RESEARCH ARTICLE

Computational Studies of Some Newly Synthesized PeryleneTetracarboxylicDiimides (PTCDIs)

*Andrea Sandra Christine D'Cruz[1], Araveti Aditya Prasad[1], K.R Sankaran[2]

[1]Department of Chemistry, School of Science and Humanities, St. Martin's Engineering College, Secunderabad.

[2]Department of Chemistry, Annamalai University, Chidambaram, Tamil Nadu.

ABSTRACT

PTCDIs are largely studied as they demonstrate great molar absorption factor and fluorescence has great quantum, exhibit good photochemical and thermal stabilities as well as good electrical presentation. They also show a direct band gap transition. Here in this paper, two new symmetrical PTCDIs are discussed namely N,N′-Bis(2-amino-4,6-dimethylpyrimidine)perylene-3,4,9,10-tetracarboxylic diimide and N,N′-bis(2-aminopyridine)perylene-3,4,9,10-tetracarboxylic diimide represented as AD-PTCDI and AP-PTCDI respectively. The compounds were synthesized by the simple condensation reaction of Perylene-3, 4, 9, 10-Tetra Carboxylic Dianhydride (PTCDA) and with suitable amines in molten imidazole. Computational studies were carried out for the synthesized compounds in order to get a better understanding of their structures. This paper aims at the computational studies such as optimized geometry, HOMO-LUMO studies, NMR shielding study, theoretical FT-IR analysis as well as Natural Bonding Orbital (NBO) analysis. The band gap for the compounds was found to be 2.59 and 2.80 eV respectively. The efficiency of these materials for use in organic electronic industry can hence be determined.

Keywords: PTCDIs, Optimized geometry, NMR shielding analysis, Mulliken charge transfer study, NBO analysis.

1. INTRODUCTION

Supramolecular chemistry is detailed the study of molecular that are joined together, and also define the intermolecular chain [1]. Supramolecular chemistry is the self-assembly and self-organization of materials through π-π stacking. In present scenario, nanotechnology plays a very important role. Many researchers and scientists alike are invading this area in a continuous attempt to create nano-scale power efficient devices from the traditional micro silicon ones. PTCDIs are widely studied as they demonstrate great molar absorption coefficient and high quantum yields of fluorescence, good electron mobility, and high fluorescence. Besides, they also exhibit excellent photochemical and thermal stabilities as well as good electrical presentation [2-4]. In dilute solutions, PTCDIs demonstrate near-unity fluorescence quantum yields. This is because it is a highly conjugated molecule. They are also known to show large visible extinction coefficients and have relatively low cost of fabrication [5]. Moreover, that shows strong absorption band in the visible region [6].A major drawback with PTCDIs is its insolubility in a vast major of organic solvents as well as its instability in air. The solubility of the PTCDI compound can be improved by the newly electron extracting sets (EWGs) at either the imide or bay positions of the parent compound PTCDA. The effect of substitution at the imide position is basically inductive [7]. Substituents added at the imide nitrogen atoms are known to show little effect on optical and electronic properties such as energy levels and redox potentials. This is because the imide positions are the nodes of the HOMO and LUMO orbitals of the molecules [8] whereas bay substituents at the 1, 6, 7 or 12 positions are known to affect the electronic and optical properties and alter as well as the photo-physical

properties of PTCDI. the invention of electron-withdrawing sets in either the ortho and/or bay-position are known to shift the lessening potential of PTCDIs to more optimistic values and thus help to rise the electron affinities [9].

Side chain of PTCDIs is therefore known to play a very important role in controlling the color, molecular stacking and other physic chemical properties of the PTCDI aggregates. Another interesting feature of PTCDIs is their self-assembly behavior. Self-assembly of PTCDIs are known to give rise to highly well-organized super molecular architectures for use in the organic electronic industry. Depending upon the increase in demand from the electronic consumer market, organic materials are highly favored as they are found to be more flexible, are easily available, have large area and are light weight [10-13] as compared to its inorganic counterparts which makes use of highly costly substrates for innovative design of materials. The strive for versatility and improvement in developing advanced functional materials has seen a high boost to meet rising market demands. PTCDI based conjugated small molecules and polymers have therefore received considerable attention in the educational and manufacturing fields due to its good possessions thereby making it suitable to extensive application. PTCDI hence finds its applications in the field of photo-electronic materials, Organic Light-Emitting Diodes (OLED), chemo sensing materials, biosensors, Photovoltaic Devices (PVCs), Organic Solar Cells (OSCs), Organic Photo Voltaic cells (OPVs), fluorescent solar collectors, Organic Field-Effect Transistors (OFETs), OLED [14-17] and etc. Another interesting feature of perylene pigments is their cool pigment behavior. This is mainly because of their ability to interact separately at varying wavelengths in the UV-Visible region. Also, their reversible n-type property makes them promising materials for electro chromic and super capacitor applications [18].They also find its applications in biochemical and pharmacological purposes as potential antitumor drugs.

