Supplemenatry Information

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S1.

Materials and Methods. All reactants and solvents were purchased from commercial sources and used as received. $RuCl_3.xH_2O$ and 4,4'-dimethyl-2,2'-bipyridine was purchased from Sigma-Aldrich, 2,2'-bipyridine, 1, 10-phenanthroline, 3-carboxaldehyde pyridine, 4-methoxyaniline, ammonium acetate, glacial acetic acid and ethylene glycol from Merck. ^1H and ^{13}C NMR spectra were recorded using a Bruker 250 MHz spectrometer. CHN analyses were recorded with a ElementarVario analyzer. Cyclic voltammoram of complexes (2×10^{-3}M, acetonitril as solvent) were carried out under a N_2 atmosphere by using SAMA500 potentiostat electrochemical analyzer with three electrode cell, Pt disk, Pt wire and Ag/AgCl as the working electrode, counter electrode and reference electrode, respectively. 0.10 M tetrabutylammonium perchlorate (TBAP) was used as supporting electrolyte and the following relation were used: formal potential $E^{o'} = (E_{pa} +/E_{pc})/2$ where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively. The HOMO/LUMO energy levels were calculated using CV data by following equation: E_{HOMO}=-(E_{ox}(vs.F_c/F_C^+)+ 4.8 eV) (E_{ox} and E_{red} are oxidation and reduction potentials. The reduction potential of ferrocene was found to be 0.43 V, $E_{LUMO} = E_{HOMO} + E_{o-o}$ eV, E_{o-o} was calculated from the intersection of absorption and emission spectra in acetonitril solutin. E_{gap}= -E_{HOMO} – E_{LUMO} [1]. UV–visible spectra and photoluminescent (PL) spectra were recorded on an Ultrospec3100 pro spectrophotometer and a Varian-Cary Eclipse fluorospectrophotometer, respectively.

The PLQY (PL quantum yields) were calculated against $[Ru(bpy)_3]^{2+}$ in degassed acetonitrile solution at 298 K as a standard ($\emptyset_{std} = 0.095$[2]) using the following equation:

$$\emptyset_{unk} = \emptyset_{std}.(\frac{I_{unk}/A_{unk}}{A_{std}/I_{std}}).(\frac{\eta_{unk}}{\eta_{std}})^2$$

In this equation,Φ_{unk} is phosphorescence quantum yields of complexes, Iunk and Istd are the integrated areas of the corrected PL spectra and standard, respectively, Aunk and Astd are the absorbances of the ruthenium complexes and the standard at the excitation wavelength (λ_{exc}= 460 nm), and ηunk and ηstd are the indexes of refraction of the respective solvents (taken to be equal to the neat solvents in both cases). Thin films of cationic ruthenium complexes for study of solid emission were obtained by drop cast from a spectrophotometric grade acetonitrile solution on a glass support with a thickness of about 90 nm. After evaporation of the solvent in air, the films were dried overnight under vacuum at room temperature.

Device fabrication and measurement : Indium tin oxide (ITO) coated glass with a sheet resistance of 20 Ω/square was used as anode. After being sufficiently cleaned by soaking in ultrasonicated isopropanol, aceton and deionized water, it was dried in the oven at 110°C for 1.5h. The devices were prepared by spin-coating a thin layer of each complex (Bn1, Bn2, Bn3) on top of an ITO glass substrate from a 7% (w/v) acetonitrile solution at RT. All solution and film preparation were performed under ambient conditions. The thicknesses of the films were ~ 85 nm, measured with profilometry. After spincoating, the thin films were annealed at 90 °C in inert atmosphere for 14h. A Ga: In (75.5:24.5 wt %, mp 15.7 °C) eutectic as cathode (ca. 3.5 mm diameter) was printed on the top of the active layer at room temperature by using a special syringe (glass syringe with needle diameter about 1.5 mm) [7] and then connected via a thin copper wire inserted into the Ga:In contact. Finally it was sealed with epoxy cement. All EL measurement were carried out in air atmosphere. The current density, luminescence versus the voltage and emission characteristics of LEC devices were measured using an AvaSpec-125 spectrophotometer, a SAMA500 electroanalayzer system and a Photo Research PR-650 spectroradiometer.

S2.

