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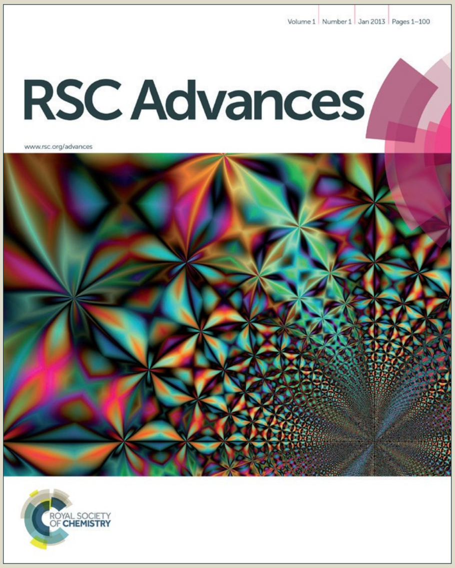

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Synthesis, Photophysical and Electrochemical Studies of Acridone-Amine based Donor-Acceptors for Hole Transport Materials

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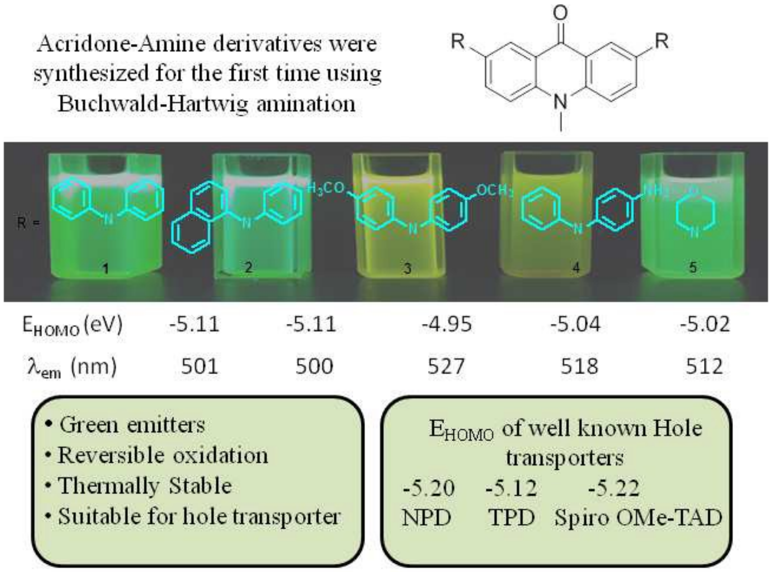


Abstract: A series of new donor-acceptor molecules based on acridone-amine containing four aryl substituted 2,7-diaminoacridones**(1-4)** and morphololine substituted acridone compounds **(5)** were synthesized in good yields using palladium catalysed Buchwald-Hartwig C-N amination. Their absorption, photoluminescence and electrochemical properties were investigated in solution and in thin films. Photophysical properties were found to be affected by electron donating capability of substituents on diaryl amines. Absorption showed an intramolecular charge transfer transitions (ICT) in a range of 447-479 nm. These acridone amine derivatives emit in green region (500-527 nm). Reversible oxidation wave were observed for compounds **1-5** in cyclic voltammetry. The HOMO (-4.95 to -5.11 eV) and LUMO (-2.36 to -2.56 eV) energy levels of **1-5** were calculated. The E_{HOMO} for compounds **1-5** are similar with the most widely used hole transporting materials **NPD**, **TPD** and **spiro-OMe-TAD**. Hence we believe that these compounds are having potential to be used as hole transporting materials in optoelectronic devices.

Introduction

Development of active materials for organic electronics is highly active field of research powered by the exciting applications inorganic light emitting devices (OLEDs), organic field effect transistors (OFETs), solar cells, solid state detectors etc.[1] Although soluble conjugated polymers remain a major class of organic materials for solution-processed electronic devices, recent years have seen the upcoming of small molecules in applications owing to their obvious advantages in well defined structures, ease of purification, reliable reproducibility and better solubility in most of the organic solvents.[2]Depending on the structure-properties relationship, small molecules also offer the control on photophysical and electrochemical properties by having various electron donating or withdrawing substituents.[3]Low molecular weight, simple structure and good overall synthetic yield present the advantage to be processable from solutions or by thermal evaporation under vacuum. It has been shown recently that interesting photovoltaic performances can be obtained with donor-acceptor molecules having triphenylamine (TPA) as donor unit. Donor-Acceptor (D/A) design approach facilitates intramolecular charge transfer in the molecule leading to smaller HOMO-LUMO energy band gap[4].Choice of suitable D/A unit could allow the simultaneous control of photophysical and electrochemical properties of such systems.[5] A variety of molecules based on donor-acceptor are available which emits in the visible region, including blue,[6] green,[7] yellow,[8] and red[9]. Bipolar molecules can accept and transport both holes and electrons along with good emission for applications in OLEDs. Many donor-acceptor molecules derived from electron-deficient and electron-rich units such as borane/amine,[10] quinoxaline/fluorine,[11] triazole/amine,[12] bathophenanthrooline/amine,[13] benzimidazole/amine[14] and oxadiazole/carbazole[15] have been synthesized for their possible applications in electroluminescent devices. Acridone derivatives also have attracted a lot of research attention because of their successful biological applications as antimicoribial[16a] fungicidal[16a] agents, anticancer,[16b] anti-inflammatory,[16c] chemosensor[16d] etc. Some of these acridone derivatives are shown in Figure 1.

