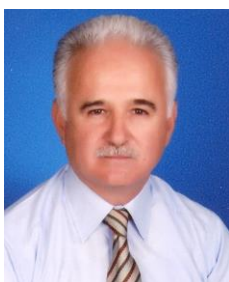


Journal of ongoing Chemical Research

Synthesis of novel naked-eye Fe^{3+} chemosensing silica particles and Rh^{3+} complex based on 4-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenol

Mehmet Ali Özler

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A Rh^{3+} complex **4** derived from 4-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenol **3** was prepared at room temperature. **3** was stirred with pentamethylcyclopentadienylrhodium chloride dimer for 30 minutes which resulted yellow precipitates which were washed with methanol, redissolved in acetone and purified chromatographically with ethanol. Phenanthroline-derived **3** was reacted with (3-chloropropyl)trimethoxysilane to obtain an alkylated compound **5**. Silica particles were functionalized by reacting with **5** at 70 °C in DMF for 6 h. Functionalized silica particles can be used for removal of different metals from aqueous and organic solutions and due to their bigger size can be easily filtered.

SYNTHESIS OF NOVEL NAKED-EYE Fe^{3+} CHEMOSENSING SILICA PARTICLES AND Rh^{3+} COMPLEX BASED ON 4-(1*H*-IMIDAZO[4,5-*f*][1,10]PHENANTHROLIN-2-YL)PHENOL

Mehmet Ali Özler^{a,*}, Said Nadeem^{a,b}

^a Department of Chemistry, Faculty of Sciences, Muğla Sıtkı Koçman University, Kötekli-48121 MUĞLA Turkey

^b Department of Aromatic and Medicinal Plants, Koyceyiz Vocational School, Mugla Sıtkı Koçman University, Mugla-48000, MUĞLA Turkey

Corresponding email: aozler@mu.edu.tr

Corresponding author's mobile number: +90-252 211 1022

ABSTRACT

A Rh^{3+} complex **4** derived from 4-(1*H*-imidazo[4,5-*f*][1,10]phenanthroline-2-yl)phenol **3** was prepared at room temperature. **3** was stirred with pentamethylcyclopentadienylrhodium chloride dimer for 30 minutes which resulted yellow precipitates which were washed with methanol, redissolved in acetone and purified chromatographically with ethanol. Phenanthroline-derived **3** was reacted with (3-chloropropyl)trimethoxysilane to obtain an alkylated compound **5**. Silica particles were functionalized by reacting with **5** at 70 °C in DMF for 6 h. Functionalized silica particles can be used for removal of different metals from aqueous and organic solutions and due to their bigger size can be easily filtered.

Keywords: 1,10-phenanthroline, fluorescence, functionalized silica particles, Rh-complex, metal removal

INTRODUCTION

Clean and non-polluted water is as necessary for life as the presence of water itself. Both organic[1-3] and inorganic[4-7] pollution of water is on the rise due to modernization and industrialization of human being. Inorganic pollution is due to metals and their salts dissolved[8] or suspended in water.[9] Common metals found in water as pollutant are Fe, Ag, Cd, Cu, Cr, Hg, Ni, Pb, Mn, and Zn.[8, 10] Heavy metals have been detected by numerous techniques[11] e.g. microelectrode array chips,[12] bioindicators,[13] living organisms,[14] atomic absorption,[15] UV-spectroscopy,[16, 17] fluorescence spectroscopy,[18] semiconductor photon counter,[19] ion-exchange X-Ray fluorescence,[20] chemosensors,[21-23] etc.

There are different methods applied for the removal of metals from drinking water. Activated carbon is widely used in different forms e.g. charcoal,[24, 25] coal,[26] coal fly ash,[27, 28] coal ash,[29] activated biomass[30] etc. Different other materials are also used for the removal of metals like steel slag filter,[31] beech sawdust,[32] solvent extraction,[33] amine-functionalized nanoporous carbon,[34] lignin-based ion-exchange resin,[35] titania-silica nanoparticles,[36] nanocomposites on rice husk,[37] organic soil modified by alkyl quaternary ammonium,[38] and the list goes on. Due to extensive work in this field, it is not possible to cover this topic even in a single book.

