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THE SYNTHESIS OF 2,2-BIS(1-INDOL-3-YL)ACENAPHTHYLENE-1(2)-ONES USING NANOCATALYSIS: FLUORESCENT SENSING FOR Cu^{2+} IONS

Abstract: 2,2-bis(1H-indol-3-yl)acenaphthylene-1(2H)-ones were synthesised by the reaction of acenaphthenequinone and 2 equivalents of indole using Fe_3O_4@SiO_2@Si-Pr-NH-$CH_2CH_2NH_2$ as the basic magnetic nanocatalyst, assembled under greener and sustainable conditions in high purity and yields. Furthermore, the photoluminescence properties of 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-one were exploited for the sensing of copper ions in the mixed solvent systems comprising H_2O and CH_3CN in excitation wavelength at 410 nm with a detection limit of $9.5 \cdot 10^{-6}$ M.

Keywords: fluorescent sensor, 2,2-bis(1H-indol-3-yl)acenaphthylene-1(2H)-ones, indole, acenaphthenequinone, Fe_3O_4@SiO_2@Si-Pr-NH-$CH_2CH_2NH_2$, MCRs

Introduction

Copper is one of the most pertinent elements in industrial activities and human life with the benefits of melanin secretion and protection of the skin cells [1-4]. Moreover, this element prevents the growth and expansion *E. coli* bacteria [5]. The deficiency of this metal can be caused many problems in the human body such as anemia, hair loss, increased blood cholesterol, and immunodeficiency [6-9]. Importantly, this element has been widely deployed as catalyst in organic reactions for the synthesis of heterocycle, medicinal and natural compounds via assorted methods [10-23]. The advantageous methods for determining copper ions in various samples comprise electrochemical methods such as voltammetry, colorimetric, potentiometric chromatography, atomic adsorption (AAs), techniques inductively coupled plasma (ICP), UV-Vis, and photoluminescence techniques (among them, optical methods are excellent means for measuring the copper ions due to their high selectivity, sensitivity, inexpensive nature, and a wide linear range) [24-36].

Indole is a heterocycle compound, which is endowed with numerous illustrated pharmacological properties such as anti-cancer, anti-inflammatory, anti-bacterial, and

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anti-microbial [37-41]. Indole derivatives serve as a valuable starting material, which is applied as a synthon for the preparation of medicinal compounds and natural products [42-44]. In recent years, inherently sustainable multi-component reactions (MCRs) have attracted immense attention in organic chemistry, for generating primary materials of huge utility in medicine, natural, sensor, and polymer compounds [45-49]. Furthermore, MCRs can be carried out by various catalysts [50-55]. The efficient parameters in the application of catalysts in MCRs typically comprise atomic economy, high turnover number (TON), and turnover frequency (TOF), which have attained the benchmark status in green chemistry [56-60]. MCRs are performed under greener conditions namely lack of by-product production, using safe solvents and auxiliaries, prevention of hazardous materials creation, and the deployment of renewable material for the synthesis of organic compounds [61-65].

