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#### Photocatalytic and Luminescent Properties of Three Novel Complexes Based on

#### a Pyridine-Pyrimidine-Hydrazone Ligand

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Abstract: Three novel complexes, namely  $\{[Zn_3(L)_2(SO_4)_2(H_2O)_4] \cdot 2H_2O\}_n$  (1),  $\{[Cd(L)(OAc)]\}_n$ (2) and  $[Hg_2(L)(I)_3]_2$  (3) (HL = N' - isonicotinoylpyrimidine -2- carbohydrazonamide), have been synthesized and characterized by elemental analyses, infrared spectra and single-crystal X-ray diffraction analyze. The 1D complex 1 and complex 2, and the binuclear complex 3 are expanded to 3D networkers by the strong hydrogen bonds and  $\pi$ - $\pi$  stacking interactions. The photocatalytic degradation of methylene blue (MB) results indicate that complexes 1-3 are excellent candidates as photocatalysts in decomposing MB with the presence of H<sub>2</sub>O<sub>2</sub>. In addition, the luminescent properties of these three complexes have been studied in the solid state.

Key words: metal-organic framework; luminescent property; photocatalytic degradation

Up to now, in view of the intense desire for "green life", organic dyes, one of the main pollutants in wastewater, have been given tremendous attention because of their reduction the quality of water and adverse effects on human health. <sup>[1-2]</sup> In this regard, removing the poor biodegradable dyes from water has been attracting a great deal of attention and becoming a hot

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research topic <sup>[3-4]</sup>. There have been considerable efforts in treating wastewater based on adsorption and separation, <sup>[5-6]</sup> chemical treatment, <sup>[7]</sup> and photocatalytic methods. <sup>[8]</sup> Among these, photocatalysis offers a convenient and recyclable approach and has been applied in ecologically eliminating organic dyes and other noxious contaminants. Therefore, the investigation of inexpensive, stable, and efficient materials with improved photocatalytic properties is extremely urgent.

Recently, a new emerging application of metal-organic frameworks (MOFs) is photocatalysis, and some results have demonstrated that MOFs are efficient photocatalysts on the degradation of organic dyes, water splitting, or photoreduction of CO<sub>2</sub>.<sup>[9-10]</sup> How to achieve inexpensive, stable, efficient, and band-gaptunable photocatalysts based on MOFs is still a big challenge. Because the ligand could adopt different conformations and alternative linking modes in the crystallization, the rational selection of ligand always plays crucial role in the construction of the targeted MOFs. Hydrazone, a kind of schiff base ligand, have been attracting much attention because of their strong tendency to chelate to transition metals. Especially, the hydrazone asymmetrically decorated by different aza-aromatics possessing tridentate chelating and bridging coordinating sites may be a good candidate to construct novel MOFs with unique structure characters and interesting properties. However, this kind of organic compounds have rarely used as linkers to construct MOFs.

Motivated by the above-mentioned facts, we employed N'-isonicotinoylpyrimidine-2-carbohydrazonamide (HL) as ligand to achieve three novel complexes:  $\{[Zn_3(L)_2(SO_4)_2(H_2O)_4] \cdot 2H_2O\}_n$  (1),  $\{[Cd(L)(OAc)]\}_n$  (2) and  $[Hg_2(L)(I)_3]_2$  (3). The photocatalytic research result indicates that complexes 1-3 are excellent candidates as

photocatalysts in decomposing MB with the presence of  $H_2O_2$ . In addition, the luminescent properties of these three complexes have been studied in the solid state.

#### **1. Experimental section**

#### 1.1. Materials and measurements

All chemicals were commercially purchased except for HL which was synthesized according to the literature. <sup>[11]</sup> Elemental analyses for carbon, hydrogen and nitrogen were performed on a Thermo Science Flash 2000 element analyzer. FT-IR spectra were obtained in KBr disks on a PerkinElmer Spectrum One FTIR spectrophotometer in 4000-450 cm<sup>-1</sup> spectral range. Diffuse reflectance data were collected using a Shimadzu UV-3600 spectrophotometer, and the Kubelka– Munk function was used to estimate the optical band gap. The X-ray powder diffraction (XRPD) data were collected on a Bruker D8 ADVANCE diffractometer using monochromatic CuK $\alpha$ radiation, and the recording speed was 0.5s/step over the 2 $\theta$  range of 5-40° at room temperature. Thermogravimetric analyses (TGA) were performed using a TG-DTA 2010S MAC apparatus between 30 and 800 °C in atmosphere with heating rate of 10 °C min<sup>-1</sup>. The photoluminescent properties were measured on an F-4500 FL Spectrophotometer.

