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# A novel Co(II) based multifunctional metal-organic framework: synthesis, fluorescence sensing and magnetic analysis

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Abstract: A new coordination Co(II) complex, namely,  $[Co_2(DIPT)_4(PClA)_2Cl_2] \cdot H_2O(NCl-1)$  (DIPT= 2-(2,4-dichlorophenyl) -1H-imidazo [4,5-f]-[1,10]phenanthroline, HPClA=3-(2-chlorophenyl)acrylie ) has been synthesized under solvothermal conditions and structurally characterized by elemental analysis, IR spectroscopy, single-crystal X-ray diffraction analysis, nitrogen adsorption analysis and powder X-ray diffraction. NCl-1 constructed by six coordinated mode with metal center and connected different ligands and ions, exhibits a three-dimensional structure under interactions of hydrogen bond and  $\pi$ - $\pi$  stacking interactions. The luminescence explorations demonstrated that NCl-1 exhibits highly selective and sensitive sensing for organic solvents (MeOH) and metal ion (Fe<sup>3+</sup>). Furthermore, magnetic analysis indicated that NCl-1 also own the property of anti ferromagnetic.

**Keywords:** Hydrothermal synthesis; Crystal structure; Fluorescent sensing; Magnetic property.

#### **1. Introduction**

In the field of organometallic chemistry and crystal engineering, the design and assembly of metal-organic coordination frameworks ( MOFs ) with appealing structures and properties have stimulated interests of chemists in recent years. MOFs show potential applications in areas such as luminescence, catalysis, magnetism, gas storage, guest species recognition and so on<sup>[1-3]</sup>. Nowadays intensive researches in the field of metal organic frameworks ( MOFs ) containing transition metal ions are explored. Usually, the structures and properties of coordination polymers greatly depend on the elaborate selection of metal ions, organic ligands and synthetic methods, and ome of them consisting of metal ions coordinated to organic molecules capable of forming chains, layers or even 3D structures present remarkable properties.

Many MOFs have now been considered to be compelling and promising sensors for detecting small inorganic, organic molecules, and metal ions<sup>[4-6]</sup>. some significant progress has been made based on the rational choice of metal ions and organic ligands as well as the structural features ( open metal sites, the highly regular channel structures, controllable pore sizes, and so on ) of constructed MOFs<sup>[7,8]</sup>. It's well known that Fe<sup>3+</sup> ion is a kind of ubiquitous element in human body and also plays an important role in all biological system. It influences electron transfer and oxygen metabolism processes in DNA and RNA synthesis. Both excess and deficiency from the normal permissible limit can induce serious disorders. Accordingly, the selective detection of Fe<sup>3+</sup> is very important for human health. In recent decades, water pollution has become a global environmental issue<sup>[9-11]</sup>, and the organic pollutants among them made the problem more serious<sup>[12,13]</sup>. Therefore, the selective detection of organic pollutants are very important<sup>[14, 15]</sup>. While transition metal ions, such as Co(II), can produce a variety of complexes that not only exhibit novel structures but can detect and authenticate of small organic molecules and metal ions<sup>[16-18]</sup>.

In this paper, we synthesized a kind of novel Co(II) complex, The fluorescent investigation demonstrated that NCl-1 can select and sense  $Fe^{3+}$  ions and methanol

molecules with high sensitivity, indicating that **NCl-1** shows potential applications in fluorescent sensor. The magnetic properties are investigated as well.

#### 2. Experimental techniques

#### 2.1 Materials and Measurements

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The photoluminescence spectra for the powdered solid samples were measured at room temperature and collected with a Hitachi F-4600 fluorescence spectrophotometer. FT-IR spectra (KBr pellets) were carried out on a PerkinElmer Frontier FT-IR spectrometer, the statistics were recorded in the range of 4000-400 cm<sup>-1</sup>. The TGA were performed with a Rigaku Thermo Plus-EVO thermal analyzer under N<sub>2</sub> Atmosphere with a heating rate of 10 °C/min. Elemental analysis (N, C and H) was conducted on a EuroVector EA3000 elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from  $2\theta$  = 1.5° up to 60° with 0.02° increment. Temperature dependent magnetic susceptibility data for polycrystalline NCI-1 were obtained on a MPMS XL-7 SQUID magnetometer under an applied field of 2000 Oe over the temperature range of 1.8-300 K. Before measurement, the samples were degassed in vacuum at 150 °C for more than 10 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The nonlocal density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution. nitrogen sorption isotherms were measured at 273 K with a Bel Japan Inc. model BELSORP-max analyzer, respectively. Before measurement, the samples were also degassed in vacuum at 120 °C for more than 10 h.