In this paper, two newly synthesized molecules namely AD-PTCDI and AP-PTCDI are studied computationally in order to get a better idea of the structure of these compounds.

2. EXPERIMENTAL

2.1. Instrumentation

Compounds AD-PTCDI and AP-PTCDI were synthesized by the condensation reaction of PTCDA with suitable primary amines/anilines in molten imidazole as mentioned in [19].The FT-IR measurements were carried out in the regions ranging from 4000-400 cm^{-1} on NICOLET AVATAR 360 instrument.
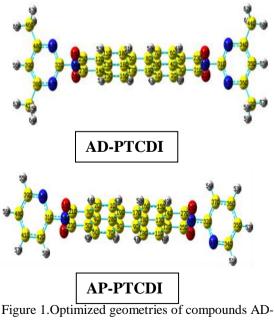
2.2. Procedure

The following computational studies such as the molecular geometry optimization, MEP analysis, NBO analysis, NMR shielding analysis and Mulliken charge transfer studies were carried out by using the Gaussian 09W software package (Becke-Lee-Yang-Parr hybrid density functional method) with a 6-31++ G (d, p) basis set combination for compounds AD-PTCDI and AP-PTCDI respectively. A comparison study between the experimental and theoretical spectra of the IR and NMR for compounds AD-PTCDI and AP-PTCDI was performed in order to help predict their correct assignments. The studies along with their data thereby provide us an in-depth understanding of the basic chemical molecular structure relationship.

3. RESULTS AND DISCUSSION (Computational studies)

3.1. Optimized geometries (molecular modelling)

The geometry of the molecules was optimized. The optimized geometries of compounds AD-PTCDI and AP-PTCDI were visualized using the GaussView5.0 molecular visualization program and are displayed in Figure 1 respectively.

AD-PTCDI

AP-PTCDI

Figure 1.Optimized geometries of compounds AD-PTCDI and AP-PTCDI

3.2. HOMO-LUMO studies

The molecular frontier orbitals are responsible for the electronic characteristics of PTCDIs by the substitution of the conjugated aromatic core [19] which in turn plays a key role for application of organic electronic materials.

PTCDI dyes demonstrate good characteristic electron mobility's up to 2.10 cm^2 $V^{-1}S^{-1}$ [20]. PTCDI core is fairly electron deficient and thus it is easy to reduce and difficult to oxidize [21, 22]. Therefore the electron acceptor character is an important feature observed in PTCDIs which arises from the strong electron-withdrawing nature of the imides groups. Thus the electron transport properties in molecular and organic electronics devices are mainly dependent upon the orientation of the molecular orbitals i.e., Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbitals (LUMO) [23]. Addition of a second electron into the next LUMO, almost equivalent to the addition of an electron into the second imide group, can involve a lower energy [24]. PTCDIs and naphthalene diimides (NDIs) possess good electron affinities, have low-lying LUMOs and hence demonstrate reversible redox behavior which makes them suitable for the design of n-doped materials [25].HOMO acts as electron deficient and hence it is subjected to nucleophile attack [26].The energy of the HOMO is directly The energy of the LUMO is totally related to electron affinity (EA). The energy difference between the HOMO and the LUMO is called as the optical band gap (E_g). Low energy gap are found suitable for the semiconducting nature of the organic materials used. PTCDIs show a direct band gap. PTCDI molecule(s) with small or no HOMO-LUMO gap are found to be chemically reactive. Lower the energy gap between the two orbitals indicates the influence on the intermolecular charge transfer of the molecule. The energy gap values also helps to determine the global chemical reactivity description of the molecules such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity [27].

As additional aromatic rings are added to the PTCDI system, additional bonding and anti-bonding levels are introduced with a resulting reduction of the energy of the lowest $\pi \rightarrow \pi*$ transition. Substitution at the imide position negligibly affects the absorption and emission of PTCDIs due to the presence of nodes in the HOMO and LUMO orbitals of the imide nitrogen [28]. Previous literature studies of PTCDIs revealed that the thermodynamic studies lower the LUMO energies which are capable of demonstrating greater stability to an organic radical anion attack by water and oxygen. This has found to be beneficial for developing much n-type air –stable devices [29].

