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Communication

Exploring the Halogen-Bonded Cocrystallization Potential of a Metal-Organic Unit Derived from Copper(II) Chloride and 4-Aminoacetophenone

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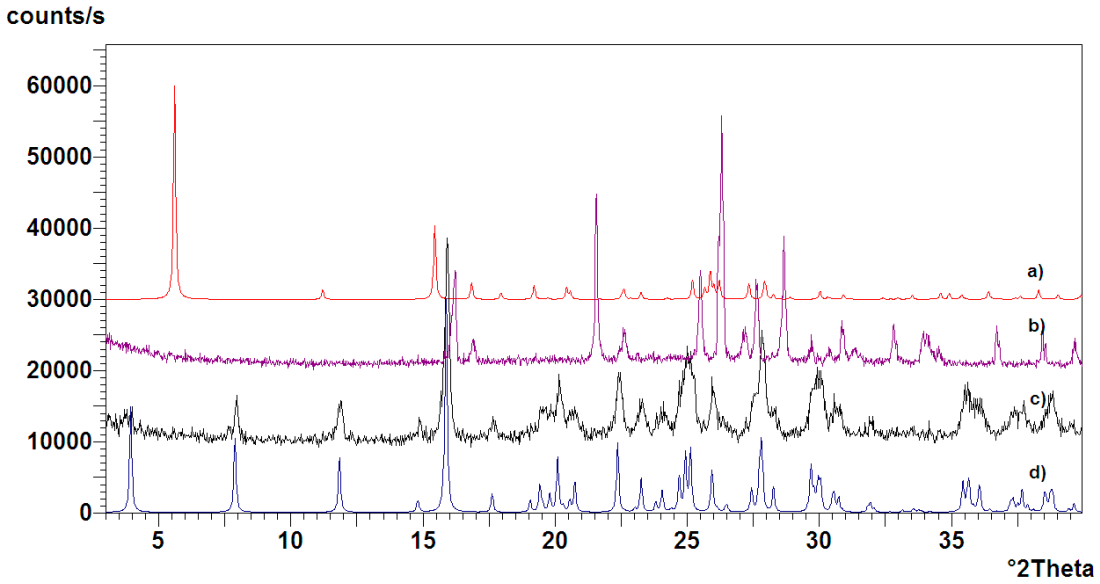

Figure S1. PXRD patterns of **a**) $CuCl_2$(**aap**)$_2$, **b**) **14tfib**, **c**) product obtained by grinding $CuCl_2$(**aap**)$_2$ and **14tfib** in a 1:1 stoichiometric ratio, d) calculated pattern from [$CuCl_2$(**aap**)$_2$](**14tfib**) single crystal data.

