Supporting Information

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Synthesis of heteroleptic terpyridyl complexes of Fe(II), Ru(II): Optical and electrochemical studies

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Solvents and reagents

2-acetyl pyridine, pyridine-4-carboxaldehyde, p-nitro-benzaldehyde, p-tolualdehyde, $RuCl_3.3H_2O$, $FeCl_2$ and ammonium hexafluorophosphate were purchased from Sigma-Aldrich. n-tetrabutyl ammonium hexafluorophosphate ($TBAP_6$) was purchased from Alfa-Aesar and it was recrystallized before use. All the deuterated solvents such as $CDCl_3$, DMSO-d_6 and CD_3CN were purchased from Sigma-Aldrich and stored as directed. Benzaldehyde, aqueous ammonia (30%), iodine, ammonium acetate, 10% Pd-C, hydrazine monohydrate, triethyl amine and hydrogen peroxide (30%) were purchased from s. d. fine chemicals (Mumbai, India). Other chemicals were used as received without any further purification. Solvents (AR grade) were purchased from Merck (Mumbai, India) and s. d. fine chemicals and used after distillation. The common solvents were distilled following the reported methods.[S1] Chloroform and dichloromethane were distilled over anhydrous $CaCl_2$ using laboratory distillation unit. Methanol and ethanol were distilled using two steps: (i) the alcohols have been refluxed using solid I_2 and activated over magnesium turnings, (ii) the solvents were distilled and stored over molecular sieves. THF was distilled using benzophenone and sodium metal and stored over molecular sieves under N_2 atmosphere.

Physical measurements

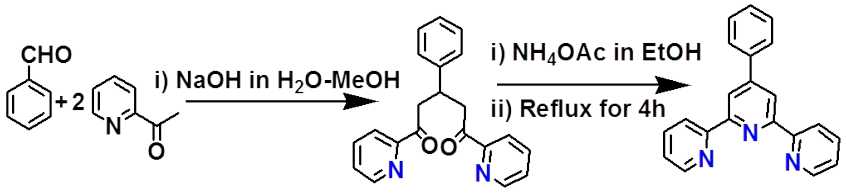
UV-vis spectra were recorded at room temperature on a double beam JASCO (Model V-670) spectrophotometer. One cm path length quartz cuvette equipped with Teflon stopper was used for data collection of solution samples. FT-IR spectra were recorded on a Perkin Elmer spectrometer in the range 4000–400 cm^{-1} region using solid KBr as medium. ^1H and ^1H-^1H COSY NMR spectra were recorded on JEOL 400 NMR (JNMECX 400P). All electrochemical experiments were performed using a CH Instruments (Model 660D) Electrochemical workstation and a conventional three-electrode cell. CV and DPV were measured on 1 mM solution of the complexes in dry CH_3CN with $TBAPF_6$ (0.1 M) as supporting electrolyte using a glassy carbon as working electrode (WE), a Pt wire as counter electrode (CE) and Ag-AgCl (1 M KCl) as the reference electrode (RE). The potentials were mentioned versus Ag-AgCl. The TBAP was dried at 100^{o}C temperature for 30 min before use. The solution was degassed by N_2 bubbling for 30 min afore the experiment. All experiments were performed at room temperature unless otherwise mentioned.

Preparation of 4'-phenyl-terpyridine

The 4'-phenyl-terpyridine was prepared by literature method[S2] which consists of two consecutive steps as follows (Scheme S1).

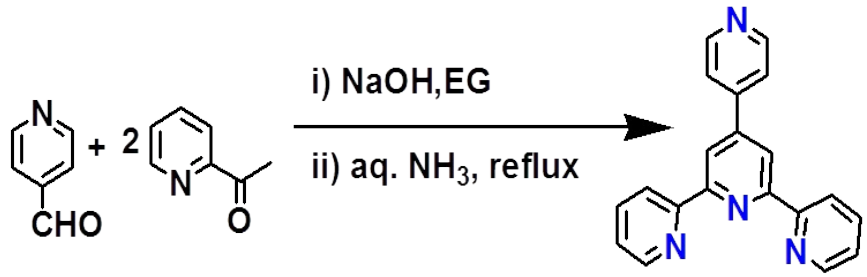
(i) Preparation of 3-phenyl-1,5-bis(2-pyridyl)-l,5-pentane-dione: 2-acetyl pyridine (2.1 mL, 18.5 mmol) was added dropwise to the stirred solution of benzaldehyde (0.9 mL, 8 mmol) followed by the addition of NaOH (500 mg) in a mixture of 10 mL ethanol-water (10:7, v/v) and then the whole reaction mixture was stirred for 1h at room temperature. The white product was obtained after addition of 30 mL distilled water to the reaction mixture. The resultant mixture was stirred at room temperature for another 4h. The white solid was filtered and properly washed with cold ethanol (20 mL) followed by drying under vacuum. The product was recrystallized from ethanol-dimethyl formamide (1:l, v/v) to obtain the white needle shape crystals. ^{1}H NMR ($CDCl_3$) δ/ppm: 8.56 (2H, dt, J = 8.03 & 3.68 Hz, H^6), 7.88 (2H, dt, J = 8.70 & 3.85 Hz, H^3),7.71 (2H, dt, J = 9.2, 6.7 & 2.7 Hz, H^4), 7.37(2H, dt, J = 9.37, 4.35 & 1.2 Hz, H^5), 7.35 (2H, d, J = 6.8 Hz, H^o), 7.30 (2H, t, J = 7.2 Hz, H^m), 7.14 (lH, t, J = 7.06 Hz, H^m), 4.0 (lH, tt, J = 8.03, 7.7 Hz, $H^{4'}$), 3.64 (2H, dd, J = 17.9, 7.7 Hz, H^a), 3.77 (2H, dd, J = 17.9, 7.8 Hz, H^b). FTIR (KBr): 3060 (w), 2882 (w), 1699 (vs), 1585 (s), 1354 (s), 1282 (s), 995 (s), 702 (s) cm^{-1}.

