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P.M. Anbarasanan, P. Senthil Kumar, K. Vasudevan, S. Moorthy Babu, V. Aroulmoji. DFT and TD-DFT Calculations of Some Metal Free Phthalonitrile Derivatives for Enhancement of the Dye Sensitized Solar Cells. *Acta Physica Polonica A*, 2011, 119 (3), pp.395-404. 10.12693/APhysPolA.119.395 . hal-03101189

HAL Id: hal-03101189

<https://hal.science/hal-03101189>

Submitted on 26 Jan 2021

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DFT and TD-DFT Calculations of Some Metal Free Phthalonitrile Derivatives for Enhancement of the Dye Sensitized Solar Cells

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(Received January 1, 2010; revised version April 20, 2010; in final form May 10, 2010)

The geometries, electronic structures, polarizabilities, and hyperpolarizabilities of organic dye sensitizers 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile were studied based on density functional theory using the hybrid functional B3LYP. Ultraviolet-visible spectra were investigated by time dependent density functional theory. The features of electronic absorption spectra in the visible and near-UV regions were assigned based on time dependent density functional theory calculations. The absorption bands are assigned to $\pi \rightarrow \pi^*$ transitions. Calculated results suggest that the three lowest energy excited states of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile are due to photoinduced electron transfer processes. The interfacial electron transfer between semiconductor TiO₂ electrode and dye sensitizers 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile is due to an electron injection process from excited dyes to the semiconductor's conduction band. The role of amide and methyl groups in phthalonitrile in geometries, electronic structures, and spectral properties were analyzed in a comparative study of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile for the improvement of dye sensitized solar cells.

PACS: 78.66.Qn, 31.10.+z, 71.15.Mb, 32.30.-r

1. Introduction

New technologies for direct solar energy conversion have gained more attention in the last few years. In particular, dye sensitized solar cells (DSSCs) are promising in terms of efficiency and low cost [1–3]. The leading feature of DSSC consists in a wide band gap nanocrystalline film grafted with a quasi-monolayer of dye molecules and submerged in a redox electrolyte. This elegant architecture can synchronously address two critical issues of employing organic materials for the photovoltaic applications: (i) efficient charge generation from the Frenkel excitons and (ii) long-lived electron–hole separation up to the millisecond time domain. The latter attribute can often confer an almost quantitative charge collection for several micrometer-thick active layers, even if the electron mobilities in nanostructured semiconducting films are significantly lower than those in the bulk crystalline materials. Benefited from systematic device engineering and continuous material innovation, a state of the art DSSC with a ruthenium sensitizer has achieved a validated efficiency of 11.1% [4] measured under the Air Mass 1.5 Global (AM1.5G) conditions. In view of the limited ruthenium resource and the heavy-metal toxicity, metal-free organic dyes have received surging research interest in recent years [5–21]. Because of their high molar absorption coefficient, relatively simple synthesis proce-

dures, various structures and lower cost in contrast to a ruthenium dye and the flexibility in molecular tailoring of an organic sensitizer provides a large area to explore [22–24]. In addition, recently a rapid progress of organic dyes has been witnessed reaching close to 10.0% efficiencies in combination with a volatile acetonitrile-based electrolyte [25]. In this paper the performance of following metal free dyes that can be used in DSSC namely 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile is analyzed.

2. Computational methods

The computations of the geometries, electronic structures, polarizabilities and hyperpolarizabilities for dye sensitizers 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile were done using density functional theory (DFT) with Gaussian 03 package [26]. The DFT was treated with hybrid functional Becke's three parameter gradient-corrected exchange potential and the Lee–Yang–Parr (B3LYP) [27–29]. The calculations were performed without any symmetry constraints by using polarized triple-zeta 6-311++G(d,p) basis sets. The vibrational wave numbers were also calculated with the same method and the calculated Raman activities (S_i) were converted to relative Raman intensities (I_i) using the following relationship derived from the intensity theory of the Raman scattering [30–32]:

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$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i [1 - \exp(hc\nu_i/kt)]},$$

where ν_0 is the exciting wave number in cm^{-1} , ν_i is the vibrational wave number of the i -th normal mode, h , c and k are fundamental constants and f is a suitably chosen common normalization factor for all peak intensities. Simulation of calculated IR and Raman spectra have been plotted using pure Lorentzian band shape with a bandwidth (FWHM) of 10 cm^{-1} . The electronic absorption spectra require calculation of the allowed excitations and oscillator strengths. These calculations were done using TD-DFT with PBE1PBE [20] correlation functional and same 6-311++G(d,p) basis sets in vacuum and solution, and the non-equilibrium version of the polarizable continuum model (PCM) [33, 34] was adopted for calculating the solvent effects.

