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Two 3D Metal-Organic Frameworks based on Co^{II} and Zn^{II} clusters for Knoevenagel Condensation Reaction and Highly Selective Luminescence Sensing

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ABSTRACT: Two MOFs with 3D structures, $\{[Co_{24}(BDPO)_{12}(H_2O)_{12}] \cdot 18DMF \cdot 40H_2O\}_n$ (namely **1**) and $\{[NH_2(CH_3)_2]_4[Zn_3(HBDPO)_2(SO_4)_2]\}_n$ (namely **2**), both successfully synthesized based on Co^{II} and Zn^{II} inorganic nodes with the same bridging organic ligand (namely H₄BDPO). **1** possesses relatively high BET surface area (*ca.* 1014 m² g⁻¹) with multiple pore systems and basic catalytic centers to apply as an efficient heterogeneous catalytic. The resultant **2** exhibits a 3D structure based on $Zn(COO)_4$ and $Zn_2(SO_4)_2(COO)_2$ as inorganic secondary building units. Thanks to its luminescence property, **2** is able to consider as a platform of recyclable bi-responsive luminescence sensor for explosive and antibiotics *via* luminescence quenching effect. The high selectivity of TNP can be estimated by the K_{sv} value about 1.2×10^4 M⁻¹. Significantly, **2** can efficiently detect NFT or NFZ, and the corresponding K_{sv} values are 4.5 $\times 10^4$ and 4.9×10^4 M⁻¹, respectively.

INTRODUCTION

Metal–organic frameworks (MOFs)^[1-5] are fascinating crystal materials and capture the public's attentions in virtue of their designability, porosity and multiformity. They exhibit various potential applications in gas sorption and separation,^[6-11] catalysis,^[12-16] enzyme carrier,^[17, 18] optical material,^[19, 20] and so on. Notably, MOFs can be easily constructed by the organic ligands and inorganic metals in the assembly, which both play significantly important influence factors for the properties of MOFs. The functional groups can be introduced in the organic ligands to synthesize functional materials for targeting applications. In addition, the different metal ions can remarkably change the structure and property of MOFs, such as luminescence, catalysis and so on. MOFs have been widely investigated as heterogeneous catalysts in catalysis fields. Some MOFs based on some organic ligands with nitrogen atoms have been investigated their basic catalytic performance to date.^[21-24] Triazine ring fragments are always imported into the ligands as central parts to construct such basic MOFs catalytic.^[25-30] Nevertheless, there is lots of demand to study and develop such MOFs to catalyze organic reactions. In addition, luminescent MOFs possess various advantages, including distinct luminescence spectrum, visible color, simple operation, high selectivity and sensitivity. Therefore, luminescence MOFs become the

Crystal Growth & Design

greatest potential sensor materials towards pollutants, such as explosives and heavy metals.^[31–39] Many luminescence MOFs have been widely applied as luminescence sensors to detect heavy metal ions, nitroaromatic compounds (NACs), organic vapors and so on. Notably, antibiotics are very useful and have a variety of benefits in many fields; however they produce a sequence of concurrency problems. The residual antibiotics can be founded in agricultural products, food and river, prompting concerns about the transmission of antibiotic resistance through the food chain in human society.^[40, 41] Whereas, only few investigations have been reported to detect antibiotics by using luminescence MOFs.^[42–49] Hence, it spurred further sustained attentions to explore novel sensing MOF materials for efficient detecting antibiotics.

Herein, we firstly prepared two MOFs with 3D structures, ${Co_{24}(BDPO)_{12}(H_2O)_{12}] \cdot 18DMF \cdot 40H_2O_n$ (1) and ${[NH_2(CH_3)_2]_4[Zn_3(HBDPO)_2(SO_4)_2]_n}$ (2) $(H_4BDPO = 2,4-bis(3,5-dicarboxyphenylamino)-6-ol triazine)$ based on Zn^{II} and Co^{II} metal nodes. The cobalt ion comes from $Co(NO_3)_2 \cdot 6H_2O$, thus the valence of cobalt ion should be +2. In addition, the whole neutral structure contains $Co_{24}(BDPO)_{12}$ and the value of BDPO is -4, which also confirms that the valence of cobalt ion is +2 in MOF 1.

