Mechanistic investigation of photocatalytic degradation of organic dyes by a novel zinc coordination polymer†

Jianqiang Huo, Donghui Yu, Haiqiang Li, Bingcai Luo and Navamoney Arulsamy

A new coordination polymer ([Zn(TIPA)(seb)$_{0.5}$](NO$_3$)$_3$.3.5H$_2$O)$_n$ (1) (TIPA = tris(4-(1H-imidazol-1-yl)phenyl)amine, seb = sebacic acid) is prepared and characterized by elemental analysis, Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD) and single crystal X-ray diffraction. Complex 1 has a three-dimensional (3D) 2-fold interpenetrating diamondoid network, and can be represented by the Schl"afli symbol (3$^3$.4$^3$.5$^4$.6$^6$.7). The luminescent, optical, and thermal properties of 1 in the solid state are investigated. Significantly, 1 assists in the photodegradation of organic dyes in the presence of H$_2$O$_2$ and upon irradiation with UV light ($\lambda = 254$ nm). A mechanistic study toward understanding the photocatalytic degradation of organic dye molecules is carried out. The study reveals that the band gap of the fluorophore TIPA is lowered by the charge interaction between the Zn$^{2+}$ cation and ligand seb$^2-$dianion. The enhanced photocatalysis of 1 is also accompanied by the selective sensing of polar organic solvent nitromethane (NM) and antibiotic ofloxacin (OFX) by a luminescence quenching process. Concurrently, 1 demonstrates excellent ability to adsorb inorganic pollutant permanganate ions likely due to the presence of its unique 3D structural network.

Introduction

Dye wastewater is an industrial effluent which remains difficult to treat, containing large quantities of highly chromophoric complex chemicals that do not easily degrade under biochemical conditions. Industrial processing of dye wastewater often includes physicochemical methods such as filtration, sedimentation, and coagulation. As a result, photocatalytic degradation of dye wastewater by oxidation has recently become an area of intensive research, where metal–organic frameworks (MOFs) have attracted extensive attention as a new category of semiconductor material for photocatalytic degradation of organic dyes.

Mechanistic studies of photocatalytic decomposition of organic dyes reveal that catalysis consists of three major steps:

(1) Photo driven electron–hole pair generation:

(2) Photogenerated electron–hole pair migration and recombination:

Under the influence of the electric field, photogenerated electrons and holes migrate rapidly to the surface of the semiconductor material. Since photogenerated electrons and holes have a short lifetime and opposing charges, they recombine at the surface, or inside of the material, by electrostatic attraction to release energy.

(3) Surface reaction:

For the process to be effective the photogenerated electrons and holes undergo a redox reaction at the surface. The photogenerated holes can oxidize electron donors such as OH$^-$ and H$_2$O to hydroxyl radicals (·OH), which have strong redox capabilities, and can interact with organic dye molecules to achieve degradation. A schematic representation of the mechanism is shown in Fig. 1.

Zinc-based semiconductor catalysts, including simple oxides and metal complexes, have been shown to effectively degrade organic substances such as dyes in wastewater. Among those, ZnO is the most commonly used photocatalytic material as it has a high uptake of sunlight with a high quantum
yield. More intricate complexes such as Zn(INA)2 [INA = iso-

nicotinic acid] demonstrate better photocatalytic properties

compared to ZnO. Similarly, [Zn(H2biiim)(bpy)H2O][NO3]2,

Zn(TPP)(IQNO), Zn(bba)(phen) show analogous performance

(where H2biiim = bis(benzimidazole), bpy = 4,4′-bipyridyl, TPP

= tetraphenylporphyrin, IQNO = iso-quinoline N-oxide, bba =

2-benzoylbenzoate and phen = 1,10-phenanthroline).55

The triphenylamine-based imidazole-containing tripodal

ligand, TIPA; is an excellent fluorophore in many photo-

luminescent applications.56 In this study, its band gap, between

the highest occupied molecular orbital (HOMO) and the lowest

unoccupied molecular orbital (LUMO), has been calculated to

be 4.1 eV. The HOMO and LUMO energy level difference of the

MOFs corresponds to the MOF conduction band valence energy

level difference. When coordinated to Zn(n) the resulting polymer

environment sharply reduces the band gap to 3.25 eV. The

narrower band gap explains the excellent photocatalytic

performance of the Zn–TIPA coordination polymer. A mecha-
nistic study is undertaken towards explaining the enhanced

photocatalytic performance. The Zn2+ complex has a dramati-
cally smaller band gap by almost 1 eV in comparison to the band

gap of the florescent ligand, a reduction of 30%. A narrow band
gap for fluorophores is a necessary requirement for efficient

photocatalysis.

