Abstract

The rapid monitoring of food safety plays a key role in the food industry. Here, we have prepared a lanthanide metallo-organic framework Eu-TCPP, which can selectively detect aflatoxin B1, showing an ultrafast response of 5 min, a detection limit (LOD) of 44.17 ng/mL, and potential to develop point-of-care testing (POCT) sensing materials. Moreover, the emission wavelength of Eu-TCPP is at 617nm, which can effectively avoid aflatoxin autofluorescence interference, which is rarely reported in other mycotoxin fluorescence detection sensors. Combined experimental analysis and density functional theory (DFT) calculations show that the high selectivity, high sensitivity and rapid response ability of Eu-TCPP to detect aflatoxin B1 may be due to the LUMO level of the ligand higher than the LUMO level of aflatoxin, which transfers electrons to the object to be detected, resulting in weakened fluorescence. This study not only provides a potential probe for aflatoxin detection, but also providing a horizon that can guide the development of sensing materials for point-of-care testing (POCT) application.

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Keywords
Photoelectron transfer | Fluorescence | Aflatoxin | Sensors | Metal-organic frameworks

Comprehensive Summary

The rapid monitoring of food safety plays a key role in the food industry. Here, we have prepared a lanthanide metallo-organic framework Eu-TCPP, which can selectively detect aflatoxin B1, showing an ultrafast response of 5 min, a detection limit (LOD) of 44.17 ng/mL, and potential to develop point-of-care testing (POCT) sensing materials. Moreover, the emission wavelength of Eu-TCPP is at 617nm, which can effectively avoid aflatoxin autofluorescence interference, which is rarely reported in other mycotoxin fluorescence detection sensors. Combined experimental analysis and density functional theory (DFT) calculations show that the high selectivity, high sensitivity and rapid response ability of Eu-TCPP to detect aflatoxin B1 may be due to the LUMO level of the ligand higher than the LUMO level of aflatoxin, which transfers electrons to the object to be detected, resulting in weakened fluorescence. This study not only provides a potential probe for aflatoxin detection, but also providing a horizon that can guide the development of sensing materials for point-of-care testing (POCT) application.
Background and Originality Content

Aflatoxins are a group of secondary toxic metabolites produced by Aspergillus flavus and Aspergillus parasiticus, including aflatoxin B1 (AFB1), aflatoxin B2 (AFB2), aflatoxin G1 (AFG1), aflatoxin G2 (AFG2) and others[1]. As the most toxic one, AFB1 is a crucial risk factor for liver cancer and was classified as a class I carcinogen by the International Agency for Research on Cancer (IARC)[2]. Cereals and cereal byproducts are frequently contaminated by AFB1, and the mycotoxin is usually not destroyed by food processing or cooking due to its high chemical and thermal stability[3, 4]. To prevent health risks from AFB1 contamination, it is of vital importance to determine and assess the level of AFB1 in food. Conventional approaches for detecting mycotoxins mainly include chromatography-based methods such as high performance liquid chromatography (HPLC) [5], liquid chromatography–mass spectrometry (LC–MS/MS) [6], and enzyme-linked immunosorbent assay (ELISA) [7]. However, these methods suffer from the restrictions such as sophisticated instrumentation, time-consuming sample pretreatment, or skilled personnel. Therefore, it is of great importance to develop a simple, rapid, low-cost, and sensitive aflatoxin detection method. Compared with the above methods, fluorescence analysis methods have attracted increasing attention due to their simplicity, high speed, low cost and high sensitivity[8,9]. Especially recently, the development of sensors using luminescent metal-organic frameworks has become a research hotspot, with promising prospects for detecting fluorescent sensors for cations[10], anions[11], vapor[12], or small molecules[13]. So far, some studies have found that the sensors of luminescent MOF can detect mycotoxins[14-17], but these luminescent MOF still have the problem of wide emission, overlapping with the emission wavelength of AFB1, and interference detection, which requires the development of new luminescent MOF materials.

