

# Ruthenium Phenanthroimidazole complexes for Near Infrared Light-Emitting Electrochemical Cell

## Experimental section

**General information** : All reagents were used as received without further purification. RuCl<sub>3</sub>·3H<sub>2</sub>O, 4,4'-Dimethyl-2, 2'-dipyridyl (dmbpy), ammonium acetate, 2, 2'-bipyridine (bpy), 4, 7-diphenyl-1, 10-phenanthroline (bathophen) were purchased from sigma Aldrich. 1,10-phenanthroline (phen), potassium bromide, sodium perchlorate, sodium hydroxide, 4-methoxy aniline, 4- methyl benzaldehyde, glacial acetic acid, DMF, ethylene glycol, acetonitrile, nitric acid, sulfuric acid, chloroform and tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>, used as the supporting electrolyte for electrochemical measurements) were purchased from Merck. IR spectra were recorded on a Perkin-Elmer 597 spectrometer. <sup>1</sup>H-NMR spectra were recorded using a Bruker 250 MHz, spectrometer. Elemental analyses were performed on ElementarVario EL CHN elemental analyzer. The Electrochemical studies of complexes (2×10<sup>-3</sup>M) were performed with a SAMA500 electrochemistry system. In cyclic voltammetry (CV) the following parameters and relation were used: scan rate, 30 mV s<sup>-1</sup>; formal potential E<sup>o</sup> = (E<sub>pa</sub> + E<sub>pc</sub>)/2 where E<sub>pa</sub> and E<sub>pc</sub> are anodic and cathodic peak potentials, respectively; ΔE<sub>p</sub> is the peak-to-peak separation. All experiments were done under a dry N<sub>2</sub> atmosphere at 298 K in a three-electrode configuration by using a Pt-disk working electrode and a Pt-wire auxiliary electrode. The potentials are referenced to a saturated Ag/AgCl reference electrode. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (TBAP) in CH<sub>3</sub>CN solutions. The oxidation (E<sub>ox</sub>) and reduction (E<sub>red</sub>) potentials were used to determine the HOMO/LUMO energy levels and energy gap (E<sub>gap</sub>) using the equations E<sub>HOMO</sub> = [-e(E<sub>ox</sub>(vs. Ag/AgCl) - E<sub>1/2</sub>(FC/Fc<sup>+</sup> vs. Ag/AgCl))] - 4.8 eV and E<sub>LUMO</sub> = [-e(E<sub>red</sub>(vs. Ag/AgCl) - E<sub>1/2</sub>(FC/Fc<sup>+</sup> vs. Ag/AgCl))] - 4.8 eV and E<sub>gap</sub> = -E<sub>HOMO</sub> - E<sub>LUMO</sub> which E<sub>1/2</sub>(FC/Fc<sup>+</sup> vs. Ag/AgCl) is the reduction potential of ferrocene which was found to be 0.43 V. UV-visible absorption spectra were carried out in a 1 cm path length quartz cell using Ultrospec3100 pro spectrophotometer in CH<sub>3</sub>CN solutions (1×10<sup>-5</sup>M). Photoluminescence (PL) emission spectra of complexes (λ<sub>exc</sub> = 460 nm) in degassed acetonitrile solutions, hbbp in chloroform (λ<sub>exc</sub> = 405 nm) at 298 K and neat films were made on glass substrates with a thickness of about 90 nm were recorded using Varian-Cary Eclipse fluorescence spectrophotometer and AvaSpec-125 spectrophotometer at the excitation wavelength of 460 nm, respectively. The emission quantum yields were calculated by comparison with [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in degassed acetonitrile solution at room temperature as a standard (Φ<sub>std</sub> = 0.095<sub>2</sub>). Quantum yields were calculated using the following equation:

$$\Phi_{unk} = \Phi_{std} \cdot \left( \frac{I_{unk}/A_{unk}}{A_{std}/I_{std}} \right) \cdot \left( \frac{\eta_{unk}}{\eta_{std}} \right)^2$$

Where Φ<sub>unk</sub> is the relative radiative quantum yield of the sample, I<sub>unk</sub> and I<sub>std</sub> are the integrated areas of the corrected emission spectra of the sample and standard respectively, A<sub>unk</sub> and A<sub>std</sub> are the absorbances of the sample and the standard at the excitation wavelength, and η<sub>unk</sub> and η<sub>std</sub> 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. After evaporation of the solvent in air, the films were dried overnight under vacuum at room temperature.

**Fabrication and measurements of LEC devices:** Indium tin oxide (ITO) coated glass with a sheet resistance of 15-18 Ω/ was used as anode. After being sufficiently cleaned with isopropanol, ethanol and deionized water, it was dried in the oven at 90 °C for 4 h. The devices were prepared by spin-coating a thin layer of each complex (NE01-04) from a 4% (w/v) acetonitrile solution at room temperature, on top of an ITO glass substrate. All solution and film preparation were carried out under ambient conditions. The thicknesses of the films were ~ 85 nm, measured with profilometry. After spincoating, the thin films were baked at 75 °C in inert atmosphere for 12 hours to remove the solvent residue (acetonitril). A Ga: In (75.5:24.5 wt %, mp 15.7 °C) eutectic cathode (ca. 3.5 mm diameter) was printed on the films at room temperature by using a special syringe 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 electrical and emission characteristics of LEC devices were measured using a SAMA500 electroanalyzer system and an AvaSpec-125 spectrophotometer and a Photo Research PR-650 spectroradiometer.

**Quantum chemical calculations:** The molecular and electronic structure calculations were performed with density functional theory (DFT) using the Gaussian 03(G03) software package. The B3LYP functional with the LANL2DZ basis set was carried out. <sup>3</sup> All geometry optimizations were performed in either C1 or C2 symmetry with subsequent frequency analysis to show that the structures are at the local minima on the potential energy surface. The electronic orbitals were visualized using Gauss View 3.0.

