Article

Two Cd(II)-Based MOFs Constructed from Tris(3′-F-4′-carboxybiphenyl)amine: Synthesis, Crystal Structure, Luminescence Sensing towards Nitrophenols and Acetylacetone

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Abstract: Two new luminescent metal-organic frameworks (MOFs), namely [Cd₄(TFBA)₃(H₂O)₁]ₙ (CdMOF-1) and [Cd(TFBA) (bipy)₁]ₙ (CdMOF-2) (H₃TFBA = tris(3′-F-4′-carboxybiphenyl)amine, 4,4′-bipy = 4,4′-bipyridine), have been prepared and successfully constructed via solvothermal conditions. Single-crystal structure analysis reveals that CdMOF-1 are two-dimensional network containing [Cd₄O₂₆] units. CdMOF-2 shows a non-interpenetration 3D microporous structure with a hexagon pore of 24.6 × 25.9 Å. Notably, CdMOF-2 exhibits turn off fluorescence behavior towards picric acid (TNP) and 4-Nitrophenol (PNP) with a limit of detection (LOD) value of 9.2 × 10⁻⁶ M and 1.81 × 10⁻⁵ M, respectively. Furthermore, CdMOF-2 shows obvious turn-on luminescence responses toward acetylacetone (Acac) with luminescence red-shift and a detection limit of 19.40 ppm. Additionally, the possible quenching or enhancing mechanism during the sensing process were evaluated by PXRD, UV-vis, and luminescence decay lifetime.

Keywords: metal-organic framework; luminescence; dual-responsive; quenching or enhancing mechanism; X-ray Single-crystal analysis

1. Introduction

Nowadays, the detection of toxic and harmful organic compounds has obtained increasing attention due to the industrial advancement, wide applications of organic intermediates, and the increasing growth of environmental pollution [1,2]. Nitrophenols are commonly employed in dyes and pesticides, but nitrophenols are difficult to degrade and could cause irreversible damage to the environment and pose a serious threat to human health [3–5]. On the other hand, acetylacetone (Acac) is extensively employed as an organic synthetic intermediate, important raw ingredient, and analytic reagent [6–8]. However, as a toxic, volatile, and combustible chemical, traces of acetylacetone in inappropriate places could generate severe environmental issues and human diseases such as headache, nausea, and vomiting [9,10]. Numerous traditional methods including atomic absorption spectrophotometry (AAS) [11], liquid chromatography-tandem mass spectrum (LC-MS) [12], inductively coupled plasma atomic emission spectrometry (ICP-AES) [13], and UV-visible spectrophotometry, still suffer from time-consuming, complicated recognition procedures, and sophisticated devices. Thus, there is a pressing need to exploit reliable, facile, and efficient detection methods/technologies for Acac and nitrophenols.

Metal-organic frameworks (MOFs), assembled from metal ions and organic ligands, have drawn widespread attention in absorption, magnetism, catalysis, medical delivery, proton conduction, and chemical sensing due to their predictable properties and controllable structure and porosity [14–19]. The exploration of neoteric chemical sensors is...
currently an extremely interesting research topic [20,21]. Among them, luminescent MOF sensors have been designed and utilized in various sensing fields, including toxic metal ions/anions, nitroaromatic compounds, antibiotics, and small organic molecules [22]. For example, Qin’s group reported two new Co-MOFs in 2019, exhibiting outstanding selectivity and sensitivity to picric acid (TNP) [23]. Liu’s group demonstrated Zn-based MOFs with high sensitivity and selectivity to detect Acac in DMF solution with the detection limit of 0.10 ppm and obvious luminescence shift [24]. Therefore, it is worthwhile to design luminescent MOFs with unique topologies and potential applications as luminescent sensors.

