# Supporting Information

## Structures, Fluorescence and Magnetism of a Series of Coordination Polymers Driven by Tricarboxypyridine Ligand

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### 1. Synthesis

**1.1 Synthesis of complex [Zn(μ$_3$-Hcppa)•2H$_2$O]$_n$ (1), [Cd(μ$_4$-Hcppa) • H$_2$O]$_n$(2), [Co(μ$_2$-H$_2$cppa)$_2$ • 2H$_2$O]$_n$ (6) and [Fe(μ$_2$-H$_2$cppa)$_2$ • 2H$_2$O]$_n$ (8)**

A mixture of $H_3$cppa (0.3 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ ($Cd(NO_3)_3 \cdot 4H_2O$ or $FeSO_4 \cdot 7H_2O$) (1 mmol) and distilled $H_2O$ (10 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 160 °C at 10.8°C·h$^{-1}$. After maintained for 72 h, the reaction vessel was cooled to 10 °C at a rate of 5°C h$^{-1}$.

**[Zn(μ$_3$-Hcppa)•2H$_2$O]$_n$ (1):** Light yellow crystals were collected with ca. 63% yield based on $H_3$cppa. Elemental Anal. Calc. for Zn $C_{14}H_{10}NO_9$: (C, 41.87%; H, 2.51%; N, 3.49% Found: C, 41.56%; H, 2.37%; N, 3.16%. FT-IR (KBr pellets, cm$^{-1}$): 3420, 3016, 1736, 1682, 1556, 1394, 1257, 1161, 1033, 985, 923, 835, 760, 683.

**[Cd(μ$_4$-Hcppa) • H$_2$O]$_n$(2) :** Light yellow crystals were collected with ca. 47% yield based on $H_3$cppa. Elemental Anal. Calc. for $CdC_{14}H_9NO_8$: C, 38.96%; H, 2.10%; N, 3.25% Found: 39.32%; H, 2.51%; N, 3.54% FT-IR (KBr pellets, cm$^{-1}$): 3435, 3037, 1618, 1540, 1373, 1261, 1160, 1073, 993, 917, 864, 772, 685.

**[Co(μ$_2$-H$_2$cppa)$_2$ • 2H$_2$O]$_n$ (6):** Light red crystals were collected with ca. 49% yield based on $H_3$cppa. Elemental Anal. Calc. for $CoC_{28}H_{20}N_2O_{16}$: C, 48.08%; H, 2.88%; N, 4.01% Found: C, 48.35%; H, 3.11%; N, 4.43%. FT-IR (KBr pellets, cm$^{-1}$): 3403, 3051, 1709, 1596, 1552, 1464, 1385, 1313, 1255, 1176, 1034, 947, 761, 691.

**[Fe(μ$_2$-H$_2$cppa)$_2$ • 2H$_2$O]$_n$ (8):** Yellow crystals were collected with ca. 39% yield based on $H_3$cppa. Elemental Anal. Calc. for $FeC_{28}H_{20}N_2O_{16}$: C, 48.30%; H, 2.90%; N, 4.02% Found: C, 47.89%; H, 3.33%; N, 4.36%. FT-IR (KBr pellets, $cm^{-1}$): 3408, 3052, 1709, 1553, 1463, 1394, 1312, 1223, 1178, 1033, 980, 912, 828, 762, 687.

**1. 2 Synthesis of complex [Mn($\mu_2$-Hcppa) • (phen) • $H_2O$] (4) and [Co($\mu_3$-Hcppa) • (phen) • $2H_2O$]$_n$ (7)**

A mixture of $H_2$cppa (0.2 mmol), $Mn(NO_3)_2{\cdot}4H_2O$ or $Co(NO_3)_3{\cdot}6H_2O$ (0.25 mmol), NaOH (0.2mmol) and distilled $H_2O$ (8 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 120 °C at 10.8°C·$h^{-1}$. After maintained for 72 h, the reaction vessel was cooled to 10 °C at a rate of 5°C $h^{-1}$.

