

Microwave Assisted Synthesis, Solvatochromic, Photophysical and DFT Studies of Newer naphthalenoethyl N-methyl imidazolium bromide

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Abstract: Newer imidazolium bromide compound was prepared by reacting 1-methyl imidazole and 2-bromo-1-(naphthalen-2-yl)ethanone under microwave irradiation. The structure of the imidazolium compound was confirmed by spectral analysis, further photophysical, solvatochromic, and thermal properties were investigated. The Lippert-Mataga plot and solvent polarity empirical parameter $E_T(30)$ were used to examine solvent dependent optical properties of imidazolium compounds with a range of solvents with varying polarities. The thermal stability and phase behavior were studied by TGA and DSC analysis with a heating rate of 10 deg min⁻¹. DFT computation was performed to get the optimized molecular orbitals and HOMO - LUMO energies.

Index Terms: Lippert–Mataga plot, Microwave assisted synthesis, Photophysical, Solvatochromism, TD-DFT.

I. INTRODUCTION

“As a material class”, ILs are organic salts comprised fully of ions. Ionic liquids chemically comprise a bulky, asymmetrical organic cation and inorganic anion. The most stunning features of ILs are their negligible vapor pressure, also they show tunability in physicochemical properties with varying ion structures (Freemantle, 1998; Plechkova, 2007). Ionic liquids show high ionic conductivity and good thermal stability, wide electrochemical window of potential, good solvation ability. The properties possessed by ionic liquids make them excellent applications for a range such as solvent in synthesis, catalyst, lubricants, electrolytes (Tao, 2014; Welton, 1999; Zhou, 2009; Valkenburg, 2005; Galiński, 2006). Most of the ILs are nonvolatile, nonflammable and can have good solvation ability to dissolve organic and inorganic materials. These are thermally

stable and can remain in liquid state over a wide range of temperatures. ILs also show conducting behavior along with electrochemical stability and have low toxicity, hence ILs can be used as “green” substitutes to volatile organic solvents in chemical synthesis, separation and electrochemical processes (Sarbu, 2001; Shamsipur, 2010). Ionic liquids show high thermal stability, they can be thermally stable about 450 °C temperatures. The thermal stability is credited by the strength of molecular interactions in ionic liquids such as heteroatom–hydrogen bonds and heteroatom–carbon bonds (Wasserscheid, 2000).

Imidazolium cation possesses an ample number of promises in relation to the functionalities that are introduced at the N-1 and N-3 positions. Several researchers have been attentive to understanding the thermodynamic and thermophysical properties of imidazolium-based ionic liquids with a variety of functionalities attached to both nitrogen atoms. The groups present on N-atoms of imidazolium contain combinations of functionalities as alkyl, fluoroalkyl, ether, nitrile, alcohol, and silicon-based substituents. Amongst a variability of ionic liquids, n-alkyl imidazolium based ionic liquids are the most studied in the literature. Even though aryl substituted imidazolium-based ionic liquids are less commonly studied as compared to alkyl substituted (Tao, 2015; Tao, 2014; Mahurin, 2011; Bara, 2009; Bara, 2019). Microwave (MW) irradiation is a non-conventional energy source, has developed as a prevailing technique for promoting a diverse chemical reaction and employed as a useful greener synthetic strategy in organic chemistry (Lidström, 2001). The numerous imidazolium cation based ionic liquids yet synthesized under microwave irradiation (Namboodiri, 2002, Kim, 2005; Leveque, 2007; Aupoix, 2010). In this work we have synthesized newer 3-(2-(3,4-dihydronaphthalen-2-yl)-2-

oxoethyl)-1-methyl-1H-imidazol-3-ium bromide compound by greener approach under microwave irradiation and characterized it using analytical techniques. The synthesized imidazolium salt was investigated for its photophysical, solvatochromic behavior and DFT study..