From a synthetic perspective, an excellent combination of metal centers and scheduled organic chromophores is the elementary tactics of luminescent MOFs. Cd(II) belongs to d10 metal ions and possess a variety of coordination numbers, geometric configurations, and Cd-MOFs hold great potential applications in sensing filed [25–30]. Meanwhile, multi-carboxylic acids tris(3′-F'-4'-carboxybiphenyl)amine (H₃TFBA) were based on π-conjugated aromatic backbones, which may endow them luminescent multifunctionality [31,32]. Herein, we obtained two new luminescent crystalline [Cd₄(TFBA)₃(H₂O)₄]ₙ (CdMOF-1) and [Cd(TFBA) (bipy)]ₙ (CdMOF-2) (H₃TFBA = tris[(3′-F'-4'-carboxyl)-phenyl-duryl]amine, 4,4'-bipy = 4,4'-bipyridine) by solvothermal method. These Cd (II)-based MOFs were further studied with X-ray Structure Determination, powder X-ray diffraction (PXRD), infrared spectroscopy (IR), thermal analysis (TGA), and luminescence sensing experiment. Notably, CdMOF-2 was proven to be a dual-responsive luminescent sensor for sensing nitrophenols and Acac in DMF.

2. Materials and Methods

2.1. Materials

All the reagents and solvents (analytical grade) were purchased from pharmaceutical corporation and applied directly. The synthesis method of CdMOF-1 and CdMOF-2 were summarized in Scheme 1. Tri-carboxylic acid H₃TFBA was prepared according to the reported procedure via the Suzuki coupling reaction [32]. The corresponding NMR data and detailed synthesis procedure of H₃TFBA were provided in the Experiment Section of the Supporting information. Under a N₂ atmosphere, thermalgravimetric analysis (TGA) were tested on a Netzsch STA-449F5 thermo analyzer at a heating rate of 10 °C min⁻¹. Infrared (IR) spectra were carried out in the range of 4000–400 cm⁻¹ on a NICOLET 5700-IR spectrometer (Figure S1). Powder X-ray diffraction (PXRD) patterns were measured under Cu-Kα radiation at room temperature via Bruker D8 Advance diffractometer. Luminescence lifetime was recorded on Edinburgh FLS 1000 fluorescence spectrometer. Luminescence spectra tests were proceeded with a Hitachi F-7000 spectrometer. The UV-vis absorption spectra were conducted on a UV-UH4150 spectrophotometer.

![Scheme 1. Synthesis of the CdMOF-1 and CdMOF-2.](image-url)
2.2. Synthesis of MOFs

Preparation of CdMOF-1. A mixture of Cd(NO$_3$)$_2$·6H$_2$O (40.0 mg, 0.08 mmol) and H$_3$TFBA (13.5 mg, 0.02 mmol) was dissolved in 0.4 mL H$_2$O, 0.4 mL CH$_3$OH, and 1.6 mL DMF solution. After ultrasound 15 min, to make a transparent solution, the reaction mixture was placed in a Teflon vessel within the autoclave. The vessel was heated at 85 °C for 48 h and then cooled to room temperature. Faint yellow triangle block crystals were obtained by filtration and washed with DMF. The yield was ca.65% (based on H$_3$TFBA). IR (KBr, m/cm$^{-1}$): 3370(s), 1659(s), 1596(s), 1518(s), 1381(s), 1186(w), 904(w), 826(w), 788(w).

Preparation of CdMOF-2. A mixture of H$_2$O (0.4 mL)/DMF (1.6 mL) containing Cd(NO$_3$)$_2$·6H$_2$O (40.0 mg, 0.08 mmol) in 0.8 mL CH$_3$OH, 4,4′-bipy and H$_3$FTBA (13.5 mg, 0.02 mmol) was placed in a Teflon vessel within the autoclave. The vessel was heated at 85 °C for 48 h and then cooled to room temperature. Yellow block crystals were obtained by filtration and washed with DMF. The yield was ca.55% (based on H$_3$TFBA). IR (KBr, m/cm$^{-1}$): 3037(w), 1663(m), 1598(s), 1519(s), 1384(s), 1187(s), 904(m), 819(s), 786(s), 631(s), 525(w).

