QUANTUM EFFICIENCY OF 3, 5-DIMETHYL PYRIDINE 2-CARBONITIRLE FOR DYE SENSITIZED SOLAR CELL AND VIBRATIONAL SPECTRAL ANALYSIS OF THE DYE MOLECULE

Uthayakumar.B[1], G.Meenakshi[2], S.Ramadasse[3]

[1]Research Scholar, [2,3] Associate Professor, Department of Physics, Kanchi Mamunivar Centre for Post Graduate Studies, Lawspet, Puducherry, India

Abstract

Dye-sensitized solar cells (DSSC) attain consideration because of their sky-scraping light to electricity conversion efficiencies, simple and low cost manufacturing. Fruitful efficiency of a DSSC is that it should convert photon into current even at wavelength of UV. Present work aimed at quantum efficiency (Light Harvesting Efficiency) of 3,5-dimethyl pyridine 2-carbonitirle. Density functional theory (DFT) has been used to determine the ground state geometries of dye 3,5-dimethyl pyridine 2-carbonitirle. The time dependant density functional theory (TDDFT) has been used to calculate the excitation energies. All the calculations were performed in both gas and solvent phase. The improved light harvesting efficiency (LHE) and free energy change of electron injection of newly designed sensitizers revealed that these materials would be an excellent sensitizers. It may also be due to dendrites of methyl group and cyno group which is present in the study material. The experimental spectrum of FTIR and FT-Raman supports the absorption levels.

Key Words: *3,5-dimethyl pyridine 2-carbonitirle,Dye-sensitized solar cells, Light harvesting efficiency, Density functional Theory, FTIR, FT-Raman spectroscopy*

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1. INTRODUCTION

Dye-sensitized solar cells (DSSC) attain consideration because of their sky-scraping light to electricity conversion efficiencies, simple and low cost manufacturing.[1-3] The sensitizer is a critical element in DSSC, which improves the power conversion efficiency and increases the stability of the devices. The Ruthenium base photosensitizers give a solar energy to electricity conversion efficiency of 10% in average.[2] Metal free organic DSSCs have benefits over metal holding sensitizers, e.g., easy and cheap preparation methods, environment friendly and elevated molar extinction coefficient.[4] Different metal free dyes have been examined which have comparable efficiencies to metal holding sensitizers.[5-7] Designing of dye sensitizer plays an important role in the optimization of DSSC,[8] and it depends on the quantitative information of dye sensitizer. In most of the organic sensitizers presence of donor, bridge and acceptor (DBA) moieties is very important to get better performance of the photo induced intramolecular charge transfer.
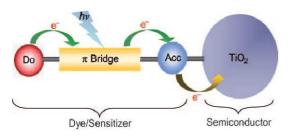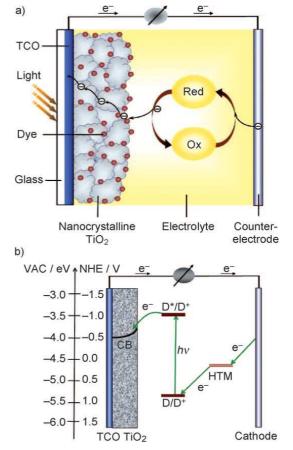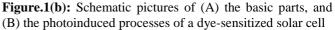

Figure 1(a). Schematic illustration of the dye-sensitized TiO$_2$ interface

Figure.1(b): Schematic pictures of (A) the basic parts, and (B) the photoinduced processes of a dye-sensitized solar cell

During electronic transition, charge transfer depends on the conjugation across the donor and anchoring groups. Efficiency of organic sensitizers decreases due to dye aggregation and charge recombination.[9] To model and design efficient metal-free sensitizers for DSSC, suitable DBA systems are needed whose properties can be altered by applying the drivable structural modifications. In this research work, we report an organic dye 3,5-dimethyl pyridine 2-carbonitrile, shows the light harvesting efficiency which is overall of 12% . We also investigated its Molecular structure, vibrational spectroscopic FT-IR,FT-Raman analysis.