II. EXPERIMENTAL

A. Materials and equipment:

The microwave assisted synthesis was performed using sineo microwave technology synthesizer. The compound was characterized by spectroscopic methods such as FT-IR, ^1H NMR, ^{13}C NMR spectroscopies and MASS spectrometry. Mass spectrum was recorded on Shimadzu mass spectrometer, ^1H NMR and ^{13}C NMR spectrum were recorded on Bruker Avance II Spectrometer at 400 MHz and Infrared spectrum (IR) was recorded on a Shimadzu FTIR-8400 Spectrophotometer. The absorption and emission were studied on Shimadzu UV-2450 spectrophotometer and Horiba Jobin Yvon Fluoromax-4 spectrophotometer. Auto lab PGSTAT 101 used to determine oxidation and reduction potential. Thermo gravimetric analysis and differential scanning calorimetric measurement were carried using SDT Q600 thermal analyser. Gaussian 16 software used to perform DFT computations with semiempirical AM1 calculations. The chemicals and solvents were procured Ar-grade, used as such.

B. Microwave assisted synthesis:

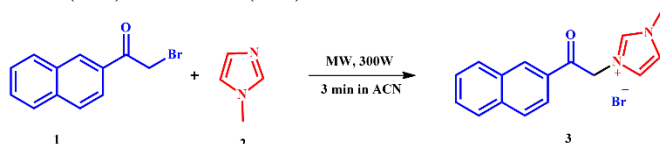
The mixture of 1-methyl imidazole (1.0 mmol), 2-bromo-1-(naphthalen-2-yl)ethanone (1.1 mmol) in dry acetonitrile was irradiated in a microwave synthesizer at 300 W. The quaternization of nitrogen of imidazole was completed in 3 minutes. The quaternized product formed in the reaction was separated as a solid. The obtained solid product was then filtered, washed with hot acetonitrile to remove the unreacted starting materials. The new imidazolium salt product was dried under vacuum, the solid isolated (yield = 88 %), the synthetic route for newer imidazolium salt is depicted in Scheme 1.

IR: ν_{max} = 3150, 1680, 1560, 1200 and 785 cm^{-1}

^1H NMR: (DMSO- d_6 , 400 MHz): δ = 9.21 (s, 1H), 8.80 (s, 1H), 8.20 (s, 1H), 8.08 (m, 2H), 8.0 (d, 1H), 7.80 (d, J = 8.0, 2H), 7.72 (m, 2H), 6.25 (s, 2H), 4.02 (s, 3H) ppm.

^{13}C NMR: (DMSO- d_6 , 400 MHz): δ = 191.2 (1C), 137.6 (1C), 135.3 (1C), 131.9 (1C), 130.8 (1C), 130.4 (1C), 129.5 (1C), 129.1 (1C), 128.6 (1C), 127.7 (1C), 127.2 (1C), 123.8 (1C), 123.2 (1C), 123 (1C), 55.3 (1C), 35.8 (1C) ppm.

HR-MS (ESI) m/z = 251 (M^+)



Scheme 1: Microwave assisted synthetic route for synthesis of newer imidazolium compound.

C. Absorption and Emission Studies:

The optical studies of imidazolium salt were performed in solutions prepared in sequence of solvents with varying polarities and dielectric constants. The absorption spectrums were recorded over the wavelength range of 200 – 800 nm using double beam Shimadzu spectrophotometer, with solution concentration of 2×10^{-5} M in a quartz cuvette having path length 10 mm. The fluorescence emission was recorded with identical prepared solutions using the Fluoromax-4 spectrophotometer.

D. Thermal Analysis:

Thermal properties of imidazolium compound were analysed using thermogravimetric analyser under inert nitrogen atmosphere. The sample was heated in an aluminium pan between 25 to 700 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}$ per minute.

III. RESULT AND DISCUSSION

A. Synthesis:

The newer imidazolium salt 3-(2-(3,4-dihydronaphthalen-2-yl)-2-oxoethyl)-1-methyl-1H-imidazol-3-ium bromide **3** was synthesized by greener approach under microwave irradiation. A mixture of 1-methyl imidazole **1** and -bromo-1-(naphthalen-2-yl)ethanone **2** in dry acetonitrile was irradiated for about 3 minutes to give the desired product. The structure of the synthesized imidazolium salt was confirmed by FT-IR, Mass, ^1H NMR, and ^{13}C NMR analysis. The corresponding data are provided in the supporting information.

B. Optical Studies:

The absorption spectrum of imidazolium compound was recorded in sequence of solvents of varying polarity such as, dioxane, dimethyl sulfoxide, N, N-dimethylformamide, ethanol, and methanol at 2×10^{-5} M concentration. It is observed that solution of imidazolium compound in different solvents displays maximum absorption in the wavelength range of 280 – 300 nm, as these are shown in Fig. 1.

