

# Computational Studies of the water splitting by using Ruthenium organometallic compounds

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Molecular geometries, electronic structures, and optical absorption spectra were investigated using density functional theory (DFT) at the HF/3-21G and B3LYP/3-21G levels for heteroleptic ruthenium dye, both in the gas phase and in water solution. The vertical excitation energies were calculated within the framework of the time-dependent DFT (TD-DFT) approach, whereas the solvent effects were taken into account using the conductor like polarizable continuum model (CPCM). Our results show that the three highest occupied molecular orbitals (HOMOs) are composed of Ru 4d orbitals. The spectra in the range of 350-600 nm were found to originate from metal-to-ligand charge-transfer (MLCT) transitions. The solvent effects lead to changes in both the geometries and the absorption spectra. The results of this work suggest that Ruthenium -based complexes might be effective sensitizers for next-generation dye-Sensitized Photoelectrochemical Cell.

**Keywords:** DFT; TD-DFT; Heteroleptic Ruthenium dye; Water splitting

## Introduction

Hydrogen and oxygen evolution from water using semiconductors and light is an important issue in the exploitation of solar radiation as a sustainable energy . As the cost of fossil fuels increases, the development of alternative, renewable, and environmentally benign (i.e., carbonfree) sources of energy is paramount. Hydrogen, as a potential alternative fuel, has a higher energy density (per kg) than gasoline or alcohols and a viable storage capacity

under high pressure. Hydrogen generation from clean and environmentally friendly sources such as solar energy is required. Photoelectrochemical (PEC) water splitting, also known as solar-driven water splitting, is one of the most promising means of producing hydrogen from a renewable source. In 1972, Fujishima and Honda first reported the photo-assisted splitting water into  $H_2$  and  $O_2$  on  $TiO_2$ , providing the possibility for the human being to convert solar energy into chemical/electrical energy in a renewable and cheap way. In this process, water molecules are broken into hydrogen and oxygen, using sunlight. There are several advantages to this approach, such as abundance of solar energy, inexpensive raw materials, and ease of mass production. In addition, the production of hydrogen by sunlight will minimize the need for expensive infrastructure for transport in a future prospective  $H_2$  economy[1].

Since then, considerable efforts have been devoted into relevant research fields, such as photocatalysis, dye-sensitized solar cells, and so on. More recently, the importance of hydrogen energy has been recognized again due to the imperative requirements of solving the global energy issues and environmental problems associated with fossil fuels. Hydrogen from water splitting by using solar energy is even called “solar-hydrogen”, representing a kind of clean and low-cost fuel. Unfortunately, a satisfactory system under visible light irradiation has not been obtained yet.

Under irradiation with an energy equivalent to or greater than the bandgap ( $E_g$ ) of the semiconductor photocatalyst, the electrons ( $e^-$ ) of the valence band are excited into the conduction band (CB) while the holes ( $h^+$ ) are left in VB. Electrons and holes that migrate to the surface of the semiconductor without recombination can respectively reduce and oxidize the water

molecules adsorbed on the semiconductor surface. To achieve overall water splitting, the bottom of the CB must be located at a more negative potential than the reduction potential of  $\text{H}^+/\text{H}_2$ , while the top of the VB must be positioned more positively than the oxidation potential of  $\text{H}_2\text{O}/\text{O}_2$ . Therefore, according to this theoretical value, it can drive water splitting only if the photon energy is equal or superior to 1.23 eV. This energy is equivalent to the energy of a photon with a wavelength of around 1010 nm, indicating that visible light is energetically sufficient for the decomposition of water[2].

