

# A three-component hydrogen bonded framework

Phonlakrit Muang-Non,<sup>a</sup> Meabh K. S. Perry-Britton,<sup>a</sup> Lauren K. Macreadie,<sup>b</sup> and Nicholas G. White<sup>a\*</sup>

A porous three-component hydrogen bonded framework, **1-biphen-TP**, was prepared from a tetra-amidinium component (**1<sup>4+</sup>**) and two different dianions, benzene-1,4-dicarboxylate (terephthalate, **TP<sup>2-</sup>**) and biphenyl-4,4'-dicarboxylate (**biphen<sup>2-</sup>**). Interestingly, when the framework was prepared in ethanol/water, **1-biphen-TP** forms even when an excess of either dicarboxylate is present. However, when only water is used as solvent, only two-component frameworks are formed.

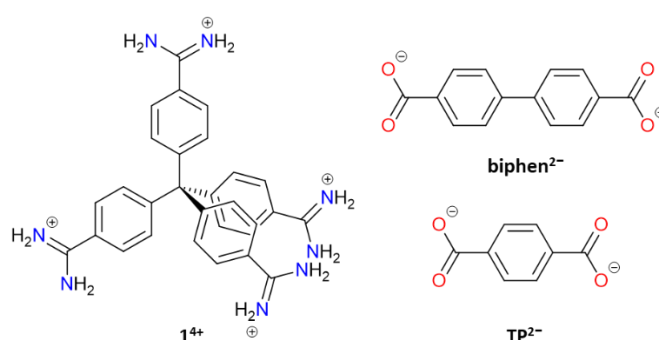
Metal organic frameworks (MOFs) containing two or more ligands are a well-established class of framework material.<sup>1</sup> They can be either multicomponent (MTC),<sup>2,3</sup> where each ligand occupies a distinct position in the crystal lattice, or multivariate (MTV),<sup>4</sup> where the ligands are “scrambled” and not ordered in the crystalline lattice. Both types of frameworks offer sophisticated pore environments, which can result in improved gas adsorption properties<sup>3,5–8</sup> and catalytic activity<sup>9,10</sup> compared to single ligand MOFs. MTC MOFs are of specific interest as the ordered arrangement of the ligands leads to controllable and uniform pores.

Wuest reported the first example of what may now be termed a hydrogen-bonded organic framework (HOF) in 1991,<sup>11</sup> shortly after Robson’s report of open 3D frameworks assembled through metal–ligand coordination.<sup>12</sup> However, the development of porous hydrogen-bonded frameworks has been slower than the development of MOFs. In the last decade or so, however, this area has advanced rapidly and many of the achievements made in MOF chemistry are now finding analogues in HOF chemistry.<sup>13,14</sup>

Very recently, multivariate HOFs were reported by the groups of Hisaki,<sup>15</sup> and Chen and Li.<sup>16</sup> In these reports tetracarboxylic acids based on pyrene scaffolds were used to form frameworks through carboxylic acid self-recognition. In Hisaki’s report,<sup>15</sup> two similar

components were incorporated into the framework with the mole fraction of one matching closely the fraction of that component in the reaction mixture, and the components distributed inhomogeneously. Chen and Li reported the synthesis of HOFs containing up to four components and showed that the hydrophobicity of the MTV-HOFs could be tuned systematically.<sup>16</sup>

We have reported a series of amidinium-carboxylate frameworks assembled through charge-assisted hydrogen bonding between tetra-amidinium components such as **1<sup>4+</sup>** and tetracarboxylates or dicarboxylates such as the biphenyl species **biphen<sup>2-</sup>** or the phenyl-containing species **TP<sup>2-</sup>** (Figure 1).<sup>17,18</sup> We decided to investigate whether multicomponent HOFs could be prepared using the combination of two different dicarboxylate species. While this work was in progress, Champness and co-workers reported a related material: an amidinium-carboxylate framework where a framework assembled from a bis-amidinium and tetra-carboxylate encapsulates a third species, which is the decomposition product of the bis-amidinium.<sup>19</sup> In the current work, we demonstrate that it is possible to make a ternary multicomponent HOF, where two different anionic components combine with **1<sup>4+</sup>** to form the three-component framework **1-biphen-TP**.<sup>20</sup>



**Figure 1** Structures of tetraamidinium (**1<sup>4+</sup>**), biphenyldicarboxylate (**biphen<sup>2-</sup>**), and terephthalate (**TP<sup>2-</sup>**) used in this work.

