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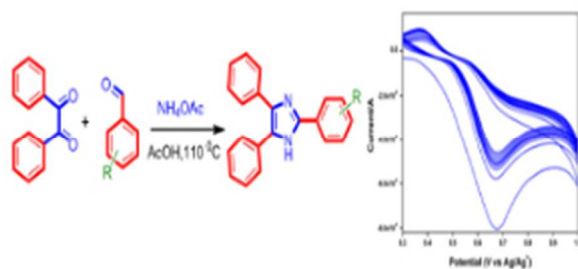


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ARTICLE TYPE

Synthesis and studies of electrochemical properties of lophine derivatives

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Abstract

A versatile series of Lophine (2,4,5-triphenyl-1H-imidazole) derivatives (1-13) were synthesized and characterized using melting point, Fourier transform infra red (FTIR), Liquid Chromatography-Mass Spectrometry (LC-MS), ^1H and ^{13}C Nuclear magnetic resonance (NMR) spectra. Their photophysical and electrochemical parameters were evaluated using Ultra violet-Visible (UV-Vis), Fluorescence spectrophotometric and cyclic voltammetric experiments. The optical band gap and quantum yield for the derivatives were in the range of 3.05-3.55 eV and 0.06 to 0.36 respectively. The HUMO-LUMO and associated energy gaps (E_g) calculated through cyclic voltammetric experiments were found to be in the range of 0.068 – 0.194 eV. Among them, the derivatives with electron donating groups such as $\text{N}(\text{Me})_2$, phenyl and methoxy efficiently facilitated the redox process when compared to lophine. The $\text{N}(\text{Me})_2$ was found to more effective because of the enhancement of electron density on nitrogen due to the electron donating ability of two methyl groups.

Introduction

The hetero aromatic push-pull system with various functional groups exhibits interesting chemical and physical properties. Introduction of various chromophores through extended π -conjugated molecules with readily polarizable hetero atoms and groups by facile synthetic route plays an important role in the area of optoelectronic, optical data storage and light emitting materials.¹ These push-pull systems which spring up by optimal Donor- π -Acceptor functional groups can effectively enhance the charge transfer ability and thereby find various newer applications as functional materials.²⁻⁵ The chemical nature including electronic effect of the substituent and molecular backbone plays a crucial role on their linear and non-linear optical properties.⁶ Recently, hetero aromatic π -conjugated molecules have been investigated in order to explore the charge transport properties for their effectiveness in the field of electronic devices.⁷ Further, these organic molecules are susceptible for structural modifications which in turn can alter the optical band gap, redox potentials and charge transport properties.⁸ Among the heterocyclic systems, imidazole derivatives have drawn considerable attraction because of their unique optical, thermal and electronic properties.⁹ Coupling of strong electron donating

groups and strong electron withdrawing moieties are commonly used to generate dipolar push-pull systems that feature low-energy and intense charge transfer absorption. Further, substitution of various electron donating/accepting groups to imidazole moiety increased polarisability, stability, and thermal and chemical robustness.¹⁰ Imidazole derivatives with various donor and acceptor groups are attractive blue-emitting materials.¹¹ Lophine (2,4,5-triphenyl-1H-imidazole) is a gorgeous fluorescent and chemiluminescent molecule with the property to emit yellow light on reaction with oxygen in the presence of strong base.¹² Derivatives of lophine are also known for efficient hole transportation¹³, enhancement of chemiluminescence¹⁴ and fluorescent chemosensing¹⁵. Moreover, the lophine derivatives can be tailored with various donor and acceptor groups on the phenyl ring present in the C-2, C-4 and C-5 positions of the imidazole ring. Tailoring the electronic nature of these derivatives by substitution of different electron donating and/or accepting functional groups or elongation of π -conjugation through these phenyl rings makes them promising candidates for light emitting applications.¹⁶ These modifications could also be used to modulate the band gap of the imidazole derivatives.¹⁷ The energy difference between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) often called band gap of the material must be quite small in order to achieve multi-functional material applications.¹⁸

Absorption/emission spectral studies reveal basic understanding about the photophysical properties including Stokes shift, quantum yield and optical band gap.¹⁹ Further, these imidazole

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derivatives exhibit halochromism and shown to have discrete color change on pH variation.²⁰ The absorption maxima (λ_{max}) increases with increase of pH.²¹ The protonation–deprotonation equilibria for donor/acceptor under varying pH conditions for imidazole derivatives have already been established.²²

So understanding the effect of substituents on imidazole moieties using its absorption/emission spectra and the effect of pH on the spectral characteristics would give more clear insight about the successive application in various fields including fluorescent labelling reagent²³ and fluorescent probes.²⁴ This has made the development of imidazole based functional material with improved transport properties by balanced injection of charges interesting. Hence in order to develop a material with these properties, the photo physical and electrochemical properties of lophine derivatives were studied by modifying the lophine with the electron donating and attracting groups at para-position of C-2 phenyl ring.