3. Results and discussion

3.1. The geometrical structures

The optimized geometries of the 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile are shown in Fig. 1, and the selected bond lengths, bond angles and dihedral angles are listed in Table I. The similar geometrical character induces the similar geometrical parameters of 3,4-

pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile. Among these dyes 4-aminophthalonitrile has the largest conjugate bridge between carbonyl and amide group.

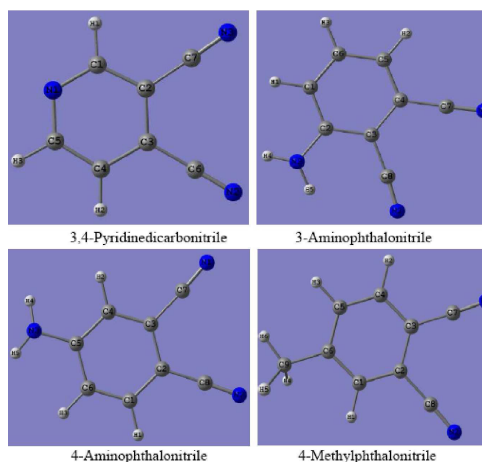


Fig. 1. Optimized geometrical structures of dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile with atomic serial numbers.

TABLE I

Selected bond lengths (in Å), bond angles (in degree) and dihedral (in degree) of the dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile.

3,4-pyridinedicarbonitrile		3-aminophthalonitrile		4-aminophthalonitrile		4-methylphthalonitrile	
C2-C3	1.4095	C2-C3	1.4169	C2-C3	1.4131	C2-C3	1.4131
C2-C7	1.4269	C2-N3	1.3691	C2-C8	1.4255	C2-C8	1.4306
C3-C6	1.4299	C3-C4	1.4144	C3-C7	1.4314	C3-C7	1.4291
C6-N2	1.154	C3-C8	1.4232	C5-N3	1.3774	C6-C9	1.5073
C7-N3	1.1545	C4-C7	1.4307	C7-N1	1.1548	C7-N1	1.1551
C1-C2-C7	119.843	C2-C1-H1	118.9322	C2-C1-H1	118.9278	C2-C1-C6	121.3942
C3-C2-C7	122.1911	C6-C1-H1	120.0877	C6-C1-H1	119.8277	C2-C1-H1	118.5861
C2-C3-C4	118.2039	C1-C2-C3	118.1636	C1-C2-C3	118.241	C6-C1-H1	120.0196
C2-C3-C6	121.5964	C1-C2-N3	120.9201	C1-C2-C8	119.9354	C1-C2-C3	119.725
C4-C3-C6	120.1997	C3-C2-N3	120.8926	C3-C2-C8	121.8236	C1-C2-C8	119.1516
C3-C4-C5	118.7099	C2-C3-C4	120.054	C2-C3-C4	120.4646	C3-C2-C8	121.1233
C1-N1-C5	117.8072	C4-C5-C6	119.0469	C4-C5-C6	118.4398	C5-C4-H2	120.3986
N1-C1-C2-C3	0.0018	C6-C1-C2-N3	178.0814	C6-C1-C2-C3	0.015	C6-C1-C2-C8	180.0004
N1-C1-C2-C7	180.0012	H1-C1-C6-C5	179.6242	H1-C1-C2-C3	179.953	H1-C1-C2-C8	0.0006
H1-C1-N1-C5	180.0022	C1-C2-C3-C4	0.2714	H1-C1-C2-C8	0.0431	C2-C1-C6-C9	180.0002
C7-C2-C3-C6	0	N3-C2-C3-C8	2.4607	C2-C1-C6-C5	0.0423	H1-C1-C6-C5	179.9989
H2-C4-C5-N1	180.0017	C1-C2-N3-H5	169.5011	C1-C2-C3-C4	0.0003	C1-C2-C3-C4	0.0018
H3-C5-N1-C1	180.0021	C2-C3-C4-C7	179.9751	C8-C2-C3-C4	179.9084	C1-C2-C3-C7	180.0008

3.2. Electronic structures and charges

Natural bond orbital (NBO) analysis was performed in order to analyze the charge populations of the

dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile. Charge distributions in C, N and H atoms were observed

because of the different electronegativity, the electrons transferred from C atoms to C, N atoms, C atoms to H, N atoms to H atom. The natural charges of different groups are the sum of every atomic natural charge in the group. These data indicate that the cyanine and amide groups are acceptors, while the acetic groups are donors, and the charges were transferred through chemical bonds.

The frontier molecular orbitals (MO) energies of the dyes 3,4-pyridinedicarbonitrile, 3-nitrophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile are shown in Fig. 2. The HOMO–LUMO gap of the dye 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile in vacuum is 5.96 eV, 5.54 eV, 5.57 eV, and 5.76 eV, respectively.

