Electronic Supplementary Information for

Enhancing CO_2 adsorption of a Zn-phosphonocarboxylate framework by pore space partitions

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1. Materials and physical measurements

All reagents were purchased from commercial sources and used as received, except for the H_4pbdc, which was synthesized by the method described previously. IR spectra were measured on a Nicolet 470 FT-IR spectrometer in the range 4000 – 400 cm^{-1} with KBr pellets. Absorptions are described as follows: very strong (*vs*), strong (*s*), medium (*m*), weak (*w*), shoulder (*sh*), and broad (*br*). Powder X-ray diffraction (PXRD) patterns were measured using a Bruker D8 powder diffractometer with Cu *K*α radiation (λ = 1.5406 Å). The simulated powder patterns for the three iso-structures were calculated using Mercury 1.4. The phase purity of the bulk products were determined by comparison of the simulated and experimental PXRD patterns. Thermogravimetric-Mass analysis (TG-MS) experiments were carried out on the TA Q600 analyzer in the temperature range of 30–500 ^{o}C under N_2 flow with a heating rate of 10 $^{o}C\cdot min^{-1}$. SEM images for each as-made sample were obtained on a Philips XL-30 scanning electron microscope. CO_2 (288K and 298 K) and N_2 (298 K) adsorption isotherms were measured on IGA adsorption apparatus. Before each adsorption experiment, all the samples were degassed at 150 °C for 8 hours.

2. Synthesis of ZnPC-2, HPYR@ZnPC-2, HPIP@ZnPC-2

ZnPC-2: A solution of H_4pbdc (0.051 g, 0.2 mmol) and triethylamine (0.082 g, 0.8 mmol) in isopropanol (5 ml) was carefully layered onto a solution of $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.065 g, 0.3 mmol) in deionized water (5 mL) in a telflonlined stainless steel autoclave (15 mL), and then heated at 140 °C for 3 days, followed by cooling at room temperature. Colorless rod-shape crystals of **ZnPC-2** were collected by filtration (Yield: 33 % based on H_4pbdc).

HPYR@ZnPC-2 and HPIP@ZnPC-2: The procedure for preparation of HPYR@ZnPC-2 and HPIP@ZnPC-2 was similar to that of **ZnPC-2** except replacing tea by pyrrolidine for HPYR@ZnPC-2 and by piperidine for HPIP@ZnPC-2. Light yellow rod-like crystals of Hpyr@ZnPC-2 and Hpip@ZnPC-2 were collected by filtration (Yield: 42 % and 44 % respectively). For Hpyr@ZnPC-2, IR (cm^{-1}): 3434m, 3065w, 2959w, 2862w, 1614s, 1568m, 1435m, 1380m, 1209w, 1114m, 1011m, 989m, 777m, 729w, 687w, 573m, 455m. For Hpip@ZnPC-2 IR (cm^{-1}): 3434m, 3066w, 2863w, 1614s, 1568m, 1435m, 1380m, 1210w, 1114m, 1011m, 989m, 777m, 729w, 687w, 573m, 455m.

3. Crystal Structure determination

Suitable single crystals of HPIP@ZnPC-2 were mounted on glass capillaries and data collection were carried out on a Bruker Apex CCD diffractometer with graphite monochromated Mo Kα radiation (λ□= 0.71073 Å) at 293 K. Data reduction was performed with the SAINT and semi-empirical absorption corrections were applied by SADABS program. The structures were solved by direct methods using SHELXS program and refined with SHELXL program. The heavy atoms and other non-hydrogen atoms are directly obtained from difference Fourier map. The final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. Generally, C-bonded H atoms were placed geometrically and refined as riding modes. The hydrogen atoms on the lattice water and hydrated protons are hardly located from Fourier map, which are theoretically calculated.