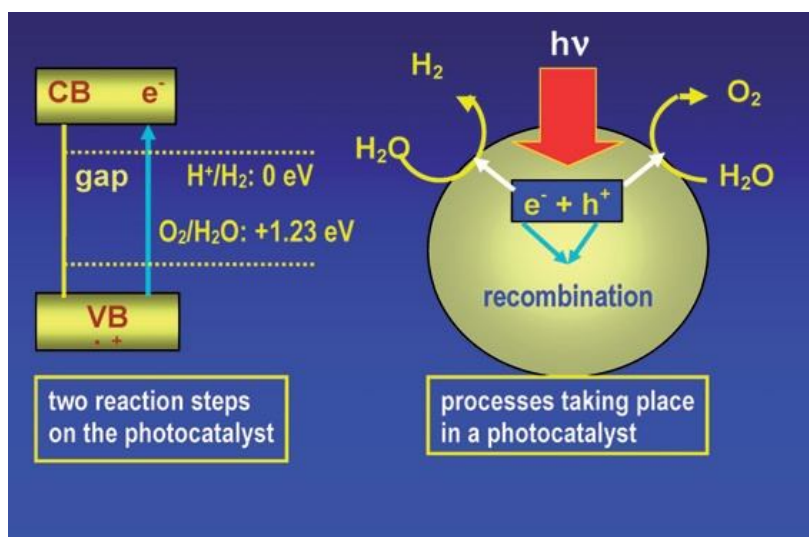


Fig. 1 diagram of the basic principle of overall water splitting[2].

## Computational Details

Geometry optimizations of the heteroleptic ruthenium dye sensitizers (Figure 2) in the ground state and in water solution have been performed with two different computational levels: HF and B3LYP. Calculations were performed with DFT using the Gaussian 98W program[6]. The geometries were fully optimized in gas at hybrid DFT levels by B3LYP functions, which combine Becke's three-parameter exchange function (B3)

with the correlation function of Lee, Yang, and Parr (LYP). For Ru we use a LanL2DZ basis set.

All geometry optimizations were computed in water solution using the CPCM solvation model and with the 3-21G basis set. The vertical excitation energies were calculated for all geometries by the B3LYP functional within the TD-DFT methodology. Natural bond orbital (NBO) analysis was also conducted on optimized geometries with the NBO program included in the Gaussian program package in order to understand the nature and magnitude of the intermolecular interactions.

## Results and Discussion

The simplest system for exploring the idea of visible light water splitting with a sensitized oxide semiconductor is a photoelectrochemical cell[3]. In an electrochemical cell, one can avoid the possible complication of  $H_2$ - $O_2$  recombination by making  $H_2$  in a physically separated cathode compartment[4]. The  $[Ru(bpy)_3]^{2+}$  sensitizer is modified with both phosphonate and malonate ligands in the 4-positions of the 2,2'-bipyridyl ligands in order to adsorb strongly to  $TiO_2$ [5].

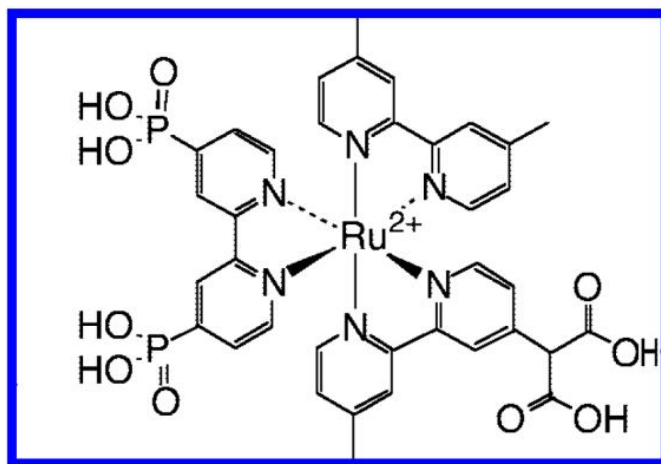


Fig. 2 heteroleptic ruthenium dye.

**Electronic Structures.** In the heteroleptic ruthenium dye complexes, the 4d ruthenium center is surrounded by three pairs of nitrogen atoms of bipyridines. Such a configuration would be of great help for photoexcitations and electronic transitions. Usually, the primary photoexcitation in the visible region occurs from the transfer of one of the transition-metal d electrons to an unoccupied  $\pi^*$  molecular orbital (MO) of the conjugated ligands, coupled with the transition from the ground state to an excited state favoring the metal-to-ligand charge transfer (MLCT). A detailed analysis of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the Ru-based complexes is obtained.

