Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

pH dependent synthesis of Zn(II) and Cd(II) coordination polymers with dicarboxyl-functionalized arylhydrazone of barbituric acid: Photoluminescence properties and catalysts for Knoevenagel condensation

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1. X-ray analysis

Table S1. Crystal data and structure refinement details for compounds **1-4**.

Identification name	**1**	**2**	**3**	**4**
Formulae	$C_{12}H_{10}N_4O_9Zn$	$C_{12}H_{10}CdN_4O_9$	$C_{12}H_{18}N_4O_{13}Zn$	$C_{12}H_{20}CdN_4O_{14}$
Mol. wt.	419.61	466.64	491.67	556.72
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P-1	P-1	$P2_1/c$	C2/c
Temperature /K	296	296	296	296
Wavelength /Å	0.71073	0.71073	0.71073	0.71073
a /Å	7.7271(7)	7.8701(5)	7.5088(5)	22.127(4)
b /Å	9.6737(8)	10.0231(6)	13.6816(9)	15.583(4)
c /Å	10.9425(10)	10.5151(7)	18.8063(12)	14.931(3)
α/°	69.740(3)	107.894(2)	90	90
β/°	87.236(2)	91.326(3)	96.493(3)	106.340(10)
γ/°	67.112(3)	113.088(2)	90	90
V/ Å^3	703.38(11)	716.27(8)	1919.6(2)	4940.4(18)
Z	2	2	4	8
Density/Mgm^{-3}	1.981	2.164	1.701	1.497
Abs. Coeff. /mm^{-1}	1.813	1.590	1.357	0.950
F(000)	424	460	1008	2240
Refl. collected	6693	11614	32059	34149
Refl. unique	2528	2899	3947	4726
Max. 2θ/°	25.344	26.394	26.408	25.909
Ranges (h, k, l)	-9 <= h <= 9	-9 <= h <= 9	-9 <= h <= 9	-26 <= h <= 27

	-11 <= k <= 11 -13 <= l <= 13	-12 <= k <= 12 -13 <= l <= 13	-17<= k <= 17 -23 <= l <= 23	-18<= k <= 18 -18 <= l <= 18
Complete to 2θ (%)	97.9	98.6	99.9	98.0
Refl. with I > 2σ(I)	2148	2808	2844	3059
Data/ Restraints/Parameters	2528/0/ 235	2899/0/235	3947/6/289	4726/0/ 253
Goof (F^2)	1.090	1.132	1.048	1.053
R1 [I > 2s(I)]	0.0381	0.0302	0.0444	0.0580
wR2 [I > 2s(I)]	0.0972	0.0768	0.1015	0.1601
R1 [all data]	0.0475	0.0310	0.0768	0.0898
wR2 [all data]	0.1013	0.0775	0.1156	0.1734