Other approaches for the removal of metals are the use of functionalized particles,[39] immobilized magnetite nanoparticles,[40] latex particles,[39] filtration and adsorption on expanded polypropylene media.[41] Most of the reported functionalized particles and immobilized materials are expensive and their preparation is time consuming. We decided to prepare functionalized silica particles which can be used for metal removal and can be easily filtered out after use. Titania-silica nanoparticles are already reported for the removal of Cr, Co and Pb.[36] Functionalized nanoporous silica have been also reported for the removal of As, Cd, Hg, and Pb from biological systems.[42] Micelle-templated modified silica, [43] copolymer of iron and aluminum impregnated with active silica derived from rice husk ash,[44] mesoporous silica,[45, 46] carbamoylphosphonic acids on mesoporous silica,[47] silica-titania gel[48] etc. are

current examples of growing interest in use of silica-based materials for the removal of metals. Silica is a cheap material and can be functionalized using various type of chemicals.

1,10-phenanthroline (phen) is bidentate ligand and used in almost all areas of organic and coordinate chemistry. Incorporation of phen on silica is also a hot area and has been studied in oxygen sensor,[49] optical oxygen sensors,[50] oxidative catalysis,[51] visible light sensitized red emission,[52] solid phase extraction,[53] specific adsorption,[54] luminescence,[55] inner sphere complexation,[56] silver pre-concentration and determination,[57] and silica sol-gels.[58]

Keeping in mind all these properties of phen and silica, it was decided to functionalize silica particles using phen. Phen was oxidize at 5,6-positions and reacted with *p*-hydroxybenzaldehyde to obtain 4-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)phenol. Silica particle contains terminal –OH groups which can be used as nucleophile. The prepared phenol was alkylated by reacting with (3-chloropropyl)trimethoxysilane. The methoxysilane compound was reacted with silica which result phen-functionalized silica particles (Figure 1). The obtained particles are under study for metal removal from aqueous solutions.

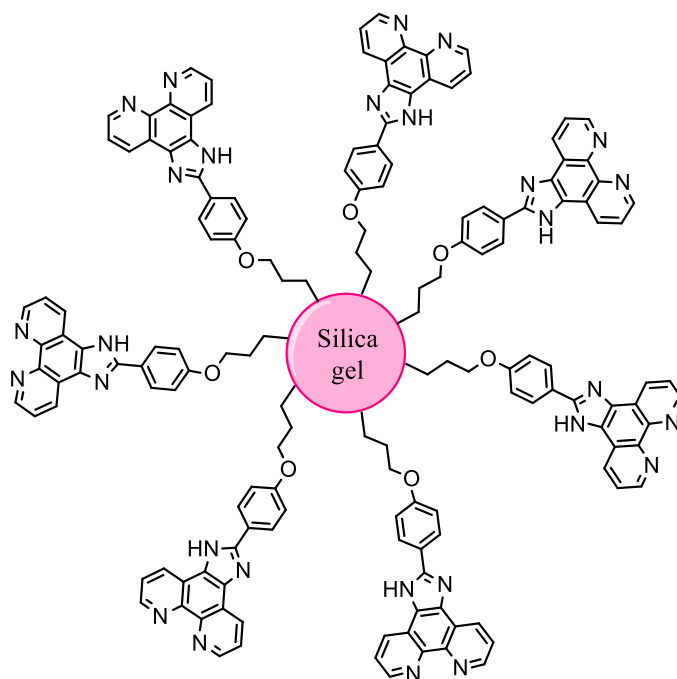
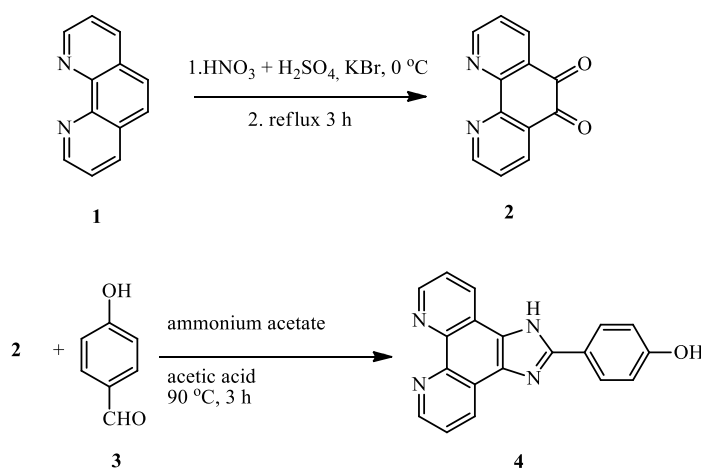