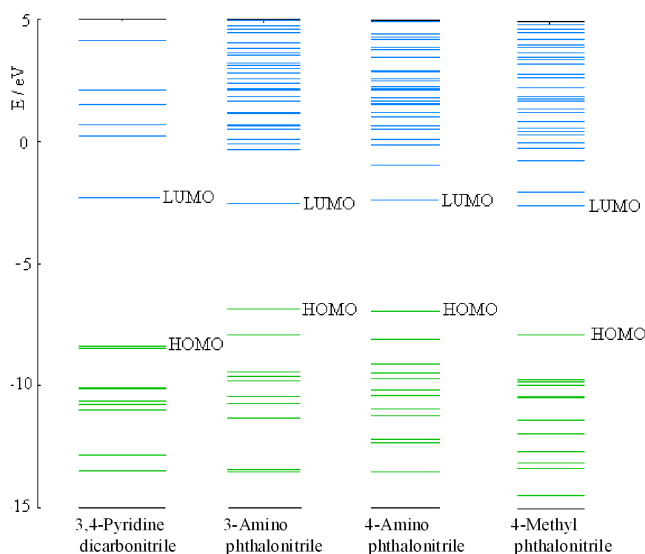


Fig. 2. The frontier molecular orbital energies of the dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile.

While the calculated HOMO and LUMO energies of the bare $\text{Ti}_{38}\text{O}_{76}$ cluster as a model for nanocrystalline are -6.55 and -2.77 eV, respectively, resulting in a HOMO–LUMO gap of 3.78 eV, the lowest transition is reduced to 3.20 eV according to TD-DFT, and this value is slightly smaller than typical band gap of TiO_2 nanoparticles with nm size [35]. Furthermore, the HOMO, LUMO and HOMO–LUMO gap of $(\text{TiO}_2)_{60}$ cluster is -7.52 , -2.97 , and 4.55 eV (B3LYP/VDZ), respectively [36]. Taking into account of the cluster size effects and the calculated HOMO, LUMO, HOMO–LUMO gap of the dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile, $\text{Ti}_{38}\text{O}_{76}$ and $(\text{TiO}_2)_{60}$ clusters, we can find that the HOMO energies of these dyes fall within the TiO_2 gap.

The above data also reveal the interfacial electron transfer between semiconductor TiO_2 electrode and the dye sensitizers 3,4-pyridinedicarbonitrile, 3-amino-

phthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile are electron injection processes from excited dyes to the semiconductor conduction band. This is a kind of typical interfacial electron transfer reaction [37].

3.3. IR and Raman frequencies

Figures 3–6 show the IR and Raman spectra of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile. The strongest IR absorption for 3,4-pyridinedicarbonitrile corresponds to the vibrational mode 28 near about 1614 cm^{-1} , which corresponds to stretching mode of $\text{C}=\text{C}$ bonds. The next stronger IR absorption is attributed to vibrational mode 16 near about 867 cm^{-1} , corresponding to the torsion mode of $\text{C}-\text{H}$ bonds. In the Raman spectra, however, the strongest activity mode is the vibrational mode 29 near about 2345 cm^{-1} , which corresponds to stretching mode of $\text{C}\equiv\text{N}$. The strongest IR absorption for 3-aminophthalonitrile corresponds to the vibrational mode 6 near about 290 cm^{-1} , which is the out of plane bending mode of $\text{C}\equiv\text{N}$. The next stronger IR absorption is attributed to vibrational mode 35 near about 1664 cm^{-1} , corresponds to stretching mode of $\text{C}=\text{C}$ bonds. In the Raman spectra, however, the strongest activity mode is the vibrational mode 37 near about 2338 cm^{-1} , which corresponds to stretching mode of $\text{C}\equiv\text{N}$. The strongest IR absorption for 4-aminophthalonitrile corresponds to the vibrational mode 8 near about 387 cm^{-1} , which is the wagging mode of $\text{C}-\text{H}$ bonds. The next stronger IR absorption is attributed to vibrational mode 35 near about 1666 cm^{-1} , corresponds to stretching mode of $\text{C}=\text{C}$ bonds. In the Raman spectra, however, the strongest activity mode is the vibrational mode 36 near about 2329 cm^{-1} , which corresponds to stretching mode of $\text{C}\equiv\text{N}$. The strongest IR absorption for 4-methylphthalonitrile corresponds to the vibrational mode 19 near about 846 cm^{-1} , which is the ring breathing mode of $\text{C}-\text{C}$ bonds. The next stronger IR absorption is attributed to vibrational mode 37 near about 1639 cm^{-1} , corresponds to stretching mode of $\text{C}=\text{C}$ bonds. In the Raman spectra, however, the strongest activity mode is the vibrational mode 38 near about 2337 cm^{-1} , which corresponds to stretching mode of $\text{C}\equiv\text{N}$.

