"Super hybrid tridentate ligands": 4-substituted-2-(1-butyl-1*H*-1,2,3-triazol-4-yl)-6-(1*H*-pyrazol-1-yl)pyridine ligands coordinated to Fe(II) ions display above room temperature spin transitions†

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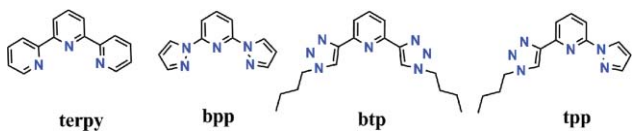
A series of novel "super hybrid tridentate ligands" based on (2-(1-butyl-1*H*-1,2,3-triazol-4-yl)-6-(1*H*-pyrazol-1-yl)pyridine (tpp) derivatives were synthesized. Their Fe(II) complexes display around ($T_{\frac{1}{2}}$ = 287 K) and above room temperature ($T_{\frac{1}{2}} \gg$ 375 K) spin transition temperatures.

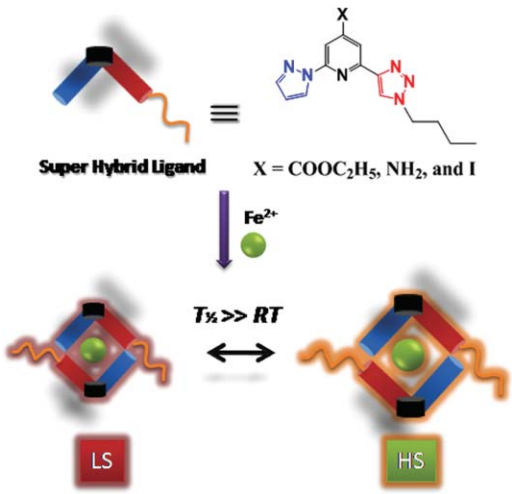
1. Introduction

A variety of iron(II) complexes are known to show reversible spin transition (ST) between two different spin states (high-spin, HS ↔ low-spin, LS) with respect to external stimulus such as temperature, light irradiation and pressure.[1–10a–d,11] Recently, there has been a growing interest in obtaining ST complexes displaying technologically appealing around and above room temperature ST due to their possible applications in molecular electronic devices and MRI contrast agents.[9,10a–d] Among spin transition compounds, 2,6-bispyrazolylpyridine (bpp) ligand derivatives coordinated to Fe(II) ion have been attracting considerable interest.[1h,i,10a–d,11] A recent new member to the club of tridentate ligands is 2,6-bis(1*H*-1,2,3-triazol-4-yl)pyridines (btp) synthesized using Click chemistry.[10g,12]

In the literature a number of reports are available on the syntheses of various tridentate ligands by combining various heterocyclic rings (*e.g.* pyridine, bipyridine, pyrazole, triazole, tetrazole, *etc.*).[1–11] These heterocyclic rings are very fascinating due to the tunable ligand properties they offer in a chelating ligand unit (*e.g.* terpy, bpp, btp, *etc.*).



Nevertheless, the preparation of novel hybrid tridentate ligands also involves serious organic synthetic protocols. We[10] and other group[11] have reported on the syntheses of several Fe(II) complexes using various bpp ligand derivatives exhibiting diverse ST temperatures. Recently, the groups of Flood and Hecht have independently reported the synthesis of $Fe(btp)_2 \cdot X_2$ complex.[12] In both reports the spin state of the Fe(II) ion was diamagnetic (S = 0; low-spin) due to the strong ligand field strengths of the btp units.[12] Motivated by our previous successful results on synthesizing several $Fe(bpp)_2 \cdot X_2$ (X = counter anion) type spin transition complexes,[10] in order to fine tune the ligand field strength of the btp unit, we have designed and prepared a new class of mixed tridentate ligand system (tpp) with three different coordination units by combining triazole, pyridine, and pyrazole units. We have used pyrazole unit, since in most cases, it forms switchable HS↔LS Fe(II) complexes due to its moderate ligand-field strength (Scheme 1).[1i–h,10,11]



Scheme 1 Representation of the components used for the synthesis of Fe(II) spin transition complexes (**I–III**).

In this article, we report a new synthetic protocol for the preparation of "super hybrid ligands" by connecting pyrazole, and triazole units to the 2,6-position of the pyridine ring to form a novel 2-(1-butyl-1*H*-1,2,3-triazol-4-yl)-6-(1*H*-pyrazol-1-yl)pyridine (tpp) derivatives (L_1–L_3). We also report the preparation of their Fe(II) compounds (**I–IV**), single crystal X-ray structures of **I**, **II** and **IV**, variable temperature magnetic properties of **I–III** displaying technologically attractive above room temperature ST and also the powder XRD studies of the Fe(II) complexes.

