Supporting Information: Multifunctional Cu(I) Coordination Polymers with Aromatic Mono- and Ditopic Thioamides

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S1. Crystallographic Details

1. Structural determination of 1

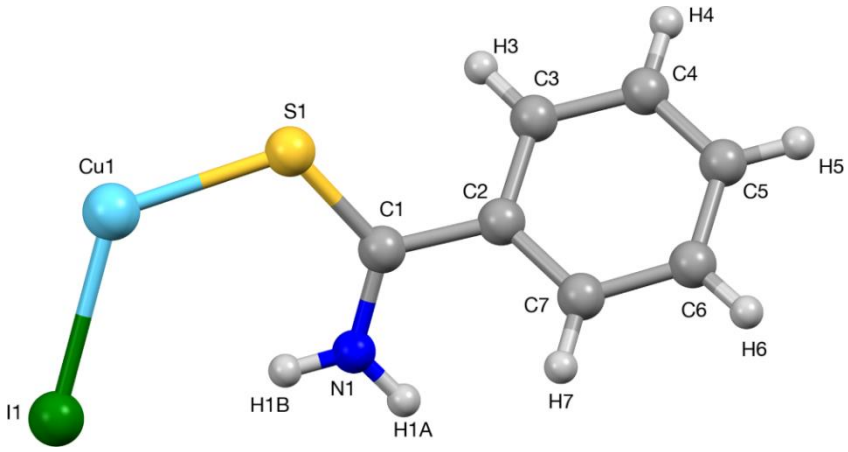

Figure S1. Asymmetric unit of polymeric compound **1** with atoms labeled.

a. 1 at room temperature

Table S1. Sample and crystal data for 1RT

CSD number	CCDC 1835539	
Chemical formula	C_7H_7CuINS	
Formula weight	327.64 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.023 x 0.032 x 0.154 mm	
Crystal habit	clear intense orange needle	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.9143(4) Å	α = 90°
	b = 5.6030(3) Å	β = 94.722(2)°
	c = 21.0033(9) Å	γ = 90°
Volume	928.21(8) $Å^3$	
Z	4	
Density (calculated)	2.345 g/cm^3	
Absorption coefficient	5.838 mm^{-1}	
F(000)	616	

Table S2. Data collection and structure refinement for 1RT

Theta range for data collection	1.95 to 25.34°	
Index ranges	-9<=h<=9, -6<=k<=6, -25<=l<=25	
Reflections collected	9966	
Independent reflections	1704 [R(int) = 0.0595]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8770 and 0.4670	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	1704 / 0 / 100	
Goodness-of-fit on F^2	1.073	
Final R indices	1166 data; I>2σ(I)	$R_1 = 0.0365$, $wR_2 = 0.0882$
	all data	$R_1 = 0.0733$, $wR_2 = 0.1297$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0662P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.367 and -1.737 eÅ^{-3}	
R.M.S. deviation from mean	0.727 eÅ^{-3}	

b. 1 at low temperature

Table S3. Sample and crystal data for 1LT

CSD number	CCDC 1835540	
Chemical formula	C_7H_7CuINS	
Formula weight	327.64 g/mol	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.023 x 0.032 x 0.154 mm	
Crystal habit	clear intense orange needle	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 7.8649(6) Å	α = 90°
	b = 5.5400(4) Å	β = 94.375(4)°
	c = 20.878(2) Å	γ = 90°
Volume	907.0(1) Å^3	
Z	4	
Density (calculated)	2.399 g/cm^3	
Absorption coefficient	5.974 mm^{-1}	
F(000)	616	

Table S4. Data collection and structure refinement for 1LT

Theta range for data collection	2.85 to 25.34°

Index ranges	-9<=h<=9, -6<=k<=6, -25<=l<=24
Reflections collected	10375
Independent reflections	1669 [R(int) = 0.0522]
Coverage of independent reflections	99.9%
Absorption correction	multi-scan
Max. and min. transmission	0.8750 and 0.4600
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1669 / 0 / 100
Goodness-of-fit on F^2	1.024
Final R indices	1291 data; I>2σ(I) $R_1 = 0.0311$, $wR_2 = 0.0596$
	all data $R_1 = 0.0522$, $wR_2 = 0.0672$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0275P)^2+1.5311P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.852 and -0.786 eÅ^{-3}
R.M.S. deviation from mean	0.166 eÅ^{-3}

2. Structural determination of 1·THF

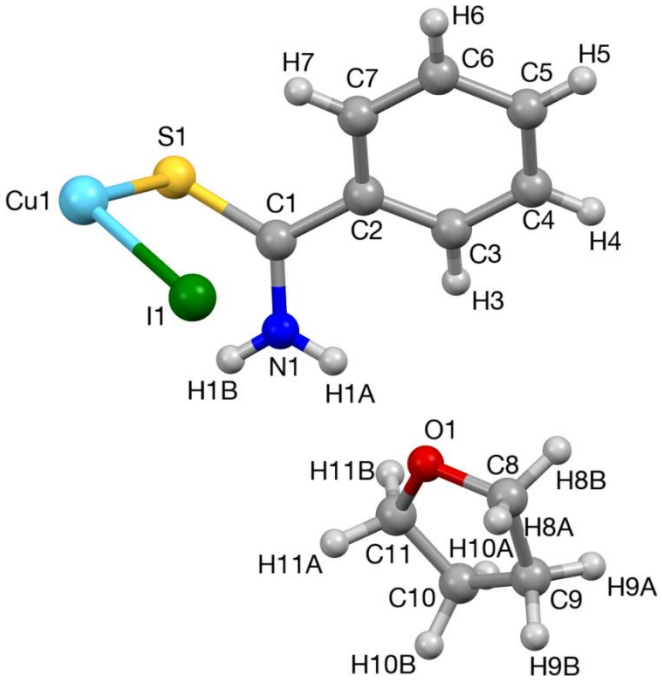

Figure S2. Asymmetric unit of polymeric compound **1**·THF with atoms labeled.

a. 1·THF at room temperature

Table S5. Sample and crystal data for 1·THF RT

CSD number	CCDC 1835543	
Chemical formula	$C_7H_7CuINS \cdot C_4H_8O$	
Formula weight	399.74 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.010 x 0.040 x 0.210 mm	
Crystal habit	clear intense orange needle	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.889(3) Å	α = 90°
	b = 18.26(1) Å	β = 96.23(3)°
	c = 13.131(8) Å	γ = 90°
Volume	1403.9(14) $Å^3$	
Z	4	
Density (calculated)	1.891 g/cm^3	
Absorption coefficient	3.884 mm^{-1}	
F(000)	776	

Table S6. Data collection and structure refinement for 1·THF RT

Theta range for data collection	1.92 to 25.42°	
Index ranges	-7<=h<=7, -21<=k<=22, -13<=l<=15	
Reflections collected	15133	
Independent reflections	2576 [R(int) = 0.0531]	
Coverage of independent reflections	99.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9600 and 0.8100	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2576 / 0 / 145	
Goodness-of-fit on F^2	1.158	
Final R indices	1793 data; I>2σ(I)	R_1 = 0.0367, wR_2 = 0.0954
	all data	R_1 = 0.0718, wR_2 = 0.1463
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0769P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.908 and -1.343 $eÅ^{-3}$	
R.M.S. deviation from mean	0.406 $eÅ^{-3}$	

b. 1·THF at low temperature

Table S7. Sample and crystal data for 1·THF LT

CSD number	CCDC 1835544	
Chemical formula	$C_7H_7CuINS \cdot C_4H_8O$	
Formula weight	399.74 g/mol	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.010 x 0.030 x 0.140 mm	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.8404(4) Å	α = 90°
	b = 18.388(1) Å	β = 94.598(4)°
	c = 12.5344(9) Å	γ = 90°
Volume	1341.8(2) $Å^3$	
Z	4	
Density (calculated)	1.979 g/cm^3	
Absorption coefficient	4.063 mm^{-1}	
F(000)	776	

Table S8. Data collection and structure refinement for 1·THF LT

Theta range for data collection	1.97 to 25.35°	
Index ranges	-7<=h<=7, -21<=k<=21, -15<=l<=15	
Reflections collected	18989	
Independent reflections	2424 [R(int) = 0.1124]	
Max. and min. transmission	0.9600 and 0.6000	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2424 / 0 / 139	
Goodness-of-fit on F^2	1.054	
Final R indices	1667 data; I>2σ(I)	R_1 = 0.0428, wR_2 = 0.0970
	all data	R_1 = 0.0841, wR_2 = 0.1400
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0754P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.046 and -1.850 $eÅ^{-3}$	
R.M.S. deviation from mean	0.412 $eÅ^{-3}$	

3. Structural determination of 1·acetone

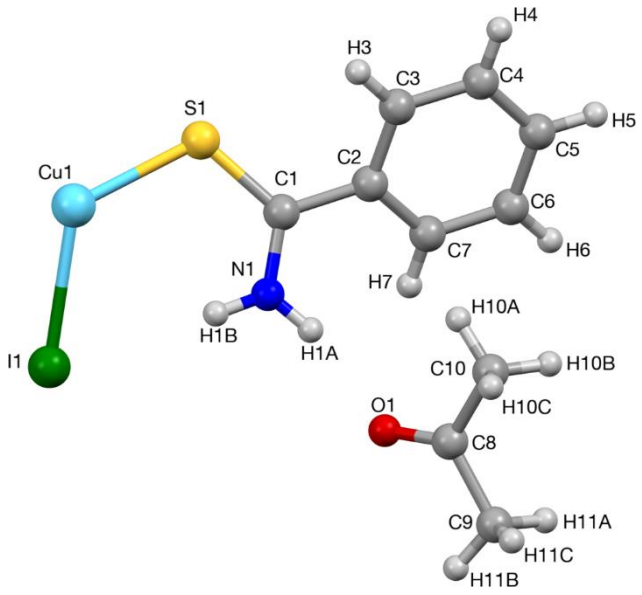

Figure S3. Asymmetric unit of polymeric compound **1**·acetone with atoms labeled.

a. 1·acetone at room temperature

Table S9. Sample and crystal data for 1·acetone RT

CSD number	CCDC 1835541	
Chemical formula	$C_7H_7CuINS·C_3H_6O$	
Formula weight	385.71 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.120 x 0.240 mm	
Crystal habit	clear orange prismatic	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 5.6938(1) Å	α = 90°
	b = 19.3276(4) Å	β = 96.839(1)°
	c = 12.7453(3) Å	γ = 90°
Volume	1392.61(5) $Å^3$	
Z	4	
Density (calculated)	1.840 g/cm^3	
Absorption coefficient	3.911 mm^{-1}	
F(000)	744	

Table S10. Data collection and structure refinement for 1·acetone RT

Theta range for data collection	1.92 to 25.35°	
Index ranges	-6<=h<=6, -23<=k<=23, -15<=l<=15	
Reflections collected	24333	
Independent reflections	2541 [R(int) = 0.0563]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7990 and 0.4540	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2541 / 0 / 138	
Goodness-of-fit on F^2	1.157	
Final R indices	2001 data; I>2σ(I)	$R_1 = 0.0277$, $wR_2 = 0.0768$
	all data	$R_1 = 0.0483$, $wR_2 = 0.1106$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0600P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.706 and -1.431 eÅ^{-3}	
R.M.S. deviation from mean	0.401 eÅ^{-3}	

b. 1·acetone at low temperature

Table S11. Sample and crystal data for 1·acetone LT

CSD number	CCDC 1835542	
Chemical formula	$C_7H_7CuINS \cdot C_3H_6O$	
Formula weight	385.71 g/mol	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.120 x 0.240 mm	
Crystal habit	intense yellow needle	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 5.6434(2) Å	α = 90°
	b = 18.8307(8) Å	β = 96.919(2)°
	c = 12.7580(5) Å	γ = 90°
Volume	1345.91(9) Å^3	
Z	4	
Density (calculated)	1.904 g/cm^3	
Absorption coefficient	4.047 mm^{-1}	
F(000)	744	

Table S12. Data collection and structure refinement for 1·acetone LT

Theta range for data collection	1.94 to 25.34°	
Index ranges	-6<=h<=6, -22<=k<=22, -15<=l<=15	
Reflections collected	20991	
Independent reflections	2464 [R(int) = 0.0381]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.7930 and 0.4430	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2464 / 0 / 138	
Goodness-of-fit on F^2	1.354	
Final R indices	2223 data; I>2σ(I)	R_1 = 0.0254, wR_2 = 0.0822
	all data	R_1 = 0.0342, wR_2 = 0.1053
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0551P)^2+1.4820P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.767 and -1.493 eÅ^{-3}	
R.M.S. deviation from mean	0.419 eÅ^{-3}	

4. Structural determination of 1·MeOH

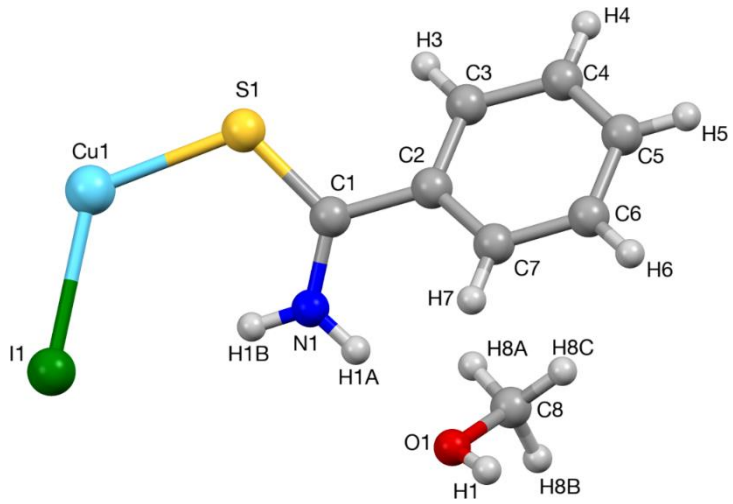

Figure S4. Asymmetric unit of polymeric compound **1**·MeOH with atoms labeled

c. 1·MeOH at room temperature

Table S13. Sample and crystal data for 1·MeOH RT

CSD number	CCDC 1835545	
Chemical formula	$C_7H_7CuINS \cdot CH_4O$	
Formula weight	359.68 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.046 x 0.048 x 0.239 mm	
Crystal habit	clear intense orange prismatic	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.4019(1) Å	α = 90°
	b = 16.2402(4) Å	β = 96.352(1)°
	c = 13.0710(3) Å	γ = 90°
Volume	1139.65(4) $Å^3$	
Z	4	
Density (calculated)	2.096 g/cm^3	
Absorption coefficient	4.771 mm^{-1}	
F(000)	688	

Table S14. Data collection and structure refinement for 1·MeOH RT

Theta range for data collection	2.01 to 25.34°	
Index ranges	-6<=h<=6, -19<=k<=19, -15<=l<=15	
Reflections collected	20009	
Independent reflections	2098 [R(int) = 0.0415]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8100 and 0.3950	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2098 / 0 / 120	
Goodness-of-fit on F^2	1.176	
Final R indices	1855 data; I>2σ(I)	R_1 = 0.0216, wR_2 = 0.0656
	all data	R_1 = 0.0265, wR_2 = 0.0682
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0362P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.575 and -0.803 $eÅ^{-3}$	
R.M.S. deviation from mean	0.237 $eÅ^{-3}$	

d. 1· MeOH at low temperature

Table S15. Sample and crystal data for 1·MeOH LT

CSD number	CCDC 1835546	
Chemical formula	$C_7H_7CuINS \cdot CH_4O$	
Formula weight	359.68 g/mol	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.046 x 0.048 x 0.239 mm	
Crystal habit	clear intense orange prismatic	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.3389(2) Å	α = 90°
	b = 16.2890(7) Å	β = 95.618(2)°
	c = 12.7887(6) Å	γ = 90°
Volume	1106.83(8) $Å^3$	
Z	4	
Density (calculated)	2.158 g/cm^3	
Absorption coefficient	4.912 mm^{-1}	
F(000)	688	

Table S16. Data collection and structure refinement for 1·MeOH LT

Theta range for data collection	2.50 to 25.35°	
Index ranges	-6<=h<=6, -19<=k<=18, -15<=l<=15	
Reflections collected	14089	
Independent reflections	2035 [R(int) = 0.0402]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8060 and 0.3860	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014 (Sheldrick 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2035 / 0 / 120	
Goodness-of-fit on F^2	1.043	
Final R indices	1889 data; I>2σ(I)	R_1 = 0.0173, wR_2 = 0.0352
	all data	R_1 = 0.0198, wR_2 = 0.0362
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0100P)^2+0.6767P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.369 and -0.322 $eÅ^{-3}$	
R.M.S. deviation from mean	0.083 $eÅ^{-3}$	

5. Structural determination of 2

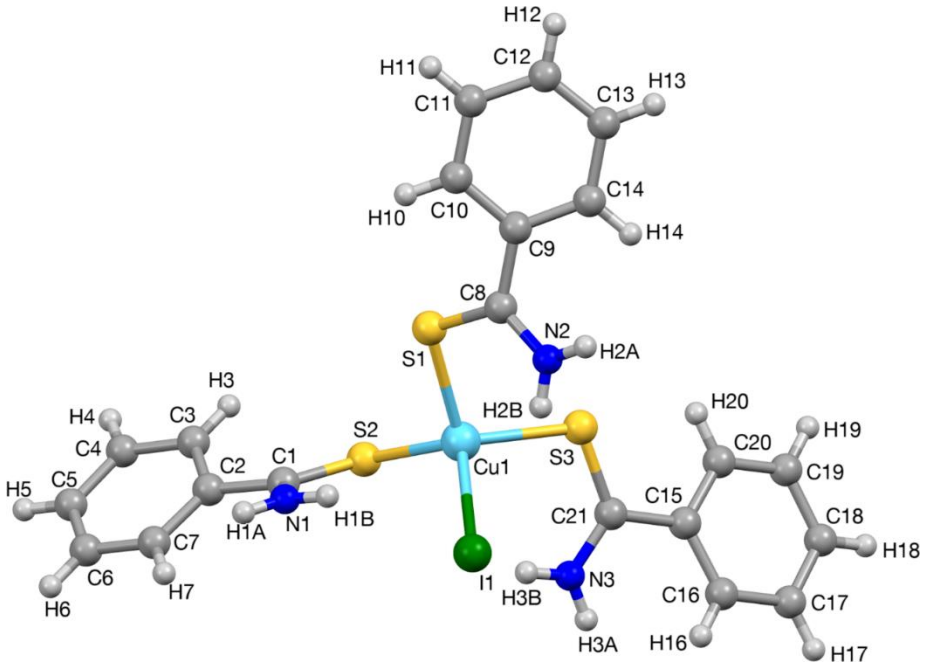

Figure S5. Asymmetric unit of molecular compound **2** with atoms labeled

Table S17. Sample and crystal data for 2

CSD number	CCDC 1835547	
Chemical formula	$C_{21}H_{21}CuIN_3S_3$	
Formula weight	602.03 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.080 x 0.120 mm	
Crystal habit	yellow prismatic	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.433(2) Å	α = 90°
	b = 12.158(1) Å	β = 92.113(4)°
	c = 11.488(1) Å	γ = 90°
Volume	2433.1(5) $Å^3$	
Z	4	
Density (calculated)	1.644 g/cm^3	
Absorption coefficient	2.436 mm^{-1}	
F(000)	1192	

Table S18. Data collection and structure refinement for 2

Theta range for data collection	1.17 to 25.34°	
Index ranges	-20<=h<=20, -14<=k<=14, -13<=l<=13	
Reflections collected	42798	
Independent reflections	4448 [R(int) = 0.1030]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8680 and 0.7590	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4448 / 0 / 262	
Goodness-of-fit on F^2	1.061	
Final R indices	2725 data; I>2σ(I)	R_1 = 0.0403, wR_2 = 0.0993
	all data	R_1 = 0.0884, wR_2 = 0.1376
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0590P)^2+0.7261P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.453 and -0.509 eÅ^{-3}	
R.M.S. deviation from mean	0.113 eÅ^{-3}	

6. Structural determination of 3

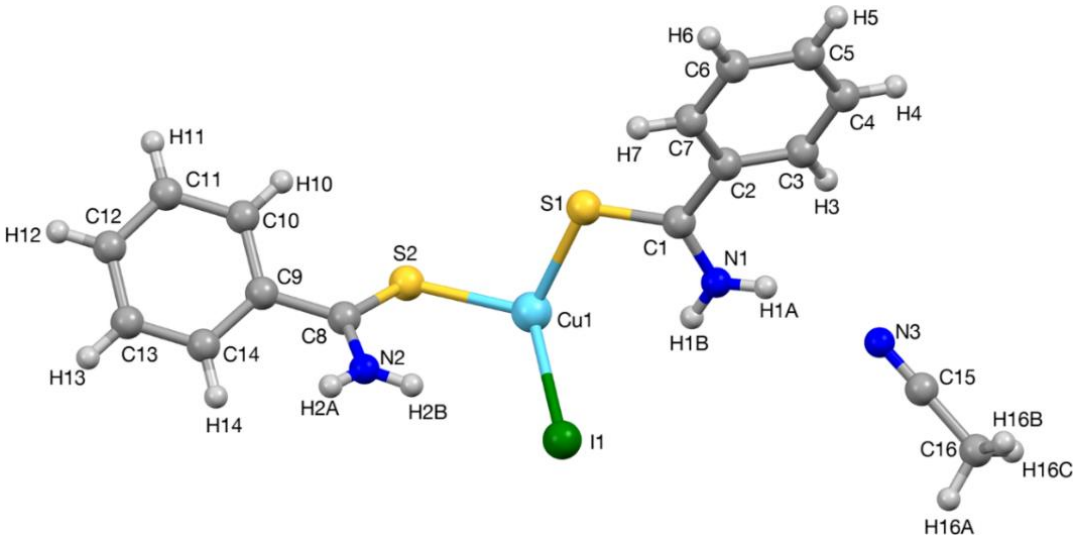

Figure S6. Asymmetric unit of dimeric compound **3** with atoms labeled

e. 3 at room temperature

Table S19. Data collection and structure refinement for 3RT

CSD number	CCDC 1835548	
Chemical formula	$C_{12}H_{11}CuIN_2S_2 \cdot C_2H_3N$	
Formula weight	505.88 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.053 x 0.307 x 0.311 mm	
Crystal habit	clear intense orange prismatic	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 12.2449(2) Å	α = 90°
	b = 7.3873(1) Å	β = 104.399(1)°
	c = 23.0545(4) Å	γ = 90°
Volume	2019.93(6) $Å^3$	
Z	4	
Density (calculated)	1.664 g/cm^3	
Absorption coefficient	2.817 mm^{-1}	
F(000)	992	