(ii) 3-phenyl-1,5-bis(2-pyridyl)-1,5-pentanedione (500 mg, 1.57 mmol) and solid NH_4OAc (1.30 g) were dissolved in 20 mL ethanol. Then the whole reaction mixture was refluxed for 4 h and then cooled to room temperature followed by the addition of 20 mL distilled water. The white precipitate appeared from the reaction mixture was filtered, washed with cold ethanol, diethyl ether and then dried under vacuum. The crude product was recrystallized from ethanol to get the needle shape yellow crystals. ^{1}H NMR ($CDCl_3$) δ/ppm: 8.74 (s, 2H, $H^{3'}$), 8.74 (d, 2H, J = 6.8 Hz, H^6), 8.68 (d, 2H, J = 8.48 Hz, H^3), 7.92 (m, 4H, H^4 +H^o), 7.53 (t, 2H, J = 7.8 Hz, H^m), 7.48 (dd, 1H, J = 8.2 & 4.2 Hz, H^p), 7.36 (dd, 2H, J = 7.8 & 3.8 Hz, H^5). UV-vis ($CHCl_3$) λ_{max}: 321 and 248 nm. FTIR (KBr): 1599 (m), 1583 (vs), 1392 (vs), 1074 (w), 1040 (w), 893(m), 796 (s), 791 (vs) cm^{-1}.



Scheme S1: Schematic presentation for preparation of 4'-phenyl-terpyridyl.

Preparation of 4'-pyridyl-terpyridyl. 4'-pyridyl-terpyridine (ligand **2**) was synthesized using reported procedure[S3] (Scheme S2). In brief**,** 2-acetylpyridine (0.94 mL, 8.24 mmol) was added to a stirred suspension of crushed NaOH (0.34 g, 8.24 mmol) in 6 mL ethylene glycol at 0°C. After 10 min, pyridine-4-carboxaldehyde (0.4 mL, 4.12 mmol) was added at 0°C. Then the resulting suspension kept at 0°C over 2h with constant stirring. Consequently aq. NH_3 (5 mL, 30%) was added dropwise and it was refluxed at 100°C for 2h and cooled at room temperature. The yellow precipitate was obtained and it was filtered and washed properly with cold ethanol. The product was recrystallized from ethanol and a little amount of water. After 3 days, needle shaped white crystals were obtained and dried under vacuum. ^{1}H NMR ($CDCl_3$) δ/ppm: 8.78 (s, 2H, $H^{3'}$), 8.77 (d, 2H, J = 8.6 Hz, H^m), 8.75 (d, 2H, J = 8.2 Hz, H^6), 8.68 (d, 2H, J = 8.05 Hz, H^3), 7.89 (t, 2H, J = 6.8 Hz, H^4), 7.8 (d, 2H, J = 8.4 Hz, H^o), 7.39 (t, 2H, J = 6.72 Hz, H^5). UV-vis ($CHCl_3$) λ_{max}: 316, 278 and 245 nm. ESI-MS: m/z: 310, 232, 153 and 77. FTIR (KBr): 1582 (vs), 1564 (m), 1470 (m), 1392 (vs), 792 (vs) cm^{-1}.



Scheme S2: Schematic presentation for preparation of 4'-pyridyl-terpyridyl.

Preparation of 4'-nitrophenyl-terpyridine. Synthesis of ligand **4** involves two steps (Scheme S3), (i) preparation of (E)-3-(4″-nitrophenyl)-1-(pyrid-2′-yl)prop-2-enone[S3] and (ii) cyclization using pyridacyl pyridinium iodide.[S4]

(i) Preparation of (E)-3-(4''-nitrophenyl)-1-(pyrid-2'-yl)prop-2-enone: Sodium hydroxide (0.5 mL, 10% aq.) was added to a suspension of p-nitro benzaldehyde (1.26 g, 8.34 mmol) in 10 mL ethanol. The reaction mixture was stirred at 0°C for 4h. The yellow product was collected by filtration and washed with a small amount of cold ethanol followed by recrystallization in boiling ethanol. The needle shaped yellow crystals were obtained. ^{1}H NMR ($CDCl_3$) δ/ppm: 8.78 (d, 1H, J = 4.8 Hz, H^6), 8.46 (d, 1H, J = 16.72 Hz, H^7), 8.30 (d, 2H, J = 8.4 Hz, H^{10}), 8.23 (d, 1H, J = 8.2 Hz, H^3),7.94 (m, 1H, H^4), 7.94 (d, 1H, J_{trans} = 15.6 Hz, H^8), 7.89 (d, 2H, J = 9.6 Hz, H^9), 7.55 (m,

