

Copper(II) Acetate/Bis(4-pyridylthio)methane System: Synthesis, Structural Diversity and Single-Crystal to Single-Crystal Transformation.

Ana Belén Lago, Rosa Carballo, Sabina Rodríguez-Hermida, Ezequiel M. Vázquez-López.

^a Departamento de Química Inorgánica, Facultade de Química, Universidade de Vigo, E-36310 Vigo, Galicia, Spain.

*Corresponding authors: A. B. Lago, e-mail: ablago@uvigo.es and R. Carballo, e-mail: rcrial@uvigo.es

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Table S1. Synthetic conditions of compounds **1-4**:

Compound	Synthesis.	Molar ratio M:L	Solvent	Yield. (%)
1 [Cu ₂ (AcO) ₄ (SCS)]	R(3h)	1:1	MeOH	75
	Diff	2:1	H ₂ O/EtOH	
2 [Cu ₂ (AcO) ₄ (SCS)].solv	mw	1:1	DMF/EtOH 2:1	30
3 [Cu ₄ (AcO) ₈ (SCS) ₅ (H ₂ O) ₄].4H ₂ O	Hydrot.	1:1	H ₂ O	23
	Diff.	2:1	H ₂ O/EtOH	
4 [Cu ₄ (OH) ₂ (AcO) ₆ (SCS) ₂].10H ₂ O	Diff.	2:1	H ₂ O/CH ₃ CN	10

Table S2. Diffusion conditions of **1, 3** and **4**:

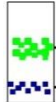
Compound	Salt	Solvent	Molar ratio	Solvent (ligand)	Scheme
1	Cu(AcO) ₂ .H ₂ O	H ₂ O	2:1	EtOH	Green: 1 (top) Blue: 3 (bottom) 
3	Cu(AcO) ₂ .H ₂ O	H ₂ O	2:1	EtOH	
4	Cu(AcO) ₂ .H ₂ O	H ₂ O	2:1	CH ₃ CN	

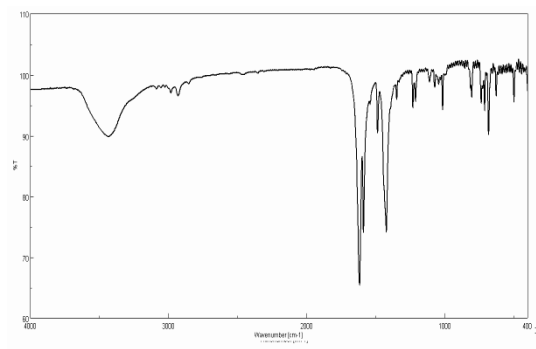
Table S3. Symmetric and Antisymmetric Stretches in the Acetate Ion for compounds **1-4**:

Compound	Coordination mode	$\nu_{\text{asym}}(\text{OCO})$	$\nu_{\text{sym}}(\text{OCO})$	$\Delta a\text{-s exp (cm}^{-1}\text{)}$
1	bridging	1616s	1422s	194
2 dmf	bridging	1680m ^b , 1625s	1430s	195
2.desol.	bridging	1618s	1422s	196
3	unidentate	1596s	1390m	206
4	unidentate bidentate bridging	1585s	1403s 1410sh	182 175

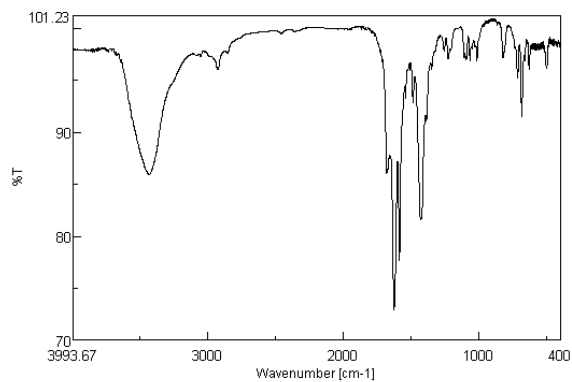
Table S4. Significant IR bands for the ligand and compounds **1-4** in the range 2000-400 cm^{-1}