Results and discussion

Characterization

The structure of all the synthesized lophine and their derivatives (1-13) was ascertained using melting point (mp), Fourier transform-infrared spectra (FTIR), Liquid chromatography-Mass spectrometry (LC-MS), ¹H and ¹³C Nuclear magnetic resonance (NMR) spectral techniques. The results were in good agreement with the previous literature reports. FTIR spectra of all the derivatives showed four important characteristic stretching vibration bands. The band near 3440 cm⁻¹ to NH stretching, the band near 3100 cm⁻¹ to aromatic C-H stretching, the band near 1600 cm⁻¹ to aromatic C=C stretching and the band near 1500 cm⁻¹ to C=N stretching vibrations.²⁵ In order to determine the structure of all the synthesized products affirmatively, ¹H and ¹³C NMR spectral analysis was done. The NMR chemical shift of the N-H proton of imidazole ring was observed at around δ 12.80 ppm.²⁶ Further, the peaks in the range of δ 6.8-8.0 ppm were attributed to the C-2, C-4 and C-5 phenyl ring protons of imidazole moiety.²⁷ Due to the complex nature of NMR, the splitting pattern was not clear for these derivatives. In ¹³C NMR spectra, the peaks at around 120-140 ppm for the aromatic carbons of the derivatives and the peak above 140 ppm for C-2 carbon of imidazole ring confirmed all synthesized derivatives.²⁸ M+1 peak of LC-MS spectra also added evidence to the product formation.

2,4,5-triphenyl-1H-imidazole (1)

mp: 267-268 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3444, 3082, 1641, 1462; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 7.24-7.62 (m, 15H), 12.57 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 125.20, 126.52, 127.09, 127.78, 128.19, 128.26, 128.47, 128.66, 128.69, 130.36, 131.09, 135.18, 137.13, 145.52; LCMS: calculated 296.1, found 297.2 (M+1).

4-(4,5-diphenyl-1H-imidazol-2-yl)phenol (2)

mp: 232-233 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3448, 3178, 1641, 1240; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 6.86-8.31 (m, 14H), 9.75 (s, OH), 12.42 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 115.45, 121.67, 126.37, 126.89, 127.08, 127.40, 127.53, 128.16, 128.33, 128.62, 131.34, 135.44, 136.63, 146.12, 157.82; LCMS: calculated 312.1, found 313.2 (M+1).

2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole (3)

mp: 230-232 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3439, 1612, 1492, 1247; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 3.85 (s, 3H), 7.07-8.06 (m, 14H), 12.55 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 54.73, 113.62, 122.63, 125.95, 126.23, 126.58, 127.17, 127.70, 127.88, 128.17, 130.74, 134.82, 136.28, 145.16, 158.94; LCMS: calculated 326.1, found 327.2 (M+1).

2-(2,5-dichlorophenyl)-4,5-diphenyl-1H-imidazole (4)

mp: 223-225 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3415, 3174, 1448, 1398; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 7.36-8.32 (m, 13H), 12.77 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 127.37, 128.44, 129.72, 130.10, 130.57, 131.29, 131.73, 132.05, 142.02; LCMS: calculated 364.0, found 365.1 (M+1).

4,5-diphenyl-2-p-tolyl-1H-imidazole (5)

mp: 233-235 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3446, 3176, 1629, 1492, 1400; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 2.38 (s, 3H), 7.26-7.6 (m, 12H), 8.04 (m, 2H), 12.67 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 20.90, 125.21, 126.46, 127.11, 127.67, 127.74, 127.97, 128.18, 128.42, 128.62, 129.26, 131.20, 135.30, 136.98, 137.68, 145.74; LCMS: calculated 310.0, found 311.1 (M+1).

2-(3,4-dimethoxyphenyl)-4,5-diphenyl-1H-imidazole (6)

mp: 215-216 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3417, 3132, 1496, 1253; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 3.85-3.89 (s, 6H), 7.09-7.71 (m, 13H), 12.60 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 55.54, 55.59, 108.82, 111.82, 117.94, 123.20, 127.09, 127.76, 145.70, 148.80, 149.07; LCMS: calculated 356.1, found 357.2 (M+1).