We wish to report that a novel Zn–TIPA coordination poly-

mer prepared in this study also exhibits selective photo-
luminescent sensing properties for nitromethane (NM) among

nine other polar organic solvents as well as an antibiotic,
iofloxicin (OFX). We have also studied if the Zn–MOF’s is

capable of adsorbing a number of common pollutant oxyanions

such as the permanganate anion.

Experimental section

Materials and methods

TIPA was synthesized according to reported procedures.77

Reagents (such as H2seb) and solvents were obtained from

commercial sources and were used as received without further

purification. Double-deionised water was used in hydrothermal

synthesis. Fourier-transform infrared (FTIR) spectra (Fig. S3†)

were obtained from KBr pellets in the range of 4000–400 cm−1

using an FTS 3000 (DIGILAB) spectrometer. Thermogravimetric

analysis (TGA) data were obtained using a PerkinElmer Pyris

Diamond TG/DTA TG-7 Thermal Analyzer. Experiments were

performed in the 25–800 °C temperature range in a nitrogen

atmosphere with a heating rate of 10 °C min−1. Morphology

analysis was performed using an ULTRA Plus scanning electron

microscope (SEM, Germany). Single-crystal X-ray diffraction was

carried out using a Bruker Apex Smart CCD diffractometer
equipped with a graphite crystal monochromator at 293 K.

Data collection, cell refinement and data reduction were

performed with Crysalis PRO from Agilent Technologies. The

structure was solved by direct methods using the SHELX-97

program,44 and final refinement performed by the full-matrix

least-squares method with anisotropic thermal parameters for

non-hydrogen atoms on F2. The non-hydrogen atoms were

located in successive Fourier maps and refined anisotropically,

and the H atoms were placed in calculated positions and refined

isotropically with fixed thermal parameters. Although, electron

densities attributable to a highly disordered nitrate anion could

be observed in the Fourier maps, no satisfactory disorder model

could be achieved. In addition, unaccounted for electron

densities were also observed throughout the map. The electron
densities associated with the nitrate and other atoms were

removed by the SQUEEZE/PLATON program, which led to

a significantly better refinement of the overall structure.

Specifically, the calculated scattering of 265 electrons in a void

volume of 703 Å3 per unit cell were assigned to 4NO3− anions

and 14H2O molecules. Crystallographic data collection and

refinement details are given in Table S1.† Selected bond
distances and angles are listed in Table S2.† Crystallographic
data for the structural analysis have been deposited with the

Cambridge Crystallographic Data Centre, CCDC no. 1967331.

Powder X-ray diffraction (XRD) patterns were measured using a Philips PW 1710-BASED diffractometer at 293 K.

Simulated powder XRD pattern for [[Zn(TIPA)(seb)0.5][NO3]−

Fig. 1 Schematic diagram of the proposed mechanism for malachite green oxalate (MGO) photocatalytic degradation over the fluorophore compounds.
3.5H₂O)ₖ 1 (Fig. S8†) was obtained from the final CIF file using the Mercury 2.0 program.²⁹ Solid-state fluorescence emission spectra were obtained at ambient temperature using a LS-55 (PE USA Inc.) fluorescence spectrophotometer.

**Synthesis of \([\text{[Zn(TIPA)(seb)₀.₅](NO₃)}]·3.5\text{H₂O})ₖ (1)\)**

A mixture of ZnNO₃·6H₂O (66.04 mg 0.2 mmol), TIPA (66.47 mg, 0.15 mmol), H₂seb (30.33 mg, 0.15 mmol), DMF (2 mL) and H₂O (6 mL) was sealed in a Teflon-lined stainless steel container and heated at 105 °C for 3 days. When cooled to room temperature colorless cubic crystals of 1 were obtained in 53% yield. Anal. calcld for C₁₂H₆₅N₈O₈Zn: C, 52.39; H, 4.91; N, 15.28%. Found: C, 51.26; H, 4.86; N, 15.37%. IR (KBr pellet, cm⁻¹): 3458 (m), 3118 (m), 2923 (m), 1665 (s, v asym(CO₂)), 1513 (s), 1407 (m, v sym(CO₂)), 1279 (s), 1128 (m), 1053 (s), 962 (m), 751 (w), 646 (m), 548 (m).