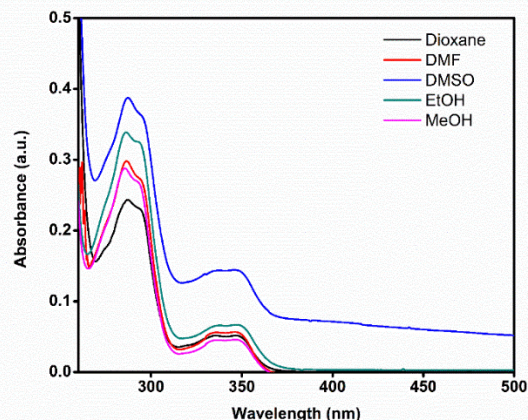


Fig. 1: Absorption spectrum of imidazolium compound in different solvents.

The fluorescence emission of the compound was investigated at their excitation wavelengths, the fluorescence emission of the compound was observed in the wavelength range 334 – 432 nm (Fig. 2). The Stokes shifts were calculated and observe in the range 3504 – 12566 cm^{-1} . The collective data of photophysical parameters is summarized in the Table 1 & Table 2.

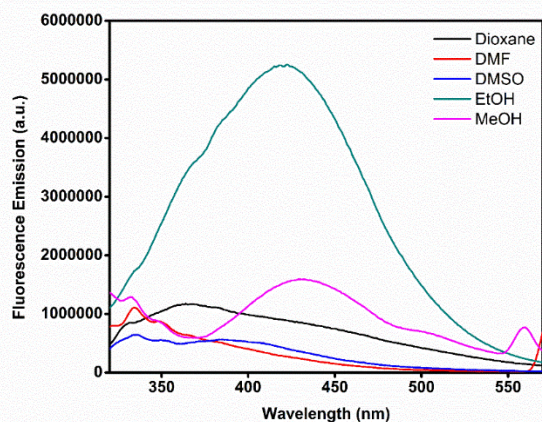


Fig. 2: Emission Spectrum of imidazolium compound in different solvents.

Table 1: Photophysical parameters of imidazolium compound in different solvents.

Solvent	Orientation Polarizability	$E_T(30)$	Absorption maxima ($\lambda_{\text{abs}}/\text{nm}$)
Dioxane	0.021	36	295
DMF	0.275	43.8	288
DMSO	0.265	45	299
Ethanol	0.29	51.9	292
Methanol	0.309	55.5	280

Table 2: Photophysical parameters of imidazolium compound in different solvents

Solvent	Molar Absorptivity ($\epsilon/1 \text{ mol}^{-1} \text{ cm}^{-1}$)	Emission Maxima ($\lambda_{\text{emi}}/\text{nm}$)	Stokes shift (cm^{-1})
Dioxane	11355	367	6650
DMF	14735	334	4782
DMSO	8575	334	3504
Ethanol	16290	418	10323
Methanol	12315	432	12566

C. Solvatochromism

Lippert- Mataga equation interprets energy difference between the ground and excited states due to the interactions between the solvent and organic molecule. Lippert-Mataga equation offers measure of variation in dipole moment of molecules upon photo-excitation. Lippert- Mataga equation (1) gives a plot of Stokes shift against orientation polarizability of solvents (Aggarwal, 2014; Kumar, 2011; Valeur, 2002; Zhang, 2016; Patil, 2019; Patil, 2021).

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc} \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n - 1} \right) \frac{(\mu_e - \mu_g)^2}{a^3} + \text{constant} \quad (1)$$

where “ h is Planck’s constant (6.6256×10^{-27} erg), c is velocity of light (2.9979×10^{10} cm/s), a is radius of cavity in which molecule resides, $\bar{\nu}_A$ is wave numbers (cm^{-1}) of the absorption, $\bar{\nu}_F$ is wave numbers (cm^{-1}) of the emission, ϵ is dielectric constant of the solvent, n is refractive index of the solvent”.

The orientation polarizability of solvent is calculated using the equation (2)

$$\Delta f = \left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n - 1} \right) \quad (2)$$

The Lippert-Mataga plot of imidazolium compound is depicted in Fig. 3, higher Stokes shift is observed in methanol whereas lower Stokes shift is observed in DMSO. Possibly methanol interacts greatly with the charge centre of the molecule affecting the electron excitation process significantly prompting a large Stokes shift.

