Supplementary Information

A new class of color-tunable electroluminescence of ruthenium(II) phenanthroline emitters

Hashem Shahroosvand[a]*, Parisa Abbasi[a], Alireza Faghih[a], Ezeddin Mohajerani[b], Mohammad Janghouri[b]

[a]Chemistry Department, University of Zanjan, Zanjan, Iran.
[b]Laser and Plasma Research Institute, Shahid Beheshti University, Tehran, Iran

S1:

The wavelength of electroluminescence (EL) and photoluminescence (PL) emissions of reported ruthenium polypyridine complexes.

Complex/reactant	λ_{em} (nm)	λ_{el} (nm)	ref
$Ru(bpy)_3^{2+}$	608	608	1,2,3
$Ru(bpy)_3^{2+}/C_2O_4^{2-}$	610	610	4
$Ru(bpy)_3^{2+}/C_2O_4^{2-}$		591	5
$Ru(bpy)_3^{2+}/S_2O_8^{2-}$	625	625	4,6
$Ru(bpy)_3^{2+}$ /TPrA	610	610	7
$Ru(dmbp)_3^{2+}/C_2O_4^{2-}$		594	5
$Ru(phen)_3^{2+}$	590	590	8
$Ru(phen)_3^{2+}/C_2O_4^{2-}$		585	5
$Ru(dmphen)_3^{2+}/C_2O_4^{2-}$		591	5

Ru(terpy)$_3^{2+}$		660	8
Ru(bpz)$_3^{2+}$	585	585	9,10
Ru(bpz)$_3^{2+}$/$S_2O_8^{2-}$	585	590	11
Ru(dp-bpy)$_3^{2+}$	635	635	12
Ru(dp-phen)$_3^{2+}$	615	615	12
(bpy)$_2$Ru(bphb)$^{2+}$	624	624	13
(bpy)$_2$Ru(bphb)$^{2+}$ /TPrA	624	624	13
(bpy)$_2$Ru(bphb)$^{2+}$/$S_2O_8^{2-}$	624	624	13
[(bpy)$_2$Ru]$_2$(bphb)$^{4+}$	624	624	13
[(bpy)$_2$Ru]$_2$(bphb)$^{4+}$/TPrA	624	624	13
[(bpy)$_2$Ru]$_2$(bphb)$^{4+}$/$S_2O_8^{2-}$	624	624	13
(bpy)$_2$Ru(AZA-bpy)$^{2+}$/TPrA	603	603	14
(bpy)$_2$Ru(AZA-bpy)$^{2+}$/TPrA	613	613	14
(bpy)$_2$Ru(CE-bpy)$^{2+}$/TPrA		650	15
(bpy)$_2$Ru(CE-bpy)$^{2+}$/TPrA		655	15
Ru(v-bpy)$_3^{2+}$	630	650	16
(bpy)$_2$Ru(DC-bpy)$^{2+}$	629	629	17
(bpy)$_2$Ru(DM-bpy)$^{2+}$	605	605	17

$(bpy)_2Ru(dpen\text{-}bpy)^{2+}$ /PF_6^-	612	612	18
$Ru(m\text{-}bpy)_3^{2+}$ /PF_6^-	609	612	18
$Ru(dtb\text{-}bpy)_3^{2+}$ /PF_6^-	610	611	18
$(bpy)_2Ru(DIM)^{2+}$	600	600	19
$(bpy)_2Ru(PBIm\text{-}H)^{2+}$ /PF_6^-		680	20
[Ru(tpy)(tpy-COOEt)] /PF_6^-	706	706	21
$Ru(DM\text{-}bpy)_3^{2+}$	604	615	22
$(bpy)_2Ru(dbeb)^{2+}$ /PF_6^-	642	640	23
$(bpy)_2Ru(pbq)^{2+}$	900	900	24
$(PBIm\text{-}H)_2Ru(pbq)^{2+}$	945	945	24
$(PBIm\text{-}H)_2Ru(acac)^{2+}$	850	880	24
$[Ru(PBIM\text{-}H)_2]_2(pbq)^{+2}$	1040	1040	24
$Ru(tpy)(trz)^{2+}$ /PF_6^-	723	717	25
$Ru(tpy\text{-}COOEt)(trz)^{2+}$ /PF_6^-	717	725	25
$(bpy)_2Ru(Mt\text{-}bpy)^{2+}$ /PF_6^-	625	557	26

RuTRu	625	598	26
$(bpy)_2Ru(aa\text{-}bpy)^{2+}$ /PF_6^-	649	699	27
Ru_2 $(bpy)_4$ (im-phen) / ClO_4^-	638	655	28
$(bpy)_2Ru(Eh\text{-}bpy)^{2+}$ /PF_6^-	427	600	29
$(bpy)_2Ru(Hmh\text{-}bpy)^{2+}$ /PF_6^-	427	600	29
(H2MPy3,4DMPP)Ru(bpy)2Cl /PF_6^-	655	656	30
$Ru_2(bpy)_2(tpy)_2(BTB)^{2+}$	680	710	31
$Ru_2(bpy)_2(tpy)_2(4\text{-}TBN)^{3+}$	676	680	31
$[Ru(bpy)_2]_2(bmpa\text{-}bpy)^{+2}$/ PF_6^-	642	596	32
$[Ru(bpy)_2]_2(bmdpa\text{-}bpy)^{+2}$/ PF_6^-	638	570	32
$[Ru(bpy)_2]_2(bmna\text{-}bpy)^{+2}$/ PF_6^-	636	570	32