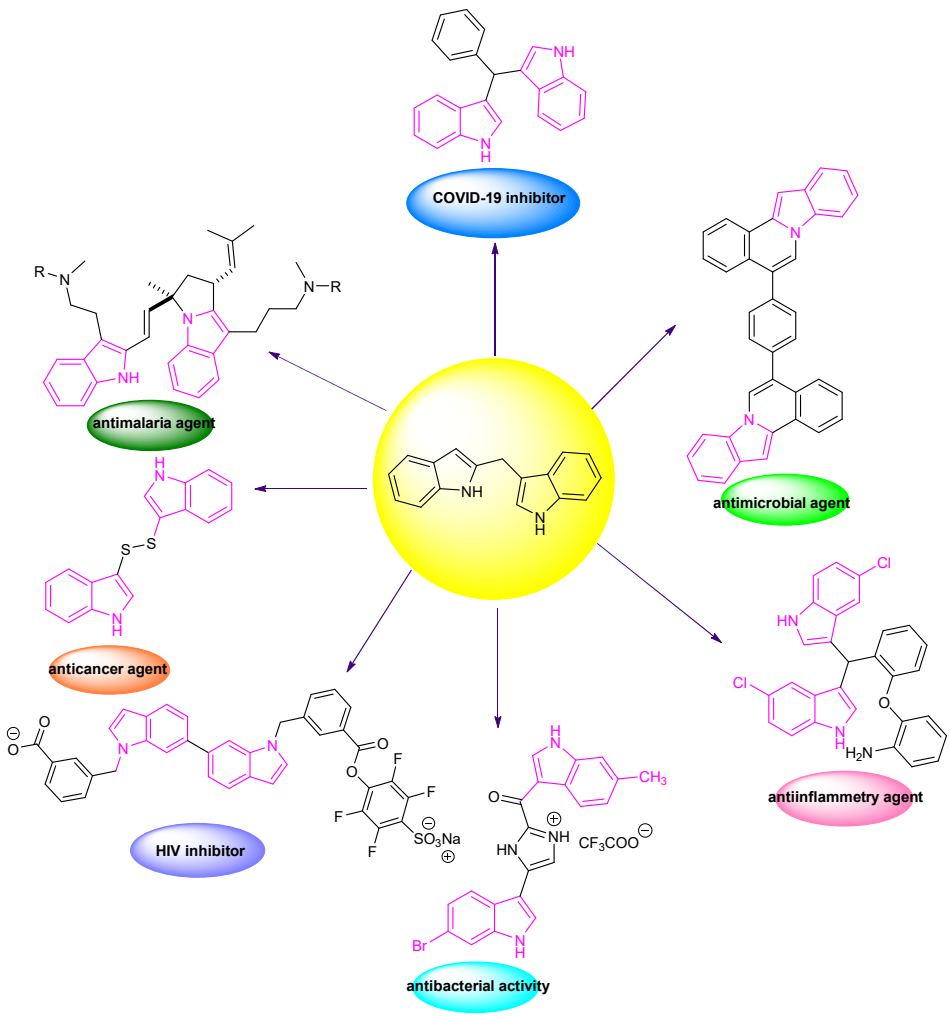


Fig. 1. The pharmacological properties of bis-indole derivatives

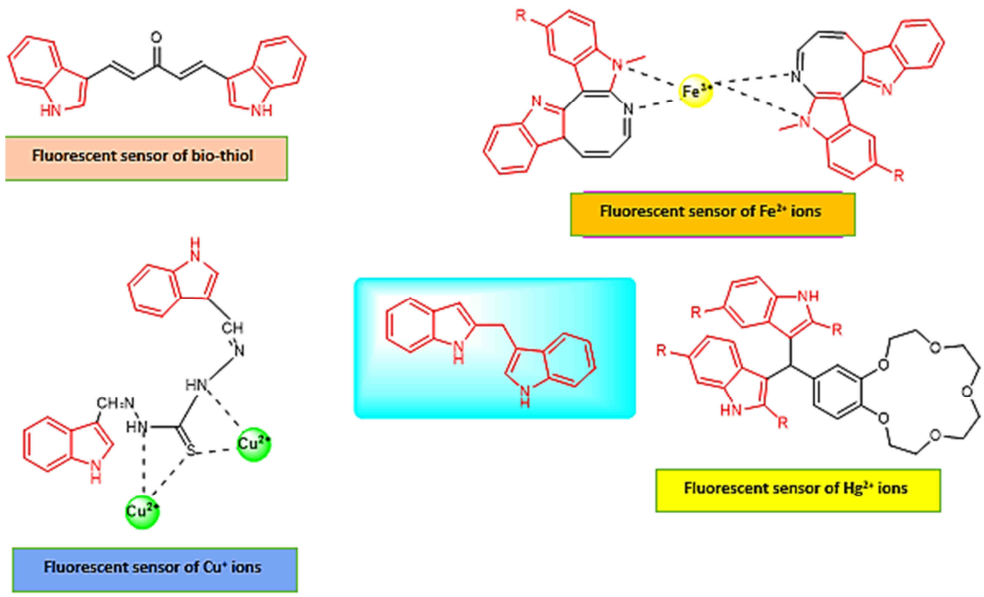


Fig. 2. The sensing properties of bis-indoles

The representative materials discussed in this study, 2,2-bis(1H-indol-3-yl)acenaphthylene-1(2H)-one derivative has been synthesised through the usage of various catalysts such as SO_4^{2-}/TiO_2, P-TSA, SBA-Pr-NH_2, and Ceric ammonium nitrate (CAN) in the various conditions [66-69]. The bis-indoles structure has been interested in organic and medicinal chemistry, which have used for the synthesis of various pharmacological materials such as anti-malaria, inhibitors of HIV-1, anti-microbial, anti-inflammatory, anti-bacterial, anti-cancer, and COVID-19 inhibitor (Fig. 1) [70-76]. As well as the bis-indole derivatives have optical properties, which can detect via numerous methods in various environments containing inorganic ions and heavy metals (Fig. 2) [77-79]. Consequently, the other bis-indole derivative can function as a medicinal sensor to detect toxic and hazardous materials in biological and blood samples.

Experimental section

Synthesis of Fe_3O_4@SiO_2@Si-Pr-NH-$CH_2CH_2NH_2$

This catalyst was prepared according to the previously described procedure [80].

General producer the preparation of 2,2-bis(1H-indol-3-yl)acenaphthylene-1(2H)-ones derivative (3a-3e)

The Fe_3O_4@SiO_2@Si-Pr-NH-$CH_2CH_2NH_2$ (0.02 g) was activated at vacuum at 100 ^oC after that, cooling to room temperature. Acenaphthenequinone **1** (1 mmol) and indoles **2** (2 mmol) were added to it. The mixture was stirred under solvent-free conditions at 100 ^oC for suitable time to result in the formation of 2,2-bis(1H-indol-3-yl)acenaphthylene-1(2H)-one derivatives **3a-3e**. This reaction was indicated by TLC in a mixture of solvents of