2. Result and discussion

2.1 Synthesis and characterization

For the synthesis of tpp ligand derivatives (L_1–L_3), a multi-step synthetic protocol from the low-priced citrazinic acid was developed (Scheme 2). Conversion of citrazinic acid into

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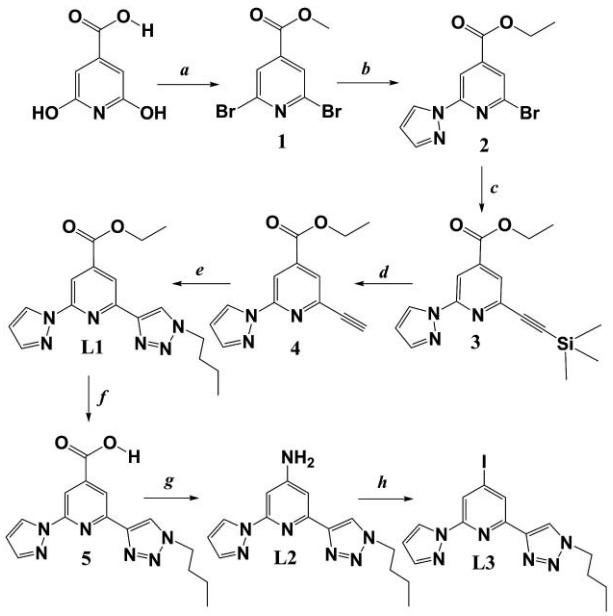
† Electronic supplementary information (ESI) available: Spectroscopic and experimental data for **1-5**, **L1-L3** and metal complexes **I**, **II** and **IV**. CCDC reference numbers 772647–772649. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00373e



Scheme 2 Syntheses of ligands ($\mathbf{L}_1$, $\mathbf{L}_2$ and $\mathbf{L}_3$), Reagents and conditions: (*a*) $PBr_3/Br_2/P_2O_5/CH_3OH$/18 h (*b*) (i) K/diglyme/pyrazole/3 d/110 °C (ii) HCl/C_2H_5OH/Conc. H_2SO_4 (*c*) TMSA/$[Pd(PPh_3)_4]$/CuI/THF/$(C_2H_5)_3N$/4 h/RT (*d*) KF/Methanol/30 min/RT (*e*) Butyl azide/Sodium ascorbate/Copper(II) sulfate/10 h/RT (*f*) LiOH/THF/HCl (2M) (*g*) $C_2O_2Cl_2/NaN_3$/TFA/K_2CO_3 (*h*) $NaNO_2$/Conc. HCl/aq. KI.

2,6-dibromo-isonicotinicacidmethylester **1** was carried out as reported. The mononucleophilic substitution of the pyrazole unit on **1** was successfully carried out to isolate ethyl-2-bromo-6-(1*H*-pyrazol-1-yl)isonicotinate **2** in 74% yield. Transformation of compound **2** into **3** was achieved *via* Sonogashira coupling reaction conditions by using trimethylsilylacetylene (TMSA) in $(Et)_3N$/THF solvents using $Pd(PPh_3)_4$ catalyst to prepare compound **3** in 78% yield. Deprotection of **3** in the presence of KF/MeOH gave the Click precursor **4** in 99% yield. Formation of triazole units on **4** was realized by employing Click reaction conditions *i.e.*, by using $Cu(SO_4)_2$ and sodium ascorbate in the presence of butylazide. This Click reaction provided an ester derivative of btp ligand $\mathbf{L}_1$ in a quantitative 99% yield. The saponification reaction readily converted compound $\mathbf{L}_1$ into its carboxylic acid derivative. Furthermore sequential conversion of the carboxylic acid into acyl azide followed by a thermal Curtius rearrangement and succeeding hydrolysis of the trifluoroacetamide provided the amino derivative $\mathbf{L}_2$ (74% yield). From $\mathbf{L}_2$, the 4-iodo derivative $\mathbf{L}_3$ was synthesized by diazotization and reaction with KI in a modest 40% yield. The ligands were characterized by employing NMR (^{1}H and ^{13}C), LC-MS, FTIR and elemental analysis techniques. The mononuclear iron(II) complexes $[Fe^{II}(\mathbf{L}_1)_2](ClO_4)_2$ (**I**) and $[Fe^{II}(\mathbf{L}_1)_2](BF_4)_2$ (**II**), were synthesized from $\mathbf{L}_1$ by using the respective Fe^{II} salts in acetonitrile. Complexes $[Fe^{II}(\mathbf{L}_2)_2](ClO_4)_2$ (**III**) and $Fe^{II}(\mathbf{L}_3)_2](ClO_4)_2$ (**IV**) were prepared from ligands $\mathbf{L}_2$ and $\mathbf{L}_3$, respectively by using $Fe^{II}(ClO_4)_2$. Single crystals suitable for XRD studies were obtained in a quantitative yield by diffusing diisopropylether into an acetonitrile solution of complexes under N_2 atmosphere at RT. After a week, wine-red color crystals of complexes **I–II** and yellow color crystals of complex **IV** were obtained.

2.2. Crystallographic studies

The single crystal X-ray diffraction crystallographic parameters, and selected bond lengths are given in Table 1 and Table 2. The crystallographic molecular structures of the octahedral $Fe^{(II)}N_6$ type complexes **I**, **II** and **IV** are displayed in Fig. 1 and 2. At 100 K, complex **I** displayed an orthorhombic *Pbcn* symmetry with four complex molecules per unit cell. The asymmetric units in **I** consist of the $[Fe(\mathbf{L}_1)_2]$ cation, two corresponding ClO_4 anions and one CH_3CN solvate molecule. The average Fe–N bond distance (1.944 Å) obtained at 100 K showed the LS state of the Fe(II) cation. Interestingly, the Fe–N bond distances decreased in the following order: $Fe(1)–N(4)_{pyrazole}$ = 1.974(3) Å > $Fe(1)–N(1)_{triazole}$ = 1.952(3) Å > $Fe(1)–N(2)_{pyridine}$ = 1.906(3) Å. The variation in the Fe–N bond lengths clearly indicated the metal ion biting ability of the ring nitrogens in the following order: pyrazole > triazole > pyridine. Complex **II** revealed a monoclinic $P2_1/n$ symmetry. The asymmetric units in **II** consist of the $[Fe(\mathbf{L}_1)_2]$ cation, two corresponding BF_4 anions and one CH_3CN molecule. At 100 K, the average Fe–N bond distance (1.938 Å) signified the LS state of the Fe(II) cation. Moreover, in comparison to complex **I**, a notable variation in the $Fe–N_{pyrazole}$ and $Fe–N_{triazole}$ bond lengths was found with no change in the $Fe–N_{pyridine}$ distances at 100 K. The increasing order of the Fe–N bond distances are as follows: $Fe(1)–N(8)_{pyridine}$ = 1.905(3) Å < $Fe(1)–N(2)_{pyridine}$ = 1.907(3) Å, < $Fe(1)–N(11)_{triazole}$ = 1.947(3) Å < $Fe(1)–N(4)_{pyrazole}$ = 1.947(3) Å, $Fe(1)–N(1)_{triazole}$ = 1.959(3) Å < $Fe(1)–N(9)_{pyrazole}$ = 1.967(3) Å. Complex **IV** revealed a triclinic $P\bar{1}$ symmetry. The asymmetric units in **IV** consist of the