2. EXPERIMENTAL

Freshly prepared 3,5-dimethyl pyridine 2-carbonitrile has been purchased from Sigma Aldrich and used without further purification. Fourier transform infrared spectra of the title compound is measured at the room temperature in the region 4000-400 cm^{-1} using a BRUCKER IFS-66 V FTIR spectrometer at a resolution of ± 1cm^{-1} equipped with a MCT detector, a KBr beam splitter and globar source. The FT-Raman spectrum of 3,5-dimethyl pyridine 2-carbonitrile is recorded on a BRUKER IFS -66 V model interferometer equipped with FRA-106 FT-Raman accessory in the 3500–100 cm^{−1} Stokes region using the 1064 nm line of a Nd: YAG laser for excitation operating at 200 mW power. The reported wave numbers are believed to be accurate within ±1 cm^{−1}.
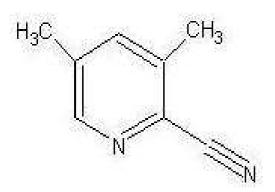

Figure.2: Chemical Structure of 3,5-dimethyl pyridine 2-carbonitrile

3. COMPUTATIONAL DETAILS

Density functional theory (DFT) and time dependant density functional theory (TD-DFT) calculations were performed to determine geometries, electronic structures and electronic absorption spectra selected dye. All the calculations, both in gas and solvent phase, were performed using Gaussian09 package.[12] All calculations were performed by employing CAM-B3LYP functional and 6-311+G* basis set. The free energy change for electron injection onto a titanium dioxide (TiO$_2$) surface and dye's excited state oxidation potential were calculated using mathematical equations.

The **light harvesting efficiency** (**LHE**) was determined by formula[14]:

$$LHE = 1 - 10^{-f}$$

Where **f** is the oscillator strength of dye

4. RESULTS AND DISCUSSION

4.1. The geometric structure:

The optimized geometry of the 3,5-dimethylpyridine 2-carbonitrile is shown in Figure.3, and the bond lengths, bond angles and dihedral angles are listed in Table.1(a),(b),(c). Since the crystal structure of the exact title compound is not available till now, the optimized structure can be only be compared with other similar systems for which the crystal structures have been solved. From the theoretical values we can find that most of the optimized bond lengths, bond angles and dihedral angles. The optimized bond lengths of C-C single and double bond inside and outside the pyridine ring differs. These values are reported in Table 1(a),(b),(c). The bonds length between Carbon atoms C1-C2=1.4087Å, C3-C4 =1.3961 Å and C2-C3=1.3935 Å, C4-C5 =1.3998 Å these C-C bonds are skeletal C-C bonds of the pyridine ring which are having merely same value of bond length this is due to interaction made by localized electron inside the ring. Bond angle betweenC1-N6-C5 is 117.768 which support the presence of Nitrogen in pyridine ring. Dihedral angle implies the sample under study have a ring structure.
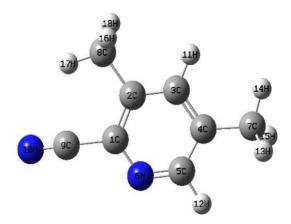

Figure.3: Optimized geometrical structure of dye 3,5-dimethylpyridine 2-carbonitrile.

Table 1(a): Bond lengths (Å) of the dye 3,5-dimethylpyridine 2-carbonitrile

Bond length	B3LYP/6-311++G(d,p)(Å)
C1-C2	1.4087
C1-N6	1.3384
C1-C9	1.4405
C2-C3	1.3935
C2-C8	1.5055
C3-C4	1.3961
C3-H11	1.0861
C4-C5	1.3998
C4-C7	1.5056
C5-N6	1.3299
C5-H12	1.0868
C7-H13	1.0914

C7-H14	1.094
C7-H15	1.094
C8-H16	1.0936
C8-H17	1.0936
C8-H18	1.091
C9-N10	1.1549

Table 1(b): Bond angle (°) of the dye 3,5-dimethylpyridine 2-carbonitrile

Bond angle	B3LYP/6-311++G(d,p) (°)
C2-C1-N6	124.1532
C2-C1-C9	119.4946
N6-C1-C9	116.3521
C1-C2-C3	116.1263
C1-C2-C8	121.822
C3-C2-C8	122.0517
C2-C3-C4	121.1168
C2-C3-H11	119.1001
C4-C3-H11	119.783
C3-C4-C5	116.8421
C3-C4-C7	121.7516
C5-C4-C7	121.4063
C4-C5-N6	123.9938
C4-C5-H12	120.1051
N6-C5-H12	115.9011
C1-N6-C5	117.7678
C4-C7-H13	111.2781
C4-C7-H14	111.0938
C4-C7-H15	111.0924
H13-C7-H14	107.9317
H13-C7-H15	107.9312
H14-C7-H15	107.3447
C2-C8-H16	111.2016
C2-C8-H17	111.2009
C2-C8-H18	110.8354
H16-C8-H17	106.8458
H16-C8-H18	108.3013
H17-C8-H18	108.3014