Comp .	$\nu(\text{OH})$	$\nu(\text{CC}) + \nu(\text{CN})$	$\omega(\text{CH}, \text{CH}_2)$	$\nu(\text{CH}) + \delta(\text{C-H})$	$\gamma(\text{C-H})$	$\nu(\text{CS})$	$\delta(\text{C-H})$
1	-	1588m, 1486m	1211m	1072m	804m	736m	498m
2	3437m	1586m, 1486m	1225m	1065m	821m	712m	502m
2.desol.	3437m	1588m, 1485m	1230m	1070m	805m	707m	498m
3	3421br	1596s, 1486m	1226m	1066m	807m	733m	501m
4	3429m	1585s, 1482m	1216m	1067m	805m	730m	506m

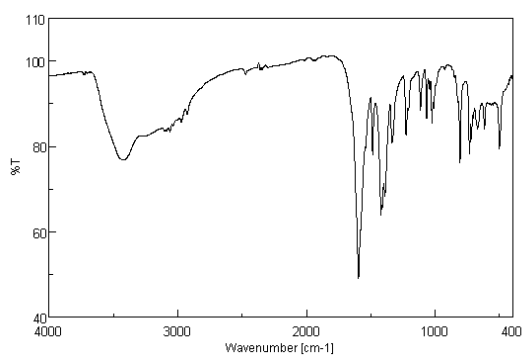
Figure S1. IR spectra of the compounds **1-4** in the range 2000-400 cm^{-1}



