Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

An unusual chiral 3D inorganic connectivity featuring a $\{Pb_{18}\}$ wheel: rapid and highly selective and sensitive sensing of Co(II)

1.Experimental procedures

Materials and Physical Measurements: All reagents were commercially purchased and no any further purified. The TGA were performed on a TGA/NETZSCH STA449C instrument heated from room temperature to 1000ºC under a nitrogen atmosphere at a heating rate of 10ºC/min. Powder X-ray diffraction was recorded on a PANalytical X`pert PRO X-ray Diffraction using Cu-Kα radiation in the 2θ range of 5-50°. The Fourier transform infrared (FT-IR) spectra using KBr pellets were collected on a Spectrum-One FT-IR spectrophotometer in the range of 4000-450cm^{-1}. Elemental analyses (C, H and N) were measured with an Elemental Vairo EL III Analyzer. The UV-vis absorption spectra were measured at room temperature with a PE Lambda 900 UV-visible spectrophotometer. Fluorescence spectra were performed on an Edinburgh Analytical instrument FLS920.

Synthesis of 1: A mixture of $Pb(NO_3)_2$ (0.50 mmol,170 mg) and 5-Methyisophthalic acid (0.35mmol,640 mg) was sealed in a 20mL of Teflon-lined stainless steel vessel with a mixed-solvent (10mL) of acetonitrile and water (V/V=1:1). The mixture was heated to 120ºC in 4 hours and kept this temperature for 3 days. Then the reaction system was cooled slowly to room temperature during another 3 days. The light yellow prismatic crystals of **1** were collected, washed with water and ethanol and dried in air (yield 67% based on $Pb(NO_3)_2$). Elemental analysis Calcd.(%) for $C_{63}H_{42}N_6O_{48}Pb_{10}$ (3723.03): C 20.32,H 1.14, N 2.26; found: C 20.89, H 1.70, N 2.42.IR (KBr, cm^{-1}): 3425s, 2924w, 1850vw, 1603vs, 1527vs, 1508vs, 1426vs, 1351vs, 1240w, 1116vw, 1023vw, 947vw, 924vw, 778vs, 723vs, 585s, 496vw, 468s.

Single-Crystal Structure Determination: Single-crystal X-ray diffraction data were collected on a Rigaku Diffractometer with a Mercury CCD area detector (Mo Kα: λ = 0.71073 Å) at room temperature. Crystal Clear software was used for data reduction and empirical absorption correction. The structures were solved by direct methods using SHELXTL and refined by full-matrix least-squares on F^2 using SHELX-97 program. Metal atoms in each compound were located from the E-maps, and other non-hydrogen atoms were located in successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The organic hydrogen atoms were positioned geometrically. Crystallographic data and other pertinent information for **1P** and **1M** are summarized in Table S1. CCDC numbers for **1P** and **1M** are 988800 and 988801, respectively.

2. Characterization

IR spectroscopy: The IR spectrum of **1** shows the characteristic bands of the carboxylic groups in the usual region at 1156–468 cm^{-1} for symmetric vibrations and at 1581–1182 cm^{-1} for asymmetric vibrations (Fig. S5, right). The absence of strong absorption associated with the carboxyl group at around 1605 cm^{-1} indicates that the H_2mip ligand is completely deprotonated.

UV-vis spectra: The UV-vis Spectrum of **1** displays the absorption peaks at λ = 220 and 300 nm (Fig. S5, left), which well match with the CD spectrum.

PXRD and TGA analysis: To check the phase purity of the bulk sample, the PXRD was recorded at room temperature. The peak positions of the simulated pattern closely match those of the experimental one, indicating the phase purity of as-synthesized sample (Fig. S6, left). The framework is quite robust as shown in the PXRD of the dehydrated sample which is slightly different from that of the as-synthesized. The TGA was examined in dry nitrogen from 26 to 1000ºC to study the thermal stability of the sample. The first step from 26 to 349ºC with *ca*. 1.06% weight loss is due to the sustained loss of acetonitrile and water molecules (weight *ca*. 0.967%) from solvent, then it begins to decompose upon further heating till approximately 350ºC (Fig. S6, right).

