

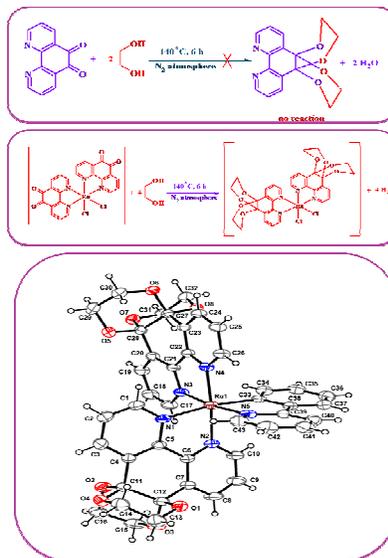
A new cyclometalated Ru(II) complex, [Ru(phpy- κ^2N,C^2')(phen-diox)₂](PF₆):
by the metal-assisted effect of [Ru(phen-dione)₂Cl₂] *via* condensation of the
coordinated phen-dione ligands with ethylene glycol

M. Daryanavard^{1,2*}, H. Hadadzadeh¹

¹Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran

²Department of Chemical and Physical Sciences, University of Toronto at Mississauga,
Mississauga, Ontario, Canada L5L 1C6

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)₂Cl₂] complex leading to the synthesis of the novel cyclometalated complex, [Ru(phpy- κ^2N,C^2')(phen-diox)₂](PF₆), where phpy- κ^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:

- [1] S. Aiki, A. Taketoshi, J. Kuwabara, T. Koizumi, T. Kanbara, J. Organomet. Chem. 689 (2011) 1301–1304.
- [2] C.R. Wade, F.P. Gabbaï, Inorg. Chem. 49 (2010) 714–720.
- [3] H. Hadazaheh, M.C. DeRosa, G.P.A. Yap, A.R. Rezvani, R.J. Crutchley, Inorg. Chem. 41 (2002) 6521–6526.