3.4. Polarizability and hyperpolarizability

Polarizabilities and hyperpolarizabilities characterize the response of a system in an applied electric field [38]. They determine not only the strength of molecular interactions (long-range intermolecular induction, dispersion forces, etc.) as well as the cross-sections of different scattering and collision processes, but also the nonlinear optical properties (NLO) of the system [39, 40]. It has been found that the dye sensitizer hemicyanine system, which has high NLO property, usually possesses high photoelectric conversion performance [41]. In order to investigate the relationships among photocurrent generation, molecular structures and NLO, the polarizabilities and hyperpolarizabilities of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and

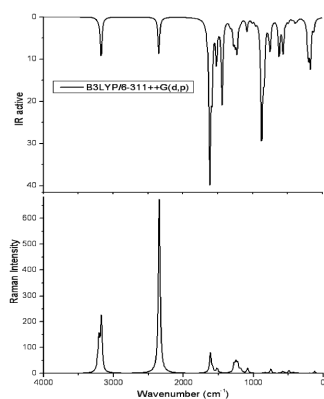


Fig. 3. The calculated IR activity and Raman activity vs. vibration frequency of 3,4-pyridinedicarbonitrile.

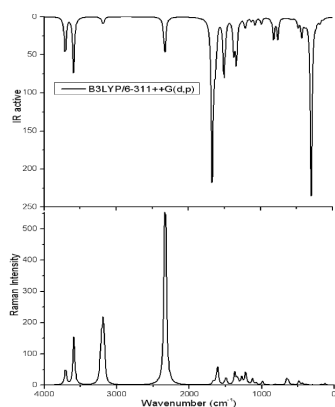


Fig. 4. As in Fig. 3, but for 3-aminophthalonitrile.

4-methylphthalonitrile were calculated. Here, the polarizability and the first hyperpolarizabilities are computed using B3LYP/6-311++G(d,p) method. The definition [39, 40] for the isotropic polarizability is:

$$\alpha = \frac{1}{3}(\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}).$$

The polarizability anisotropy invariant is

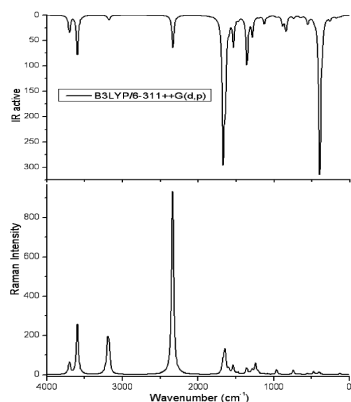


Fig. 5. As in Fig. 3, but for 4-aminophthalonitrile.

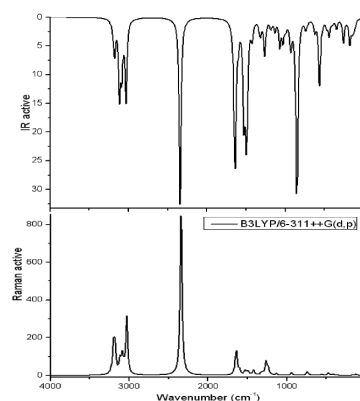


Fig. 6. As in Fig. 3, but for 4-methylphthalonitrile.

$$\Delta\alpha = \left\{ \frac{1}{2}[(\alpha_{XX} - \alpha_{YY})^2 + (\alpha_{YY} - \alpha_{ZZ})^2 + (\alpha_{ZZ} - \alpha_{XX})^2] \right\}^{\frac{1}{2}}$$

and the average hyperpolarizability is

$$\beta_{\parallel} = \frac{1}{5} \sum_i (\beta_{iiz} + \beta_{izi} + \beta_{zii}),$$

where α_{XX} , α_{YY} and α_{ZZ} are tensor components of polarizability; β_{iiz} , β_{izi} , and β_{zii} (i from X to Z) are tensor components of hyperpolarizability.

Tables II and III list the values of the polarizabilities and hyperpolarizabilities of the dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile. In addition to the individual tensor components of the polarizabilities and the first hyperpolarizabilities, the isotropic polarizability, polarizability anisotropy invariant and hyperpolarizability are also calculated. The calculated isotropic polarizability of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile is 94.76, 112.71, 115.49 and 115.10 atomic units (a.u.), respectively. However, the calculated isotropic polarizability of JK16, JK17, dye 1, dye 2, D5, DST and DSS is 759.9, 1015.5, 694.7, 785.7, 510.6, 611.2 and 802.9 a.u., respectively [42, 43]. The above data indicate that the donor-conjugate π bridge-acceptor (D- π -A) chain-like dyes have stronger response for external electric field. Whereas, for dye sensitizers D5, DST, DSS, JK16, JK17, dye 1 and dye 2, on the basis of the published photo-to-current conversion efficiencies, the similarity and the difference of geometries, and the calculated isotropic polarizabilities, it is found that the longer the length of the conjugate bridge in similar dyes, the larger the polarizability of the dye molecule, and the lower the photo-to-current conversion efficiency. This may be due to the fact that the longer conjugate π bridge enlarged the delocalization of electrons, thus it enhanced the response of the external field, but the enlarged delocalization may be not favorable to generate charge separated state effectively. So it induces the lower photo-to-current conversion efficiency.