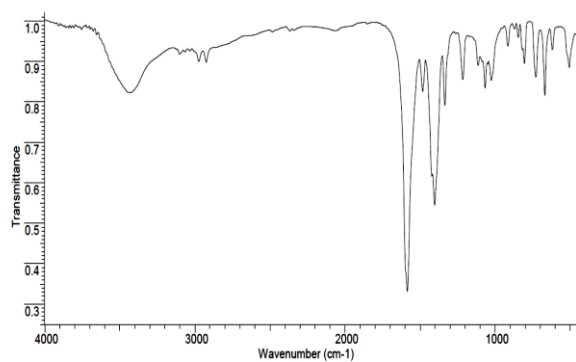
A) Spectra of **1**



B) Spectra of **2**

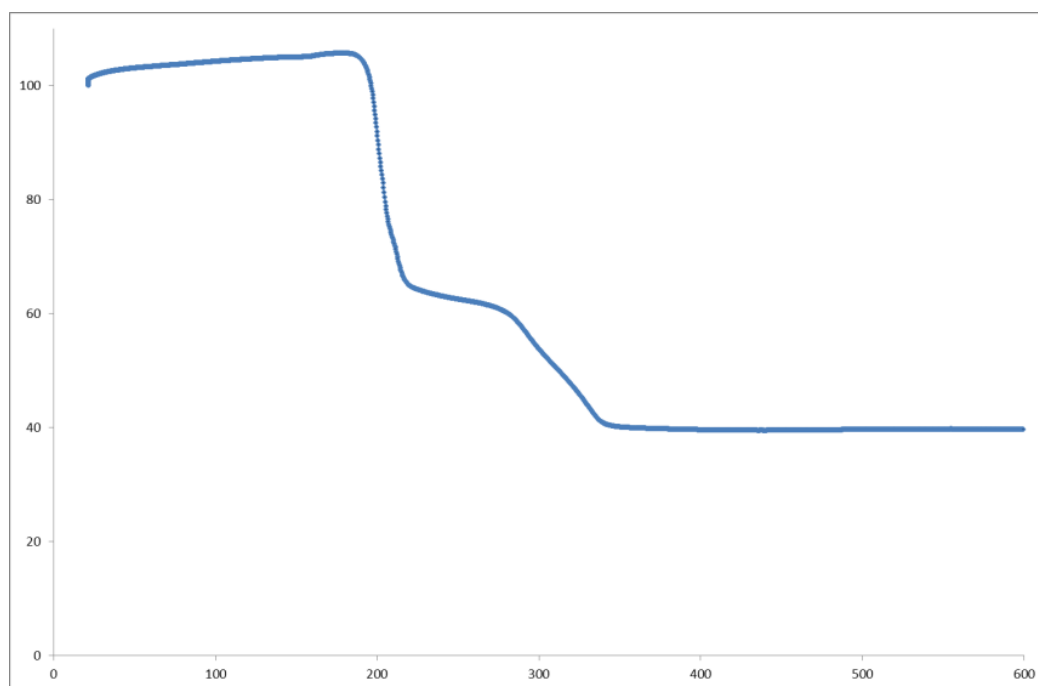


C) Spectra of **3**

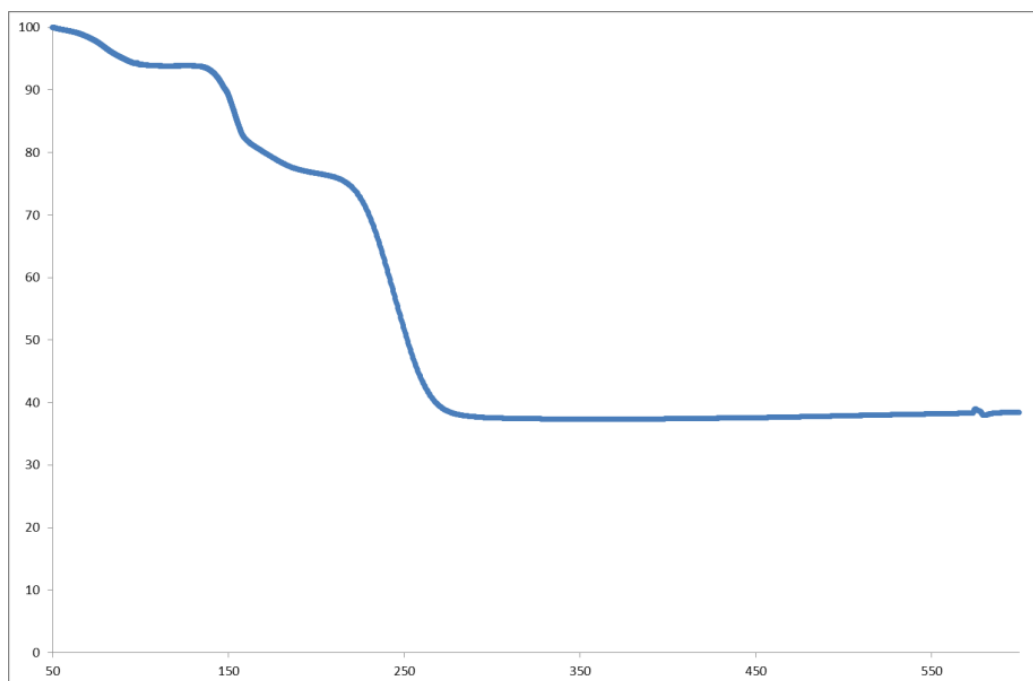


D) Spectra of **4**

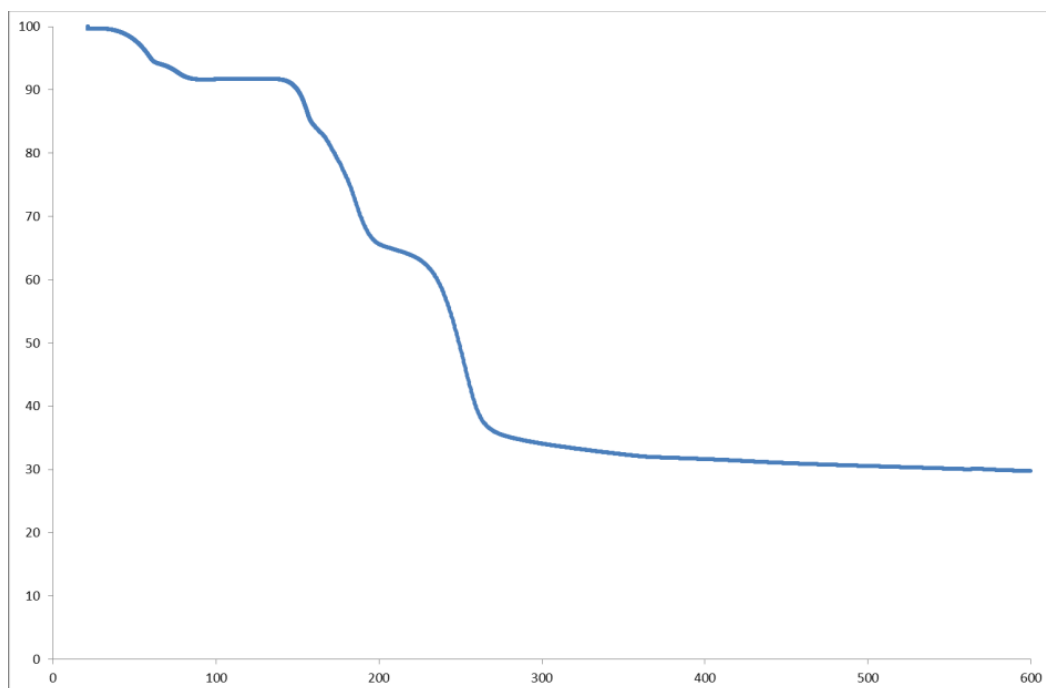
Figure S2. Thermogravimetric analysis (TGA) of **1-4** carried out between 25 and 600°C



