

# A Three-Component Hydrogen Bonded Framework

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# Synthesis and characterisation of building blocks

## Details of instruments and characterisation data

NMR spectra were collected on a Bruker Avance 400 spectrometer and are referenced to the residual solvent signal.<sup>1</sup> Infrared spectra were recorded on a Perkin-Elmer Spectrum 2 FT-IR Spectrometer fitted with an ATR2 Single Reflection Diamond. PXRD data were collected using D2 Phaser with Cu K $\alpha$  radiation and a LYNXEYE detector. TGA data were recorded on a TA Instruments Q500 analyser under flowing nitrogen at a ramp speed of 5 °C/minute. Details of instruments used for single crystal X-ray diffraction studies and water vapour sorption are given in subsequent sections of this document.

## Synthesis of building blocks

The tetraamidinium chloride (**1·Cl<sub>4</sub>**),<sup>2</sup> and the tetrabutylammonium (TBA<sup>+</sup>) salts of 4,4'-biphenyldicarboxylate (**biphen<sup>2-</sup>**)<sup>3</sup> and 1,4-benzenedicarboxylate (**TP<sup>2-</sup>**)<sup>4</sup> were synthesised as previously described.

# Synthesis of multi-component framework: 1·biphen·TP

## General remarks

We were able to prepare **1·biphen·TP** at different ratios of **1<sup>4+</sup>·biphen<sup>2-</sup>·TP<sup>2-</sup>** (1:1:1, 1:2:1, 1:1:2 and 1:2:2) in 1:1 ethanol:water. However, the crystallisation at 1:2:2 ratio crystallised fastest with a reasonable yield, so this ratio was used to prepare the framework in bulk.

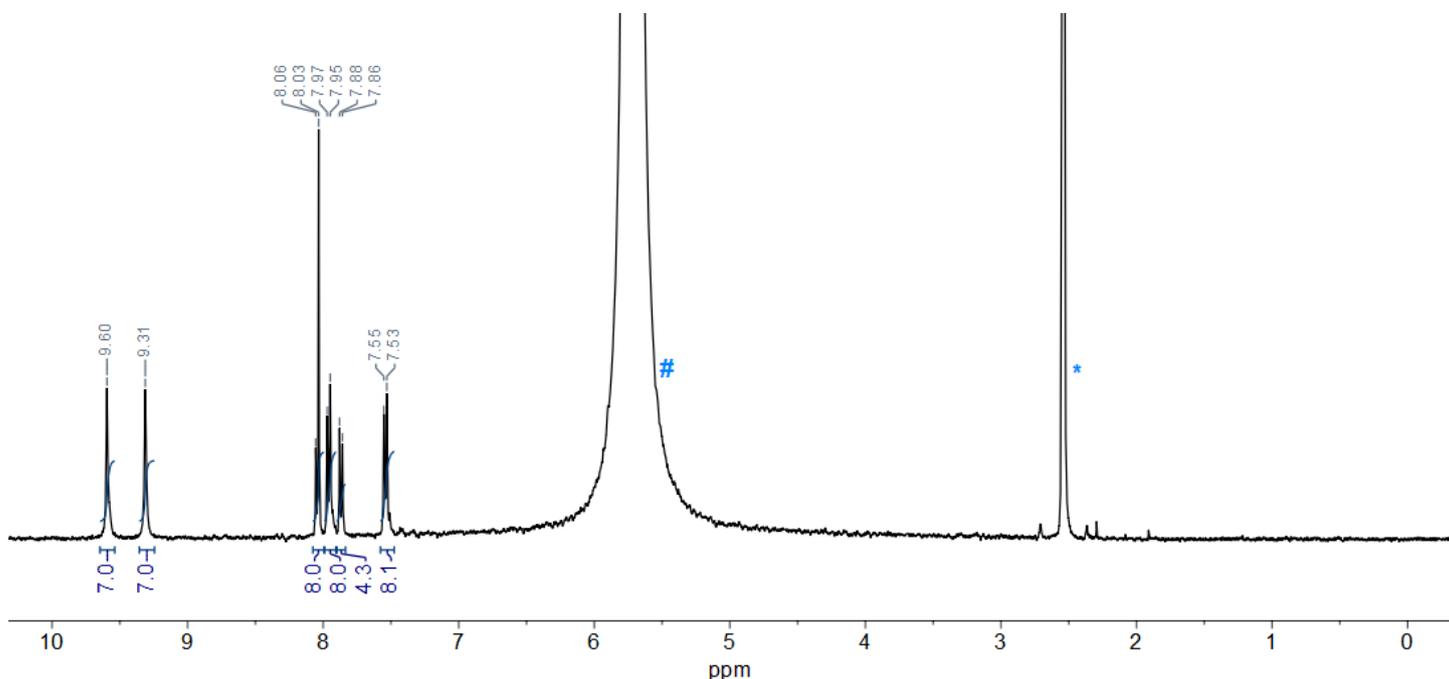
## Synthesis of 1·biphen·TP at 1:2:2 ratio

**TBA<sub>2</sub>·biphen** (88 mg, 120 μmol) and **TBA<sub>2</sub>·TP** (79 mg, 120 μmol) were separately dissolved in 1:1 EtOH:H<sub>2</sub>O (7.5 mL each). The two solutions were mixed together and then added to a solution of **1·Cl<sub>4</sub>** (38 mg, 60 μmol) in 1:1 EtOH:H<sub>2</sub>O (15 mL) at room temperature. Crystal formation was observed within 2 minutes of mixing. After 3 days, the crystals were isolated by filtration, washed with water (~ 6 mL) and suction-dried.

