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Hydrogen-bonded organic frameworks (HOFs) constructed from naphthalene-diimide bearing tectons undergo photochromic changes whilst forming radical bearing species within the framework structure.

HOFs have emerged as an exciting new class of materials^{1–4} that offer a potential alternative to the more widely studied metal–organic frameworks (MOFs)^{5,6} and covalent-organic frameworks (COFs).⁷ HOFs are crystalline framework materials constructed by the self-assembly of organic molecules through intermolecular hydrogen bonding.^{1–4,8} HOFs demonstrate attractive features due to ease of formation by simple crystallization processes, low weight and environmentally friendly structures due to the absence of metals. In contrast to MOFs and COFs, it is also potentially possible to regenerate HOFs by a simple recrystallization process.⁹ Although, the term HOF has not been formally defined it seems reasonable to describe HOFs as hydrogen-bonded frameworks with ‘potential’ porosity, analogously to MOFs.¹⁰ In the examples reported here our HOFs contain guest molecules.

A potential drawback of HOFs is a perceived fear of framework instability, due to the relatively weak nature of H-bonding interactions, which is, in some instances, encountered experimentally.² However, HOFs assembled with charge-assisted hydrogen bonds tend to be significantly more robust than those assembled without charge assistance, due to the presence of electrostatic interactions in these assemblies.¹¹ Of particular note are the family of charge-assisted HOFs based on amidinium and carboxylate components which have been developed by White *et al.*^{12–14}

Photoinduced radical formation in hydrogen-bonded organic frameworks†

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In this study we seek to establish HOFs as alternatives to photochromic MOFs that form radicals as a result of photoexcitation. MOFs that undergo colour changes as a result of photoexcitation have received extensive investigation with the family of MOFs composed of naphthalene-diimide (NDI) groups an area of particular focus.¹⁵ Such materials have been identified as attractive targets due to robust behaviour of the NDI fragment and its ability to undergo photoexcitation using simple LED light sources.^{16–20} We have chosen to develop HOFs that contain NDI groups as constituents of one component of a dual-component framework. In order to incorporate NDI into a suitable hydrogen-bonding tecton we functionalise the NDI core with isophthalic acid groups at either terminus of the molecule, providing carboxylate groups that can form robust charge-assisted hydrogen bonding interactions. In combination with amidinium tectons, these four carboxylic acids form intermolecular hydrogen bonds to generate extended framework structures. Our highly adaptable dual-component approach contrasts with the single component NDI-containing HOF reported by Wang *et al.*²¹ who observe radical formation upon photo-excitation, although this is associated with only a small colour change of the material.

The NDI-containing tecton, **1H₄**, was prepared by a simple condensation reaction between 5-aminoisophthalic acid and 1,4,5,8-naphthalene dianhydride. **1H₄** exhibits a high degree of insolubility in all organic solvents except hot DMF, and in order to form aqueous solutions deprotonation is required resulting in a tetracarboxylate species, **1** (Fig. 1a), capable of forming charge-assisted hydrogen bonds with amidinium donors.

Three different crystalline HOF materials were prepared through self-assembly of **1** with the bisamidinium cation, **2** (Fig. 1a). The specific HOF product formed was found to be sensitive to crystallisation conditions, including pH. A general procedure for HOF synthesis involved dissolving each component, **1** and **2**, in water with the addition of sufficient NaOH to ensure solubility of **1**. The two components were then combined by slow addition of the solution of **2** to that of **1**. Naphthalene diimides are sensitive to basic conditions and **1**

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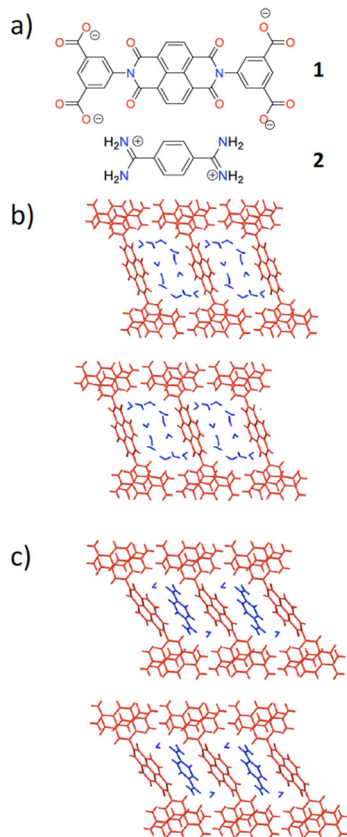



