Structural Diversity in Zn(II)/Cu(II) Complexes with salicylic/acetylsalicylic acids and Bis(4-pyridylthio)methane: Coordination Polymers, one organic Cocrystal, and one organic Salt

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Supplementary material

Table S1. Reported crystal structures of Zn/Cu salicylate coordination polymers with N,N'-divergent ligands (CSD Search[1]).

Compound	**D**	**Coordination mode**	**NC(M)/geometry**	**Synthesis**	**Ref**
$Zn(bpp)(Hsal)_2$	1D	Monodentate (Hsal)	4/tetrahedral	Hasp/solvothermal	2
$[\{Zn(Hsal)_2\}_2(bpe)]_2$	0D	Monodentate (Hsal)	4/tetrahedral	Hasp/solvothermal	2
$Zn(Hsal)_2(bbmi)$	1D	Carboxylate chelate (Hsal)	6/octahedral	H_2sal/solvothermal	3
$[Cu_2(Hsal)_4(4,4'\text{-bipy})(H_2O)_2(DMF)_2]$	0D	Monodentate (Hsal)	5/square pyramidal	H_2sal/diffusion	4
$Cu(Hsal)_2(4,4'\text{-bipy})\bullet H_2O\bullet H_2sal$	2D	Bis-monodentate bridging (Hsal)	5/square pyramidal	H_2sal/diffusion	4
$(Hsal)_2(4,4'\text{-bipy})\bullet DMF$	1D	Carboxylate chelate (Hsal) Bis-monodentate bridging (Hsal)	6/octahedral	H_2sal/diffusion	5
$Cu(Hsal)_2\text{-}(4,4'\text{-bipy})\bullet 2H_2O$	1D	Carboxylate chelate (Hsal)	6/octahedral	H_2sal/diffusion	5
$Cu_2(Hsal)_4(4,4'\text{-bipy})$	1D	Bis-monodentate bridging (Hsal)	6/octahedral	H_2sal/diffusion	5
$Cu(Hptz)_2(Hsal)_2$	2D	Monodentate (Hsal)	6/octahedral	H_2sal/hydrothermal	6

D= dimensionality; bpp=1,3-bis(4-pyridyl)propane; bpe= 1,2-bis(4-pyridyl)ethane; bbmi= 1,10-(1,4-butanediyl)bis(2-methylbenzimidazole); 4,4'-bipy= 4,4'-bipyridine; Hptz= 5-(4-pyridyl)-1H-tetrazole.

1- CCDC (2017). CSD web interface – intuitive, cross-platform, web-based access to CSD data. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, UK.

2- S. Chooset, A. Kantacha, K. Chainok, S. Wongnawa. Synthesis, crystal structure, luminescent properties and antibacterial activities of zinc complexes with bipyridyl and salicylate ligands. Inorg. Chim. Acta 471 (2018), 493-501. DOI: 10.1016/j.ica.2017.11.053.

3- Y-Y. Liu, Y-Y. Jiang, J. Yang, Y-Y. Liu, J-F. Ma. Syntheses, structures and photoluminescence of zinc(II) and silver(I) coordination polymers based on 1,10-(1,4-butanediyl)bis(2 methylbenzimidazole) and different carboxylate ligands. CrystEngComm, 13 (2011), 6118-6129. DOI: 10.1039/c0ce00990c.

4- L-G. Zhu, S. Kitagawa. The dimeric and two-dimensional copper(II) complexes constructed from salicylic acid and 4,4'-bipyridine. Inorg. Chem. Commun. 6 (2003) 1051–1055. DOI: 10.1016/S1387-7003(03)00173-4.

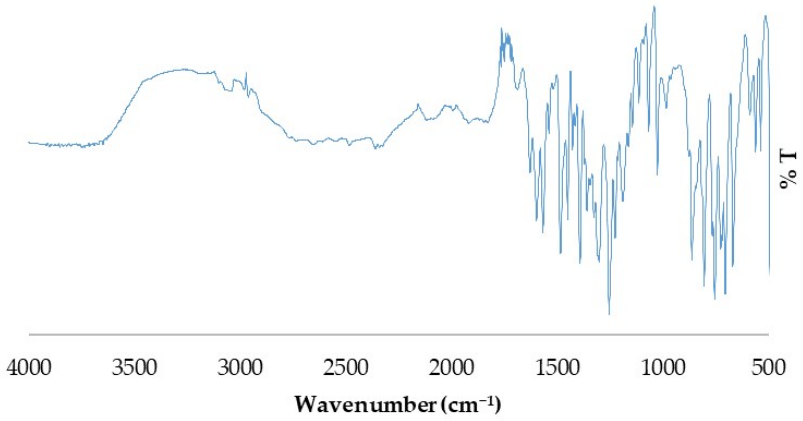
5-L-G. Zhu, S. Kitagawa, H. Miyasaka, H-C. Chang. Syntheses and crystal structures of three one-dimensional copper(II) complexes constructed by salicylate and 4,4'-bipyridine: ladder,

zig-zag, and linear polymeric assembly. Inorg. Chim. Acta 355 (2003) 121-126. DOI: 10.1016/S0020-1693(03)00254-8.

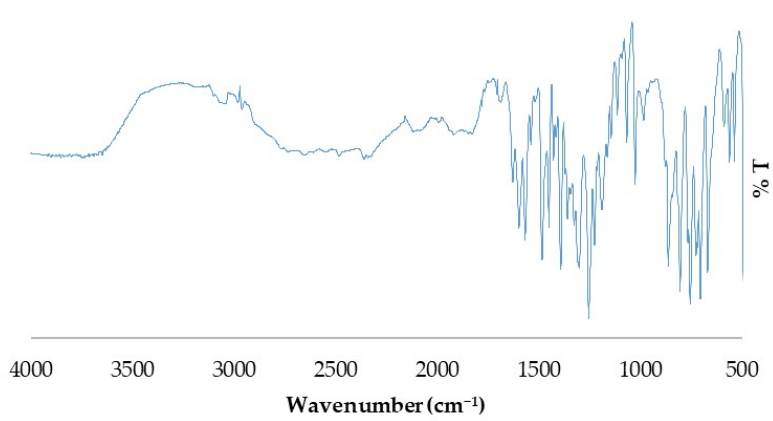
6-S-R. Zheng, X-L. Wen, Z-M. Liu, T. Xie, J-B. Tan, J. Fan, S-S. Hou, and W-G. Zhang. Two Coordination Polymers Constructed from 5-(4-Pyridyl)-1H-tetrazole Ligands with Different Organic Carboxylates: Structure and Luminescence Properties. Z. Anorg. Allg. Chem. 640 (2014), 2057–2061. DOI: 10.1002/zaac.201400093.

1. Characterization

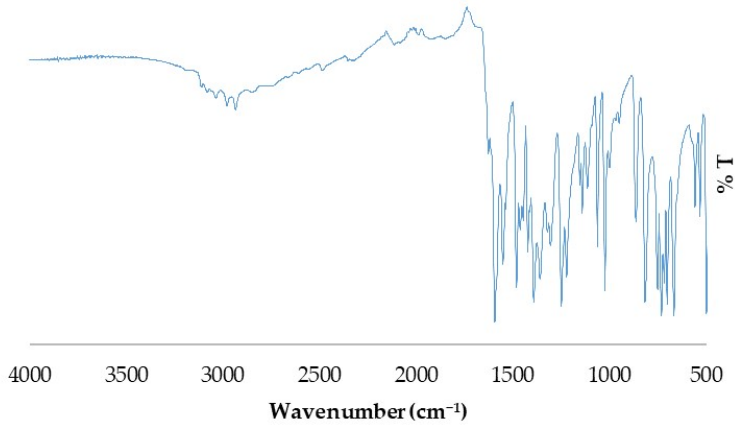
$^{1}_{\infty}Zn(Hsal)_2(SCS)$ **(1m)**



$^{1}_{\infty}Zn(Hsal)_2(SCS)$ **(1m')**



$^{1}_{\infty}Zn(Hsal)_2(SCS)$ **(1o)**



$^{1}_{\infty}Zn(Hsal)_2(SCS)\cdot H_2O$ **(1w)**

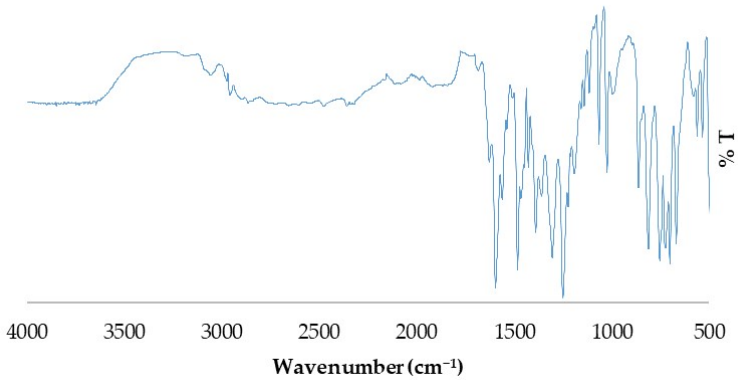


Figure S1: Infrared spectra (IR) of the Zn(II) coordination polymers **1m, 1m', 1o** and **1w**.

