Supplementary Material

Solid-state structural transformation and photoluminescence properties of supramolecular coordination compounds

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1. Characterization of the SCMs

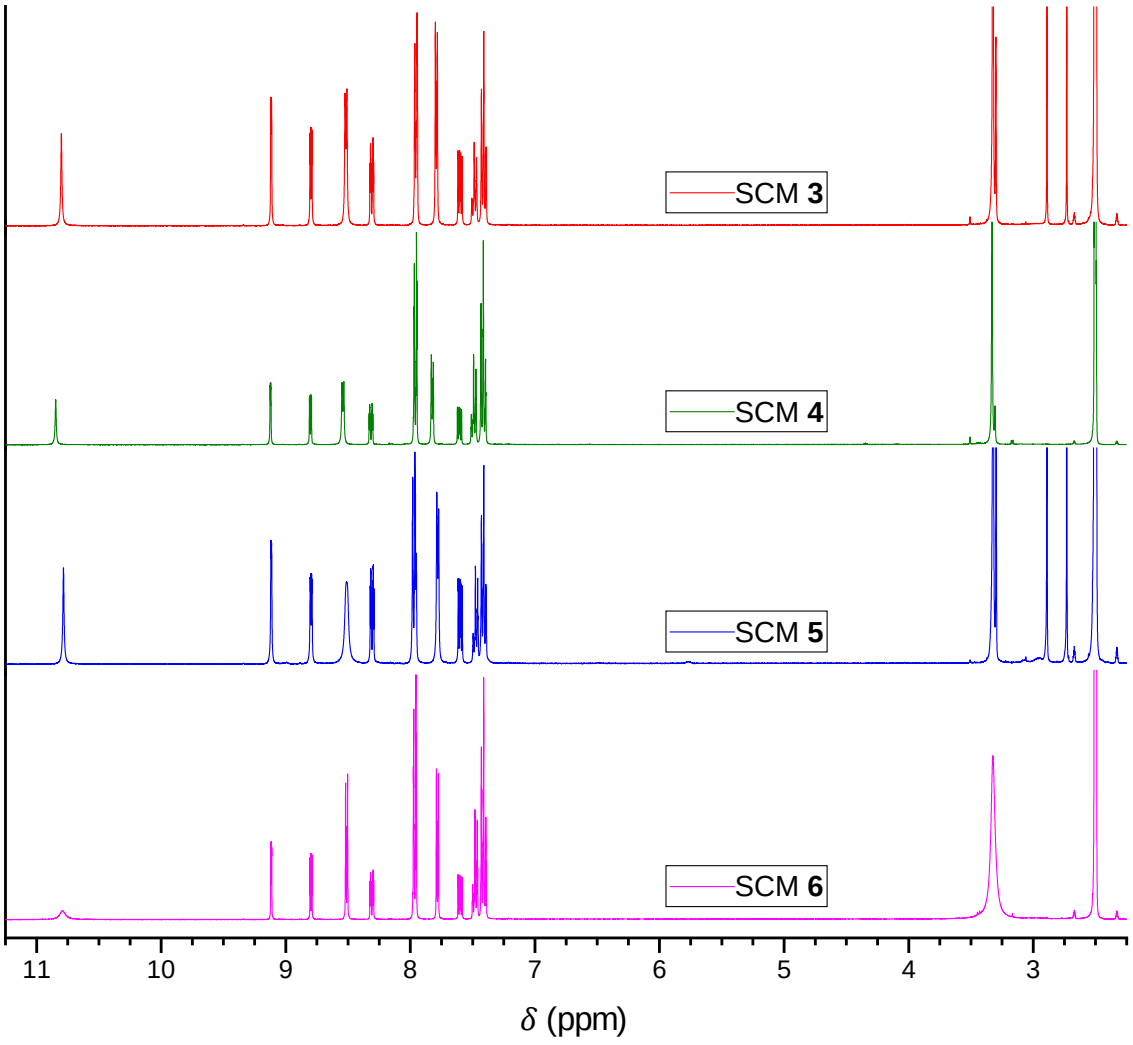

Figure S1: ^{1}H-NMR spectra of the SCMs **3**-**6** in DMSO-d_6 (400 MHz).

2. Crystal structure

(a)

(b)

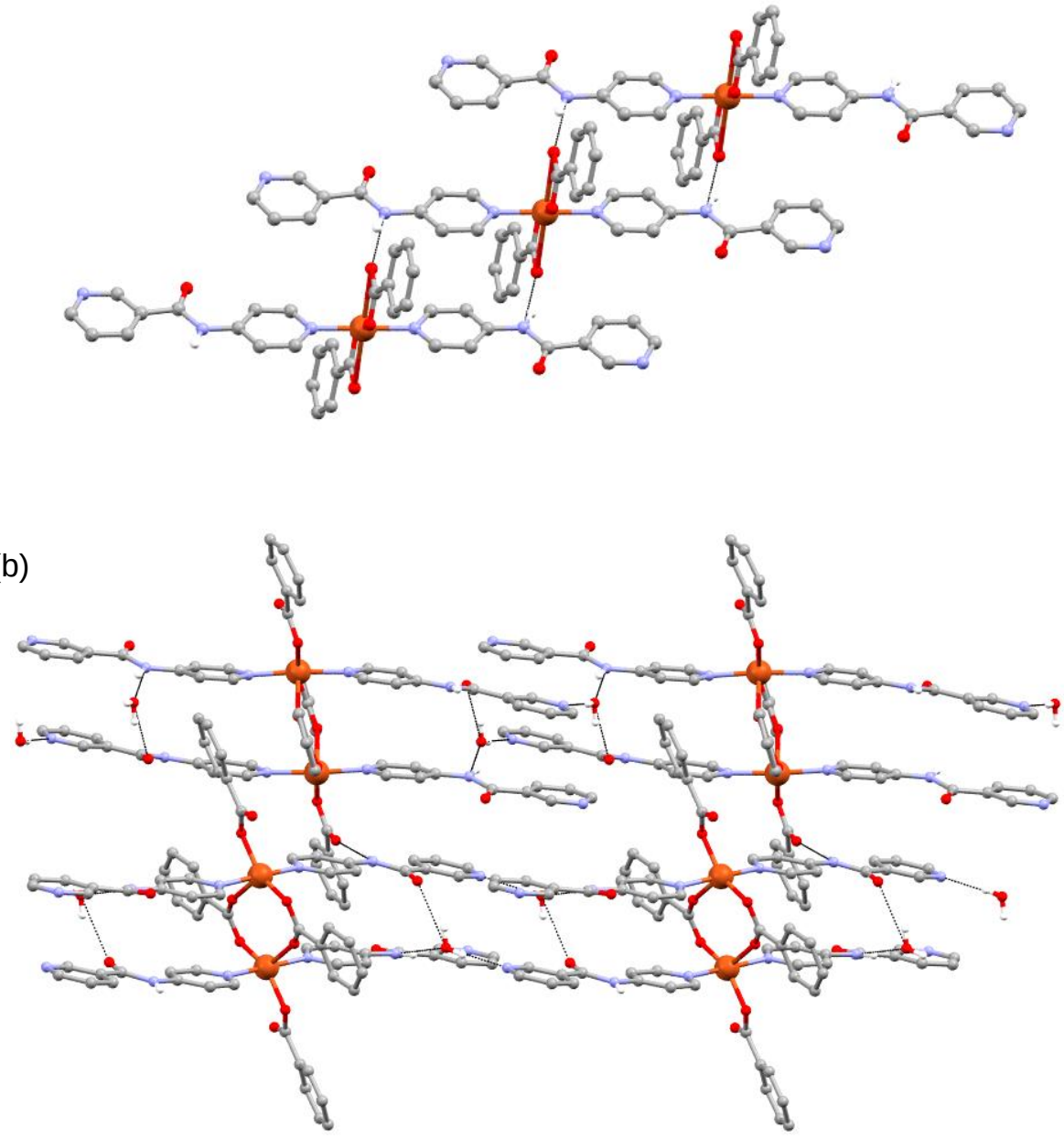

Figure S2: Hydrogen bonding interactions (dotted lines) observed in copper(II) SCMs: (a) **1**, and (b) **2** (hydrogen atoms except for the donor atoms are were omitted for clarity).