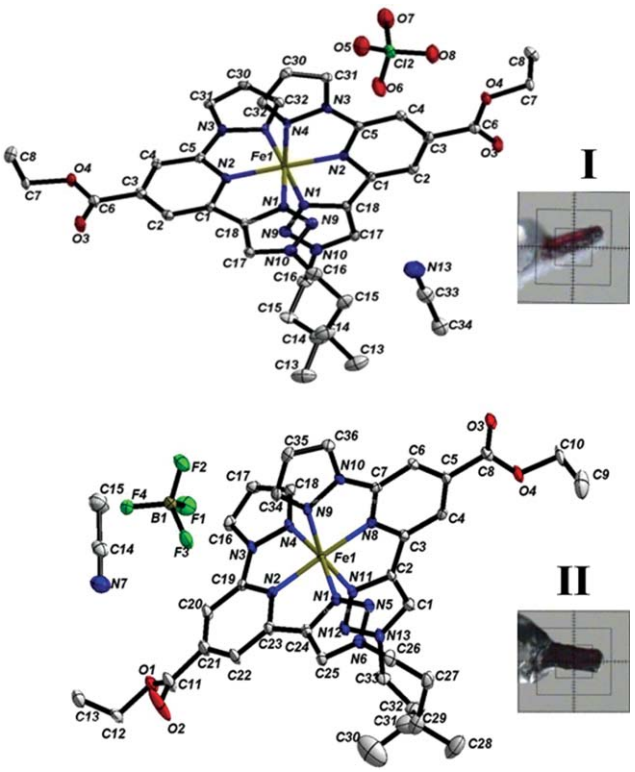


Fig. 1 ORTEP view of low-spin complexes $[Fe^{II}(\mathbf{L}_1)_2](ClO_4)_2{\cdot}CH_3CN$ (**I**) and $[Fe^{II}(\mathbf{L}_1)_2](BF_4)_2{\cdot}CH_3CN$ (**II**) (50% probability thermal ellipsoids) at 100 K. All hydrogen atoms and remaining counter ions are omitted for clarity. The right side photographs show the low-spin state wine-red color of the single crystals **I** and **II** at 100 K.

Table 1 Crystallographic parameters of complexes **I**, **II** and **IV**

	$[Fe^{II}(L_1)_2](ClO_4)_2\cdot CH_3CN$ (**I**)	$[Fe^{II}(L_1)_2](BF_4)_2\cdot CH_3CN$ (**II**)	$[Fe^{II}(L_2)_2]\cdot(ClO_4)_2$ (**IV**)
Formula	$C_{38}H_{46}N_{14}O_{12}Cl_2Fe$	$C_{36}H_{44}N_{13}O_4B_2F_8Fe$	$C_{28}H_{34}Cl_2FeN_{14}O_8$
Formula weight	1017.64	952.30	821.44
Crystal colour	Wine red	Wine red	yellow
T/K	100(2) K	100(2) K	100(2) K
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system,	Orthorhombic	Monoclinic	Triclinic
Space group	*Pbcn*	$P2_1/n$	$P\bar{1}$
a, (Å)	21.3932(19)	12.8665(11)	11.9124(13)
b, (Å)	13.5171(12)	20.8850(18)	12.0189(13)
c, (Å)	15.5665(14)	15.9996(14)	14.8282(16)
α, (deg.)	90	90	66.581(2)
β, (deg.)	90	93.515(2)	76.138(2)
γ, (deg.)	90	90	62.629(2)
V, (Å^3)	4501.4(7)	4291.3(6)	1725.8(3)
Z, ρ_c. (mg m^{-3})	4, 1.502	4, 1.474	2, 1.581
μ (Mo, Kα) (mm^{-1})	0.531	0.442	0.663
F(000)	2112	1960	848
Crystal size/mm	$0.38\times0.16\times0.12$	$0.38\times0.18\times0.10$	$0.32\times0.22\times0.04$
theta range for the data collection (deg.)	1.78 to 26.09	1.61 to 28.31	1.50 to 26.00
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0754$, w$R_2 = 0.1397$	$R_1 = 0.0901$, w$R_2 = 0.1906$	$R_1 = 0.0873$, w$R_2 = 0.1783$
R indices (all data)	$R_1 = 0.0855$, w$R_2 = 0.1439$	$R_1 = 0.1114$, w$R_2 = 0.1996$	$R_1 = 0.1241$, w$R_2 = 0.1948$
GoF on F^2	1.264	1.201	1.119