#### **1.2 Preparations**

#### 1.2.1 Preparations of ligand

HL was prepared by standard procedures (Scheme 1). 0.1 mol (10.5 g) of 2-cyanopyrimidine was dissolved in 100 cm<sup>3</sup> of methanol with 0.7 g of sodium and heated under reflux for 4 h. Equimolar amounts of 4-pyrazylhydrazide ((as to the 2-cyanopyrimidine, 13.7 g) was added to the solution and heated for 1 h. The solution was cooled to room temperature and the precipitate formed (yellow) was filtered off and air-dried for 2 h. Yield 16.1 g, 68%. 1H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.93 (2H, d), 8.60

(2H, d), 7.96 (2H, d), 7.62 (1H, s). MS: m/z = 242.105; calcd for  $C_{11}H_{10}N_6O$ , m/z = 242.36. Mp: 185 °C. IR (KBr) cm<sup>-1</sup>: 3393, 3137, 1665, 1624, 1573, 1550, 1476, 1375, 1312.



Scheme 1. Synthetic scheme and synthetic details of the ligand.

#### 1.2.2 Preparations of the complexes 1 - 3

{[Zn<sub>3</sub>(L)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]·2H<sub>2</sub>O}<sub>n</sub> (**1**). A mixture of HL (0.05 mmol, 12.1 mg), ZnSO<sub>4</sub>·7H<sub>2</sub>O (0.10 mmol, 28.7 mg), absolute ethanol (5 mL) and H<sub>2</sub>O (5 mL) was placed in a Teflon-lined stainless steelvessel (25 mL), heated to 80 °C for 3 days, and then cooled to room temperature at a rate of 5 °C/h. Pale yellow block crystals of **1** were obtained and picked out, washed with distilled water and dried in air. Yield: 18.4 mg, 75 % (based on HL). Elemental analysis (%): calcd for  $C_{22}H_{30}N_{12}O_{16}S_2Zn_3$  (Mr = 978.81): C 26.99, H 3.09, N 17.17 %; found: C 26.82, H 3.08, N 17.87 %. IR (KBr) cm<sup>-1</sup>: 3422, 3304, 1675, 1608, 1571, 1512, 1442, 1363, 1312.

{[Cd(L)(OAc)]}<sub>n</sub> (2). A mixture of HL (0.03 mmol, 7.4 mg), Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (0.06 mmol, 16.0 mg), absolute ethanol (1 mL) and H<sub>2</sub>O (4 mL) was placed in a sealed flask (10 mL), heated to 80°C for 3 days. Yellow block crystals of **2** were obtained and picked out, washed with distilled water and dried in air. Yield: 8.5 mg, 68 % (based on HL). Elemental analysis (%): calcd for  $C_{10}H_{11}CdClN_6O_2$  (Mr = 412.68): C 37.84, H 2.93, N 20.36; found C 37.21, H 2.88, N 21.18. IR (KBr) cm<sup>-1</sup>: 3458, 3273, 1654, 1607, 1567, 1521, 1438, 1341, 1312.

 $[Hg_2(L)(I)_3]_2$  (3). 3 was synthesized in the similar way as that described for 2, except that  $Cd(OAC)_2 \cdot 2H_2O$  and absolute ethanol (1 mL) were replaced by  $HgI_2(13.6 \text{ mg})$  and DMF (1 mL), respectively. Reddish-brown crystals of 3 were obtained and picked out, washed with distilled water

and dried in air. Yield: 18.4 mg, 60 % (based on HL). Elemental analysis (%): calcd for  $C_{22}H_{18}Hg_4I_6N_{12}O_2$  (Mr =2046.24): C 12.91, H 0.88, N 8.21; found C 12.52, H 0.81, N 8.35. IR (KBr) cm<sup>-1</sup>: 3473, 3354, 1657, 1607, 1564, 1516, 1437, 1347, 1310.

