An uncommon 3D 3,3,4,8-c Cd(II) metal–organic framework for highly efficient luminescent sensing and organic dye adsorption: experimental and theoretical insight†

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A new Cd(II) based metal–organic framework (MOF), having formula ([CH$_3$)$_2$NH$_2$)$_6$[Cd$_4$(L)$_3$(H$_2$)O·3DMF]$_n$ (1), has been synthesized based on a rigid tetracarboxylate ligand of terphenyl-3,3,4,8-tetracarboxylic acid (H$_4$L). 1 shows a complicated 3D tetranodal 3,3,4,8-c network with uncoordinated –COO$^-$ groups. The highly selective luminescent sensing of 2,4-dinitrophenol (2,4-DNP), 2,4,6-trinitrophenol (TNP) and ferric ions was studied for 1 through the alleviation in its fluorescence intensity. The detection limit of 2,4-DNP was found to be 0.84 ppm, which is 20 times higher than that of 1,3,5-trimethylbenzene, demonstrating greater and selective quenching ability. The possible mechanism associated with the decrease in fluorescence intensity of 1 in the presence of nitroaromatics (NACs) has been addressed by theoretical calculations. Furthermore, 1 displays excellent capacity to adsorb methylene blue (MB) with high selectivity, and it maintains an almost identical adsorption performance after being recycled five times.

In recent years, the “chemosensors” based on metal–organic frameworks (MOFs) have created enormous interest amongst synthetic chemists as the MOFs are highly sensitive and selective candidates for the detection of analytes by various energy/charge transfers occurring among different ligands and metal centers viz. from ligands to metal centers or from metal centers to ligands.1–4 The traditional selective recognition of such small molecules needs expensive instruments and multiple spectrometry as well as intricate characterization approaches.5 It has also been revealed that MOFs containing active Lewis basic/acidic sites and hydrophilicity/hydrophobicity significantly affect their recognition capability and selectivity towards a variety of analytes.5–8 Thereinto, MOF is one of the competitive materials for detecting heavy metal ions and small molecules, which is considered to be inexpensive, simple and efficient.9,10

The large volumes of dye-wastewater discharge cause a significant hazard to the environment because of the drawbacks of toxicity and carcinogenicity related with the aromatic dyes.11 The approaches that have been employed at the industrial scale for the removal of dyes from the waste-water are by deploying activated carbon and zeolites and so on. However, these methods are generally inefficient when selective removal of the targeted organic dye molecules having varied chemical characteristics from waste-water is concerned.12

Generally, porous MOFs are designed and synthesized by the rational choice of molecular building blocks (MBBs) that involve various di-, tri-, and tetranuclear or higher metal clusters, viz. paddle-wheel {M$_2$(COO)$_4$}, trigonal prismatic {M$_3$(COO)$_6$} and octahedral {M$_4$(COO)$_8$} etc.13 These metal clusters are often assembled using multicarboxylate (such as di-, tetra-, hexa and octacarboxylates) ligands. The use of high symmetry linkers has paved a pathway to promote the formation of porous materials.14,15 In addition, several cadmium based luminescence MOFs have also been well used as a model system for understanding aspects of explosive sensing.6a Indeed, an interesting paper regarding the
explosive sensing mechanism was reported by Ghosh and coworkers.14

The rigid tetracarboxylate ligand of type terphenyl-3,3″,5,5″-tetracarboxylic acid (H4L) was chosen to fabricate an interesting (5,5)-connected Zn(u) MOF \([(\text{Me}_{2}\text{NH})_{2}\text{Zn}_{3}(\text{H}_{2}\text{O})]\cdot 0.5\text{DMF}]_{n}\) in our recent work.16 In order to obtain larger MBBs and to improve the resulting stability, we attempted to explore a larger radius Cd(u) as nodes and successfully obtained a new luminescent Cd(u)-MOF \([(\text{CH}_{3})_{2}\text{NH}_{2}]_{2}\text{Cd}_{2}(\text{L})_{4}\cdot \text{H}_{2}\text{O}-3\text{DMF}]_{n}\) (1) having Cd3(CO2)6 clusters and displaying uncommon topology of tetranodal 3,3,4,8-c framework, which could be described as \((4\cdot 6\cdot 3\alpha\cdot 6\cdot 6\cdot 8\cdot 8\alpha)^{n}\) (Schläfli symbol). The synthesized MOF not only displayed excellent selectivity to detect nitroaromatics and ferric ions but also proved to be an efficient adsorbent for the selective adsorption of methylene blue (MB) with high selectivity.

