Understanding The Behavior Of 5, 10, 15, 20-Tetrakis (4 -Hydroxyphenyl) Porphyrin and Its Cation in Methanol: Insights from Electronic Structure Calculations

Anju[1]*, L.K. Saini[1], Mukesh Pandey[2]

[1] *Department of Physics, Sardar Vallabhbhai National Institute of Technology, Surat, - 395007, INDIA*

[2]*Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai, - 400085, INDIA*

Abstract

This research investigates the solvation dynamics and interactions of neutral 5,10,15,20-tetrakis(4-hydroxyphenyl) porphyrin (TPPH) and its cationic form (TPPH^{2+}) with methanol as the solvent. HOMO-LUMO analysis and Global Chemical Reactive Descriptors (GCRD) results were reported using DFT method with BP86 functional. The study reveals contrasting charge transfer behaviors: neutral TPPH demonstrates an enhanced charge transfer rate upon dissolution in methanol, while cationic TPPH exhibits a reverse trend. This solvation-induced reduction in energy gap presents a potential avenue for optimizing optoelectronic devices like light-emitting diodes and laser diodes. These findings elucidate the intricate interplay between porphyrin derivatives and solvents, offering valuable insights for tailored applications across diverse scientific and technological fields.

Keywords: Solvation, porphyrin, DFT, energy gap, charge transfer.

Introduction

Porphyrins belong to a category of aromatic heterocyclic compounds that are widespread in nature. They play a pivotal role in essential biochemical processes, including oxygen transport - heme), photosynthesis (chlorophylls), photovoltaic devices [1] to oxidative catalysis, sensors, nonlinear optics, nanomaterials for cancer photodynamic therapy [2]. In the context of measuring the solvation ability of solvents, porphyrin-based solvation/de-solvation indicators can be used to study the interaction between solvents and solutes. The solvation ability of a solvent refers to its capacity to dissolve or interact with a solute, which could be a different chemical compound. Understanding solvation abilities is crucial in various fields, including chemistry, biochemistry, and material science.

Porphyrin-based indicators are often chosen for these studies because they can undergo changes in their electronic structure, fluorescence properties, or other physical properties when they interact with solvents. These changes can be used to probe the strength and nature of solvent-solute interactions. The study conducted by Rica Boscencu et. al, shows that the TPPH molecule is insoluble in water but soluble in alcohol, acetone, and ethyl acetate [3]. This paper aims to explore how solvation effects occur on neutral and cationic TPPH.

Method

The ORCA program package (version-4.1.2) [4] was used for all quantum chemical calculations carried out in this work. Optimized molecular structures were calculated using DFT with Hybrid functional BP86 in conjunction with the triple-ζ quality def2-TZVP basis set and D3BJ dispersion correction [5]. To get the insight of the molecular orbitals of molecules, Avogadro software was used. The solvent effects were estimated at BP86 level of theory using conductor-like polarizable continuum model (CPCM) with methanol as solvent (dielectric constant ε=32.63) [6]. To check the kinetic stability, reactivity, hardness and softness of the specified molecule, a global reactivity descriptor parameter was calculated based on *Koopman's theorem* [7]. According to this theory, the Ionization Potential (I) and Electron Affinity (A) can be specified through HOMO (E_H) and LUMO (E_L) orbital energy, as:

$$I = -E_H \qquad (1)$$

$$A = -E_L \qquad (2)$$

Using the above relations, the electronegativity (χ) and chemical hardness (η) of a molecule were determined and are given by,

$$\chi = \frac{[I+A]}{2} = -\frac{[E_L + E_H]}{2} \qquad (3)$$

$$\eta = \frac{[I-A]}{2} = \frac{[E_L - E_H]}{2} \qquad (4)$$

The softness (s) and maximum charge transfer (ΔN_{max}) properties of molecule are calculated by,[8]

$$s = \frac{1}{\eta} \qquad (5)$$

$$\Delta N_{max} = \frac{\chi}{\eta} \qquad (6)$$

Results

The computational techniques, employed to facilitate a comprehensive analysis of the chemical arrangement of molecules neutral and cationic TPPH. Our primary focus was to attain the optimized molecular structure of TPPH neutral and cation.

Table 1: Calculated HOMO-LUMO energy values, their differences and GCRD parameters before and after solubility of TPPH and derivative in methanol. The values for all parameters are in eV except s is in (eV)$^{-1}$ and ΔN_{max} is unit less.

Parameters	TPPH	TPPH^{2+}	TPPH (in methanol)	TPPH^{2+} (in methanol)
E_H	-4.691	-9.506	-4.844	-5.303
E_L	-2.999	-8.676	-3.252	-4.338
ΔE	1.692	0.830	1.592	0.965
η	0.846	0.415	0.796	0.482
s	1.182	2.409	1.256	2.074
χ	3.845	9.091	4.048	4.820
I	4.691	9.506	4.844	5.303
A	2.999	8.676	3.252	4.338
ΔN_{max}	4.544	21.906	5.085	10.00

We evaluated the energy difference of HOMO-LUMO (ΔE), global chemical reactivity descriptors (GCRD) like hardness (η), softness (s), electronegativity (χ), ionization potential (I), electron affinity (A) and charge transfer properties (ΔN_{max}) of the titled molecules by studying the frontier orbital energies [9] given in Table 1. The charge density plots for the two molecular orbitals (MO) that were examined in this study—the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO)—for TPPH and TPPH^{2+} are shown in figure 1.