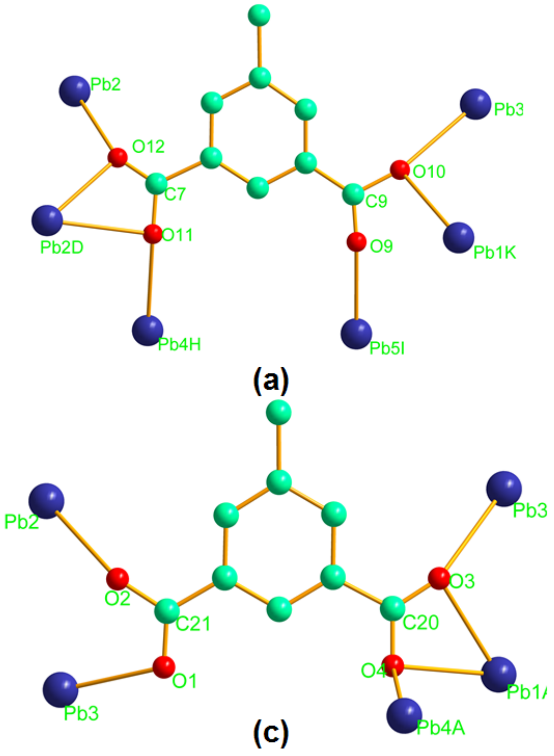


Fig.S1 The coordination environment of ligands in compounds **1P** and **1M**.

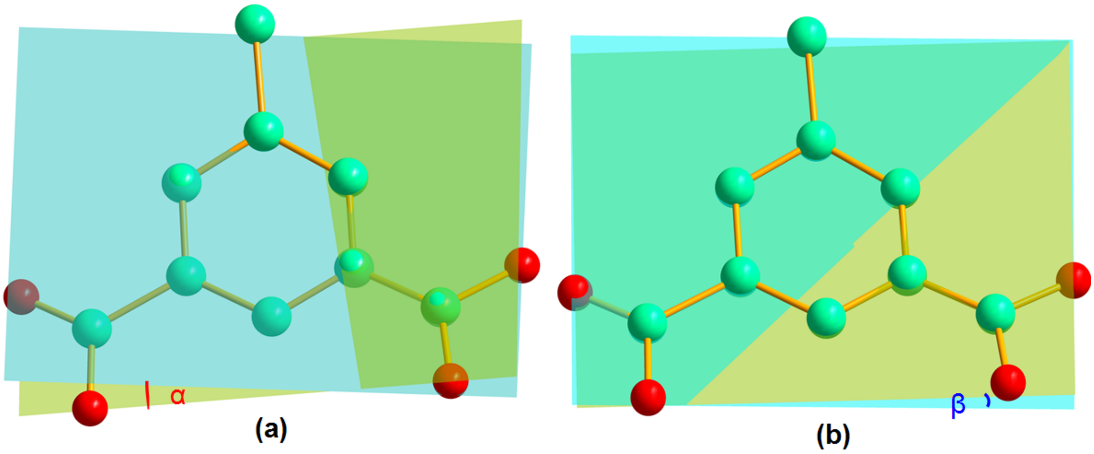


Fig. S2 View of the distortion angle(α) between two carboxylate groups of the ligand and the bending angle(β) between the carboxylate group and the aromatic ring.