2-(3-nitrophenyl)-4,5-diphenyl-1H-imidazole (7)

mp: 264-265 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3435, 1541, 1521, 1348; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 7.37-8.52 (m, 13H), 8.96 (s, 1H), 13.11 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 119.4, 122.61, 127.21, 128.49, 130.43, 131.18, 131.83, 143.39, 148.36; LCMS: calculated 341.1, found 342.2 (M+1).

2-(4-fluorophenyl)-4,5-diphenyl-1H-imidazole (8)

mp: 190-192 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3441, 3132, 1492, 1400; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 7.26-8.15 (m, 14H), 12.73 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 115.54, 115.76, 126.54, 126.98, 127.01, 127.04, 127.27, 127.35, 127.79, 128.18, 128.23, 128.39, 128.66, 131.01, 135.08, 137.05, 144.68, 160.89, 163.33; LCMS: calculated 314.1, found 315.2 (M+1).

2-(4-chlorophenyl)-4,5-diphenyl-1H-imidazole (9)

mp: 263-265 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3417, 3130, 1485, 1402; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 7.25-8.12 (m, 14H), 12.80 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 126.81, 127.05, 127.86, 128.23, 128.39, 128.64, 128.76, 129.16, 130.87, 132.72, 134.96, 137.24, 144.40; LCMS: calculated 330.0, found 331.1 (M+1).

2-(4-bromophenyl)-4,5-diphenyl-1H-imidazole (10)

mp: 247-248 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3417, 3136, 1483, 1402; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 7.35-8.05 (m, 14H), 12.80 (s, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 121.38, 127.09, 128.42, 129.52, 131.66, 144.46; LCMS: calculated 374.0, found 375.0 (M+1).

4-(4,5-diphenyl-1H-imidazol-2-yl)-N,N-dimethylaniline (11)

mp: 256-258 °C; IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3446, 3132, 1508, 1406, 1361; ¹H NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 3.00 (s, 6H), 6.82-7.95 (m, 14H), 12.03-12.35 (b, NH); ¹³C NMR (400 MHz, DMSO-*d*₆): δ_{ppm} 111.92, 118.24, 126.32, 126.87, 127.70, 128.37, 146.47, 150.28; LCMS: calculated 339.17, found 340.3 (M+1).

2-(biphenyl-4-yl)-4,5-diphenyl-1H-imidazole (12)

mp: 229-230 °C; IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3468, 3132, 1485, 1400; ^1H NMR (400 MHz, DMSO- d_6): δ_{ppm} 7.23-8.32 (m, 19H), 12.76 (b, NH); ^{13}C NMR (400 MHz, DMSO- d_6): δ_{ppm} 125.72, 126.54, 126.88, 127.09, 127.60, 127.78, 128.19, 128.39, 128.44, 128.65, 128.97, 129.37, 131.04, 135.16, 137.29, 139.48, 139.66, 145.21; LCMS: calculated 372.2, found 373.3 (M+1).

1,4-bis(4,5-diphenyl-1H-imidazol-2-yl)benzene (13)

mp: 232-235 °C; IR (KBr tablet) $\nu_{\max}/\text{cm}^{-1}$: 3500, 1637, 1402; ^1H NMR (400 MHz, DMSO- d_6): δ_{ppm} 7.23-8.18 (m, 24H) 12.75 (s, NH); ^{13}C NMR (400 MHz, DMSO- d_6): δ_{ppm} 125.37, 126.58, 127.09, 127.82, 128.19, 128.40, 128.66, 130.98, 135.10, 145.14; LCMS: calculated 514.1, found 515.2 (M+1).

Absorption and emission spectra

Fig. 1 shows the absorption spectra of lophine and its derivatives in *N,N*-dimethylformamide (DMF) solution. Absorption maxima (λ_{\max}), molar absorptivity coefficient (ϵ) and optical band gap (E_{opt}) for all derivatives (1-13) are presented in the table 1. Highly aromatic substituted molecules such as lophine act as efficient π -conjugated system. This type of extended π -conjugated molecules exhibit charge transfer processes, which play vital role in order to achieve newer electronic applications. The Charge transfer ability of these molecules could be modified by substituting suitable donor and/or acceptor substituents.¹⁶ The blue or red shift will be based on the nature of the substituents in the π -conjugated system.²⁹ Further, the π -electron delocalization due to either effective donor/acceptor group or efficient π -conjugation resulted in a red shifted peak when compared with parent molecule in their absorption pattern.¹⁰