**[Mn($\mu_2$-Hcppa) • (phen) • $H_2O$](4):** Yellow crystals were collected with ca. 53% yield based on $H_3$cppa. Elemental Anal. Calc. for $MnC_{26}H_{17}N_3O_8$: C, 56.33%; H, 3.09%; N, 7.58% Found: C, 56.63%; H, 3.42%; N, 7.86%. FT-IR (KBr pellets, $cm^{-1}$): 3080, 1697, 1621, 1568, 1518, 1428, 1372, 1227, 1145, 973, 840, 777, 701, 672.

**[Co($\mu_3$-Hcppa) • (phen) • $2H_2O$]$_n$ (7):** Dark red crystals were collected with ca. 67% yield based on $H_3$cppa. Elemental Anal. Calc. for $CoC_{26}H_{19}N_3O_9$: C, 54.18%; H, 3.32%; N, 7.29% Found: C, 54.56%; H, 3.60%; N, 7.61%. FT-IR (KBr pellets, $cm^{-1}$): 2928, 1709, 1591, 1515, 1464, 1393, 1297, 1228, 1160, 990, 817, 752.

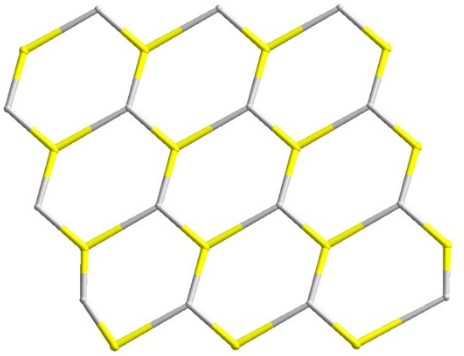
**1. 3 Synthesis of complex [Cd($\mu_2$-$H_2$cppa)$_2$ • $2H_2O$]$_n$ (3)**

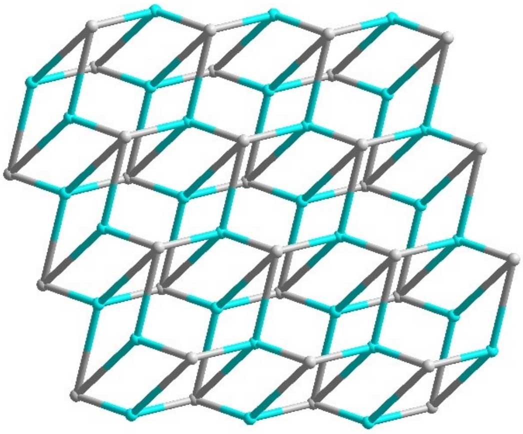
A mixture of $H_2$cppa (0.2 mmol), $Cd(NO_3)_2{\cdot}4H_2O$ (0.5 mmol), 4,4'-Bipyridine (0.2mmol) and distilled $H_2O$ (10 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 120 °C at 10.8°C·$h^{-1}$. After maintained for 72 h, the reaction vessel was cooled to 10 °C at a rate of 5°C $h^{-1}$. Light brown crystals were collected with ca. 42% yield based on $H_3$cppa. Elemental Anal. Calc. for $CdC_{28}H_{20}N_2O_{16}$: C, 44.67%; H, 2.68%; N, 3.72% Found: C, 44.86%; H, 2.96%; N, 3.49%. FT-IR (KBr pellets, $cm^{-1}$): 3419, 3053, 1713, 1682, 1600, 1556, 1415, 1386, 1220, 1157, 1045, 1008, 912, 827, 729, 630.

