

Synthesis of Novel Tetrazole Transition Metal Complexes for Advanced Photonic Applications

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As tetrazole themselves revealed a rich photochemistry and are piquantly affected by the presence of substituents on tetrazole ring. This exertion explores the harmony of two bidentate ligands-pyridine tetrazole (Hpytz) and pyridine tetrazole-N-oxide (Hpytzo) as "antennae" and their complexes with transition metals (Fe^{3+} , Co^{2+} , Ni^{2+} , Zn^{2+} and Ru^{3+}). The erections of these pyridine tetrazole metal complexes were elucidated by UV, IR and ^1H NMR by using DMSO, acetonitrile as solvents in which these metal complexes persist in undissociated form and also show high melting point $>360^\circ\text{C}$. These pyridine tetrazole ligands ("antennae") sensitize efficiently the metal centre and stimulus the absorption window of pyridine tetrazole transition metal complexes, which was appreciably stretched towards the UV-visible region of 400-800 nm. The wavelength of these ligands $\lambda_{\text{emission}}$ was found to be amplified upto 522-540 nm ($\lambda_{\text{excitation}} = 270$ nm) that might enlightens the extremely conjugated unsaturated system which triggers the UV-region and for metal complexes ($\lambda_{\text{excitation}}$, $\text{Fe}^{3+} = 270$ nm, $\text{Co}^{2+} = 280$ nm, $\text{Ni}^{2+} = 285$ nm, $\text{Zn}^{2+} = 270$ nm and $\text{Ru}^{3+} = 260$ nm ($\lambda_{\text{emission}}$, $\text{Fe}^{3+} = 522.5$ nm, $\text{Co}^{2+} = 576$ nm, $\text{Ni}^{2+} = 554$ nm, $\text{Zn}^{2+} = 521$ nm and $\text{Ru}^{3+} = 522$ nm). The escalation in $\lambda_{\text{emission}}$ of the metal complexes with novel designed tetrazole ligands spectacles a drift on complex formation due to the augmented conjugation and conformation, which might sensitizes luminescence properties as reported with La(III) complexes more proficiently. The fluorescent property revealed with these neutral pyridine tetrazole derivatives stipulate an efficient alternative to that of usual dipicolinate analogues.

Keywords: Transition metal complexes, Heteronuclear, Pyridine, Tetrazole, Luminescence.

INTRODUCTION

Heterocycles predominantly containing nitrogen have been renowned as a class of auspicious and handy structures for the novel tetrazole chromophore design (e.g., pyridine tetrazole, bis-tetrazole pyridine, bipyridine tetrazole and terpyridine tetrazole ligands) [1-7] and synthesis of the elevated energy materials. Due to their higher thermal stability, higher heat of formation of these pyridine based derivatives found much imperative applications embracing the improvement of photoluminescent materials [8], protein crystallography [9] and immense variety of many other applications ranging from material science to medicinal field [10-12]. One of the most imperative and sensational applications of tetrazole based derivative as the pyridine tetrazole, which has been set up to display extensive appliances particularly in luminescent applications such as indicators, imaging and signal sensors [13,14].

These tetrazole based derivatives can be used as a ligand in the configuration of eclectic range of complexes liable upon the nature of the central metal. Recently, lanthanide complexes equipped, which has publicized much more boosted photo luminescent property [15]. Correspondingly, the complexes