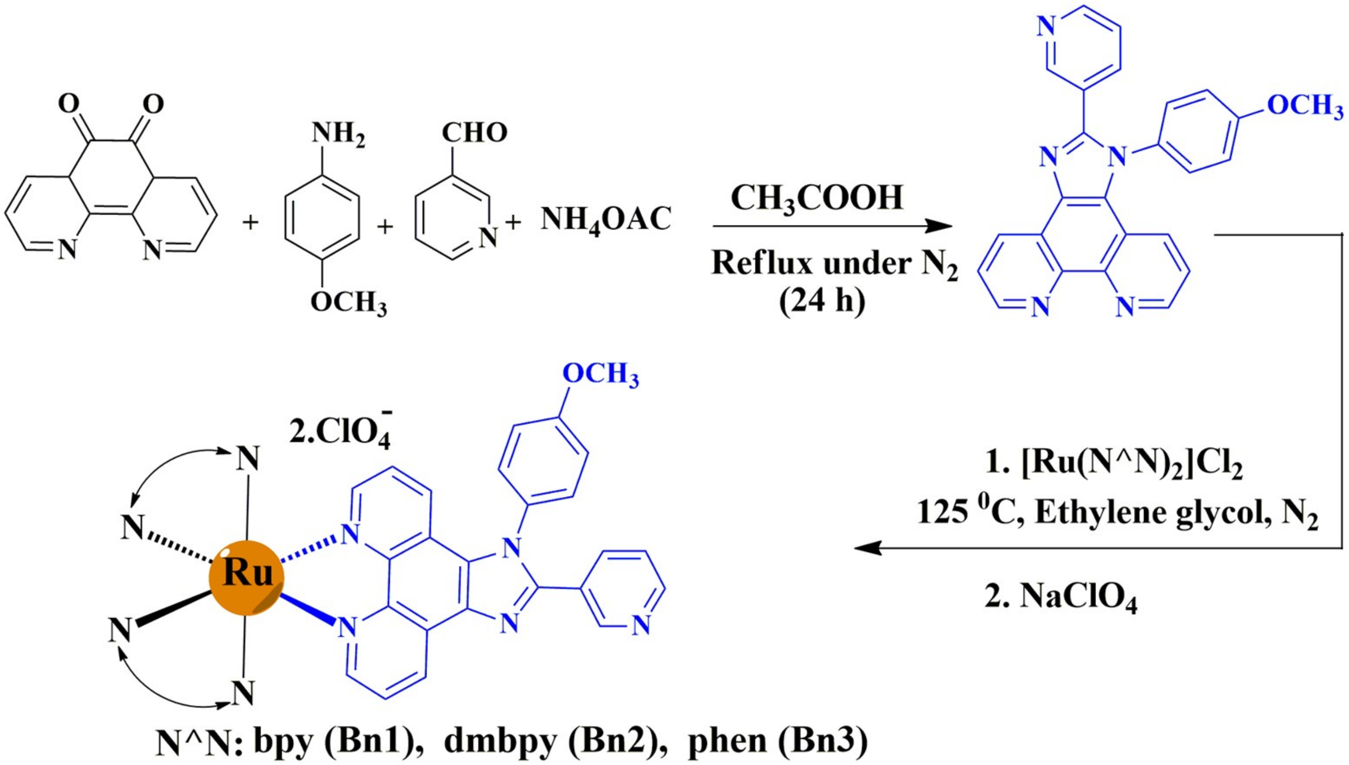

Figure S1. Synthesis of phenanthroimidazole ligand based (mpip) and their ruthenium(II) complexes

Synthesis and characterization: The precursor compounds of ruthenium complexes with formula of cis-[Ru(N^N)$_2$Cl$_2$].2H$_2$O (N^N: bpy, dmbpy, phen) and 1,10-phenanthroline-5,6-dione were synthesized according to reference methods [3-6].

1-(4-methoxyphenyl)-2-(pyridin-3-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (mpip). The ligand was prepared by refluxing phendione (0.212 g, 1.0 mmol), 3- pyridine carboxaldehyde (0.11 g, 1 mmol), 4-meyhoxyaniline (0.13 g, 1 mmol), and ammonium acetate (770 mg, 10 mmol, excess) in glacial acetic acid (7 mL) for 24 h under an nitrogen atmosphere. The sultion was cooled to room temperature, then added 25 mL deionized water and neutralized with a 25% aqueous ammonia solution and extracted with 40 mL of chloroform. After removed the solvent, the residue was washed with cool ethanol /acetone (1:3). The solid was dissolved in a minimum of CHCl$_3$ and then added 10 fold acetone. The solution keep in refrigrator at -5 ^{0}C for a 12h and then the precipitate was isolated and dried to give the product as a grey solid. Yield: 41%. mp. 281°C, Anal. calcd. For $C_{25}H_{17}N_5O$ (%): C, 74.433; H, 4.255; N, 17.367. Found (%): C, 74.429; H, 4.251; N, 17.369. ^{1}HNMR (250 MHz, CDCl$_3$): 9.16 (d, 1H), 9.07(m, 2H), 8.78 (s, 1H), 8.56 (d, 1H), 7.96 (d, 1H), 7.74 (m, 1H), 7.51-7.41(m, 3H), 7.32-7.25 (m, 2H), 7.12 (d, 2H), 3.94 (s, 3H, methoxy). ^{13}CNMR (62 MHz, D$_6$-DMSO): 160.92, 149.88, 149.63, 149.13, 148.16, 146.4, 136.38, 130.39, 129.62, 128.04, 126.34, 123.57, 123.19, 122.22, 119.75, 115.84, 55.68 (carbon of methoxy group).

General procedure for synthesis of [Ru(N^N)$_2$(mpip)](ClO$_4$)$_2$: A mixture of cis-[Ru(N^N)$_2$Cl$_2$].2H$_2$O (0.1 mmol) and mpip (0.1 mmol) was degassed by N$_2$ and heated under N$_2$ at 126 °C in ethylene glycol (5 ml) for 16.0 h. After this time, the dark purple solution was cooled to room temperature, precipitated by dropwise addition to an saturated NaClO$_4$ solution and allowed to rapidly stir for 10 min. The orange precipitate was collected and several time washed with deionized water to remove trace of salts. The product was purified by column chromatography on alumina with acetonitril-toluene (3/1, v/v) as an eluent. Then, the solvent was removed under reduced pressure and red solid were obtained.

[Ru(bpy)$_2$(mpip)](ClO$_4$)$_2$ (Bn1). Yield: 74% (73 mg). Anal. calcd. For $C_{45}H_{33}Cl_2N_9O_9Ru$(%): C, 53.216; H, 3.275; N, 12.414 Found (%): C, 53.212; H, 3.279; N, 12.411. ^{1}HNMR (250 MHz, D$_6$-DMSO): 9.19 (d, 1H), 8.83 (m, 5H), 8.60 (d, 1H), 8.30-8.09 (m, 5H), 8.02-7.96 (m, 3H), 7.82 (t, 2H), 7.74-7.63(m, 3H), 7.65 (m, 5H), 7.47 (m, 1H), 7.35 (t, 2H), 7.23 (t, 2H), 3.87 (s, 3H, methoxy). ^{13}CNMR (62 MHz, CDCl$_3$): 161.14, 157.00, 152.04, 150.82, 149.86, 146.04, 145.82, 138.45, 138.36, 137.06, 136.55, 131.01, 130.39, 128.82, 128.70, 128.22, 127.43, 126.37, 125.97, 125.92, 124.90, 121.95, 116.31, 56.14 (carbon of methoxy group of mpip).