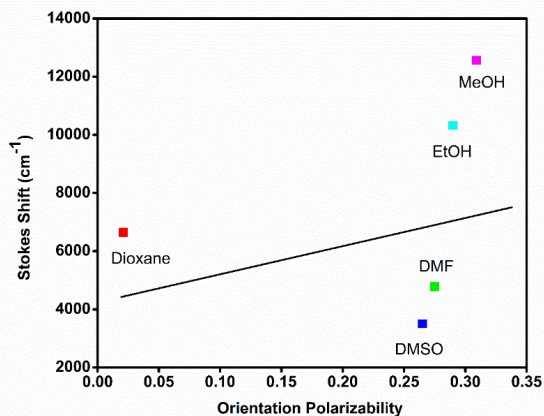


Fig. 3: LM plot of imidazolium compound.

The solvent polarity indicator scale $E_T(30)$ is seen to be effectively applicable to study the charge transfer in a compound. Plot of Stokes shift against $E_T(30)$ values of solvents is shown in Fig. 4, describes stabilization of ground state and

excited state of imidazolium compound by the different solvents as a function of polarities (Aggarwal, 2014; Kumar, 2011).

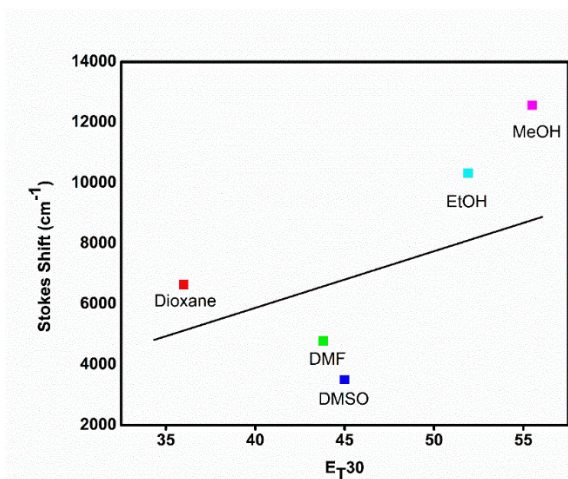


Fig. 4: Plot of Stokes shift of imidazolium compound Vs E_{T30} of different solvents.

D. Thermal Analysis: Thermal stability and phase behavior of synthesized imidazolium compound was investigated by differential scanning calorimetry and thermogravimetric analysis.

Thermogravimetric investigation was performed using a thermogravimetric analyser under inert nitrogen atmosphere. The thermal decomposition of the synthesized product was carried out as a function of temperature, the sample was heated at a rate of 10 °C per minute from 25 to 700 °C. The thermogravimetric analysis is shown in Fig. 5, the decomposition temperature was noted to be above 235 °C and $T_{10\%} = 275$ °C. The one step weight loss process observed in the TGA thermogram.

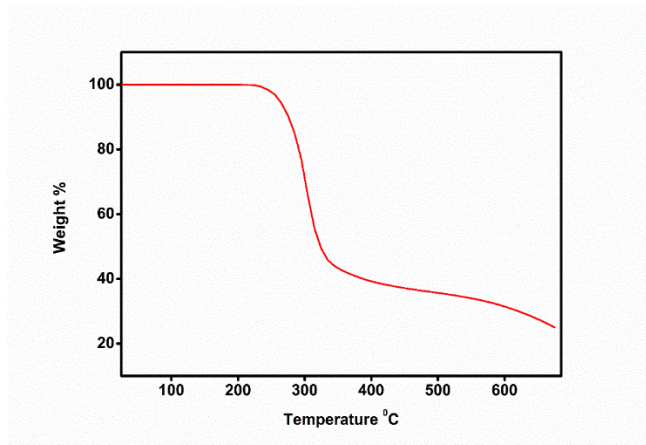


Fig. 5: Thermogram of imidazolium compound

Differential scanning calorimetry was carried out under nitrogen atmosphere with the heating rate of 10 deg min⁻¹. The thermogram displayed in Fig. 6. It was noted that increase in temperature results in endothermia and an exothermic peak

arises at about 245 °C due to decomposition of imidazolium compound.