Table S20. Data collection and structure refinement for 3RT

Theta range for data collection	2.80 to 25.35°	
Index ranges	-14<=h<=14, -8<=k<=8, -26<=l<=27	
Reflections collected	19392	
Independent reflections	3696 [R(int) = 0.0408]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8650 and 0.4740	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3696 / 0 / 209	
Goodness-of-fit on F^2	1.142	
Final R indices	3113 data; I>2σ(I)	R_1 = 0.0262, wR_2 = 0.0671
	all data	R_1 = 0.0362, wR_2 = 0.0846
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0436P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.314 and -0.473 $eÅ^{-3}$	
R.M.S. deviation from mean	0.088 $eÅ^{-3}$	

7. Structural determination of 4

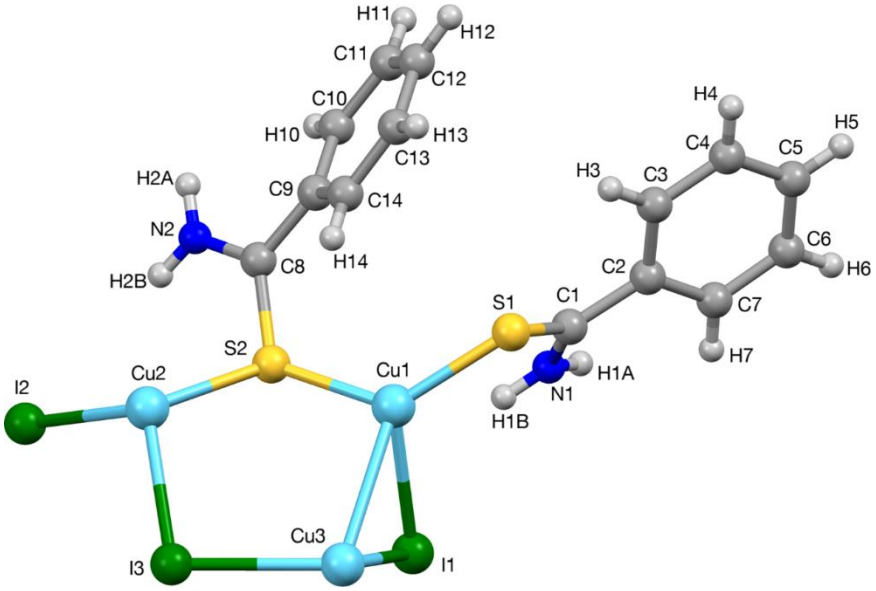

Figure S7. Asymmetric unit of polymeric compound **4** with atoms labeled

Table S21. Sample and crystal data for 4

CSD number	CCDC 1835550	
Chemical formula	$C_{14}H_{14}Cu_3I_3N_2S_2$	
Formula weight	845.71 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.054 x 0.063 x 0.077 mm	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.4652(5) Å	α = 90°
	b = 8.4163(4) Å	β = 101.066(2)°
	c = 20.241(1) Å	γ = 90°
Volume	2084.0(2) $Å^3$	
Z	4	
Density (calculated)	2.695 g/cm^3	
Absorption coefficient	7.678 mm^{-1}	
F(000)	1560	

Table S22. Data collection and structure refinement for 4

Theta range for data collection	1.78 to 25.35°	
Index ranges	-15<=h<=14, -10<=k<=10, -24<=l<=24	
Reflections collected	30944	
Independent reflections	3797 [R(int) = 0.0709]	
Coverage of independent reflections	99.9%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6820 and 0.5890	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3797 / 0 / 217	
Goodness-of-fit on F^2	1.096	
Final R indices	2906 data; I>2σ(I)	$R_1 = 0.0333$, $wR_2 = 0.0755$
	all data	$R_1 = 0.0573$, $wR_2 = 0.0963$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0486P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.972 and -1.143 eÅ^{-3}	
R.M.S. deviation from mean	0.412 eÅ^{-3}	

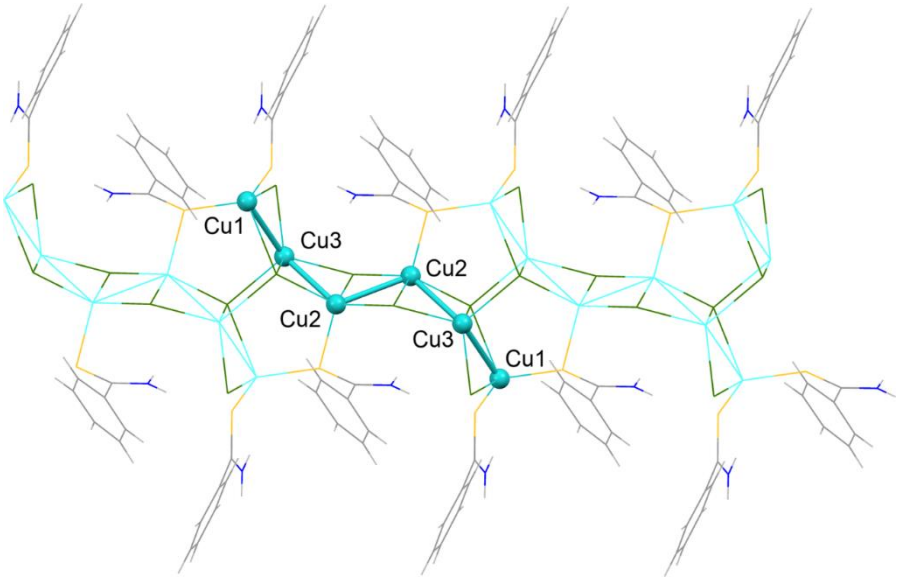

Figure S8. Detail of a Cu-Cu chain in **4.**

8. Structural determination of 5

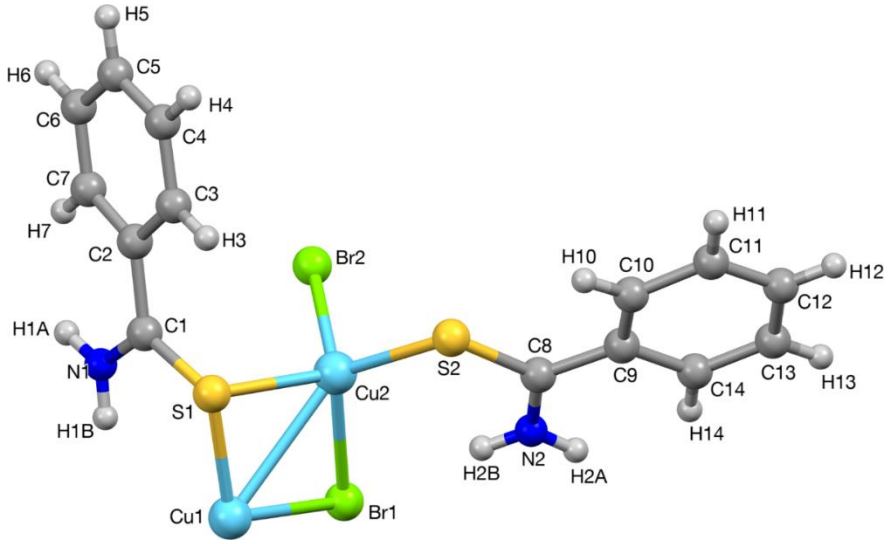

Figure S9. Asymmetric unit of polymeric compound **5** with atoms labeled

f. 5 at 250 K

Table S23. Sample and crystal data for 5 250K

CSD number	CCDC 1835552	
Chemical formula	$C_7H_7BrCuNS$	
Formula weight	280.65 g/mol	
Temperature	250(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.083 x 0.149 mm	
Crystal habit	clear intense orange prismatic	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.945(1) Å	α = 90°
	b = 5.7360(5) Å	β = 107.705(4)°
	c = 22.770(2) Å	γ = 90°
Volume	1735.1(3) $Å^3$	
Z	8	
Density (calculated)	2.149 g/cm^3	
Absorption coefficient	7.292 mm^{-1}	
F(000)	1088	

Table S24. Data collection and structure refinement for 5 250K

Theta range for data collection	1.53 to 25.34°	
Index ranges	-14<=h<=16, -6<=k<=6, -27<=l<=27	
Reflections collected	29074	
Independent reflections	3162 [R(int) = 0.0630]	
Coverage of independent reflections	99.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8680 and 0.4100	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3162 / 0 / 199	
Goodness-of-fit on F^2	1.187	
Final R indices	2543 data; I>2σ(I)	$R_1 = 0.0877$, $wR_2 = 0.2361$
	all data	$R_1 = 0.1032$, $wR_2 = 0.2458$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0418P)^2+120.5269P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	3.075 and -1.591 eÅ^{-3}	
R.M.S. deviation from mean	0.319 eÅ^{-3}	

g. 5 at low temperature

Table S25. Sample and crystal data for 5LT

CSD number	CCDC 1835553	
Chemical formula	$C_7H_7BrCuNS$	
Formula weight	280.65 g/mol	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.083 x 0.149 mm	
Crystal habit	orange prismatic	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.8859(7) Å	α = 90°
	b = 5.6849(4) Å	β = 107.618(3)°
	c = 22.665(2) Å	γ = 90°
Volume	1705.3(2) Å^3	
Z	8	
Density (calculated)	2.186 g/cm^3	
Absorption coefficient	7.420 mm^{-1}	
F(000)	1088	

Table S26. Data collection and structure refinement for 5LT

Theta range for data collection	1.54 to 25.35°	
Index ranges	-13<=h<=16, -6<=k<=6, -27<=l<=27	
Reflections collected	12389	
Independent reflections	3120 [R(int) = 0.0545]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8660 and 0.4040	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3120 / 57 / 157	
Goodness-of-fit on F^2	1.223	
Final R indices	2549 data; I>2σ(I)	$R_1 = 0.0922$, $wR_2 = 0.2550$
	all data	$R_1 = 0.1077$, $wR_2 = 0.2708$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0536P)^2+198.6284P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	4.007 and -2.272 eÅ^{-3}	
R.M.S. deviation from mean	0.409 eÅ^{-3}	

9. Structural determination of 5·THF

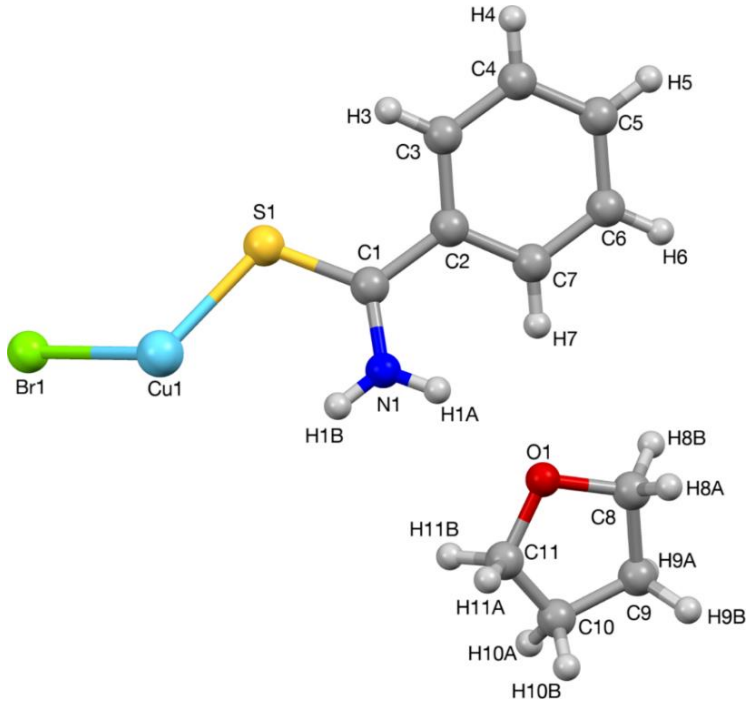

Figure S10. Asymmetric unit of polymeric compound **5**·THF with atoms labeled.

h. 5·THF at room temperature

Table S27. Sample and crystal data for 5· THF RT

CSD number	CCDC 1835555	
Chemical formula	$C_7H_7BrCuNS \cdot C_4H_8O$	
Formula weight	352.75 g/mol	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.020 x 0.070 x 0.260 mm	
Crystal habit	clear intense orange needle	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.7667(1) Å	α = 90°
	b = 17.6731(4) Å	β = 97.122(1)°
	c = 13.3180(3) Å	γ = 90°
Volume	1346.84(5) $Å^3$	
Z	4	
Density (calculated)	1.740 g/cm^3	
Absorption coefficient	4.722 mm^{-1}	
F(000)	704	

Table S28. Data collection and structure refinement for 5·THF RT

Theta range for data collection	1.92 to 25.35°	
Index ranges	-6<=h<=6, -21<=k<=21, -14<=l<=16	
Reflections collected	21171	
Independent reflections	2454 [R(int) = 0.0461]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9110 and 0.3730	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2454 / 0 / 145	
Goodness-of-fit on F^2	1.099	
Final R indices	1809 data; I>2σ(I)	R_1 = 0.0374, wR_2 = 0.1050
	all data	R_1 = 0.0634, wR_2 = 0.1270
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0735P)^2+0.3524P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.933 and -0.899 $eÅ^{-3}$	
R.M.S. deviation from mean	0.299 $eÅ^{-3}$	

i. 5·THF at low temperature

Table S29. Sample and crystal data for 5·THF LT.

CSD number	CCDC 1835556	
Chemical formula	$C_7H_7BrCuNS \cdot C_4H_8O$	
Formula weight	352.75 g/mol	
Temperature	110(2) K	
Wavelength	0.71073 Å	
Crystal size	0.010 x 0.070 x 0.410 mm	
Crystal habit	clear orange needle	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.6970(3) Å	α = 90°
	b = 16.9195(9) Å	β = 95.109(3)°
	c = 13.4156(7) Å	γ = 90°
Volume	1288.00(12) $Å^3$	
Z	4	
Density (calculated)	1.819 g/cm^3	
Absorption coefficient	4.938 mm^{-1}	
F(000)	704	

Table S30. Data collection and structure refinement for 5·THF LT

Theta range for data collection	1.94 to 25.35°	
Index ranges	-6<=h<=6, -20<=k<=20, -16<=l<=16	
Reflections collected	19593	
Independent reflections	2350 [R(int) = 0.0478]	
Coverage of independent reflections	100.0%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9520 and 0.2370	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2350 / 0 / 145	
Goodness-of-fit on F^2	1.151	
Final R indices	1949 data; I>2σ(I)	R_1 = 0.0297, wR_2 = 0.0730
	all data	R_1 = 0.0438, wR_2 = 0.0914
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0532P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.422 and -0.816 $eÅ^{-3}$	
R.M.S. deviation from mean	0.308 $eÅ^{-3}$	

10. Structural determination of 5·acetone

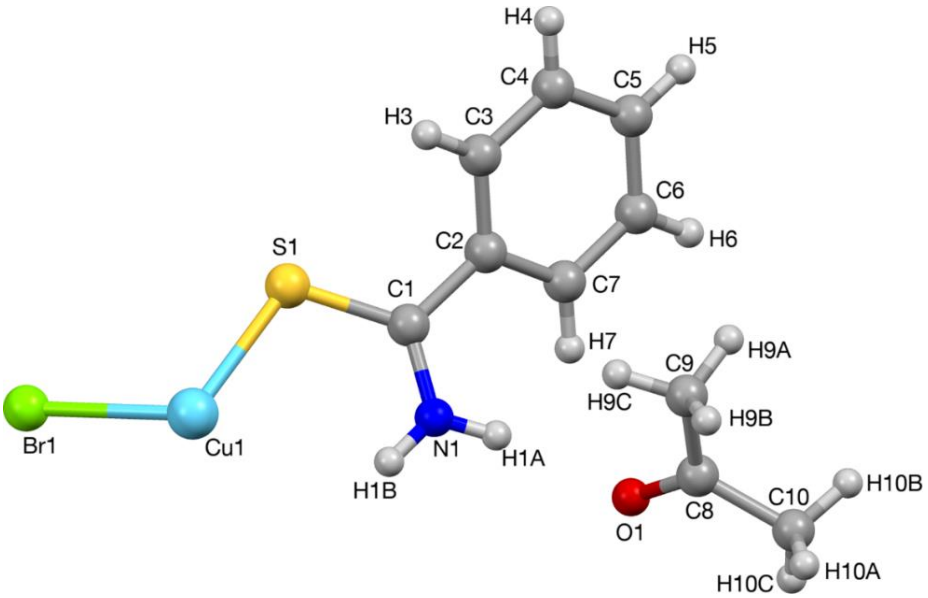

Figure S11. Asymmetric unit of polymeric compound **5**·acetone with atoms labeled

Table S31. Sample and crystal data for 5·acetone

CSD number	CCDC 1835554	
Chemical formula	$C_7H_7BrCuNS \cdot C_3H_6O$	
Formula weight	338.72 g/mol	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.120 x 0.170 mm	
Crystal habit	orange needle	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 5.7617(8) Å	α = 90°
	b = 14.019(3) Å	β = 90.003(6)°
	c = 15.885(3) Å	γ = 90°
Volume	1283.1(4) $Å^3$	
Z	4	
Density (calculated)	1.754 g/cm^3	
Absorption coefficient	4.953 mm^{-1}	
F(000)	672	

Table S32. Data collection and structure refinement for 5·acetone

Theta range for data collection	1.94 to 25.35°
Index ranges	-6<=h<=5, -16<=k<=15, -19<=l<=19
Reflections collected	16643

Independent reflections	2283 [R(int) = 0.2257]	
Coverage of independent reflections	97.6%	
Absorption correction	multi-scan	
Max. and min. transmission	0.6930 and 0.4860	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2283 / 0 / 132	
Goodness-of-fit on F^2	1.005	
Final R indices	1198 data; I>2σ(I)	$R_1 = 0.0590$, $wR_2 = 0.1156$
	all data	$R_1 = 0.1638$, $wR_2 = 0.1777$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0723P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.951 and -1.091 eÅ^{-3}	
R.M.S. deviation from mean	0.347 eÅ^{-3}	

11. Structural determination of 6·DMF

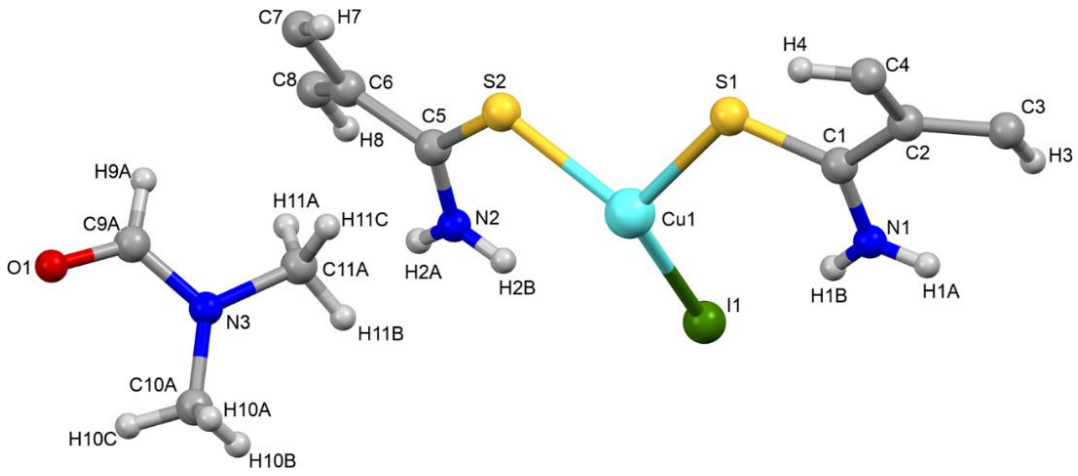

Figure S12. Asymmetric unit of polymeric compound **6**·DMF with atoms labeled. The DMF molecule is represented at the most position found in both **6**·DMF RT and **6**·DMF LT.

