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Computational Study on Optoelectronically Important Novel 1,3,4-Oxadiazole Chromophore

By

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Abstract

In this work, we report on computational studies of a novel optoelectronically important chromophore 2-(4-((E)-2-(5-((E)-4-(5-(4-tert-butylphenyl)-1, 3, 4-oxadiazol-2-yl) styryl) thiophen-2-yl) vinyl)-5-(4-tert-butylphenyl) 1, 3, 4-oxadiazole (3TPO). Density functional theory (DFT) and time dependant density functional theory (TD-DFT) computations were carried out to demonstrate various intramolecular interactions that cause the stabilization of the compound leading to its optoelectronic applications. The solvation effects were tested using integral equation formalism for the polarizable continuum model (IEF-PCM) model. The highest occupied molecular orbital energy (HOMO), lowest unoccupied molecular orbital energy (LUMO), the energy gap, ground and excited state dipole moments, chemical hardness (η), softness (σ), electronegativity (χ) and chemical potential (μ_c) were estimated with the help of frontier molecular orbitals. It is observed that the experimental results agree well with the computed values.

Keywords: DFT and TDDFT, FRET, Oxadiazole, Salvatochromism, ZnSe/ZnS QDs.

1. Introduction

Oxadiazoles are class of heterocyclic aromatic chemical compound having five membered rings belonging to the azole family. The design, synthesis and development of novel organic chromophores with efficient optical and optoelectronic properties have caught peoples interest due to their significant applications in field effect transistors, organic light-emitting diodes (OLEDs), organic solid-state lasers and sensors and light emitting electrochemical cells, lasers, photodetectors etc. (Narahari et al., 2017 and references therein). In addition, these oxadiazoles have also been extensively used in pharmaceutical and medical applications (Kappor, 2012), (Shyma et al., 2013), (Liang et al., 2013 and references therein).

Computational studies are the crucial ones in developing new materials as they explore the material properties. There are various computational studies and one of them is density functional theory (DFT) formalism which accurately estimates physicochemical behaviors of probes. DFT calculations have been effectively used to study the interactions between solute and solvents and estimation of electronic ground and excited state dipole moments (Tomasi et al., 2005), (Mitra et al., 2007), (Rekha et al., 2017). In the present paper, we have investigated substituted 1,3,4-oxadiazole derivative with a view to understand its solvatochromism, chemical stability and kinetics, energy gap, electron delocalization, charge distribution and its potential candidacy as an optoelectronically important probe with the support of DFT and TD-DFT computations. The solvent effects on geometry were studied by PCM that models the solvent as a polarizable continuum (Caricato et al., 2004), (Caricato et al., 2006) rather than isolated probe.