2.3. X-ray Structure Determination

The X-ray diffraction intensity data for suitable crystals of CdMOF-1-2 were measured on Bruker SMART CCD detector with monochromatic radiation (Mo Kα radiation, λ = 0.71073 Å) at 296(3) K. The obtained structural information was solved by the direct methods and Fourier synthesis method. Positional and thermal parameters were enhanced by the full-matrix least-squares method on $F^2$ with the SHELXTL [33]. Final Single-crystal data and refinement values were filled in Table 1, and other selected data of CdMOF-1-2 were given in Tables S1 and S2. CCDC references number for CdMOF-1 and CdMOF-2 were 2,179,531 and 2,179,530, respectively.

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3. Results and Discussion

3.1. Structural Description

3.1.1. Crystal Structure of CdMOF-1

X-ray Single-crystal analysis exhibited that CdMOF-1 crystallized in the monoclinic space group C2 coordination polymers. As depicted in Figure 1a, the asymmetric unit...
composed of four distinct Cd(II) centers and three TFBA\(^{3-}\) ligands. Notably, there were two kinds of Cd(II) centers as follows, Cd1 and Cd2 center was hepta-coordinated (Figure 1b) to seven oxygen atoms (for Cd1 O16, O17, O18, O19, O20, O21, O22 and for Cd2 O11, O12, O13, O14, O15, O16, O17) from three different (TFBA)\(^{3-}\) anions. The Cd3 and Cd4 centers were hexa-coordinated (Figure 2b) to six oxygen atoms; for Cd3 the equatorial plane was comprised by four O from three different TFBA\(^{3-}\) (O6, O7, O9), one from H\(_2\)O molecular (O7), while the vertex location was engaged by two oxygen atoms from H\(_2\)O molecular (O8, O10). For Cd4, the equatorial plane was composed of four O from three different TFBA\(^{3-}\) (O2, O4, O5, O6), while the vertex location was occupied by two oxygen atoms, one from H2O and another from TFBA\(^{3-}\). The Cd–O bond lengths lied in 2.127(19) to 2.507(15) Å, which were similar to those reported Cd-MOFs [34]. Additionally, the independent Cd(II) center was bridged by two carboxylate groups from TFBA\(^{3-}\) ligands to form 2D layers which exist as hexagon pores. As described in Figure 1c, all the ligands were completely deprotonated and displayed four kinds of coordination modes: \(\mu_1-\eta^1\), \(\mu_2-\eta^1\eta^1\), \(\mu_2-\eta^1\eta^2\), and \(\mu_3-\eta^1\cdot\eta^2-\eta^3\) (Figure 1d). After removing the disordered solvent molecules, the porosity of CdMOF-1 was calculated to be 39.2% (5559.5 Å\(^3\) of 14191.0 Å\(^3\) unit cell volume) by PLATON [35].

![Figure 1](image)

**Figure 1.** (a) The asymmetry of CdMOF-1. (b) Coordination environment of Cd(II) center. (c) The view of 2D space filling mode of CdMOF-1 (for clarity, the H atoms were deleted). (d) The diverse coordination modes of H\(_3\)TFBA in CdMOF-1(\(\mu_1-\eta^1\cdot\eta^1\), \(\mu_2-\eta^1\cdot\eta^1\), \(\mu_2-\eta^1\cdot\eta^2\), and \(\mu_3-\eta^1\cdot\eta^2-\eta^3\)).