of the transition metals like Fe, Co, Ni, Zn and Ru are also foreseeable to display eclectic range of photonic applications due to the neighbouring resemblance in physio-chemical properties because of availability of empty *d*-orbitals. Pyridine tetrazole derivatives plays essential role in coordination chemistry as ligands, in medicinal chemistry as metabolically secure alternatives for carboxylic acids [16]. Nevertheless, tetrazole themselves exhibit no pharmacological activity but several of their derivatives possess fascinating biological (antihypertensive, antiallergic and antibiotic) activities [17]. The two ligands which acts as chromophore pyridine tetrazole and pyridine tetrazole-N-oxide (Hpytz, Hpytzo) having elevated extinction coefficient, which engrosses the maximum portion of the light "antennae" and transmissions that gripped light to the metal centre, causing excitation among the metal *d*-orbitals "antenna effect" [18,19]. The competence of ligand to metal energy transfer requires the compatibility amongst the energy levels of ligand excited states and accepting levels of the metal ions, which is decisive in designing the elevated precise analyses. To counter act the deactivation of metal centre by spending the pyridine tetrazole as a ligand which has been revealed to have alerting property in the ancient and supreme property of ligand was that it counter

acts the water binding to the metal centre which ultimately upsurges the luminescent lifetime of the metal in the excited state and displays considerable fluorescent property as rivalled to carboxylate analogues which were used previously [20-22]. Alternative vital entity about the tetrazole derivatives was π -acceptance capability and higher thermal stability which exhibit fascinating glowing property [23]. Utmost ratio of the sensitizing ligand to metal proliferates the fluorescence consistently, since more and more energy is absorbed by ligands "antennae" which is conveyed to the metal centre.

Moreover the pyridine tetrazole, former chelating organic ligands like terpyridine derivatives that existed set up act as potential ligands for sensitizing the metal centre, consequently opening a innovative age of investigation in the pitch of coordination chemistry [24]. The synthesis of numerous functionalized terpyridine ligands and terpyridine complexes, ranging from mononuclear complexes *via* dyads and triads (ruthenium (II) complexes and their optical properties) to extensive supramolecular styles. Likewise the custom of di-tetrazolate pyridine ligands, owing to their elevated stability in thermal and acidic situations too custom a potential chromophore in formulating the complexes, which are estimated to display the elevated luminescent property as rivalled to carboxylate, mono-tetrazole ligands, *etc.* The complexes of di-tetrazole ligands were set with the lanthanides (Ln = Nd, Eu, Tb) which are questioned and their photoluminescent properties was sound upto the streak, analogous opinion was initiated with transition metals (Fe, Co, Ni, Zn and Ru) on complexation with pyridine tetrazole ligands *viz.*, pyridine tetrazole (Hpytz) and pyridine tetrazole-N-oxide (Hpytzo).

Thiophene substituents were also reced having potential sensitizing power, OLED elaboration and operative tuned luminescence properties [25]. The augmented permeation of the metal centre and to eradicate the water molecules from the metal centre, triphenyl phosphine oxide (TPPO) and their correspondents were extensively studied and initiate as impending sensitizers now a days. Triphenyl phosphine oxide was found to enrich the total luminescence by nearly 20 % in lanthanide complexes predominantly in Eu(III) complexes [26]. Also passionate orange luminescence in complexes enclosing TPPO as co-ligand with samarium complexes as rivalled with water coordinated complexes. Numerous phosphine oxide derivatives have been set with improved sensitizing power in Ln(III) complexes [27]. A like marks are anticipated to originate on the changeover of water molecules with TPPO referents in occasion of the lower transition complexes also. Thus, escalation in the luminescent property in complexes on changeover of water with co-ligand TPPO was due to the amendment in the geometry of complex, which in turn endorses faster radiation rates or boosts the communication flanked by ligands, the metal centre and consistently (LS-coupling) singlet-triplet states [28], thus amassed the photoluminescent property excellently.

