A DFT and TDDFT Study of PCM Effect on N3 Dye Absorption in Ethanol Solution

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Abstract. Dye Sensitized Solar Cell (DSSC) is one kind of low-cost third generation solar cell which employed organic or complex dye molecule as photon harvester. [Ru(H2dcbpy)(SCN)2], known as N3 dye, one of the best sensitizer for DSSC, was the focus of this research. All calculations were carried out with Gaussian03, using B3LYP hybrid functional DFT and TDDFT for ground state geometry optimization and excited states calculations respectively. Basis set used in all calculations was 3-21G* for all elements. Polarized Continuum Model was used for modelling the complex in ethanol solution. Combination of 3-21G* basis set with PCM in N3 dye calculation achieve the better approach regarding to experimental absorption spectra. The last two maximum absorption peaks dominated by charge transfer excitation are red shifted in ethanol solution with respect to the gas phase. Electronic polarization between complex and solvent caused the structure to relax, permitting a greater charge separation.

1. Introduction
Since founded in 1990s, dye-sensitized solar cell (DSSC) has attracted many researchers’ attention and the number of publication related to this research topic increasing quite rapidly in recent years. DSSC attracts many interests because this new kind of molecular solar cell achieved lower cost-efficiency ratio than the first and second generation solar cell, moreover, the development of DSSC still have wide area to be investigated in order to achieve higher efficiency while maintaining the low cost production [1]. Many research subtopics arises from DSSC investigation, such as finding new sensitizer, new semiconductor, new electrolyte system, electrolyte additives, controlling the semiconductor pore size, etc., both experimentally and computationally [2-7].

DSSC is a solar cell that employed a dye (usually an organic or metal complex molecule) as a photon catcher, called sensitizer. DSSC provides an efficient source of renewable energy, environmentally friendly, and quite economical [8]. In the DSSC cells, the properties of components such as the sensitizer absorption spectra (UV-Vis spectra) [9] and redox properties [10] play an important role in the photovoltaic performance of DSSC cells. Solar energy absorbed by the sensitizer is used to inject electrons into the semiconductor photoanode then transferred to the conductor part. Hence, sensitizer material has a critical influence to the overall cell efficiency.

One of the best sensitizers comes from ruthenium polypyridyl complexes and its derivatives, such as N3 dye and black dye [11]. N3 dye is a famous name for dithiocyanatobis(2,2-bipyridine-4,4-
dicarboxylicacid)ruthenium (II) \([\text{Ru(H}_2\text{dcbpy)}_2(\text{SCN})_2]\), having an overall cell efficiency up to 11.18% [11] and can be enhanced by modifying the electrolyte systems [12]. However, computational study to investigate the electronic structure, photonic properties, and excitation mechanism of this material is still not fully understood.

2. Computational Details

All calculations were carried out with Gaussian03 [13] program package using Becke, three-parameter, Lee-Yang-Parr (B3LYP) hybrid functional [14] density functional theory (DFT). Ground state geometry optimization of neutral form of N3 dye were carried out using 3-21G* basis set for all elements with no symmetry applied. Time-dependent density functional theory (TD-DFT) excited state calculations were determined based on geometry optimization results in both the gas phase and ethanol solution. The approach to embed N3 molecule in a dielectric medium in order to include the solvent polarization effect was used in calculation for N3 dye in ethanol solution. The cavity was defined as the union of a series of interlocking atomic spheres using Tomasi’s Polarized Continuum Model (PCM) for the ground state geometry optimization and TD-DFT calculations for 70 singlet to singlet transition states. Mixed (GENECP) basis set with PCM ethanol solvent was used to predict the absorption spectra of N3 dye. Visualization was carried out using Chemcraft 1.6 [15].

3. Results and Discussion

3.1. Molecular Structure

The optimized geometry of N3 dye is shown in figure1. Ruthenium (II) ion is coordinated to four N atoms from two 2,2-bipyridine 4,4-dicarboxylic acid ligands and to two N atoms from two SCN- ligands forming an octahedral-like molecular shape in the center. Comparison of the calculated structure parameter with experimental data was presented in table 1. The calculated structure parameters were slightly different with the experimental result because of the different condition of measurement with the model in computational study. Experimental structure parameter is usually obtained from a single crystal (solid phase) while the calculated values were for gas and aqueous phase in ethanol solvent. However, the experimental value still can be used to make a rough comparison. From the table above, it can be seen that the calculated structure parameters were in quite good agreement with the experimental data. Values from each method were slightly different with each other. Interatomic distance values after the solvation effect applied were longer than the values in gas phase in order to overcome intermolecular interactions between N3 molecule (solute) and ethanol solvent.