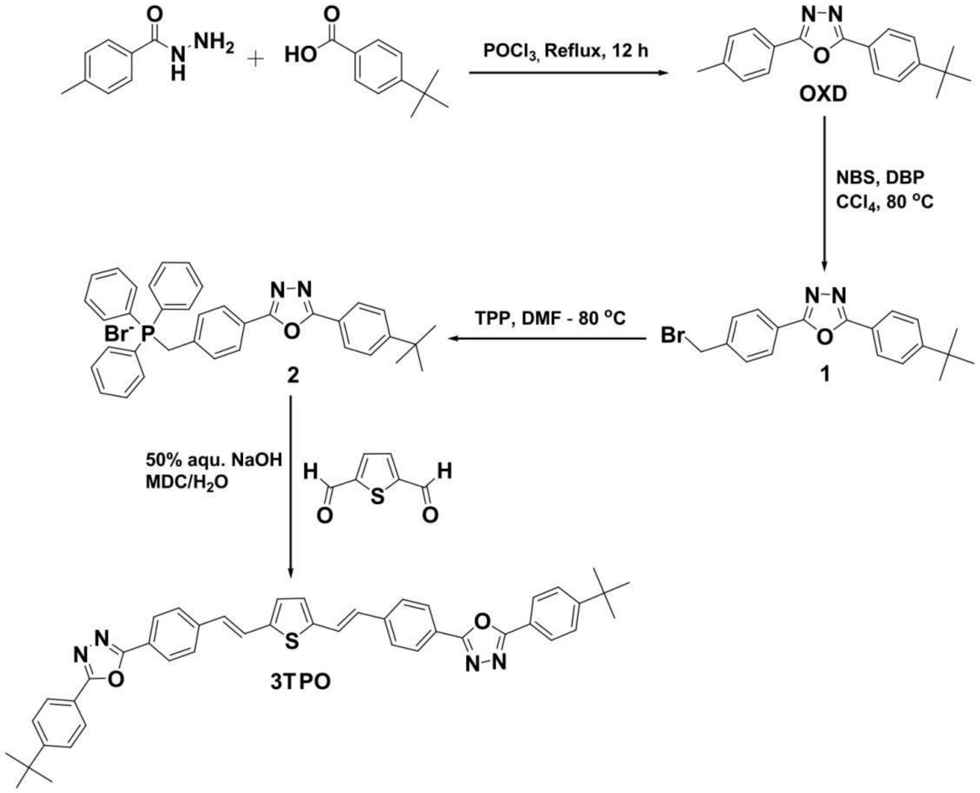
2. Materials and Methods

All the computations were done with Gaussian 09 software package (Frisch et al., 2016). The optimized ground states geometries of 3TPO was estimated using density functional theory (DFT) model using the hybrid functional Becke3–Lee–Yang–Parr (B3LYP) with a basis set 6311+G(d) to calculate ground state dipole moments and vector, frontier HOMOs and LUMOs values and plots, bond lengths, angles and dihedral angles, etc. Meanwhile, the molecular electrostatic potential energy surfaces (ESP) were scanned for ground states (S_0) in gas phase. Vertical transition energies of the singlet excited state were approximated employing time dependent density functional (TD-DFT) method at the B3LYP/6-311+G(d) level to compute excited state dipole moments and absorption transition energies**.** The integral equation formalism for the polarizable continuum model (IEF-PCM) model was used to explore ground and excited state solvation effects on titled probe 3TPO at DFT/B3LYP/6311+G(d)/IEF-PCM and TD-DFT/B3LYP/6311+G(d)/IEF-PCM level, respectively, in all the selected solvents. This above mentioned basis set is preferred throughout because of its sufficient flexibility to describe the system. On the other hand, the size of 3TPO restricted from using other larger basis sets and the above level is sufficient to handle the correlation energy properly.

3. Results and Discussion

3.1. Synthesis and characterization

The mentioned chromophore 3TPO was synthesized as per the reference (Pujar et al.) as shown in the **schem**e **1**. The structural purities and identities were characterized by ^{1}H NMR, ^{13}C NMR, HRMS and FT-IR which confirmed the proposed structure.