**1.4 Synthesis of complex [$Co_3$($\mu_3$-cppa)$_2$ • $19H_2O$]$_n$ (5)**

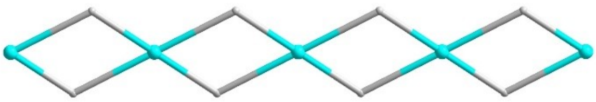
A mixture of $H_2$cppa (0.25 mmol), $Co(NO_3)_2{\cdot}6H_2O$ (0.75 mmol), NaOH (0.75mmol) and distilled $H_2O$ (10 mL) was sealed in a 25 mL Teflon-lined autoclave and heated to 120 °C at 10.8°C·$h^{-1}$. After maintained for 72 h, the reaction vessel was cooled to 10 °C at a rate of 5°C $h^{-1}$. Red crystals were collected with ca. 51% yield based on $H_3$cppa. Elemental Anal. Calc. for $C_{28}H_{50}Co_3N_2O_{33}$: C, 30.04%; H, 4.50%; N, 2.50% Found: C, 30.43%; H, 4.72%; N, 2.85%. FT-IR (KBr pellets, $cm^{-1}$): 3181, 1556, 1473, 1385, 1305, 1263, 1157, 1031, 986, 839, 799, 773, 692.

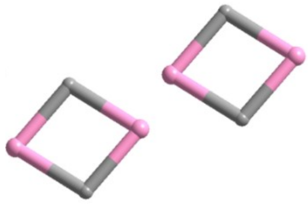
**2. Topology diagram**



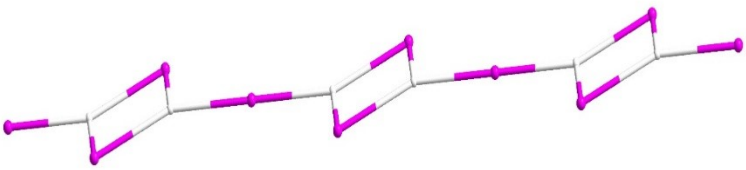


**a** **b**





**c** **d**



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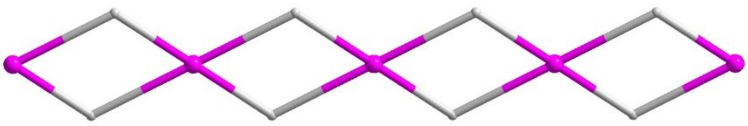

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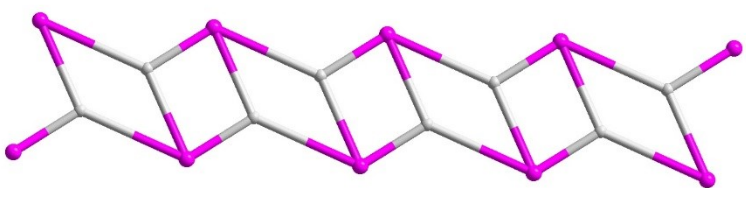
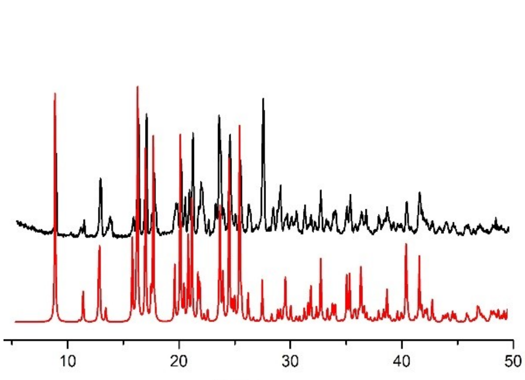


g

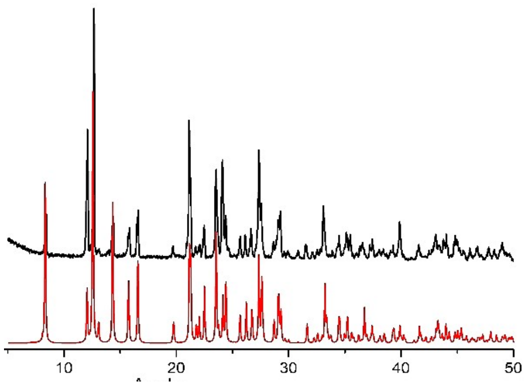
h

Fig. S1Topology diagram complexes 1-8; a (Zn: yellow code, $Hcppa^{2-}$: grey code); b (Cd: Cyan code, $Hcppa^{2-}$: grey code); c (Cd: Cyan code, $H_2cppa^{2-}$: grey code); d (Mn: pink code, $Hcppa^{2-}$: grey code); e (Co: purple code, $cppa^{3-}$: grey code); f (Co: purple code, $H_2cppa^{-}$: grey code); g (Co: purple code, $Hcppa^{2-}$: grey code); h (Fe: green code, $Hcppa^{2-}$: grey code).