As we discussed in the above, due to the different metal ions of Co^{II} and Zn^{II} , the resultant samples displayed completely different structures and properties. **1** displayed excellent basic catalysis ability because of its high surface area with multiple pores and various Lewis basic sites. On the other hand, the resultant **2** was constructed by the organic ligand and two different $Zn(COO)_4$ and $Zn_2(SO_4)_2(COO)_2$ inorganic clusters. Compared with Co^{II} -MOFs, the luminescence properties of the organic ligand can be well preserved in Zn^{II} -MOFs. Hence, **2** exhibited the similar luminescence properties like the free organic ligand H₄BDPO so that it is considered as a luminescence sensing for explosive and antibiotics.

Experimental Section

Materials and Methods. All chemicals without any treatment were directly acquired from companies. The selected organic ligand H₄BDPO was prepared as the previous reported literature.^[28] The data of elemental analysis for carbon, hydrogen and nitrogen was collected on a CE-440 (Leeman-labs) analyzer. Thermogravimetric analysis (TGA) trials were executed on a DTG-60A (Shimadzu) instrument in air from 30 to 800 °C (10 °C min⁻¹). Fourier-transform (FT) infrared spectra, using KBr as pellets, was performed on an Avatar-370 (Nicolet) spectrometer. Powder X-ray diffraction (PXRD) patterns were measured on a Rigaku D/max-2500 diffractometer. Shimadzu UV-2700 spectrophotometer was used to gain UV-Vis results. Cary Eclipse fluorescence spectrophotometer was applied for luminescence measurements. The N₂, CO₂ and CH₄ sorption measurements were measured on a Micrometrics ASAP 2020 machine. Gas chromatograph for the catalysis results were collected from Agilent 7890A.

Synthesis of { $Co_{24}(BDPO)_{12}(H_2O)_{12}$]•18DMF•40H₂O}_n, 1. Co(NO₃)₂•6H₂O (0.035 g) and H₄BDPO (0.02g) were both directly dissolved in DMF/H₂O (5/0.5 mL) mixed solution in a 20 mL Teflon–lined autoclave. Another 0.5 mL HNO₃ was further added in the solution. The autoclave was sealed well and heated at 135 °C. The purple block crystals were directly collected after 4 days (63% yield based on H₄BDPO). Element analysis of C, N and H for 1 (C₂₈₂H₃₃₈O₁₇₈N₇₈Co₂₄). Calc. (%) C, 37.28; N, 12.03; H, 3.72; Found: C, 37.33; N, 12.15; H, 3.79. IR (cm⁻¹): 3341 (br), 2931 (s), 1644 (s), 1593 (s), 1557 (s), 1531 (s), 1434 (s), 1375 (s), 1149 (s), 1086 (s), 894 (s), 807 (s), 774 (s), 735 (s), 665 (s), 640 (s), 592 (s), 490 (s) (Figure S1).

Synthesis of $\{[NH_2(CH_3)_2]_4[Zn_3(HBDPO)_2(SO_4)_2]\}_n$, 2. $ZnSO_4 \cdot 7H_2O$ (0.03 g) and H_4BDPO (0.02 g) were dissolved in a mixture solution of DMF (5 mL) and EtOH (0.5 mL). The solution was added HNO₃ solution (0.6 mL, 2.0 mol L⁻¹). Then it was sealed into a 20 mL Teflon–lined