Fig. 1 (a) Compounds **1** and **2** used in the construction of HOFs **A–C**; (b) crystal structure of HOF **A** showing the bilayer structure and guest water molecules; (c) crystal structure of HOF **B** viewed along the *c*-axis.

is no exception with one of the two imide groups in **1** opening between pH 7.5 and 8, and both rings opening above pH 8.^{22,23} Concomitantly, the basic conditions used during HOF formation can also lead to hydrolysis of **2** forming carboxamides.²⁴

HOF **A** was synthesised by layering an aqueous solution of **1** over a solution of **2**, followed by the addition of a 2.5 mM solution of **1** in DMF. After 24 h a cloudy brown precipitate was observed followed by honey-coloured plates after a further week. HOF **A** crystallizes in the triclinic space group $P\bar{1}$, with the crystal structure revealing the formation of 2D sheets constructed from a combination of **1** and **2**, with a framework formula of 1.2_2 (Fig. 1b). The isophthalate termini of **1** adopt hydrogen bonds such that each molecule of **1** interacts with eight separate bisamidinium cations. Ten $O \cdots H-N$ hydrogen bonding interactions occur between the isophthalate or NDI imide oxygen and amidinium hydrogen atoms, with distances ranging from 1.88(2) Å to 2.09(17) Å, as depicted by the d_{norm} Hirshfeld surface (Fig. S1, ESI†). The isophthalate moiety displays two distinct geometries of hydrogen bonding interactions: $R_2^2(8)$ double H-bonds and $R_1^1(6)$ bifurcated H-bonds. As anticipated²⁵ the bifurcated interaction adopts longer interactions, suggesting a weaker interaction. The hydrogen bonding interactions are in good agreement with similar interactions previously reported.^{26,27} HOF **A** forms rectangular channels

with pore size of 8.5 Å × 5.7 Å (Fig. 1b) which accommodate water molecules that also, in some instances, adopt weak interactions with **1** through $O-H \cdots O$ hydrogen bonds.

HOF **B** was prepared by adding an excess of **2** (8 eq.) to an aqueous solution of **1**. Initially a yellow precipitate formed with a few crystals of honey-coloured plates growing over a three-month period. HOF **B** crystallizes in triclinic space group $P\bar{1}$, with a similar bilayer structure to that observed in HOF **A** (Fig. 1c). HOF **B** also forms channels that sit within the bilayer structure but in contrast to **A**, where these channels are occupied by guest water molecules, in **B** the channels accommodate a guest bis-carboxamide (shown in blue in Fig. 1c), leading to a structure with the stoichiometry of one bis-carboxamide per 1.2_2 framework. As noted above, amidiniums hydrolyse to carboxamides in basic conditions such as those used for the crystallisation of **B**. The guest bis-carboxamides hydrogen bond to the imide carbonyl of **1** through $N-H \cdots O$ interactions ($N-H \cdots O = 2.21(10)$ Å, $> N-H \cdots O = 148.74(9)^\circ$) which are longer than the charge-assisted amidinium \cdots carboxylate $N-H \cdots O$ interactions in the same HOF ($N-H \cdots O = 2.03(10)$ Å, $> N-H \cdots O = 163.814(9)^\circ$) (see Fig. 2b and Fig. S2 for further representations and analysis of interactions, ESI†). The guest bis-carboxamides also interact with the NDI groups on either side of the framework channels, with a closest contact of 3.48(2) Å. It is evident that the guest bis-carboxamides sit comfortably in the channels of the bilayer structure (Fig. 1c). Residual space in the structure, both within the bilayer channels and between bilayers, is occupied by water molecules that interact with residual hydrogen bond accepting sites. The structure of **B** can be viewed as a three component HOF, to our knowledge the first example, or alternatively as HOF **A** but with guest bis-carboxamides sitting in the framework channels.

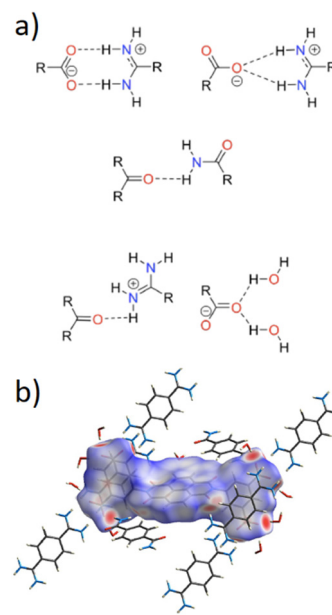


Fig. 2 (a) H-bonding motifs observed in HOFs **A–C** between **1**, **2** and bis-carboxamide molecules; (b) d_{norm} surface Hirshfeld plot showing the interactions between **1** and **2** or bis-carboxamide in HOF **B**.