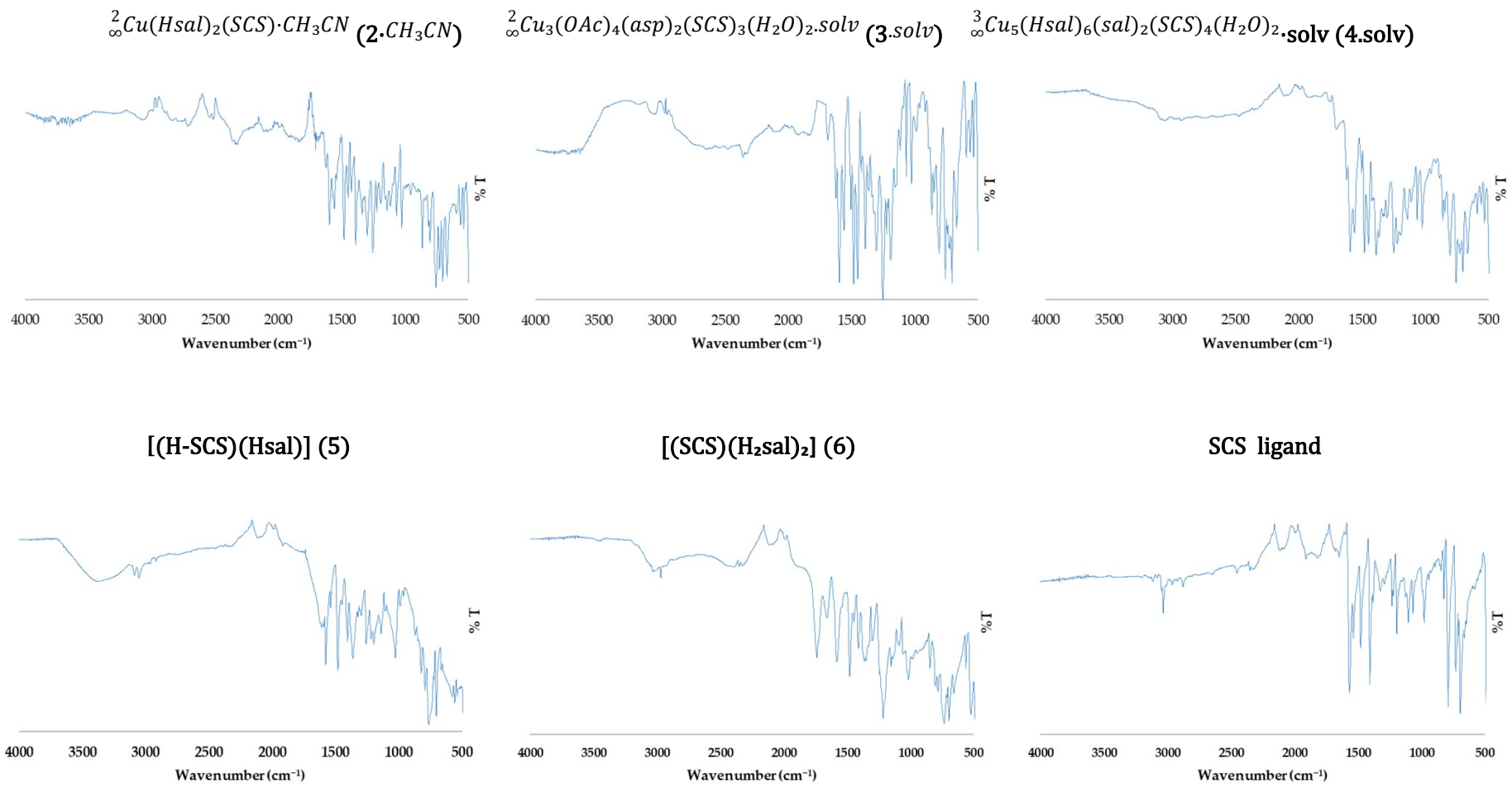
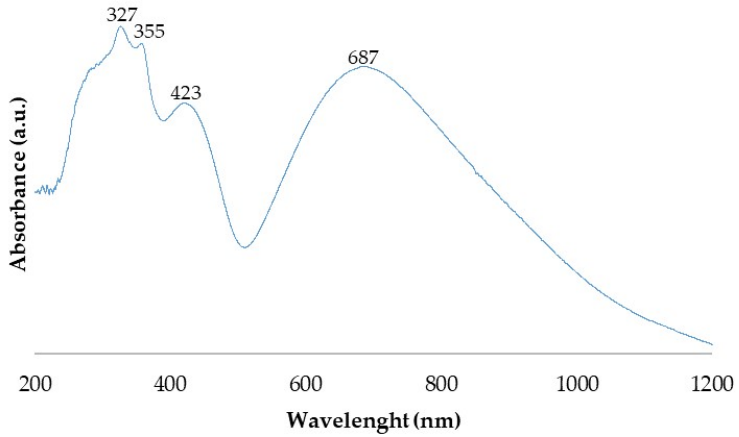
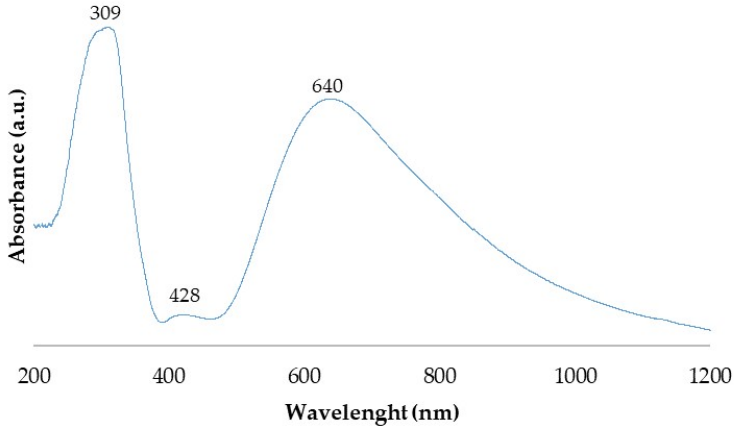


Figure S2: Infrared spectra (IR) of the Cu(II) complexes **2·CH₃CN, 3·solv, 4·solv,** and the salt **5**, the cocrystal **6** and free **SCS ligand**.

$^{2}_{\infty}Cu(Hsal)_2(SCS)\cdot CH_3CN$ (**2**·CH_3CN)

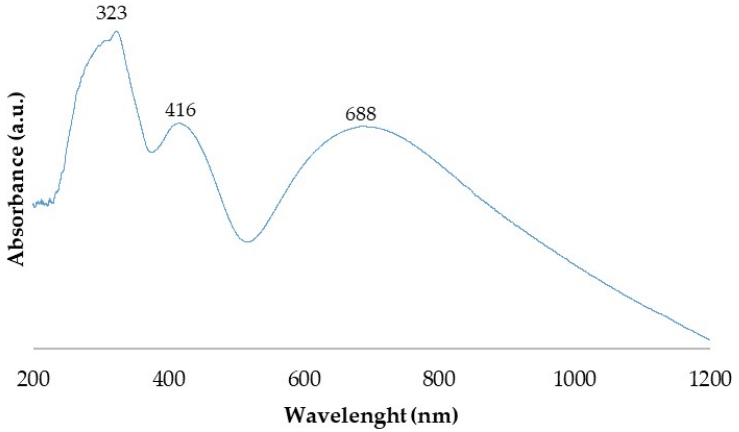


$^{2}_{\infty}Cu_3(OAc)_4(asp)_2(SCS)_3(H_2O)_2\cdot solv$ (**3**·$solv$)



3

$_{\infty}Cu_5(Hsal)_6(sal)_2(SCS)_4(H_2O)_2\cdot solv$ (**4.solv**)



SCS ligand

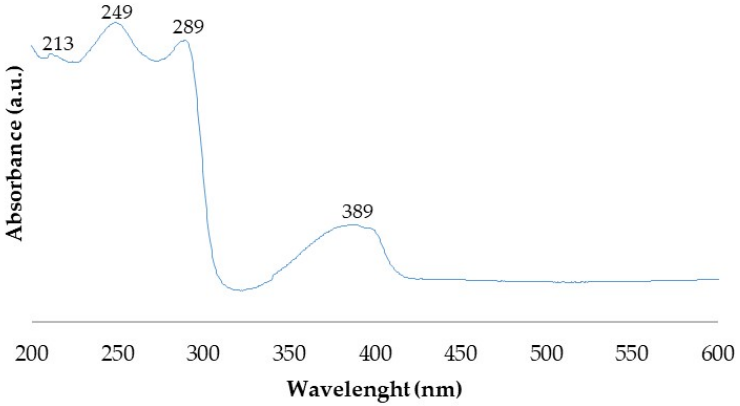


Figure S3: UV-Vis spectra (diffuse reflectance) of the Cu(II) coordination polymers **2-4** and the free **SCS ligand**.

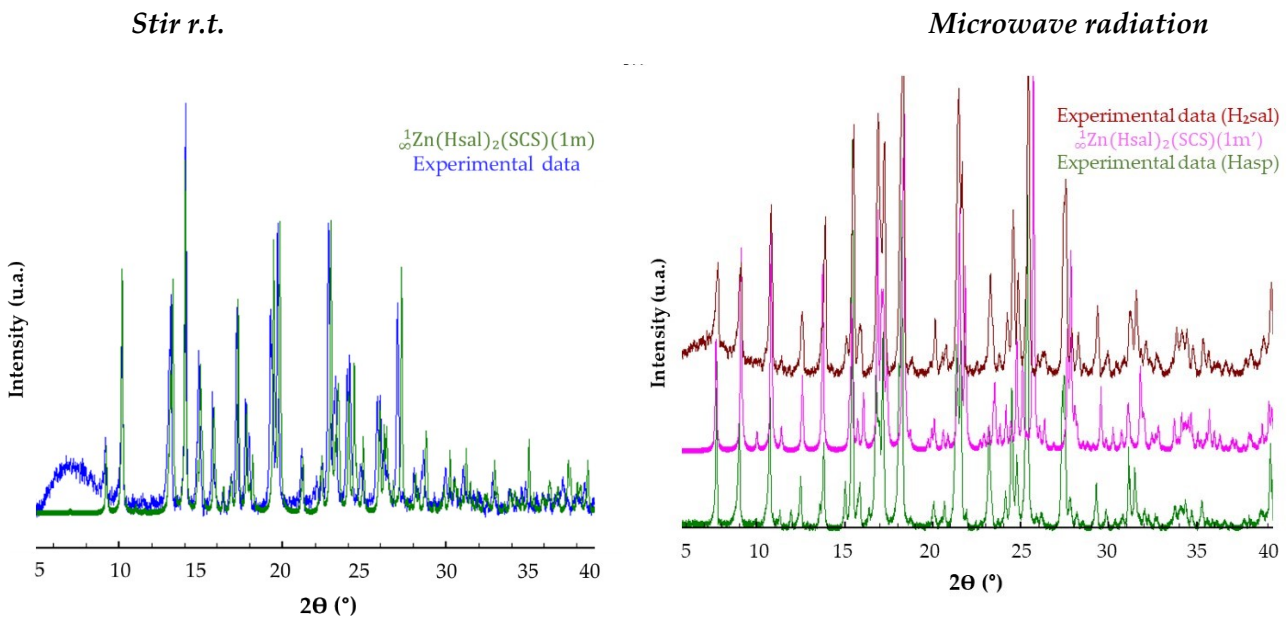


Figure S4: Powder X-ray diffraction (PXRD) comparison between bulk experimental data and simulation based on single crystal X-ray diffraction of **1m** and **1m′**

