

New Metal-Organic Frameworks Based on 2,5-Thiophenedicarboxylate and Pyridine- or Imidazole-Based Spacers: Syntheses, Topological Structures, and Properties

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X-Ray crystallography.

The crystallographic data for **1-7** were collected on a Bruker Smart Apex CCD area-detector diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K using the ω -scan technique. The diffraction data were integrated by using the *SAINTE* program,¹¹ which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the *SADABS* program.¹² The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the *SHELXL-97* crystallographic software package except for the disordered atoms.¹³ The hydrogen atom positions were generated theoretically, allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters. For

4, the distribution of peaks in the channels was chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining water molecule was removed by the SQUEEZE routine in PLATON. The residual electron density count amounted to 61 e per unit cell, corresponding to nearly 1 molecules of DMF and 2 molecules of H₂O, which was in agreement with the results of element analysis and TG. For **5**, the H atoms of free water molecules (O17, O18, O20) could not be found. For **6**, the H atoms of free water molecules (O8) and oxygen (O6) atom of free CH₃OH could not be located. To assist the refinement, several restraints were applied: for **2**, O-H bonds of coordinated water (O5) and free aqua (O6 and O7) were restrained by DFIX, the H...H distances were restrained by DANG; for **3**, possible hydrogen atoms of the solvent water molecules were found from difference Fourier maps, and then initially refined making use of DFIX restraints; For **5**, the free CH₃OH is disordered over two positions with site occupancy factors of 0.50/0.50, the C-O bonds of CH₃OH were restrained by DFIX; 'similar' Uij values of C91 and C91', O19 and O19' were obtained by using SIMU and ISOR instructions; the C1 and C2 atoms of imidazole group also exhibit disordered over two positions with site occupancy factors of 0.50/0.50, atoms C1, C1b, C2, C2b were restrained by SIMU, plus SADI restraints to make C1-C2 and C1b-C2b, N1-C1 and N1-C1b, N2-C2 and N2-C2b, C1-C3 and C1b-C3, C2-C3 and C2b-C3 distances approximately equal; for **6**, the free DMF is disordered over two positions with equal site occupancy factors, the C-N and C-O bonds of free DMF were restrained by DFIX, equal C34 and C34', C35 and C35', C36 and C36' displacement parameters were obtained by EADP instruction, the anisotropic displacement components of N7 and C36' along the line joining them are restrained to be equal by DELU; for **7**, atoms C26, C27 and O6 were restrained by ISOR, the C-N and C-O bonds of free DMF were restrained by DFIX. Crystallographic data and other pertinent information for **1-7** are summarized in Table S1, while the selected bond lengths and angles are listed in Table S2. More details on the crystallographic studies as well as atom displacement parameters are presented in the CIF.

Crystal Structures

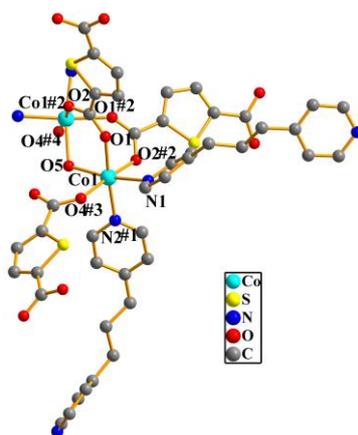


Figure S1 The dinuclear $[\text{Co}_2(\text{CO})_2(\mu^2\text{-H}_2\text{O})]$ in compound **1**. Symmetry codes : #1 $y, -1+x, 1-z$; #2 $y, x, 1-z$; #3 $1/2-x, -1/2+y, 3/2-z$; #4 $-1/2+y, 1/2-x, -1/2+z$.

Table S1. Crystal data and structure refinement for **1-7**.