Table 2 Selected bond lengths of complexes **I**, **II** and **IV**

Bond distances (Å)	**$[Fe^{II}(L_1)_2](ClO_4)_2\cdot CH_3CN$ (I)**
Fe(1)–N(2)	1.906(3)
Fe(1)–N(4)	1.974(3)
Fe(1)–N(1)	1.952(3)
Bond distances (Å)	**$[Fe^{II}(L_1)_2](BF_4)_2\cdot CH_3CN$ (II)**
Fe(1)–N(8)	1.905(3)
Fe(1)–N(4)	1.907(3)
Fe(1)–N(9)	1.967(3)
Fe(1)–N(5)	1.947(3)
Fe(1)–N(3)	1.959(3)
Fe(1)–N(11)	1.907(3)
Bond distances (Å)	**$[Fe^{II}(L_2)_2](ClO_4)_2$(IV)**
Fe(1)–N(9)	2.204(5)
Fe(1)–N(4)	2.131(4)
Fe(1)–N(1)	2.173(4)
Fe(1)–N(2)	2.186(4)
Fe(1)–N(8)	2.202(5)
Fe(1)–N(11)	2.122(4)

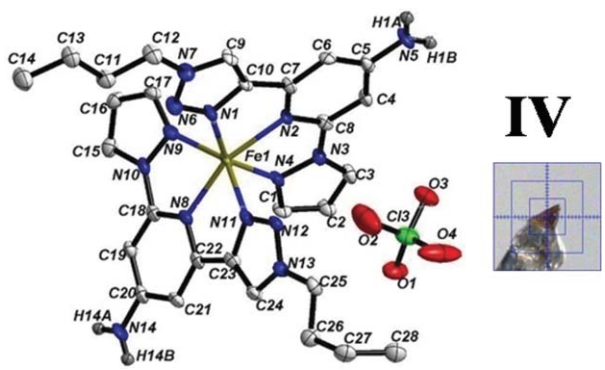


Fig. 2 ORTEP view of the high-spin complex $[Fe^{II}(L_2)_2](ClO_4)_2$ (**IV**) (50% probability thermal ellipsoids) at 100 K. All hydrogen atoms and remaining counter ions are omitted for clarity. The right hand photograph shows the high-spin state orange color of the single crystal **IV** at 100 K.

$[Fe(L_2)_2]$ cation and two corresponding ClO_4 anions. The Fe–N bond lengths Fe(1)–N(8) = 2.122(4) Å, Fe(1)–N(2) = 2.131(4) Å, Fe(1)–N(1) = 2.173(4) Å, Fe(1)–N(11) = 2.186(4) Å, Fe(1)–N(9) = 2.202(5) Å and Fe(1)–N(4) = 2.204(5) Å clearly showed the HS state of the iron(II) cation even at 100 K, which is in line with the yellow colour of the crystals. Unfortunately, we were unable to get single crystals of complex **III** suitable for X-ray diffraction, but the wine-red color of the crystals clearly indicated the LS state of the Fe(II) ion even at room temperature.

2.3. Bulk magnetic properties

The temperature dependent magnetic susceptibilities of powdered polycrystalline samples of **I–III** were measured on a quantum design vibrating sample magnetometer (VSM-SQUID) set-up in the temperature range of 375–4 K at continuous heating (↑) and cooling (↓) cycle with an applied DC magnetic field of 0.1 T (Fig. 3). In order to improve the accuracy of the measurements, many data points were collected at 0.1 K intervals. Compound **I** revealed a reversible ST behavior with a wide hysteresis loop. At 375 K the product of the molar magnetic susceptibility and temperature (χT) of compound is 3.8 emu K mol^{-1}, which is an expected value for a HS iron(II) ion in the S = 2 state. The temperature dependent magnetic behaviour showed the involvement of two types of ST behaviour: (i) upon cooling the χT value of the HS state abruptly decreased down to 2.5 emu K mol^{-1} at *ca.* 260 K; (ii) followed by a steady but gradual decrease of the magnetic moment reaching the minimum value of *ca.* 1.0 emu K mol^{-1} at 4 K displaying an incomplete ST. Calculation of the number of fraction (f_a) involved in the first steep transition showed that *ca.* 45% of the molecules undergo abrupt ST behaviour with the ST temperatures of 292 K for the heating ($T_{\frac{1}{2}}\uparrow$) and 282 K for the cooling ($T_{\frac{1}{2}}\downarrow$) mode cycle with 10 K wide thermal hysteresis loop. Importantly, the observed $T_{\frac{1}{2}}$ value of **I** is very close to room temperature *i.e.* 287 K. The remaining fraction (f_b = 55%) of the molecules displayed a gradual and incomplete ST

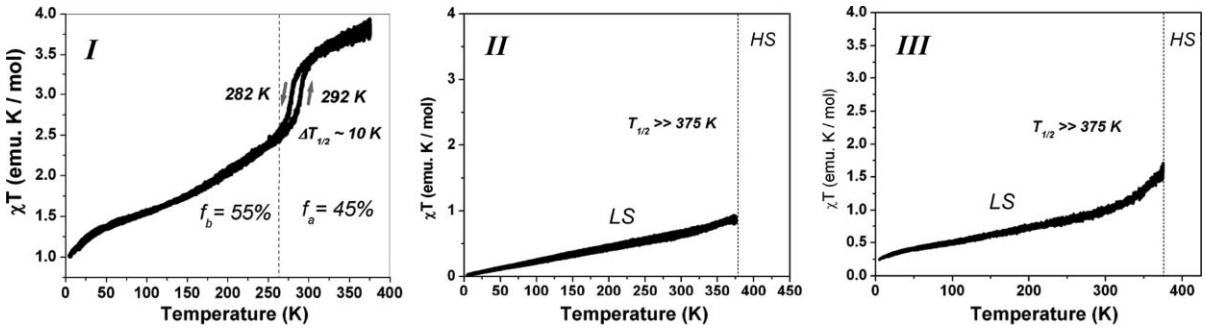


Fig. 3 The χT *vs.* T plot for the complexes **I–III** measured in the temperature range of 4–375 K in the (↓) cooling and (↑) heating mode cycle with an applied magnetic field of 0.1 T.