[Ru(dmbpy)$_2$(mpip)](ClO$_4$)$_2$(Bn2). Yield: 67% (69 mg). Anal. calcd. For $C_{49}H_{41}Cl_2N_9O_9Ru$ (%): C, 54.916; H, 3.86 N, 11.767 Found (%): C, 54.911; H, 3.864 N, 11.762. ^{1}HNMR (250 MHz, D$_6$-DMSO):): 9.15 (d, 1H), 8.77 (d, 1H), 8.68 (m, 4H), 8.58 (d, 1H), 8.14 (d, 1H), 7.97 (m, 3H), 7.75-7.63 (m, 5H), 7.58-7.39 (m, 6H), 7.26-7.18 (m, 4H), 3.87 (s, 3H, methoxy), 2.45 (s, 12H, overlap with DMSO peak). ^{13}CNMR (62 MHz, D$_6$-DMSO):): 161.18, 156.59, 151.97, 150.92, 150.40, 150.15, 150.06, 149.83, 146.25, 146.02, 137.05, 136.52, 130.41, 129.71, 129.00, 128.85, 128.68, 128.22, 127.32, 126.24, 125.99, 125.83, 125.46, 123.99, 122.87, 116.29, 56.13 (carbon of methoxy group of mpip), 21.10 (carbon of methyl group of dmbpy).

[Ru(phen)$_2$(mpip)](ClO$_4$)$_2$(Bn3). Yield: 63% (68 mg). Anal. calcd. For $C_{49}H_{33}Cl_2N_9O_9Ru$ (%): C, 55.322; H, 3.13; N, 11.857 Found (%): C, 55.328; H, 3.19; N, 11.852. ^{1}HNMR (250 MHz, D$_6$-DMSO):): 9.17 (d, 1H), 8.75 (m, 4H), 8.62 (d, 1H), 8.35 (m, 4H), 8.09-7.98 (m, 8H), 7.75 (m, 8H), 7.54-7.41 (m, 3H), 7.2 (m, 2H), 3.85 (s, 3H, hydrogen of methoxy group of mpip). ^{13}CNMR (62 MHz, D$_6$-DMSO):): 161.17, 153.15, 153.04, 151.96, 151.64, 151.05, 150.95, 149.84, 147.67, 147.55, 146.44, 146.22, 137.34, 137.04, 136.55, 130.92, 130.40, 128.82, 128.69, 128.52, 127.28, 126.78, 126.23, 125.97, 125.85, 124.02, 121.89, 116.3, 56.12 (carbon of methoxy group of mpip).

S3.

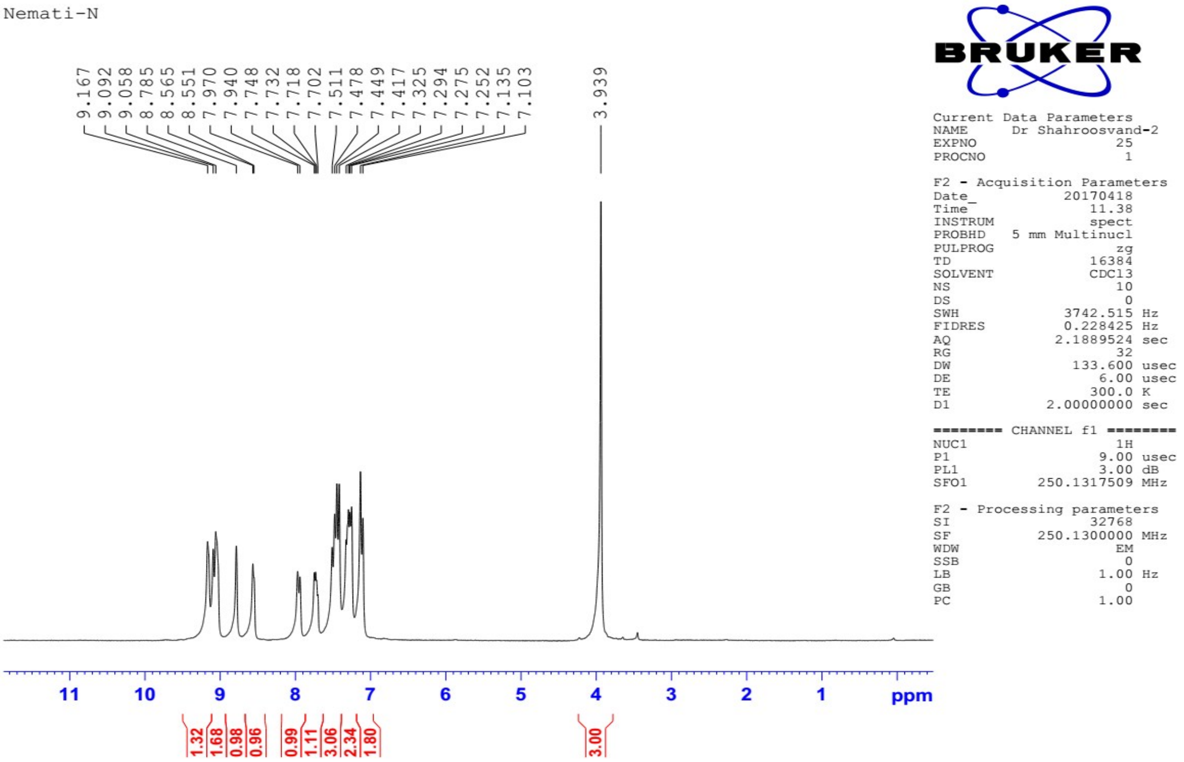

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Figure S2. ^{1}HNMR spectra of phenanthroimidazole ligand (mpip) in $CDCl_3$.

