Supplementary Material (ESI) for CrystEngComm

Syntheses and Conversions of Dinuclear Cadmium(II) Compounds Containing N_2O/N_2O_2 Donor Tridentate/Tetradentate Asymmetrical Schiff Base Ligands

Hua-Cai Fang, Ying-Ying Ge, Yin Ying, Sheng-Run Zheng, Qing-Guang Zhan, Zheng-Yuan Zhou, Li Chen, and Yue-Peng Cai*

School of Chemistry and Environment, Key Lab of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, *Engineering Research Center of Materials and Technology for Electrochemical Energy Storage (Ministry of Education),, South China Normal University, Guangzhou, 510006, China*

Materials and physical measurements: All reagents were commercially available and used without further purification. Infrared spectra were obtained from KBr pellets on a Bruker TENSOR 27 Fourier transformation infrared spectrometer in the 400-4000 cm^{-1} region. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/M-2200T automated diffractometer. The luminescent spectra for the solid state were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5.0 nm.

Crystallographic Studies: X-ray diffraction data were collected on a Bruker Apex II diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 298 K. Absorption corrections were applied by using multi-scan program SADABS. All the structures were solved by direct methods and refined with full-matrix least-squares technique using SHELXTL. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms on organic ligands were generated by the riding mode (C-H 0.96 Å).

Syntheses of 1 and 1a. An ammount of 0.75 mmol $CdCl_2$ and 0.50 mmol of HL[1] were added to 15 mL of methanol, and the mixture was stirred for 30 min at room temperature/50°C. After filtration, the filtrate was kept at room temperature for several days to give colorless crystals **1**, and **1a** upon slow evaporation of the solvent. The crystals were filtered and dried in air. For **1**, yield: 57% (based on Cd). Found: C, 38.75; H, 5.23; N, 7.51. Anal. Calcd for $C_{24}H_{38}N_4O_4Cl_2Cd_2$: C, 38.80; H, 5.12; N, 7.54. IR (KBr, cm^{-1}): ν 3565(br, s), 2996 (m), 2965(s), 2893(s), 2799(s), 1634 (vs), 1597(s), 1539(s), 1471 (vs), 1446(vs), 1290 (vs), 1189(vs), 1150 (s), 1021 (vs), 900 (vs), 792(m), 765 (s), 676(m), 639 (m), 600(m), 571 (m), 528(m), 465 (w). For **1a**, yield: 50% (based on Cd). Found: C, 38.89; H, 4.57; N, 8.28. Anal. Calcd for $C_{22}H_{30}Cl_2N_4O_2Cd_2$: C, 38.93; H, 4.42; N, 8.26. IR (KBr, cm^{-1}): ν 3249-3207 (br, m), 2945 (m), 1653 (vs), 1463 (s), 1385 (w), 1279 (s), 1151 (m), 1040 (m), 897 (w), 761 (s), 641 (m), 569 (w), 475 (w).

Syntheses of 2 and 2a. The compounds **2** and **2a** were obtained using the same reaction procedure as described in compounds **1** and **1a** taking HL^2 in place of HL^1. The colorless crystals of **2** were isolated in about 52% yield (based on Cd). Found: C, 38.91; H, 5.01; N, 9.25. $C_{25}H_{38}Cl_2N_4O_5Cd_2$ calcd.: C, 38.95; H, 4.93; N, 9.27 %. IR (KBr, cm^{-1}): ν 3494-3692(br., w), 2958(m), 2980(m), 2841(m), 1637(vs), 1599(s), 1467(s), 1448(s), 1396(w), 1375(w), 1337(w), 1298(s), 1236(s), 1217(vs), 1082(s), 967(m), 936(m), 886(m), 848(m), 783(m), 744(s), 732(s), 629(w), 561(w), 476(w). For **2a**, 65% yield (based on Cd). Found: C, 38.88 H, 4.70; N, 7.54. $C_{24}H_{34}Cl_2N_4O_4Cd_2$ calcd.: C, 39.01; H, 4.61; N, 7.59 %. IR (KBr, cm^{-1}): ν 2925(m), 2875(w), 1634(m), 1567(s), 1470(w), 1438(m), 1411(w), 1385(w), 1343(w), 1110(w), 1020(w), 927(w), 653(m), 528(w), 479(w).

Table **S2** Distances (Å) and angles (°) of hydrogen bonds for the compounds **1**-**2**.

D-H···A	d(H···A)	d(D···A)	□D-H···A
		1	
O(2)-H(2A)···O(1)#1	1.769(12)	2.600(5)	175(5)
		2	
O1W-H1W···O1W#2	2.163(11)	2.774(8)	132(6)

*Symmetry transformation used to generate equivalent atoms: #1 -x,y,-z+1/2; #2 y+1/4,-x+1/4,z+1/4.

Table **S1** Crystal data and structure refinement for the compounds **1a** and **2a**.