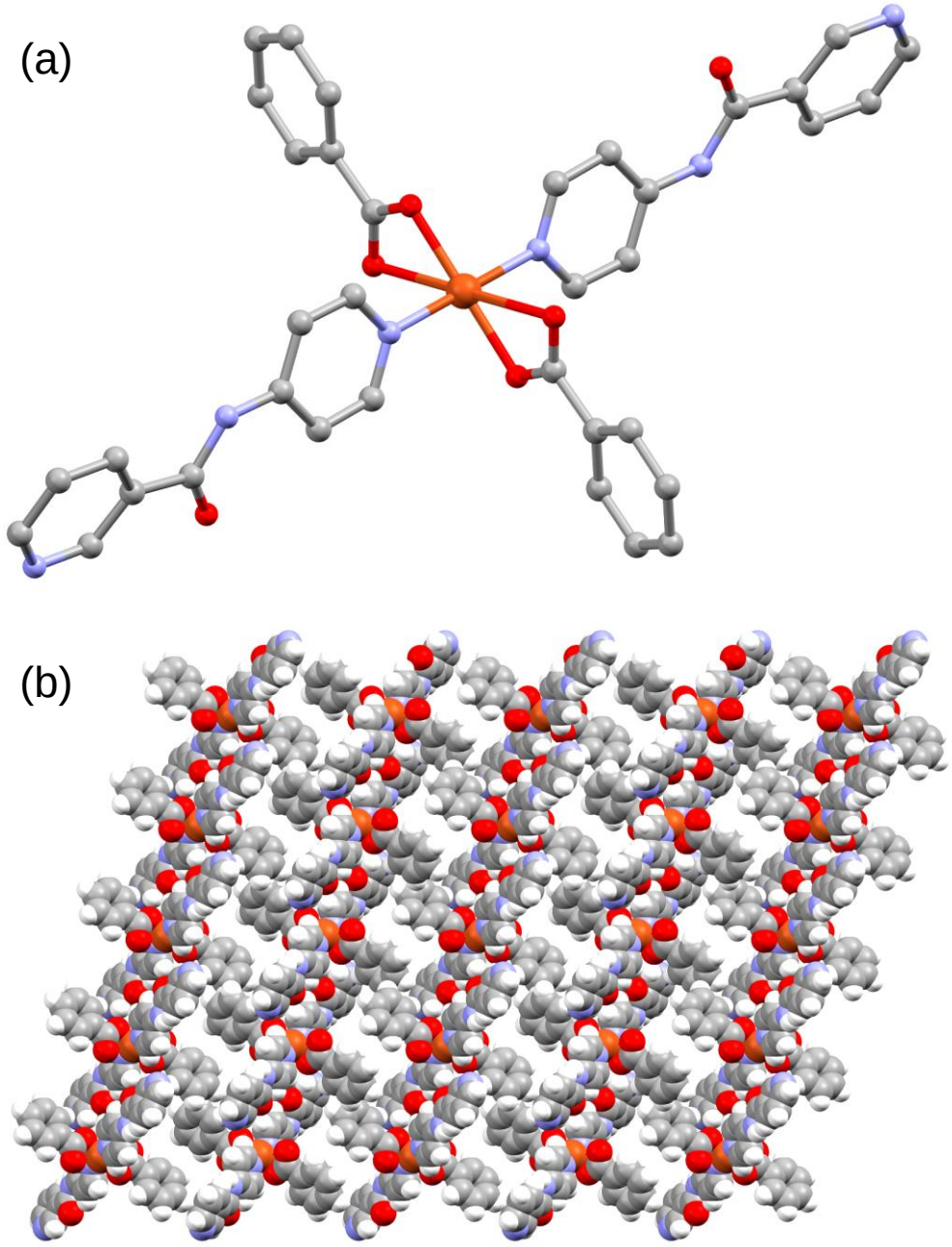

Figure S3: (a) Molecular structure of **1.S** (hydrogen atoms were omitted for clarity) after excluding the electron densities from solvent molecules using PLATON/SQUEEZE and (b) spacefill model showing the solvent accessible voids.

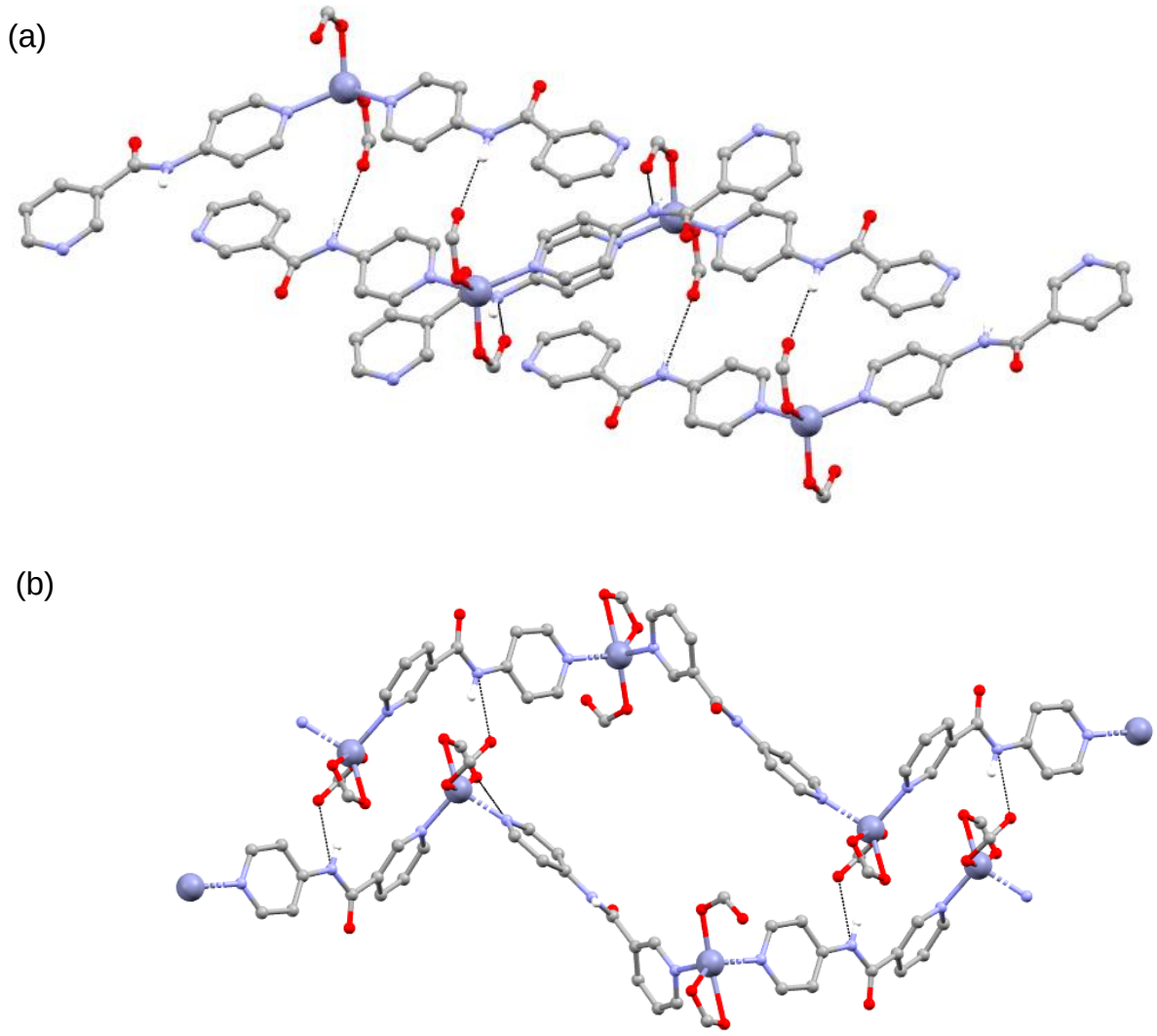

Figure S4: Hydrogen bonding interactions (dotted lines) observed in the zinc(II) SCMs: (a) **3** and (b) **4** (phenyl moiety of the benzoate and the hydrogen atoms except for the donor atoms are were omitted for clarity).