	1	2	3	4	5	6	7
Formula	C ₃₈ H ₃₆ Co ₂ N ₄ O ₁₀ S ₂	C ₁₉ H ₂₂ CdN ₂ O ₇ S	C ₃₂ H ₃₆ N ₈ O ₁₀ S ₂ Zn ₂	C ₉₉ H ₈₁ Co ₄ N ₁₇ O ₂₄ S ₄	C ₉₁ H ₇₂ N ₁₆ O _{19.25} S ₃ Zn ₄	C ₁₄₆ H ₁₂₆ Cd ₄ N ₂₈ O ₂₂ S ₄	C ₅₄ H ₄₆ Co ₂ N ₁₄ O ₁₄ S ₃
Formula weight	890.71	534.87	887.55	2256.77	2055.42	3202.67	1329.12
Crystal system	Tetragonal	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P4₂2₁2</i>	<i>P2₁/c</i>	<i>P-1</i>	<i>P1</i>	<i>Pc</i>	<i>P2₁/c</i>	<i>Pbcn</i>
Flack parameter	0.01(3)			0.037(7)	0.373(9)		
<i>a</i> /Å	16.038(2)	10.5078(18)	9.4224(7)	11.196(3)	22.559(2)	10.6974(13)	22.9568(15)
<i>b</i> /Å	16.038(2)	18.163(3)	12.2481(9)	13.020(3)	9.9836(10)	37.268(5)	13.2642(9)
<i>c</i> /Å	15.787(3)	11.574(2)	18.7629(14)	16.520(4)	20.465(2)	9.4058(12)	19.3659(13)
<i>α</i> /°	90	90	108.9110(10)	84.072(3)	90	90	90
<i>β</i> /°	90	104.499(2)	91.0620(10)	85.182(3)	103.164(2)	101.263(2)	90
<i>γ</i> /°	90	90	110.1020(10)	79.138(3)	90	90	90
<i>V</i> /Å ³	4060.7(11)	2138.6(6)	1903.0(2)	2347.2(10)	4488.0(7)	3677.6(8)	5897.0(7)
<i>Z</i>	4	4	2	1	2	1	4
<i>ρ</i> _{calcd} /g cm ⁻³	1.457	1.661	1.549	1.597	1.521	1.446	1.497
<i>μ</i> /mm ⁻¹	0.980	1.162	1.435	0.872	1.206	0.703	0.746
collected	29927	13422	13358	22151	33248	28810	50326
Reflections							
Unique	4440	3951	6617	16580	15523	7751	7115
reflections							
<i>R</i> ₁ [<i>I</i> > 2σ (<i>I</i>)]	0.0606	0.0455	0.0310	0.0281	0.0455	0.0574	0.0495
<i>wR</i> ₂ (all data)	0.1477	0.1378	0.1297	0.0922	0.1227	0.1287	0.1586