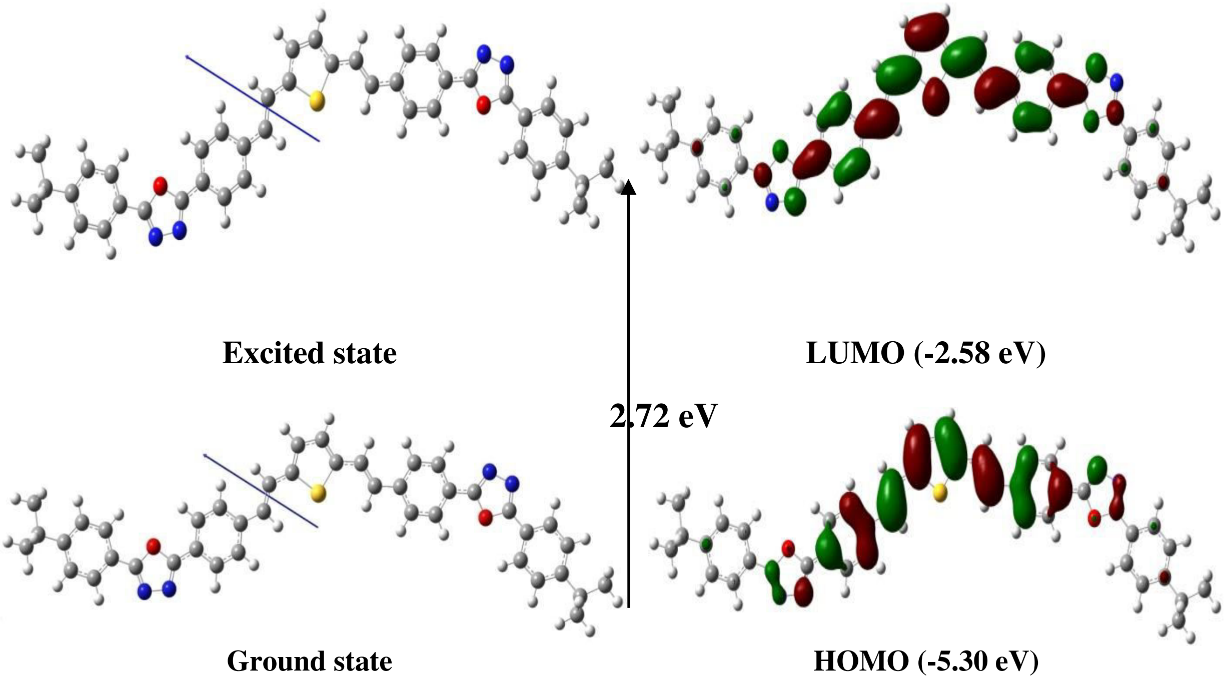
Scheme 1. Synthetic route for the target compound 3TPO

3.2. DFT and TD-DFT studies

In order to gain better insight into the electronic structure, geometry properties and spectroscopic properties, DFT and TD-DFT computations were carried out on compound 3TPO. **Fig. 1** shows ground, excited-state optimizations and frontier molecular orbitals, HOMOs and LUMOs of compound in gas phase. The values of HOMO/LUMO and energy bandgap (E_g) are tabulated in **Table 1** whereas **Table 2** collects the $E_T(30)$ relevant absorption maxima, transition energy, oscillator strengths and electronic states dipole moments.

Theoretically, the excitation energies of molecules have been successfully approximated using the combination of TD-DFT/PCM models to explain the solvatochromic behavior particularly. TD-DFT quantum mechanical level calculations provide accurate results for the systems under study. Therefore, large sized molecules, such as 3TPO considered in the present work, are better approximated by TD-DFT combined with IEF-PCM. The detailed computational formalism behind the TD-DFT/PCM method has been presented in some earlier reports (Caricato et al., 2004), (Caricato et al., 2006).

The electronic transition energies are affected by solvation. Such solvatochromic behaviors have been calculated and analyzed by TD-DFT/IEF-PCM formalism in all the solvents studied. The prediction of electronic excitation energies by this method is most popular because of its accuracy and precise approximations over other formal models. Herein, the TDDFT-PCM calculations on 3TPO compound are presented. The transition energies and their dependence on solvent polarity scale, $E_T(30)$, are analyzed and compared with that of experimental data. **Fig. 2a** and **b** shows the typical E vs. $E_T(30)$, plot for 3TPO probe in alcohols and general solvents and corresponding data are tabulated in **Table 2.** The alcohols (methanol-


Excited state

LUMO (-2.58 eV)

Ground state

HOMO (-5.30 eV)

Fig. 1. Optimized ground and excited state molecular structures of compound 3TPO and calculated molecular orbital amplitude plots of HOMO and LUMO levels. The molecular orbitals were calculated at the DFT/B3LYP/6-311+G(d) level of theory in vacuum. Contour surfaces of orbital amplitude (red) and (green) are shown. The arrow indicates the direction of dipole moments.