### 3.1.2. Crystal Structure of CdMOF-2

X-ray Single-crystal determination illustrated that CdMOF-2 exhibited an interpenetrating 3D microporous structure and crystallized in the monoclinic space group C2/c. The asymmetric unit of CdMOF-2 consisted of one Cd(II) center, one TFBA\(^{3-}\) ligand, and one coordinated 4,4’-bipy molecule (Figure 2a). The Cd1 ion was linked by four O from three distinct TFBA\(^{3-}\), and two N from 4,4’-bipy, showing distorted octahedral coordination geometry. Interestingly, the independent Cd(II) centers were bridged by two carboxylate groups from TFBA\(^{3-}\) ligands to form 2D layers, which a hexagon pore of 24.6 × 25.9 Å based on Cd–N distances (Figure 2b). Then, these 2D layers were extended by bipy to form a 3D framework along b axial, which was a typical 1D channel that has seldom been recorded in the molecular cycling fashion of coordination polymers (Figure 2c). In CdMOF-2, completely deprotonated tricarboxylate ligand shown: \(\mu_1-\eta^1\cdot\eta^1\) and \(\mu_1-\eta^1\) coordination modes to Cd(II) centers (Figure 2d). The calculation of PLATON showed that the porosity was 21.7% (2001.4 Å\(^3\) of 9205.9 Å\(^3\) unit cell volume) [35].
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Figure 1. (a) The asymmetry of CdMOF-1. (b) Coordination environment of Cd(II) center. (c) The view of 2D space filling mode of CdMOF-1 (for clarity, the H atoms were deleted). (d) The diverse coordination modes of H3TFBA in CdMOF-1 (μ₁–η₁: η₁, μ₂–η₁: η₁, μ₂–η₁: η₂, and μ₃–η₁: η₂: η₁).

Figure 2. (a). The asymmetric of CdMOF-2. (b). 2D layers of CdMOF-2. Enlarged part: A hexagon pore with 66-members ring with pore size of 24.6 × 25.9 Å. (c). Single 3D network of CdMOF-2. (d) Coordination modes of TFBA³⁻ to Cd(II) center.

3.1.2. Crystal Structure of CdMOF-2
X-ray Single-crystal determination illustrated that CdMOF-2 exhibited an interpenetrating 3D microporous structure and crystallized in the monoclinic space group C2/c. The asymmetric unit of CdMOF-2 consisted of one Cd(II) center, one TFBA³⁻ ligand, and one coordinated 4,4′-bipy molecule (Figure 2a). The Cd1 ion was linked by four O from three distinct TFBA ³⁻, and two N from 4,4′-bipy, showing distorted octahedral coordination geometry. Interestingly, the independent Cd(II) centers were bridged by two carboxylate groups from TFBA³⁻ ligands to form 2D layers, which a hexagon pore of 24.6 × 25.9 Å based on Cd–N distances (Figure 2b). Then, these 2D layers were extended by bipy to form a 3D framework along b axial, which was a typical 1D channel that has seldom been recorded in the molecular cycling fashion of coordination polymers (Figure 3).

3.2. Stability of CdMOF-1 and CdMOF-2
It is well-known that stability is an indispensable trait for evaluating the luminescent sensors. To explore the thermal ability of CdMOF-1 and CdMOF-2, under a N₂ atmosphere, thermogravimetric analysis was proceeded with stability from 30 to 800 °C. For CdMOF-1 (Figure S2a), an initial weight loss of 8.61% occurring before the 120 °C region was attributed to the loss of the twelve water molecules (with a calculated value of 8.95%). Coordinated four H₂O and six DMF molecules lose between 120 and 260 °C (experimental, 12.58%; calculated, 15.85%), and finally the framework collapsed at 260 °C, decreased smoothly, and attained a minimum value at 800 °C. The TGA curves of CdMOF-2 (Figure S2b) showed a weight loss of 11.71% (calculated, 12.07%) from room temperature to 212 °C, suggesting the guest three H₂O and one DMF molecules were removed. The framework of CdMOF-2 begins to collapse at 265 °C. The result indicated CdMOF-2 had good thermal stability. In order to check the phase purity of CdMOF-1-2, its Powder X-ray diffraction was carried out (Figure 3). The diffraction peaks of samples (after DMF immersed and calculated) were unified with those of the simulated ones, which verified the pure bulk samples. Additionally, we selected CdMOF-2 for the chemical stability experiment due to its good stability. Each finely ground powder of CdMOF-2 was immersed in methanol, ethanol, DMF, CH₂Cl₂, CHCl₃, toluene, toluene, and Acac solvents for 24 h. Following, the PXRD of each sample was tested (Figure S3). Almost unchanged peaks positions shown that the framework of CdMOF-2 maintained after the various solvent treatment, further indicating the high chemical stability of CdMOF-2. Otherwise, the PXRD patterns of CdMOF-1 after being immersed in different solvents except DMF were not satisfactory.
Nitroaromatic compounds (NACs) are commonly adopted in the manufacturing processes of industrial explosives and industrial products, such as nitrobenzene (NB), ONP, PNP, 1,3-dinitrobenzene (1,3-DNB), 2,6-dinitrotoluene (2,6-DNT) and 2,4,6-trinitrophenol (TNP), etc. Therefore, it is vital to screen new materials for the efficient detection of NACs. Thus, the photoluminescent properties of CdMOF-1 and CdMOF-2 were evaluated. Different DMF solutions containing the above NACs were added to the CdMOF-1 and CdMOF-2 suspensions of (TNP), etc. Therefore, it is vital to screen new materials for the efficient detection of NACs.