**Synthesis and characterization:** The compounds cis-[Ru(bpy)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O (bpy: 2, 2'-Bipyridine), cis-[Ru(dmbpy)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O (dmbpy: 4,4'-Dimethyl-2,2'-dipyridyl), cis-[Ru(phen)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O (Phen: Phenanthroline), cis-[Ru(bathophen)<sub>2</sub>Cl<sub>2</sub>].H<sub>2</sub>O.DMF(4,7-Diphenyl-1,10-phenanthroline), and 1,10-phenanthroline-5,6-dione (phendione) were synthesized according to literature methods.<sup>4-6</sup>

**Synthesis of 2-(4-Methylphenyl)-1-(4-Methoxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (MPIP):** A mixture of 1,10-phenanthroline-5,6-dione (0.212 g, 1.0 mmol), 4-methylbenzaldehyde (0.120 g, 1.0 mmol), p-anisidine (0.123 g, 1 mmol) and ammonium acetate (770 mg, 10 mmol, excess) was refluxing in glacial acetic acid (10 mL) for 24 h under a N<sub>2</sub> atmosphere. The reaction mixture was cooled to room temperature,

poured into water (30 mL), treated with a 25% NH<sub>3</sub> solution until the pH=6, giving rise to a thick dark blue suspension. The suspension was extracted with 40 mL of chloroform and then removed the solvent by rotary evaporation and the residue was washed with methanol and acetone. The recrystallization from CH<sub>2</sub>Cl<sub>2</sub>-acetone was repeated one more time to give the product as a white solid. Yield: 46%. mp. 286°C, Anal. calcd. For C<sub>27</sub>H<sub>20</sub>N<sub>4</sub>O (%) : C, 77.87; H, 4.84; N, 13.45. Found (%): C, 77.89; H, 4.81; N, 13.39. IR (KBr):  $\tilde{\nu}$  = 3065 (C-H aromatic), 2943 (C-H aliphatic), 1613 (C=C), 1598 (C=N), 1378 cm<sup>-1</sup>. <sup>1</sup>HNMR (250 MHz, CDCl<sub>3</sub>): 9.12-9.19(m, 2H), 9.06(t, 1H), 7.77 (dd, 1H), 7.49-7.53 (m, 3H), 7.43 (d, 2H), 7.33 (dd, 1H), 7.10-7.16 (m, 4H), 3.96(s, 3H), 2.35 (s, 3H). <sup>13</sup>CNMR (62 MHz, CDCl<sub>3</sub>): 160.5, 148.82, 147.72, 139.27, 130.42, 129.78, 129.11, 129.07, 127.91, 127.06, 123.97, 123.38, 122.06, 119.92, 115.46, 55.63, 21.31.

**General procedure for synthesis of [Ru(L)<sub>2</sub>(MPIP)](ClO<sub>4</sub>)<sub>2</sub>:** A mixture of cis-[Ru(N<sup>^</sup>N)<sub>2</sub>Cl<sub>2</sub>].2H<sub>2</sub>O (0.1 mmol) and MPIP (41.6 mg, 1 mmol) was deoxygenated by N<sub>2</sub> and heated under N<sub>2</sub> at 126 °C in ethylene glycol (3 ml) for 12.0 h (except NE04, 24h) to give a clear red solution. Upon cooling, the solution was treated with saturated aqueous solution of NaClO<sub>4</sub> and gave a pale orange precipitate and washed several times with water to remove traces of salts. The crude product was purified by column chromatography on alumina with CH<sub>3</sub>CN-toluene (1/1, v/v) as an eluent. The mainly red band was collected. The solvent was removed under reduced pressure and red crystals were obtained.

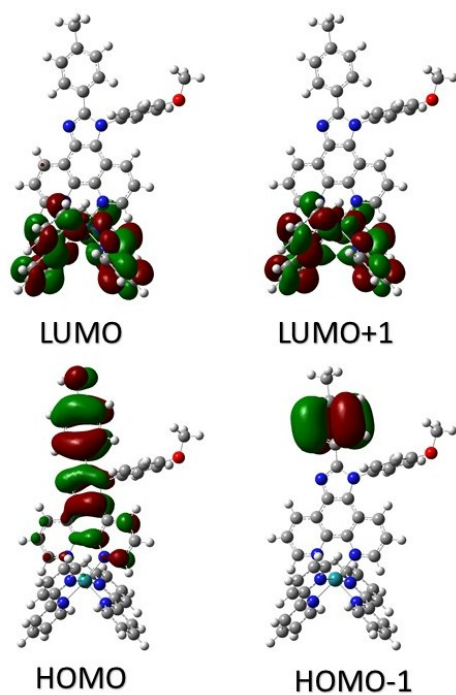
**CAUTION:** Perchlorate salts of metal complexes with organic ligands are potentially explosive, and only small amounts of the material should be prepared and handled with great care!