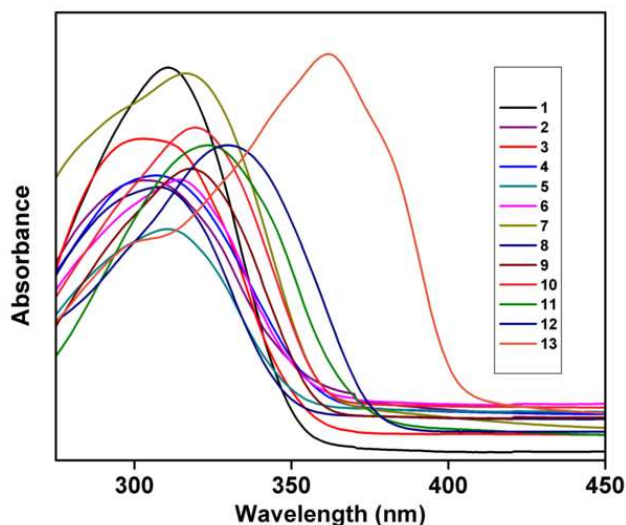


Fig. 1 Absorption spectra of lophine derivatives

The absorption maximum of all these derivatives lies in the range of 300-361 nm.³⁰ The planarity and dependence of polarizing ability of substituents were clearly shown by absorption patterns of these synthesized lophine derivatives.¹⁰ Moreover, the derivatives with substituents such as CH_3 , Cl, Br, $\text{N}(\text{Me})_2$, Ph, NO_2 , and 3,4-dimethoxy groups showed red shift whereas F, OH, OMe, and 2,5-dichloro showed a slight blue shift in the absorption spectrum. This behaviour could be due to the charge transfer ability from benzene ring to the imidazole controlled by

the substituent.⁹ Derivatives substituted with Cl and Br showed red shift but fluorine substituted derivative showed blue shift. This might be due to the mesomeric effect (electron donating) of the fluorine atom substituted at the para-position.³¹ Further, the ortho substituted chlorine atom disturbed the planarity between the benzene ring and imidazole in 2,5-dichloro substituted derivative.¹⁰ The derivatives containing substituent such as $\text{N}(\text{Me})_2$, phenyl and NO_2 showed large red shift with enhanced intensity and the extended π -conjugation in bis-imidazole derivative (13) showed red shift with higher molar extinction coefficient.³²

Table 1 Physical properties of lophine derivatives 1-13.

Compound	λ_{\max} (nm)	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	E_{opt}^{\S} (eV)	$\lambda(\text{em})_{\max}^{\P}$ (nm)	Stokes shift (cm^{-1})	$\Phi_{\text{f}}^{\Upsilon}$
Lophine	311	32890	3.53	390	6513	0.27
4-OH	303	32500	3.49	406	8373	0.28
4-OMe	304	38080	3.51	401	7957	0.23
2,5-Dichloro	307	33160	3.45	338	2988	0.06
4-F	308	31590	3.55	393	7022	0.17
4-Me	311	25970	3.49	395	6838	0.40
3- NO_2	313	34500	3.46	340	2537	0.04
3,4-(OMe) ₂	314	32500	3.47	403	7034	0.27
4-Cl	317	34000	3.47	389	5839	0.28
4-Br	319	39570	3.45	343	2193	0.05
4- $\text{N}(\text{Me})_2$	323	37190	3.34	452	8836	0.15
4-Ph	338	37200	3.29	416	5547	0.36
Bis	361	49420	3.08	425	4171	0.29

^{\S} E_{opt} = optical band gap derived from the onset wavelength of the UV-vis absorption spectra.

^{\P} molecules are excited at their respective absorption maximum

^{\Upsilon} fluorescence quantum yield were measured using lophine as standard

Effect of pH

The effect of pH on the absorption spectra of all the derivatives in DMF was studied in order to understand the influence of pH on the charge transport behaviour of these derivatives. All the derivatives showed halochromic behaviour at different pH in DMF. Further, all derivatives showed significant shift when the pH was lowered from 7 to 1 but no significant shift was observed when the pH was increased from 7-14. The results are summarized in table 2. The λ_{\max} of lophine shifted from 311 nm to 295 nm with reduced absorption intensity when the pH was decreased from 7 to 1. The isobestic point was observed at 285 nm. These observations clearly indicated the formation of protonated lophine with the decrease in pH. Protonation occurred at the N-3 position of imidazole ring when the pH was lowered, as shown in Fig .2.²²