The ideal reason for performing the structural studies is to study the relationship between the optical properties and the structural modifications by using different substituents. HOMO- LUMO studies are hence found to be very useful for the characterization of organic compounds in both the ground and excited state as they help to determine the molecular electron transport properties as they are a measure of electron conductivity. In addition, they play a very important role in the chemical stability of the molecule and its calculations reveal the charge transfer within the molecule.

The theoretical HOMO and LUMO values of compounds AD-PTCDI and AP-PTCDI are given in Table 1. From the E_{HOMO} and E_{LUMO} values as seen in Table 1, it is observed that different side chains at the imide position of the PTCDIs enhances the localizability of the π-system which helps in stacking of the molecules. This is observed in the π-$\pi*$ transitions. In simpler words, it can be said that as the number of side chain substituent increases, there could be a possible reduction in the electron density of the central part of the molecule. This is seen by the less favoured π-stacking. The easier the electrons are exited the greater is their mobility. It is noted that the energy of the LUMO can be shifted or changed by an introduction or rather the substitution of nitrogen atom with an electronegative atom as oxygen. This observation also makes easier the possibility of understanding the behaviour of the molecule during excitation and π-$\pi*$ transition.

Table.1.Theoretical values of HOMO and LUMO (eV) at 6-31G ++ (d, p) level of DFT

Compounds	HOMO	LUMO	E_g
AD -PTCDI	-5.90	-3.30	2.59
AP -PTCDI	-6.20	-3.40	2.80
Perylene core	-6.49	-4.38	-2.11

The cyclic voltammogram of compound AD-PTCDI is shown in Figure 2. The experiment was performed at room temperature in DMSO solution containing 0.1 M Tetra Butyl Ammonium Perchlorate (TBAP) as a supporting electrolyte. A three electrode cell consisting of a glossy carbon

working electrode, a Pt counter electrode and an Ag/AgCl reference electrode were used. CV analysis of this compound showed a single reduction peak at -1.605 V having a cathodic peak current, i = -3.403e -6A. It was found that the cyclic voltammogram are almost unaffected by the methyl groups in pyrimidine side chains.
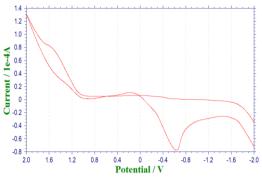

Figure 2.Cyclic voltammetry curve of AD-PTCDI in DMSO

HOMO and LUMO values are calculated from the CV redox potentials as carried out by [30] which are shown in (1) and (2)

$$E_{HOMO} = eE_{ox} + 4.5 \text{ eV} \qquad (1)$$
$$E_{LUMO} = -eE_{red} - 4.5 \text{ eV} \qquad (2)$$

Where, E_{ox} and E_{red} are oxidation and reduction potentials in volts versus the normal hydrogen electrode potential.

The cyclic voltammetry study of compound AD-PTCDI showed the presence of only reversible reduction peak at ~ -1.605 eV. It was observed that the reduction step occurred at less negative potential and that values are considerably less negative than the reduction potentials of perylene carboxylate. It is noted that the cyclic voltammogram of compound AD-PTCDI are almost unaffected by the methyl groups in pyrimidine side chains.

The experimental values of LUMO of this compound was obtained from (3) proposed by [30]

Compound AD-PTCDI:

$$E_{LUMO} = 1.605 - 4.5 \text{ eV} = -2.89 \text{ eV} \qquad (3)$$

The LUMO values alone have been taken into consideration as they represent the level where electronic excitation and delocalization take place.

The theoretically obtained E_{LUMO} of compound AD-PTCDI is – 3.30 eV. It is observed that the value of compound AD-PTCDI is not in good agreement with the theoretical and experimental LUMO value. The molecular frontier orbitals of compounds AD-PTCDI and AP-PTCDI are presented in Figure B1. The red regions indicate the positive region whereas the violet coloured regions represents negative surfaces. It is observed that the HOMO is localized on the terminal substituents whereas the LUMO are located on the central perylene moiety.

3.3. Theoretical FT-IR analysis

In order to have a better understanding about the distribution of the various band assignments of the compounds AD-PTCDI and AP-PTCDI, a theoretical FT-IR analysis study was carried out. The comparison study showed in Table A1 that the experimental and theoretical modes of vibrations are found to be good agreement with each other.

