



NONLINEAR OPTICAL AND ELECTRONIC PROPERTIES OF (N1E, N4E)-N1-(2-NITROBENZYLIDENE)-N4-(3-NITROBENZYLIDENE)BENZENE-1,4-DIAMINE (NNBD) DENSITY FUNCTIONAL APPROACH

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Introduction

- Nonlinear optical (NLO) materials are essential materials in modern photonics technology.
- They are applicable in optical computing, laser systems, and telecommunication.
- Organic molecules with π -conjugated systems and strong electron donor-acceptor characteristics exhibit promising NLO properties.
- Schiff bases have gained significant attention due to their excellent charge transfer capabilities and thermal stability.

Aims

This study investigates the nonlinear and electronic properties of NNBD using the density functional theory (DFT) approach

Objectives

- Geometrical optimization.
- Quantum parameters calculation (HOMO-LUMO energies and energy gaps).
- Solvent effects on the electronic absorption properties of NNBD.
- Determination of hyperpolarizability parameters (α , β , γ).
- Evaluate potential applications as a semiconductor and photosensitizer.

Computational Study

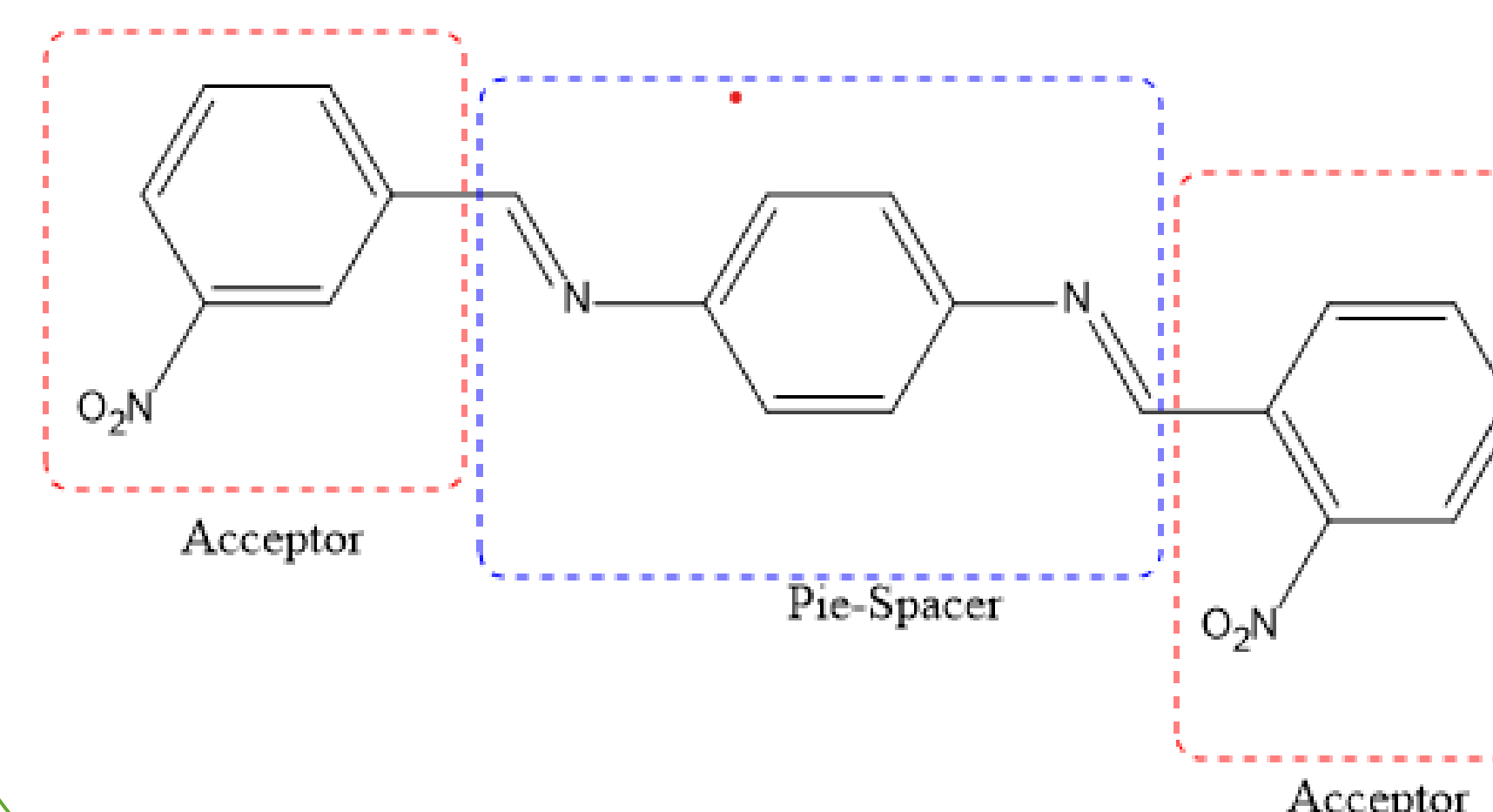
DFT Calculation

- Functional:** B3LYP and ω B97XD
- Basis Set:** 6-311++G(d,p)
- Software:** Gaussian 16
- Solvents:** Cyclohexane, THF, DCM, Ethanol, Methanol, and Acetonitrile.

