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

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By adopting a ligand-based solid solution approach, the sulphonic acid functional group can be successfully incorporated into a porous coordination polymer with UiO-66
10 **structure type. $Zr_6O_4(OH)_4(BDC-SO_3H)_{1.1}(BDC)_{4.9}$ possess enhanced heat of adsorption for carbon dioxide and acetone compared to $Zr_6O_4(OH)_4(BDC)_6$.**

In the past decade, the field of metal organic frameworks (MOF) or porous coordination polymers (PCPs)[1] has seen explosive
15 growth due to the modular nature of their synthesis, crystalline nature and porous structures. Possible applications of these materials are in gas separation/storage, catalysts, ion conductivity and drug delivery.[2] However, for practical usage, PCPs should be thermally, hydrolytically and chemically stable.[3]
20 $Zr_6O_4(OH)_4(BDC)_6$ or **1**, is a recently reported compound that exhibits robust stability due to its strong Zr-O bonds and 12-coordinated 'Maltese Cross' Structural Building Unit (SBU).[4] By utilizing 2-substituted 1,4-benzene carboxylic acids such as -Br, -NH_2 and -NO_2, various functionalised UiO-66 can be
25 successfully synthesized.[5]

The incorporation of sulphonic acid, -SO_3H functional group into PCPs is potentially interesting due to the strong acidity of its acidic proton. This renders the resultant material useful for proton conductivity and catalysis, as best embodied by Nafion.[6]
30 However, despite reports of PCPs with *alkyl* sulphonic acid groups using post-synthetic methods,[7] reports of MOFs with *aryl* sulphonic acid groups has thus far been limited. Recently, Cr-MIL-101 with aryl sulphonic acid functional groups has been reported using the sodium salt of 2-sulfonylterephtalic acid (2-
35 $NaSO_3$-H_2BDC) as the starting material.[8] The sodium ion was exchanged in-situ with H^+ by HCl in the reaction solvent. Another approach is to graft sulphonic acid groups via post-synthetic treatment.[9]

To achieve modulation of the physical properties of a target PCP
40 crystal structure in a designed fashion, one approach is to combine different ligands of the same denticity in different proportions while keeping the crystal structure invariant. This approach has been termed solid solution[10] (from classical solid state chemistry), mixed MOFs[11] (MIXMOF) or multivariate
45 MOFs.[12] By using this strategy, properties such as optimization of gas separation property,[10,12] catalytic activity[11] have been successfully modulated.

In this communication, we demonstrate the synthesis of an aryl

substituted sulphonic acid,
50 $[Zr_6O_4(OH)_4(HSO_3BDC)_6]⊃(CH_3COOH, DMF, H_2O)$ or **2**⊃G via in-situ ion exchange of Na^+ for H^+ of the $NaSO_3$-H_2BDC ligand in the acidified reaction solvent. However, the synthesized PCP is unstable to loss of guest molecules, strongly limiting its utility. In order to overcome this instability and obtain a high surface area
55 porous solid, a ligand-based solid solution approach to *stabilisation* was employed using a mixed ligand approach. By utilising a mixture of 2-$NaSO_3$-H_2BDC and H_2BDC as starting ligands, it is postulated that at certain intermediate compositions, the resultant mixed ligand PCP will be stable to evacuation since
60 **1** is stable but **2** is not. Indeed, we succeeded in obtaining a series of frameworks, $Zr_6O_4(OH)_4(HSO_3BDC)_{6x}(BDC)_{6-6x}⊃G$ or **1/2** (x = 0.18, 0.40, 0.69)⊃G where (x = fraction of sulphonated ligand) and observed that when x = 0.18, the resultant PCP is stable to evacuation.
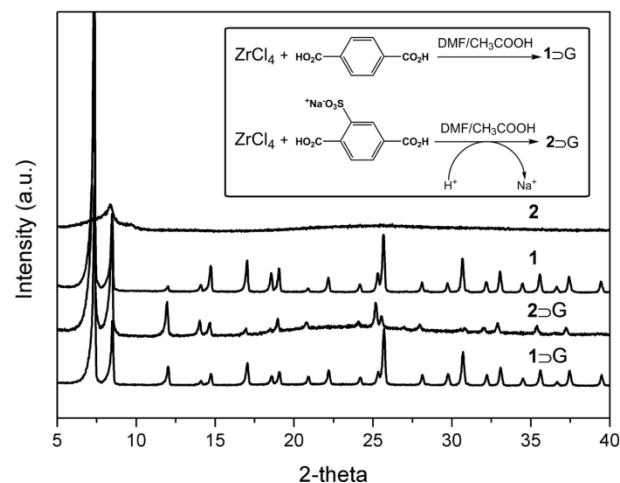
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Fig. 1 Powder XRD of as-synthesized and evacuated state of **1** and **2**.