Ln-MOFs are promising chemosensing materials[18], and lanthanide ions can be used as fine fluorophores, although specific recognition of the detected molecules is usually ignored, leading to non-specific and slow detection[19]. In fact, the photoinduced electron transfer (PET) between Ln-MOF and the motif-detected object, fluorescence resonance energy transfer (FRET) or fluorescence internal filtration (IFE) can effectively affect the fluorescence intensity of Ln-MOF, which has great potential to improve the recognition ability of different molecules[20-24]. For example, Yuan’s[25] team successfully synthesized a multinuclear lanthanide metal-organic framework (Tb-L1). Based on the IFE mechanism, the absorption spectrum of tetracycline and the excitation spectrum of Tb-L1 are well-overlapped, which can efficiently hinder the excitation light for the Tb-L1 and providing good sensitivity to tetracycline. Xiao et al.[26] demonstrated a photo-induced electron transfer (PET) process from Eu-DPA to the BA-leucodopachrome polymers. Thereby, the fluorescence turn-off response of Eu-MOF is achieved. In addition, the 5D0 -7FJ (J= 1,2,3,4) transition of Eu3+ ions can generate characteristic emission wavelengths at 591, 616, 650 and 698 nm that do not overlap with the mycotoxin fluorescence wavelengths, which can avoid interference.

Herein, we proposed a novel europium (III) (Eu3+) -based luminescent metal–organic framework Eu-TCPP for mycotoxin sensing. The enhanced emission from the antenna effect between the ligand and the Eu3+ ions enable Eu-TCPP excellent photoluminescent properties. Due to the lowest unoccupied molecular orbital (LUMO) energy levels of aflatoxins are lower than the LUMO energies of the ligand, a photoinduced electron transfer (PET) process occurs from ligands to aflatoxins, leading to the attenuation of antenna effect between the ligand and the Eu3+ ions. The developed Eu-TCPP sensor exhibited rapid and efficient luminescence quenching response toward aflatoxins. Furthermore, the proposed method showed robust performance for sensitive AFB1 detection in real oil samples. Thereby, our work expects to inspire further research into luminescent Ln-MOFs for advanced practical applications in point-of-care testing (POCT) biochemical sensors.

Results and Discussion

Characterization and structural analysis of Eu-TCPP

The Eu-TCPP is a typical Eu3+-based metal–organic framework prepared by utilizing hydrothermal synthesis
method. The SEM image revealed the uniform nanorod morphology of Eu-TCPP with a length about 7-12 μm (Figure 1A). The Fourier transform infrared (FTIR) spectra of H4TCPP and Eu-TCPP were recorded (Figure 1B). The characteristic stretching vibration νC=O (1700 cm\(^{-1}\)), νC-O (1280 cm\(^{-1}\), 1220 cm\(^{-1}\)), and νO-H (3140 cm\(^{-1}\)) of TCPP nearly disappear in Eu-TCPP, which illustrates that the ligands in Eu-TCPP are coordinated with Eu\(^{3+}\) ions through the carboxyl group. Before study the luminescent sensing properties of Eu-TCPP, the stability of the MOF material was also tested. We evaluated the thermal stability of Eu-TCPP by thermogravimetric analysis (TGA) (Figure 1C). The first weight loss of 12.73% for Eu-TCPP compound in the range of 25–400 °C corresponds to the removal of internal solvent molecules. A sharp weight loss of 23.52% in the range of 400–600 °C is ascribed to the decomposition of the compounds and release of organic moieties. To test the effect of analyte (AFB1) on MOF crystal structure, the powder X-ray diffraction (PXRD) patterns were recorded (Figure 1D). The PXRD pattern of Eu-TCPP treated with AFB1 is coincident to that of Eu-TCPP control, indicating that the parent crystal structure of Eu-TCPP has not changed after being treated with AFB1.

![Figure 1](image1.png)

**Figure 1** (A) SEM image of Eu-TCPP. Scale bar: 10 μm. (B) Fourier transform infrared (FTIR) spectra of H4TCPP and Eu-TCPP. (C) Thermogravimetric analysis (TGA) curve of Eu-TCPP material. (D) Powder X-ray diffraction (PXRD) patterns of Eu-TCPP before and after being treated with AFB1.

The surface component of the nanoprobe was also studied by XPS (Fig.S1), and it displayed four specific peaks of C 1s, N 1s, O 1s and Eu 3d at respective energies of 284.08, 399.08, 531.08 and 1134.08 eV. The europium content of 7.16% manifested the successful coordination of Eu\(^{3+}\) with H4TCPP.