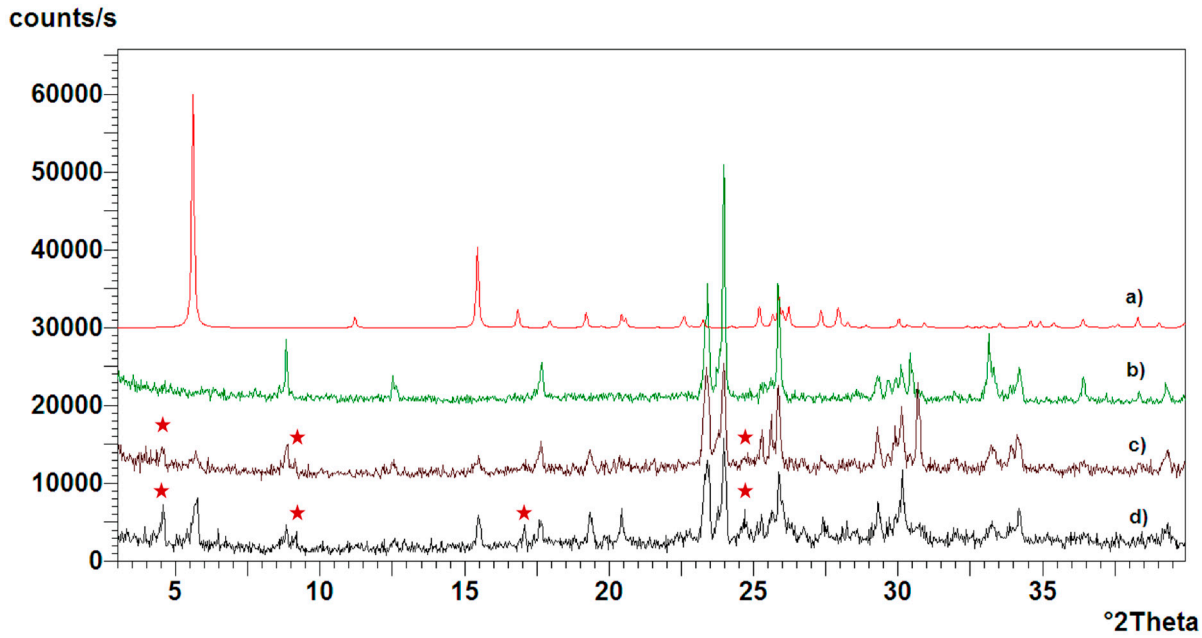

Figure S2. PXRD patterns of **a**) $CuCl_2$(**aap**)$_2$, **b**) **12tfib**, **c**) product obtained by grinding $CuCl_2$(**aap**)$_2$ and **12tfib** in a 1:2 stoichiometric ratio, d) product obtained by grinding $CuCl_2$(**aap**)$_2$ and **12tfib** in a 1:1 stoichiometric ratio. Stars denote small peaks not belonging to either reactant.

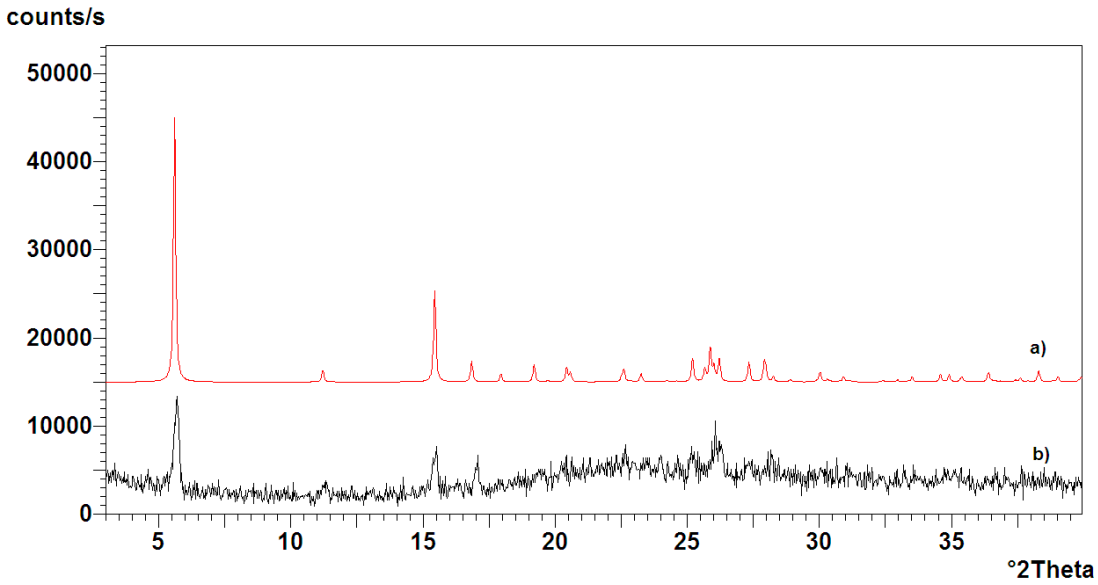

Figure S3. PXRD patterns of **a**) $CuCl_2$(**aap**)$_2$, **b**) product obtained by grinding $CuCl_2$(**aap**)$_2$ and **13tfib** in a 1:1 stoichiometric ratio. The other reagent (**13tfib**) is a liquid, so its PXRD pattern is omitted.