EXPERIMENTAL

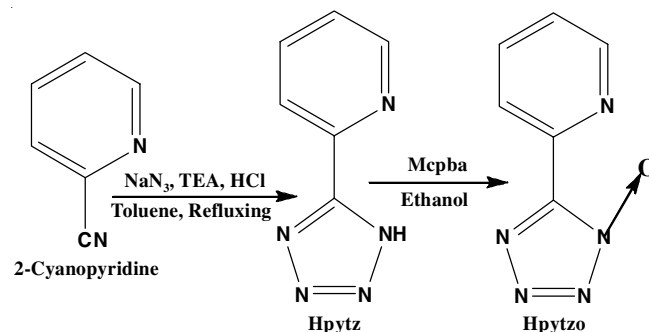
All the chemicals and solvents were obtained from Fluka Chemicals Co., Germany and used as received. Low-resolution visible luminescence measurements in solution were recorded on a Perkin-Elmer spectrometer at 298 K. The other instruments

viz. UV spectrum (Shimadzu UV-1800 series), IR spectrum (FTIR-8400S Shimadzu), ^1H NMR spectrum (Bruker Avance II 400 NMR Spectrometer) using TMS as internal standard ($\text{DMSO}-d_6$) are used to characterize the structures of the metal complexes and photoluminescence properties.

Synthesis of ligands

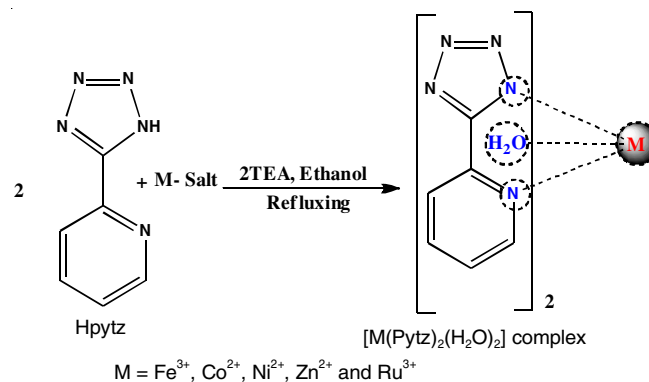
Synthesis of pyridine tetrazole (Hpytz): 2-Cyanopyridine (10 mmol) was taken in 300 mL of toluene followed by the addition of sodium azide (130 mmol) and triethylamine (130 mmol). Conc. HCl (130 mmol) was added dropwise to this solution and stirred without heating for 0.5 h, reflux the reaction mixture for 12-16 h. Now this reaction mixture was added with 30 mL of water and stirred for another 0.5 h. The aqueous layer was separated from the organic layer and added 100 mmol of acetic acid after few minutes till white crystals are formed [29,30]. Yield: 7.5 g; 65 % and m.p. 215-220 °C.

Synthesis of pyridine tetrazole-N-oxide (Hpytzo): 1 mmol of pyridine tetrazole (Hpytz) and 2.5 mmol of *m*-chloroperoxybenzoic acid (Mcpba) were added in 180 mL of ethanol and stirred at room temperature. Haziness occurred after 30 min which indicated the formation of white precipitate of crystals of pyridine tetrazole-N-oxide (Scheme-I). Yield: 2.55 g; 70 % and m.p. 255-260 °C.