3.3. Solid-State Photoluminescent Spectra

The solid-state luminescence properties of CdMOF-1 and CdMOF-2 were studied at ambient temperature. The luminescence emission peak of H3TFBA ligand was observed at 503 nm, which excited at 336 nm (Figure 4). The maximum of emission bands of CdMOF-1-2 were 493 (λex = 369 nm) and 496 nm (λex = 363 nm), which reveals a slight shift compared to the H3TFBA. As we know, red/blue shift could be ascribed to the π*→π or π*→n of organic ligands to metal coordination transformations [36]. Furthermore, the luminescence decay curves were drawn in Figure S4, and the corresponding luminescence lifetime of CdMOF-1-2 were 2.93, and 3.27 μs. As shown in Figure S5, CdMOF-1 and CdMOF-2 exhibit emission at 490, and 486 nm in DMF solution, respectively, which were similar to the emission in the solid state. Given above stability studies and solid-state photoluminescent spectra, we selected CdMOF-1 (as a comparison) and CdMOF-2 to continue further luminescence sensing experiment.

3.4. Sensing of Nitrobenzene Explosive

Nitroaromatic compounds (NACs) are commonly adopted in the manufacturing processes of industrial explosives and industrial products, such as nitrobenzene (NB), ONP, PNP, 1,3-dinitrobenzene (1,3-DNB), 2,6-dinitrotoluene (2,6-DNT) and 2,4,6-trinitrophenol (TNP), etc. Therefore, it is vital to screen new materials for the efficient detection of NACs. Inspired by the above, the sensing behaviors of CdMOF-1 and CdMOF-2 toward NACs were evaluated. Different DMF solutions containing the above NACs were added to the suspensions of CdMOF-2 (Figure 5a). Notably, nitrophenols (especially for PNP and TNP) lead to obvious quenching of the intensity of CdMOF-2. The anti-interference experiments of CdMOF-2 toward TNP and PNP were also fully studied. As we expect, when TNP/PNP was dropped in the existence of other NACs, the emission of CdMOF-2 declined obviously, indicating that other NACs do not disturb with TNP/PNP (Figures 5b and S6).
Figure 4. Emission spectra of H₃TFBA 503 (λex = 336 nm); CdMOF-1-2 in the solid state at room temperature.

Figure 5. (a). The emission intensities of CdMOF-2 dispersed in DMF solution with different NACs (10⁻² M). (b) Anti-interference performance of CdMOF-2 before and after adding with TNP and other NACs. (c) Emission intensities of CdMOF-2 with increasing concentrations of TNP in DMF solution, inset into liner correlation at low concentration. (d) Emission intensities of CdMOF-2 with increasing concentrations of PNP in DMF solution, inset into liner correlation at low concentration.