The dicarboxylate ligands are expected to act as metal antisymmetrically (see below). IR spectra, although the sebacate dianion coordinates to the metal, reveal the ligands bonding three different asymmetrically equivalent Zn atoms. Therefore the zinc is five-coordinate and its geometry distorted square pyramidal with the N’s of three different TIPA ligands occupying one face of the square pyramid as shown in Fig. 2a. Each of the carboxylates coordinates to the metal ion antisymmetrically with two significantly different Zn–O bond distances, 2.110(12) and 2.477(11) Å. The dinucleating μ₂–η¹–η⁰–η¹–η⁻ bridges as the Δν values are observed at 240 and 258 cm⁻¹. The crystallographic structure is consistent with the IR spectra, although the sebacate dianion coordinates to the metal antisymmetrically (see below).

**Results and discussion**

**Crystal structure of \([\text{[Zn(TIPA)(seb)₀.₅](NO₃)}]·3.5\text{H₂O})ₖ (1)\) (1)

Complex 1 crystallizes in the centrosymmetric monoclinic space group P2₁/n and the asymmetric unit consists of one Zn²⁺ cation, one TIPA ligand, a half seb⁻² anion. A two fold axis of symmetry passes through the central C–C bond of the sebacate ligand. All atoms of the cation are located on general positions. The TIPA ligand coordinates through all of its imidazole N atoms binding three different symmetrically equivalent Zn atoms. Therefore the zinc is five-coordinate and its geometry distorted square pyramidal with the N’s of three different TIPA ligands occupying one face of the square pyramid as shown in Fig. 2a. Each of the carboxylates coordinates to the metal ion antisymmetrically with two significantly different Zn–O bond distances, 2.110(12) and 2.477(11) Å. The dinucleating μ₂–η¹–η⁻ and trinucleating μ₃–η¹–η⁻–η⁻ coordination modes of the seb⁻² and TIPA ligands lead to a fascinating three dimensional network structure. The structure features channels formed exclusively by the TIPA ligands and Zn²⁺ cations (Fig. 2b). The channels are further linked together by the dinucleating (μ₁–η¹–η⁻) seb⁻² ligands (Fig. 2c). A simplified view of the network with the representation of the TIPA and seb⁻² ligands and the Zn²⁺ cation as 3-, 2- and 4-connected nodes reveals a two-fold interpenetrating diamondoid network as shown in Fig. 2d, The Schlöflı symbol for the network is \(\{3^3·4^1·5^1·6^1·7\}\) as determined by the TOPOS software. As outlined in the experimental section, scattering due to nitrate anions and a number of solvated water molecules is observed during the refinement of the structure, and could not be adequately modeled. We suggest that the anion and water solvates are highly disordered over a large volume. We also point out that the water solvates are readily lost on drying the product as confirmed by the elemental analysis data. The ready loss of water solvates also explains the host-guest properties of 1. SEM images of complex 1 are shown in Fig. S9.† The material exhibits a uniformly distributed and loose block morphology. The SEM image with 2 μm scale plate, shows random-shaped aggregation composed by many macroscopic tiny balls.

**Thermogravimetric analysis**

Crystals of 1 are quite stable showing no sign of decomposition or disintegration under ambient conditions. TGA data (Fig. S2, ESi) were measured in the 25–800 °C temperature range, in order to determine the robustness of the 3D framework present in the crystals. The TGA data reveal a gradual loss of mass corresponding to the loss of the solvated water molecules in the 100–200 °C temperature region. This gradual loss over a wide temperature range are consistent with the presence of strong H-bonding interactions deduced from the crystallographic data analysis. Complex 1 appears to regain its MOF architecture up to ca. 300 °C and exhibits a one-step or two closely-spaced steps of mass loss due to the decomposition of the TIPA ligand. We conclude that the multiply bridged network framework is robust up to T > 300 °C.