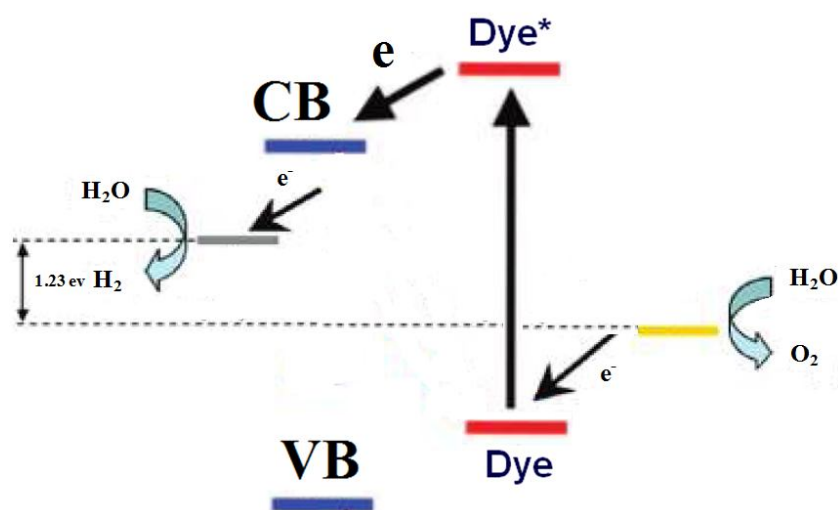


Fig. 3 Energy level diagram showing the electron transfer from and to the sensitizer molecule.

In the heteroleptic ruthenium dye, the five HOMOs (HOMO to HOMO- 4) show predominantly 4d character. Usually, the octahedral configuration of Ru-based complexes results in ligand-field splitting, which makes the five nondegenerate orbitals. However, the situation is completely different for

our calculations. In fact, this situation also appears in the Ru-based complexes in water solution. The four LUMOs in heteroleptic ruthenium dye (LUMO to LUMO+3), lying at least 3.2eV above the HOMO, result from the antibonding combinations of the C orbitals ( $2p_y$  and  $2p_z$ ) of the bipyridines.

**NBO analysis.** NBO analysis shows that the electron occupancies of these four lumo orbitals range from 0.907 to 0.645. The LUMO + 1 and LUMO + 2 also show the  $\pi^*$  character of 2p orbitals ( $2p_y$  and  $2p_z$ ), but they originate from the C and O atoms of the carboxylic groups, which serve as anchoring groups to semiconductor surfaces.