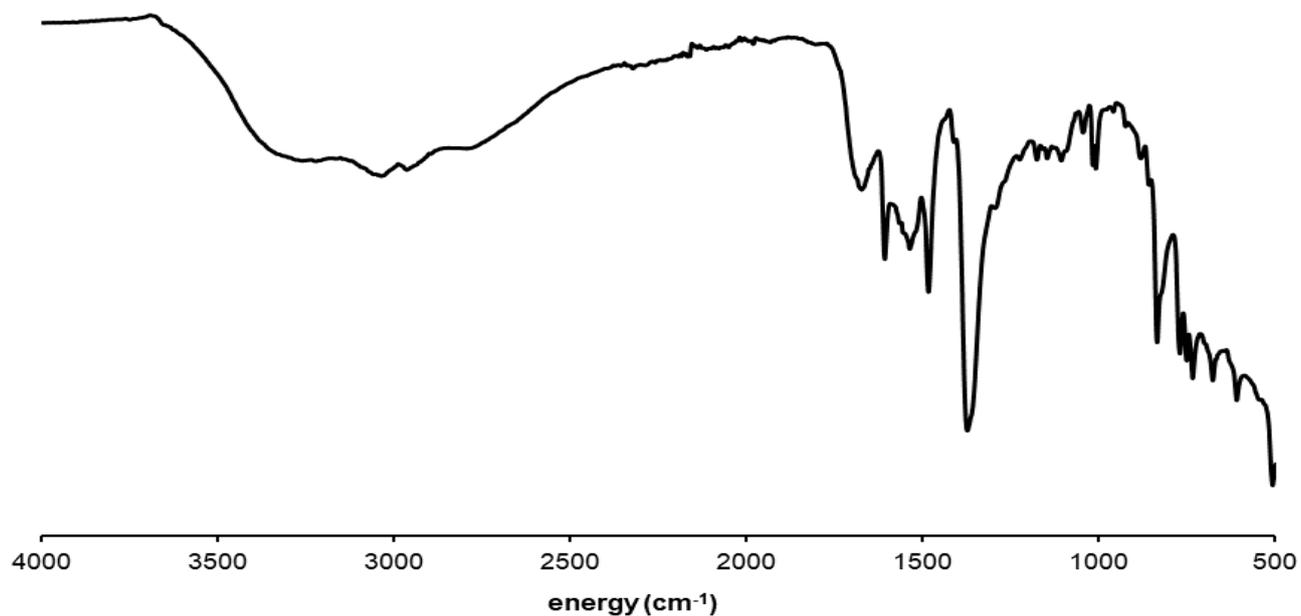
**Yield:** 38 mg (36 μmol, 60%). *Yield calculated assuming 8 H<sub>2</sub>O (as indicated by TGA); M.W. = 1040.64 g.mol<sup>-1</sup>.*

**<sup>1</sup>H NMR** (400 MHz, d<sub>6</sub>-DMSO containing a drop of conc. DCl<sub>(aq)</sub>): 9.60 (s, 8H), 9.31 (s, 8H), 8.03 – 8.06 (m, 8H), 7.95 – 7.97 (d, *J* = 8.6 Hz, 8H), 7.86 – 7.88 (d, *J* = 8.5 Hz, 4H), 7.53 – 7.55 (d, *J* = 8.6 Hz, 8H) ppm.

**ATR-IR** (*inter alia*): 1678 (br., C=N stretch), 1595 (**biphen<sup>2-</sup>** C=O stretch), 1587 (**TP<sup>2-</sup>** C=O stretch), 1368 (br., **biphen<sup>2-</sup>** & **TP<sup>2-</sup>** C=O stretches) cm<sup>-1</sup>. Peaks assigned based on comparison with IR spectra of **1·(biphen)<sub>2</sub>** and **1·(TP)<sub>2</sub>**.

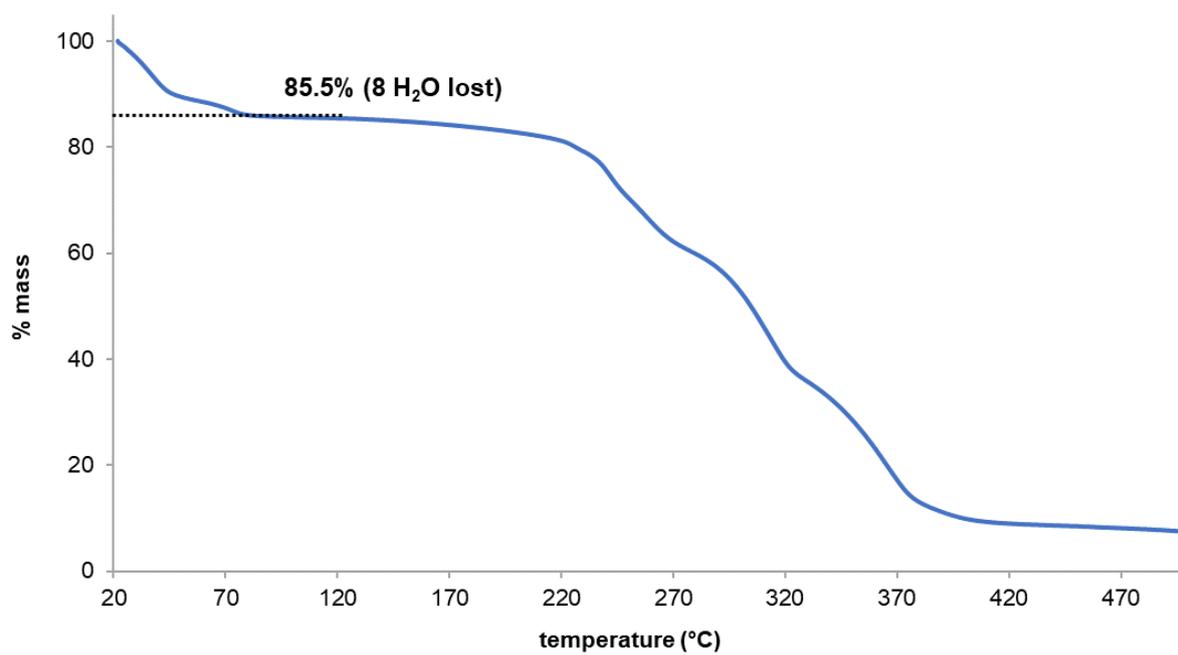


**Figure S1.** <sup>1</sup>H NMR spectrum of acid-digested **1·biphen·TP**; peak labelled \* results from incompletely deuterated NMR solvent, peak labelled # results from water (d<sub>6</sub>-DMSO containing 1 drop DCl<sub>(aq)</sub>, 400 MHz, 298 K).



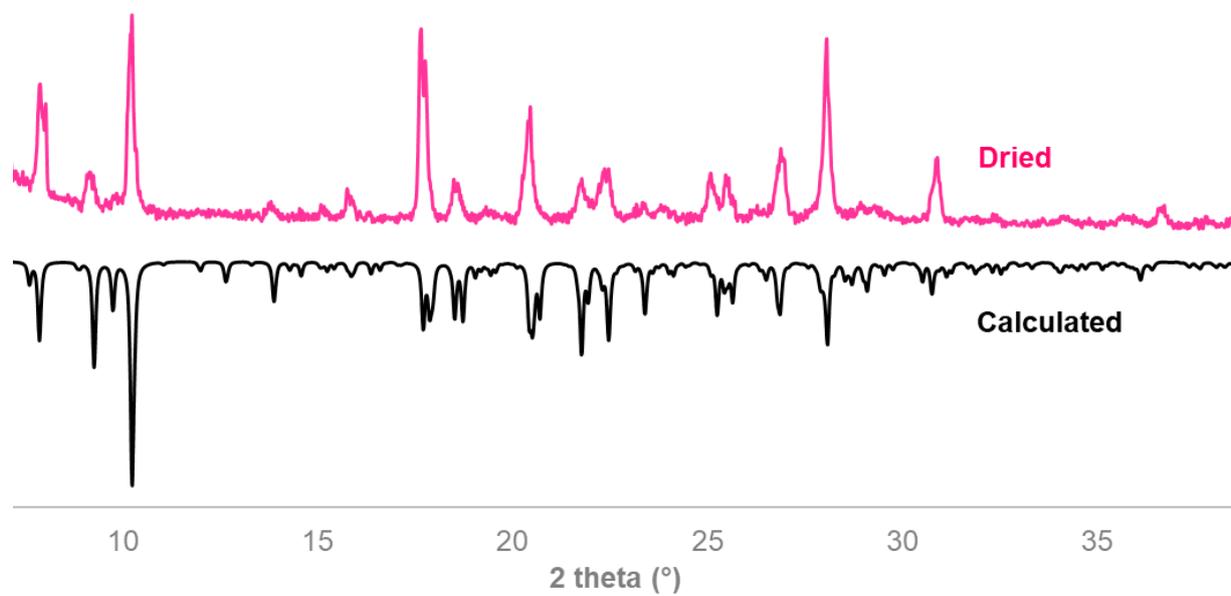
**Figure S2.** ATR-IR spectrum of **1-biphen-TP**.