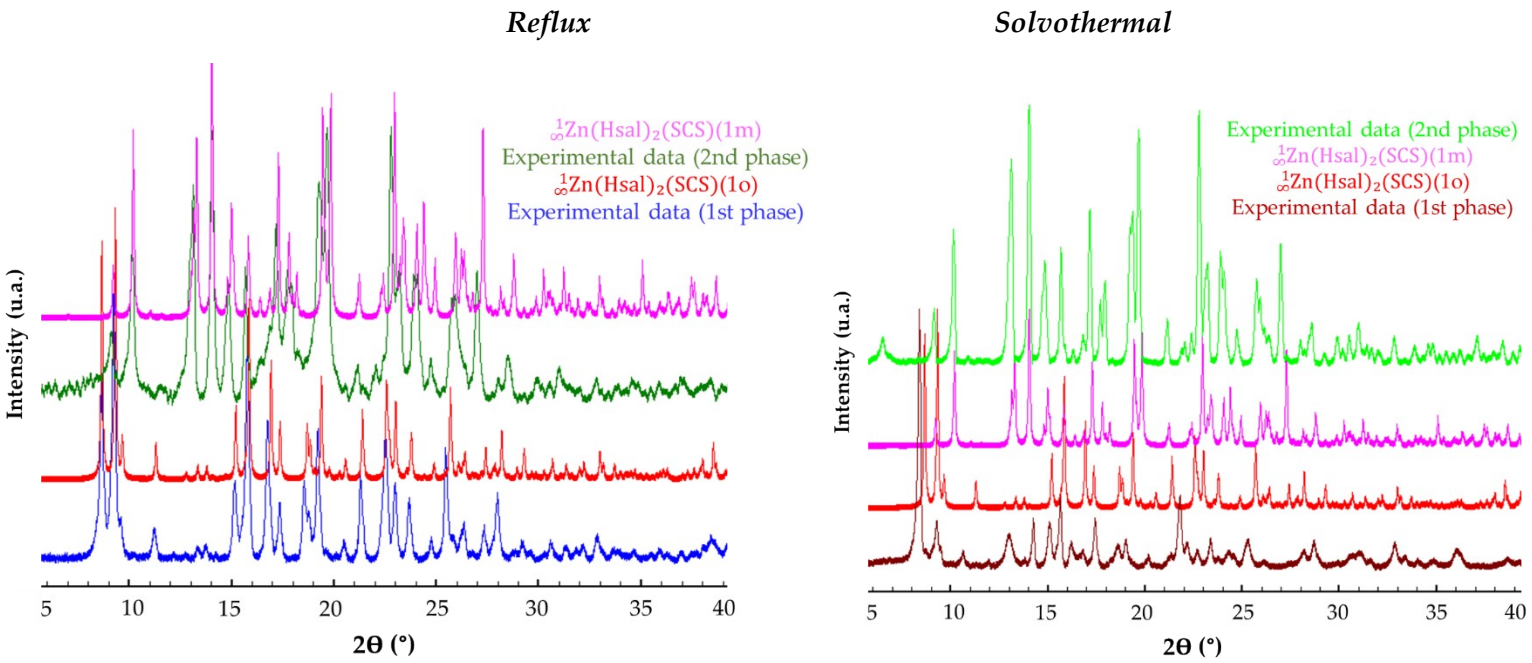


Figure S5: Powder X-ray diffraction (PXRD) comparison between bulk experimental data and simulation based on single crystal X-ray diffraction of **1o.**

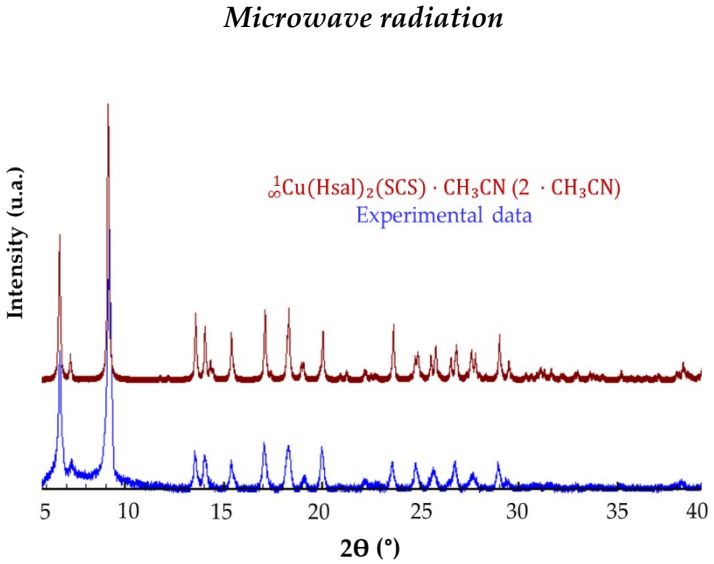


Figure S6: Powder X-ray diffraction (PXRD) comparison between bulk experimental data and simulation based on single crystal X-ray diffraction of **2·CH₃CN.**

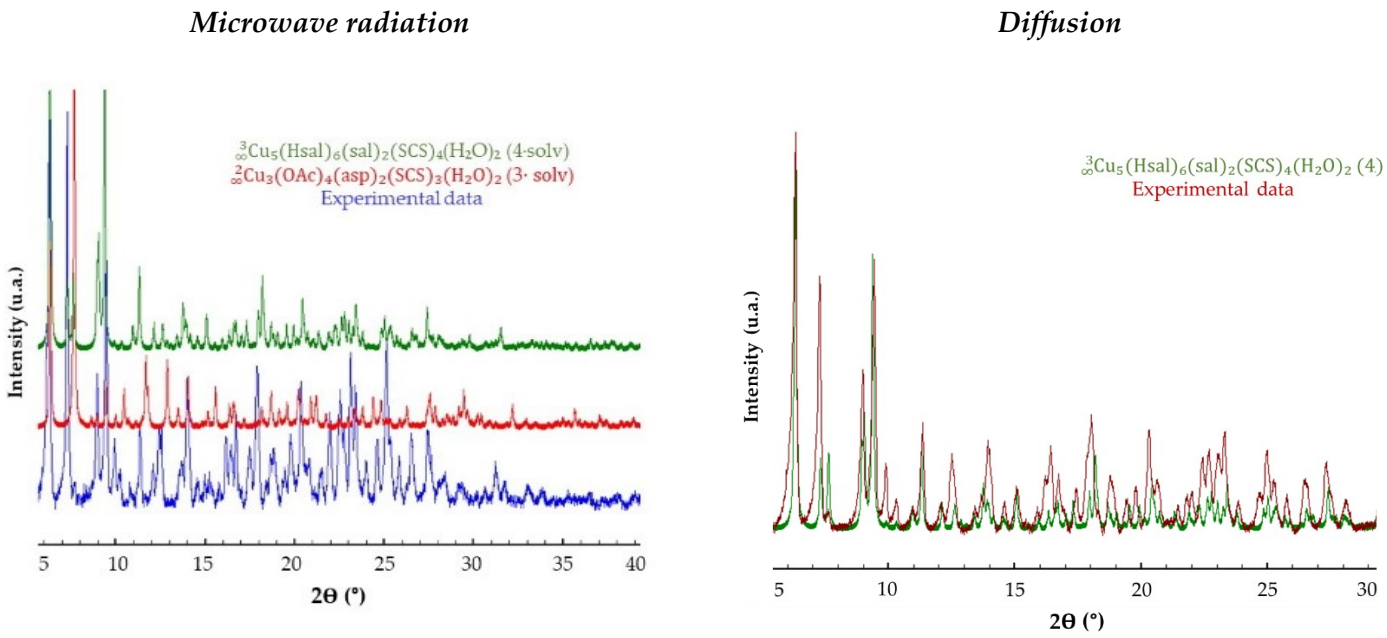


Figure S7: Powder X-ray diffraction (PXRD) comparison between bulk experimental data and simulation based on single crystal X-ray diffraction of **3·solv** and **4·solv.**

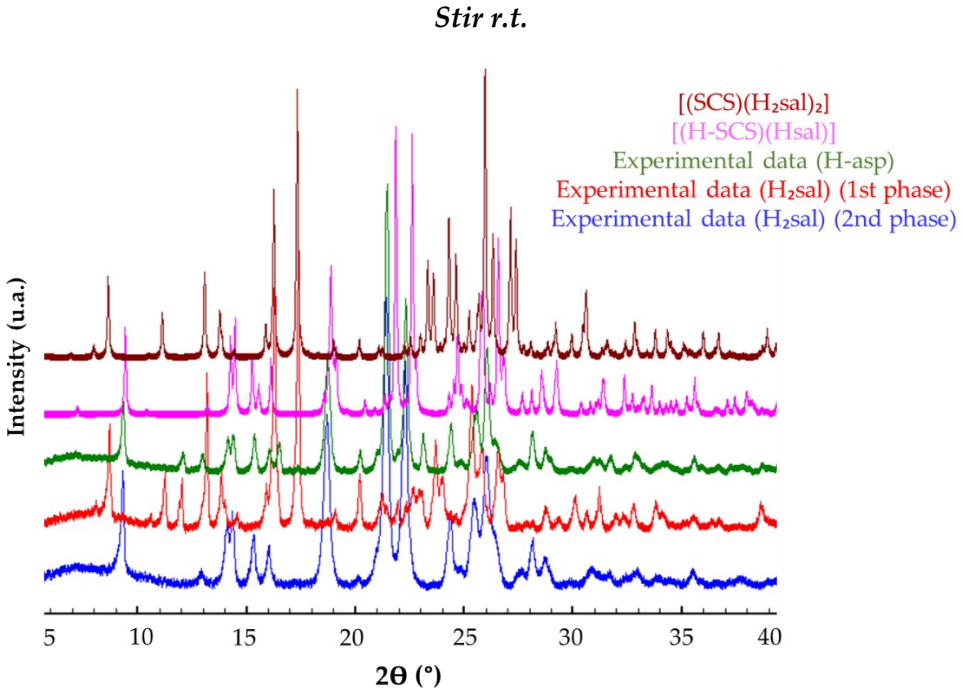


Figure S8: Powder X-ray diffraction (PXRD) comparison between bulk experimental data and simulation based on single crystal X-ray diffraction of **5** and **6.**

2. Crystallography

Table S2: Crystal data and structure refinement

Compound		1m	1m′	1o	1w
Empirical formula		$C_{25}H_{20}N_2O_6S_2Zn$	$C_{25}H_{20}N_2O_6S_2Zn$	$C_{25}H_{20}N_2O_6S_2Zn$	$C_{25}H_{21}N_2O_{6.5}S_2Zn$
Formula weight		573.92	573.92	573.92	582.93
Crystal system, space group		Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/c$
CCDC reference		2487460	2487459	2487457	2487461
Unit cell dimensions	a/Å	12.6079(3)	11.7291(13)	12.1962(4)	19.0306(5)
	b/Å	11.9634(3)	11.6093(12)	13.8436(4)	13.8281(3)
	c/Å	16.0231(4)	17.996(2)	15.1045(5)	20.5871(5)
	α/°	-	-	-	-
	β/°	90.5900(10)	100.984(5)	-	115.5680(10)
	γ/°	-	-	-	-
Volume/A^3		2416.69(10)	2405.5(5)	2550.23(14)	4887.1(2)
Z, ϱ_{calc}/mg·m^{-3}		4/1.577	4/1.585	4/1.495	8/1.585
F(000)		1176	1176	1176	2392
Crystal size (mm^3)		0.281 x 0.273 x 0.213	0.273 x 0.132 x 0.031	0.298 x 0.264 x 0.251	0.255 x 0.167 x 0.106
Abs. coeff. (mm^{-1})		1.234	1.240	1.170	1.224
θ Range (°)		2.542-28.303	2.600-28.321	2.602-28.275	1.891-28.299
Max./min. transmission		0.7457/0.6022	0.7457/0.6427	0.7457/0.5497	0.7457/0.6751
Reflections collected		40213	47524	26179	96639
Independent reflections (R_{int})		5997 (0.0308)	5966 (0.0409)	6322 (0.0272)	12133 (0.0431)
Final R indices [I>2σ(I)]		R1 = 0.0230, wR2 = 0.0565	R1 = 0.0295, wR2 = 0.0693	R1 = 0.0198, wR2 = 0.0452	R1 = 0.0289, wR2 = 0.0691