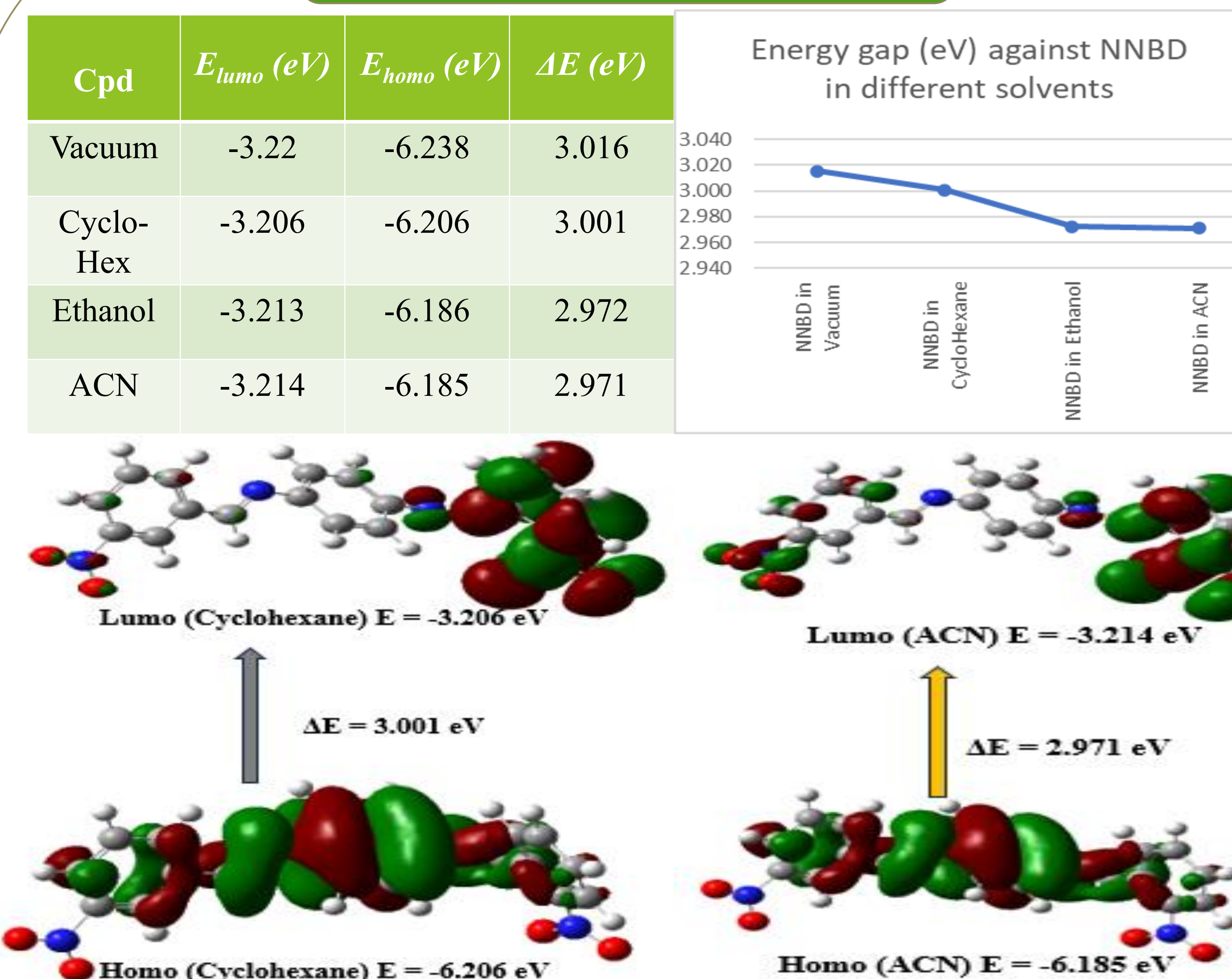
Properties Calculation

- Geometrical and frequency analysis
- Quantum parameters analysis
- TD-DFT for UV - Vis absorption
- NLO properties calculation

Molecular Structure

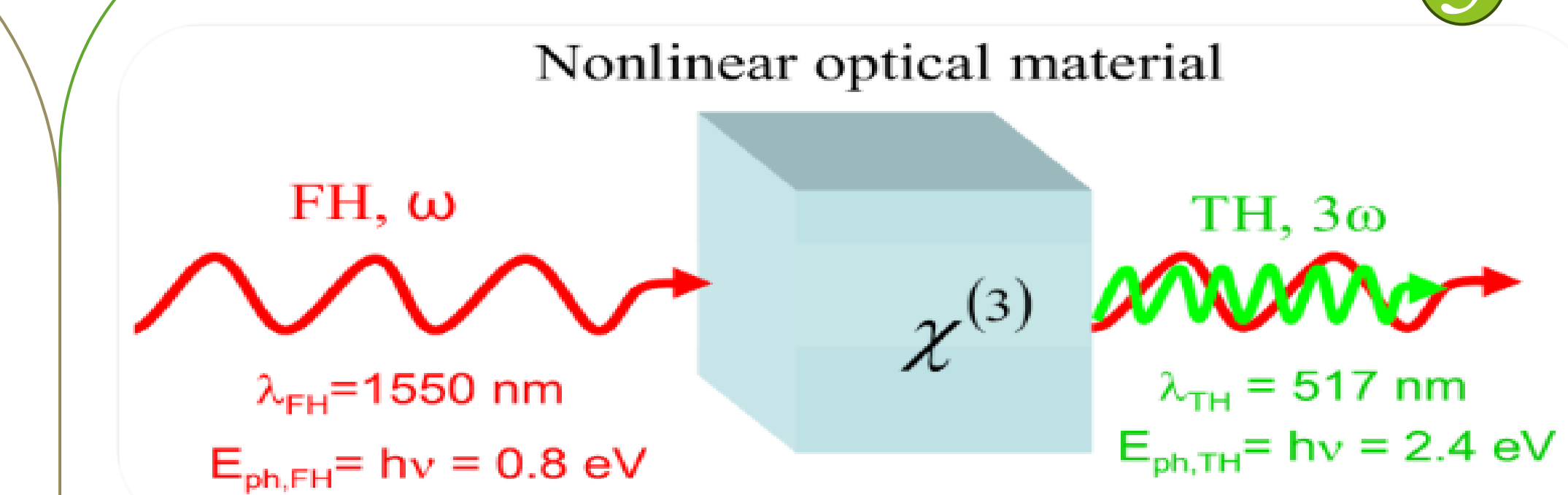


Frontier Molecular Orbital Parameters



- NNBD shows its best performance in acetonitrile with an energy gap of 2.971 eV.
- It was therefore suggested that NNBD has the potential to be an organic semiconductor material.