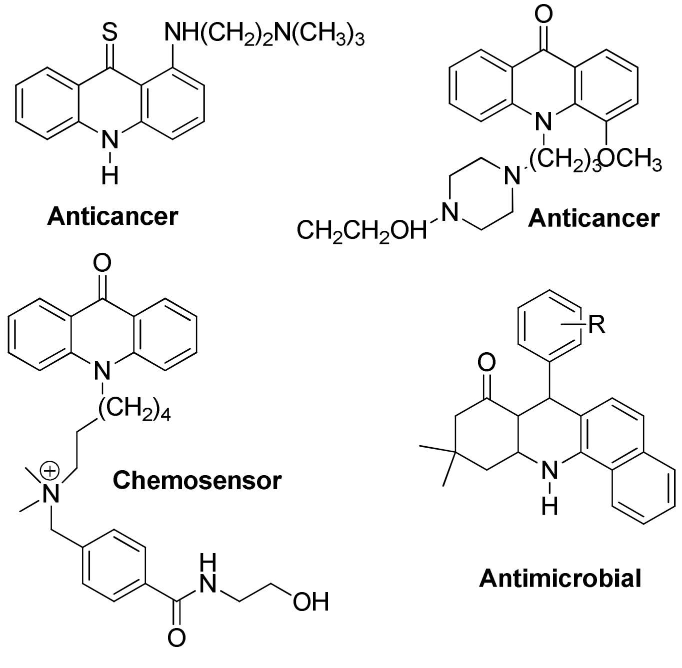


Figure 1: Biologically active acridone derivatives

Recently, acridone derivatives found applications in organic electronics. Nitrogen substituted triarylamines acridone derivatives,[17] 2,7-organosilane acridone,[18a] acridonediyneplatinum(II) complexes[18b] and quinacridone derivatives[18c] were synthesized and used as host materials for phosphorescent dopants and as well as emitting materials in OLEDs (Figure 2). To the best of our knowledge, substitution of groups affecting electronic properties of acridone, at 2,7- positions are very rare and have not been studied extensively.[19]

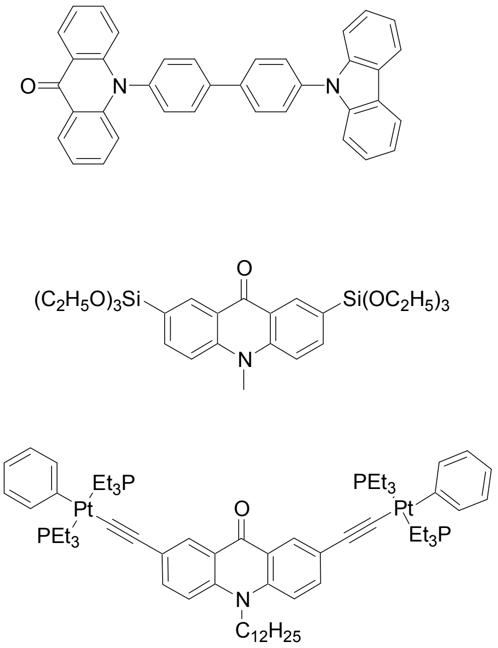


Figure 2: Literature reported acridone derivatives used in optoelectronic devices

There is no report on the synthesis and studies of 2,7-diarylamino acridone. Herein we report the synthesis of 2,7-diarylamine substituted acridone derivatives, **1-4** and morpholine substituted acridone derivative **5** (Figure 3) and study their photophysical, electrochemical and thermal properties for their possible applications in organic electronic devices. Morpholine amine was used to see the effect of rigid cyclic aliphatic amines on the properties of acridone. The design of triarylamines based acridone derivatives is mainly based on the considerations that triarylamine derivatives are well known hole transporting materials and acridone is selected for its known electron injection/transporting abilities due to the presence of the electron-withdrawing carbonyl group.[17] Further the incorporation of arylamines at 2,7-positions of acridone are expected to affect the electronic properties effectively.