Complex	**1a**	**2a**
Empirical formula	$C_{22}H_{30}N_4O_2Cl_2Cd_2$	$C_{24}H_{34}N_4O_4Cl_2Cd_2$
Formula weight	678.20	740.37
Temperature	298(2) K	298(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	Cc
Unit cell dimensions		
a (Å)	11.1065(14)	15.373(8)
b (Å)	7.3027(9)	14.399(7)
c (Å)	16.939(2)	14.621(9)
α (°)	90	90
β (°)	105.5740(10)	113.82(3)
γ (°)	90	90
V (Å^3)	1323.5(3)	2981.6(3)
Z	2	4
ρ (cald.) (mg m^{-3})	1.702	1.647
μ (m^{-1})	1.833	1.338
F(000)	672	1473
Crystal size (mm)	0.30 × 0.22 × 0.17	0.16 × 010 × 0.08
θ range for data collection (°)	1.90 to 25.50	1.95 to 25.50
$h/k/l$ (max, min)	-8,13/-8,8/-20,20	-15,14/0,14/0,14
Reflections collected	7034	6352
Unique	4565 [R(int) = 0.0213]	3918[R(int) = 0.0275]
Completeness to θ = 27.13	100 %	100 %
Absorption correction	empirical	empirical
Max. and min. transmission	full-matrix least-squares on F^2	full-matrix least-squares on F^2
Data / restraints / parameters	4565 / 1 / 294	3918 / 0 / 323
Goodness-of-fit on F^2	1.039	1.052
Final $R1$[a],$wR2$ [b] indices [$I > 2\sigma(I)$]	0.0220, 0.0482	0.0468, 0.1185
$R1$, $wR2$ indices (all data)	0.0232, 0.0488	0.0572, 0.1219
Largest diff. Peak and hole (e Å^{-3})	0.272 / -0.237	0.629/ -1.035

[a] $R = \Sigma \| \|F_o\| - \|F_c\| / S \|F_o\|$. [b] $wR = [\Sigma w(\|F_o\|^2 - \|F_c\|^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2)+(0.0086\ P)^2+\ 0.1674P]$ for **1a** and $w = 1/[\sigma^2(F_o^2)+(\ 0.1075P)^2+\ 2.1118P]$ for **2a**, $P = (F_o^2 + 2\ F_c^2)/3$.

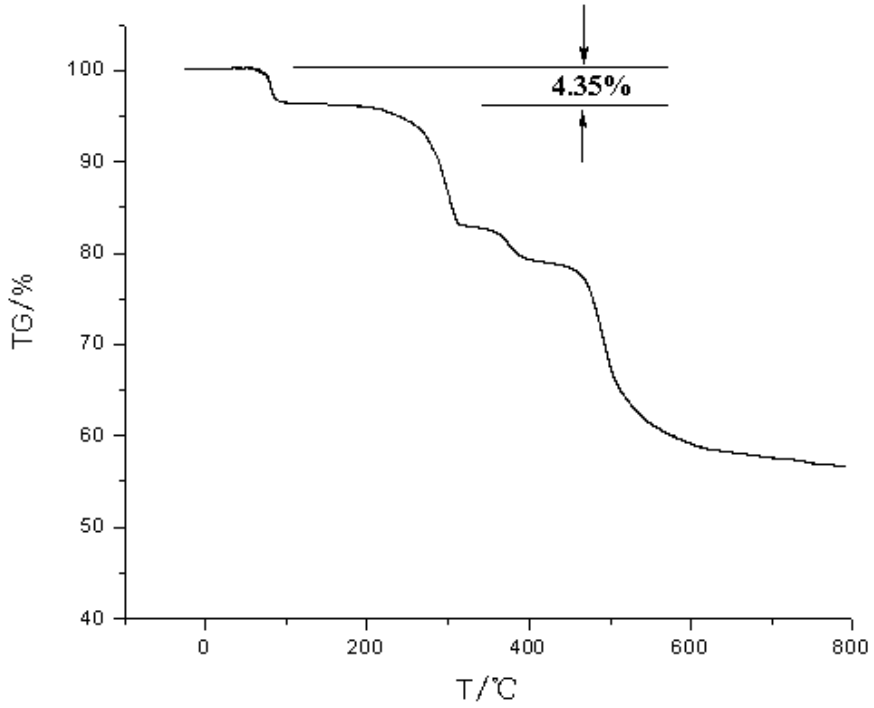
Table S2 Fluorescence lifetimes (τ), fluorescence quantum yields (Φ), optical density (A), maximum excitation wavelength (λ_{max}), fitted value (χ^2)

compound	Φ	A	$\lambda_{max\text{-}ex}$	$\lambda_{max\text{-}em}$	τ (ns)	χ^2
1	0.87	0.031	371	558	16.8	0.97
1a	0.82	0.029	371	556	15.6	0.99
2	0.86	0.035	371	507	17.2	0.97
2a	0.85	0.032	371	509	18.5	0.98
$\mathbf{L^1}$	0.65	0.013	370	553	10.5	0.96
$\mathbf{L^2}$	0.58	0.015	370	503	9.5	0.95

Notes: Samples were prepared to have an optical density of $\leq$0.05 at the λ_{max}. The χ^2 for each decay profile is also presented. All of these photophysical properties were measured in DMF/acetonitrile, except for the fluorescence quantum yields measured in ethanol.

Figure S1 TGA curves for compounds **1** and **2**.