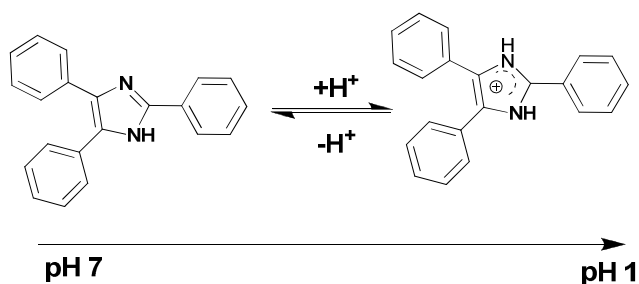


Fig. 2 Protonation of lophine with decrease in pH

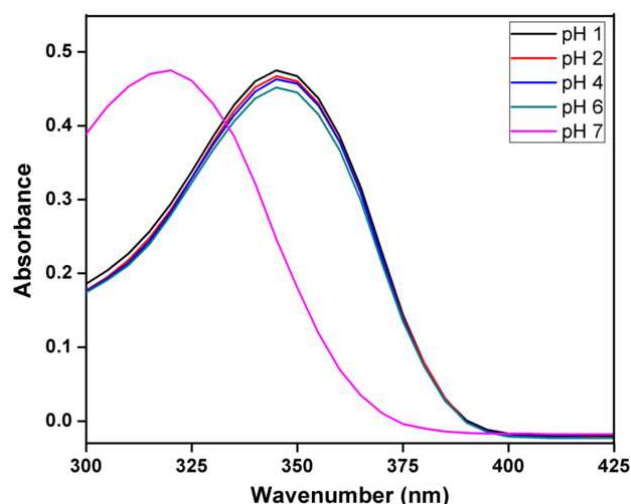


Fig. 3 Absorption spectra of (11) at different pH

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The protonation at imidazole ring may be attributed to the shift in the $\lambda_{(\max)}$ of the absorption spectrum. The electron donation ability of N-3 of imidazole ring can be greatly influenced by the substituent present at the C-2 phenyl ring. As a consequence, the various electron donating and accepting groups could cause significant shift when compared to lophine in their absorption spectra. Derivatives with substituents such as 2,5-dichloro, CH_3 , 3,4-dimethoxy, NO_2 , Cl, F and Ph showed blue shift, with the decrease in pH from 7–1. The derivatives with substituents such as OH, OMe and highly conjugated bis-imidazole showed very slight red shift with decreased absorption intensity with reduction from 7 to 1. This might be due to the less pronounced conjugation between these substituent bearing phenyl ring and protonated imidazole ring. The $\text{N}(\text{Me})_2$ group imparted good electron donating ability to N-3 of imidazole and showed larger red shift. Moreover, the $\lambda_{(\max)}$ of $\text{N}(\text{Me})_2$ substituted lophine (11) showed red shift from 323 nm to 345 nm with decrease in pH from 7 to 1. The isobestic point was observed at 333 nm. Further, the absorption intensity of that derivative increased with a decrease in pH from 7 to 1 as shown in the Fig. 3. The bromine substituted lophine also showed significant red shift compared with chlorine and fluorine due to its lower electronegativity. These observations clearly indicated the influence of substituents present at C-2 phenyl ring of imidazole moiety and the pH on charge transfer.

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Table 2 Halochromic behaviour of lophine derivatives 1-13

Compound	$\lambda_{(\max)}$ (Absorbance (arb.units))				
	pH 7	pH 6	pH 4	pH 2	pH 1
Lophine	311 (0.288)	310 (0.252)	310 (0.251)	310 (0.251)	310 (0.251)
4-OH	303 (0.353)	305 (0.345)	305 (0.339)	305 (0.335)	305 (0.326)
4-OMe	304 (0.384)	305 (0.383)	305 (0.382)	305 (0.382)	305 (0.382)
2,5-Dichloro	307 (0.310)	297 (0.286)	297 (0.286)	297 (0.286)	297 (0.286)
4-F	308 (0.315)	305 (0.309)	305 (0.309)	305 (0.309)	305 (0.309)
4-Me	311 (0.259)	304 (0.257)	304 (0.256)	304 (0.254)	304 (0.254)
3- NO_2	313 (0.396)	311 (0.382)	311 (0.368)	311 (0.368)	311 (0.368)
3,4-(OMe) ₂	314 (0.366)	310 (0.346)	310 (0.342)	310 (0.342)	310 (0.342)
4-Cl	317 (0.285)	305 (0.257)	305 (0.256)	305 (0.254)	305 (0.254)
4-Br	319 (0.394)	317 (0.336)	317 (0.333)	317 (0.333)	317 (0.333)
4- $\text{N}(\text{Me})_2$	323 (0.473)	345 (0.451)	345 (0.462)	345 (0.467)	345 (0.475)
4-Ph	338 (0.355)	320 (0.343)	320 (0.342)	320 (0.341)	320 (0.331)
Bis	361 (0.526)	364 (0.418)	364 (0.411)	364 (0.410)	364 (0.398)