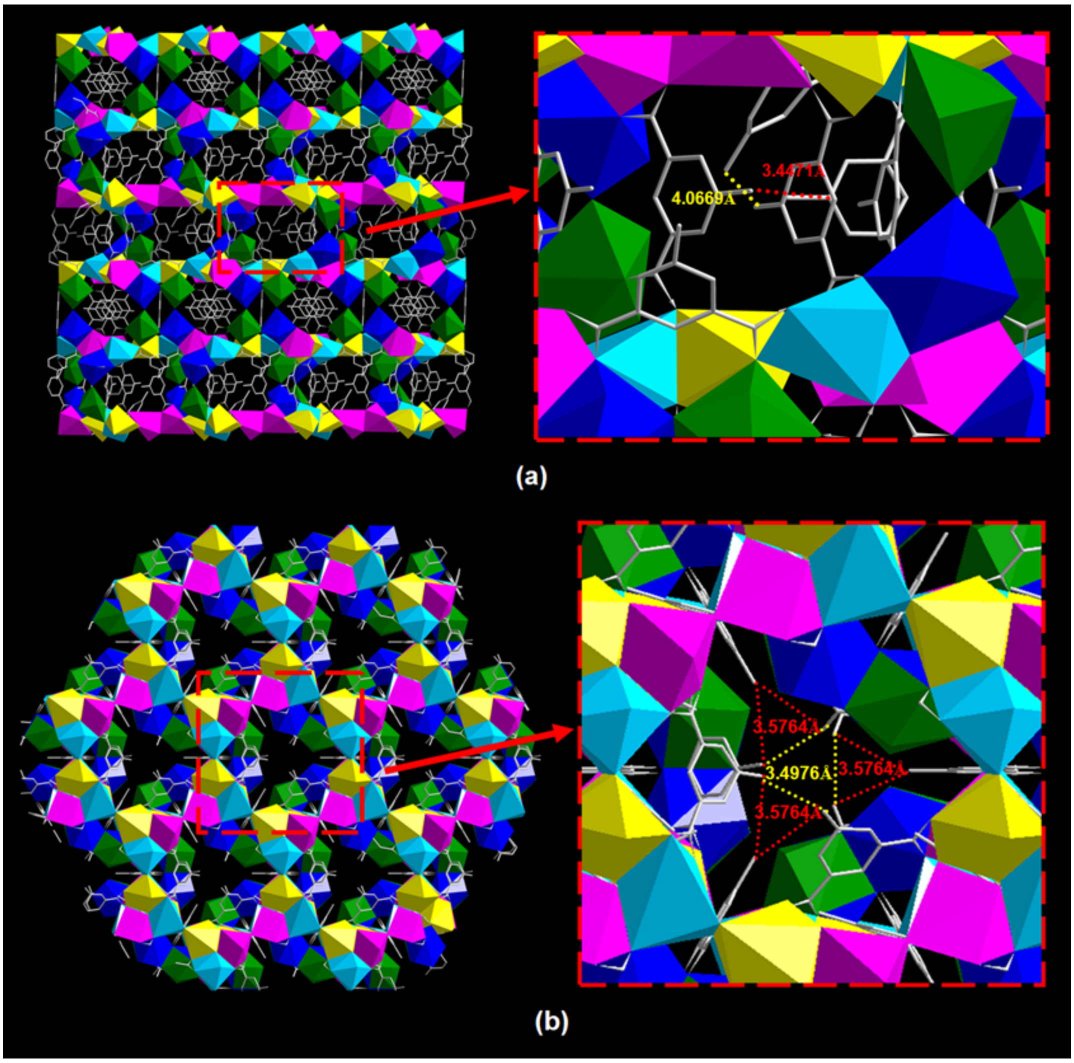


Fig. S3 The space hindrance of the methyl groups of the mip^{2-} ligands in the framework when viewed down from the *b*- (a) and the *c*-axes (b).