Subsequently, to study the relationship between the concentration of TNP/PNP and the fluorescence intensity of the CdMOF-2, the quantitative sensing behavior of the CdMOF-2 on TNP and PNP were studied by fluorescence concentration gradual titration experiment (79.6%, 57.6%), and the emission spectrum was examined (Figure 5c,d). This quenching effect can be quantified by the quenching effect constant (KSV), which is evaluated by using the Stern-Volmer formula [37] I_0/I = KSV [M] + 1 (I_0 is initial intensity; I is intensity after adding analytes). The KSV values of TNP and PNP were 2.59 × 10⁵ M⁻¹ and 1.41 × 10⁵ M⁻¹, respectively, for CdMOF-2. The limit of detection (LOD) of CdMOF-2 sensing TNP and PNP were evaluated to be 9.2 × 10⁻⁶ M and 1.81 × 10⁻⁵ M, respectively.
For comparison, the sensing nitrophenols experiments of CdMOF-1 were also carried out and listed in the supporting information (Figure S7). The LOD of CdMOF-1 sensing TNP and PNP were evaluated to be $2.6 \times 10^{-5}$ M and $3.0 \times 10^{-5}$ M, respectively. The results were competitive with the homologous examples (Table S3) [38,39].

3.5. Luminescence Sensing Properties for Organic Molecules

Inspired by the excellent sensing performance of CdMOF-2 toward the NACs, we further explored the application in detection of organic solvents because it is vital to effectively detect the various organic molecules in environment. In this work, we screen the various organic solvents including CH$_3$OH, EtOH, acetone, Acac, CH$_2$Cl$_2$, CHCl$_3$, DMA, CH$_3$CN, and toluene. As above, CdMOF-1 and CdMOF-2 exhibited suitable stability in DMF (Figure 3b). So, the luminescence detection experiments for different solvents were implemented with CdMOF-1 and CdMOF-2 in DMF solution. For the luminescence selectivity experiment, 6 µL of different organic solvents were titrated into 2 mL of pre-prepared suspension, respectively. The corresponding emission spectra are in Figure 6a and Figure S8; the titration of Acac induced a slight enhancing effect (about 1.8 times of blank) on the emission intensity of CdMOF-1. For CdMOF-2, the titration of Acac led to an obvious enhancing response (about 3.7 times of blank) and a slight luminescence red shift. Hence, the subsequent experiments mainly aimed at CdMOF-2. The suspension of CdMOF-2 containing Acac (3000 ppm) varied the visible emission color from light blue to green when excited by a UV lamp at 365 nm (Figure 6c), which is further certified by the CIE chromaticity diagram (Figure S6). The anti-interference tests were carried out to certify the selectivity of CdMOF-2 toward Acac, with the presence of equal equivalence of other solvents in the sample suspensions. CdMOF-2 displayed an analogous emission reply without showing any influence by the titration of other solvents, which was revealed in Figure 6b.

![Figure 6.](image)

Figure 6. (a). Emission intensities of CdMOF-2 in DMF with different organic solvents (3000 ppm). (b). Anti-interference performance of CdMOF-2 for sensing Acac with the coexistence of other organic solvents (3000 ppm) in DMF solutions. (c). Sample of CdMOF-2 in DMF containing 3000 ppm Acac converted the visible emission color from blue to green (under 365 nm UV-lamp). (d). Emission intensities of CdMOF-2 with increasing concentrations of Acac (0–36 µL) in DMF solution.

Further investigations on the correlation of luminescence of MOF-2 and the proportion of acetylacetone in DMF were determinate in detail. The results showed that the
luminescence intensity of MOF-2 was improved with the slowly addition of Acac, a valued luminescence red shift was surveyed (Figure 6d). Furthermore, a positive linear relationship was found (Figure S10). According to the $3\sigma/k$ formula, the detection limit was calculated with 19.4 ppm, which are competitive with other reported examples [24].

In addition, the repeatable stability was also crucial for luminescent sensors in practical applications, and thus the repeatability experiment of CdMOF-1 and CdMOF-2 was arranged. The repeatability result of CdMOF-1 was not satisfactory, perhaps induced by framework collapse, which could be owning to the large porosity and the departure of coordinated H$_2$O. After three cycles, the luminescence intensity remained stable, which proved that CdMOF-2 holds great potential as a recyclable energy-saving material (Figures S11–S13).