**Luminescence properties**

Considering that d¹⁰ metal complexes usually exhibit excellent luminescent properties, the emission of 1 was investigated in the solid state at room temperature. Upon excitation at 276 nm, the complex exhibits an intense emission peak centered at ca. 392 nm. To gain further insight, the luminescence spectrum was also measured for the free TIPA ligand at the excitation wavelength set at 276 nm. The ligand emits a broad emission band from 370 to 550 nm with the maximum (λmax) being 415 nm. The emission band can be ascribed to π* → π or π* → n transitions within the molecular orbital manifolds of the imidazolyl and phenyl rings of TIPA moieties. Therefore, we conclude that the luminescent properties of the TIPA ligand is preserved upon complexation with the Zn²⁺ ions. However, the metal complex exhibits responsive emission properties in the presence of certain organic compounds. The blue shift of emission bands observed for 1 is due to the coordination interactions between Zn²⁺ and the added organic compounds (Fig. 3 and 4).

**Optical band gaps**

Since the Zn²⁺ complex 1 has potential application in semiconductor materials, we measured its optical diffuse-reflection. The absorption data \(F = \alpha/S\) were calculated from the reflectance using the Kubelka–Munk function: \(F = \frac{(1-R)^2}{2R}\), where \(\alpha = \text{absorption}, S = \text{scattering coefficient, and } R = \text{reflectance of an infinitely thick layer at a given wavelength. The energy band gap, } E_g, \text{ is defined as the intersection point among the energy axis and line extrapolated of the linear portion. The } E_g \text{ value obtained for the complex is 3.25 eV. The reflectance spectrum shows that the optical band gap and semiconductor behaviour exist in this complex. The band gap also suggests that 1 may}
respond to UV light and possess the potential capacity for photocatalytic reactions.

To investigate the HOMO to LUMO energy band gap of solo ligand compounds, density functional theory (DFT) computations were carried out for pure TIPA molecules. All computations were performed with the Gaussian09 software package using the density functional B3LYP method and the standard 6-311++G(d,p) basis set.$^{39-42}$

As it can be seen from Fig. 5, the energy band gap for the free TIPA based on the calculated HOMO ($-5.825$ eV) to LUMO ($-1.724$ eV) molecular energy levels is $4.10$ eV. The study also reveals that when TIPA is coordinated to Zn$^{2+}$, the energy band gap can be dramatically reduced by $30\%$ to $3.25$ eV. A detailed rationale for Zn$^{2+}$ narrowing the band gaps by the formation of metal–organic complexes is given as follows:

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**Fig. 2** (a) Coordination environment of the Zn atom in 1. (b) Channels formed by the TIPA ligands and Zn$^{2+}$ cations. (c) Seb$^{2-}$ ligands bridging Zn–TIPA channels forming additional channels. (d) Two-fold interpenetrating diamondoid network.

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**Fig. 3** The emission spectra of compound and TIPA in solid state ($\lambda_{\text{ex}} = 276$ nm).

**Fig. 4** Solid-state optical diffuse-reflection spectrum for 1 at room temperature.
The Zn$^{2+}$ cation plays an important role in ligand to metal charge transfer (LMCT) as this occurs with the charge transition on the empty p orbitals from the oxygen of the dicarboxylate ligand and nitrogen of the TIPA ligand to the metal centre. The HOMO orbital of the metal complex consists mainly of 2p (valence band) empty orbitals of O and N atoms, whilst the LUMO orbital of the complex is mainly composed of an empty orbit (guide band orbit) of the Zn atom. The splitting effect on the charge transfer from the p orbitals of TIPA nitrogen atoms to the empty guide band orbit of the Zn$^{2+}$ cation has significantly reduced the energy level of LUMO in the metal complex. Thus, under the influence of the LMCT, the HOMO to LUMO energy band gap for Zn$^{2+}$–MOF is much smaller compared to that of the free TIPA ligand.

**Photocatalysis properties**

The Zn$^{2+}$–MOF complex 1 was screened for its contribution to the photo-degradation of a variety of dyes. The dyes studied were rhodamine B (RHB), crystal violet, fuchsin basic, malachite green oxalate (MGO) and methyl orange (MO). The photo-degradation experiments were performed for 0.01 mM solutions of the dyes in a 3 mL cuvette by monitoring the intensity of one of the peaks in their UV-vis spectra in the presence of the MOF complex (1 mg) or aq. H$_2$O$_2$ (30%, 1 drop). The experiments were also repeated after irradiation of the dye solutions containing the MOFs with UV light for 30 min. The data measured reveal that complex 1 is of assistance in the degradation reactions. Significantly, enhanced degradation is observed for MGO when both complex 1 and H$_2$O$_2$ are present and when the mixture is irradiated with UV light. The spectra measured for the dyes under various conditions are given in Fig. 6.