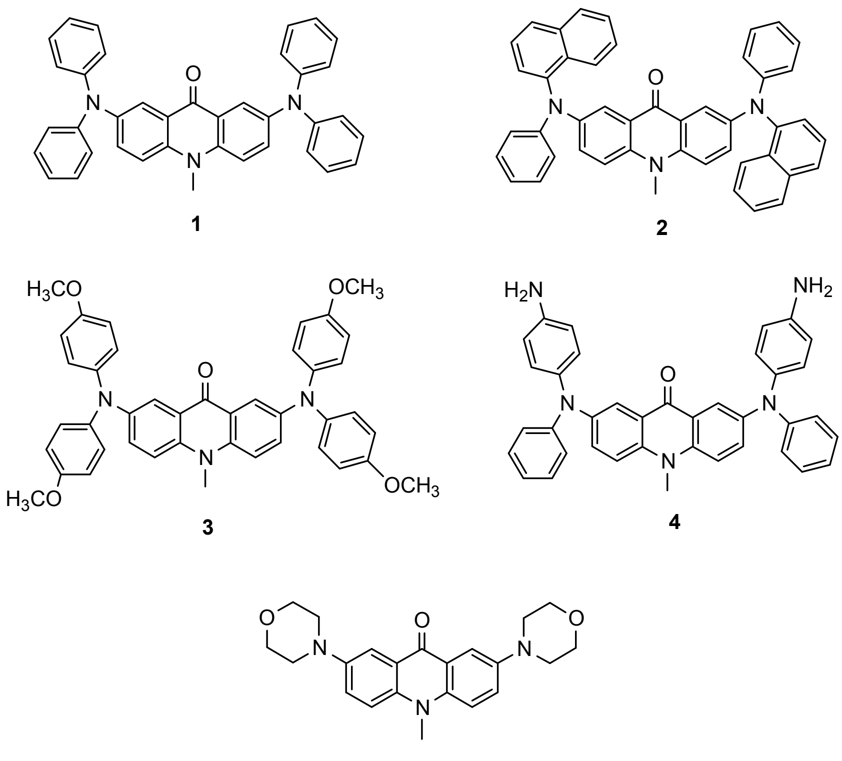
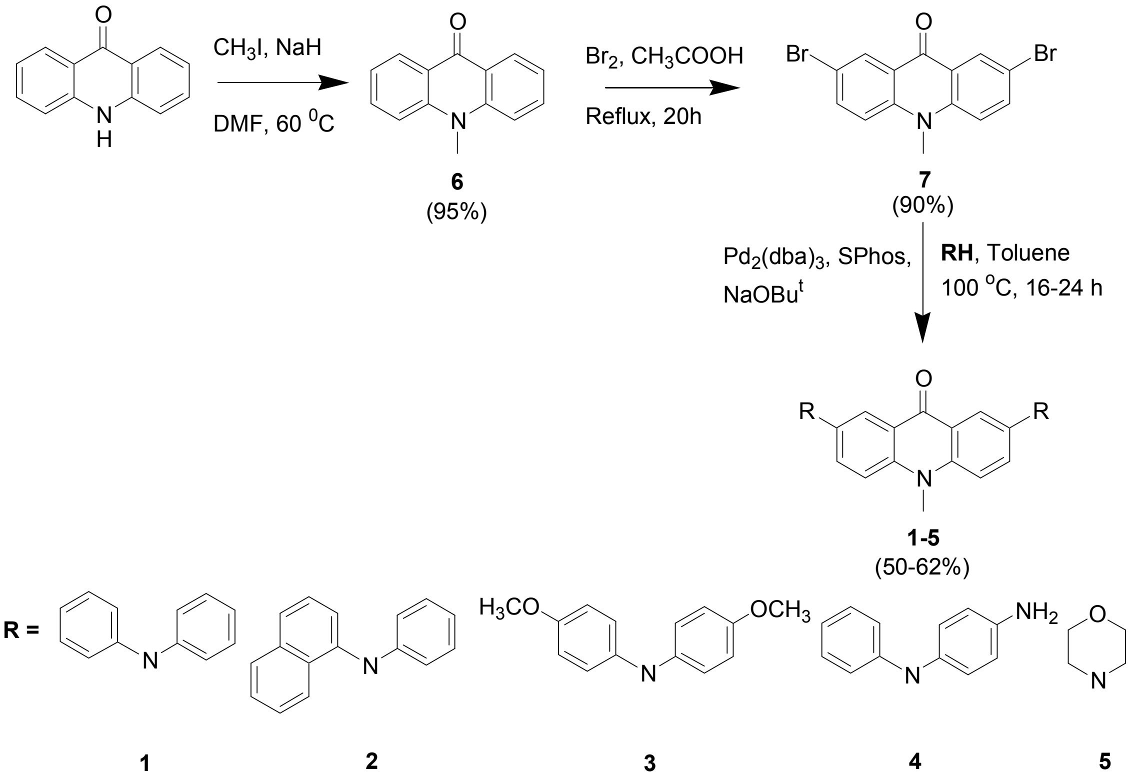