Table S2 Selected bond lengths (Å) and bond angles (deg) for **1-7**

1^a									
Co1–O1	2.077(3)	Co1–O5	2.166(3)	Co1–N1	2.225(5)	Co1–N2#1	2.186(5)	Co1–O2#2	2.080(3)
Co1–O4#3	2.098(3)	O2#2–Co1–O4#3	174.73(13)	O5–Co1–N1	169.90(15)	O1–Co1–N2#1	173.83(16)		
2^b									
Cd1–O1	2.404(5)	Cd1–O2	2.425(5)	Cd1–O5	2.3171	Cd1–N1	2.337(6)	Cd1–N2	2.340(6)
Cd1–O3#1	2.346(5)	Cd1–O4#1	2.598(5)	O1–Cd1–O2	53.97(17)	O3#1–Cd1–O4#1	53.06(16)	O1–Cd1–N1	133.14(18)
O4#1–Cd1–N1	138.80(17)	O5–Cd1–N2	161.8(2)						
3^c									
Zn1–O1	1.964(2)	Zn1–O5	1.988(2)	Zn1–N1	2.058(2)	Zn1–N3	2.003(3)	Zn2–O7	1.952(2)
Zn2–N5	2.020(3)	Zn2–N7	2.040(2)	Zn2–O3#1	1.968(2)	O1–Zn1–N1	96.13(10)	O5–Zn1–N3	110.67(10)
O5–Zn1–N1	109.07(10)	O1–Zn1–N3	130.73(11)	O7–Zn2–N5	118.93(10)	O3#1–Zn2–O7	108.00(8)	O3_d–Zn2–N7	111.78(10)
4^d									
Co1–O1	2.063(2)	Co1–O17	2.136(2)	Co1–O20	2.200(2)	Co1–N1	2.107(3)	Co1–N8#1	2.116(3)
Co1–O4#2	2.094(2)	Co2–O2	2.092(2)	Co2–O5	2.101(2)	Co2–O18	2.103(2)	Co2–O20	2.206(2)
Co2–N5	2.095(2)	Co2–N4#3	2.118(3)	Co3–O8	2.112(2)	Co3–O9	2.104(2)	Co3–N12#1	2.094(3)
Co3–N16#4	2.114(2)	Co3–O11#5	2.088(2)	Co4–O7	2.119(2)	Co4–O19	2.138(2)	Co4–O21	2.169(2)
Co4–N9	2.133(2)	Co4–N13	2.091(3)	Co4–O12#5	2.078(2)	O1–Co1–O4#2	175.90(9)	O20–Co1–N1	175.83(9)
O17–Co1–N8#1	177.24(9)	O2–Co2–N4#3	175.49(9)	O5–Co2–O18	173.49(9)	O20–Co2–N5	174.05(9)	O8–Co3–N12#1	170.37(9)
O9–Co3–O11#5	171.63(8)	O21–Co3–N16#4	172.94(9)	O12#5–Co4–N13	177.83(9)	O7–Co4–O19	177.30(9)	O21–Co4–N9	171.95(9)
5^e									
Zn1–O1	1.948(5)	Zn1–O5	1.924(5)	Zn1–N1	2.022(4)	Zn1–N5	1.969(4)	Zn2–N16	2.009(4)
Zn2–O7#1	1.947(4)	Zn2–O12#3	1.961(5)	Zn2–N12#4	2.026(4)	Zn3–O9	1.930(4)	Zn3–O10	1.994(4)
Zn3–N9	2.003(4)	Zn3–N13	2.003(5)	Zn4–O4	1.951(5)	Zn4–O9	1.911(4)	Zn4–N4#1	1.994(4)
Zn4–N8#2	2.005(4)	O1–Zn1–O5	102.43(19)	N1–Zn1–N5	111.13(19)	N12#4–Zn2–N16	109.44(19)	O7#1–Zn2–O12#3	106.5(2)
O10–Zn3–N13	101.7(2)	O9–Zn3–N9	110.5(2)	O4–Zn4–N8#2	102.19(18)	O9–Zn4–N4#1	118.10(18)		
6^f									
Cd1–O1	2.433(4)	Cd1–O2	2.454(3)	Cd1–N1	2.315(4)	Cd1–N3	2.367(4)	Cd1–N5	2.317(4)
Cd1–O3#1	2.552(3)	Cd1–O4#1	2.373(3)	O1–Cd1–O3#1	150.35(13)	O4#1–Cd1–N3	131.18(14)	N1–Cd1–N5	173.54(15)
7^g									
Co1–O1	2.158(2)	Co1–O2	2.274(2)	Co1–N1	2.141(2)	Co1–N5#1	2.141(2)	Co1–O3#2	2.027(2)
Co1–N3#3	2.101(2)	O1–Co1–O3#2	151.40(9)	O2–Co1–N3#3	153.15(8)	N1–Co1–N5#1	177.51(9)	O3#2–Co1–N3#3	114.41(9)

^aSymmetry codes for **1**: #1 y, -1+x, 1-z; #2 y, x, 1-z; #3 1/2-x, -1/2+y, 3/2-z