**[Ru(bpy)<sub>2</sub>(MPIP)](ClO<sub>4</sub>)<sub>2</sub>(NE01).**Yield: 82% (84 mg). Anal. calcd. For C<sub>47</sub>H<sub>36</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>9</sub>Ru (%) : C, 54.87; H, 3.53; N, 10.89. Found (%): C, 54.80; H, 3.52; N, 10.79 (MW, 1029). IR (KBr):  $\tilde{\nu}$  = 3072 (C-H aromatic), 2922 (C-H aliphatic), 1617 (C=C), 1602 (C=N), 1513, 1089 (ClO<sub>4</sub>) cm<sup>-1</sup>. <sup>1</sup>HNMR (250 MHz, D<sub>6</sub>-DMSO): 9.11 (d, 2H), 8.82 (q, 4H), 8.31 (d, 2H), 8.16 (d, 2H), 8.06-8.11 (m, 2H), 7.92-7.97 (m, 3H), 7.8 (t, 2H), 7.61-7.66 (m, 3H), 7.49-7.59(m, 4H), 7.37 (t, 2H), 7.21-7.22 (m, 4H), 3.89 (s, 3H), 2.30 (s, 3H).<sup>13</sup>CNMR (62 MHz, CDCl<sub>3</sub>): 161.02, 157.20, 157.12, 157.03, 154.60, 151.85, 150.24, 145.80, 145.70, 140.25, 138.34, 136.45, 131.03, 130.41, 129.60, 129.45, 128.38, 128.25, 127.33, 126.83, 126.24, 124.94, 122.01, 116.21, 56.14, 21.31. ESI-MS: m/z, 928.556, [M-H -2ClO<sub>4</sub>]<sup>+</sup>.

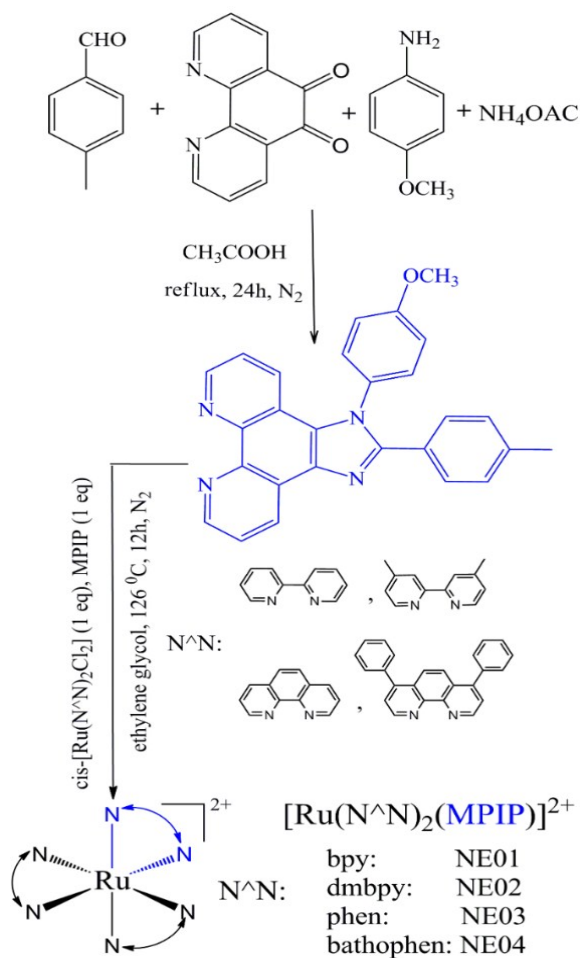
**[Ru(dmbpy)<sub>2</sub>(MPIP)] (ClO<sub>4</sub>)<sub>2</sub>(NE02).**Yield: 79% (86 mg). Anal. calcd. For C<sub>51</sub>H<sub>44</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>9</sub>Ru (%) : C, 56.46; H, 4.09; N, 10.33. Found (%): C, 56.41; H, 4.13; N, 10.32 (MW, 1085). IR (KBr):  $\tilde{\nu}$  = 3079 (C-H aromatic), 2931 (C-H aliphatic), 1610 (C=C), 1597 (C=N), 1550, 1087 (ClO<sub>4</sub>) cm<sup>-1</sup>. <sup>1</sup>HNMR (250 MHz, D<sub>6</sub>-DMSO): 9.15 (d, 2H), 8.61-8.77 (m, 4H), 8.1 (d, 2H), 7.94 (d, 4H), 7.82 (m, 2H), 7.63 (m, 4H), 7.5 (d, 2H), 7.36 (d, 2H), 7.19-7.23(m, 4H), 3.87 (s, 3H), 2.29 (s, 3H).<sup>13</sup>CNMR (62 MHz, CDCl<sub>3</sub>): 160.99, 156.55, 150.90, 150.13, 140.24, 136.39, 130.38, 129.59, 129.56, 129.43, 129.06, 128.39, 127.21, 126.80, 125.85, 125.49, 121.92, 116.21, 100.97, 56.12, 21.29, 21.12. ESI-MS: m/z, 984.754, [M-H -2ClO<sub>4</sub>]<sup>+</sup>.

**[Ru(phen)<sub>2</sub>(MPIP)] (ClO<sub>4</sub>)<sub>2</sub>(NE03).**Yield: 85% (91.5 mg). Anal. calcd. For C<sub>51</sub>H<sub>36</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>9</sub>Ru (%) : C, 56.88; H, 3.37; N, 10.41. Found (%): C, 56.87; H, 3.35; N, 10.43 (MW, 1077). IR (KBr):  $\tilde{\nu}$  = 3070 (C-H aromatic), 2926 (C-H aliphatic), 1608 (C=C), 1598 (C=N), 1558, 1088 (ClO<sub>4</sub>) cm<sup>-1</sup>. <sup>1</sup>HNMR (250 MHz, D<sub>6</sub>-DMSO): 9.12 (d, 2H), 8.71-8.76 (m, 4H), 8.33 (d, 4H), 8.03 (m, 4H), 7.92 (m, 2H), 7.58-7.83 (m, 6H), 7.49 (d, 4H), 7.11-7.23 (m, 4H), 3.87 (s, 3H), 2.28 (s, 3H).<sup>13</sup>CNMR (62 MHz, CDCl<sub>3</sub>): 161.02, 153.09, 151.44, 150.70, 147.68, 143.31, 140.22, 137.31, 130.92, 130.36, 129.56, 128.48, 126.77, 126.10, 125.88, 121.91, 116.22, 56.10, 21.24. ESI-MS: m/z, 976.588, [M-H -2ClO<sub>4</sub>]<sup>+</sup>.