EtOAc: *n*-Hex. as eluent (4 : 1). Then, this reaction was carried out and the resulting solid product was dissolved in hot EtOH solvent to give a yellow solid, and the basic magnetic nanocatalyst was separated by means of an external magnet. Finally, the recovered catalyst could be reused after washing sequentially with diluted aqueous $NaHCO_3$ solution, water, and acetone [68].

The preparation of 10^{-3} M aqueous solution of 2,2-bis(1H-indol-3-yl)acenaphthylene-1(2H)-one in H_2O : CH_3CN (50 : 50) solvents

In the volumetric flasks, 100 mL, the aqueous solution of 2,2-bis(1H-indol-3-yl)acenaphthylene-1(2H)-one (0.0426 g) was prepared in the mixed solvents of CH_3CN : H_2O (50 : 50 v/v). Its solution (2.5 mL) put into the sample tubes, and then an aqueous solution of different cation nitrate salt (200 μL, 10^{-2} M) were added.

Result and discussion

Synthesis of 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-ones

Fe_3O_4@SiO_2@Si-Pr-NH-$CH_2CH_2NH_2$ was synthesised according to the previously described procedure [80]. Its catalytic activity was applied in the synthesis of 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-ones **(3a-3e)** (Table 1) via the reaction of acenaphthenequinone and 2 equivalent of indoles as illustrated in Figure 3 [68].

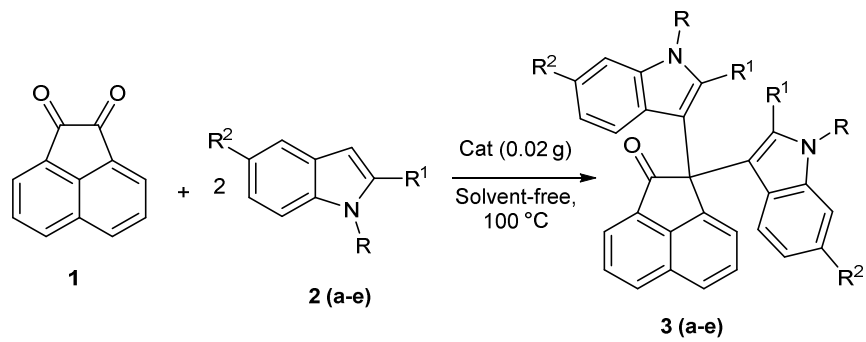


Fig. 3. The synthesis of 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-ones **(3a-3e)** in the presence of Fe_3O_4@SiO_2@Si-Pr-NH-$(CH_2)_2NH_2$ catalyst