behaviour without reaching the minimum magnetic moment value corresponding to the LS state. In contrary, compound **II** showed a near completion of the ST event even above room temperature. At 375 K, the χT value of 0.8 emu K mol^{-1}. Upon further cooling the magnetic moment decreased gradually and reached a lowest value of *ca.* 0.02 emu K mol^{-1} at 5 K indicating the completion of the ST event. Complex **III** also displayed a similar ST trend as complex **II**. The ST event was almost completed at room temperature and below this temperature the χT value gradually decreased down to 4 K to reach a minimum χT value of *ca.* 0.25 emu K mol^{-1}. The χT value steeply increased above 350 K and only reached the minimum value of *ca.* 1.5 emu K mol^{-1} at 375 K. This behaviour clearly demonstrated that the HS state and the ST temperature is somewhere above 375 K for both **II** and **III**. Furthermore the ST properties of complexes **I** and **II** are independent of lattice-solvents, since the powdered crystalline sample used for the magnetic studies showed no characteristic bands for the lattice-acetonitrile molecules in the FTIR data (ESI,† Figure S19 and S20).[10c] Additionally, the experimental powder XRD data of powdered samples of **I** and **II** showed different diffraction peak patterns in comparison to their calculated data (obtained from their single crystal data). This further confirmed the loss of lattice-acetonitrile molecules from the crystals during the preparation of the powdered samples (ESI,† Figure S1 and S2).

3. Conclusions

We have demonstrated the synthesis of a family of novel "super hybrid tridentate ligand derivatives" containing pyridine, pyrazole and triazole rings ($\mathbf{L_1}$–$\mathbf{L_3}$). These hybrid btp ligands were efficiently used to prepare iron(II) complexes **I–III** exhibiting around and above room temperature ST temperatures.

4. Experimental section

4.1 Materials

The materials citrazinic acid, $[Pd(PPh_3)_4]$, triflouroacetic acid, 1-bromo butane, $Fe(ClO_4)_2{\cdot}xH_2O$ and $Fe(BF_4)_3{\cdot}6H_2O$ were purchased from Aldrich USA. Sodium azide, KI, K_2CO_3, ethanol, $NaNO_2$, sodium thiosulfate and diethylether were procured from Merck, India. Oxalylchloride, PBr_3, iodine, Cu(I)I, $NaHCO_3$ and trimethylsilyl acetylene were obtained from Avra Snthesis, Hyd and Acros USA respectively. Br_2 was purchased from Spectrochem Pvt. Ltd., Mumbai. Column chromatography was performed using Merck silica gel (particle size 100–200 mesh). THF, triethylamine, benzene, dichloromethane, hexane, petroleum ether, $CHCl_3$ and methanol solvents were obtained from Finar Chemicals Limited, Ahmadabad, India. The solvents were used as dried and distilled for reactions. All solvent were used after distillation.

4.2 Instrumental methods

^{1}H and ^{13}C NMR spectroscopic data were recorded on a Bruker DPX 400 spectrometer with solvent proton as internal standard ($CDCl_3$-d_1 = 7.26). Deuterated solvent $CDCl_3$-d_1 was obtained from Aldrich. LC mass spectrometry was performed on a Shimadzu LCMS-2010A mass spectrometer. IR spectra were recorded on JASCO FT/IR-5300. Elemental analyses were recorded on a Thermo Finnigan Flash EA 1112 analyzer. For thin-layer chromatography (TLC), silica gel plates Merck 60 F254 were used and compounds were visualized by irradiation with UV light. Magnetic susceptibilities were measured in the temperature range 375–4 K on a Quantum Design VSM-SQUID operating at 0.1 Tesla. Single Crystal-XRD data for complexes **I**, **II** and **IV** were collected on a Bruker SMART CCD Diffractometer with Mo-Kα (λ = 0.71073 Å) radiation. Data reduction was performed using Bruker SAINT software. Structures were solved and refined using SHELXL-97 with anisotropic displacement parameters for non-H atoms.

4.3 Syntheses of Ligands (L_1–L_3) and their Fe(II) complexes

Methyl-2,6-dibromoisonicotinate (1). Compound (**1**) was prepared according to literature procedure.[13]

Ethyl-2-bromo-6-(1*H*-pyrazol-1-yl)isonicotinate (2). In a clean and dry 250 mL three-neck flask, small pieces of K metal flakes (0.9, 20 mmol, 1.1 eq) were dispersed completely in diglyme (100 mL) by vigorously stirring the mixture for 1 h under N_2 atmosphere. To this solution pyrazole (1.4 g, 20.0 mmol, 1.2 eq) was added slowly to minimize the violent reaction that occurred due to the formation of potassium salt of pyrazole. The mixture was stirred for about 30 min at 60 °C until all the K was reacted to pyrazole to afford a white turbid solution. Methyl-2,6-dibromoisonicotinate **1** (5.2 g, 16.8 mmol, 1.0 eq) was added into this reaction mixture and heated at 110 °C for 3 d under N_2 atmosphere. The mixture was poured into water and neutralized

by conc. HCl (10 mL), the white precipitate that formed was filtered and dried. (If precipitate forms upon pouring into water, no neutralization is required).

