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SYNTHESIS , STRUCTURAL AND DFT INVESTIGATION OF $\text{Zn(nba)}_2(\text{meim})_2$ FOR ADSORPTIVE REMOVAL OF EOSIN YELLOW DYE FROM AQUEOUS SOLUTION

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Abstract

A novel Zn(II) mixed-ligand complex, $\text{Zn(nba)}_2(\text{meim})_2$ (**1**), synthesized from $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, nitrobenzoic acid (Hnba) and 1-methylimidazole (meim) is reported. The complex was characterized by elemental analysis, FT-IR, powder and single crystal X-ray crystallography and TGA/DSC. **1** exhibits a tetrahedral geometry for Zn(II) , which is coordinated to two carboxylate oxygen atoms from two nba anions and two imidazole nitrogen atoms from two meim molecules. Thermal analysis shows the stability of **1** up to 260 °C. The adsorption of eosin yellow (EY) dye on **1** was investigated. The adsorption capacity of **1** for EY amounted to 65.32 mg/g, fitting best into Langmuir isotherm and pseudo second order kinetic models. From DFT studies, it was determined that adsorption is predominantly due to electrostatic, hydrogen bonding and π - π interactions.

Keywords: Zn(II) complexes; adsorptive separation; eosin yellow dye.

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Introduction

Accumulation of dyes in wastewater as a result of discharges from chemical industries *e.g* paper, plastic and paper manufacturing is an issue of environmental concern worldwide. About one fifth of the dyes used in these industries end up in the environment. They cause detrimental effects to human wellbeing and the ecosystem at large ^[1]. Eosin yellow dye (EY) is a highly water-soluble dye. It is a fluorescein dye mainly used in bacterial staining ^[2]. It gives a yellow-fluorescence red colour, it is also used in wool and silk ^[3]. These result in its significant discharge into water. Fluorescein dyes cause irritation of the eyes and skin, and like other dyes, can cause damage to vital organs in the human body ^[4,5]. It is therefore important to remove such dyes from water. However, their complex structure and high water solubility make their removal through biological processes difficult ^[6].

Adsorptive separation is an efficient and cost effective way of removing dyes ^[7]. Activated carbon ^[8,9], chitosan ^[10] have been applied in the adsorption of dyes, among other adsorbents. Recently, there is increasing research around the use of coordination complexes in the adsorption of dyes ^[11–20]. Apart from the adsorptive removal of dyes, coordination complexes have been used as photocatalysts for the remediation of pollutants ^[21]. Our group previously reported the adsorption of fluorescein dye using a copper-isonicotinate metal-organic framework ^[22] and also the use of Zn(II) coordination polymers for the adsorption of methyl orange dye^[23].

A well explored class of linkers for the synthesis of complexes are the carboxylates due to their versatile complexing behaviour toward a wide range of metal ions. Benzene carboxylic acids have been particularly a good choice due to the feasibility of incorporating additional groups on the ring to provide useful properties and interactions for desired applications. Functionalities such as thio, hydroxyl, nitro, amino and halogens can confer hydrogen bonding interactions either by acting as hydrogen donors or acceptors ^[24–26]. Also, the benzene ring aromaticity can lead to π - π interactions with other aromatics and can be useful for adsorptive separation. The use of N-donor ligands such as imidazole, pyridine and phenanthroline alongside the carboxylate ligands in the construction of coordination complexes offers structural diversity ^[27,28].

Herein, we report the use of Zn(nba)₂(meim)₂ (**1**) constructed from 4-nitrobenzoic acid and 1-methylimidazole in the adsorptive uptake of EY dye (**Figure 1**) from water.

Figure 1: Structure of Eosin yellow

Results and discussion

1 was initially obtained in powder form **1a**. There was a need to obtain single crystals of **1a** for crystallographic analysis. Recrystallization of **1a** was not successful, therefore an attempt to grow crystals directly from the reaction mixture was made, hence, **1b** was synthesized in DMF.

FT-IR, CHN, PXRD and TGA analyses results compared for both **1a** and **1b** clearly show that the two are identical. The percentage yield of **1a** was higher than that of **1b**. **1a** was also successfully scaled up by a factor of 10, thereby indicating the feasibility for industrial applications.