The optical band gap corresponds to the formation of Frenkel exciton with the electron and hole in the same molecule or a charge transfer exciton with the electron and hole with adjacent molecules.³³ Extended π -conjugation and the nature of substituents could affect the optical band gap.³⁴ The difference in the band gap value compared with lophine clearly showed the donor-acceptor effect of the substituent, which destabilized the HOMO and LUMO levels. The optical band gap determined by the absorption edge of the solution spectra was found to be in the range of 3.08 to 3.54 eV given in table 1. Among the substituents investigated, strongly electron donating $\text{N}(\text{Me})_2$ group showed much lower optical band gap in **11**. The blue shifted optical band gap value for **12** and **13** could be due to the extended π -conjugation.¹⁰ Further the optical band gap value clearly indicated lophine materials can be used as potential candidates in the optoelectronic applications.³⁵

The emission band maxima, $\lambda_{(\text{em})\max}$, the Stokes shift along with fluorescence quantum yield of lophine and its derivatives are summarized in table 1. The normalized emission spectra of derivatives **1-13** were measured in dimethyl sulfoxide (DMSO) solution (Fig. 4), and the characteristic band in the blue region (386-452 nm) was observed.³⁰ Further, the value of emission wavelength (table 1) clearly evidenced that the substituents greatly influenced the fluorescence property of lophine

derivatives. The reason for this behavior might be due to the charge transfer from benzene ring to imidazole ring. The materials emitted blue light. The lophine derivatives exhibited red shift in emission spectra relative to parent lophine except **4**, **7** and **10**. Among the derivatives, **11-13** showed higher red shift value. The exhibited fluorescence in these derivatives might be due to the resonance effect between the phenyl ring and the imidazole ring. This red shift could be due to the substituent on the phenyl ring that carried the unshared pair of electron and delocalized π -electrons in the ground state.

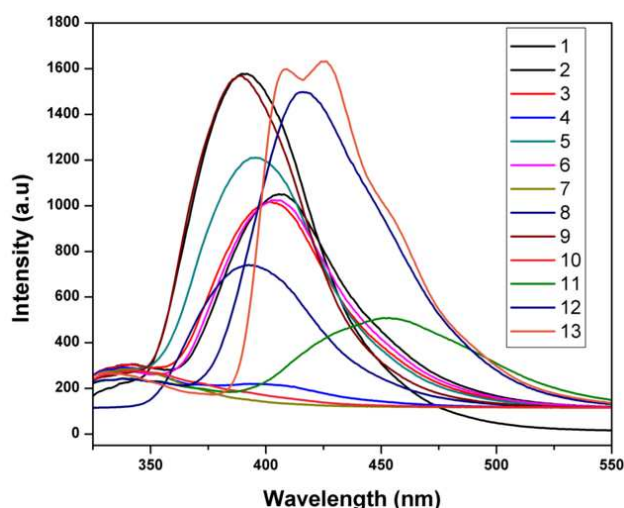


Fig. 4 Emission spectra of lophine derivatives

The effect of extended conjugation was also observed in the fluorescence quantum yield (Φ_f). The derivative **11** showed higher Stokes shift relative to others. Derivative **11**, with $N(Me)_2$ group possessed higher red shift compared to the highly π -conjugated **12** and **13** too. This might be due to the electron donating ability of them.²² Derivatives **5** and **12** with electron donating substituent such as CH_3 and Ph also exhibited higher Φ_f value compared to highly π -conjugated **13**. Fluorescence quantum yield (Φ_f) for all the synthesized derivatives was measured and compared with lophine as a reference (Φ_f of 0.27 in methanol).³⁰ Quantum yield Φ_f was calculated by the formula,

$$\Phi_f = \Phi_{std} (I/I_{std}) (A/A_{std}) (\eta/\eta_{std})^2$$

Where, Φ_f and Φ_{std} are the fluorescence quantum yield of the sample and standard, I and I_{std} are the integrated emission intensities of the sample and standard. A and A_{std} are the absorbance of the sample and standard, η and η_{std} are the refractive indices of the solution.³⁶ Derivative with substituents such as $N(Me)_2$ and OH showed larger Stokes shift. The larger Stokes shift indicated the structural reorganization of the nucleus after the conformational changes resulted due to the emission.³⁷ The low Stokes shift in derivatives **4**, **7**, **12** and **13** might be due to the distortion in the planarity. In the halogen substituted derivatives, the Stokes shift exhibited the trend $F > Cl > Br$. This phenomenon may be due to the increase in atomic weight of the substituents.³⁸ From the results it was clearly evident that the lophine molecule could be effectively used as versatile fluorescent materials with extended π -conjugation without affecting its planarity.