decanol) being class of polar protic solvents have strong tendency to interact with solute probes. From the experimental data it is noticed that a red shift of the transition energy of 3TPO with the solvent polarity decreasing from methanol to decanol. Interestingly, the same trend is observed by TD-DFT/PCM computations. The maximum difference among the calculated and experimental data for 3TPO in alcohols is found be 0.02 eV, being very close to each other. In case of general solvents, a blue shift is observed when solvents changing from toluene to DMSO as computationally backed by TD-DFT/PCM having difference 0.05 eV. This shift is attributed to the dipole interaction forces which cause the solvation of the solutes. It is noticed that the maximum differences for alcohols are smaller than for general solvents, possible be due to strong interaction between 3TPO and polar solvents. In conclusion, the calculated absorption transition energies trend is almost in good agreement with that of experimental data for all the selected solvents. The TD-DFT computations also reveal that the transition of 3TPO molecule from the gas phase to solution is accompanied by bathochromic shift (**Table 1**). These calculations confirm that the lowest transitions for the titled compound in various solvents do not change much, which is comparable with the experimental absorption data.

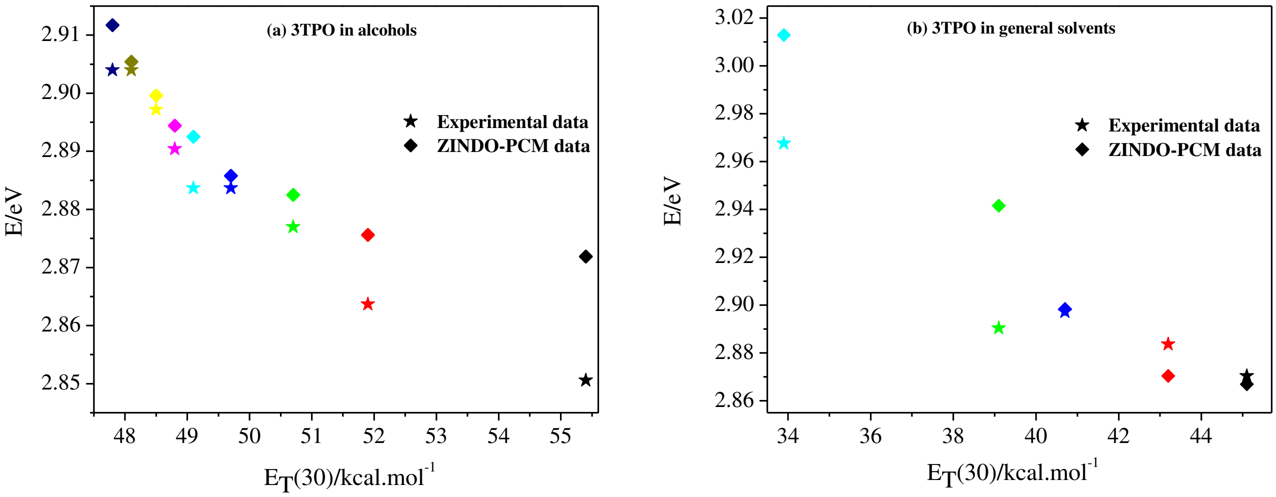


Fig. 2. Comparison of experimental transition energies of 3TPO in (**a**) alcohols and (**b**) general solvents with calculated TD-DFT/IEF-PCM on solvent polarity scale $E_T(30)$.

Table 2 also shows that the small shift in absorption band observed both computationally and experimentally with various solvent polarities is due to the small change in polarity of the ground state of solvated 3TPO. It implies that the ground state energy distribution of 3TPO is not affected to a larger extent. Therefore, electronic singlet excited state dipole moment value is expected to be larger compared its ground state and the same is observed by DFT and TD-DFT computations. In addition, the dipole moment difference of two electronic states is found to be positive (i.e., $\Delta\mu>0$) and its ratio is also greater than unity (i.e., $\mu_{e/}\ \mu_g >1$) for 3TPO probe which confirms that excited states are more polar than ground state.