<sup>a</sup> Research School of Chemistry, Australian National University, Canberra, ACT, Australia. E-mail: [nicholas.white@anu.edu.au](mailto:nicholas.white@anu.edu.au); Web: <https://www.nwhitegroup.com>

<sup>b</sup> School of Chemistry, University of New South Wales, Sydney, NSW, Australia.

†Supporting Information available: experimental details and characterisation, CCDC 2335839.

Initially, we mixed the three components in water in a 1:1:1 **14<sup>+</sup>:biphen<sup>2-</sup>:TP<sup>2-</sup>** ratio (see ESI for full details of crystallisation experiments). The mixture immediately turned cloudy, and then after a few hours the cloudiness disappeared and single crystals slowly formed. Analysing the unit cell parameters of several crystals by single crystal X-ray diffraction (SCXRD) experiments revealed that the unit cells of all of these matched those of previously-reported **1(biphen)<sub>2</sub>**.<sup>18</sup> <sup>1</sup>H NMR spectroscopy of the acid-digested product showed that **biphen<sup>2-</sup>** was the only anion incorporated into the framework. We have previously shown that **1(TP)<sub>2</sub>** forms crystals of a highly open phase very rapidly (crystals begin to form in less than one minute),<sup>17</sup> while **1(biphen)<sub>2</sub>** forms a less open structure more slowly.<sup>18</sup> It appears that the addition of **biphen<sup>2-</sup>** acts as a hydrogen bonding modulator<sup>21</sup> to prevent rapid formation of **1(TP)<sub>2</sub>** and allows the system time to form the denser (although still open) structure **1(biphen)<sub>2</sub>**.

We next investigated the effect of using different ratios of linkers by combining 1:1:2, 1:2:1 and 1:2:2 ratios of **14<sup>+</sup>:biphen<sup>2-</sup>:TP<sup>2-</sup>**. At the 1:1:1, 1:2:2 or 1:2:1 ratios, *i.e.* when **biphen<sup>2-</sup>** was present in equal or greater concentrations to **TP<sup>2-</sup>**, SCXRD unit cell checks and <sup>1</sup>H NMR spectroscopy of the acid-digested frameworks indicated that the only ligand incorporated into the crystals was **biphen<sup>2-</sup>**.

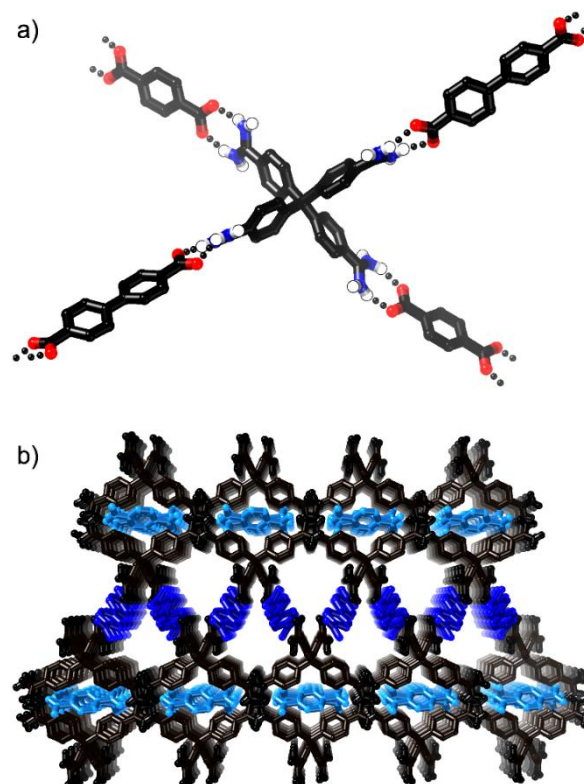
When **TP<sup>2-</sup>** was present in excess, an approximately equal ratio of **biphen<sup>2-</sup>** and **TP<sup>2-</sup>** was observed in the <sup>1</sup>H NMR spectrum of the acid-digested material (Figure S6). However, no peaks corresponding to the mixed framework **1-biphen-TP** (see later) were visible in the powder X-ray diffraction PXRD trace of the material, and unit cell screening identified crystals of **1(TP)<sub>2</sub>** as well as **1(biphen)<sub>2</sub>**. We thus conclude that this crystallisation results in a mixture of **1(biphen)<sub>2</sub>** and **1(TP)<sub>2</sub>**.

