Supporting Information

Ligand-based solid solution approach to stabilisation of sulphonic acid groups in porous coordination polymer $Zr_6O_4(OH)_4(BDC)_6$ (UiO-66)

Maw Lin Foo,[a,d] Satoshi Horike,[b,c] Tomohiro Fukushima,[b] Yuh Hijikata,[b] Yoshiki Kubota,[e] Masaki Takata[f] and Susumu Kitagawa*[a,b,d]

[a] *Japan Science and Technology Agency, ERATO, Kitagawa Integrated Pores Project, Kyoto Research Park Bldg #3, Shimogyo-ku, Kyoto 600-8815, Japan*

[b] *Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. Fax: +81-75-383-2732; Tel: +81-75-383-2733*

[c] *Japan Science and Technology Agency, PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

[d] *Institute for Integrated Cell-Material Sciences (WPI-iCeMS), Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan*

[e] *Osaka Prefecture University*

[f] *Japan Synchrotron Radiation Research Institute/SPring-8 Sayo-gun, Hyogo 679-5198 (Japan)*

**E-mail: kitagawa@sbchem.kyoto-u.ac.jp*

Supplementary Information Contents Page

^{1}H NMR Digestion and Analysis. Approximately 10 mg of microcrystalline UiO-66 was digested by sonication in 570 μL of d^6-DMSO and 30 μL of 49% HF (caution!). After complete dissolution of the material, the solution was used to collect a ^{1}H NMR spectrum recorded on a JEOL ECA spectrometer (500 MHz).

Thermal Gravimetric Analysis. TGA data was collected from room temperature to 700 ^{o}C with a ramp rate of 10^{o}C/min in flowing N_2 (20 ml/min) using a Rigaku TG8120 TGA.

PXRD Analysis. Laboratory PXRD data were collected at ambient temperature on a Rigaku RINT powder X-ray diffractometer at 40 kV, 40 mA for Cu K_α with a 2 theta range of 5-45^o, step size of 0.02^o with 3s dwell time. Lattice parameters were calibrated with Si standard. Cell parameters were obtained via least square refinements via Celref v3 (Laboratoire des Materiaux et du Génie Physique de l'Ecole Supérieure de Physique de Grenoble http://www.inpg.fr/LMGP/) software. Le-Bail fitting was obtained by using Rietica v1.7.7 (http:// http://www.rietica.org/) software. A pseudo-voigt function was used for peak profile and background was set to ‘automatically smoothed’.

Synchrotron data were collected at ambient temperature at Spring-8 synchotron source (Hyogo, Japan) in the transmission mode with image plate. Lattice parameters were calibrated with ceria standard.

FT-IR Analysis.

FT-IR spectra were collected using a Nicolet iD5 diamond ATR.

Adsorption measurements

N_2 and CO_2 gas adsorption. N_2 surface area adsorption experiments were conducted at 77 K using a Bel-Mini with ultra-high purity nitrogen gas. CO_2 adsorption experiments were made at 288 K and 293 K using a Bel-Mini with ultra-high purity CO_2

Acetone vapour adsorption. Acetone adsorption/desorption measurements were collected at 298 K using Belsop-8 volumetric adsorption apparatus. The acetone was degassed via free-pump-thaw procedure.

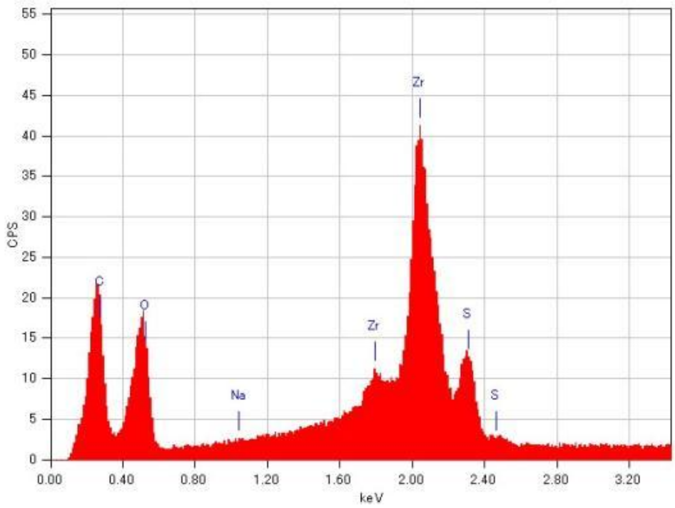


Fig. S1 SEM-EDX of **2**⊃G showing absence of Na in the framework.