### Materials and Method

#### General considerations

All the purchased chemicals were used without further purification. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 ADVANCE X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å) at 50 kV, 20 mA with a scanning rate of 6° min\(^{-1}\) and a step size of 0.02°. Fourier transform infrared (FT-IR) spectra as KBr pellet were measured using a Nicolet Impact 750 FTIR in the range of 400–4000 cm\(^{-1}\). Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere from room temperature to 650 °C at a heating rate of 10 °C min\(^{-1}\), using a SDT Q600 thermogravimetric analyzer.

#### X-ray crystallography

Single crystal X-ray diffraction data collection for 1 was carried out on a Bruker SMART APEX diffractometer that was equipped with graphite monochromated MoKα radiation (λ = 0.71073 Å) using an θ-scan technique. The intensities of the absorption effects were corrected using SADABS. The structure was solved by direct method (SHLEXS-2014) and refined by a full-matrix least-squares procedure based on \(F^2\) (Sheld1-2014).17 All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. Attempts to determine the final formula of these compounds from the SQUEEZE results,18 combined with elemental analysis and thermogravimetric analysis data, were unsuccessful because of the volatility of crystallisation solvents during measurements. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic details and selected bond dimensions for 1 are listed in Tables S1 and S2;‡ CCDC number: 1570452.

#### Synthesis of \([(\text{CH}_{3})_{2}\text{NH}_{2}]_{2}\text{Cd}_{2}(\text{L})_{4}\cdot \text{H}_{2}\text{O}-3\text{DMF}]_{n}\) (1)

A mixture of terphenyl-3,3″,5,5″-tetracarboxylic acid (H4L) (0.1 mmol) and Cd(NO₃)₂·4H₂O (0.2 mmol) was dissolved in DMF (2 mL) in a screw-capped vial, and two drops of HNO₃ (65%,aq) were added to the mixture. The resulting solution was placed in a 25 mL vial container and heated to 105 °C for 72 h. Thereafter the reaction mixture was cooled to room temperature at a rate of 2 °C h\(^{-1}\). Colorless block shaped crystals of 1 were obtained in 39% yield based on Cd. anal. (%) calcd for \(\text{C}_{1907}\text{N}_{162}\text{O}_{36}\text{Cd}_{5}\text{H}_{111}\): C, 48.76%; H, 4.17%; N, 4.69%; found: C, 47.88%; H, 4.00%; N, 4.31%. IR (KBr disk): 3440(s); 2798(m), 2479(m); 1616(s); 1554(v); 1451(v); 1390(m); 1279(m); 862(m); 732(v); 681(m); 535(m).

#### Computational details

The possible mechanism associated with the alleviation in fluorescence intensity of 1 in the presence of nitroaromatics (NACs) was addressed using theoretical calculations. To establish the nature of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) of different nitro-aromatic analytes, the ligand H₄L as well as MOF 1, density functional theory (DFT) calculations were performed. Optimized molecular geometries were calculated using the B3LYP exchange-correlation functional.19 The 6-31G** basis set for all the atoms except Cd was used for geometry optimization. For Cd centers, LANL2DZ basis set was employed. All the calculations were executed using the Gaussian 09 programme.20

#### Results and discussion

\([(\text{CH}_{3})_{2}\text{NH}_{2}]_{2}\text{Cd}_{2}(\text{L})_{4}\cdot \text{H}_{2}\text{O}-3\text{DMF}]_{n}\) (1)

The structure of 1 contains two unique L ligands and three unique Cd centres (Fig. 1a). The Cd1 and Cd2 centres form a linear trinuclear cluster with a Cd1 lying at the inversion centres and two Cd2 positioned at each end. The Cd centres are bridged within the cluster by the carboxylate groups of six different L ligands, with a further carboxylate chelating to the Cd2 at each end of the cluster. Cd1 and Cd2 have the same coordination environments, but they have different coordination modes. Cd1 is coordinated by three symmetry oxygen atoms (O2, O8 and O18) from two \(\mu_{2}^{-}\eta^{1-1}\) carboxylate groups and one \(\mu_{2}^{-}\eta^{2-1}\) carboxylate group (Scheme S1a†). The third Cd centre Cd3 is not a part of the cluster, but instead is chelated by three \(\mu_{3}^{-}\eta^{1-1}\) carboxylate groups from three L ligands (Scheme S1b†), with a coordination geometry significantly distorted from that of octahedral.

