

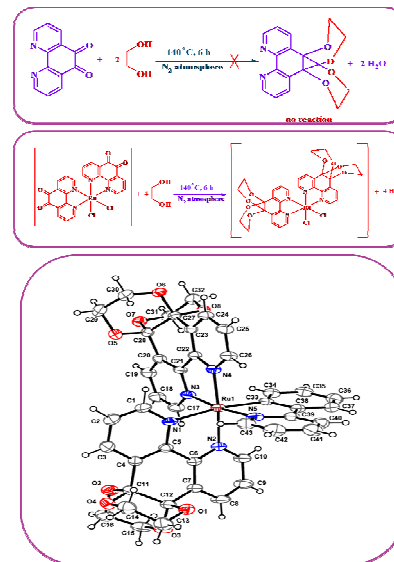
A new cyclometalated Ru(II) complex, [Ru(phpy- $\kappa^2N, C^2'$ )(phen-diox)<sub>2</sub>](PF<sub>6</sub>):  
by the metal-assisted effect of [Ru(phen-dione)<sub>2</sub>Cl<sub>2</sub>] *via* condensation of the  
coordinated phen-dione ligands with ethylene glycol

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In recent years, there have been an increasing number of reports on the synthesis of cyclometalated ruthenium complexes bearing 2,2'-bipyridine analogous (N,C) bidentate ligands such as 2-phenylpyridine, 2-phenylquinoline, 2-phenylimidazole, N,N-dimethylbenzylamine, benzo[h]-quinoline, and so on, and their photo- and electro-chemical properties have been investigated from the viewpoints of the comparison with analogous ruthenium polypyridyl complexes [1-3]. Herein, we report the unprecedented condensation of coordinated phen-dione ligands with ethylene glycol caused by the metal-assisted effect of [Ru(phen-dione)<sub>2</sub>Cl<sub>2</sub>] complex leading to the synthesis of the novel cyclometalated complex, [Ru(phpy- $\kappa^2N, C^2'$ )(phen-diox)<sub>2</sub>](PF<sub>6</sub>), where phpy- $\kappa^2N, C^2'$  is 2-phenylpyridine and phen-diox is 2,3-dihydro-



4a,12b-(epoxyethanoxy)[1,4]dioxino[2,3-f][1,10]phenanthroline. No condensation reaction was observed for the free phen-dione ligand with ethylene glycol under the same experimental conditions. The DFT calculations show that the electronic and energy parameters are involved in this unusual condensation reaction. Coordination of phen-dione to Ru(II) tends to decrease the energy of the LUMO and correspondingly the condensation of a diol becomes much easier. The cyclometalated complex has been structurally characterized revealing a distorted octahedral environment around of ruthenium center. In acetonitrile solution, the complex exhibits metal-to-ligand charge transfer transitions (MLCT) in the visible region and is a poor emitter at room temperature with a quantum yield of approximately 0.02%. The complex showed good reversibility upon oxidation as evidenced by spectroelectrochemical studies.

#### References:

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