Table S2. Hydrogen bond geometry (Å, °) in compounds **1-4.**

Compound	D-H---A	D-H (Å)	H···A (Å)	D···A (Å)	<D−H···A(°)	Symmetry
1	O8−H8A···O7	0.96	2.20	3.125(3)	160.7	x+1, y+1, z
	O8−H8B··· O5	0.96	2.62	3.159(4)	115.6	x+1, y, z
	O8−H8B··· O6	0.96	2.18	2.981(3)	140.5	-x+1, -y+1, -z
	N4−H4N···O6	0.86	1.96	2.824(3)	178.7	-x, -y, -z
	O9−H9A···O2	0.96	1.91	2.789(4)	151.4	-x+2, -y+1, -z+1
	O9−H9B···O7	0.96	1.90	2.703(4)	139.8	-x+2, -y, -z+1
	N3−H3N···O2	0.86	2.03	2.767(4)	143.0	-
	N1−H1N···O5	0.86	2.03	2.680(4)	131.7	-x+1, -y+1, -z
2	N1−H1N···O9	0.86	2.49	3.178(3)	137.0	x-1, y, z
	N1−H1N···O5	0.86	2.14	2.742(3)	126.7	-
	O8−H8A···O7	0.96	2.09	2.684(3)	118.3	-x+2, -y+1, -z+1
	O8−H8B···O1	0.96	1.84	2.788(3)	169.2	-x+2, -y, -z+1
	O9−H9A···O8	0.96	2.01	2.952(4)	167.2	-x+3, -y, -z+1
	O9−H9B···O6	0.96	1.93	2.875(3)	167.6	-x+1, -y, -z
	N3−H3N···O1	0.86	2.27	2.994(3)	142.4	-x+1, -y, -z
	N3−H3N···O5	0.86	2.60	3.203(4)	127.9	-x, -y, -z
	N4−H4N···O6	0.86	2.03	2.887(3)	173.8	-x, -y+1, -z
3	O11−H11B···O1	0.88	1.88	2.762(4)	176.0	x, y+1, z
	O11−H11A···O2	0.88	1.93	2.798(4)	169.0	-x+2, -y, -z+1
	O12−H12A···O3	0.93	1.83	2.761(4)	178.0	-x+2, y+1/2, -z+3/2
	O12−H12B···O6	0.93	1.95	2.844(4)	159.0	-x+1, -y+1, -z+1
	O13−H13B···O2	0.89	1.96	2.836(4)	169.0	-x+2, y+1/2, -z+3/2
	O13−H13A···O4	0.89	1.92	2.789(5)	164.0	-
	O8−H8B···O13	0.96	2.21	3.100(5)	153.4	-x+1, -y, -z+1
	O8−H8A···O11	0.96	2.38	3.208(4)	144.0	-x+1, y-1/2, -z+1/2
	O10−H10B···O4	0.96	1.99	2.951(4)	174.0	x-1, -y+1/2, z-1/2
	O10−H10A···O3	0.96	2.03	2.962(4)	164.3	-x+1, -y, -z+1
	O9−H9B···O13	0.96	2.13	3.027(5)	156.0	x, -y+1/2, z-1/2
	O9−H9A···O7	0.96	2.09	3.013(4)	160.2	x, -y+1/2, z-1/2

	N1–H1N···O5	0.86	1.91	2.590(3)	134.4	-
	N4–H4N···O11	0.86	2.06	2.866(4)	156.7	-x+1, -y+1, -z+1
	O3–H3o···O8	0.79	2.41	3.198(4)	170.0	-x+2, -y, -z+1
4	O9–H9B···O1	0.96	2.13	2.815(6)	127.2	-x, y, -z+1/2
	O9–H9A···O5	0.96	1.98	2.894(6)	159.2	-x+1/2, -y+1/2, -z+1
	O10–H10B···O4	0.96	2.61	3.367(7)	135.8	-x, -y+1, -z
	O10–H10A···O7	0.96	2.36	2.982(6)	122.3	-
	N4–H4···O11	0.86	2.07	2.899(7)	163.0	x-1/2, -y+3/2, z-1/2
	O8–H8B···O6	0.96	1.93	2.873(5)	165.7	-x+1/2, y-1/2, -z+1/2
	O8–H8A···O4	0.96	1.93	2.855(7)	161.3	-x, -y+1, -z
	O4–H4O···O11	0.82	2.00	2.722(6)	146.6	x-1, y, z-1
	N1–H1···O7	0.86	1.92	2.591(5)	134.0	-