2⊃G was synthesized in polycrystalline form by mixing $ZrCl_4$,
70 2-$NaSO_3$-H_2BDC with a 9:1 DMF: acetic acid mixture and heating at 120 °C. All attempts at formation of single crystals did not succeed. Addition of acetic acid is crucial since no crystalline product was formed without its presence. The role of acetic acid is presumably a modulator for slowing down the reaction of Zr^{4+}
75 with the ligand via formation of a zirconium acetate complex, similar to the revised synthesis of UiO-67,

$Zr_6O_4(OH)_4(BPDC)_6$.[13] The X-ray diffraction (XRD) pattern (Fig. 1) verifies that a crystalline structure isoreticular to **1**⊃G has been synthesized, which can be indexed to $a = 20.885(5)$ Å. The lattice parameter of **2**⊃G is slightly larger than the parameters obtained from **1**⊃G synthesized under similar conditions, $a = 20.786(6)$ Å. No sodium ions was detected in **2** via SEM-EDX, X-ray fluorescence and ^{23}Na NMR suggesting the sulphonate oxygen may be binding to Zr or in-situ ion-exchange of Na^+ for H^+ has occurred. From infra-red (IR) spectroscopy, the symmetric O=S=O (1080 cm^{-1}) and S=O (1024 cm^{-1}) stretching frequencies of **2** did not vary greatly from the free ligand, suggesting that the environment of the sulphonate group is quite similar in the PCP and free ligand, i.e. no binding of the sulphonate oxygen to Zr has occured. However, in comparison to **1**, which retains porosity of evacuation, **2** was unstable to removal of guests, losing crystallinity even after evacuation at room temperature (Fig. 1). It is known that on evacuation, the SBU of UiO-66 undergoes rearrangement due to loss of μ^3-OH with no loss of crystallinity.[4] However for **2**⊃G, this same loss induces significant loss of crystallinity. This is probably due to the anionic charge or protons from the sulphonate group interacting with the 12-coordinated SBU.

In order to obtain a robust framework stable to evacuation, a series of frameworks with different proportions of H_2BDC and 2-$NaSO_3$-H_2BDC ligands, **1/2** (x)⊃G were synthesized. The initial starting stiochiometry employed was $x' = 0.25, 0.50$ and 0.75 (Scheme 1) with respect to 2-$NaSO_3$-H_2BDC ligand.
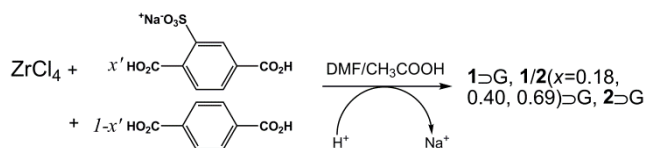
The actual composition of the frameworks was obtained by digesting the PCPs in HF (caution!)/d^6-DMSO mixture, followed by performing ^{1}H NMR on the resulting solution to obtain the actual composition of $x = 0.18, 0.40, 0.69$ for the mixed ligand frameworks.
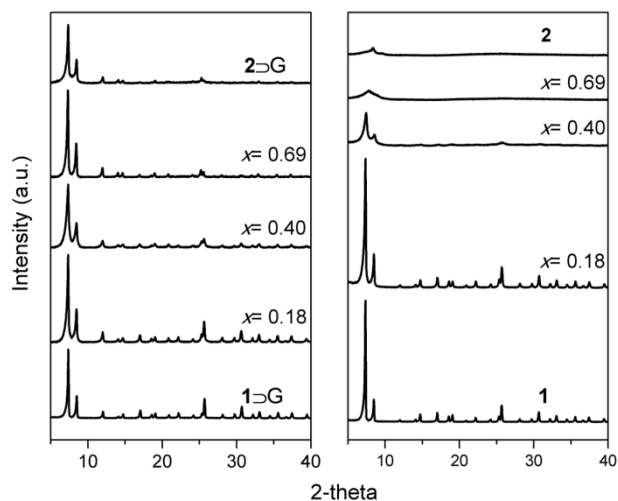
Fig. 2 (left panel) Powder XRD for as-synthesized mixed ligand frameworks **1**⊃G, **2**⊃G, **1/2** ($x = 0.18, 0.40$ and 0.69)⊃G. (right panel) The same frameworks after solvent exchange and evacuation at 120 °C.