**Photoluminescence properties of Eu-TCPP**

The photoluminescence excitation spectrum of Eu-TCPP, collected by utilizing a characteristic emission wavelength (617 nm) at room temperature, indicated a broad excitation with the peak at about 340 nm (Figure 2A). 340 nm excitation of Eu-TCPP provided four characteristic emission peaks at 592, 617, 652 and 697 nm, which are attributed to the\(^{5}D_{0}^{-7}F_{J}(J = 1, 2, 3 \text{ and } 4, \text{ respectively})\) transition of Eu\(^{3+}\) ions\(^{[19]}\). In addition, a bright red color fluorescence can be observed by the naked eye under 365 nm UV light (Figure 2B, inset), with the maximum fluorescence yield come from the transition the\(^{5}D_{0}^{-7}F_{2}\)transition of Eu-TCPP.
Figure 2  (A) The schematic energy transfer process that induces the antenna effect in Eu-TCPP.  (B) The excitation and emission spectrum of Eu-TCPP. Inset: the corresponding photograph under 365 nm UV light irradiation.  (C) Molecular structures of organic ligands H₄TCPP, H₄TCPE, H₄TCPB.  (D) The emission spectrum of the Eu-TCPP, Eu-TCPE and Eu-TCPB suspended in acetonitrile (0.2 mg/mL) at room temperature under 340 nm excitation.

To study the photoluminescence features, the luminescence intensities of H₄TCPP, Eu³⁺ and Eu-TCPP were gathered. At the same concentration, the ligand and Eu³⁺ don’t have fluorescence signal at 617 nm (Figure S2). We analyzed the energy relationship between ligand H₄TCPP and Eu³⁺ ions in Eu-TCPP to study the photoluminescence mechanism of antenna effect. Figure 2C illustrates the energy transition of ligand (singlet state, S₁) - ligand (triplet state, T₁) - Eu³⁺ (excited state, ⁵D₀) in Eu-TCPP material. Based on density functional theory (DFT) calculation, the S₁ energy of H₄TCPP is 32201.69 cm⁻¹, the T₁ energy is 26409.82 cm⁻¹ (Table S1). Thus, the energy gap ΔE₁(S₁-T₁) between S₁ and T₁ is 5791.84 cm⁻¹, indicating that H₄TCPP can be excited to its triplet state through intersystem crossover process, according to Reinhold’s empirical rule[27] that the intersystem crossing becomes effective when the ligand energy gap ΔE₁ is larger than 5000 cm⁻¹. On the other hand, the energy gap ΔE₂(T₁-⁵D₀) between triplet state of H₄TCPP and the excited state of Eu³⁺ (⁵D₀, 17500 cm⁻¹) is calculated to be 8909.82 cm⁻¹, which is larger than 3500 cm⁻¹, an energy level sufficient for achieving irreversible energy transfer to sensitize Ln³⁺ ions[28]. Collectively, Eu³⁺ ions can be efficiently sensitized by the ligand H₄TCPP, which is excited to its triplet state through intersystem crossing from its singlet state after absorbing photons. These data together suggest that Eu-TCPP harbors excellent photoluminescent properties based on antenna effect between the ligand and the Eu³⁺ ions.

To testing the Eu³⁺-based MOFs with the optical behavior of antenna effect, The other two kinds of carboxyl-modified tetratopic ligands were selected as organic linkers to prepare MOFs by hydrothermal synthesis. As indicated by Figure 2C, the organic ligands containing four carboxylic groups are tetrakis(4-carboxyphenyl)ethylene (H₄TCPE) and 1,2,4,5-tetrakis(4-carboxyphenyl) benzene (H₄TCPB), which belong to rectangular derivatives of tetraphenylethylene and tetraphenylbenzene, respectively. Thus, we obtained the other two Eu³⁺-based MOFs, named as Eu-TCPE and Eu-TCPB. According to scanning electron microscopy (SEM,
Figure S3), the two Eu-MOFs are in the shape of block and schistose, respectively. Then, photoluminescence emission spectrum of the Eu-MOFs (0.2 mg/mL) suspended in acetonitrile at room temperature were recorded and compared in Figure 2D. The Eu-TCPP and Eu-TCPB samples exhibit red color emission at about 617 nm when excited by 340 nm UV light, while that of Eu-TCPE showed no significant emission peak. Compared with the other two Eu-MOFs, the strongest emission of Eu-TCPP under 340 nm excitation can be attributed to its best antenna effect and optimal sensitization of Eu$^{3+}$. Therefore, the following study in this work mainly focuses on Eu-TCPP, a typical luminescent MOF.