#### 1.3.1 X-ray crystallography

X-ray Single-crystal diffraction analysis of 1-3 was carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-*Ka* radiation ( $\lambda = 0.071073$  nm) by using  $f/\omega$  scan technique at room temperature. The structures were solved via direct methods and successive Fourier difference synthesis (SHELXS-97), <sup>[12]</sup> and refined by the full-matrix least-squares method on F<sup>2</sup> with anisotropic thermal parameters for all non-H atoms (SHELXL-97). The empirical absorption corrections were applied by the SADABS program. <sup>[13]</sup> The H-atoms of carbon were assigned with common isotropic displacement factors and included in the final refinement by the use of geometrical restraints. H-atoms of water molecules were first located by the Fourier maps and then refined by the riding mode. The crystallographic data for complexes 1-3 are listed in Table 1. Moreover, the selected bond lengths and bond angles are listed in Table 2. CCDC: 1443982, **1**; 1443983, **2**; 1443984, **3**.

#### **1.4 Photocatalytic experiments:**

To evaluate the photocatalytic activities of these three complexes, the photocatalytic degradation of methylene blue (MB) aqueous solution was performed at ambient temperature. The procedure was as follows: 30 mg of the desolvated samples was dispersed into 100 mL of methylene blue aqueous solution (12.75 mg  $\cdot$  L<sup>-1</sup>), followed by the addition of four drops of hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30%). The suspensions were magnetically stirred in the dark for over 1 h to ensure adsorption equilibrium of methylene blue onto the surface of samples. A 300 W xenon arc lamp was

used as a light source. An optical filter in the equipment of xenon arc lamp was used to filtering out the UV emission below 400 nm. Visible light then irradiated the above solutions for 0, 20, 40, 60 and 80 min, and the corresponding reaction solutions were filtered and the absorbance of methylene blue aqueous solutions was then measured by a spectrophotometer. For comparison, the constrast experiment was completed under the same conditions without any catalyst. The characteristic peak ( $\lambda = 664$  nm) for MB was employed to monitor the photocatalytic degradation process.

#### 2. Result and discussion

#### 2.1 Crystal structures of complexes 1-3

Single-crystal X-ray crystallographic analysis reveals that complex **1** crystallizes in the monoclinic space group p21/c and its asymmetric unit consists of one and a half Zn(II) ions, one L<sup>-</sup> ligand, one SO<sub>4</sub><sup>2-</sup> anion, two coordinated water molecules and one lattice water molecule. We were gratified to note that the HL ligand indeed coordinate to two Zn atoms from the tridentate chelating and the bridging sites. As shown in Figure 1a, the Zn1 ion is coordinated by two N atoms and one carbonyl oxygen atom from one L<sup>-</sup> ligand, one oxygen atom from the SO<sub>4</sub><sup>2-</sup> anion and one coordinated water molecule, thus creating distorted trigonal bipyramid coordination geometry. The Zn2 ion adopts a slightly distorted octahedral geometry coordinated to two N atoms from two L<sup>-</sup> ligands, two oxygen atoms from two SO<sub>4</sub><sup>2-</sup> anions and two coordinated water molecules. The Zn-O bond distances are in the range of 1.966(3) Å to 2.128(3) Å, and the Zn-N bond length is in the range of 2.002(4)) Å to 2.257(4) Å. 8.745 Å. The SO<sub>4</sub><sup>2-</sup> anion in **1** connects two Zn(II) ions adopting a  $\mu_{2n}\eta^{i}\eta^{i}$ -coordination mode. In this way, two SO<sub>4</sub><sup>2-</sup> anions bridge two Zn1 and one Zn2 ions to yield a trinuclear unit. Then the trinuclear units are connected by the L<sup>-</sup>



ligands to form an interesting corrugated 1D chain (Fig. 1c).