m-bpy = 4-methyl-2,2′-bipyridine

dtb-bpy = 4,4′-di-tert-butyl-2,2′-bipyridine

dpen-bpy = 4,4′-di-n-pentyl-2,2′-bipyridine

DIM = 4,7-dimethyl-1,10-phenanthroline

PBIm-H =2-(2-pyridyl)-1H-benzoimidazole

tpy= 2,2′,6′,2″-terpyridine

tpy-COOEt = 2,2′,6′,2″, terpyridine-4′-carboxylic acid ethyl ester

DM-bpy = 4,4′-dimethyl-2,2′- bipyridine

dbeb= 4,4′-dibutyl ester-2,2′-bipyridine

pbq=2,3-bis(2-pyridyl)benzoquinoxaline

acac=acetylacetone

trz= 2-phenyl-4,6-dipyridin-2-yl-1,3,5-triazine

RuTRu = bis-2,2′-bipyridyl-ruthenium-bis-[2-((E)-4′-methyl-2,2′-bipyridinyl-4)-ethenyl]-thienyl-bis-2,2′-bipyridyl-ruthenium tetra hexafluorophosphate

Mt-bpy =4-methyl-4′-(2-thienylethenyl)-2,2′-bipyridine

aa-bpy= Acrylic acid 4′-acryloyloxymethyl-2,2′-bipyridinyl-4-ylmethyl ester

im-phen =1,2-bis(4-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)phenoxy)ethane

Eh-bpy =4,4′-bis(3-ethylheptyl)-2,2′-bipyridine

Hmh-bpy =4-dihexylmethyl-4′-heptyl-2,2′-bipyridine

H2MPy3,4DMPP = meso-tris-3,4-dimethoxyphenyl-mono-(4-pyridyl)porphyrin

4-TBN = 4-(1H-tetrazol-5-yl)benzonitrile

BTB = bis(1H-tetrazol-5-yl)benzene

bpy = 2,2′-bipyridine

$C_2O_4^{2-}$ = oxalate ion

$S_2O_8^{2-}$ = persulfate or peroxydisulfate

TPrA = tri-n-propylamine

dmbp = 4,4′-Me2bpy and DM-bpy = 4,4′-dimethyl-2,2′-bipyridine

phen = 1,10-phenanthroline

terpy = 2,2′,2″-terpyridine

bpz =2,2′-bipyrazine

dp-bpy = 4,4′-biphenyl-2,2′-bipyridyl

dp-phen =4,7-diphenyl-1,10-phenanthroline

dmphen = 4,7-dimethyl-1,10-phenanthroline

bphb = 1,4-bis(4′-methyl-2,2′-bipyridin-4-yl)benzene

AZA-bpy = 4-(N-aza-18-crown-6-methyl-2,2′-bipyridine

CE-bpy= bipyridine ligand where a crown ether (15-crown 5) is bound to the bpy ligand in the 3- and 3′-positions

v-bpy =4-vinyl-4′-methyl-2,2′-bipyridine

DC-bpy = 4,4′-dicarboxy-2,2′-bipyridine

PF_6^- =hexafluorophosphate

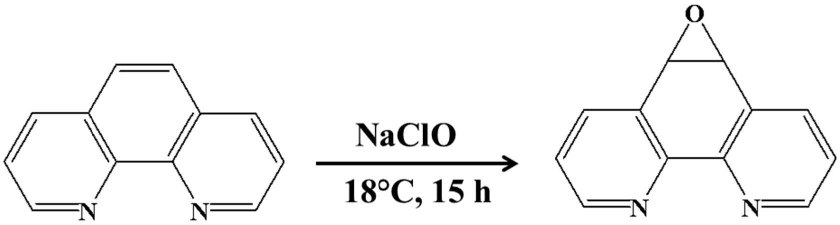
bmpa-bpy =bis(4′-methyl-2,2′-bipyridinyl-4-carbonyl)-(1,4-phenylediamine)

bmdpa-bpy =bis(4′-methyl-2,2′-bipyridinyl-4-carbonyl)-(1,4-diphenylediamine)

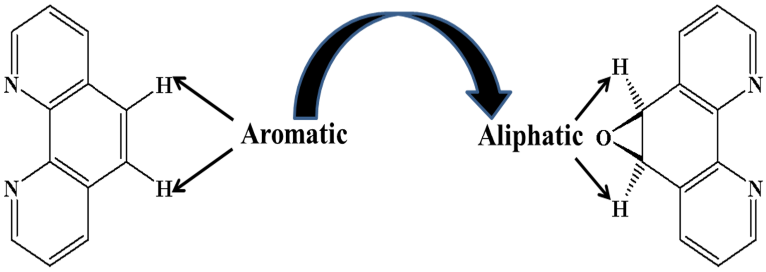
bmna-bpy =bis(4′-methyl-2,2′-bipyridinyl-4-carbonyl)-(1,4-naphthalenediamine)

S2.