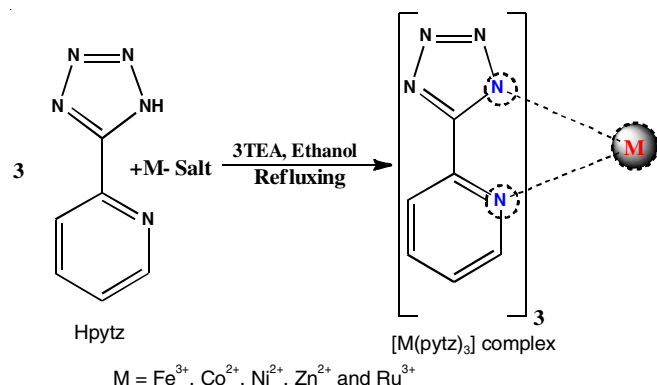
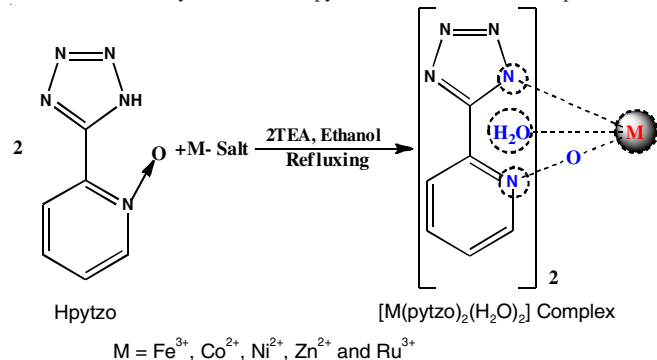
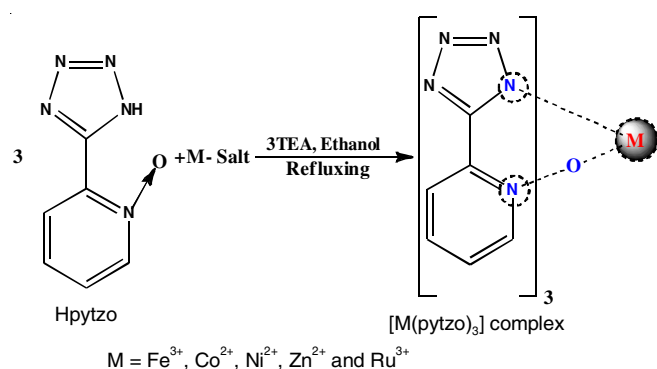
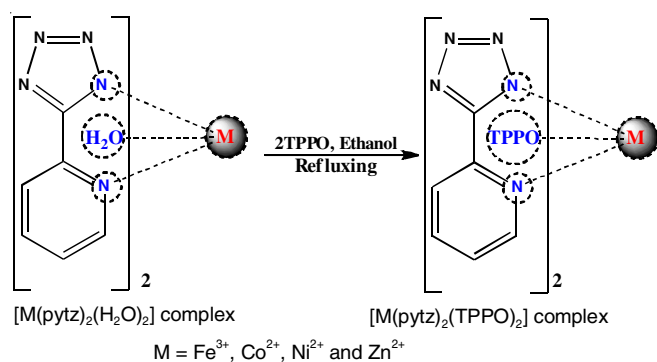


Scheme-I: Synthesis of pyridine tetrazole/pyridine tetrazole-N-oxide

Synthesis of bis- and tris-pyridine tetrazole and pyridine tetrazole-N-oxide (Hpytz/Hpytzo) metal complexes: Pyridine tetrazole/pyridine tetrazole-N-oxide (Hpytz/Hpytzo) (2/3 mmol) and triethyl-amine (2/3 mmol) were mixed in 20 mL ethanol taken in 250 mL round bottom flask. Now added corresponding metal salt (1 mmol) dissolved in 2 mL ethanol to the mixture and refluxed for 12-16 h. Washed the corresponding colour metal precipitate by ethanol and finally with cold distilled water (Schemes II-VI).



Scheme-II: Synthesis of bis-pyridine tetrazole metal complexes

Scheme-III: Synthesis of *tris*-pyridine tetrazole metal complexesScheme-IV: Synthesis of *bis*-pyridine tetrazole-N-oxide metal complexesScheme-V: Synthesis of *tris*-pyridine tetrazole-N-oxide metal complexesScheme-VI: Synthesis of [M(pytz)₂(TPPO)₂] complexes

RESULTS AND DISCUSSION

Absorption spectroscopy: The photoluminescence spectra of all the *bis* and *tris*-metal complexes of (Fe³⁺, Co²⁺, Ni²⁺, Zn²⁺ and Ru³⁺) was taken in relevant solvents methanol or ethanol. Solubility of the metal complexes and their absorption spectra can also be taken in DMSO and acetonitrile. From the