Figure. 1 Crystal structure of complex **1** showing a) the coordination environment of centre ions, b) the hydrogen bonds, c) the corrugated 1D chain, d) the 3D supramolecular network. Symmetry code: i = 0.5-x, 0.5-y, -z; ii = 0.5+x, 0.5-y, 0.5+z; iii = -x, -y, -0.5-z, iv = 0.5-x, 0.5+y, 0.5-z; v = x, 1+y, z.

The most fascinating feature of the structure is that the lattice water molecule (O8) occupy the cavity inside the networks and adopt an interesting orientation so that four O–H···O hydrogen bonds are generated between O8 and four circumjacent oxygen atoms (O6, O7,  $O5^{iv}$ ,  $O5^{v}$ ) (Fig. 1b). A closer inspection of the structure reveals that the amino group in the backbone forms strong hydrogen bonding with  $O2^{ii}$  and  $N2^{iii}$  (Fig. 1b). Thereupon, adjacent corrugated 1D chain is connected by the aforementioned hydrogen bonds to construct the three 3D network of **1** (Fig. 1d). X-ray single crystal structure analysis reveals that **2** crystallizes in the monoclinic space group p21/c. The asymmetric unit of crystal **2** consists of one Cd(II) ion, one L<sup>-</sup> ligand and one OAc<sup>-</sup> anion. As shown in Figure 2a, each Cd(II) ion in 2 possesses a distorted trigonal bipyramid coordination environment built by two N atoms and one carbonyl oxygen atom from one L<sup>-</sup> ligand, one nitrogen atom from other L<sup>-</sup> ligand and one oxygen atom from the OAc<sup>-</sup> anion (Cd-N =

2.225(5) - 2.448(6) Å, and Cd-O = 2.255(6) - 2.376(5) Å). In this fashion, L<sup>-</sup> ligands hold Cd(II) ions together, leading to the formation of a wavelike chain with the Cd···Cd distance across the L<sup>-</sup> ligand of 9.529(6) Å (Figure 2b). The neighboring chains are then joined by the N3-H3A···O2 hydrogen bonds, forming a supermolecule 2D-layered structure (Figure 2c and 2d).



Figure 2. Crystal structure of complex **2** showing a) the coordination environment of centre ions, b) the wavelike 1D chain, c), the hydrogen bonds d) the 2D supramolecular network. Symmetry code: i = -1+x, 0.5–y, -0.5+z.

Single-crystal structure determination shows that **3** crystallizes in a triclinic system with p-1 space group. The asymmetric unit of **3** contains two Hg(II) ions, one L<sup>-</sup> ligand and three iodide ions. One Hg(II) ion is coordinated by two N atoms and one oxygen atom of one ligand and three iodide ions resulting in a tetragonal plane geometry. The other mercury is coordinated by one N atom of pyridine group and two I ions (Figure 3a). The measured Hg-O distance is 2.454(7) Å, Cu-N distance is in the range of 2.178(8) to 2.646(9) Å, and Hg-I distance is in the range of 2.544(10) to 2.783(17) Å, respectively. The bond angle around the Hg(II) center lies in the range of 68.0(3)–143.0(6)°. As illustrated in Figure 3b, the pyridine moiety of one molecule very close to the pyrimidine part of the adjacent molecule and results in strong  $\pi$ - $\pi$  stacking, which give rise to the formation of the 1D chain. Furthermore, the  $\pi$ - $\pi$  interactions formed chains are connected



by the intermolecular hydrogen bonds N3-H3B···I2 into extended plane structure (Fig. 3c).

Figure 3. Crystal structure of complex **3** showing a) the coordination environment of centre ions, b) the 1D chain, c) the hydrogen bonds and the 2D supramolecular network.