Table S3. Selected bond distances (Å) and angles (°) for compounds **1-4.**

	Bond distances		Bond angles		Bond angles
1					
Zn1–O1	1.968(2)	<O4–Zn1–O3	130.17(10)	<O3–Zn1–O1	101.77(10)
Zn1–O3	1.964(2)	<O4–Zn1–O1	128.01(10)	<O3–Zn1–O8	90.61(10)
Zn1–O4	1.964(2)	<O4–Zn1–O9	89.29(12)	<O1–Zn1–O8	91.59(11)
Zn1–O9	2.095(3)	<O4–Zn1–O8	86.55(10)	<O1–Zn1–O9	91.15(13)
Zn1–O8	2.215(3)	<O3–Zn1–O9	91.89(11)	<O9–Zn1–O8	175.84(10)
2					
Cd1–O4	2.209(2)	<O4–Cd1–O2	134.38(8)	<O2–Cd1–O3	93.80(9)
Cd1–O2	2.231(2)	<O4–Cd1–O3	131.04(9)	<O4–Cd1–O8	84.19(9)
Cd1–O3	2.244(2)	<O2–Cd1–O8	95.51(10)	<O3–Cd1–O9	84.54(8)
Cd1–O8	2.347(2)	<O3–Cd1–O8	82.72(9)	<O8–Cd1–O9	157.90(9)
Cd1–O9	2.356(2)	<O4–Cd1–O9	90.71(8)	<O4–Cd1–O1	82.74(7)
Cd1–O1	2.525(2)	<O2–Cd1–O9	103.30(9)	<O2–Cd1–O1	54.66(8)
		<O3–Cd1–O1	145.66(8)	<O9–Cd1–O1	89.76(8)
		<O8–Cd1–O1	110.80(8)		
3					
Zn1–N3	2.010(3)	<N3–Zn1–O10	117.72(12)	<O10–Zn1–O9	104.37(16)
Zn1–O10	2.018(3)	<N3–Zn1–O8	109.47(12)	<O8–Zn1–O9	109.04(17)
Zn1–O8	2.021(3)	<N3–Zn1–O9	107.99(13)		
Zn1–O9	2.043(4)	<O10–Zn1–O8	107.91(13)		
4					
Cd1–N3	2.246(4)	<N3–Cd1–O10	107.07(17)	<O10–Cd1–O2	83.87(15)
Cd1–O10	2.284(5)	<N3–Cd1–O9	90.48(15)	<O9–Cd1–O2	84.06(15)
Cd1–O9	2.334(4)	<O10–Cd1–O9	93.5(2)	<O8–Cd1–O2	93.45(15)
Cd1–O8	2.348(5)	<N3–Cd1–O8	90.67(15)	<N3–Cd1–O1	116.15(14)
Cd1–O2	2.425(4)	<O10–Cd1–O8	93.04(19)	<O10–Cd1–O1	136.62(16)
Cd1–O1	2.450(4)	<O9–Cd1–O8	172.72(17)	<O9–Cd1–O1	89.77(16)
		<N3–Cd1–O2	168.10(14)	<O8–Cd1–O1	83.26(15)
		<O2–Cd1–O1	53.46(13)		

2. Catalysis

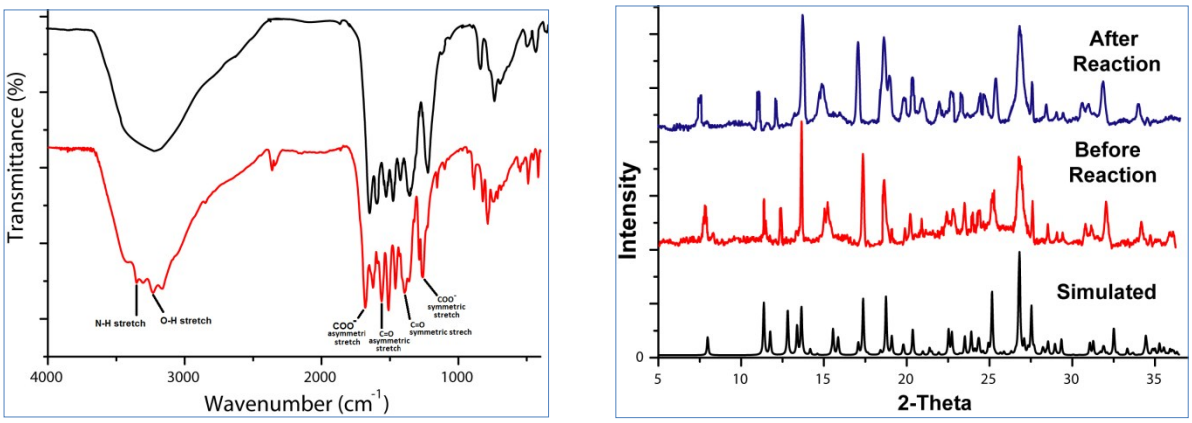

Figure S1. FT-IR spectra and X-ray powder diffractograms of catalyst **3** before (red line) and after (black line) the Knoevenagel condensation reaction.