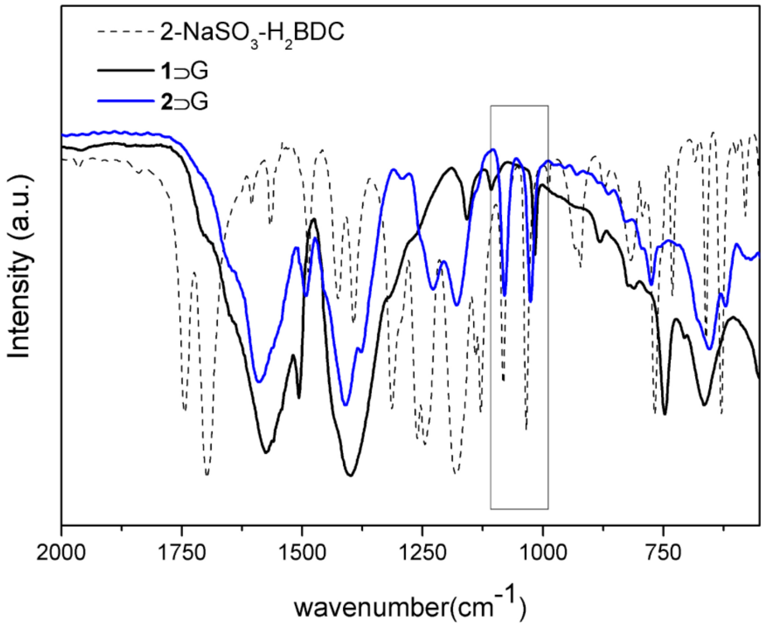


Fig. S2 IR spectra of **1**⊃G, **2**⊃G and ligand 2-NaSO$_3$-H$_2$BDC. The relevant S=O bands are highlighted.