We subsequently looked at crystallisation in the mixed solvent system 1:1 ethanol:water, which we have previously observed to slow crystallisation relative to pure water.<sup>17,21</sup> Mixing the three components resulted in a clear solution, and within two minutes needle-like crystals were observed.

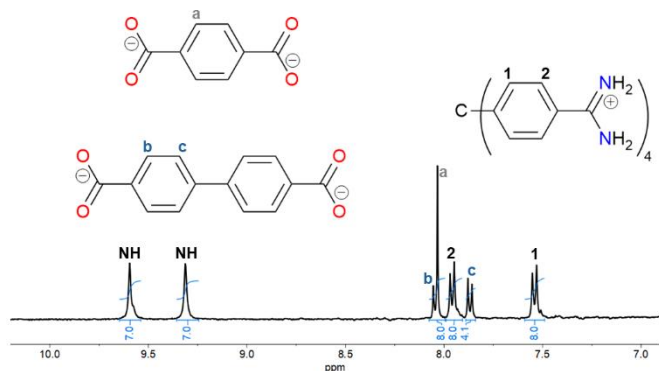
SCXRD studies revealed that these crystals are **1-biphen-TP**, containing all three components. The diamondoid framework is assembled by charged-assisted “paired”  $R_2^2(8)$  hydrogen bonds<sup>22</sup> between the amidinium groups of **14<sup>+</sup>** and the carboxylate groups of both **biphen<sup>2-</sup>** (H–O distances = 1.92 – 2.20 Å) and **TP<sup>2-</sup>** (H–O distances = 1.92 – 2.11 Å).<sup>23</sup> The structure is highly interpenetrated (17 interpenetrated nets, Figure S11) but still contains solvent-filled channels (Figure 2).

The solvent molecules could not be modelled satisfactorily, and so the OLEX2 solvent mask feature<sup>24</sup> was used to include the electron density in the model.

The structure of the bulk material was characterised by <sup>1</sup>H NMR spectroscopy of the acid-digested material (Figure 3), which confirmed the expected 1:1 ratio of the two dicarboxylate species. PXRD experiments confirmed phase purity of the framework, which retained its crystallinity after drying under mild conditions (Figure S4). Further characterisation by IR spectroscopy and thermogravimetric analysis is provided in the ESI.



**Figure 2** Single crystal structure of **1-biphen-TP** showing (a) hydrogen bonds (b) the packing of the structure containing small channels; each dicarboxylate is shown in a different shade of blue. C–H atoms and one disorder omitted for clarity, the OLEX2 solvent mask feature was used.<sup>24</sup>



**Figure 3** Partial  $^1\text{H}$  NMR spectrum of acid-digested **1-biphen-TP** showing 1:1 ratio of **biphen<sup>2-</sup>**:**TP<sup>2-</sup>** ( $d_6$ -DMSO containing a drop of  $\text{DCl}_{(\text{aq})}$ , 400 MHz, 298 K). N-H peaks integrate to a lower value than expected due to H/D exchange.