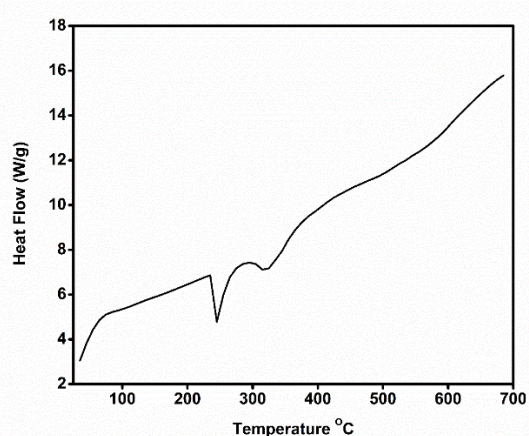


Fig. 6: DSC Thermogram for imidazolium compound

E. DFT Study:

The ground state and excited state molecular orbitals having electronic energies varying with electron density of imidazolium compound were computationally optimized by quantum chemical calculations using Gaussian 16 program [Aggrawal,2014; Patil, 2019; Patil, 2021) at DFT/TD-DFT-B3LYP and the corresponding optimized molecular geometries data are collected in Fig. 7. The highest occupied molecular orbital (HOMO) displays the electron density is mainly localized over the imidazolium ring, whereas in lowest unoccupied molecular orbital (LUMO) electron density appears to be localized over the naphthalene ring. The calculated energy of HOMO is found to be -0.18141 and energy of LUMO observed is 0.05357 , the data for chemical hardness and energy gap for imidazolium compound is summarized in Table 3.

Table 3: Calculated energy values with excited states of Imidazolium compound.

E_{LUMO}	0.05357
E_{HUMO}	-0.18141
Energy Gap (ΔE)	0.23498
Chemical Hardness (η)	0.11749

* The units for E_{HUMO} , E_{LUMO} and ΔE are expressed in 'Hartree'

DECLARATION OF INTEREST

The authors declare no conflict of interest.

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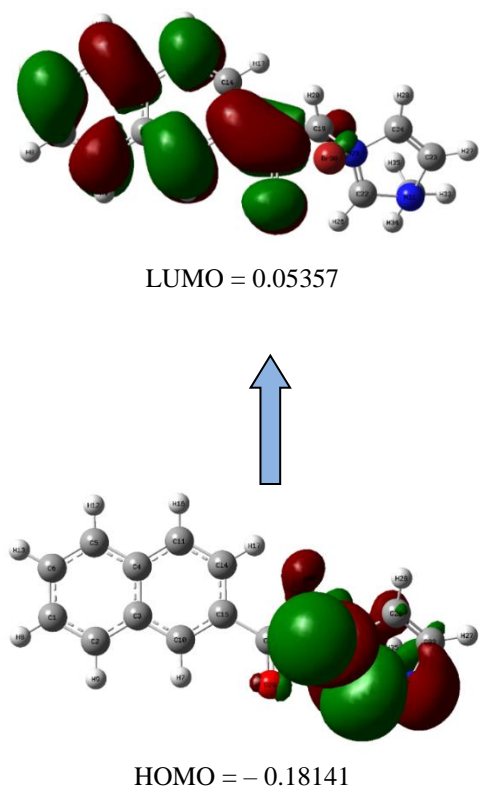


Fig. 7: Molecular orbitals of imidazolium compound determined by TD-DFT

IV. CONCLUSION

In current work, an expeditious microwave assisted synthetic pathway is developed for the synthesis of newer imidazolium-based ionic compound 3-(2-(3,4-dihydronaphthalen-2-yl)-2-oxoethyl)-1-methyl-1H-imidazol-3-ium bromide by greener approach. The synthesized imidazolium bromide was characterized by spectral, thermal properties, which confirms its structure. The solvent dependent optical properties were examined with a series of solvents having varying polarities. The effect of solvent on optical properties of predicted using Stokes shift against $E_T(30)$ parameter and Lippert Mataga plot. The Lippert Mataga plot of imidazolium compound with different solvent does not show linear behavior, which suggests the involvement of solute-solvent interactions, similarity observed with the plot of Stokes shift against $E_T(30)$. The theoretical study determined the HOMO and LUMO energies, which confirms that charge transfer occurs within the molecule.

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