we investigated the luminescence of Eu-TCPP in different solvents (Figure S4), including acetonitrile, DMF, MeOH, DCM, and water. Eu-TCPP exhibits the solvent-dependent luminescent behavior, similar to other luminescent MOFs. Among these solvents, the strong emission peak at 617 nm was observed in ACN and DMF. After spending 7 days in an ACN solution, the luminescence stability of Eu-TCPP was remarkable (Figure S5A, B). Also, the photostability of the nanoprobe was explored in Fig. S5C. The fluorescence intensity of Eu-TCPP maintaining stability after continuous UV light (365 nm) irradiation for 60 min, indicating that the nanoprobe has good resistance to photobleaching. To sum up, Eu-TCPP has excellent optical properties, prompting the potential function of Eu-TCPP as fluorescent nanoprobes.

Conditions optimization and determination of AFB1

We tested the proposed Eu-TCPP on responding to mycotoxin AFB1. As shown in Figure 3A and Figure 3B, a dose-dependent quenching response of fluorescence intensities was distinctly observed after exposure of the Eu-TCPP to the mycotoxin AFB1 for 5 min. Specifically, the Eu-TCPP dosage were changed (0.8, 0.6, 0.4, 0.2, 0.1, 0.05, and 0.025 mg/mL) to optimize the fluorescence quenching of the luminescent MOFs, while the experimental concentration of AFB1 was fixed to be 25 ppm (Figure S6B). The highest fluorescence intensity change ($\Delta F/F_0$) was achieved with 0.2 mg/mL of Eu-TCPP, thus this Eu-TCPP dosage was adopted for evaluating the sensing performance of Eu-TCPP for AFB1 in the following work. Under 340 nm excitation, the fluorescence intensity change of Eu-TCPP at 617 nm emission wavelength was monitored at different timepoint (Figure S6C). Rapid fluorescence quenching was achieved after AFB1 exposing and the response time was found to be 60 s ($\Delta F/F_0 = 0.74$), which is advantageous compared to other reported AFB1 sensors. The effect of solvent on the fluorescence quenching of Eu-TCPP after exposing to AFB1 (5 min) was also measured and the results are presented in Figure S6A. The fluorescence quenching reaction has excellent adaptability and tolerance to organic solvents including acetonitrile (ACN), N, N-dimethylformamide (DMF), methanol (MeOH), dichloromethane (DCM), while that reaction was relatively weak in water solvent with a $\Delta F/F_0$ of 59%. Take reaction in acetonitrile solvent as a representative, a linear correlation between fluorescence intensity changes and the logarithmic AFB1 concentration (50 ng mL$^{-1}$ to 1000 ng mL$^{-1}$) can be expressed by the equation of $\Delta F/F_0 = 0.0638 \log_{10} C_{\text{AFB1} \text{ng mL}^{-1}} - 0.0752$, with a correlation coefficient ($R^2$) of 0.9714 (Figure 3C, red line). Also noted in Figure 3C (black line) is that the relationship curve can be well-fitted to $\Delta F/F_0 = 0.8144 \log_{10} C_{\text{AFB1} \text{ng mL}^{-1}} - 2.7484$ ($R^2 = 0.9964$) at higher concentrations within the range of 5 ppm to 30 ppm.
Figure 3 (A) Fluorescence spectrum of Eu-TCPP after being exposed to AFB1 in acetonitrile under 340 nm excitation, with mycotoxin concentrations given from 25 ng mL\(^{-1}\) to 30 ppm. (B) A magnified view of the fluorescence spectrum from the area indicated by dotted box in (A). (C) The linear relationship between the fluorescence intensity changes (\(\Delta F/F_0\)) of Eu-TCPP and the logarithmic AFB1 concentration (LgCAFBI), within the range of 50 ng mL\(^{-1}\) to 1000 ng mL\(^{-1}\) (red line) and 5 ppm to 30 ppm (black line). (D) Stern–Volmer plots of Eu-TCPP acquired at 340 nm excitation and 617 nm emission for aflatoxin B1 (AFB1, black), aflatoxin G1 (AFG1, red), aflatoxin G2 (AFG2, blue) and ochratoxin A (OTA, green).