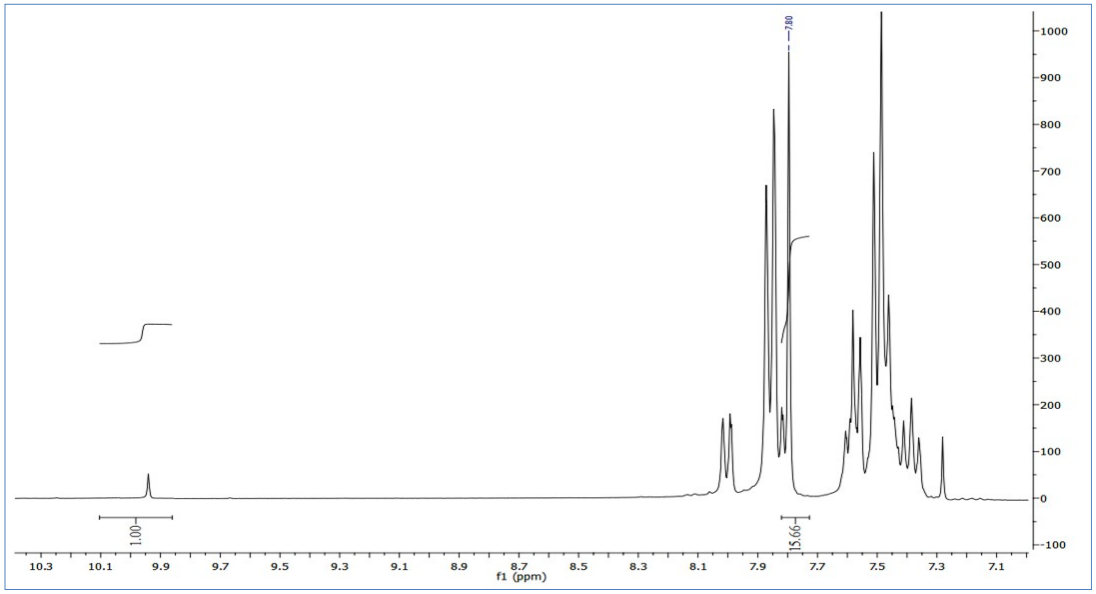

Figure S2. Example of integration in the ^{1}H-NMR spectrum for the determination of the product of the Knoevenagel condensation reaction of benzaldehyde with malononitrile (Table 1, entry 5)

*Calculation of the product yield in the Knoevenagel condensation reaction of benzaldehyde with malononitrile catalyzed by **3***

Total amount of compounds at the end (see Fig. S2):

Unreacted bezaldehyde (10.03 ppm) + 2-benzylidenemalononitrile (7.80 ppm) = 1 + 15.66=16.66

Yield of 2-benzylidenemalononitrile = 15.66/16.66 X 100 = 94.0 %

3. Thermogravimetric analyses

Thermogravimetric analyses were carried out under N_2, from room temperature to ca. 750 ˚C at a heating rate of 5˚C min^{-1}. Features of the thermal stability of complexes **1**-**4** are illustrated in Figure S3.