The two different L ligands in turn show significantly different bonding modes. For the first ligand, only three of the four carboxylate groups are coordinated. One coordinates to a Cd1 and a Cd2 of a cluster, and another chelates to a Cd2 but also bridges to a Cd1 in the same cluster via a \(\mu_{3}^{-}\text{O}\), and a third chelates to a Cd3 centre. This ligand thus bridges two clusters and one Cd3 ion. All the carboxylate groups of the second ligand are used in coordination i.e. two carboxylate groups chelate to Cd3, one chelates to Cd2, and the other bridges Cd1 and Cd2 ions in a cluster. This ligand thus bridges two Cd3 ions and two clusters (Fig. 1b).

The L ligands overall connect the Cd3(CO2)₆ clusters and Cd3 ions into a complicated 3D network (Fig. 1c and S1†). Each cluster is coordinated to eight L ligands, the Cd3 ion is...
coordinated to three ligands, and each L ligand bridges either two clusters and a Cd3 ion, or two clusters and two Cd3 ions. This generates a tetranodal 3,3,4,8-c net with (4 · 62)2(63)2(42 · 620 · 86) topology (Fig. 1d). A porous Zn(II) metal–organic framework based on a tetracarboxylate H4L ligand possessing a NbO-type framework was reported.21 The difference between the topologies of this MOF and H4L can be attributed to the feature of cluster modes. The combination of the 3, 8-c net connected {Cd3(CO2)8} molecular building blocks (MBBs) and Cd3 ion and the 3,4-connected ligands in a 1 : 1 ratio leads to the formation of a 3D framework that exhibits elliptical channels of dimensions 11.3 × 13.9 Å2 along the a crystallographic direction (atom-to-atom separation). Disordered solvent molecules and cations are located in these channels. The effective free volume is ∼68.7%, as calculated by PLATON.16 The thermogravimetric analysis indicates that the framework of 1 is stable up to 300 °C (Fig. S2†). The permanent porosity of the framework of 1 has been found to be of N2 adsorption profile (Fig. S3†), indicating that 1 is a microporous material with a pore volume of 58.52 cm3 (STP) g−1, and the BET surface area is 40.837 m2 g−1.20 Usually, this strange sorption feature can be attributed to the fact that the framework may be blocked by the large and unremovable [(CH3)2NH2]2 cations.

Luminescence sensing

The solid-state photoluminescence (PL) spectra of H4L and 1 (λex = 285 nm) were collected at room temperature (Fig. S4†). An intense emission peak at 370 nm observed in the PL spectrum of H4L corresponds to linker-localized n → π* or π → π* transition.22 In contrast, 1 exhibits obvious red shift displaying intense peak at 405 nm possibly because of the Cd–L coordination, which can increase the ligand conformational rigidity and reduce non-radiative decay.23 The different emission red shifts may be attributed to the different coordination modes of the metal ions.23 The outstanding fluorescence property of 1 prompted us to explore its potential for fluorescence sensing of nitro-explosives in various solvents. The fluorescence property of 1, as a dispersion in different solvents, was recorded, and it was observed that the dispersion of 1 in nitrobenzene showed the lowest fluorescence intensity. Moreover, the emissive property of 1 in nitrobenzene was different from fluorescence properties of 1 recorded in dispersions of other solvents (Fig. 2a and S5†). Taking inspiration from these results, the DMF dispersion of 1 was prepared to detect different types of aromatics (ACs). The different types of aromatics (ACs) used in the investigation are 2,4,6-trinitrophenol (TNP), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2-nitrotoluene (2-NT), 4-nitrotoluene
(4-NT), 1,3-dinitrobenzene (1,3-DNB), 1,2,4-trimethylbenzene (1,2,4-TMB), 1,3,5-trimethylbenzene (1,3,5-TMB), o-nitrophenol (MNP), p-nitrophenol (PNP), and 2,4-dinitrophenol (2,4-DNP). All the twelve ACs can decrease the luminescence intensity of 1 to a different extent and the order of quenching efficiency is 2,4-DNP \approx TNP > PNP \approx MNP > 4-NT > 2-NT > 2,4-DNT > 2,6-DNT > NB > 1,3-DNB > 1,2,4-TM > 1,3,5-TMB (Fig. 2b). Furthermore, the fluorescence intensity decreases steadily along with an increase in the concentrations of 2,4-DNP and TNP. Moreover, upon addition of 130 ppm of 2,4-DNP and TNP, the fluorescence intensity of 1 was almost nullified (Fig. 2c and d and Fig. S6 and S7†). In addition, upon addition of 400 ppm of 1,3,5-TMB and 1,2,4-TMB, the fluorescence intensity of 1 remained almost unaffected (Fig. 2b). However, all other nitro-aromatics also showed effect to different degrees on the fluorescence intensity of 1 (Fig. 2b and S8–S23†). These results demonstrated that 1 possesses high selectivity for 2,4-DNP and TNP in the presence of different NACs (Fig. 2c and d and S6 and S7†).