Figure 3: 2,7-Diamine substituted acridone derivatives **1-5.**

Results and discussion

The synthesis of the target compounds,**1-5** is shown in Scheme 1. The building block, 2,7-dibromo-10-methyl acridone was synthesized in two steps. The 9(10*H*)-acridone possesses a low solubility in most of the organic solvents while N-methylation of acridone increases the solubility effectively, therefore 9(10*H*)-acridone was first methylated using methyliodide and sodium hydride as a base to get 10-methylacridone **(6)**. Further, bromination of **6** was carried out with molecular bromine in acetic acid at reflux temperature to get the desired 2,7-dibromo-10-methyl acridone **(7)** in overall 85% yield for these two steps. Acridone derivatives **1-5** were synthesized by Buchwald-Hartwig coupling[20] reaction of different diarylamines with 2,7-dibromo-10-methylacridone **(7)** in the presence of a palladium catalyst, co-ligand and strong base. The $Pd_2(dba)_3$ (5-8 mol%), was used as the source of palladium catalyst. The SPhos (2-dicyclohexylphoshpino-2´,6´-dimethylbiphenyl), XPhos **(**2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl**)** and DPPF (1,1'-bis(diphenylphosphino)ferrocene) were tried as co-ligands with bases such as sodium *t*-butoxide, potassium *t*-butoxide and potassium phosphate however the best results were obtained with SPhos and sodium *t*-butoxide along with palladium catalyst. Further it was observed that the yield of the reaction was significantly affected by the substituent attached to the diarylamines. Amines with electron-donating groups like $-OCH_3$ and $-NH_2$ were resulted in better yield compared to electron-withdrawing groups like Br, CN etc. It is worth to mention that no coupling reaction was observed when rigid polycyclic heteroamines such as phenothiazine, phenoxazine and carbazole were used in this reaction. The five target compounds were obtained in 50-62 % yield as yellow to orange solids. Compounds **1-5** (except **4**) showed good solubility in common organic solvents *e.g.* ~ 20 mg/ml in dichloromethane and chloroform.



Scheme 1: Synthesis of acridone-amine derivatives **1-5**

The identity and purity of all new compounds were confirmed by several characterization methods such as ^{1}H-NMR, ^{13}C-NMR, MALDI mass, FTIR, elemental analysis etc. Figure 4 shows the ^{1}H-NMR and ^{13}C-NMR of 2,7-bis(anisylamino)-10-methylacridone **(3)** in $CDCl_{3.}$ A singlet of two hydrogens at 1,8-positions appeared at 8.04 ppm and shows the symmetric nature of molecule. A multiplet of four protons at ~7.41 ppm is assigned for acridone hydrogens at -3,6 and -4,5 positions. 4-Methoxyphenyl hydrogens appeared at 7.00 and 6.81 ppm. The presence of a singlet at 3.83 ppm indicates the N-methyl and four methoxy groups are shown at 3.77 ppm in compound **3**. A characteristic signal for carbonyl group was observed 176 ppm in ^{13}C-NMR. N-methyl and methoxy carbons appeared at 33 and 55 ppm respectively. All other peaks observed in ^{13}C-NMR spectrum can be assigned to aromatic carbons.

