the isosteric heats of CO_2 adsorption (Q_{st}):

The CO_2 Q_{st} was modeled using a virial-type expression with the parameters a_i and b_i, as following:

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

Where, P is the pressure of the adsorption, N is the uptake, T is the temperature, a_i and b_i are the virial coefficirnts, and m and n determine the number of terms required to adequately describe the isotherm. The values of the virial coefficients a_0, a_1, a_2, a_3, a_4 and a_5 are then used to calculate the Q_{st}, as follows:

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i$$

While the Q_{st} shows the interactions between the CO_2 molecules and the porous skeletons.

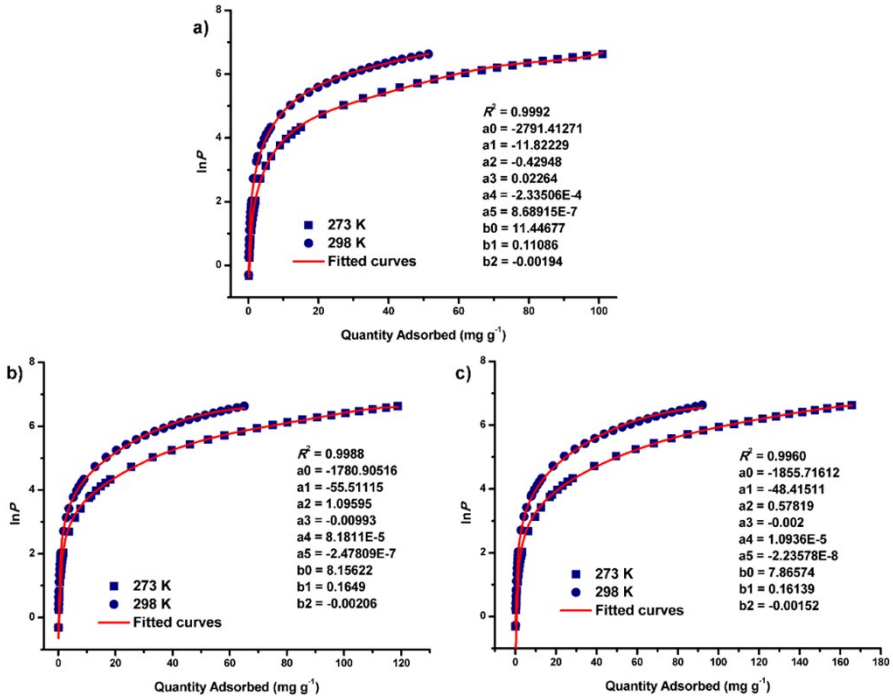

Fig. S13 Fitted CO_2 adsorption isotherms of (a) CMP-1, (b) **KCMP-F1** and (c) **KCMP-M1**.

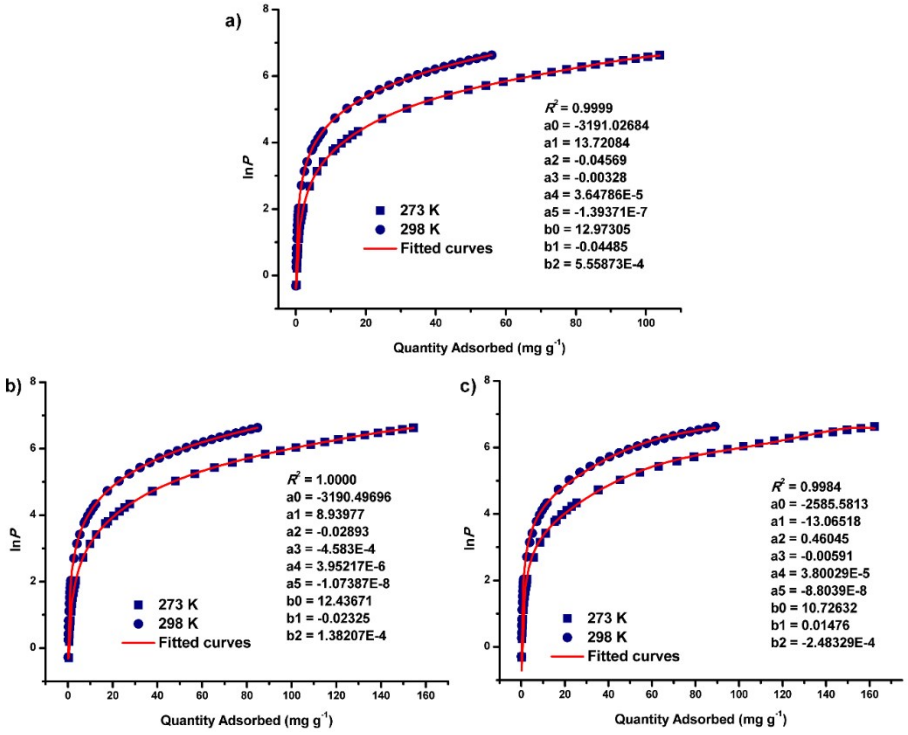

Fig. S14 Fitted CO_2 adsorption isotherms of (a) CMP-2, (b) **KCMP-F2** and (c) **KCMP-M2**.