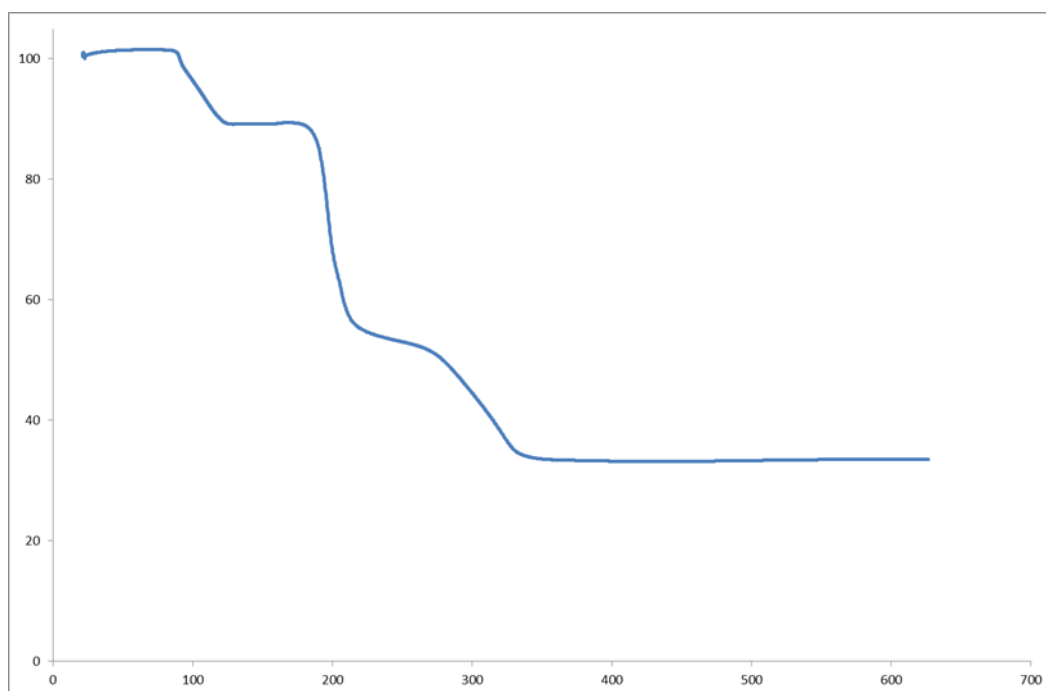
A) Compound **1**



B) Compound **2**



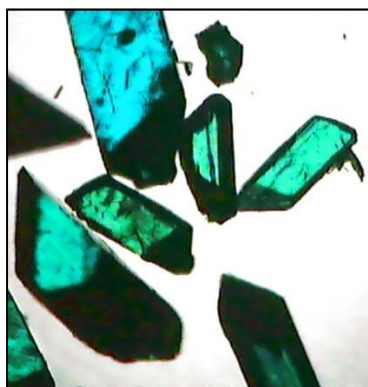
C) Compound **3**



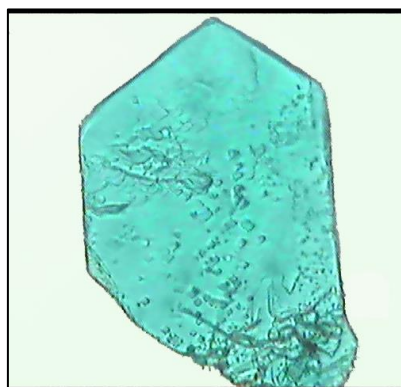
D) Compound **4**

Study of structural transformation in 2

Figure S3. At first glance, it is possible to distinguish both compounds by the shape of the crystals, green rectangular prism in **1** and green thin sheets in **2**:



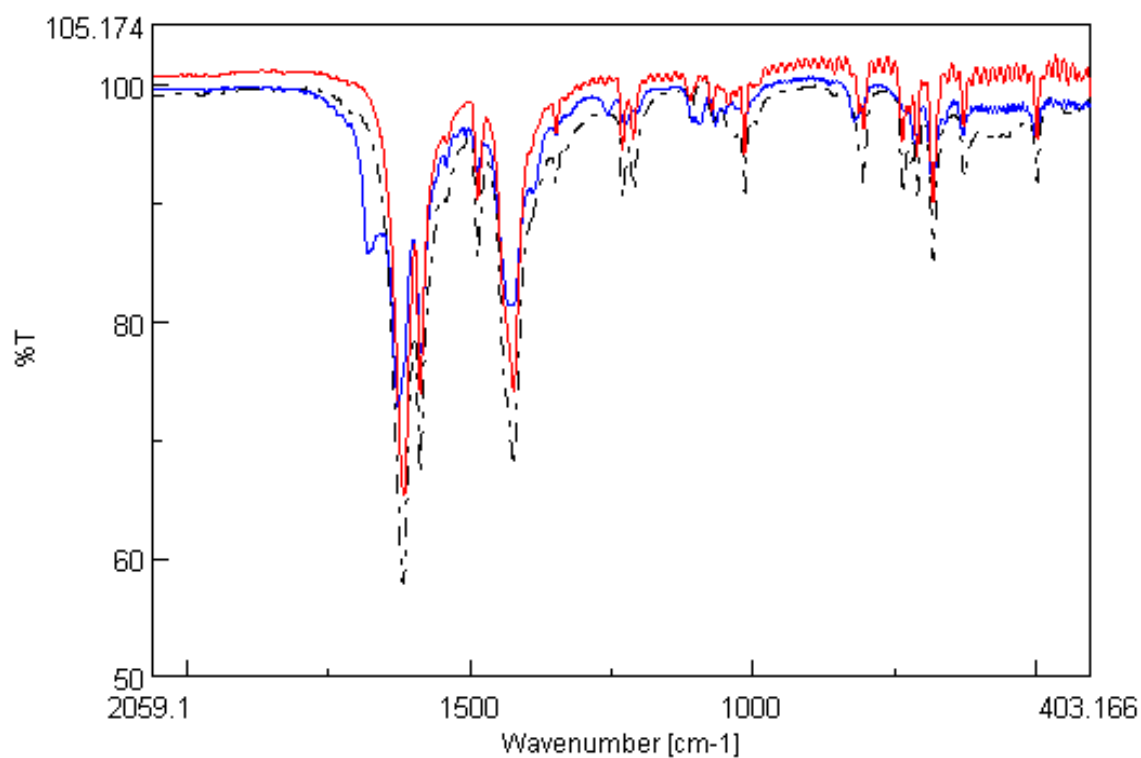
A) compound 1



B) Compound 2

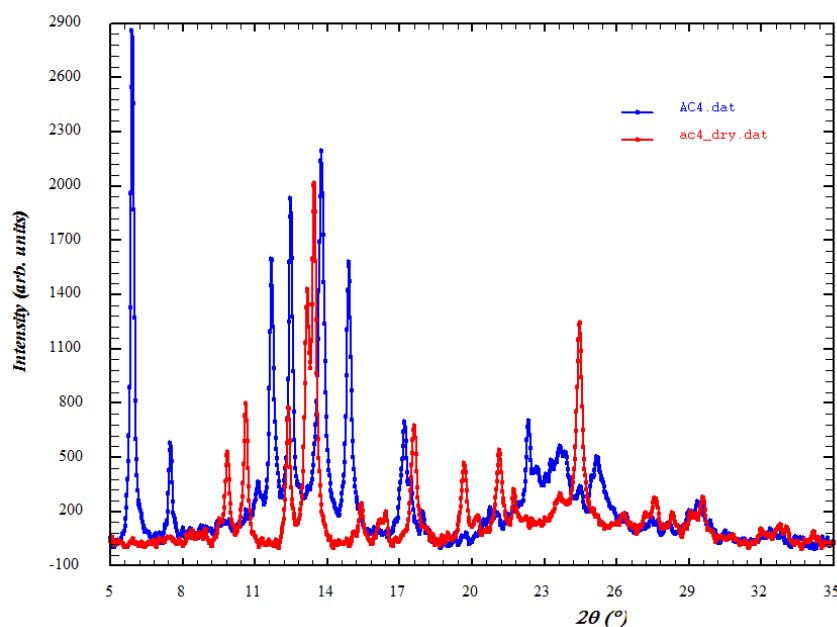
A suspension of **2** was soaked in dichloromethane for 2 hours, over the course of which the solvent was replaced and then heating at 80°C for 24 hours. The resulting solid was characterized as anhydrous compound by X-ray powder diffraction (XRPD) and IR. The IR spectra do not show the characteristic bands of dmf molecules. Structural transformation was confirmed by Powder X-ray diffraction.