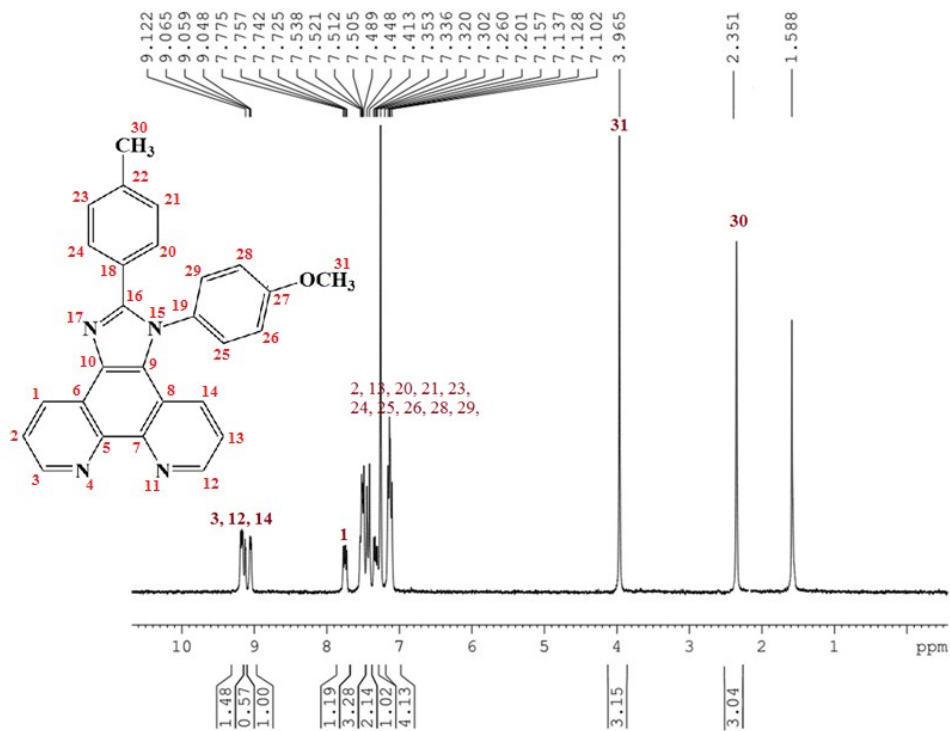
**[Ru(bathophen)<sub>2</sub>(MPIP)] (ClO<sub>4</sub>)<sub>2</sub>(NE04).** Yield: 73% (100 mg). Anal. calcd. For C<sub>75</sub>H<sub>52</sub>Cl<sub>2</sub>N<sub>8</sub>O<sub>9</sub>Ru (%) : C, 65.22; H, 3.79; N, 8.11. Found (%): C, 65.21; H, 3.78; N, 8.13 (MW, 1381). IR (KBr):  $\tilde{\nu}$  = 3068 (C-H aromatic), 2929 (C-H aliphatic), 1611 (C=C), 1600 (C=N), 1551, 1087 (ClO<sub>4</sub>) cm<sup>-1</sup>. <sup>1</sup>HNMR (250 MHz, D<sub>6</sub>-DMSO): 9.21 (d, 1H), 8.14-8.35 (m, 10H), 7.94 (m, 2H), 7.55-7.82 (m, 27H), 7.24 (m, 6H), 3.87 (s, 3H), 2.30 (s, 3H).<sup>13</sup>CNMR (62 MHz, CDCl<sub>3</sub>): 161.01, 154.67, 152.61, 148.45, 148.45, 146.18, 140.25, 136.25, 135.92, 130.38, 130.08, 129.61, 128.65, 128.46, 126.84, 126.55, 125.98, 122.07, 119.34, 116.24, 56.12, 21.29. ESI-MS: m/z, 1280.654, [M-H -2ClO<sub>4</sub>]<sup>+</sup>.