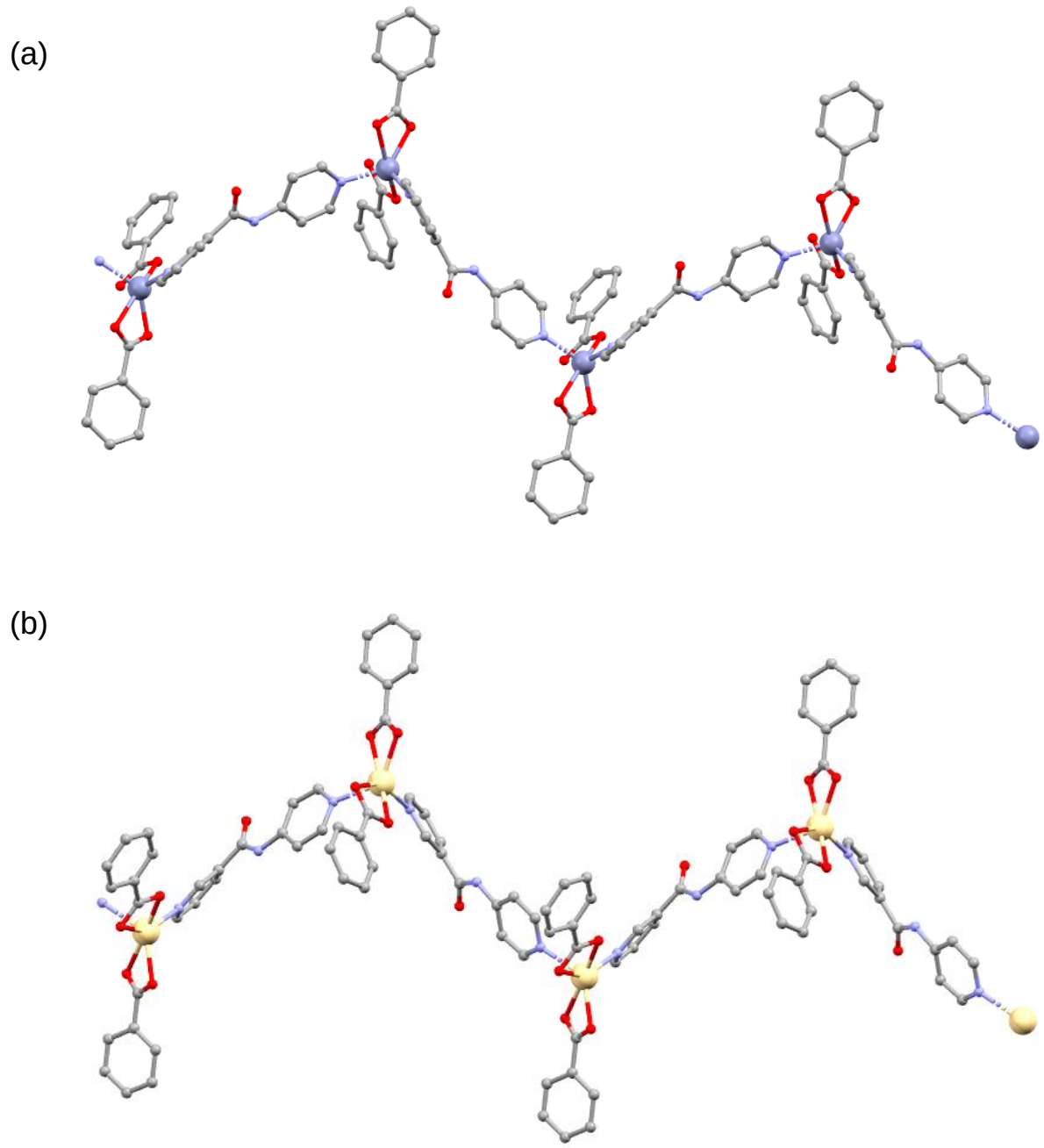

Figure S5: Molecular structure of the coordination polymers (a) **4** and (b) **6** showing the 1-D network (hydrogen atoms were omitted for clarity).

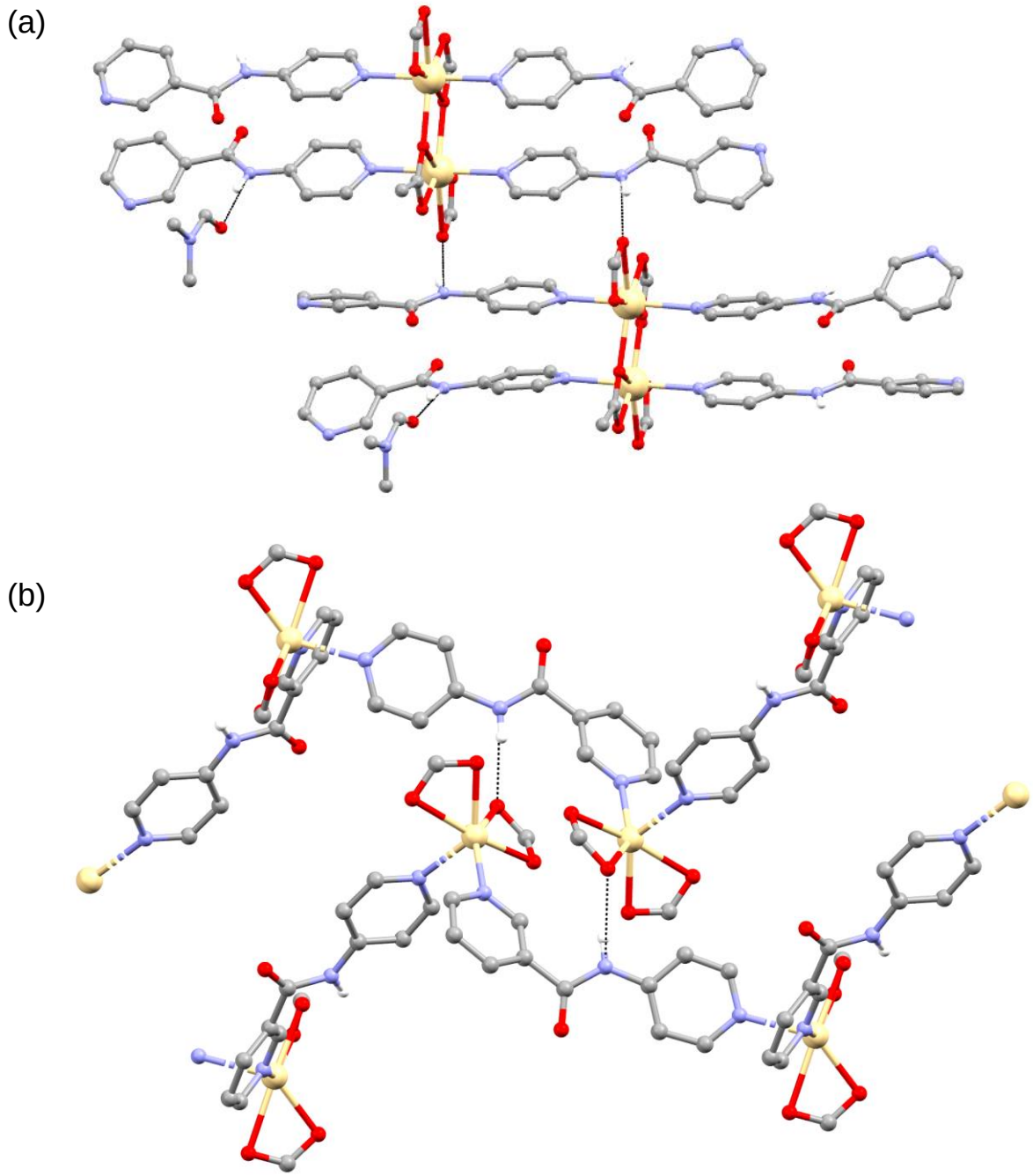

Figure S6: Hydrogen bonding interactions (dotted lines) observed in the cadmium(II) SCMs: (a) **5** and (b) **6** (phenyl moiety of the benzoate and the hydrogen atoms except for the donor atoms are were omitted for clarity).