TABLE II

Polarizability (α) of the dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile (in a.u.).

Dyes	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	α	$\Delta\alpha$
3,4-pyridinedicarbonitrile	129.215	-2.938	107.116	0.000059	-0.00014	47.965	94.76	72.76
3-aminophthalonitrile	144.22	5.113	136.74	0.1023	-0.2269	57.19	112.71	83.54
4-aminophthalonitrile	169.10	1.50	120.18	-0.33	-0.12	57.19	115.49	97.17
4-methylphthalonitrile	162.04	2.072	122.60	-0.00013	-0.00018	60.68	115.10	88.49

TABLE III

Hyperpolarizability (β) of the dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile (in a.u.).

Dyes	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxx}	β_{xyz}	β_{yyz}	β_{xzz}	β_{yzz}	β_{zzz}	β_{ii}
3,4-pyridinedicarbonitrile	-8.221	-52.465	-43.089	77.523	-0.0008	-0.0001	-0.0001	-38.806	12.305	0.0002	0.0042
3-aminophthalonitrile	103.03	-43.33	17.187	-127.09	5.527	-0.6355	4.663	-52.414	-47.17	5.167	9.214
4-aminophthalonitrile	-0.0663	-265.78	-14.77	96.71	12.58	2.968	3.623	64.93	-15.89	7.56	14.257
4-methylphthalonitrile	175.92	-75.168	-0.716	10.05	0.0037	-0.0001	-0.0013	-48.98	-11.33	0.0032	0.00336

3.5. Electronic absorption spectra and sensitized mechanism

Electronic absorption spectra of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile in vacuum and solvent were performed using TD-DFT(PBE1PBE)/6-311++G(d,p) calculations, and the results are shown in Figs. 7–10. It is observed that the absorption in the visible region is much weaker than that in the UV region for 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile. The results of TD-DFT have an appreciable redshift in vacuum and solvent. The discrepancy between vacuum and solvent effects in TD-DFT calculations may result from two aspects. The first aspect is smaller gap of materials which induces smaller excited energies. The other is solvent effects. Experimental measurements of electronic absorptions are usually performed in solution. Solvent, especially polar solvent, could affect the geometry and electronic structure as well as the properties of molecules through the long-range interaction between solute molecule and solvent molecule. For these reasons, the TD-DFT calculation is more difficult to make consistent with quantitatively, so TD-DFT calculation with polar solvent measurable. Though the discrepancy exists, the TD-DFT calculations are capable of describing the spectral features of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile, because of the agreement of line shape and relative strength as compared with the vacuum and solvent.

The HOMO–LUMO gap of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile in acetonitrile at PBE1PBE/6-311++G(d,p) theory level is smaller than that in vacuum. This fact indicates that the solvent effects stabilize the frontier orbitals of 3,4-pyridinedicarbonitrile,

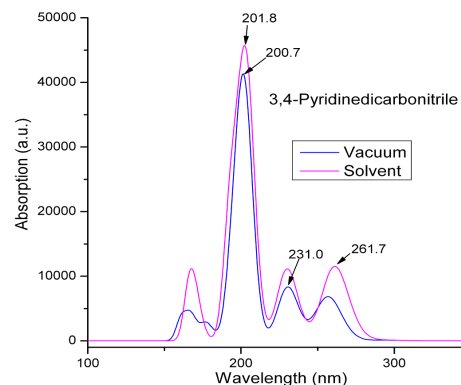


Fig. 7. Calculated electronic absorption spectra of 3,4-pyridinedicarbonitrile.

nitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile, so it induces the smaller intensities and redshift of the absorption as compared with that in vacuum.

In order to obtain the microscopic information about the electronic transitions, the corresponding MO properties are checked. The absorption in visible and near-UV region is the most important region for photo-to-current conversion, so only the 20 lowest singlet/singlet transitions of the absorption band in visible and near-UV region for 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile are listed in Tables IV–VII. The data of Tables IV–VII and Fig. 11 are based on the 6-311++G(d,p) results with solvent effects involved.

This indicates that the transitions are photoinduced charge transfer processes, thus the excitations generate charge separated states, which should favour the electron injection from the excited dyes to semiconductor surface.

The solar energy to electricity conversion efficiency (η) under AM 1.5 white-light irradiation can be obtained

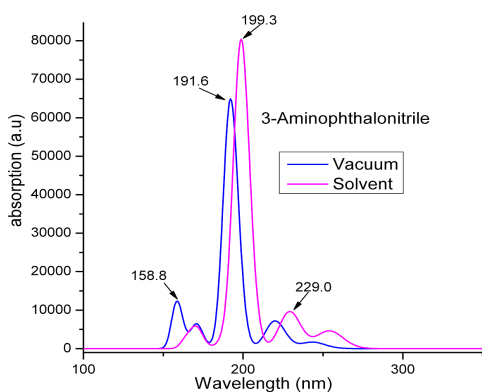


Fig. 8. As in Fig. 7, but for 3-aminophthalonitrile.

