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Synthesis and Photophysical Study of Heteroleptic Ru(II) Complexes with Bipys and Conjugated 4,4′-Dicarboxamide-2,2′-Bipyridine

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Solar photovoltaic cells (photovoltaic devices, PV) are the most promising eco-friendly technology for obtaining energy and this utopia became reality thanks to the pioneer works by O'Regan and Grätzel that provided the development of solar cell dye sensitive devices (DSSC, Dye Sensitizer Solar Cell), also known as "Grätzel cell".[1] The sensitizers used in the DSSCs described by Grätzel are ruthenium complexes endowed with bipyridine ligands and thiocyanate (**N3**, **N719** or "black dye"). Despite the notable progress made to date with more modern dyes, these compounds still have maintained leadership in commercial use since they are, until now, the best and most attractive method for energy generation for solar energy-electricity interconversion with relatively large-scale and low production cost, good potential for transparency, flexibility and mechanical robustness.[2] The strong metal-to-ligand charge transfer allows these bipyridine coordination compounds to have unique redox, photophysical, and electrochemical properties in the excited state. The present work reports the synthesis of the 4,4′-dicarboxamide-2,2′-bipyridine ligands (**L**) and their corresponding heteroleptic complexes [Ru(**L**)(bipy)$_2$](PF$_6$)$_2$. These functionalized ligands **L** were prepared through the following synthetic route: oxidation of 4,4'-dimethyl-2,2'-bipy (**1**) with potassium dichromate in sulfuric acid to the 4,4'-dicarboxy-2,2′-bipy (**1i**) (85%), followed by quantitative transformation into the corresponding 4,4′-diacylchloride derivative (**1ii**) that is the direct precursor to the analogous aromatic diamide ligands **1.2a** and **1.2b** through reaction with amines, such as 2-naphthylamine (**2a**) and 2-aminofluorene (**2b**). Finally, the ruthenium complexes [Ru(**1.2a** or **1.2b**)(bipy)$_2$](PF$_6$)$_2$ are obtained by reacting [RuCl$_2$(bipy)$_2$] or [RuCl$_2$(COD)]$_n$ with the ligands **1.2a** or **1.2b**. All compounds have been fully characterized. Suitable single crystals for X-ray crystallography study of [Ru(**1.2a**)(bipy)$_2$](PF$_6$)$_2$ (Fig. 1) were obtained through the slow evaporation of acetone and water, and shows the Ru coordination geometry defined as slightly distorted octahedral. Preliminary photophysical studies of the Ru(II) complexes indicate that these compounds are promising new agents for DSSCs.

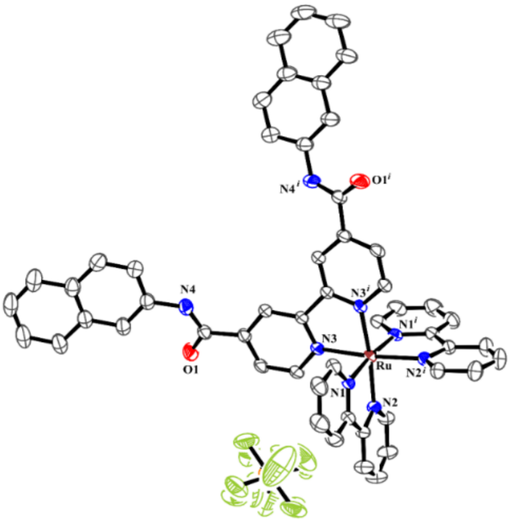

Figure 1. ORTEP representation of [Ru(**1.2a**)(bipy)$_2$](PF$_6$)$_2$

Acknowledgments:

DQ-UFMG, FAPEMIG (CEX PPM 00281-17), CNPq/FAPEMIG (INCT-MIDAS), CAPES (FC 001)

References

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