Table 1

The synthesis of 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-one in the presence of Fe_3O_4@SiO_2@Si-Pr-NH-$(CH_2)_2NH_2$ catalyst

Entry	R	R^1	R^2	Product	Time [min]	Yields [%]	m.p.* [°C]	m.p.* [°C] [74]
1	H	H	H	3a	1	92	290-292	290-292
2	H	CH_3	H	3b	1	89	289-291	289-291
3	H	H	CH_3	3c	1.5	85	263-265	263-265
4	H	H	Cl	3d	2	87	263-265	263-265
5	*N*-Hexyl	H	H	3e	2	82	255-257	255-257

*m.p. melting point

The activity of Fe_3O_4@SiO_2@Si-Pr-NH-$(CH_2)_2NH_2$ was compared with other applied catalysts in the synthesis of compounds **(3a-3e)** as presented in Table 2. The obtained results demonstrated that Fe_3O_4@SiO_2@Si-Pr-NH-$(CH_2)_2NH_2$ catalyst has high catalytic activity among the others.

Table 2

The comparison of Fe_3O_4@SiO_2@Si-Pr-NH-$(CH_2)_2NH_2$ catalyst with the other catalysts

Entry	Catalyst	Solvent	Conditions	Time [min]	Yields [%]	Reference
1	SO_4^{2-}/TiO_2	-	grinding	30-60	70-90	[66]
2	*p*-TSA[a]	CH_2Cl_2	rt	15-120	82-95	[67]
3	SBA-Pr-NH_2	-	100 °C	10-40	60-82	[68]
4	CAN[b]	EtOH	Reflux	120	80-93	[69]
5	Fe_3O_4@SiO_2@Si-Pr-NH-$(CH_2)_2NH_2$	-	100 °C	1-2	82-92	This work

[a] *p*-toluene sulfonic acid, [b] Ceric ammonium nitrate

A plausible mechanism involves the activation of the carbonyl functional group of acenaphthoquinone **1** through hydrogen bonding. After that, the indole was attacked from position 3 through the Knoevenagel condensation and removing the H_2O molecule to generate intermediate **(I)**. Finally, indole **2** was added to intermediate **(I)** as a Michael acceptor to generate the final desired product **3** (Fig. 4).

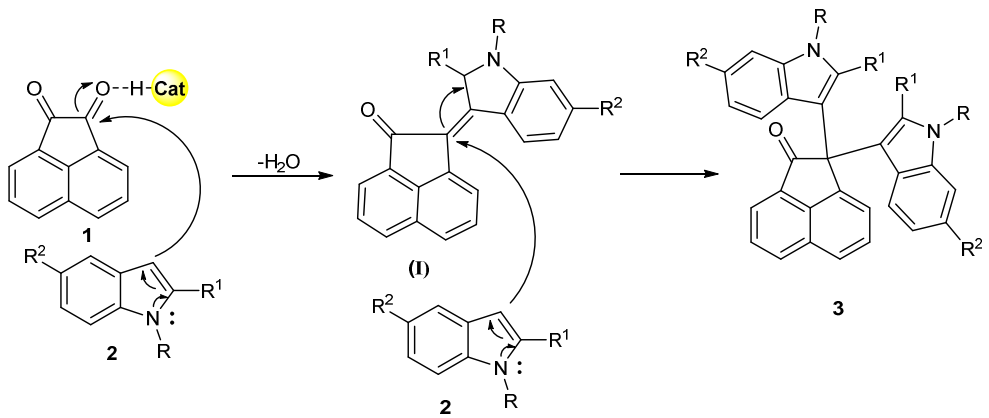


Fig. 4. The plausible mechanism for the synthesis of bis-indole derivatives

The fluorescent analysis of 2,2-bis(2-methyl-indol-3-yl)-1(2H)-one for sensing Cu^{2+} ions