Table S1: Crystal data

Crystal data	**1**	**1.S**	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{36}H_{28}N_6O_6Cu$	$C_{36}H_{28}N_6O_6Cu$	$C_{72}H_{60}N_{12}O_{14}Cu_2$	$C_{39}H_{35}N_7O_7Zn$	$C_{25}H_{19}N_3O_5Zn$	$C_{78}H_{70}N_{14}O_{14}Cd_2$	$C_{25}H_{19}N_3O_5Cd$
Color	Purple	Purple	Blue	Colorless	Colorless	Colorless	Colorless
Formula weight	704.18	704.18	1444.40	779.11	506.80	1652.28	553.83
Crystal size (mm)	0.2x0.14x0.06	0.23x0.2x0.05	0.16x0.14x0.02	0.2x0.08x0.06	0.31x0.12x0.07	0.22x0.12x0.075	0.27x0.11x0.02
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	P_{-1}	$C_{2/c}$	$P2_1/c$	P_{-1}	$P2_1/n$	P_{-1}	$P2_1/n$
a (Å)	8.3460(6)	18.9445(5)	18.8516(4)	11.3277(12)	12.3027(3)	15.4400(12)	12.5377(5)
b (Å)	10.1680(8)	8.0644(2)	12.1741(3)	11.9052(13)	11.5304(3)	15.8539(12)	11.7553(4)
c (Å)	10.7139(9)	25.7527(7)	15.2361(4)	14.2976(16)	15.6293(4)	16.7878(14)	15.6731(6)
α (°)	97.407(3)	90	90	72.605(3)	90	69.068(2)	90
β (°)	90.984(2)	106.5410(10)	110.1010(10)	82.496(3)	94.3390(10)	88.466(3)	97.0200(10)
γ (°)	109.905(2)	90	90	85.032(3)	90	79.660(2)	90
Volume (Å^3)	845.93(12)	3771.57(17)	3283.71(14)	1821.9(3)	2210.74(10)	3772.7(5)	2292.65(15)
Z	1	4	2	2	4	2	4
$D_{calc.}$ (g/cm^3)	1.382	1.240	1.461	1.420	1.523	1.454	1.605
F(000)	363	1452	1492	808	1040	1688	1112
μ K_α (mm^{-1})	μMoK_α = 0.700	μCuK_α = 1.229	μCuK_α = 1.449	μMoK_α = 0.735	μCuK_α = 1.916	μMoK_α = 0.638	μCuK_α = 7.991
Temperature (K)	296(2)	130(2)	296(2)	150(2)	131(2)	295(2)	296(2)
Reflections collected/ unique/observed [I>2σ(I)]	32635/3885/ 3353	31534/4016/ 3893	60323/7017/ 5705	81501/9870/ 7742	61911/4648/ 4618	137725/16722/ 10995	47312/4914/ 4571
Data/restraints/parameters	3885/0/ 223	4016/0/223	7017/0/ 459	9870/0/489	4648/0/307	16722/0/987	4914/0/307
Goodness of fit on F^2	1.074	1.155	1.072	1.040	1.059	1.025	1.067
Final R indices [I>2σ(I)]	R_1 = 0.0352 wR_2 = 0.0847	R_1 = 0.0394 wR_2 = 0.0932	R_1 = 0.0464 wR_2 = 0.1054	R_1 = 0.0399 wR_2 = 0.0784	R_1 = 0.0250 wR_2 = 0.0657	R_1 = 0.0418 wR_2 = 0.0751	R_1 = 0.0232 wR_2 = 0.0565
R indices (all data)	R_1 = 0.0477 wR_2 = 0.0878	R_1 = 0.0404 wR_2 = 0.0938	R_1 = 0.0605 wR_2 = 0.1119	R_1 = 0.0629 wR_2 = 0.0854	R_1 = 0.0252 wR_2 = 0.0658	R_1 = 0.0885 wR_2 = 0.0880	R_1 = 0.0254 wR_2 = 0.0577

Table S2: Hydrogen-bonding table

1						
No	Donor–H···Acceptor	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/°	Symmetry operation
1	N(7)–H(7)···O(17)	0.86	2.01	2.849(2)	163	-1+x,y,z
2	C(2)–H(2)···O(9)	0.93	2.37	3.238(3)	155	1-x,-y,2-z
3	C(5)–H(5)···O(17)	0.93	2.55	3.269(2)	134	-1+x,y,z
4	C(6)–H(6)···N(12)	0.93	2.62	3.489(3)	155	1+x,1+y,z
5	C(15)–H(15)···O(17)	0.93	2.36	3.256(2)	160	-1+x,y,z
1.S						
No	Donor–H···Acceptor	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/°	Symmetry operation
1	N(7)–H(7)···O(17)	0.88	1.99	2.844(2)	162	x,1+y,z
2	C(3)–H(3)···O(17)	0.95	2.53	3.240(2)	132	x,1+y,z
3	C(6)–H(6)···O(9)	0.95	2.38	3.280(2)	159	1/2-x,1/2-y,1-z
4	C(11)–H(11)···O(17)	0.95	2.34	3.257(2)	161	x,1+y,z
2						
No	Donor–H···Acceptor	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/°	Symmetry operation
1	N(7)–H(7)···O(41)	0.86	2.12	2.951(3)	161	1-x,-1/2+y,3/2-z
2	N(22)–H(22)···O(49)	0.86	2.07	2.901(3)	161	x,y,z
3	O(49)–H(49A)···N(12)	0.81(4)	2.01(4)	2.811(4)	169(4)	-1+x,y,-1+z
4	O(49)–H(49B)···O(9)	0.82(5)	2.20(6)	2.944(3)	152(4)	1-x,1-y,1-z
5	C(5)–H(5)···O(41)	0.93	2.46	3.239(3)	142	1-x,-1/2+y,3/2-z
6	C(14)–H(14)···N(29)	0.93	2.45	3.322(4)	157	1+x,-1+y,1+z
7	C(15)–H(15)···O(41)	0.93	2.35	3.267(3)	169	1-x,-1/2+y,3/2-z
8	C(18)–H(18)···O(49)	0.93	2.58	3.289(4)	133	x,y,z
9	C(26)–H(26)···O(49)	0.93	2.43	3.265(4)	150	x,y,z
3						
No	Donor–H···Acceptor	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/°	Symmetry operation
1	N(7)–H(7)···O(32)	0.88	2.06	2.902(2)	160	-x,1-y,1-z
2	N(22)–H(22)···O(41)	0.88	2.06	2.904(2)	160	1-x,1-y,1-z
3	C(5)–H(5)···O(32)	0.95	2.36	3.141(2)	139	-x,1-y,1-z
4	C(6)–H(6)···O(49)	0.95	2.34	3.193(3)	149	x,y,z
5	C(15)–H(15)···O(32)	0.95	2.47	3.343(2)	152	-x,1-y,1-z
6	C(17)–H(17)···O(49)	0.95	2.31	3.174(3)	151	x,y,z
7	C(18)–H(18)···O(41)	0.95	2.38	3.164(2)	139	1-x,1-y,1-z

8	C(26)–H(26)···O(41)	0.95	2.47	3.236(2)	138	1-x,1-y,1-z
9	C(28)–H(28)···N(29)	0.95	2.59	3.471(3)	154	2-x,1-y,2-z
10	C(52)–H(52A)···O(40)	0.95	2.56	3.398(3)	143	x,1+y,z
4						
No	Donor–H···Acceptor	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/°	Symmetry operation
1	N(9)–H(9)···O(17)	0.88	2.50	3.1043(15)	126	1-x,1-y,1-z
2	N(9)–H(9)···O(26)	0.88	2.06	2.7830(15)	139	1-x,1-y,1-z
3	C(15)–H(15)···O(26)	0.95	2.50	3.2044(16)	131	1-x,1-y,1-z
4	C(29)–H(29)···O(17)	0.95	2.54	3.3451(17)	143	1-x,1-y,1-z
5						
No	Donor–H···Acceptor	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/°	Symmetry operation
1	N(7)–H(7)···O(97)	0.86	2.06	2.905(4)	165	x,y,z
2	N(22)–H(22)···O(79)	0.86	2.17	2.994(3)	160	x,y,z
3	N(55)–H(55)···O(102)	0.86	1.99	2.830(5)	167	1+x,y,z
4	N(70)–H(70)···O(31)	0.86	2.06	2.857(3)	153	x,y,z
5	C(5)–H(5)···O(97)	0.93	2.46	3.232(4)	141	x,y,z
6	C(15)–H(15)···O(97)	0.93	2.35	3.161(4)	146	x,y,z
7	C(18)–H(18)···O(79)	0.93	2.56	3.308(4)	138	x,y,z
8	C(26)–H(26)···O(79)	0.93	2.34	3.257(4)	170	x,y,z
9	C(53)–H(53)···O(102)	0.93	2.53	3.254(5)	134	1+x,y,z
10	C(63)–H(63)···O(102)	0.93	2.48	3.180(5)	132	1+x,y,z
11	C(66)–H(66)···O(31)	0.93	2.60	3.278(4)	130	x,y,z
12	C(83)–H(83)···O(9)	0.93	2.53	3.235(4)	133	1-x,1-y,1-z
13	C(98)–H(98)···O(24)	0.93	2.47	3.354(6)	159	1-x,1-y,1-z
14	C(103)–H(103)···O(72)	0.93	2.54	3.417(6)	157	1-x,-y,1-z
6						
No	Donor–H···Acceptor	D–H/Å	H···A/Å	D···A/Å	∠D–H···A/°	Symmetry operation
1	N(9)–H(9)···O(16)	0.86	2.08	2.900(2)	158	1-x,1-y,1-z
2	C(20)–H(20)···O(25)	0.93	2.54	3.363(3)	147	1-x,1-y,1-z