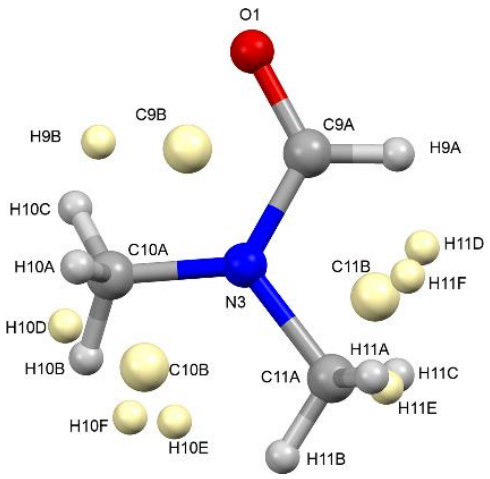

Figure S13. Carbon and hydrogen atoms from the interstitial DMF molecule in both **6**·DMF RT and **6**·DMF LT are located in two different positions. In this image, the most frequently occupied positions (70% and 90% in **6**·DMF RT and **6**·DMF LT respectively), have been depicted with the usual color code (grey for C and white for H) while the minoritarian ones are in yellow.

j. 6·DMF at room temperature

Table S33. Sample and crystal data for 6·DMF RT

CSD number	CCDC 1835557	
Chemical formula	$C_8H_8CuIN_2S_2 \cdot C_3H_7NO$	
Formula weight	459.82	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.02 x 0.05 x 0.08 mm	
Crystal habit	clear intense orange plate	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions	*a* = 7.5033(2) Å	α = 98.385(1)°
	b = 9.6766(3) Å	β = 93.378(1)°
	c = 11.4138(3) Å	γ = 106.284(1)°
Volume	771.58(13) $Å^3$	
Z	2	
Density (calculated)	1.941 Mg/cm^3	
Absorption coefficient	3.610 mm^{-1}	
F(000)	448	

Table S34. Data collection and structure refinement for 6·DMF RT

Theta range for data collection	1.81 to 25.34°	
Index ranges	-8<=h<=9, -11<=k<=11, -13<=l<=13	
Reflections collected	12680	
Independent reflections	2844 [R(int) = 0.0309]	
Coverage of independent reflections	98.9%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXL-2014/7 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2844 / 8 / 186	
Goodness-of-fit on F^2	1.134	
Final R indices	2477 data; I>2σ(I)	$R_1 = 0.0242$, $wR_2 = 0.0672$
	all data	$R_1 = 0.0327$, $wR_2 = 0.0829$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0497P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.605 and -0.818 eÅ^{-3}	
R.M.S. deviation from mean	0.221 eÅ^{-3}	

k. 6·DMF at low temperature

Table S35. Sample and crystal data for 6·DMF LT

CSD number	CCDC 1835558	
Chemical formula	$C_8H_8CuIN_2S_2 \cdot C_3H_7NO$	
Formula weight	459.82	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.02 x 0.05 x 0.08 mm	
Crystal habit	clear intense orange plate	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 7.4490(6) Å	α = 98.018(4)°
	b = 9.609(1) Å	β = 93.683(4)°
	c = 11.440(1) Å	γ = 106.772(4)°
Volume	771.6(1) Å^3	
Z	2	
Density (calculated)	1.979 Mg/cm^3	

Absorption coefficient	3.681 mm^{-1}
F(000)	448

Table S36. Data collection and structure refinement for 6·DMF LT

Theta range for data collection	1.81 to 25.30°	
Index ranges	-8<=h<=8, -11<=k<=11, -13<=l<=13	
Reflections collected	18572	
Independent reflections	2790 [R(int) = 0.0332]	
Coverage of independent reflections	99.5%	
Absorption correction	multi-scan	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2790 / 8 / 180	
Goodness-of-fit on F^2	1.199	
Final R indices	2446 data; I>2σ(I)	R_1 = 0.0217, wR_2 = 0.0615
	all data	R_1 = 0.0300, wR_2 = 0.0763
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0461P)^2]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.840 and -0.687 eÅ^{-3}	
R.M.S. deviation from mean	0.237 eÅ^{-3}	

12. Structural determination of 6·2MeCN

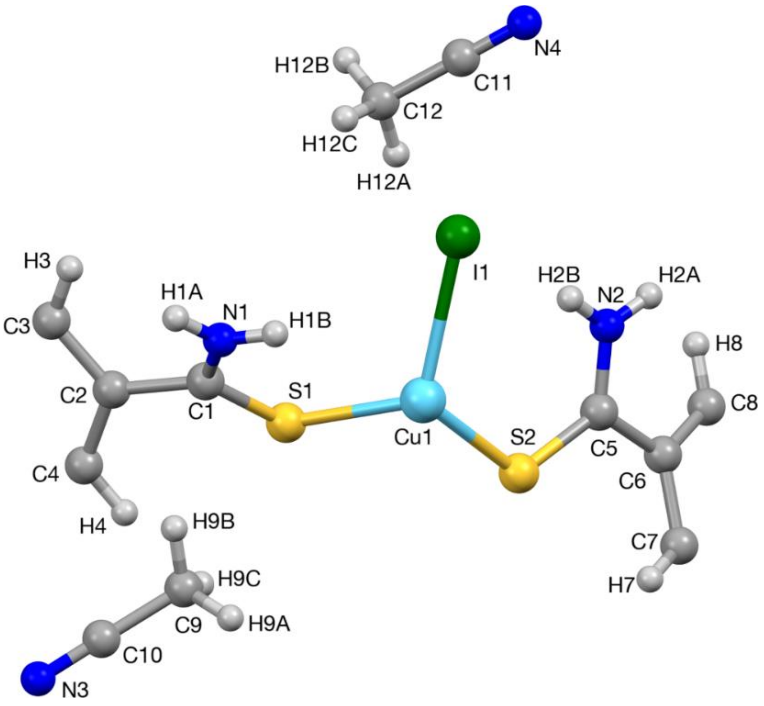

Figure S14. Asymmetric unit of polymeric compound **6**·2MeCN with atoms labeled.

Table S37. Sample and crystal data for 6·2MeCN

CSD number	CCDC 1835559	
Chemical formula	$C_8H_8CuIN_2S_2 \cdot 2C_2H_3N$	
Formula weight	468.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.03 x 0.07 x 0.11 mm	
Crystal habit	clear orange plate	
Crystal system	triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 7.3536(5) Å	α = 100.230(3)°
	b = 10.7182(8) Å	β = 93.032(3)°
	c = 10.8755(8) Å	γ = 101.538(3)°
Volume	823.02(10) $Å^3$	
Z	2	
Density (calculated)	1.892 Mg/cm^3	
Absorption coefficient	3.450 mm^{-1}	
F(000)	456	

Table S38. Data collection and structure refinement for 6·2MeCN

Theta range for data collection	1.91 to 25.35°	
Index ranges	-8<=h<=8, -12<=k<=12, -13<=l<=13	
Reflections collected	19851	
Independent reflections	3004 [R(int) = 0.0281]	
Coverage of independent reflections	99.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9036 and 0.7027	
Structure solution technique	direct methods	
Structure solution program	SHELXL-2014/7 (Sheldrick, 2014)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3004 / 0 / 183	
Goodness-of-fit on F^2	1.136	
Final R indices	2781 data; I>2σ(I)	R_1 = 0.0163, wR_2 = 0.0461
	all data	R_1 = 0.0200, wR_2 = 0.0652
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0346P)^2+1.2771P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.576 and -0.703 $eÅ^{-3}$	

R.M.S. deviation from mean	0.208 eÅ^{-3}

13. Metal coordination environments

Table S39. Copper environment distances (Å) in 1		
	1 RT	**1 LT**
Cu1—S1	2.277 (2)	2.282 (2)
Cu1—S1^{i}	2.511 (2)	2.472 (2)
Cu1—I1	2.612 (1)	2.6166 (8)
Cu1—I1^{ii}	2.650 (1)	2.6446 (8)
Cu1—Cu1^{i}	2.967 (2)	2.911 (1)
Cu1—Cu1^{ii}	2.689 (2)	2.671 (1)
Symmetry codes: (i)−*x*, −*y*+1, −*z*+1; (ii) −*x*, −*y*, −*z*+1.		

Table S40. Copper environment angles (°) in 1		
	1 RT	**1 LT**
S1—Cu1—I1	122.93 (7)	122.27 (4)
S1^{i}—Cu1—I1	99.25 (6)	98.82 (4)
S1—Cu1—I1^{ii}	102.67 (6)	102.12 (4)
S1^{i}—Cu1—I1^{ii}	108.12 (6)	108.68 (4)
I1—Cu1—I1^{ii}	118.55 (5)	118.98 (3)
S1—Cu1—Cu1^{ii}	138.10 (8)	136.96 (5)
S1^{i}—Cu1—Cu1^{ii}	117.56 (7)	117.86 (5)
I1—Cu1—Cu1^{ii}	59.97 (4)	60.00 (3)
I1^{ii}—Cu1—Cu1^{ii}	58.57 (4)	58.97 (3)
S1—Cu1—Cu1^{i}	55.34 (6)	55.24 (4)
S1^{i}—Cu1—Cu1^{i}	48.25 (6)	49.33 (4)
I1—Cu1—Cu1^{i}	123.59 (6)	123.27 (4)
I1^{ii}—Cu1—Cu1^{i}	115.56 (5)	115.88 (3)
Cu1^{ii}—Cu1—Cu1^{i}	164.32 (8)	165.81 (5)
Cu1—I1—Cu1^{ii}	61.45 (5)	61.02 (3)
Symmetry codes: (i)−*x*, −*y*+1, −*z*+1; (ii) −*x*, −*y*, −*z*+1.		

Table S41. Copper environment distances (Å) in 1·THF		
	1·THF RT	**1·THF LT**
Cu1—S1^{i}	2.295 (2)	2.305 (3)
Cu1—S1	2.534 (3)	2.480 (3)
Cu1—I1	2.622 (2)	2.627 (1)
Cu1—I1^{ii}	2.629 (2)	2.638 (1)
Cu1—Cu1^{ii}	2.940 (3)	2.917 (2)
Cu1—Cu1^{i}	3.003 (3)	2.969 (2)
Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) −*x*, −*y*, −*z*+2.		

Table S42. Copper environment angles (°) in 1·THF		
	1·THF RT	**1·THF LT**
S1^{i}—Cu1—S1	103.27 (8)	103.40 (8)
S1^{i}—Cu1—I1	107.33 (7)	106.18 (8)
S1—Cu1—I1	107.73 (6)	107.35 (7)
S1^{i}—Cu1—I1^{ii}	123.17 (7)	122.94 (8)
S1—Cu1—I1^{ii}	102.05 (7)	102.89 (7)
I1—Cu1—I1^{ii}	111.89 (6)	112.71 (4)
S1^{i}—Cu1—Cu1^{ii}	139.00 (9)	137.96 (9)
S1—Cu1—Cu1^{ii}	117.27 (8)	118.05 (8)
I1—Cu1—Cu1^{ii}	56.07 (4)	56.54 (4)
I1^{ii}—Cu1—Cu1^{ii}	55.83 (4)	56.17 (4)
S1^{i}—Cu1—Cu1^{i}	55.20 (7)	54.35 (7)
S1—Cu1—Cu1^{i}	48.07 (6)	49.05 (6)
I1—Cu1—Cu1^{i}	118.99 (6)	117.74 (6)
I1^{ii}—Cu1—Cu1^{i}	126.46 (6)	127.48 (7)
Cu1^{ii}—Cu1—Cu1^{i}	164.47 (8)	165.81 (9)
Cu1—I1—Cu1^{ii}	68.11(6)	67.29 (4)
Symmetry codes: (i) −*x*+1, −*y*, −*z*+2; (ii) −*x*, −*y*, −*z*+2.		

Table S43. Copper environment distances (Å) in 1·acetone		
	1 RT	**1 LT**
Cu1—S1	2.292 (2)	2.295 (1)
Cu1—S1^{i}	2.530 (2)	2.480 (1)
Cu1—I1	2.6137 (8)	2.6149 (7)
Cu1—I1^{ii}	2.6356 (8)	2.6319 (7)
Cu1—Cu1^{i}	2.870 (2)	2.815 (1)
Cu1—Cu1^{ii}	2.877 (1)	2.870 (1)
Symmetry codes: (i)−*x*, −*y*+1, −*z*+1; (ii) −*x*, −*y*, −*z*+1.		

Table S44. Copper environment angles (°) in 1·acetone		
	1·ac RT	**1·ac LT**
S1—Cu1—S1^{i}	107.15 (5)	107.87 (4)
S1—Cu1—I1	122.51 (5)	121.79 (4)
S1^{i}—Cu1—I1	100.28 (4)	100.95 (4)
S1—Cu1—I1^{ii}	104.79 (5)	104.11 (4)
S1^{i}—Cu1—I1^{ii}	107.59 (4)	107.68 (4)
I1—Cu1—I1^{ii}	113.55 (3)	113.69 (2)
S1—Cu1—Cu1^{i}	57.39 (4)	56.97 (4)
S1^{i}—Cu1—Cu1^{i}	49.76 (4)	50.89 (4)
I1—Cu1—Cu1^{i}	125.93 (4)	126.64 (4)
I1^{ii}—Cu1—Cu1^{i}	118.05 (4)	117.80 (3)
S1—Cu1—Cu1^{ii}	136.24 (6)	134.72 (5)

S1^{i}—Cu1—Cu1^{ii}	116.05 (5)	116.85 (5)
I1—Cu1—Cu1^{ii}	57.14 (3)	57.13 (2)
I1^{ii}—Cu1—Cu1^{ii}	56.41 (2)	56.56 (2)
Cu1^{i}—Cu1—Cu1^{ii}	164.59 (6)	166.30 (5)
Symmetry codes: (i) −*x*, −*y*+1, −*z*+2; (ii) −*x*−1, −*y*+1, −*z*+2.		

Table S45. Copper environment distances (Å) in 1·MeOH		
	1·MeOH RT	**1·MeOH LT**
Cu1—S1	2.294 (1)	2.2963 (7)
Cu1—S1^{i}	2.503 (1)	2.4726 (7)
Cu1—I1	2.6118 (5)	2.6158 (3)
Cu1—I1^{ii}	2.6583 (5)	2.6526 (3)
Cu1—Cu1^{ii}	2.7128 (9)	2.6914 (6)
Cu1—Cu1^{i}	2.743 (1)	2.6963 (6)
Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1.		

Table S46. Copper environment angles (°) in 1· MeOH		
	1· MeOH RT	**1· MeOH LT**
S1—Cu1—S1^{i}	110.39 (3)	111.26 (2)
S1—Cu1—I1	121.50 (3)	121.18 (2)
S1^{i}—Cu1—I1	97.62 (2)	97.285 (17)
S1—Cu1—I1^{ii}	102.12 (3)	101.57 (2)
S1^{i}—Cu1—I1^{ii}	106.33 (2)	106.33 (2)
I1—Cu1—I1^{ii}	118.05 (2)	118.56 (1)
S1—Cu1—Cu1^{ii}	135.14 (4)	134.49 (3)
S1^{i}—Cu1—Cu1^{ii}	113.78 (3)	113.60 (2)
I1—Cu1—Cu1^{ii}	59.86 (2)	59.95 (1)
I1^{ii}—Cu1—Cu1^{ii}	58.18 (2)	58.61 (1)
S1—Cu1—Cu1^{i}	58.78 (3)	58.72 (2)
S1^{i}—Cu1—Cu1^{i}	51.61 (3)	52.54 (2)
I1—Cu1—Cu1^{i}	123.91 (3)	123.86 (2)
I1^{ii}—Cu1—Cu1^{i}	115.60 (2)	115.38 (2)
Cu1^{ii}—Cu1—Cu1^{i}	163.84 (4)	164.57 (3)
Cu1—I1—Cu1^{ii}	61.96 (2)	61.44 (1)
Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*, −*y*+1, −*z*+1.		

Table S47. Copper environment distances (Å) in 2	
Cu1—S1	2.280 (2)
Cu1—S2	2.311 (2)
Cu1—S3	2.294 (2)
Cu1—I1	2.7276 (9)

Table S48. Copper environment angles (°) in 2	
S1—Cu1—S2	104.26 (7)
S1—Cu1—S3	114.91 (7)
S2—Cu1—S3	108.05 (7)
S1—Cu1—I1	114.65 (6)

S2—Cu1—I1	107.76 (5)
S3—Cu1—I1	106.83 (5)

Table S49. Copper environment distances (Å) in 3	
Cu1—S1	2.276 (1)
Cu1—S2	2.276 (1)
Cu1—I1	2.6724 (5)
Cu1—I1^{i}	2.7240 (6)
Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1	

Table S50. Copper environment angles (°) in 3	
S1—Cu1—S2	108.28 (5)
S1—Cu1—I1	108.99 (3)
S2—Cu1—I1	119.69 (4)
S1—Cu1—I1^{i}	111.73 (3)
S2—Cu1—I1^{i}	105.53 (3)
I1—Cu1—I1^{i}	102.46 (2)
Cu1—I1—Cu1^{i}	77.54 (2)
Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1	

Table S51. Copper environment distances (Å) in 4	
Cu1—S1	2.236 (2)
Cu1—S2	2.263 (2)
Cu1—I1	2.648 (1)
Cu1—I3^{i}	2.932 (1)
Cu1—Cu3	2.859 (1)
Cu2—S2	2.345 (2)
Cu2—I2	2.642 (1)
Cu2—I2^{ii}	2.654 (1)
Cu2—I3	2.672 (1)
Cu2—Cu2^{ii}	2.878 (2)
Cu2—Cu3^{i}	2.781 (1)
Cu3—I1	2.581 (1)
Cu3—I2^{iii}	2.695 (1)
Cu3—I3	2.712 (1)
Cu3—I3^{i}	2.717 (1)
Cu3—Cu2^{i}	2.781(1)
Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*, −*z*+1; (iii) *x*, *y*+1, *z*.	

Table S52. Copper environment angles (°) in 4	
S1—Cu1—S2	129.47 (8)
S1—Cu1—I1	116.68 (7)
S2—Cu1—I1	99.23 (6)
S1—Cu1—Cu3	128.75 (7)

S2—Cu1—Cu3	100.35 (6)
I1—Cu1—Cu3	55.75 (3)
S1—Cu1—I3^{i}	93.77 (7)
S2—Cu1—I3^{i}	106.76 (6)
I1—Cu1—I3^{i}	109.76 (4)
Cu3—Cu1—I3^{i}	55.95 (3)
S2—Cu2—I2	109.46 (6)
S2—Cu2—I2^{ii}	102.49 (6)
I2—Cu2—I2^{ii}	114.16 (4)
S2—Cu2—I3	108.45 (6)
I2—Cu2—I3	104.86 (4)
I2^{ii}—Cu2—I3	117.23 (4)
S2—Cu2—Cu3^{i}	107.35 (6)
I2—Cu2—Cu3^{i}	143.07 (5)
I2^{ii}—Cu2—Cu3^{i}	59.40 (3)
I3—Cu2—Cu3^{i}	59.73 (3)
S2—Cu2—Cu2^{ii}	120.35 (7)
I2—Cu2—Cu2^{ii}	57.30 (3)
I2^{ii}—Cu2—Cu2^{ii}	56.86 (4)
I3—Cu2—Cu2^{ii}	131.10 (6)
Cu3^{i}—Cu2—Cu2^{ii}	105.32 (6)
I1—Cu3—I2^{iii}	101.52 (4)
I1—Cu3—I3	114.46 (4)
I2^{iii}—Cu3—I3	112.63 (4)
I1—Cu3—I3^{i}	119.07 (4)
I2^{iii}—Cu3—I3^{i}	114.32 (4)
I3—Cu3—I3^{i}	95.52 (3)
I1—Cu3—Cu2^{i}	141.48 (5)
I2^{iii}—Cu3—Cu2^{i}	57.97 (3)
I3—Cu3—Cu2^{i}	103.87 (4)
I3^{i}—Cu3—Cu2^{i}	58.15 (3)
I1—Cu3—Cu1	58.00 (3)
I2^{iii}—Cu3—Cu1	141.37 (5)
I3—Cu3—Cu1	105.88 (4)
I3^{i}—Cu3—Cu1	63.40 (3)
Cu2^{i}—Cu3—Cu1	115.77 (5)
Cu3—I1—Cu1	66.25 (4)
Cu2—I2—Cu2^{ii}	65.84 (4)
Cu2—I2—Cu3^{iv}	114.94 (4)
Cu2^{ii}—I2—Cu3^{iv}	62.63 (3)
Cu2—I3—Cu3	98.72 (3)
Cu2—I3—Cu3^{i}	62.12 (3)
Cu3—I3—Cu3^{i}	84.48 (3)
Cu2—I3—Cu1^{i}	116.85 (3)
Cu3—I3—Cu1^{i}	100.23 (3)
Cu3^{i}—I3—Cu1^{i}	60.65 (3)
Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+2, −*y*, −*z*+1; (iii) *x*, *y*+1, *z*;	

Table S53. Copper environment distances (Å) in 5		
	5 HT	**5 LT**
Cu1—S1	2.280 (5)	2.274(5)
Cu1—S2^{ii}	2.341 (5)	2.341(5)

Cu1—Br1	2.498(3)	2.498(3)
Cu1—Br2^{ii}	2.600 (3)	2.595(3)
Cu1^{i}—Br2	2.600 (3)	2.595(3)
Cu1—Cu2	2.857 (3)	2.832(4)
Cu1—Cu2^{ii}	2.885 (3)	2.860(4)
Cu2—S1	2.342 (5)	2.336(5)
Cu2—S2	2.271 (5)	2.265(5)
Cu2—Br1	2.581(3)	2.575(3)
Cu2—Br2	2.494(3)	2.496(3)
Cu2—Cu1^{i}	2.885 (3)	2.860(4)
Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *y*−1, *z*.		

Table S54. Copper environment angles (°) in 5		
	5 HT	**5 LT**
S1—Cu1—S2^{ii}	117.7 (2)	117.9(2)
S1—Cu1—Br1	109.2 (2)	109.5(2)
S2^{ii}—Cu1—Br1	110.1 (1)	109.7(1)
S1—Cu1—Br2^{ii}	118.2 (1)	118.4(2)
S2^{ii}—Cu1—Br2^{ii}	103.2 (1)	103.7(2)
Br1—Cu1—Br2^{ii}	96.4 (1)	95.2(1)
S1—Cu1—Cu2	52.8 (1)	53.1(1)
S2^{ii}—Cu1—Cu2	126.4 (2)	125.7 (2)
Br1—Cu1—Cu2	57.17 (8)	57.36 (8)
Br2^{ii}—Cu1—Cu2	128.5 (1)	128.3 (1)
S1—Cu1—Cu2^{ii}	131.5 (2)	131.6 (2)
S2^{ii}—Cu1—Cu2^{ii}	50.2 (1)	50.4 (1)
Br1—Cu1—Cu2^{ii}	119.1 (1)	118.5 (1)
Br2^{ii}—Cu1—Cu2^{ii}	53.79 (8)	54.19 (8)
Cu2—Cu1—Cu2^{ii}	174.8 (1)	174.3 (1)
S2—Cu2—S1	116.4 (2)	116.4 (2)
S2—Cu2—Br2	108.8 (2)	109.3 (2)
S1—Cu2—Br2	110.3 (1)	110.0 (1)
S2—Cu2—Br1	118.0 (1)	118.0 (2)
S1—Cu2—Br1	104.5 (1)	105.0 (2)
Br2—Cu2—Br1	97.1 (1)	96.1 (1)
S2—Cu2—Cu1	130.9 (2)	130.8 (2)
S1—Cu2—Cu1	50.9 (1)	51.1 (1)
Br2—Cu2—Cu1	120.2 (1)	119.7 (1)
Br1—Cu2—Cu1	54.40 (8)	54.78 (8)
S2—Cu2—Cu1^{i}	52.4 (1)	52.8 (1)
S1—Cu2—Cu1^{i}	124.8 (2)	124.0 (2)
Br2—Cu2—Cu1^{i}	57.27 (8)	57.49 (8)
Br1—Cu2—Cu1^{i}	129.2 (1)	129.1 (1)
Cu1—Cu2—Cu1^{i}	174.8 (1)	174.3 (1)
Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, *y*−1, *z*.		