The fluorescence quenching efficiency can be calculated by the modified Stern–Volmer (SV) equation\(^{[30]}\) as shown below:

\[
\ln \left( \frac{I_0}{I} \right) = K_{SV} [Q] + 1
\]

Where \(I_0\) and \(I\) represent the emission peak intensity of Eu-TCPP in the absence and presence of quencher, respectively; \(K_{SV}\) is the Stern–Volmer quenching efficiency; and \([Q]\) is the molar concentration of the added quencher. The \(K_{SV}\) plots for different mycotoxins are shown in Figure 3D, which indicate linear relationships between the Ln (\(I_0/I\)) and \([Q]\) for the four mycotoxins. Thus, the Eu-TCPP has demonstrated efficient quenching effect towards aflatoxin B1 (AFB1), aflatoxin G1 (AFG1), aflatoxin G2 (AFG2), as the \(K_{SV}\) value for AFB1, AFG1, AFG2 and ochratoxin A (OTA) calculated to be to be 20988 M\(^{-1}\), 16532 M\(^{-1}\), 12655 M\(^{-1}\) and 1829.8 M\(^{-1}\), respectively. The \(K_{SV}\) for AFB1 is largest compared with that for AFG1, AFG2 and OTA, indicating its higher selectivity toward AFB1.

Quenching mechanism of Eu-TCPP’s emission for mycotoxin sensing

We further studied quenching mechanism to better understand the luminescence quenching response of Eu-TCPP toward mycotoxins. In general, the presence of the analyte may lead to the fluorescence quenching of LMOFs through mechanism including causing structural collapse of the material, fluorescence resonance energy transfer (FRET)\(^{[31]}\), inner filter effect (IFE)\(^{[32]}\), or photoinduced electron transfer (PET)\(^{[33]}\). As the PXRD patterns show the parent crystal structure of Eu-TCPP has not changed after being treated with AFB1 (Figure 3D), the fluorescence quenching effect is not caused by the structural collapse of Eu-TCPP.
When the distance between the two fluorophores is suitable (typically less than 100 Å), the transfer of fluorescence energy from the donor to the acceptor can be considered. To achieve successful fluorescence resonance energy transfer, the emission spectrum of one fluorophore (the donor) usually overlaps the absorption spectrum of the other group (the acceptor). As shown in Fig. 5A, the UV–Vis absorption spectrum demonstrated that the UV absorption of the analytes (mycotoxins) did not overlap with the Eu-TCPP emission spectrum, indicating that the mycotoxin-induced quenching of Eu-TCPP’s emission is not suitable to be explained by the FRET mechanism. On the other hand, the UV absorption peaks of the four mycotoxins (especially the AFB1, AFG1, AFG2) overlapped with the excitation spectrum of Eu-MOF (Figure 4B), indicating that there is likely to be an IFE process when the Eu-TCPP was treated with the mycotoxin. Nevertheless, AFG1, AFG2, and OTA exhibited significant emission peaks under 340 nm excitation wavelength, while the excitation spectrum and emission spectrum of AFB1 showed weak peaks (Figure 4C). We also observed different fluorescence quenching effects of Eu-TCPP caused by the four mycotoxins (Figure 4D). These data suggest that the mycotoxin-induced fluorescence quenching of Eu-TCPP could not be fully attributed to the inner filter effect between mycotoxin and Eu-TCPP.

Figure 4 (A) Comparison of the emission spectrum of Eu-TCPP with the UV–Vis absorption spectrum of four mycotoxins. (B) Spectral overlap of the excitation spectrum of Eu-TCPP between the UV–Vis absorption spectrum of four mycotoxins. (C) The excitation (dotted line) and emission (solid line) spectrum of AFB1, AFG1, AFG2 and OTA in acetonitrile. (D) Responses of AFB1, AFG1, AFG2, OTA on the fluorescence attenuation of standard concentration Eu-TCPP.