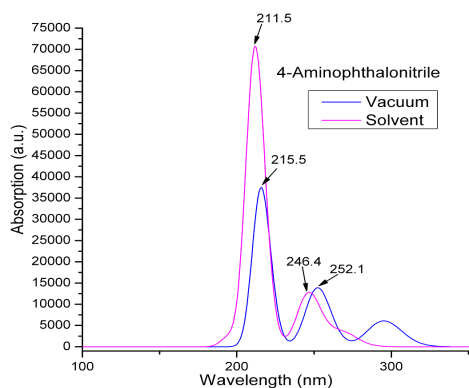


Fig. 9. As in Fig. 7, but for 4-aminophthalonitrile.

from the following formula:

$$\eta(\%) = \frac{J_{sc}[\text{mA cm}^{-2}]V_{oc}[\text{V}]\text{ff}}{I_0[\text{mW cm}^{-2}]} \times 100,$$

where I_0 is the photon flux, J_{sc} is the short-circuit photocurrent density, and V_{oc} is the open-circuit photovoltage, and ff represents the fill factor [44]. At present, the J_{sc} , the V_{oc} , and the ff are only obtained by experiment, the relationship among these quantities and the

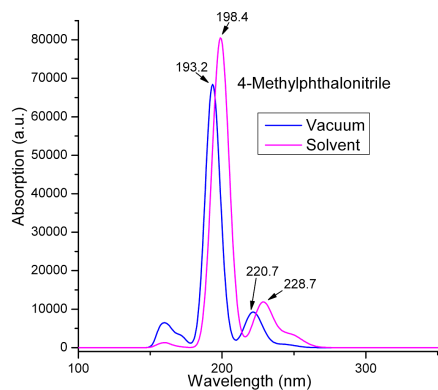


Fig. 10. As in Fig. 7, but for 4-methylphthalonitrile.

electronic structure of dye is still unknown. The analytical relationship between V_{oc} and E_{LUMO} may exist. According to the sensitized mechanism (electron injected from the excited dyes to the semiconductor conduction band) and single electron and single state approximation, there is an energy relationship

$$eV_{oc} = E_{LUMO} - E_{CB},$$

where E_{CB} is the energy of the semiconductor's conduction band edge. So the V_{oc} may be obtained applying the following formula:

$$V_{oc} = (E_{LUMO} - E_{CB})/e.$$

It induces that the higher the E_{LUMO} , the larger the V_{oc} .

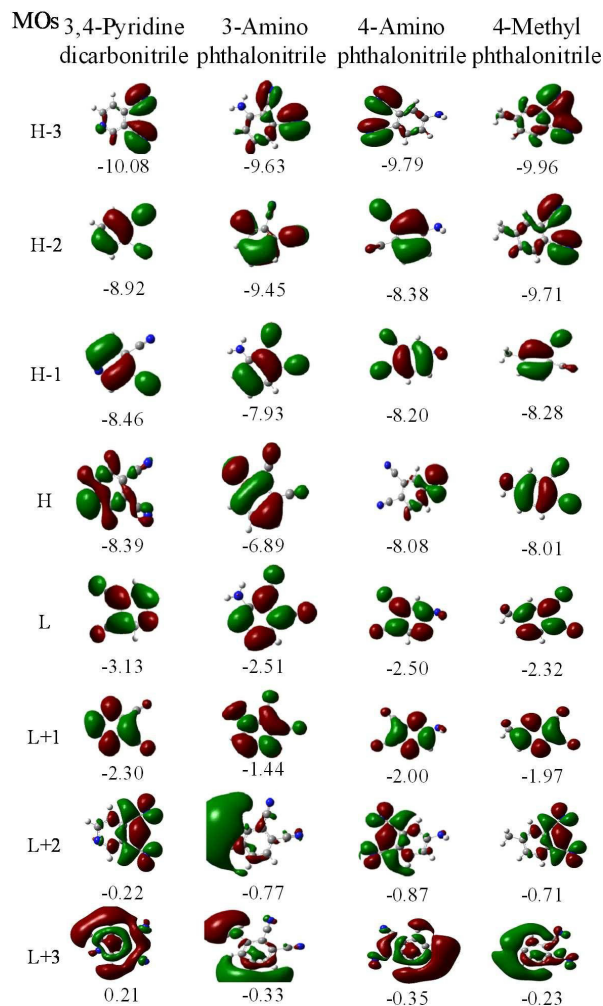


Fig. 11. Isodensity plots (isodensity contour = 0.02 a.u.) of the frontier orbitals of the dyes and corresponding orbital energies (in eV).