Table S1. Crystallographic data and structure refinement

	ZnPC-2	**Hpyr@ZnPC-2**	**Hpip@ZnPC-2**
Formula	$C_{16}H_{12}O_{16}P_2Zn_3$	$C_{20}H_{27}NO_{19}P_2Zn_3$	$C_{21}H_{31}NO_{20}P_2Zn_3$
F.W.	718.31	843.51	875.52
Space group	I-42d	I-42d	I-42d
a (Å)	18.310(6)	18.450(4)	18.453(7)
b (Å)	18.310(6)	18.450(4)	18.453(7)
c (Å)	23.222(11)	23.201(7)	23.283(12)
V(Å^3)	7785(5)	7898(3)	7928(6)
Z	8	8	8
Dc (g cm^{-3})	1.215	1.400	1.442
μ(mm^{-1})	1.964	1.953	1.950
F(000)	2800	3320	3432
T(K)	293	293	293
Total collected	19410	19669	22955
Unique data, R(int)	3510, 0.058	4545, 0.165	4567, 0.105
Observed [$I > 2\sigma(I)$]	3105	3312	3048
GOF on F^2	1.21	0.96	0.98
Flack	0.00(6)	0.00(7)	0.00(7)
R_1,[a] wR_2[b] [$I>2\sigma(I)$]	0.0409, 0.1374	0.0540, 0.1314	0.0520, 0.1485
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.81, -0.47	0.76, -1.14	1.07, -0.43
CCDC	746203	776925	894708

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(Fo^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. The occupied volume, free volume, surface area per unit cell calculated by a probe atom (radii 1.84 Å) and the theoretical surface area calculated by the formula of Å^2/(Dc × V), V = cell volume, and Dc = density of the sample.

	Occupied Volume (Å^3)	**Free Volume (Å^3)**	**Surface Area (Å^2)**	**Surface area (m^2/g)**
ZnPC-2	7058.01	758.79	1429.28	1497
HPYR@ZnPC-2	7427.49	470.19	909.17	822
HPIP@ZnPC-2	7499.69	428.48	811.91	709
MOF-5	10515.95	6721.54	3669.25	2739

Table S3. Adsorption and selectivity of CO_2 over N_2 for some amino-modificated MOFs

MOF	**Strategy** [a]	**CO_2 (mmol/g)**[b]	**Selectivity** [c]	**Q_{st}** [d] **(kJ/mol)**	**Ref**
bioMOF-1	PE	0.32		35	16a
TMA-bioMOF-1		0.46		40	16a
TEA-bioMOF-1		0.53		35	16a
TBA-bio-MOF-1		0.47		60	16a
Cu(BTTri)	PE	0.65	19	20	16b
en-Cu(BTTri)		0.52	44	90	16b
mmen-Cu(BTTri)		2.1	165	96	16b
ZnPC-2	PSP	0.26	9	40	Here
Hpyr@ZnPC-2		0.71	27	36	Here
Hpip@ZnPC-2		1.13	94	32	Here

[a] PE: Post-Exchange with amines, PSP: pore space partition; [b] CO_2 uptake amount at 0.15 bar and 298K, [c] selectivity is calculated by the method mentioned in ref. 2e; [d] Q_{st} at zero coverage.

Figure S1 (a) 6-connected Zn_3-SBU and tritopic ligand of pbdc in the rutile-type framework; (b-d) the 3D framework of ZnPC-2, HPYR@ZnPC-2, HPIP@ZnPC-2 respectively (up: the (3,6)-connected topology, below: the related 3D structure. Symmetry code used to generate the pyrrolidine and piperidine: i: 0.5-x, y, 1.75-z; ii: x, 1.5-y, 1.25-z)