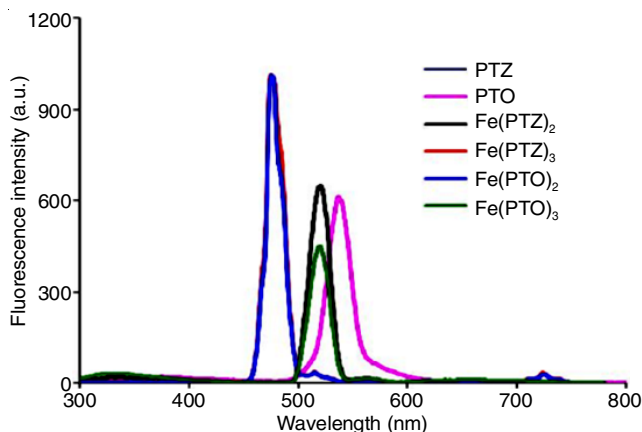
absorption spectra of all the metal complexes, it was clearly marked that there was substantial bathochromic shift in the absorption maxima in all the complexes, depicted that the complexation has occurred. This bathochromic shift in the absorption band were merely because of existence of exceedingly conjugated pyridine and tetrazole rings which succors energy transfer from ligand to metal center, that might benefit for making of singlet¹ to triplet³ state due to crossing over and followed by spin inversion after excitation and emission of absorbed energy from the metal complex. The above progression was built by two fascinating sensations *viz.*, fluorescence and phosphorescence, which elucidates singlet¹, triplet³ states, lifetime of both sequences was dignified, recorded and are creative in phosphorescence-long lived triplet³ state in the emission spectra that delivers coloured visualization in the UV-visible region. The graphical exemplification of luminescence property of all the metal complexes, laterally with data are given in Table-1 [31-34].

TABLE-1
PHOTOLUMINESCENCE DATA OF
LIGANDS AND METAL COMPLEXES

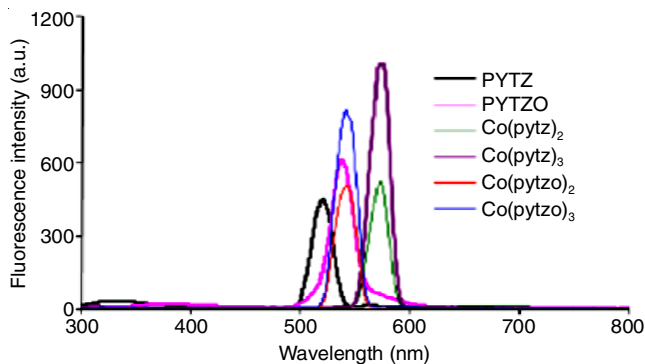
Ligand/metal complexes	$\lambda_{\text{excitation}}$ (nm)	$\lambda_{\text{emission}}$ (nm)
Hpytz	270	522
Hpytzo	270	540
[Fe(pytz) ₂ (H ₂ O) ₂]	270	522.5
[Fe(pytz) ₃]	250	478.5
[Fe(pytzo) ₂ (H ₂ O) ₂]	250	477.5
[Fe(pytzo) ₃]	250	521.5
[Co(pytz) ₂ (H ₂ O) ₂]	285	561
[Co(pytz) ₃]	280	576
[Co(pytzo) ₂ (H ₂ O) ₂]	285	532
[Co(pytzo) ₃]	280	543
[Ru(pytz) ₂ (H ₂ O) ₂]	260	522
[Ni(pytz) ₂ (H ₂ O) ₂]	285	553.5
[Ni(pytz) ₃]	285	554
[Ni(pytzo) ₂ (H ₂ O) ₂]	285	554
[Ni(pytzo) ₃]	280	478
[Ru(pytzo) ₂ (H ₂ O) ₂]	260	522
[Zn(pytz) ₂ (H ₂ O) ₂]	250	475
[Zn(pytz) ₃]	270	475
[Zn(pytzo) ₂ (H ₂ O) ₂]	250	519
[Zn(pytzo) ₃]	270	521

