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ARTICLE TYPE

Synthesis of an extended halogen-bonded metal-organic structure in a one-pot mechanochemical reaction that combines covalent, coordination and supramolecular synthesis

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We describe a four-component one-pot mechanochemical reaction which combines the formation of covalent bonds, coordination bonds and halogen bonds to obtain an extended
10 **structure based on halogen-bonded metal-organic units.**

Mechanochemistry,[1] conducted by milling or grinding, is a powerful approach for clean and environmentally-friendly synthesis, applicable to a wide range of targets, including organic molecules,[2] functional organic solids,[3]
15 organometallics,[4] metal-organic materials,[5] as well as inorganic materials[6] and nanoparticles.[7] While the majority of reports have focused on adapting mechanochemistry to conduct a particular type of transformation, recent work has highlighted the possibility to combine multiple orthogonal[8]
20 reactions into a one-pot, "all-at-once"[9] synthesis of complex products.[10] The development of multi-component synthetic procedures is driven by the attractive prospect to extend the benefits of mechanochemistry in solvent-free synthesis with the ability to synthesise complex products rapidly and from
25 the simplest possible precursors.

   We now demonstrate a one-pot mechanochemical reaction that combines the synthesis of covalent bonds, coordination bonds and halogen bonds[11] to form an extended structure consisting of metal-organic complexes connected by halogen
30 bonds (Figure 1a,b). The assembly of metal-organic units is an attractive target for crystal engineering by halogen bonding, due to their potential to provide new magnetic, optical or electrical properties.[12] However, while engineering halogen-bonded structures has focused largely on organic solids and
35 liquid crystals,[13] the design of halogen-bonded cocrystals based on metal-organic building blocks remains of continuing interest.[14-16]

   Herein, we show a synthetic design addressing this challenge, and a mechanochemical methodology that allows a
40 material based on this design to be synthesised cleanly, in one step and from the simplest precursors. Central to this design is a metal complex with a terminal electron donor that can link to a halogen bond donor such as 1,4-diiodotetrafluorobenzene (**tfib**, Figure 1c). As a candidate for such a metal-organic
45 building block we considered the Cu(II) complex of the chelating Schiff base (**Hnaap**, Figure 1c) derived from 4–aminoacetophenone (**aap**) and 2-hydroxy-1-naphthaldehyde
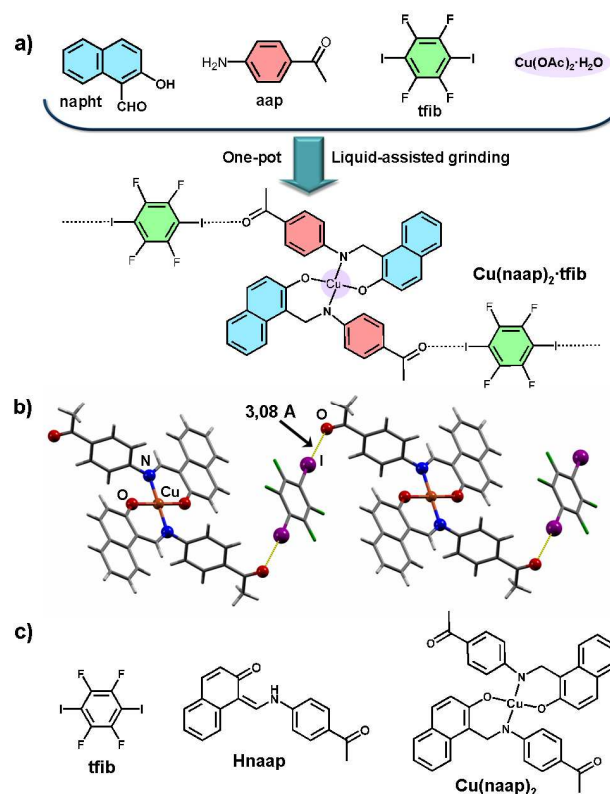

Figure 1. (a) Mechanosynthesis of a halogen-bonded metal-organic
50 structure by combining covalent bond formation, coordination chemistry and halogen bonding in a single milling process; (b) fragment of the crystal structure of the resulting halogen-bonded metal-organic polymer; (c) diagrams of **tfib**, the Schiff base ligand and its copper(II) complex.

(**napht**).[17] Copper(II) was chosen because of its preference for
55 square-planar coordination with chelating Schiff bases,[18,19] expected to facilitate the participation of the terminal acetyl group of the complex Cu(**naap**)₂ in halogen bonding.