The results of organic dye sensitizer JK16 and JK17 [42], D-ST and D-SS also proved the tendency [45] (JK16: $E_{LUMO} = -2.73$ eV, $V_{oc} = 0.74$ V; JK17: $E_{LUMO} = -2.87$ eV, $V_{oc} = 0.67$ V; D-SS: $E_{LUMO} = -2.91$ eV, $V_{oc} = 0.70$ V; D-ST: $E_{LUMO} = -2.83$ eV, $V_{oc} = 0.73$ V).

TABLE IV

Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions with $f > 0.01$ of the absorption bands in visible and near-UV region for the dye 3,4-pyridinedicarbonitrile in acetonitrile.

State	Configurations composition (corresponding transition orbitals)	Excitation energy [eV/nm]	Oscillator strength (f)
2	-0.13 (31 → 34) -0.24 (31 → 35) 0.61 (33 → 34) -0.13 (33 → 35)	4.79/258.55	0.14
4	0.57 (31 → 34) 0.17 (33 → 34) 0.27 (33 → 35)	5.44/227.70	0.14
6	0.12 (27 → 34) -0.26 (31 → 34) 0.54 (33 → 35)	6.17/200.75	0.52
8	-0.13 (28 → 34) 0.60 (31 → 35) 0.12 (33 → 34) -0.12 (33 → 35)	6.47/191.57	0.29
11	-0.11 (27 → 34) 0.63 (28 → 34) 0.10 (29 → 37) 0.12 (31 → 35) -0.12 (32 → 36)	7.24/171.25	0.03
15	0.49 (27 → 34) 0.11 (30 → 36) -0.44 (32 → 36)	7.41/167.31	0.03
18	0.37 (27 → 34) 0.16 (28 → 34) 0.51 (32 → 36)	7.59/163.34	0.06
20	0.10 (27 → 35) 0.67 (32 → 37)	7.97/155.44	0.08

TABLE V

Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions with $f > 0.01$ of the absorption bands in visible and near-UV region for the dye 3-aminophthalonitrile in solvent.

State	Configurations composition (corresponding transition orbitals)	Excitation energy [eV/nm]	Oscillator strength (f)
3	0.35749 (35 → 39) 0.59993 (36 → 38)	4.8856/253.77	0.0635
4	0.60145 (35 → 38) -0.26698 (36 → 39)	5.4165/228.90	0.1330
5	0.13865 (33 → 38) 0.21405 (35 → 38) 0.13087 (35 → 39) 0.55944 (36 → 39)	6.2145/199.51	0.3921
6	0.54145 (35 → 39) -0.25188 (36 → 38) -0.14768 (36 → 39)	6.2609/198.03	0.7261
8	0.67969 (37 → 40) -0.16019 (37 → 41)	6.6025/187.78	0.0274
12	0.64383 (33 → 38) -0.14077 (34 → 40)	7.1527/173.34	0.0181
13	0.15701 (37 → 40) 0.64019 (37 → 41) 0.17806 (37 → 45)	7.2886/170.11	0.0588
18	-0.17371 (37 → 41) 0.60718 (37 → 42) 0.27148 (37 → 45)	7.5653/163.89	0.0308

Certainly, this formula expects further test by experiment and theoretical calculation. The J_{sc} is determined by two processes, one is the rate of electron injection from the excited dyes to the conduction band of semiconductor, and the other is the rate of redox between the excited dyes and electrolyte. Electrolyte affect on the redox processes is very complex, and it is not taken into account in the present calculations. On the basis of the analysis of excitation energies, electronic transition configurations, oscillator strengths and molecular orbitals

of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile in UV-Vis region, we find that most oscillator strengths for the excited states with intramolecular electron transfer character of 4-aminophthalonitrile are larger than that of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile and 4-methylphthalonitrile.

This indicates that most of excited states of 4-aminophthalonitrile have larger absorption coefficient, and then with shorter lifetime for the excited states, so it results in

TABLE VI

Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions with $f > 0.01$ of the absorption bands in visible and near-UV region for the dye 4-aminophthalonitrile in solvent.