It is notable that crystals of HOF **B** grew over approximately a month, allowing hydrolysis of **2** to give the bis-carboxamide. Crystallisation of a further HOF over a much longer period of a year led to a further framework, HOF **C** (Fig. S3 and S4, ESI†). Crystals of this HOF were prepared by mixing 2.5 mM solutions of **1** and **2** which led to the formation of a light yellow powder after one day, followed by the formation of a few crystals of HOF **C** over the period of a year. Like HOFs **A** and **B**, HOF **C** crystallizes in the triclinic space group $P\bar{1}$ but, in contrast to **A** and **B**, hydrolysis of both **1** and **2** is observed. One imide of **1** is hydrolysed leading to ring opening and the formation of an additional carboxylate hydrogen bond acceptor (Fig. S7, ESI†) and, as with **B**, **2** is partially hydrolysed to make the bis-carboxamide derivative. The resulting material exhibits a plethora of different hydrogen bonds and π - π interactions between the various components forming a framework structure. The data collected for HOF **C** is weak and as a result the model does not justify analysis beyond simple molecular connectivity. HOF **C** serves as a warning of the potential complexity of these systems, particularly when crystals are grown over long periods (such as those afforded by a pandemic) allowing multiple reaction processes to occur.

Due to the prolonged times required to prepare both **B** and **C** we decided to focus on HOF **A** for subsequent studies. The phase purity of samples of **A** were established by powder X-ray diffraction (PXRD). PXRD studies were performed on air-dried crystals without subjecting the sample to grinding, and the observed diffraction pattern exhibited good agreement with the calculated pattern derived from the crystal structure (Fig. 3d). The stability of the framework after activating the sample under vacuum for two days was assessed by PXRD (Fig. 3d) which showed only negligible changes in the overall structure, illustrating a stable framework even after removing solvent. A good agreement can be found between this conclusion and the published work of Luo *et al.*²¹ Grinding the sample resulted in a PXRD pattern with notable changes in the peak intensities indicating a high degree of preferred orientation in unground samples, consistent with the plate morphology of crystals of this material. The thermal stability of HOF **A** was examined by TGA which showed a gradual release of guest water molecules from 40 °C until *ca.* 230 °C, accounting for approximately 11% of the total weight (Fig. S3, ESI†) followed by a sharp weight loss of 30% above 230 °C attributed to amidinium cation decomposition.