3.4. Mulliken population analysis

Mulliken population analysis is a powerful technique to investigate the charge transfer of quantified charges per atom in the molecules [31].Mulliken atomic charge calculation plays a very significant role in the application of quantum chemical calculations to that of molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure and a lot of properties of molecular systems [32]. Besides, Mulliken charge transfer helps in providing information regarding the charge distributions over the atoms which suggest the formation of donor and acceptor pairs involving the charge transfer in the molecule [33].

The atomic charge distribution of the various atoms present in the compounds AD-PTCDI and AP-PTCDI is obtained by Mulliken population analysis and the corresponding Mullikan's plot is shown in Figure B2.

Table 2.Overall distribution of highly electro-positive and electro-negative atoms of compounds AD-PTCDI and AP-PTCDI

Compound	Highly electro positive atom(s)	Highly electro negative atom(s)
AD -PTCDI	C23, C27	C35, C39
AP -PTCDI	C21, C23	C35, C40

From the listed charge values as shown in Table 2, varying highly electropositive and electronegative atoms are observed. From the Mulliken population analysis, it was observed that

electropositive atoms have been found to be located at 23C for compounds while electronegative atoms are observed at 35C for both the compounds. The presence of other varying electropositive and electronegative atoms indicated the presence of both electrophilic and nucleophilic sites. This suggested the presence of intermolecular hydrogen bonding interactions in these compounds. Thus compounds AD-PTCDI and AP-PTCDI showed the presence of both electrophilic and nucleophilic sites which suggested the presence of intermolecular hydrogen bonding interactions in these compounds.

3.5. Natural Bond Orbital (NBO) analysis

NBO analysis is an efficient tool in elucidating the stereo electronic interactions on the reactivity and dynamic behavior of chemical compounds [34]. NBO helps us analyze the interactions between the intra and intermolecular bonding as well as provides a solid platform for investigating charge transfer or conjugative interactions in molecular system [35, 36].

NBO analysis was performed for compounds AD-PTCDI and AP-PTCDI in order to find out if there is any significant electronic population in the virtual states where electrons move on excitation or during delocalization. This level can be identified using Rydberg population scheme of NBO. [37] These states represent exactions whose understanding has led to the improvement in the semiconductor devices and solar cells. In this study, it is noted that the central part of the molecule has sufficient Rydberg population which is in complete agreement with the DFT calculations on molecular orbital delocalization listed in Table A2 and Table A3.

For compound AD-PTCDI, the strong intramolecular hyper conjugative interactions of π-electrons are derived as π (C1-C19) to π* (C2-C3) is 20.34 kJmol-1, π (C2-C3) to π* (C21-O22) is 22.70 kJmol-1, π (C4-C5) to π* (C6-C7) is 22.20 kJmol-1, π (C6-C7) to π* (C8-C20) is 22.76 kJmol-1, π (C8-C20) to π* (C4-C5) is 21.10 kJmol-1, π (C9-C18) to π* (C12-C13) is 21.11 kJmol-1, π (C10-C11) to π* (C9-C18) is 22.76 kJmol-1, π (C12-C13) to π* (C12-C11) is 22.20 kJmol-1, π (N33-N34) to π* (C31-N37) is 37.44 kJmol-1 and π (C35-C36) to π* (N33-C34) is 32.11 kJmol-1.

For compound AP-PTCDI, the strong intramolecular hyper conjugative interactions of π-electrons are derived as π (C1-C19) to π* (C2-C3) is 20.37 kJmol-1, π (C2-C3) to π* (C21-O22) is 22.68 kJmol-1, π (C5-C6) to π* (C23-O24) is

22.68 kJmol-1, π (C7-C8) to π* (C5-C6) is 20.38 kJmol-1, π (C9-C10) to π* (C11-C12) is 20.37 kJmol-1, π (C13-C14) to π* (C15-C16) is 22.15 kJmol-1, π (C15-C16) to π* (C17-C18) is 22.78 kJmol-1, π (C17-C18) to π* (C13-C14) is 21.13 kJmol-1 and π (C39-C40) to π* (C41-C42) is 20.94 kJmol-1. Lone pair of electrons available on nitrogen atoms N (29) and N (30) is delocalized on the anti-bonding orbitals of (C21-O22), (C23-O24) and (C25-O26), (C27-O28) bonds and the delocalization energy is found to be 55.54 kJmol-1respectively.