Table S3*:* Crystal data and structure refinement

Compound		2·CH_3CN	3·solv	4·solv	5	6
Empirical formula		$C_{27}H_{23}CuN_3O_6S_2$	$C_{43}H_{51}Cu_2N_7O_{13}S_4$	$C_{100}H_{82}Cu_5N_8O_{26}S_8$	$C_{18}H_{16}N_2O_3S_2$	$C_{25}H_{22}N_2O_6S_2$
Formula weight		613.14	1129.22	2385.91	372.45	510.56
Crystal system, space group		Orthorhombic, *Pna2₁*	Triclinic, *P-1*	Monoclinic, *P2₁/c*	Monoclinic, *P2₁/c*	Orthorhombic, *P2₁2₁2₁*
CCDC reference		2487455	2487463	2487462	2487458	2487456
Unit cell dimensions	a/Å	24.5240(7)	10.3233(9)	17.1409(16)	12.6042(8)	4.0567(3)
	b/Å	15.8085(5)	13.6855(12)	24.162(2)	7.2044(5)	22.3227(13)
	c/Å	7.1593(2)	18.7340(17)	13.1999(12)	19.3267(12)	25.5311(16)
	α/°	-	92.024(4)	-	-	-
	β/°	-	101.552(3)	92.494(3)	103.951(2)	-
	γ/°	-	97.723(3)	-	-	-
Volume/A^3		2775.57(14)	2564.3(4)	5461.6(9)	1703.21(19)	2312.0(3)
Z, ϱ_{calc}/mg·m^{-3}		4/1.467	2/1.462	2/1.451	4/1.452	4/1.467
F(000)		1260	1168	2438	776	1064
Crystal size (mm^3)		0.165 x 0.022 x 0.019	0.223 x 0.131 x 0.109	0.075 x 0.053 x 0.044	0.291 x 0.273 x 0.173	0.273 x 0.082 x 0.069
Abs. coeff. (mm^{-1})		0.983	1.059	1.185	0.333	0.277
θ Range (°)		2.577-26.367	2.107-28.346	2.161-24.795	2.397-28.300	1.991-28.284
Max./min. transmission		0.7454/0.5695	0.0962/0.0613	0.7451/0.5752	0.7457/0.6651	0.7457/0.6347
Reflections collected		25226	100153	97133	35800	27484
Independent reflections (R_{int})		5432 (0.0781)	12750 (0.0389)	9333 (0.1792)	4236 (0.0412)	5751 (0.0324)
Final R indices [I>2σ(I)]		R1 = 0.0380, wR2 = 0.0704	R1 = 0.0617, wR2 = 0.1629	R1 = 0.0803, wR2 = 0.2068	R1 = 0.0315, wR2 = 0.0760	R1 = 0.0275, wR2 = 0.0655

Table S4: Selected bond lengths (Å) and angles (°) for polymorphs **1m, 1m′, 1o** and **1w**

	1m	**1m′**	**1o**	**1w**		**1m**	**1m′**	**1o**	**1w**
Zn(1)-O(1)	1.9437(10)	1.9440(13)	2.1211(18)	1.9719(12)	O(1)-Zn(1)-N(1)	99.74(4)	113.73(6)	92.37(6)	108.19(5)
Zn(1)-O(3)	1.9398(10)	1.9541(13)	1.9956(14)	1.9419(12)	O(1)-Zn(1)-N(2)$^{\#1}$	114.71(4)	100.47(6)	109.05(6)	
Zn(1)-N(1)	2.0385(11)	2.0281(14)	2.0505(16)	2.0182(14)	O(3)-Zn(1)-O(1)	125.74(4)	119.12(6)	138.24(6)	105.80(5)
Zn(1)-N(2)$^{\#1}$	2.0410(10)	2.0366(15)	2.0501(16)		O(3)-Zn(1)-N(1)	112.06(4)	97.10(6)	108.38(6)	118.40(6)
Zn(1)-O(2)			2.2626(16)		O(3)-Zn(1)-N(2)$^{\#1}$	95.30(4)	115.25(6)	102.27(6)	
Zn(1)-N(3)				2.0455(14)	N(1)-Zn(1)-N(2)$^{\#1}$	109.17(4)	111.83(6)	100.78(7)	
Zn(2)-O(7)				1.9449(12)	O(3)-Zn(1)-O(2)			90.90(6)	
Zn(2)-O(5)				1.9523(12)	O(1)-Zn(1)-O(2)			59.86(6)	
Zn(2)-N(4)$^{\#1}$				2.0574(14)	N(2)$^{\#1}$-Zn(1)-O(2)			95.27(6)	
Zn(2)-N(2)				2.0216(14)	N(1)-Zn(1)-O(2)			151.40(6)	
					O(3)-Zn(1)-N(3)				118.61(5)
					O(1)-Zn(1)-N(3)				100.30(5)
					N(1)-Zn(1)-N(3)				103.76(6)
					O(7)-Zn(2)-N(4)$^{\#1}$				115.64(5)
					O(7)-Zn(2)-O(5)				112.02(5)
					O(7)-Zn(2)-N(2)				114.58(5)
					O(5)-Zn(2)-N(4)$^{\#1}$				97.42(5)
					O(5)-Zn(2)-N(2)				110.27(5)
					N(2)-Zn(2)-N(4)$^{\#1}$				105.48(6)

Symmetry code: (**1m**) $^{\#1}$ x-1,y,z; (**1m′**) $^{\#1}$ x-1,-y+3/2,z-1/2; (**1o**) $^{\#1}$ -x+1,y-1/2,-z+1/2; (**1w**) $^{\#1}$ x,y-1,z

Table S5: Selected bond lengths (Å) and angles (°) for **2·CH₃CN, 3·solv** and **4·solv**

	2·CH₃CN	**3·solv**	**4·solv**		**2·CH₃CN**	**3·solv**	**4·solv**
Cu(1)-N(1)	2.007(3)	2.008(3)	1.998(7)	N(1)-Cu(1)-N(2)$^{\#1}$	172.93(15)		
Cu(1)-N(2)$^{\#1}$	2.022(3)			N(1)-Cu(1)-O(3)$^{\#2}$	92.49(15)	94.81(12)	
Cu(1)-O(1)	1.961(3)	1.991(5)	2.010(5)	N(2)$^{\#1}$-Cu(1)-O(3)$^{\#2}$	94.46(13)		
Cu(1)-O(3)$^{\#2}$	2.345(3)	2.346(4)		O(1)-Cu(1)-N(1)	87.86(13)	89.71(16)	92.6(2)
Cu(1)-O(4)	1.949(3)		1.946(6)	O(1)-Cu(1)-N(2)#1	93.09(13)		
Cu(1)-N(3)		2.013(3)		O(1)-Cu(1)-O(3)#2	92.51(12)	99.23(17)	
Cu(1)-O(2)		2.667(5)	2.553(6)	O(4)-Cu(1)-N(1)	92.10(14)		87.8(3)
Cu(1)-O(3)		2.095(5)		O(4)-Cu(1)-N(2)$^{\#1}$	87.74(13)		
Cu(2)-N(2)		2.007(2)	2.019(6)	O(4)-Cu(1)-O(1)	173.47(13)		154.6(2)
Cu(2)-O(10)		1.955(2)	1.894(5)	O(4)-Cu(1)-O(3)$^{\#2}$	80.97(12)		
Cu(2)-O(11)		2.675(2)	2.089(8)	N(1)-Cu(1)-N(3)		172.65(13)	
Cu(3)-N(4)		2.010(3)		N(1)-Cu(1)-O(2)		86.28(14)	89.6(2)
Cu(3)-O(5)		2.577(3)		N(1)-Cu(1)-O(3)$^{\#2}$		92.45(12)	
Cu(3)-O(6)		1.964(2)		N(1)-Cu(1)-O(3)		88.98(15)	
Cu(1)-N(4)$^{\#1}$			2.021(7)	N(3)-Cu(1)-O(2)		87.78(15)	
Cu(1)-O(5)$^{\#2}$			2.324(6)	N(3)-Cu(1)-O(3)		91.10(17)	
Cu(2)-O(7)			2.405(11)	O(1)-Cu(1)-N(3)		90.27(18)	
Cu(2)-O(8)			1.923(5)	O(1)-Cu(1)-O(2)		53.80(17)	56.5(2)
Cu(3)-N(3)			2.023(6)	O(1)-Cu(1)-O(3)		178.58(13)	
Cu(3)-O(8)			2.537(5)	O(3)$^{\#1}$-Cu(1)-O(2)		152.97(17)	
Cu(3)-O(9)			1.945(5)	O(3)-Cu(1)-O(2)		126.62(15)	
				O(3)-Cu(1)-O(3)$^{\#2}$		80.30(15)	
				N(2)-Cu(2)-N(2)$^{\#1}$		180.0	
				N(2)$^{\#1}$-Cu(2)-O(11)		90.97(9)	
				N(2)-Cu(2)-O(11)		89.03(9)	93.0(3)

Symmetry code: (**2·CH₃CN**) $^{\#1}$ x+1/2,-y+3/2,z ; $^{\#2}$ x,y,z+1; (**3·solv**) $^{\#1}$ -x,-y+1,-z+2; $^{\#2}$ -x+1,-y+1,-z+1, $^{\#3}$ -x+1,-y,-z; (**4·solv**) $^{\#1}$ -x+1,y+1/2,-z+3/2; $^{\#2}$ -x+1,-y+1,-z+1; #3 -x,-y,-z+1

Table S5 (continuation): Selected bond angles/° for **3·solv** and **4·solv**

	2·CH$_3$CN	**3·solv**	**4·solv**		**2·CH$_3$CN**	**3·solv**	**4·solv**
				O(10)-Cu(2)-N(2)$^{\#1}$		89.88(9)	
				O(10)-Cu(2)-N(2)		90.12(9)	89.3(3)
				O(10)$^{\#1}$-Cu(2)-O(11)		125.26(8)	
				O(10)-Cu(2)-O(11)		54.74(8)	174.5(3)
				N(4)-Cu(3)-O(5)		86.68(9)	
				N(4)$^{\#3}$-Cu(3)-O(5)		93.32(9)	
				O(6)-Cu(3)-N(4)		89.66(10)	
				O(6)-Cu(3)-N(4)$^{\#3}$		90.34(10)	
				O(6)$^{\#3}$-Cu(3)-O(5)		83.54(8)	
				O(6)-Cu(3)-O(5)		96.46(8)	
				N(1)-Cu(1)-N(4)$^{\#1}$			175.5(3)
				N(1)-Cu(1)-O(5)$^{\#2}$			90.5(2)
				N(4)$^{\#1}$-Cu(1)-O(2)			89.0(2)
				N(4)$^{\#1}$-Cu(1)-O(5)$^{\#2}$			93.5(3)
				O(1)-Cu(1)-N(4)$^{\#1}$			90.3(2)
				O(1)-Cu(1)-O(5)$^{\#2}$			78.4(2)
				O(4)-Cu(1)-N(4)$^{\#1}$			88.1(3)
				O(4)-Cu(1)-O(2)			98.1(2)
				O(4)-Cu(1)-O(5)$^{\#2}$			127.0(2)
				O(5)$^{\#2}$-Cu(1)-O(2)			134.9(2)
				N(2)-Cu(2)-O(7)			91.2(3)
				O(8)-Cu(2)-N(2)			175.8(3)
				O(8)-Cu(2)-O(7)			92.1(3)
				O(8)-Cu(2)-O(11)			85.1(2)
				O(10)-Cu(2)-O(7)			103.6(4)