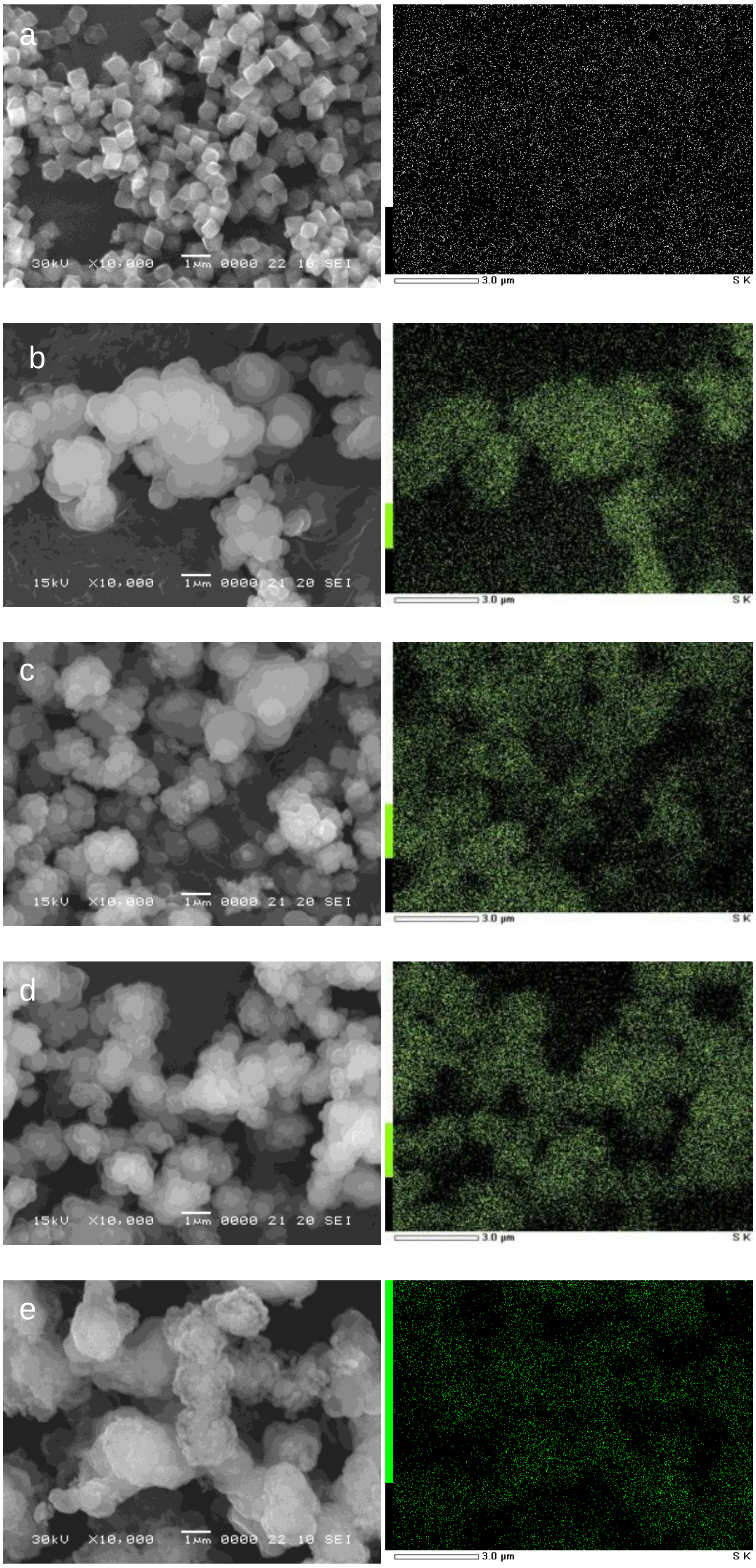


Fig. S3 SEM and sulphur EDX mapping of a: **1**⊃G; b: **1**/**2** (*x* = 0.18)⊃G; c: **1**/**2** (*x* = 0.40)⊃G; d: **1**/**2** (*x* = 0.69)⊃G and **2**⊃G.