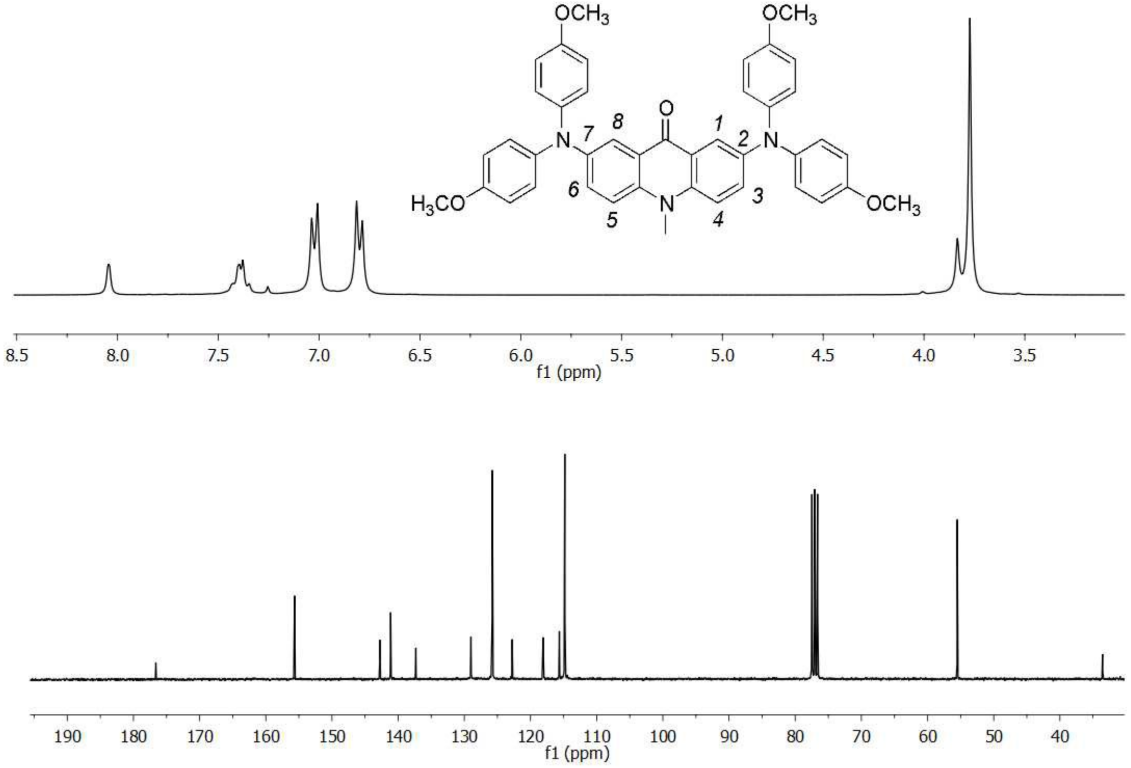


Figure 4:^{1}H-NMR (above) and ^{13}C-NMR (below) of compound **3** recorded in $CDCl_3$

Absorption and fluorescence properties of compounds **1-5** were studied in various solvents and as neat solid film. The photophysical data for compounds **1-5** is summarized in Table 1. The absorption spectra of compounds **1-5**,in toluene and in neat solid films, are shown in Figure 5. The 10-methylacridone (**6**) shows two absorption maxima at 376 and 396 nm due to π-π^*transition. **1-5** showed absorption at 303-342 nm showing a blue shift of ~ 30-65 nm as compared high energy transition of **6**. The π-π^* transitions were found at ~348-391 nm in **1-5**. However, this transition was weak in compound **5** where aliphatic substituent, morpholine, was used. All these new acridone derivatives showed a broad feature with relatively low molar absorption coefficient in further lower energy region (~ 447-479 nm).

This band is assigned to the transitions based on the intramolecular charge transfer transitions originating from electron-donating, arylamines in **1-4** and morpholine in **5,** to electron-withdrawing acridone core. A set of solvents of different polarity was used to study the effect of solvents polarity on photophysical properties of **1-5** and were correlated with their donor-acceptor architecture. Compounds **1-5** showed blue shift in the absorption peaks in ethylacetate due to possible H-bonding of acridone derivatives with solvent molecules. Charge transfer band showed a bathochromic shift in **1-5** with increase of solvent polarity. Absorption of compounds **1-3** and **5** in neat solid films was observed in a range of ~450-500 nm. The red shift observed in thin film absorption maxima along with broadening of peaks suggests the intermolecular aggregation in these acridone derivatives.

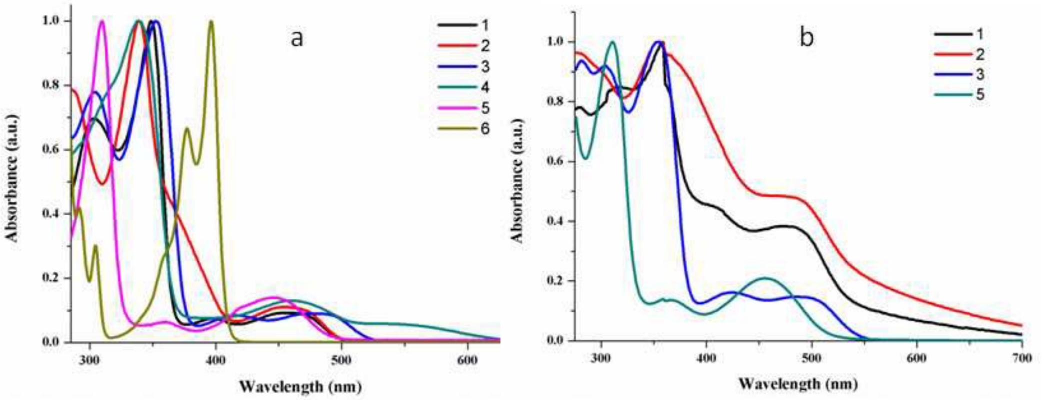


Figure 5: Absorption spectra of acridone derivatives in (a) toluene and (b) neat solid film.

Compounds **1-5** showed emission in green region with emission maxima in range of 500-527 nm (Figure 6) in toluene. A red shift of ~ 65-90 nm was observed for **1-5** as compare to unsubstituted 10-methylacridone, **6** (445 nm). Considerable Stokes shifts of about 50 nm were observed for **1-5** which suggest the change in the ground and excited state geometry.