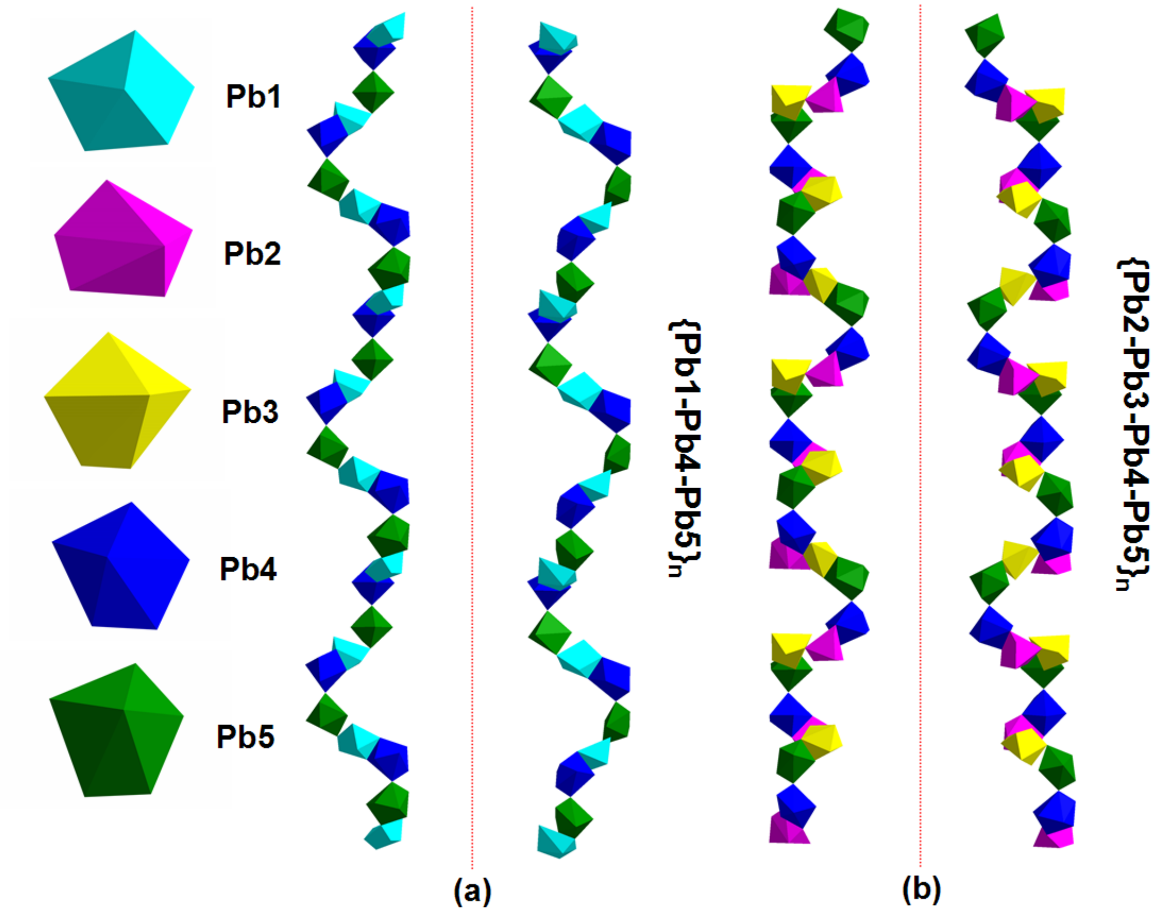


Fig. S4 View of the {Pb1-Pb4-PB5}$_n$ and {Pb4-Pb2-Pb3-Pb5}$_n$ helices in **1P** and **1M**.

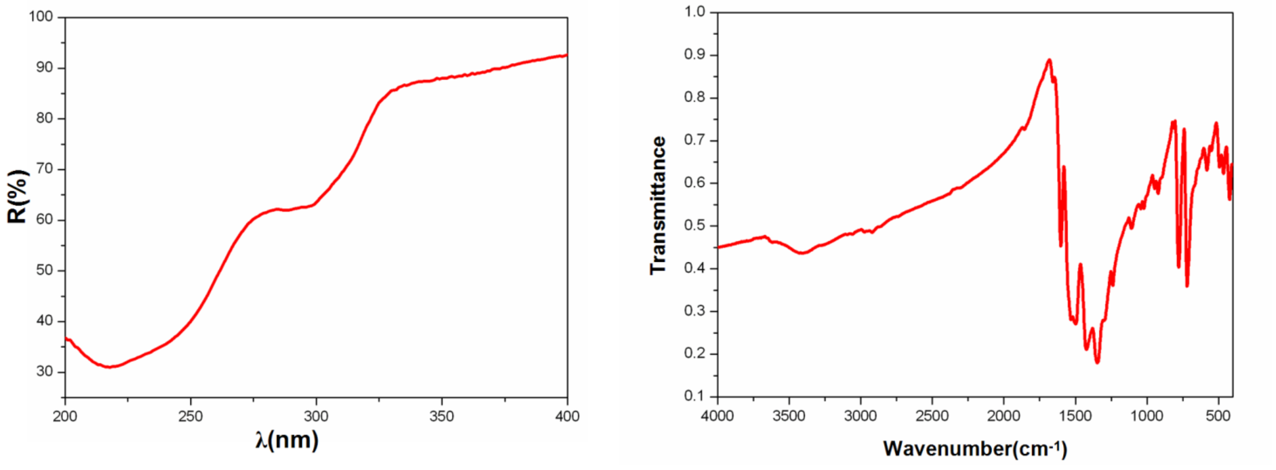


Fig. S5 View of the UV-vis and the IR spectra of **1**.