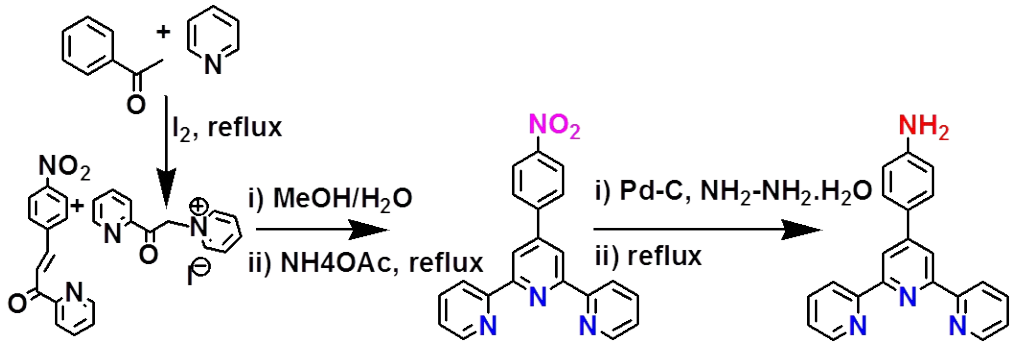
1H, H^5). FTIR (KBr): 1673 (m), 1604 (m), 1582 (s), 1339 (m), 1320 (m) 1028 (m), 850 (m), 753 (m) cm^{-1}.

(ii) Preparation of pyridacyl pyridinium iodide: 2-acetyl pyridine (6.05 g, 50 mmol) was added drop wise to the stirred solution of I_2 (12.69 g, 50 mmol) in 60 mL of dry pyridine. The mixture was refluxed for 1 h, followed by cooling at ice-bath. The black precipitate obtained was filtered and washed with a mixture of ether/ethanol (9:1, v/v, 50 mL). Subsequently the black solid was redissolved in 50 mL hot methanol and a little amount (100 mg) of activated charcoal was added. After refluxing for 30 min, the solution was filtered through a celite pad while hot to yield a clear yellow solution. On cooling at room temperature, the golden yellow crystals were obtained. The crystals were washed with cold methanol and then properly dried under vacuum. ^{1}H NMR (DMSO-d_6) δ/ppm: 9.01 (d, 2H, J = 8.8 Hz, H^8 +H^{12}), 8.86 (d, 1H, J = 8.4 Hz, H^6), 8.74 (t, 1H, J =7 .8 Hz, H^{10}), 8.28 (d, 2H, J = 8.6 Hz, H^9 +H^{11}), 8.13 (dt, 1H, J = 8.4 & 4.2 Hz, H^5), 8.06 (d, 1H, J = 8.4 Hz, H^3), 7.84 (ddd, 1H, J = 7.8 & 4.8 Hz, H^4) and 6.50 (s, 2H, H^7). FTIR (KBr): 3052 (m), 2876 (s), 1712 (vs), 1630 (s), 1484 (s), 1332 (s), 998 (s), 786 (vs) cm^{-1}.

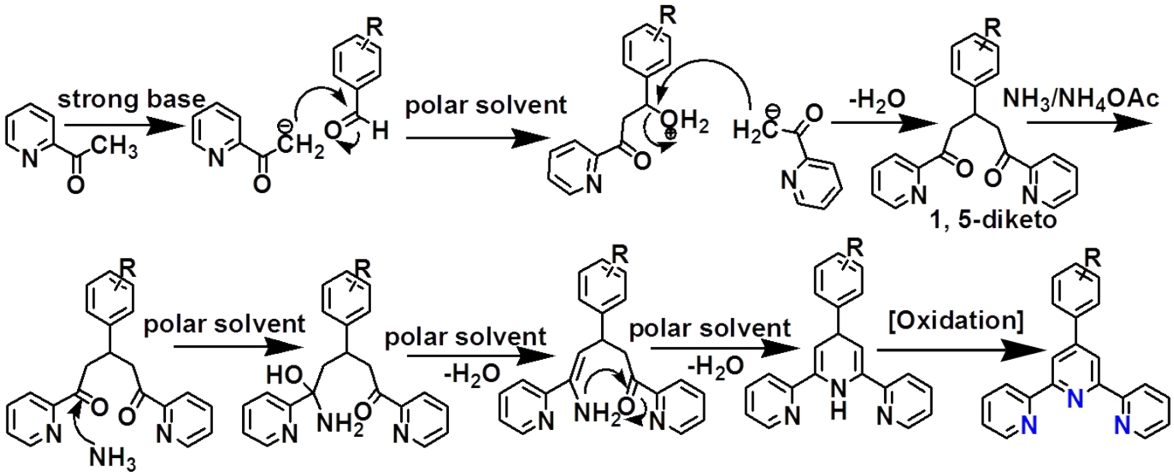
A mixture of (E)-3-(4”-nitro phenyl)-1-(pyrid-2’-yl) prop-2-enone (123 mg, 0.485 mmol) and pyridacyl pyridinium iodide (0.16 g, 0.485 mmol) were added into a mixture of methanol/water (2:1, v/v, 10 mL). Subsequently solid NH_4OAc (187 mg, 2.4 mmol) was added to the reaction mixture and refluxed for 12h. It was recrystallized from a mixture of ethanol/water (1:1, v/v). The purple compound of 4’-nitrophenyl terpyridine was obtained. ^{1}H NMR ($CDCl_3$) δ/ppm: 8.77 (s, 2H, $H^{3'}$), 8.75 (d, 2H, J = 4.6 Hz, H^6), 8.69 (d, 2H, J = 8.6 Hz, H^3), 8.38 (d, 2H, J = 8.2 Hz, H^m), 8.09 (d, 2H, J = 8.6 Hz, H^o), 7.91 (dt, 2H, J = 8.2, 5. 6 & 2.2 Hz, H^4), 7.39 (dd, 2H, J = 6.4 & 4.2 Hz, H^5). UV-vis ($CHCl_3$) λ_{max}: 245, 286 nm. FTIR (KBr): 1586 (s), 1514 (vs), 1352 (vs), 788 (m) cm^{-1}.