FT-IR spectroscopy

From **Figure 2**, it is obvious that the FT-IR spectra of **1a** and **1b** are identical. Symmetric and asymmetric stretching of the coordinated carboxylate groups were observed at 1654 and 1395 cm^{-1} respectively. These are similar to those reported for complexes of carboxylate and meim [27]. The separation $\Delta\nu [\nu_{\text{as}}(-\text{COO})-\nu_{\text{s}}(\text{COO})]$ indicates the bonding mode of the COO^- groups [29]. Its value is 251 cm^{-1} which indicates monodentate coordination of the COO^- groups [30]. The broad band for -OH observed around 2576 - 3096 cm^{-1} in the FT-IR spectrum of Hnba is absent in the spectra of **1a** and **1b**, indicating deprotonation. Also, the C=O band of around 1732 cm^{-1} is absent in the spectrum of **1**. The absorption bands of the aromatic C-H of meim are found in the range 3138 -2933 cm^{-1} . The band at 663 cm^{-1} indicates Zn-N and 438 cm^{-1} indicates Zn-O stretching vibrations [31]. The **complex (1a and 1b)** is anhydrous as the FT-IR spectra have no -OH bands expected around 3400 -3200 cm^{-1} for anhydrous complexes.

Figure 2: FT-IR spectra of Hnba, meim, 1a and 1b

Powder X-ray diffraction

The PXRD patterns of **1a** and **1b** are presented in **Figure 3**. The similarity of the patterns further confirms that **1a** is the same as **1b** as well as the phase purity of the bulk material of **1b**. Differences in relative peak intensities between measured and simulated patterns are due to preferred orientation effects.

Figure 3: Simulated and as-prepared PXRD patterns of $\text{Zn}(\text{nba})_2(\text{meim})_2$ (**1a** and **1b**).

Single crystal X-ray crystallography

The ORTEP diagram and the atom numbering scheme is as shown on **Figure 4**. The coordination geometry around the $\text{Zn}(\text{II})$ atom is tetrahedral. Two meim and two nba ligand molecules coordinate in a monodentate manner to the zinc atom through the deprotonated oxygen atoms the nitrogen atoms and the deprotonated oxygen atoms respectively. The crystal data and structure refinement parameters of **1** are presented in **Table 1**, while bond distances and angles are summarized in **Table 2**. **1** crystallizes in the centrosymmetric monoclinic space group $C2/c$. $\text{Zn}(\text{II})$ is located on a two-fold axis; the asymmetric unit consists of a Zn atom, a nba and a meim. The observed Zn-O bond length of 1.9717(10) Å and Zn-N distance of 2.0081 (2) Å (Table 2), agree with reported lengths of $\text{Zn}(\text{II})$ coordinated to nba^[32] and this indicates stronger coordination of the imidazolate nitrogen than the carboxylate oxygen atoms to the $\text{Zn}(\text{II})$. The C-O distance of the coordinated oxygen atoms is slightly longer than the uncoordinated ones (1.284 Å vs 1.232 Å), confirming the

coordination of the deprotonated oxygen atom. The bond angles around Zn(II) vary between 96.20(6)-121.83(5)°, showing a distorted tetrahedral coordination sphere [ZnN₂O₂]. The crystal structure of **1** reveals that there are no H-bonded atoms in the coordination sphere but some weak C-H...O interactions were observed as shown in **Figure 5**, some of which are C10-H10....O6B (2.546 Å), C5-H5...O2 (2.705 Å), C12-H12B...O2(2.359 Å). The nearly antiparallel overlapped arrangement of nba rings of the neighbouring molecules has a centroid to centroid distance of >4 Å, indicating that there are no π - π interactions. The packing of **1** is represented using a spacefill model in **Figure 6**. **Figure 7** shows the voids present in the packing of **1**. The void volume, calculated using PLATON, was 543.15Å³.

Figure 4: Structure of **1** with thermal ellipsoids drawn at 50% probability level. (Symmetry codes: ¹1-X,+Y,1/2-Z)

Table 1: Crystal data and structure refinement parameters for **1**.