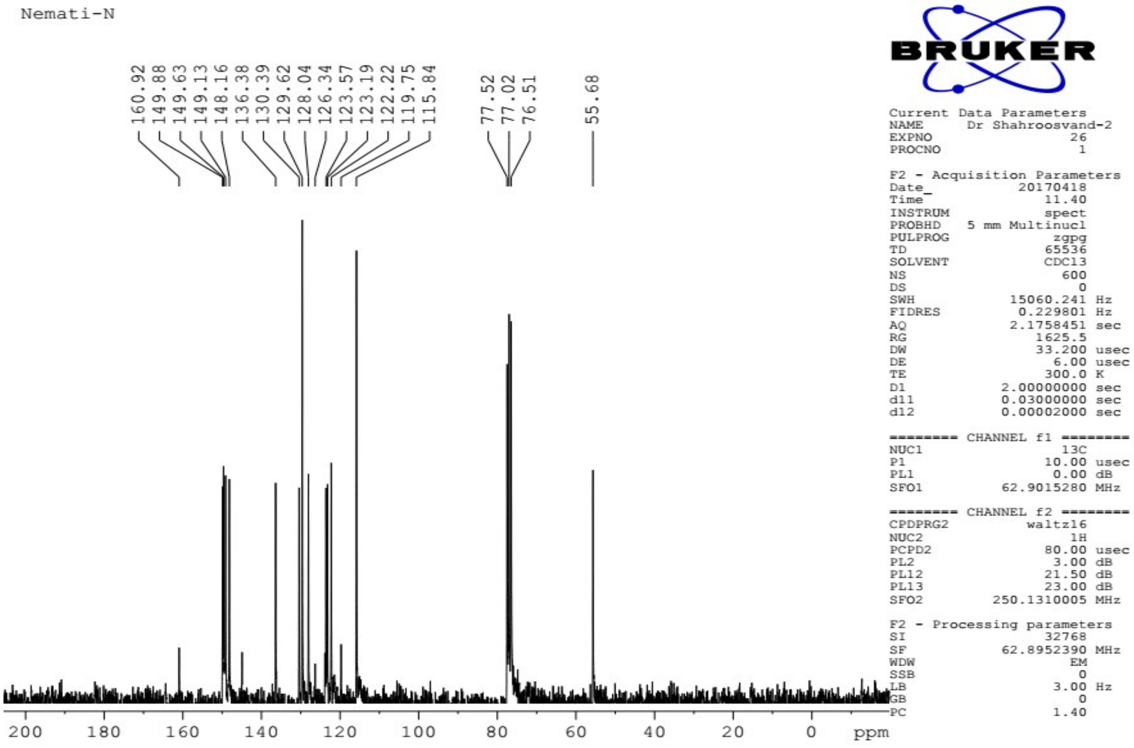

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Figure S3. ^{13}CNMR spectra of phenanthroimidazole ligand(mpip) in $CDCl_3$