Powder XRD (Fig. 2) demonstrated that the isostructure of **1** was successfully obtained using mixed ligands. The lattice parameters of the mixed ligand frameworks were obtained by least square refinement of the powder X-ray data. By plotting the obtained lattice parameters against the actual composition of x, solid solution formation is suggested (Fig. 3). This is further supported by SEM-EDX data, verifying that the homogeneous distribution of sulphur in the mixed frameworks, indicating that only one phase is present.
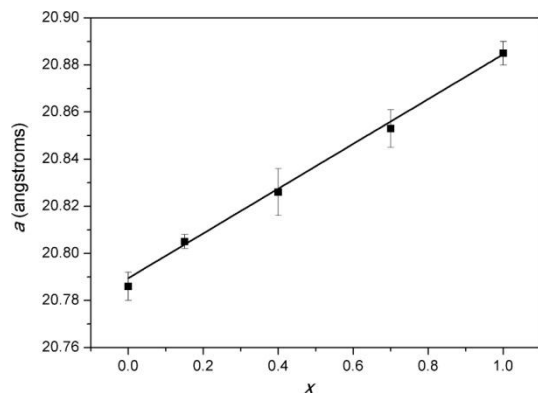
Fig. 3 Plot of lattice parameters against composition for as-synthesized frameworks, **1**⊃G, **2**⊃G, **1/2** ($x = 0.18, 0.40$ and 0.69)⊃G. Note that $x = 0.0$ is equivalent to **1**⊃G, and $x = 1.0$ is equivalent to **2**⊃G.

After solvent exchange with acetone/water mixture and evacuation at 120 °C, the crystallinity of the frameworks was determined by X-ray diffraction. It is observed that besides the **1** composition, the only other composition to stay intact was $x = 0.18$ (and lower x). Hence for **1/2** ($x = 0.18$) or $Zr_6O_4(OH)_4(HSO_3BDC)_{1.1}(BDC)_{4.9}$⊃G, a composition that incorporates the –SO_3H group but is stable to evacuation at elevated temperatures is synthesized. The presence of a limiting stiochiometry is consistent with previous results on UiO-67 synthesized with 1,4-biphenyldicarboxylic acid and functionalized ligands.[14] Le-Bail fitting of synchrotron XRD data acquired from an evacuated sample of **1/2** ($x = 0.18$) affords $a = 20.7382(3)$ Å, which is larger than the previously synchrotron determined lattice parameters of **1** $a = 20.7004(2)$ Å.[4] This increase in lattice parameters of the evacuated mixed ligand framework **1/2** ($x = 0.18$) compared to **1** is consistent with the results obtained from the as-synthesized samples.

The use of Hammett indicators[15] on **1, 2, 1/2** ($x = 0.18$) reveals that the latter two compounds possess acidic protons compared to **1**. Upon addition of the indicator, 4-o-tolylazo-o-toluidine ($pK_a = 2.0$) in cyclohexanone, **1** is coloured orange (negative test) via physical adsorption of indicator, **1/2** ($x = 0.18$) is dark brown (positive test) and **2** is light brown (positive test). Despite having nominally more protons, the lighter colour of **2** is due to its non-porosity. This suggests that exchange of Na^+ for H^+ has occurred in **1/2** ($x = 0.18$) as well. The exchange is further substantiated by SEM-EDX measurements showing absence of Na^+ for **1/2** ($x = 0.18$).

Thermogravimetric Analysis (TGA) of the frameworks in nitrogen shows initial weight loss (~20%) from room temperature

till 200 °C, which is due to solvent molecules such as acetic acid, DMF and water. From 200 to 480 °C, a weight loss of 7.75% is observed for **1** but increases with increasing amounts of *x*, culminating at 19.6% for **2**. There is no drastic difference in the temperature of decomposition, ~500 °C for all the different frameworks.