Symmetry code: (**2·CH$_3$CN**) $^{\#1}$ x+1/2,-y+3/2,z ; $^{\#2}$ x,y,z+1; (**3·solv**) $^{\#1}$ -x,-y+1,-z+2; $^{\#2}$ -x+1,-y+1,-z+1, $^{\#3}$ -x+1,-y,-z; (**4·solv**) $^{\#1}$ -x+1,y+1/2,-z+3/2; $^{\#2}$ -x+1,-y+1,-z+1; #3 -x,-y,-z+1

Table S5 (continuation): Selected bond angles/° for **4·solv**

	2·CH₃CN	**3·solv**	**4·solv**		**2·CH₃CN**	**3·solv**	**4·solv**
				O(10)-Cu(2)-O(8)			92.3(2)
				O(11)-Cu(2)-O(7)			81.3(5)
				N(3)#3-Cu(3)-O(8)			89.3(2)
				N(3)-Cu(3)-O(8)			90.7(2)
				O(9)-Cu(3)-N(3)#3			90.2(2)
				O(9)-Cu(3)-N(3)			89.8(2)
				O(9)-Cu(3)-O(8)			56.64(18)
				O(9)#3-Cu(3)-O(8)			123.36(18)
Symmetry code: (**2·CH₃CN**) #1 x+1/2,-y+3/2,z ; #2 x,y,z+1; (**3·solv**) #1 -x,-y+1,-z+2; #2 -x+1,-y+1,-z+1, #3 -x+1,-y,-z; (**4·solv**) #1 -x+1,y+1/2,-z+3/2; #2 -x+1,-y+1,-z+1; #3 -x,-y,-z+1							

Table S6: Selected bond lengths (Å) and angles (°) for **5** and **6**

	5	**6**		**5**	**6**
S(2)-C(7)	1.7559(13)	1.7557(18)	C(7)-S(2)-C(6)	102.02(6)	104.20(9)
S(2)-C(6)	1.8075(14)	1.8078(19)	C(3)-S(1)-C(6)	104.51(6)	104.60(9)
S(1)-C(3)	1.7495(13)	1.7579(18)	C(14)-O(3)-H(3)	109.5	109.5
S(1)-C(6)	1.7992(13)	1.8067(19)	O(2)-C(12)-O(1)	123.04(12)	123.58(16)
O(1)-C(12)	1.2782(16)	1.310(2)	S(1)-C(6)-S(2)	108.70(7)	118.75(11)
O(2)-C(12)	1.2585(16)	1.235(2)	O(5)-C(19)-O(4)		123.1(4)
O(3)-H(3)	0.8400	0.8400			
N(1)-H(1)	0.8800				
O(1)-H(1A)		0.8400			

Table S7: Main hydrogen bonds (A,°) of the Zn(II) coordination polymers **1m, 1m'** and **1o**

	D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
1m	O(12)-H(12)...O(2)	0.84	1.82	2.5613(15)	146.5
	O(34)-H(34)...O(4)	0.84	1.80	2.5492(16)	146.9
	C(8)-H(8)...O(12)$^{\#3}$	0.95	2.65	3.2890(16)	125.1
	C(9)-H(9)...O(3)$^{\#2}$	0.95	2.54	3.0254(15)	112.1
	C(10)-H(10)...O(2)$^{\#4}$	0.95	2.52	3.3827(16)	151.0
	C(5)-H(5)...O(34)$^{\#5}$	0.95	2.45	3.2975(17)	148.9
1m'	O(12)-H(12)...O(2)	0.84	1.79	2.5342(19)	147.2
	O(34)-H(34)...O(4)	0.84	1.82	2.568(2)	147.1
	C(2)-H(2)...O(4)$^{\#3}$	0.95	2.55	3.187(2)	124.9
	C(5)-H(5)...O(3)	0.95	2.56	3.074(2)	113.9
	C(10)-H(10)...O(1)$^{\#2}$	0.95	2.50	3.110(2)	121.9
	C(10)-H(10)...O(34)$^{\#4}$	0.95	2.52	3.114(2)	120.7
	C(6)-H(6A)...O(12)$^{\#5}$	0.99	2.51	3.435(2)	156.2
	C(15)-H(15)...O(12)$^{\#6}$	0.95	2.45	3.388(2)	170.9
1o	O(12)-H(12)...O(2)	0.84	1.81	2.550(2)	146.5
	O(34)-H(34)...O(4)	0.84	1.83	2.577(2)	146.7
	C(4)-H(4)...O(3)$^{\#3}$	0.95	2.52	3.280(2)	136.6
	C(6)-H(6A)...O(2)$^{\#3}$	0.99	2.44	3.263(3)	140.2
	C(6)-H(6B)...O(4)$^{\#4}$	0.99	2.22	3.159(3)	157.8
	C(11)-H(11)...O(34)$^{\#5}$	0.95	2.60	3.254(3)	126.3
	C(10)-H(10)...O(2)$^{\#2}$	0.95	2.57	3.193(3)	123.3
	C(1)-H(1)...O(12)$^{\#6}$	0.95	2.24	3.130(2)	155.8

Symmetry code: (**1m**) $^{\#2}$ x+1,y,z; $^{\#3}$ -x+1,y+1/2,-z+1/2; $^{\#4}$ x+1,-y+3/2,z+1/2; $^{\#5}$ x,-y+3/2,z+1/2; (**1m'**) $^{\#2}$ x+1,-y+3/2,z+1/2; $^{\#4}$ -x+1,y+1/2,-z+1/2; $^{\#5}$ x,-y+3/2,z+1/2; $^{\#6}$ -x+1,-y+2,-z; (**1o**) $^{\#2}$ -x+1,y+1/2,-z+1/2; $^{\#3}$ x+1/2,-y+1/2,-z+1; $^{\#4}$ -x+3/2,-y+1,z-1/2; $^{\#5}$ x,y,z-1; $^{\#6}$ -x+1,y+1/2,-z+3/2.

Table S8: Main hydrogen bonds (A,°) of the Zn(II) coordination polymer **1w**

	D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
1w	O(56)-H(56)...O(6)	0.84	1.81	2.5558(17)	147.1
	O(78)-H(78)...O(8)	0.84	1.83	2.5679(18)	146.5
	O(12)-H(12)...O(1)	0.84	1.80	2.5390(18)	145.8
	O(34)-H(34)...O(4)	0.84	1.87	2.6051(19)	145.3
	C(21)-H(21)...O(78)$^{\#4}$	0.95	2.53	3.286(2)	137.1
	C(20)-H(20)...O(8)$^{\#2}$	0.95	2.48	3.236(2)	136.2
	C(5)-H(5)...O(4)	0.95	2.29	3.080(2)	139.6
	C(4)-H(4)...O(12)$^{\#7}$	0.95	2.29	3.093(2)	142.4
	C(16)-H(16)...O(2)$^{\#8}$	0.95	2.37	3.111(2)	134.1
	C(22)-H(22)...O(5)$^{\#2}$	0.95	2.44	3.049(2)	122.1
	C(2)-H(2)...O(3)$^{\#10}$	0.95	2.52	3.212(2)	129.7

Symmetry code: (**1w**) $^{\#2}$ x,y+1,z; $^{\#4}$ x,-y+3/2,z-1/2; $^{\#7}$ x,-y+3/2,z+1/2; $^{\#8}$ -x,y+1/2,-z+1/2; $^{\#10}$ -x,y-1/2,-z+1/2.

Table S9: Main hydrogen bonds (A,°) of **2·CH₃CN, 3·solv** and **4.solv**

	D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
2·CH₃CN	O(3)-H(3)...O(2)	0.84	1.77	2.521(4)	147.9
	O(6)-H(6)...O(5)	0.84	1.83	2.577(5)	147.2
	C(1)-H(1)...O(5)	0.95	2.52	3.324(5)	142.3
	C(2)-H(2)...N(3)$^{\#5}$	0.95	2.65	3.448(6)	141.8
	C(9)-H(9)...O(3)$^{\#6}$	0.95	2.52	3.178(5)	126.5
	C(11)-H(11)...O(2)$^{\#3}$	0.95	2.39	3.059(5)	126.7
3·solv	C(6)-H(6B)...O(9)$^{\#1}$	0.99	2.41	3.240(4)	141.2
	C(9)-H(9)...O(10)$^{\#2}$	0.95	2.43	2.919(3)	111.5
	C(16)-H(16)...O(4)	0.95	2.42	3.191(6)	138.5
	C(17)-H(17A)...O(2)$^{\#5}$	0.99	2.57	3.293(6)	130.0
	C(21)-H(21)...O(6)$^{\#3}$	0.95	2.47	2.942(4)	110.5
	C(35)-H(35C)...O(1)$^{\#1}$	0.98	2.44	3.365(8)	156.3
4·solv	O(3)-H(3)...O(2)	0.84	1.77	2.506(8)	145.1
	O(6)-H(6)...O(5)	0.84	1.89	2.599(10)	140.9
	O(13)-H(13A)...O(12)	0.84	1.84	2.526(17)	138.3
	C(40)-H(40)...O(2)$^{\#9}$	0.95	2.36	3.291(10)	165.8
	C(10)-H(10)...O(10)	0.95	2.23	2.784(10)	116.1
	C(12)-H(12)...O(9)$^{\#3}$	0.95	2.42	2.926(10)	113.1
	C(1)-H(1)...O(5)$^{\#2}$	0.95	2.47	3.069(11)	120.9
	C(6)-H(6A)...O(12)$^{\#6}$	0.99	2.33	3.136(13)	137.5

Symmetry code: (**2·CH₃CN**) $^{\#3}$ x-1/2,-y+3/2,z; $^{\#5}$ -x+1,-y+1,z-1/2; $^{\#6}$ x-1/2,-y+3/2,z+1; (**3·solv**) $^{\#1}$ -x+1,-y+1,-z+1; $^{\#2}$ -x,-y+1,-z+2; $^{\#3}$ -x+1,-y,-z; $^{\#5}$ -x+2,-y+1,-z+1; (**4·solv**) $^{\#2}$ -x+1,-y+1,-z+1; $^{\#3}$ -x,-y,-z+1; $^{\#6}$ x,-y+1/2,z-1/2; $^{\#9}$ -x+1,y-1/2,-z+1/2.