A suction-dried sample of **1-biphen-TP** was analysed by TGA. The percentage mass of the framework decreases by 14.5% and then plateaus (Figure S3), suggesting loss of solvent in the channels. This mass % corresponds to 8 water molecules.



**Figure S3.** TGA trace of **1-biphen-TP**. The black dotted line indicates the expected mass loss corresponding to eight waters from the framework (85.5%).

The PXRD pattern of dried **1·biphen·TP** is shown in Figure S4. The pattern shows a good match for that calculated based on the single crystal structure, suggesting that the framework does not collapse after suction drying.



**Figure S4.** PXRD pattern of dried **1·biphen·TP**, and the calculated trace derived from the SCXRD structure.

## Summary of crystallisation outcomes

All crystallisations were carried out using a concentration of 2.0 mM in  $1^{4+}$ , with varying ratios of components (1:1:1, 1:1:2, 1:2:1, 1:2:2  $1^{4+}$ :biphen $^{2-}$ :TP $^{2-}$ ) and in either water or 1:1 ethanol:water (Table S1). The outcomes of the crystallisation experiments were analysed by SCXRD unit cell checks,  $^1\text{H}$  NMR spectroscopy of the digested crystals and PXRD experiments. When a large excess of one dicarboxylate was used (five or ten equivalents), it was generally not possible to conduct SCXRD unit cell checks as crystals formed rapidly and were very small; the exception was the crystallisation conducted at a 1:1:5 ratio, where crystals were relatively large, and SCXRD unit cell checks confirmed that  $1\cdot\text{biphen}\cdot\text{TP}$  had formed. We note that PXRD experiments are limited for checking phase-purity in these systems as  $1\cdot(\text{TP})_2$  loses crystallinity upon drying so is unlikely to be observed.

**Table S1.** Summary of crystallisation conditions and outcomes.

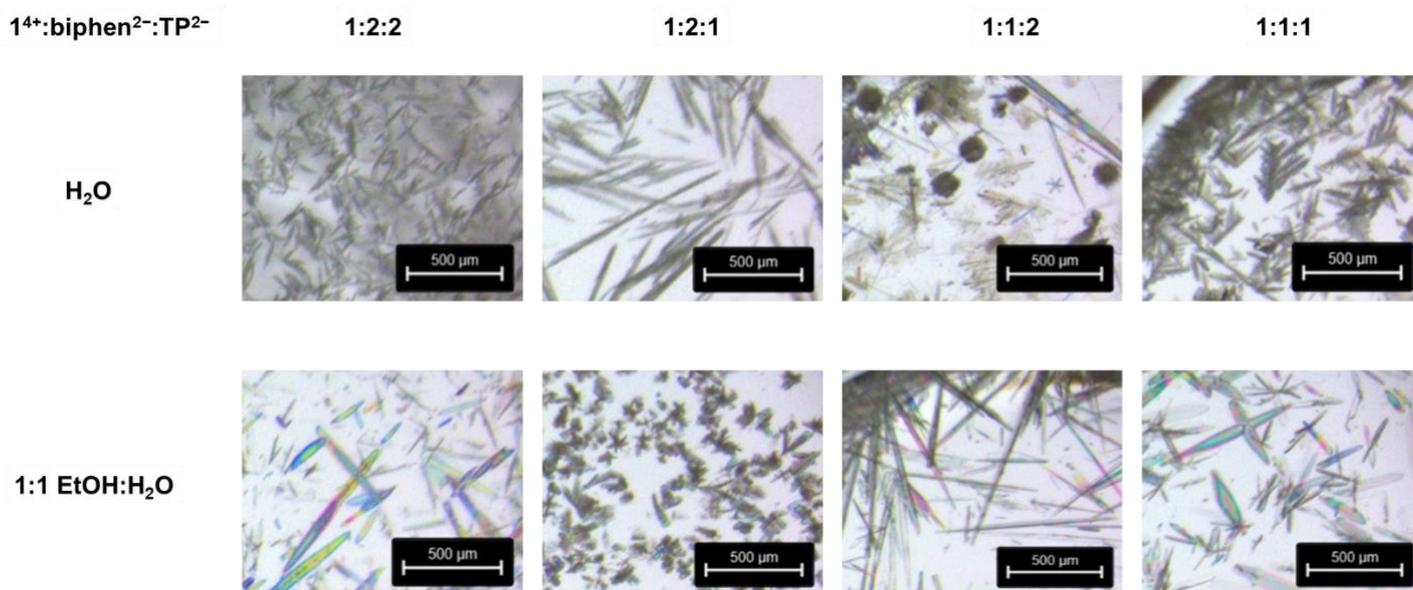
Solvent	[ $1^{4+}$ ] (mM)	[biphen $^{2-}$ ] (mM)	[TP $^{2-}$ ] (mM)	Molar ratio 1:biphen:TP	Crystal formation?	Framework
H <sub>2</sub> O	2.0	2.0	2.0	1:1:1	✓	$1\cdot(\text{biphen})_2$
	2.0	4.0	4.0	1:2:2	✓	$1\cdot(\text{biphen})_2$
	2.0	2.0	4.0	1:1:2	✓ <sup>a</sup>	$1\cdot(\text{biphen})_2$ & $1\cdot(\text{TP})_2$
	2.0	4.0	2.0	1:2:1	✓	$1\cdot(\text{biphen})_2$
1:1 EtOH:H <sub>2</sub> O	2.0	2.0	2.0	1:1:1	✓	$1\cdot\text{biphen}\cdot\text{TP}$
	2.0	4.0	4.0	1:2:2	✓	$1\cdot\text{biphen}\cdot\text{TP}$
	2.0	2.0	4.0	1:1:2	✓	$1\cdot\text{biphen}\cdot\text{TP}$
	2.0	2.0	10	1:1:5	✓	$1\cdot\text{biphen}\cdot\text{TP}$
	2.0	2.0	20	1:1:10	✓	$1\cdot(\text{TP})_2$
	2.0	4.0	2.0	1:2:1	✓	$1\cdot\text{biphen}\cdot\text{TP}$
	2.0	10	2.0	1:5:1	✓	$1\cdot(\text{biphen})_2$
	2.0	20	2.0	1:10:1	✓	$1\cdot(\text{biphen})_2$

<sup>a</sup> Two different crystals observed.