Table 1(c): Dihedral angle (°) of the dye 3,5-dimethylpyridine 2-carbonitrile

Dihedral angle	B3LYP/6-311++G(d,p) (°)
N6-C1-C2-C3	0.001
N6-C1-C2-C8	180.0002
C9-C1-C2-C3	-179.9972
C9-C1-C2-C8	0.002

C2-C1-N6-C5	-0.0013
C9-C1-N6-C5	179.997
C1-C2-C3-C4	0.0001
C1-C2-C3-H11	-179.9997
C8-C2-C3-C4	-179.9992
C8-C2-C3-H11	0.001
C1-C2-C8-H16	59.4652
C1-C2-C8-H17	-59.4652
C1-C2-C8-H18	179.9961
C3-C2-C8-H16	-120.5356
C3-C2-C8-H17	120.526
C3-C2-C8-H18	-0.0047
C2-C3-C4-C5	-0.0007
C2-C3-C4-C7	-180.0027
H11-C3-C4-C5	-180.0009
H11-C3-C4-C7	-0.0029
C3-C4-C5-N6	0.0004
C3-C4-C5-H12	180.0012
C7-C4-C5-N6	180.0012
C7-C4-C5-H12	0.0032
C3-C4-C7-H13	-180.0068
C3-C4-C7-H14	59.7042
C3-C4-C7-H15	-59.7194
C5-C4-C7-H13	-0.009
C5-C4-C7-H14	-120.2979
C5-C4-C7-H15	120.2785
C4-C5-N6-H11	0.0006
H12-C5-N6-C1	-180.003

4.2. Vibrational spectral Analysis

Figure 5 and 6 shows the observed IR and Raman spectra of 3,5-dimethylpyridine 2-carbonitrile respectively. The 3,5-dimethylpyridine 2-carbonitrile molecule give rise to three C-H stretching, two C-H torsion vibrations, two C-H out of plane bending vibrations ,one C-H in-plane bending vibration, four wagging C-C-N vibrations, one C-C-N bending vibration, two C=C stretching vibrations, three C-N stretching vibrations, one C-C-C torsion vibration, one C-C-C in plane vibration, one ring stretching and one ring deformation were assigned using experimental spectrum. The strongest IR absorption for 3,5-dimethylpyridine 2-carbonitrile corresponds to the vibrational mode 28 near about 1455 cm^{-1}, which is corresponding to stretching mode of C=C bonds. The next stronger IR absorption is attributed to vibrational mode 16 near about 895 cm^{-1}, corresponding to the Torsion mode of C-H bonds. In the Raman spectrum, however, the strongest activity mode is the vibrational mode 29 near about 2213 cm^{-1}, which is corresponding to stretching mode of C-N triple bond. This peak is also observed in FTIR spectrum at 2224 cm^{-1}.

4.3. C–H vibrations

The C–H stretching vibrations in the benzene derivatives arises from non-degenerate mode (3072 cm^{-1}) and two degenerate modes (3047 cm^{-1}), (3099 cm^{-1}). In this region, the bands are not appreciably affected by the nature of substituents. Hence in the present investigation, the FT-IR bands at 3057, 3022 cm^{-1} and FT-Raman bands at 3059, 3009 cm^{-1} have been assigned to C–H stretching vibrations. In general most of them are weak in either the FT-Raman or FT-IR, with the exception of 3059 cm^{-1} which appears as very strong band in the FT-Raman spectra is assigned C–H