We believe that a large change in the dipole moment is a result of intramolecular charge transfer from donor to acceptor moieties in compounds **1-5**. The Stokes shift were further increased in the more polar solvents which suggests the charge transfer complex formation in **1-5** and interaction with the polar solvents (see supporting information Table 1). The lone pair of electrons in non-bonding orbitals of amines interacts strongly with polar solvents which may lead to the stabilization of polarized molecules in the excited state by polar solvent. The emission of compounds **1-3** and **5** (540-586 nm) in the neat solid film were bathochromically shifted (upto ~60 nm) as compared to emission in toluene. It may be due to intermolecular aggregations of molecule in the solid state.[21] Compound **4** could not be used in thin film absorption and emission studies as it did not produce uniform neat solid films due to poor solubility in common organic solvents.

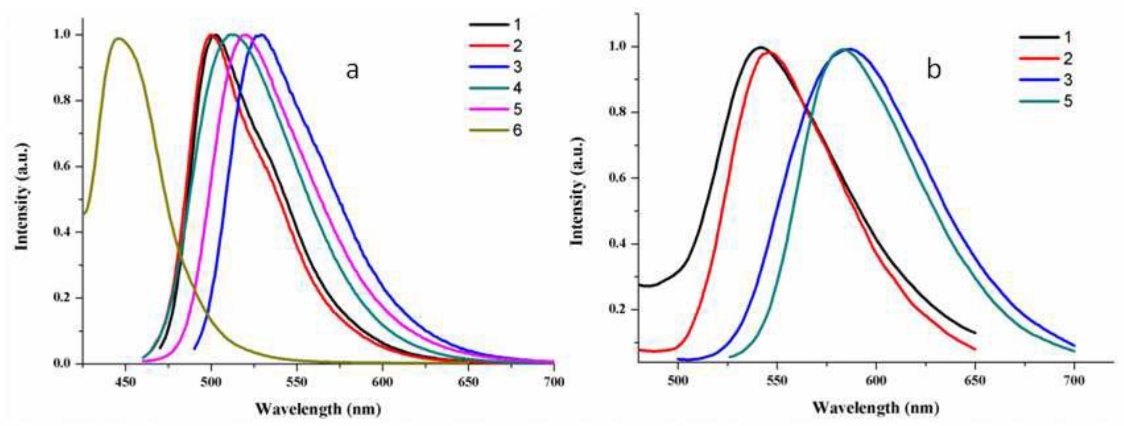


Figure 6: Emission spectra of **1-5** in (a) toluene and (b) neat solid films.

Table 1: Photophysical data of compounds **1-5** in toluene and thin film

Comp	**$\lambda_{abs}{}^{a}$,nm (log $\varepsilon_{max}$$M^{-1}cm^{-1}$)^{a}**	**$\lambda_{em}{}^{a}$, nm**	**Stokes shift^{a}, nm**	**$\Phi_F{}^{b}$**	**$\lambda_{abs}{}^{c}$,nm**	**$\lambda_{em}{}^{c}$, nm**	**$E_g{}^{d}$ eV**
1	303 (5.52), 348 (5.67), 397 (4.54), 458 (4.65)	501	43	0.41	358, 407, 477	540	2.41
2	338 (5.40), 360 (5.06), 459 (4.45)	500	41	0.19	354, 479	545	2.50
3	303 (5.55), 351 (5.66), 415 (4.60), 479 (4.61)	527	48	0.10	303, 353, 423, 494	586	2.32
4	342 (5.69), 391 (4.55), 462 (4.68)	518	56	0.01	-	-	-
5	310 (5.07), 358 (3.83), 447 (4.22)	512	65	0.25	311, 364, 456	583	2.31

^{a}in toluene, ^{b}Quantum yield with reference to Fluorescein (Φ =0.79 in ethanol, ^{c}in neat solid film, ^{d}optical band gap estimated using emission and excitation spectra in neat solid film form.

The quantum yields of **1-5** were calculated using Fluoresceine (Φ = 0.79 in ethanol) as reference and are tabulated in table 1. Quantum yields were found to be dependent on the electron-donating nature of diarylamine at 2,7-positions. Substitution of strong electron-donating amine resulted in decrease in quantum yield. Compounds **1-5** showed red shift of emission maxima and low quantum yields with increasing polarity of solvents (See Table 1, supporting information). It can be explained according to energy gap law, which says, excited state internal conversion efficiency and fluorescence is reduced with a decrease in energy gap between ground and excited states. Fluorescence life time for compounds **1-5** were measured on TCSPC and are summarized in supporting information. All the compounds show a double-exponential decay. A short lifetime (1-2 ns) combined with a longer lifetime (10 ns) components are observed. Interestingly, the short/long fluorescence lifetimes composition seems to follow a trend related to the energy distribution of the emission spectrum.