3. X-ray powder diffraction

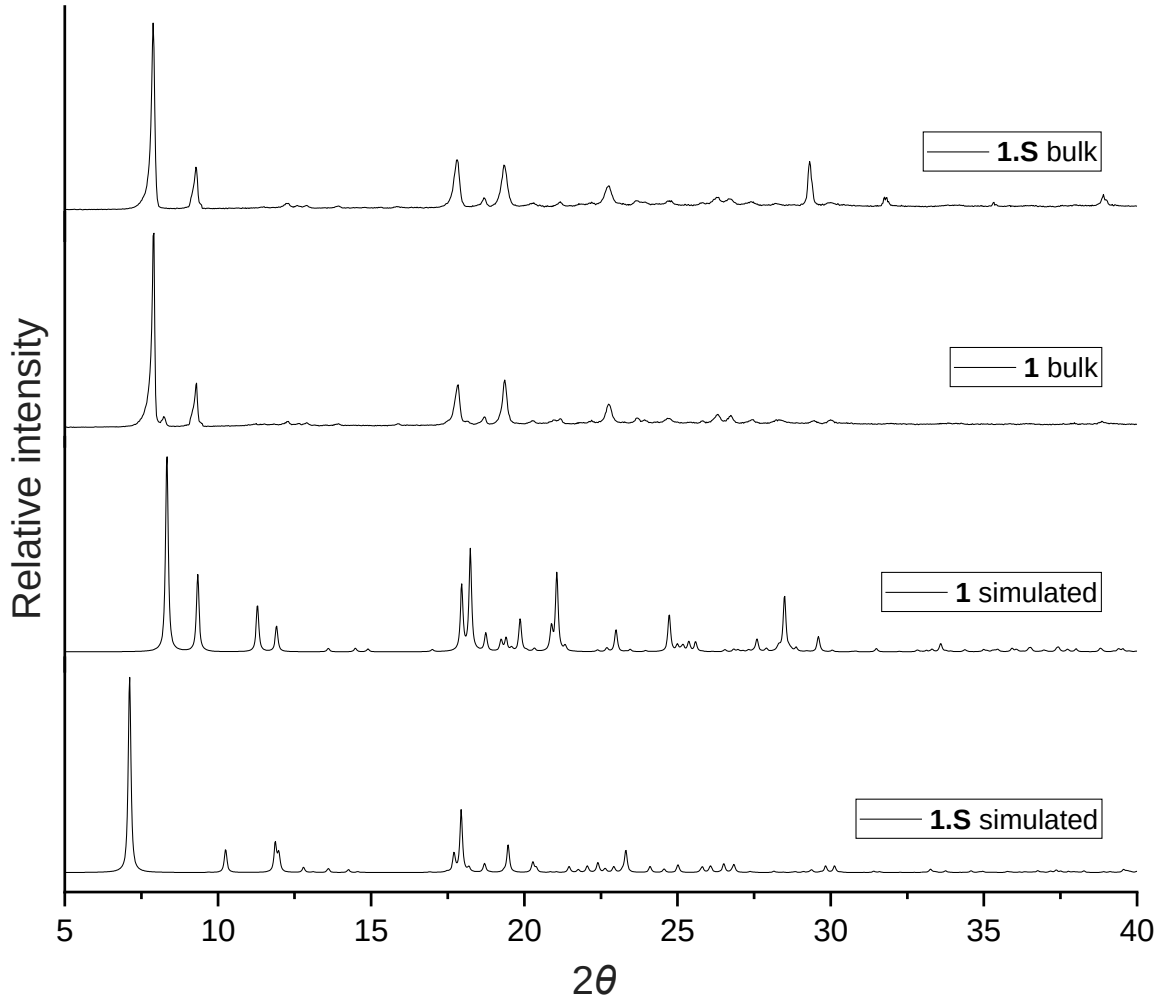

Figure S7: Comparison of XRPD pattern of complex **1** and **1.S** simulated and as synthesized.

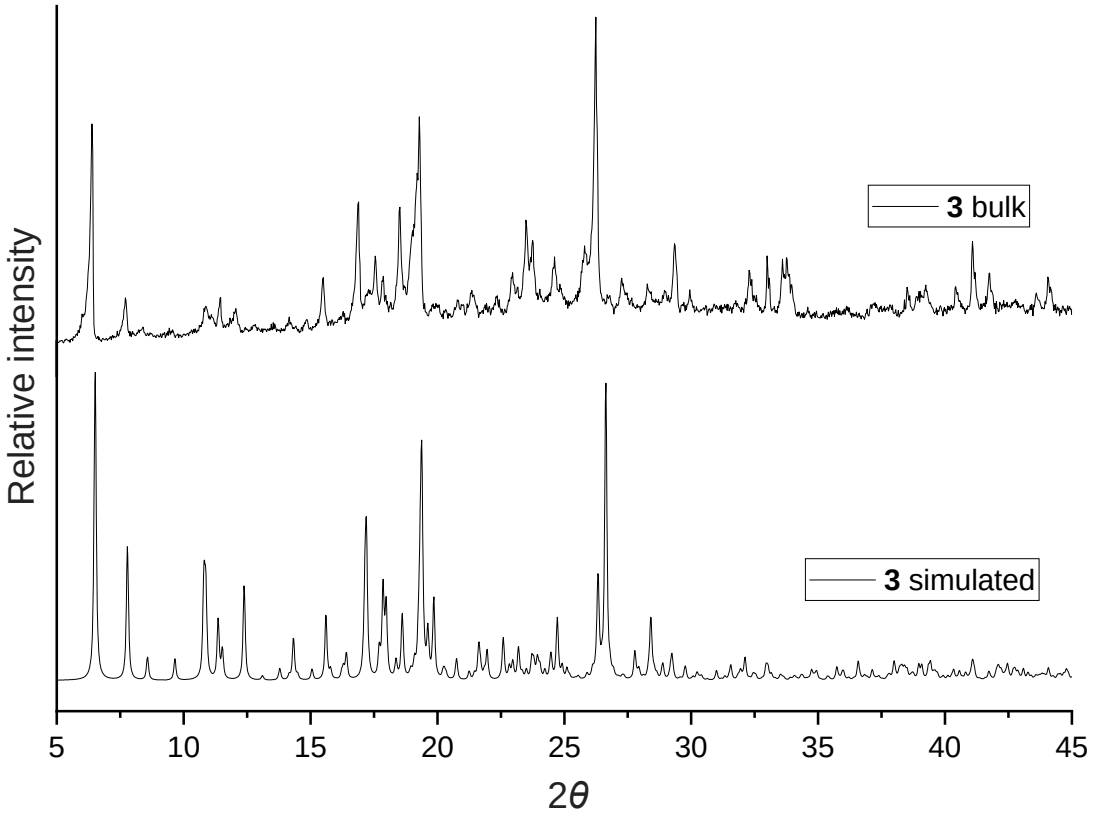

Figure S8: Comparison of XRPD pattern of complex **3** simulated and as synthesized.

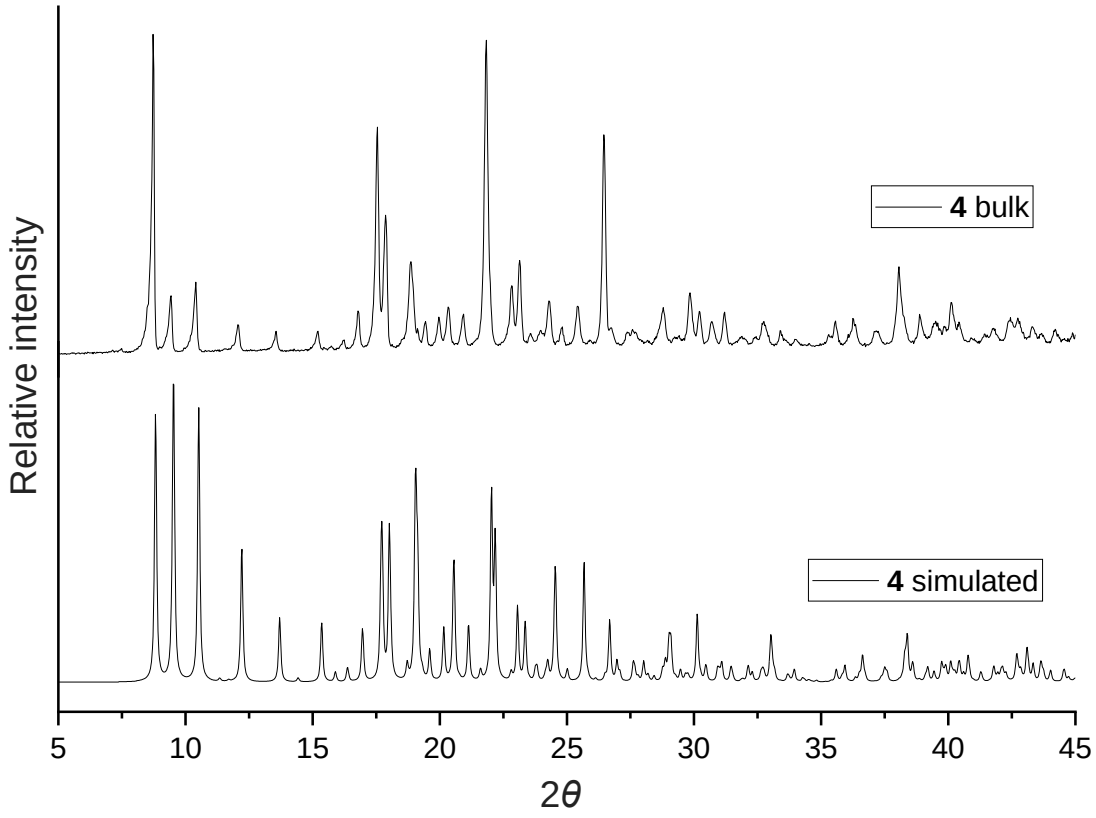

Figure S9: Comparison of XRPD pattern of coordination polymer **4** simulated and as synthesized.