The fluorescence quenching efficiency can quantitatively be explained with the help of Stern–Volmer (SV) equation: \( \frac{I_0}{I} = 1 + K_{sv}[Q] \). The Stern–Volmer plots for 2,4-DNP and TNP are nearly linear at low concentrations with the \( K_{sv} \) value of \( 2.37 \times 10^4 \) and \( 1.61 \times 10^4 \) M\(^{-1}\), respectively (Fig. S6 and S7†). These values are a little smaller than those of their corresponding MOFs (Table S4†), implying the effect of the preconcentration of analytes on the fluorescence quenching. The 2,4-DNP and TNP detection limits are calculated to be 0.84 and 1.57 ppm based on the 3σ/slope, respectively. Therefore, 1 can be used to distinguish the NACs having electron-donor and electron-withdrawing substituents. To further
elucidate the detection mechanism associated with 1, the luminescence sensing of H₄L dispersions in the presence of 2,4-DNP was recorded, which remained almost unchanged at different concentrations of 2,4-DNP (Fig. S24†). This suggests that there are interactions between 2,4-DNP and Cd(I) ions, and changes in emission intensities are not related to the interactions between 2,4-DNP and the ligands H₄L.²⁴–²⁶

The fluorescence intensity of 1 was observed to be alleviated in the presence of NACs, and this phenomenon would have the same mechanism. Hence, to propose the probable mechanism, the HOMO–LUMO energies of the NACs along with those of MOF 1 and H₄L were calculated using density functional theory (DFT) at the B3LYP level (Fig. S34† and Table 1). The most probable reason behind complete quenching or partial alleviation in fluorescence intensity may be the charge transfer taking place from the framework of 1 to the LUMO of the analytes. This charge transfer will be successful only when LUMO of the acceptor analytes can accept the charge from LUMO of the donor MOF, and to facilitate this phenomenon, the LUMO of 1 should have higher energy level in comparison to that of the LUMOs of the acceptor.²⁵–²⁷ The LUMO energies of 1 as well as aromatic analytes, presented in Table 1, indicate that the LUMO energy levels for all the NACs are low in comparison to that of 1, and hence they can accept charge from the photo-excited 1, which eventually results in the alleviation in the fluorescence intensity of 1 in the presence of these NACs. It is worthy to mention here that the aromatics deprived of the nitro group viz. 1,2,4-TMB and 1,3,5-TMB possess LUMOs at higher energy levels than 1, and hence in presence of these aromatic compounds, practically negligible change in fluorescence intensity of 1 is observed. Moreover, the observed order of decrease in the emission intensity of 1 by these NACs is not in full agreement with the corresponding LUMO energies of NACs, which indicates that the electron transfer phenomenon is not the sole mechanism for the quenching in intensity. There may be the existence of electrostatic interaction between 1 and NACs in addition to electron and energy transfer processes, which contribute to the fluorescence quenching.²⁵–²⁷

The metal ion interaction studies were also performed by addition of nitrate salts of Zn²⁺, Cd²⁺, Ca²⁺, Al³⁺, K⁺, Na⁺, Mg²⁺, Ni²⁺, Hg²⁺, Pb²⁺, Co²⁺ and Fe³⁺ to 1·H₂O emulsions with the concentration of the metal ion of 1.0 × 10⁻⁴ M. The luminescence intensities of M⁺₁ solution were recorded and compared (Fig. 3a and S25†). M⁺₁ solution showed

![Fig. 3](image-url)
markedly different luminescence intensities. Zn$^{2+}$, Cd$^{2+}$ and Al$^{3+}$ metal ions have positive effects on the luminescence intensity, while others exhibit different levels of quenching effect on the luminescence intensity, particularly Fe$^{3+}$ exhibiting the most significant quenching effect. The absorption maximum at longer wavelength in Pb$^{2+}$ compared to that in other metal ions may be assigned to the result of the weak coordination of Pb$^{2+}$ with the free carboxyl group. This restricts the photoinduced electron-transfer process and changes the fluorescence output. To further explore the sensitivity of 1 towards Fe$^{3+}$, the concentration gradient experiments were performed by changing the concentration of Fe$^{3+}$ solutions from 0 to 600 ppm. As shown in Fig. 3a, it is evident that the luminescence intensity of Fe$^{3+}$@1 solution gradually decreases with an increase in the amount of Fe$^{3+}$.