**Figure S1.** Electron density contours calculated for the HOMOs and the LUMOs of NE01 in the ground state.

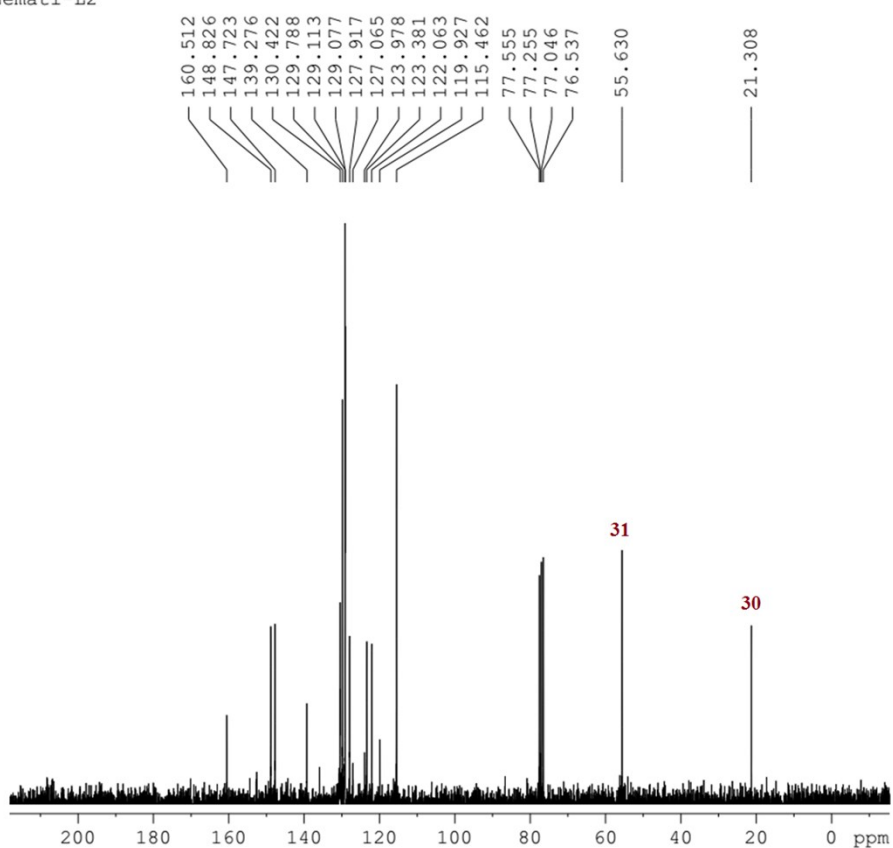


**Scheme S1.** Synthesis of phenanthroimidazole ligand (MPIP) and their derivative Ru(II) complexes



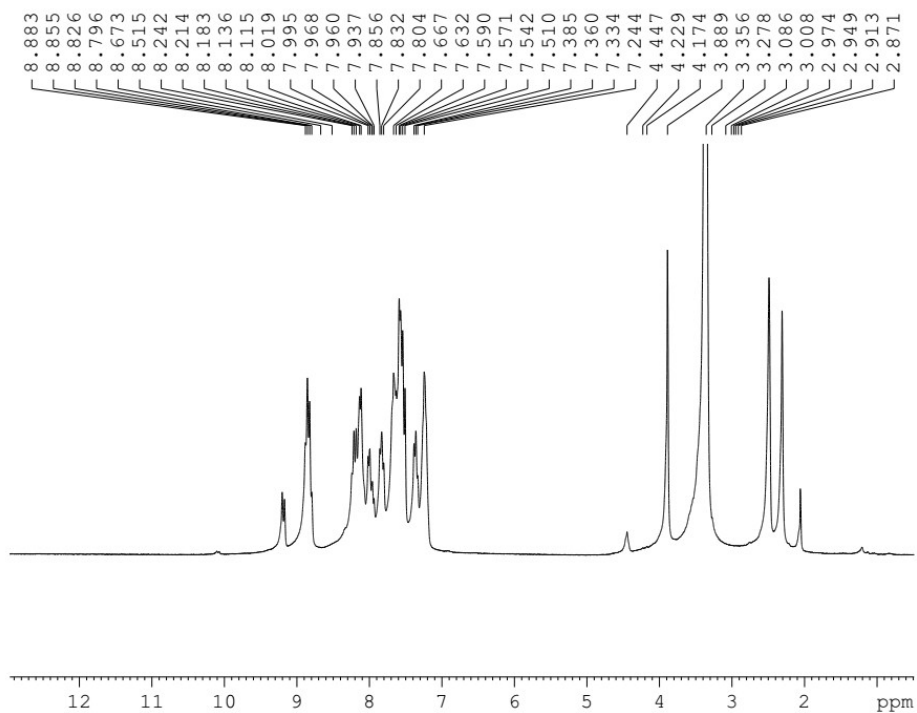
S2.  $^1\text{H NMR}$  of phenanthroimidazole ligand (MPIP) in  $\text{CDCl}_3$

Nemati-L2



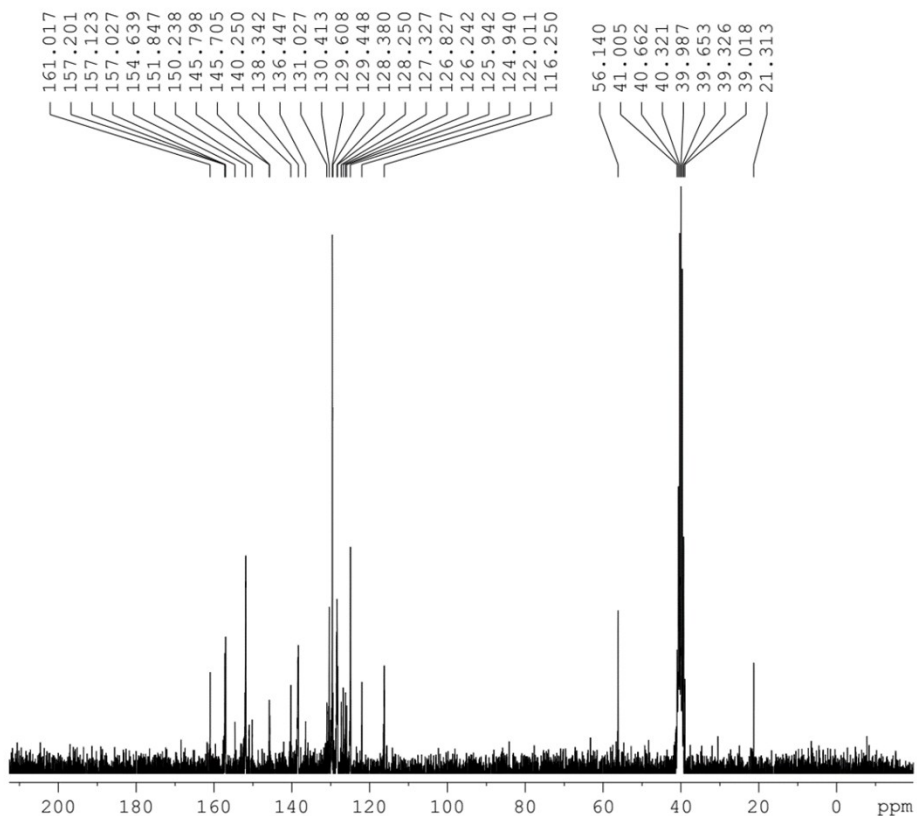
S3.  $^{13}\text{C NMR}$  of phenanthroimidazole ligand (MPIP) in  $\text{CDCl}_3$