## Microscopy images of frameworks crystallised at different ratios of $1^{4+}:\text{biphen}^{2-}:\text{TP}^{2-}$

In water, different crystal morphologies were obtained depending on the ratio of the components used. While the crystallisation at 1:2:2, 1:2:1 and 1:1:1  $1^{4+}:\text{biphen}^{2-}:\text{TP}^{2-}$  gave large needles, a mixture of small and large needles were obtained at a 1:1:2 ratio (Figure S5). In this case, SCXRD unit cell screening of ~10 crystals indicated that all crystals were  $1\cdot(\text{biphen})_2$ , apart from those obtained at a 1:1:2 ratio, which were a mixture of crystals of  $1\cdot(\text{biphen})_2$  and  $1\cdot(\text{TP})_2$ .

In 1:1 ethanol:water, the crystallisation at 1:2:2, 1:1:2 and 1:1:1 gave needle-like crystals, whereas 1:2:1 gave small blocks. SCXRD unit cell screening of ~10 crystals indicated that all crystals were  $1\cdot\text{biphen}\cdot\text{TP}$ . We are unsure why a different crystal morphology was obtained at the 1:2:1 ratio but suggest it may be due to modulation<sup>5</sup> caused by the excess  $\text{biphen}^{2-}$  present.

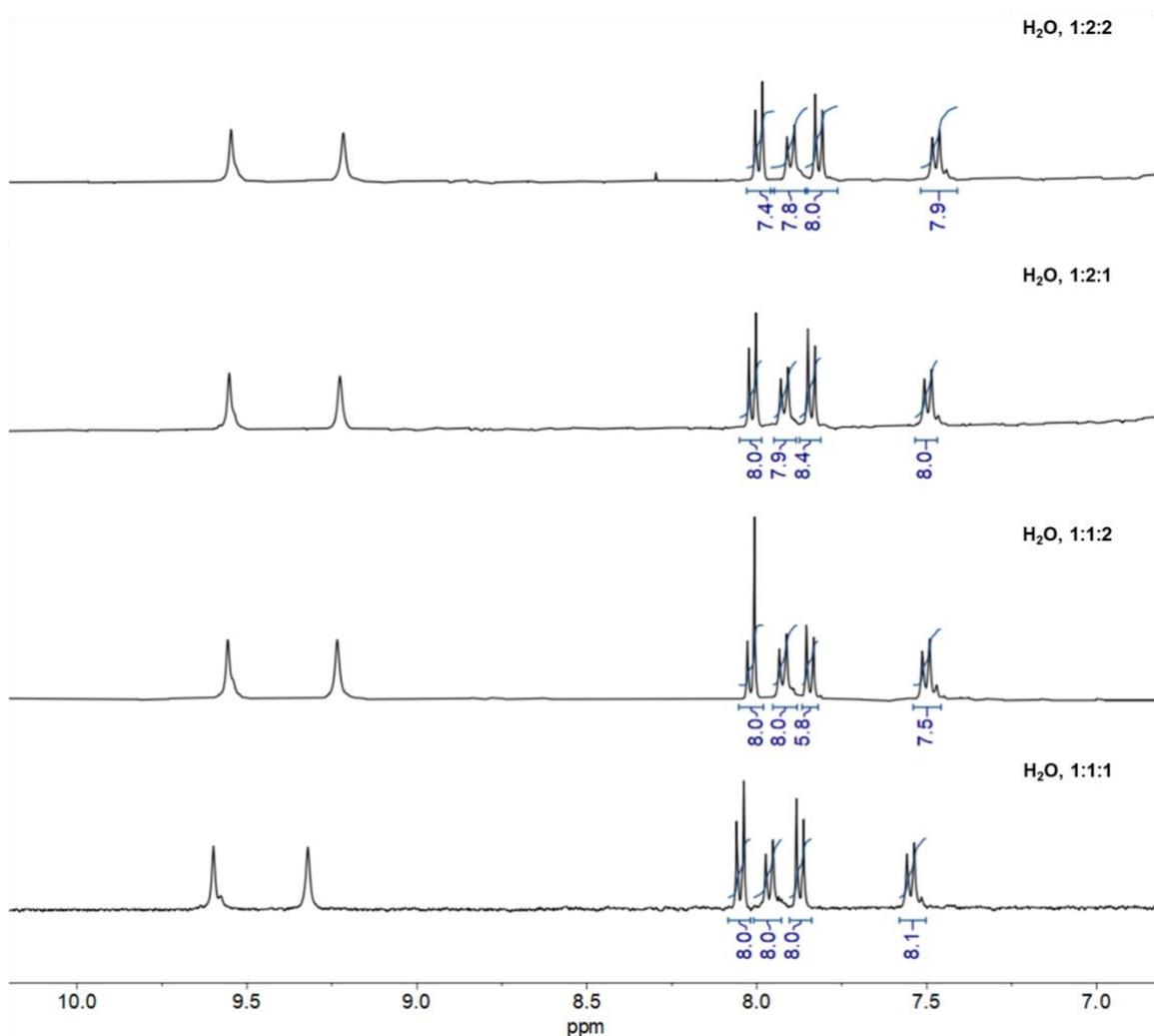


**Figure S5.** Optical microscope images of the crystals formed in water ( $\text{H}_2\text{O}$ ) and 1:1 ethanol:water (EtOH: $\text{H}_2\text{O}$ ) at different ratios of  $1^{4+}:\text{biphen}^{2-}:\text{TP}^{2-}$ .