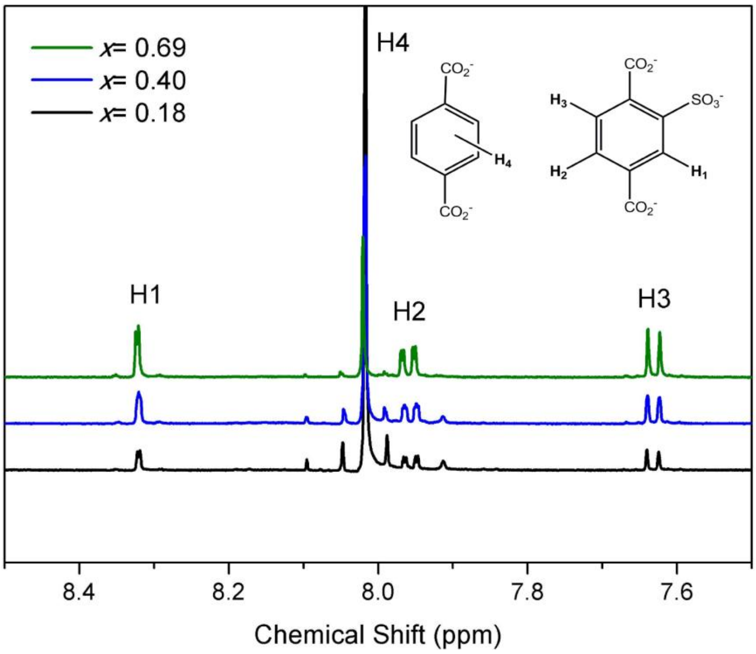


Fig. S4 ^{1}H NMR of digested mixed ligand frameworks **1/2** (*x*=0.18, 0.40 and 0.69). ^{1}H NMR (500MHz, d^6-DMSO/HF) δ 8.32 (d, 1H, J=1.0 Hz, H1) 7.96 (dd, 1H, J=1.0Hz, 4.0 Hz, H2) 7.63 (d, 1H, J=4.0 Hz, H3) 8.02(s, 1H, H4). The ratio of BDC to 2-HSO_3-BDC ligand in the frameworks was obtained from the ratio of normalized H4/H1 integrals.

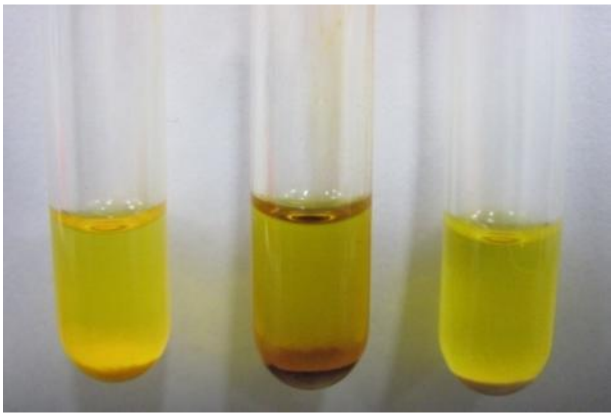


Fig. S5 a) **1**⊃indicator (left), and **1/2** (*x*=0.18)⊃indicator (center) and **2**⊃indicator (right).

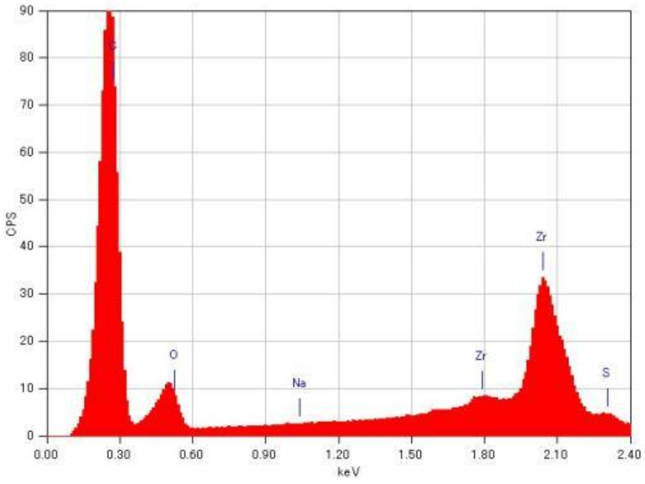


Fig. S6 SEM-EDX of **1/2** (*x* = 0.18), showing the absence of Na in the framework.

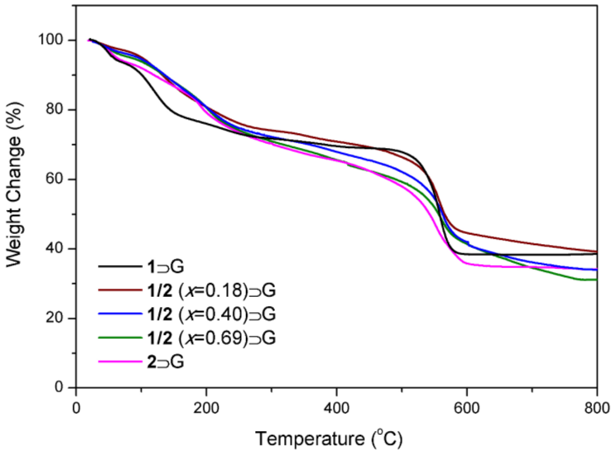


Fig. S7 TGA of **1**⊃G, **1**/**2** (*x* = 0.18, 0.40, 0.69)⊃G and **2**⊃G in flowing N_2.