Empirical formula	C ₂₂ H ₂₀ N ₆ O ₈ Zn
Molar mass	561.81
Temperature (K)	150 (2)

Crystal system	Monoclinic
Space group	C2/c
a / Å	29.8237(4)
b / Å	6.59478 (4)
c / Å	14.73868(19)
α /°	90
β /°	126.6480(19)
γ /°	90
Volume/Å ³	2325.77(6)
Z	4
ρ_{calc} (g/cm ³)	1.604
M (mm ⁻¹)	2.021
F (000)	1152.0
Crystal size (mm ³)	0.5 × 0.4 × 0.1
Radiation	CuKα (λ = 1.54184)
2 Θ range for data collection/°	7.39 to 156.132
Index ranges	-37 ≤ h ≤ 37, -8 ≤ k ≤ 8, -18 ≤ l ≤ 18
Reflections collected	22340
Independent reflections	2481 [R_{int} = 0.0357, R_{sigma} = 0.0149]
Data/ restraints/ parameters	2481/0/169
Goodness-of-fit on F^2	1.068
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0287$, $wR_2 = 0.0811$
Final R indexes [all data]	$R_1 = 0.0289$, $wR_2 = 0.0813$
Largest diff. peak/hole/eÅ ⁻³	0.36/-0.27

Figure 5: C-H...O interactions in the crystal structure of **1**.

(Symmetry codes: $^11-X,+Y,1/2-Z$)

Figure 6: Space filling representation showing the packing of **1**.

Figure 7: Packing of **1** showing the voids; Probe radius 0.2Å, Void volume = 543.15Å³, unit cell = 23.4%

Table 2: Some bond distances and angles around Zn(II).

Bond	Length (Å)	Bond	Angle(°)
Zn1-O1	1.9717(10)	O1-Zn1- O1 ¹	96.20(6)
Zn1-O1 ¹	1.9718(10)	O1 ¹ -Zn1- N9	107.55(5)
Zn1-N9 ¹	2.0081(12)	O1-Zn1- N9	121.83(5)

Zn1-N9	2.0080(12)	O1 ¹ -Zn1- N9 ¹	121.83(5)
		O1-Zn1- N9 ¹	107.56(5)
		N9-Zn1- N9 ¹	103.27(7)

Thermogravimetric analysis and differential scanning calorimetry

Figure 8: TGA/DSC profiles of $\text{Zn}(\text{nba})_2(\text{meim})_2$ (**1**)

Thermal analysis of **1a** (**Figure 8**) reveals four weight loss steps. The first weight loss of 15% (calc. 14.6%) with an endothermic peak around 250-300 °C accounts for the loss of a meim molecule. The second weight loss of 28% (calc. 29.6%) with a little exothermic peak at 300-360 °C corresponds to the loss of a nba molecule. The third and fourth weight losses were observed around 360-440 °C and 440-525 °C, and they are attributed to the loss of the other nba and meim ligands which are 15% (calc 14.6%) and 28% (calc. 29.6%) of the total weight of **1** respectively. Zinc oxide which remains (observed 14%, calculated 14.43%) is seen to be stable up to 800 °C.

Adsorption studies

The adsorption of EY dye from water using **1** was investigated. The effects of operational parameters; pH, initial concentration of the adsorbate, contact time, solution temperature and adsorbent mass were studied.

Effect of pH

The acidity/basicity level of the adsorbate solution influences, to a great extent, the adsorption of ions at the solid-liquid interfaces. EY dye adsorption over **1** was studied with 25 mL of 100 mg/L EY solution for 240 min from pH 2 to 12. Changes in point of zero charges of Zn(nba)₂(meim)₂ with pH and changes in absorption of EY dye on **1** with pH are shown in **Figures S1** and **9**, respectively. The pH_{pzc} of **1** is 7.3 as shown in **Figure S1**. **Scheme 1** shows the acid-base behaviour of EY. It exists in four different forms in equilibrium, the spirocyclic and the ring-opened forms which are the neutral forms of EY; also the monoanionic and dianionic forms which are the anionic forms (with pK_a of 2 and 3.8 in water) formed when there is deprotonation of one and two protons respectively ^[33].

Scheme 1: Acid-base behaviour of EY

Adsorption is highest and constant from pH 1 to 7. This is due to the elevated pH value at the point of zero charge of the adsorbent which makes it effective in a wide range of pH. In this pH range, the adsorbent surface remains positively charged and consequently, electrostatic interactions between the adsorbent and the anionic adsorbate are enhanced. Increasing pH

beyond 7 led to a drastic reduction in the amount of EY dye adsorbed by **1** due to electrostatic repulsion between the like-charges ^[34]. As a result, pH 7.0 was employed for subsequent adsorption process considering that most water bodies in the environment are around pH 7 or higher ^[35].