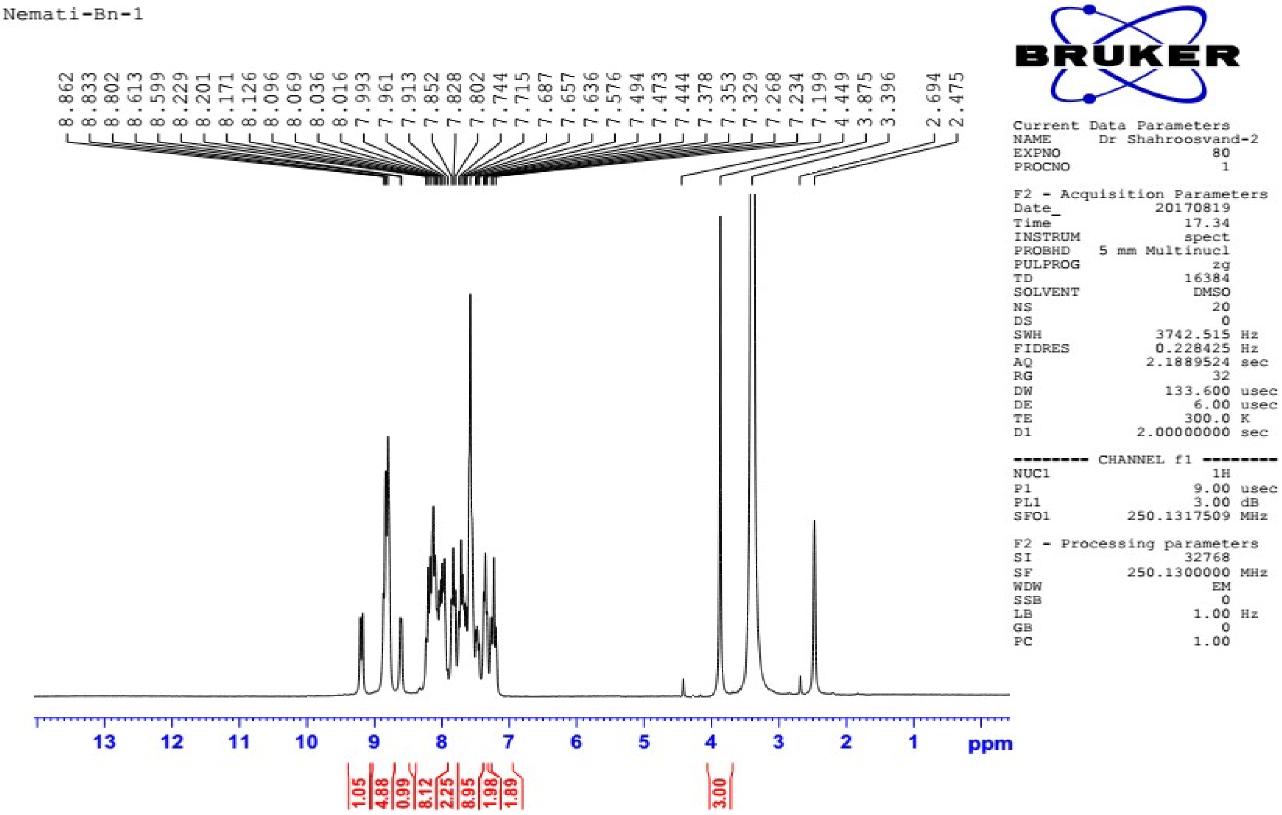


Figure S4. ^{1}HNMR spectra of Bn1 in D_6-DMSO.

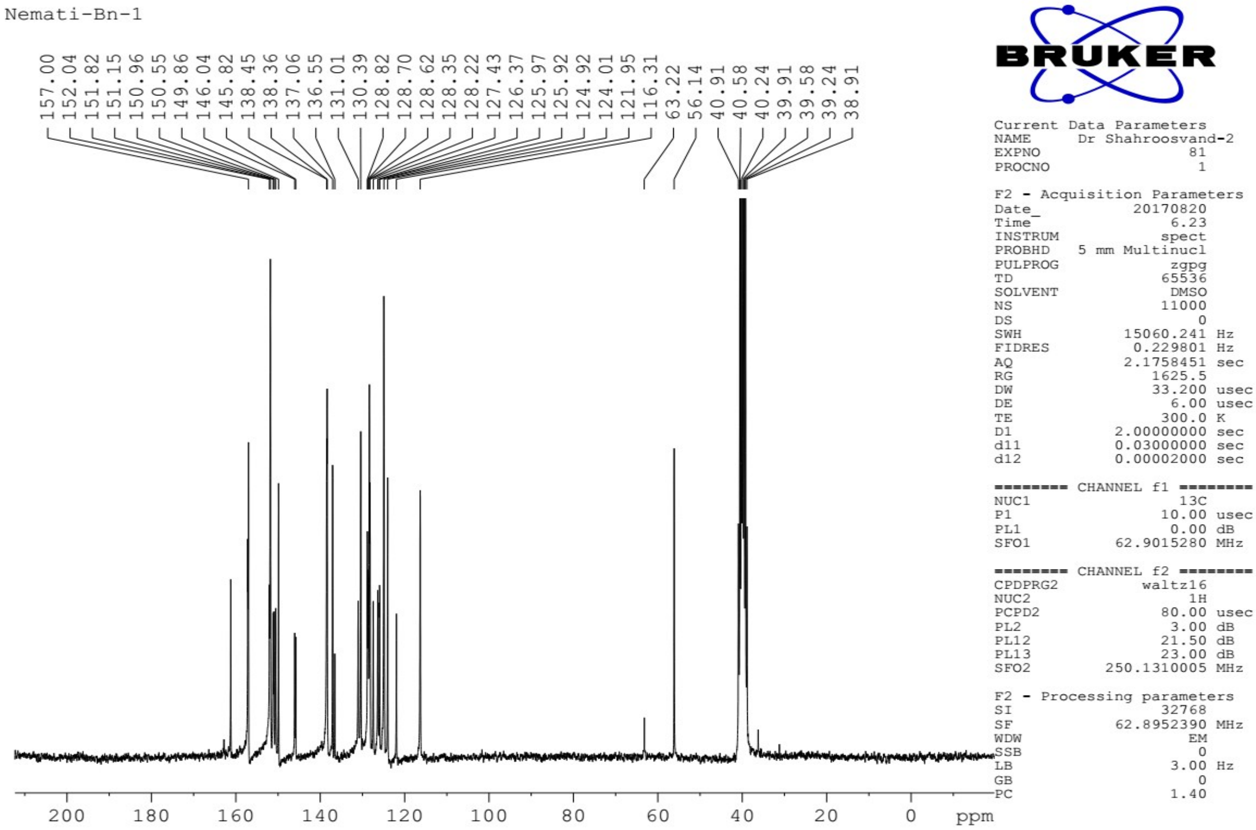
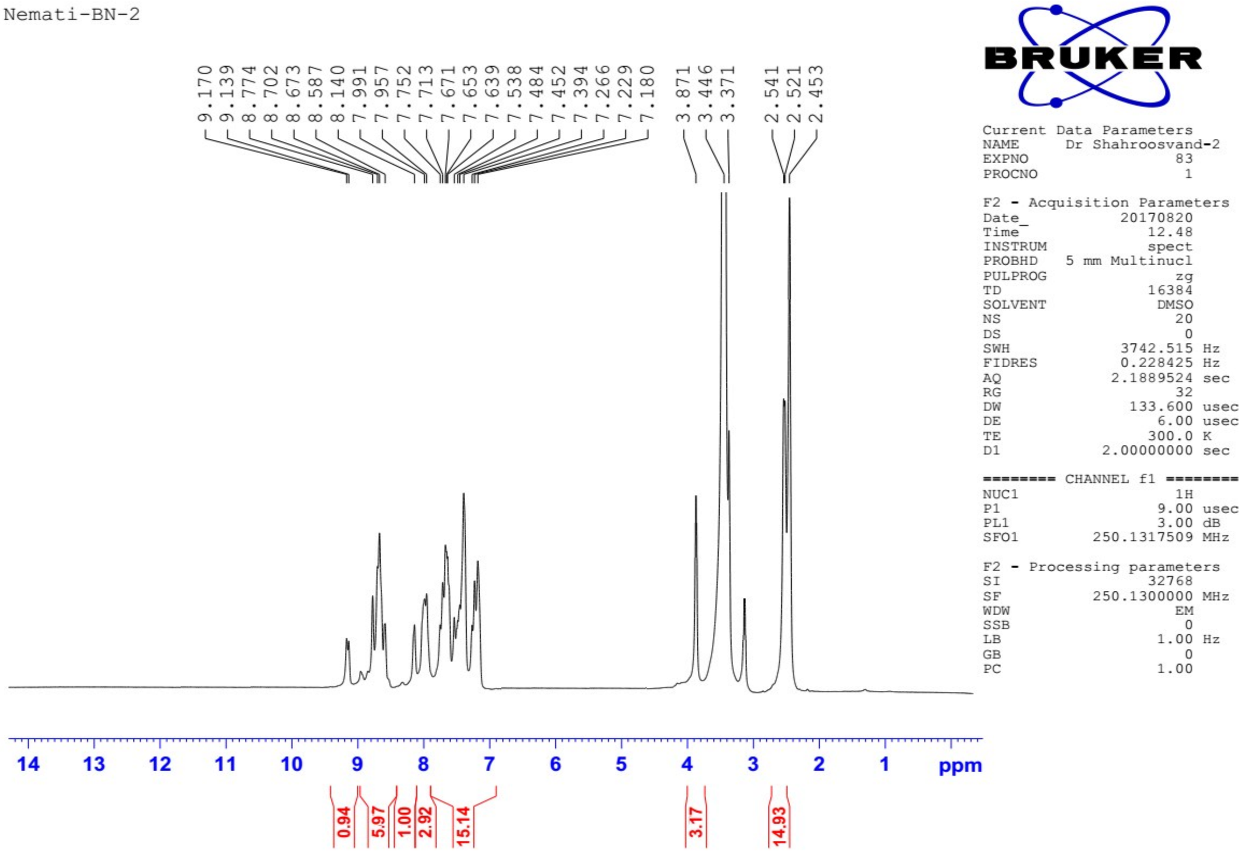