Table 1. HOMOs, LUMOs and energy gap calculated from DFT model and its comparison with experimental data.

Compound	HOMO/ LUMO[a]	HOMO/ LUMO[b]	E_g	$E_g^{opt\,[c]}$
3TPO	-5.30/-2.58	-5.20/-2.54	2.72 [a] /2.66 [b]	2.60 (477 nm)

(a) Obtained from DFT computations (present work). (b) Obtained from cyclic voltammetry measurements (Pujar et al.). (c) Calculated from experimental UV-Vis spectra (Pujar et al.).

Table 2. Calculated spectroscopic properties of 3TPO in various solvents at 300 K and its comparison with experimental data.

Solvent	$E_T(30)^*$	λ_{abs} [a]	E[a]	λ_{abs} [b]	E[b]	f [b]	μ_g [c]	μ_e [b]	$\Delta\mu$	$\mu_{e/}\,\mu_g$
Gas Phase				405	3.0173	0.3124	2.5027	2.8901	0.3874	1.1547
Methanol	55.4	435	2.8506	432	2.8719	0.2971	3.7657	4.2467	0.4810	1.1277
Ethanol	51.9	433	2.8637	431	2.8756	0.2989	3.7400	4.2190	0.4790	1.1280
Butanol	50.7	431	2.8770	430	2.8825	0.3018	3.6946	4.1702	0.4756	1.1287
Pentanol	49.7	430	2.8837	430	2.8858	0.3031	3.6734	4.1475	0.4741	1.1290
Hexanol	49.1	430	2.8837	429	2.8925	0.3054	3.6393	4.1109	0.4716	1.1295
Heptanol	48.8	429	2.8904	428	2.8944	0.3060	3.6191	4.0892	0.4701	1.1298
Octanol	48.5	428	2.8972	427	2.8996	0.3070	3.5885	4.0885	0.4600	1.1393
Nonanol	48.1	427	2.9040	426	2.9054	0.3082	3.5546	4.0200	0.4654	1.1309
Decanol	47.8	427	2.9040	425	2.9117	0.3091	3.5182	3.9809	0.4627	1.1315
DMSO	45.1	432	2.8704	433	2.8669	0.2942	3.7913	4.2741	0.4828	1.1273
DMF	43.2	430	2.8837	432	2.8704	0.2964	3.7761	4.2578	0.4817	1.1275
Chlorofor	39.1	429	2.8904	421	2.9415	0.3100	3.3590	3.8100	0.4510	1.1342
DCM	40.7	428	2.8972	427	2.9594	0.3058	3.5643	4.0304	0.4661	1.1307
Toluene	33.9	425	2.9176	411	3.0129	0.2963	3.0332	3.4600	0.4268	1.1407

* $E_T(30)$ (in kcal-mol^{-1}) referred from the reference (Reichardt et al., 2005).

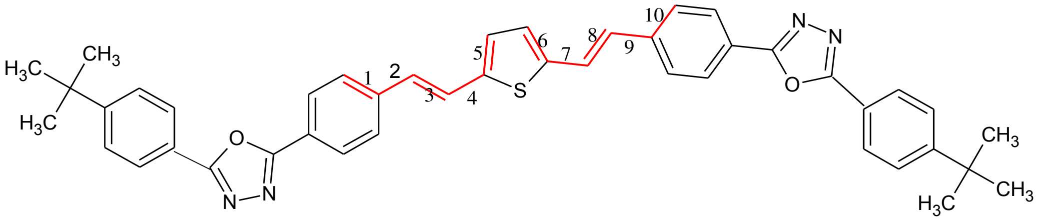
(a) Experimental absorption maxima and excitation energy referred from (Pujar et al.). (b) Calculated using TD-DFT/B3LYP/6311+G(d)/IEF-PCM level. (c) obtained at DFT/B3LYP/6311+G(d)/IEF-PCM level. Where, λ_{abs} -absorption maxima (in nm), E-electronic excitation energy (in eV), f-oscillator strength, μ_g and μ_e -Ground and excited state dipole moments (in D).