^bSymmetry codes for **2**: #1 1+x, y, z

^cSymmetry codes for **3**: #1 2+x, 1+y, z

^dSymmetry codes for **4**: #1 -1+x, -1+y, z; #2 -1+x, y, z; #3 -1+x, y, 1+z; #4 1+x, y, -1+z; #5 1+x, y, z

^eSymmetry codes for **5**: #1 x, y, 1+z; #2 -1+x, 1-y, -1/2+z; #3 1+x, 2-y, 1/2+z; #4 1+x, 2-y, 3/2+z

^fSymmetry codes for **6**: #1 1+x, y, z

^gSymmetry codes for **7**: #1 x, -1+y, z; #2 3/2-x, 1/2-y, -1/2+z; #3 1-x, 1-y, -z

PXRD

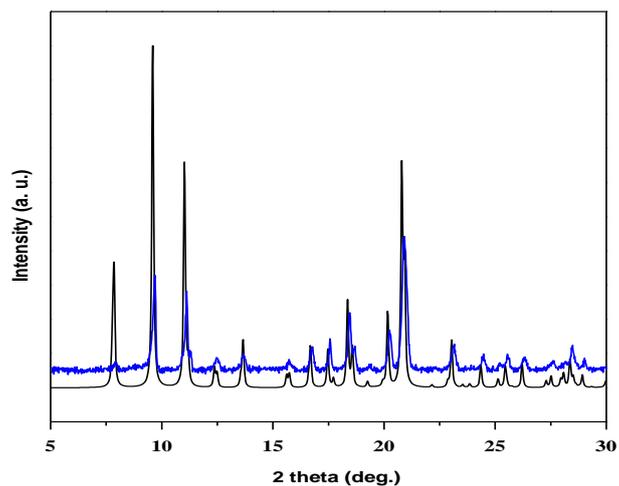


Figure S2 X-ray power diffraction diagram of the simulated spectra from single crystal data of **1** (black), compound **1** (blue).

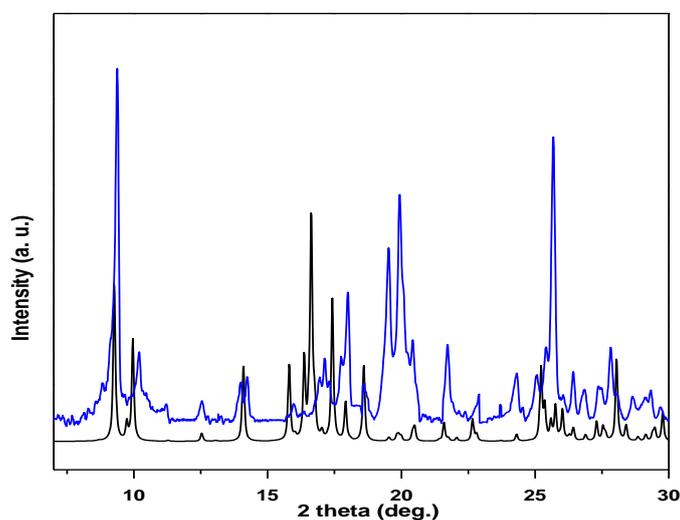


Figure S3 X-ray power diffraction diagram of the simulated spectra from single crystal data of **2** (black), compound **2** (blue).