#### 2.2 IR spectrum

As shown in Figure 4, the v(OH) bands of the ligand appear at 3393 cm<sup>-1</sup> and the aqueous v(OH) bands of the complexes appear at 3422 cm<sup>-1</sup> in **1**, 3458 cm<sup>-1</sup> in **2** and 3473 cm<sup>-1</sup> in **3**. This shows that there are some crystal water molecules in the complexes. The v(NH) bands at 3137 cm<sup>-1</sup> in the ligand and 3304 cm<sup>-1</sup> in 1, 3273 cm<sup>-1</sup> in **2** and 3354 cm<sup>-1</sup> in **3**, showing the strong hydrogen bonding between amino group in the backbone with O2(ii) and N2(iii) (Fig. 1b).<sup>[14]</sup> The v(C=O) band of the ligand appears at 1624 cm<sup>-1</sup>, however, the bands of the complexes occur at 1607 cm<sup>-1</sup> in complexes, which makes a shift towards lower frequency by 17 cm<sup>-1</sup>. The  $v(C=N)_{pyrimidine}$   $v(C=N)_{pyridine}$  band of the ligand appears at 1573 cm<sup>-1</sup> and 1550 cm<sup>-1</sup>, however, the bands of the complexes of the bands of the ligand appears at 1573 cm<sup>-1</sup> and 1550 cm<sup>-1</sup>.

**3.** As to the v(C=N) of the group NH<sub>2</sub>-C=N, the band of ligand appears at 1476 cm<sup>-1</sup>, while the bands of the complexes occur at 14422 cm<sup>-1</sup> in **1**, 1438 cm<sup>-1</sup> in **2** and **3**. The shift towards lower frequency of the v(C=N) and v(C=O) showing the nitrogen atom of these two N atoms and the O atom take part in the coordination.<sup>[15]</sup>



Figure 4. The IR spectra of the ligand (HL) and complexes.

#### 2.3 Thermal analysis (TGA)

To estimate the stability of the coordination architectures, thermogravimetric analyses (TGA) were carried out (Figure 5). The TGA curve of **1** shows two steps weight loss 2.81% at 85.6 - 136.5 °C and 2.95% at 136.5 - 224.5 °C, corresponding to the loss of two lattice water molecules and two coordinated water molecules (calcd: 2.83%), respectively. The removal of the organic components and sulfate anions occurs in the range 344.5 - 418.0 °C. The remaining weight corresponds to the formation of ZnO (obsd, 24.05%; calcd, 24.95%). As for complex **2**, the initial weight losses in the range of 153.8 - 243.9 °C correspond to the losses of the coordinated acetate anion (obsd, 14.08%; calcd, 14.31%). The further weight losses represented the decomposition of the anhydrous

compounds, leading to the formation of a pale residue of CdO (obsd, 30.10%; calcd, 31.11%). The TGA data of complex **3** show that it is stable up to 280 °C and then keeps losing weight from 280 to 405 °C, corresponding to the losses of ligands and iodide anions. A red amorphous residue of HgO (observed 41.68%, calculated 42.34%) is remained.



Figure 5. TG plots of complexes.

2.4 Photoluminescent Properties.

In order to evaluate the phase purity of 1-3, powder X-ray diffraction experiments have been performed at room temperature (Figure 6). Their high purity solid state phases were confirmed by the good match of the patterns for the as-synthesized samples and simulated ones from the single-crystal data. Luminescent properties of MOFs based on d<sup>10</sup> metal ions are of special interest due to their prospective applications in electroluminescent displays, nonlinear optical (NLO) devices and so on. The combination of organic linkers and metal centers in MOFs provides an

efficient route to a new type of photoluminescent materials with potential applications because of their structure- and metal-dependent emission. In this context, solid-state photoluminescent behavior of HL as well as complexes 1-3 are examined in the solid state at room temperature.



Figure 6. a) The PXRD patterns of complex 1, b) The P XRD patterns of complex 2, c) The PXRD patterns of complex 3 and d) The emission spectra of the ligand and complexes 1-3 at room temperature.

As shown in figure 6d, the HL ligand are nearly nonfluorescent in the range 400-650 nm for excitation wavelength of 370 nm at ambient temperature.<sup>[16]</sup> The intense emissions occur at 570 and 625 nm for complexes **1** and **2** with the excitation wavelength of 370 nm. The emissions are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since ZnII is difficult to oxidize or reduce due to its d<sup>10</sup> configuration. <sup>[17]</sup> Thus, they may be assigned to intraligand ( $\pi^* \rightarrow$  n or  $\pi^* \rightarrow \pi$ ) emission. The enhancement of luminescence in d<sup>10</sup> complexes may be attributed to ligand chelation to the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.<sup>[18]</sup> In comparison, complex **3** shows relatively weak emission bands. This significantly weakened intensity of the emission is probably attributed to the quenching effect of iodide ions. <sup>[19]</sup> The observation

indicates that the complexes of 1 and 2 may be candidates for potential photoactive materials.

