

N-(1H-Benzo[d]imidazol-2-yl)-1-(3-Substituted phenyl)methanimines as optoelectronic and nonlinear optical materials: spectroscopic and computational approaches

OJO N. D.^{1*}, ADEKUSIBE O. D.¹ and OBI-EGBEDI N. O.¹

¹ Department of Chemistry, Faculty of Science, University of Ibadan, Ibadan, Nigeria

* Corresponding author: dammynath@yahoo.com; nd.ojo@ui.edu.ng; Tel. +234 806 480 2584

ABSTRACT

Negative environmental impact of fossil fuel and ever-increasing need for renewable energy materials necessitate rigorous search for optoelectronic materials. Photon reabsorption due to small Stokes shift limits the light-emitting potentials of many optical materials. In this research, two benzimidazole Schiff bases (1H-benzo[d]imidazol-2-yl)-1-(3-nitrophenyl)methanimine (BINM) and N-(1H-benzo[d]imidazol-2-yl)-1-(3-hydroxyphenyl)methanimine (BIHM) were synthesized via one-pot single step condensation and characterized using spectrometric (¹H NMR, ¹³C NMR, ESI-MS, FTIR) techniques. Optoelectronic and nonlinear optical (NLO) properties of BINM and BIHM were, herein, explored using spectroscopic, density functional theory (DFT) and Monte Carlo simulation approaches. Absorption, light-harvesting efficiency (LHE) and fluorescence properties were studied in different solvent. LHE, first and second hyperpolarizabilities, and parameters for power conversion efficiency (V_{oc} and ΔG_{inj}) were computed using time-dependent-DFT/B3LYP/6-311++G(d,p) method. Hyperpolarizabilities were compared with urea (standard). Binding properties of BINM and BIHM on TiO₂ (anatase 101) were investigated using MC method. Calculated properties agree remarkably with experiment. The compounds display large Stokes shift (> 200 nm), appreciable quantum yield and low band gap. High LHE (80%) and large hyperpolarizabilities were obtained for BINM. BINM displayed higher V_{oc} and ΔG_{inj} than BIHM. Negative adsorption energies of BIHM-TiO₂ (-52.7 kJ/mol) and BINM-TiO₂ (-57.3 kJ/mol) interfaces indicate their strong binding interactions on anatase. The materials possess potentials for optoelectronic and nonlinear optical applications.

Key Words: Schiff base; optoelectronics; dye-sensitizer; nonlinear optical property; Stokes shift

INTRODUCTION

The demand on clean and affordable energy is both global and ever-increasing.

Recent report by international energy agency shows a rising shift towards exploitation of renewable energy sources in the last decade [1]. Although fossil fuel contributes a large percentage to energy source globally, its fast depletion and negative impact on the environment spur research on renewable alternatives.

PROBLEM

- Fossil fuel depletion
- Negative environmental impact of fossil fuel
- Need for systems that can interconvert energy
- Photon reabsorption in most organic systems due to small Stokes shift [2-6]