Compounds **1-5** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) to get an insight on the redox properties and molecular orbital energy levels (HOMO and LUMO). Thus, the electrochemical properties obtained by CV measurements are reported in Table 2 and cyclic voltammogram for compound **1** is shown in Figure 7. Cyclic voltammetry of 10-methyl acridone (**6**) showed an irreversible oxidation wave at 1.55 V whereas two reversible oxidation peaks were obtained for compounds **1-5**. Oxidation at lower potential (0.71 to 0.91 V) is assigned for the oxidation of peripheral amines while other at higher potential (1.02 to1.78 V) is attributed to oxidation of 10-methylacridone core. Additional peak at 0.58 and 0.66 V were observed in **3** and **5** respectively and these were assigned to the oxidation of aliphatic methoxy and morpholine groups. First oxidation potentials decrease with the increasing electron donating ability of substituents in **1-5**. Compounds **1-5** did not show substantial changes in the peak potential even after repeated scans, revealing that compounds **1-5** are electrochemically stable during these oxidation conditions. None of these compounds showed electrochemical reduction and decomposition of compounds was observed, which was visible by change in color (dark brown) near the working electrode during negative scan hence no reduction wave was observed. The energy levels of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) were calculated from first oxidation potential and optical band gap and are found in the range of-4.95 to -5.11 eV and -2.36 to -2.56 eV, respectively.

Table 2: Electrochemical and thermal data of compounds **1-5**:

Comp	(V)[a]	E_{HOMO} (eV)[b]	E_{LUMO} (eV)[c]	T_m (°C)[d]	T_d (°C)[e]
1	0.74, 1.02	-5.11	-2.56	170	391
2	0.73, 1.05	-5.11	-2.56	240	428
3	0.58, 0.78, 1.24	-4.95	-2.51	178	402
4	0.71, 1.42	-5.04	-2.49	198	302
5	0.66, 0.91, 1.78	-5.02	-2.36	217	345

[a]oxidation peak potential, [b]E_{HOMO} = - (E_{ox} *w.r.t. Fc/Fc*$^+$+ 4.8) eV, [c] E_{LUMO} = E_{HOMO}-optical band gap, [d] Melting points, [e]decomposition temperature obtained from the onset of TGA.

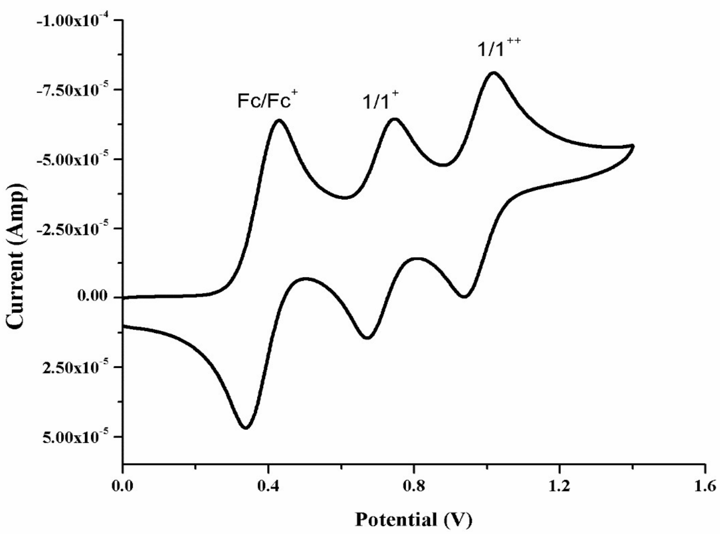


Figure 7: Cyclic voltammogram of compound **1** and ferrocene (**Fc)** in acetonitrile.

To know the thermal stabilty of compounds **1-5** they were subjected for the thermal gravimetric analysis (TGA). Thermograms of **1-5** are given in supporting information. Melting points of **1-5** were recorded using capillary method and were observed in the range of 170-240 °C. Decomposition temperature for these compounds were calculated using the onset of weight loss in TGA. **1-5** showed no decomposition in the range of their melting points. It was found that these compounds are thermally stable and decompose > 300 °C. These decomposition temperatures are much higher than the usually used hole transporting materials.[15,22b]

The E_{HOMO} for compounds **1-5** are similar to that of most widely used hole transporting material **NPD** (*N,N′*-Di(1-naphthyl)-*N,N′*-diphenyl-(1,1′-biphenyl)-4,4′-diamine), **TPD** (*N,N′*-Bis(3-methylphenyl)-*N,N′*-diphenylbenzidineand **spiro-OMe-TAD** (2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene.[22] Electrochemical (HOMO energy levels) properties along with thermal stability of these compounds are promising which make these acridone derivatives suitable for hole transporter for OLEDs.