The fluorescence property means the transition from the excited state to the ground state at the same energy level. While the photocatalytic property requires the excited electrons stay at the surface of the material long enough to participate surface oxidation-reduction reaction. Therefore, the fluorescence properties and photocatalytic properties are theoretically reverse process. In general, materials with good photocatalytic performance will not be too strong fluorescence. By the above points, the photocatalytic properties of complexes **1-3** need to be investigated.

Complexes	1	2	3
Empirical formula	$C_{22}H_{30}N_{12}O_{16}S_2Zn_3\\$	$C_{13}H_{12}CdN_6O_3$	$C_{22}H_{18}Hg_4I_6N_{12}O_2$
Formula weight	978.81	412.69	2046.24
Temperature (K)	296	296	296
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	c2/c	p21/c	p-1
<i>a</i> (Å)	28.759(5	7.497(7)	7.9081(14)
<i>b</i> (Å )	7.4727(12)	14.608(13)	9.1706(17)
<i>c</i> (Å )	18.024(3)	15.010(10)	14.576(3)
$\alpha(\text{deg})$	90	90	78.838(3)
β(deg)	121.890(5)	118.66(3)	87.184(3)
γ(deg)	90	90	68.896(3)
Volume (Å <sup>3</sup> )	3288.7(10)	1442(2)	967.3(3)
Z	4	4	1
Calculated density	1.977	1.977	3.513
Absorption	2.393	2.393	20.650
F(000)	1984	816	888
Crystal sizes (mm)	0.3 x 0.2 x 0.2	0.3×0.2×0.2	0.2×0.1×0.1
R(int)	0.0754	0.0754	0.0257
Reflections collected/	10015 / 3960	6842 / 2527	4982 / 3375
Goodness-of-fit on $F^2$	0.974	0.974	1.058
Final $R^a$ indices $[I > 2\sigma(I)]$	R1 = 0.0490	R1 = 0.0491	R1 = 0.0399
	wR2 = 0.0927	wR2 = 0.0928	wR2 = 0.0932
R indices (all data)	R1 = 0.0994	R1 = 0.0993	R1 = 0.0519
	wR2 = 0.1118	wR2 = 0.1118	wR2 = 0.0986