Preparation of 4’-aminophenyl terpyridyl: 4’-aminophenyl terpyridiyl have been synthesized following the reported method[S5] (Scheme S3). Solid 4’-nitro-phenyl-terpyridine (375 mg, 1.06 mmol) was dissolved in hot EtOH/THF (50 mL, 1:1 v/v) solution. 10% Pd-C (160 mg) was added to the mixture followed by drop wise addition of 1.3 mL hydrazine hydrate over a period of 30 min. The solution was filtered over celite pad in hot and cooled at room temperature. Yellow needle crystals appeared after 3 days. It was washed with cold ethanol and dried under vacuum. ^{1}H NMR (DMSO-d_6) δ/ppm: 8.75 (d, 2H, J = 5.2 Hz, H^6), 8.65 (d, 2H, J = 8.2 Hz, H^3), 8.64 (s, 2H, $H^{3'}$), 8.02 (dt, 2H, J = 8.6 & 1.8 Hz, H^4), 7.65 (d, 2H, J = 8.6 Hz, H^o), 7.52 (dt, 2H, J

= 8.4, 4.6 & 1.8 Hz, H^5), 6.75 (d, 2H, J = 8.4 Hz, H^m) and 5.59 (br, 2H, -NH_2). UV-vis (EtOH): λ_{max}: 229, 288, 325 nm. FTIR (KBr): 3386 (s), 1584 (s), 1308 (m), 790 (s) cm^{-1}.



Scheme S3: Proposed mechanism for synthesis of 4'-substituted-terpyridines.



Scheme S4: Proposed mechanism for synthesis of 4'-substituted-terpyridines.

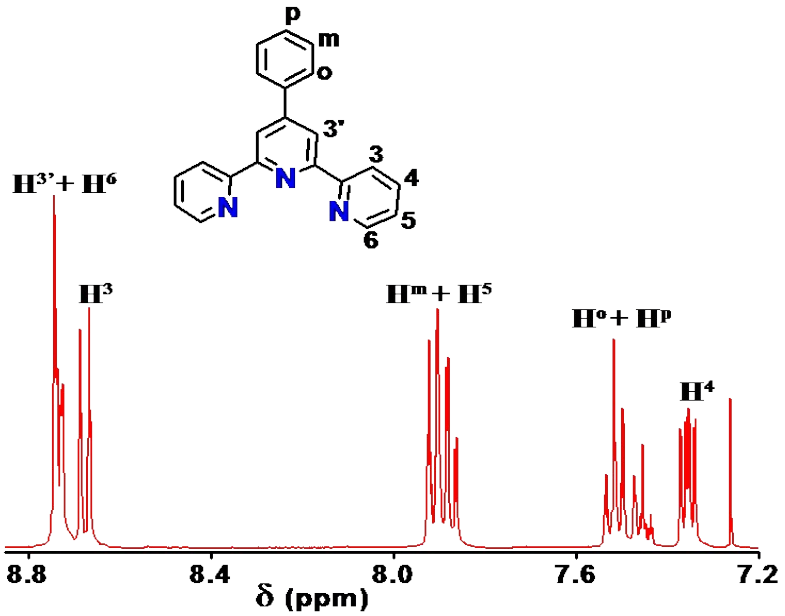


Figure S1: ^{1}H NMR spectrum of ligand 3 in $CDCl_3$.