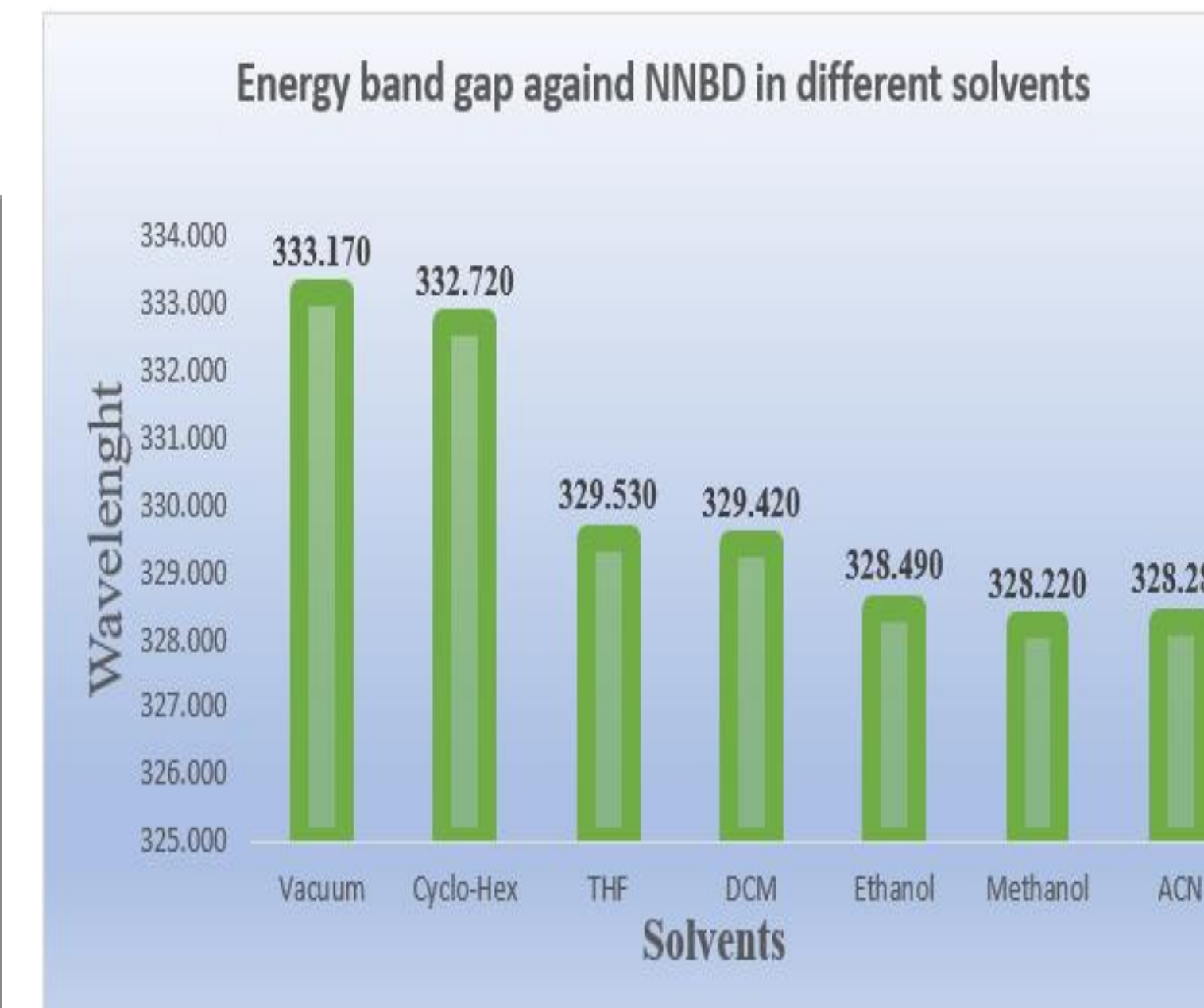