Furthermore, the fluorescence lifetime of 110.41 ns in 1 gets reduced to 8.19 ns in the presence of 1.0 mM Fe$^{3+}$ (Fig. S26†). Hence, we infer that the electrostatic interaction may be responsible for the quenching phenomenon. To elucidate the possible mechanism for such luminescence quenching by metal cations, O1s X-ray photoelectron spectroscopy (XPS) studies were carried out on 1 and Fe$^{3+}$@1.
O1s peak for the free oxygen atoms of coordinated carboxylate at 531.69 eV in 1 gets shifted to 532.07 eV on the addition of Fe³⁺ (Fig. S27a†), indicating weak binding of oxygen atoms to Fe³⁺ in Fe³⁺@1.

The stabilities of Fe³⁺@1 and NACs@1 dispersions were also confirmed by the IR spectroscopy and PXRD, which indicated almost unaltered band positions compared with the simulated one (Fig. S28–S31†). The robustness of the framework of Cd–L is attributed to the [Cd₃(CO₂)₈] geometry subunit, for which ligand displacement is not as favorable for this arrangement.28

The Stern–Volmer plots for Fe³⁺ are nearly linear at low concentrations (R² = 0.995) with the Ksv value of 1.67 × 10⁴ M⁻¹ (Fig. 3b). Following the 3δ/slope, the Fe⁴⁺ detection limit is calculated to be 1.25 ppm.28,29 As presented in Table S3,† most of the reported MOFs can detect Fe³⁺ in the concentration ranging between 10⁻³ and 10⁻⁵ M, and the lowest detected concentration of Fe³⁺ was recorded in MIL-53(Al).29

In comparison to these reports, 1 also displays potentially high sensitivity and selectivity towards Fe³⁺.

### Selective adsorption dyes

We also tried to explore the ability of 1 to adsorb different pollutant dyes from water. Three different types of dye viz. methylene blue (MB), methyl orange (MO) and rhodamine B (Rh B) with different sizes and charges were chosen as model adsorbates.30 In a typical reaction, 50 mg of adsorbent 1 was added in 50 mL 5 × 10⁻⁵ M of aqueous solution of dye at room temperature, and the mixture was continually stirred. In the given time period, the ability of 1 to adsorb dyes from aqueous solution was determined through UV-vis adsorption spectroscopy. The UV-vis spectroscopy results showed that 1 exhibited an excellent capacity to adsorb MB (Fig. 4), while the ability to adsorb MO and Rh B dyes was almost negligible. A proposed mechanism of the selective adsorption between MB and 1 could be explained through matching of the size of the MB molecule and the pore size of 1.31 The adsorption capacity of 1 toward MB is completely different from that of the other two dyes. The selectivity of 1 for dyes could be attributed to the anionic framework, in which the [(CH₃)₂NH₂]⁺ cations may be exchanged with cationic dyes. The adsorption rate is higher than 80% in the first 30 s; moreover, it is worthy to mention that 1 can adsorb MB completely within 25 minutes.

The removed quantity of MB by 1 was calculated using the following equation.32–35

\[ Q_{eq} = \frac{C_0 - C_{eq}}{m} \cdot t \]  

(1)

The above equation indicates that each gram of 1 can adsorb 68.5 mg of MB. This fast and high-capacity adsorption process is also very important for adsorbents in practical wastewater treatment. Moreover, the color of the crystals of 1 changed from colorless (before adsorption) to transparent blue (after adsorption) (Fig. 5), which indicated that MB molecules penetrated into the crystal lattice of 1 instead of on the surface of the crystals.