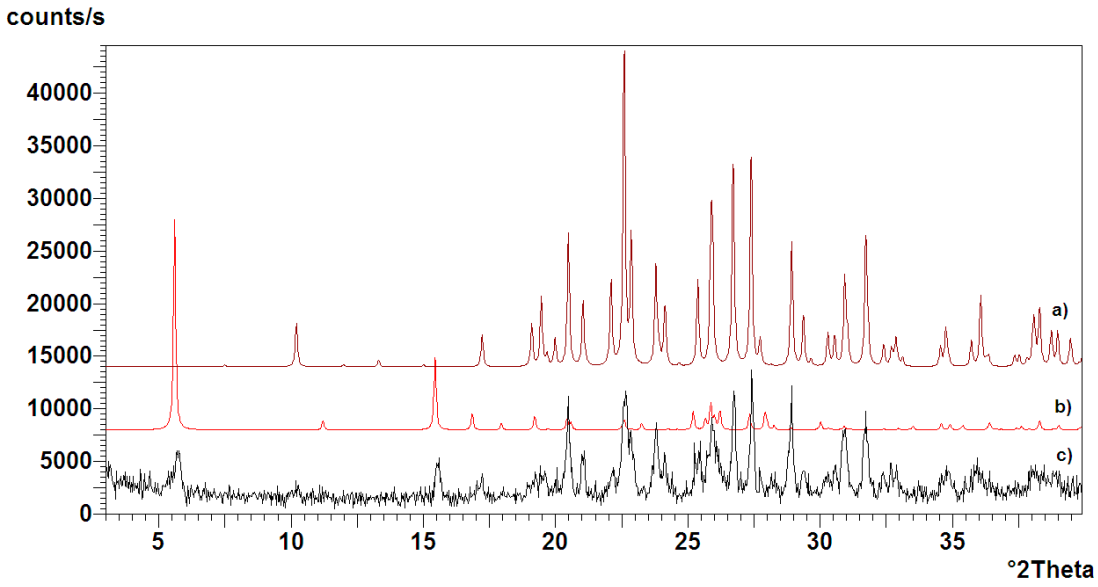

Figure S4. PXRD patterns of **a**) **135tfib**, **b**) $CuCl_2$(**aap**)$_2$, **c**) product obtained by grinding $CuCl_2$(**aap**)$_2$ and **135tfib** in a 1:1 stoichiometric ratio.

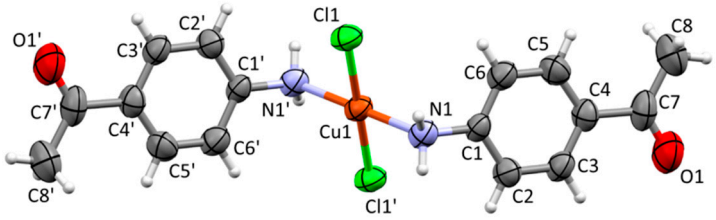

Figure S5. Molecular structure of $CuCl_2$(**aap**)$_2$ showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, and H atoms are shown as small spheres of arbitrary radius. Symmetry codes of symmetry equivalent atoms marked with an ' symbol are listed in Table S4.

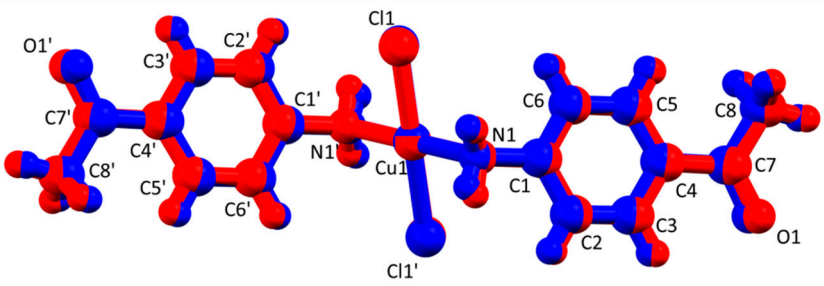

Figure S6. Molecular overlay of the metal complex molecule obtained from $CuCl_2$(**aap**)$_2$ data (colored red) with the metal complex molecule obtained from [$CuCl_2$(**aap**)$_2$](**14tfib**) data (colored blue). The metal complex structures are in good agreement with a root mean square deviation (RMSD) value of 0.1418 and a maximum distance of 0.2619.