Figure 1: Immobilization of compound 6 on silica gel particles

RESULT & DISCUSSION

Synthesis of ligands

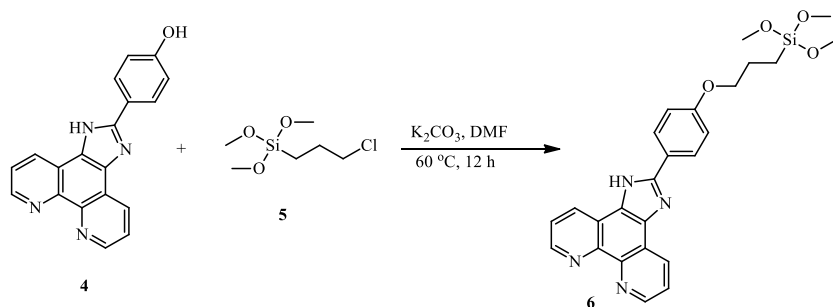
Compound **4** was synthesized according to literature procedure[59] with slight modification. Phenanthroline was oxidized at 5,6-positions in a mixture of nitric acid, sulfuric acids and potassium bromide. In normal cases, nitration occurs at 5-position to give 5-nitro-1,10-phenanthroline when nitric acid and sulfuric acids are added to 1,10-phenanthroline.[60] But when potassium bromide is added to the same reaction conditions, phen-5,6-dione **2** is formed (Scheme 1). Crude compound was dissolved in acetone and this solution accidentally touched the nails which resulted reddish color similar to “Hina”. Interestingly, the color retained for 20 days. The synthesis of **2** provided excellent starting material for the synthesis of very complex and important architectures. Phen-dione upon reaction with aldehyde in the presence of ammonium acetate and acetic acid introduces variety of functional groups via imidazole derivatives (Scheme 1).



Scheme 1: Synthesis of 4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenol **4**

Before immobilize compound **4** on silica particles, there was a need to convert it into an electrophile. For this purpose, the phenol **4** was reacted with (3-chloropropyl)trimethoxysilane **5** to obtain the required alkylated product **6** (Scheme 2). Compound **5** was an attractive option because it can anchor the molecule on the surface of silica particles. The reaction was performed

in dry DMF while potassium carbonate was used as a base. Alkylated phenanthroline-derivative **6** was obtained in the form of brownish gel which could be easily separated from the reaction mixture with a spatula. **6** was purified by column chromatography using ethanol as eluent. Pure compound was characterized through NMR and mass.



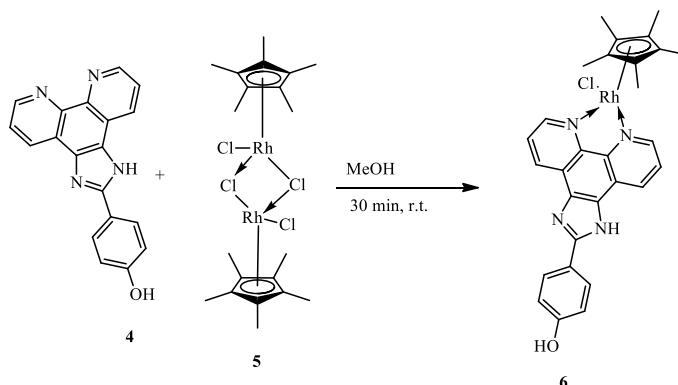
Scheme 2: Alkylation of compound **4**

Rh³⁺ complex

Literature is very rich about the complexation of phen with various metals e.g. Ru(II),[49] Ru(III),[61] Ru(IV),[62] Eu(III),[63] Fe(II),[64] Cu(II),[65] Tb(III),[66] Ni(II),[67] Bi(III),[68]Pb(II),[69] Mn(II),[70] Co(III),[71] Cr(III),[72] Pt(II),[73] Pt(III),[74] Ho(II),[75] Sm(III),[76] Ag(I),[77] Cd(II),[78] Pd(II),[79] Au(III),[80] Zn(II),[81] Re(I),[82] and quantum dot Sn(II)Se(V).[83] Phen and its derivatives were used for the detection of toxic metals in water. Similarly metals complexation of phen **1** has been used for the template mediated formation of macrocycles and catenanes. Model studies for metal complexation with molecule **4** were carried out to explore the effect of metals on photophysical properties of compound **4**. Pentamethylcyclopentadienylrhodium chloride dimer **5** was reacted with phenol phen-derivative **4** as shown in scheme 3.