### Table 2

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<th>Model</th>
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<td>Pseudo-first-order</td>
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<td>qₑ (mg g⁻¹)</td>
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<td></td>
<td>R</td>
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<tr>
<td>Pseudo-second-order</td>
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<td>qₑ (mg g⁻¹)</td>
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<tr>
<td></td>
<td>R</td>
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<td>Second-order</td>
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<td></td>
<td>R</td>
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<tr>
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<td></td>
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Fig. 5 UV-vis spectral changes of the dye mixtures of MB and MO for (a) and Rh B and MB for (b), respectively.
To validate whether \( \textbf{1} \) possesses the ability to selectively adsorb MB from a solution containing mixture of dyes. Hence, the capability of \( \textbf{1} \) to selectively adsorb MB in mixture of dyes comprising of Rh B + MB and MB + MO was tested. The UV-vis spectra show that after soaking \( \textbf{1} \) in these solutions having compositions Rh B + MB and MB + MO, in both the cases only MB molecules could be efficiently adsorbed over a period of time (Fig. 5a and b), while Rh B and MO could not be encapsulated by \( \textbf{1} \). As presented in the photographs (see inset pictures in Fig. 5a and b), after soaking \( \textbf{1} \) in the mixed-dye solution, the solution color changed and finally retained the characteristic colors of Rh B and MO. This result also confirmed that \( \textbf{1} \) could effectively and selectively adsorb MB molecules into its pores, leaving Rh B and MO molecules in the solution. Furthermore, the adsorption capacity of \( \textbf{1} \) was found to be fully maintained after recycling the same batch of \( \textbf{1} \) five times, and its stability was also confirmed (Fig. S32\textsuperscript{†}). After absorption, MB@\( \textbf{1} \) could expediently release MB by simply washing the sample with ethanol after recycling 5 times. Furthermore, \( \textbf{1} \) showed almost identically rapid and quantitative adsorption of MB (Fig. S33\textsuperscript{†}). Thus, \( \textbf{1} \) can be a potential candidate as a selective adsorption material, which can be applied practically to adsorb MB in mixed-dye containing wastewater.

**Adsorption kinetics**

The rate of dye adsorption depends on the contact time of \( \textbf{1} \) and dye solution as well as on the diffusion process. During the process of adsorption, MB molecules migrate to the outer surface of \( \textbf{1} \), diffuse into the layers of the MOF, and are then adsorbed via pore diffusion. To further explore the adsorption kinetics, pseudo-first order, pseudo-second-order, second-order and intra-particle diffusion kinetics models were employed. The constants of all of the kinetics models were calculated using the following equations.

The pseudo-first-order rate equation:

\[
\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t
\]

The pseudo-second-order rate equation:

\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}
\]
The second-order rate equation:

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_t t
\]

(4)

\[
q_t = K_t t^{1/2} + C
\]

(5)

As can be seen in Table 2 and Fig. 6, there are four \( R^2 \) for MB obtained from the aforementioned equation. The fitting of the experimental results show that the pseudo-second-order model possesses the highest \( R^2 \) value in comparison to the other adsorption kinetics models.\(^{34,36} \) Therefore, the results indicate that the adsorption kinetics can be best described by a pseudo-second-order model. The calculated value of \( K_t \) for the adsorption of MB on 1 is 0.01379 g mg\(^{-1}\) min\(^{-1}\), which is much higher than those of the previously reported MOFs viz. MOF-235 (0.000218 g mg\(^{-1}\) min\(^{-1}\)),\(^{37} \) activated carbon (0.0127 g mg\(^{-1}\) min\(^{-1}\)),\(^{38} \) amino-MIL-101(Al) (0.0026 g mg\(^{-1}\) min\(^{-1}\))\(^ {39} \) and graphene (0.0001 g mg\(^{-1}\) min\(^{-1}\)).\(^ {40} \) This is mainly because the framework of 1 may be interacting with the MB molecules. It is proved that 1 can quickly adsorb MB compared to many other adsorbents.\(^ {41} \)

**Conclusion**

The luminescent MOF 1 comprising Cd(II) centres exhibited dual sensing capability for Fe\(^{3+}\) ions and nitro-aromatics and also acted as an efficient and selective adsorbent for MB dye. The possible mechanism for the alleviation in the luminescence intensity was proposed using theoretical calculations, which indicated that the alleviation in fluorescence intensity arises because of the occurrence of both electron and energy transfer processes, in addition to electrostatic interaction between the MOF 1 and nitro-aromatics. We conclude that the synthesized Cd(II) based luminescent MOF having symmetrical terphenyl-3,3\(^d\),5,5\(^e\)-tetracarboxylate ligand is not only an effective sensor for nitroaromatics and ferric ions but it also proves to be an efficient and selective adsorbent for organic dye MB. Such systems will be useful to develop new and versatile materials as sensors and adsorbents.

**Conflicts of interest**

There are no conflicts to declare.

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