## Electronic Absorption Spectra of Platinum (II) complexes used for Sensitized Solar Cells: DFT/ TDDFT Study

## S Brahim

University of Saida, Algeria

## **Abstract:**

Using the time dependent density functional theory, we studied in this work the electronic absorption spectra of a series of heteroleptic complexes the form [M(dppf)L] [where dppf =1,10-bis(diphenylphosphino)ferrocene, M=Pt and L= p-tolylsulfonyl dithiocarbimate, p-CH<sub>2</sub>C6H<sub>4</sub>SO<sub>2</sub>NCS<sub>2</sub> (1). M=Pt and L= p-chlorobenzene sulfonyl dithiocarbimate, p-CIC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>NCS<sub>2</sub> (2). M=Pt and L= p-bromobenzene sulfonyl dithiocarbimate, p-BrC<sub>e</sub>H<sub>4</sub>SO<sub>2</sub>NCS<sub>2</sub> (3). M=Pt and L= 1-ethoxycarbonyl-1cyanoethylene-2,2-dithiolate(ecda). These complexes have been synthesized and characterized experimentally using the spectroscopy methods (IR, 1H, 13C and 31P NMR and UV-Vis) and crystal X-ray diffraction. Due to their photo-physical and photochemical properties, they have been used as photo sensibilisator in the DSSC (Dye Sensitized Cell Solar). The conversion efficiency of DSSC is defined by the ability of the electron transport, cheap fabrication, flexibility and intense absorption in the visible region of the spectrum. In order to find dyes satisfying these restrictions, many experimental researches have been done to synthesize and to analyze different molecules. In this sense, the Pt (II) complexes quoted above have been selected as efficient photosensitizer because they have shown the best conversion efficiency. In this work, our contribution to study these complexes is set theorical spectra from quantinum calculation. For each complex the contribution is made in two main steps. The first is a geometry optimization to find the optimal structure with the density functional theory (DFT). We using the hybrid functional B3LYP and PBE0, using 6-31G (d,p) and 6-31+G(d) basis as implemented in Gaussian09. The study of HOMO, LUMO has been used to explicate information about charge transfer in molecules. Lastly, from the frontier molecular orbitals we elucidate the UV-vis spectra and electronic absorption proprieties. The calculated spectrums have been compared with the experimental result.

The influences of functional, substitution and solvent on electronic spectra have been assessed. According to the computed results, the geometry optimization was in good agreement with the experimental results from X-ray diffraction. As experimentally observed, computations results reveal that all complexes show a tree absorption bands in UV region and very low absorption one in visible region. We have assigned these bands to the electronic transitions answerable for their appearance; they are characterized by mixed character mainly dominated by MLCT and LLCT character,

which is arising due to the d–d transition from the dz2 orbital of Fe of ferrocenyl fragment to the others ligands.

It should be noted that the electronic system and optical properties of these complexes can be modified by altering ligands and/or metal. In particular, absorption spectra and photo physical properties can be improved by fixing appropriate substituting groups on the N=CS2 ligand.

Several studies have been carried out with the aim of evaluating the effects of the introduction of a thiophen motif into the ligand structure on the DSSC functions of ruthenium, copper, nickel complexes. Or they showed that the integration of hetero-aromatic donor substituents, usually thiophene-based fragments embedded between bipyridine and carboxy groups, greatly improves the optical properties of sensitizers in terms of bathochromic and hyperchromic shift. Other studies were conducted to assess the effect of the number of thiophenes on UV/visible spectra of organic dyes. The results show that the absorption spectra are gradually widened and shifted to the red with an increasing number of thiophene units.

Based on the above points and based on literature research, we have chosen to improve the efficacy of the dye in DSSC by introducing an anchor ligand –COOH with a thiophen auxiliarygroupin M(dppf) NCS2 (M=Pt(II), and substitute the ligand L=p-XC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub> (X=CH<sub>3</sub>, Cl, Br) with 2-Thiophene carboxylic acid which has a hypso chrome effect on the absorption spectrum due to the  $\pi$ -conjugation and the strong auxo chrome resulting from the thiophene.

Our contribution will therefore be the theoretical study of geometric structures and the spectroscopic properties of these complexes. Based on the results of the tests carried out, we selected for our study the functional CAM-B3LYP with 6-31+G (d) on the one hand. On the other hand we studied the aspect and effect of the COOH number and its position. We also focused on the effect of the number of units of thiophen.

We have conclude that the thiophene offers a high efficiency of light capture over a wide range of light, and that the introduction of a thiophen group into the auxiliary ligand leads directly to absorption transitions in the range of 350–550 nm. The intense  $\pi$   $\pi^*$  transitions are observed at 452 nm, 397 nm and 386 nm. For complexes the low energy bands have mixed character MLCT, LLCT

and ILCT. However, no experimental and theoretical studies have been reported for this type of complex. For this, the study of the thermodynamic stability of these complexes may be necessary to see whether these complexes are synthesizable or not.

Absorption spectroscopy alludes to spectroscopic procedures that measure the retention of radiation, as an element of recurrence or frequency, because of its cooperation with an example. The example ingests vitality, i.e., photons, from the transmitting field. The power of the retention fluctuates as a component of recurrence, and this variety is that the range. Retention spectroscopy is performed over the electromagnetic range.

Absorption spectroscopy is utilized as a scientific science apparatus to work out the nearness of a particular substance during an

example and, by and large, to evaluate the amount of the substance present. Infrared and bright noticeable spectroscopy is especially normal in investigative applications. Retention spectroscopy is also utilized in investigations of atomic and atomic material science, galactic spectroscopy and remote detecting.

There is a decent scope of exploratory methodologies for estimating ingestion spectra. The most widely recognized course of action is to coordinate a produced light emission at an example and distinguish the force of the radiation that goes through it. The transmitted vitality are frequently wont to figure the retention. The source, test game plan and recognition method change fundamentally depending on the recurrence go and in this manner the motivation behind the examination.