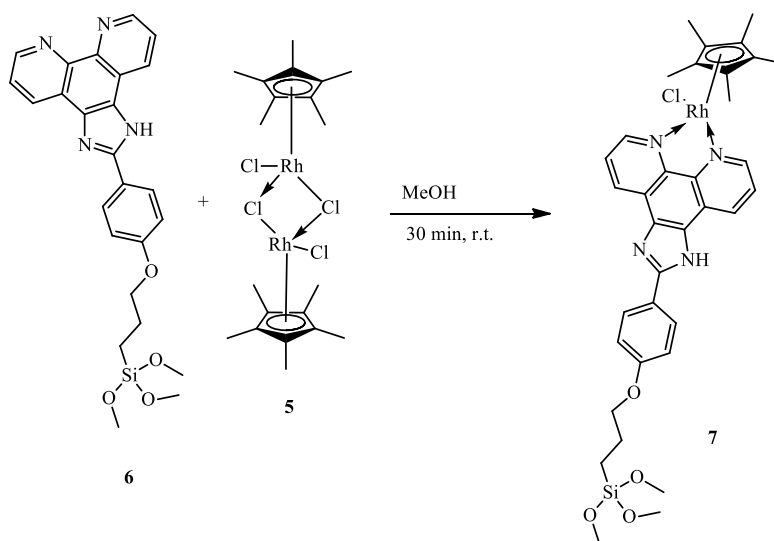
The reactants were mixed together in dry methanol and stirred for 30 minutes at room temperature. Yellow precipitates were obtained which were filtered and washed with methanol. Reactants were soluble in methanol but the obtained complex **6** was insoluble which make it easier to remove impurities by washing. After washing and removing of the unreacted starting

materials with methanol, **6** was dissolved in acetone, while the residual starting material was insoluble. The solvent was evaporated and dried in vacuum.



Scheme 3: Synthesis of Rh³⁺ complex from compound **4**

The ¹H NMR spectrum of the rhodium complex supported the successful formation of the product with a finger print peak of fifteen protons belongs to five –CH₃ located on cyclopentadiene ring, and were observed as a singlet at δ 1.73. A proton belongs to imidazole-NH was observed as a single. In the reactant compound **4**, this singlet was observed at 14 ppm but in the complex, it shifted to δ 12.1 ppm. Protons of aromatic region were observed as a doublet at δ 6.81 of two protons with a coupling constant of 8.9 Hz, a four protons multiplet at δ 7.93-7.64 while other peaks were observed at δ 8.48, 8.7, 8.82, 9.11 and 9.18.



Scheme 4: Synthesis of Rh³⁺ complex from compound **6**

Molecule **6**, which was ready to immobilize was also subjected to complexation. Rhodium dimer **5** and phen-methoxysilane-derivative **6** were mixed in dry methanol and stirred for 30 minutes at room temperature (Scheme 3).

After completion of the reaction, yellow precipitates were obtained which were filtered and washed with methanol. Product **7** was washed with acetone and dried in vacuum.

Fluorescence studies

The compound **6** was subjected to fluorescent studies in DMSO to evaluate the effect of introduced substituents on the photophysical properties of the molecule. The excitation and emission spectra are given in Figure 2.

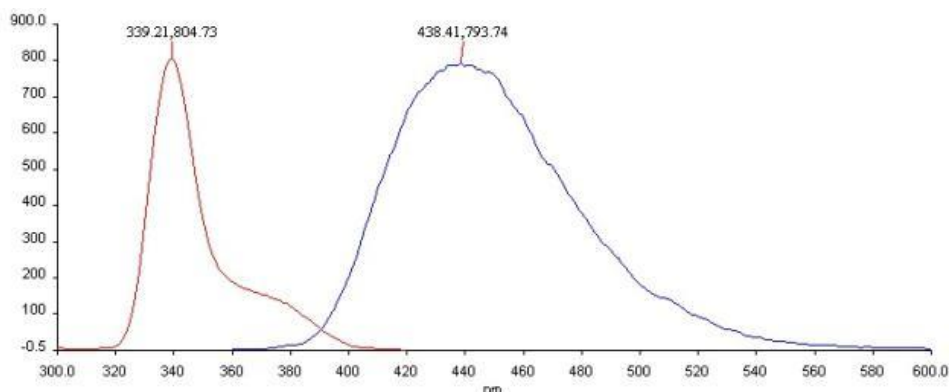


Figure 2: Excitation and emission spectra of compound **6**

The spectrum showed the excitation maxima at 339 nm and the emission maxima at 438 nm with almost 100 nm of Stokes shift. The spectrum also showed small shoulder in excitation around 360-380 nm. Both the excitation and emission band were almost similar to that of the reactant molecule as the change in the maxima is very less.

