

# Study of Coumarin NKX-2697 Dye for photo water splitting by Computational Method

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The electronic, structural and spectroscopic properties of the Coumarin NKX-2697 dye in gas and water solvent by the conductor-like polarizable continuum model (CPCM) to account for solute-solvent interactions have been investigated by means of combined DFT/TD-DFT calculations. Using time dependent density functional theory (TD-DFT), we calculate excitation energies and oscillator strengths. The spectra in the range of 470-1100 nm were found to originate from transitions. We also have investigated HOMO and LUMO levels in gas and solvent phases for this dye. Inclusion of the solvent leads to important changes of the energies and composition of the molecular orbitals of the dye.

**Keywords:** DFT; TD-DFT; Coumarin NKX-2697 dye; Water splitting

## Introduction

Development of new energy sources is a major need for the 21<sup>st</sup> century. Hydrogen has considerable potential as an alternative fuel, especially if it can be generated inexpensively from an abundant raw material such as water. However, the efficient photocatalytic splitting of water to generate hydrogen using sunlight remains an as yet unachieved goal from a

technological standpoint[1]. New fundamental knowledge is needed regarding how potential photocatalyst materials can be made (more) active in the visible.

So far ruthenium polypyridyl complexes [2] are the most promising sensitizers for photo-electrochemical water splitting to hydrogen generation by visible light, achieving power conversion with high efficiency and good long-term stability. In addition to metal complex dye sensitizers, metal-free organic dye[3] sensitizers are also promising due to their higher extinction coefficients and facile molecular design. In the past decades, various kinds of organic dyes have been designed and employed as dye sensitizers in DSSCs[4], achieving gradual improvement of  $\eta$  through wise molecular design. Among the organic dyes employed for DSSCs so far, coumarin dyes are one kind of promising dye for photo-electrochemical water splitting[5].

### **Computational Details**

Geometry optimizations of the NKX-2697 coumarin dye (Figure 1) in the ground state and in water solution. Calculations were performed with DFT using the Gaussian 98W program[6]. The geometries were fully optimized in vacuo 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).

All geometry optimizations were computed in water solution using the CPCM solvation model and with the 6-311G(d) 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.

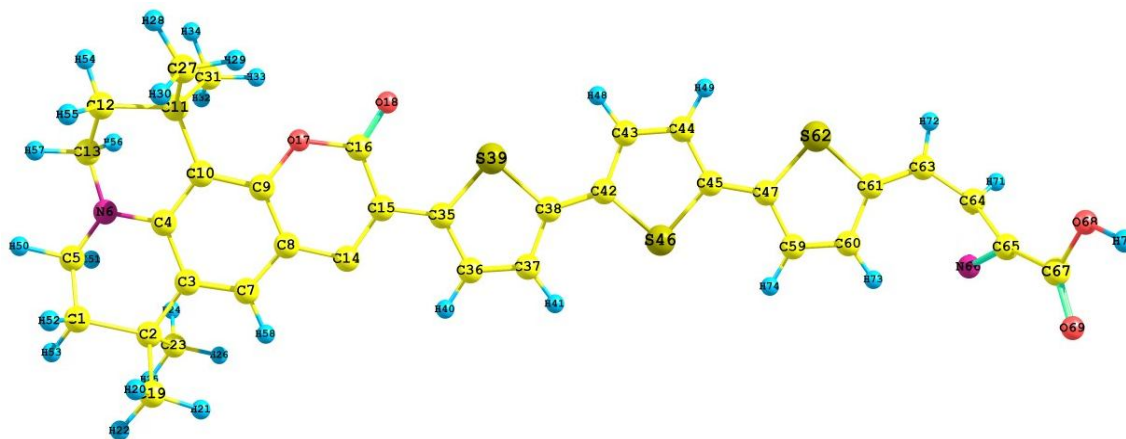


Fig. 1. Molecular structures of the NKX-2697 coumarin dye.