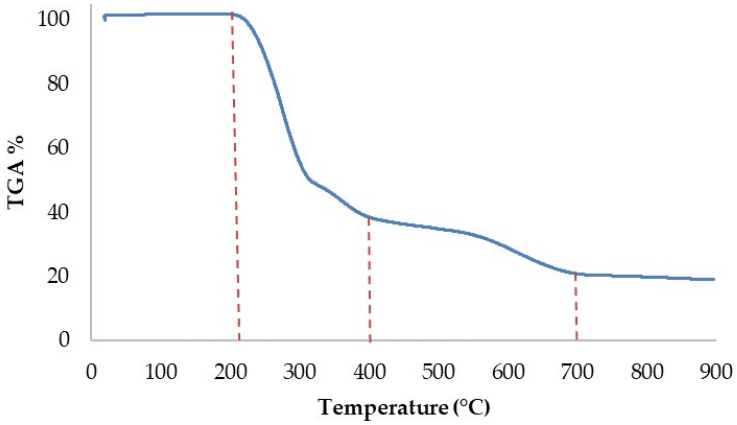
Table S10: Main hydrogen bonds (A,°) of **5** and **6**

	D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
5	O(3)-H(3)...O(2)	0.84	1.81	2.5525(14)	146.9
	N(1)-H(1)...O(1)	0.88	1.69	2.5701(15)	173.6
	N(1)-H(1)...O(2)	0.88	2.61	3.1595(15)	121.2
	C(2)-H(2)...N(2)$^{\#1}$	0.95	2.46	3.3265(17)	151.7
	C(5)-H(5)...O(2)	0.95	2.48	3.1155(17)	124.2
	C(4)-H(4)...O(1)$^{\#3}$	0.95	2.50	3.4106(17)	160.9
	C(1)-H(1A)...S(1)$^{\#2}$	0.95	2.74	3.6546(14)	161.9
6	O(1)-H(1A)...N(1)	0.84	1.80	2.640(2)	175.3
	O(3)-H(3)...O(2)	0.84	1.85	2.5873(19)	145.7
	O(4)-H(4A)...N(2)	0.84	1.75	2.586(3)	179.2
	O(6)-H(6)...O(5)	0.84	1.85	2.588(4)	146.5
	C(8)-H(8)...S(1)	0.95	2.88	3.5300(19)	126.8
	C(1)-H(1)...O(2)	0.95	2.40	3.129(2)	133.7
	C(4)-H(4)...S(2)	0.95	2.98	3.6175(19)	125.8
	C(15)-H(15)...O(5)$^{\#2}$	0.95	2.41	3.201(3)	140.5
	C(9)-H(9)...O(5)$^{\#3}$	0.95	2.54	3.110(3)	118.6

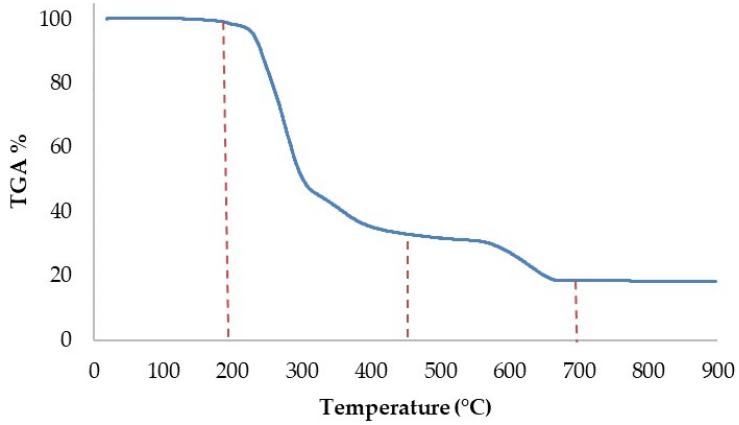
Symmetry code: (**5**) $^{\#1}$ -x+2,-y+1,-z+1; $^{\#2}$ x,y+1,z; #3 x,y-1,z; (**6**) $^{\#2}$ x+1/2,-y+1/2,-z+1; #3 x-1,y,z.

3. Thermal stability

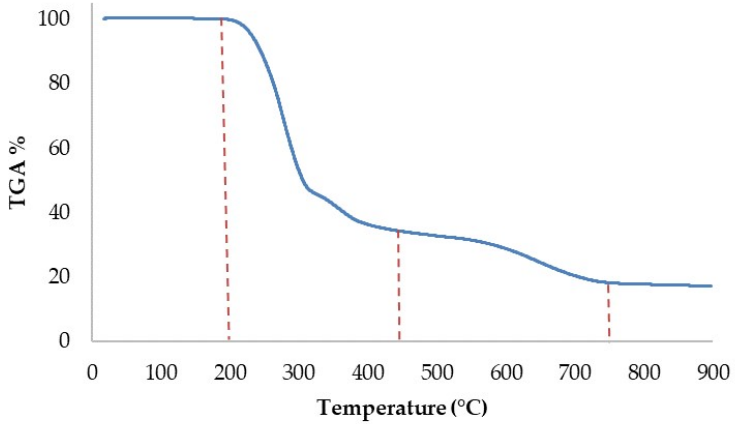
$^{1}_{\infty}Zn(Hsal)_2(SCS)$ **(1m)**



$^{1}_{\infty}Zn(Hsal)_2(SCS)$ **(1m')**



.....$^{1}_{\infty}Zn(Hsal)_2(SCS)$ **(1o)**



$^{2}_{\infty}Cu(Hsal)_2(SCS)\cdot CH_3CN$ **(2·CH_3CN)**

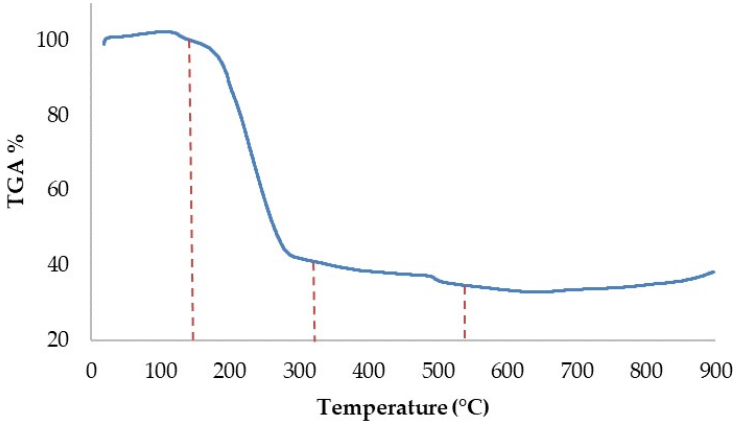
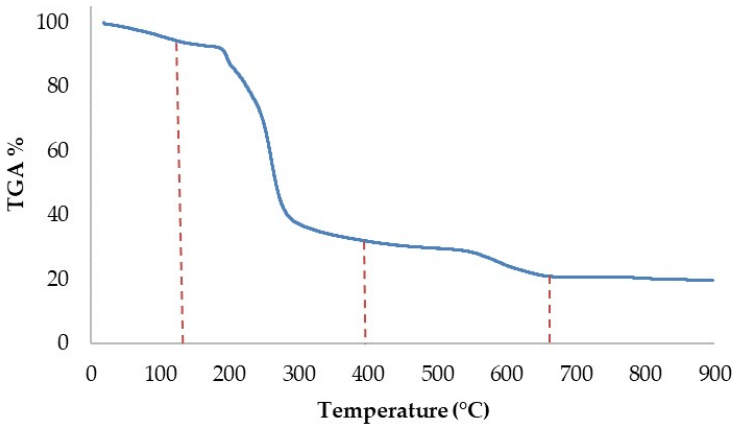
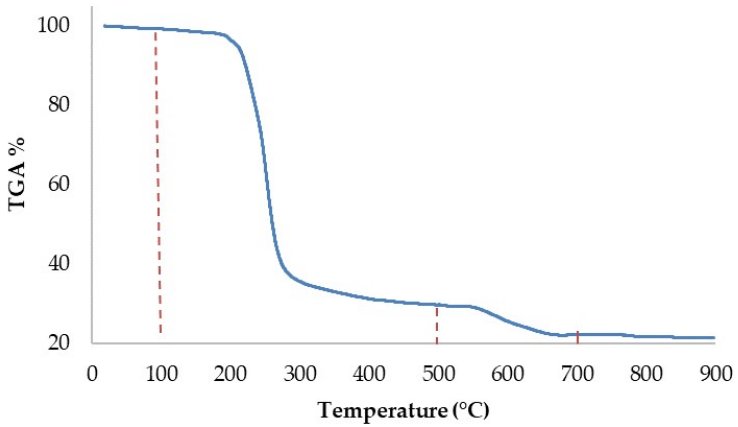


Figure S9: Thermogravimetric analysis of polymorphs **1** and **2·CH₃CN**

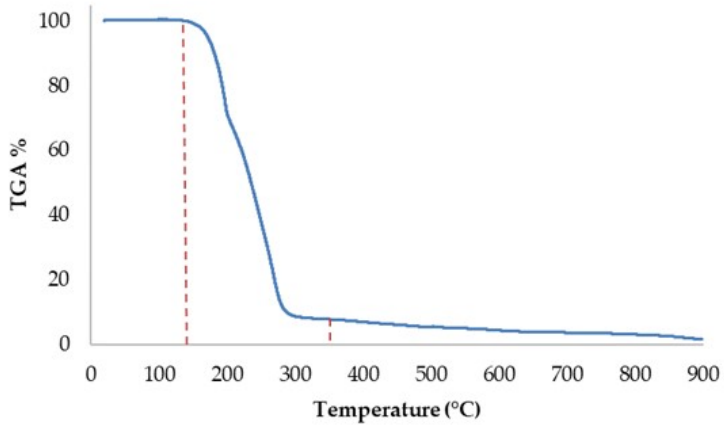
$^{2}_{\infty}Cu_3(OAc)_4(asp)_2(SCS)_3(H_2O)_2$ **(3·*solv*)**



$^{3}_{\infty}Cu_5(Hsal)_6(sal)_2(SCS)_4(H_2O)_2$ **(4.solv)**



[(H-SCS)(Hsal)] (5)



[(SCS)(H₂sal)₂ (6)

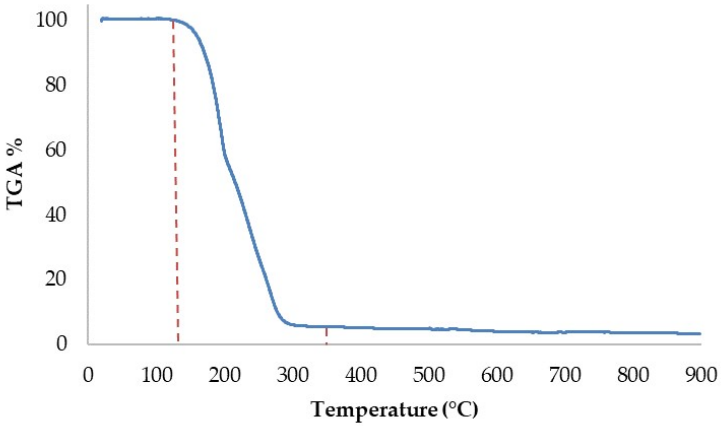
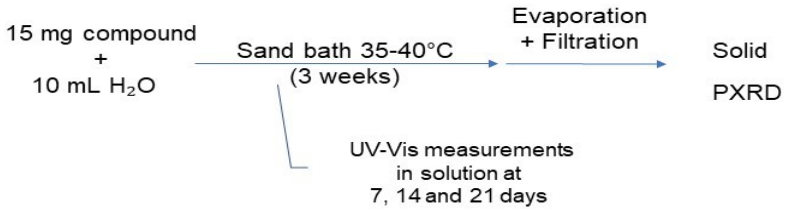


Figure S10: Thermogravimetric analysis of **3·solv, 4.solv, 5** and **6**

4. Stability in water, acidic conditions and in PBS

- **In water**



Scheme S1: Experimental procedure to study the stability in water.