3.2. Excitation Energies of N3Gas Phase and N3 in Ethanol Solution

70 singlet to singlet transition states were calculated for both N3 optimized structure (gas phase and solution phase) and excitation energies for wavelength larger than 380 nm using both methods were presented in table 2. A detailed analysis of several N3 dye molecular orbital composition are presented in table 3.
Figure 1 N3 dye optimized geometry obtained using 3-21G* basis set in ethanol solution.

Table 1 Structure parameter comparison between experimental [16] and computational results.

| Structure parameter | Expt [16] | N3 Gas phase | N3 in Ethanol Solution |
|---------------------|-----------|--------------|------------------------|
| R (Ru-N1)           | 2.030     | 2.073        | 2.072                  |
| R (Ru-N2)           | 2.036     | 2.074        | 2.083                  |
| R (Ru-N3)           | 2.058     | 2.075        | 2.082                  |
| R (Ru-N4)           | 2.048     | 2.072        | 2.072                  |
| R (Ru-N5)           | 2.046     | 2.049        | 2.078                  |
| R (Ru-N6)           | 2.048     | 2.048        | 2.078                  |
| < N1 – Ru – N2      | 79.8      | 78.8         | 78.8                   |
| < N2 – Ru – N3      | 90.6      | 92.4         | 90.9                   |
| < N3 – Ru – N4      | 79.1      | 78.8         | 78.8                   |
| < N2 – Ru – N4      | 97.8      | 99.7         | 98.5                   |

Table 1 Excitation energies for λ>380 nm, oscillator strength (f)> 0.01, and %composition>10%.

| State | E (eV) | f   | Composition                      | E (eV) | f   | Composition                      |
|-------|--------|-----|----------------------------------|--------|-----|----------------------------------|
| 1     | 0.9178 | 0.0154 | 87% (HOMO to LUMO)            | 1.8154 | 0.0326 | 95% (HOMO to LUMO)            |
| 2     | 1.1969 | 0.0195 | 90.3% (HOMO-2 to LUMO+1)       | 1.8439 | 0.0143 | 85% (HOMO to LUMO+1)          |
| 3     | 1.3133 | 0.0367 | 43.8% (HOMO-3 to LUMO), 24.3% (HOMO-1 to LUMO+1), 17.3% (HOMO to LUMO+1) | 2.1554 | 0.1091 | 55.3% (HOMO-2 to LUMO+1), 40.4% (HOMO-1 to LUMO+1) |
| 4     | 1.3955 | 0.0367 | 91.3% (HOMO-3 to LUMO+1)       | 2.2480 | 0.0206 | 52.2% (HOMO-2 to LUMO+1), 27.1% (HOMO-1 to LUMO), 11% (HOMO to LUMO+3) |
| 5     | 1.6770 | 0.0333 | 95.6% (HOMO to LUMO+2)         | 2.5992 | 0.0559 | 93.8% (HOMO to LUMO+2)        |
| 6     | 1.7565 | 0.0421 | 89% (HOMO to LUMO+3)           | 2.6718 | 0.0469 | 94.8% (HOMO-3 to LUMO+1)       |
| 7     | 1.8098 | 0.0147 | 92.3% (HOMO-1 to LUMO+2)       | 2.6946 | 0.0794 | 73.5% (HOMO to LUMO+3), 12.8% (HOMO-3 to LUMO) |
| 8     | 2.0223 | 0.0238 | 64.2% (HOMO-3 to LUMO+3), 21.5% (HOMO-1 to LUMO+4) | 2.8546 | 0.0477 | 77.1% (HOMO-2 to LUMO+2), 15.2% (HOMO to LUMO+4) |
| 9     | 2.0237 | 0.0258 | 51.2% (HOMO to LUMO+5), 21.1% (HOMO-3 to LUMO+3), 19% (HOMO-3 to LUMO+2) | 3.0831 | 0.0368 | 91.5% (HOMO-4 to LUMO)        |
|       |        |       |                                  | 3.1299 | 0.0488 | 90.1% (HOMO-5 to LUMO+1)      |
Table 2 Percent composition of the highest occupied and lowest unoccupied orbitals of N3 dye in terms of Ru, bipyridine-dicarboxylic ligand, and SCN⁻ ligand for N3.