Snthesis of 1,10 phenanthroline 5, 6 epoxide. 1 mmol (198 mg) of 1,10 phananthroline , dissolved in 20 mL of chloroform, is added to 50 mL of 0.6 M aqueous sodium hypochlorite, the pH of which has been adjusted to 8.5 with concentrated HCl. Tetrabuthyl ammonium hydrogen sulfate(0.2-1 ev) is added and the mixture is stirred at room temperature while cooling in a water bath. The conversion of the reaction was followed by NMR because the reaction time varies due to the quality of the bleach. The yield decreases over 2 hours. The best conversion was obtained after2 hours at room temperature. After the completion of the reaction, the organic layer was isolated and washed with water (3×100 ml). The washed organic layer was dried with sodium carbonate anhydrous and filtered, and the solvent was evaporated by rotary at room temperature. The crude epoxide was purified by recrystallization from chloroform/hexan (5:1) to give the pure product (yield:74%), m. p. 163-165 ^{0}C, Anal. Calc for C12H8N2O: C,73. 465; H, 4116; N, 14, 281. Found: C, 73,312; H, 4.158; N, 14.376.

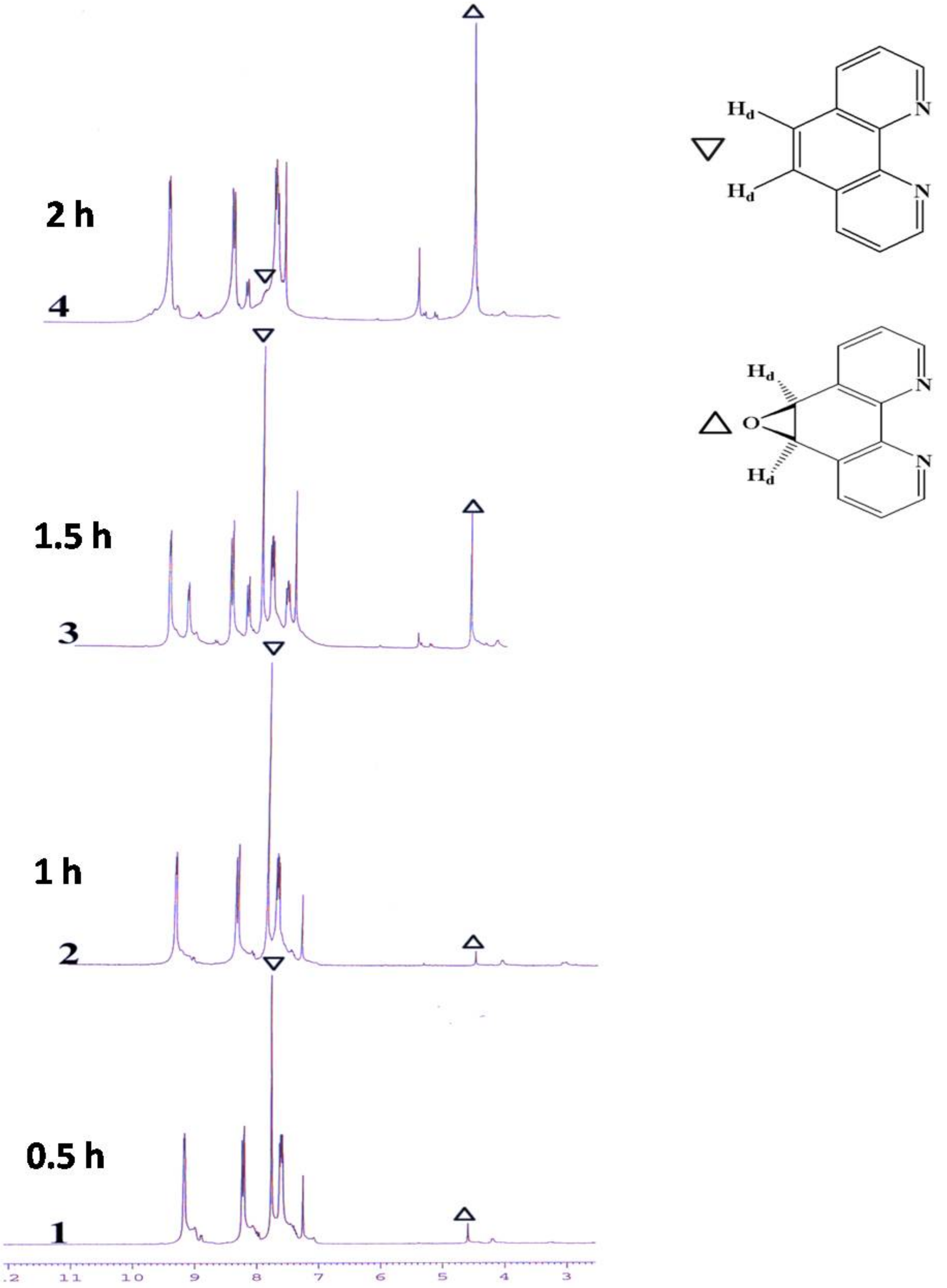


S3.