Cyclic voltammetry

Electronic structures (HOMO and LUMO) of the lophine derivatives were characterized by Cyclic voltammetry (CV) at a scan rate of 20 mV s^{-1} . Further, from the oxidation (E_{ox}) and reduction (E_{re}) potential, the HOMO and the LUMO energy levels were calculated using the relationship $E_{HOMO} = -(E_{ox} + 4.4)$ and $E_{LUMO} = -(E_{re} + 4.4)$ respectively.³⁹ All the synthesized lophine derivatives exhibited stable and consistent voltammograms indicating the stability of the compounds as depicted from Fig. 5. All the derivatives of lophine showed one electron reversible redox process. It can be seen from table 3 that all the lophine derivatives (**1-13**) were oxidized in the potential range of 0.505 to 0.702 V and got reduced in the potential range of 0.572 to 0.821 V. The impact of various substituents on the electrochemical properties of lophine derivative was evaluated (Table 3) by the variation in E_{ox} and E_{re} value. Lophine derivatives possessing OH (**2**), OMe (**3**), $N(Me)_2$ (**11**) and Ph (**12**) exhibit low oxidation potential value when compared to parent lophine. This trend evidently showed that the oxidation process was efficiently facilitated by electron-donating group $N(Me)_2$ (**11**) when compared to other group such as CH_3 (**5**) and Ph (**12**). Moreover, these **2**, **3** and **11** derivatives showed red shifted peak in their absorption spectra when pH was lowered from 7-1. Fluoro substituted derivatives showed a different trend compared to chloro and bromo substituted derivatives. This could be due to the anomalous behaviour of fluorine. Fluorine atom as a substituent exhibit both inductive effect (electron-withdrawing) and mesomeric effect (electron-donating). Inductive effect will have the same influence at any position, where as mesomeric effect will be dominant over inductive effect when fluorine atom is present at para-position.³²

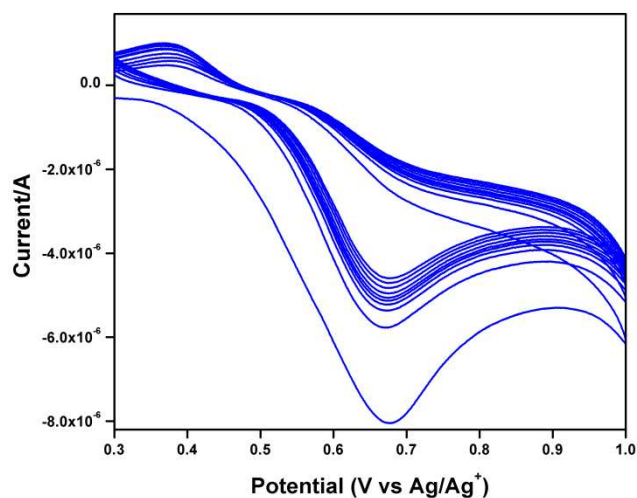


Fig. 5 Cyclic voltammograms of 2-(4-methoxyphenyl)-4,5-diphenyl-1H-imidazole (**3**)

In the redox processes, $N(Me)_2$ (**11**) and Ph (**12**) substituted derivatives efficiently facilitated the reduction. The extensively π -conjugated bis-imidazole (**13**) had minimal impact on redox process. This behavior was observed on the HOMO-LUMO level too, where the lophine and its various derivatives differed much on their E_{gap} value.

The E_{gap} value was found to depend mainly on the charge transport ability or the promotion of electron or hole in organic

molecules. Here in the lophine derivatives, the charge transport ability lies on the imidazole ring and so the substitution in the aromatic ring could make predominant impact on it. From the E_{gap} value, it was evident that the substituent present on the phenyl ring could play a vital role on the charge transport ability of the lophine. Among the derivatives, the lophine substituted with $\text{N}(\text{Me})_2$ (**11**) and Ph (**12**) showed significant impact on the charge transport phenomena.