Table 1 Crystal data and structural refinement of complexes 1-3

### Table 2 Selected bond lengths (Å) and angles (°) for complexes 1-3

Complex 1					
Zn(1)-O(2)	1.965(3)	Zn(1)-N(1)	2.257(4)	Zn(2)-O(7)#1	2.130(3)
Zn(1)-O(6)	1.995(3)	Zn(2)-O(3)	2.102(3)	Zn(2)-N(6)#2	2.160(4)
Zn(1)-N(4)	2.001(4)	Zn(2)-O(3)#1	2.102(3)	Zn(2)-N(6)#3	2.160(4)
Zn(1)-O(1)	2.084(3)	Zn(2)-O(7)	2.130(3)	O(7)-Zn(2)-N(6)#2	90.41(12)
O(2)-Zn(1)-O(6)	114.32(13)	O(1)-Zn(1)-N(1)	150.64(13)	O(7)#1-Zn(2)-N(6)#2	89.59(12)
O(2)-Zn(1)-N(4)	117.51(14)	O(3)-Zn(2)-O(3)#1	180.00(18)	O(3)-Zn(2)-N(6)#3	89.87(12)
O(6)-Zn(1)-N(4)	127.43(15)	O(3)-Zn(2)-O(7)	84.08(12)	O(3)#1-Zn(2)-N(6)#3	90.13(12)
O(2)-Zn(1)-O(1)	103.40(13)	O(3)#1-Zn(2)-O(7)	95.92(12)	O(7)-Zn(2)-N(6)#3	89.59(12)
O(6)-Zn(1)-O(1)	99.91(13)	O(3)-Zn(2)-O(7)#1	95.92(12)	O(7)#1-Zn(2)-N(6)#3	90.41(12)
N(4)-Zn(1)-O(1)	76.50(13)	O(3)#1-Zn(2)-O(7)#1	84.08(12)	N(6)#2-Zn(2)-N(6)#3	180.0(2)
O(2)-Zn(1)-N(1)	94.39(14)	O(7)-Zn(2)-O(7)#1	180	O(7)-Zn(2)-N(6)#2	90.41(12)
O(6)-Zn(1)-N(1)	93.61(13)	O(3)-Zn(2)-N(6)#2	90.13(12)		
N(4)-Zn(1)-N(1)	74.59(13)	O(3)#1-Zn(2)-N(6)#2	89.87(12)		
Complex 2					
Cd(1)-N(4)	2.225(5)	Cd(1)-O(2)	2.255(6)	Cd(1)-N(1)	2.448(6)
Cd(1)-N(6)#1	2.254(5)	Cd(1)-O(1)	2.367(5)		
N(4)-Cd(1)-N(6)#1	136.7(2)	O(2)-Cd(1)-O(1)	93.24(19)	N(6)#1-Cd(1)-O(1)	92.61(19)
N(4)-Cd(1)-O(2)	111.4(2)	N(4)-Cd(1)-N(1)	69.40(18)	O(1)-Cd(1)-N(1)	137.60(17)
N(6)#1-Cd(1)-O(2)	108.5(2)	N(6)#1-Cd(1)-N(1)	112.5(2)		
N(4)-Cd(1)-O(1)	68.99(18)	O(2)-Cd(1)-N(1)	109.11(19)		
		Complex 3	3		
Hg(1)-N(4)	2.178(8)	Hg(2A)-N(6)	2.485(11)	Hg(2B)-N(6)	2.391(13)
Hg(1)-O(1)	2.454(7)	Hg(2A)-I(2)	2.589(7)	Hg(2B)-I(3)	2.544(10)
Hg(1)-I(1)	2.5644(9)	Hg(2A)-I(3)	2.642(6)	Hg(2B)-I(2)	2.783(17)
Hg(1)-N(1)	2.646(9)	Hg(2A)-I(2)#1	3.247(5)	N(6)-Hg(2B)-I(3)	107.8(5)
N(4)-Hg(1)-O(1)	69.2(3)	N(6)-Hg(2A)-I(2)	101.2(3)	N(6)-Hg(2B)-I(2)	98.3(4)
N(4)-Hg(1)-I(1)	171.3(2)	N(6)-Hg(2A)-I(3)	102.1(3)	I(3)-Hg(2B)-I(2)	143.0(6)
O(1)-Hg(1)-I(1)	114.78(18)	I(2)-Hg(2A)-I(3)	150.0(3)	N(6)-Hg(2B)-I(2)#1	92.9(5)
N(4)-Hg(1)-N(1)	68.0(3)	N(6)-Hg(2A)-I(2)#1	88.5(3)	I(3)-Hg(2B)-I(2)#1	111.1(5)
O(1)-Hg(1)-N(1)	135.1(2)	I(2)-Hg(2A)-I(2)#1	94.05(17)	I(2)-Hg(2B)-I(2)#1	92.9(2)
I(1)-Hg(1)-N(1)	105.95(17)	I(3)-Hg(2A)-I(2)#1	105.25(18)	N(6)-Hg(2B)-I(3)	107.8(5)

Symmetry transformations used to generate equivalent atoms: For 1: #1 x-1,-y+1/2,z-1/2, #2 x+1,-y+1/2,z+1/2; for 2: #1 -x+1/2,-y+1/2,-z, #2 -x,y,-z-1/2, #3 x+1/2,-y+1/2,z+1/2; for 3: #1 -x+2, -y+1, -z+1.