Figure S5. ^{13}CNMR spectra of Bn1 in D_6-DMSO.



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RG                      32
DW                 133.600 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec

======== CHANNEL f1 ========
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PL1                   3.00 dB
SFO1           250.1317509 MHz

F2 - Processing parameters
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WDW                     EM
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GB                       0
PC                    1.00
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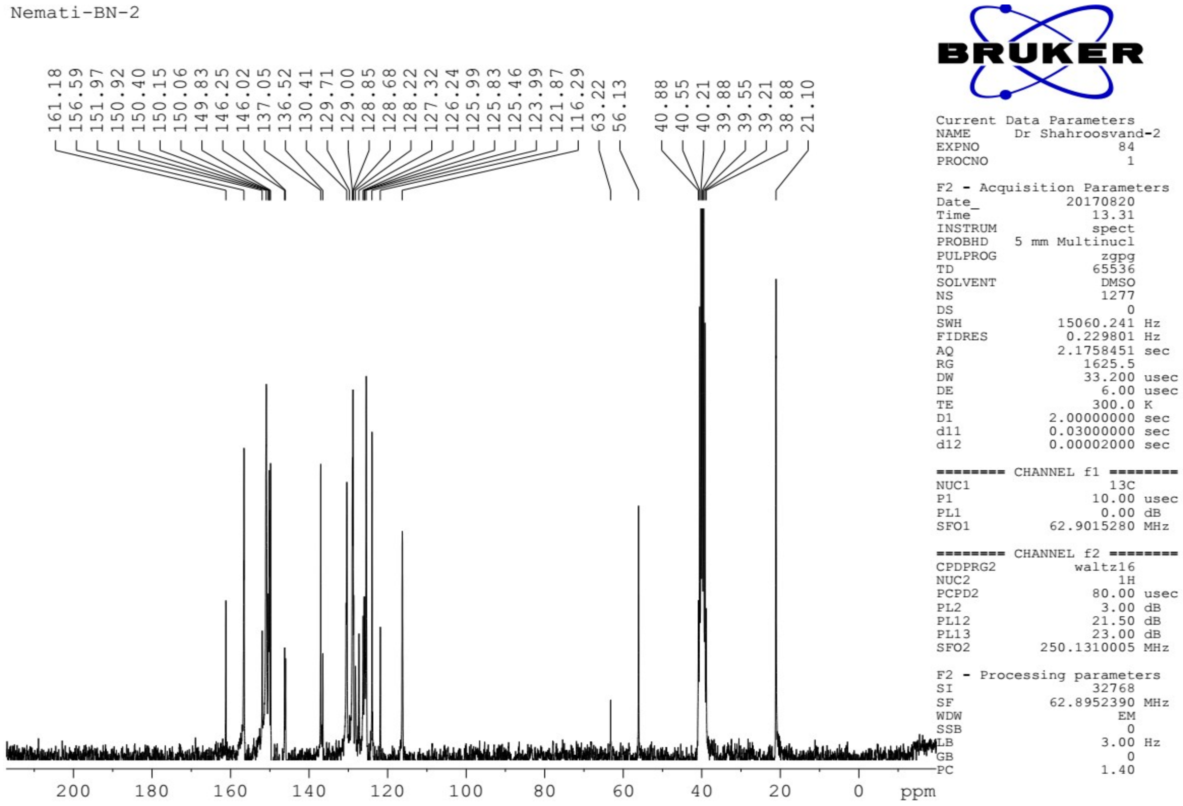
Figure S6. ^{1}HNMR spectra of Bn2 in D_6-DMSO.