The degradation rate was monitored in the presence of both 1 and H$_2$O$_2$, and with the irradiation of UV light. The study revealed that the absorption peak due to MGO significantly reduced in intensity as the photocatalytic reaction progressed within a short time period of 35 min (Fig. 7).

A complete degradation mechanism for the combined effect of the photocatalyst in the degradation of MGO can be explained by eqn (1)–(5).

\[
\text{Zn–MOF photocatalyst } 1 + h\nu \rightarrow e^- + h^+ \quad (1)
\]

\[
\text{MGO} \text{ dyes (MD) } + h^+ \rightarrow \text{MD}^+ \quad (2)
\]

\[
\text{O}_2 + e^- \rightarrow \cdot\text{O}_2^- \quad (3)
\]

\[
\text{H}_2\text{O}_2 + \cdot\text{O}_2^- \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2 \quad (4)
\]

\[
\text{MD}^+ + (h^+ + \cdot\text{OH} + \cdot\text{O}_2^-) \rightarrow \text{degradation products} \quad (5)
\]

During irradiation under UV light, electrons (e$^-$) in the HOMO (valence band, VB) were excited to the LUMO (conduction band, CB), and equal numbers of positive vacancies (holes, h$^+$) were left in the VB. Initially, oxygen radicals (·O$_2^-$) are generated by combining the electrons and O$_2$ absorbed on the surfaces of the Zn–MOF photocatalyst. O$_2$ is reduced into ·O$_2^-$ with the combination of electrons (e$^-$), which further transformed into hydroxyl radicals (·OH). Such hydroxyl radicals are known to be highly efficient in the degeneration of malachite green oxalate. It is notable that H$_2$O$_2$ provides part of the O$_2$ and hydroxyl (OH$^-$) adsorbed on the surfaces of the Zn–MOF catalyst 1 and significantly accelerates the photocatalytic reaction.

From the perspective of molecular orbital study, the irradiation of MOF 1 by UV light must cause an empty orbital transition of the 2p electrons of the ligand O or N atoms to the Zn$^{2+}$ cation, which will be the LMCT transition. According to the representation, the process of semiconductor photocatalysis can be regarded as the electrons that transition to the Zn$^{2+}$ empty orbit as photogenerated electrons, and the empty orbitals left behind by the electronic transition associated with the 2p of O or N atoms as the photogenerated holes. The HOMO orbital that loses electrons must capture an electron from the water molecule back to the ground state. Correspondingly, a molecule that loses an electron is oxidized into the active species, ·OH radical. Thus the highly reactive ·OH radical can effectively oxidize organic dye molecules to complete the photocatalytic process.

**Sensing of organic solvents**

Nitromethane is listed as a group 2B carcinogen by the World Health Organization’s International Agency for Research on
Cancer. Therefore, towards evaluating the ability of the current Zn–MOF complex 1 to detect nitromethane we have studied the effect of various organic solvents on the emission spectra of 1, and observe that the complex is capable of detecting nitromethane as discussed below.

The solvents included in the study are dimethylformamide (DMF), 1,4-dioxane, dimethylsulfoxide (DMSO), dimethylacetamide (DMA), ethanol (CH₃CH₂OH), methanol (CH₃OH), acetonitrile (CH₃CN), 1-methyl-2-pyrrolidinone (NMP), acetone and nitromethane (NM). Each sample was tested for fluorescence intensity, as shown in Fig. 8.

The luminescence sensing studies indicate that complex 1 might have potential use as a highly sensitive probe for selective detection of NM.

Additional experiments were also carried out to determine the quenching efficiency of NM by varying the volume of it added to a suspension of 1. The spectra measured are shown in Fig. S5.† When 2 μL of NM was added, a decrease in relative intensity from 100% to 60% was observed. For the addition of 4 μL of NM, the emission intensity decreased sharply, and a further rise in the volume of NM, added gradually, reduced the emission intensity, with 50 μL of NM completely quenching the fluorescence of the suspension.