autoclave for 3 days at 120°C in an oven to generate colorless pale crystals. The resultant sample can be collected by simply filtering and washed by fresh DMF several times. The crystal yield is about 59 % on account of the ligand. Element analysis of C, N and H for **2** $(C_{46}H_{52}O_{26}N_{14}S_2Zn_3)$: Calc. (%) C, 37.42; N, 13.29; H, 3.53; Found: C, 37.59; N, 13.33; H, 3.52. IR (cm⁻¹): 3134 (br), 2803 (s), 2482 (s), 1708 (s), 1647 (s), 1578 (s), 1560 (s), 1552 (s), 1467 (s), 1364 (s), 1273 (s), 1261 (s), 1234 (s), 1036 (s), 977 (s), 851 (s), 780 (s), 764 (s), 733 (s), 715 (s), 677 (s), 607 (s), 460 (s) (Figure S2).

Typical procedure for catalysis experiments. 1 was soaked into toluene, as reactive solvent, for one day before using it as a catalytic. Then it was filtered and directly dried in air. Substrate (0.001 mol) and malononitrile (0.0011 mol) were both added into a glass reactor with 5 mL toluene. When the reaction temperature reached 80 °C, **1** (0.1 g) was introduced into the reaction system and stirred at this reaction condition. The GC instrument was employed to analyze the yields.

Recyclable catalysis experiments. The recyclability of **1** was easily recollected by centrifugation and washed by fresh toluene after the catalysis experiment. The recollected samples were reused as a base catalyst.

Luminescence sensing experiments. The powder sample of **2** was dispersed in 3 mL DMF containing different nitro-compounds (0.01 mol L^{-1}) or antibiotics (0.00005 mol L^{-1}). The luminescence results were directly collected after 2 min.

Typical procedure for luminescence titration study. The powder sample of **2** was dispersed in DMF solution (3 mL, 0.1 mg mL⁻¹) and putted into a quartz cell. The quenching experiments were performed by gradually adding analyte of NACs (0.001 mol L⁻¹), nitrofurantoin (NFT) and

nitrofurazone (NFZ) (0.001 mol L^{-1}) DMF solution. The experiment was parallelly duplicated three times.

Recyclable luminescence experiments. The recyclability of **2** was explored in DMF solution. After the first quenching trial, the **2** powder was recollected by centrifugation and washed by fresh DMF. The recovered crystals were collected and reused in the next quenching experiments. **Single Crystal X-ray Analysis.** The structures of **1** and **2** were both measured on Bruker SMART APEX II with Cu– K_{α} graphite radiation (λ = 1.54184 Å). Adsorption correction was performed by multi–scan absorption corrections by using *SADABS* program.^[50] These two frameworks were determined by direct methods, which was further refined by using the *SHELXTL* program.^[51] The anisotropical technology was used for all non–hydrogen atoms. The *PLATON/SQUEEZE* method was applied to delete the contributions from solvent molecules and counter cations.^[52, 53] The solvent–free structure of **1** and **2** were obtained by the *SQUEEZE* routine. Crystal data of complex **1** and **2** were both listed in Table 1 and the characteristic bond lengths and angles are summarized in Table S1.

Comp	Compound		2
Empii	rical formula	$C_{282}H_{338}O_{178}N_{78}Co_{24}$	C46H52O26N14S2Zn3
Form	ula weight	9078	1475
Crysta	al system	Cubic	Monoclinic
Space	group	Im-3m	C2/c
a (Å)		27.9163(6)	30.5668(7)
$b(\mathbf{A})$		27.9163(6)	11.8581(3)
<i>c</i> (Å)		27.9163(6)	21.7723(5)
α (°)		90	90.00
β(°)		90	109.8560(10)
γ (°)		90	90.00
$V(Å^3)$)	21755.8(9)	7422.5(3)
Z		24	4
ρ calc	g cm ⁻³	1.101	1.155
μ (mn	n ⁻¹)	7.548	2.256
Nref		2060	7330
F(000))	7224.0	2584.0
R(int)		0.0866	0.0365
Goof		1.012	1.047
R_1 , wh	$R_2[I > 2\sigma(I)]$	0.0534, 0.1201	0.0742, 0.2071
R_1 , wh	R_2 (all data)	0.0546, 0.1207	0.0785, 0.2122
RESULTS AND DI	SCUSSION		

 Table 1 Crystal parameters for 1 and 2.