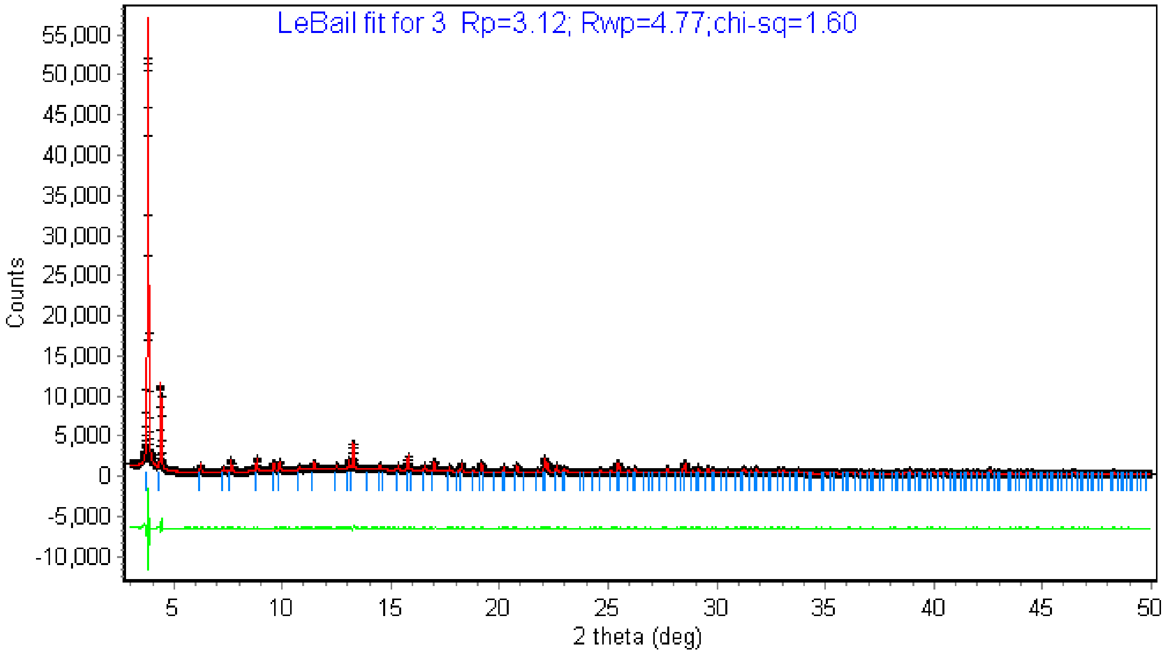


Fig. S8 Le-Bail fitting of **1**(*x* = 0.18) using synchrotron X-ray data. Crosses denote experimental points. The black crosses denote observed data, red line denotes calculated profile, blue bars denote positions calculated for Bragg reflections and green line is the difference plot between observed and calculated profile. R_p=3.12, R_{wp}=4.77, χ^2=1.60.

Table 1 BET and Langmuir surface areas for **1**, **1/2** (*x* = 0.18, 0.40, 0.69), and **2**.

	BET (m^2/g)	**Langmuir(m^2/g)**
1	1210	1361
1/2 (*x*=0.18)	1222	1436
1/2 (*x*=0.40)	503	655
1/2 (*x*=0.69)	195	255
2	5	6

For adsorption isotherms, fits were performed using the virial equation with R software.