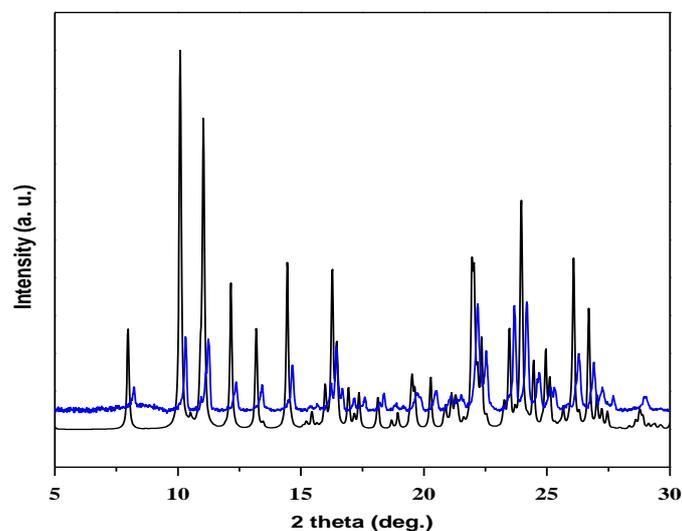


Figure S4 X-ray power diffraction diagram of the simulated spectra from single crystal data of **3** (black), compound **3** (blue).

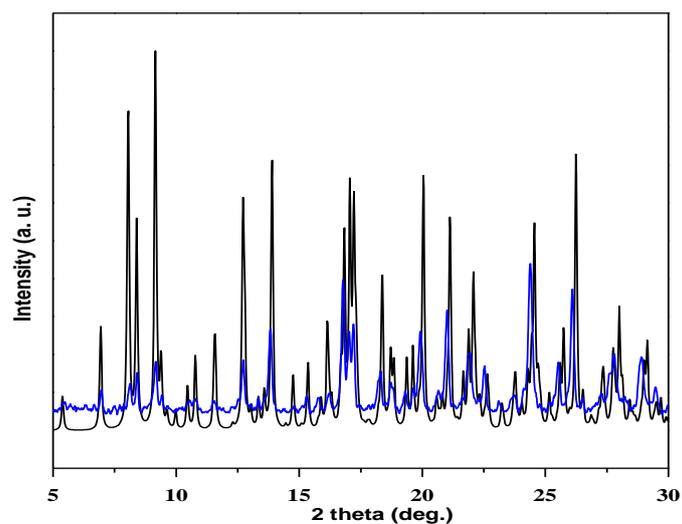


Figure S5 X-ray power diffraction diagram of the simulated spectra from single crystal data of **4** (black), compound **4** (blue).

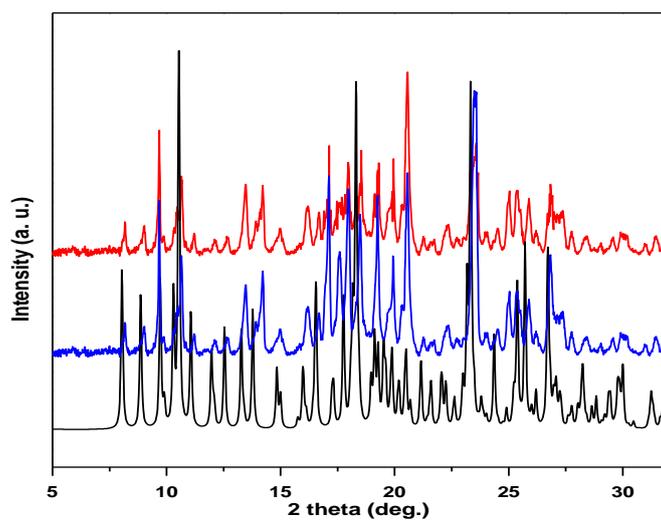


Figure S6 X-ray power diffraction diagram of the simulated spectra from single crystal data of **5** (black), compound **5** ((blue), **5** after photocatalysis process (red).