#### 2.2 Synthesis of Ligands ( DIPT and HPClA )

The synthesis of DIPT ( 2-(2,4-dichlorophenyl)-1H- imidazo[4,5-f]-[1,10]phenanthroline ) involves a four components assembling of a mixture of 1,10-Phenanthroline-5,6-dione (2.10 g, 10 mmol), ammonium acetate (2.5 g, 30 mmol) and 2,4-dichlorobenzaldehyde (1.1 ml, 10 mmol) in distilled ethanol medium (20 ml).

The reaction mixture was refluxed in ethanol  $(78^{\circ}C)$  and the completion of the reaction was monitored by thin layer chromatography (TLC) technique, using benzene : ethyl acetate (9:1) as the eluent. The reaction mixture was then extracted by dichloromethane and the resultant products was purified by column chromatography.

The synthesis process of HPClA ( 3-(2-chlorophenyl)acrylie ) was as follows, malonic acid (9.4 mmol), toluene (12 mL), and triethylamine (12.5 mmol) were added in a round bottom and mixed for 5 min. 2-chlorobenzaldehyde (9.4 mmol) and piperidine (1.7 mmol) were added slowly then. The mixed solution was refluxed for 2–3 h. The solvent was taken away under vacuum and the resulting viscous liquid was cooled to room temperature. Wash the reaction solution with 5% bicarbonate and ethyl acetate. The organic layer was neutralized by HCl solution, and the resulting solid was filtered and dried in vacuum, then target compound was obtained.

#### 2.3 Synthesis and growth of NCl-1 single crystal

A mixture of  $CoCl_2 \cdot 6H_2O$  59.4 mg ( 0.2 mmol ), DIPT 145.6 mg ( 0.4 mmol ), HPCIA 36.4 mg ( 0.2 mmol ), 150 mL of deionized water and 5 mL of methanol solution were stirred for 90 min, then adjusted the pH value to 6.5 by adding NaOH solution. The reactants solution was heated at 423 K in a 50 mL Teflon stainlesssteel autoclave for five days. The reaction mixture was then slowly cooled to room temperature. Colorless crystals suitable for single-crystal X-ray diffraction analysis were collected by filtration which was washed several times with distilled water and then saved in the clean saturated mother liquor. Yield: 47.8 % based on Co (II). Anal. for  $Co_2 C_{94} H_{40} Cl_{14} N_{14} O_5$  ( % ): calcd. C 50.60, H 1.79, N 10.04; found C 51.07, H 1.60, N 10.14. FT/IR data ( cm<sup>-1</sup>): 3446 ( w ), 1637 ( s ), 1572 ( m ), 1463 ( m ), 1368 ( m ), 1108 ( m ), 811 ( s ), 804 ( s ) ( Fig. S1 ).

#### 3. Results and discussion

#### **3.1. Single crystal X-ray diffraction**

Crystal structures measurement were performed on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatic Mo K $\alpha$  [ $\lambda$  = 0.71073 Å] radiation by using the  $\phi$  and  $\omega$  scan mode at 293. The structures were determined by

direct methods and refined by full-matrix least-squares procedures using the SHELXTL. Crystallographic parameters and the data collection statistics are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: deposition numbers CCDC 1850613. These data may be obtained free of charge from the Cambridge Crystallographic Data Center through <a href="http://www.ccdc.cam.ac.uk/data\_request/cif.">http://www.ccdc.cam.ac.uk/data\_request/cif.</a>