Figure 9: Effect of pH on the adsorption of EY on **1**.

Optimizing adsorbent loading

The optimal loading of EY dye on **1** was investigated by introducing 0.02 g of adsorbent to 25 mL of different concentrations of EY dye (from 2 to 100 mg/L) at 26 °C and pH 7 for 240 minutes (**Figure 10**). The percentage of EY adsorbed decreased with an increase of dye concentration from 2 to 100 mg/L, but the adsorption capacity per gram of **1** increased with an increase in EY dye concentration. This is as a result of the easily accessible large vacant sites on the adsorbent surface, hence, higher EY adsorption.

Figure 10: Effect of initial concentration on the adsorption of EY on **1** at pH 7.

Optimizing adsorption time

The optimal time adsorption of EY on **1** was investigated at room temperature using 25 mL of 100 mg/L dye concentration, 0.02 g adsorbent dosage and pH 7 up to 240 minutes. The adsorption capacity increased with time and the maximum amount adsorbed was about 54 mg/g at 210 minutes as shown in **Figure 11**.

Figure 11: Effect of time on the adsorption of EY on **1** at pH 7.

Effect of adsorbent dosage

The effect of adsorbent dosage was investigated by introducing different masses of the adsorbent to a 25 mL solution of 100 mg L⁻¹ EY dye solution at pH 7 and shaking for 210

minutes at room temperature (**Figure 12**). The amount of adsorbed EY dye increased with an increase of adsorbent dosage up to 40 mg where an amount adsorbed of 65 mg/g was obtained.

Figure 12: Effect of adsorbent dosage on the adsorption of EY on **1** at pH 7

Effect of temperature

To study the effect of temperature on the adsorption of EY dye, the adsorption procedure was carried out by introducing 0.02 g of **1** to 25 mL of 100 mg/L EY solutions at five different temperatures (299, 308, 318, 328, 333 K) and shaking for 210 minutes.

Figure 13: (a) Effect of temperature and (b) van't Hoff plot for the adsorption of EY on **1**.

The amount of EY dye adsorbed decreased from 57.43 to 37.34 mg/g on increasing solution temperature from 26 to 60 °C (**Figure 13a**). The van't Hoff plot from which the

thermodynamic parameters were calculated is shown in **Figure 13b**. The equations are given in the supplementary information. The van't Hoff plot indicates that the adsorption process is exothermic in nature, shown by the negative ΔH value obtained. Related observations were also noted from previous reports ^[36]. When ΔH° is less than 40 kJ mol⁻¹, the adsorption process is physisorption ^[37]. Therefore, ΔH obtained for this adsorption process indicates that it is physisorption. The parameters ΔG° , ΔS° and ΔH are presented in **Table 3**. The negative values of ΔG° indicate the spontaneity and feasibility in the temperature range. ΔS° value is also negative and it indicates decreased randomness at the solid-solution interface ^[38].

Table 3: Thermodynamic parameters of the adsorption of EY on **1**.

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
308	-8.09	-25.35	-56.42
318	-7.53		
328	-6.97		
333	-6.69		

Adsorption isotherm study

For practical applications, the adsorption isotherm study is necessary. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isothermal models were used to determine the mode of adsorption of EY on **1**. The equations are shown in **Table S1**. This was carried out by introducing 0.04 g of adsorbent to 25mL of different concentrations of EY dye (from 2 to 100 mg/L) at 26°C and pH 7 for 210 minutes. The isotherm parameter values are given in **Table S2**.

The linear plots of the isotherm models are shown in **Figure 14** and **Figures S2(a-c)**. The relevant parameters are shown in **Table S2**. The Langmuir isotherm best fits the adsorption process with an R^2 value of 0.9823. The Langmuir model assumes that adsorption is limited to a monolayer coverage, the adsorbent surface is homogenous and there is no interaction among molecules adsorbed on neighbouring sites ^[39,40]. The maximum monolayer adsorption capacity (q_m) of the adsorbent was 60.39 mg/g. The R_L value was 0.1, indicating favourable adsorption. K_f and $1/n$ from the Freundlich plot, were found to be 5.08 and 0.6, respectively. The E value calculated from the D-R plot, was 1.78 kJmol⁻¹, indicating a physisorption process.