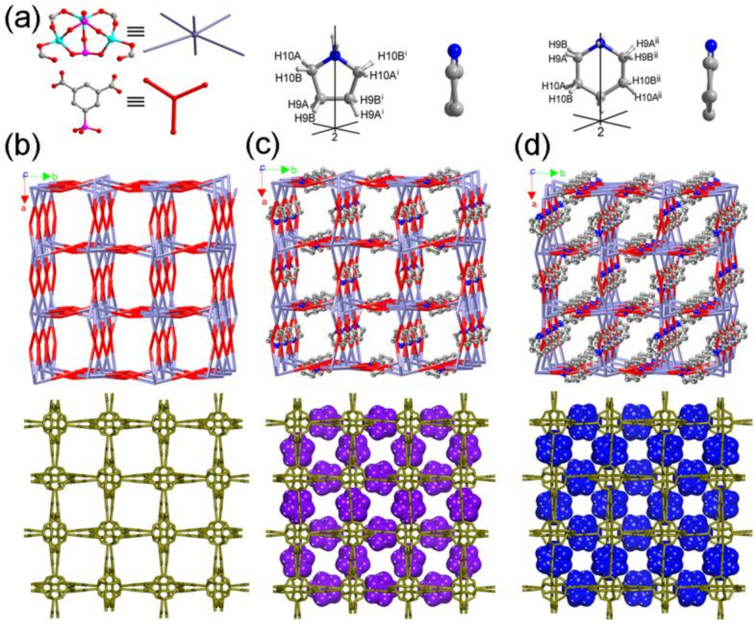


Figure S2. the PXRD data of ZnPC-2 (a), HPYR@ZnPC-2 (b) and HPIP@ZnPC-2 (c) showing well agreement with simulated one for as-made, activated and after adsorbed samples (red: the simulated data; black: as-made sample; blue: activated sample; dark yellow: after adsorption)

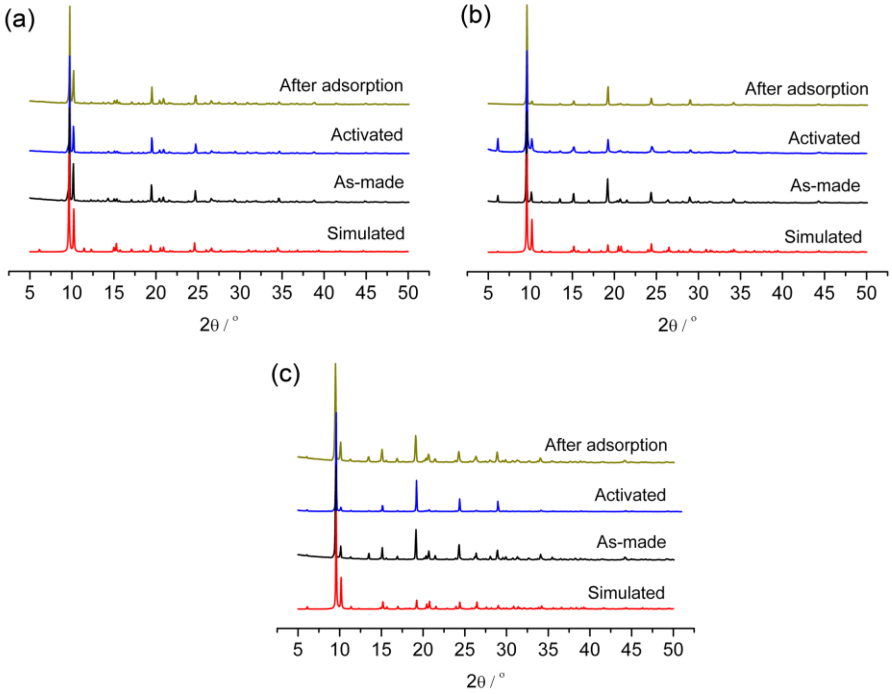


Figure S3. The SEM images for ZnPC-2 (a), HPYR@ZnPC-2 (b) and HPIP@ZnPC-2 showing the pure rod-like morphology.