#### **3.2. Compound Structure**

#### **3.2.1 Detail Description**

Crystallographic analysis reveals that NCI-1 crystallizes in the triclinic space group P-1. The asymmetric unit of NCI-1 consists of one crystallographically independent Co<sup>2+</sup> ion, two DIPT ligands, one HDHTA ligand and one Cl<sup>-</sup> ligand (Fig. 1). As shown in Fig. 2, the coordination environment of  $Co^{2+}$  cation and the linkage modes of four ligands are well denoted.  $Co^{2+}$  is in a six-coordinated environment, supplied by four nitrogen atoms (N1, N2, N5, N6) from two DIPT, and the two remaining positions are respectively occupied by one oxygen atom (O1) and one chlorine atom( Cl1 ) from the HDHTA and Cl-1 ligands. The neighboring rings interact through  $\pi$ - $\pi$  stackings between the ligands ( in total nine kinds of  $\pi$ - $\pi$  stacking, such as: Cg (1)-Cg (3), Cg (4)-Cg (7), Cg (4)-Cg (8), Cg (7)-Cg (4), Cg (8)-Cg (4), Cg (9)-Cg (5) and son on ) to generate a three-dimensional layer structure( Table.S1 ). Besides, the adjacent layers are stacked to furnish a 3D supramolecular network structure via  $\pi$ - $\pi$  interactions between DIPT and HAHTA. In the network structure, there are C (19)-H (63)...Cl (10)#3, C (44)-H (87)...OW#4, C (46)- H(115)...Cl (8)#5 and C (12)- H (32)...Cl (3)#2 as well as halogen bonds (Table.S2) which may stabilize the structure of NCI-1and extend into a 3D layered supramolecular architecture (Fig. 3a, Fig. 3b). The three-dimensional structure is formed by the action of hydrogen bond and  $\pi$ - $\pi$ stacking interactions.

#### 3.2.2 Quantum chemistry calculation for NCI-1( Electron cloud distribution )

The quantum chemistry calculation of NCI-1 was performed with Gaussian09<sup>[29]</sup>

program at the B3LYP/GenECP level ( the 6-31+G(d) basis set for C, H, O, N and LANL2DZ basis set for Co ) to model the initial guess of the title complexes obtained from the X-ray refinement data ( cif ). In order to save computing time, the structures were not optimized in the calculations.

The calculation covered 90 atoms, 1332 basis functions, 2576 primitive gaussians, 290  $\alpha$  electrons and 289  $\beta$  electrons for the model of NCI-1. The total molecular energy is = -7599.053066 a.u., the energies of HOMO and LUMO are -0.190 and -0.107 a.u., respectively, and the  $\Delta E$  (E<sub>LUMO</sub>-E<sub>HOMO</sub>) value to be -0.083 a.u., which shows the complex is stable in the ground state <sup>[30]</sup>. The HOMO and LUMO are presented in Fig. 9, from which we can see the HOMO electron cloud is mainly located at HPCIA and the LUMO electron cloud at the DIPT. Selected atom net charges and electronic configuration of the title complex at the B3LYP/(6-31+G(d))(for C, H, N, O and Cl) and Lanl2dz (for Co) levels are listed in Table. 3. The calculation results show that electronic configurations of the central Co atoms are  $4S^{0.26}3d^{7.57}4p^{0.53}4d^{0.01}$ those of 0 and Ν and atoms are  $2s^{1.66\sim1.71}2p^{4.97\sim5.08}3p^{0\sim0.01}3d^{0\sim0.01}$  and  $2s^{1.30\sim1.32}2p^{4.05\sim4.08}3p^{0.01\sim0.02}4p^{0\sim0.01}$ , as well as the Cl atom is  $3S^{1.90}3p^{5.63}$ . The valence of cobalt is +2. The cobalt partially obtains electrons from the DIPT and HPCIA ligands, illustrating that the charge of the central Co metals for NCI-1 has positive charge, and it is 0.63426 for Co. Based on the above results, one can conclude that the Co(II) ion coordination with N and O atoms is mainly on the 2s and 2p orbitals. All O atoms supply electrons of 2s and 2p to the Co (II) ion and form coordination bonds. N atoms form coordination bonds with the Co (II) ion using 2s, 2p and 3p orbitals. Therefore, the Co (II) ion obtained some electrons from O atoms of HPClA ligand and N atoms of DIPT ligand. Thus, according to valence-bond theory the atomic net charge distribution in the NCI-1 show obvious covalent interactions between the coordinated atoms and Co (II) ion.