Table S55. Copper environment distances (Å) in 5·THF		
	5·THF RT	**5·THF LT**
Cu1—S1^{ii}	2.498 (2)	2.445 (1)
Cu1—S1	2.274 (1)	2.271 (1)

Cu1—Br1	2.4674 (8)	2.4749 (6)
Cu1—Br1^{i}	2.4931 (8)	2.4738 (6)
Cu1—Cu1^{ii}	2.824 (1)	2.7640 (9)
Cu1—Cu1^{i}	3.001 (1)	2.9781 (9)
Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1.		

Table S56. Copper environment angles (°) in 5·THF		
	5·THF RT	**5·THF LT**
S1—Cu1—Br1	113.06 (4)	111.46 (3)
S1—Cu1—Br1^{i}	121.10 (4)	120.86 (3)
Br1—Cu1—Br1^{i}	105.55 (3)	106.00 (2)
S1—Cu1—S1^{ii}	107.61 (4)	108.53 (3)
Br1—Cu1—S1^{ii}	107.64 (4)	107.64 (4)
Br1^{i}—Cu1—S1^{ii}	100.58 (4)	100.72 (3)
S1—Cu1—Cu1^{ii}	57.49 (4)	57.34 (3)
Br1—Cu1—Cu1^{ii}	125.70 (4)	125.40 (3)
Br1^{i}—Cu1—Cu1^{ii}	125.34 (4)	125.92 (3)
S1^{ii}—Cu1—Cu1^{ii}	50.12 (4)	51.18 (3)
S1—Cu1—Cu1^{i}	138.70 (5)	136.89 (4)
Br1—Cu1—Cu1^{i}	53.16 (2)	52.98 (2)
Br1^{i}—Cu1—Cu1^{i}	52.38 (2)	53.02 (2)
S1^{ii}—Cu1—Cu1^{i}	113.68 (4)	114.54 (3)
Cu1^{ii}—Cu1—Cu1^{i}	163.78 (5)	165.63 (4)
Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1.		

Table S57. Copper environment distances (Å) in 5·ac	
Cu1—S1	2.270 (3)
Cu1—S1^{ii}	2.471 (3)
Cu1—Br1^{i}	2.475 (2)
Cu1—Cu1^{ii}	2.813 (3)
Cu1—Cu1^{i}	2.989 (2)
Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1.	

Table S58. Copper environment angles (°) in 5·ac	
S1—Cu1—Br1	110.8 (1)
S1—Cu1—S1^{ii}	107.4 (1)
Br1—Cu1—S1^{ii}	108.95 (9)
S1—Cu1—Br1^{i}	121.1 (1)
Br1—Cu1—Br1^{i}	105.58 (6)
S1^{ii}—Cu1—Br1^{i}	102.33 (9)
S1—Cu1—Cu1^{ii}	56.99 (8)
Br1—Cu1—Cu1^{ii}	124.90 (8)
S1^{ii}—Cu1—Cu1^{ii}	50.39 (8)
Br1^{i}—Cu1—Cu1^{ii}	127.18 (9)
S1—Cu1—Cu1^{i}	136.1 (1)
Br1—Cu1—Cu1^{i}	52.90 (5)
S1^{ii}—Cu1—Cu1^{i}	116.4 (1)
Br1^{i}—Cu1—Cu1^{i}	52.68 (5)
Cu1^{ii}—Cu1—Cu1^{i}	166.6 (1)

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1.

Table S59. Copper environment distances (Å) in 6·DMF		
	6·DMF RT	**6·DMF LT**
Cu1—S1	2.276 (1)	2.283 (1)
Cu1—S2	2.280 (1)	2.284 (1)
Cu1—I1	2.6635 (6)	2.6751 (6)
Cu1—I1^{i}	2.7741 (6)	2.7448 (6)
Symmetry code: (i) −*x*+1, −*y*+1, −*z*+2		

Table S60. Copper environment angles (°) in 6·DMF		
	6·DMF RT	**6·DMF LT**
S1—Cu1—S2	101.50 (4)	101.29 (4)
S1—Cu1—I1	119.93 (3)	119.97 (3)
S2—Cu1—I1	121.05 (3)	121.06 (3)
S1—Cu1—I1^{i}	108.71 (4)	109.41 (3)
S2—Cu1—I1^{i}	108.16 (4)	109.08 (3)
I1—Cu1—I1^{i}	96.71 (2)	95.48 (2)
Cu1—I1—Cu1^{i}	83.29 (2)	84.52 (2)
Symmetry code: (i) −*x*+1, −*y*+1, −*z*+2		

Table S61. Copper environment distances (Å) in 6·2MeCN	
Cu1—S1	2.2886 (8)
Cu1—S2	2.2728 (9)
Cu1—I1	2.6142 (4)
Cu1—I1^{i}	2.7261 (5)
Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.	

Table S62. Copper environment angles (°) in 6·2MeCN	
S1—Cu1—S2	105.05 (3)
S1—Cu1—I1	115.50 (2)
S2—Cu1—I1	119.18 (3)
S1—Cu1—I1^{i}	105.12 (3)
S2—Cu1—I1^{i}	102.45 (3)
I1—Cu1—I1^{i}	108.00 (1)
Cu1—I1—Cu1^{i}	72.04 (2)
Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.	

14. Hydrogen bonds

Table S63. Hydrogen bond geometry in 1 and 1·S (Å, °)					
	D—H···A	**D—H distance**	**H···A distance**	**D···A distance**	**D-H-A angle**
1RT	N1—H1*A*···I1^{i}	0.86	3.19	3.648(7)	116
	N1—H1*B*···I1	0.86	2.85	3.703(7)	174
Symmetry code: (i) −*x*+1, −*y*, −*z*+1.					
1LT	N1—H1*A*···I1^{i}	0.88	3.13	3.600(4)	115
	N1—H1*B*···I1	0.88	2.79	3.670(5)	175
Symmetry code: (i) −*x*+1, −*y*, −*z*+1.					
1 · THF RT	N1—H1*A*···O1	0.86	1.98	2.79(1)	155

	N1—H1*B*···I1 [i]	0.86	2.75	3.611(7)	177
Symmetry code: (i) *x*+1, *y*, *z*.					
1 · THF LT	N1—H1*A*···O1	0.88	1.94	2.77(1)	156
	N1—H1*B*···I1[i]	0.88	2.72	3.597(7)	177
	C8—H8*B*···I1[ii]	0.99	3.28	3.97(1)	128
Symmetry codes: (i) *x*+1, *y*, *z*. (ii) *x*+1/2, −*y*+1/2, *z*−1/2;					
1 · acetone RT	C11—H11*B*···I1[i]	0.96	3.21	4.03(1)	145
	N1—H1*A*···O1	0.86	2.04	2.871(7)	162
	N1—H1*B*···I1	0.86	2.80	3.652(5)	170
Symmetry code: (i) −*x*-1, −*y*+*1*, −*z*+1.					
1 · acetone LT	N1—H1*A*···O1	0.88	2.01	2.845(6)	159
	N1—H1*B*···I1	0.88	2.75	3.620(5)	171
Symmetry code: (i) *x*+1, *y*, *z*.					
1 · MeOH RT	C8—H8*A*···I1[i]	0.96	3.19	4.119(5)	165
	N1—H1*A*···O1	0.86	2.06	2.853(4)	153
	N1—H1*B*···I1	0.86	2.86	3.697(3)	167
	O1—H1···I1[ii]	0.82	3.13	3.895(3)	156
	O1—H1···S1[iii]	0.82	2.97	3.511(3)	126
Symmetry codes: (i) *x*+1, *y*, *z*; (ii) *x*+1/2, −*y*+1/2, *z*+1/2; (iii) −*x*+3/2, *y*−1/2, −*z*+3/2.					
1 · MeOH LT	C8—H8*A*···I1[i]	0.98	3.15	4.096(3)	164
	C8—H8*B*···S1[ii]	0.98	3.02	3.568(3)	117
	N1—H1*A*···O1	0.88	2.02	2.829(3)	153
	N1—H1*B*···I1	0.88	2.81	3.677(2)	168
	O1—H1···I1[iii]	0.84	3.02	3.756(2)	148
	O1—H1···S1[ii]	0.84	2.90	3.507(2)	131
Symmetry codes: (i) *x*+1, *y*, *z*; (ii) −*x*+3/2, *y*−1/2, −*z*+3/2; (ii) *x*+1/2, −*y*+1/2, *z*+1/2.					

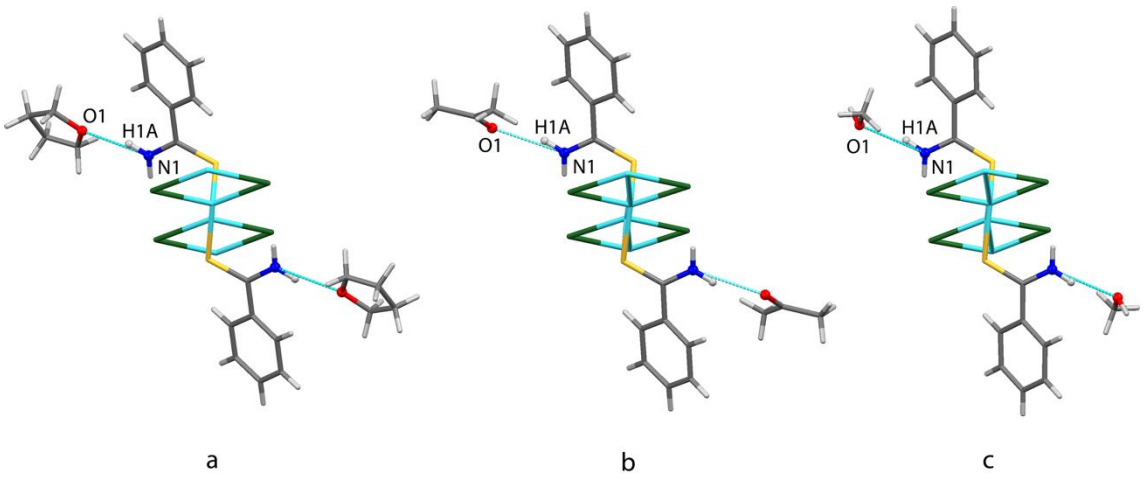

Figure S15. Detail of the supramolecular N-H···O hydrogen bonds in **1**·S between the chains and the solvent molecules: **1**·THF (a); **1**·acetone (b) and **1**·MeOH (c). Atoms in the asymmetric unit participating in the H bonds are labelled.

Table S64. Hydrogen bond geometry in 2 and 3 (Å, °)					
	D—H···A	**D—H distance**	**H···A distance**	**D···A distance**	**D-H-A angle**
2	N1—H1*A*···S1^{i}	0.86	2.69	3.387(5)	139
	N1—H1*B*···I1	0.86	2.85	3.682(6)	163
	N2—H2*A*···I1^{ii}	0.86	2.86	3.547(6)	138
	N2—H2*B*···I1	0.86	2.85	3.641(6)	153
	N3—H3*B*··S2^{iii}	0.86	2.76	3.504(6)	146
	N3—H3*B*···I1	0.86	2.91	3.593(5)	137
Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) −*x*, −*y*+1, −*z*+1; (iii) *x*, −*y*+1/2, *z*+1/2.					
3	C16—H16*B*···I1^{i}	0.96	3.10	3.968(5)	151
	N1—H1*A* ···N3	0.86	2.24	3.066(6)	160
	N1—H1*B*···I1	0.86	3.22	3.832(3)	130
	N1—H1*B*···I1^{ii}	0.86	3.21	3.914(3)	141
	N2—H2*A*···S1 ^{iii}	0.86	2.80	3.588(3)	153
	N2—H2*B*···I1	0.86	2.76	3.615(3)	176
Symmetry codes: (i) −*x*+1, *y*+1/2; (ii)−*x*+1, −*y*+1, −*z*+1;, −*z*+3/2; (iii) *x*, *y*−1, *z*.					

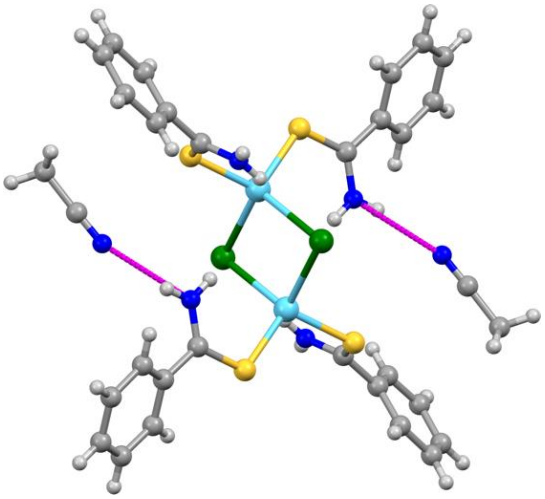

Figure S16. Detail of the molecular packing in **3** with supramolecular N-H···N hydrogen bonds depicted in magenta.

Table S65. Hydrogen bond geometry in 4 (Å, °)					
	D—H···A	**D—H distance**	**H···A distance**	**D···A distance**	**D-H-A angle**
4	N1—H1*A* ···I2^{i}	0.86	3.20	4.006(8)	158
	N1—H1*B*···I1	0.86	2.99	3.753(8)	148
	N2—H2*A*···S1^{ii}	0.86	2.60	3.437(7)	164
	N2—H2*B*···I1^{ii}	0.86	3.24	3.842(6)	129
	N2—H2*B*···I2	0.86	3.27	4.016(6)	147
Symmetry codes: (i) −*x*+3/2, *y*+1/2, (ii) −*z*+1/2 *x*, *y*−1, *z*.					

Table S66. Hydrogen bond geometry in 5 and 5·S (Å, °)					
	D—H···A	**D—H distance**	**H···A distance**	**D···A distance**	**D-H-A angle**
5 RT	N2—H2*B*···Br1	0.87	2.48	3.35(1)	177
	N2—H2*A*···Br1^{i}	0.87	2.58	3.38(1)	154
	N1—H1*B*···Br2^{ii}	0.87	2.47	3.34(2)	176
	N1—H1*A*···Br2^{iii}	0.86	2.58	3.38(2)	153
Symmetry codes: (i) −*x*+1, −*y*, −*z*+1 (ii) *x*, *y*−1, *z*;; (iii) −*x*+2, −*y*, −*z*+1.					
5LT	N2—H2*B*···Br1	0.88	2.46	3.34(2)	177
	N2—H2*A*···Br1^{i}	0.88	2.55	3.37(2)	155
	N1—H1*B*···Br2^{ii}	0.88	2.45	3.33(2)	176
	N1—H1*A*···Br2^{iii}	0.88	2.55	3.37(2)	154
Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) *x*, *y*−1, *z*;					
5 · THF RT	N1—H1*A*···O1	0.86	2.05	2.874(7)	160
	N1—H1*B*···I1 ^{i}	0.86	2.56	3.411(4)	173
5 · THF LT	N1—H1*A*···O1	0.88	2.08	2.911(5)	158
	N1—H1*B*···Br1^{i}	0.88	2.57	3.446(3)	173
Symmetry code: (i) -*x*+2, -*y*+1, -*z*+1.					
5 · acetone LT	N1—H1*A*···O1	0.88	2.00	2.86(2)	167
	N1—H1*B*···Br1^{i}	0.88	2.55	3.420(9)	170
Symmetry code: (i) −*x*+2, −*y*,+1 −*z*+1.					

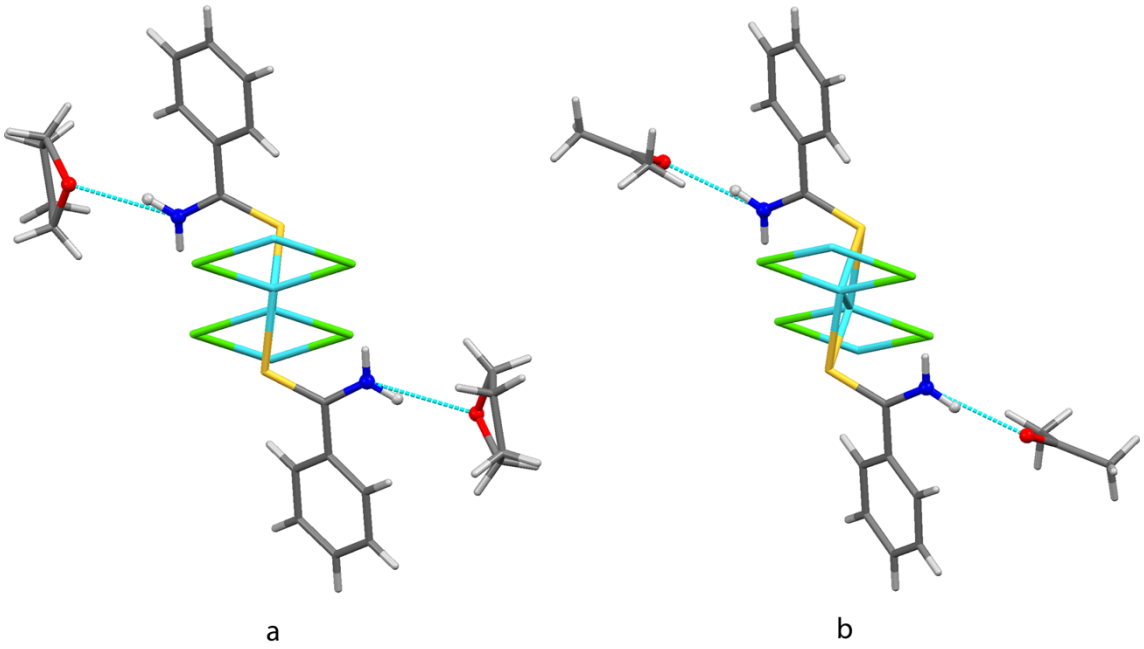

Figure S17. Detail of the supramolecular N-H···O hydrogen bonds in **5**·S between the chains and the solvent molecules: **5**·THF (a) and **1**·acetone (b).

Table S67. Hydrogen bond geometry in 6 · S (Å, °)					
	D—H···A	**D—H distance**	**H···A distance**	**D···A distance**	**D-H-A angle**
6 · DMF RT	N1—H1A···O1^{i}	0.86	2.03	2.860(5)	162
	N1—H1B···I1	0.86	2.92	3.771(3)	170
	N2—H2A···I1^{ii}	0.86	2.90	3.697(3)	156
	N2—H2B···I1	0.86	2.90	3.710(3)	159
	C11A—H11B···I1^{iii}	0.96	3.13	3.92(1)	141
Symmetry codes: (i) *x*, *y*+1, *z*+1; (ii) −*x*+2, −*y*+1, −*z*+2; (iii) −*x*+1, *y*+1, −*z*+2.					
6 · DMF LT	N1—H1A···O1^{i}	0.88	2.01	2.856(5)	161
	N1—H1B···I1	0.88	2.89	3.760(3)	171
	N2—H2A···I1^{ii}	0.88	2.87	3.695(3)	156
	N2—H2B···I1	0.88	2.89	3.717(3)	158
	C11A—H11E···O1^{iii}	0.98	3.28	3.28(8)	133
Symmetry codes: (i) *x*, *y*+1, *z*+1; (ii) −*x*+2, −*y*+1, −*z*+2; (iii) −*x*+1, −*y*, −*z*+1.					
6 · 2MeCN	N1—H1A···I1^{i}	0.88	3.04	3.822(3)	149
	N1—H1B···I1	0.88	3.22	3.940(3)	140
	N2—H2A···N3^{ii}	0.88	2.16	2.996 (4)	158
	N2—H2B···I1	0.88	2.78	3.652(3)	171
Symmetry codes: (i) –*x*, −*y*+1, −*z*+1; (ii) *x*, *y*−1, *z*−1.					

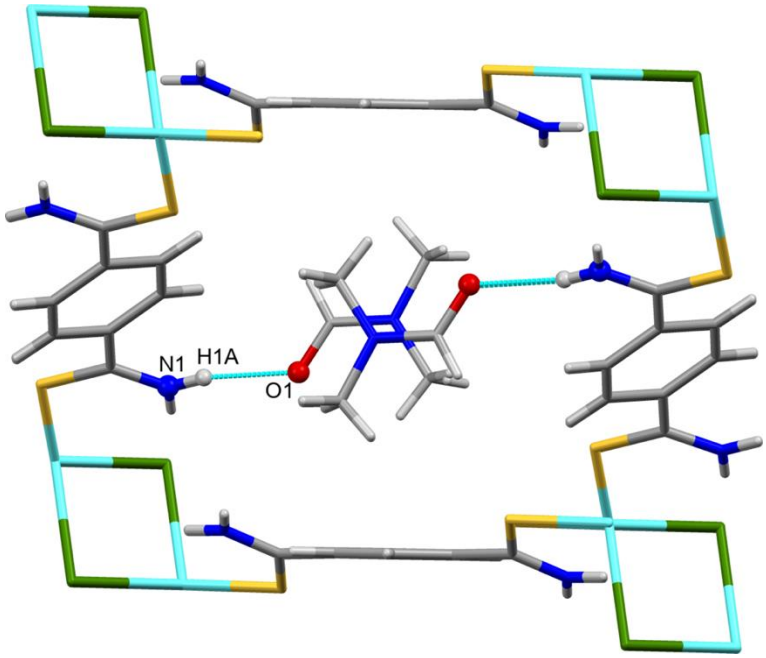

Figure S18. Detail of the molecular packing in $[Cu_2I_2(TBA)_4]\cdot DMF$ with supramolecular N-H···O hydrogen bonds depicted in cyan. Atoms in the asymmetric unit participating in the H bonds are labelled.