in-phase stretching mode. The upper limit of frequency comparatively decreases may be due to the presence of methyl group. The C–H in-plane bending vibrations appear in the region 1000–1520 cm^{-1} and C–H out of- plane bending vibrations in the range of 700–1000 cm^{-1}. The bands corresponding to the C–H in-plane bending modes of pyridine are observed at 1177 and 1081 cm^{-1} in the FT-IR spectra. The corresponding calculated modes are dominated by C-H in plane bending, and coupled mostly with CC stretching. The medium strong bands observed at 947, 898 and 866, 812 cm^{-1} in the FT-IR spectrum modes of pyridine.
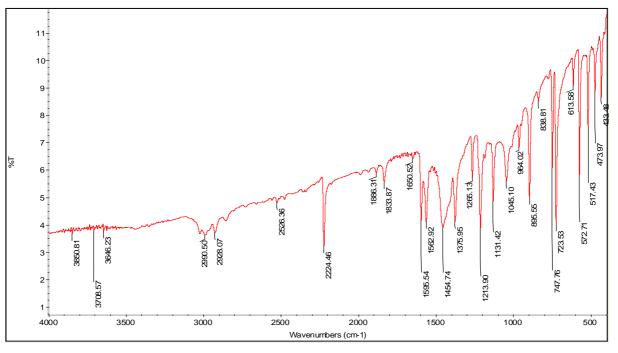

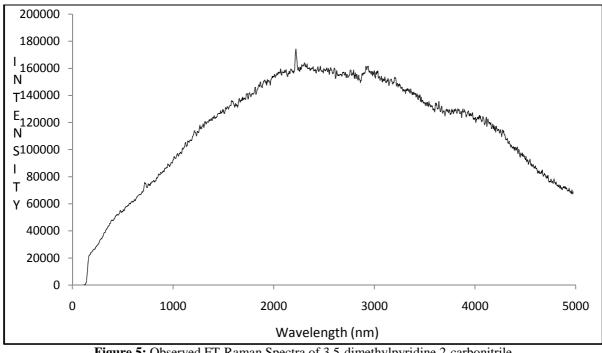**Figure.4:** Observed FT-IR Spectra of 3,5-dimethylpyridine 2-carbonitrile

Figure.5: Observed FT-Raman Spectra of 3,5-dimethylpyridine 2-carbonitrile

4.4. C–C vibrations

The C–C stretching frequencies are generally predicted in the region 650–1650 cm^{-1}. In pyridine, the C–C stretching frequencies arise from the two doubly degenerated vibrations (1596 cm^{-1}) and (1485 cm^{-1}) and two non-degenerate modes at (1300 cm^{-1}) and (998 cm^{-1}) which corresponds to skeletal vibrations. The doubly degenerated (1485 cm^{-1}) mode is basically a ring deformation, since it involves both stretching and bending of the C–C bonds. The frequency of the vibrational pair in substituted pyridine is rather insensitive of substitution. The strong bands observed at 1318, 1305 cm^{-1} in FT-IR spectrum are assigned to 40% contribution of the CC-stretching mode. The CC in-plane bending modes result from non-degenerate value (1010 cm^{-1}).

4.5. Methyl group vibrations

The asymmetric and symmetric stretching modes of methyl group attached to the pyridine ring are usually downshifted due to electronic effects and are expected in the range 2850–3000 cm^{-1} for asymmetric and symmetric stretching vibrations. From spectrum the asymmetric stretching CH$_3$ mode in which two C–H bonds of the methyl group are extending while the third one is contracting. The second arises from symmetrical stretching CH$_3$ in which all three of the C–H bonds extend and contract in phase. The two CH$_3$ frequencies are calculated to be 2933 and 2931 cm^{-1}, which are well comparable with the experimental values observed at 2913(m) cm^{-1}, 2862(m) cm^{-1} in FT-IR and 2915 (m) cm^{-1}, 2862 (m) cm^{-1} in FT-Raman spectra. The frequency of calculated values of CH$_3$ frequencies and 2979 cm^{-1} observed only in FT-IR spectra at 2933 (m) cm–1. The two CH$_3$ out of plane modes are calculated at 2830 and 2824 cm^{-1} both are not observed from experiment. In many molecules the symmetric deformation labeled CH$_3$ symmetric bending and CH$_3$ in plane bending appears with an intensity varying from medium to strong and expected in the range 1380±25 cm^{-1}. The two CH$_3$ stretching bending frequencies are observed at 1379 and 1361 cm^{-1}. Out of these two modes one is observed in the FT-IR and FT-Raman spectra at 1377 and 1379 cm–1. The out-of-plane rocking in the region 970±70 cm^{-1} is more difficult to find among the C–H out-of-plane deformations.