#### 3.3. PXRD, TGA and N<sub>2</sub> adsorption analysis

PXRD analyses of NCI-1 were carried out at room temperature (Fig. S2). The experimental PXRD patterns are closely matched with those in the simulated patterns

from single-crystal structures, revealing the phase purity of the bulk crystalline materials. The thermal properties of NCl-1 is investigated by TGA under an N<sub>2</sub> atmosphere with a heating rate of 10 °C min<sup>-1</sup>. As depicted in Fig. S3, the only one weight loss in the temperature range of 100–750 °C is consistent with the removal of one water molecules and four DIPT ligands ( obsd 39.85%, calcd 40.36 % ). The remaining residue corresponds to the formation of CoCl<sub>2</sub> and two PClA ligands ( obsd 61.15 %, calcd 60.64 % ). The NCl-1 had exhibited excellent thermal stabilities. As well as we studied the N<sub>2</sub> adsorption-desorption isotherm of the complex as shown in Fig. S4. It can be seen that the adsorption-desorption isotherms of 77 K and 1 atm show a type III isotherm with a Brunauer-Emmett-Teller surface area (  $S_{BET}$  ) of 27.70 m<sup>2</sup> g<sup>-1</sup>.

#### **3.4 Magnetic properties**

The temperature dependence data of the magnetic susceptibilities for NCI-1 was collected in the temperature range of 2-300 K with an applied field of 1000 Oe. The reciprocal susceptibility versus temperature plot above 10 K obeys the Curie-Weiss law. The magnetic behavior of NCI-1 also obeys the Curie-Weiss law from 50 K to 300 K with C = 5.484 cm<sup>3</sup> mol<sup>-1</sup> K and  $\theta = -1.925$  K (Fig. 4a)<sup>[20-22]</sup>. The  $\chi_m$  value increases smoothly, reaching a maximum of 1.78 cm<sup>3</sup> mol<sup>-1</sup> at 2.0 K as the temperature decreases. On the other hand, the  $\chi_m T$  value at 300 K is 5.47 cm<sup>3</sup> mol<sup>-1</sup> K, which is larger than the spin-only value of 1.875 cm<sup>3</sup> mol<sup>-1</sup> K expected for one high-spin Co(II) centers (S = 3/2 and g = 2.0)<sup>[23-25]</sup>. This larger value benefits from the contributions of orbital angular momentum at high temperatures to the susceptibility. After cooling, the  $\gamma_m T$  value decreases monotonically and reaches a minimum value of 3.54 cm<sup>3</sup> mol<sup>-1</sup> K at 2 K, suggesting a dominant antiferromagnetic interaction between Co(II) centers. To further investigate the magnetic interactions, other mal magnetic hysteresis loop (M-H) measurements at 2 K (Fig. 4b) was performed . The M value at 2 K and 6 T is 2.88 N $\beta$ , lower than the saturated value 3.0 NB. which is characteristic of strong anti ferromagnetic interactions and Co(II) ion at high spin state.

### 3.5 Luminescent property of NCl-1 with high sensitivity for MeOH and $\mathrm{Fe}^{3+}$

#### 3.5.1 Luminescent property of NCI-1

Luminescence is an important property for  $d^{10}$  metal complexes, so the solid-state emission and excitation spectra of NCI-1 at room temperature are tested and showed in Fig. 7a. An obvious emission are observed at 472nm for NCI-1. In order to explore the influence of the free DIPT and HPCIA ligands to NCI-1, luminescence properties of the two ligands were recorded for comparison under same conditions. The DIPT ligand exhibits emission bands locating at 472 and 494 nm, respectively. The result of experiments indicates that HPCIA ligands have no fluorescence. The emissions of NCI-1 may be assigned to the metal-to-ligand charge-transfer (MLCT).

The luminescence of NCI-1 was examined in solid state and the spectrum exhibits a slight blue shift, compared with that of the luminous ligand ( DIPT ). The reason may be that the metal ion [Co(II)] coordinates to the ligands, which probably forms the back-coupling  $\pi$ -bond between the metal and ligands, and decreases the electron transition energy of intra ligand charge transfer. Otherwise, the ligand coordinated with metal ions also forms additional five-membered rings, which also increases the  $\pi$ - $\pi$ \* conjugation length and the conformational coplanarity of the ligand, accordingly reduces the energy gap between the  $\pi$  and  $\pi$ \* molecular orbitals of the ligand.