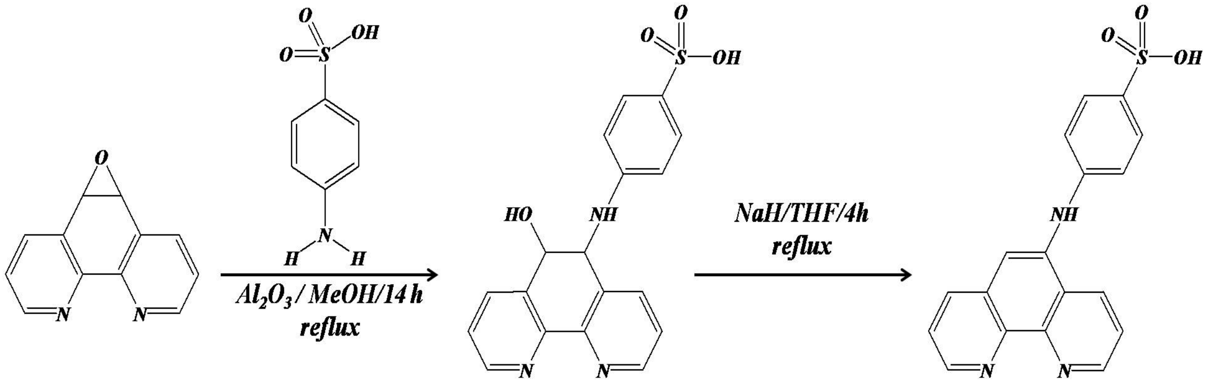
S4.

^{1}H-NMR spectra of conversion of phen to ephen in different reaction times dissolved in DMSO solvent at room temperature.



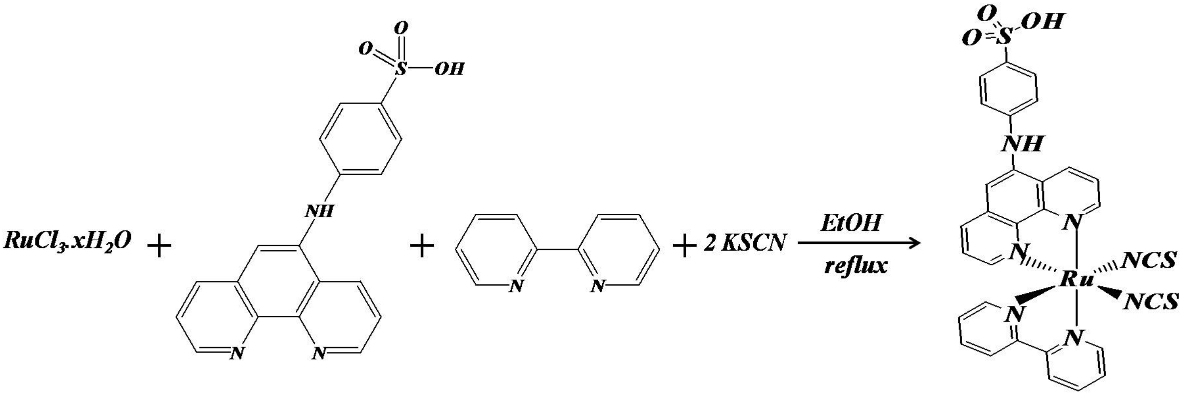
S5.

Synthesis of 4-(1, 10-phenanthroline-6-ylamino)benzenesulfonic acid. A mixture of L (0.1 g, 0.5 mml) and 4-amino-benzen sulfunic acid (0.0885g, 0.5 mmol) in 50 mL of dry methanol was created and alumina (5 mmol) was added as the catalyst. The mixture was refluxed for 14 hours. After the mixture had cooled to room temperature, the solvent was removed by rotary evaporation. This product was further purified by column chromatography using silica as the column support and acetone/ methanol (3: 10, v/v) as the eluent. The major band was collected and corresponds to the desired ligand. 57% yield. In order to remove the hydroxyl group from L1, a suspension of NaH (0.174 g) in 10 mL of dry THF was added to L1 (0.143g, 4.593 mmol). The mixture was refluxed for 4 hours under a nitrogen atmosphere. After completion, the excess NaH was quenched by the addition of 2.5 mL of methanol. The solution was then removed by rotary evaporation and was thrice washed with ethanol.



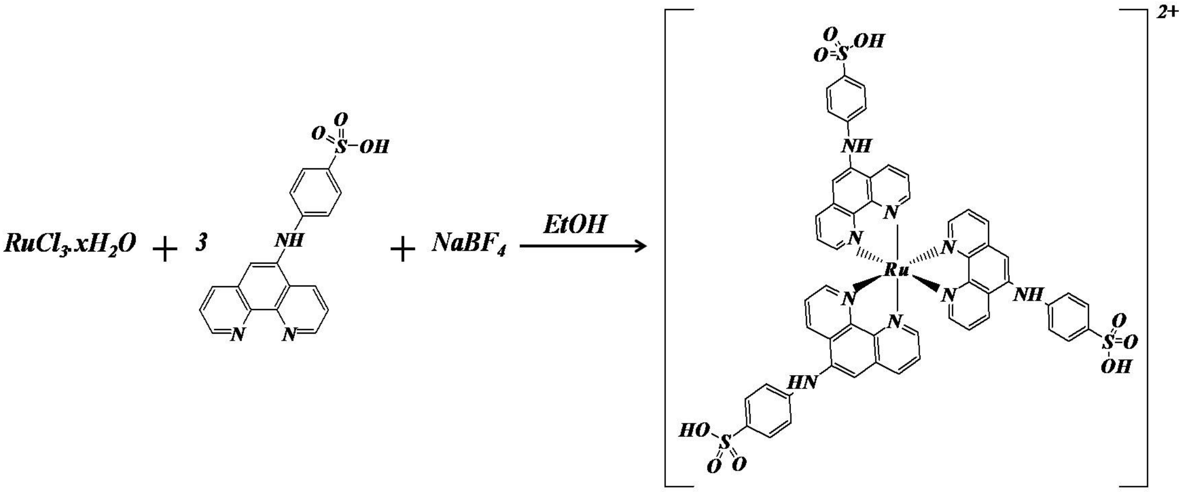
S6.