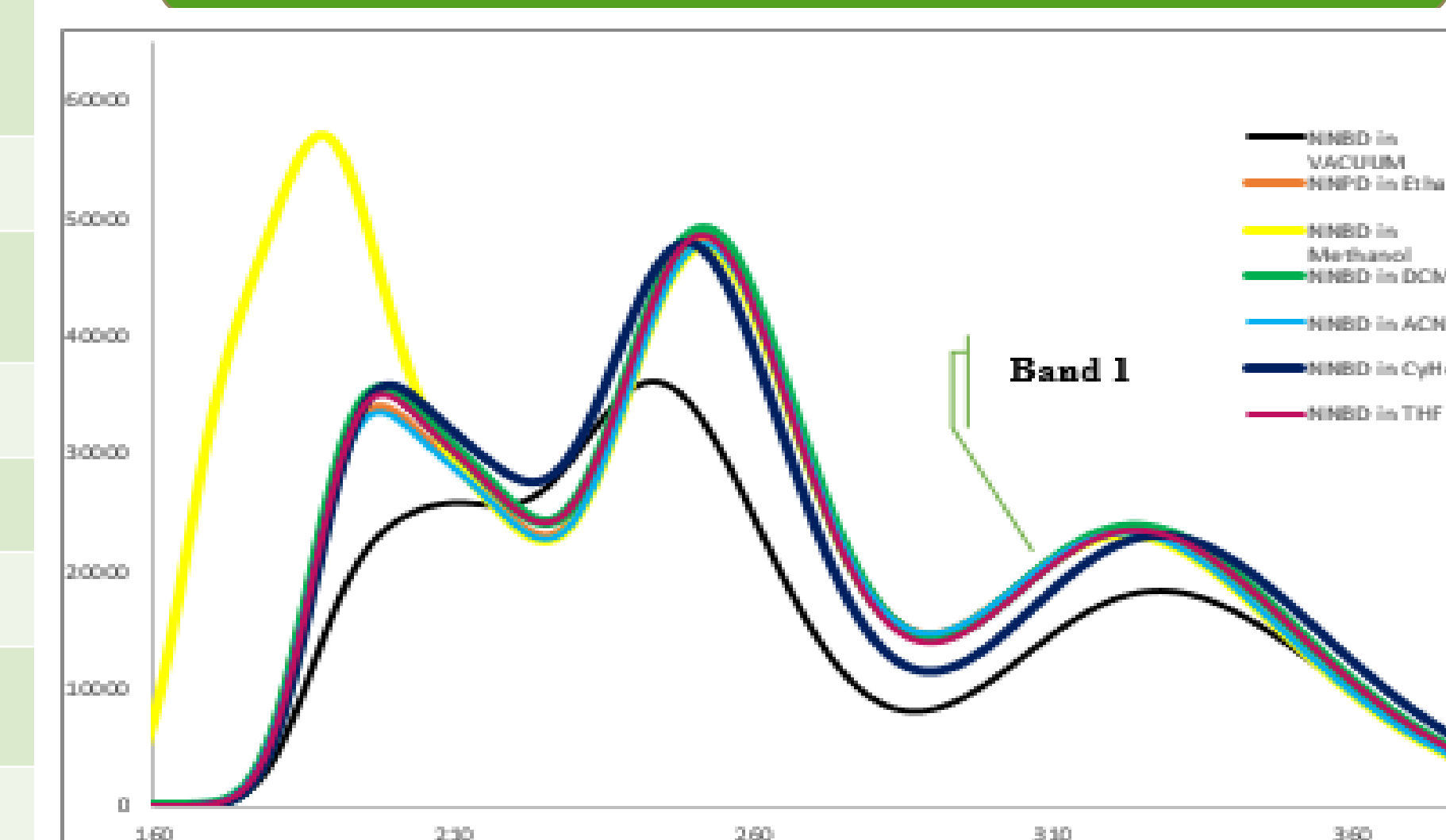
Nonlinear Optical Parameters