Nemati-NEO1



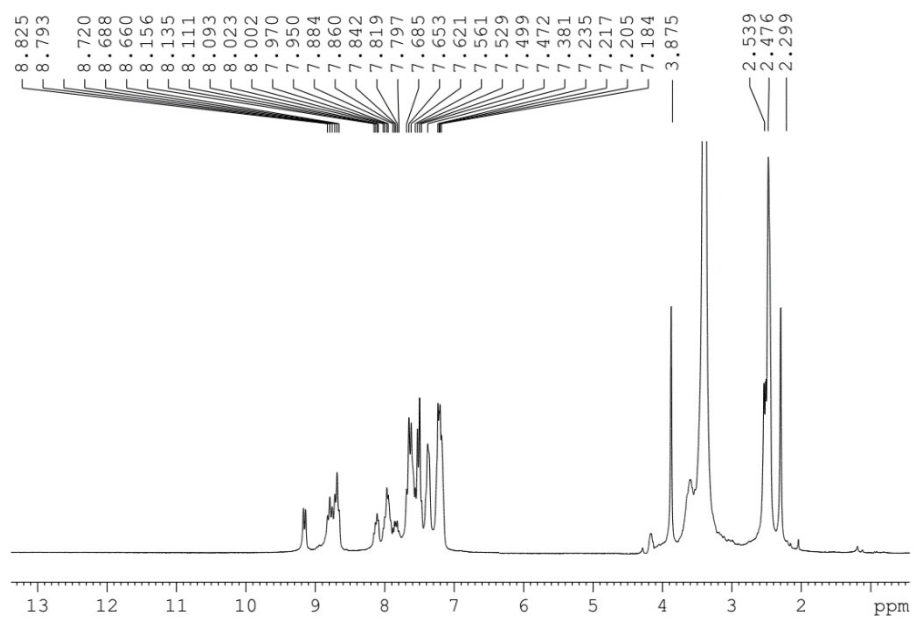
S4. <sup>1</sup>H NMR of NEO1 in D<sub>6</sub>-DMSO

Nemati-NEO1



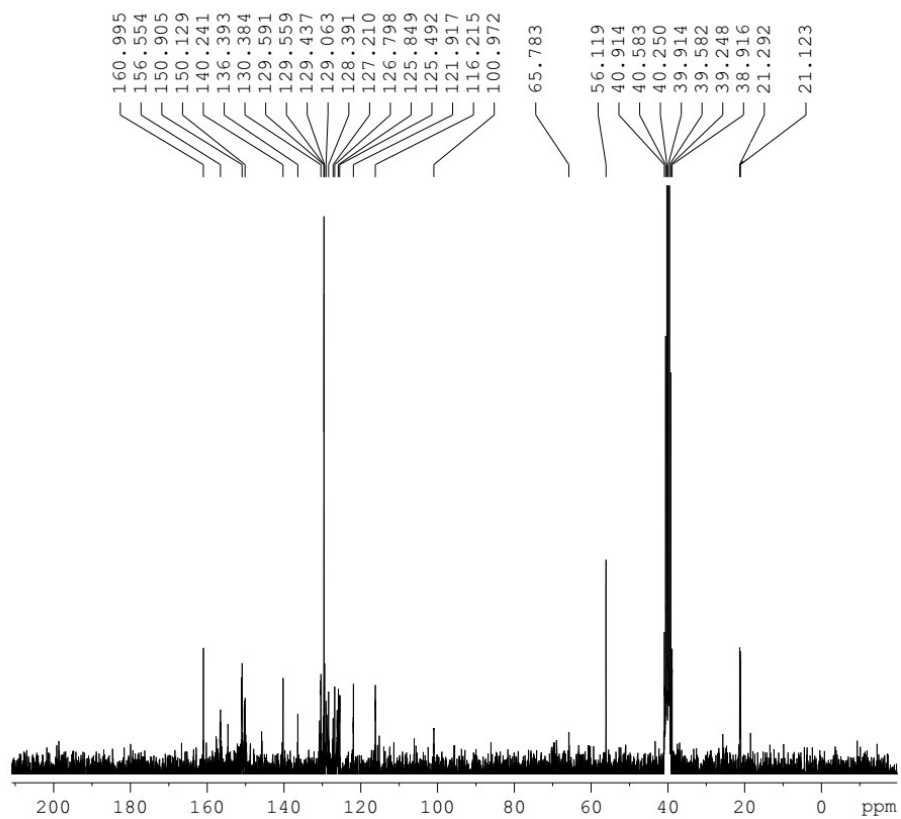
S5. <sup>13</sup>C NMR of NEO1 in D<sub>6</sub>-DMSO