| MO No. | N3 Gas Phase | % Ru | % Bipyridine | % SCN | MO No. | % Ru | % Bipyridine | % SCN |
|--------|--------------|------|--------------|-------|--------|------|--------------|-------|
|        | 4d | 5s | 5p | other | ring 1 | ring 2 | 1 | 2 | 4d | 5s | 5p | other | ring 1 | ring 2 | 1 | 2 |
| LUMO+3 | 181 | 0.6 | 0 | 5.5 | 46.6 | 46.9 | 0.2 | 0.2 | 181 | 0.5 | 0 | 4.4 | 46.2 | 48.5 | 0.2 | 0.2 |
| LUMO+2 | 180 | 0.1 | 0 | 0.8 | 49.6 | 49.3 | 0.1 | 0.1 | 180 | 0.1 | 0 | 0.8 | 50.7 | 48.3 | 0 | 0 |
| LUMO+1 | 179 | 0.6 | 0.1 | 13.6 | 41.5 | 39.9 | 1.7 | 1.8 | 179 | 1 | 0.1 | 10.5 | 42.1 | 44.8 | 0.7 | 0.7 |
| LUMO   | 178 | 0.6 | 0.1 | 45 | 47 | 0.7 | 0.6 | 178 | 0.5 | 0.1 | 5.6 | 47.9 | 45.2 | 0.4 | 0.4 |
| HOMO   | 177 | 2.5 | 0 | 22.2 | 5 | 4.5 | 32.2 | 33.6 | 177 | 5.7 | 0 | 49.1 | 3.9 | 3.9 | 18.7 | 18.7 |
| HOMO-1 | 176 | 1.4 | 0 | 13 | 3 | 2.9 | 34.9 | 44.8 | 176 | 4.1 | 0 | 36.1 | 5.3 | 5.4 | 23.8 | 25.3 |
| HOMO-2 | 175 | 1.2 | 0.1 | 11.2 | 3.1 | 3.2 | 45.6 | 35.6 | 175 | 4.3 | 0.1 | 38.3 | 3.7 | 3.7 | 25.6 | 24.4 |
| HOMO-3 | 174 | 0 | 0.1 | 1.1 | 0.8 | 1 | 49.5 | 47.6 | 174 | 0 | 0 | 0.3 | 0.4 | 0.4 | 49.5 | 49.4 |
| HOMO-4 | 173 | 7.6 | 0 | 65.6 | 5.2 | 5.1 | 8.3 | 8.2 | 173 | 5.5 | 0.1 | 48.1 | 5.9 | 5.9 | 18.7 | 15.9 |
| HOMO-5 | 172 | 6.9 | 0.1 | 60.1 | 10.3 | 10.3 | 5.9 | 6.3 | 172 | 4.4 | 0.1 | 39 | 7.7 | 7.7 | 18.9 | 22.1 |
| HOMO-6 | 171 | 7.2 | 0.1 | 64.1 | 8.4 | 8.4 | 5.9 | 5.7 | 171 | 4.8 | 0 | 42 | 5.9 | 5.8 | 20.7 | 20.7 |

It can be inferred from table 2 and table 3 that the gas phase N3 dye excitation energies with wavelength larger than 380 nm were mainly charge transfer. It can be seen from the large metal (Ru) contribution in mostly HOMO orbital that known to be the source of donor electron to LUMO orbital which is dominated by ligand (bipyridine ring) orbital contribution. From HOMO to HOMO-6, Ru atomic orbital contribution was larger than 10% except for HOMO-3. Donor electron in HOMO-4 to HOMO-6, where Ru contribution was larger than 67%, will be transferred to LUMO, LUMO+1, and LUMO+3 where the bipyridine ligands orbital contribution was larger than 81%. HOMO to HOMO-3 orbital, originated from more than 65% contribution of SCN⁻ ligands atomic orbital, will transfer its electron to LUMO, LUMO+1, LUMO+2, LUMO+3, LUMO+4, and LUMO+5 orbitals (dominated by bipyridine ligands atomic orbital) via Ru contribution ranging from to 2.1% to 35.9% from the HOMO-LUMO excitation pairs.