#### 3.5.2 High sensitivity for MeOH

**NCI-1** is luminescent both in the solid and liquid state, so we have studied their potential as a fluorescent probe for the selective and sensitive detection to organic solvents commonly used in chemical industry. In this study, the following organic solvents were chosen: Petroleum ether ( PE ), ethyl acetate ( EAC ), trichloromethane ( CHCl<sub>3</sub> ), methylbenzene ( MB ), acetonitrile ( CH<sub>3</sub>CN ) and methanol ( MeOH ). Meanwhile, deionized water was selected as the blank control. The suspensions were prepared by introducing 2.00 mg of complex powders into 4.00 mL of these organic solvents. All of the titration experiments were executed by gradually adding suspensions solution in an incremental mode. As **NCI-1** showed intensity at 473 nm emission band. A significant red shift and blue shift was observed in aqueous solution

compared with that of its solid state, which may be caused by the solvatochromism effect.

As presented in Fig. 5, a significant quenching effect to the luminescent intensities exists of **NCI-1** in MeOH which may act as a high-performance luminescence for detecting this organic solvent, whereas other organic solvent showed no quenching effect on the luminescence intensity. The difference originating from the distinct saturations and functional groups of the central carbon atom, None fluorescence quenching occurred for solvent ( PE, EAC, CHCl<sub>3</sub>, MB and CH<sub>3</sub>CN ) due to none alcohol hydroxyl in their compound structure or low saturation of the central carbon atom is.

The higher the saturation degree of carbon atom, the lower the sterically hindered of conjugate acid, so the electron absorption capacity is enhanced and transfer of the excitation energy to metal ions effectively suppressesed. The phenomenon leads to a sharp decrease in the luminescent intensities or even quenching, ultimately. These are all attributed to that the central carbon atom is highly saturated and attached to an alcohol-hydroxyl group with forms conjugate acids in its aqueous solution. This fluorescence quenching phenomenon provides a new detection method and research direction for the detection of organic solvent pollutants containing MeOH<sup>[26,27]</sup>.

### 3.5.3 High sensitivity for Fe<sup>3+</sup>

Metal–organic frameworks with d<sup>10</sup> transition metal ions have attracted intense interest from chemists owing to their potential applications in photoactive materials. Thereby, the fluorescence properties of complex and DIPT ligand were investigated in the solid state. The fluorescence spectra of the free DIPT ligand and the as-synthesized complex possess strong broad emission bands centered at 470 and 482 nm in the solid state under the excitation of 350 nm, which may be attributed to the  $\pi^*$ - $\pi$  transitions and the DIPT intra ligand charge transfer, respectively.

Owing to the excellent fluorescence property and water stability, NCI-1 has attracted our interest to explore its application in sensing metal ions in aqueous solution. To investigate the ability of its selective sensing for metal ions, NCI-1 (5.0

mg ) was and immersed in the individual aqueous solutions of  $M(NO_3)_x$  ( 3.0 mL, 0.001 mol·L<sup>-1</sup>, M = Co<sup>2+,</sup> Cd<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Ba<sup>2+</sup>, Na<sup>2+</sup>, Ca<sup>2+</sup>, Cr<sup>2+</sup>, Pb<sup>2+</sup> and Fe<sup>3+</sup>, respectively ) for 1 d to form uniform dispersion suspensions for fluorescence study. Emission intensities of the different suspensions heavily depend on the species of metal ions. As shown in Fig. 6, the presence of Fe<sup>3+</sup> aqueous solution almost absolutely quenched the luminescence intensity of complex for the given metal ions compared with that of the original NCI-1 in water [quenching percentage =  $(I_0 - I)/I_0 \times 100\%$ , where I<sub>0</sub> and I are fluorescent intensities of NCI-1 before and after addition of metal ions].