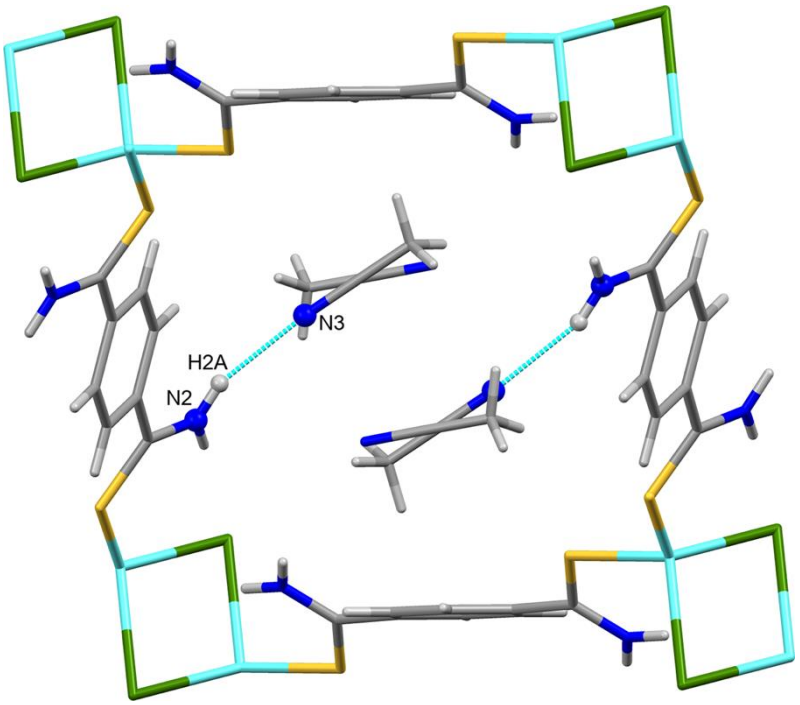

Figure S19. Detail of the molecular packing in $[Cu_2I_2(TBA)_4]\cdot 2MeCN$ with supramolecular N-H···N hydrogen bonds depicted in cyan. Atoms in the asymmetric unit participating in the H bonds are labelled.

15. Cell parameters orientation in the measured single crystals

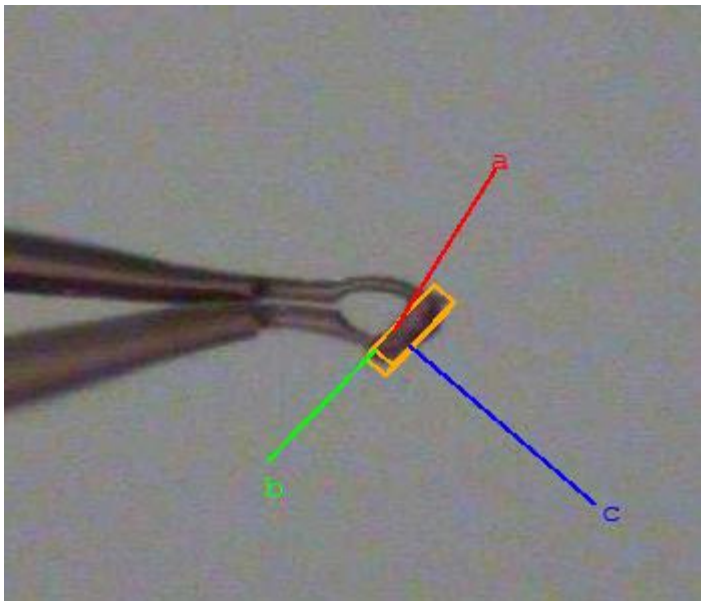

Figure S20. Cell axes orientation in the measured single crystal of **1**.

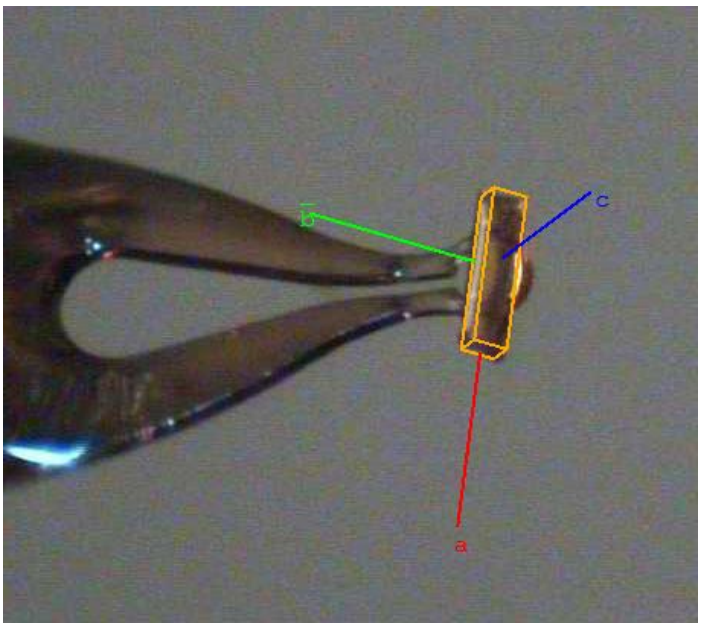

Figure S21. Cell axes orientation in the measured single crystal of **1·MeOH.**

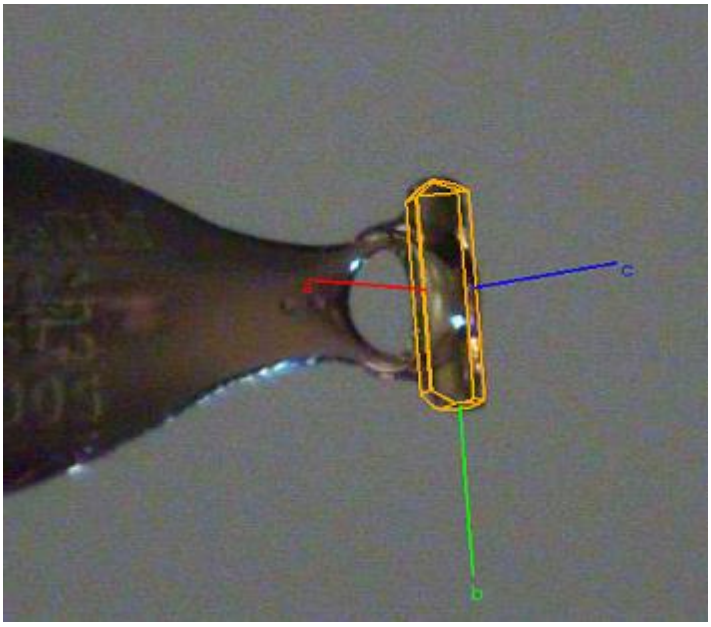

Figure S22. Cell axes orientation in the measured single crystal of **4**.

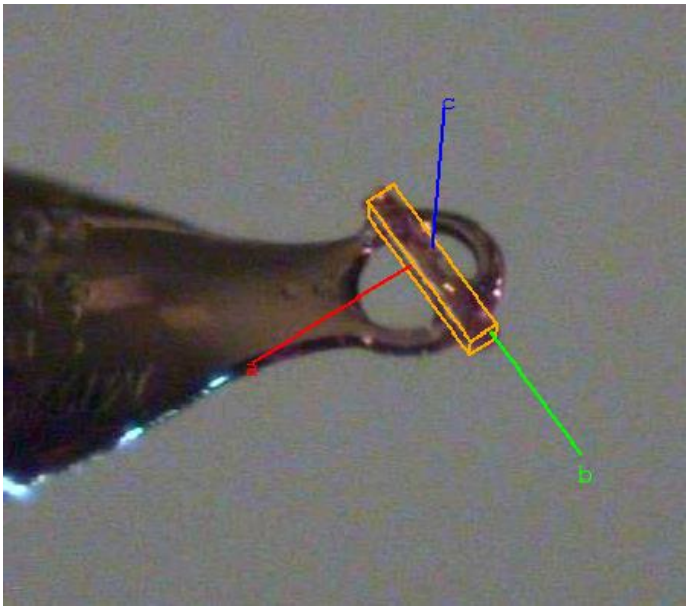

Figure S23. Cell axes orientation in the measured single crystal of **5**.

S2. XRPD Patterns of Synthesized Compounds

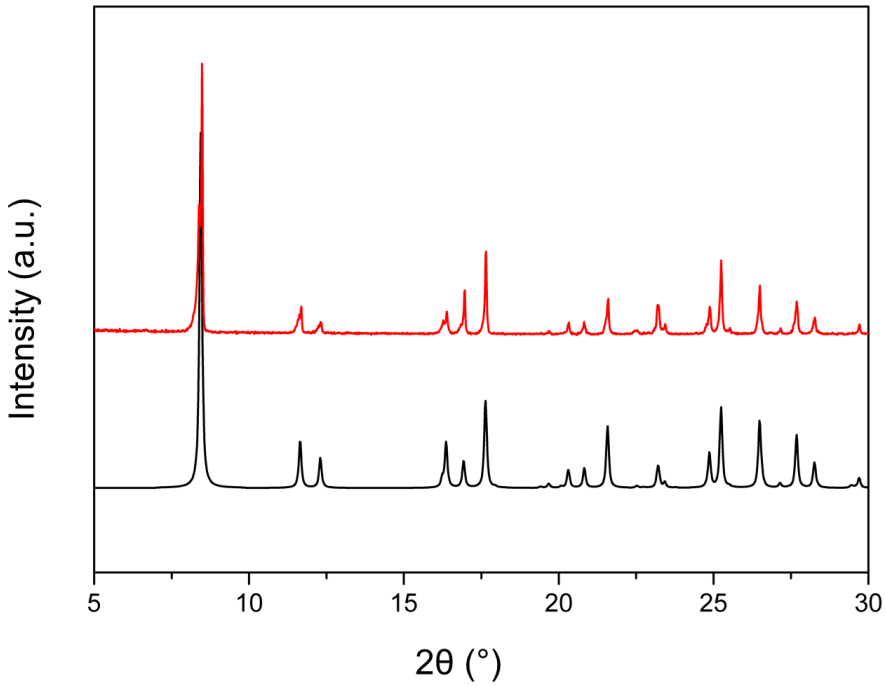

Figure S24. Experimental (red) and simulated (black) XRPD patterns of **1**.

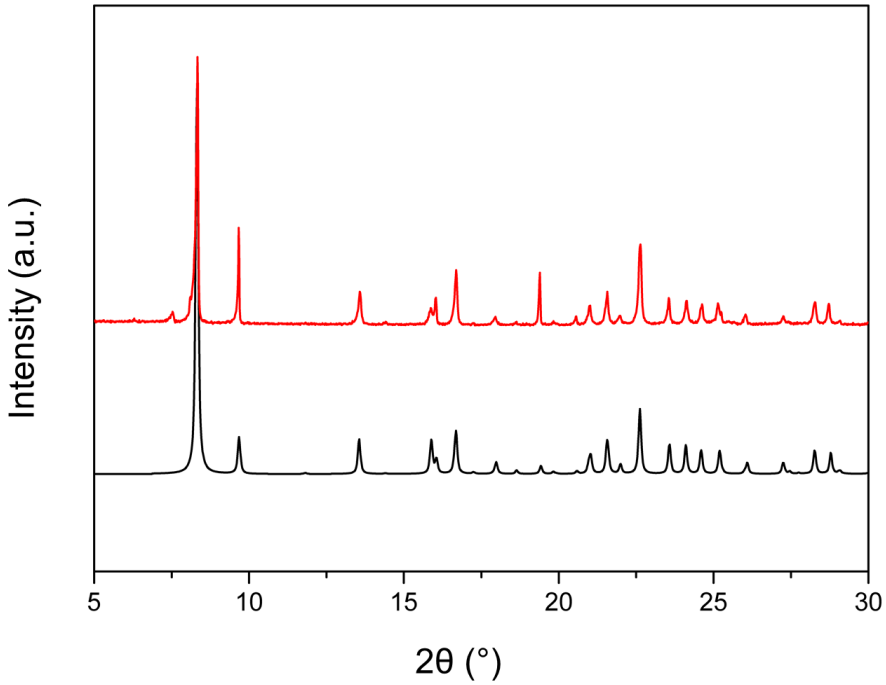

Figure S25. Experimental (red) and simulated (black) XRPD patterns of **1**·THF.

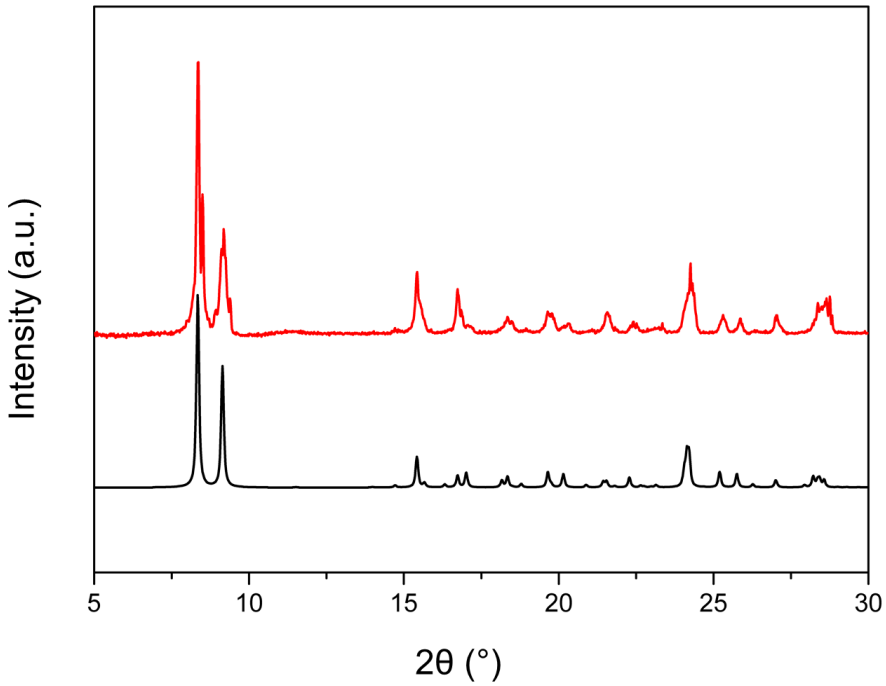

Figure S26. Experimental (red) and simulated (black) XRPD patterns of **1**·acetone.

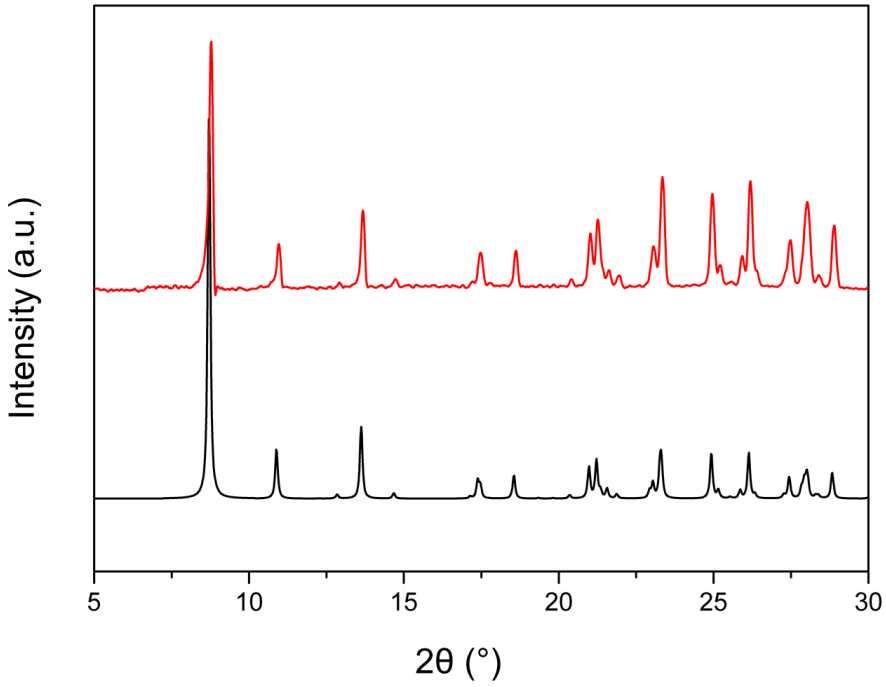

Figure S27. Experimental (red) and simulated (black) XRPD patterns of **1**·MeOH.

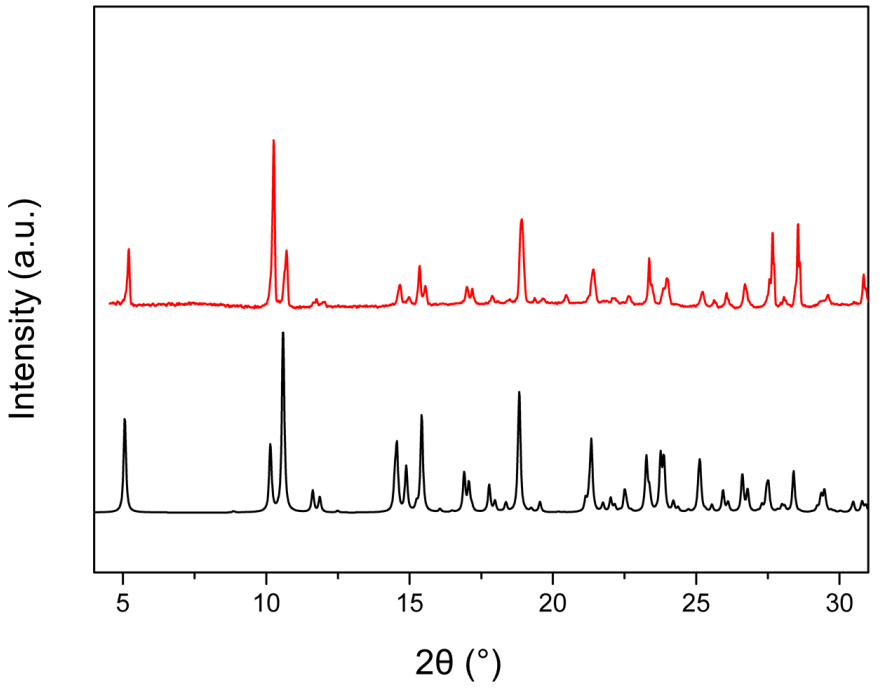

Figure S28. Experimental (red) and simulated (black) XRPD patterns of **2**.

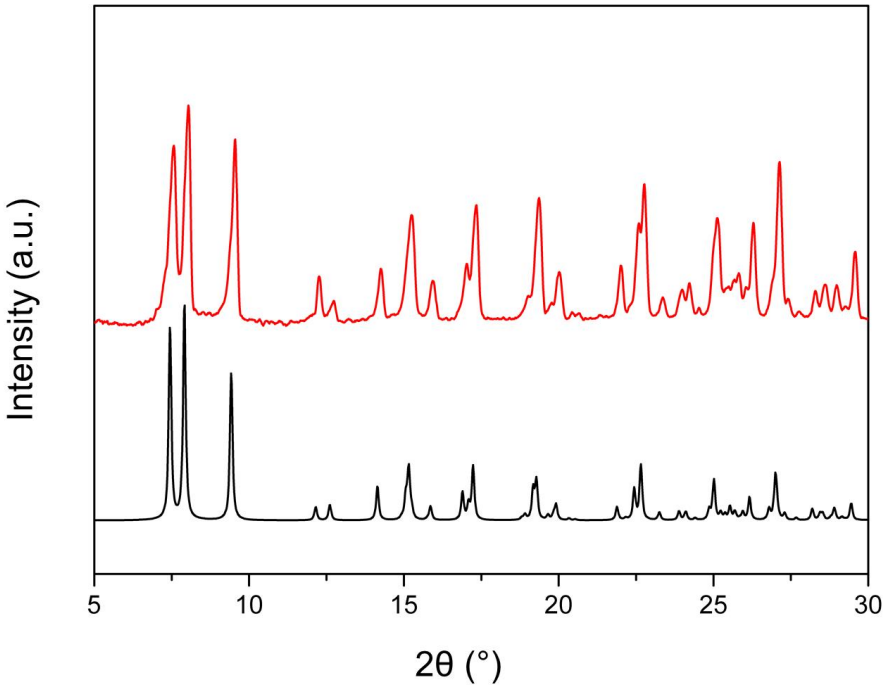

Figure S29. Experimental (red) and simulated (black) XRPD patterns of **3**.

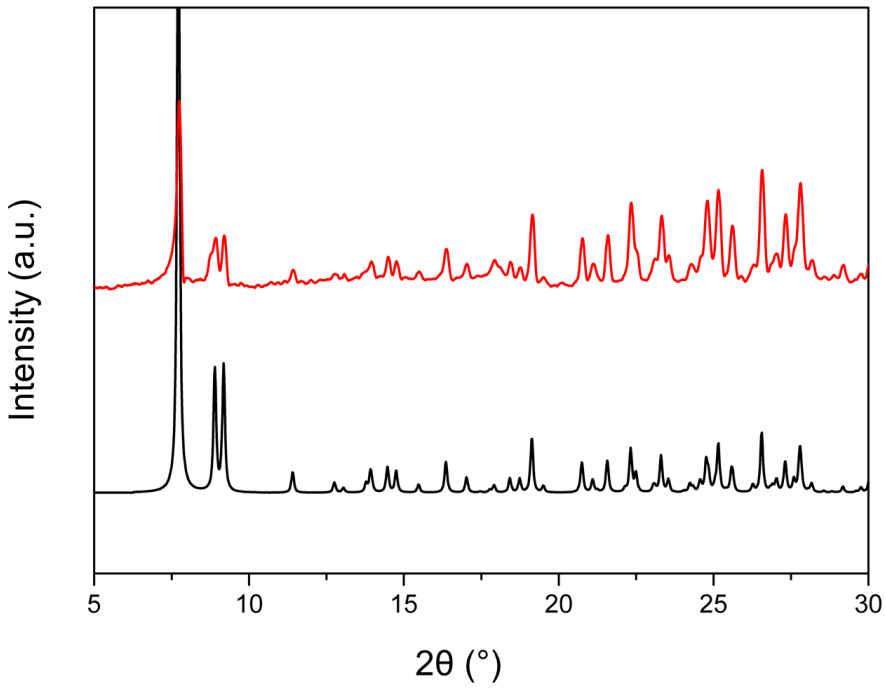

Figure S30. Experimental (red) and simulated (black) XRPD patterns of **4**.