## 3. Powder X-ray diffraction




**1**

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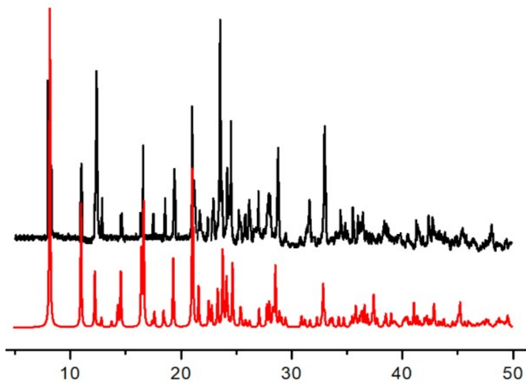
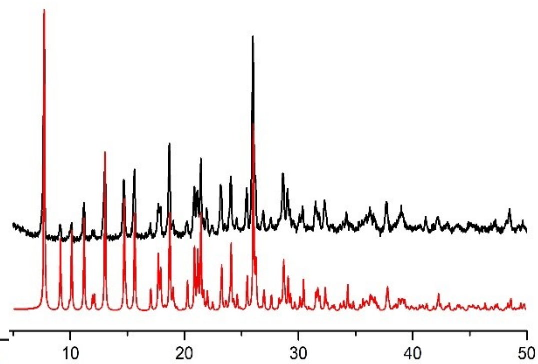



**3**

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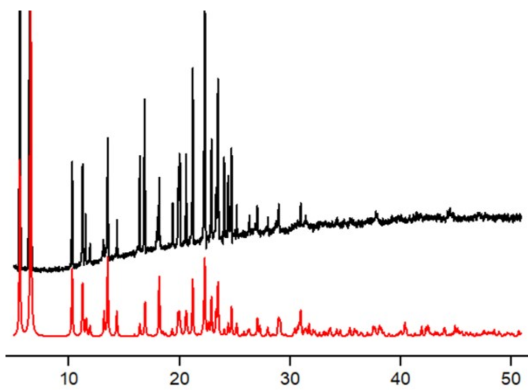


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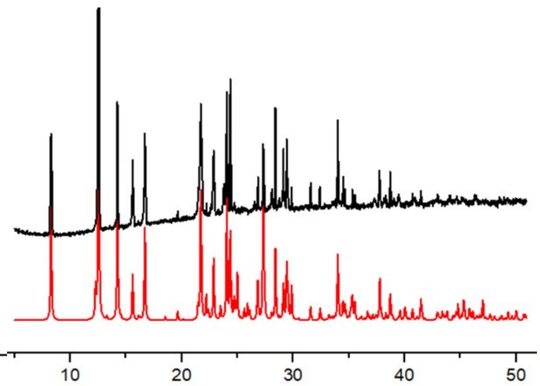
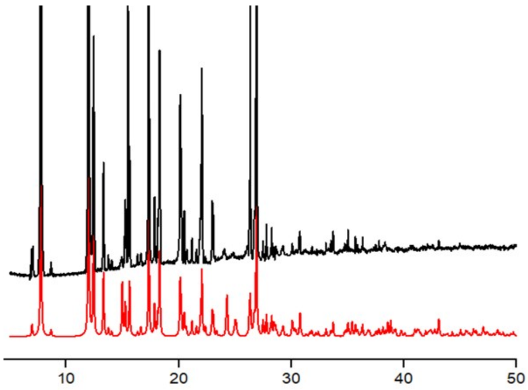