The anti-interference sensing experiments further conducted NCl-1( 2.0 mg ) were immersed in aqueous solutions containing  $Fe^{3+}$  ion and other metal ions (  $Co^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ ,  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Ba^{2+}$ ,  $Na^{2+}$ ,  $Cr^{2+}$ ,  $Pb^{2+}$ ) with a concentration of  $1 \times 10^{-3}$  mol·L<sup>-1</sup>. Therein, the mixed addition of other metal ions only resulted in a slight reduction in fluorescence intensity, and the emission was quenched after the addition of Fe<sup>3+</sup> ion, verifying that the Fe<sup>3+</sup> ion can still be sensed in the presence of several other metal ions ( Fig. 8a ). Moreover, a reversible processing was performed: NCl-1 was immersed in aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub> for 24 h and then centrifuged and washed with aqueous solution until the solution became colorless. Strong fluorescence intensity was observed after three sensing-recovery cycles. After this treatment, PXRD pattern of NCl-1 was tested, which matched well with the simulated one as well as the as-synthesized one. In view of the above-mentioned superior fluorescent sensing properties of complex, this crystal material might act as a potential practical fluorescence sensor for detecting Fe<sup>3+</sup> ion with high reversibility.

To further assess sensing sensitivity toward  $\text{Fe}^{3+}$  ion, with gradually increasing  $\text{Fe}^{3+}$  concentration in **NCI-1**. Five concentrations from  $1 \times 10^{-5}$  to  $1 \times 10^{-1}$  mol·L<sup>-1</sup> were prepared to test the emissive response. The emission intensity of **NCI-1** at 462 nm was gradually quenched with increasing addition of  $\text{Fe}^{3+}$  (Fig. 7b). Slight red shift was observed by increasing the concentration of  $\text{Fe}^{3+}$ , which may be caused by the solvatochromism effect. It is apparent that the higher the concentration of iron ions, the better the fluorescence quenched. This experiment proves that the **NCI-1** has

sensitive and efficient identification to  $Fe^{3+}$  ion.

On the basis of the above pieces of evidence, NCl-1 may be a practical promising fluorescence sensor for detecting  $Fe^{3+}$  ion with high selectivity and sensitivity.

The underlying mechanism of luminescence quenched by  $\text{Fe}^{3+}$  ion was further investigated in detail. Firstly, considering the collapse of the framework, the PXRD was measured after this sample immersed in metal ion solutions. As confirmed by PXRD patterns (Fig. 8b), the crystal structure remains unchanged, shows that this quenching phenomenon has no relation with the framework of the crystal. Secondly, the resonance energy transfer was another possible reason for the quenching phenomena<sup>[28,29]</sup>. If the emission spectrum of the fluorophore (donor) has a certain degree of overlap with the absorption band of the analyte (acceptor), in case of an appropriate distance between them, the resonance energy transfer can be observed from the donor to the acceptor. Therefore, this quenching phenomenon may be attributed to the competition absorption of the excitation wavelength (460nm) energy between Fe<sup>3+</sup> aqueous solution and NCI-1. In consideration of these pieces of evidence, we then draw the conclusion that the competitive absorption mechanism may be responsible for the quenching effect, as reported in other literature reports.

#### 4. Conclusion

In summary, by using 2-(2,4-dichlorophenyl) -1H-imidazo[4,5-f] -[1,10]phenanthroline (DIPT) as the N-heterocyclic ligand and the 3-(2-chlorophenyl)acrylie (HPCIA) acid as the carboxylic acid, a novel Co(II) MOF with 2D double-layer and 3D framework structure is successfully synthesized. Solid-state fluorescent properties of NCI-1 indicate that it is a super candidate for blue-light luminescent materials. NCI-1 shows good sensing capabilities for organic solvents and metal ions, especially for MeOH and Fe<sup>3+</sup> ions by a fluorescent technique. It is significant for. The quenching mechanism is due to the combined processes of electrostatic interactions between NCI-1 and organic ligands, and

electron-transfer between the metal ions and organic frameworks, respectively. Meanwhile, magnetic analysis revealed that it is also a potential antiferromagnetic material.

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#### **Figure Captions**

Fig.1 Coordination environment of Co(II) atoms in NCl-1.

- **Fig.2** The coordination environment of Co(II) ions in **NCl-1**, the probability of ellipsoid is 30%.
- Fig.3 (a) The 1D structure of NCl-1.
  - (b) The 3D structure of NCI-1 constructed by the  $\pi$ - $\pi$  interactions (Dotted Line) between neighboring planes.