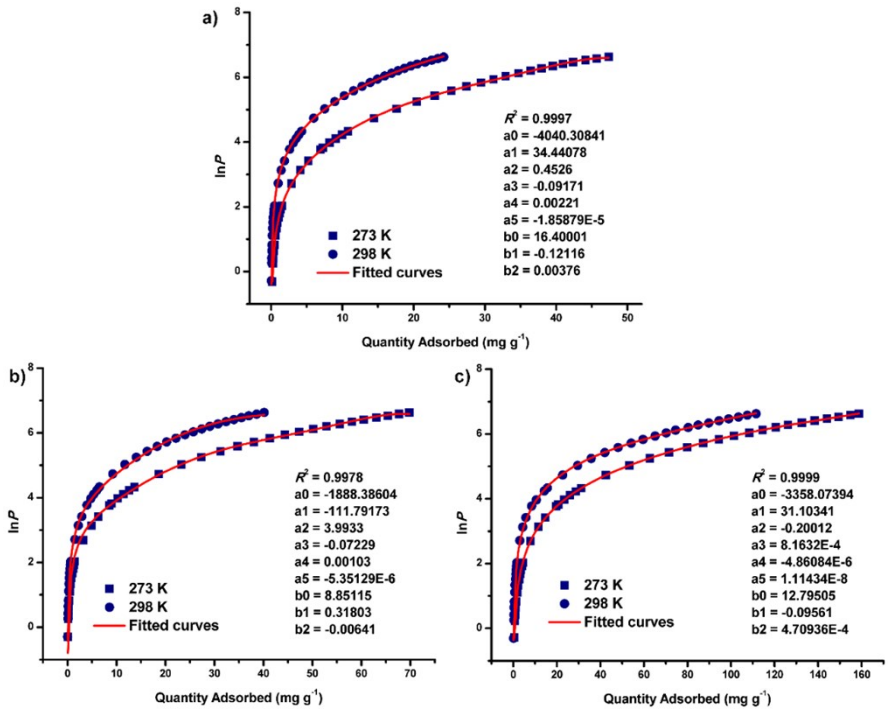

Fig. S15 Fitted CO_2 adsorption isotherms of (a) CMP-3, (b) **KCMP-F3** and (c) **KCMP-M3**.

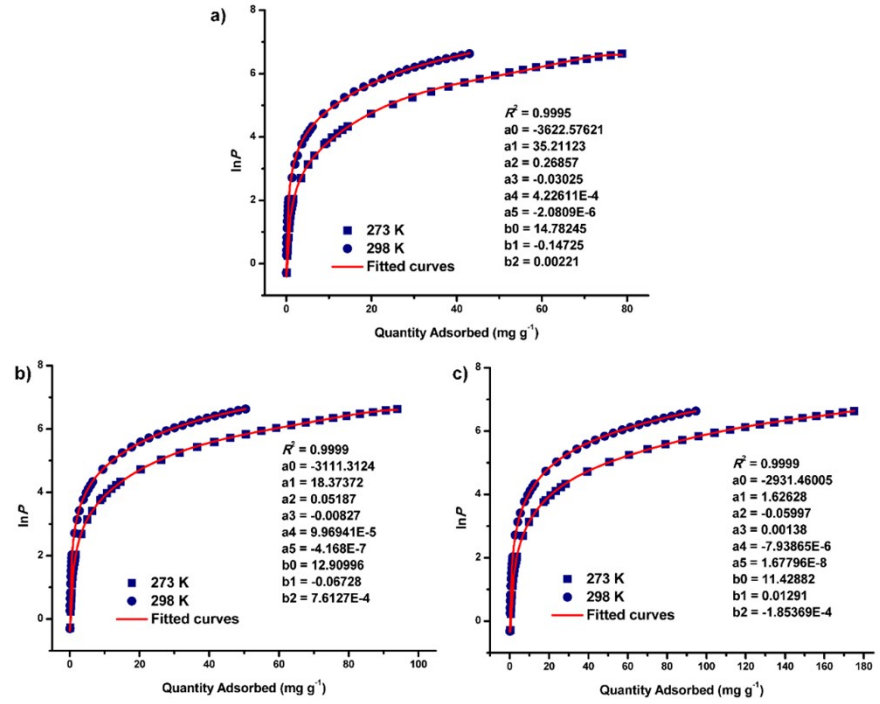

Fig. S16 Fitted CO_2 adsorption isotherms of (a) CMP-4, (b) **KCMP-F4** and (c) **KCMP-M4**.

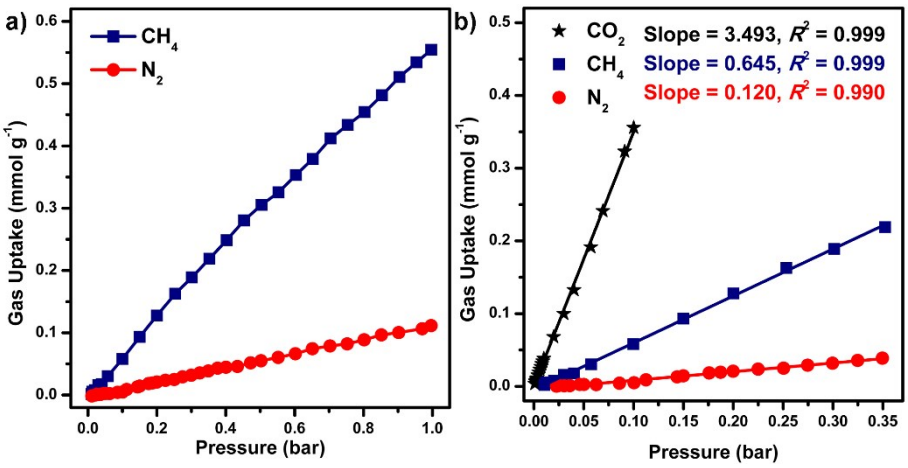

Fig. S17 (a) CH_4 and N_2 adsorption isotherms of **KCMP-M3** at 298 K. (b) Linear fitting of the low-pressure region of gas adsorption isotherms of **KCMP-M3**.