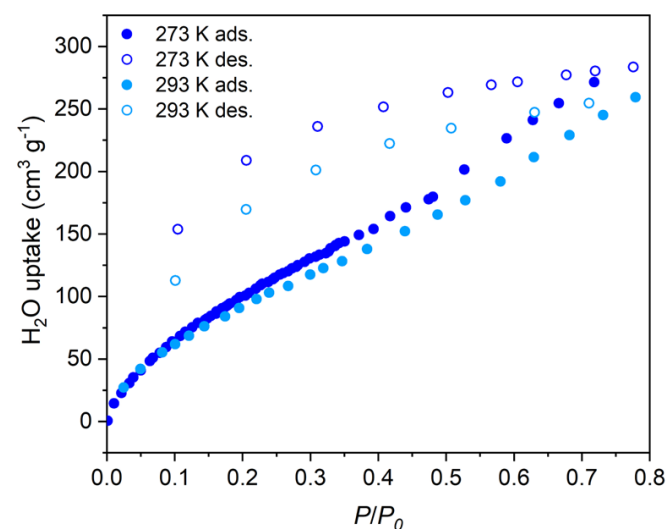
We investigated the effect of varying the ratio of **1<sup>+</sup>**:**biphen<sup>2-</sup>**:**TP<sup>2-</sup>** during synthesis of the framework. Interestingly, at 1:1:1, 1:1:2, 1:1:5, 1:2:1 and 1:2:2 and **1<sup>+</sup>**:**biphen<sup>2-</sup>**:**TP<sup>2-</sup>** ratios in the mixed ethanol:water solvent system, the only product observed was the multicomponent framework **1-biphen-TP** as confirmed by SCXRD unit cell checks of the crystals, PXRD studies, and  $^1\text{H}$  NMR spectroscopy of the acid-digested frameworks (see Figures S7, S9 and Table S1). While there is clearly some tolerance for "incorrect" equivalents of anions, this has its limitations: using five or more equivalents of **biphen<sup>2-</sup>**, or ten equivalents of **TP<sup>2-</sup>** gave two-component frameworks instead of **1-biphen-TP**.

We have previously demonstrated that amidinium-carboxylate frameworks do not adsorb  $\text{N}_2$  or  $\text{CO}_2$  but can reversibly adsorb water vapour at low partial pressures.<sup>25,26</sup> While highly interpenetrated, the structure of **1-biphen-TP** contains solvent-accessible channels, and so we studied its water vapour sorption properties. As shown in Figure 4, **1-biphen-TP** demonstrates reversible adsorption of a significant volume of water vapour, demonstrating its porosity. The amount of water adsorbed by the framework is approximately that expected based on the number of disordered water molecules in the pores of the framework indicated by X-ray crystallography (see ESI for details). While the water vapour capacity of the multicomponent framework is slightly lower than that of the two-component material **1-(TP)<sub>2</sub>**, we note it is still a high level of water sorption for a hydrogen bonded framework.<sup>16,27–30</sup>

In summary, this work has shown for the first time that three-component hydrogen bonded frameworks can be synthesised from one cationic building block and two different dicarboxylate components. In water,

two-component frameworks were preferred, whereas a three-component system was formed when ethanol was added as a co-solvent.

We gratefully acknowledge funding from the Australian Research Council (AGRTP scholarship to PMN, DE210101627 to LKM, FT210100495 to NGW) and assistance with X-ray crystallography from Dr Michael Gardiner. Parts of this work were conducted using beamline MX2 of the Australian Synchrotron and made use of the Australian Cancer Research Foundation detector.<sup>31</sup>



**Figure 4** Water adsorption isotherms for **1-biphen-TP** at 273 and 293 K.

## Conflicts of interest

There are no conflicts to declare.

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