Nemati-Neo2



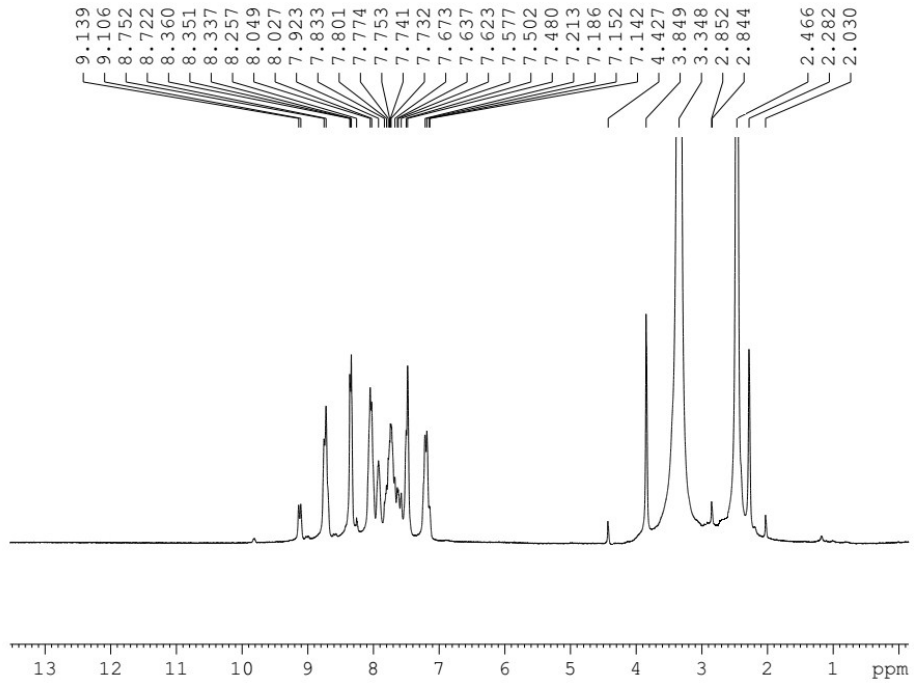
S6. <sup>1</sup>H NMR of NE02 in D<sub>6</sub>-DMSO