   While the synthesis and structure of **Hnaap** were previously reported,[17] we found that it can be quantitatively
60 obtained by 60 min milling of **napht** and **aap** with a catalytic amount of a 5% *v/v* solution of triethylamine (TEA) in ethanol (EtOH).[20,21] Milling was conducted in a Retsch MM400 mill using a stainless steel milling assembly (see ESI). Formation of **Hnaap** by such liquid-assisted grinding (LAG)[21] was

confirmed by comparing its powder X-ray diffraction (PXRD) pattern to the one calculated for the reported structure (Figure 2a,b),[17] and to the pattern of a sample of **Hnaap** made by solution techniques (75% yield).
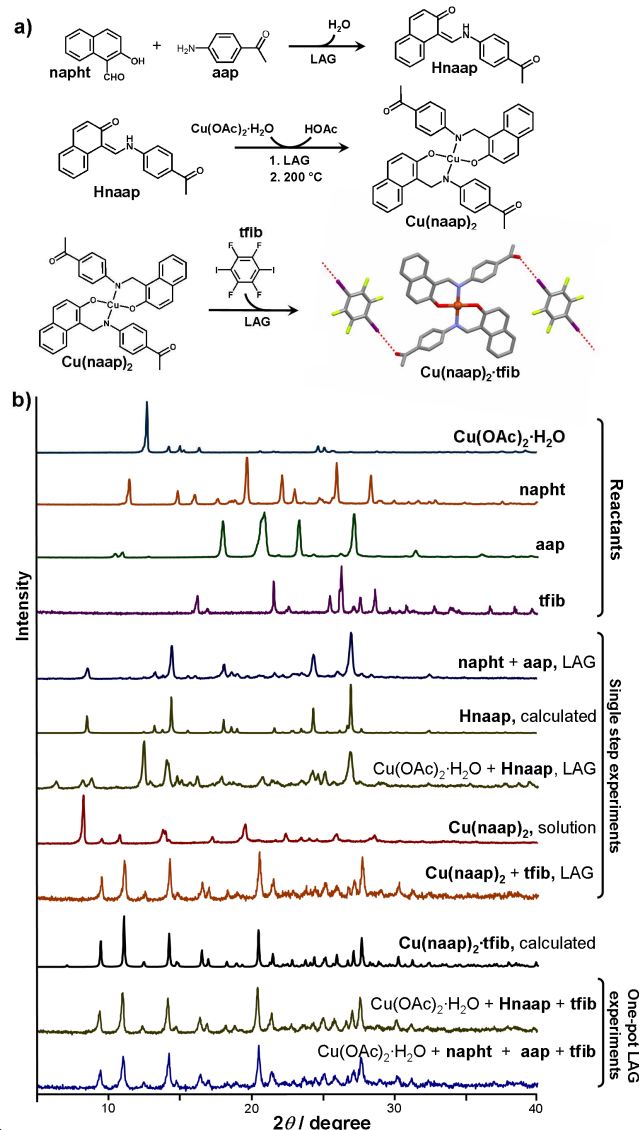
a)

Figure 2. (a) Sequential synthesis of Cu**(naap)₂·tfib** involving the formation of **Hnaap** followed by metal complexation, thermal desolvation and cocrystallisation with **tfib**; (b) relevant calculated and experimental PXRD patterns: (top) reactants; (middle) selected patterns for sequential synthesis and (bottom) for one-pot mechanosynthesis.

Next, we pursued the synthesis of Cu**(naap)₂** by LAG of a 1:2 stoichiometric mixture of copper(II) acetate monohydrate (Cu(OAc)₂·H₂O) and **Hnaap** in the presence of 5% TEA/EtOH solution[21] as the grinding liquid. After 50 min the reaction gave a green powder characterised by PXRD, Fourier-transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). The latter revealed that the product is an acetic acid (AcOH) solvate of composition Cu**(naap)₂·2AcOH.**[22,23] In contrast, a solution-based reaction of **Hnaap** and Cu(OAc)₂·H₂O provided a brown powder identified by TGA as Cu**(naap)₂** (80% yield). Annealing of the mechanochemical product at 200 °C for 30 min gave

Cu**(naap)₂**, as indicated by comparing its FTIR spectrum and PXRD pattern to a solution-made sample (Figures 2a,b). As the final step, we conducted[21] LAG of Cu**(naap)₂** with **tfib**. After 50 min milling, PXRD analysis of the brown reaction mixture revealed the complete disappearance of reactants and formation of a new crystalline solid (see ESI). Recrystallisation of the product from a mixture of EtOH and tetrahydrofuran led to partial decomposition into Cu**(naap)₂** but also gave single crystals suitable for X-ray diffraction.¶ Structure determination revealed that the crystals are the hoped for halogen-bonded chain Cu**(naap)₂·tfib**, consisting of alternating units of Cu**(naap)₂** and **tfib** (Figure 1b).