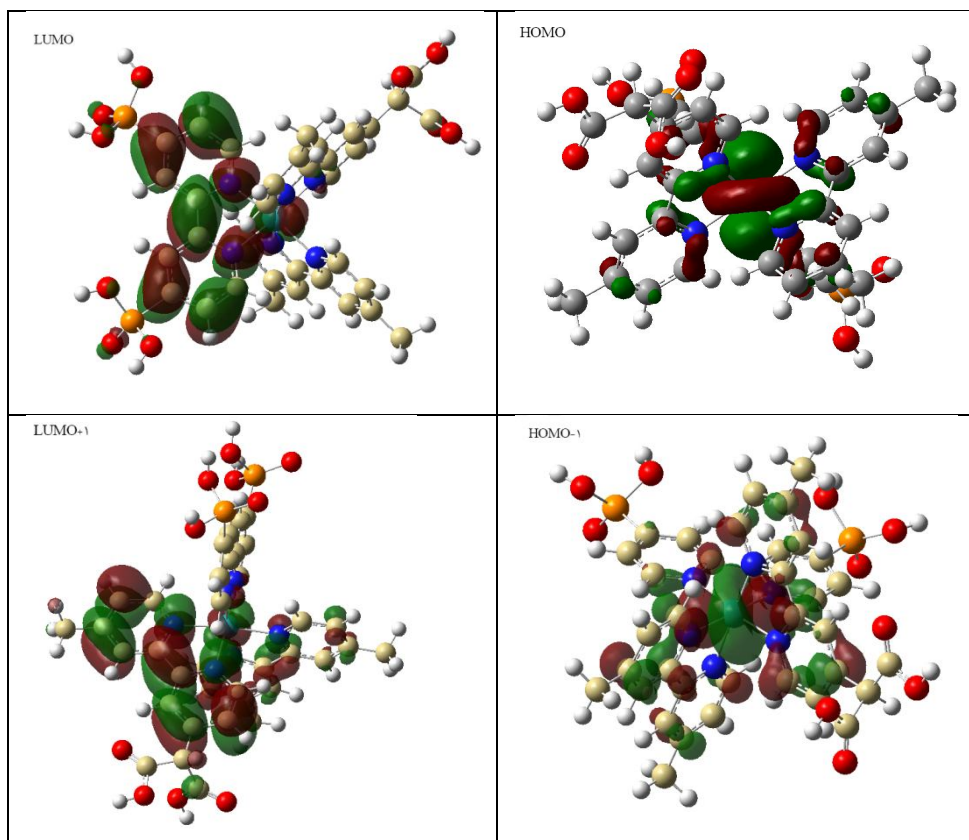


Fig. 4 Frontier molecular orbitals of the gas-phase heteroleptic ruthenium complexes calculated at the B3LYP/3-21G level.

Note that the HOMO-LUMO gap was calculated to be 3.3 eV for the heteroleptic ruthenium dye complex in the gas phase. When the water solvent is considered, all of the energies of the MOs in the heteroleptic ruthenium dye are shifted upward. Using the form of CPCM model, the HOMO was calculated to shift from -10.52 to -6.15 eV.

Even though switching from the gas phase to water solution does not change the composition of the Ru 4d orbital contributions. Similarly, the solution also destabilizes the six LUMOs (LUMO to LUMO+5) of heteroleptic ruthenium dye .

**Electronic Excitations and Absorption Spectra.** The TD-DFT-simulated absorption spectra of the Ru-based complexes are shown in Figure 5 and 6. Figure 5 shows the spectra calculated in the gas phase, and the Figure 6 shows the spectra obtained in water solution.

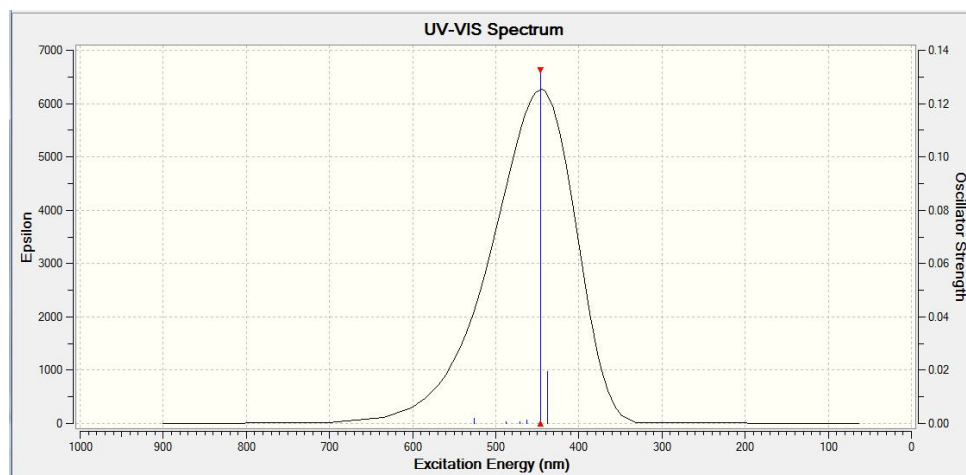


Fig 5. Simulated absorption spectra of heteroleptic ruthenium dye in the gas phase (at the B3LYP/3-21G levels).