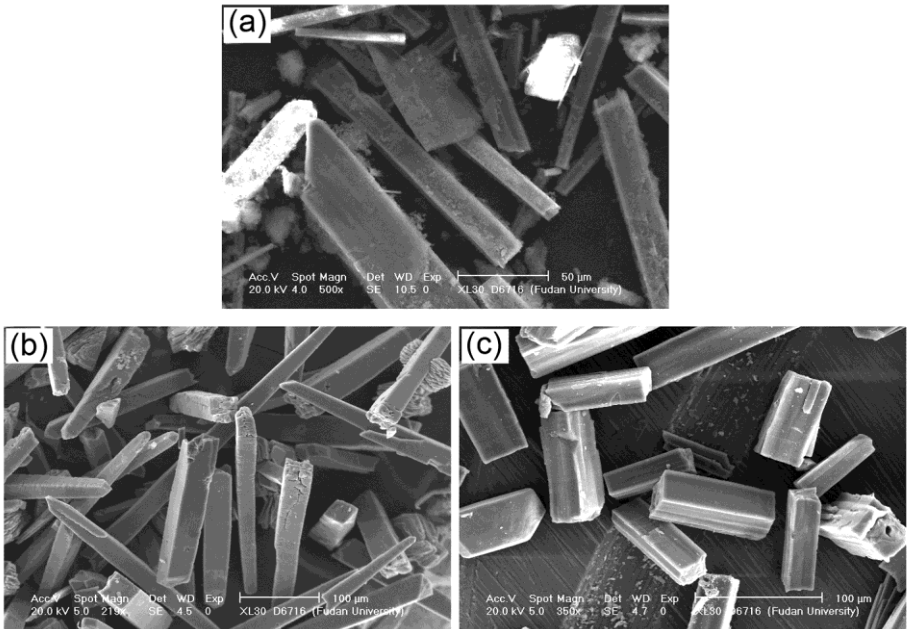


Figure S4. the isostructures of ZnPC-2 (a), HPYR@ZnPC-2 (b) and HPIP@ZnPC-2 (c) in packing structures showing along *c* and *a* axes (the pore size along *c* axis is slightly decreased after embedded HPYR or HPIP, which are strong bonded to host framework by hydrogen bonding interactions)

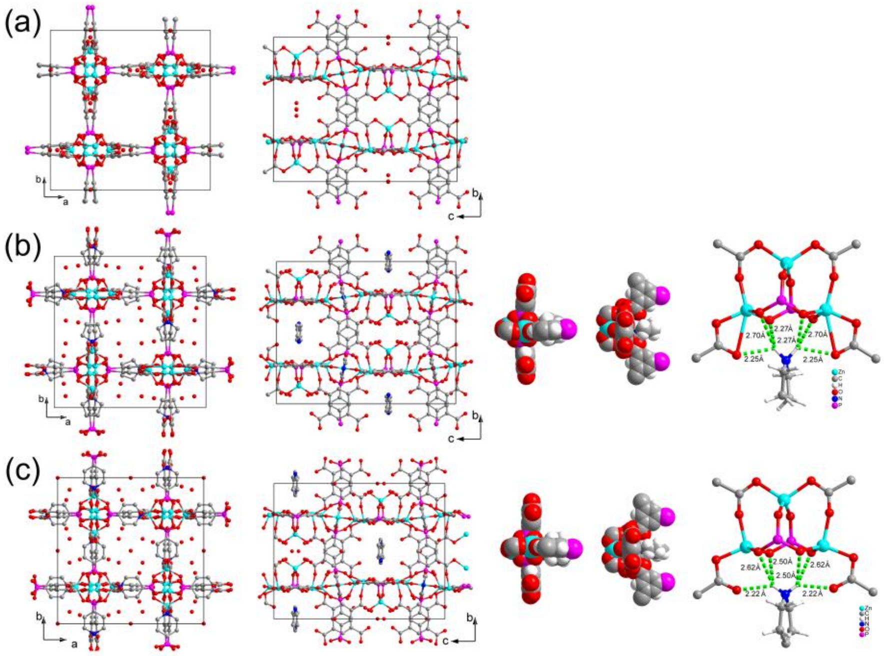


Figure S5. The size of the entrance for ZnPC-2 (a), HPYR@ZnPC-2 (b) and HPIP@ZnPC-2 are calculated to be ca. 6.8, 5.3 and 4.8 Å respectively, based on the Connolly surface (Connolly radius sets to be 1.4 Å and vdW scale factor sets to be 1.)