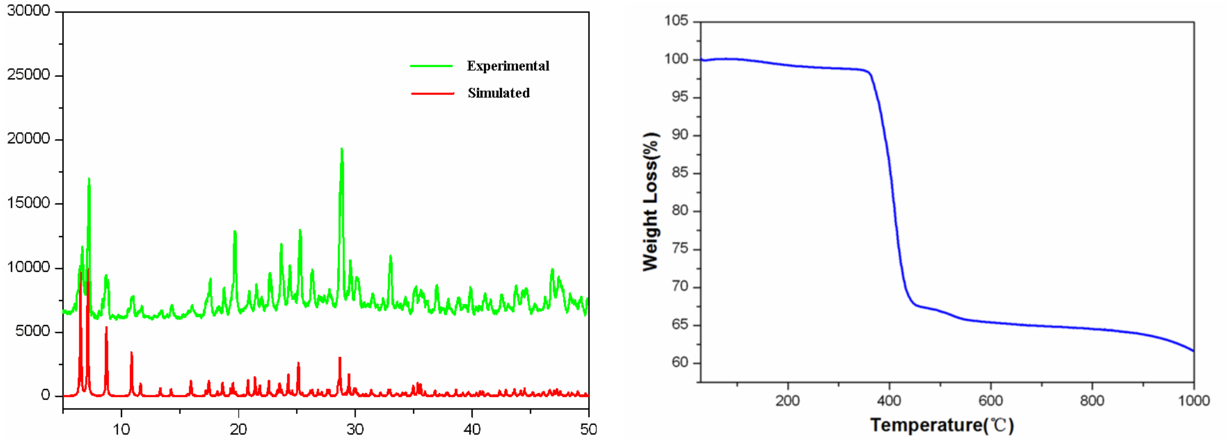
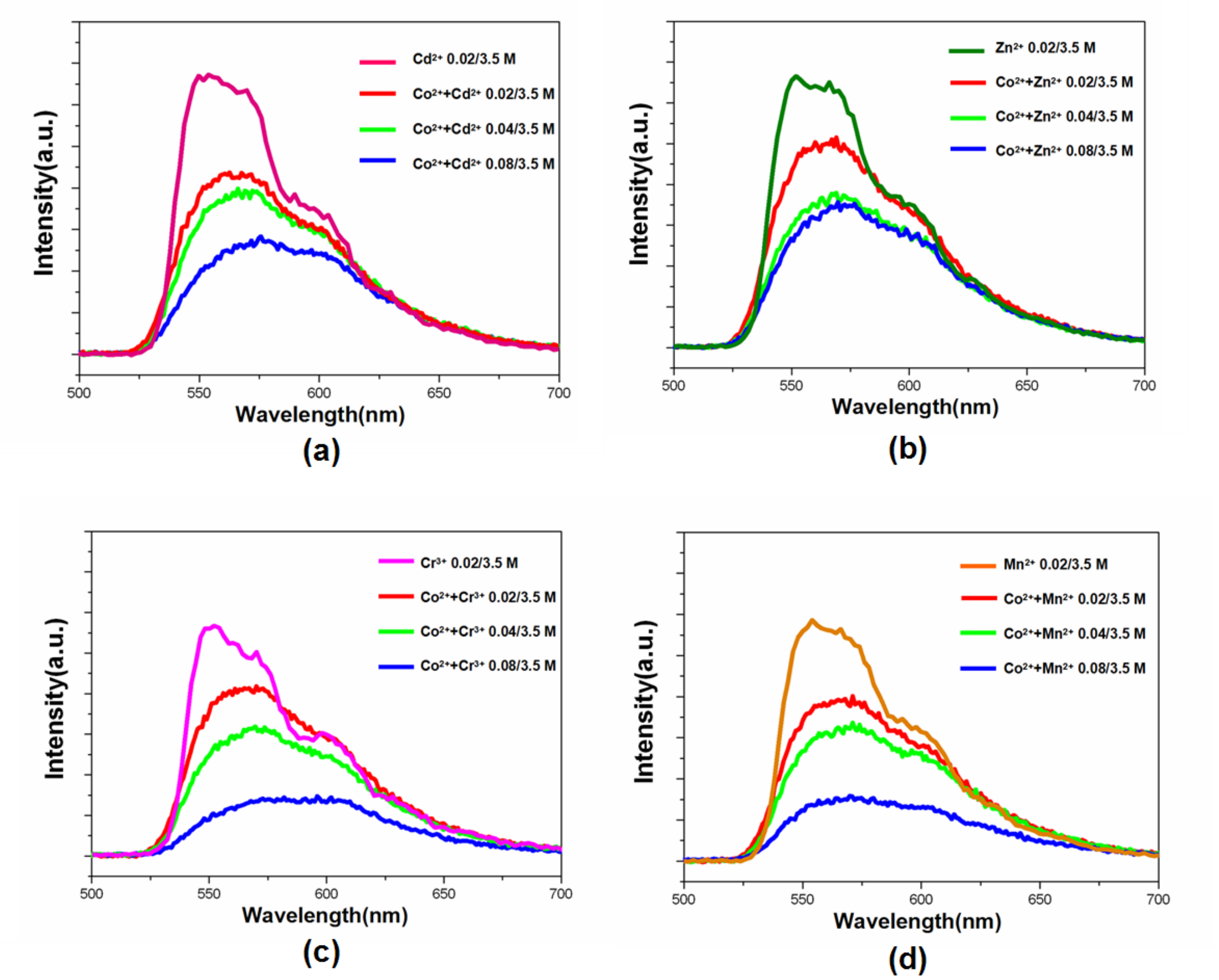
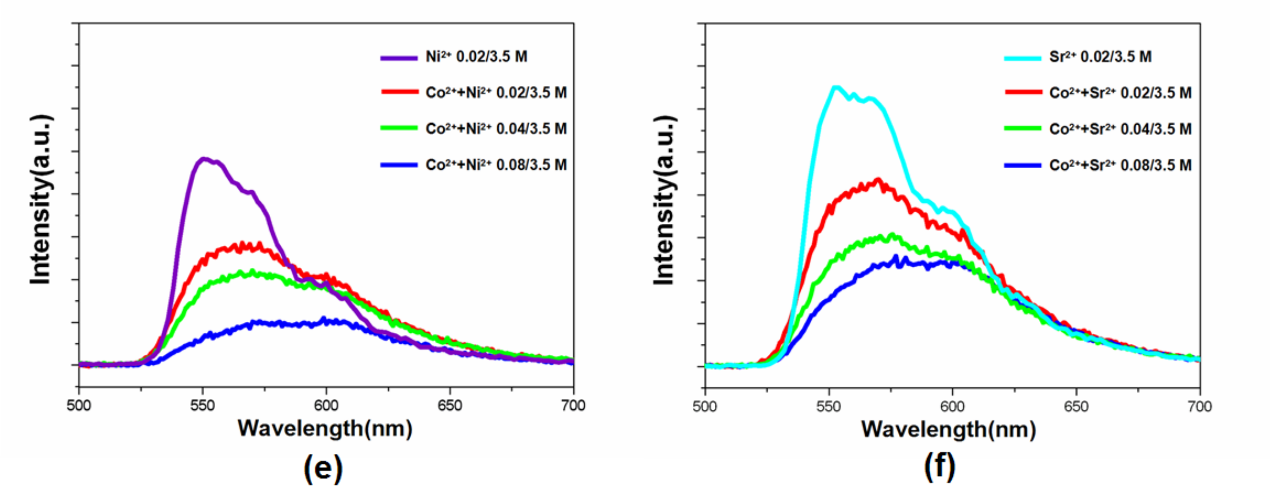