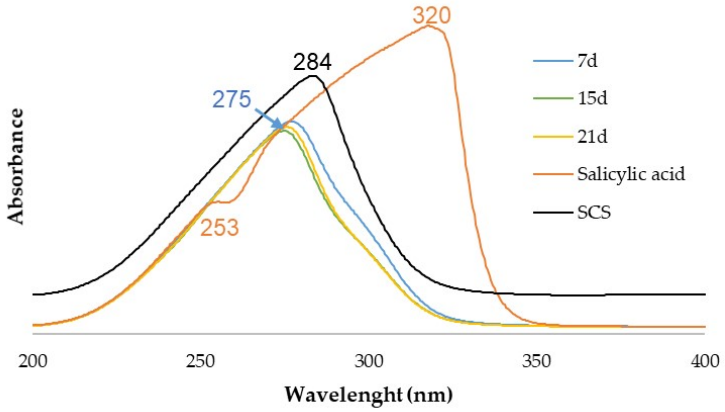


Figure S11: UV-Vis absorption spectrum of the solution of **1m** after 4, 14 and 21 days.

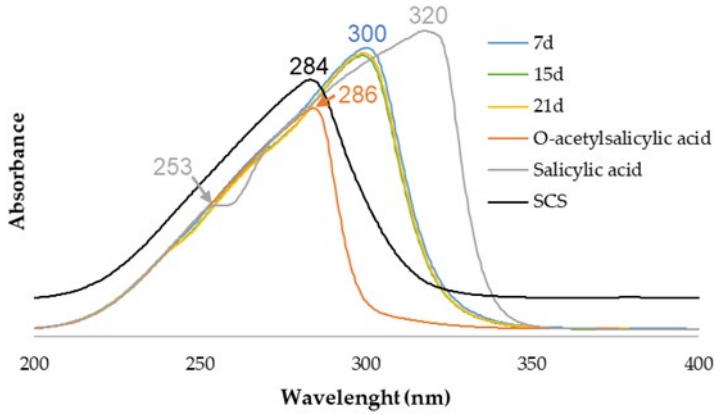


Figure S12: UV-Vis absorption spectrum of the solution of **3·solv** after 4, 14 and 21 days.

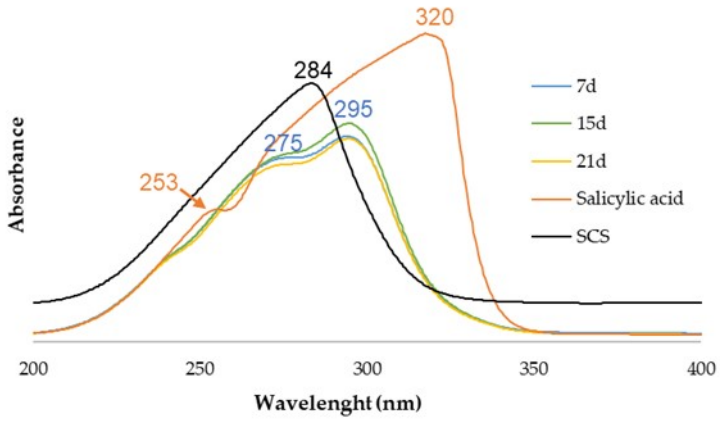


Figure S13: UV-Vis absorption spectrum of the solution of **4.solv** after 4, 14 and 21 days.

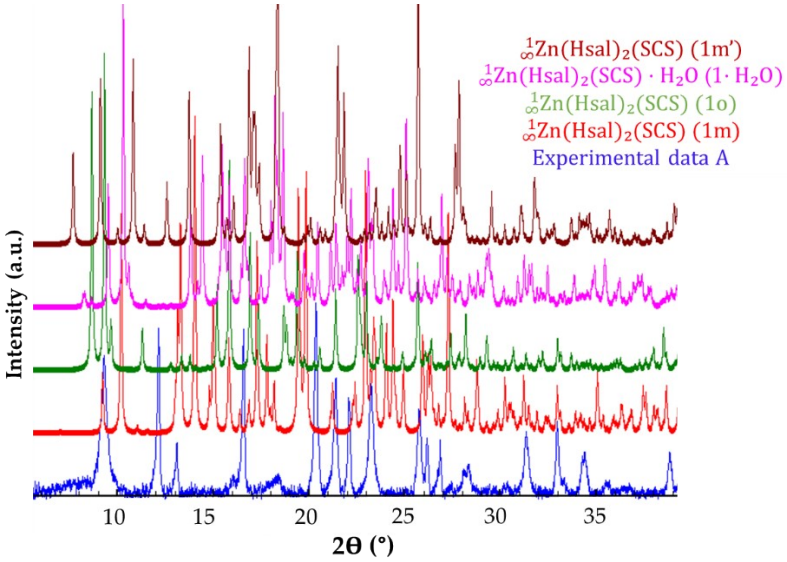


Figure S14: PXRD of **1m** after water treatment compared with theoretical patterns of all polymorphs.

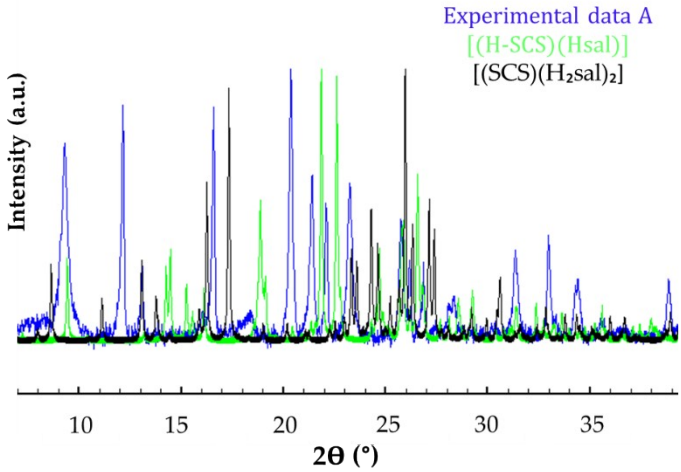
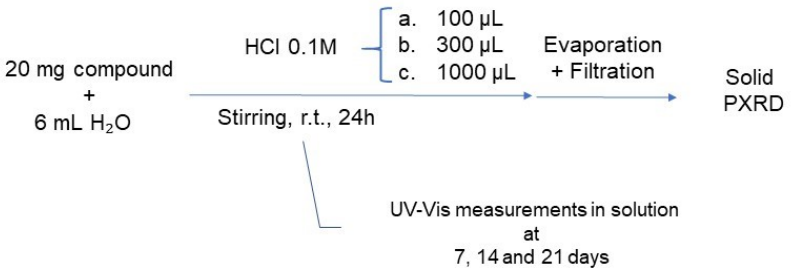


Figure S15: PXRD of **1m** after water treatment compared with theoretical patterns of **5** and **6**.

- **In acidic conditions**



Scheme S2: Experimental procedure to study the stability in acidic conditions.

Compound	100 µL			300 µL			1000 µL		
	Inicial	30min	24h	Inicial	30min	24h	Inicial	30min	24h
1m	5.60	6.85	6.72	3.62	5.43	5.33	3.13	3.90	3.87
3·solv	4.11	4.96	4.96	3.45	4.59	4.69	3.08	3.29	3.39
4·solv	3.76	5.04	4.98	3.61	4.66	4.55	2.99	3.36	3.36

Table S11: pH measurement of compounds at different times.

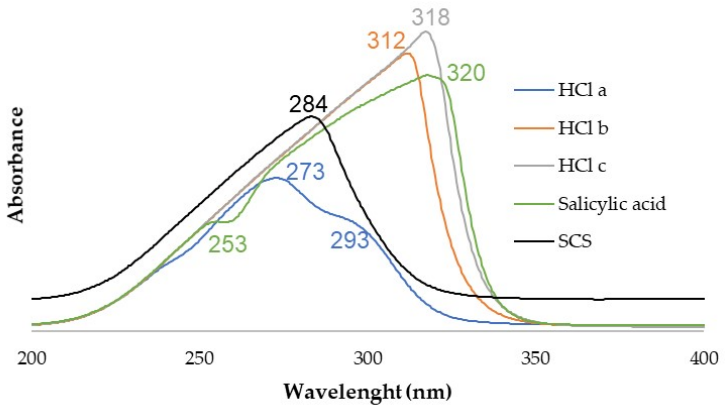


Figure S16: UV-Vis of **1m** solutions after acidic treatment (a, 100 µL; b, 300 µL; c, 1000 µL).

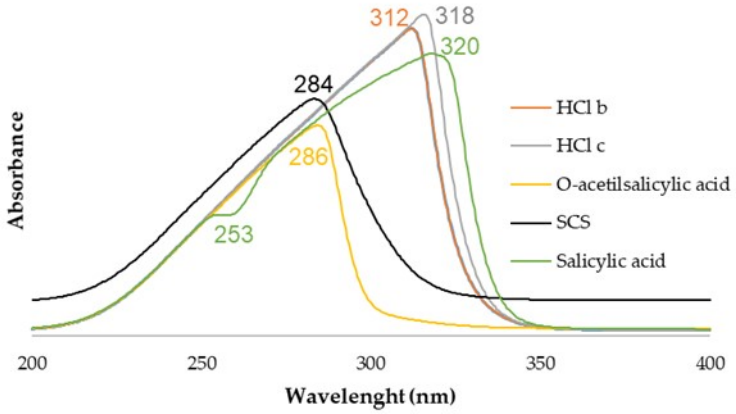


Figure S17: UV-Vis of **3·solv** solutions after acidic treatment (a, 100 μL; b, 300 μL; c, 1000 μL).

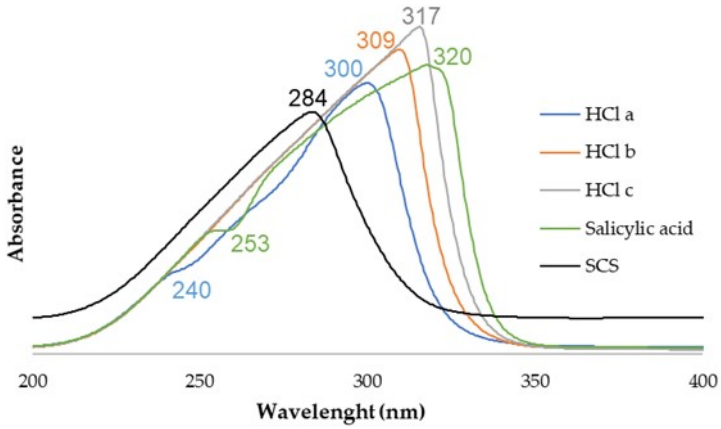


Figure S18: UV-Vis of **4·solv** solutions after acidic treatment (a, 100 μL; b, 300 μL; c, 1000 μL).