State	Configurations composition (corresponding transition orbital)	Excitation energy [eV/nm]	Oscillator strength (f)
1	-0.13772 (36 \rightarrow 39) 0.62208 (37 \rightarrow 38) -0.18956 (37 \rightarrow 39)	4.0351/307.27	0.1579
2	0.31856 (36 \rightarrow 38) 0.16886 (37 \rightarrow 38) 0.56654 (37 \rightarrow 39)	4.8193/257.27	0.2310
3	0.54733 (36 \rightarrow 38) 0.14821 (36 \rightarrow 39) -0.26869 (37 \rightarrow 39)	5.6045/221.22	0.6325
5	0.57246 (35 \rightarrow 38) -0.12001 (36 \rightarrow 38) 0.31288 (36 \rightarrow 39)	6.2357/198.83	0.1277
7	-0.34228 (35 \rightarrow 38) 0.53442 (36 \rightarrow 39)	6.4820/191.28	0.2886
11	0.12583 (34 \rightarrow 40) 0.10658 (34 \rightarrow 41) 0.62630 (35 \rightarrow 39) 0.14546 (37 \rightarrow 42)	7.2485/171.05	0.0606
13	0.40772 (32 \rightarrow 38) 0.53526 (37 \rightarrow 42)	7.5963/163.22	0.1083
16	0.22620 (30 \rightarrow 38) 0.40714 (32 \rightarrow 38) 0.13547 (33 \rightarrow 40) 0.14380 (35 \rightarrow 39) -0.32147 (37 \rightarrow 42) -0.27250 (37 \rightarrow 43) 0.13633 (37 \rightarrow 44)	7.7219/160.56	0.0354
20	0.47147 (28 \rightarrow 38) 0.45804 (29 \rightarrow 38)	7.9748/155.47	0.0149

TABLE VII

Computed excitation energies, electronic transition configurations and oscillator strengths (f) for the optical transitions with $f > 0.01$ of the absorption bands in visible and near-UV region for the dye 4-methylphthalonitrile in solvent.

State	Configurations composition (corresponding transition orbitals)	Excitation energy [eV/nm]	Oscillator strength (f)
1	-0.37690 (36 \rightarrow 38) -0.25951 (36 \rightarrow 39) 0.44013 (37 \rightarrow 38) -0.31582 (37 \rightarrow 39)	5.0105/247.45	0.0449
2	0.40666 (36 \rightarrow 38) -0.12746 (36 \rightarrow 39) 0.43828 (37 \rightarrow 38) 0.27222 (37 \rightarrow 39)	5.4316/228.27	0.1628
3	-0.35497 (36 \rightarrow 38) 0.49676 (37 \rightarrow 39)	6.1917/200.24	0.8644
4	0.58161 (36 \rightarrow 39) 0.20114 (37 \rightarrow 38) -0.11722 (37 \rightarrow 39)	6.3807/194.31	0.4258
15	0.62695 (30 \rightarrow 38) 0.12594 (32 \rightarrow 40) -0.13672 (33 \rightarrow 40) -0.16394 (34 \rightarrow 39) 0.13359 (35 \rightarrow 41)	7.6942/161.14	0.0102

the higher electron injection rate of the 4-aminophthalonitrile, then it leads to the larger J_{sc} of 4-aminophthalonitrile. On the basis of above analysis, the 4-aminophthalonitrile has better performance in DSSC than that of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile and 4-methylphthalonitrile.

4. Conclusions

The geometries, electronic structures, polarizabilities, and hyperpolarizabilities of dyes 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile were studied by using density functional theory with hybrid functional B3LYP, and the UV-Vis spectra were investigated by using TD-DFT methods. The NBO results suggest

that 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile are all ($D-\pi-A$) systems. The calculated isotropic polarizability of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile is 94.76, 112.71, 115.49 and 115.10 a.u., respectively. The calculated polarizability anisotropy invariant of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile is 72.76, 83.54, 97.17 and 88.49 a.u., respectively. The hyperpolarizabilities of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile is 0.0042, 9.214, 14.257, 0.0033 (in a.u.), respectively. The frequencies of strongest IR absorption for 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile

are 1614 cm^{-1} , 290 cm^{-1} , 387 cm^{-1} and 846 cm^{-1} and the frequencies of strongest Raman activity for 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile are 2345 cm^{-1} , 2338 cm^{-1} , 2329 cm^{-1} , 2337 cm^{-1} , respectively. The electronic absorption spectral features in visible and near-UV region were assigned based on the qualitative agreement to TD-DFT calculations. The absorptions are all ascribed to $\pi \rightarrow \pi^*$ transition. The three excited states with the lowest excited energies of 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile are photoinduced electron transfer processes that contributes sensitization of photo-to-current conversion processes. The interfacial electron transfer between semiconductor TiO_2 electrode and dye sensitizer 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile and 4-methylphthalonitrile is electron injection process from excited dyes as donor to the semiconductor conduction band. Based on the comparative analysis of geometries, electronic structures, and spectrum properties between 3,4-pyridinedicarbonitrile, 3-aminophthalonitrile, 4-aminophthalonitrile, and 4-methylphthalonitrile the role of amide and methyl groups in phthalonitrile is as follows: it enlarged the distance between electron donor group and semiconductor surface, and decreased the timescale of the electron injection rate, resulting in giving lower conversion efficiency. This indicates that the choice of the appropriate conjugate bridge in dye sensitizer is very important to enhance the performance of DSSC.

Acknowledgments

This work had been partly financially supported by University Grants Commission, Govt. of India, New Delhi, within the Major Research Project scheme under the approval-cum-sanction Nos. F.No.34-5\2008(SR) and 34-1/TN/08.

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