$\ln(p) \sim \ln(n) + (1/T) * (a_0 + a_1 * n + a_2 * n^2 + a_3 * n^3 + a_4 * n^4 + a_5 * n^5) + (b_0 + b_1 * n + b_2 * n^2 + b_3 * n^3)$

where p=pressure/ Pa
n = amount of adsorption / mmol·mol^{-1}
T= temperature / K (288 K or 293)
a_0, a_1, a_2, a_3, a_4, a_5, b_0, b_1, b_2, b_3= fitting parameters

The heat of adsorption, Q_{st} in kJ·mol^{-1}

$$Q_{st} = -\mathrm{R}\sum_{i=0}^{5} a_i n^i$$

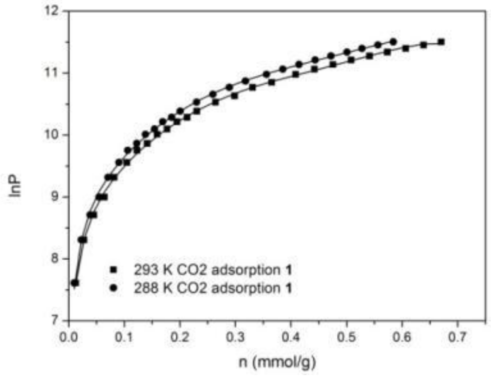
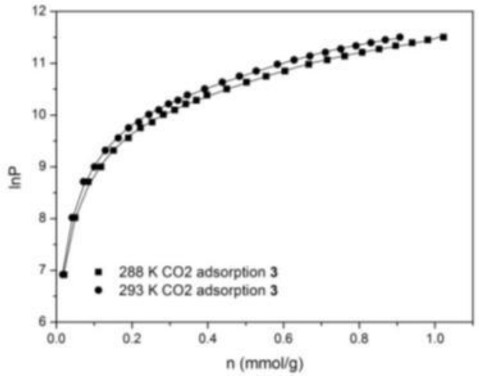


Fig. S9 (a) Adsorption isotherm of **1** for CO_2 at 288 and 293 K. Solid lines denote fit using virial equation. Obtained parameters: a_0 = -2641, a_1 = 1153, a_2 = 1682, a_3= -32672, a_4= 70589, a_5= -38660; b_0 = 21.22, b_1= -9.88, b_2= 42.55, b_3= -50.19.



s

Fig. S9 (b) Adsorption isotherm of **1/2** (*x* = 0.18) for CO_2 at 288 and 293 K. Solid lines denote fit using virial equation. Obtained a_0 = -3457, a_1 = 5094, a_2 = -12337, a_3= 16934, a_4= -13566, a_5= 4703; b_0 = 22.79, b_1= -12.11, b_2= 18.38, b_3= -8.45.

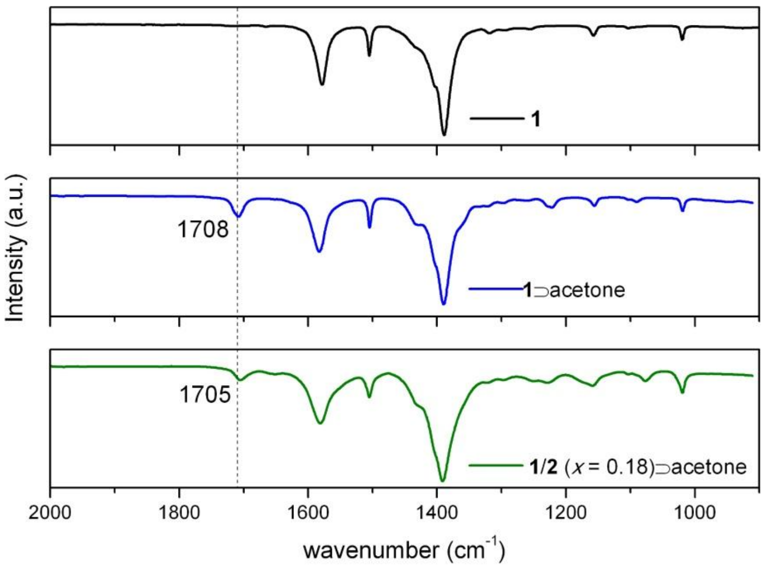


Fig. S10 IR spectra of **1**, **1**⊃acetone and **1**/**2** (*x* = 0.18)⊃acetone with emphasis on the acetone C=O stretch (dotted line).