SUPPORTING INFORMATION

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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Figure S38. a) PXRD pattern of residue after TG experiment of compound Cu(naap)$_2$:tfib and b) calculated pattern for CuO.
EXPERIMENTAL DETAILS

MATERIALS
The starting materials, 2-hydroxy-1-naphthaldehyde (napht) and 4-aminoacetophenone (aap) were obtained from Acros Organics; copper acetate monohydrate was obtained from Kemika; and 1,4-tetrafluoriodobenzene (tfib) was obtained from Merck. Napht was recrystallised from methanol and all other materials were used without further purification. Solvents were purchased from Kemika and T.T.T., Zagreb.

BALL MILLING EXPERIMENTS

Synthesis of Hnaap
For LAG experiment equimolar quantities of napht (0.129 g, 0.75 mmol) and aap (0.101 g, 0.75 mmol) were placed in a 10 mL stainless steel grinding jar along with 40 µL of a mixture of EtOH and TEA [5% v/v of TEA] and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 60 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

Synthesis of acetic acid solvate of Cu(naap)$_2$
For LAG experiment, compound Hnaap (0.174 g, 0.60 mmol) and copper acetate monohydrate (0.060 g, 0.30 mmol) were placed in a 10 mL stainless steel grinding jar along with 35 µL of a mixture of EtOH and TEA [5% v/v of TEA] and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 50 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

Synthesis of Cu(naap)$_2$·tfib

Single-step synthesis
For LAG experiment, compound Cu(naap)$_2$ (0.030 g, 0.047 mmol) and tfib (0.019 g, 0.047 mmol) were placed in a 5 mL stainless steel grinding jar along with 15 µL of nitromethane and two 4 mm-diameter stainless steel grinding balls. The mixture was then milled for 50 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

One-pot two-step synthesis
For LAG experiment, compound Hnaap (0.087 g, 0.30 mmol), copper acetate monohydrate (0.030 g, 0.15 mmol) and tfib (0.061 g, 0.15 mmol) were placed in a 10 mL stainless steel grinding jar along with 40 µL of a mixture of EtOH and TEA [5% v/v of TEA] and two 7
mm-diameter stainless steel grinding balls. The mixture was then milled for 50 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

**One-pot three-step synthesis**  
For LAG experiment, **napht** (0.052 g, 0.30 mmol), **aap** (0.041 g, 0.30 mmol), copper acetate monohydrate (0.030 g, 0.15 mmol) and **tfib** (0.061 g, 0.15 mmol) were placed in a 10 mL stainless steel grinding jar along with 40 µL of a mixture of EtOH and TEA [5% *v*/v of TEA] and two 7 mm-diameter stainless steel grinding balls. The mixture was then milled for 60 minutes in a Retsch MM200 Shaker Mill operating at 25 Hz frequency.

**SOLUTION SYNTHESIS**  
To monitor solid-state experiments, as well as to facilitate the characterisation of new materials by single-crystal X-ray diffraction, solid-state experiments were accompanied by conventional solution-based experiments. Crystal and molecular structures of **Hnaap** has been previously reported, CCDC code IXAPOM\(^1\).

**Synthesis of **Hnaap**  
Equimolar quantities of **aap** (1.35 g, 0.01 mol) and **napht** (1.72 g, 0.01 mol), were dissolved in hot methanol (15 mL and 35 mL, respectively). The solutions were mixed and the resulting mixture left at room temperature. Orange precipitate appeared after a period of 1 day. It was separated from the mother liquor by filtration, and washed with methanol.

**Synthesis of **Cu(naap)\(_2\)**  
A clear solution of copper acetate monohydrate (0.199 g, 0.001 mol) in 50 mL methanol was added to a solution of compound **Hnaap** (0.579 g, 0.002 mol) in 70 mL acetonitrile. The resultant mixture was refluxed for 3 h and the brown precipitate was separated from mother liquor by filtration, and washed with methanol.

**Synthesis of **Cu(naap)\(_2\)-tfib**  
Equimolar quantities of compound **Cu(naap)\(_2\)** (0.64 g, 1.0 mmol) and **tfib** (0.40 g, 1.0 mmol), were dissolved in a hot mixture of ethanol and tetrahydrofurane (24 mL, 1:2). The resulting mixture left at room temperature. Brown crystals appeared after a period of 1 day. It was separated from the mother liquor by filtration, and washed with methanol.
THERMAL ANALYSIS

DSC measurements were performed on a Mettler-Toledo DSC823e module in sealed aluminium pans (40 μL), heated in flowing nitrogen (150 mL min⁻¹) at a rate of 10 °C min⁻¹. TG measurements were performed on a Mettler-Toledo TGA/SDTA 851e module in sealed aluminium pans (40 μL), heated in flowing oxygen (150 mL min⁻¹) at a rate of 10 °C min⁻¹. The data collection and analysis was performed using the program package STAR® Software 9.01.2

FTIR SPECTROSCOPY

Infrared spectra were recorded on a PerkinElmer Spectrum Two FTIR spectrophotometer using a KBr pellet. The data collection and analysis was performed using the program package PerkinElmer Spectrum (version 10.4.2.279).