The sensing ability of 2,2-bis(2-methyl-indol-3-yl)-1(2H)-one (2.5 mL, 10^{-3} mol · L^{-1}) was investigated in the presence of various cations such as Ca^{2+}, Na^{+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, Fe^{3+}, Fe^{2+}, Mn^{2+}, Co^{2+}, Al^{3+}, Pb^{2+}, Ag^{+}, Cd^{2+}, Ni^{2+}, and Mg^{2+}. Upon the addition of 200 μL metal ions, only Cu^{2+} increased a distinct spectrum change remarkably, while the other metal ions were presenting weak fluorescent emission intensity. Additionally, the sensing properties of

compound **3b** were investigated to detect the various anions, wherein the result displayed no selectivity for detecting various anions (Fig. 5).

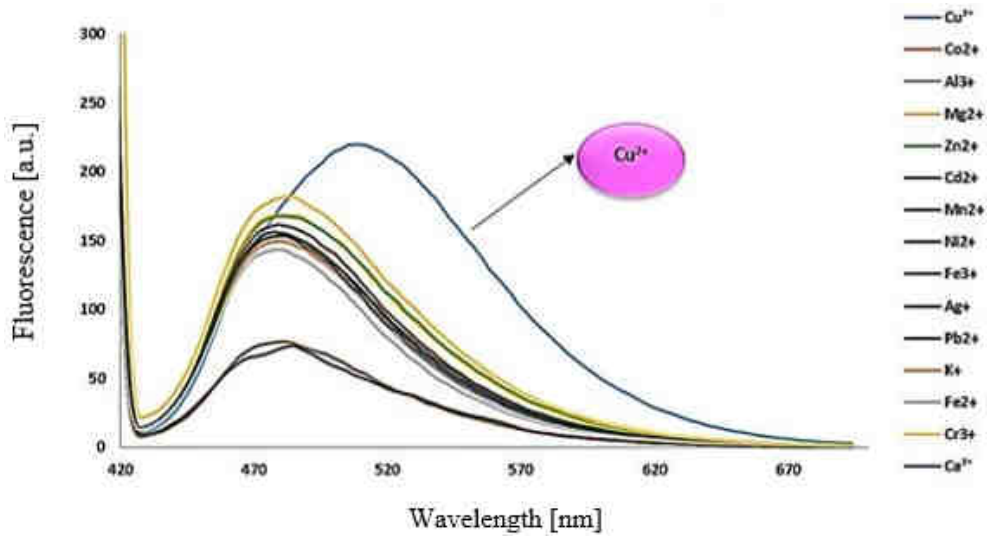


Fig. 5. The comparative photoluminescence study of 2,2-bis (2-methyl-1H-indol-3-yl)-1(2H)-one (2.5 mL, 10^{-3} mol · L^{-1}) in H_2O/CH_3CN (1 : 1 v/v) upon addition 200 μL various metal nitrate salts (10^{-2} mol · L^{-1}) in H_2O