For compound 1



For compound 2

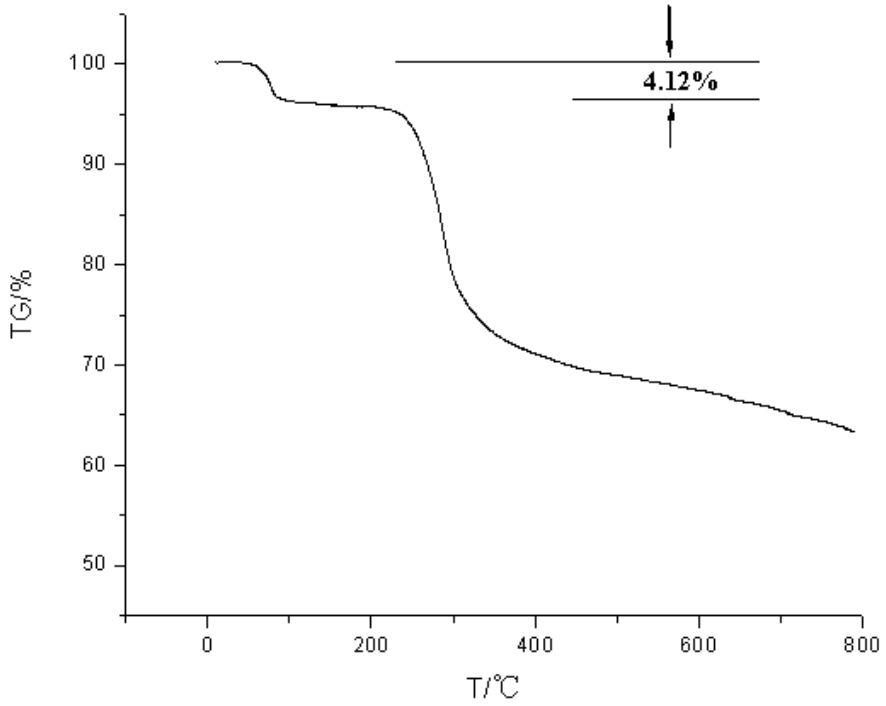


Figure S2. 1D chain in **1** constructed by intermolecular O-H···O hydrogen bonding interactions in *bc* plane.

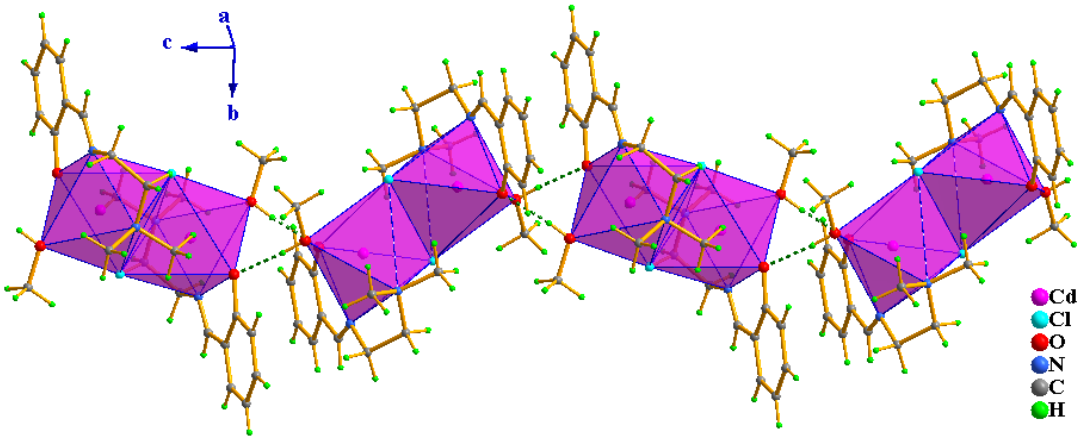


Figure **S3** 3D packing of **1a** constructed by intermolecular hydrogen bonding C-H···Cl interactions viewed along the *b* axis direction.

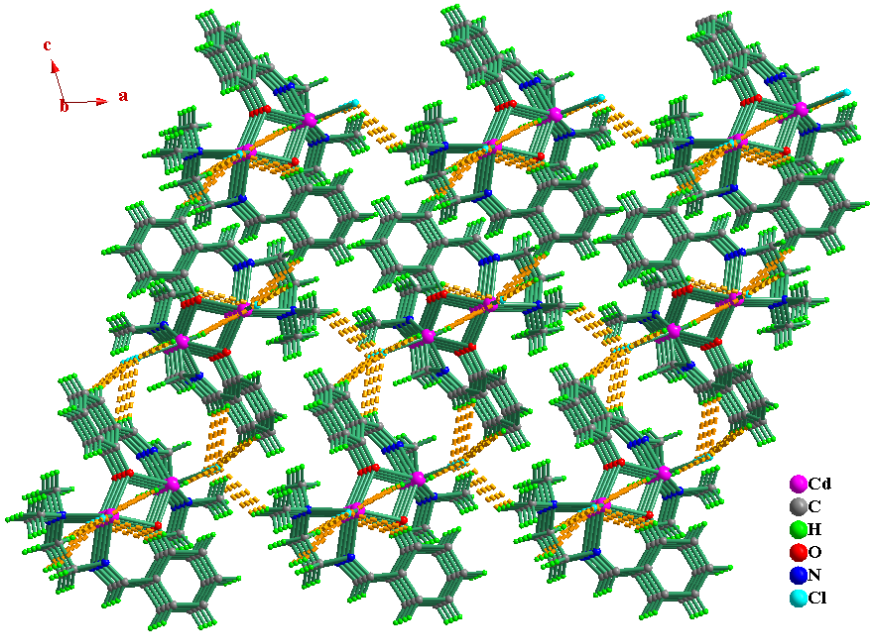


Figure S4 Right-/left-handed (*Δ*-/*Λ*-) methanol helical chains locating on the central axis of left-/right-handed (*Λ*-/*Δ*-) four-blade propeller constructed by intermolecular Van der Waals interactions in 3D packing view of **2**.