Structure { $Co_{24}(BDPO)_{12}(H_2O)_{12}]$ •**18DMF**•**40**H₂O}_n (**1**). **1** belongs to the cubic *Im*–3*m* space group, which contains 1/4 Co1, 1/4 Co2, 1/4 coordinated oxygen atom and 1/4 fully deprotonated BDPO^{4–} organic ligand in the asymmetrical unit (Figure S3). As illustrated in Figure 1, it contains a very standard and common paddle wheel motif to assemble with the carboxylic acid groups in the ligand. Interesting, one nitrogen atom form the organic ligand is further coordinated with one Co site in the paddle wheel motif. It can be found after analysis in detail that there are three different microporous cages in **1** with 14.9 Å for largest cage, 12.1 Å for the medium cage, and 8.9 Å for the small one, respectively. All the cages further were connected by the carboxylate acids and nitrogen atoms in the organic ligands to form a 3D structure. From the angle of topology, the obtained network is a 5–nodes topology with the point symbol [4⁶•6⁴]. The total accessible volume of **1** is *ca*. 49.5% without the guest and coordinated solvents in the *PLATON/VOID* method.^[52, 53] Due to its distorted solvents and the weak X-ray diffraction data, all solvents can't be located accurately by the results of the single crystal. Thus, they only can be inferred by TGA and elemental analysis.



Figure 1. View the large-size cages (a); middle-size cages (b); small-size cages (c), their 3D packing (d) and the whole structure (e) in 1 (hydrogen atoms are deleted for clarity. O, red; Co, blue; C, gray; N, green).

Structure $\{[NH_2(CH_3)_2]_4[Zn_3(HBDPO)_2(SO_4)_2]\}_n$ (2). MOF 2 crystallizes in monoclinic space group C2/c. The asymmetrical unit of **2** has a half Zn1 cation, one Zn2 cation, one $SO_4^{2^-}$ ion and one HBDPO³⁻ ligand (Figure S4). As shown in Figure 2a, there are two different Zn(COO)₄ and $Zn_2(SO_4)_2(COO)_2$ clusters as secondary building units. The Zn1 adopt distorted octahedron configuration by six-coordinated oxygen donors from two monodentate and two chelating carboxylate groups. The Zn2 adopts distorted tetrahedral configuration by four-connected from four oxygen atoms from two different SO_4^{2-} ions and one chelating carboxylate group (Zn–O, 1.9554-2.8075 Å). In addition, two different Zn2 ions were further connected by two shared SO_4^{2-} ions to form a binuclear inorganic cluster (Zn–O, 1.9502–2.6768 Å). Hence, the SO_4^{2-} ion plays a necessary role for the coordinated process between Zn^{II} ions and ligands. The Zn…Zn distance in the binuclear inorganic cluster is 4.5098 Å. The partial deprotonated HBDPO³⁻ only adopts one coordinated mode ($\mu_3 - \eta^1$: η^1 : η^1 : η^1 : η^1 : η^1 ; η^1 Figure 2b) to connect with three different Zn(II) ions. Meanwhile, the ligands can link with these two Zn-clusters to form an interesting 3D construction (Figure 2c). However, the solvents in 2 are also hard to directly make sure, which are further able to determine from the results of elemental analysis, FT-IR and TGA data.

Zn2

(b)



MOF 1 loses about 24.68% weight before 240 °C, which is similar with the calculated result after removing coordinated and guest molecules (calculated 24.79%, Figure S5). As illustrated in Figure S6, the TGA data of **2** shows a 12.49% weight lose before 250 °C, which is similar with the calculated result after removing guest cations and molecules (calculated 12.74%). The phase purity of the experimental sample can be determined by PXRD patterns based on their characteristic diffraction peaks (Figures S7 and S8). The PXRD results demonstrated the purity of MOFs 1 and 2.