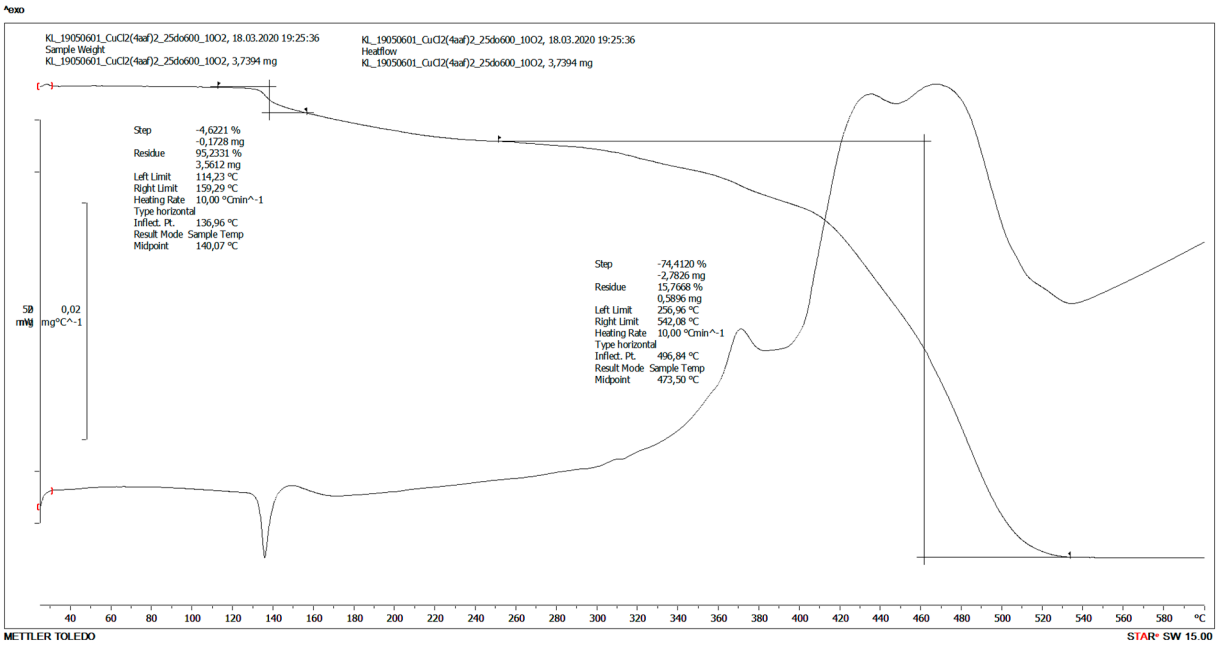

Figure S7. TG and DSC curves of $CuCl_2$(**aap**)$_2$.