Figure 14: Langmuir plot for the adsorption of EY on **1**.

Adsorption kinetics and mass transfer mechanisms

The studies were carried out by introducing 0.04 g of adsorbent to 25mL of 100 mg/L EY dye at 25°C and pH 7 for 210 minutes. The kinetic model equations are presented in **Table S3**. The data obtained was then fitted into pseudo first order and pseudo second order kinetic models (**Figures S3 (a-b)**). The Ho-Mckay pseudo second order model fits best with an R^2 value of 0.9971 while the pseudo first order has an R^2 value of 0.8472. The experimental adsorption capacity from the pseudo second order model, as shown in **Table S4**, is closer to the calculated adsorption capacity than that of the pseudo first order. Therefore, the adsorption process follows a pseudo second order process. The rate constant k_2 and the adsorption capacity q_e were found to be $1.20 \times 10^{-3} \text{ gm}^{-1}\text{min}^{-1}$ and 55.61 mg/g, respectively.

Intraparticle and Bangham diffusion models were employed to investigate the adsorption mechanism (**Figures S3 (c-d)**). The parameters of the models are presented in **Table S4**. For the intra-particle diffusion model plot (**Figure S3c**), it can be seen that the straight line obtained is non-zero and is also multilinear,, indicating that intraparticle diffusion is not the only rate-limiting step ^[41]. The first curved portion of the plot indicates a boundary layer effect, while the second linear portion (linearly fitted in red line) is due to intraparticle or pore diffusion. The third represents adsorption into the pores. The intraparticle diffusion parameter, K_{id} can be calculated from the slope of the second linear portion of the plot and was found to be $5.315 \text{ mg/ g/ min}^{1/2}$. Also, the intercept of the plot which gives information about the boundary layer effect, was found to be 24.38 mg/g. The Bangham diffusion model (**Figure S3d**) was also used to verify the proposition that not only one mechanism takes

place in the adsorption process. The Bangham diffusion model plot suggests that boundary layer diffusion was involved in the uptake of EY onto **1** but was not the only rate-determining step^[42]. To ascertain the process controlling the overall adsorption rate, the Boyd model plot was employed. In the Boyd model, a linear plot that passes through the origin indicates that particle diffusion is the rate limiting step otherwise, an external mass transfer is the rate limiting step. As seen from **Figure S3e**, the plot is linear but does not pass through the origin, therefore, the adsorption process is film diffusion controlled^[43,44]. The R^2 value for the Boyd plot at initial concentration of 100 mg/L is 0.9118.

Mechanism of adsorption

The N_2 adsorption-desorption isotherms of MOF at 77 K and pore size distribution curves are shown in **Figure S4(a and b)**. The BET SSA is estimated to be 77.51 m²/g (199.30 m²/g, Langmuir). The pore volume and pore size were found to be 0.052 cm³/g and 2.11 nm. It can be seen that surface area of **1** is relatively low compared to other coordination compounds previously used as adsorbents, this is due to the zero-dimensional structure of **1**. However, compounds possessing similarly low value of BET surface area but with high adsorption capacities for pollutants, have been reported.

The ability of these compounds to adsorb a considerable amount of the pollutants is due to some specific interactions that occur between their structures and those of the adsorbates. Some of these interactions are hydrogen bonding, electrostatic and π - π stacking interactions^[45]. For example, a copper(II) complex of 4-methoxybenzoic acid ligand with a surface area of 31.7 m²/g was found to have desulphurization capacity as a result of π - π stacking interaction between the sulphur-containing compound and the complex^[46]. A negatively charged compound was reported to have a remarkable capability to adsorb the cationic dye methylene blue, as a result of electrostatic interaction^[47]. A nickel coordination compound based on 5-(1H-benzoimidazol-2-ylsulfanylmethyl)-isophthalic acid (H₂bismip) along with 4,4-bis(1-imidazolyl)biphenylene (bimb), was reported to show a remarkable adsorption capacity for methyl orange dye due to the formation of consecutive π - π stacking with bimb^[48].

The photographs of the dye solution withdrawn at different time intervals are shown in **Figure 15**.