## Results and Discussion

A NKX-2697 coumarin dye with one -CN groups as electron acceptors and three thiophene rings were applied as dye sensitizers for photo water splitting. Using time-dependent density functional theory (TD-DFT) we investigated the absorption spectra of coumarin NKX-2697 dye which have been considered for efficient dye-sensitized water splitting.

**Vertical Excitation Energies.** To analyze the absorption bands of the coumarin NKX-2697 dye, we investigate the optically active excited states in the visible band. Result shows the vertical excitation energies and the oscillator strengths of the  $\pi \rightarrow \pi^*$  states in each chemical environment at the ground-state geometries.

Next, we discuss the solvent effect on the vertical excitation energies of the NKX-2697. The vertical excitation energies of the NKX-2697 in water solution are smaller than in the gas phase by 0.20-0.29. This shift can be divided into two contributions, namely, geometry relaxation and solvent polarization effects. The effect of geometry relaxation is evaluated by comparing the vertical excitation energies at the ground-state geometries optimized in the gas phase and in solution, and the effect of solvent polarization is evaluated by comparing the vertical excitation energy in the gas phase and solution at the same geometry optimized in solution.

The TD-DFT-simulated absorption spectra of the NKX-2697 are shown in Figure 2 and 3. Figure 2 shows the spectra calculated in the gas phase, and the Figure 3 shows the spectra obtained in water solution.

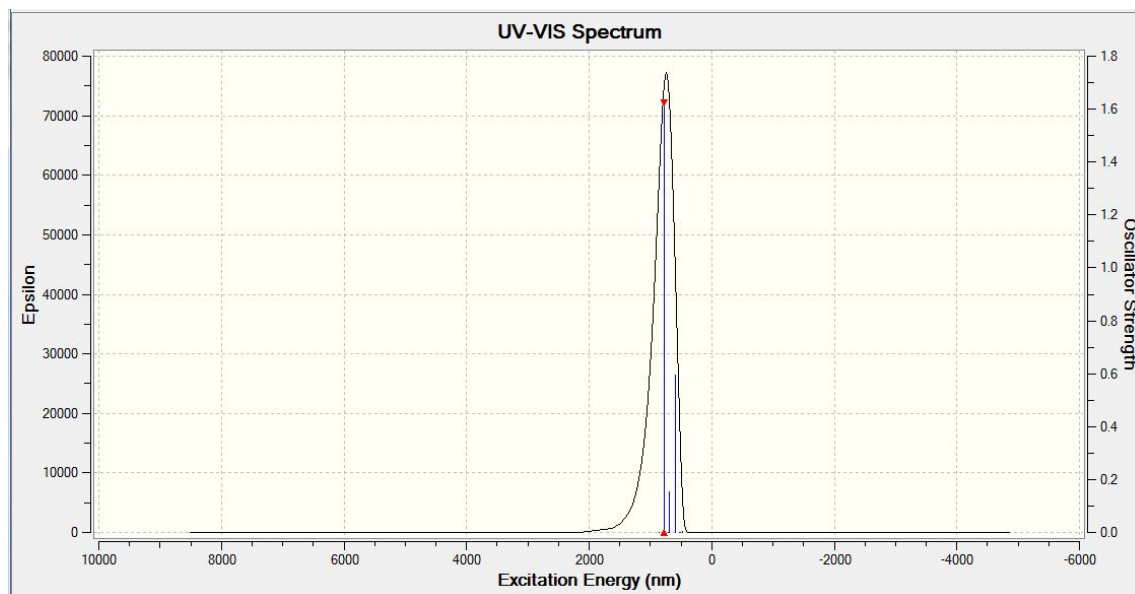


Fig 2. Simulated absorption spectra of NKX-2697 dye in the gas phase (at the B3LYP/6-311G(d) levels).