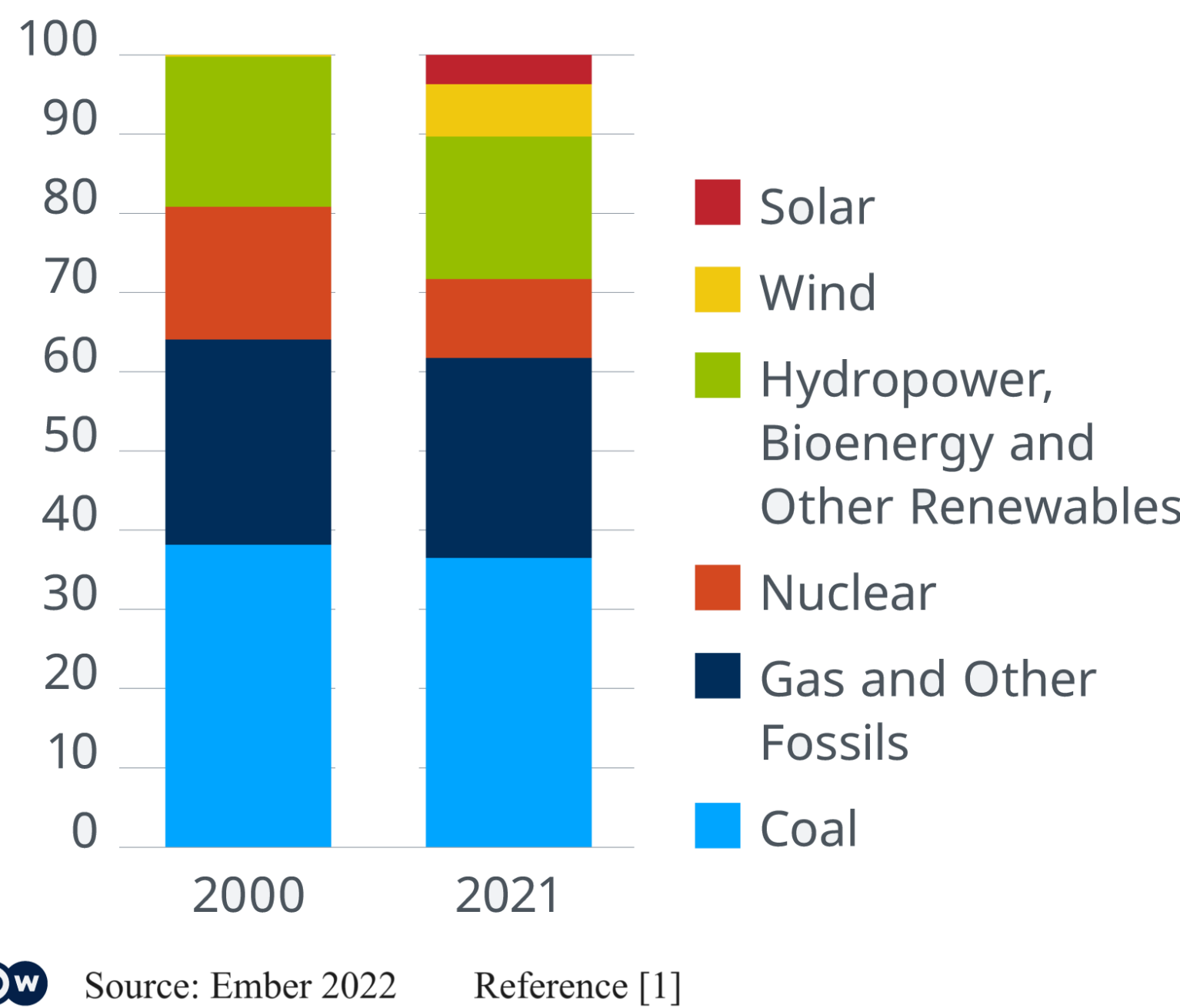
Aim of Research

- Design and synthesis of organic optical material with reduced photon reabsorption

Research Objectives

- Synthesis of BIHM and BINM
- Spectroscopic study of electronic properties
- Determination of optoelectronic properties
- Calculation of nonlinear optical properties