**Fig. 4** (a) The temperature dependence  $\chi_m$  and  $\chi_m$ T vs. T plots for NCl-1. Inset:  $1/\chi_m$ 

*vs.* T plot ( the red solid line presents the best fit of Curie-Weiss law  $\chi_m = C/(T - \theta)$  ).

- (b) The field-dependent isothermal magnetization curve at 2 K.
- Fig.5 The fluorescence quenching experiments of NCl-1 dispersed in organic solvents, respectively.

Fig.6 The fluorescence quenching experiments of NCI-1 dispersed in metal cations ( an aqueous solution with a concentration of  $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$  ), respectively.

Fig.7 (a) Solid-State Emission Spectra of NCI-1.

- (b) The fluorescence quenching experiments of NCl-1 dispersed in Fe<sup>3+</sup> solution with different concentration gradients(  $1.0 \times 10^{-1} 1.0 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ), respectively.
- Fig.8 (a) Comparison of the luminescence intensity of NCl-1 in the presence of mixed metal ions ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ).

(b)The PXRD patterns of NCl-1 before and after adsorption of  $Fe^{3+}$  ions.

Fig. 9 The molecular orbitals of the NCl-1.

#### **Table captions**

Table. 1 Crystallographic Data and Structure Refinement parameters for the NCI-1.

 Table. 2 Selected bond crystallographic data for NCI-1.

**Table.3** Selected Atom Net Charges and Electronic Configuration of NCI-1 at theB3LYP/(6-31+G(d) (for C, H, N and O) and Lanl2dz (for Co) Levels.



Fig.1 Coordination environment of Co(II) atoms in NCI-1.



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Fig. 4 (a) The temperature dependence χ<sub>m</sub> and χ<sub>m</sub>T vs. T plots for NCl-1. Inset: 1/ χ<sub>m</sub> vs. T plot (the red solid line presents the best fit of Curie-Weiss law χ<sub>m</sub>= C/(T-θ)); (b) The field-dependent isothermal magnetization curve at 2 K.



Fig.5 The fluorescence quenching experiments of NCI-1 dispersed in organic solvents,



Fig.6 The fluorescence quenching experiments of NCI-1 dispersed in metal cations

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ACE



Fig.8 (a) Comparison of the luminescence intensity of NCl-1 in the presence of mixed metal ions ( $1.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ ); (b) The PXRD patterns of NCl-1 before and after adsorption of Fe<sup>3+</sup> ions.



Fig. 9 The molecular orbitals of the NCl-1.



Par	rameter	Complex

Formula	C94 H40 Cl18 N16 O5 Co2
Formula weight	2229.38
Temperature (K)	293
Crystal system	Colourless
Space group	P-1
a (Å)	11.3513(2)
b (Å)	11.6584(2)
c (Å)	18.0376(2)
α (°)	94.2780(10)
β (°)	102.5110(10)
γ (°)	107.114(2)
Volume (Å <sup>3</sup> )	2202.57(6)
Crystal size (mm <sup>3</sup> )	0.181mm×0.105mm×0.060mm
Z	1
$\rho_{calc} g/cm^3$	1.618
Absorption coefficient (mm <sup>-1</sup> )	0.990
F (000)	1116.0
Index ranges	$-13 \le h \le 14, -14 \le k \le 13, -22 \le l \le 17$
$\theta$ range for data collection (°)	1.846 to 25.999
Reflections collected/unique/R <sub>int</sub>	22251/8462/0.0612
Refinement method	Full-matrix least-squares on F2
Data/restraints/parameters	8462/18/621
Goodness-of-fit on F2	1.0320
Final R indices [I>2 sigma (I)]	R1 = 0.0932, wR2 = 0.2593
R indices (all data)	R1 = 0.1116, wR2 = 0.2767
Largest diff. peak, hole (e $Å^{-3}$ )	1.1500/-0.9800

 Table. 2 Selected bond crystallographic data for NCI-1.