Additionally, the change in energy gap and other parameters was observed during solvation process of neutral TPPH and cationic TPPH in methanol solvent after optimization. The change in parameters of TPPH and TPPH^{2+} after solvation process are also mentioned in Table 1.

Discussion

It was observed that the value of energy gap in case of neutral TPPH decreases (from 1.692 eV to 1.592 eV) when it is dissolved in methanol solvent; however, it increases for cationic TPPH (~ 0.830 eV to 0.965 eV). The decrease in energy gap, in case of neutral TPPH explains that neutral TPPH shows good interaction with methanol solvent but, an increase in the bandgap of cationic TPPH during solvation process demonstrates that it exhibits different kind of interactions after dissolving in methanol. When neutral TPPH is added to methanol, the bonds of neutral TPPH weakens, due to which it becomes soft (more reactive and susceptible to electron donation or acceptance) with softness ranging from 1.182 to 1.256 eV. Due to the increase in softness of neutral TPPH, it becomes easier to transfer charge from HOMO to LUMO. The charge transfer characteristic (ΔN_{max}) increases from 4.544 to 5.085 for neutral TPPH after solvation; meanwhile, for cationic TPPH, the charge transfer, ΔN_{max} has significantly reduced.
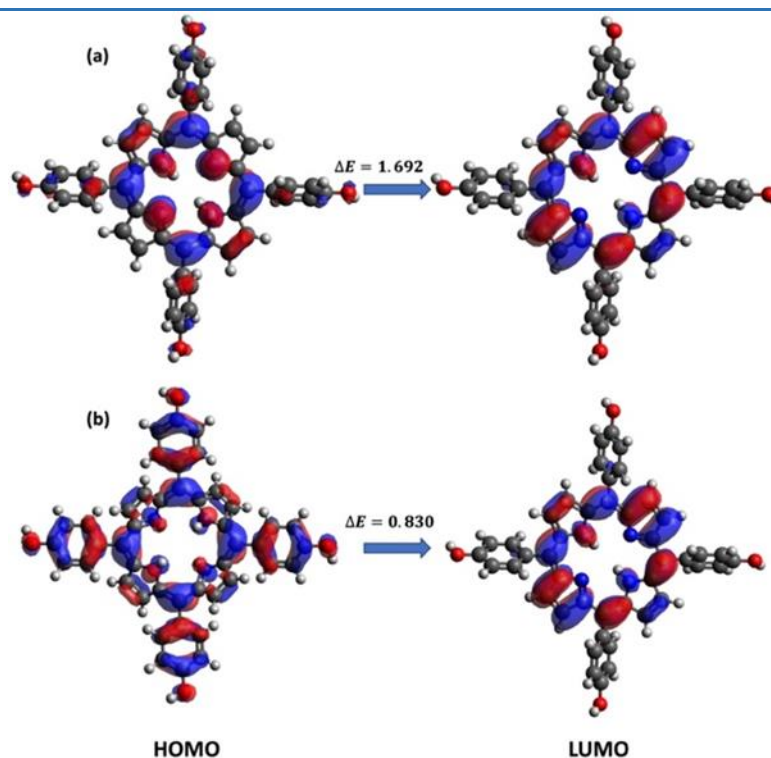
Figure 1: Change in molecule charge distribution for pure TPPH(a) and TPPH^{2+}(b) during HOMO-LUMO transition. ΔE denotes HOMO-LUMO transition energy. The regions abundant in electrons are represented in red, while electron-deficient areas are depicted in blue colour code.

Conclusion

In summary, we have investigated the solvation effects and interactions of neutral TPPH and cationic TPPH with methanol solvent. The solvation effect has revealed that charge transfer will be rapid when neutral TPPH is dissolved in methanol. But in case of cationic TPPH, the charge transfer had reduced significantly. These solvents can form charge transfer complexes with semiconductor materials, which leads to bandgap modification. These complexes can introduce new energy levels within the bandgap or alter the effective bandgap of the material. The decrease in energy gap caused by solvation offers a promising opportunity to enhance the performance of optoelectronic devices such as LEDs and laser diodes [10].

Acknowledgment

References

1. M.V. Tesakova and V.I. Parfenyuk, Surf. Engin. Appl. Electrochem. 57, 67, 2021.
2. Ioana Baldea, et. al, Processes, 11, 917, 2023.
3. Rica Boscencu et.al, Molecules, 28(3):1149, 2023.
4. F. Neese, et. al, J. Chem. Phys. 152, 22, 224108, 2020.
5. Louise M. Debefve and Christopher J. Pollock, Phys. Chem. Chem. Phys. 23, 25780, 2021.
6. M. Mohsen-Nia, H. Amiri and B. Jazi, Journal of Solution Chemistry, 39, 701, 2010.
7. Takao Tsuneda, et. al, J. Chem. Phys. 133, 174101, 2010.
8. P.K. Chattaraj, et. al, Chem. Rev. 107, 9, PR46, 2007.
9. Marzieh Miar, et. al, Journal of Chemical Research, 45, 147, 2021.
10. A.G. Pramod, et. al, Journal of Molecular Liquids, 292, 111383, 2019.