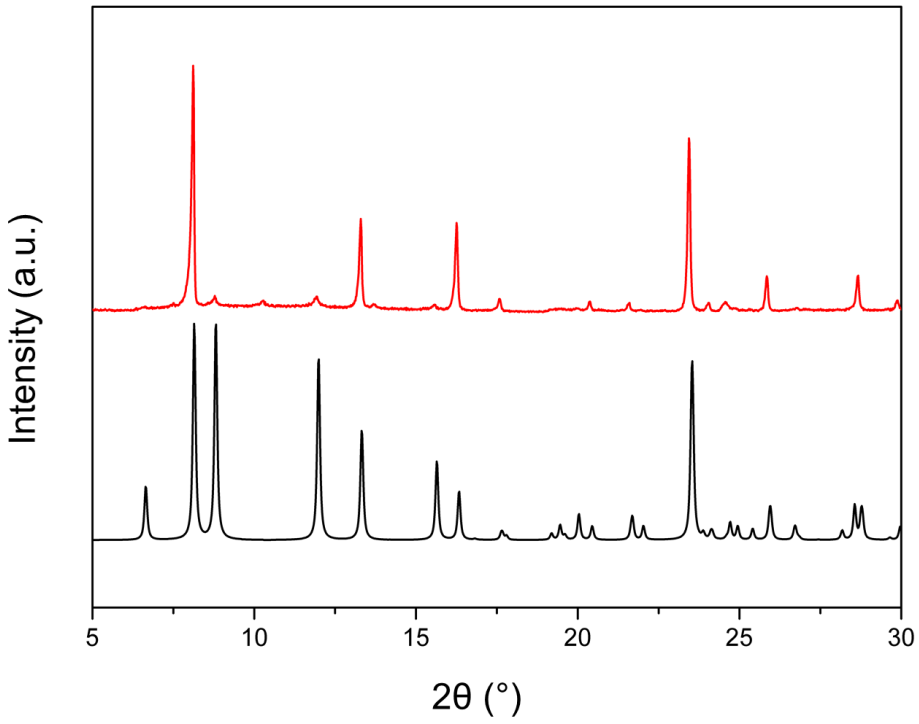

Figure S31. Experimental (red) and simulated (black) XRPD patterns of **5**.

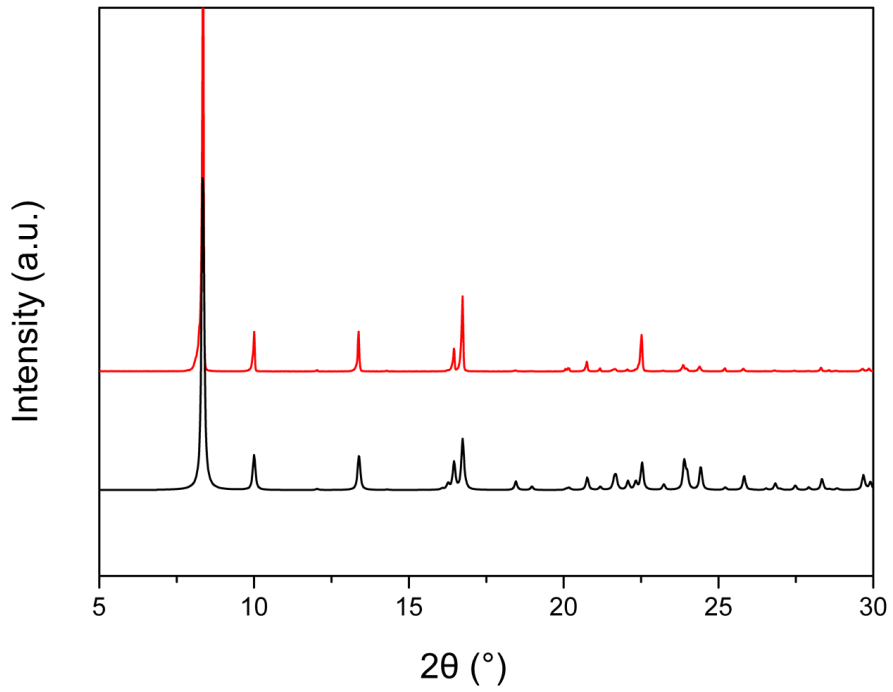

Figure S32. Experimental (red) and simulated (black) XRPD patterns of **5**·THF.

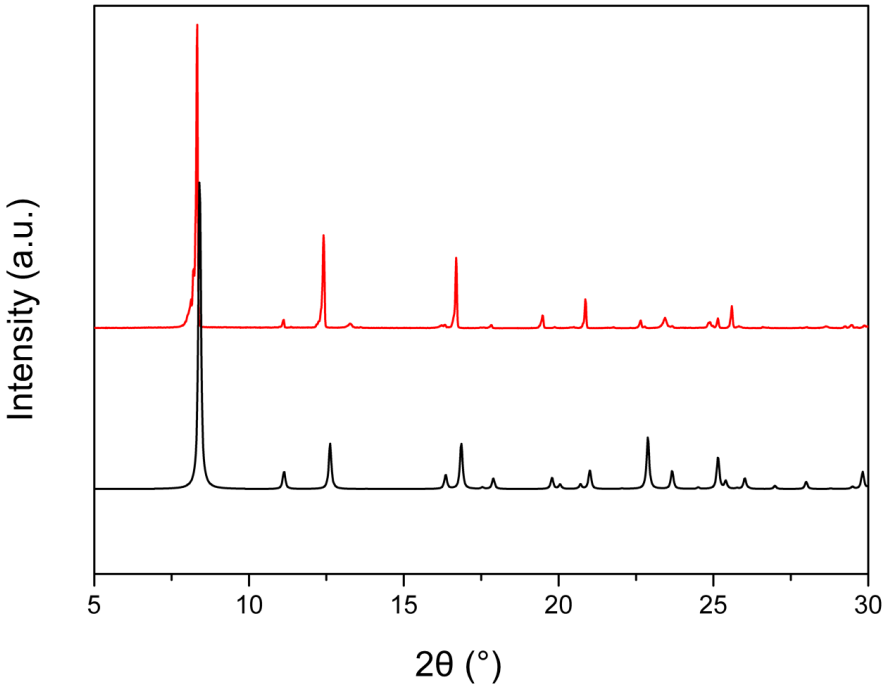

Figure S33. Experimental (red) and simulated (black) XRPD patterns of **5**·acetone.

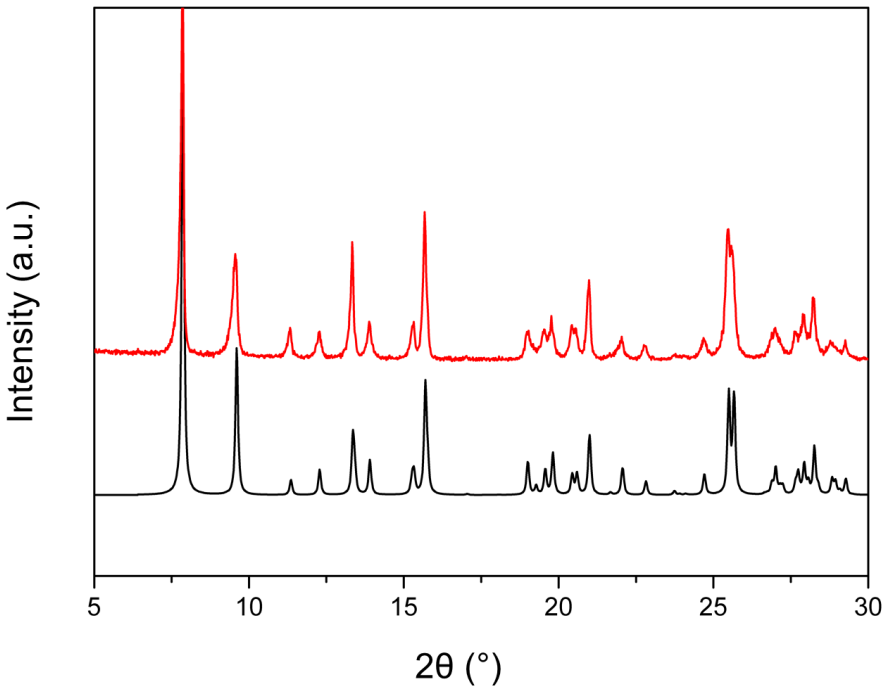

Figure S34. Experimental (red) and simulated (black) XRPD patterns of **6**·DMF.

S3. Immersion Experiments

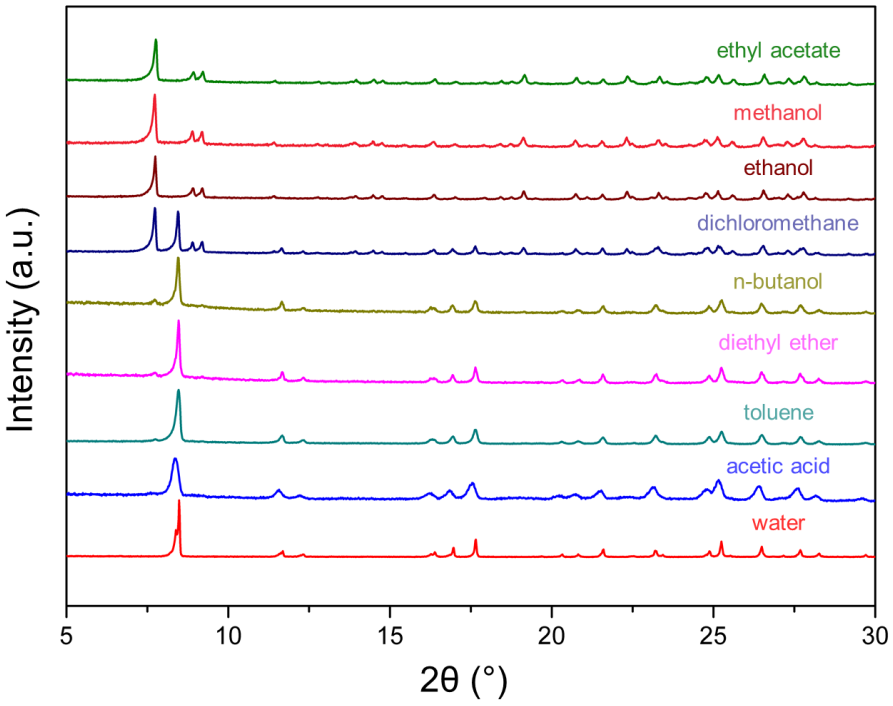

Figure S35. XRPD patterns of **1** after immersing in various solvents.

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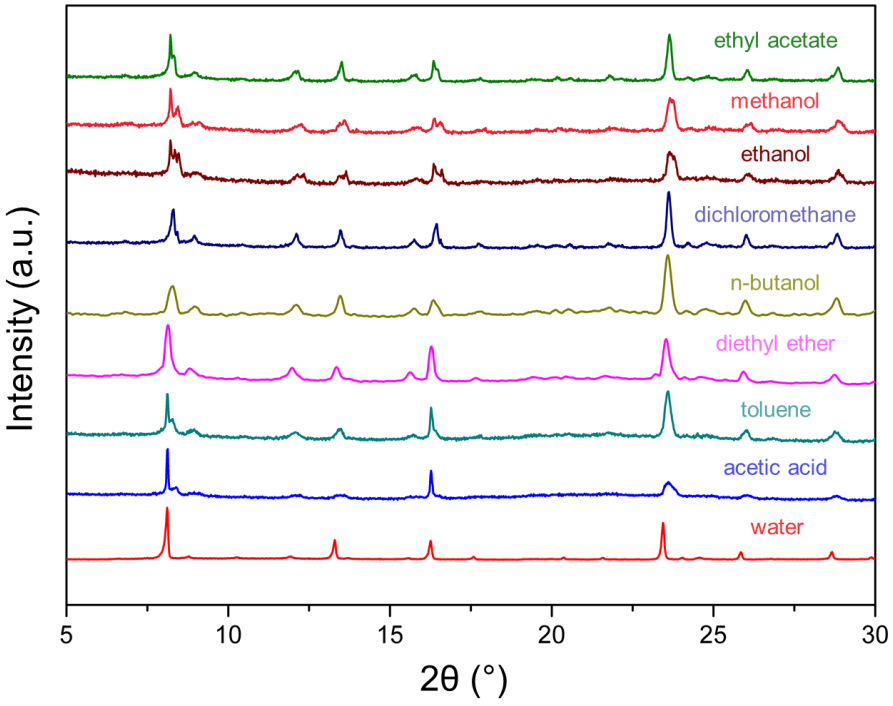

Figure S36. XRPD patterns of **5** after immersing in various solvents.

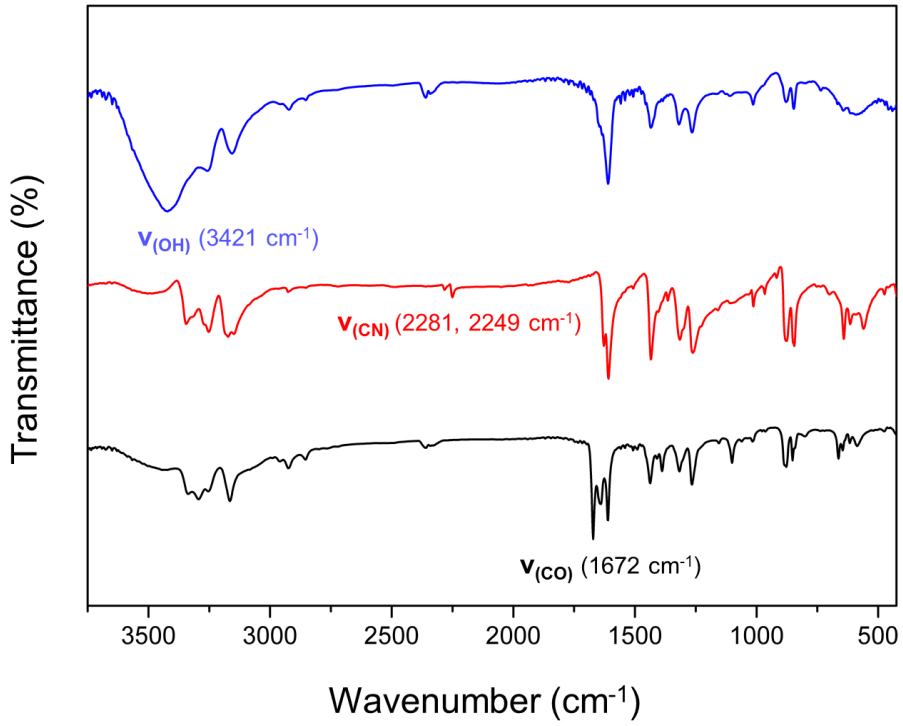

Figure S37. FT-IR spectra of **6**·DMF before (black) and after immersing in MeCN (**6**·MeCN, red) and MeOH (**6**·MeOH, blue).

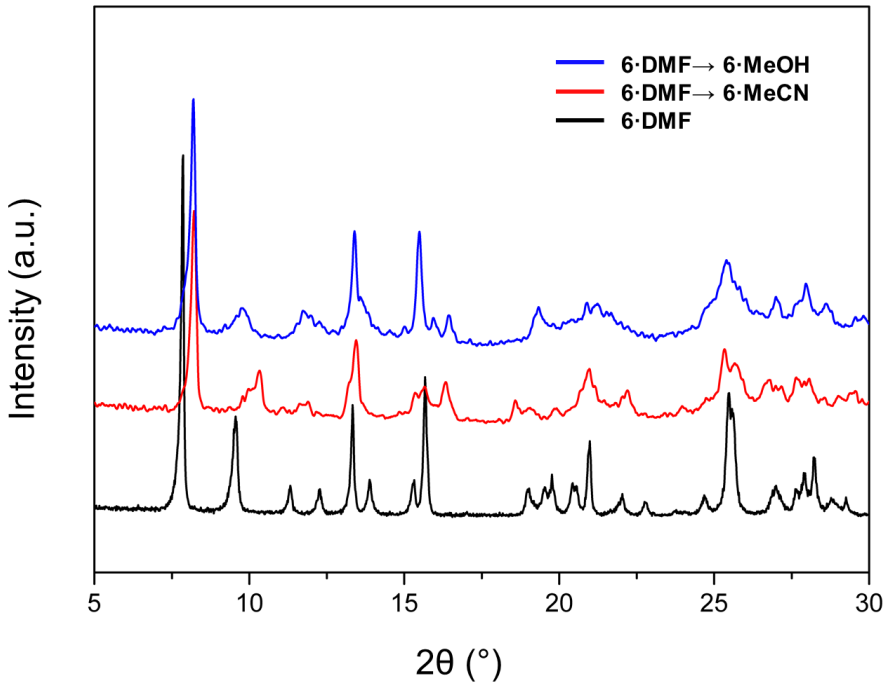

Figure S38. XRPD patterns of **6**·DMF before (black) and after immersing in MeCN (**6**·MeCN, red) and MeOH (**6**·MeOH, blue).

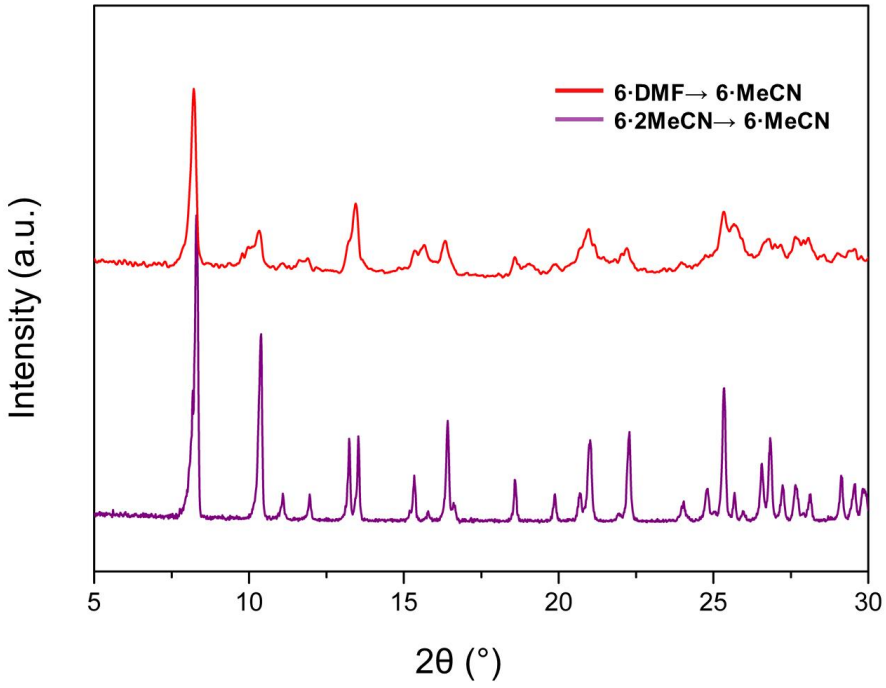

Figure S39. XRPD patterns of **6**·MeCN obtained after **6**·2MeCN drying (purple) and after immersing **6**·DMF in MeCN (red).