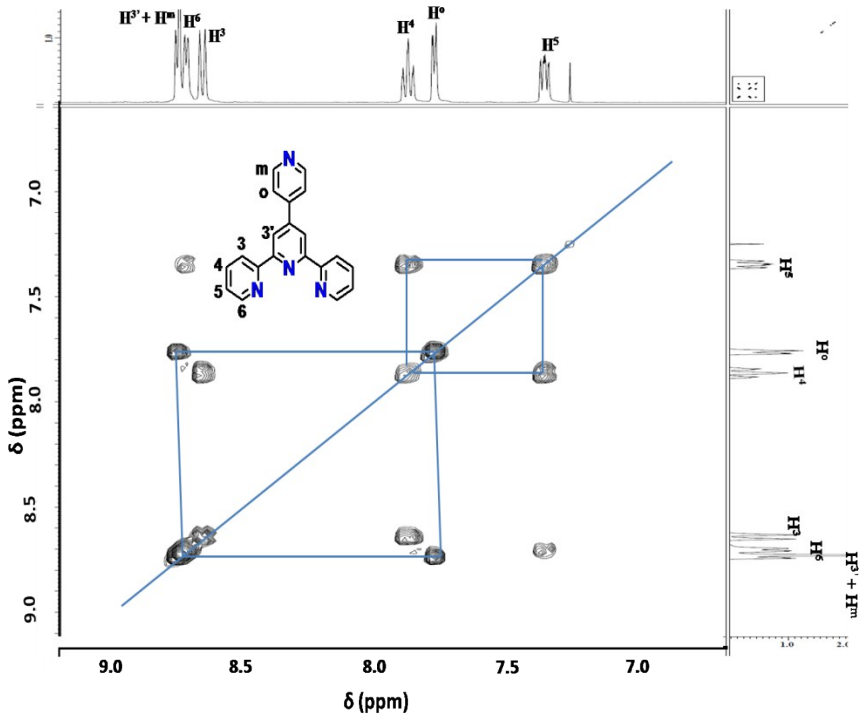


Figure S2: ^{1}H-^{1}H COSY NMR spectra of 4'-pyridyl terpyridyl in $CDCl_3$.

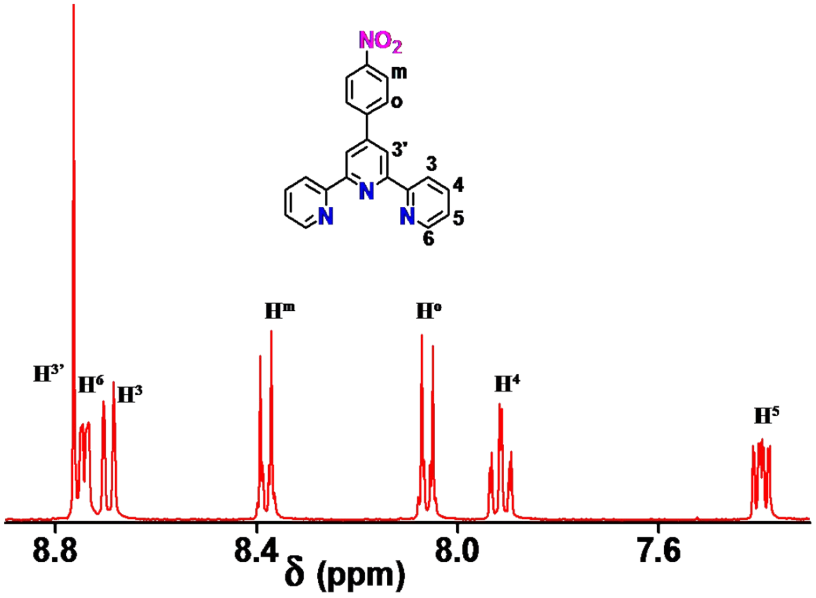


Figure S3: ^{1}H NMR spectrum of 4'-nitrophenyl terpyridyl in $CDCl_3$.

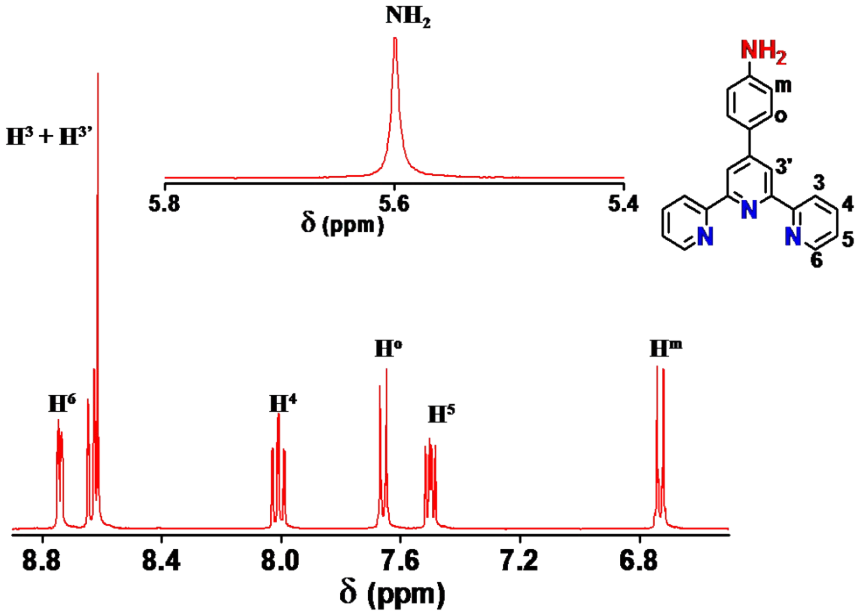


Figure S4: ^{1}H NMR spectra of 4'-aminophenyl terpyridyl in DMSO-d_6. Inset shows $-NH_2$ peak.