Nemati-neo2

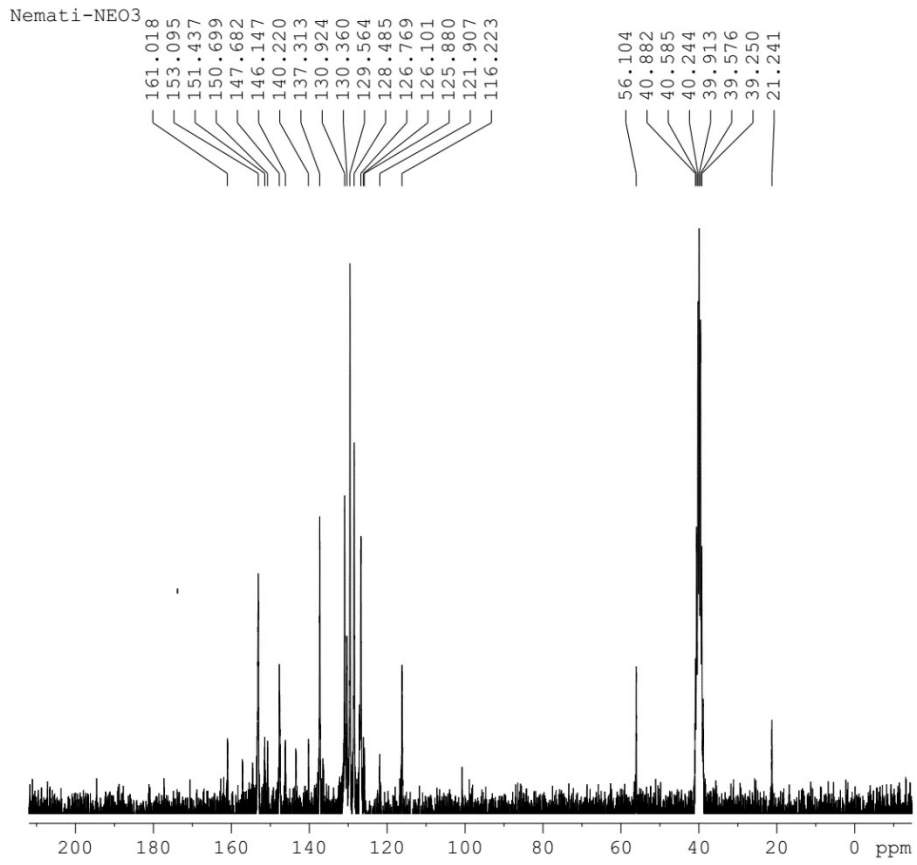


S7. <sup>13</sup>C NMR of NE02 in D<sub>6</sub>-DMSO

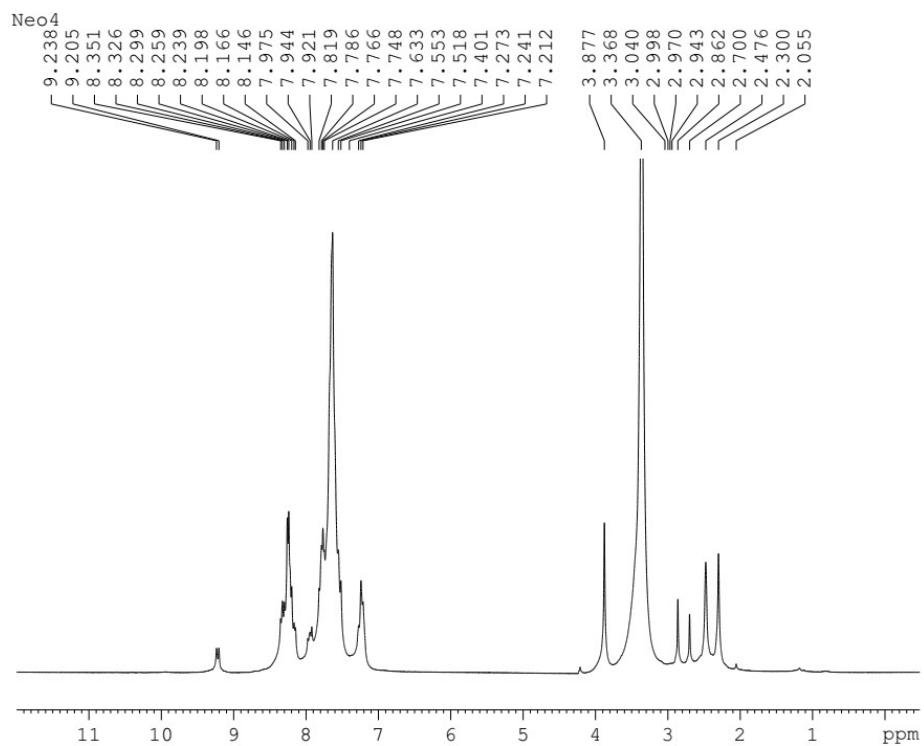
NEO-3



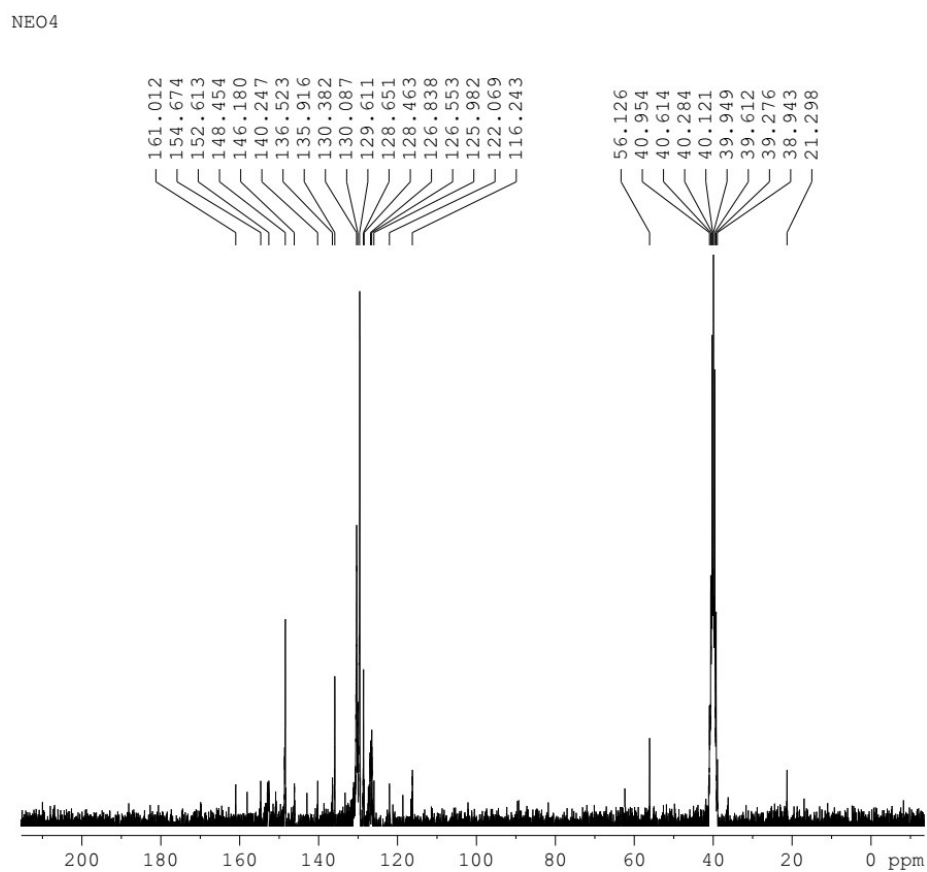
S8. <sup>1</sup>H NMR of NEO3 in D<sub>6</sub>-DMSO



S9. <sup>13</sup>C NMR of NEO3 in D<sub>6</sub>-DMSO

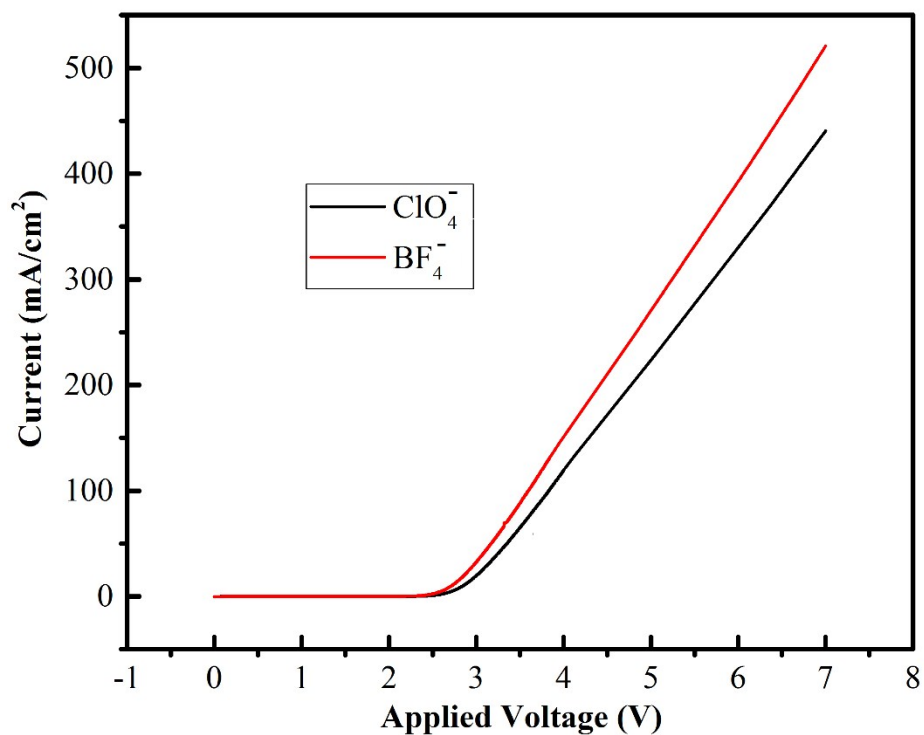


S10.  $^1\text{H}$ NMR of NE04 in  $\text{D}_6$ -DMSO



S11.  $^{13}\text{C}$ NMR of NE04 in  $\text{D}_6$ -DMSO





S12. I-V curve for NE01 with different counterion

## References

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