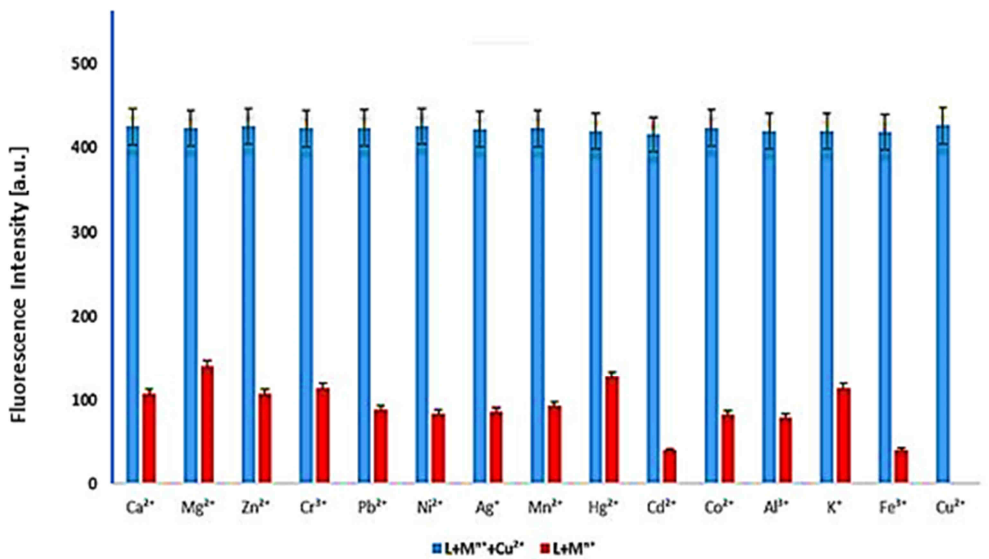


Fig 6. The selectivity of 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-one (2.5 mL, 10^{-3} M) in H_2O/CH_3CN (1 : 1 v/v) for Cu^{2+} (200 μL, $1{\cdot}10^{-2}$ M in H_2O) in relation to various metal ions (200 μL, 10^{-2} M in H_2O) from nitrate salts

Selectivity of 2,2-bis(2-methyl-indol-3-yl)acenaphthylene1(2H)-one for detecting Cu^{2+} in the presence of other cations

To evaluate the efficiency of chemical sensors in sense of Cu^{2+} in multi-analyte environments, a selectivity experiment was performed. The fluorescent emission of the chemical sensor was studied, which included 2.5 mL compound **3b** at the concentration of 10^{-3} M in CH_3CN : H_2O (1 : 1 v/v) and 200 μL Cu^{2+} (10^{-2} M in H_2O) and 200 μL the other metal ions (10^{-2} M in H_2O) from nitrate salts. The obtained results revealed that compound **3b** has no cations interference to sense the Cu^{2+} ions (Fig. 6).

The detection limit calculation of compound 3b towards Cu^{2+} ions

The measuring detection limit is the most important parameter for optical sensors, which was defined by IUPAC (CDL = 3 Sb/m) [81]. For this purpose, compound **3b** (10^{-3} M in H_2O: CH_3CN (1 : 1 v/v)) was titrated through the Cu^{2+} ions (10^{-2} M in H_2O), which indicated the changing emission intensity in excitation wavelength of 410 nm (Fig. 7). The fluorescent emission intensity of compound **3b** was increased by adding the various concentrations of Cu^{2+} ions. Moreover, compound **3b** had a linear change in the range of (0, 1000) μL Cu^{2+} ions, which has $y = 6.515\,x + 90.821$ equilibrations with the regression analysis of 0.9915 and the detection limit of compound **3b** being estimated to be $9.5 \cdot 10^{-6}$ M (Fig. 8).

