Theoretical Study of the Nickel (II) Complex Using First Principles Density

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Abstract

Photo physics and photochemistry of transition metal complexes with organic dyes is a field of worldwide research due to their applicability as photosensitizer materials in solar cells. Herein, a Ni (II) complex based on quinoxaline-2, 3-dithiolate as ancillary ligand and 4, 4'-dicarboxy-2, 2'-bipyridine as anchoring ligand is studied theoretically for application as a sensitizer. Within the framework of first-principles density functional theory (DFT), using B3LYP exchange correlation functional with 6-311G+ (d,p) basis set, geometrical structure of these dyes is fully optimized in gas phase. Molecular orbital energies, electronic structure and absorption spectra are calculated. The results demonstrate that the dye exhibits strong ligand to ligand transition in visible region and NIR region.

Keywords

Nickel, Complex, Density, Dye sensitized solar cells, Ni (II) Sensitizing Dyes.

Recently strong research efforts have been addressed to synthesize ruthenium-free sensitizers for dye sensitized solar cells (DSSCs)[1] to overcome the issue of high cost and scarce availability of ruthenium. Transition metals like copper and iron are the preferred choice for metal complex sensitizers owing to their low-cost production and significant photochemical properties. However research on use of nickel as sensitizers for DSSCs is scanty as some of the initially investigated Ni complex dyes reported insignificant photovoltaic activity.

Assessment of Literature

Linfoot et al.[2] reported the first example of a Ni(II) complex that exhibited sensitizing activity. Ni (II) iminosemibezoquinonate complexes[3] are reported to absorb strongly in near infrared (NIR) region. The heteroleptic Ni(II) diimine dithiolenes have been reported to be used as cosensitizers to known visible light absorbing dyes in order to extend the spectral window used for light harvesting in IR region. Ni (II) complexes with Rhodamine[4] and a Ni(II)-Chlorophyll[5] with 0.2% efficiency have been reported in literature. The conversion efficiency is observed to be quite low in spite of satisfactory light harvesting probably due to short lived excited state. More recently Ferrocenyl Dithiophosphonate Complexes of Nickel(II) and a new series of macrocyclic Ni (II) complexes having indolenine[6] and dibenzotetraaza annulene [7] ligand are tested for their application as sensitizers The development of sensitizers with absorption extending to nearIR is greatly desired to reduce spectral losses.

Objectives of Research

Herein we report the electronic and optical properties of a Ni (II) complex based on quinoxaline-2,3-dithiolate as ancillary ligand and 4,4'-dicarboxy-2,2'-bipyridine as anchoring ligand using first principles density functional theory (DFT). This work aims to gain an understanding of optical properties of Ni (II) dye and find the possibility of its use as a sensitising dye in solar cell.

Methodology

All calculations are performed by using the Gaussian 09 software[7] package. Geometry optimisations of both complexes are performed at the 6-311G+(d,p) level by using the B3LYP functional in gas phase. Based on the optimized ground-state structures TD-DFT calculations are then performed with the same basis set to obtain the optical property and absorption spectra. Guass Sum[8] software was used to plot density of states and absorption spectra.

Results

Molecular Geometries

The optimized molecular structure of Ni (II) dye in the gas phase is shown in Figure 1.The optimized parameters of the molecular structure (Table 1) show a very small structural variation of the atoms bonded with respect to the characteristic lengths and angles reported in literature. Good agreement of structural parameters justifies the reliability of selected model and levels of theory.

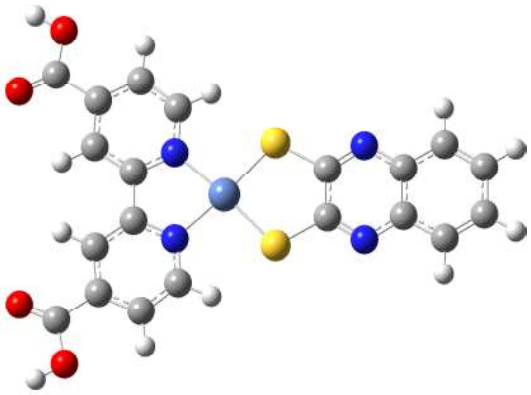

Figure 1 Optimized structure of Ni (II) dye with quinoxaline-2,3-dithiolate as ancillary ligand and 4,4'-dicarboxy-2,2'-bipyridine as anchoring ligand

Table 1: Selected bond lengths (angstroms), bond angles and dihedral angles (degrees) for nickel (II) dye