Table 3 Electrochemical properties of lophine derivatives

Compound	E_{ox}^{\S} (V)	E_{re}^{\S} (V)	HOMO [†] (eV)	LUMO [†] (eV)	E_{g}^{\ddagger} (eV)
Lophine	0.544	0.738	5.344	5.538	0.194
4-OH	0.516	0.643	5.316	5.443	0.127
4-OMe	0.553	0.674	5.353	5.474	0.121
2,5-Dichloro	0.680	0.762	5.480	5.562	0.082
4-F	0.587	0.727	5.387	5.527	0.140
4-Me	0.576	0.700	5.376	5.500	0.124
3-NO ₂	0.654	0.788	5.454	5.588	0.134
3,4-(OMe) ₂	0.538	0.686	5.338	5.486	0.148
4-Cl	0.604	0.712	5.404	5.512	0.108
4-Br	0.600	0.717	5.400	5.517	0.117
4-N(Me) ₂	0.505	0.572	5.305	5.372	0.068
4-Ph	0.537	0.624	5.337	5.424	0.087
Bis	0.702	0.821	5.502	5.621	0.119

[§] redox potentials with reference to the ferrocene, which is used as an internal standard.

[†] HOMO = $E_{\text{ox}} + 4.4$ and LUMO = $E_{\text{re}} + 4.4$

[‡] $E_{\text{g}} = \text{HOMO-LUMO}$

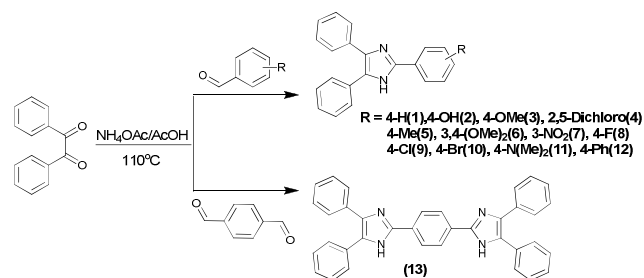
Experimental

Materials

Benzil, substituted aldehydes, ammonium acetate and solvents were purchased from Aldrich and S.D.fine chemicals and used as received. Thin-layer chromatography (TLC) was conducted on aluminium sheets coated with silica gel 60 F obtained from Merck, with visualization by UV lamp (254 or 360 nm). Melting points were measured on a Büchi B-540 melting-point apparatus in open capillaries and are uncorrected. ¹H and ¹³C NMR spectra were recorded with a Bruker AVANCE 400 MHz instrument at 25°C. Chemical shifts are reported in ppm relative to the signal trimethylsilane. Apparent resonance multiplicities are described as s (singlet), br (broad), m (multiplet) and NH (secondary amine). LC-MS were recorded in Agilent 6420 Triple quadrupole LC-MS instrument. FTIR spectra were recorded in Perkin-Elmer Spectrum-1 instrument with freshly dried KBr pellets in the range between 4000-400 cm⁻¹. Ultra violet-visible spectroscopy (UV-Vis) was analyzed using JASCO V-670 UV-VIS Spectrophotometer. Emission spectra were measured using a Perkin-Elmer LS 50-B spectro-fluorimeter. For absorption and

emission measurements, the sample concentration was maintained at 10⁻³ M. Spectroscopic grade solvents were used for spectral measurement, without further purification. CV was conducted in DMSO medium in presence of 0.1M Bu₄NPF₆ (Tetrabutylammonium hexafluorophosphate) with the use of a three-electrode cell in which a glassy carbon electrode as a working electrode, a platinum wire as an auxiliary electrode and Ag/AgCl as reference electrode was used.

General procedure for synthesis of lophine derivatives



Scheme 1 Synthesis of lophine derivatives (**1-13**)

In a round-bottomed flask, Benzil (1 mmol), suitable benzaldehyde (1 mmol), and ammonium acetate (7 mmol) were taken in boiling glacial acetic acid (16 ml) and refluxed for 5-6 h. The completion of the reaction was monitored by TLC. After completion of the reaction, crude mixture was poured into ice-cooled water and neutralized with sodium bicarbonate to give a precipitate. The precipitate was washed with water and recrystallized using suitable solvents such as methanol and ethanol. The expected products were obtained in 80–90% yield.⁴⁰

Conclusion

Lophine derivatives with different electron donating accepting groups in the para-position of C-2 phenyl ring were synthesized, and their photo physical properties were studied. These electron donor/acceptor substituted lophine derivatives and their characteristic absorption and emission spectra showed that their electronic nature was greatly influenced by their π -extension and substituent. Moreover, from the electrochemical properties it was clear that the HOMO-LUMO energy level could be engineered by the extension of π -conjugation. Further, $\text{N}(\text{CH}_3)_2$ and Ph substituted lophine derivatives showed higher absorption value and calculated quantum yield. These results confirm that the synthesized imidazole derivatives could also be used as luminescent materials.

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