Synthesis of [Ru(L_3)(bpy)($SCN)_2$] (1). Complex (1) was synthesized in a three neck balloon under an nitrogen atmosphere by refluxing a solution of bpy (0.0118 g, 0.06 mmol) and RuCl3 .xH2O (0.0089 g, 0.06 mmol) in 50 mL of ethanol for 2 hours. Then, L1(0.02 g, 0.06 mmol) was added and the solution was refluxed for an additional 2 hours. Subsequently KNCS (0.1 g) was separately added to the above solution and the mixture was again refluxed for 1 h. After this time, the reaction mixture was allowed to cool, and the precipitate was filtered and washed with ethanol and diethyl ether. This product was further purified by column chromatography using alumina as the column support and acetonitrile/methanol (2:1, v/v) as the eluent. The major brown band was collected and corresponds to the desired complex. . Yield 40%. ^{1}H NMR (250 MHz*, DMSO,d*), 4. 05 (s, 1H), 6. 70 (d, 2H), 6. 80(s,1H), 7.10(t, 2H), 7.20(s,1H), 7, 27(d, 1H), 7.65(t, 2H), 7.80(d, 3H), 8.00(d, 1H), 8.50(d, 2H), 8.60(d, 2H), 8. 80 (s, 1H).



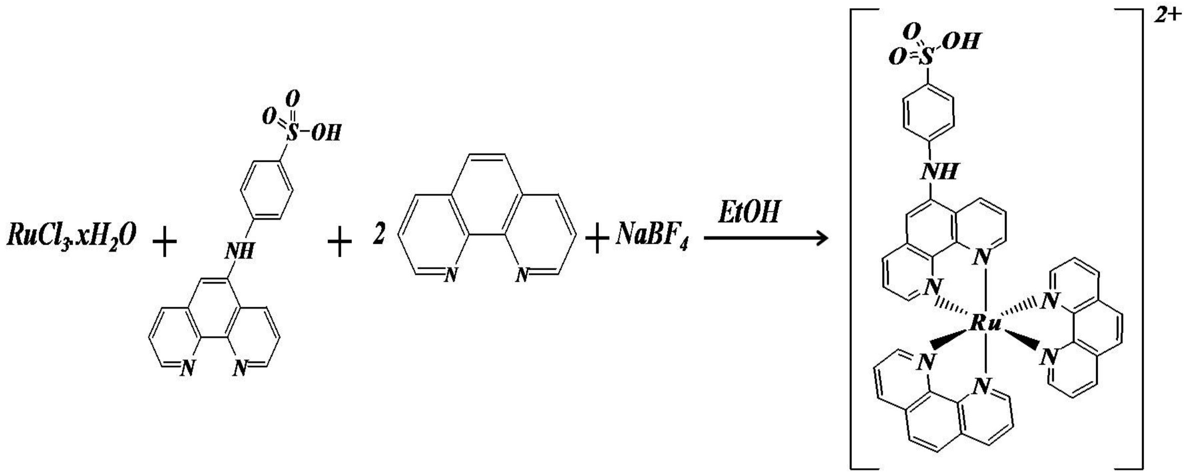
(1)

Synthesis of [Ru($L_3)_3$]($BF_4)_2$ (2). A mixture of $RuCl_3.xH_2O$ (0.0118 g, 0.06 mmol) and L1 (0.06g, 0.18 mmol) in 50 mL of ethanol was refluxed under a nitrogen atmosphere for 4 hours. Then, $NaBF_4$ (0.6g) was added and the solution was refluxed for an additional 1 h. The resulting precipitate was filtered and washed with ethanol and diethyl ether. The isolated solid was recrystallized to form methanol-diethyl ether, after which it was purified on an alumina column using methanol as eluent. Yield 42%. ^{1}H NMR (250 MHz*, DMSO,d*) δ: 4.02 (s, 3H), 6.75(d, 6H), 6. 82(s, 3H), 7. 18(t, 3H), 7.28 (t, 3H), 7. 69 (d, 6H), 7.80 (d, 3H), 8.00 (d, 3H), 8. 60(d, 3H), 8.80 (d, 3H).