Parameter	Ni (II) dye
Ni-N_1	1.96934
Ni-N_2	1.96933
Ni-S_1	2.17690
Ni-S_2	2.17687
C-S_1	1.75757
C-S_2	1.75756
N_1-Ni-N_2	82.43390
S_1-Ni-S_2	90.42732
N_1-N_2-S_1-S_2	0.11986

Electronic Structure and Molecular Orbitals

Density of states represented of Ni (II) complex in Figure 2 shows HOMO density is localised on quinoxaline-2,3-dithiolate ancillary ligand while that of LUMO is localised on 4,4'-dicarboxy-2,2'-bipyridyl anchoring ligand, resulting in ligand to ligand charge transfer or LLCT transitions. Table 2 indicates HOMO orbital is located at 5.501eV and LUMO at 3.724eV. The energy levels for the LUMOs of the dye are effectively well–matched with the conduction band of the semiconductor. Moreover a bandgap of 1.777 eV is a value suitable for its consideration as a potential sensitizing dye to inject electrons into the TiO2 electrode.

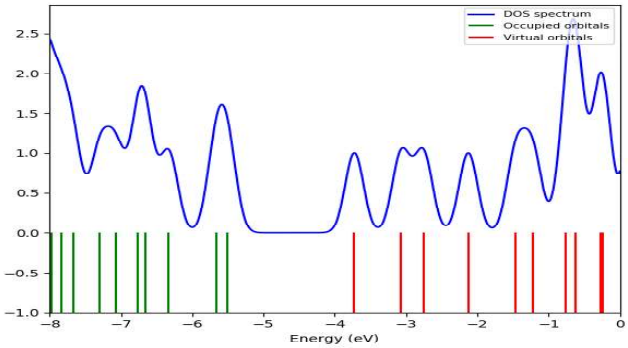

Figure 2: Density of States of Ni(II) dye

Table 2.TheHOMO and LUMO Energies, HOMO-LUMO Gaps for Ni (II) dye

Dye	HOMO (eV)	LUMO (eV)	HOMO-LUMO bandgap (eV)
Ni (II) complex	5.501	3.724	1.777

Electronic Excitations and Absorption Spectra

Ni (II) complex mainly absorbs in the visible region and extends into near infrared (NIR) region (Table 3 and Figure 3) covering a wide spectral range from ~300nm to 900nm. The first band with a maximum absorption ($\ddot{e}_{max}$) located at 347 nm involves multiple LLCT transitions and has very high extinction coefficient. Another band at 863.65 nm with a high spectral intensity and oscillator strength indicates strong absorption in near infeared (NIR) region. This suggests that Ni (II) dye can efficiently harvest the light in visible as well as infrared region, which an important prerequisite for an efficient sensitizer so as to reduce spectral losses.

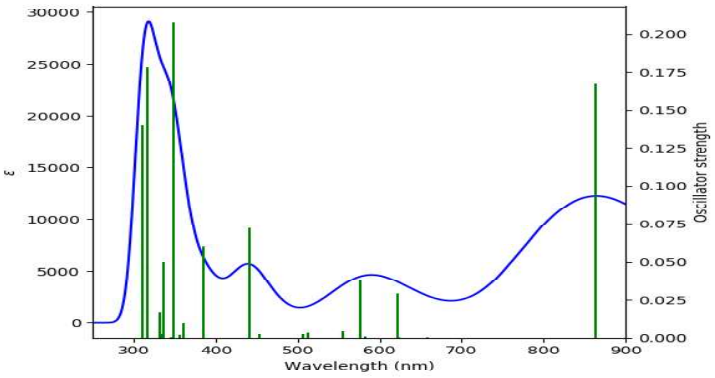

Figure 3: Absorption Spectra of Ni (II) dye

Table 3: Optical data for theoretical absorption spectra

System	E*(eV) Excited state	Excitation Energy E (eV)	Wavelength (nm) λ	Oscillator Strength f
Ni (II) dye	2	1.4356	863.65	0.1666
	15	2.8135	440.6	0.0722
	27	3.5660	347.69	0.2077
	37	3.9174	316.49	0.1783
	40	3.9959	310.28	0.1399

Conclusion

The Ni (II) dye under consideration has a well matched HOMO and LUMO energy levels, broad spectral range extending to nearIR, high absorption intensity, large oscillator strength and hence a good light harvesting capacity. Thus, theoretically, this dye fulfils most of the criteria for its consideration as a potential sensitizer for future. However low conversion efficiency reported in literature, generally attributed to the short lived excited state is an important challenge to be tackled. This suggests that high efficiency Ni complex sensitizers are possible if excited state lifetime is enhanced by suitable molecular design.

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