4.6. Quantum Efficiency

Light harvesting efficiency of 3,5-dimethylpyridine 2-carbonitrile is calculated from the oscillator value obtained from TDDFT and tabulated in Table.3 , the highest light harvesting efficiency value 0.8611 is obtained at 165.84nm in solution and 0.7882 is obtained at 163.61nm in gas phase. Each photon ejects one electron from a molecule of the dye, hence 3,5-dimethyl pyridine 2-carbonitrile achieve up to 86% of efficiency in solution and 78% in vacuum at UV region. Average light harvesting efficiency is calculated and the result is 12.7976% in solution and 12.2604% in gas phase.

Table 2: Light Harvesting Efficiency of the Dye

Light Harvesting Efficiency of the dye in SOLUTION		Light Harvesting Efficiency of the dye in GAS PHASE	
Wavelength(nm)	η%	Wavelength(nm)	η%
218.58	0.4461	215.28	0.3390
207.74	0.0579	211.14	0.0133
205.25	0.01213	207.65	0.0779
174.11	0.00757	175.47	0.00597
170.05	0.01599	173.19	0.00046
168.86	0.7418	169.43	0.00391
166.11	0.00688	165.27	0.6251
165.84	0.8611	163.61	0.7882
158.72	0.00023	160.20	0.0084
157.13	0.00459	159.51	0.00023
154.92	0.1318	156.72	0.1696
153.94	0.0000	155.86	0.0000
150.94	0.0993	153.14	0.01213
150.92	0.1104	151.84	0.3583
145.53	0.00757	147.21	0.01916
141.88	0.00207	144.45	0.00069
141.21	0.00962	141.98	0.01122
140.09	0.00574	141.36	0.0000
138.96	0.0124	139.40	0.00253
137.61	0.02634	137.16	0.01599

Table 3: Computed excitation energies, electronic transition configurations and oscillator strengths(f) for the optical transitions with f>.01 of the absorption bands in visible and near-UV region for the dye 3,5-dimethyl pyridine2-carbonitrile (in Gas phase)