4. CONCLUSION

Two new symmetrical PTCDIs were previously synthesized and were further studied for their computational properties. HOMO-LUMO studies of compounds AD-PTCDI and AP-PTCDI revealed the charge transfer taking place within the molecule. NBO analysis revealed the stability of the molecules arising from hyper-conjugative interaction and charge delocalization. Mulliken population analysis confirmed the charge transfer within the molecules. Hence it can be concluded that these compounds are found useful to serve in organic electronic and optoelectronic devices.

REFERENCES

[1] J.M.Lehn, Macrocyclic Receptor Molecules: Aspects of Chemical Reactivity, Investigations into Molecular Catalysis and Transport Processes, Pure and Applied Chemistry, Vol. 51, No. 5, 1979, pp. 979-997, https://doi.org/10.1351/pac197951050979 .

[2] O.Birel, A Review on Perylene-3, 4, 9, 10- Tetracarboxylic Acid Diimide Molecules, Celal Bayar Universitesi Fen Bilimleri Dergisi, Vol. 13, No. 2, 2017, pp. 379-386, https://dx.doi.org/10.18466/cbayarfbe.319879.

[3] J.Jayabharathi, V.Thanikachalam, K.Jayamoorthy, Optical Properties of 1, 2-Diaryl Benzimidazole Derivatives - A Combined Experimental and Theoretical Studies, Spectrochimca Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 115, 2013, pp. 74-78, https://doi.org/10.1016/j.saa.2013.06.001.

[4] J.Jayabharathi, V.Thanikachalam, K.Jayamoorthy, Synthesis of Some Fluorescent Benzimidazole Derivatives using Cobalt Hydroxide (II) as Highly

Efficient Catalyst – Spectral and Physico-Chemical Studies and ESIPT Process, Photochemical & Photobiological Science, Vol. 12, No. 10, 2013, pp. 1761-1773.

[5] K.Fang, Y.Huang, G.Chang, J.Yang, Y.Shen and X.Ye, Conjugated Polymers Based on Modified Benzo [1, 2-b:4, 5-b] Dithiophene and Perylene Diimide Derivatives: Good Optical Properties and Tunable Electrochemical Performance, Macromolecular Research, Vol. 23, No. 6, 2015, pp. 545-551.

[6] X.Zhang , Z.Lu , L.Ye, C.Zhan, J.Hou, S.Zhang, B.Jiang, Y.Zhao, J.Huang, S.Zhang and Y.Liu, A Potential Perylene Diimide Dimer-Based Acceptor Material for Highly Efficient Solution-Processed Non-fullerence Organic Solar Cells with 4.03 % Efficiency, Advanced Materials, Vol. 25, No. 40, 2013, pp. 5791-5797, https://doi.org/10.1002/adma.201300897.

[7] M.Sadrai, L.Hadel, R.R.Sauers, S.Husain, K.K.Jesperson, J.D.Westbrook and G.R.Bird, Lasing Action in a Family of Perylene Derivatives: Singlet Absorption and Emission Spectra, Triplet Absorption and Oxygen Quenching Constants, and Molecular Mechanics and Semi Empirical Molecular Orbital Calculations, Journal of Physical Chemistry, Vol. 96, No. 20, 1992, pp. 7988-7996.

[8] S.Chen, P.Slattum, C.Wang and L.Zang, Self-assembly of Perylene Imide Molecules into 1D Nanostructures: Methods, Morphologies, and Applications, Chemical Reviews, Vol. 115, No. 21, 2015, pp. 11967-11998.

[9] D.Schmidt, D.Bialas and F.Wurthner, Ambient Stable Zwitterionic Perylene Bisimide-Centered Radical, Angewandte Chemie International Edition, Vol. 54, No. 12, 2015, pp. 3611-3614, https://doi.org/10.1002/anie.201408067.

[10] D.Zhang, W.C.H.Choy, F.X.Xie and X.Li, Large-area, High-quality Self-assembly Electron Transport Layer for Organic Optoelectronic Devices, Organic Electronics, Vol. 13, No. 10, 2012, pp. 2042-2046, https://doi.org/10.1016/j.orgel.2012.06.012.

[11] M.Wright and A.Uddin, Organic-inorganic Hybrid Solar Cells: A Comparative Review, Solar Energy Materials and Solar Cells, Vol. 107, 2012, pp. 87-111, https://doi.org/10.1016/j.solmat.2012.07.006.

[12] H.Sirringhaus, N.Tessler and R.H.Friend, Integrated Optoelectronic Devices based on Conjugated Polymers, Science, Vol. 280, No. 5370, 1998, pp. 1741-1744.