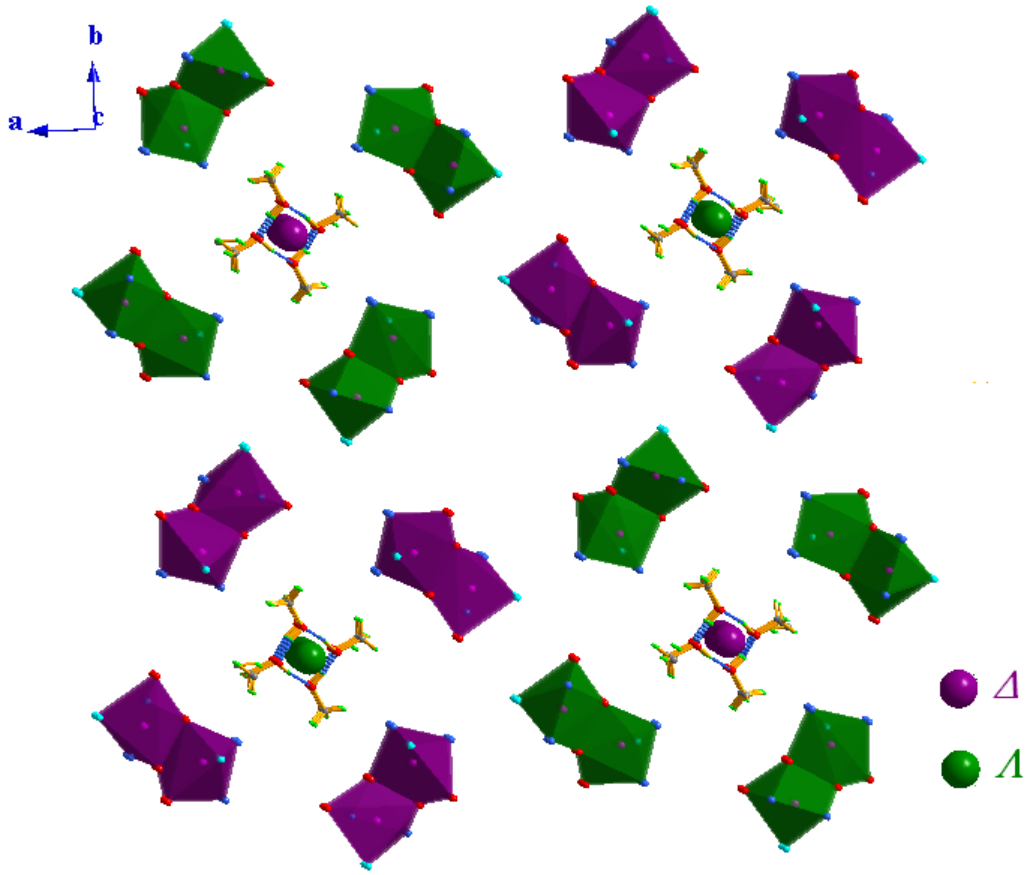
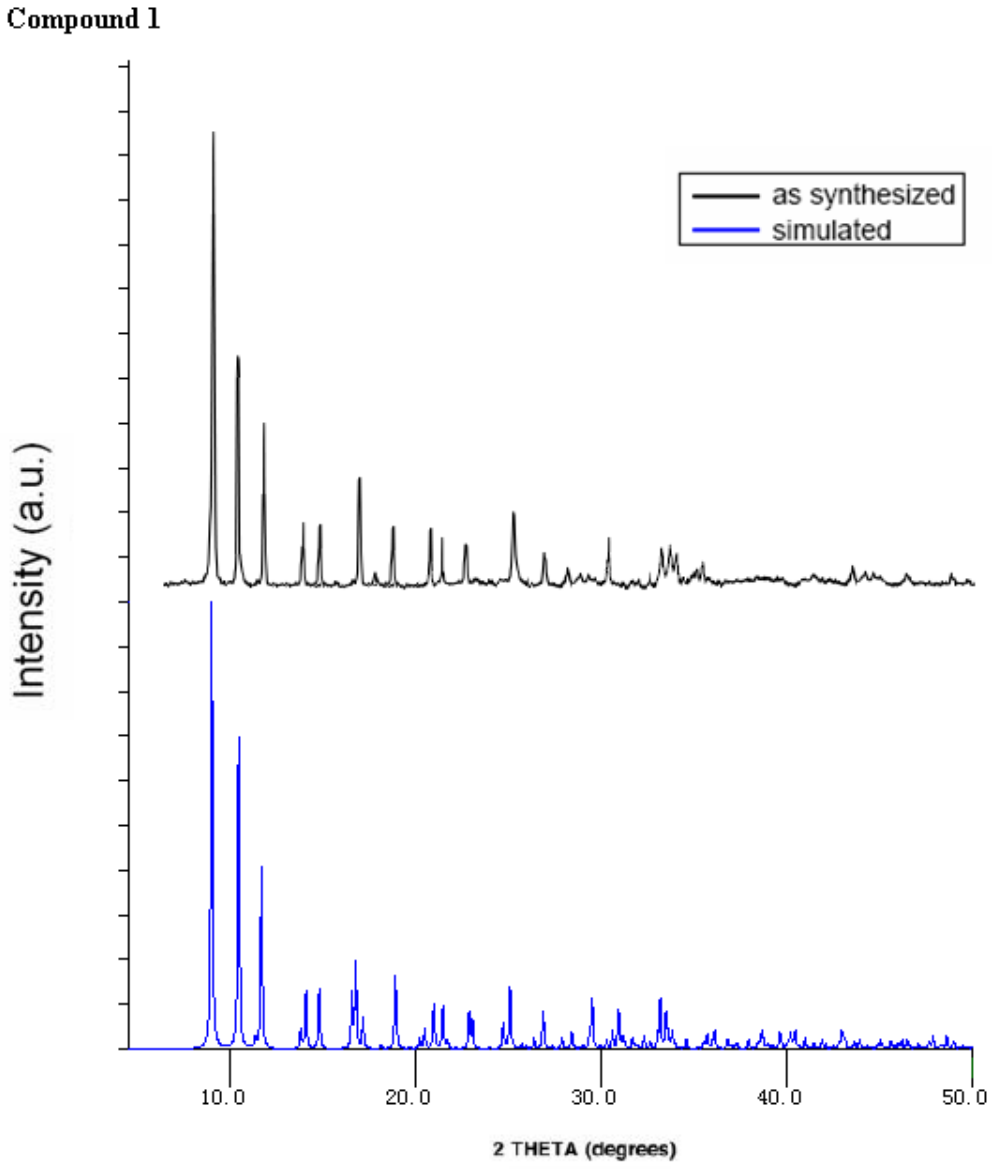