## NMR spectra of frameworks crystallised at different ratios of $1^{4+}$ :**biphen** $^{2-}$ :**TP** $^{2-}$

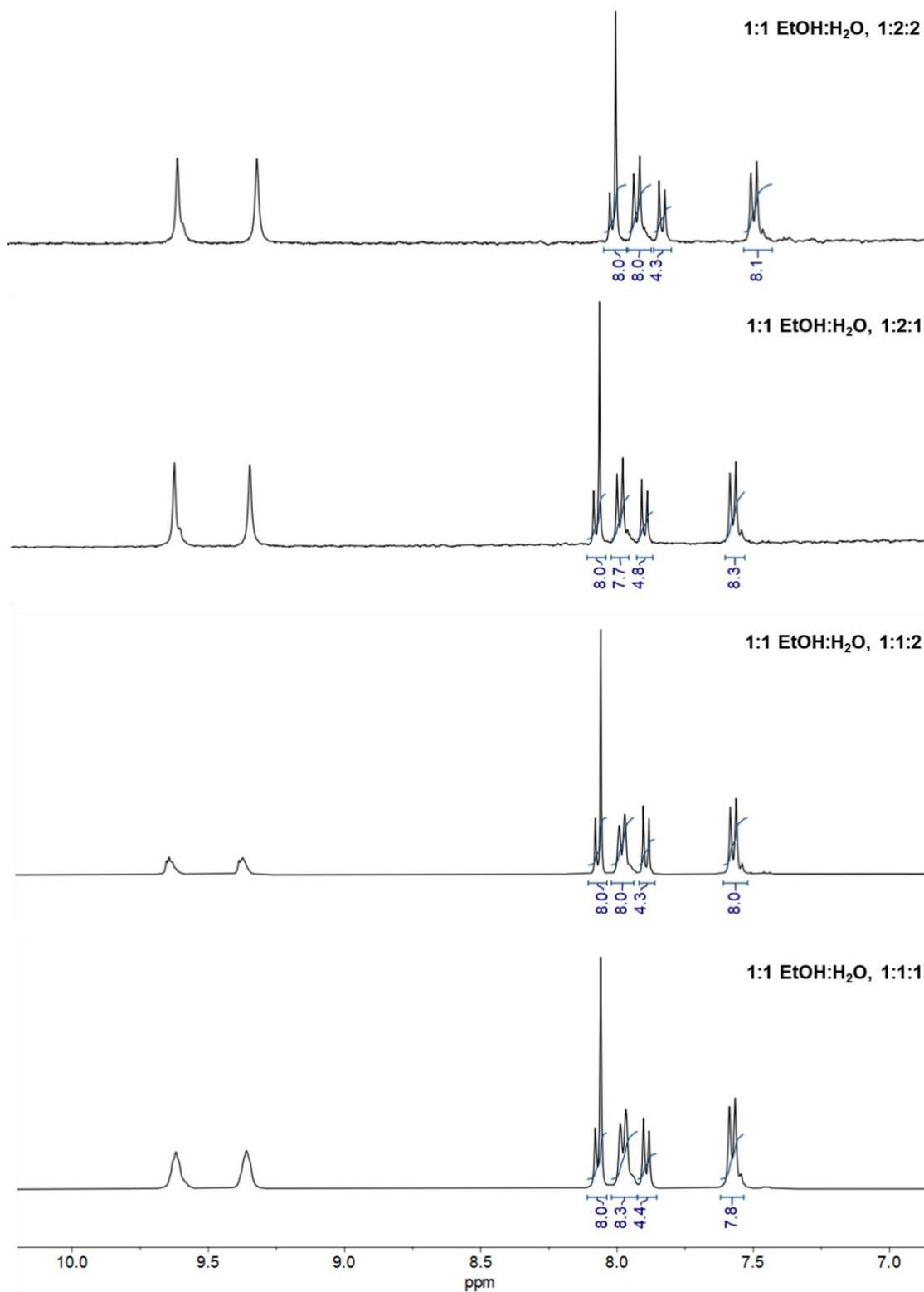
The dried crystals obtained from the crystallisation in either water ( $H_2O$ ) or 1:1 ethanol:water (EtOH: $H_2O$ ) at different precursor ratios were digested by dissolving in  $d_6$ -DMSO containing a drop of 35%  $DCl_{(aq)}$ . The  $^1H$  NMR spectra of the resulting solutions are shown in Figures S6 and S7.

### Crystallisations in water:



**Figure S6.**  $^1H$  NMR spectra of acid-digested frameworks crystallised in water ( $H_2O$ ) at different ratios of  $1^{4+}$ :**biphen** $^{2-}$ :**TP** $^{2-}$  ( $d_6$ -DMSO containing 1 drop  $DCl_{(aq)}$ , 400 MHz, 298 K). In the 1:1:1, 1:2:1 and 1:2:2 ratios, only peaks corresponding to  $1^{4+}$  and **biphen** $^{2-}$  are observed. In the 1:1:2 ratio (*i.e.* excess **TP** $^{2-}$ ), peaks for  $1^{4+}$ , **biphen** $^{2-}$  and **TP** $^{2-}$  are observed.

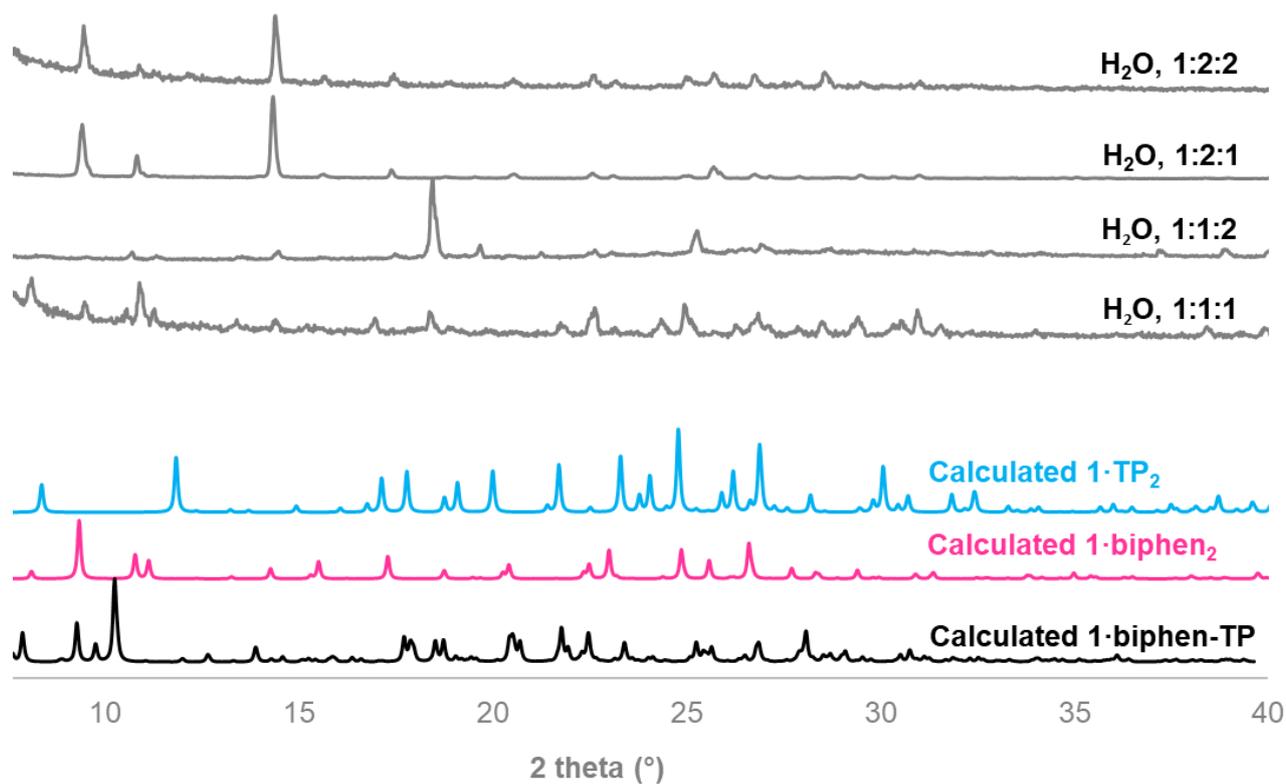
Crystallisations in 1:1 ethanol:water:



**Figure S7.**  $^1\text{H}$  NMR spectra of acid-digested frameworks crystallised in 1:1 ethanol:water (EtOH:H<sub>2</sub>O) at different ratios of **1<sup>4+</sup>:biphen<sup>2-</sup>:TP<sup>2-</sup>** (d<sub>6</sub>-DMSO containing 1 drop DCI<sub>(aq)</sub>, 400 MHz, 298 K). In all cases, a 1:1 ratio of **biphen<sup>2-</sup>:TP<sup>2-</sup>** is observed in the product.