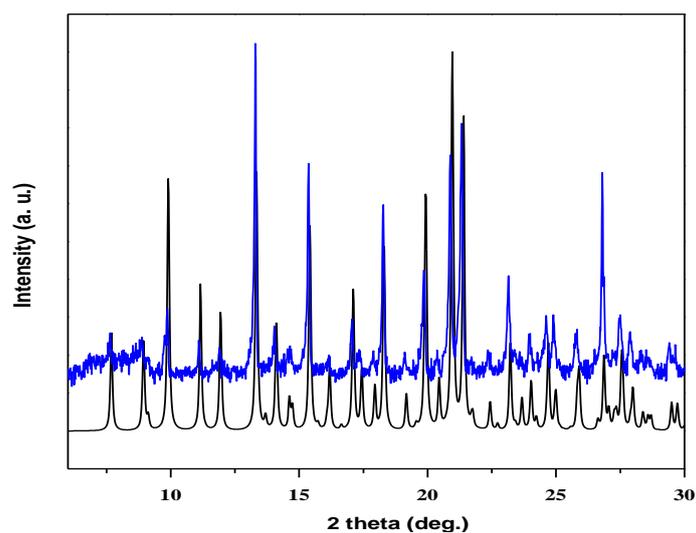


Figure S7 X-ray power diffraction diagram of the simulated spectra from single crystal data of **7** (black), compound **7** (blue).

TG

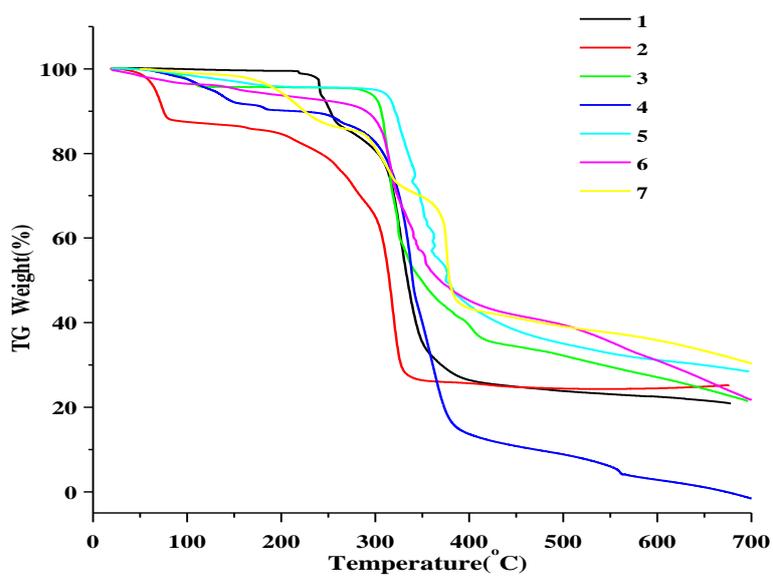


Figure S8 TG curves of compounds **1-7**.

Fluorescence Properties

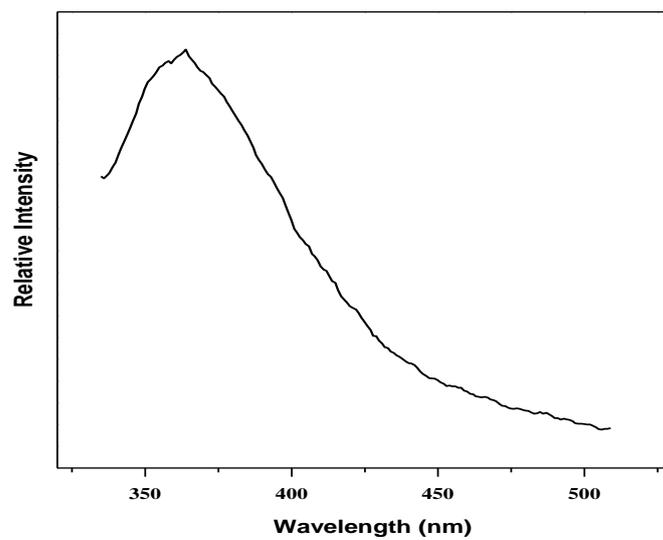


Figure S9 Fluorescent emission spectra of free ligand H₂tdc in solid state at room temperature, excited at 300 nm.