Fig. S6 Simulated and experimental XRD powder patterns and TGA diagram for **1**.





(e) (f)

Fig. S7 Emission spectra of **1** immersed in a CH_3CN solution containing a mixture of Co^{2+} and Cd^{2+}, Zn^{2+}, Mn^{2+}, Sr^{2+}, Cr^{3+}, or Ni^{2+} (excited at 397nm).

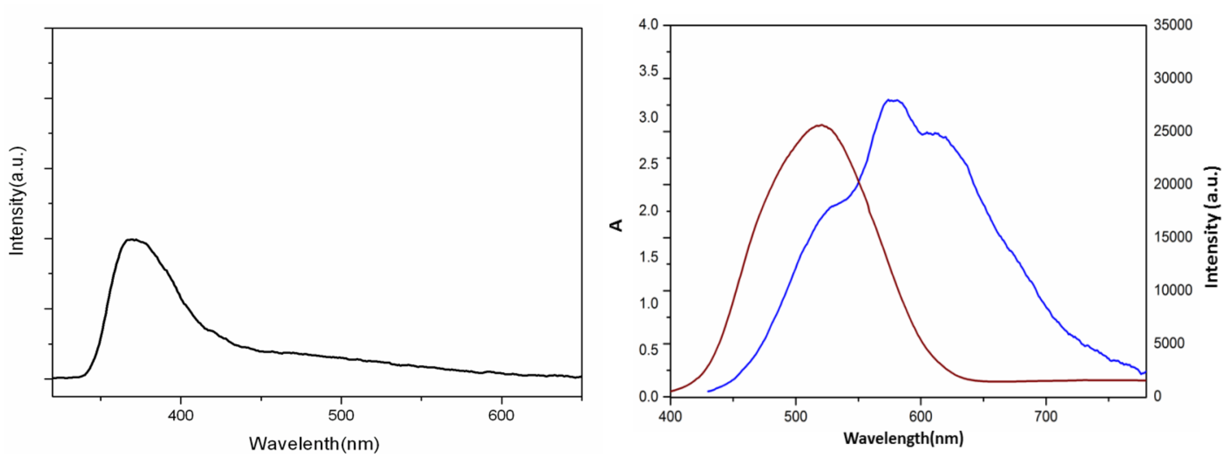


Fig. S8 The emission spectra of the ligand (left) and **1** (right, blue), and the UV absorbance of Co^{2+} (right, wine red).