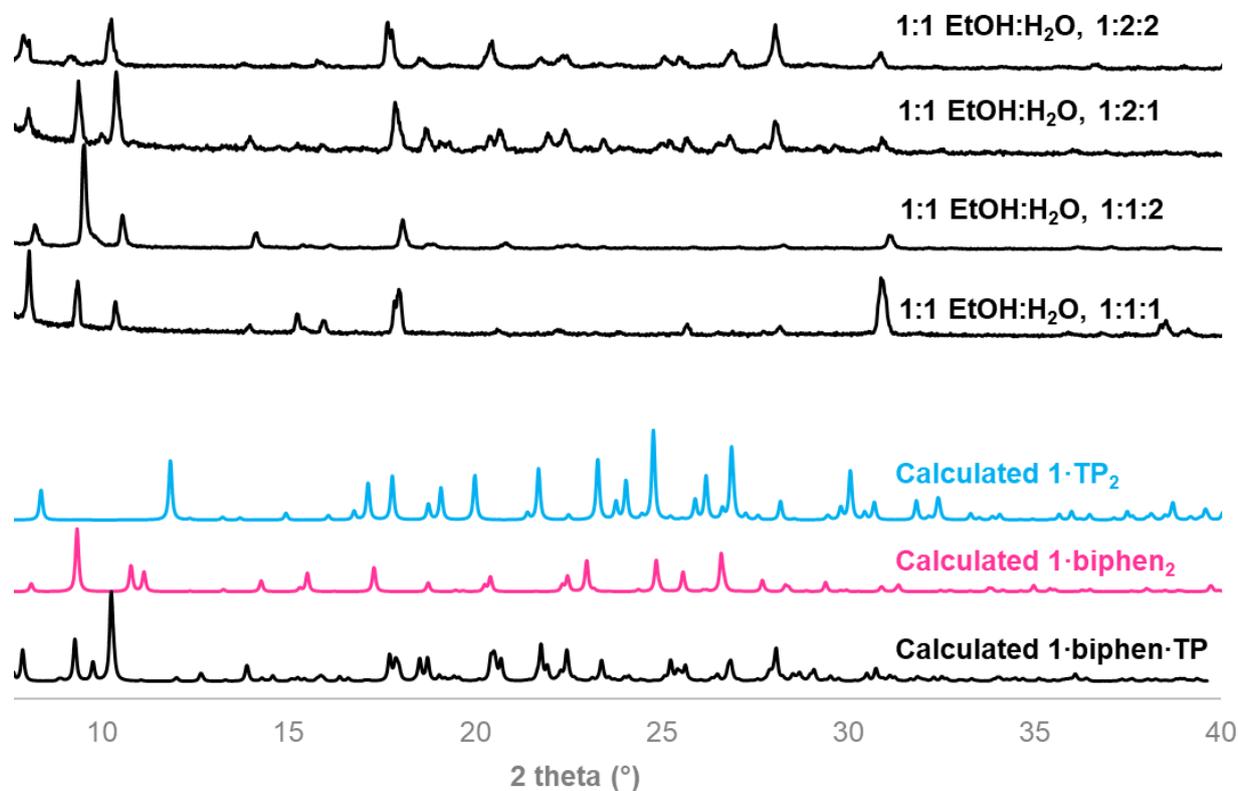
## PXRD traces of frameworks crystallised at different ratios of $1^{4+}:\text{biphen}^{2-}:\text{TP}^{2-}$

PXRD traces of frameworks crystallised at different component ratios in water are shown in Figure S8. It should be noted that  $1\cdot\text{TP}_2$  loses crystallinity upon drying so is unlikely to be observed in these experiments. While patterns do not match any phase particularly well, which we attribute to preferred orientation effects, it is clear that the patterns do not match those expected for the mixed framework  $1\cdot\text{biphen}\cdot\text{TP}$ . Instead, patterns broadly consistent with  $1\cdot(\text{biphen})_2$  are observed in most cases, which is consistent with the SCXRD unit cell checking and  $^1\text{H}$  NMR spectroscopy studies.



**Figure S8.** PXRD pattern of partially dried crystals which crystallised in water ( $\text{H}_2\text{O}$ ) at different ratio of  $1^{4+}:\text{biphen}^{2-}:\text{TP}^{2-}$ . The calculated patterns for  $1\cdot\text{biphen}\cdot\text{TP}$ ,  $1\cdot(\text{biphen})_2$ , and  $1\cdot(\text{TP})_2$  derived from the SCXRD structure are shown.

PXRD traces of frameworks crystallised at different component ratios in 1:1 ethanol:water are shown in Figure S9. It should be noted that  $1 \cdot (\text{TP})_2$  loses crystallinity upon drying so is unlikely to be observed in these experiments. While these patterns are not particularly diagnostic, traces broadly consistent with formation of  $1 \cdot \text{biphen} \cdot \text{TP}$  are observed, suggesting the three-component framework forms at all ratios. This agrees with analysis by SCXRD unit cell checking and  $^1\text{H}$  NMR spectroscopy.



**Figure S9.** PXRD pattern of partially dried crystals which crystallised in 1:1 ethanol:water (EtOH:H<sub>2</sub>O) at different ratio of  $1^{4+}:\text{biphen}^{2-}:\text{TP}^{2-}$ . The “calculated” patterns for  $1 \cdot \text{biphen} \cdot \text{TP}$ ,  $1 \cdot (\text{biphen})_2$ , and  $1 \cdot (\text{TP})_2$  are derived from the SCXRD structure.