(2)

Synthesis of [Ru(L$_3$)(bpy)$_2$](BF$_4$)$_2$ (3). [Ru(L$_3$)(bpy)$_2$](BF$_4$)$_2$ was prepared starting from RuCl$_3$.xH$_2$O (0.0236 g, 0.12 mmol), bpy (0.0178 g, 0.24 mmol) and L1 (0.04 g, 0.12 mmol) using the same procedure as described for [Ru(L$_3$)$_3$](BF$_4$)$_2$ (2) to yield the product. Yield 38%. ^{1}H NMR (250 MHz*, DMSO,d*) δ: 4. 03(s, 3H), 6. 72 (d, 2H) 6. 80(s, 3H), 7. 14(t, 6H), 7.65-7.70(m, 6H), 8. 03(d, 1H), 8. 50 (d, 6H), 8. 60(d, 4H), 8. 70 (d, 2H).



(3)

S 7.

The main absorption peaks in the IR spectra of complexes (1-3) , (cm^{-1}).

Emitter	$\nu_{sym}(SO_3)$	$\nu_{asym}(SO_3)$	**ν(C=C)**	**ν(SCN)**	**ν(C-H)**	**ν(O-H)**
L	1034	1202	-1370 1633-1450	-	2927	3439
(1)	1041	1180	-1385 1633-1450	2072	2919	3446
(2)	1034	1140	-1385 1633-1457	-	2919	3424
(3)	1041	1114	-1385 1633-1436	-	2927	3446

S 8.

CHN and ICP analysis for emitters (1-3).

No.	Formula	Experimental			Theoretical			ICP(ppm)
		%C	%H	%N	%C	%H	%N	
(1)	$RuC_{30}H_{21}N_7O_3S_3$	52.03	4.24	12.49	52.11	4.28	12.42	8.7
(2)	RuC_{54} $H_{39}0_{21}N_9O_9S_3B_2F_4$	57.86	4.61	10.21	57.80	4.58	10.20	6.5
(3)	RuC_{38} $H_{29}0_3N_7O_3SB_2F_4$	61.81	5.54	11.47	61.80	5.54	11.47	7.2

S9.

Material and Instruments. All chemicals and solvents were purchased from Merck & Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer 597 spectrometer ^{1}H-NMR spectra were recorded by use of a Bruker 250 MHz, spectrometer. The ruthenium content of the final material was determined by ICP-AES model Perkin Elmer 1100DV. Electrochemical measurements were made in THF using model 273 A potentiostat. A conventional three-electrode configuration consisting of a glassy carbon working electrode, and Pt-wires as both the counter and reference electrodes was used. The supporting electrolyte was 0.1 M $[Bu_4N]PF_6$. Ferrocene was added as an internal standard after each set of measurements, and all potentials reported were quoted with reference to the ferrocene-ferrocenium (Fc/Fc $^+$) couple at a scan rate of 100 mV/s. The oxidation (E_{ox}) and reduction (E_{red}) potentials were used to determine the HOMO and LUMO energy levels using the equations E_{HOMO} =- (E_{ox} + 4.8) eV and E_{LUMO} = -(E_{red} + 4.8) eV which were calculated using the internal standard ferrocene value of -4.8 eV with respect to the vacuum [33]. The PL spectra of the ruthenium compounds and PVK: PBD were measured in 1,2-dimethylformamide solution. The PL spectra were recorded by ocean optic spectrometer USB2000 during 405 nm irradiation. The emission quantum yields (Φ) were calculated by comparison with $[Ru(bpy)_3]^{2+}$ (Φ_{std} = 0.064) in acetonitrile solution at room temperature using eqn (1):

$$\Phi = \Phi_{std}\,(A_{std}/A)(I/I_{std}) \quad (1)$$

where Φ and Φ_{std} are the quantum yields of unknown and the standard samples; A and A_{std} are the absorbance at the excitation wavelength; I and I_{std} are the integrated emission intensities. Full geometric optimization and the calculation of the energetic for all of the structural variables were theoretically investigated by performing DFT calculations at the B3LYP/(6-31G**+LANL2DZ) level and taking singlet state of the complexes. All calculations and optimizations were performed in vacuum medium using the Gaussian 03 package [34]. Initial calculations were performed on the donor and acceptor moieties of the novel Ruthenium complexes to determine the HOMO and LUMO levels of the moieties independently. After the initial calculations, donor and acceptor moieties were paired, and the HOMO and LUMO levels were calculated and compared. The molecular orbital densities were viewed using Gauss View [35].

Preparation of EL devices and testing. The structure of the fabricated device is as follow: ITO/PEDOT:PSS(55nm)/PVK (85nm) /PBD(25nm)/Al(120nm)and, ITO/PEDOT:PSS(55nm)/ ruthenium complex (55nm)/Al(120nm), That is shown in figure 1.

