

Study of Constitutional Isomers in Ru(II) Polypyridinic Complexes

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INTRODUCTION

Changing a binder or a functional group for another can interfere in the spectroscopic properties of dyes based on ruthenium(II) polypyridinic complexes¹. These dyes may be used as sensitizers in dyes sensitized solar cells (DSSC). In order to improve the efficiency of these cells, the strategy to switch ligands and functional groups have been used and studied. As N3 (cis-Ru[(dcbH₂)₂(NCS)₂) is one of the most efficient dyes², in this work, he was chosen to make these changes.

METHODS

The structures studied in this work are shown in Figure 1. The studied structures were divided into isomers of group 1: (H), (I), (J) and (K) and isomers of group 2 (L) (M) (N) and (O). All calculations used the Gaussian 09 program, and were carried out using DFT / TD-DFT, the B3LYP functional and LANL2DZ basis set. The solvent acetonitrile was simulated for calculations of TD-DFT by IEFPCM.

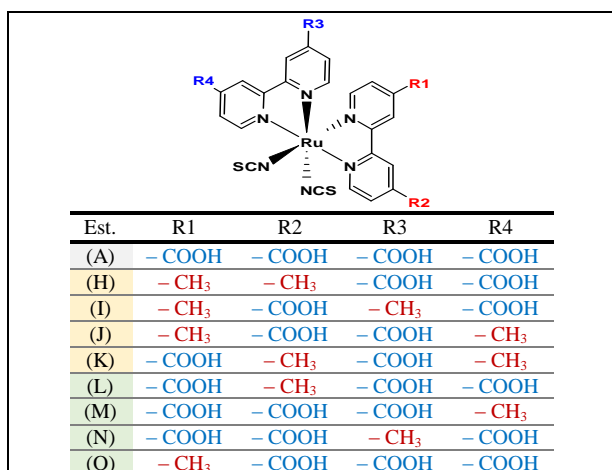


Figure 1. List of structures covered in this study.

RESULTS AND DISCUSSION

The lowest energy structures of each isomers group are (J), (K) and (L), (M), which all have a methyl attached at R2 and/or R4 position. Various structural and electronic properties of these dyes

have been studied. However due to the close structural similarity between the dyes studied, it is expected that a number of properties are similar, but what we are interested in this work, are the differences. The graph analysis of molecular orbitals indicates that replacing one or two carboxylic groups by methyl, decreases the difference between the LUMO and LUMO+1 orbitals relative to the conduction band of TiO₂. What may favor the electronic injection but on the other hand, removes orbitals LUMO+3 and LUMO+4, which also has great contribution in electronic transitions in the visible region of the electromagnetic spectrum, especially the LUMO+3.

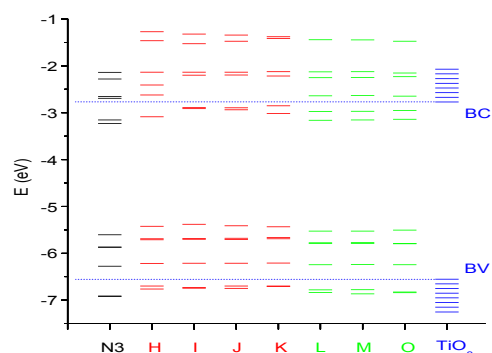


Figure 2. Orbitals energy from HOMO-5 to LUMO+5, compared with conduction bands (CB) and valence bands (VB) of TiO₂ semiconductor.

CONCLUSIONS

This is still a work in progress, in which several other properties are being studied. After this analysis, it expected to be able to say more clearly what are the most affected properties and how it can influence the DSSC performance.

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¹ L. Vandenberg, M. R. Buck, D. A. Freedman, *Inorg. Chem.*, 47, 9134, (2008).

² T. P. Brewster, et al, *Inorg. Chem.*, 50, 11938, (2011).