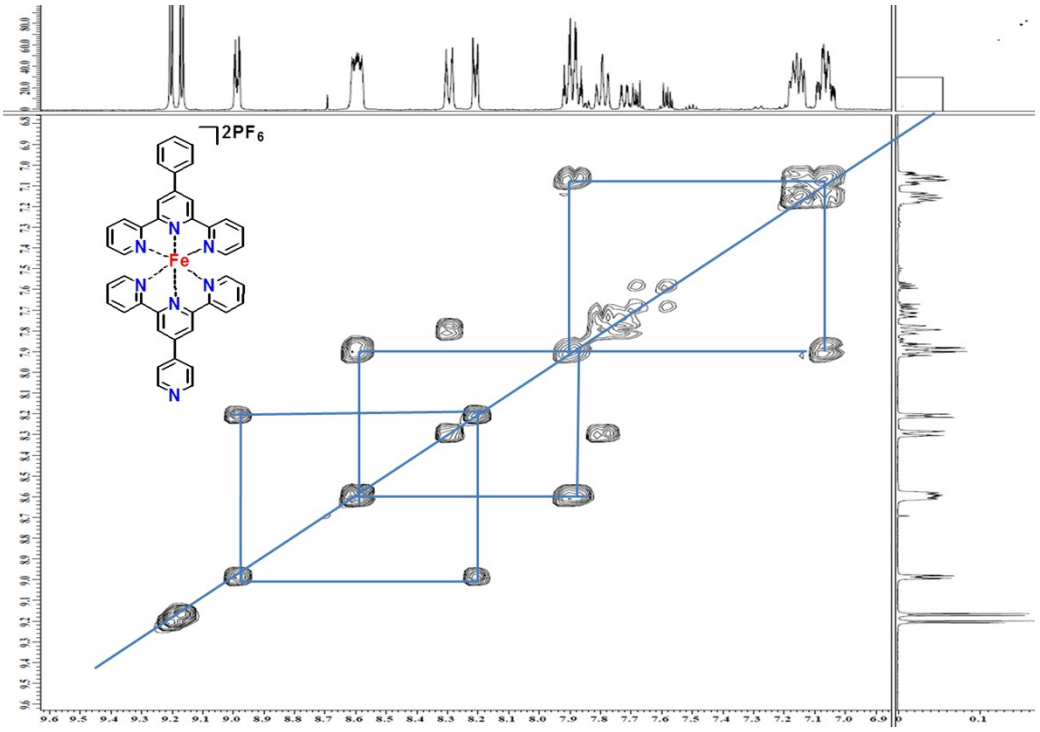


Figure S5: ^{1}H-^{1}H COSY NMR spectra of **1** in CD_3CN.

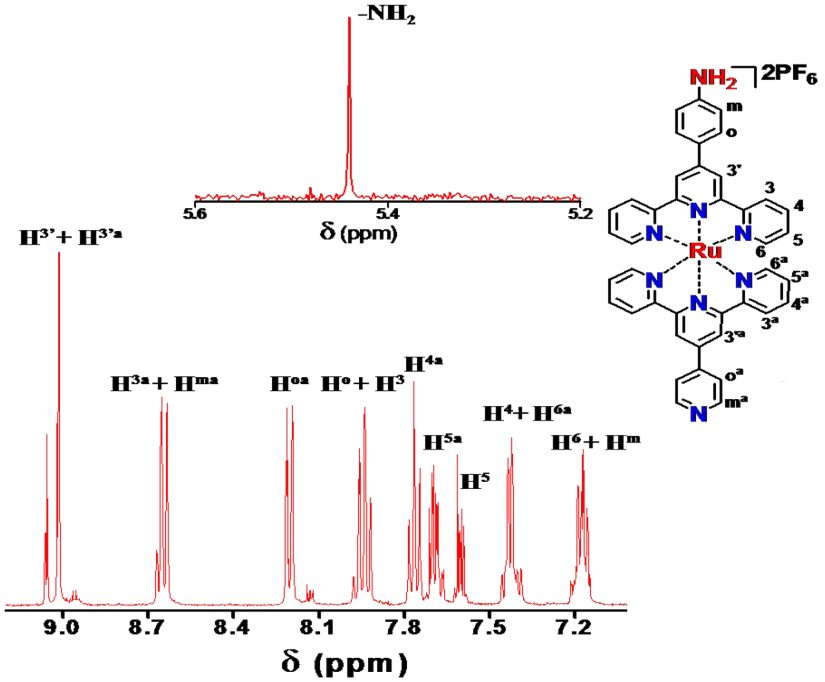


Figure S6: ^{1}H NMR spectra of **3** in CD_3CN. Inset shows $–NH_2$ peak.