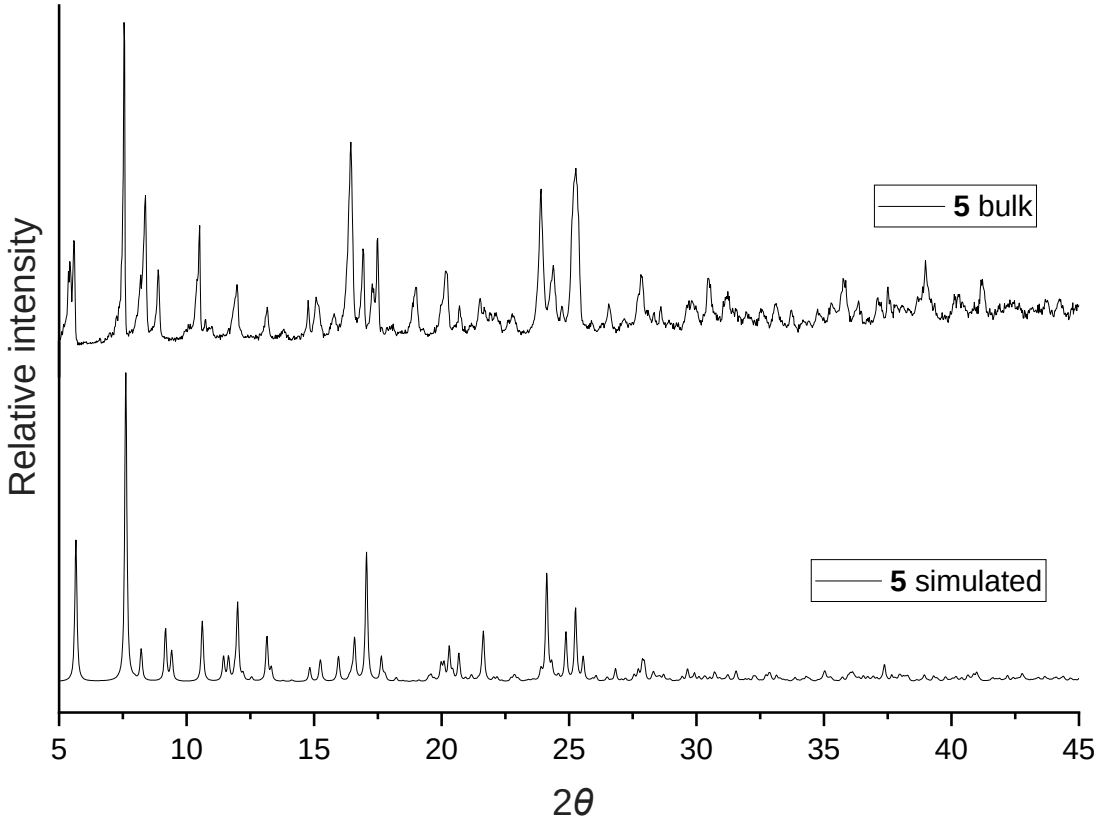

Figure S10: Comparison of XRPD pattern of complex **5** simulated and as synthesized.

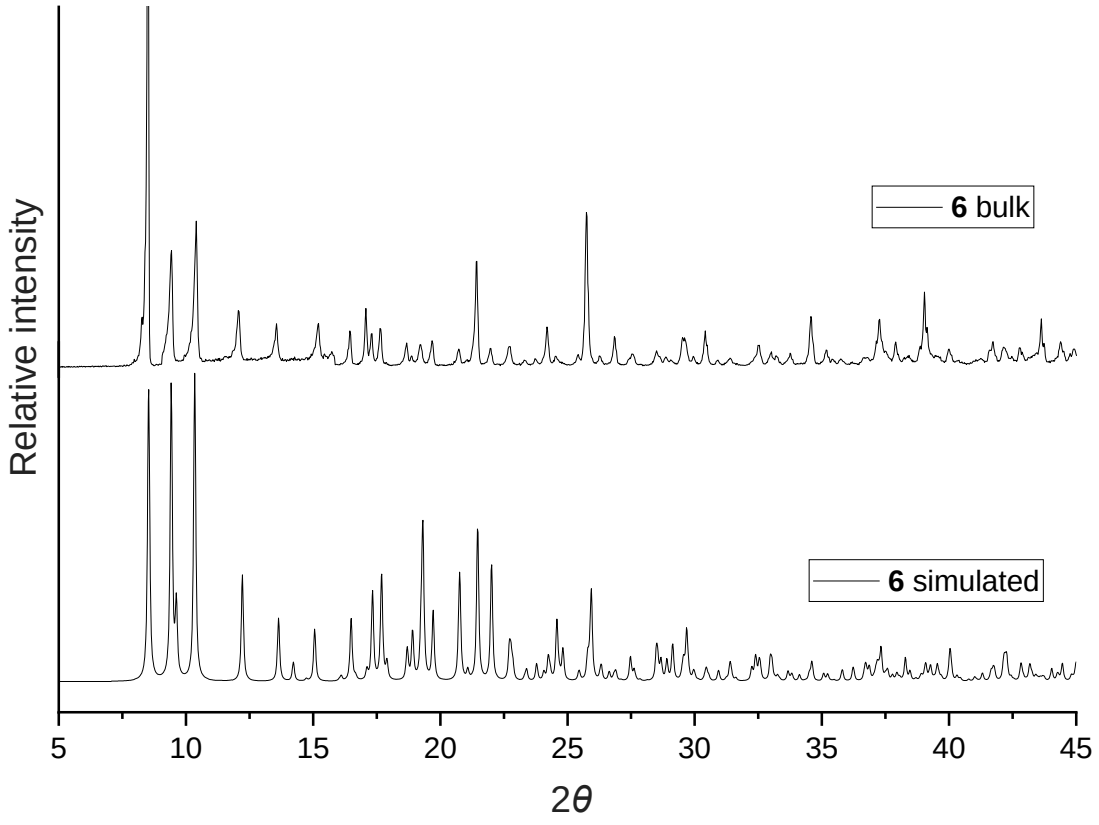

Figure S11: Comparison of XRPD pattern of coordination polymer **6** simulated and as synthesized.