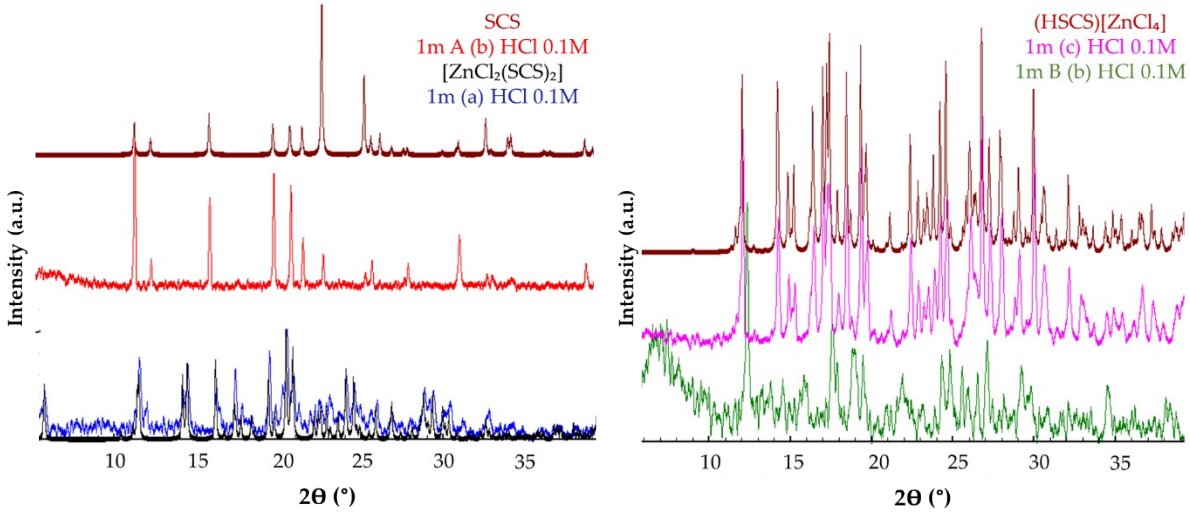


Figure S19: PXRD of **1m** after acid treatment compared with theoretical patterns of secondary compounds.

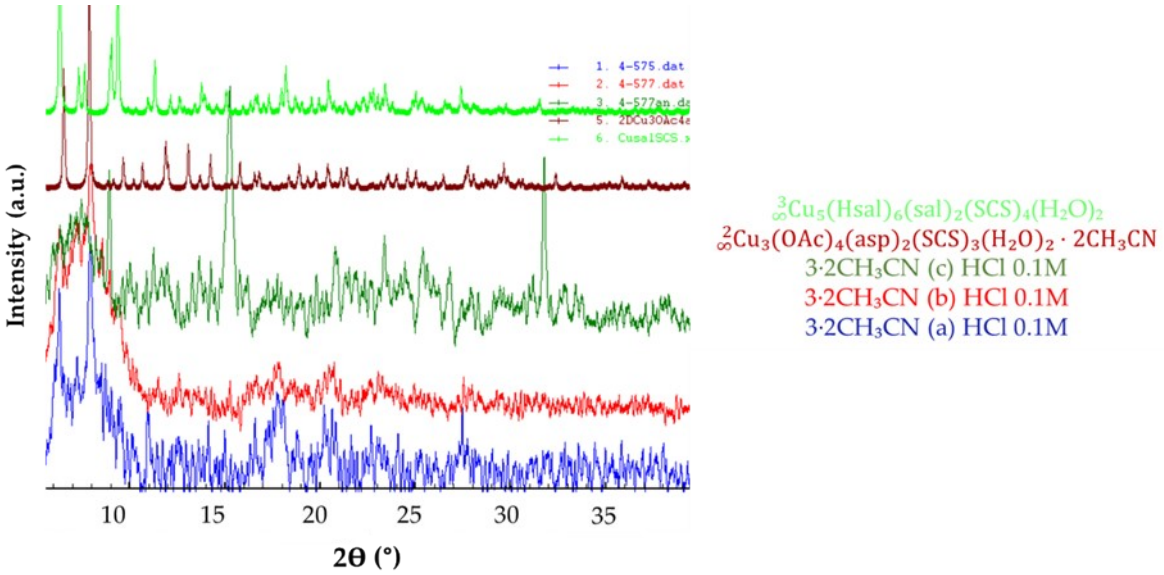
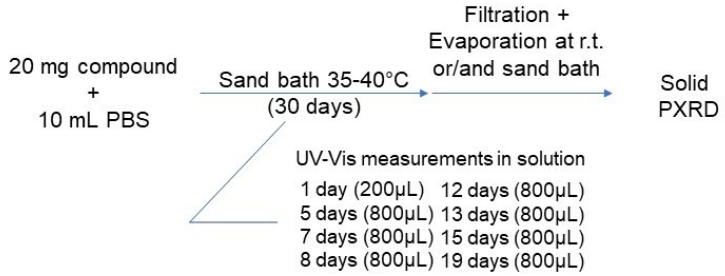


Figure S20: PXRD of **3·solv** after acid treatment compared with theoretical patterns of **3·solv** and **4.solv**.

- **In PBS (Phosphate Buffered Solution)**



Scheme S3: Experimental procedure to study the PBS stability.

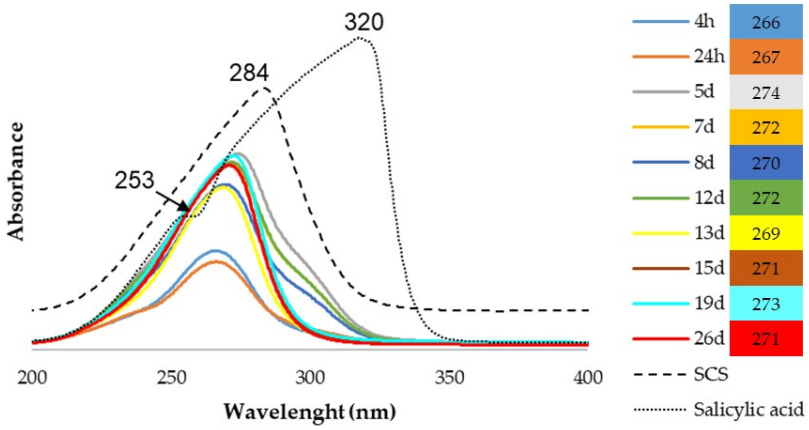


Figure S21: UV-Vis evolution of **1m** in PBS.

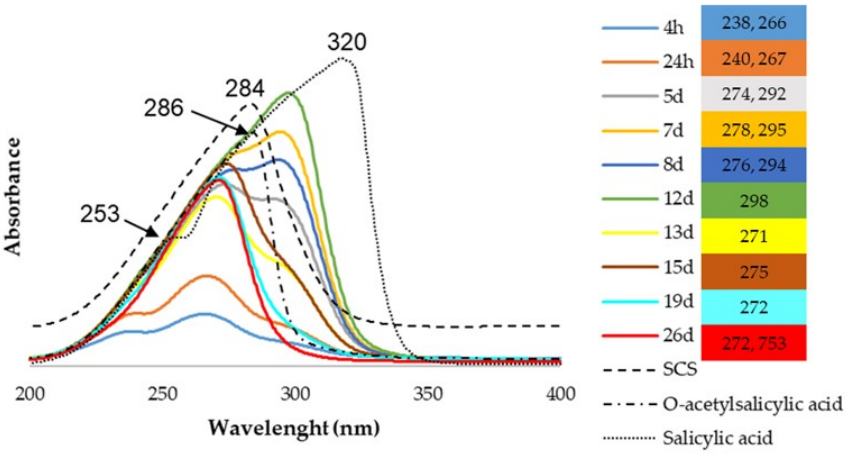


Figure S22: UV-Vis of **3·solv** evolution in PBS.

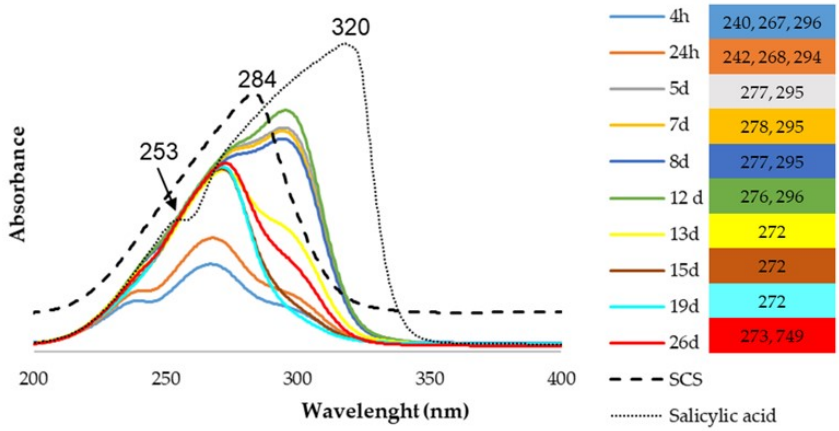


Figure S23: UV-Vis of **4·solv** evolution in PBS.

5. Citotoxicity study

The cytotoxicity experiments were carried out on MRC-5 (non-tumour human fibroblast), NCI-H460 (human lung carcinoma), A549 (human lung carcinoma), and MDA-MB231 (human breast adenocarcinoma) cell lines obtained from the American Type Culture Collection (ATCC). Cells were cultured at 37 °C in a humidified atmosphere of 95% of air and 5% CO_2 in the media showed in Table S13.

Growth inhibition induced by the compounds was evaluated by a colorimetric method based on the tetrazolium salt MTT ([3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide]), which is reduced by living cells to yield formazan (purple). Cells were seeded in 96-well plates and left to incubate for 24 h. After this time, DMSO solutions of the compounds were added to each well in such a way that the same proportion of DMSO was maintained in each well. Incubation was performed at 37 ºC/5% CO_2 for 7 days. At the end of the incubation period, 10 μL of MTT solution, 5 mg/mL in PBS (0.136 M NaCl, 1.47 mM KH_2PO_4, 8 mM NaH_2PO_4 and 2.68 mM KCl), was added and the solutions were incubated for 4 h at 37 ºC/5% CO_2. After the addition of 100 μL of SDS (10% sodium dodecyl sulfate in 0.01 M HCl) the solutions were again incubated for 12–14 h. Finally, the cell viability was evaluated by measuring the absorbance at 595 nm using a plate spectrophotometer (Tecan Ultra Evolution). The cell viability was calculated by dividing the absorbance of each well by that of the control wells (cells treated with medium containing 1% DMSO). Each experiment was repeated at least three times.

Data are expressed as % growth inhibition, calculated using the following formula:

% inhibition=100 – [(AO*100)/AT], where AO is the absorbance observed in the wells with the compounds under study and AT is the absorbance observed in the wells with DMSO controls.

Table S12: Cytotoxicity (cell line MRC-5) results for the compounds.

Compound	Concentration (μM)	%growth inhibition
SCS*	100	32±1
1m	100	46±3
1w	100	34±4
$ZnCl_2$(SCS)*	100	39±1

*A. B. Lago, A. Pino-Cuevas, R. Carballo, E. M. Vázquez-López. A new metal–organic polymeric system capable of stimuli-responsive controlled release of the drug ibuprofen. Dalton Trans. 45 (2016), 1614–1621. DOI: 10.1039/c5dt04031k.

Table S13: Conditions of the experiments with cell lines

Cell line	Celular density	Culture medium
MCR-5 (human fetal lung fibroblast cells, non tumoral)	10000	Minimum Essential Medium Eagle supplemented with 10 % FBS (Fetal Bovien Serum)
NCI-H460 (human lung carcinoma cells)	15000	RPMI 1640* supplemented with 10 % FBS (Fetal Bovien Serum)
A549 (human lung carcinoma cells) **MDA-MB231** (human breast adenocarcinoma cells)	5000	DMEM* supplemented with 10 % FBS (Fetal Bovien Serum) and 2mM de L-glutamine
(*) RPMI 1640 (Roswell Park Memorial Institute); DMEM (Dulbeco Modified Eagle's Medium low glucose)		