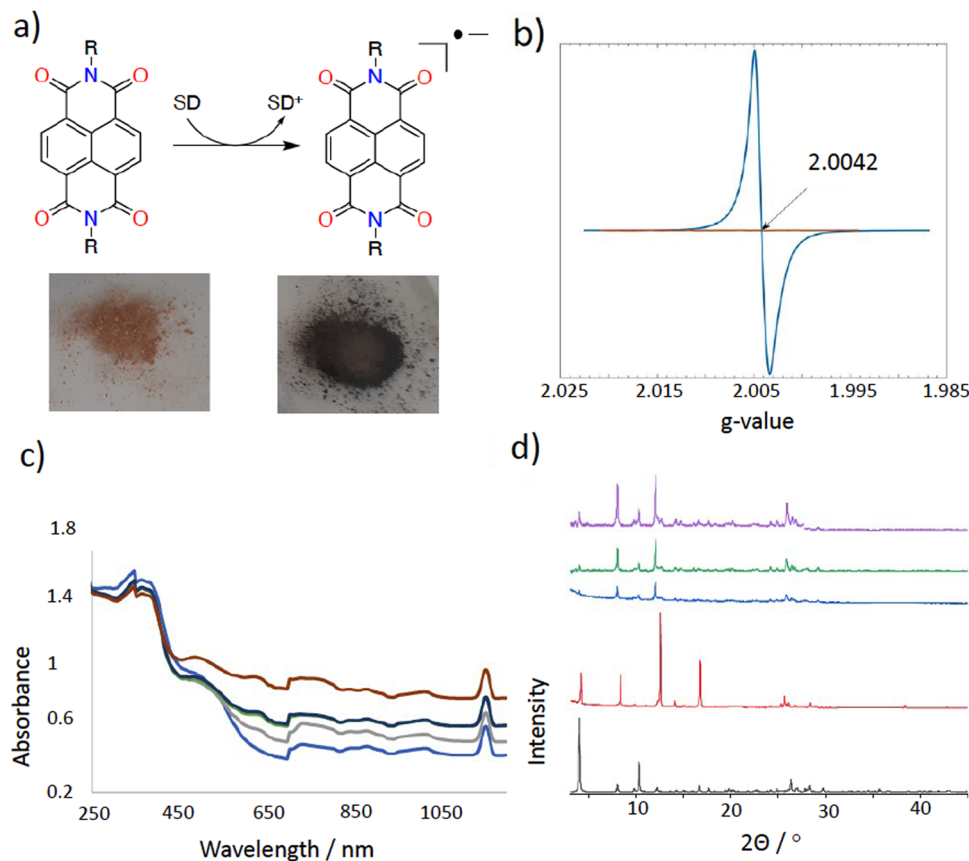


Fig. 3 (a) Photoinduced radical formation in NDI species accompanied by photographs of a sample of HOF **A** before irradiation (left) and after 5 minutes of irradiation with 369 nm light (right); (b) EPR spectra of HOF **A** before (red) and after irradiating (blue) the sample for five minutes under 369 nm light; (c) solid state UV-vis spectra of HOF **A** before and after irradiating for increments of 5 minutes (light blue – pre irradiation; grey – 5 min irradiation; green – 10 min; dark blue – 15 min; red – 20 min); (d) PXRD pattern of simulated (black), ground HOF **A** (red), vacuum dried **A** (blue), irradiated **A** (green) and as-synthesised **A** (purple).



It is known that it is possible to generate NDI-based radicals by photoexcitation in the presence of a sacrificial donor,²⁸ and we wished to explore whether the HOF was able to undergo such an excitation process. In accordance with related experiments on NDI-containing MOFs we assign the role of sacrificial donor to DMF, or decomposition products thereof.²⁹ During our studies we noted that HOF A was sensitive to sunlight with samples exhibiting photochromic behaviour resulting in a colour change from the original honey-coloured to dark brown (Fig. 3a). We anticipated that this colour change was due to photogeneration of an NDI-based radical and therefore we used EPR measurements to confirm the presence of radicals in this HOF. Non-irradiated HOF A does not exhibit any detectable EPR signal, however, when irradiated with 369 nm light for just five minutes, the photoexcited HOF produces a single-peak radical signal ($g = 2.0042$) (Fig. 3b). The intensity of this peak slowly reduces over a period of more than 48 hours (Fig S6, ESI†) indicating that the radical, once formed, is stable over prolonged periods. Solid-state UV-vis spectroscopy confirms a significant change in the overall spectrum as a result of irradiation and radical formation with a gradual increase in absorption across the spectrum (Fig. 3c). No significant alterations in the structure were observed in the irradiated samples when compared to the original sample, as demonstrated by their PXRD patterns (Fig. 3d), although we cannot rule out whether the radicals are formed solely on the surface of the HOF.

Our results demonstrate that HOFs are capable of undergoing photoinitiated radical formation whilst maintaining structural integrity. The incorporation of the photoactive NDI group within one of the HOF tectons provides significant challenges in terms of solubility. As the carboxylate...amidinium HOFs are prepared in aqueous conditions, basic conditions were required to dissolve the NDI-based component, which concurrently resulted in reaction of the two tectons to further species during prolonged crystallisation experiments. Reaction of the tectons during crystallisation clearly leads to complications in consistent synthesis of this family of HOFs but fortunately short reaction times are effective in leading to the isolation of HOF A. Subsequent studies demonstrate that photoinitiated radical formation processes is possible in HOF A accompanied by a notable colour change associated with this activation process. Thus, we conclude that HOFs offer themselves as viable alternatives to the much more widely studied MOF analogues in demonstrating photochromic behaviour, and radical formation, and opening new avenues of research for this interesting and highly adaptable class of materials.

The project was conceived and supervised by NRC. ARYA performed the synthesis and characterisation. X-ray diffraction was performed by ARYA and GRFO, and EPR experiments, performed by CR. All authors discussed the results and contributed to the final preparation of the manuscript.

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Conflicts of interest

There are no conflicts to declare.

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