4. Hirshfeld surface analysis

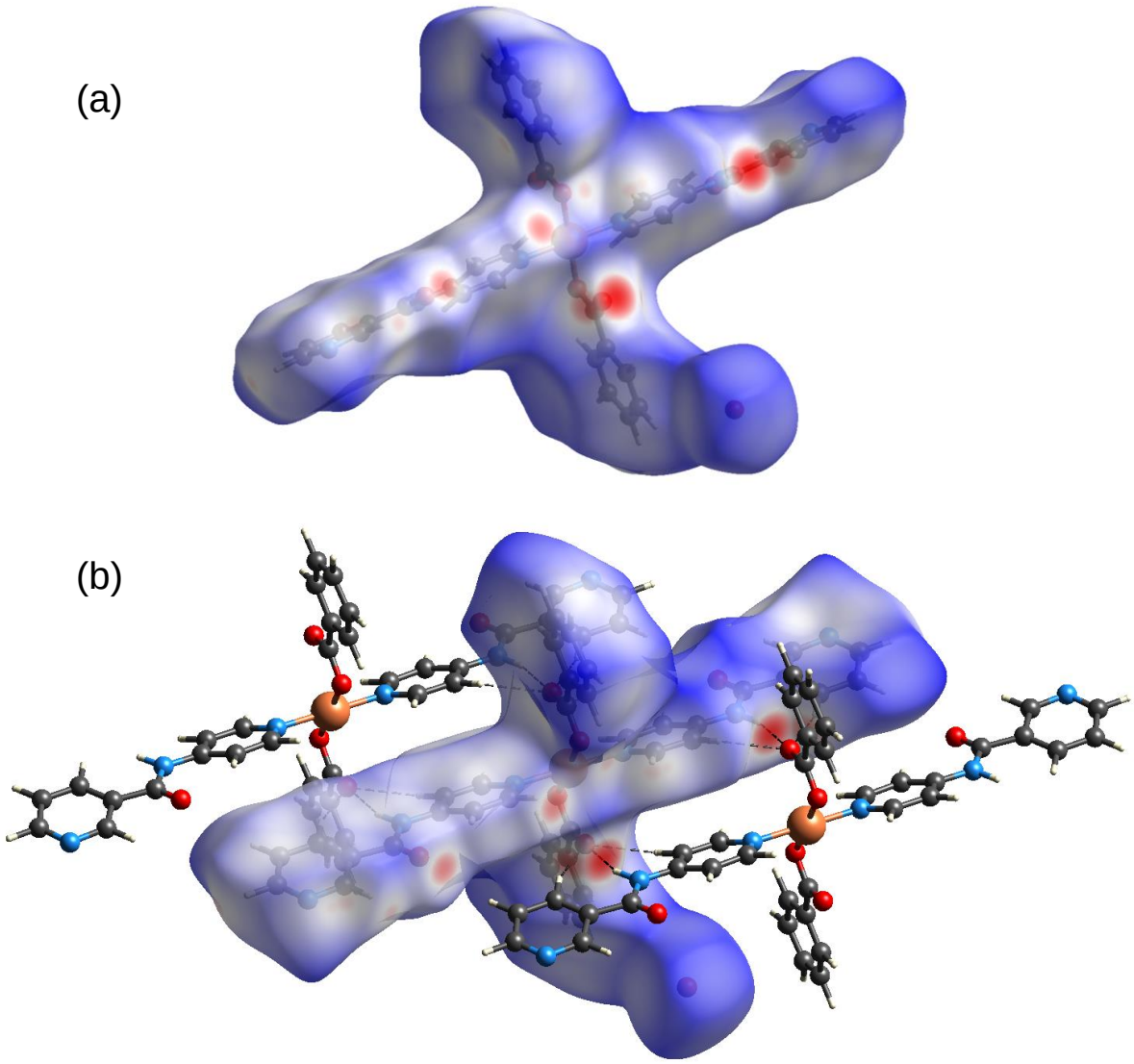

Figure S12: Hirshfeld surface analysis plotted on the d_{norm} maps of **1.S** (with unrefined solvent molecule) (a) single molecule and (b) three molecule aggregation showing the close contacts.

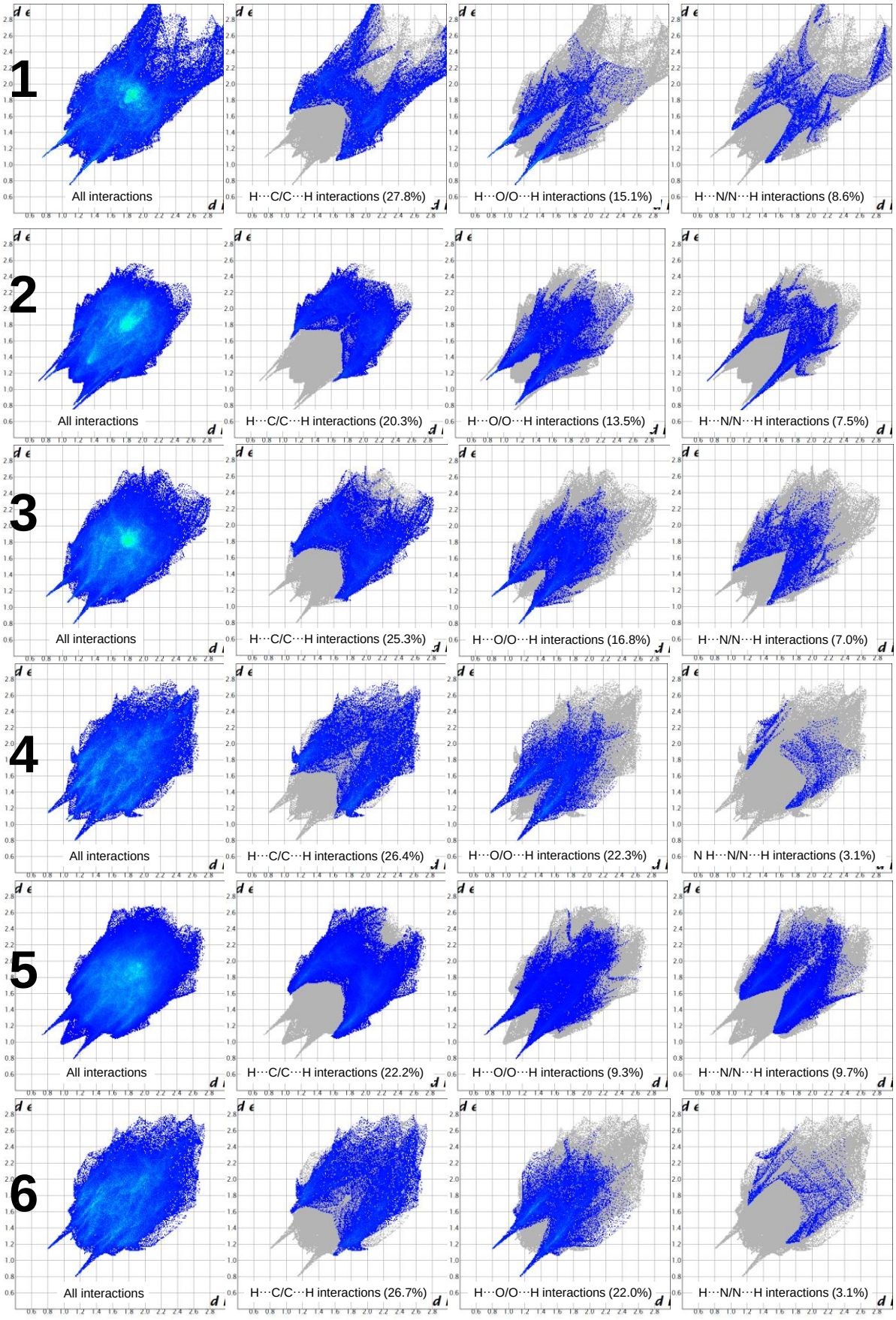

Figure S13: The overall two-dimensional fingerprint plots of the SCMs **1**-**6** and the percentage contributions from the specific non-bonding interactions.

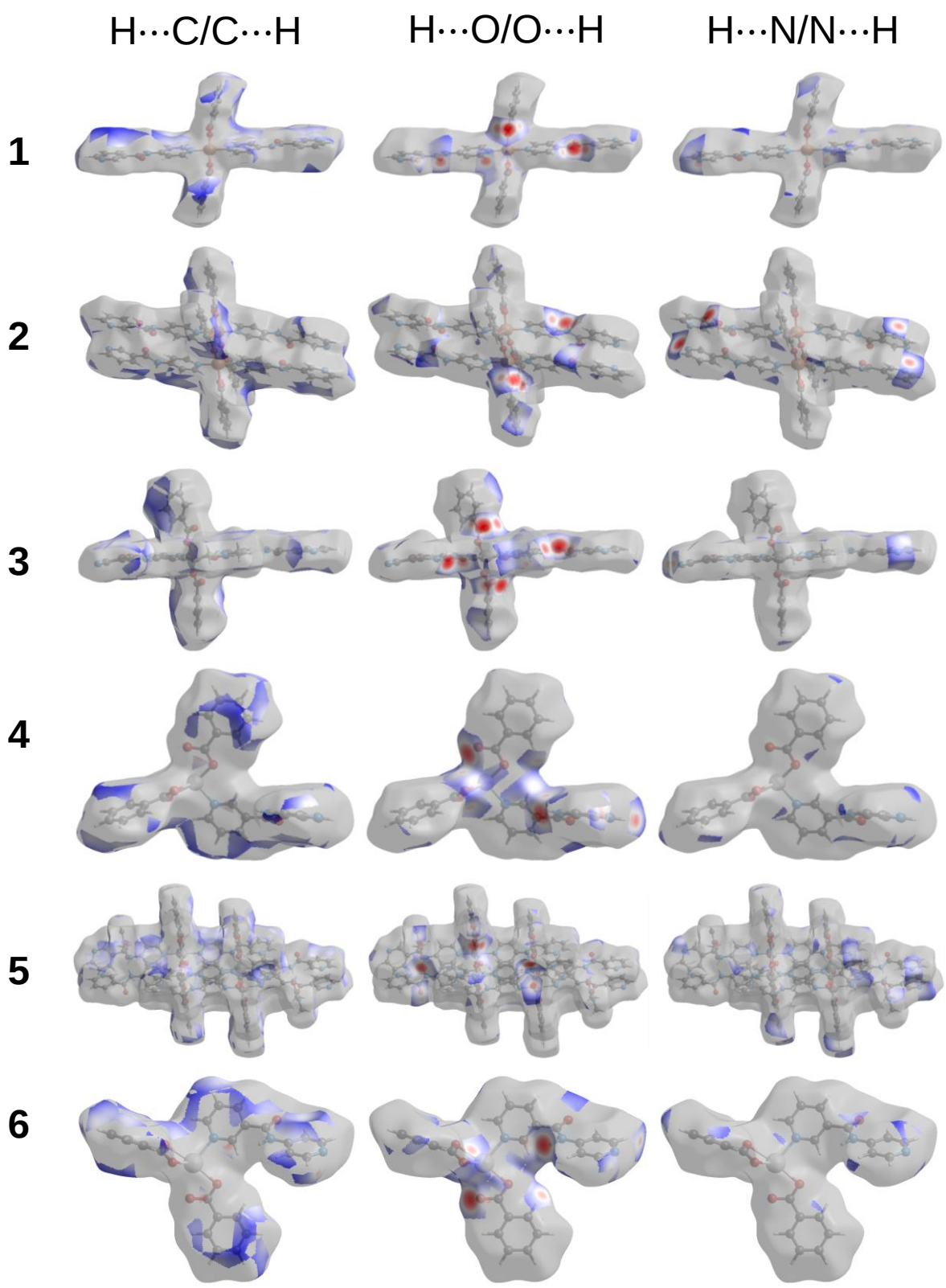

Figure S14: Hirshfeld surface analysis of the SCMs **1**-**6** based on the specific non-bonding interactions.