Figure S4. IR spectra of **1**, **2** and **2.desolvated** in the range 2000-400 cm^{-1}



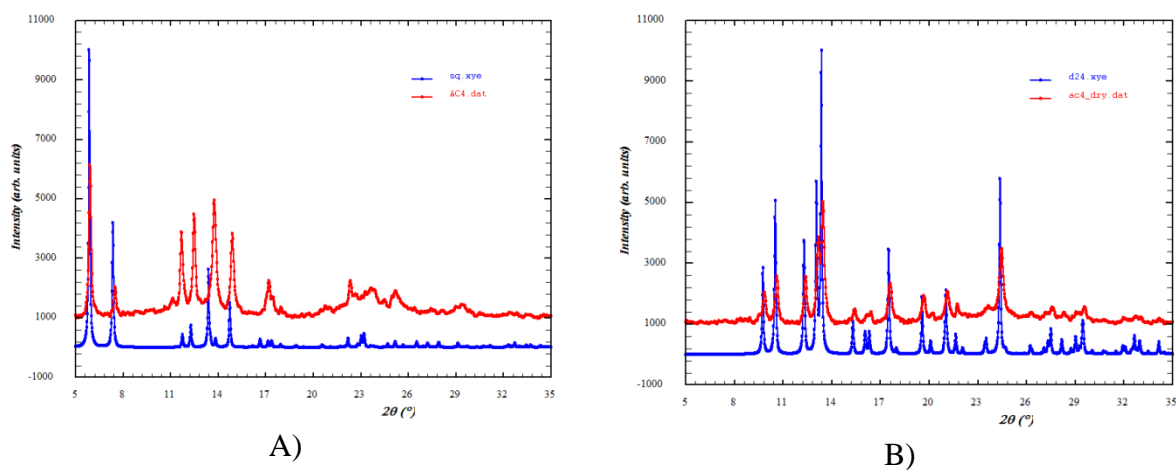
Red: compound **1**; blue: compound **2**, black dash line: **2.desolvated**.

Figure S5. Experimental powder X-ray diffractograms for **2** before and after the treatment to remove the crystallization solvents.



Powder X-ray diffractograms of as-synthesized compound **2** (blue) and **2.desolvated** (red).

Figure S6. Experimental powder X-ray diffractograms for **2** and **2.desolvated** and simulated PXRD from crystal structures **1** and **2**.



A) Calculated from single crystal data of **2** (blue) and as-synthesized **2**(red). **B)** Calculated from single crystal data of **1** (blue) and **2.desolvated** after the treatment to remove the crystallization solvents (red).

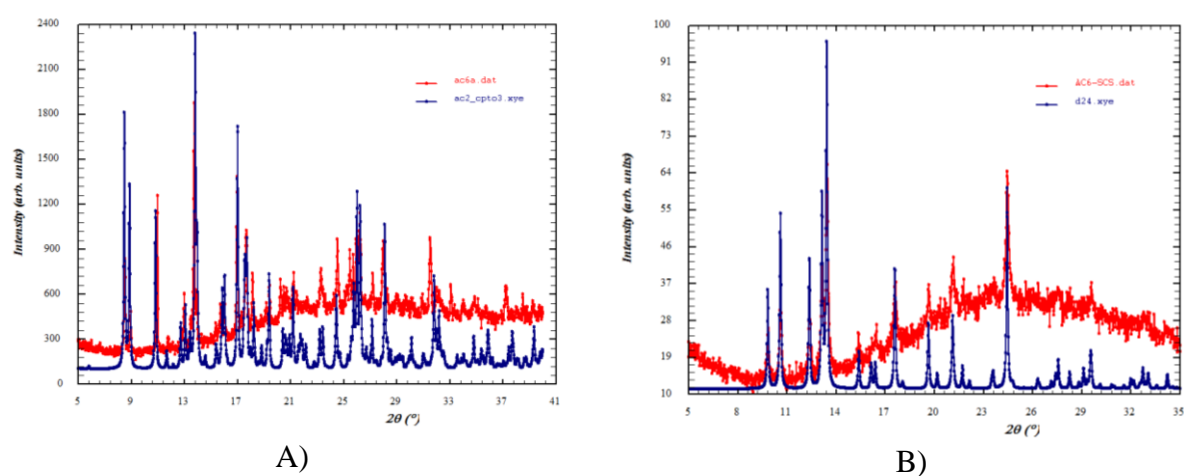
Table S5. Single crystal data before and after the phase transition in different examples:

Reference	Seki, T.; Sakurada, K.; Ito., H. <i>Angew. Chem. Int. Ed.</i> 2013 , 52, 12828	
Stimulus	Mechanical picking or solid seeding	
Crystal	INITIAL	TRANSFORMED
Empirical Formula	C ₁₅ H ₁₄ AuN	C ₁₅ H ₁₄ AuN
Formula Weight	405.25	405.25
Crystal System	monoclinic	orthorhombic
Space group	<i>P21/n</i>	<i>Ima2</i>
<i>a</i> /Å	12.813(2)	7.172(2)
<i>b</i> /Å	32.566(6)	20.048(6)
<i>c</i> /Å	19.876(4)	8.940(3)
α /°	90.0000	90.0000
β /°	97.110(4)	90.0000
γ /°	90.0000	90.0000
<i>V</i> /Å ³	8330(3)	1285.3(7)
Reference	Girad, J.; Fromm, K. <i>CrystEngComm</i> , 2012 , 14, 6487	
Stimulus	Change temperature from 273K to 200K	
Crystal	INITIAL	TRANSFORMED
Empirical Formula	C ₈ H ₁₆ Ag ₂ N ₂ O ₁₀	C ₃₂ H ₆₄ Ag ₈ N ₈ O ₄₀
Formula Weight	515.97	2063.87
Crystal System	orthorhombic	monoclinic
Space group	<i>lbca</i>	<i>P21/c</i>
<i>a</i> /Å	13.4204(6)	16.3286(8)
<i>b</i> /Å	16.5076(7)	13.4452(5)
<i>c</i> /Å	28.1263(13)	28.0645(14)
α /°	90.0000	90.0000
β /°	90.0000	90.0000
γ /°	90.0000	90.0000
<i>V</i> /Å ³	6231.1(5)	6160.7(5)
Reference	Skoko, Z.; Zamir, S.; Naumov. P.; Bernstein. J. <i>J. Am. Chem. Soc.</i> 2010 , 132, 14191	
Stimulus	Heating	UV irradiation
Crystal	INITIAL	TRANSFORMED
Crystal System	orthorhombic	orthorhombic
Space group	<i>P2₁2₁2₁</i>	<i>P2₁2₁2₁</i>
<i>a</i> /Å	7.3927(2)	7.453(3)
<i>b</i> /Å	10.1512(4)	11.220(4)
<i>c</i> /Å	24.6291(9)	22.790(7)
<i>V</i> /Å ³	1848.29(11)	1905.8(11)
Reference	Liu, G.; Liu, J.; Liu, Y.; Tao, X. <i>J. Am. Chem. Soc.</i> 2014 , 136, 590	
Stimulus	Mechanical	
Crystal	INITIAL	TRANSFORMED
Crystal System	triclinic	triclinic
Space group	<i>P-1</i>	<i>P-1</i>
<i>a</i> /Å	8.0350(5)	7.127(5)
<i>b</i> /Å	8.2606(6)	7.543(5)
<i>c</i> /Å	9.7665(7)	12.014(5)
α /°	77.260(1)	83.495(5)
β /°	73.554(1)	88.783(5)
γ /°	78.132(1)	67.724(5)
<i>V</i> /Å ³	599.26(7)	593.6(6)

Study of structural transformation in **3**

Blue single crystals of **3** were stirred in ethanol for one day and were slightly heated until the total solution. The green solution formed was concentrate and the resulting green powder was washed with acetone and vacuum dried. In order to study the structural stability X-ray powder diffraction (XRPD) was collected before (**3**) and after (**3.T**) the treatment.

Figure S7. Experimental powder X-ray diffractograms for **3** and **3.T** and simulated PXRD from crystal structures **3** and **1**.



A) Calculated from single crystal data of **3** (blue) and as-synthesized **3**(red). **B)** Calculated from single crystal data of **1** (blue) and **3.T** after the treatment to change the structure (red).