Gas sorption properties.

1 and 2 were both directly exchanged the high boiling point guest molecules with the low boiling point CH₂Cl₂ for two days. These MOFs were heated at 100 °C under vacuum for 12 h. The N₂

gas sorption measurement of the activated **1** was implemented to verify the permanent pore character at 77 K. N₂ sorption isotherms at 77 K featured a completely reversible type–I adsorption characteristic of microporous materials (Figure 3). The BET and Langmuir surface area are calculated directly as 1014 and 1147 m² g⁻¹, respectively. The corresponding pore width distributions are 7.3, 11.8 and 14.8 Å through the DFT method. The structure of the activated sample can be retained well by the PXRD measurement (Figure S9). It also exhibits more excellent CO₂ adsorption capacity than the adsorption amount of CH₄ at 273 K and 298 K (Figure S10). However, the activated **2** didn't have any N₂ sorption at 77 K (Figure S11), which is mainly attributed that the framework was collapsed completely after the activation process. The reason can be confirmed by the PXRD pattern of the activated **2** (Figure S12).



Figure 3. The N₂ sorption isotherm of 1 was measured at 77 K. The insert was the pore size distribution.

Catalysis properties.

Due to high BET surface area, multiple pore systems and lots of basic sites, **1** was further studied its catalytic properties for the Knoevenagel condensation model reaction. The fresh sample was directly soaked in toluene for one day prior this catalytic reaction. Substrate with different

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structures (0.001 mol) and malononitrile (0.0011 mol) were both added into a glass reactor with 5 mL toluene. When the reaction temperature reached 80 °C, catalytic 1 (0.1 g) was instantly putted into the reaction solution and stirred at this temperature. The GC instrument was employed to analyze the yields. Table 2 contains the yield results of all the reactions, including malononitrile and different aldehyde substrates with or without 1. As illustrated in entry 1 of Table 2, the final yield of 2-benzylidenemalononitrile is about 97% after reaction 3 hours. The kinetic catalysis performance of benzaldehyde as substrate was chosen as a model to investigate the catalytic rate in detail, which illustrated that this reaction almost completed within 3 hours in the presence of 1 (Figure 4a). Because the corresponding yield almost remained unchanged after filtering 1 at 40 minute, MOF 1 is clearly necessary for this reaction. Meanwhile, no any 2-benzylidenemalononitrile can be detected without catalytic 1 after 3 hours in entry 2 and Figure 4a. In order to investigate the substrate effect, several different substituted aldehyde reactants were used in the present of 1 under similar conditions. The yields of the aldehyde substrates with the withdrawing groups (-F and $-NO_2$) were both almost >99% (entries 3 and 4). Whereas, the yield results significantly decreased to 87% for one electron donor -OMe group (entry 5) and 80% for two –OMe groups (entry 6), respectively.







Furthermore, it is a significant importance issue to recycle the catalysis after reaction. MOF **1** was easily recollected and reused by centrifuging and washing with toluene. The catalytic effect of recycled **1** was basically no loss after reuse four times. As illustrated in Figure S13, the PXRD peaks suggested that the framework of recycled samples can keep very well. The results of FT–IR and TGA of recycle samples after further washing with fresh DMF are similar with the as-synthesized samples, which illustrates the structure of recycled **1** retained very well (Figures S14 and S15).



Figure 4. (a) The kinetics results and (b) the recycle performance for this reaction.

Luminescence properties.