[13] M.Sessolo and H.J.Bolink, Hybrid Organic-inorganic Light-emitting Diodes, Advanced Materials Vol. 23, No. 16, 2011, pp. 1829-1845, https://doi.org/10.1002/adma.201004324.

[14] S.Suresh, K.Jayamoorthy, P.Saravanan and S.Karthikeyan, Switch-Off Fluorescence of 5-amino-2-mercapto benzimidazole with Ag_3O_4 Nanoparticles: Experimental and Theoretical Investigations, Sensors and Actuators B: Chemical Vol. 225, 2016, pp. 463-468, https://doi.org/10.1016/j.snb.2015.11.056.

[15] J.Shang, H.Tang, H.Ji, W.Ma, C.Chen and J.Zhao Synthesis Characterization, and Activity of a Covalently Anchored Heterogeneous Perylene Diimide Photocatalyst, Chinese Journal of Catalysis, Vol. 38, No. 12, 2017, pp. 2094–2101, https://doi.org/10.1016/S1872-2067(17)62960-7.

[16] P.Saravanan, K.Jayamoorthy and S.A.Kumar, Switch-On Fluorescence and Photo-Induced Electron Transfer of 3-Aminopropyl Triethoxysilane to ZnO: Dual Applications in Sensors and Antibacterial Activity, Sensors and Actuators B: Chemical, Vol. 221, 2015, pp. 784-791, https://doi.org/10.1016/j.snb.2015.05.069.

[17] Jose Diego Fernandesa, Priscila Alessioa, Matheus Rodrigues Medeiros Silva, Ricardo Flavio Aroca, Agda Eunice de Souza, Carlos Jose Leopoldo Constantinoa, Physical Vapor Deposited Films of a Perylene Derivative: Supramolecular Arrangement and Thermal Stability, Materials Research, Vol. 20, No. 4, 2017, pp. 882-890, http://dx.doi.org/10.1590/1980-5373-MR-2016-069.

[18] Merve Lleri, Serife O.Hacioglu, Ali Cirpan and Levent Toppare, Syntheses and Optical Properties of Perfluorophenyl Containing Benzimidazole Derivaties: The Effect of Donor Units, Vol. 52, No. 7, 2015, pp. 510-516,

https://doi.org/10.1080/10601325.2015.10 39321.

[19] J.Jayabharathi, V.Thanikachalam, K.Jayamoorthy, Physicochemical Studies of Chemosensor Imidazole Derivatives: DFT based ESIPT process. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 89, 2012, pp. 168-176, https://doi.org/10.1016/j.saa.2011.12.053.

[20] J.Jayabharathi, V.Thanikachalam and K.Jayamoorthy, Photophysical Studies of Some Heterocyclic Chromophores as Potential NLO Materials, Spectrochim.Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 89, 2012, pp. 301-307, https://doi.org/10.1016/j.saa.2011.12.031.

[21] M.Bagui, T.Dutta, H.Zhong, S.Li, S.Chakraborty, A.Keightley and Z.Peng, Synthesis and Optical Properties of Perylene Diimide Derivatives with Triphenylene based Dendrons Linked at the Bay Positions through a Conjugated Ethynyl Linkage, Tetrahedron, Vol. 68, No. 13, 2012, pp. 2806-2818, https://doi.org/10.1016/j.tet.2012.02.008.

[22] J.Jayabharathi, V.Thanikachalam, M.Vennila, K.Jayamoorthy, DFT Based ESIPT Process of Luminescent Chemosensor: Taft and Catalan Solvatochromism, Spectrochim. Acta A: Molecular and Biomolecular Spectroscopy, Vol. 95, 2012, pp. 589-595, https://doi.org/10.1016/j.saa.2012.04.056.

[23] V.Chis, G.Mile, R.S.Tiufiuc, N.Leopold and M.Oltean, Vibrational and Electronic Structure of PTCDI and Melamine-PTCDI Complexes, Journal of Molecular Structure, Vol. 924-926, 2009, pp. 47-53, https://doi.org/10.1016/j.molstruc.2008.12 .038.

[24] J.Jayabharathi, V.Thanikachalam, M.Vennila and K.Jayamoorthy, Physico-Chemical studies of New Luminescent Chemosensor for Cu^{2+}, Spectrochimca Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 96, 2012, pp. 677-683, https://doi.org/10.1016/j.saa.2012.06.049.