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FIDRES            0.229801 Hz
AQ               2.1758451 sec
RG                  1625.5
DW                  33.200 usec
DE                    6.00 usec
TE                   300.0 K
D1              2.00000000 sec
d11             0.03000000 sec
d12             0.00002000 sec

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PL1                   0.00 dB
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======== CHANNEL f2 ========
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NUC2                    1H
PCPD2                80.00 usec
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PL12                 21.50 dB
PL13                 23.00 dB
SFO2           250.1310005 MHz

F2 - Processing parameters
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GB                       0
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Figure S7. ^{13}CNMR spectra of Bn2 in D_6-DMSO.

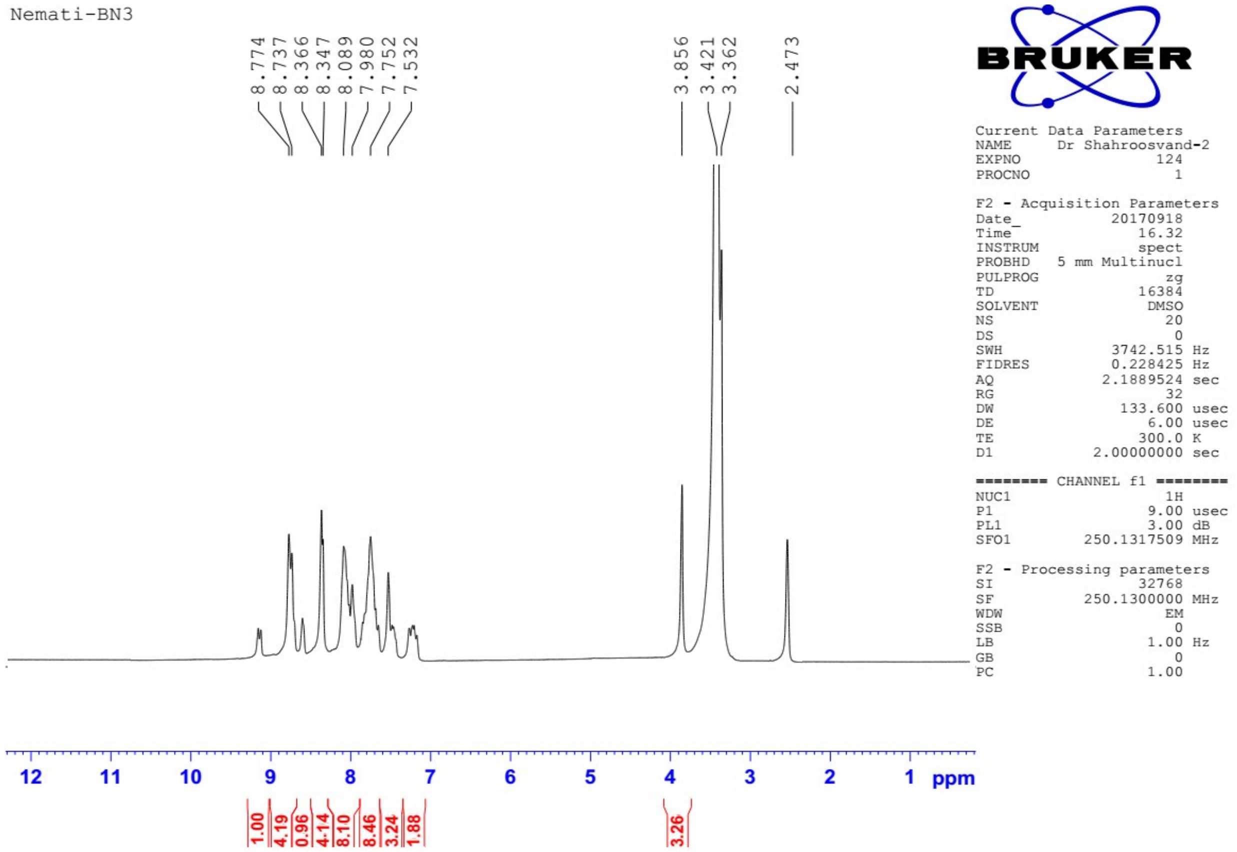

Figure S8. ^{1}HNMR spectra of Bn3 in D$_6$-DMSO.