5. Luminescence

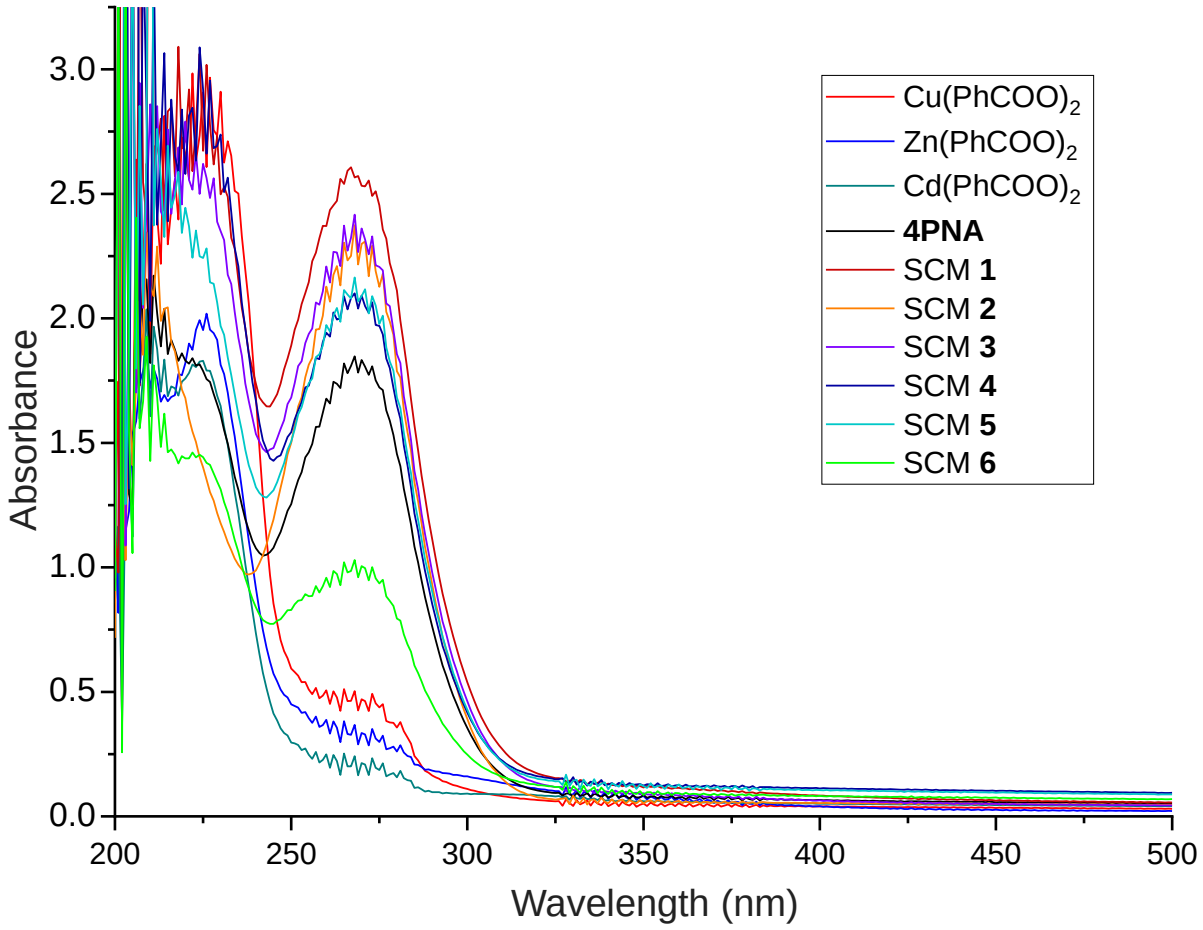

Figure S15: UV-vis absorbance spectra of the metal benzoates, **4PNA** ligand and SCMs **1**-**6** in MeCN at room temperature (10^{-4} M concentration).

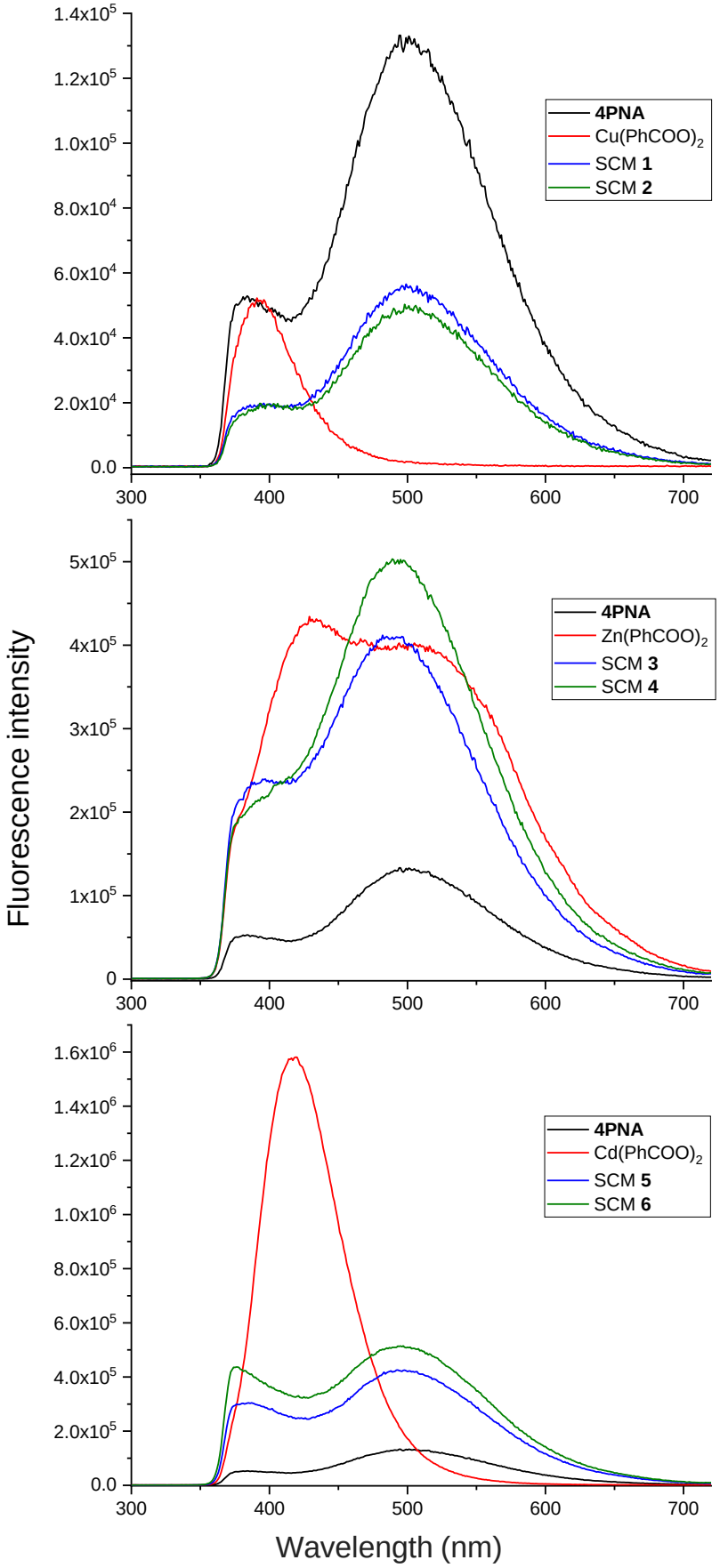

Figure S16: Comparison of fluorescence intensity of the SCMs with respect to corresponding metal benzoates and **4PNA** ligand in MeCN at room temperature (λ_{ex}= 295 nm).