**6**

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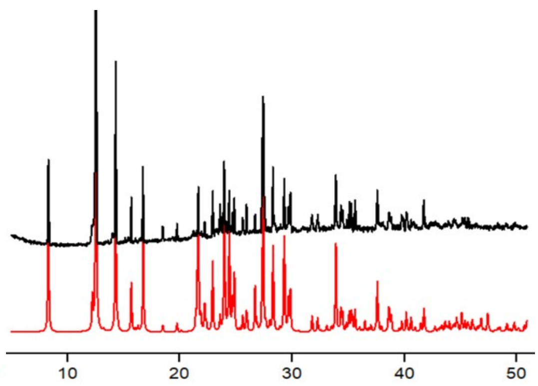
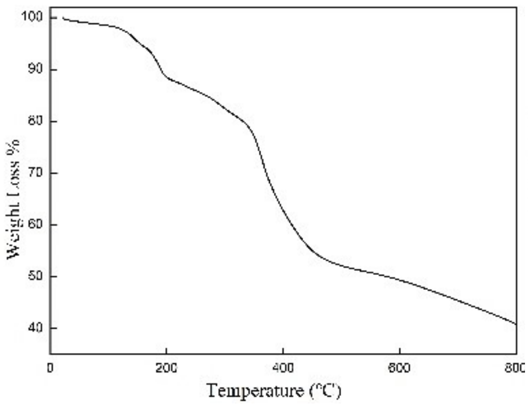



**8**

Fig. S2 Powder diffraction plot of complexes 1-8 (black: experimental value, red: simulate value)

## 4. Thermogravimetric analysis

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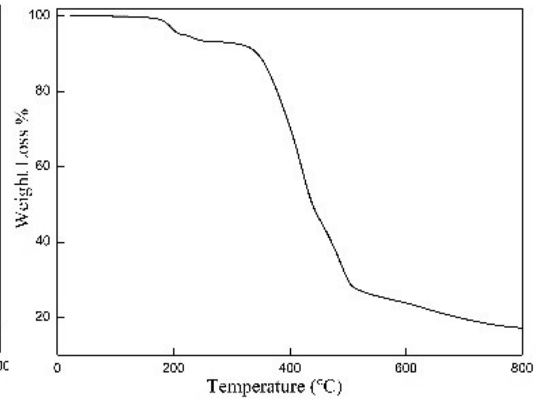


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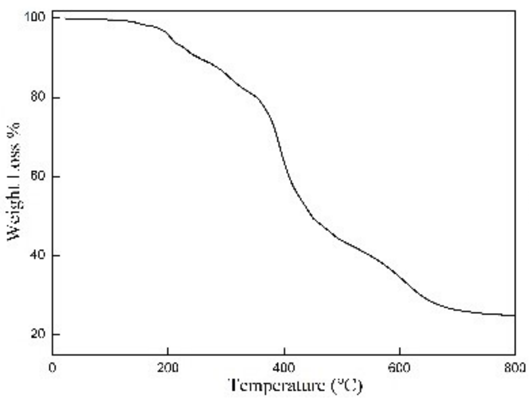


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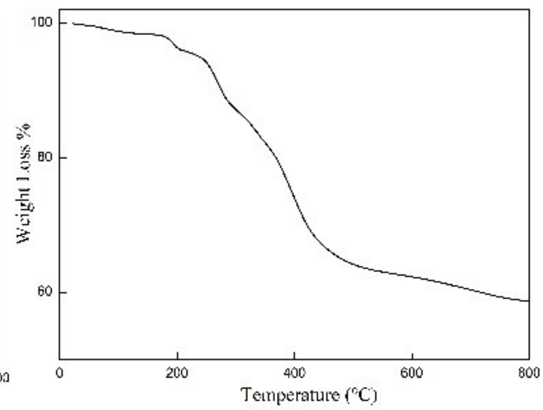