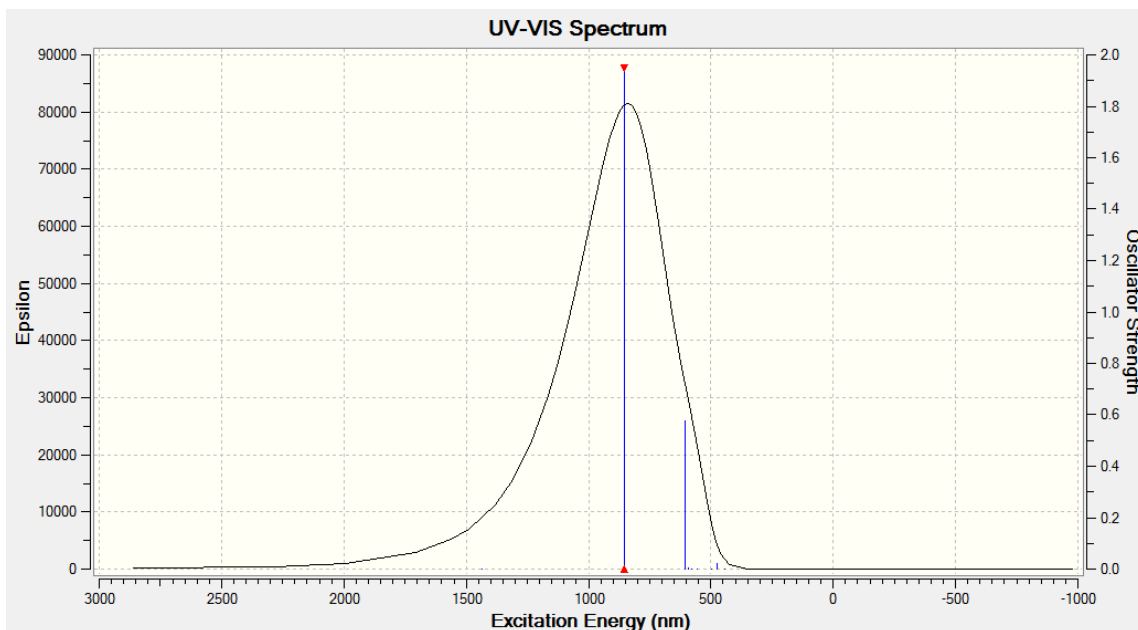


Fig 3. Simulated absorption spectra of NKX-2697 dye in the water (at the B3LYP/6-311G(d) levels.

Results shows that all of the spectra in the range of 500-1200 nm are contributed by transitions from the highest occupied orbitals to the lowest unoccupied orbitals. In this region, the simulated spectrum of the gas-phase NKX-2697 dye shows one peak at 768 nm with the oscillator strength of 1.623. This peak corresponds to the lowest-energy excitation, which shows strong HOMO  $\rightarrow$  LUMO character.

For the NKX-2697 dye in water solution calculated using the C-PCM model, the peak of the spectrum appears at 851.88 nm, a 83nm red shift from the gas-phase spectrum. The oscillator strength of the lowest-energy excitation increases from 1.623 to 1.94

**NBO analysis.** NBO analysis shows that the electron occupancies of four LUMO orbitals range from 0.00606 to 0.00127. 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.