3.6. Sensing Mechanism for Detecting TNP/PNP and Solvent Molecules

Based on the above performance, we selected CdMOF-2 to discuss the possible quenching and enhancing mechanism. Firstly, PXRD curves of CdMOF-2, CdMOF-2@PnP and CdMOF-2@TNP were basically consistent, which excluded the probability of structural damage (Figure S13). Then, luminescence lifetimes of CdMOF-2 before and after immersing TNP/PNP was examined (Figure S14); the slightly reduced luminescence lifetime and the tendency of Stern-Volmer curve confirmed static and dynamic quenching (Figure S15) [40]. The UV absorption of all TNP/PNP in DMF were recorded (Figure 7a), which displayed an obvious overlap with excitation and a minor overlap with emission (Figure S15) [40]. The UV absorption of all TNP/PNP in DMF were recorded (Figure 7a), which displayed an obvious overlap with excitation and a minor overlap with emission (Figure S15) [40].

The probable occasions for the intrinsic enhancing mechanism of Acac were explored. Firstly, PXRD curves of CdMOF-2, CdMOF-2@PnP and CdMOF-2@TNP were basically consistent, which excluded the probability of structural damage (Figure S13). Then, luminescence lifetimes of CdMOF-2 before and after immersing TNP/PNP was examined (Figure S14); the slightly reduced luminescence lifetime and the tendency of Stern-Volmer curve confirmed static and dynamic quenching (Figure S15) [40]. The UV absorption of all TNP/PNP in DMF were recorded (Figure 7a), which displayed an obvious overlap with excitation and a minor overlap with emission (Figure S15) [40]. The lower the LUMO energy of NACs is, the easier it is to electron transfer, which would make the quenching effect more evident. Thus, the electron transfer may be one factor leading to luminescence quenching.

![Figure 7](image.png)

**Figure 7.** (a) The emission and excitation spectra of CdMOF-2 and absorption spectra of NACs in DMF solution. (b) HOMO and LUMO energy level of NACs.

The probable occasions for the intrinsic enhancing mechanism of Acac were explored. Firstly, the maintenance of the PXRD pattern for the sample before and after dealing with organic solvents excluded collapse of framework (Figure S11). As above, for sensing Acac, an obvious red shift (486–496 nm) was tested in the luminescence emission spectrum after titrating Acac to the pre-prepared CdMOF-2 (Figure 6d). The shift manifested strong formation of exciplex between CdMOF-2 and Acac. From crystal structure, the F atoms in H$_3$TFBA ligand are aligned along the inner walls of the channels, and hydrogen-bonds could be easily formed between Acac and F atoms. Earlier studies suggested that this
luminescent effect was probably caused by Acac, possibly derived from host-guest interaction [43]. Furthermore, the relationship between the concentration of Acac and absorbance under UV-vis was also tested (Figure S16). The absorbance of CdMOF-2 slowly increased with the titration of Acac, further elucidating their intra-molecular interaction. Additionally, the UV-vis absorption experiments of CdMOF-2 containing different organic solvents were proceeded (Figure S17). These experimental results showed the absorption of Acac had a large overlap with the excitation of CdMOF-2, while the UV-vis adsorption of the other organic solvents displayed negligible overlap. Generally, acute turn-on luminescence response and the redshift of the emission band toward Acac was probably ascribed to the electron transfer and the formation of an interaction between Acac and CdMOF-2 [44–49].

4. Conclusions

In summary, two new Cd-MOFs (CdMOF-1 and CdMOF-2) based on H$_3$TFBA were synthesized under solvothermal conditions and fully characterized. CdMOF-1 and CdMOF-2 displayed diverse 2D or 3D structures demonstrating a mixed ligand approach in the exploitation of metal-organic frameworks. CdMOF-2 showed good thermal and chemical stability in various solvents. More importantly, it can selectively and sensitively detect nitrophenols and Acac in DMF. The fluorescence quenching mechanism for nitrophenols is due to competition absorption and luminescence resonance energy transfer (FRET). The turn-on mechanism for Acac of MOF-2 could be attributed to host-guest interaction and electron transfer. Therefore, [Cd(TFBA) (bipy)]$_n$ could act as a promising MOF-based luminescent sensor in the detection field.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst12121708/s1.

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