State	Configuration composition (corresponding transition orbital)	Excitation energy (eV/nm)	Oscillator Strength (f)
1	0.15377 (34 -> 41) -0.26138 (34 -> 45) -0.26132 (35 -> 39) 0.58476 (35 -> 42)	5.7593/215.28	.1798
2	-0.20848 (33 -> 39) -0.19004 (33 -> 41) 0.52608 (33 -> 42) 0.10413 (33 -> 45) 0.16362 (33 -> 51) -0.11259 (33 -> 92)	5.8722/211.14	.0058
3	-0.18561 (34 -> 39) 0.37295 (34 -> 42) -0.31910 (35 -> 41) 0.45852 (35 -> 45) 0.13445 (35 -> 51)	5.9707/207.65	.0352
4	0.53817 (35 -> 36) 0.24513 (35 -> 38) -0.26883 (35 -> 44) -0.10565 (35 -> 47) -0.10548 (35 -> 55)	7.0658/175.47	.0026
5	-0.11226 (31 -> 59) 0.14730 (31 -> 64) 0.31770 (32 -> 42) -0.17681 (32 -> 45) -0.13911 (32 -> 65) -0.16490 (32 -> 69) 0.14285 (33 -> 45)	7.1588/173.19	.0002
6	-0.27487 (33 -> 41) -0.23405 (33 -> 42) 0.50529 (33 -> 45) 0.11998 (33 -> 51)	7.3177/169.43	.0017
7	-0.13317 (33 -> 39) 0.33403 (33 -> 41) -0.19705 (33 -> 42) 0.46913 (33 -> 45) 0.10834 (33 -> 48) -0.11956 (33 -> 54)	7.4642/166.11	.0030
8	0.26666 (34 -> 41) -0.25917 (34 -> 42) 0.44797 (34 -> 45) 0.12710 (34 -> 48) -0.11695 (35 -> 41) -0.10233 (35 -> 42)	7.4763/165.84	.8572
9	-0.12656 (30 -> 41) 0.21151 (31 -> 56) 0.15802 (31 -> 58) -0.10103 (31 -> 64) -0.16199 (32 -> 39) 0.29416 (32 -> 41) 0.12989 (32 -> 45) -0.14783 (32 -> 63) 0.12348 (32 -> 66) -0.13215 (32 -> 69) -0.10701 (32 -> 79) -0.18415 (35 -> 56) -0.10845 (35 -> 58)	7.8115/158.72	.0001
10	0.30079 (34 -> 36) -0.12860 (34 -> 44) 0.53274 (35 -> 37) 0.11252 (35 -> 49)	7.8905/157.13	.0020
11	0.11613 (31 -> 39) -0.18478 (31 -> 41) 0.14033 (32 -> 56) 0.10430 (32 -> 58) 0.42258 (35 -> 39) 0.20340 (35 -> 41) 0.15516 (35 -> 42) 0.19827 (35 -> 48) -0.10974 (35 -> 51)	8.0032/154.92	.0614
12	0.27588 (34 -> 36) -0.11537 (34 -> 44) -0.10059 (34 -> 47) -0.17494 (35 -> 36) -0.26501 (35 -> 37) 0.45345 (35 -> 38) -0.11851 (35 -> 46) 0.11990 (35 -> 58)	8.0540/153.94	.0000
13	-0.16475 (31 -> 41) 0.13264 (32 -> 56) 0.27169 (34 -> 36) 0.10159 (34 -> 40) -0.13414 (34 -> 44) 0.12067 (35 -> 36) -0.13680 (35 -> 37) -0.21751 (35 -> 38) -0.19224 (35 -> 39) -0.18192 (35 -> 41) 0.14083 (35 -> 43)	8.2140/150.94	.0454
14	0.16955 (31 -> 41) -0.13702 (32 -> 56) -0.10160 (32 -> 58) 0.26196 (34 -> 36) -0.12746 (34 -> 44) 0.11674 (35 -> 36) -0.13559 (35 -> 37) -0.21034 (35 -> 38)	8.2154/150.92	.0508
15	-0.30245 (35 -> 36) -0.15788 (35 -> 37) -0.15912 (35 -> 38) -0.42962 (35 -> 44) -0.25239 (35 -> 47) 0.10751 (35 -> 50) -0.12375 (35 -> 53)	8.5194/145.53	.0033

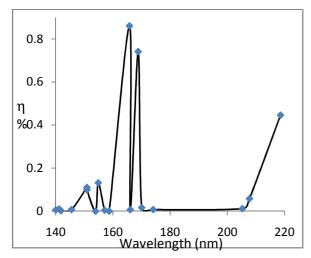|			
	-0.11797 (35 -> 55)		
16	-0.18404 (34 -> 37) -0.19197 (35 -> 38) 0.48689 (35 -> 40) -0.33905 (35 -> 43) 0.10811 (35 -> 44) -0.10276 (35 -> 65)	8.7386/141.88	.0009
17	-0.17304 (34 -> 38) 0.10398 (35 -> 37) 0.15111 (35 -> 38) 0.40633 (35 -> 40) 0.41638 (35 -> 43)	8.7799/141.21	.0042
18	-0.30212 (34 -> 39) -0.20100 (34 -> 41) -0.11772 (34 -> 42) -0.20479 (35 -> 41) 0.37188 (35 -> 42) 0.31961 (35 -> 45)	8.8504/140.09	.0025
19	-0.32104 (34 -> 37) 0.43895 (34 -> 38) -0.13453 (34 -> 40) -0.11421 (34 -> 44) -0.17331 (34 -> 46) -0.10973 (34 -> 53) 0.18038 (35 -> 43)	8.9225/138.96	.0054
20	0.39563 (33 -> 36) -0.19618 (33 -> 37) 0.34153 (33 -> 38) 0.15808 (33 -> 40) -0.11647 (33 -> 43) -0.15267 (33 -> 46) -0.13717 (33 -> 47) 0.10273 (33 -> 55) -0.10699 (33 -> 57)	9.0098/137.61	.0116