S4. Thermal Analysis

Table S68. TGA data for TBA based CPs **1**, **1**·S (S= THF, acetone, MeOH), **4**, **5** and **5**·S (S= THF, acetone)

	Temperature (°C)	% Mass loss (calc.)	Mass loss assignment
1	275	41.6 (41.9)	TBA
1·THF	100	11.3 (18.0)	THF
	275	48.2 (52.3)	TBA
1·acetone	100	13.8 (15.1)	Acetone
	275	51.8 (50.6)	TBA
1·MeOH	120	7.3 (8.9)	MeOH
	275	45.5 (47.0)	TBA
4	250	32.4 (32.4)	TBA
5	260	54.8 (48.9)	TBA
5·THF	105	19.6 (20.4)	THF
	260	64.7 (59.3)	TBA
5·acetone	90	16.3 (17.1)	Acetone
	260	60.0 (57.6)	TBA

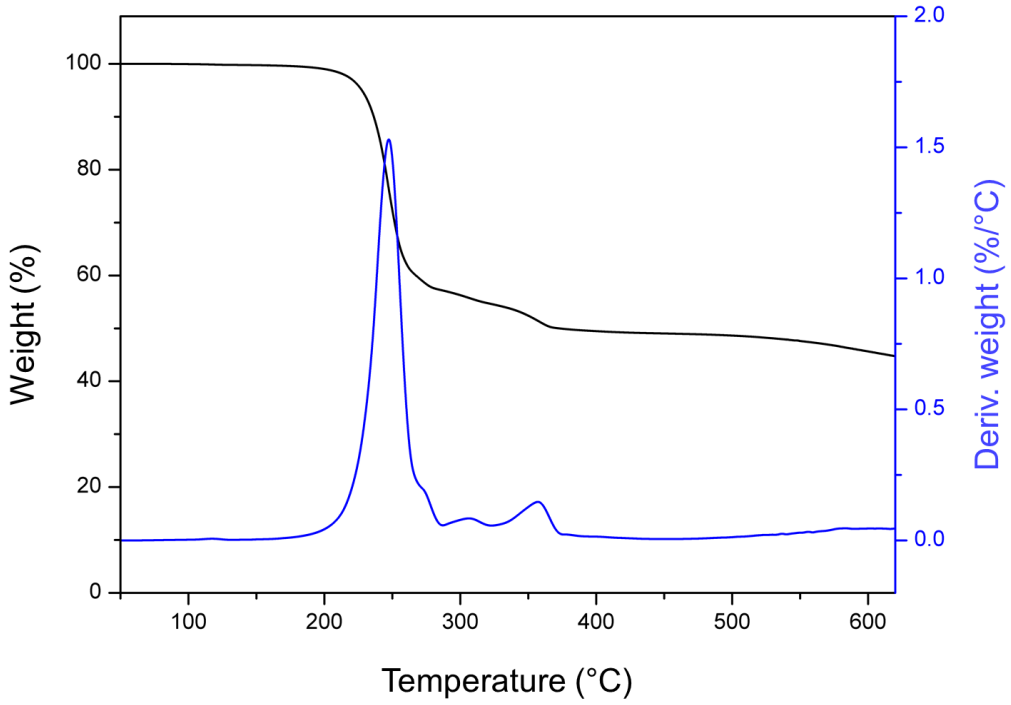

Figure S40. TGA and DTG curves of **1** in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

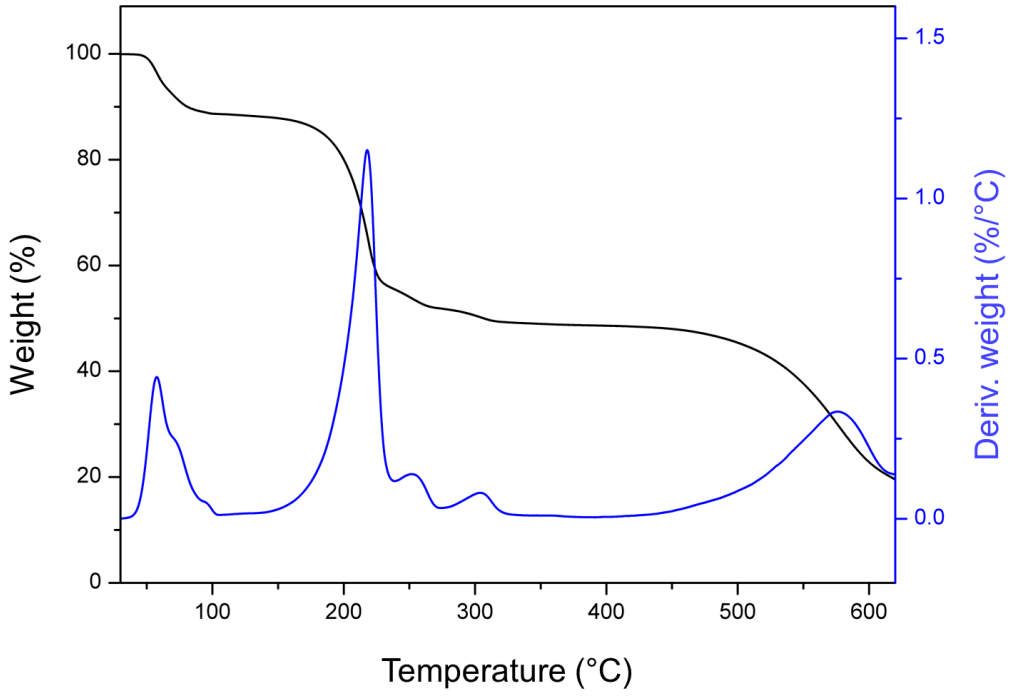

Figure S41. TGA and DTG curves of **1**·THF in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

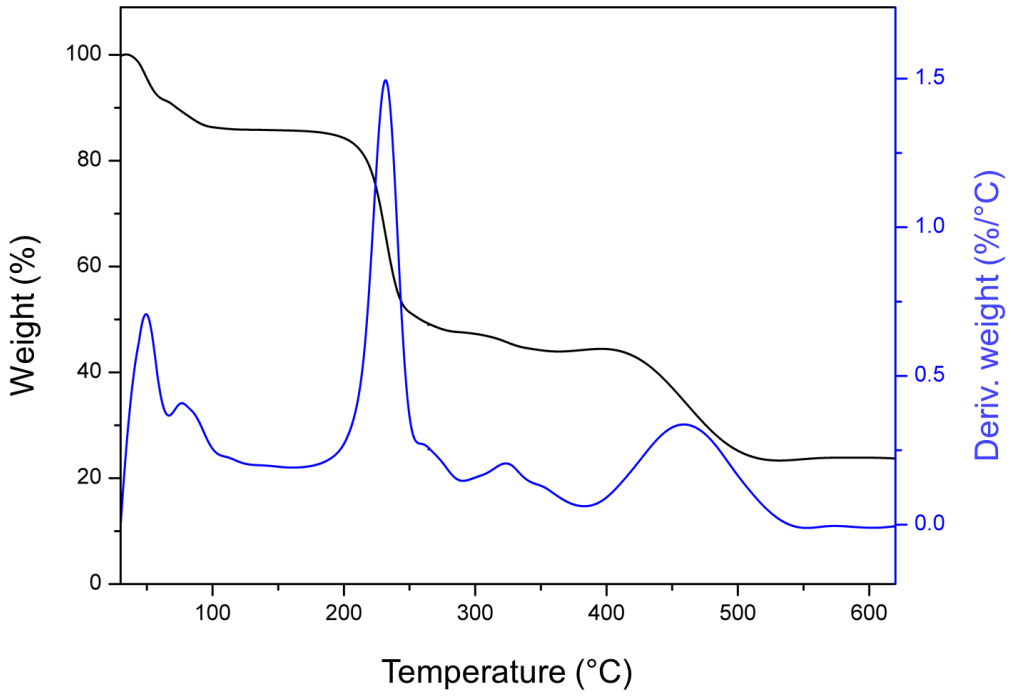

Figure S42. TGA and DTG curves of **1**·acetone in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

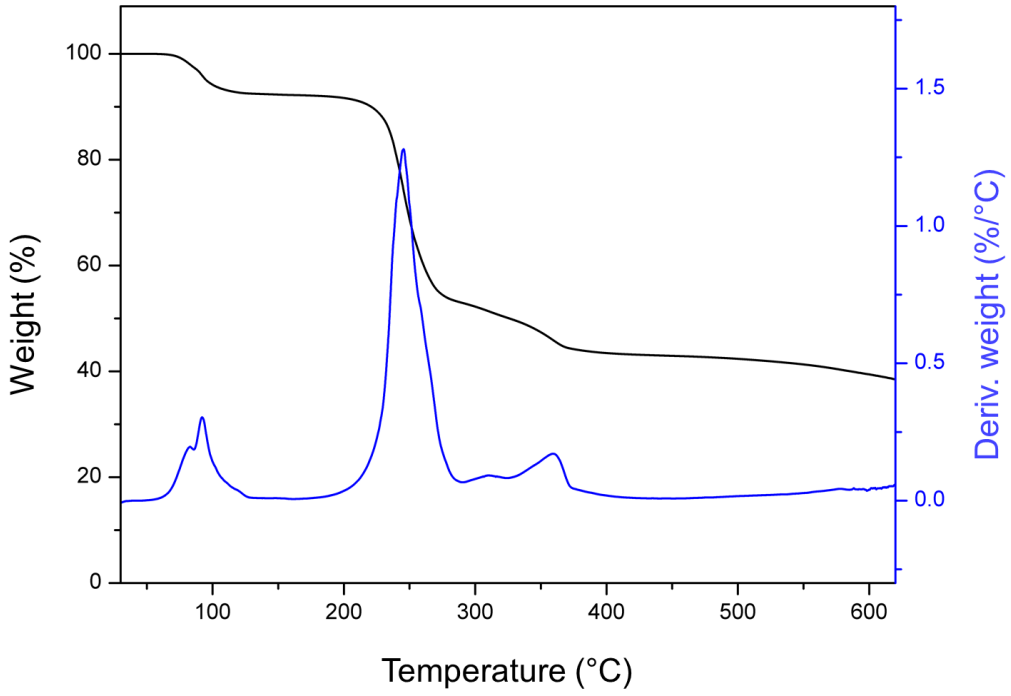

Figure S43. TGA and DTG curves of **1**·MeOH in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

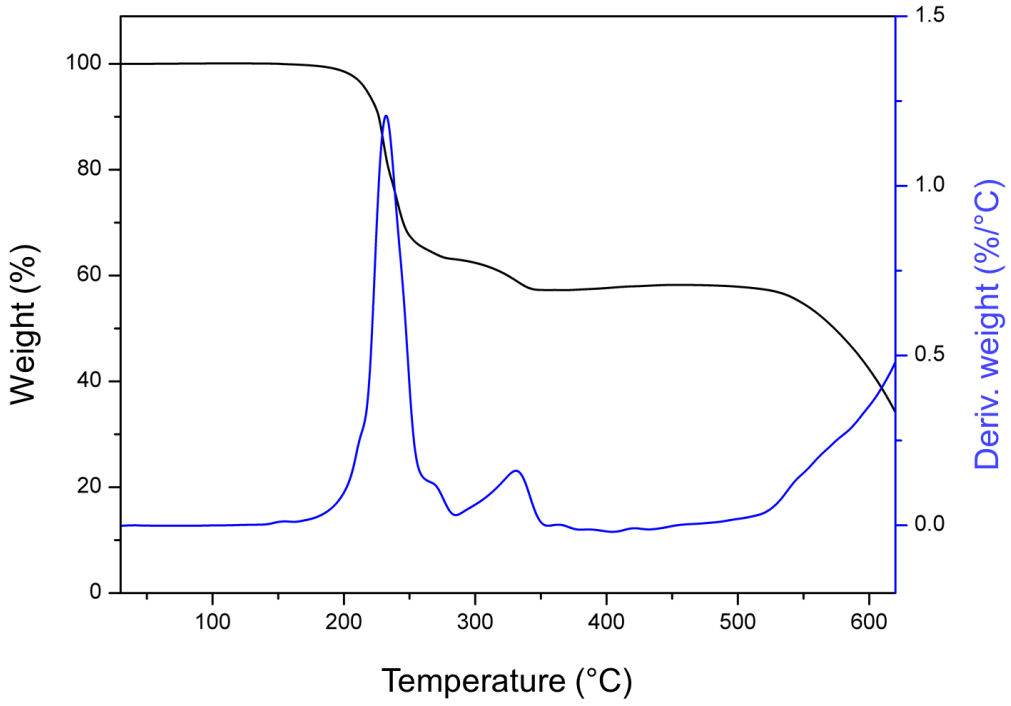

Figure S44. TGA and DTG curves of **4** in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

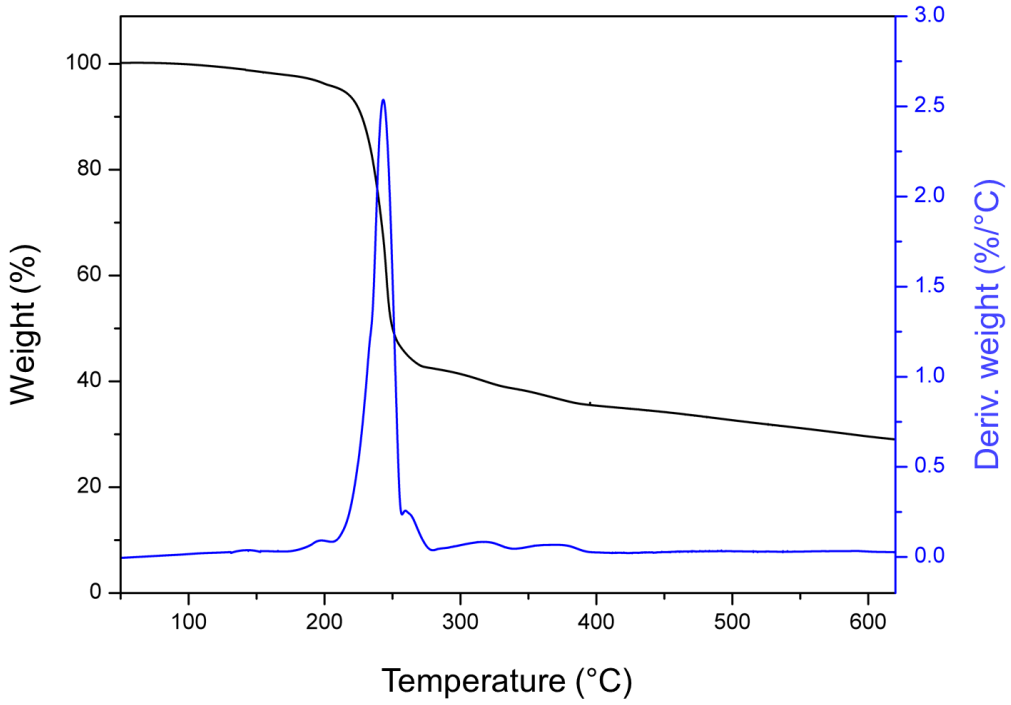

Figure S45. TGA and DTG curves of **5** in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

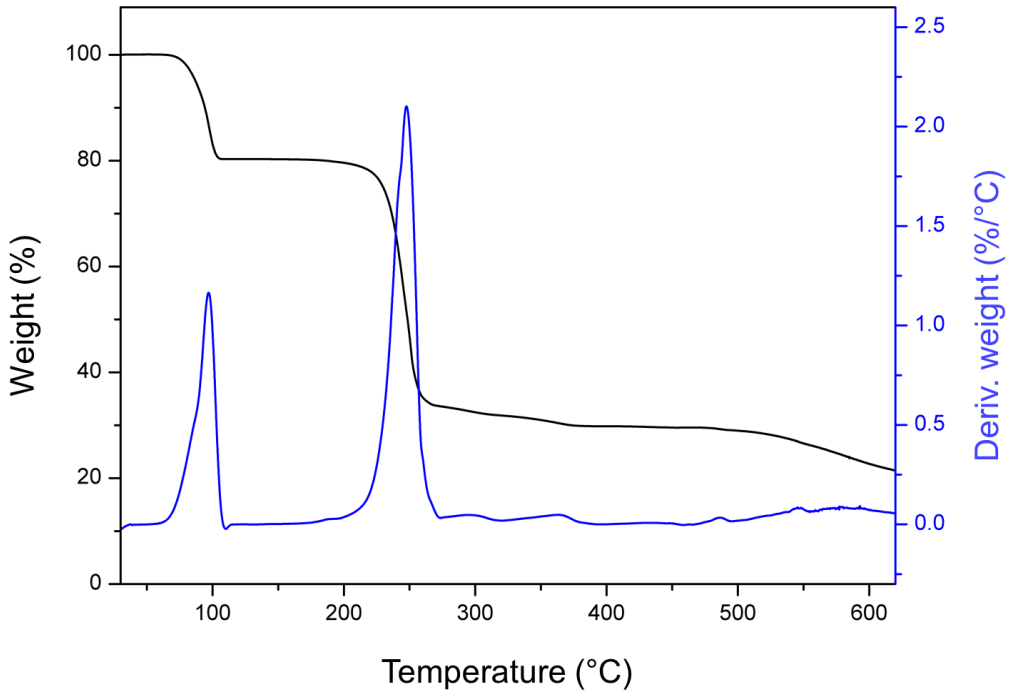

Figure S46. TGA and DTG curves of **5**·THF in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

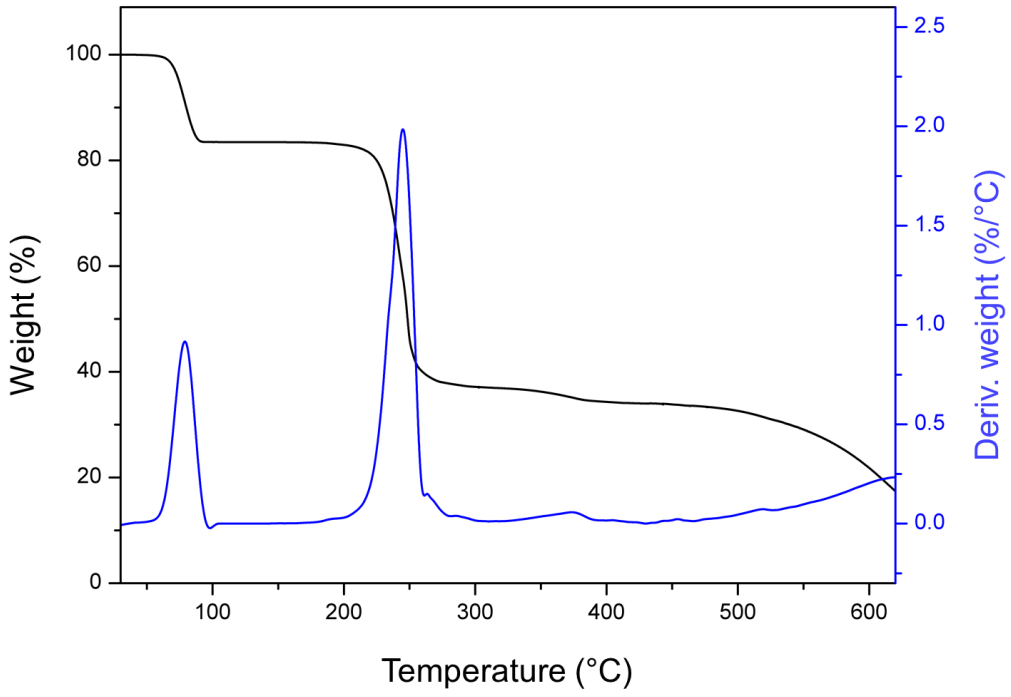

Figure S47. TGA and DTG curves of **5**·acetone in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

Table S69. TGA data for DTBA based CPs **6**·S (S= DMF, MeCN, MeOH)

	Temperature (°C)	**% Mass loss (calc.)**	**Mass loss assignment**
6·DMF	165	15.5 (15.9)	DMF
	285	37.2 (37.3)	½ DTBA
	315	59.2 (58.6)	½ DTBA
6·MeCN	155	9.6 (9.6)	MeCN
	275	31.0 (32.5)	½ DTBA
	305	54.4 (55.5)	½ DTBA
6·MeOH	150	8.0 (7.7)	MeOH
	270	31.4 (31.1)	½ DTBA
	300	54.8 (54.5)	½ DTBA

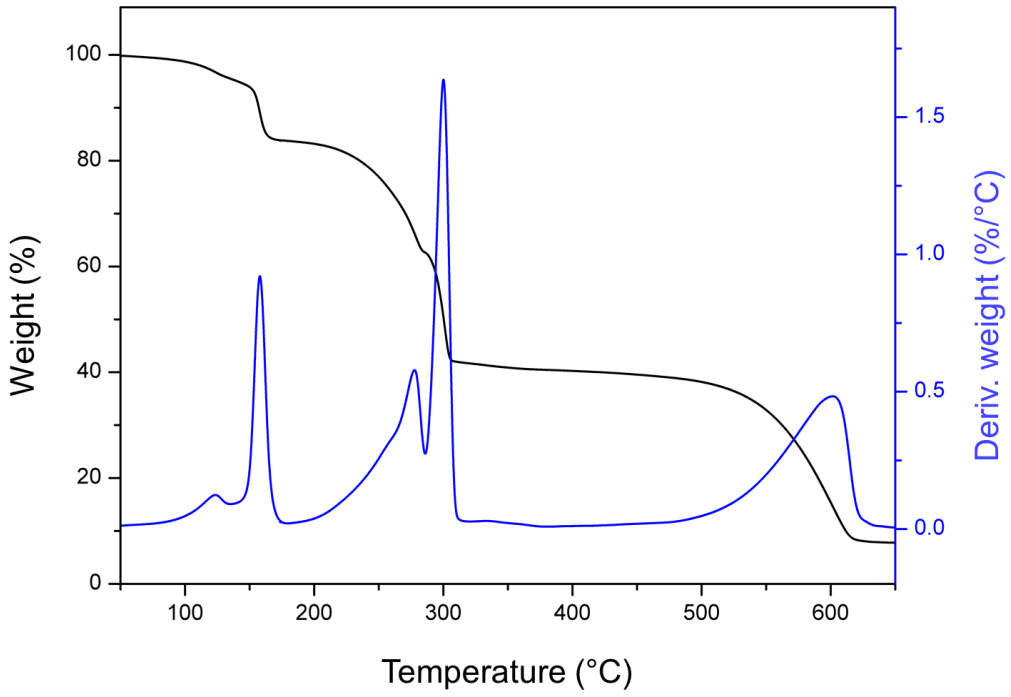

Figure S48. TGA and DTG curves of **6**·DMF in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

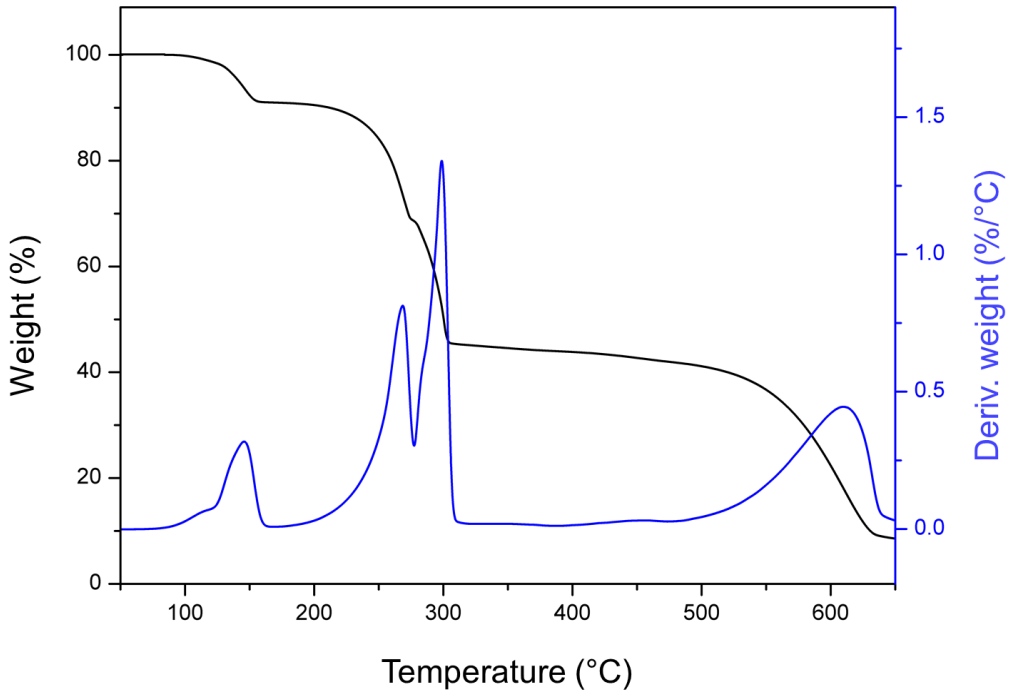

Figure S49. TGA and DTG curves of **6**·MeCN in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

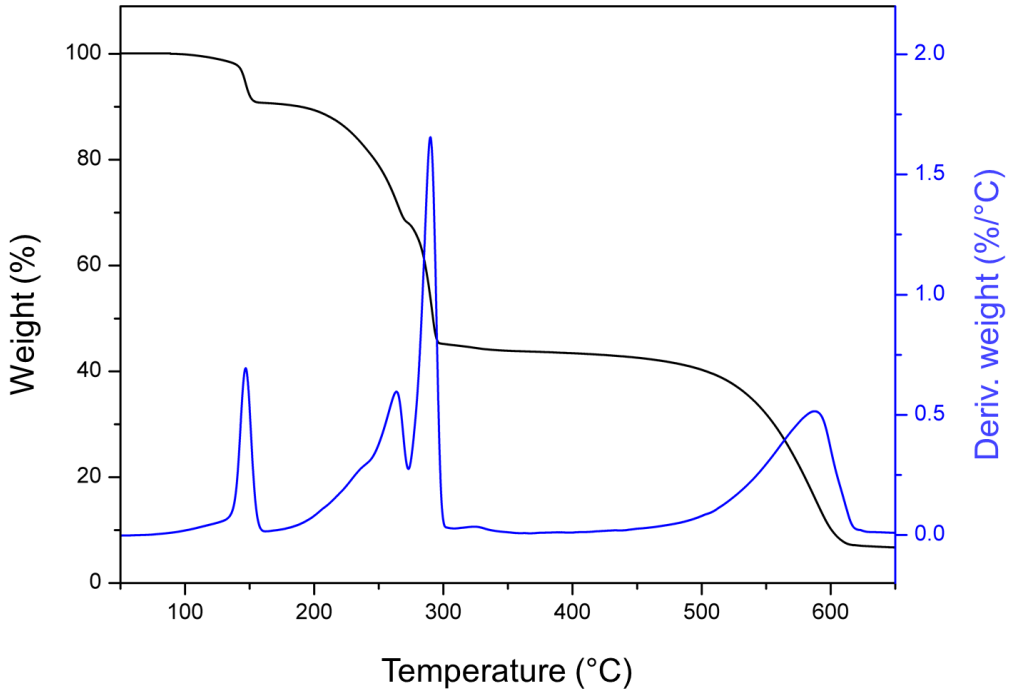

Figure S50. TGA and DTG curves of **6**·MeOH in N_2 atmosphere with a heating rate of 5 °C min^{-1}.