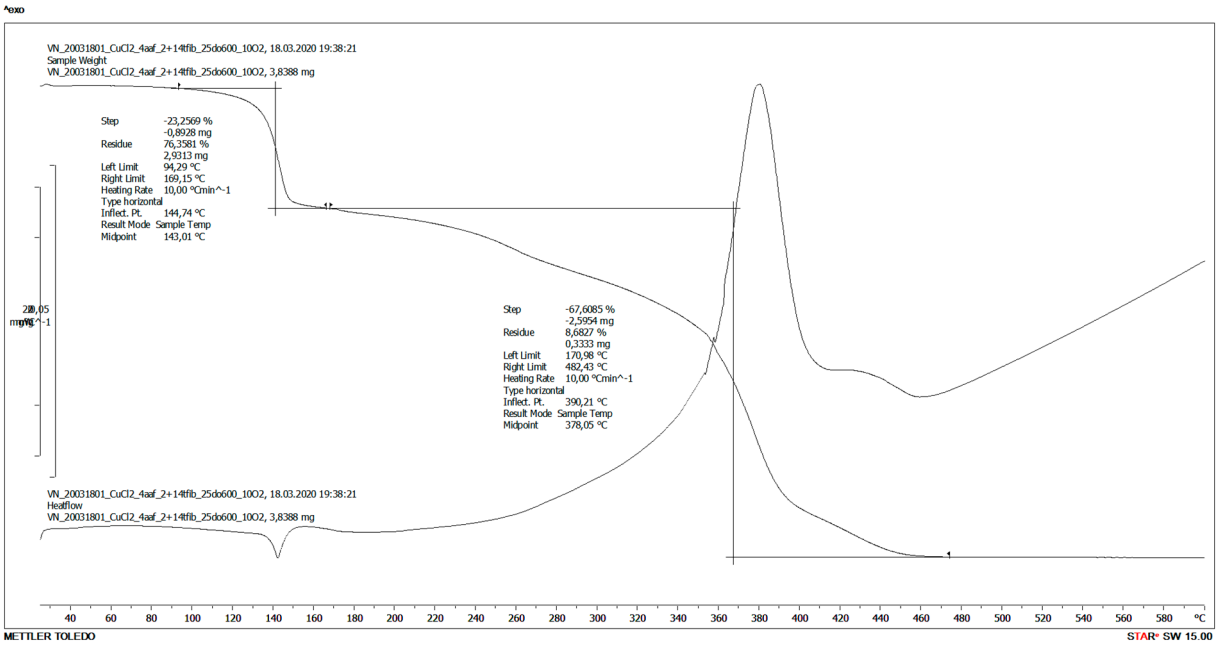

Figure S8. TG and DSC curves of [$CuCl_2$(**aap**)$_2$](**14tfib**).

Table S1. Mechanochemical Synthesis Parameters.

$t_{milling}$ = 30 min, $\nu_{milling}$ = 25 Hz.				
Reactants	**Mole Ratio**	***m*(CuCl$_2$(aap)$_2$) / mg**	***m* or *V*(donor)**	**Liquid**
$CuCl_2$(**aap**)$_2$: **14tfib**	1 : 1	99.6	100.0 mg	40.0 µL acetonitrile
$CuCl_2$(**aap**)$_2$: **12tfib**	1 : 2	67.0	133.0 mg	40.0 µL acetonitrile
	1 : 1	100.0	99.3 mg	40.0 µL acetonitrile
$CuCl_2$(**aap**)$_2$: **13tfib**	1 : 1	100.0	37.5 µL	10.0 µL acetonitrile
$CuCl_2$(**aap**)$_2$: **135tfib**	1 : 1	100.0	125.9 mg	40.0 µL acetonitrile

Table S2. Crystal data and refinement details for the prepared compounds.

	$CuCl_2(aap)_2$	$[CuCl_2(aap)_2](14tfib)$
Molecular formula	$C_{16}H_{18}CuCl_2N_2O_2$	$(C_{16}H_{18}CuCl_2N_2O_2)(C_6F_4I_2)$
M_r	404.76	806.62
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Crystal data:		
a / Å	4.5094(12)	4.6532(3)
b / Å	6.0113(14)	6.0374(3)
c / Å	15.666(4)	22.5789(12)
α / °	93.87(2)	82.905(4)
β / °	90.18(2)	89.166(4)
γ / °	92.38(2)	89.192(4)
V / Å^3	423.31(19)	629.34(6)
Z	1	1
D_{calc} / g cm^{-3}	1.588	2.928
λ(MoK_α) / Å	0.71073	0.71073
T / K	295	295
Crystal size / mm^3	0.35 x 0.26 x 0.03	0.60 x 0.40 x 0.07
μ / mm^{-1}	1.615	3.586
F(000)	207	385
Refl. collected/unique	2885 / 1481	8303 / 2400
Parameters/restraints	113/0	169/0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	1.090; −1.135	0.372; −0.556
$R[F^2 > 4\sigma(F^2)]$	0.0868	0.0276
w$R(F^2)$	0.2560	0.0664
Goodness-of-fit, S	1.092	1.066

Table S3. Parameters of the supramolecular interactions and corresponding symmetry operators present in the prepared compounds.

Cocrystal	D···A	d / Å	∠ (X–D···A) / °	Symmetry Operator
$CuCl_2$(**aap**)$_2$	C8–H8C···O1	3.61(2)	168.0	x, y, z
	N1–H2N···Cl1	3.466(8)	171(9)	x, y, z
[$CuCl_2$(**aap**)$_2$](**14tfib**)	I1···O1	2.989(2)	172.6(1)	$-x, -y, 1-z$
	N1–H1A···Cl1	3.474(3)	165(4)	x, y, z

Table S4. Atom list and symmetry codes of symmetry equivalent atoms (marked with an ' symbol) in the prepared compounds.