Photoluminescence

Iron complexes: The analysis of wavelength ($\lambda_{\text{emission}}$) of ligand Hpytz (522 nm) and Hpytzo (540 nm) was perceived that there was a sharp intensification in wavelength of Hpytzo *i.e.*, bathochromic shift. Thus, it was evidently clinched that insertion of oxygen atom directly stimuli conjugation of the ligand which ramblingly impacts photoluminescence property. Consequently, the metal complexes molded with these ligands revealed a sizeable conformational conversion in the wavelength *i.e.*, bathochromic and hypsochromic shifts are observed. Such as Fe(pytz)₂(H₂O)₂ complex (522.5 nm) formed with the ligand Hpytz (522 nm) show bathochromic shift than Fe(pytz)₃ complex (478.5 nm) and Hpytz ligand. Likewise complexes of Fe(pytzo)₂(H₂O)₂ and Fe(pytzo)₃ (477.5 nm, 521.5 nm) which was primed from the ligand Hpytzo (540 nm) displays hypsochromic shift as rivalled to the ligand. From Fig. 1, it was perceived that there was mild variance in the emission spectra but a close resemblance with Ln(III) complexes in luminescent properties.

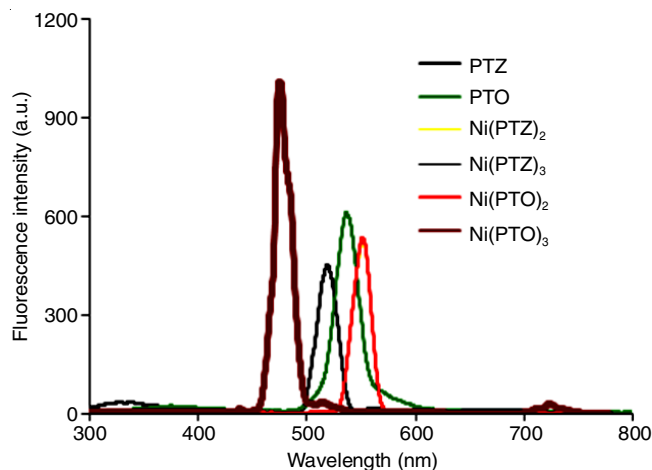
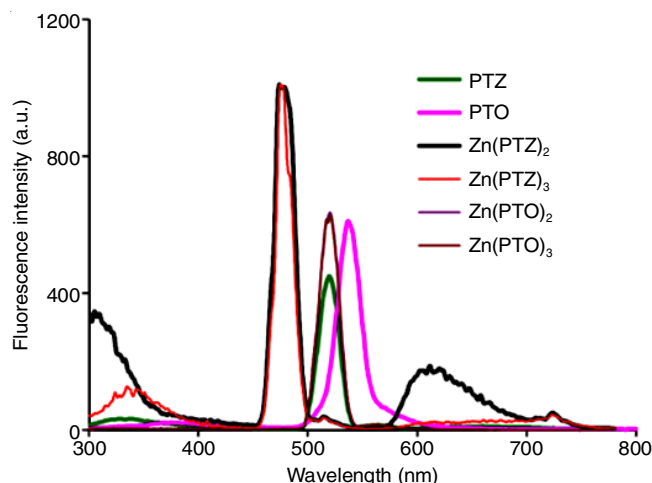
Fig. 1. Graphical representation of ligands and Fe³⁺ complexes