The white precipitate was dissolved in 50 mL of ethanol and 3 mL conc. H_2SO_4 and put under reflux for 4 h. The mixture was poured into a 50 mL of water, extracted with chloroform (2 × 50 mL) and washed with brine solution (2 × 10 mL). The collected organic layers were combined and dried over $MgSO_4$ and the chloroform was evaporated on a vacuum evaporator to obtain a pale yellow residue, which upon washing with pet-ether gave compound **2** as white powder in 74% yield (3.7 g). Anal. Calcd. for $C_{11}H_{10}N_3O_2Br$: C, 44.62; H, 3.40; N, 14.19. Found: C, 44.59; H, 3.44; N, 14.16. LC–MS *m*/*z* calcd. 296.1, found 295.8. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.53 (d, 1H), 8.43 (s, 1H), 7.88 (d, 1H), 7.76 (s, 1H), 6.49–6.47(m, 1H), 4.43 (q, 2H, ^3J = 7.04 Hz, 1″), 1.42 (t, 3H, ^3J = 7.18 Hz, 2″). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 163.2, 152.6, 143.03, 142.6, 140.4, 127.7, 124.6, 110.7, 108.5, 62.3, 14.1.

Ethyl-2-(1*H*-pyrazol-1-yl)-6-((trimethylsilyl)ethynyl)isonicotinate (3). Compound **2** (2.8 g, 9.5 mmol), CuI (0.050 g) and $[Pd(PPh_3)_4]$ (0.60 g, 0.05 mmol) were discharged in a clean and dry 250 mL three-neck round bottom flask. The flask was put under vacuum followed by flushing with argon gas for 2–3 times. To this dry THF (15 mL) and triethylamine (35 mL) were added. Trimethylsilylacetylene (TMSA) (2.0 mL, 14.2 mmol, 1.5 eq) was added drop wise within 20 min. On addition of TMSA, the yellow color turbid solution changed to deep brown color. The progress of reaction was monitored by TLC (silica, 1 : 19 ratio of ethylacetate: pet-ether). After disappearance of the starting material the reaction mixture was filtered and washed with hexane or THF. The filtrate was evaporated by rotary evaporator and the crude reaction mixture was purified by column chromatography (silica, 1 : 19 ratio of ethyl acetate: pet-ether) to get a pale yellow crystalline solid of **3** in 78% yield (2.32 g). Anal. Calcd for $C_{16}H_{19}N_3O_2Si$: C, 61.31; H, 6.11; N, 13.41. Found: C, 61.38; H, 6.20; N, 13.45. LC–MS *m*/*z* calcd 313.1, found 313.8. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.65 (d, 1H), 8.48 (d, 1H), 7.9 (s, 1H), 7.78 (s, 1H), 6.50–6.49 (m, 1H), 4.46 (q, 2H, ^3J = 7.52 Hz, 1″), 1.45 (t, 3H, ^3J = 7.45 Hz, 2″), 0.33 (s, 9H, 1‴). ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 163.95, 152.1, 142.7, 142.6, 142.0, 127.7, 124.4, 111.8, 108.2, 102.6, 96.7, 62.1, 14.2, –0.37.

Ethyl-2-ethynyl-6-(1*H*-pyrazol-1-yl)isonicotinate (4). Compound **3** (2.0 g, 6.4 mmol, 1.0 eq) was loaded in a 250 ml two-neck round bottom containing degassed methanol. To this solution, KF (0.75 g, 12.7 mmol, 2.0 eq) was added under N_2 atmosphere. After 30 min, the completion of the reaction was confirmed by TLC (silica, 1 : 9 ratios of ethyl acetate: pet-ether) and reaction mixture was concentrated in vacuo. The obtained solid compound was redissolved in chloroform and filtered. The filtrate was evaporated to get desired compound (**4**) as white powder > 99% yield (1.54 g). Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.68; H, 4.64; N, 17.39. LC–MS *m*/*z* calcd 241.1, found 241.7. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.61 (d, 1H), 8.51 (s, 1H), 7.91 (s, 1H), 7.78 (s, 1H), 6.50-6.47(m, 1H), 4.44 (q, 2H, ^3J = 7.20 Hz, 1″), 3.26 (s, 1H, 1‴), 1.43 (t, 3H, ^3J = 6.94 Hz, 2″), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 163.9, 152.3, 142.8, 141.3, 127.6, 126.3, 124.4, 112.4, 108.4, 81.8, 78.4, 62.3, 14.22.