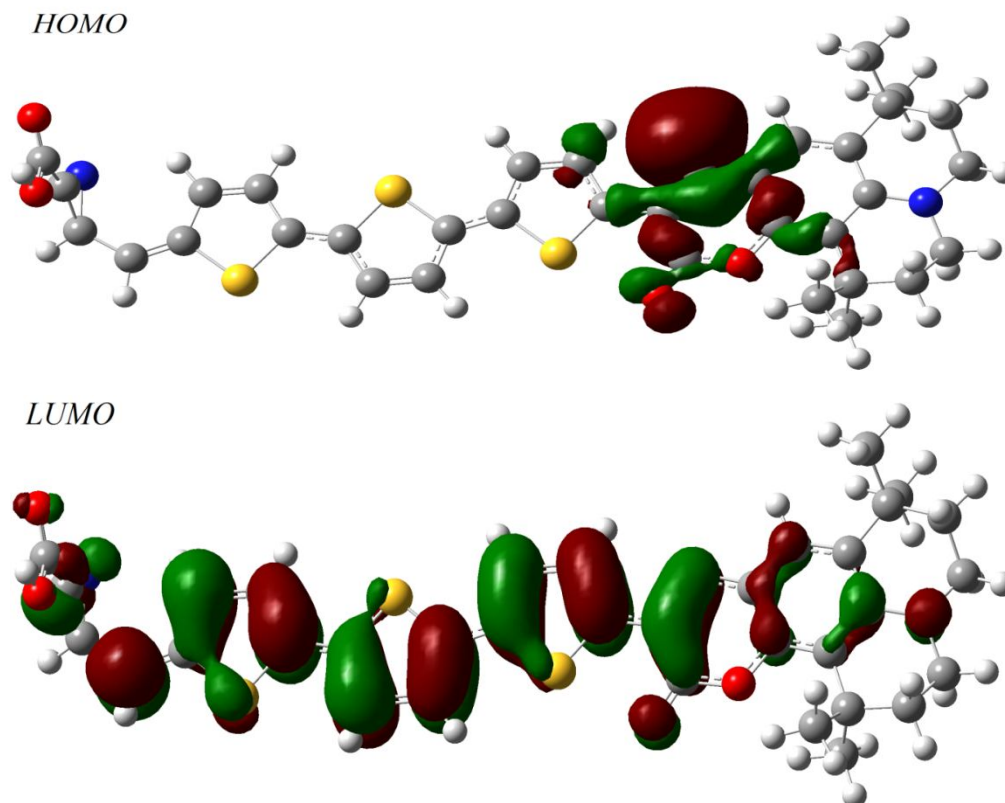


Fig. 4 Frontier molecular orbitals of the gas-phase NKX-2697 dye calculated at the B3LYP/6-311G(d) level.

Note that the HOMO-LUMO gap was calculated to be 1.041 eV for the NKX-2697 dye in the gas phase. When the water solvent is considered, all of the energies of the MOs in the NKX-2697 dye are shifted upward. Using the form of C-PCM model, the HOMO was calculated to shift from -4.44 to -5.07 eV.

## Conclusion

In this study, we have theoretically investigated the excited-state energies and properties in a NKX-2697 coumarin dye molecule for use in photo water splitting applications. For this dye, excited-state energies and properties were obtained using the TD-DFT formalism both in gas and water. The solvent effects are taken into account by the CPCM.

The water solution is found to induce a red shift in the vertical excitation energy due to the stabilization of the HOMO. We conclude that the red shift in solution is mainly caused by the polarization of the solvent.

## Reference:

- [1] C. A. G. O. K. V. S. Ranjan, *Light, Water, Hydrogen The Solar Generation of Hydrogen by Water Photoelectrolysis*: Springer, 2008.
- [2] W. J. Youngblood, S.-H. A. Lee, K. Maeda, and T. E. Mallouk, "Visible Light Water Splitting Using Dye-Sensitized Oxide Semiconductors," *Accounts of Chemical Research*, vol. 42, pp. 1966-1973, 2009.
- [3] H. Harada, C. Hosoki, and A. Kudo, "Overall water splitting by sonophotocatalytic reaction: the role of powdered photocatalyst and an attempt to decompose water using a visible-light sensitive photocatalyst," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 141, pp. 219-224, 2001.
- [4] Y. Kurashige, T. Nakajima, S. Kurashige, K. Hirao, and Y. Nishikitani, "Theoretical Investigation of the Excited States of Coumarin Dyes for Dye-Sensitized Solar Cells," *The Journal of Physical Chemistry A*, vol. 111, pp. 5544-5548, 2007.
- [5] K. S. Ryu Abe, Kohjiro Hara and Bunsho Ohtani, "Robust dye-sensitized overall water splitting system with two-step photoexcitation of coumarin dyes and metal oxide semiconductors," *The Royal Society of Chemistry*, pp. 3577-3579, 2009.
- [6] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* 37 (1988) 785.