The effect of solid solution on porosity was determined by N_2 adsorption measurements and presented in Fig. 4 and Table 1. As expected, for **1/2** (*x* = 0.40, 0.69) and **2**, the surface area of the framework decreased with increasing amounts of sulphonic acid substitution as the resulting PCP is less resistant to structural collapse upon removal of guests. However, it is surprising that for **1/2** (*x* = 0.18), the surface area is reproducibly higher than **1** with Langmuir surface area of 1436 vs 1361 m^2g^{-1}. Isostructural PCPs synthesized from 2-substituted dicarboxylic acids as ligands usually possess lower surface areas than their unsubstituted counterparts due to steric constraints and increased molecular weight.[5] There has been a recent report of using the solid solution technique to suppress interpenetration in the MOF-5 structure type and the largest surface area was experimentally observed at an intermediate composition.[16] However, in our case, this is not the case, as interpenetration is not possible in the UiO-66 structure type. The nominally (~5%) higher surface area observed here could be due to slightly higher crystallinity of the **1/2** (*x* = 0.18) framework. We note that in the literature, the Langmuir surface area of UiO-66 has increased from 1136 m^2/g from its original synthesis[4a] to its current value of 1300-1400 m^2/g.[5b,13] Therefore, the maximum obtainable Langmuir surface area for the UIO-66 structure type still remains to be optimised.
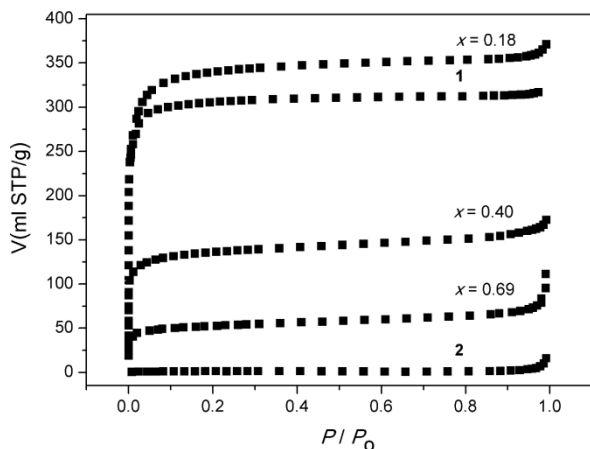
Fig. 4 N_2 adsorption isotherms (77 K) for **1, 2** and **1/2** (*x* = 0.18, 0.40 and 0.69).

In order to determine the effect of the highly polar sulphonic acid group on the adsorption uptake, **1** and **1/2** (*x* = 0.18) were subjected to acetone (298 K) and CO_2 adsorption (288 K) measurements (Fig. 5). The CO_2 adsorption isotherm demonstrated increased uptake for **1/2** (*x* = 0.18) and it can be attributed to increased surface area and higher heats of adsorption. The heat of adsorption of CO_2 for **1/2** (*x* = 0.18) ranges from 28 $kJmol^{-1}$ to 21 $kJmol^{-1}$. It is noted that heats of 30 $kJmol^{-1}$ has been observed for sulphonic acid functionalized porous polymer networks.[17] In contrast, for **1,** the heats of adsorption vary from 22 to 17 $kJ\,mol^{-1}$. This substantial increase of 6 kJ/mol for the initial heat of adsorption for **1/2** (*x* = 0.18)
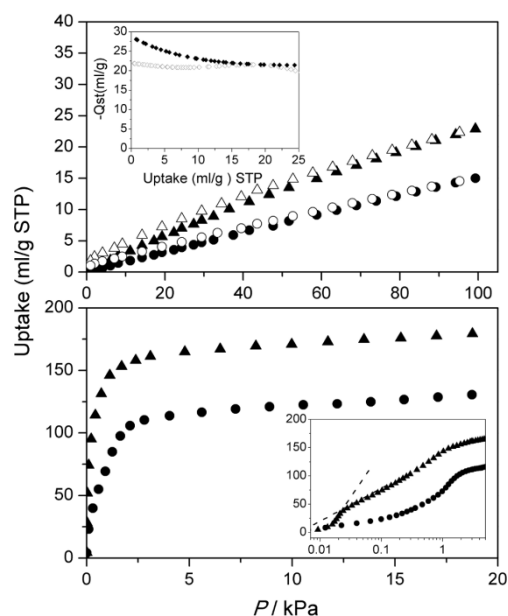
Fig. 5 (Top panel) CO_2 adsorption isotherms at 288 K for **1** (circle) and **1/2** (*x* = 0.18) (triangle). Filled symbols represent adsorption and unfilled symbols desorption. (inset) Heats of adsorption vs uptake plot for 1(unfilled diamonds), **1/2** (*x* = 0.18) (filled diamonds). (Bottom panel) Acetone adsorption isotherms at 298 K for **1** (circles) and **1/2** (*x* = 0.18) (triangles). (inset) Magnified low pressure region, showing the stepped uptake for **1/2** (*x* = 0.18).