SINGLE-CRYSTAL X-RAY DIFFRACTION EXPERIMENTS

The crystal and molecular structures of Cu(naap)₂·tfib was determined by single crystal X-ray diffraction. Details of data collection and crystal structure refinement are listed in Table S1. The diffraction data were collected at 292 K for all compounds. Diffraction measurements were made on an Oxford Diffraction Xcalibur Kappa CCD X-ray diffractometer with graphite-monochromated MoKα (λ = 0.71073Å) radiation. The data sets were collected using the ω scan mode over the 2θ range up to 54°. Programs CrysAlis CCD³ and CrysAlis RED³ were employed for data collection, cell refinement, and data reduction. The structures were solved by direct methods and refined using the SHELXS and SHELXL programs, respectively.⁴ The structural refinement was performed on F² using all data. The hydrogen atoms not involved in hydrogen bonding were placed in calculated positions and treated as riding on their parent atoms [C–H = 0.93 Å and Uiso(H) = 1.2 Ueq(C)] while the others were located from the electron difference map. All calculations were performed using the WINGX crystallographic suite of programs.⁵ The molecular structures of compounds are presented by ORTEP-3⁶ and their molecular packing projections were prepared by Mercury.⁷

POWDER X-RAY DIFFRACTION EXPERIMENTS

PXRD experiments of the samples were performed on a PHILIPS PW 1840 X-ray diffractometer with CuKα1 (1.54056 Å) radiation at 40 mA and 40 kV. The scattered intensities were measured with a scintillation counter. The angular range was from 3 to 50°.
(2θ) with steps of 0.02°, and the measuring time was 0.5 to 1 s per step. The data collection and analysis was performed using the program package Philips X'Pert.  

References
Table S1. General and crystallographic data for Cu(naap)$_2$·tfib.

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<th>Compound Cu(naap)$_2$·tfib</th>
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Figure S1. Molecular structures of Cu(naap)$_2$·tfib showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30 % probability level and H atoms are shown as small spheres of arbitrary radius.
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Figure S3. PXRD pattern of pure aap reactant.
Figure S4. PXRD pattern of pure copper acetate monohydrate.

Figure S5. PXRD pattern of pure tfib reactant.
Figure S6. PXRD patterns for mechanochemical and solution-based experiments involving napht and aap: a) napht, b) aap, c) compound Hnaap obtained by grinding in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5% v/v of TEA], d) compound Hnaap obtained by solution-based method, e) calculated pattern for compound Hnaap.

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Figure S8. PXRD patterns for mechanochemical and solution-based experiments involving compound $\text{Cu(naap)}_2$ and tfib: a) compound $\text{Cu(naap)}_2$, b) tfib, c) compound $\text{Cu(naap)}_2\cdot\text{tfib}$ obtained by solution-based method, d) compound $\text{Cu(naap)}_2\cdot\text{tfib}$ obtained by grinding in ball mill for 50 min in the presence of a small quantity of nitromethane and e) calculated pattern for compound $\text{Cu(naap)}_2\cdot\text{tfib}$.

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Figure S17. IR spectrum for the product of grinding of copper acetate monohydrate and compound Hnaap after isothermal experiment at 200 °C.
Figure S18. IR spectrum for Cu(naap)$_2$·tfib prepared by solution-based method.

Figure S19. IR spectrum for Cu(naap)$_2$·tfib prepared by grinding of compound Cu(naap)$_2$ and tfib.
Figure S20. IR spectrum for Cu(\textit{naap})$_2$·tfib prepared by grinding of compound H\textit{naap} and copper acetate monohydrate and tfib.

Figure S21. IR spectrum for Cu(\textit{naap})$_2$·tfib prepared by grinding of \textit{napht}, \textit{aap}, copper acetate monohydrate and tfib.
**Figure S22.** DSC curve for pure napht reactant.

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Figure S32. TG (black) and DTA (red) curve for Cu(naap)$_2$·tfib obtained by solution-based method.

Figure S33. TG (black) and DTA (red) curve for Cu(naap)$_2$·tfib obtained by grinding of compound Cu(naap)$_2$ and tfib in ball mill for 60 min in the presence of a small quantity of nitromethane.
Figure S34. TG (black) and DTA (red) curve for Cu\textsubscript{(naap)}\textsubscript{2}·\textit{tfib} obtained by grinding of copper acetate monohydrate, compound \textit{Hnaap} and \textit{tfib} in ball mill for 60 min in the presence of a small quantity of a mixture of EtOH and TEA [5\% \textit{v}/\textit{v} of TEA].

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