[25] J.Jayabharathi, V.Thanikachalam, M.Vennila and K.Jayamoorthy, Potential Fluorescent Chemosensor based on L-Tryptophan Derivative: DFT based ESIPT Process, Spectrochim. Acta A. Vol. 95, 2012, pp. 446-451,

https://doi.org/10.1016/j.saa.2012.04.017.

[26] J.Jayabharathi, V.Thanikachalam and K.Jayamoorthy, Computational studies of 1, 2-disubstituted benzimidazole derivatives, Spectrochim, Acta Part A: Vol. 97, 2012, pp. 131-136, https://doi.org/10.1016/j.saa.2012.05.085.

[27] C.Anbuselvan, J.Jayabharathi, V.Thanikachalam and K.Jayamoorthy, Electronic Spectral Studies of Some Fluorescent Probes: A Comparison of Two Approaches Spectrochimica Acta Part A: Vol. 96, 2012, pp. 848-853, https://doi.org/10.1016/j.saa.2012.07.119.

[28] J.Jayabharathi, V.Thanikachalam, K.Jayamoorthy and N.Srinivasan, Synthesis, Spectral Studies and Solvatochromism of Some Novel Benzimidazole Derivatives – ESIPT Process, Spectrochim, Acta Part A: Vol. 105, 2013, pp. 223-228, https://doi.org/10.1016/j.saa.2012.12.037.

[29] J.Jayabharathi, V.Thanikachalam, R.Sathishkumar and K.Jayamoorthy, Physico-chemical Studies of Fused Phenanthrimidazole Derivative as Sensitive NLO Material, Spectrochim Acta Part A: Vol. 101, 2013, pp. 249-253, https://doi.org/10.1016/j.saa.2012.09.089.

[30] X.Zhang, Y.Wu, J.Li, F.Li and M.Li, Synthesis and Characterization of Perylene Tetracarboxylic Bisester Monoimide Derivaties, Dyes and Pigments, Vol. 76, No. 3, 2008, pp. 810-816, https://doi.org/10.1016/j.dyepig.2007.02.0 06.

[31] R.S.Mulliken, Electronic Population Analysis on LCAO-MO Molecular Wave Function, 1, The Journal of Chemical Physics, Vol. 23, No. 10, 1955, pp. 1833-1840, https://doi.org/10.1063/1.1740588.

[32] J.Jayabharathi, V.Thanikachalam, K.Jayamoorthy and M.Venkatesh Perumal, A Physiochemical Study of Excited State Intramolecular Proton Transfer Process: Luminescent Chemosensor by Spectroscopic Investigation Supported by ab Initio calculations, Spectrochimica Acta Part A: Vol. 79, No. 1, 2011, pp. 6-16, https://doi.org/10.1016/j.saa.2010.12.027.

[33] J.Jayabharathi, V.Thanikachalam, N.Srinivasan, M.Venkatesh Perumal and K.Jayamoorthy, Physiochemical Studies of Molecular Hyperpolarisability of Imidazole Derivatives, Spectrochimica, Acta Part A: Vol. 79, No. 1, 2011, pp. 137-147, https://doi.org/10.1016/j.saa.2011.02.024.

[34] J.Jayabharathi, V.Thanikachalam, N.Srinivasan and K.Jayamoorthy, Physicochemical Studies of Some Novel Imidazole Derivaties as Sensitive NLO Materials, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol. 83, 2011, pp. 329-336, https://doi.org/10.1016/j.saa.2011.08.039.

[35] K.R.Sankaran, Optical and Self-Assembly Studies of Some New Perylene Tetracarboxylic Diimides, Vol. 1, No. 4, 2016, pp. 23-42, http://dx.doi.org/10.18831/djchem.org/2016041003.

[36] S.Sebastian and N.Sundaraganesan, The Spectroscopic (FT-IR, FT-IR Gas Phase, FT-Raman and UV) and NBO Analysis of 4-Hydroxypiperidine by Density Functional Method. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. Vol. 75, No. 3, 2010, pp. 941-952, https://doi.org/10.1016/j.saa.2009.11.030.

[37] K.R.Sankaran, Synthesis Characterization and Computational Studies of New Perylene Tetracarboxylic Diimides, Vol. 3, No. 1, 2018, pp. 6-27, https://dx.doi.org/10.18831/djchem.org/2018011002.