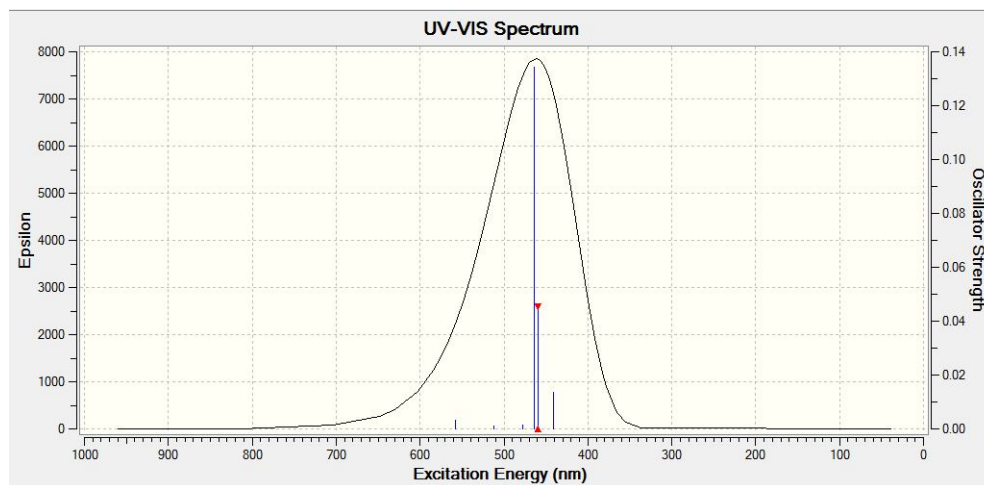


Fig 6. Simulated absorption spectra of heteroleptic ruthenium dye in the water solution at the B3LYP/6-31G levels.

Results shows that all of the spectra in the range of 350-600 nm are contributed by MLCT transitions, that is, excitation from the highest occupied Ru 4d orbitals to the lowest unoccupied bipyridine ligand  $\pi^*$  orbitals. In this region, the simulated spectrum of the gas-phase heteroleptic ruthenium dye shows one peak at 446.17 nm with the oscillator strength of 0.1325.

This peak corresponds to the lowest-energy excitation, which shows strong HOMO $\rightarrow$ LUMO character. An analysis of the HOMO and LUMO clearly shows that this excitation corresponds to an electron transfer from the metal center to the bipyridine ligands.

For the shorter wavelengths in the range of 350-400 nm, the calculated spectrum mainly contains the excitations from metal Ru 4d orbitals to the COOH  $\pi^*$  orbitals (LUMO-1 and LUMO-2). This indicates that the carboxylic group could directly mediate the electron transfer from the metal center to semiconductor surfaces in the shorter-wavelength regions.



For the heteroleptic ruthenium dye in water solution calculated using the C-PCM model, the peak of the spectrum appears at 464.23 nm, a 18.05-nm red shift from the gas-phase spectrum. The oscillator strength of the lowest-energy excitation increases from 0.132 to 0.135.

At present, the majority of studies on dye sensitizers have focused on ruthenium polypyridyl complexes for their performance in solar-to-hydrogen conversion efficiency.

## **Conclusions**

The molecular geometries, electronic structures, and optical absorption spectra of heteroleptic ruthenium dye both in the gas phase and in water solution have been investigated by means of combined DFT/TD-DFT calculations. The calculated geometries are in good agreement with the experimental results. A frontier orbital analysis shows that the five HOMOs have predominantly Ru 4d character whereas the four LUMOs are composed of the antibonding combination of the C 2p orbitals of bipyridines. The spectra in the range of 350-600 nm originate from metal-to-ligand charge-transfer (MLCT) transitions, whereas the spectra in the range of 350-400 nm are excitations mainly from the metal Ru 4d orbitals to the carboxyl group  $\pi^*$  orbitals. The solvent effect strengthens the short-range interaction by dispersing the repulsive interaction and weakens the long-range interaction by coupling the respective dipole moments of different moieties. Inclusion of solvent effects increases the oscillator strength and results in red shifts of the spectra of heteroleptic ruthenium dye.

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