Ethyl-2-(1-butyl-1*H*-1,2,3-triazol-4-yl)-6-(1*H*-pyrazol-1yl)isonicotinate (L_1). Compound **4** (1.0 g, 4.14 mol, 1.0 eq) was discharged in a clean 100 mL one-neck round bottom flask containing 30 mL of ethanol–water (1 : 1). After 5 min butyl azide (0.6 mL, 4.98 mmol, 1.1 eq) and sodium ascorbate (0.1 g, 0.45 mmol, 10 mol%) were added. To this aqueous solution a freshly prepared $CuSO_4$ (0.05 g, 0.21 mmol, 5 mol%) was added, immediately a sharp color change from pale-yellow to intense wine–red color was observed, during the course of the reaction the intense of color turned to pale–orange. The progress of the reaction was monitored by TLC (silica, 1 : 19 ratio of methanol : DCM). The crude reaction mixture was concentrated on a vacuum evaporator. The obtained solid residue was redissolved in chloroform and passed through a short celite plug and resultant solution was concentrated. The obatined pale yellow residue was washed with pet-ether to isolate a yellow solid of L_1 in 99% yield (1.57 g). Anal. Calcd for $C_{17}H_{20}N_6O_2$: C, 59.99; H, 5.92; N, 24.69. Found: C, 59.96; H, 5.94; N, 24.65. LC–MS *m*/*z* calcd 383.6, found 383.5. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.56 (d, 1H), 8.55 (d, 1H), 8.38 (s, 1H), 8.14 (s, 1H), 7.74 (s, 1H), 6.45–6.44 (m, 1H), 4.49-4.43 (m, 4H, 1″,1‴), 1.99 (q, 2H, ^3J = 7.35 Hz, 2‴), 1.46–1.40 (m, 5H, 2″, 3‴), 1.00 (t, 3H, ^3J = 7.33 Hz, 4‴), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 164.4, 151.8, 151.8, 149.9, 141.2, 142.8, 141.7, 127.05, 122.4, 116.9, 110.9, 108.0, 62.0, 50.3, 32.2, 19.7, 14.3, 13.4

2-(1-butyl-1*H*-1,2,3-triazol-4-yl)-6-(1*H*-pyrazol-1-yl)isonicotinicacid (5). Compound L_1 (1.3 g, 3.4 mmol, 1.0 eq) was dissolved in THF (25 mL) and a solution of LiOH (0.11 g, 4.4 mmol, 1.3 eq) in 75 mL of water was added to it under N_2. After stirring 20 min at RT, THF was removed on a rotary evaporator. The solution was cooled in an ice bath and 2 M HCl (pH = 2–3) (0.56 ml, 6.24 mmol) was added drop-wise until a white precipitate appeared. The mixture was then stirred for 1 h. The white powder that was formed was collected by vacuum filtration and it was dried to get compound **5** in 98% yield (1.3 g). Anal. Calcd for $C_{17}H_{16}N_6O_2$: C, 57.68; H, 5.16; N, 26.91. Found: C, 57.71; H, 5.20; N, 26.86. LC–MS *m*/*z* calcd 312.1, found 312.6. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.69 (s, 1H), 8.26 (s, 1H), 8.02 (s, 1H), 7.82 (s, 1H), 6.53 (m, 1H), 4.49 (t, 2H, ^3J = 7.02 Hz, 1‴), 2.01 (q, 2H, ^3J = 7.46 Hz, 2‴), 1.45 (m, 2H, ^3J = 7.89 Hz, 3‴), 1.02 (t,3H, ^3J = 7.02 Hz, 4‴), ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 165.9, 149.3, 147.1, 142.6, 127.4, 117.8, 111.8, 108.1, 50.6, 32.2, 19.7, 13.5.

2-(1-butyl-1*H*-1,2,3-triazol-4-yl)-6-(1*H*-pyrazol-1-yl)pyridine-4-amine (L_2). Compound L_1 (1.8 g, 5.77 mmol, 1.0 eq) was dissolved in a mixture of THF (15 mL)/CH_2Cl_2 (45 mL) solvents. To this $(COCl)_2$ (0.84 g, 0.6 mL, 1.22 eq) was added slowly while stirring under N_2 to reduce gas evolution. After stirring 4 h at RT, the solvent was removed. The residue was dissolved in dry acetone (30 mL) and added to a solution of NaN_3 (1.57 g, 24.14 mmol, 4.32 eq) in water (30 mL). The residue was extracted immediately with ether (2 × 75 mL) and dried over $MgSO_4$ followed by solvent evaporation under vacuum. The obtained solid was dissolved in dry benzene (50 mL) and trifluoroacetic acid (TFA) (1.0 g, 0.7 mL, 8.65 mmol, 1.50 eq) was added to it. After stirring 16 h at reflux, the mixture was cooled and the benzene was removed by vacuum evaporation. The residue was dissolved in methanol (50 mL) and K_2CO_3 (1.91 g, 14.4 mmol, 2.17 eq) was added to it. The mixture

was stirred vigorously for 8 h at RT $\frac{3}{4}$ of the methanol was removed and water (100 mL) was added to it. The mixture was cooled in an ice bath for 2 h to get compound as white precipitate which upon filtration gave white powder of $\mathbf{L}_2$ in 74% yield (1.2 g). Anal. Calcd for $C_{14}H_{17}N_7$: C, 59.35; H, 6.05; N, 34.60. Found: C, 59.39; H, 6.02; N, 34.58. LC–MS *m/z* calcd 283.2, found 283.4. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.60 (d, 1H), 8.11(s, 1H), 7.73 (d, 1H), 7.39 (s, 1H), 7.19 (s, 1H), 6.45–6.44 (m, 1H), 4.53 (s, 2H, $-NH_2$), 4.42 (t, 2H, ^3J = 7.12 Hz, 1‴), 1.94 (q, 2H, ^3J = 7.62 Hz, 2‴), 1.47–1.27(m, 2H, ^3J = 7.72 Hz,3‴), 0.98 (t, 3H, ^3J = 7.02 Hz,4‴).^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 155.6, 152.4, 149.3, 148.1, 141.5, 127.0, 122.0, 107.1, 103.9, 96.2, 50.2, 32.2, 19.7, 13.4.