Cobalt and ruthenium complexes: The ligand Hpytz revealed enhanced luminescent property than that of Hpytzo, as there was a substantial alteration in the wavelength ($\lambda_{\text{emission}}$) of the former one which upsurges upto 576 nm. From Fig. 2, the complexation of cobalt with the respective ligands Hpytz and Hpytzo, *bis* and *tris*-complexes of cobalt [Co(pytz)₂(H₂O)₂], [Co(pytz)₃] (561 nm, 576 nm) with Hpytz flashed improved fluorescent property as rivalled to the *bis* and *tris*-complexes of cobalt [Co(pytzo)₂(H₂O)₂], [Co(pytzo)₃] (532 nm, 543 nm) with Hpytzo as enormous implication was perceived in the wavelength. Likewise, with ruthenium, Hpytz appearances uniform assessment in the wavelength of *bis*-complex of [Ru(pytz)₂(H₂O)₂] (522 nm), but bathochromic shift was perceived with Hpytzo [Ru(pytzo)₂(H₂O)₂] (543 nm).

Fig. 2. Graphical representation of ligands and Co²⁺ complexes

Nickel complexes: The luminescent property of Hpytz and Hpytzo was prophesied supplementary and conversely penetrating to these complexes [Ni(pytz)₂(H₂O)₂], [Ni(pytz)₃], [Ni(pytzo)₂(H₂O)₂] (553.5, 554, 554 nm) except *tris* complex of [Ni(pytzo)₃] (478 nm) with Hpytzo. Thus, bathochromic shift was perceived in the $\lambda_{\text{emission}}$ of these metal complexes with reverence to Hpytz and Hpytzo (522 nm, 540 nm). From Fig. 3, it was clearly clinched that the unsaturated or exceedingly conjugated pyridine tetrazole and pyridine tetrazole-N-oxide boosts absorption interface with competent emission pattern on immersion of light in the UV-region.

Zinc complexes: From Fig. 4, the $\lambda_{\text{emission}}$ value of [Zn(pytzo)₂(H₂O)₂], [Zn(pytzo)₃] (519 nm, 521 nm) with Hpytzo was initiated, implicated with a difference of 46 nm to that of [Zn(pytz)₂(H₂O)₂], [Zn(pytz)₃] (475 nm, 475 nm) with Hpytz that shows

Fig. 3. Graphical representation of ligands and Ni²⁺ complexesFig. 4. Graphical representation of ligands and Zn²⁺ complexes

a bathochromic shift was perceived with Hpytzo. The implementation of ligands with metals exclusively elucidates the ligand design or architecture, absorbed transfer energy and hence luminescence property of metal complexes.

From the above studies, pyridine tetrazole and pyridine tetrazole-N-oxide "antennae" boosts absorption interface and transfers energy to the metal center with the assistance of extremely unsaturated, conjugated pyridine and tetrazole rings which proficiently sensitizes the metal center for excitation and emission absorption spectra which stipulates a coloured visualization in the UV-visible region. Hence, the tetrazole derivatives with transition metals illustrates parallel marks as lanthanides(III) complexes do, but the productivity set up was even enhanced than lanthanides as well.

Conclusion

The two bidentate heteronuclear nitrogen, oxygen embracing ligands-pyridine tetrazole and pyridine tetrazole-N-oxide were integrated thermally by a traditional cycloaddition reaction. These ligands were merely expanded to stimulate the metal centre and introduced for escalation of the absorption interface concerning the visible region in enriched fashion as rivalled to usual dipicolinate analogues. These chelating ligands were complexed with transition metals (Fe³⁺, Co²⁺, Ni²⁺, Zn²⁺ and Ru³⁺) to custom coloured complexes and their emission spectra was witnessed which initiated in the incidence of these metals

that riveted light energy of unsaturated conjugated ligands, conveyed to the metal center to root excitation and generates the singlet¹, triplet³ states which upon emission crop low resolution coloured visualization in the UV-visible region of 4000-8000 Å. These complexes were structurally elucidated with IR, UV, ¹H NMR, MS and their luminescence-fluorescent property was analyzed at room temperature (298 K). Moreover, due to the less solubility and higher thermal stability of these transition metal complexes, such a property ponders them as kinetically stable species. Thus, enriched these metal complexes by concerning the succeeding applications in photonic devices, biomedical field and bioimaging (MRI).

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