The quenching effects were treated quantitatively, with the Stern–Volmer equation:

\[ I_0/I = 1 + K_{sv}[M], \]
where $I_0$ and $I$ are the luminescence intensities of complex 1 and the NM-incorporated 1, respectively. $K_{sv}$ is the coefficient of the quenching effect for NM, and $[M]$ is the concentration of NM. (Fig. S5, ESI†).

**Sensing of antibiotics**

The sensing of various antibiotics by 1 was also investigated. The studies were performed by the addition of 30 μL of 0.01 M solutions of nine antibiotic compounds: Roxithromycin (RXM), Amoxicillin (AMX), Thoridazine (TDZ), Dithiazoline (DTZ), Metronidazole (MDZ), Ornidazole (ODZ), Isonicotinylhydrazide (INH), Ridinilazole (RDZ) and Ofloxacin (OFX) to a 1 mg mL$^{-1}$ suspension of the complex 1 at room temperature. We observed that the luminescence intensity of the mixture is heavily dependent on the nature of the antibiotics, and that OFX exhibited a high quenching effect on the luminescence of 1, revealing that complex 1 could be used as a sensor for OFX. The quenching effect of OFX was analysed using the Stern–Volmer equation. From the spectra measured, we calculate a $K_{sv}$ value of $1.388 \times 10^4$ M$^{-1}$ for 1, which is comparable to the value reported for a similar Cd-MOFs ($1.16 \times 10^4$ M$^{-1}$) for the sensing of antibiotic Metronidazole (MDZ). The luminescence sensing studies indicate that complex 1 may be used as a highly sensitive probe for selective detection of antibiotics OFX. (Fig. S6 and S7, ESI†).

**Adsortion of permanganate ions on MOFs**

UV-vis spectroscopy was used to examine the extent of adsorption of the anions in the Zn MOF complex. Aqueous solutions of MnO$_4^{−}$ are deeply coloured and exhibit characteristic UV-vis spectra in the 300–400 nm, and 480–600 nm wavelength regions, respectively. The intensity of absorption is reduced when the anions adsorb to the MOF complexes that remain as solids in water due to their poor solubility in water. In a typical measurement, a UV-vis spectrum was measured for an aqueous 0.1 mM solution of KMnO$_4$, and additional spectra were measured after the addition of 1 mg of the MOF complex. The spectra were measured every 10 minutes over a period of 1 hour. The UV-vis spectra for the permanganate solutions after the addition of 1 are shown in Fig. S4.† As can be seen from the spectra, complex 1 exhibits significant adsorption capability for the permanganate anion and reveals that the adsorption of the permanganate salt reaches equilibrium in 1 hour. The UV absorbance at the characteristic peak regions of 480–600 nm can be reduced by 80% relative intensity. Thus, complex 1 possesses a moderate ability to adsorb the oxyanion salt from aqueous solutions (Fig. S4, ESI†).

**Conclusions**

This study has established that the Zn$^{2+}$ cation dramatically lowers the florescent compound TIPA’s HOMO to LUMO band gap through the building up of a 3D coordination polymer. This is the first report that demonstrates the coordination of a metal ion to a fluorophore ligand could narrow the band gap of the fluorophore in the coordination polymer. Specifically, we report that the Zn$^{2+}$ coordination to TIPA dramatically narrows the band gap of the fluorescent ligand TIPA’s HOMO to LUMO energy level difference to almost 1 eV, which is a total reduction of 30%. A narrow band gap for fluorophores is a necessary requirement for efficient photocatalysis. Our investigation into the mechanism of the photocatalytic process reveals that the interactions between metal and ligand play an important role. The new zinc coordination polymer also shows selective photoluminescent sensing ability towards nitromethane among nine polar organic solvents and antibiotic ofloxacin via the luminescent quenching process. In addition, we observe that the coordination polymer is capable of adsorbing the permanganate anion, and could be applied as a crystalline sponge. These results provide important insights into the effects of the Zn$^{2+}$ ion coordination on the photoluminescent properties of the TIPA ligand and the MOF complex’s potential application in photocatalytic degradation of dyes, detection of nitromethane and ofloxacin and in the removal of pollutant oxyanion permanganate from wastewater.

**Conflicts of interest**

There are no conflicts to declare.
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References