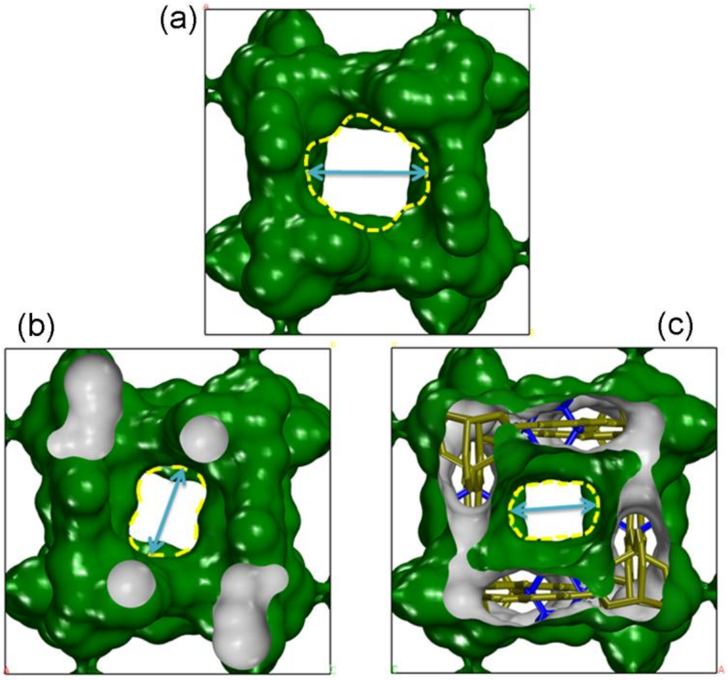


Figure S6. The TG-MS data of Hpyr@ZnPC-2 (a) and Hpip@ZnPC-2 (b) showing the release of template agent after decomposition of the host framework (the samples are washed with water (10 mL ×3) and acetone (10 mL ×3), then degased at room temperature)

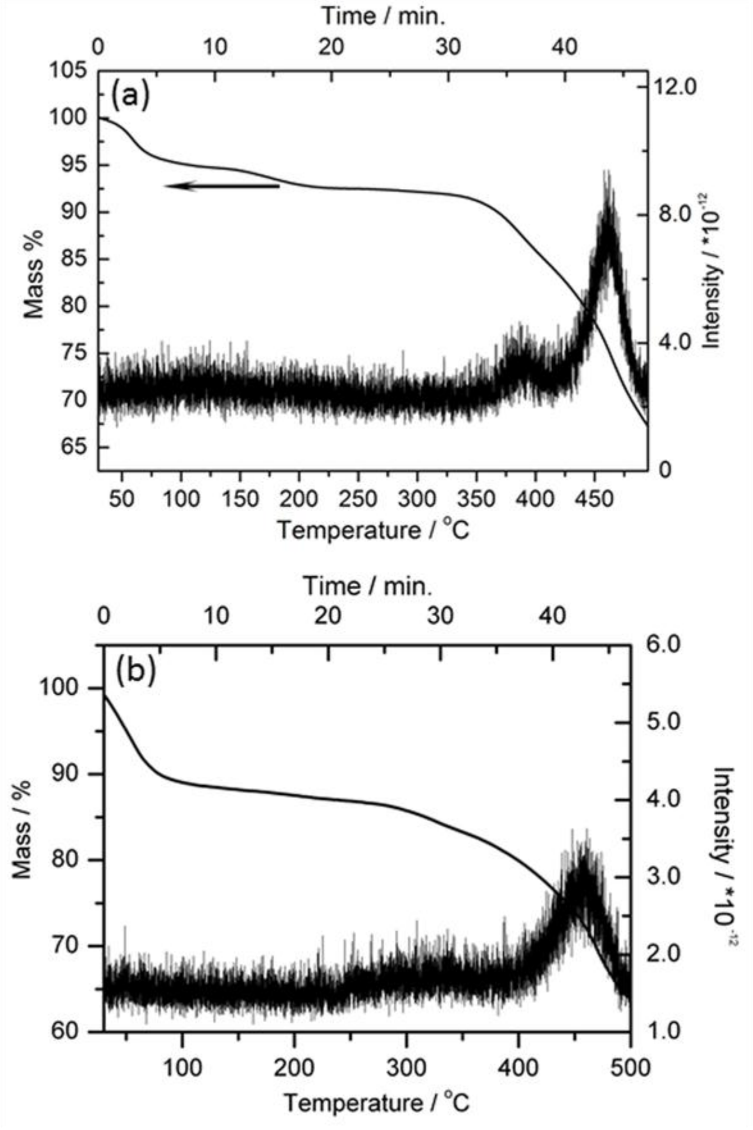


Figure S7. The CO_2 adsorption and desorption data of ZnPC-2 and HPIP@ZnPC-2 recorded on ASAP 2020 at 300 K.