Figure 15: Photographs of dye samples withdrawn at different time interval, A: 0 min; B:30 min; C: 60 min; D: 150 min; E:180 min; F: 210 min

From the figure, it is obvious that **1** could adsorb a significant amount of the dye. In order to determine the specific interactions that aided the adsorption of EY dye on **1**, DFT studies were carried out and explained.

DFT studies were carried out using the Materials Studio DMol³ module as described in the experimental section below [49,50]. EY dye exists either in the spirocyclic or ring opened form and the later was used during DFT studies. In the most plausible model acquired (**Figure 15**), EY dye molecule is strategically positioned in the confines of **1** to maximize interactions between its central xanthene aromatic ring the nitrobenzoic acid ring, as well as its phenolic ring and imidazole. It was clearly observed that π - π stacking plays a pivotal role in the adsorption of EY dye on **1**. There is no indication that coordination to Zn or hydrogen bonding played a significant role in the adsorption of EY dye on **1**. The energy difference between the substrates (EY dye and **1**) and the product (refer to **Table S5**) was found to be -115.62 kJ/mol. A negative binding energy value indicates an exothermic process between the binding of the adsorbent and the adsorbates. These findings corroborate the same discussion presented in the thermodynamics study section.

DFT studies also showed that the distribution of electron density of the highest occupied molecular orbitals (HOMO) and lowest unoccupied orbitals (LUMO) was located on the xanthene of EY dye and **1**, respectively as shown in **Figure S5**. This means that **1** has a tendency of receiving electrons from the electron rich EY dye. The electron deficiency in **1** is mostly due to the presence of the coordinated Zn(II) ion.

Figure 16. Interaction between **1** (ball and stick diagram) and EY dye (wire diagram) as modelled *via* Materials Studio DMOI³.

Reusability Study

For a feasible industrial use, the regeneration and reusability of spent adsorbents are important for cost-effectiveness. To ascertain the industrial use of **1**, the reusability study was carried out. After each adsorption cycle, the spent adsorbent was separated from the solution, washed with deionised water and dried at 80 °C. Afterwards, it was shaken in 30 mL of 95% ethanol for 1 hour, filtered, dried at 60 °C and used for the next adsorption cycle. This was done for three consecutive cycles. For the first cycle, the adsorption capacity was 65.7 mg/g, as shown on **Table 4**. At the end of the third cycle, there was only a slight reduction and an adsorption capacity of 62.4 mg/g was achieved.

Table 4: Reusability of **1** for EY dye removal after ethanol washing (Concentration = 100 mg/L and 40 mg adsorbent)

Cycle No	q _e (mg/g)
1	65.70
2	64.96
3	62.42

The FT-IR spectra of **1** and **1-EY** in the range 4000–400 cm^{-1} are shown in **Figure S6**. Little changes in the position and intensity of the FTIR bands are as a result of the adsorbed dye molecules on the adsorbent surface and different peaks were assigned to various functional groups present in both **1** and **1-EY**.

The band at 701 cm^{-1} on **1-EY** can be attributed to the C-Br bond from EY ^[51] and the –OH group band of the EY dye is observed at 3443 cm^{-1} on **1-EY**^[52], indicating its attachment onto **1**. There is a reduction in intensity of the asymmetric COO^- band coupled with its shift from 1654 cm^{-1} in **1** to 1646 cm^{-1} in **1-EY** and also the shift in the symmetric COO^- band from 1395 cm^{-1} to 1367 cm^{-1} . These indicate the participation of the carboxylate group in the adsorption process.

PXRD (**Figure S7**) analysis of **1** before and after adsorption was also carried out. No notable changes in the PXRD patterns were observed. The results show that the structural integrity of **1** is preserved even after the adsorption/desorption cycle.

In order to evaluate the efficiency of an adsorbent, the Langmuir monolayer adsorption capacity value Q_m is considered. The Q_m values of **1** and other adsorbents are presented on **Table 5**. Comparison of the Q_m values of **1**, used in this study, to those of the other adsorbents indicates its superiority for the adsorption of EY dye.