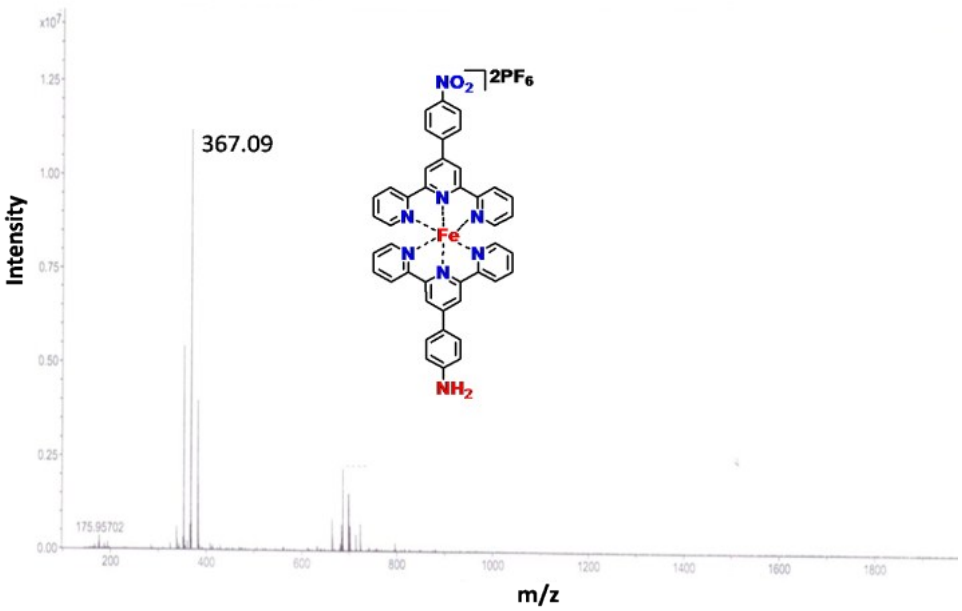


Figure S7: ESI mass spectrum of **2** in CH_3CN.

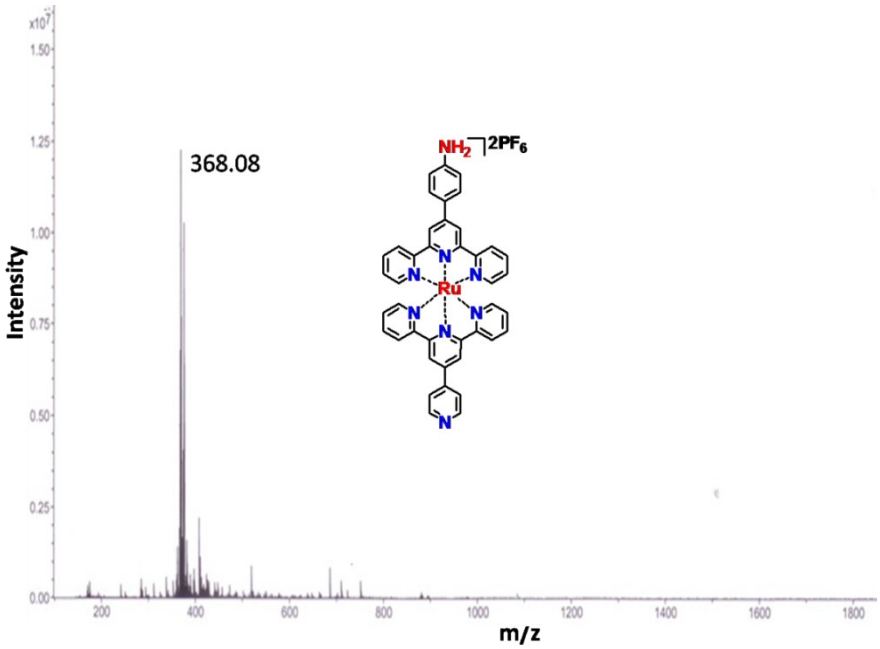


Figure S8 ESI mass spectrum of **3** in CH_3CN.

Table S1. CV characteristics of **1** at scan rate 100-1000 mV s^{-1}

ν (V/s)	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$E_{1/2}$ (V)	1.15	1.15	1.15	1.15	1.15	1.16	1.16	1.16	1.17	1.17
ΔE_p (mV)	70	72	75	78	80	84	85	88	90	94

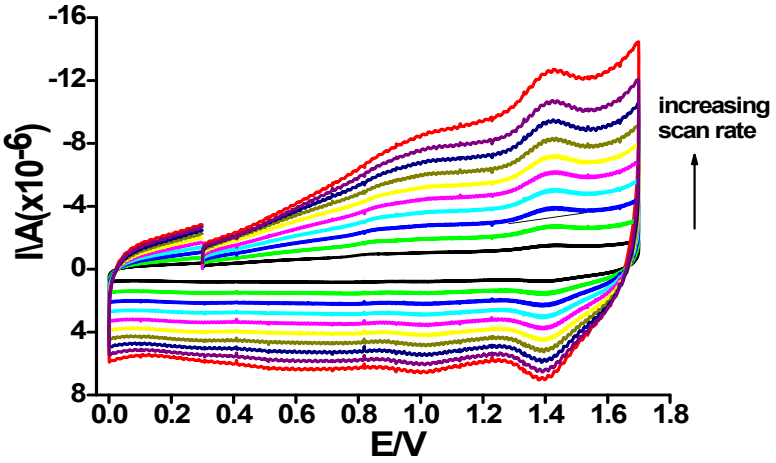


Figure S9: Cyclic voltammograms of **3** (1 mM solution, 0.1 M $TBAPF_6$) in CH_3CN recorded at 100-1000 mV s^{-1}. The potential mentioned here with respect to Ag-AgCl.