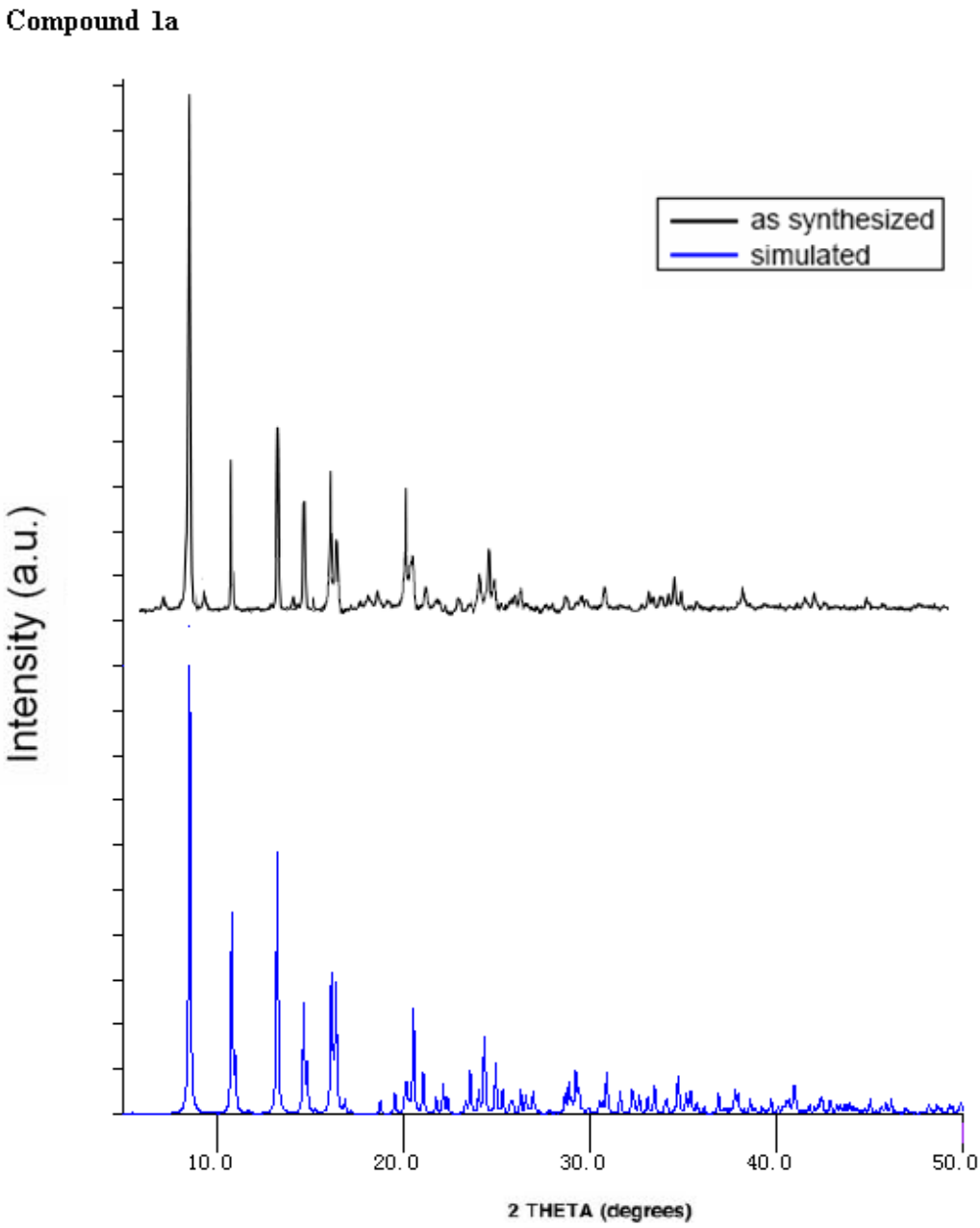