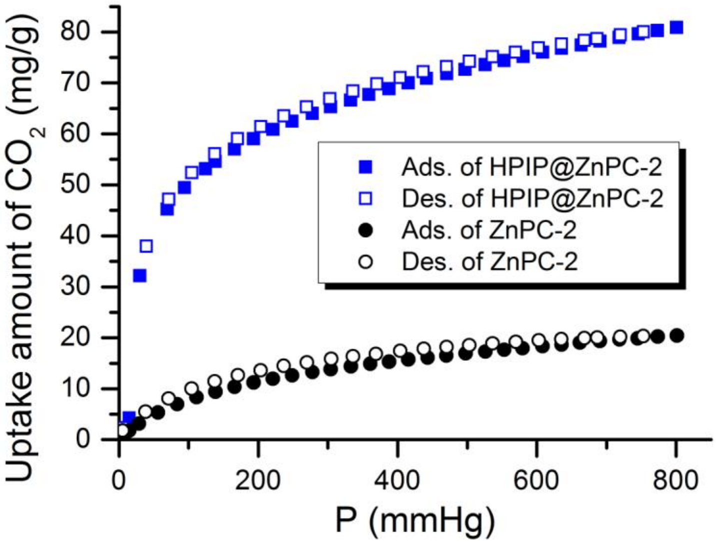
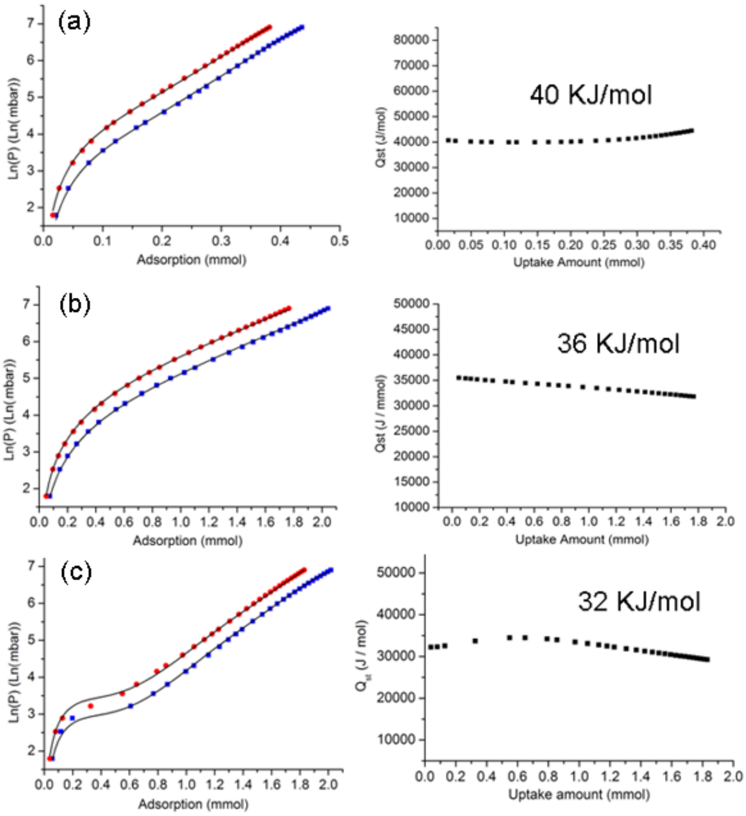


Figure S8. The adsorption data of CO2 at 298 and 288 K which were fitted by Virial Method and the calculated Q_{st} (a) for ZnPC-2; (b) for HPYR@ZnPC-2; (c) for HPIP@ZnPC-2.



Eq. (1): $$Ln(P) = Ln(x) + \frac{1}{T}\sum_{i=0}^{m} a_i x^i + \sum_{i=0}^{n} b_i x^i \tag{1}$$

Eq. (2): $$Q_{st} = -R\sum_{i=0}^{m} a_i x^i \tag{2}$$

Figure S9. The selective adsorption ability of Hpip@ZnPC-2 for the mixed gas of CO_2 and N_2 at 32 ºC measure on a thermogravimetric apparatus (The gas cycling experiment was carried out by using a flow of CO_2 and N_2 (1: 4 in V/V) and followed by a flow of pure N_2 gas at atmospheric pressure, the sample was activated using the thermogravimetric apparatus at 150 °C for 3h flow and then cooling down under N_2)