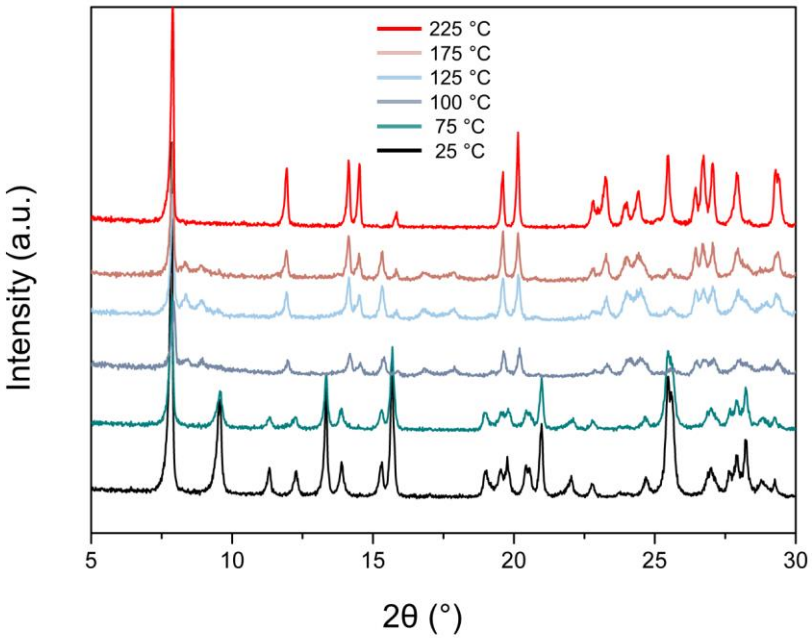

Figure S51 XRD patterns of the products obtained after heating **6**·DMF at different temperatures for1 h.

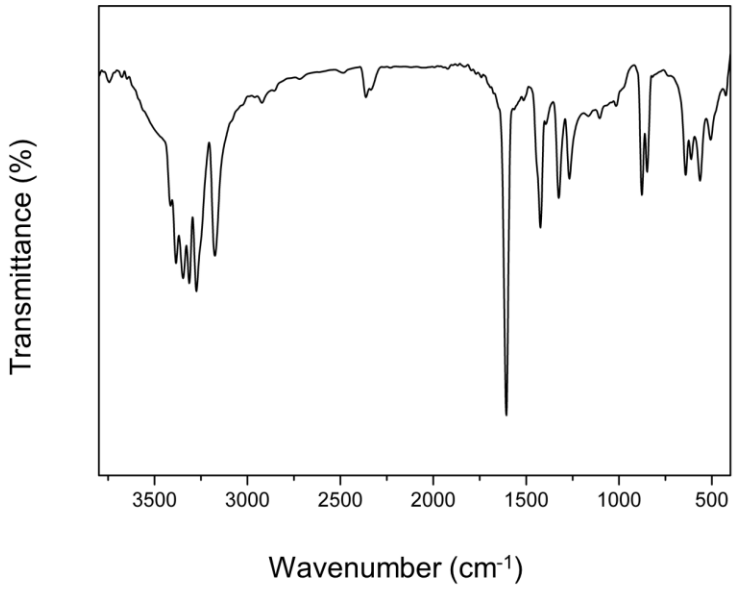

Figure S52. FT-IR spectrum of the product obtained after heating **6**·DMF at 225 °C.

Table S70. CHNS Elemental analysis of the product obtained after heating **6**·DMF at 225 °C and theoretical values for a Cu_2I_2(DTBA) composition

	C (%)	H (%)	N (%)	S (%)

6·DMF (225 °C)	16,04	1,61	4,82	10,82
Cu_2I_2(DTBA) (calcd.)	16,65	1,40	4,85	11,11

S5. Luminescent Properties

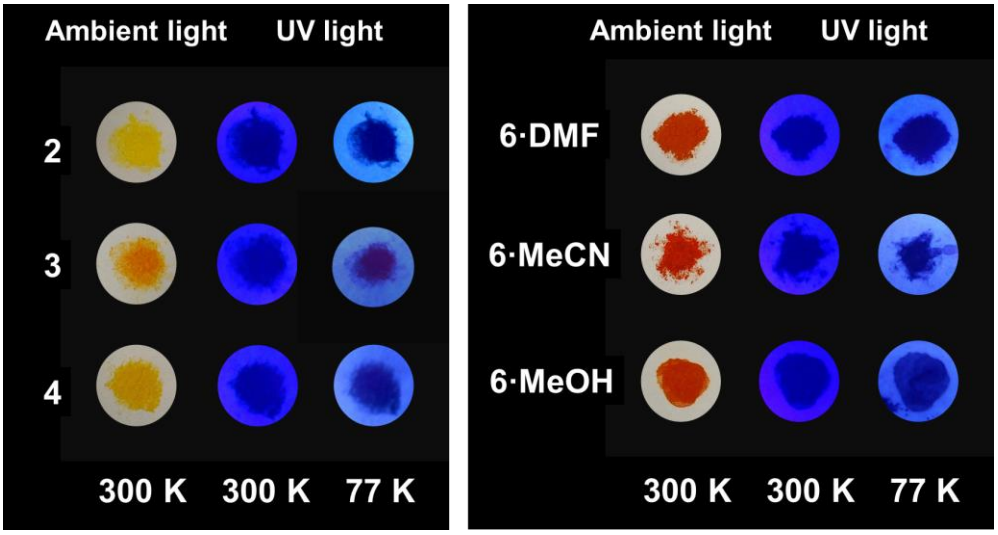

Figure S53. Photos of solid samples of **2**, **3**, **4**, and **6**·S (S= DMF, MeCN, MeOH) under ambient light and under UV lamp irradiation at 356 nm at room temperature (300 K) and in liquid nitrogen (77 K).

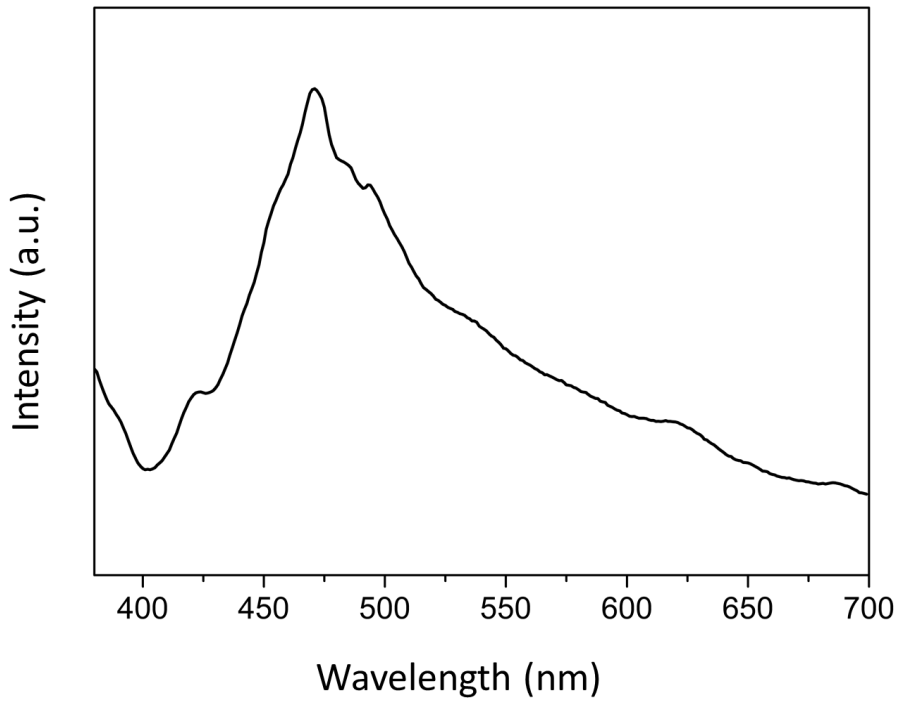

Figure S54. Emission spectra of TBA ligand in the solid state at room temperature (λ_{exc}= 359 nm).

S6. Electrical Conductivity

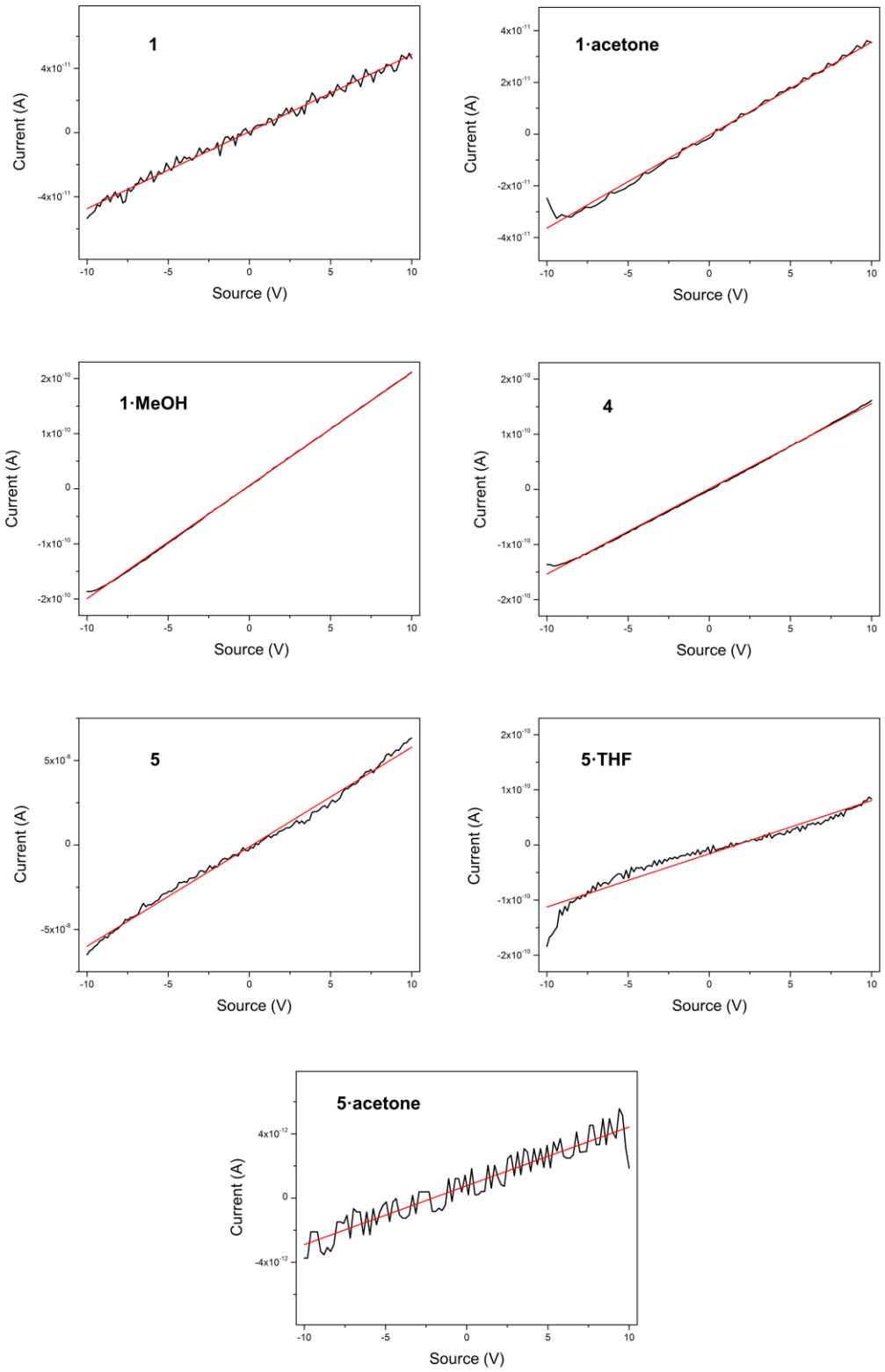

Figure S55. Intensity versus voltage (black) and linear fit (red) corresponding to compounds **1**, **1**·S (acetone, MeOH), **4**, **5** and **5**·S (THF, acetone) obtained using two contact method, with graphite paint at 300 K.

S7. Computational Analysis

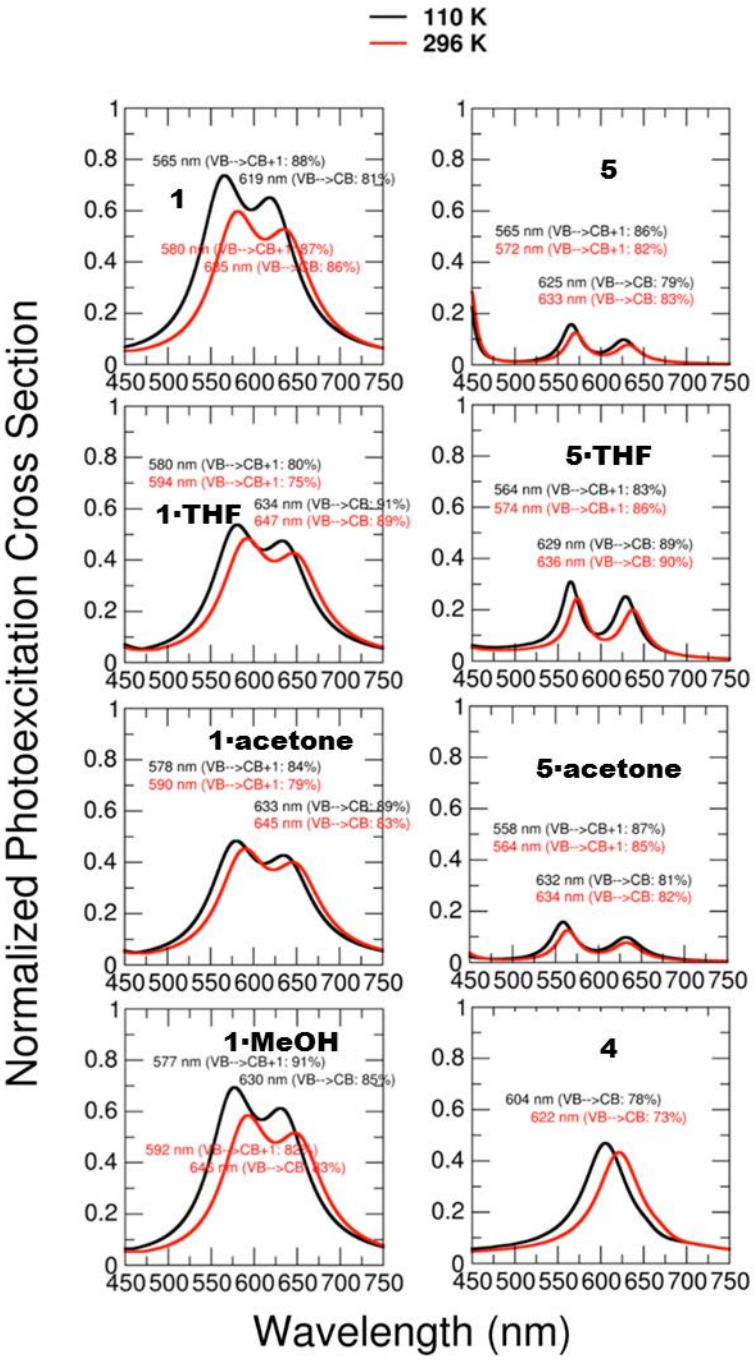

Figure S56. Computed TDDFT photoexcitation spectra for the different compounds as a function of the photon wavelength (in nm) for all the structures resolved at two different temperatures for each compound at standard pressure. Normalized ordinate-scale is the same in all the panels for a better comparison. Wavelengths of the most important peaks, as well as the

most important contributing transition and its weight percent (obtained by the CIS method), are indicated in each panel.

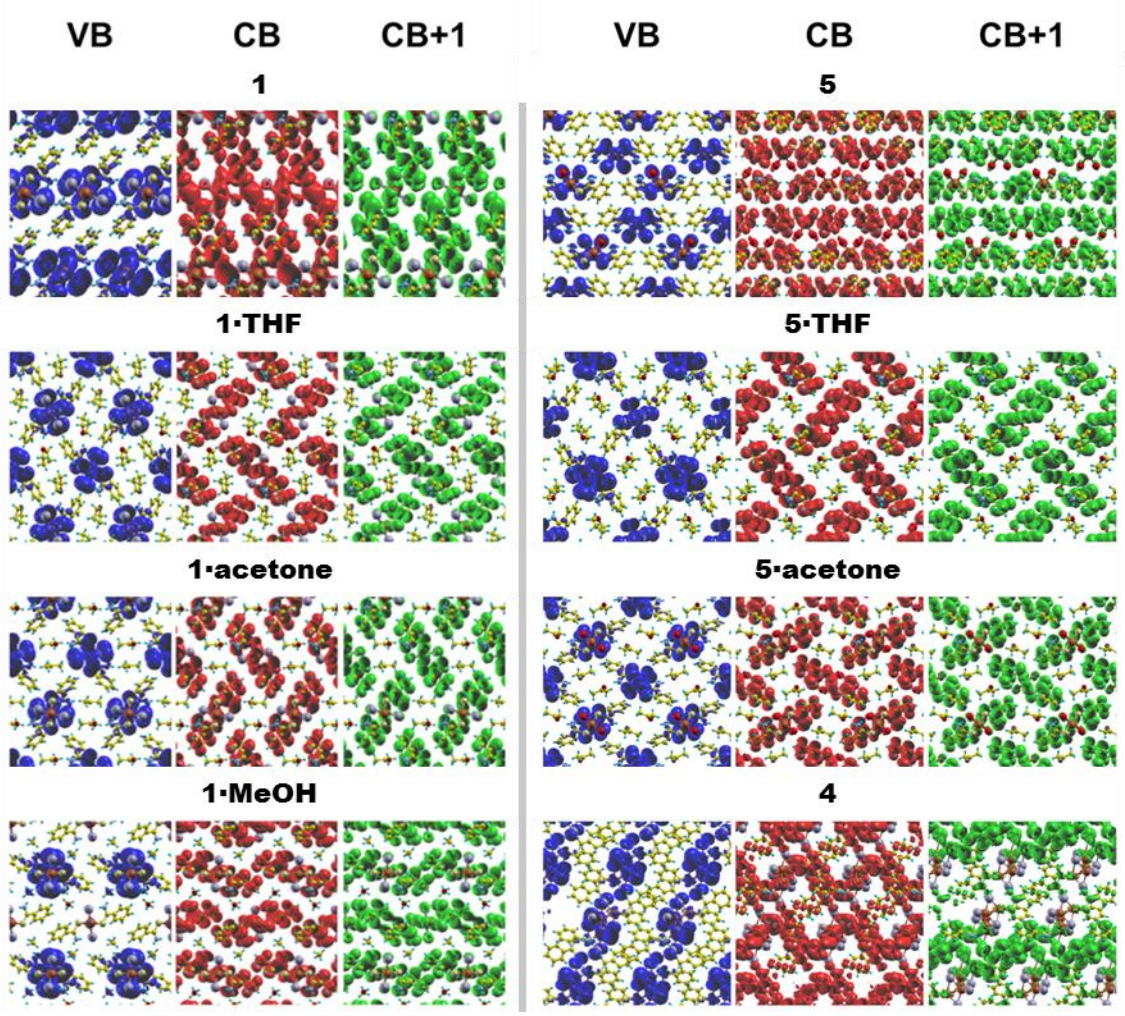

Figure S57. 3D orbital isodensities for all the compounds analysed in the present study corresponding to the VB (blue), CB (red) and CB+1 (green), all with an isodensity value of 10^{-4} a.u. For all cases, VB mostly locates at the metallic chains, whilst the CB and CB+1 are spatially located fundamentally in the organic ligands.