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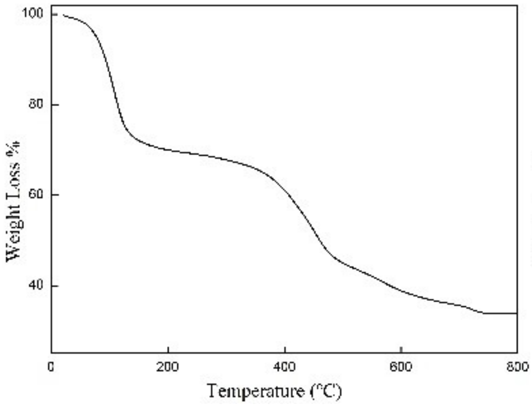


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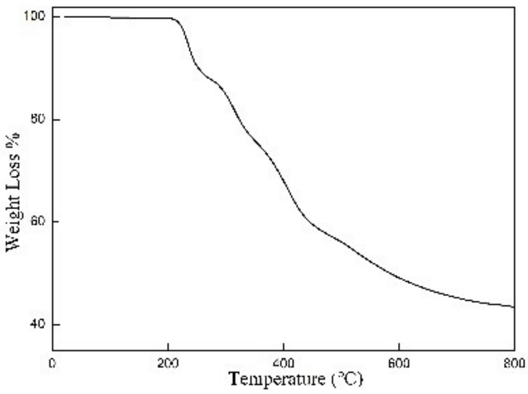
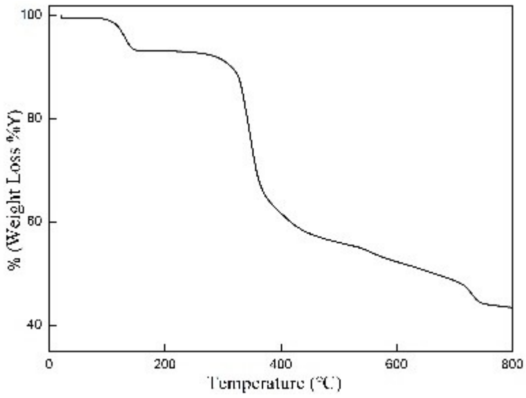



**6**

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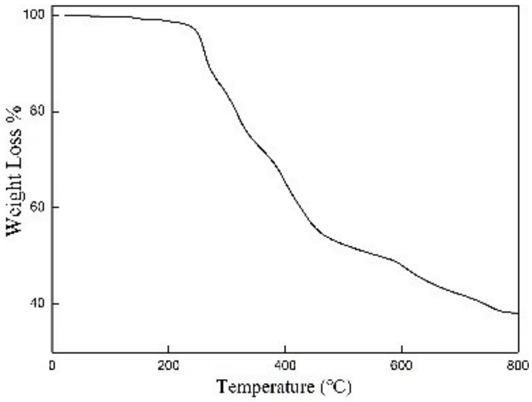
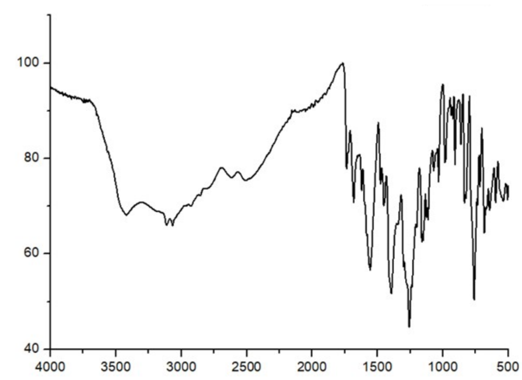