As demonstrated in **Fig. 1,** both HOMO and LUMO electrons are delocalized on the thiophene unit and on the nitrogen atoms of the oxadiazole groups. The electron clouds of HOMOs are localized on the π-electron bridge and oxadiazole groups with the attached benzene rings which act as an electron acceptor units and this strategy strongly counts for electron accepting property. The LUMO orbital is almost localized over the electron donor thiophene core rather than oxadiazole cores. It can be seen that the distribution of electron density on the S-C bonds of donor thiophene increases while electron density on N atoms decreases from HOMO to LUMO. Thus, during the excitation to the S_1 state, there is a slight effect on the shift in electron density distribution from the oxadiazole groups in the direction of the thiophene group through π-linker and this results in ICT, reducing the D-π-A form .The computationally determined HOMO/LUMO energy values (-5.30 and -2.58 eV, respectively) agree well with the ones obtained electrochemically (-5.20 and -2.54 eV). The bandgap obtained from electrochemical measurements is 2.66 eV and fairly agrees with the bandgap 2.72 eV obtained from DFT predictions. The energy gap is reflection of extended conjugation of a molecule. As the molecular size increases, the electron is delocalized over the whole molecule that results in lowering the energy gap. As stated in **Table 1,** a low bandgap is observed for 3TPO which confirms the extended conjugation of the 3TPO molecule. Such types of low bandgap chromophores are likely to work with better efficiency in the field of photovoltaics/OLEDs applications.

Frontier molecular orbital study also provides us to estimate chemical hardness ($\eta = -[E_{HOMO} - E_{LUMO}]/2$), softness ($\delta = 1/\eta$), chemical potential ($\mu_c = -[E_{HOMO} + E_{LUMO}]/2$) and electro negativity ($\chi = [E_{HOMO} + E_{LUMO}]/2$) of a molecule (Chang-Guo et al., 2003), (Udhayakala et al., 2015). The lower HOMO-LUMO energy gap indicates higher chemical reactivity and/or as a soft molecule and larger HOMO-LUMO energy gap point outs about less reactive and/or thus, as a hard molecule (Udhayakala et al., 2015). The chemical hardness (η) is an indicator of chemical stability of a compound. The estimated η, δ, μ_c and χ were found to be 1.36 eV, 0.73 eV^{-1}, 3.94 and -3.94 eV, respectively. Such values of the HOMO-LUMO gap, η, δ, μ_c and χ indicate high excitation energy, a high chemical activity and a good stability for the investigated oxadiazole compound.

Some important selected bond lengths, angles and dihedral angles in the optimized structure (gas phase and toluene) of compound 3TPO are listed in **Table 3**. The intramolecular bonds were numerically labeled from 1-10 for better description. It can be seen that the bonds on both side of thiophene donor unit (L(3), L(5), L(6) and L(8)) lengthen from ground state (GS) to excited state (S_1) for both gas phase and toluene, indicating that the intramolecular bonds are strengthened after photoexcitation. Also a marginal difference is observed in toluene compared to gas phase, suggesting that the effect of solvent significantly influences the geometry of ground as well as excited states. Whereas, the bond lengths L(1), L(2), L(4), L(7), L(9) and L(10) shorten from GS to S_1, indicating that the intramolecular bonds are weakened in the S_1 state. The bond angles A(34) and A(78) in GS change by nearly 1° compared to S_1 and A(12) and A(910) in GS alter nearly -0.200° compared to S_1. All these changes demonstrate that electronically excited state of the molecule exhibit slight structural changes compared to the ground state. Additionally, the dihedral angles in the GS and S_1 reveal that electron-withdrawing group (thiophene) makes the molecule more planar

Table 3: Calculated optimized structural parameters; L: bond lengths [Å], A: bond angles [^{o}], DA: dihedral angles [^{o}] of compound 3TPO in gas phase and toluene (values in the parenthesis bracket) for both ground and excited state.