# X-ray crystallography (SCXRD)

## Data collection and refinement

Data for **1·biphen-TP** were collected using synchrotron radiation using beamline MX2 at the Australian Synchrotron.<sup>6</sup> Raw frame data (including data reduction, interframe scaling and unit cell refinement) were processed using XDS.<sup>7</sup> The structure was solved using SHELXT<sup>8</sup> and refined using SHELXL<sup>9</sup> within the OLEX2 suite.<sup>10</sup> Diffraction data were of high quality with reflection intensity and low  $R_{\text{int}}$  (3.2%). Refinement statistics are slightly worse than might be expected based on this (e.g.  $R_1 [I > 2\sigma(I)] = 7.9\%$ ), which we attribute to a combination of a disordered anion and amidinium group, and numerous water molecules (that required inclusion using the OLEX2 mask feature, see later). Having said that, we believe this is a surprisingly high quality structure for a porous hydrogen-bonded framework. R-factors and bond length esds are relatively good, and restraints were only needed for disordered parts of the molecule (see later).

Disorder was apparent for the **biphen**<sup>2-</sup> ion and one of the amidinium groups of **1**<sup>4+</sup>. In both cases, this was modelled over two positions (occupancies of 0.5 each). It was necessary to restrain C–C and C–O bond lengths of the disordered **biphen**<sup>2-</sup> anion using DFIX commands. The C–N geometries of the disordered amidinium group were restrained using DFIX and FLAT commands. ISOR restraints were used on both disordered parts of the molecule. N–H hydrogen atoms were inserted at calculated positions and ride on the attached nitrogen atom.

While some water solvent molecules were visible in the Fourier difference map, we were not able to refine these satisfactorily. Many of these water molecules had large ellipsoids, and appear to be disordered (presumably linked to the disorder in the anion and amidinium parts of the molecule). Additionally, it seems that many of these water molecules have partial occupancies, presumably due to partial evaporation from the crystal. Even for water molecules that were relatively well-behaved, it was not possible to resolve hydrogen atom positions. Taken together, attempting to model even some of these gave a poorer quality refinement, without adding any useful information (for example about hydrogen bonding positions). For this reason, the OLEX2 solvent mask feature was instead used to incorporate electron density from solvent in the refinement.<sup>10</sup> This indicated the removal of 125 electrons per molecule of **1**<sup>4+</sup>, consistent with 12.5 water molecules per formula unit. TGA indicated eight water molecules per formula unit; this was recorded on dried material, so presumably some water molecules are lost on drying. Given the uncertainty of the number of water molecules in the asymmetric unit, and the possibility that these pores may also contain some ethanol instead, we have not estimated the solvent content as part of the formula given in the CIF or Table S2. As a result the estimated crystal density given in the CIF only accounts for the framework structure and not the whole crystal (which would be substantially higher).

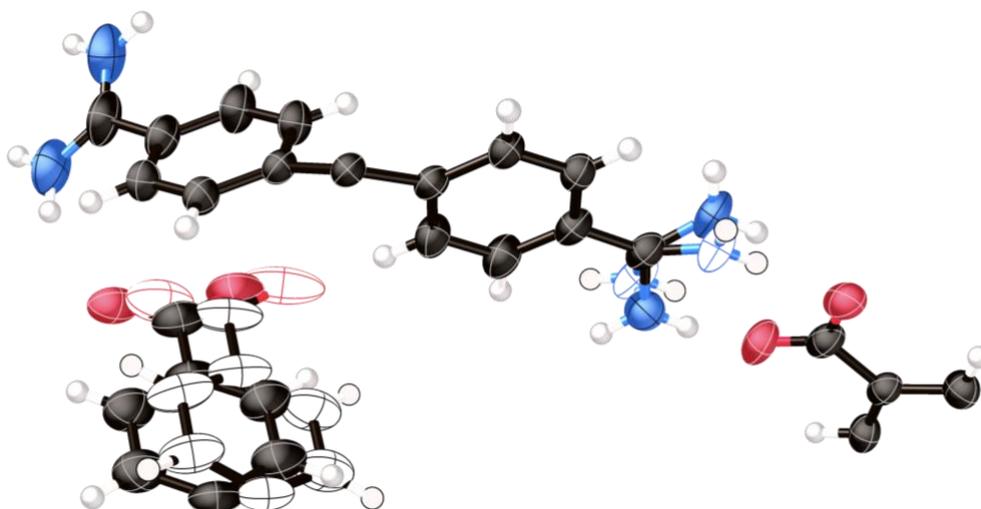
Selected crystallographic data are summarised in Table S2. Full crystallographic data in CIF format have been uploaded to the Cambridge Structural Database (CCDC: 2335839).

**Table S2.** Summary of crystallography data for **1-biphen-TP**.

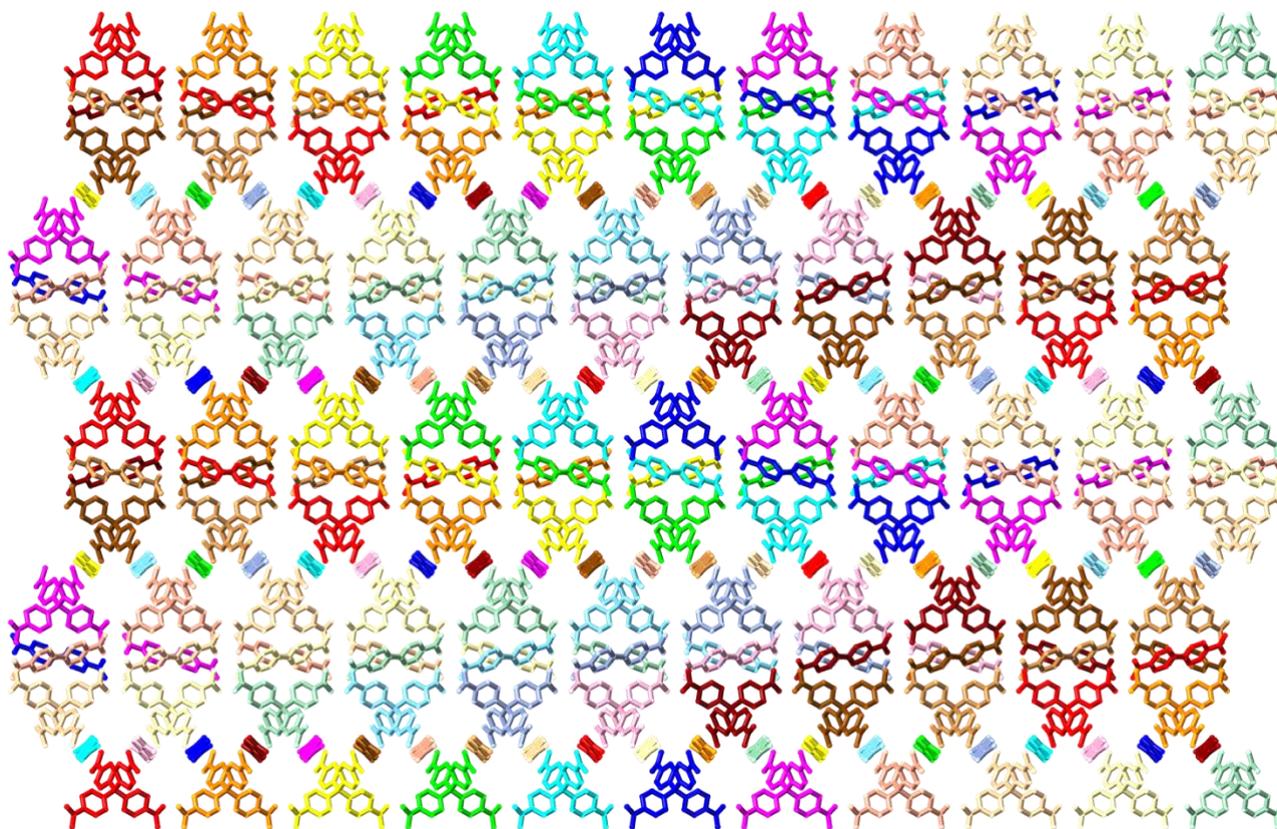
<b>Framework</b>	<b>1-biphen-TP<sup>a</sup></b>
Radiation type	Synchrotron ( $\lambda=0.71073$ Å)
Temperature (K)	100
Formula	$C_{29}H_{32}N_8 \cdot C_{14}H_8O_4 \cdot C_8H_4O_4 \cdot solvent$
Formula weight	896.94
<i>a</i> (Å)	12.402(3)
<i>b</i> (Å)	38.337(8)
<i>c</i> (Å)	12.608(3)
$\alpha$ (°)	90.0
$\beta$ (°)	111.33(3)
$\gamma$ (°)	90.0
Unit cell volume (Å <sup>3</sup> )	5584(2)
Crystal system	monoclinic
Space group	<i>I</i> 2/ <i>a</i>
<i>Z</i>	4
Reflections (all)	38173
Reflections (unique)	5735
$R_{int}$	0.0322
$R_1$ [ $I > 2\sigma(I)$ ]	0.0790
$wR_2$ (all data)	0.239
CCDC number	2335839