Figure S5 XRPD patterns of (a) **1** (experimental) and **1** (simulated); (b) **1a** (experimental) and **1a** (simulated); (c) **2** (experimental) and **2** (simulated); (b) **2a** (experimental) and **2a** (simulated).

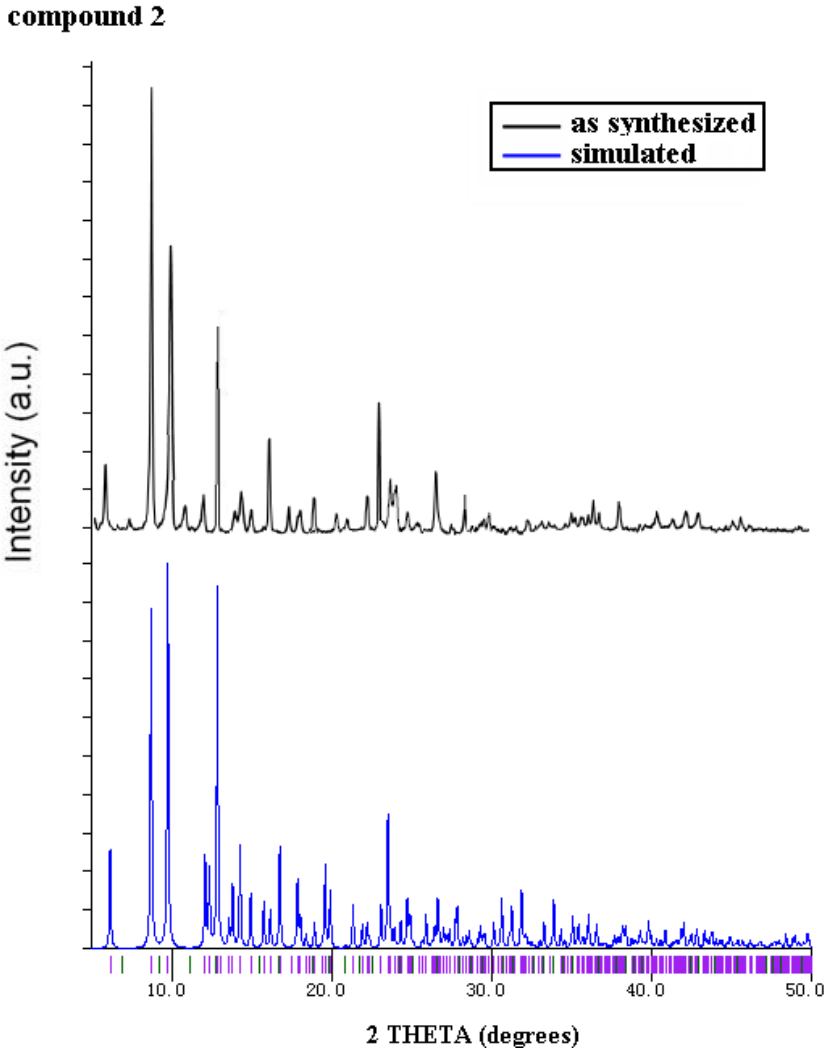
(a)



(b)


Compound 1a
as synthesized
simulated
Intensity (a.u.)
10.0
20.0
30.0
40.0
50.0
2 THETA (degrees)

(c)


compound 2
as synthesized
simulated
Intensity (a.u.)
10.0
20.0
30.0
40.0
50.0
2 THETA (degrees)

(d)