Calculation of N3 dye in ethanol solution used the same calculation parameter as gas phase, except the inclusion of PCM effect. 70 singlet to singlet transition states were calculated using the optimized geometry with PCM effect. Excitation energies for wavelength larger than 380 nm were also presented in table 2, and the detailed analysis of several solution phase N3 dye molecular orbital composition are also presented in table 3.

The excitation energies results from the addition of solvent effect are blue-shifted. This effect was expected to happen because when a molecule passes from gas phase into solution, the structure will relax to permit greater charge separation due to electronic polarization. The composition of molecular orbital in gas phase and in ethanol solution, if compared, will results in several difference of atomic orbital contribution. The solvent and solute interaction results in “shifting” composition of Ru and SCN⁻ ligand in HOMO to HOMO-2. In the case of SCN⁻, the orbital composition in these orbitals is decreased.

Inspite of its role as donor electron, the decrease of SCN⁻ orbital contribution in HOMOs might be the reason of blue-shifting phenomena in excitation energies due to decreasing the donor electron...
strength, so the excitation became more difficult than before. This atomic orbital contribution difference was indirectly resulted from the interaction between molecule and solvent. When molecule interacts with solvent, polar-polar and polar-nonpolar interactions were occurred. This intermolecular interaction could make the interatomic bond in N3 molecule change, some become longer, some become shorter than its initial state. It caused the atomic orbital contribution to change.

HOMO and LUMO orbital energy levels of gas phase N3 were -0.191840 Hartree and -0.131480 Hartree, while HOMO and LUMO orbital energy levels of N3 in ethanol solvent were -0.201030 Hartree and -0.104770 Hartree. HOMO orbital stabilization and LUMO orbital destabilization occurred when N3 dye moves to solvent environment.

3.3. Absorption Spectra

N3 dye absorption spectra obtained from gas phase calculation (figure 2) using 3-21G* basis set was overestimating the absorbed wavelength compared to the experimental data. Hence, calculation results of the molecule in gas phase were not representative enough to model the system. Since the experiment data was obtained from measuring the N3 dye in ethanol solution, the next approach was to carried out calculation in ethanol solution. This approach was done with the inclusion of polarized continuum model (PCM) in the calculation. The result was presented in figure 2.

In ethanol solution, calculated N3 dye absorption peaks shifted to shorter wavelength due to solute-solvent dielectric field. The calculated absorption spectra of N3 dye in ethanol solution have four absorption peaks for both basis sets used, as well as with the experimental absorption spectra. Peak with the largest wavelength located at 533-543 nm wavelength and 576 nm for the results of experimental measurements and calculations results using 3-21G* basis sets in solution, respectively. Wavelength absorption peak with the second largest in the experimental absorption spectrum lies at a wavelength between 403 to 409 nm. This peak was close to two absorption peaks in each calculation, it is almost in the middle of both peaks as if it is the result of the superposition of the two peaks. This peaks were at 391 nm and 455 nm on the results using the 3-21G* basis set in solution. Meanwhile, the third largest experimental absorption peak lies at a wavelength of 328 nm. This peak adjacent to the fourth peak from the calculation results in which lies at 285 nm for 3-21G* basis set in ethanol solution.

![Absorption Spectra](image)

**Figure 2** Calculated N3 dye absorption spectra using 3-21G* in gas phase (blue line) and 3-21G* in ethanol solution (brown line).

4. Conclusion

Computational study of N3 dye has been carried out by using B3LYP exchange correlation 3-21G* basis set and comparing its properties in gas phase and in ethanol solution (using PCM model). The calculation results and the comparison have been discussed above. 3-21G* basis set combined with
PCM solvation effect yields better approximation to molecular structure, excitation energies, and absorption spectra. Electronic excitation in N3 dye both in gas phase and in ethanol solution were mainly charge transfer. Solvation effect results in greater charge separation due to structure relaxation in order to overcome intermolecular interaction between N3 dye and solvent molecules.

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