Cpd	Vacuum	Cyclo-Hex	Ethanol	ACN	Urea
$\alpha_{aniso}(-w; w)(a.u.)$	189.503	190.514	186.121	185.83	13.657
$\beta_{ }(2w; w, w)(a.u.)$	1813.23	2365.41	2135.06	2110.15	34.412
$\gamma_{ }(-2w; w, w, 0)(a.u.)$	399085	576064	580505	575581	7058.210

- The polarizability (α) response of NNBD is 14x higher than that of urea across all the media. It shows the best performance in cyclohexane
- The first hyperpolarizability (β) response of NNBD is 53-69x higher than urea across all the media. It displays the best second-order character in cyclohexane.
- The second hyperpolarizability (γ) response of NNBD is 57-82x higher than urea across all the media. It exhibits a higher third-order response in ethanol.

UV-Vis Electronic Absorption



Conclusion

- NNBD demonstrates exceptional NLO properties with high hyperpolarizability values
- Polar solvents (acetonitrile) enhance the reactivity properties of NNBD
- Low band gap enables its semiconductor application.
- Moderately strong UV-Vis absorption for photosensitizer application.
- Asymmetric nitro substitution enhances charge transfer of NNBD

Applications

- Organic electronic semiconductor
- Solar Cell Sensitizers
- Nonlinear optical devices

- NNBD exhibits hypsochromic (n to π^* transition) and hypochromic shift as the solvent's polarity increases.
- Light harvesting efficiency (LHE) of NNBD ranges from 56.2% to 65.3% which is moderately high.
- Therefore, NNBD is suggested to exhibit potential as a photosensitizer in a solar cell.