Table 5: Performance evaluation of $\text{Zn(nba)}_2(\text{meim})_2$ (**1**) in EY dye removal

Adsorbent	Q_m (mg/g)	Reference
$\text{Zn(nba)}_2(\text{meim})_2$ (1)	65.32	This work
Chitosan/polyvinyl alcohol blend	52.91	[53]
$\gamma\text{-Al}_2\text{O}_3$ Nanoparticles	47.78	[54]
Teak leaf litter powder	31.64	[55]
Silica functionalized with 1-propyl-3-methylimidazolium chloride	17.73	[56]
Pineapple peels	11.76	[57]
Clay/Carbon Composite`	11.15	[51]

Conclusions

The synthesis and characterization of a Zn(II) complex, $\text{Zn(nba)}_2(\text{meim})_2$ was reported. The Zn(II) complex exhibits a tetrahedral geometry. The complex was used for the removal of EY dye from aqueous medium. Adsorption of EY on **1** is highest at pH 7 or below. The maximum adsorption capacity was determined to be 65.32 mg/g. Langmuir and pseudo second order models fitted most for the isotherm and kinetic theories respectively. The thermodynamic studies revealed that the adsorption process is physisorption. DFT studies revealed that adsorption of EY on **1** is primarily due to π - π interactions. Overall, the study presents a suitable material for the removal of eosin from wastewater.

Experimental

Materials

$\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98%), 4-nitrobenzoic acid, Hnba (98%), 1-methylimidazole, meim (99%), dimethylformamide, DMF (99%), trimethylamine (99.5%), hydrochloric acid (37%), sodium hydroxide pellets (97%) and eosin yellow dye were purchased from Sigma Aldrich and used as supplied.

Synthesis

Synthesis of the powder form of $\text{Zn(nba)}_2(\text{meim})_2$ (1a): Sample **1a** was synthesized by dissolving $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.296 g, 1 mmol) in 10 mL of methanol and 4-nitrobenzoic acid (Hnba) (0.167 g, 1 mmol) in 10 mL of DMF with two drops of trimethylamine for deprotonation. These solutions were mixed together followed by the addition of 1-methylimidazole (meim) (0.09 mL, 1 mmol) and stirring at room temperature ($\sim 27^\circ\text{C}$) for 1 hour. Precipitate was obtained immediately and washed with ethanol (**Scheme S1**). Yield = 89%, Mol. Wt. = 561.81 g/mol, Melting pt. = 252°C , Elemental analysis for $\text{C}_{22}\text{H}_{20}\text{N}_6\text{O}_8\text{Zn}$: Calc.(Found) C, 46.99 (46.69); H, 3.56 (3.42); N, 14.95 (14.53), IR; KBr pellets (cm^{-1}): 3138 (m), 1653 (m), 1628(s), 1551 (s), 1416 (m), 1338(s), 1246 (w), 663 (m), 429 (w).

Synthesis of the crystal form of $\text{Zn(nba)}_2(\text{meim})_2$ (1b): Sample **1b** was synthesized by dissolving $\text{Zn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.296 g, 1 mmol), 4-nitrobenzoic acid (Hnba) (0.167 g, 1 mmol) and 1-methylimidazole (meim) (0.09 mL, 1 mmol) in 15 mL DMF. Two drops of triethylamine were added for the deprotonation of the carboxylic acid and the mixture was stirred for 2 hours at room temperature ($\sim 27^\circ\text{C}$). Block-shaped crystals were formed after 15 days and collected by filtration (**Scheme 1**). Yield = 72%, Mol. Wt. = 561.81 g/mol, Melting pt. = 247°C , Elemental analysis for $\text{C}_{22}\text{H}_{20}\text{N}_6\text{O}_8\text{Zn}$: Calc.(Found) C, 46.99 (47.01); H, 3.56

(3.58); N, 14.95 (14.86), IR; KBr pellets (cm^{-1}): 3138 (m), 1654 (m), 1628(s), 1552 (s), 1416 (m), 1395(s), 1247 (w), 663 (m), 438 (w).