Figure 1: Renewable and non-renewable energy sources in 2000 and 2021



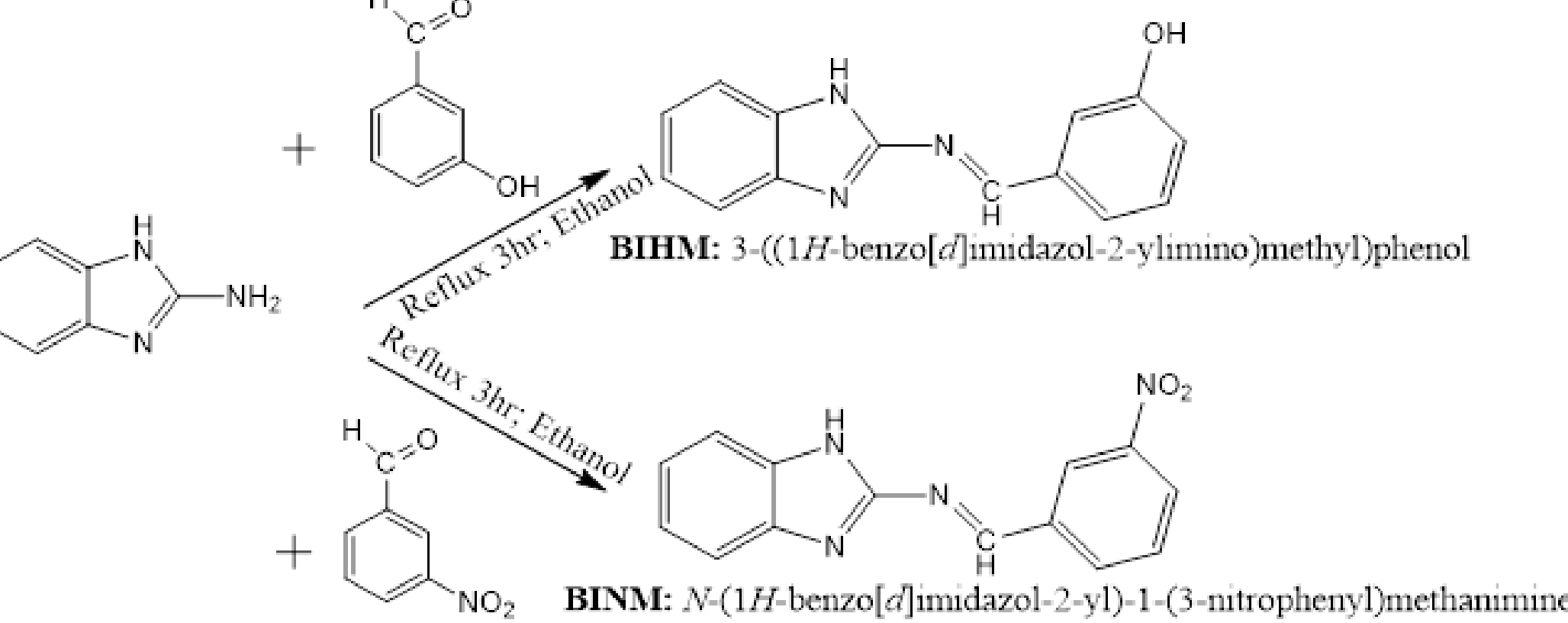
METHODS

Experimental Method

Synthesis

One pot single step condensation reaction of 2-aminobenzimidazole with 3-hydroxybenzaldehyde and 3-nitrobenzaldehyde (Figure 2) [7-9]

Figure 2: Synthetic route for BIHM and BINM



Characterization

- ¹H and ¹³C NMR spectrometry
- High-resolution electrospray ionization mass spectrometry
- ATR-FTIR
- Melting point determination

Computational Method

- Geometry optimization: DFT/B3LYP/6-311++G(d,p)
- Frequency calculation: No imaginary frequency
- Energy calculation: electronic and optoelectronic properties
- Adsorption simulation: Monte Carlo method [9-10]

RESULTS AND DISCUSSION

CHARACTERIZATION

BIHM: Yield (0.89 g, 75 %); Melting point 220 - 222 °C; Molecular weight [M+1]⁺ 238.10; Selected ATR-FTIR peaks ($\bar{\nu}$, cm⁻¹): 3376 (N-H_{str}, sh), 3200 (O-H_{str}, br), 3053 (=C-H_{str}, aromatic), 1605 (C=N_{str}, imine), 1575 (C=C_{str}, aromatic). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.34 (s, 1H), 7.61 – 7.50 (m, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.18 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.13 – 7.09 (m, 1H), 7.08 – 6.99 (m, 1H), 2.07 (s, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 165.59, 157.99, 155.78, 137.72, 136.53, 130.41, 130.29, 122.09, 121.51, 120.33, 114.80.

BINM: Yield (1.03g, 77 %) Melting point 199 – 201 °C; ATR-FTIR (selected peaks, $\bar{\nu}$ cm⁻¹): 3474 (N-H), 3072(C-H), 1605 (C=N), 1569 (C=C), 1526, 1422; Mass spec [M+1]⁺: 267.09; ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.82 (s, 1H), 9.57 (s, 1H), 8.83 (s, 1H), 8.43 (d, *J* = 7.7 Hz, 1H), 8.38 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.82 (t, *J* = 7.9 Hz, 1H), 7.59 (s, *J* = 50.7 Hz, 1H), 7.47 (s, 1H), 7.20 (d, *J* = 3.1 Hz, 1H), 7.19 (d, *J* = 3.1 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 163.18, 154.81, 148.31, 136.68, 135.70, 130.74, 126.62, 122.97, 122.55, 118.98, 111.40.

Figure 3:(a) Orbital energies and (b) computed absorption spectra of BIHM and BINM