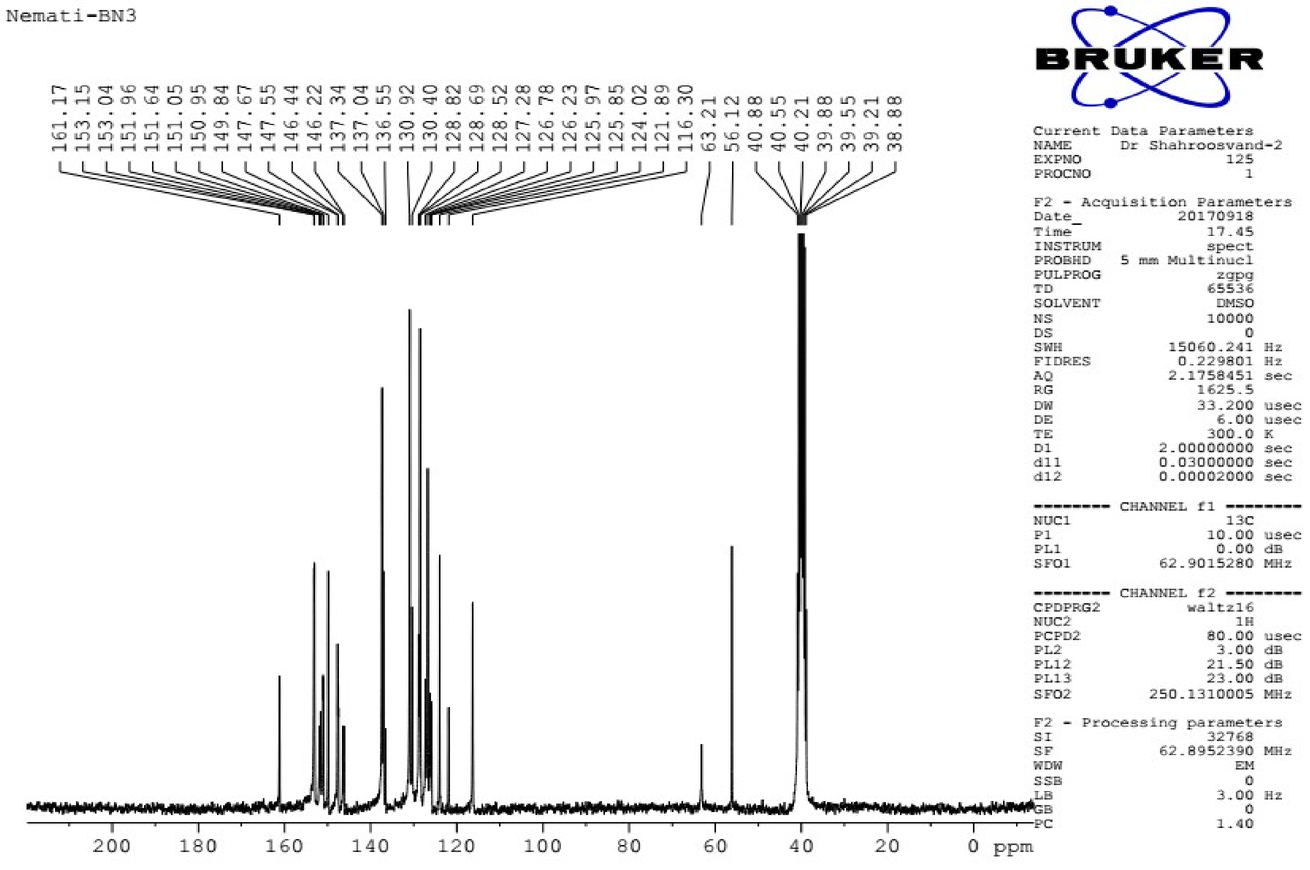

Figure S9. ^{13}CNMR spectra of Bn3 in D$_6$-DMSO.

Com.	**Absorbance** [a] $\lambda_{max}[nm]$ $(log\varepsilon)$		**Emission** $\lambda_{max}[nm](\varphi^{d})$		**Ru(II/III) Oxi.**	**Ligand Red.**	**E_{HOM}** [f] **(eV)**	**E_{LUMO}** [g] **(eV)**	**E_{gap}** [h] **(eV)**
	Ligand Transitions	MLCT	Solution [b]	Film [c]	$E_{1/2}(\Delta E)$(V)[e]	E_{red} (V)			
NE01	233 (4.61), 255 (4.10), 285 (4.98)	456 (4.25)	605 (0.119)	632	1.31 (0.075)[i]	-1.33[i]	-5.68	-3.04	2.64
NE02	221 (4.95), 259 (4.11), 285 (4.96)	462 (4.22)	618 (0.091)	636	1.24 (0.084)[i]	-1.23[j]	-5.61	-3.14	2.47
NE03	227 (4.87), 263 (4.98), 276 (4.18)	453 (4.21)	595 (0.089)	633	1.31 (0.063)[i]	-1.40[j]	-5.68	-2.97	2.71
$Ru(bpy)_3^{2+}$	**245 (4.4), 290 (4.91)**	**451 (4.17)**	**621 (0.095)**	**648**	**1.29 (0.079)[i]**	**-1.31[i]**	**-5.74**	**-3.14**	**2.60**

[a] In CH_3CN solutions (1×10^{-5}M). [b] In degassed CH_3CN solutions at 298 K. [c] Neat films were made on glass substrates with a thickness of about 90 nm. [d] The emission quantum yields were calculated by comparison with $[Ru(bpy)_3]^{2+}$ (φ_{std} = 0.095) in acetonitrile solution at room temperature. [e] From CV measurements, $E_{1/2} = 1/2(E_{pa}+E_{pc})$; 0.1 M acetonitrile/TBAP versus Ag/AgCl. [f] From the formula $E_{HOMO}= [-e(E_{ox} - E_{1/2(Fc/Fc+)}] - 4.8$ eV. [g] From the formula $E_{LUMO}=[-e(E_{red} - E_{1/2(Fc/Fc+)}] - 4.8$ eV . [h] From the formula $E_{gap}= E_{HOMO}- E_{LUMO}$. [i] An reversible electrochemical process. [j] A irreversible electrochemical process . Reference [8].

Table S1. UV/Vis, Emission, and Redox Properties of NE01-03[8]

References:

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