2-(1-butyl-1*H*-1,2,3-triazol-4-yl)-4-iodo-6-(1*H*-pyrazol-1-yl)-pyridine ($\mathbf{L}_3$). Compound $\mathbf{L}_2$ (0.72 g, 2.54 mmol, 1.0 eq) was suspended in conc. HCl (20 mL) and stirred for 24 h at RT. The mixture was cooled in an ice bath and $NaNO_2$ (0.35 g, 5.1 mmol, 2.0 eq) dissolved in a minimum amount of water (2 mL) was added drop-wise. To this KI (1.05 g, 6.35 mmol, 2.5 eq) in water (5 mL) was slowly added and the solution was stirred for 5 min. THF (10 mL) was added into the reaction mixture and the solution was neutralized by adding solid $NaHCO_3$. The product was extracted with diethylether (2 × 50 mL) and washed with $Na_2S_2O_3$ solution. The collected organic layers were combined, dried over $MgSO_4$ and the solvent was evaporated by vacuum evaporator to afford a white color product $\mathbf{L}_3$ in 40% yield (0.4 g). Anal. Calcd for $C_{14}H_{15}N_6I$: C, 42.65; H, 3.84; N, 21.32. Found: C, 42.60; H, 3.86; N, 21.29. LC–MS *m/z* calcd. 394.2, found 394.1. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 8.58 (d, 1H), 8.46(d, 1H), 8.36 (d, 1H), 8.15(s, 1H), 7.77 (d,1H), 6.5–6.49 (m, 1H), 4.44 (t, 2H, ^3J = 7.21 Hz, 1‴), 1.96 (q, 2H, ^3J = 7.6 Hz, 2‴), 1.48–1.39 (m, 2H, ^3J = 7.32 Hz,3‴), 0.99 (t, 3H, ^3J = 7.02 Hz, 4‴).^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ (ppm): 150.9, 149.1, 146.5, 133, 142.5, 127.0, 126.5, 122.4, 120.4, 108.0, 50.3, 32.2, 19.7, 13.4. FT-IR (KBr) ν in cm^{-1}: 3439, 3352, 3240, 3080, 2959, 2930, 2872, 1645, 1618, 1554, 1469, 1427, 1402, 1263, 1229, 1198, 1166, 1086, 1045, 984,922, 881,800, 752, 669, 625, 440.

$[Fe^{II}(L_1)_2](ClO_4)_2\cdot CH_3CN$ (I). In a 100 mL Schlenk tube, a solution of $\mathbf{L}_1$ (103 mg, 0.33 mmol) and $Fe(ClO_4)_2\cdot 6H_2O$ (40 mg, 0.15 mmol) in acetonitrile (15 mL) was heated at 80 °C for 6 h. The reaction mixture was cooled to RT and 80 mL of diisopropyl ether was added to it under a N_2 flow to yield a red–orange precipitate of the complex (**I**). Wine–red colour crystals were grown from diffusing the diisopropyl ether into an acetonitrile solution of the complex (**I**) under N_2. Yield *ca.* 65 mg. Anal. calcd for $C_{38}H_{46}Cl_2FeN_{14}O_{12}$: C, 44.85; H, 4.56; N, 19.27%. Found: C, 44.68; H, 4.61; N, 19.12%. FT-IR (KBr) ν in cm^{-1}: 3117, 2963, 2932, 2872, 1726, 1631, 1562, 1524, 1481, 1408, 1263, 1211, 1101, 768, 623, 536.

$[Fe^{II}(L_1)_2](BF_4)_2\cdot CH_3CN$ (II). A similar procedure as for **I** was applied using $Fe(BF_4)_2\cdot 6H_2O$ (50 mg, 0.15 mmol). Crystallization gave wine-red crystalline blocks (Yield *ca.* 55 mg). Anal. calcd for, $C_{40}H_{30}B_2FeN_{14}O_8F_8$: C, 45.99; H, 4.67; N, 19.76%. Found: C, 45.78; H, 4.58; N, 19.88%. FT-IR (KBr) ν in cm^{-1}: 3130, 2963, 2934, 2876, 1732, 1632, 1562, 1528, 1481, 1441, 1408, 1373, 1288, 1254, 1209, 1055, 966, 912, 860, 769, 611, 523.

$[Fe^{II}(L_3)_2](ClO_4)_2\cdot CH_3OH$ (III). In a 100 mL Schlenk tube, a solution of $\mathbf{L}_3$ (100 mg, 0.26 mmol) and $Fe(ClO_4)_2\cdot 6H_2O$ (33 mg, 0.13 mmol) in methanol (25 mL) was heated at 80 °C for 6 h. The reaction mixture was cooled to RT and 100 mL of diisopropyl ether was added to the flask under a N_2 atmosphere to yield wine–red precipitate of the complex (**III**). Wine–red coloured crystals were grown from diffusing the diisopropyl ether into a methanol solution of the complex (**III**) under N_2. Elemental analysis calcd for, $C_{29}H_{33}Cl_2FeI_2N_{12}O_9$: C, 34.16; H, 3.12; N, 17.43%. Found: C, 34.25; H, 3.26; N, 17.36%. FT-IR (KBr) ν in cm^{-1}: 3511, 3117, 3081, 2961, 2866, 1614, 1548, 1474, 1408, 1254, 1213, 1088, 1011, 845, 752, 623.

$[Fe^{II}(L_2)_2](ClO_4)_2$ (IV). A similar procedure as for **I** was applied using $Fe(ClO_4)_2\cdot 6H_2O$ (50 mg, 0.15 mmol). Crystallization yielded yellow color crystals (Yield *ca.* 40 mg). FT-IR (KBr) ν in cm^{-1}: 3462, 3352, 3225, 3127, 2963, 1636, 1526, 1493, 1408, 1277, 1215, 1088, 1007, 972, 768, 623

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