In those Ln-MOFs containing antennas and transmitters, the antenna effect can be interrupted by the presence of the analyte, resulting in fluorescence quenching of the sensing material. The electron transfer from ligand to analyte often contributes significantly to fluorescence quenching in these cases. Photoinduced electron transfer (PET) is a fundamental process that photoinduced transfer of excited electrons from a photoexcited fluorophore to the lowest unoccupied molecular orbital (LUMO) of a quencher. When the excited state of the ligand is located at a higher energy level than the LUMO of the analyte, it can lead to a driving force for electron transfer from the ligand to the analyte. Calculated by density functional theory (DFT), the relative orbital energies of the highest occupied molecular orbitals (HOMOs) and LUMOs of ligands and analytes were obtained as shown in Figure 5 and Table S2. The LUMO energy levels of AFB1
(2.05 eV), AFG1 (1.96 eV), AFG2 (2.16 eV) all lie below the LUMO energies of the ligand H4TCPP (2.78 eV), indicating a typical PET process exists from H4TCPP to these aflatoxins. In contrast, the LUMO energy levels of OTA (2.81 eV) is higher than that of the ligand H4TCPP (2.78 eV), which accounts for inefficient electron transfer and lower degree of quenching effect. Additionally, AFB1 did not have significant fluorescence quenching effect on the ligand H_4TCPP itself (Figure S7), indicating that there is no specific interaction between AFB1 and the ligand (free state) to support efficient electron transfer.

![Energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of H_4TCPP, Eu-TCPP and aflatoxins for analysis of electron transfer.](image)

**Figure 5** Energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of H_4TCPP, Eu-TCPP and mycotoxins for analysis of electron transfer.

**Application in the edible oil samples**

To evaluate sensing performance for practical applications, the Eu-TCPP material were applied to detect AFB1 in the spiked samples. The corn oil and sunflower oil samples were purchased from a local supermarket and then spiked with AFB1 at different level (50, 500, and 1000 ng mL\(^{-1}\)). As shown in Table 1, high recoveries were achieved by Eu-TCPP-based method in corn oil samples (82.3–114.5%) and sunflower oil samples (92.2–95.3%). The edible oil samples were also analyzed by LC-MS/MS as a comparison. As shown in Table 1, there is considerable correlation between the results of AFB1 in edible oil determined with our fluorescence sensing strategy and by LC-MS/MS. Thus, these results suggest that the proposed detection method has satisfactory selectivity and tolerance to interfering substance in real oil samples, endowing the sensing material with promising practical applications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eu-TCPP Fluorescence Sensing</th>
<th>LC-MS/MS</th>
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<tbody>
<tr>
<td>corn oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 ppb</td>
<td>1144.61 114.5 4.4</td>
<td></td>
</tr>
<tr>
<td>500 ppb</td>
<td>468.75  93.8 4.3</td>
<td></td>
</tr>
<tr>
<td>50 ppb</td>
<td>41.16   82.3 0.8</td>
<td></td>
</tr>
<tr>
<td>sunflower oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1000 ppb</td>
<td>953.29  95.3 4.4</td>
<td></td>
</tr>
<tr>
<td>500 ppb</td>
<td>555.33  111.1 0.8</td>
<td></td>
</tr>
<tr>
<td>50 ppb</td>
<td>61.16   122.3 3.0</td>
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</table>

**Table 1** Application of the Eu-TCPP for AFB1 determination in edible oil samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eu-TCPP Fluorescence Sensing</th>
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<tr>
<td>corn oil</td>
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<td>1000 ppb</td>
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<td>500 ppb</td>
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<td>sunflower oil</td>
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Conclusions

In summary, we demonstrated that a lanthanide metal–organic framework Eu-TCPP exhibits rapid and efficient luminescence quenching response toward aflatoxins. Since the ligand H₄TCPP successfully embedded into the Eu³⁺-based metal–organic framework, the ligand can act as “antennas” to absorb photons and generate their triplet states, thereby resulting in Eu³⁺ sensitization and enhanced emission. When the Eu-TCPP exposed to aflatoxins, photoinduced electron transfer (PET) can take place from ligands to aflatoxins because the LUMO energy levels of aflatoxins are lower than that of the ligand. Take advantage of the PET process to attenuate the antenna effect, the Eu-TCPP material poses an analyte-induced luminescence quenching mechanism to realize the ultrafast detection of aflatoxins. The developed Eu-TCPP sensor exhibited satisfactory performance for rapid and sensitive AFB1 detection with a detection limit of 44.17 ng mL⁻¹. It was also applied to detect AFB1 in spiked edible oil samples and high recoveries (82.3–114.5%) were achieved. These data suggest that the luminescent Ln-MOF material has great potential to develop facile, rapid and sensitive sensors for small molecules and other biochemical hazards. These Ln-MOF sensors may greatly facilitate point-of-care testing (POCT) practical application.