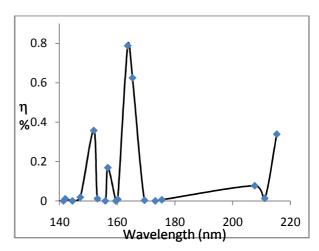**Figure .4:** Light Harvesting Efficiency of the dye in SOLUTION

Figure .5: Light Harvesting Efficiency of the dye in GAS PHASE

5. CONCLUSION

The electronic absorption spectral features in FTIR, FT-Raman, visible and near-UV region qualitatively agrees with TD-DFT calculations. The absorptions are all ascribed to $\pi \rightarrow \pi^*$ transition. Three excited states with the lowest excited energies of 3,5-dimethylpyridine 2-carbonitrile is the result of photo induced electron transfer that contributes sensitization of photo-to current conversion. The interfacial electron transfer between semiconductor TiO_2 electrode and dye sensitizer3,5-dimethylpyridine 2-carbonitrile is due to electron injection from excited dye as donor to the semiconductor conduction band. Based on the analysis of geometries, quantum efficiency, and spectral properties of 3,5-dimethylpyridine 2-carbonitrile, the nitro group and methyl group enlarges the distance between electron donor group and semiconductor surface, and decreases the time scale of the electron injection rate, which results in higher conversion efficiency at maximum absorption. This indicates that the choice of the appropriate conjugate bridge in dye sensitizer is very important to improve the performance of DSSC.

REFERENCES

[1]. Regan, B. O.; Gratzel, M. Nature 1991, 353, 737-740.

[2]. Nazeeruddin, M. K.; De Angelis, F.; Fantacci, S.; Selloni, A.;Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. J. Am. Chem. Soc. 2005, 127, 16835-16847.

[3]. Zhang, Q. F.; Dandeneau, C. S.; Zhou, X. Y.; Cao, G. Z. Adv Mater 2009, 21, 4087-4108.

[4]. Li, G.; Jiang, K. J.; Li, Y. F.; Li, S. L.; Yang, L. M. J Phys Chem C 2008, 112, 11591-11599.

[5]. Wong, B. M.; Codaro, J. G. J. Chem. Phys. 2008, 129, 214703-214710.

[6]. Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. J. Am. Chem.Soc. 2004, 126, 12218-12219.

[7]. Ferrere, S.; Zaban, A.; Gregg, B. J. Phys. Chem. B 1997, 101,4490-4493.

[8]. Robertson, N. Angew. Chem. Int. Ed. 2006, 45, 2338-2345.

[9]. Liu, D.; Fessenden, R. W.; Hug, G. L.; Kamat, P. V. J. Phys. Chem.B 1997, 101, 2583-2590.

[10]. Hagfeldt, A.; Gratzel, M. Acc. Chem. Res. 2000, 33, 269-277.

[11]. Sayama, K.; Tsukagochi, S.; Hara, K.; Ohga, Y.; Shinpou, A.; Abe, Y.; Suga, S.; Arakawa, H. J. Phys. Chem. B 2002, 106, 1363-1371

[12]. Frisch, M. J. et al. Gaussian 09, Revision A.1. Gaussian Inc,Wallingford, CT, 2009.

[13]. Katoh, R.; Furube, A.; Yoshihara, T.; Hara, K.; Fujihashi, G.;Takano, S.; Murata, S.; Arakawa, H.; Tachiya, M. J. Phys. Chem B 2004, 108, 4818-4822.

[14]. Nalwa, H. S. Handbook of advanced electronic and photonic materials and devices; Academic: San Diego, 2001.

[15]. Wichien, S.; Samarn, S.; Vittaya, A. J. Photochem. Photobiol. A 2012, 236, 35-40.

[16]. Preat, J.; Michaux, C.; Jacquemin, D.; Perpète, E. A. J. Phys.Chem. C 2009, 113, 16821-16833.

[17]. Tomkinson John, Bacci Mauro, Picollo Marcello, Colognesi Daniele. Vib. Spectrosc. 2009, 50, 268-276.

[18]. Zollinger, hristie, 2007 Methods of Determining Indigo: Handbook of Natural Colorants Edited by Thomas Bechtold and Rita Mussak©2009 John Wiley & Sons: Ltd., 2003; p 106-107