The fluorescent studies were performed to check the electronic behavior in comparison with the reactant. The excitation and emission spectra are given in Figure 3. The fluorescent studies were carried out to explain the difference in the photophysical properties between reactant and the product.

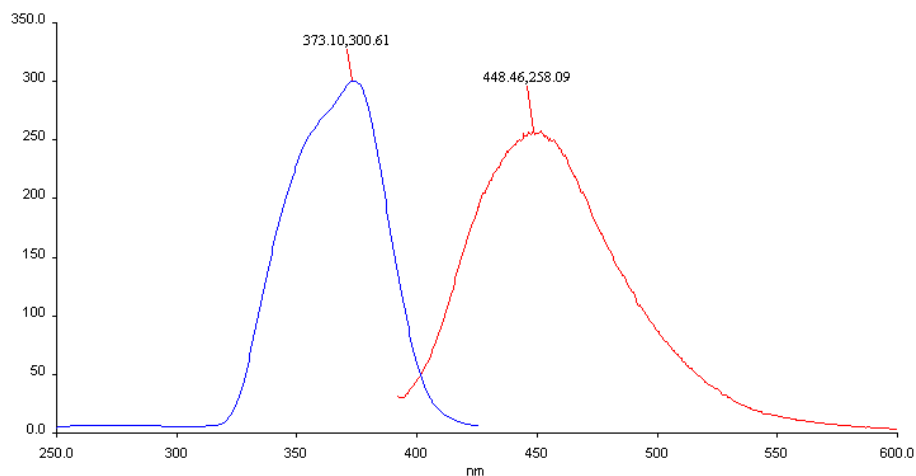


Figure 3: Excitation and emission maxima of rhodium complex of phen derivative 7

The excitation maximum of the product **7** was observed at 373 nm while the emission maximum was observed at 448 nm. The excitation maximum after metallation increased from 339 to 373 nm. The Stokes shift dropped to 75 nm in this complex as compared to the reactant which was almost 100 nm. The decrease in the Stokes shift is due to the complexation of the molecule with rhodium which is quenching the electronic excitations.

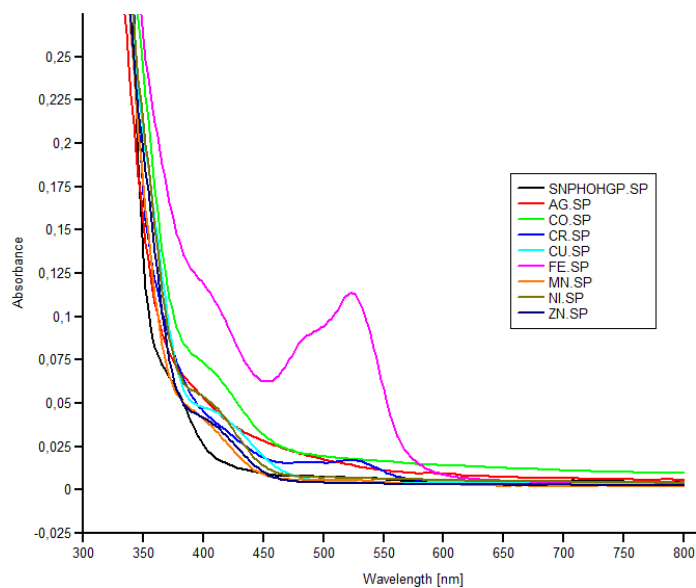


Figure 4: UV-visible spectra of compound 4 in the presence of different metal

As the reactant compound **4** was fluorescent and could be used for the separation of metals from the solutions, so the easiest characterization techniques would be the analyses of the reactant and the product by comparing their photophysical studies. The fluorescent studies of the reactant molecule **4** has been discussed in earlier pages and presented in figure 2, so the fluorescent study of the compound was concluded to investigate the effect of metal complexation on the fluorescence behavior of compound.

The fluorescent spectrum of the rhodium complex shows the excitation maxima at 340 nm and the emission maxima at 445 nm with a Stokes shift of 105 nm. After metalation, the emission maximum increased by 3 nm while only 1 nm change was observed in the excitation maximum. But the spectrum showed a big shoulder at the right side of the excitation peak around 360-400 nm.

UV studies

The UV spectrum of compound **4** was obtained in ethanol with concentration of 30 $\mu\text{mol L}^{-1}$. The compound showed λ_{max} at 278 nm and no peak was observed in the range of 800 to 350 nm.