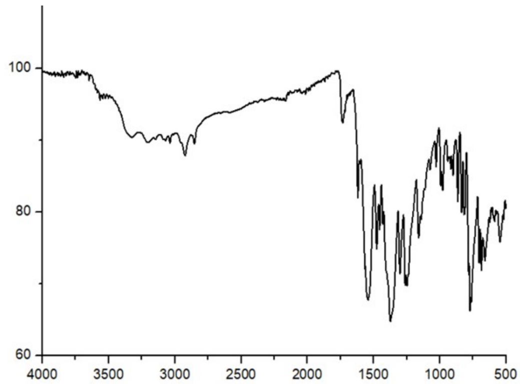

**8**

Fig. S3 Thermogravimetric analysis curve of complex 1-8

**5. Infra-red spectrogram**




**1**

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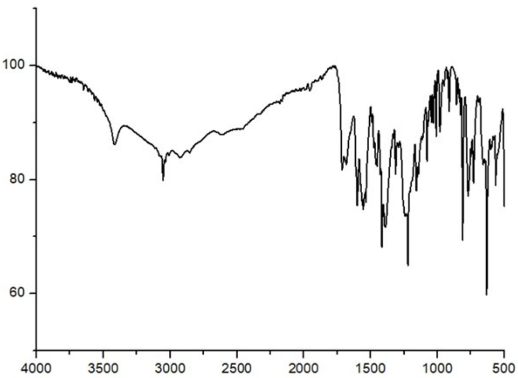


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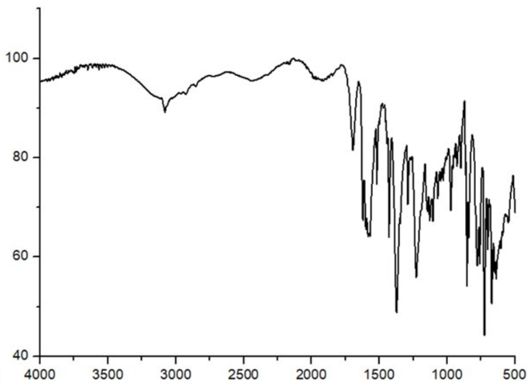


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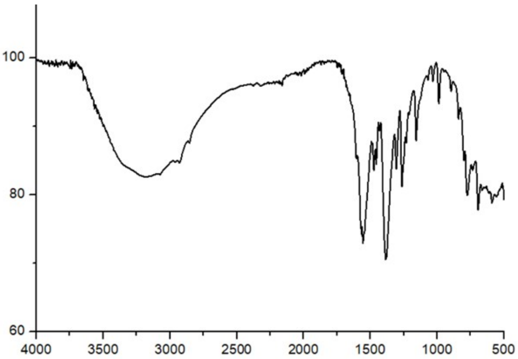


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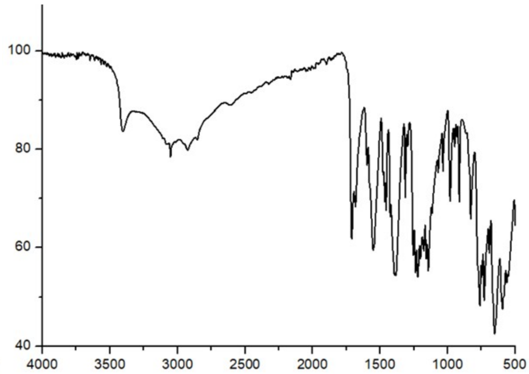


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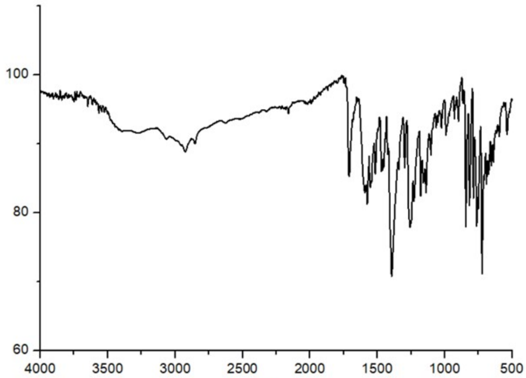


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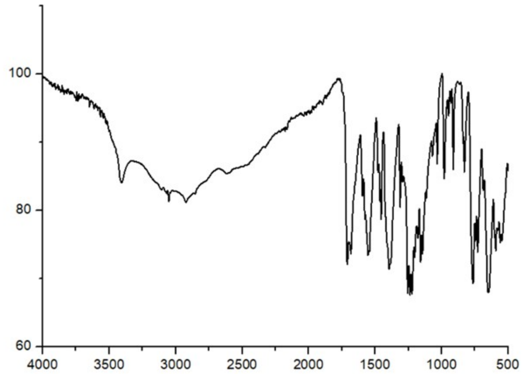