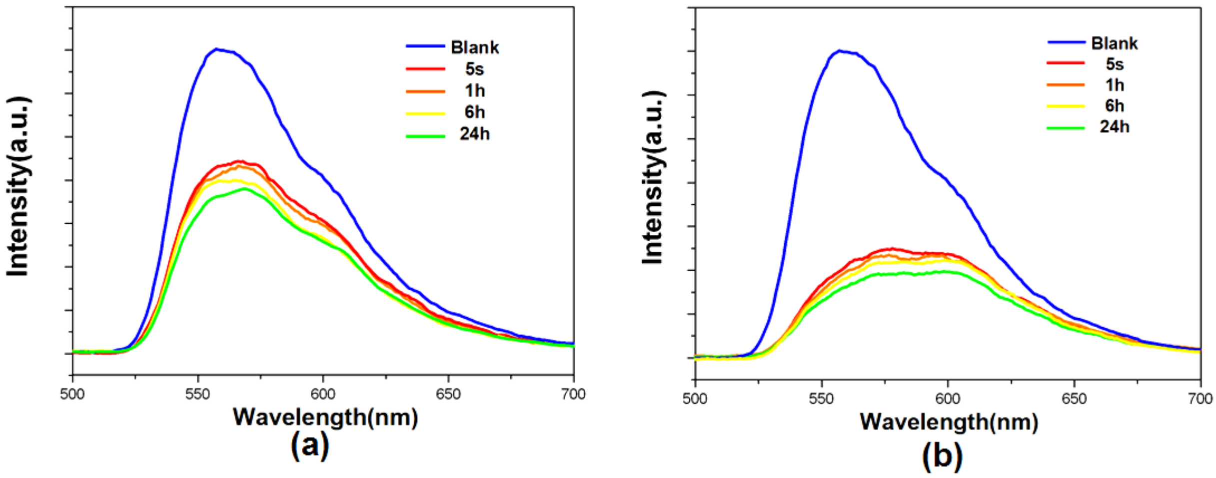


Fig. S9 The emission spectra of **1** in CH_3CN containing Co^{2+} [0.006M (a) and 0.023M (b)] for 5 s, 1 h, 6 h and 24 h, respectively.

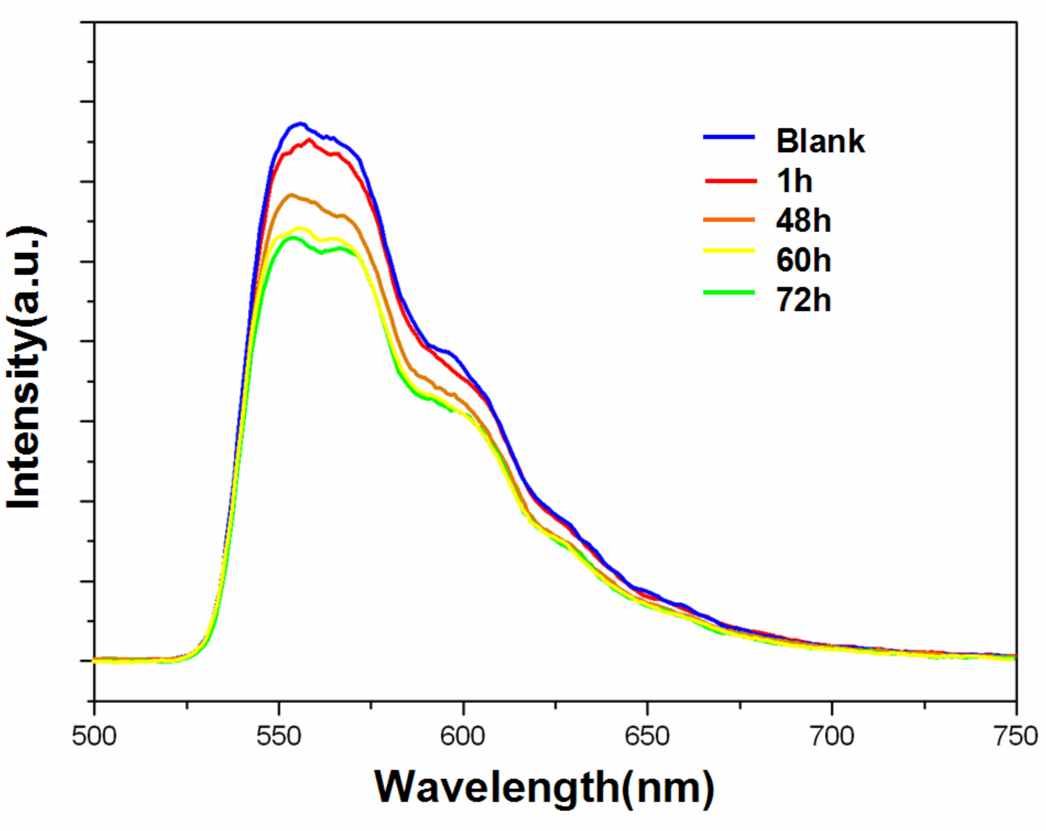


Fig. S10 Emission spectra of **1** in CH_3CN after being immersed with 0.03 M of $Co^{2+}$for 1, 48, 60 and 72h, and then washed several times with CH_3CN.