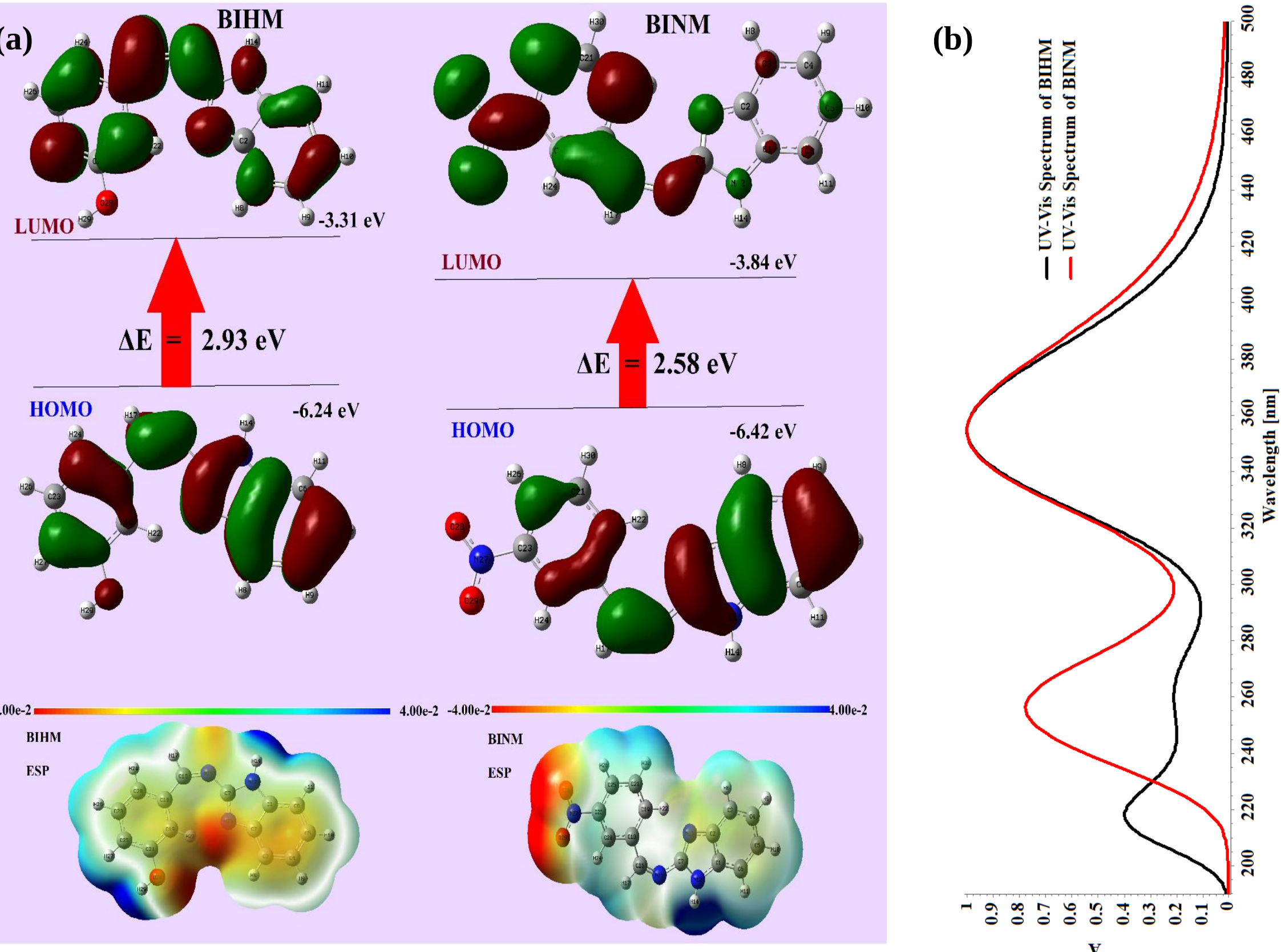


Table 1: Wavelength (λ), oscillator strength (*f*) and light-harvesting efficiency (LHE), Stokes shift ($\Delta\lambda$) and fluorescence quantum yield (ϕ_f) of BINM and BIHM

Dyes	λ_{max}^{Abs} nm	<i>f</i>	LHE (%)	λ_{max}^{Em} nm	$\Delta\lambda$	ϕ_f
BINM: DCM	357	0.90	87	626	269	0.21
BINM: Ethanol	335	0.05	11	615	280	0.21
BIHM: Ethanol	349	0.21	38	621	272	0.26

Table 2: Calculated optoelectronic and adsorption (Dye-Anatase 101) properties of BIHM and BINM

Dyes	E _{ox} eV	E _{red} eV	λ_{el} eV	E _H eV	E _L eV	ΔE eV	μ (D)	V _{oc} /V	E _{ox} eV	ΔG_{inj} eV	E _{ad} kJ/mol
BIHM	1.71	-1.22	0.44	-6.24	-3.31	2.93	2.15	0.69	-3.31	-0.74	-52.7
BINM	1.89	-0.69	0.35	-6.42	-3.84	2.58	2.92	0.85	-3.84	-0.21	-57.3

Table 3: Optical properties of BIHM and BINM

Compound	α (a.u)	$\Delta\alpha$ (a.u)	$\beta_{tot}/10^{-51}$ (C ³ m ³ J ⁻²)	$\gamma/10^{-63}$ (C ⁴ m ⁴ J ⁻³)
BIHM	221.25	48.01	3.05	150.85
BINM	238.52	30.94	18.46	287.36

Urea: $\beta_{tot} = 0.58 \times 10^{-53} \text{ C}^3\text{m}^3\text{J}^{-2}$, $\gamma = 5.91 \times 10^{-63} \text{ C}^4\text{m}^4\text{J}^{-3}$

Conclusion

- Design and synthesis of two benzimidazole dyes has been achieved
- The dyes exhibit large Stokes shifts and appreciable quantum yield indicating good photoluminescent properties
- BIHM and BIHM displayed larger hyperpolarizabilities than urea indicating good potential for nonlinear optical application
- The dyes gave good V_{oc} and ΔG_{inj} suggesting optoelectronic applications

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