**8**

Fig. S4 Infra-red spectrogram of complex 1-8

## 5. Fluorescence spectrum

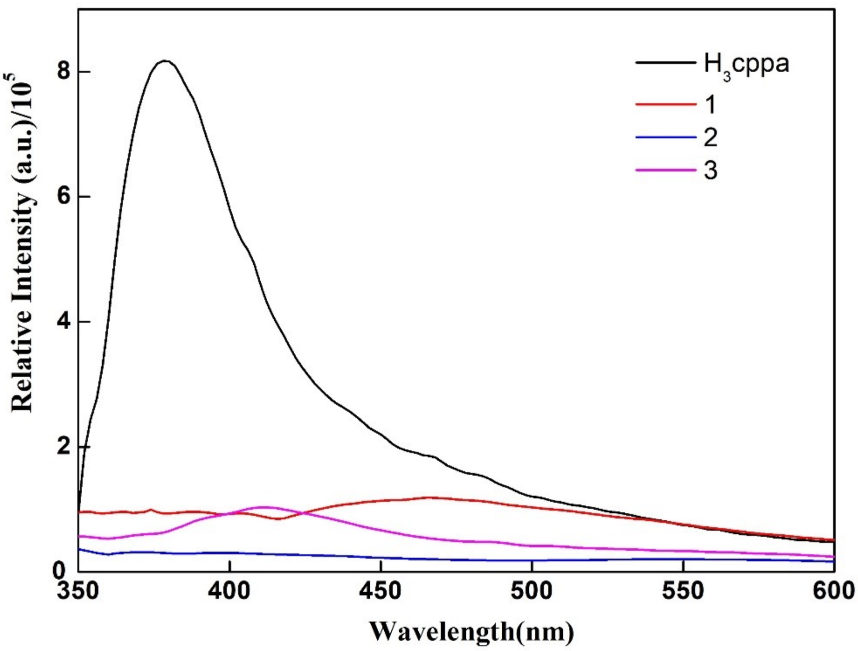


Fig. S5 Solid-state fluorescence spectra of $H_3$cppa, 1, 2 and 3 at room temperature

The solid-state fluorescence spectra of $H_3$cppa, complex **1, 2** and **3** were recorded at room temperature on a FLS980 spectrophotometer under an excitation of 330 nm. The test results of the solid-state fluorescence of ligands and complexes are shown in Fig. 9, the ligand has a strong emission peak at 379 nm, while complex 1 has a weak fluorescence emission peak at 460 nm, complex **2** has a very weak fluorescence emission peak at 550 nm and complex **3** has a relatively weak fluorescence emission peak at 410 nm. The positions of the fluorescence emission peaks of complexes **1**, **2** and **3** are all red-shifted relative to the ligands, which is caused by the charge transfer caused by the coordination reaction. The formation of coordination bonds reduces the ability of the oxygen atom and N atom to withdraw electrons, resulting in a decrease in the electron density on the ligand, Then, the energy level of the frontier orbital of the ligand changes [1,2]. Ultimately leading to a red shift of the fluorescence emission peak. At the same time, the fluorescence intensities of complexes **1**, **2** and **3** are much weaker than that of ligand.


[1]. Resch-Genger U, Li Y Q, Bricks J L, Bifunctional Charge Transfer Operated Fluorescent Probes with Acceptor and Donor Receptors. 1. Biphenyl-Type Sensor Molecules with Protonation-Induced Anti-Energy Gap Rule Behavior, J. Phys. Chem. A, 2006, 110, 10956-10971.

[2]. Wang X Y, Wei H Y, Wang Z M, etal. FormateThe Analogue of Azide: Structural and

Magnetic Properties of $M(HCOO)_2(4,4'\text{-bpy})\cdot nH_2O$ (M = Mn, Co, Ni; n = 0, 5)[J], Inorg. Chem., 2005, 44, 572-583.