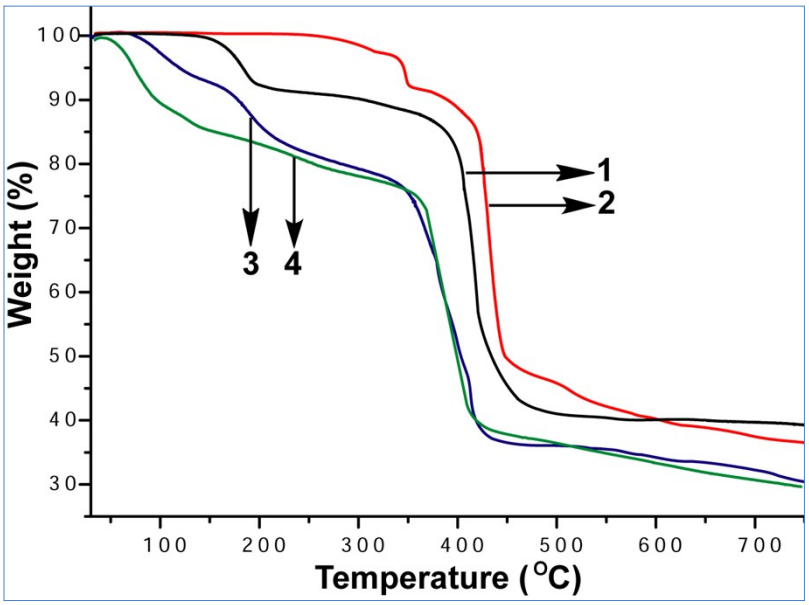

Figure S3. Thermogravimetric curves for **1**-**4**.

Compound **1** shows two step decompositions and loses 8.9% of its weight within 127-218˚C, most likely due to loss of two coordinated water molecules (calcd: 8.6%). The remaining material then decomposes from 351˚C until 527˚C. Similarly, compound **2** shows a weight loss of 7.5 % within 271-358˚C, corresponding to the release of two coordinated water molecules (calcd: 7.7%); above this temperature, further decomposition occurs until 750°C.

Compounds **3** and **4** show a similar type of decomposition. In compound **3**, a continuous weight loss of 21.5 % occurs in the temperature range of 87-320˚C, which accounts for the total removal of six water molecules (calcd: 21.9%). However, compound **4** loses seven water molecules between 44 and 350 °C (calcd: 22.9%). Above this temperature, both compounds decompose.

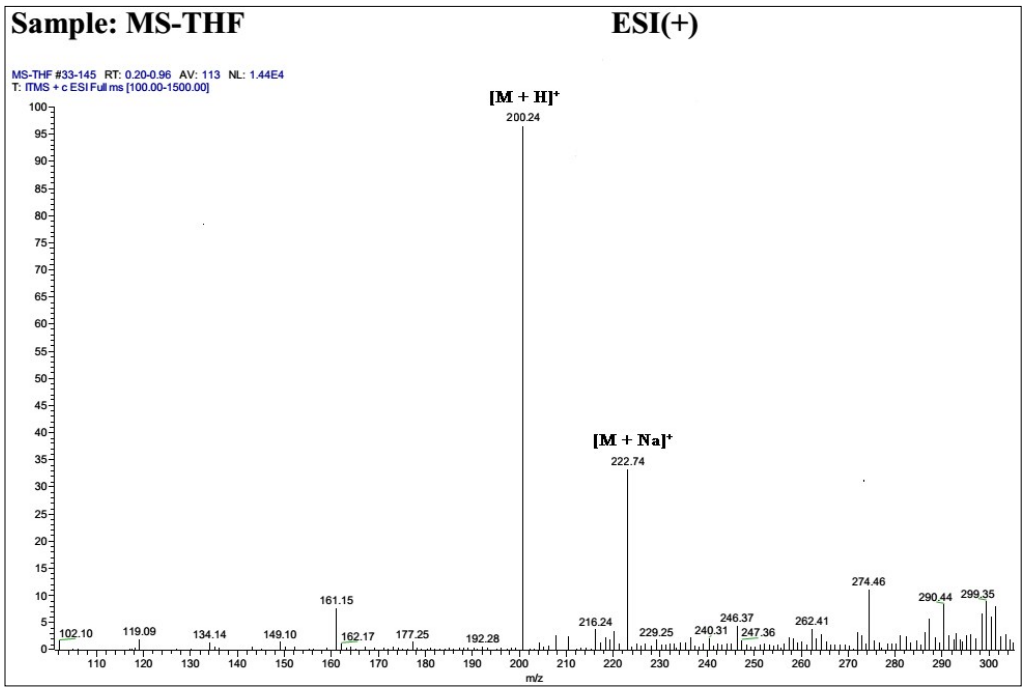

Figure S4. Mass spectrum of the Knoevenagel product 2-(4-nitrophenylmethylidene)malononitrile (Table 2, Entry 1).