The luminescence behaviors of H_4BDPO ligand and ground 2 were both investigated in detail. Figure 5a shows the maximum emission of the free ligand at 382 nm under 337 nm. The resultant 2 showed a significant emission peak at 379 nm under excitation wavelength at 292 nm (Figure 5b), revealing that the luminescence property of 2 belongs to the organic ligand. To study the luminescence detection capability towards NACs, the maximum emission peak of the

ground samples in DMF with different detectable substances were collected under 292 nm (Figure 5c). Significantly, it appeared remarkably luminescence quenching behavior in nitrobenzene (NB) DMF solution. In addition, the luminescence intensity can keep well in DMF for one day (Figure S16). To further detect the luminescence response, the resultant **2** was titrated with NB to vary the concentrations (Figure 5d). The corresponding luminescence intensity quickly reduced to 81% and 24% at 1×10^{-3} and 1×10^{-2} M, respectively, which may be ascribed to the electron transfer from the host structure of **2** to electron-deficient NB.



Figure 5. The maximum emission and excitation spectra of the free organic ligand (a) and 2 (b). The maximum emission peak of 2 in DMF with different detectable substances (c) and at different NB concentrations (d).

Hence, the luminescence sensing ability of **2** was further discussed in detail to detect several typical NACs, including 1,3–dinitrobenzene (1,3–DNB), 2,4–dinitrotoluene (2,4–DNT) and 2,4,6–Trinitrophenol (TNP). The luminescence intensities were monitored with the different concentration of the analytes in DMF solution (Figures 6a–6c), which almost quenched

completely at last. The quenching efficiency is able to quantitatively determinate by Stern–Volmer equation as $I_0/I = 1 + K_{sv}[Q]$, in which I_0 is the initial intensity without any analyte, I is the intensity after treating with the analyte, [Q] is the molar concentration of substances (M^{-1}) , and K_{sv} is the Stern-Volmer constant. When $(I_0/I) - 1$ vs. [Q] plot exhibits a linear relationship, the K_{sv} value can be determine exactly. As shown in Figure S17, the Sterm-Volmer data for these NACs all close to the linear relationship in the relatively low concentration range. The corresponding K_{sv} values are 3.0×10^2 , 9.8×10^2 , 1.9×10^3 and 1.2×10^4 M⁻¹ for NB, 1,3–DNB, 2,4–DNT and TNP, respectively. The order of quenching efficiency is TNP >2,4-DNT > 1,3-DNB > NB due to the enhancement of the electron transfer from 2 to NACs with the increasing amount of nitro groups (Figure 6d). Notably, the UV-Vis result illustrated that the absorption band of TNP and the emission spectrum of 2 have the most overlap area in DMF to significantly enhance the quenching effect (Figure S18). In addition, 2 was easily recollected by centrifuging 8000 r min⁻¹ for 3 minutes and washed with DMF. As demonstrated in Figure S19, the luminescence sensing ability of 2 shows a very little change after reusing five times. Meanwhile, the structure can be keep well after the recycle experiment by the PXRD data (Figure S20).



Figure 6. The emission spectra of **2** was titrated in DMF solutions with 1,3–DNB (a), 2,4–DNT (b) and TNP (c), respectively; (d) the relationships between the maximum emission intensities and the concentrations of NACs.

Selective sensing of antibiotics.

As we known, only few luminescence MOFs have been used as sensors to detect different antibiotics.^[42–49] In this work, ten frequently–used antibiotics were selected as models to investigate the antibiotics detectable ability of **2**, including florfenicol (FFC), penicillin (PCL), thiamphenicol (THI), chloramphenicol (CAP), azithromycin (AZM), sulfamethazine (SMZ), ronidazole (RDZ), ornidazole (ODZ), nitrofurazone (NFZ) and nitrofurantoin (NFT). The luminescence data of **2** were detected in the presence of various antibiotics (FFC, PCL, THI, CAP, AZM, SMZ, RDZ, ODZ, NFZ and NFT) in DMF, demonstrating a clearly luminescence quenching phenomenon for NFZ or NFT, respectively (Figure 7a). The quenching order of **2** towards these antibiotics is NFT > NFZ > ODZ > RDZ > SMZ > AZM > CAP > THI > PCL > FFC. The results obviously showed that **2** can be considered as a potential luminescence sensor to recognize NFZ or NFT via luminescence quenching. In addition, the luminescence response