Each molecule of the Cu(II) complex is associated with two **tfib** molecules *via* almost linear I···O contacts (I···O distance 3.08 Å, C–I···O angle 168°),[11] forming halogen-bonded metal-organic chains. Geometry of Cu**(naap)₂** in the chains is consistent with that normally observed for Cu(II) complexes of chelating Schiff bases with an O,N-donor set:[18] Cu(II) ion adopts a square planar geometry with a *trans*-distribution of O and N donor atoms. The Cu–N and Cu-O bond lengths are 1.980(3) Å and 1.881(2) Å, respectively, and the O–Cu–N angle 90.66(1)°. Notable detail of the Cu**(naap)₂·tfib** structure is the C=O···I angle of 105°, instead of 120° ideally expected for a halogen bonding to an sp^2-hybridised oxygen atom. The deviation is comparable to that previously observed for halogen bonding to ketones.[24]

Crystal structure of Cu**(naap)₂·tfib** can be described by juxtaposition of halogen-bonded chains to form layers in the (-11-2) plane, assisted by C–H···F contacts[25] between naphthalene and **tfib** moieties from adjacent chains (C···F distance: 3.50 Å, Figure 3). The overall structure results from the stacking of such layers, involving C–H···O (C···O distance: 3.52 Å) and C–H···C contacts (C···C distance: 3.57 Å)[26] between molecules in neighboring layers. The calculated PXRD pattern for the structure of Cu**(naap)₂·tfib** is in full agreement with that measured for the final product of LAG (see ESI), confirming the success of the reaction sequence involving one thermal and three mechanochemical steps.
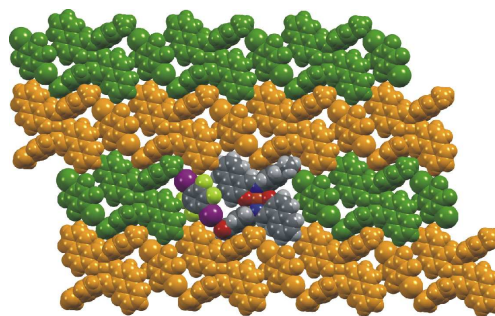
Figure 3. Assembly of halogen-bonded chains of Cu**(naap)₂·tfib** into layers. For clarity, adjacent chains are colour-coded orange or green.

Next, we attempted to simplify the mechanochemical procedure by milling the mechanochemically prepared **Hnaap** with Cu(OAc)₂·H₂O and **tfib**. As evidenced by PXRD, this one-pot two-step approach quantitatively gave Cu**(naap)₂·tfib** after 50 min LAG.

Finally, we attempted a one-pot, "all at once" approach in which a single milling process would lead to the synthesis of

Hnaap, its reaction with Cu(OAc)$_2$·H$_2$O to form Cu**(naap)$_2$** and halogen bond-driven self assembly to form Cu**(naap)$_2$**·**tfib** (Figure 1a). Indeed, the 4-component grinding of **napht**, **aap**, Cu(OAc)$_2$·H$_2$O and **tfib** in the required 2:2:1:1 stoichiometric ratios and with a small quantity[21] of the TEA/EtOH solution, yielded Cu**(naap)$_2$**·**tfib** (Figure 2b). PXRD pattern of the product was identical to that calculated from single crystal data. This one-pot "all-at-once" experiment provided the final product within 60 min grinding, which is *ca.* three times shorter than the initially explored three-step sequence, and without thermal annealing.

In summary, we have demonstrated the synthesis of a one-dimensional halogen-bonded metal-organic architecture using a one-pot milling process that couples covalent bond formation to coordination synthesis and cocrystallisation by halogen bonds. The one-pot four-component reaction exhibits notable advantages over the corresponding sequential process, not only by reducing the reaction time and allowing the use of simpler reactants, but also by circumventing the need for a thermal annealing step. The presented design for a halogen-bonded metal-organic structure is also an advance in halogen bond-driven crystal engineering by demonstrating the assemby of metal-organic units without using kinetically inert building blocks of late transition metals.[14]

Notes and references

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‡ Electronic Supplementary Information (ESI) available: details of mechanochemical and solution syntheses, instrumental analysis, PXRD, FTIR, TG/DSC data. CCDC 1013917 contains crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. See DOI: 10.1039/b000000x/

¶ Attempts to synthesise Cu**(naap)$_2$**·**tfib** in solution from **tfib** and Cu**(naap)$_2$** were only partly successful, giving rise to a product (70%yield) contaminated with Cu**(naap)$_2$** (see ESI).

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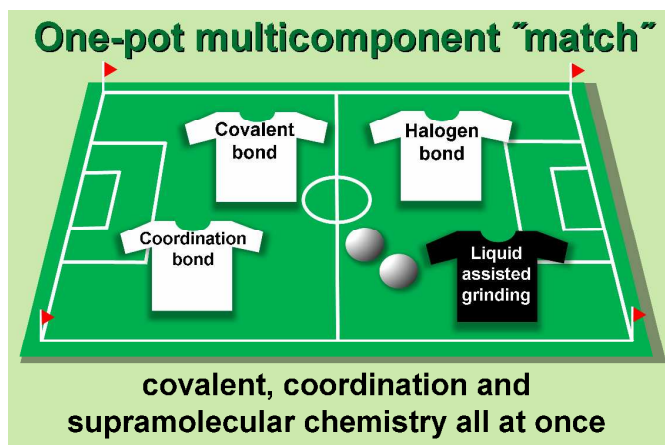
We describe a four-component one-pot mechanochemical reaction which combines the formation of covalent bonds, coordination bonds and halogen bonds to obtain an extended structure based on halogen-bonded metal-organic units