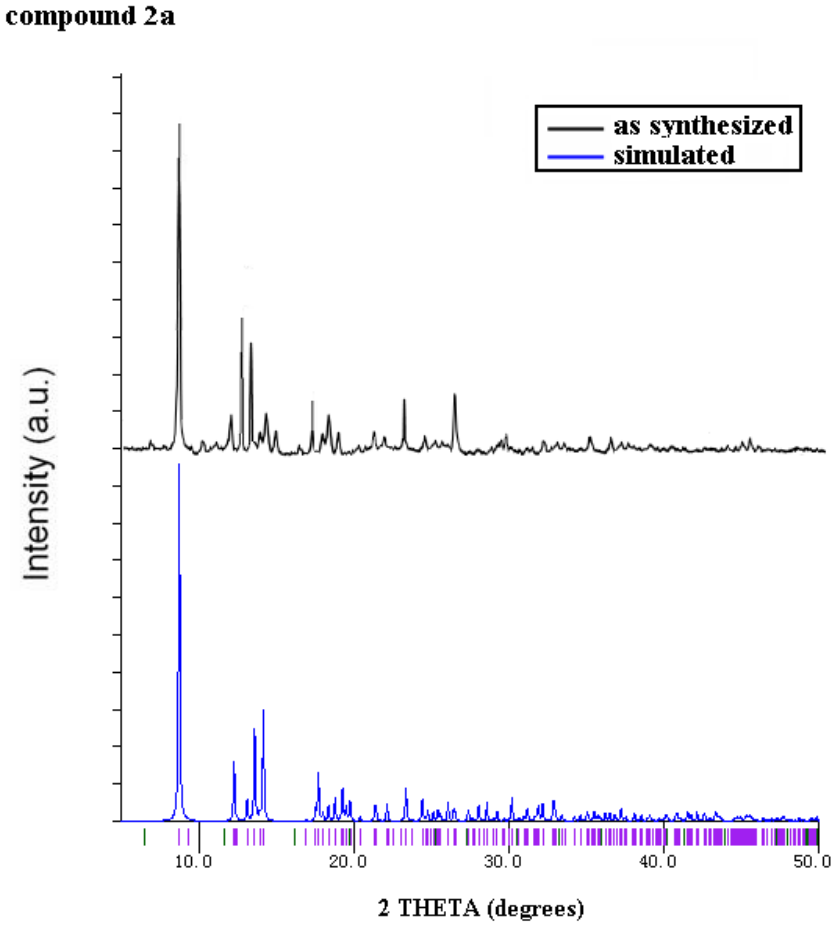
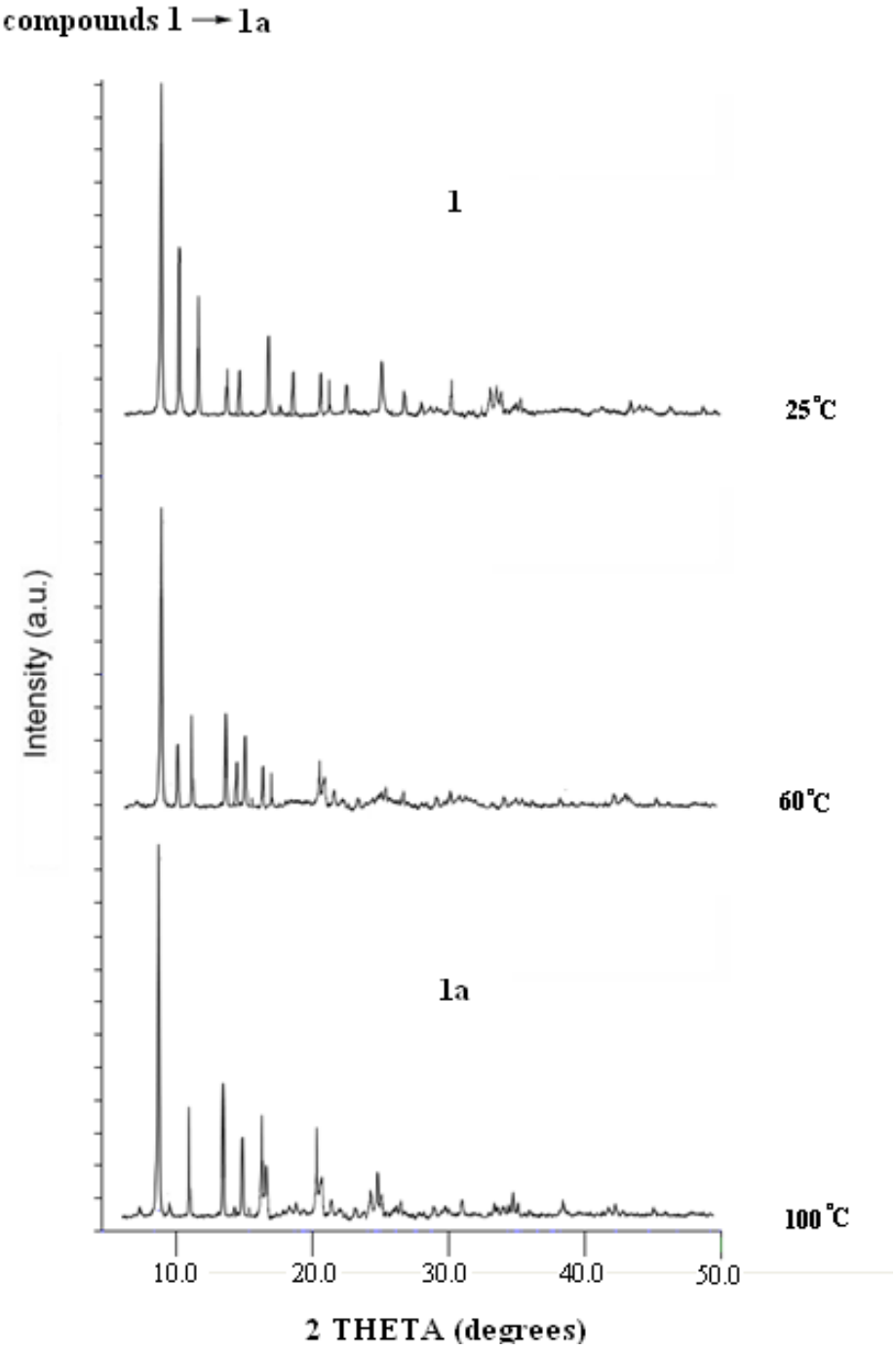

compound 2a
as synthesized
simulated
Intensity (a.u.)
10.0
20.0
30.0
40.0
50.0
2 THETA (degrees)

Figure S6 In the single-crystal-to-single-crystal transformation process, the powder diffraction patterns of the samples at different temperatures.