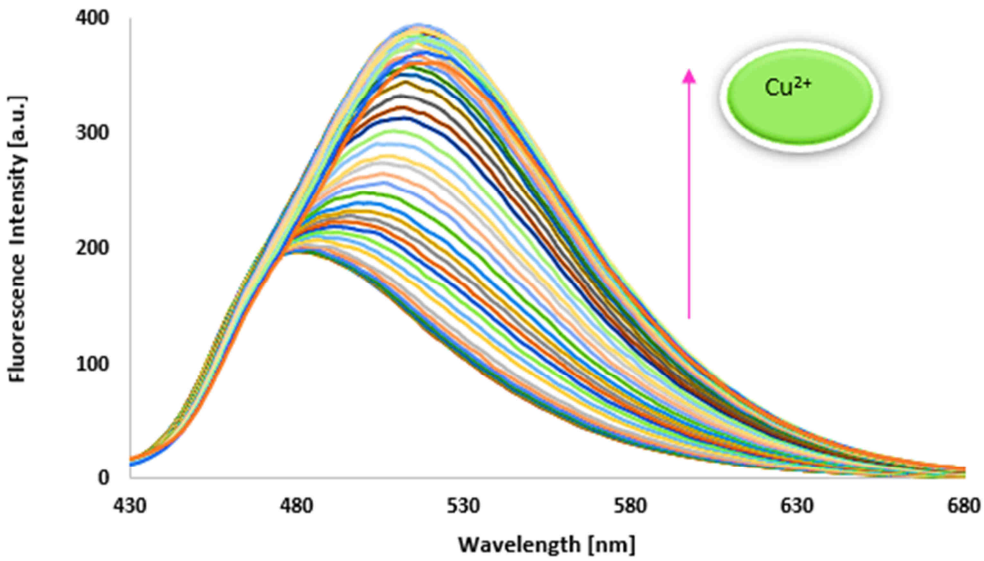


Fig. 7. The changing fluorescent emission intensity 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-one (2.5 mL, 10^{-3} M) in H_2O/CH_3CN (1 : 1 v/v) by adding various concentrations of Cu^{2+} (0, 1000) μL in H_2O, λ_{ex}: 410 nm, λ_{em}: 520 nm

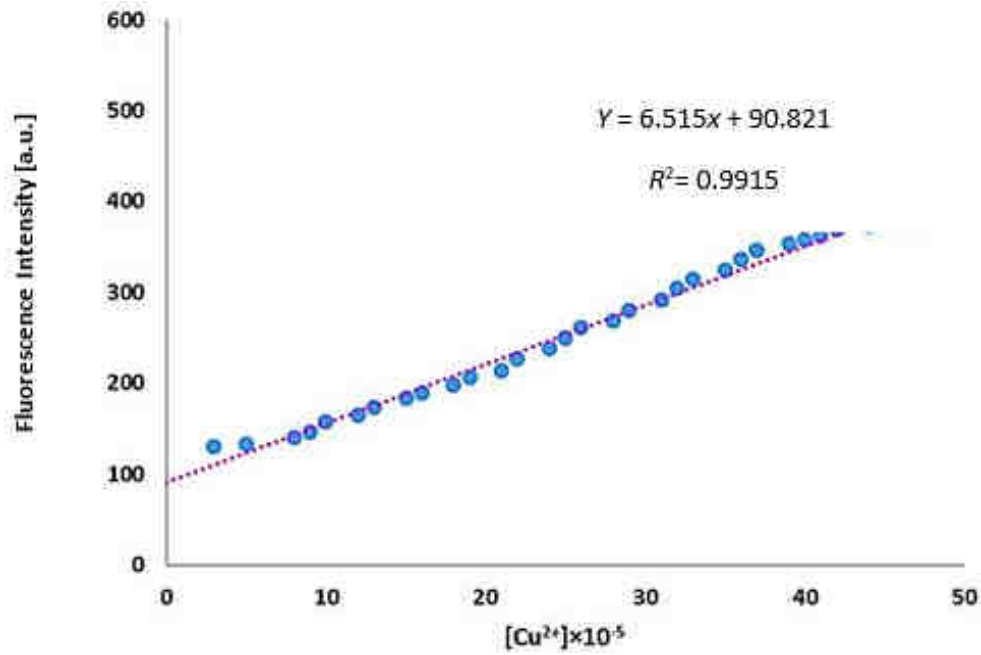


Fig. 8. Cu^{2+} calibration curve, 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-one (2.5 mL, 10^{-3} M) in H_2O/CH_3CN (1 : 1 v/v) by adding several solutions of Cu^{2+} (10 μL · 10^{-2} M in H_2O) λ_{ex}: 410 nm, λ_{em}: 520 nm

The determination of the proposed mechanism for the detection of Cu^{2+} ions through the fluorescent sensor

The proposed mechanism for the detection of Cu^{2+} ions by compound **3b** was presented in Figure 9.

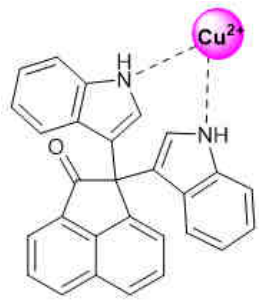


Fig. 9. The proposed mechanism for the coordination of Cu^{2+} with 2,2-bis(2-methyl-1H-indol-3-yl) acenaphthylene-1(2H)-one in λ_{ex}: 410 nm, λ_{em}: 520 nm

Ligand stoichiometry determination of Cu^{2+} through the Jobs plot test

The method of continuous variation (often referred to as Job's method) is an easy and common method for the determination of the reactant stoichiometry of chemical equilibria.