suggests that the polar sulphonic acid substituent groups (even at relatively low 15% substitution) increases CO_2 uptake and heat of adsorption. The acetone sorption isotherms for both compounds also demonstrated Type I behaviour, with adsorption saturating at $P/P_0 < 0.1$. From examining the adsorption isotherms at low pressure carefully (Fig. 5 inset), it is observed that while the adsorption of acetone for **1** increases monotonically with pressure, the **1/2** (*x* = 0.18) phase had a stepped increase at $P = 0.0015$ kPa with an adsorption amount ~20% of the total saturation uptake. This is in good correspondence with the doping level of sulphonic acid groups in the **1/2** (*x* = 0.18). Interaction of the sulphonic acid group with acetone is further substantiated by infra-red (IR) spectroscopy, as the C=O stretch of acetone (neat, \1715 cm^{-1}) for **1/2** (*x* = 0.18)⊃acetone (1705 cm^{-1}) is more downshifted compared to **1**⊃acetone (1708 cm^{-1}).

In conclusion, we have synthesized and characterized sulphonic acid substituted **2**⊃G via in-situ ion exchange of Na^+ for H^+ of the 2-NaSO$_3$-H$_2$BDC ligand during solvothermal synthesis. However, it is unstable to loss of guest molecules via evacuation, which places severe restriction on its utility. Using a ligand-based solid solution approach with H_2BDC as a co-ligand, we have arrived at a composition **1/2** (*x* = 0.18) with 18% sulphonic acid substitution, which is robust to evacuation. The solid solution stabilisation approach suggests an alternative route to stabilise PCPs which are inherently unstable with respect to loss of guest molecules. It is thus possible to incorporate a highly acidic sulphonic acid group in UiO-66 with judicious crystal design. We also show that even at relatively low levels of incorporation, the sulphonic acid group increases both the heat of adsorption and total uptake for carbon dioxide.

Notes and references

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20 ‡ *Synthesis of Zr frameworks*

$Zr_6O_4(OH)_4(BDC)_6⊃G$ **or 1⊃G**: 53 mg of $ZrCl_4$ (Aldrich) was added to 37.8 mg of H_2BDC (TCI) in a 20 ml glass vial. 9 ml of DMF (Wako) and
25 1 ml of acetic acid (Wako) was then added. The vial was sealed with a Teflon cap and heated for 40 hrs at 120°C. The product was then centrifuged (2,000 rpm for 15 min) and washed with DMF. This process was repeated for three times. The mixture was then washed with diethylether, followed by air-drying. Weight of product = 50 mg.
30

$Zr_6O_4(OH)_4(HSO_3BDC)_6⊃G$ **or 2⊃G**: 53 mg of $ZrCl_4$ (Aldrich) was added to 61 mg of $2-NaSO_3-H_2BDC$ (TCI) in a 20 ml glass vial. 9 ml of DMF (Wako) and 1 ml of acetic acid (Wako) was then added. The vial was sealed with a Teflon cap and heated for 40 hrs at 120°C. The product
35 was then suction filtered and washed with DMF and diethylether, followed by air-drying. Weight of product = 61 mg.

$Zr_6O_4(OH)_4(HSO_3BDC)_{6-6x}(BDC)_{6x}⊃G$ **or 1/2** $(x)⊃G$: To obtain the PCPs with mixed ligands, the procedure followed is the same as the
40 synthesis of **2**, except for addition of nominal stoichiometric amounts of H_2BDC and $2-NaSO_3-H_2BDC$ for x'= 0.25, 0.50 0.75 For example when x'= 0.25, 25.5mg of H_2BDC and 15.25 mg of $2-NaSO_3-H_2BDC$ were used.

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