(a)



(b)

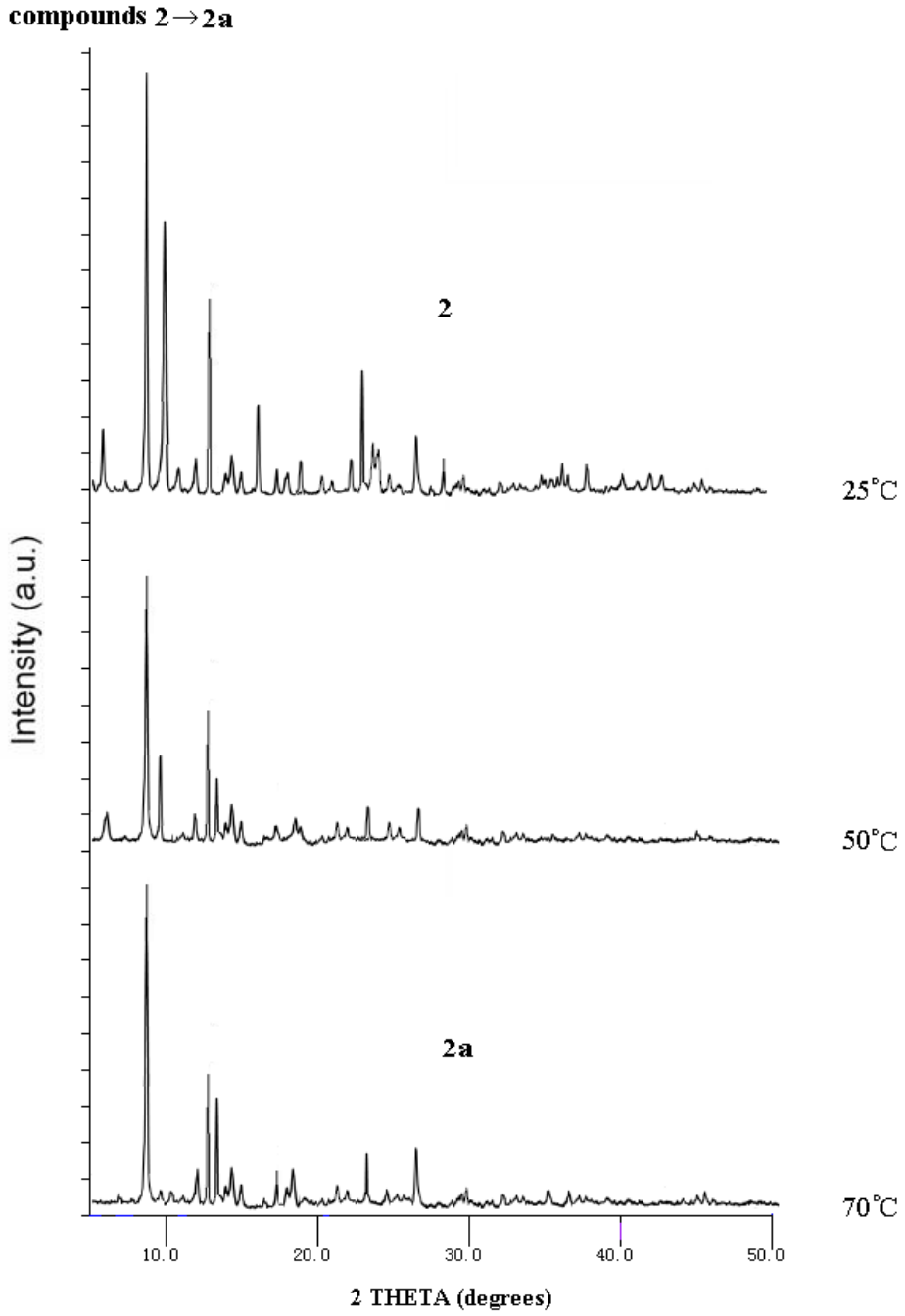

compounds 2→2a
2
25°C
Intensity (a.u.)
50°C
2a
70°C
10.0
20.0
30.0
40.0
50.0
2 THETA (degrees)

Figure S7 The green emission for the complexes **1-2** and $\mathbf{L}^{1\text{-}2}$ can be observed, where the maximum emission wavelength is at 553 and 503 nm (under 370 nm excitation) for the ligands $\mathbf{L}^1$ and $\mathbf{L}^2$, 558, 556 and 507, 509 nm (under 371 nm excitation) for the complexes **1, 1a** and **2, 2a**.