The traditional interpretation of Job plots has been restricted to complex association equilibria of the type Na + Mb ⇌ $A_{(n)}B_{(m)}$, while little focus has been placed upon displacement-type reactions (e.g., A+B ⇌ C + D), which can elasticity Job plots that look quite similar. The novel method was extended, which allowed the user to accurately distinguish between 1 : 1 complex association, 2 : 2 complex association, and displacement reactions using nothing more than a pocket calculator. To determine the stereochemistry of ligand to metal the solution of ligand (compound **3b)** and metal (Cu^{2+} ions) was prepared with the concentration of 10^{-3} in H_2O : CH_3CN (1 : 1 v/v) solvents, which were mixed through the different ratios in the total volume 3 mL in tube samples. To determine the coordination part of ligands (compound **3b**) to metal Cu^{2+} ions, the jobs plot test has been done. For this purpose, the solution of ligand and metal with the various mol ratios was obtained, and their fluorescent emission intensity of them was recorded in excitation wavelength at 410 nm. The intensity of emission was increased while the mol ratios of the solution were increased from 0 to 0.5. While the fluorescent emission intensity was decreased in the mole ratios of 0.6 to 1 as shown in Figure 10. The found result illustrated that the portion of ligand to metal was 1 : 1 [82].

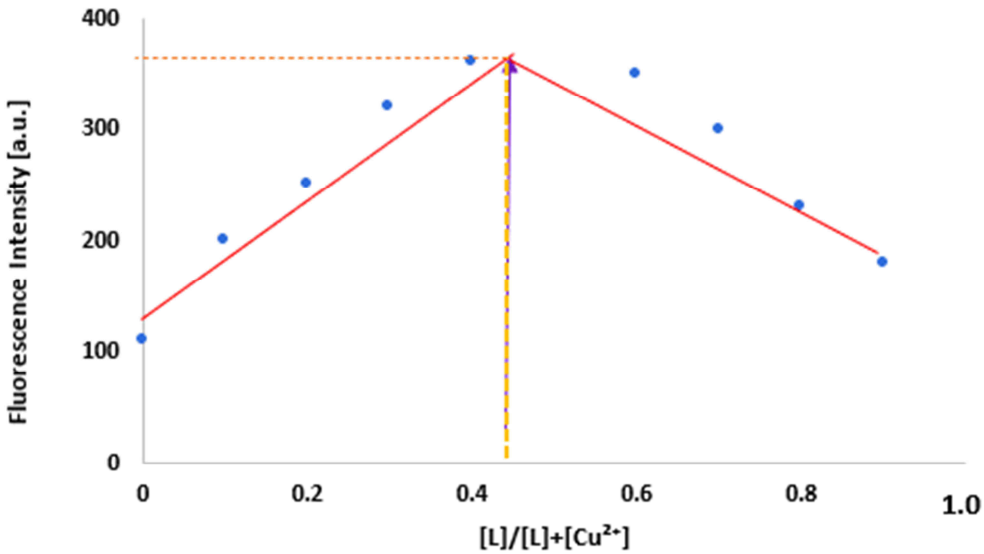


Fig. 10. The jobs plot test for determining the ratio of ligand to Cu^{2+} ions in λ_{ex} = 410 nm, λ_{em} = 520 nm

Conclusion

Herein, 2,2-bis(1H-indol-3-yl)acenaphthylene-1(2H)-ones were synthesised in one pot through the inherently sustainable three-component reaction in the presence of basic magnetic nanocatalyst Fe_3O_4@SiO_2@Si-Pr-NH-$(CH_2)_2NH_2$ under mild and greener reaction condition which displayed superiority in comparison of the other catalysts, which have been used in the preparation of compound **3a-3e**. Furthermore, the sensing properties of 2,2-bis(2-methyl-1H-indol-3-yl)acenaphthylene-1(2H)-one **(3b)** were analysed, which

revealed that copper ions fluorescent sensor with an appropriate detection limit ($9.5 \cdot 10^{-6}$ M) is attainable.

Acknowledgments

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