experiments of **2** towards NFZ were measured at different time intervals (Figure 7b). After the concentration of NFZ (1.0×10^{-5} or 7.0×10^{-5} mol L⁻¹), the luminescence intensities both immediately decreased and achieved a minimum value after about 50 s. The intensity further can be kept for a long time to illustrate that the luminescence intensity can completely quench at a very short time.

To further investigate the detection ability of 2 towards NFZ or NFT, the titration experiments were performed by adding NFZ or NFT drop by drop, respectively. With the increasing concentration of NFZ or NFT, the corresponding luminescence intensity obviously decreased (Figures 7c and 7d). Meanwhile, the corresponding quenching performance can be quantitatively determinated by the values of $(I_0/I) - 1$ vs the concentrations of NFZ or NFT. As shown in Figures 7e and 7f, the K_{sv} values for NFZ and NFT are calculated to be 4.5×10^4 and 4.9×10^4 M^{-1} with the R^2 values of 0.9989 and 0.9993, respectively. Meanwhile, the recyclability is also a vital important issue to detect NFZ or NFT. The reused samples were easily recollected and reused. The recycled crystals can perfectly preserve the luminescence properties like the fresh samples, which can be further used as a luminescence sensor to redetect NFZ or NFT at least five times (Figure S21). The integrity of skeleton can be confirmed by PXRD patterns, which can retain the characteristic peak to prove the stability during the tests (Figure S20). It is significant work to investigate the luminescence quenching mechanism for NFZ and NFT with high selectivity of **2**. The results illustrated the quenching effect is not trigged by the skeleton broken. In addition, the quick test results of 2 demonstrated that the quenching effect is also not caused by guest molecule adsorption. It is easily found that the overlap between the absorption spectra of NFT or NFZ and the emission spectrum of 2 in DMF from the UV-Vis results (Figure S22), which illustrated that the excitation energy may be competitively absorbed by the NFZ or NFT

molecules to obviously reduce the energy transfer to 2 to produce luminescence quenching phenomenon. All the luminescence data of 2 have been tabularized in Table S2.



Figure 7 (a) The luminescence intensities of 2 in different antibiotics DMF solutions; (b) the luminescence response rate of 2 in the NFZ at different concentrations; (c, d) the emission spectra of 2 after titrating with NFT or NFZ; (e, f) the Stern–Volmer plots for the intensity of 2 with different concentrations of NFT or NFZ, respectively.

CONCLUSION

In summary, we have successfully obtained two 3D MOFs. The different metal ions (Co^{II} and Zn^{II}) directly generate different structures and properties. The resultant 1 shows high catalysis effect for the Knoevenagel condensation reaction with outstanding recyclability. In addition, 2 exhibited an excellent luminescence property to use as a fast, recycle, and multi–responsive

luminescence sensor towards TNP, NFZ and NFT, respectively. Further work about novel and functional MOFs is ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Electronic Supplementary Information (ESI) available: IR, TGA, PXRD and so on. The supplementary crystallographic data were deposited with a Cambridge Crystallographic Data Centre (CCDC) No. 1465197 for **1** and 1580838 for **2**.

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Notes

The authors declare no competing financial interest.

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Two 3D Metal-Organic Frameworks based on Co^{II} and Zn^{II} clusters for

Knoevenagel Condensation Reaction and Highly Selective Luminescence

Sensing

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Two 3D metal-organic frameworks were successfully synthesized under solvothermal conditions. Co-MOF exhibited highly catalysis effect for Knoevenagel condensation reaction. Meanwhile, Zn-MOF can be served as a fast, recycle, and multi-responsive luminescence sensor towards TNP, NFZ and NFT, respectively.