State										
Bond Lengths (Å)										
	L(1)	L(2)	L(3)	L (4)	L(5)	L(6)	L(7)	L(8)	L(9)	L(10)
GS	1.414 (1.415)	1.458 (1.459)	1.358 (1.358)	1.435 (1.435)	1.382 (1.382)	1.382 (1.382)	1.435 (1.435)	1.358 (1.359)	1.458 (1.458)	1.416 (1.416)
S_1	1.412 (1.413)	1.432 (1.430)	1.372 (1.377)	1.397 (1.392)	1.405 (1.410)	1.405 (1.410)	1.397 (1.392)	1.372 (1.376)	1.432 (1.430)	1.413 (1.414)
Δ	0.002 (0.002)	0.026 (0.029)	-0.014 (-0.019)	0.038 (0.043)	-0.023 (-0.028)	-0.023 (-0.028)	0.038 (0.043)	-0.014 (-0.017)	0.026 (0.028)	0.003 (0.002)
Bond Angles										
	A(12)	A(23)	A(34)	A(45)	A(67)	A(78)	A(89)	A(910)		
GS	123.6 (123.8)	126.9 (126.7)	126.6 (126.5)	127.2 (127.2)	127.2 (127.2)	126.6 (126.5)	126.7 (126.6)	123.5 (123.5)		
S_1	123.7 (123.8)	126.7 (126.5)	125.6 (125.7)	127.1 (127.0)	127.1 (127.0)	125.6 (125.6)	126.7 (126.6)	123.7 (123.7)		
Δ	-0.100 (0.000)	0.200 (0.200)	1.000 (0.800)	0.100 (0.200)	0.100 (0.200)	1.000 (0.900)	0.000 (0.000)	-0.200 (-0.200)		
Dihedral angles										
	DA(123)	DA(234)	DA(345)	DA(678)	DA(789)	DA(8910)				
GS	-0.007 (-0.005)	179.998 (180.000)	179.998 (179.998)	179.999 (179.999)	179.999 (179.999)	-0.004 (-0.006)				
S_1	-0.001 (-0.004)	180.000 (179.999)	180.000 (179.998)	179.999 (179.997)	179.999 (180.000)	-0.001 (-0.006)				
Δ	-0.0060 (-0.0010)	-0.0020 (0.0010)	-0.0020 (0.0000)	0.0000 (0.0020)	0.0000 (0.0010)	-0.0030 (0.0000)				

GS- ground state; S_1- first excited state and Δ=GS-S_1

(See **Table 3**) as all the dihedral angles are centered either around 180° or 0°. This planarity of the 3TPO moiety that contains the π-linkage imparts extended π-conjugation and rigidity between two oxadiazole units along with a thiophene unit. This decreases the potential pathways for non-radiative decay and hence results in efficient fluorescence emission.

On the basis of the conventional color spectrum with the potential increase from red to blue, the ESP maps follow an order of red < orange < yellow < green < blue in which red coloured regions indicate the most negative electrostatic potential and the blue coloured region represents the most positive electrostatic potential. As shown in **Fig. 3**, the region of nitrogen atoms in oxadiazole units are entirely red, indicating existence of main local negative electrostatic potential and the regions over the thiophene unit are slightly bluish, showing the existence of positive electrostatic potential. On either side of thiophene unit the potential distribution is uniform over the regions of nitrogen atoms due to symmetry of molecule. Thus, the ESP map confirms the donor-π-acceptor strategy in novel fluorescent highly conjugated 1,3,4-oxadiazole derivative where acceptor oxadiazole unit is electronically rich (red) and donor thiophene is electron deficient (blue).