$CuCl_2(aap)_2$				$[CuCl_2(aap)_2](14tfib)$			
Atom	**Symmetry Operator**	**Atom**	**Symmetry Operator**	**Atom**	**Symmetry Operator**	**Atom**	**Symmetry Operator**
C1	x, y, z	H5	x, y, z	C1	x, y, z	F1'	$-x, -y, 1-z$
C2	x, y, z	H6	x, y, z	C2	x, y, z	F2'	$-x, -y, 1-z$
C3	x, y, z	H8A	x, y, z	C3	x, y, z	I1	x, y, z
C4	x, y, z	H8B	x, y, z	C4	x, y, z	I1'	$-x, -y, 1-z$
C5	x, y, z	H8C	x, y, z	C5	x, y, z	N1	x, y, z

C6	*x*, *y*, *z*	H1N'	−*x*, 1−*y*, −*z*	C6	*x*, *y*, *z*	N1'	1−*x*, −*y*, −*z*
C7	*x*, *y*, *z*	H2N'	−*x*, 1−*y*, −*z*	C7	*x*, *y*, *z*	O1	*x*, *y*, *z*
C8	*x*, *y*, *z*	H2'	−*x*, 1−*y*, −*z*	C8	*x*, *y*, *z*	O1'	1−*x*, −*y*, −*z*
C1'	−*x*, 1−*y*, −*z*	H3'	−*x*, 1−*y*, −*z*	C9	*x*, *y*, *z*	H1A	*x*, *y*, *z*
C2'	−*x*, 1−*y*, −*z*	H5'	−*x*, 1−*y*, −*z*	C10	*x*, *y*, *z*	H1B	*x*, *y*, *z*
C3'	−*x*, 1−*y*, −*z*	H6'	−*x*, 1−*y*, −*z*	C11	*x*, *y*, *z*	H2	*x*, *y*, *z*
C4'	−*x*, 1−*y*, −*z*	H8A'	−*x*, 1−*y*, −*z*	C1'	1−*x*, −*y*, −*z*	H3	*x*, *y*, *z*
C5'	−*x*, 1−*y*, −*z*	H8B'	−*x*, 1−*y*, −*z*	C2'	1−*x*, −*y*, −*z*	H5	*x*, *y*, *z*
C6'	−*x*, 1−*y*, −*z*	H8C'	−*x*, 1−*y*, −*z*	C3'	1−*x*, −*y*, −*z*	H6	*x*, *y*, *z*
C7'	−*x*, 1−*y*, −*z*			C4'	1−*x*, −*y*, −*z*	H8A	*x*, *y*, *z*
C8'	−*x*, 1−*y*, −*z*			C5'	1−*x*, −*y*, −*z*	H8B	*x*, *y*, *z*
Cu1	*x*, *y*, *z*			C6'	1−*x*, −*y*, −*z*	H8C	*x*, *y*, *z*
Cl1	*x*, *y*, *z*			C7'	1−*x*, −*y*, −*z*	H1A'	1−*x*, −*y*, −*z*
Cl1'	−*x*, 1−*y*, −*z*			C8'	1−*x*, −*y*, −*z*	H1B'	1−*x*, −*y*, −*z*
N1	*x*, *y*, *z*			C9'	−*x*, −*y*, 1−*z*	H2'	1−*x*, −*y*, −*z*
N1'	−*x*, 1−*y*, −*z*			C10'	−*x*, −*y*, 1−*z*	H3'	1−*x*, −*y*, −*z*
O1	*x*, *y*, *z*			C11'	−*x*, −*y*, 1−*z*	H5'	1−*x*, −*y*, −*z*
O1'	−*x*, 1−*y*, −*z*			Cu1	*x*, *y*, *z*	H6'	1−*x*, −*y*, −*z*
H1N	*x*, *y*, *z*			Cl1	*x*, *y*, *z*	H8A'	1−*x*, −*y*, −*z*
H2N	*x*, *y*, *z*			Cl1'	1−*x*, −*y*, −*z*	H8B'	1−*x*, −*y*, −*z*
H2	*x*, *y*, *z*			F1	*x*, *y*, *z*	H8C'	1−*x*, −*y*, −*z*
H3	*x*, *y*, *z*			F2	*x*, *y*, *z*		