Tuble 5 Hydrogen bonds of complexes 1 5				
D-HA	<i>d</i> (D-H) (Å)	$d(\mathrm{HA})(\mathrm{\AA})$	$d(\mathbf{D}\mathbf{A})$ (Å)	(D-HA)(deg)
		Complex 1		
N(3)-H(3A)O2	0.85	2.34	3.036(5)	154.0
N(3)-H(3B)N2	0.85	2.60	3.227(5)	131.7

#### Table 3 Hydrogen bonds of complexes 1-3

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O(6)-H(6A)O8	0.85	1.98	3.783(5)	156.7	
O(7)-H(7B)O4	0.85	1.85	2.695(5)	171.6	
O(7)-H(7A)O8	0.85	2.09	2.934(5)	170.5	
O(8)-H(8A)O5	0.85	1.99	2.838(5)	177.2	
O(8)-H(8B)O5	0.85	2.15	2.988(5)	171.5	
Complex 2					
N(3)-H(3A)O(2)	0.92	2.10	2.970(8)	159.3	
N(3)-H(3B)N(2)	0.91	2.26	2.730(8)	111.6	
Complex 3					
N(3)-H(3B)I(2)	0.86	3.22	3.924(9)	140.5	

#### 2.3 Photocatalysis Property.

The band gap of complexes **1-3** was measured by a solid state ultraviolet–visible (UV–vis) diffuse reflection measurement method at room temperature. In a figure of K-M function versus energy, the band gap  $E_g$  is defined as the intersection point among the energy axis and line extrapolated of the linear portion. <sup>[20]</sup> The K-M function,  $F = (1-R)^2/2R$  (R is the reflectance of an infinitely thick layer at a given wavelength), can be converted from measured diffuse reflectance data. As shown in Figure 7, the Eg values for complexes 1-3 are 2.20, 2.05, and 2.25 eV, respectively. The reflectance spectra show that there exist the optical band gap and semiconductive behaviors in complexes **1-3**, and these complexes can be employed as potential semiconductive materials (the  $E_g$  of a semiconductor is about 1-3 eV). <sup>[21]</sup>

In order to evaluate the photocatalytic effectiveness of the insoluble complexes 1-3, the photocatalytic degradation of methylene blue (MB) aqueous solution was performed at ambient temperature. Excitingly, complexes 1-3 exhibit good photocatalytic activities in the presence of  $H_2O_2$  under a 300 W xenon lamp irradiation.



Figure 7. a) UV-vis absorption spectrum of complexes 1-3; b) Kubelka-Munk-transformed diffuse reflectance of



Figure 8. The absorption spectra of the solution of methylene blue a) without catalyst, b) with complex 1 as catalyst, c) with complex 2 as catalyst, and d) with complex 3 as catalyst.

As can be seen in Figure 8, the characteristic absorption peak of MB (664 nm) were gradually reduced with time, increasing from 0 to 80 min. Besides, the changes in the  $C_t/C_0$  plot of MB solutions versus irradiation time are shown in Figure 9 to clarify the photocatalytic results (wherein  $C_t$  is the concentration at time t=t of the MB solutions and  $C_0$  is the concentration at time t=0 of the MB solutions). From figure 7, the degradation ratio of MB reaches 28% without any

photocatalyst, while it increases to 82%, 88% and 87%, respectively, when complexes **1**, **2** and **3** are added to the mixture as catalyst. We know that the efficiency of the photocatalyst is a function of the balance between charge separation, interfacial electron transfer, and charge recombination.



Figure 9. Photodegradation of MB with complexes 1-3.

In general, a narrow band gap leads to the ease of the charge separation, so the photocatalytic degradation rate of MB should follow the reverse order of band gaps of the complexes. As calculated, the band gaps of complexes 1-3 are 2.20, 2.05 and 2.25 eV, respectively. The  $E_g$  of 1-3 follows the sequence 2 < 1 < 3, and the reverse sequence of band gaps agrees with the degradation rate of MB. In addition, the stabilities of these three complexes are investigated by measuring the powder PXRD patterns after photocatalytic reactions. The PXRD patterns are consistent with those of the original ones, which confirm that these complexes keep their skeleton well after the photocatalytic process. The photocatalytic research result indicates that complexes 1-3 are excellent candidates as photocatalysts in decomposing MB with the presence of H<sub>2</sub>O<sub>2</sub> and may have possible application in decomposing other dyestuff.

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## Highlights

> A hydrazone derivative ligand N'-isonicotinoylpyrimidine-2-carbohydrazonamide (HL) have been used to constructed functional MOFs.

> Three MOFs are excellent candidates as photocatalysts in decomposing MB with

the presence of  $H_2O_{2.}$