NCI-1	NCI-1	l

Bond lengths		Bond angles	
C(43)-H(103)	0.9300	O(1)-Co(1)-N(5)	87.94(17)
C(5)-Cl(2)	1.737(8)	O(1)-Co(1)-N(1)	97.63(16)
C(28)-Cl(7)	1.745(7)	N(5)-Co(1)-N(1)	171.81(18)
C(3)-H(110)	0.9300	O(1)-Co(1)-N(6)	162.88(17)
C(29)-N(6)	1.310(7)	N(5)-Co(1)-N(6)	76.88(17)
C(29)-H(111)	0.9300	N(1)-Co(1)-N(6)	96.71(16)
C(6)-H(113)	0.9300	O(1)-Co(1)-N(2)	86.52(18)
C(46)-H(115)	0.9300	N(5)-Co(1)-N(2)	98.08(16)
Cl(5)-Cl(2)#1	2.165(9)	N(1)-Co(1)-N(2)	76.38(15)
Cl(1)-Co(1)	2.4240(16)	N(6)-Co(1)-N(2)	87.80(18)
Co(1)-O(1)	2.047(4)	O(1)-Co(1)-Cl(1)	100.90(14)
Co(1)-N(5)	2.136(4)	N(5)-Co(1)-Cl(1)	92.67(13)
Co(1)-N(1)	2.150(4)	N(1)-Co(1)-Cl(1)	92.16(12)
Co(1)-N(6)	2.169(5)	N(6)-Co(1)-Cl(1)	87.84(14)
Co(1)-N(2)	2.179(4)	N(2)-Co(1)-Cl(1)	167.17(12)
N(8)-H(4)	0.8600	C(19)-N(2)-Co(1)	126.7(4)
N(3)-H(21)	0.8600	C(18)-N(2)-Co(1)	114.3(3)

Symmetry transformations used to generate equivalent atoms: 1: #1 -x,-y+1,-z+1.

**Table 3** Selected Atom Net Charges and Electronic Configuration of NCI-1 at theB3LYP/(6-31+G(d) (for C, H, N and O) and Lanl2dz (for Co) Levels.

Atom	Charge	Electron configuration	
Co1	0.63426	[core]4S( 0.26 )3d( 7.57 )4p( 0.53 )4d( 0.01 )	
N1	-0.41221	[core]2S( 1.31 )2p( 4.08 )3p( 0.01 )	
N2	-0.38980	[core]2S( 1.30 )2p( 4.06 )3p( 0.02 )4p( 0.01 )	
N5	-0.39444	[core]2S( 1.32 )2p( 4.05 )3p( 0.01 )	
N6	-0.41286	[core]2S( 1.32 )2p( 4.07 )3p( 0.02 )4p( 0.01 )	
01	-0.76482	[core]2S( 1.66 )2p( 5.08 )3p( 0.01 )	
O2	-0.69815	[core]2S( 1.71 )2p( 4.97 )3d( 0.01 )	
Cl1	-0.53031	[core]3S( 1.90 )3p( 5.63 )	

#### **Graphical abstract**



A new Co(II) compound,  $[Co_2(DIPT)_4(PClA)_2Cl_2]\cdot H_2O$  (NCl-1) ( DIPT= 2-(2,4-dichlorophenyl) -1H-imidazo [4,5-f]-[1,10]phenanthroline, HPClA=3-(2-chlorophenyl)acrylie ), have been successfully synthesized under mild hydrothermal conditions. By hydrogen bond and  $\pi$ - $\pi$  stacking interactions constitute a stable three-dimensional space structure. The luminescent properties of the NCl-1 dispersed in different solvents have been investigated systematically, demonstrating unique selectivity for the detection of MeOH via a fluorescence quenching mechanism. The luminescent intensity of NCl-1 was selectively quenched by Fe<sup>3+</sup> ions. In addition, the magnetic property of NCl-1 is investigated, which shows the anti ferromagnetic behavior induced by the external field.

### Highlights

- A. One new Co(II) MOF have been synthesized under mild condition and characterized.
- B. Compound calculated by electronic cloud have novel coordination modes.
- C. The compound demonstrates unique selectivity for MeOH. The luminescent intensity of compound was selectively quenched by Fe<sup>3+</sup> ions.
- D. The magnetic study reveals the dominant anti ferromagnetic interactions.