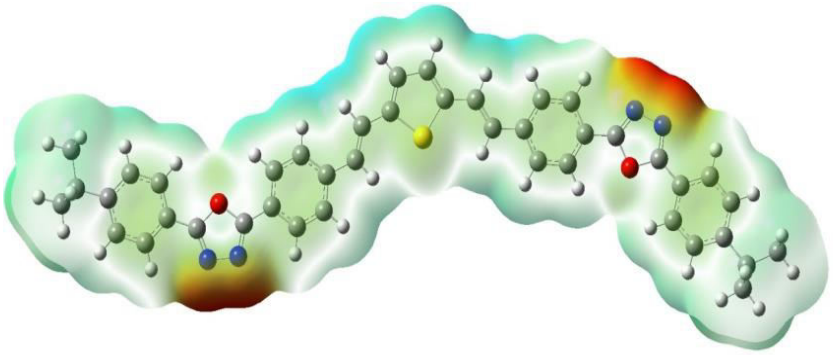


Fig. 3. Optimized structure of 3TPO in the ground state and the ESP map.

4. Conclusion

Ground and excited states optimized molecular structure and fundamental intramolecular interactions of optoelectronically important oxadiazole 3TPO have been precisely assigned and analyzed using DFT and TD-DFT formalisms. The solvatochromism behavior has been tested over solvent polarity scale, E_T (30) which raveled that computational data was well correlated and reproduced with that of experimental. The more polar nature of excited states was confirmed by TD-DFT model. Presence of a thiophene and oxadiazole groups as well as the lower band gap values confirms the optoelectronic importance and intramolecular charge transfer within the compound. The values of η, δ, μ_c and χ confirms the high excitation energy, a high chemical activity and a good stability and showed compatibility for the investigated compound.

5. Acknowledgments

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References

1. Caricato, M., Mennucci B., Tomasi, J. Mol Phys (2006), 104, 875–87.
2. Caricato, M., Mennucci B., Tomasi, J. J Phys Chem A (2004), 108, 6248–56.
3. Chang-Guo, Z., Jeffrey A. N, David A. D. J. Phys. Chem. A (2003), 107, 4184-4195.
4. Frisch, M. J. et al., (2009), Gaussian 09, Revision D.01., Gaussian, Inc., Wallingford CT. http://www.rsc.org/suppdata/c5/sc/c5sc02423d/c5sc02423d1.pdf
5. Kappor, V. K., A. Textbook of medicinal & pharmaceutical industry, (2012), 6, 264, 455.
6. Liang, M., X. Yu, L. Cong, X. Zheng-Lu, L. Dong-Dong, W. Yan-Ting, (2013), Bioorg. Med. Chem., 21, 6763–6770.
7. Mitra, S., Singh T. S., Mandal a, Mukherjee S. Chem Phys (2007), 342, 309–317.
8. Narahari, D. G. H. Pujar, Manjunath, G. S., Supreet, G., Ningaraddi, S. B., S. R. Inamdar, Chinna, B. and I. M. Khazi. Chemistry Select (2017), 2, 1793 – 1801.
9. Narahari Deshapande, G. H. Pujar, M. S. Sannaikar, M.N. Wari, I.M. Khazi and S.R. Inamdar. Synthesis, Photophysics of a Novel Green Light Emitting 1, 3, 4-oxadiazole and its application in FRET with ZnSe/ZnS QDs donor. (Unpublished work).

10. Reichardt, C., (2005), Solvents and Solvent Effects in Organic Chemistry, third ed., Wiley-VCH, Weinheim Germany.
11. Rekha, K., Anitha V., Louis G. J. Fluoresc, (2017), 27, 151–165.
12. Shyma, P. C., K. Balakrishna. Eur. J. Med. Chem., (2013), 68, 394-404.Tomasi, J., Mennucci B., Cammi R. Chem Rev, (2005), 105, 2999–3093.
13. Tomasi, J., Mennucci, B., Cammi, R., Chem Rev 2005, 105, 2999–3093.
14. Udhayakala, P., J. Chem Pharm Res, (2015), 7, 803–810.