World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:11, No:03, 2017

Homoleptic Complexes of a Tetraphenylporphyrinatozinc(II)-conjugated 2,2':6',6"-Terpyridine

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Abstract : We recently described the synthesis of a new tetraphenylporphyrinatozinc(II)-conjugated 2,2':6',6"-terpyridine (1) in which the tpy domain enables the molecule to act as a metalloligand. The synthetic route to 1 has been optimized, the importance of selecting a particular sequence of synthetic steps will be discussed. Three homoleptic complexes have been prepared, $[Zn(1)_2]^{2+}$, $[Fe(1)_2]^{2+}$ and $[Ru(1)_2]^{2+}$, and have been isolated as the hexafluoridophosphate salts. Spectroelectrochemical measurements have been performed and the spectral changes ascribed to redox processes are partitioned on either the porphyrin or the terpyridine units. Compound 1 undergoes a reversible one-electron oxidation/reduction. The removal/gain of a second electron leads to a further irreversible chemical transformation. For the homoleptic $[M(1)_2]^{2+}$ complexes, a suitable potential can be chosen at which both the oxidation and the reduction of the {ZnTPP} core are reversible. When the homoleptic complex contains a redox active metal such as Fe or Ru, spectroelectrochemistry has been used to investigate the metal to ligand charge transfer (MLCT) transition. The latter is sensitive to the oxidation state of the metal, and electrochemical oxidation of the metal center suppresses it. Detailed spectroelectrochemical studies will be presented.

Keywords : homoleptic complexes, spectroelectrochemistry, tetraphenylporphyrinatozinc(II), 2,2':6',6"-terpyridine
Conference Title : ICCCA 2017 : International Conference on Coordination Chemistry and Applications
Conference Location : Paris, France
Conference Dates : March 29-30, 2017