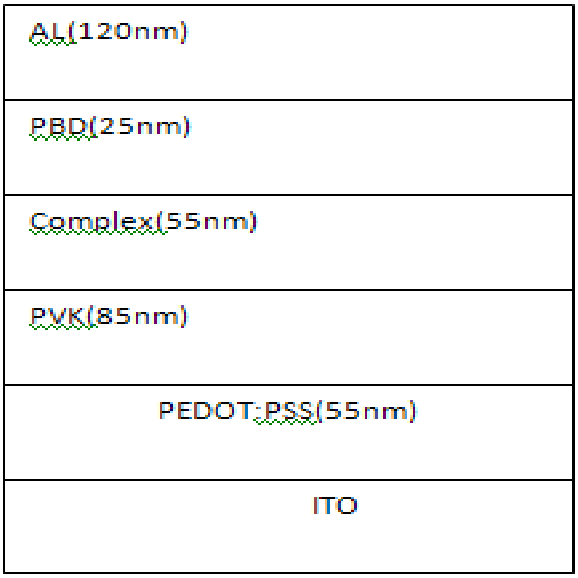
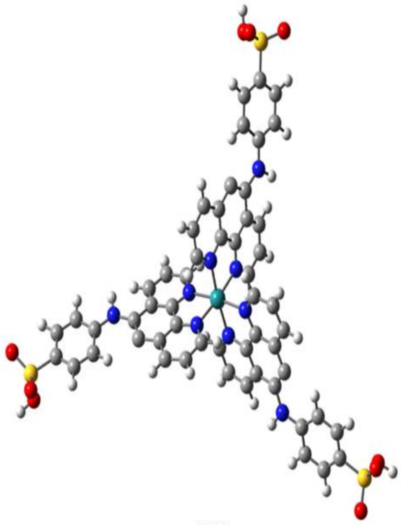


Figure 1. The layer arrangement of Ru based LED-device.

PVK as a hole-transporting and PBD as an electron-transporting material were used. Glass substrates, coated with ITO (sheet resistance of 70 Ω/m^2), were used as the conducting anode PEDOT: PSS(poly(3,4-ethylenedi-oxythiophene):poly(styrenesulfonate)) was used as a hole injection and transporting layer. All polymeric layers were successively deposited onto the ITO coated-glass by using spin-coating process from the solution. A metallic cathode of Al was deposited on the emissive layer at 8×10^{-5} mbar by thermal evaporation. The PEDOT: PSS was dissolved in DMF , spin coated on ITO and was held in an oven at 120 ^{o}C for 2 hours after deposition. PVK, PBD and ruthenium complexes with weight ratio of 0.03: 0.004: 0.01 were separately dissolved in 8 mL of dichloromethane, and then spin coated and baked at 80°C for 1 hour. The thickness of the polymeric thin film was determined by a Dektak 8000. The EL intensity and spectra were measured with an ocean optic USB2000, under ambient conditions. In addition, Keithley 2400 source meter was used to measure the electrical characteristics of the devices.

S 10.

The optimized structures of synthesized novel ruthenium complexes.



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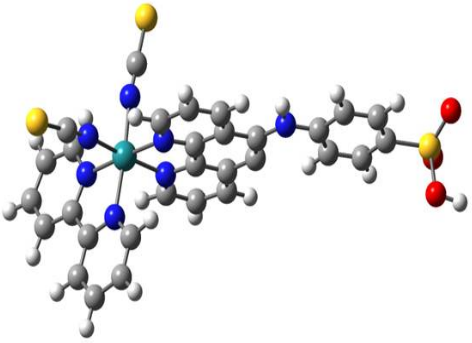
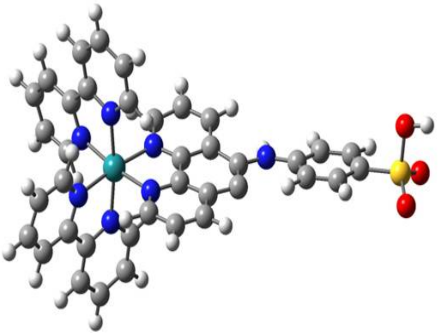


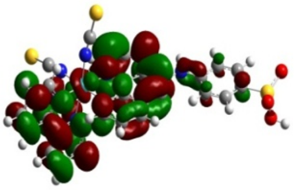
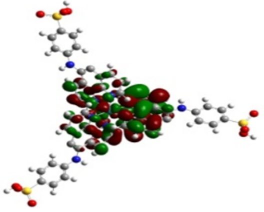
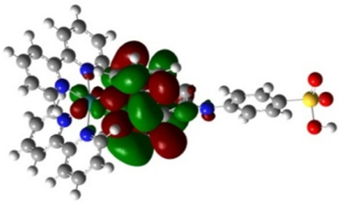
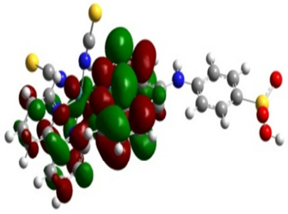
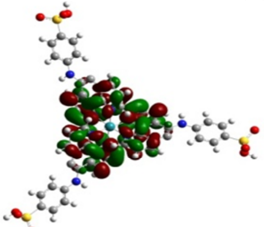
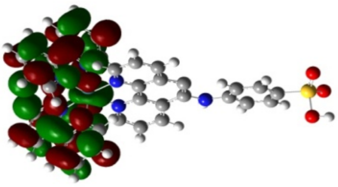
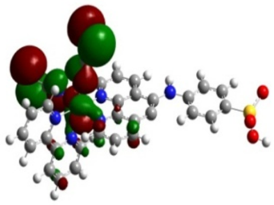
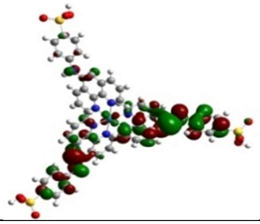
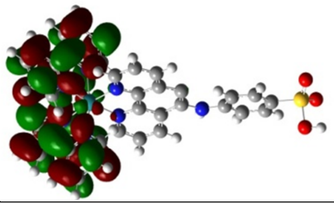
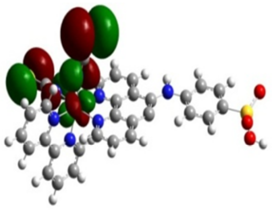
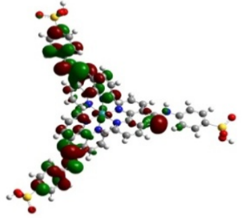
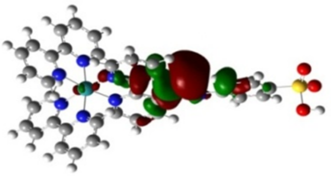
(1)