APPENDIX A

Table A1.Comparative study of theoretical and experimental IR values of AD-PTCDI and AP-PTCDI

Compounds	Ar C-H$_{str}$		C=O		C-N$_{str}$		Ar C=C	
	T	E	T	E	T	E	T	E
AP-PTCDI	3059	3056	1688	1649	1362	1353	1505	1585
AD-PTCDI	3196	3051	1695	1687	1375	1352	1505	1592

*T: theoretical IR value, E: experimental IR value

Table A2.Second order perturbation theory analysis of fock matrix in NBO basis of AD-PTCDI

Donor (i)	Acceptor (j)	E$^{(2)}$kJ mol	E(j)-E(i) a.u	F(i, j) a.u
π(C1-C19)	π*(C2-C3)	20.34	0.29	0.06
π(C2-C3)	π*(C21-O22)	22.70	0.26	0.07
π(C4-C5)	π*(C6-C7)	22.20	0.27	0.07
π(C6-C7)	π*(C8-C20)	22.76	0.27	0.07
π(C8-C20)	π*(C4-C5)	21.10	0.27	0.06
π(C9-C18)	π*(C12-C13)	21.11	0.27	0.06
π(C10-C11)	π*(C9-C18)	22.76	0.27	0.07
π(C12-C13)	π*(C10-C11)	22.20	0.27	0.07
π(N33-C34)	π*(C31-N37)	37.44	0.28	0.09
π(C35-C36)	π*(N33-C34)	32.11	0.26	0.08

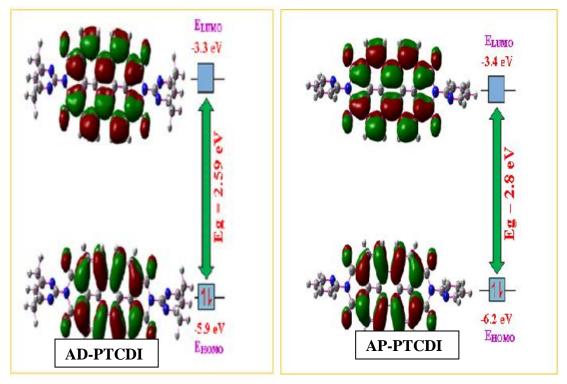Table A3 .Second order perturbation theory analysis of fock matrix in NBO basis of AP-PTCDI

Donor (i)	Acceptor (j)	E$^{(2)}$kJ mol	E(j)-E(i) a.u	F(I, j)a.u
π(C1-C19)	π*(C2-C3)	20.37	0.29	0.06
π(C2-C3)	π*(C21-O22)	22.68	0.26	0.07
π(C5-C6)	π*(C23-O24)	22.68	0.26	0.07
π(C7-C8)	π*(C5-C6)	20.38	0.29	0.06
π(C9-C10)	π*(C11-C12)	20.37	0.29	0.06
π(C13-C14)	π*(C15-C16)	22.15	0.27	0.07
π(C15-C16)	π*(C17-C18)	22.78	0.27	0.07
π(C17-C18)	π*(C13-C14)	21.13	0.27	0.06
π(C39-C40)	π*(C41-C42)	20.94	0.28	0.06
π(C41-C42)	π*(C31-N38)	28	0.26	0.07
LP (1) N29	π*(C21-O22)	55.54	0.25	0.10
LP (1) N29	π*(C23-O24)	55.54	0.25	0.10
LP (1) N30	π*(C25-O26)	55.54	0.25	0.10
LP (1) N30	π*(C27-O28)	55.54	0.25	0.10

Where,
E$^{(2)}$ is the energy of hyper conjugative interactions
Energy difference between donor and acceptor *i* and *j* NBO orbitals
F (i, j) is the fock matrix element between *i* and *j* NBO orbital

APPENDIX B

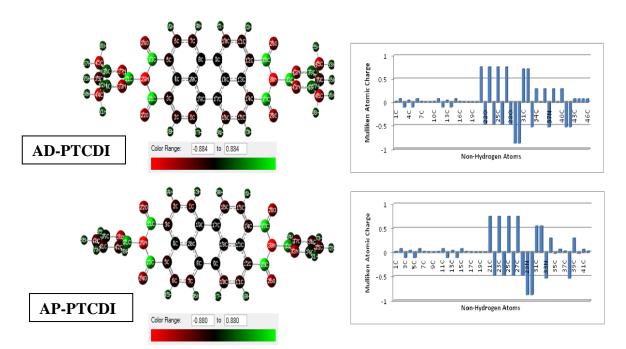Figure B1. Molecular frontier orbitals of compounds AD-PTCDI and AP-PTCDI

Figure B2.Mulliken atomic charge distribution (a) and plot of atomic charge distribution (b) of AD-PTCDI and AP-PTCDI