Experimental

Reagents and chemicals

The europium nitrate hexahydrate (Eu(NO₃)₃·6H₂O) used in this experiment was purchased from Sinopharm Chemical Co., Ltd. with a purity of 98%; organic ligands 4,4’,4″,4‴-(pyrazine-2,3,5,6-tetrayl)tetrabenzoic acid, 1,1,2,2-Tetra(4-carboxylphenyl)ethylene, 1,2,4,5-Tetrakis(4-carboxyphenyl)benzene were purchased from Shanghai McLean Biochemical Technology Co., Ltd. with a purity of 98%; Solvent N,N-Dimethylformamide (DMF, analytical grade) was purchased from Inokai Technology Co., Ltd.; Acetonitrile was purchased from Beijing Huihai Keyi Technology Co., Ltd.; AFB1, AFG1, AFG2, OTA were purchased from Shanghai McLean Biochemical Technology Co., Ltd.; ultrapure water was prepared by Milli-Q water purification system.

Instrument

The instruments used for characterization are as follows: Sigma-3000 scanning electron microscope (Zeiss, Germany), UV/Vis spectrophotometer (Shimadzu, Japan), powder X-ray diffractometer (Bruker, Germany), Nicolet i50 infrared spectrophotometer (Thermo Fisher Scientific, USA), Simultaneous Thermal Analyzer (DSC/DTA–TG) STA 449 F5 Jupiter (NETZSCH, Germany), ASAP2020 Automatic Surface Area and Porosity Analyzer (Micromeritics, USA), Electric Blast Drying Oven (Zhonghuan Electric Furnace, China), ZK-2BYT Vacuum Dryer (Zhonghuan Electric Furnace, Tianjin), Ultrasonic Cleaner (KH220V, 300 Hz, Kunshan, China).

Preparation of Eu-MOF

The preparation of Eu-TCPP was modified according to the references. Typically, a mixture of europium (III) nitrate hexahydrate (Eu (NO₃)₃·6H₂O) (0.075 mmol, 0.0335 g) and H₄TCPP (0.0375 mmol, 0.021 g), DMF (15 mL) were added in a 25 mL autoclave, followed by heating at 150 °C for 24 h. The precipitates were washed three times with DMF and twice with ethanol. After 60 °C drying overnight, colorless bulk crystals of Eu-TCPP were obtained.

The synthesis of Eu-TCPB MOF and Eu-TCPE MOF was similar to that of Eu-TCPP MOF, only replace H₄TCPP with H₄TCPB (0.0375 mmol, 0.019 mg) or H₄TCPE (0.0375 mmol, 0.021 mg), respectively.

Luminescence Sensing Experiments
A standard Eu-TCPP suspension was prepared by dispersing Eu-TCPP (1 mg) in acetonitrile (1 mL) and sonicated for 15 min. All mycotoxin standards including AFB1, AFG1, AFG2, OTA were dissolved and diluted in acetonitrile to desired concentration. Typically, 100 μL Eu-TCPP suspension (0.4 mg/mL) and 100 μL mycotoxin solution were mixed in a 1.5 mL centrifuge tube. After reaction for 5 minutes, the mixture was transferred to a quartz cuvette for fluorescence detection using an F97 fluorescence spectrophotometer at room temperature.

Real sample analysis

Corn oil and Sunflower oil as real samples, the performance of the sensor was evaluated. Firstly, the 5 g of the oil sample was vigorously mixed with 20 mL of extraction reagent (acetonitrile:water = 84:16) using a vortex mixer for 30 min. After centrifuging at 12,000 rpm for 10 min, the supernatant was filtered through a 0.22 μm membrane, and then oil sample solutions with different concentrations of aflatoxin B1 were prepared by standard addition method. Finally, the samples were detected and analyzed by fluorescence spectroscopy.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2023xxxxx.

Acknowledgement

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The Authors

After acceptance, please insert a group photo of the authors taken recently.

Left to Right: Authors Names

Entry for the Table of Contents

Fast Fluorescence Sensing of Aflatoxin B1 Employing a Europium Metal–Organic Framework Avoiding Self-Fluorescence In Text for Table of Contents. **Figure 1** (A) SEM image of Eu-TCPP. Scale bar: 10 µm. (B) Fourier transform infrared (FTIR)...