Table S1. Crystallographic data and structure refinement details for ten randomly selected crystals.

compound	**1P-1**	**1M-1**	**1P-2**	**1M-2**	**1P-3**
formula	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$
fw	3726.96	3726.96	3726.96	3726.96	3726.96
cryst syst	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal
space group	$P3_12_1$	$P3_22_1$	$P3_12_1$	$P3_22_1$	$P3_12_1$
a, Å	15.729(2)	15.651(6)	15.714(4)	15.6635(5)	15.7138(5)
c, Å	30.451(6)	30.325(2)	30.402(11)	30.3625(19)	30.4093(15)
V, Å^3	6524.6(18)	6433.5(5)	6501(3)	6451.3(5)	6502.8(4)
Z	3	3	3	3	3
μ, mm^{-1}	19.377	19.652	19.447	19.598	19.442
D_{calcd},g cm^{-3}	2.843	2.886	2.856	2.878	2.855
Flack	0.07(2)	0.08(3)	0.049(19)	0.098(3)	0.06(3)
GOF	0.981	0.998	1.054	0.952	1.119
R_1	0.0679	0.0787	0.0658	0.0818	0.0856
wR_2	0.1777	0.1855	0.1597	0.2206	0.2017
compound	**1M-3**	**1M-4**	**1M-5**	**1M-6**	**1M-7**
formula	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$	$C_{63}H_{46}N_6$ $O_{48}Pb_{10}$
fw	3726.96	3726.96	3726.96	3726.96	3726.96
cryst syst	Hexagonal	Hexagonal	Hexagonal	Hexagonal	Hexagonal
space group	$P3_22_1$	$P3_22_1$	$P3_22_1$	$P3_22_1$	$P3_22_1$
a, Å	15.7229(4)	15.7331(11)	15.729(5)	15.7649(5)	15.6729(6)
c, Å	30.3930(18)	30.406(3)	30.475(15)	30.479(2)	30.3753(18
V, Å^3	6506.8(5)	6518.0(9)	6530(5)	6560.2(5)	6461.7(5)
Z	3	3	3	3	3
μ, mm^{-1}	19.430	19.397	19.362	19.272	19.566
D_{calcd},g cm^{-3}	2.853	2.848	2.843	2.830	2.873
Flack	0.05(2)	0.07(2)	0.08(3)	0.19(2)	0.14(3)
GOF	0.889	1.104	0.916	1.086	1.100
$^{a}R_1$	0.0638	0.0722	0.0844	0.0808	0.0.0971
$^{b}wR_2$	0.1708	0.1898	0.2200	0.1896	0.2360

Table S2 Quenching effect coefficients (K_{sv}) of different metal ions on the luminescence intensity at λ_{em} = 565nm of **1**.

Metal ions	K_{sv} (M^{-1})
Cd^{2+}	0.3510
Zn^{2+}	0.5036
Rb^{+}	0.9171
K^{+}	1.2335
Sr^{2+}	2.3865
Mg^{2+}	1.8284
Mn^{2+}	6.4709
Pb^{2+}	6.9646
Ni^{2+}	7.5435
Eu^{3+}	8.1385
Cr^{3+}	14.5489
Fe^{3+}	21.0806
In^{3+}	26.6888
Cu^{2+}	32.4197
Co^{2+}	421.9444
The con. of Co^{2+} ion	
0.01/3.5	58.5264
0.02/3.5	120.8633
0.03/3.5	81.5261
0.04/3.5	64.0663
0.05/3.5	71.4040
0.06/3.5	86.9846
0.07/3.5	83.5227
0.08/3.5	83.7035
0.09/3.5	123.3399
0.1/3.5	421.9444
0.2/3.5	290.9375
0.3/3.5	204.7807

Table S3 Observed Co^{2+} amount in sample **1** after being immersed in the CH_3CN solution containing 6×10^{-3} M of Co^{2+} for 5 s, and 1, 6, 24 h.

The Atomic Absorption Spectroscopy

The amount of Co^{2+} ion added in aqueous solution	The immersed time	Observed Co^{2+} ion amount in the sample
5.82 mg	5s	$<7\times10^{-5}$mg
	1h	9.5×10^{-3}mg
	6h	1.8×10^{-2}mg
	24h	3.45×10^{-2}mg

The Inductively Coupled Plasma-Atomic Emission Spectroscopy

The amount of Co^{2+} ion added in aqueous solution	The immersed time	Observed Co^{2+} ion amount in the sample
5.82 mg	5s	7.0×10^{-5}mg
	1h	8.5×10^{-3}mg
	6h	1.78×10^{-2}mg
	24h	3.38×10^{-2}mg