Instrumentation

Elemental analysis was performed using a PerkinElmer PE-2400 CHN analyser. Fourier Transform Infrared (FT-IR) measurements were carried out on a Shimadzu 8400 spectrophotometer (8400, Shimadzu, Japan). Powder X-ray diffraction (PXRD) spectra were acquired using a Siemens D5000 diffractometer operating with Cu $K\alpha_{1/2}$ radiation in flat-plate geometry. TGA/DSC analysis was done using a Mettler Toledo TGA/DSC 1-600 instrument from 25 °C to 800 °C at a heating rate of 10 °C per minute. For single crystal X-ray crystallography, a single crystal was chosen and placed on a glass fibre with Fomblin oil and mounted on an Xcalibur Gemini diffractometer with a Ruby CCD area detector and kept at 150 (2) K during data collection. Using Olex2 ^[58], the structure was solved with the ShelXT ^[59] structure solution program using intrinsic phasing and refined with the ShelXL ^[60] refinement package using Least Squares minimisation. The nitrogen adsorption-desorption isotherms were acquired on NOVA 4200e Quantachrome (USA) The total surface area was determined using Branauer-Emmett-Teller (BET) method. Pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method. The surface area and porosity measurement of the **1** were determined volumetrically from N₂ adsorption. The specific surface area of **1** based on the BET and Langmuir equation were calculated.

Adsorption procedure

The batch adsorption procedure was used to study the adsorption of EY dye on **1**. The adsorption studies were carried out using 25 mL of 100 mg/L EY solution in 100 mL volumetric flasks. The effect of pH on the adsorption was investigated from a pH of 1 to 12, adjustments were done using 0.1 M HCl and 0.1 M NaOH. Different concentrations in the range 2-100 ppm were prepared by the serial dilution of EY stock solution to investigate the effect of initial concentration on adsorption using 0.02 g adsorbent dosage at optimum pH. The effect of contact time on the adsorption efficiency was investigated within 30-250 minutes at the 'optimum' pH and concentration. Effect of adsorbent dosage in the range 0.01-0.05 g was studied at the 'optimum' pH, concentration and time using 0.02 g of adsorbent. The effect of temperature was investigated within 298-333 K at the optimum pH, initial concentration, time and dosage. The flasks were shaken at 165 rev per minute for 240 minutes in an incubator shaker.

For analysis, the adsorbents were removed from the supernatant by centrifuging at 1200 rev per minute for 20 minutes. The final dye concentration was quantified using a UV–Vis spectrophotometer by taking the absorbance of the solution at 517 nm. The amount (q_e) of the sorbed adsorbate per gram of adsorbent was deduced using the equation:

$$q_e = \frac{(C_0 - C_e) V}{W} \dots\dots\dots \text{(Equation 1)}$$

Where C_0 and C_e are the initial and equilibrium concentrations of the adsorbate in mg/L, V is the volume of the adsorbate solution in litres and W is the mass of adsorbent used in gram.

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models; pseudo-first order, pseudo-second order, intraparticle diffusion, Bangham and Boyd kinetic models were all employed in analyzing the adsorption data and their characteristic parameters were calculated.

Density functional theory (DFT) studies

The forcite tool from Biovia Materials Studio 2018 was applied for geometry pre-optimization of drawn structures to ultra-fine quality and to determine the most plausible starting position (the position with the lowest total energy) to model the interaction between EY dye and **1**. DFT studies were then carried out by modifying literature methods using the Biovia Materials Studio 2018 DMol³ module with convergence threshold parameters set at default (medium); energy = 0.00002, gradient = 0.004 and displacement = 0.005 [49,50]. The generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) parametrization functional was applied with Grimme for DFT-D correction. Density functional semi-core pseudopotentials were fitted to all electrons with a double numerical plus (DNP) polarization basis set and 4.4 basis file. A real-space orbital global cut-off of 4.4 Å was applied. The studies were first carried out in gas phase before the conductor-like screening model (COSMO) was applied using water at a dielectric constant of 78.54. The binding energy between **1** [$\text{Zn}(\text{nba})_2(\text{meim})_2$] and EY dye was then determined by subtracting the sum of the energies of **1** and EY dye from the total energy of the **1**/EY dye cluster, i.e.

$$\Delta E (\text{BE}) = E_{\text{Complex 1/EY dye}} - (E_{\text{Complex 1}} + E_{\text{EY dye}}) \dots\dots\dots \text{(Equation 2)}$$

HOMO-LUMO diagrams were acquired using Gaussian 4.1 at 6-311+G level.

Supplementary data

CCDC **1954761** contains the crystallographic data of $[\text{Zn}(\text{nba})_2(\text{meim})_2]$ (**1**). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Conflict of Interest

The authors declare no conflict of interests.

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