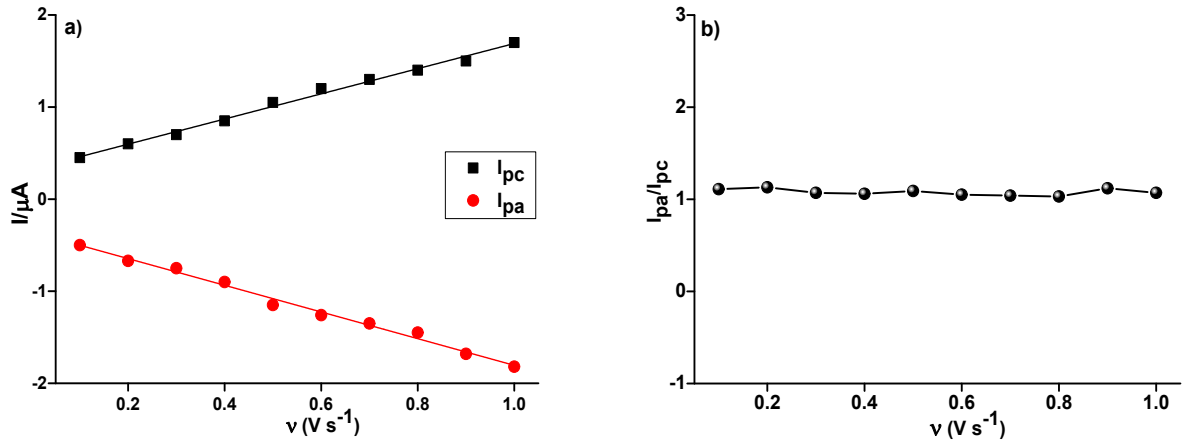


Figure S10: (a) Linear behavior (R^2 = 0.99) of the cathodic and anodic current density as a function of the scan rates (ν), and (b) the plot of the ratio of anodic to cathodic current density (Ipa/Ipc) as a function of scan rates measured for **3**.

Table S2: HOMO-LUMO gaps for complexes 1, 2 and 3 in acetonitrile solvent calculated by DFT employing different XC functional using 6-31+G(d,p) basis set for light atoms and LANL2DZ basis set for metals with ECP for the core electrons.

Complex	ΔE_{H-L} (eV) / ωB97XD	ΔE_{H-L} (eV) /CAM-B3LYP	ΔE_{H-L} (eV) /B3LYP
1	7.61	6.45	3.74
2	6.36	5.20	2.68
3	6.59	5.48	3.03

Table S3: Excitation energy calculated by TDDFT for complexes 1, 2 and 3 in acetonitrile solvent using different XC functional employing 6-31+G(d,p) basis set for light atoms and LANL2DZ basis for metals with ECP for the core electrons. Values within bracket represent oscillator strengths for each excitation. Significant molecular orbital replacements associated with each excitation and characters of each state are also listed. (LMCT: ligand-to-metal charge-transfer, MLCT: metal-to-ligand charge-transfer and LLCT: ligand-to-ligand charge-transfer).

Complex	Excitation Energy (nm)/ ωB97XD	Excitation Energy (nm)/ CAM-B3LYP	Excitation Energy (nm)/ B3LYP	Experimental (nm)
1 (HOMO=169)	**470.62 (0.0005)** 169 → 196 (LMCT) 469.34 (0.0005) 167 → 196 (LMCT) 360.89 (0.0032) 168 → 170 (MLCT) 356.09 (0.0034) 168 →171 (MLCT) 344.90 (0.001) 169 → 170 (MLCT) 334.11 (0.2589) 167 → 170 (LLCT)	491.21 (0.0006) → LMCT 489.52 (0.0005) → LMCT 372.97 (0.0028) → MLCT 369.44 (0.0028) → MLCT 339.43 (0.0005) → MLCT 336.42 (0.2684) → LLCT	483.18 (0.0021) → LMCT 480.02 (0.0016) → LMCT 449.30 (0.0046) → MLCT 434.98 (0.0061) → MLCT 418.13 (0.2302) → LLCT	**567**

2 (HOMO=184)	**475.46 (0.0005)** 181→212 (LMCT) 472.39 (0.0005) 182→212 (LMCT) 362.50 (0.0033) 183→188 (MLCT) 353.59 (0.0037) 183→186 (MLCT) 348.06 (0.0014) 181→188 (MLCT) 340.06 (0.6779) 184→186 (LLCT)	494.17 (0.0006) → LMCT 490.23 (0.0005) → LMCT 375.78 (0.0029) → MLCT 368.82 (0.0029) → MLCT 358.68 (0.0002) → MLCT 346.48 (0.7717) → LLCT	514.69 (0.0001) → LLCT 489.94 (0.0029) → MLCT 480.25 (0.0014) → MLCT 466.96 (0.0018) → MLCT 446.89 (0.6133) → LLCT	**576**
3 (HOMO=173)	**404.46 (0.0141)** 172→174 (MLCT) 396.51 (0.0003) 170 →174 (MLCT) 387.69 (0.4830) 171→174 (MLCT) 386.90 (0.0175) 172→175 (MLCT)	400.16 (0.0129) → MLCT 394.83 (0.0003) → MLCT 383.64 (0.5312) → MLCT 382.38 (0.0161) → MLCT	511.79 (0.0001) → MLCT 486.83 (0.0111) → MLCT 465.57 (0.4889) → MLCT 459.79 (0.0142) → MLCT	**501**

References:

S1. (a) E. C. Constable and A. M. W. C. Thompson, *New J. Chem*. 1996, **20**, 6; (b) S. A. Moya, R. Pastene, H. Bozec, P. J. Baricelli, A. J. Pardey and J. Gimeno, *Inorg. Chim. Acta* 2001, 7.

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