Compound **4** was screened with different metals i.e. Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Ag^{+} , and Zn^{2+} through UV-visible spectroscopy for their sensing properties for these metals. **4** was mixed in 1:1 ration with the stated metals with concentration of 30 $\mu\text{mol L}^{-1}$ and stirred in a 10 mL conical flask for 30 minutes. The flask having Fe^{3+} showed pinkish color while the solutions containing other metals did not show any color (Figure 4). This mixture was subjected to UV-visible analysis and a broad peak was found at 524 nm while no peak was observed in the presence of other metals.

EXPERIMENTAL

Preparation of solutions:

Stock solutions of all metal nitrates (Co^{2+} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Ni^{2+} , Ag^{+} , and Zn^{2+}) and compound **4** were prepared in ethanol having 1 mmol L^{-1} concentration. For analytical study, 3 mL solutions were prepared by diluting stock solution to 30 $\mu\text{mol L}^{-1}$ by ethanol.

UV-visible study:

UV-Visible spectra were obtained by using Perkin-Elmer's LAMBDA 35 UV/Vis Systems spectrophotometer in the range of 800-200 nm. 30 $\mu\text{mol L}^{-1}$ of compound **4** was stirred with all the metals of the same concentration for 30 min followed by UV-visible studies.

3.3. Synthesis

1,10-Phen-5,6-dione (2):

1 g (5.5 mmol) of 1,10-phenanthroline and 1 g (8.4 mmol) of KBr were taken in an ice cold flask. 10 mL of concentrated H_2SO_4 and 5 mL HNO_3 were added slowly with stirring at 0 °C. The mixture was then refluxed for 3h. The color of mixture changed to yellow and was poured into 500 mL of ice water and sodium hydroxide was added slowly to make the pH 4. The aqueous phase was extracted three times with DCM and dried with Na_2SO_4 . The solvent was evaporated under vacuum and 1.5 g of target compound was obtained with 96 % yield. The product was crystallized out from ethanol. M. p. 247–248 °C; EIMS m/z : 212 (M+2); ^1H NMR (300 MHz, CDCl_3) δ : 9.12 (dd, 2H, 4J = 1.8 Hz, 3J = 4.8 Hz), 8.51 (dd, 2H, 3J = 7.8, 4J = 1.5 Hz), 7.69 (dd, 2H, 3J = 4.8, 4.8 Hz). ^{13}C NMR (400 MHz, CDCl_3) δ : 178.7, 156.4, 152.9, 137.3, 129.7, 128.1, 125.6

4-(1H-Imidazo[4,5-f][1,10]phenanthroline-2-yl)phenol (4):

500 mg (2.4 mmol) of 1, 10 phenanthroline-5,6-dione and 350 mg (2.8 mmol) of 4-hydroxybenzaldehyde were dissolved in 10 ml of glacial acetic acid. After stirring for 5 minutes at room temperature, 3.70 g (48 mmol) of ammonium acetate (48 mmol 20 eq.) was added. Temperature was increased to 100 °C and then stirred at this temperature for three hours. After the desired time, the mixture was poured in 50 mL of ice cold water and neutralized with ammonium hydroxide solution. Kept in freezer at -20 °C for overnight and then filtered, washed with water and then acetone successively. 500 mg of the product was obtained as yellow powder

in 65 % yield. The compound was dried under vacuum at 50 °C for 24 h. EIMS m/z : 312.5; ^1H NMR (300 MHz, DMSO-d_6) δ : 13.50 (br, s, -NH-), 9.01 (dd, 2H, $3J = 4.5$ Hz, $4J = 1.8$ Hz), 8.91 (dd, 2H, $3J = 8.1$ Hz, $4J = 1.5$ Hz), 8.13 (d, 2H, $3J = 8.4$ Hz), 7.84 (dd, 2H, $3J = 8.1$, 8.1 Hz), 6.99 (d, 2H, $3J = 8.4$ Hz); ^{13}C NMR (300 MHz, DMSO-d_6) δ : 159.38, 151.49, 147.82, 143.64, 143.59, 136.00, 129.85, 128.41, 123.60, 121.48, and 116.27; Elemental analyses ($\text{C}_{19}\text{H}_{12}\text{N}_4\text{O}_1$) calculated C, 67.24%; H, 4.45%; N, 16.51%: found C, 67.20%; H, 4.61%; N, 16.07%.

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