<sup>a</sup> OLEX2 solvent mask used.<sup>10</sup>

## Pictures of the crystal structure of 1-biphen-TP



**Figure S10.** Thermal ellipsoid plot showing the asymmetric unit of **1-biphen-TP**; ellipsoids shown at 50% probability level. The two positions of disordered groups are shown in different colours. The OLEX2 solvent mask feature was used.<sup>10</sup>



**Figure S11.** Diagram showing 17 interpenetrated networks in **1-biphen-TP**. Each network is shown in a different colour. Disorder and hydrogen atoms omitted for clarity.

# Water vapour sorption

## General remarks

Approximately 25 mg of dried sample was weighed in a pre-dried and weighed Quartz BET tube. Adsorption isotherms for pressures in the range of 0 – 1.2 bar were measured by a volumetric method using a Micromimetics 3Flex. Measurements were performed using ultra-high purity (99.99%) N<sub>2</sub> gas and degassed distilled water. Samples were evacuated and activated at 80 °C under dynamic vacuum at 10<sup>-6</sup> Torr for 24 hrs to remove residual solvent molecules.

Initially, a water adsorption isotherm was recorded with five collection pressure points between 0 and 100 % relative humidity (RH) to find the optimum pressure steps to run the experiment. The sample was then degassed again by heating under vacuum and the next measurement was taken with several more collection pressure points. We note that three isotherms were collected on the sample, and no change was observable in the isotherms at a given temperature, indicating that water vapour sorption is reversible.

## Comparison with X-ray crystal structure of 1·biphen·TP

The OLEX2 mask routine<sup>10</sup> removed 499 electrons from a volume of 1463 Å<sup>3</sup>. Accounting for the number of molecules in the unit cell, this corresponds to 125 electrons per formula unit, or 12.5 water molecules. We assume that all solvent is water (rather than ethanol) as this is what is commonly observed in amidinium···carboxylate frameworks, although this may be an over-simplification. Accounting for the molecular mass of the framework, this would correspond to 14.0 mmol of water per gram of framework, or 253 cm<sup>3</sup> g<sup>-1</sup>. This analysis makes a number of assumptions (for example that no water is lost from the crystal on mounting, and that all solvent is water) but this expected value matches relatively well with the observed vapour sorption values (Figure 4 in main text).

## Enthalpy of adsorption

The isosteric heat of adsorption ( $Q_{st}$ ) was calculated from the sorption data measured at 273 K and 293 K. The data were fit to Equation 1.

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

To calculate the  $Q_{st}$  equation 2 was applied using the fitting parameters from Equation 1.

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (2)$$

This gave a calculated value of 61.5 kJ mol<sup>-1</sup>. This is similar to related HOFs prepared from charged components. For example, the  $Q_{st}$  value for water sorption in CPOS-6 (containing 1<sup>4+</sup> and a tetra-sulfonate anion) ranges from 48.7 – 83.8 kJ mol<sup>-1</sup>.<sup>11</sup>

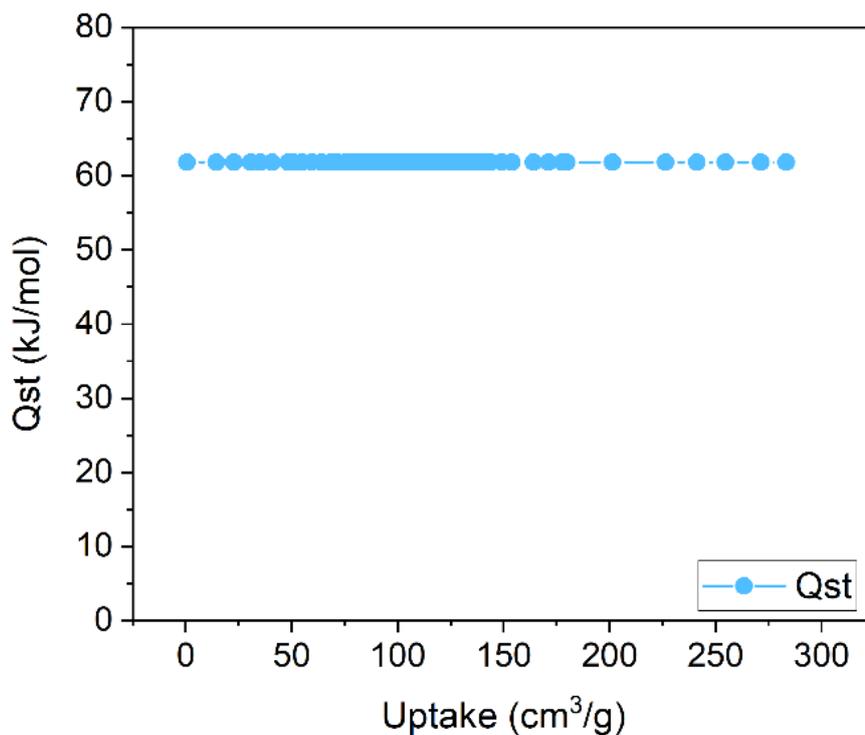


Figure S12.  $Q_{st}$  values for 1-biphen-TP.

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