(3)

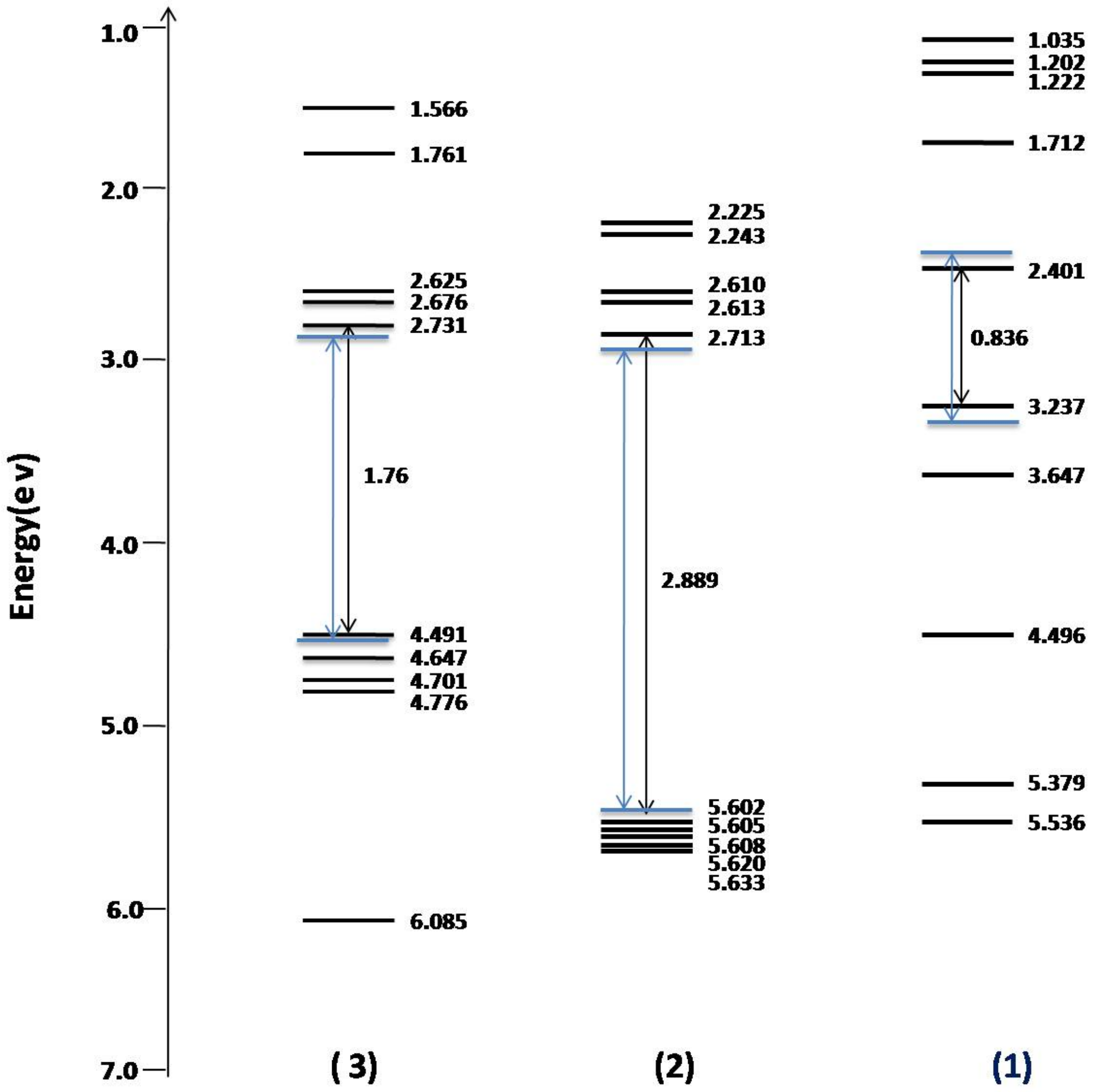
S 11.

Isodensity plots for LUMO+1 (a), LUMO (b), HOMO (c) and HOMO-1 (d) of Ru complexes (1-3) obtained by DFT calculations.

	Complex (1)	**Complex (2)**	**Complex (3)**
LUMO+1	(a) 	(a) 	(a) 
LUMO	(b) 	(b) 	(b) 
HOMO	(c) 	(c) 	(c) 
HOMO-1	(d) 	(d) 	(d) 

S 12.

Diagram of five highest occupied and five lowest unoccupied molecular orbital levels of novel Ru complexes by DFT calculation (black line). Estimated HOMO-LUMO energy level by CV analysis (blue line).



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