Figure 8 shows the schematic representation of energy levels of **1-5** along with well known and widely used hole transporters **NPD**, **TPD** and **spiro-OMe-TAD**. We further believe that these compounds may show better stability in solid state devices as the oxidation of these compounds are reversible as observed in cyclic voltammetry. The combination of the hole-transporting arylamine moiety and the electron-transporting acridone in **1-5** may provide bipolar charge transport property.

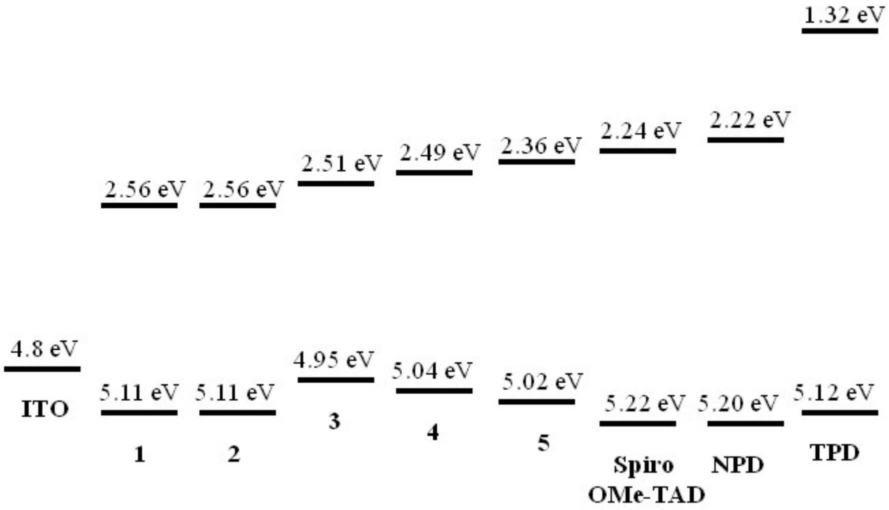


Figure 8: Schematic representation of HOMO and LUMO energy levels of **1-5**, **spiro-OMe-TAD**, **NPD** and **TPD**

Conclusions

Five new acridone/amine derivatives were synthesized in good yield under mild conditions using palladium-catalyzed Buchwald-Hartwig amination. These compounds were characterized by several spectroscopic methods and their photophysical and electrochemical properties were studied in solution and thin films. It was observed that the absorption, emission and electrochemical properties of these new compounds were affected by the electro-donative nature of the peripheral diarylamine substituents. All compounds were found to emit in the green region (500-527 nm) in toluene. A broad absorption band was observed on substitution of aryl amines on acridone which was attributed to charge transfer transitions from the electron donating peripheral arylamine to electron acceptor acridone. Electrochemical studies reveal the stability of these compounds under oxidative conditions. The HOMO energy levels of these compounds are found in the range of -4.95 to -5.11 V which is very similar with well known hole transporter eg. **NPD**, **TPD** and **spiro-OMe-TAD**. The combination of the hole-transporting arylamine moiety and the electron-transporting acridone in **1-5** may provide bipolar charge transport property. Electrochemical properties along with thermal stability of these compounds are promising which make these acridone derivatives suitable hole transporter for OLEDs. We further believe that these compounds may show better stability in solid state devices owing to their reversible oxidation potentials.

Experimental

General

All the reagents were purchased from commercial sources (Sigma Aldrich and Alfa Aesar) and were used without any further purification. The organic solvents were of analytical or spectroscopic grade and were dried and freshly distilled using the standard procedures whenever anhydrous solvents were required. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (75 MHz) spectra were recorded on a Bruker Avance II 300 MHz Ultrashield spectrometer with tetramethylsilane (TMS) as internal reference and residual $CHCl_3$ in $CDCl_3$ as reference. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier 91579. Mass spectrometric measurements were recorded using MALDI-TOF (Bruker). Melting points of the products were determined by open capillary method. Elemental analyses were obtained on Elemental Analyser-EURO Vector Italy EA-3000. Cyclic voltammetry and differential pulse voltammetry were carried out on a computer controlled (CH instruments, 620D). Typically, a three electrode cell equipped with a glassy carbon working electrode, Ag/AgCl (non–aqueous) reference electrode and platinum (Pt) wire as counter electrode were employed. The measurements were carried at room temperature in anhydrous acetonitrile with tetrabutyl ammonium hexafluorophosphate solution (0.1 M) as supporting electrolyte with a scan rate of 100 mVs^{-1}. The potential of Ag/AgCl reference electrode was calibrated by using ferrocene/ferrocenium redox couple. Absorption and fluorescence data were acquired using ~2 X 10^{-6} M solutions of **1-5**. UV-Visible spectra were recorded on SHIMADZU U.V–A114548 and fluorescence studies were done on Horiba Flurolog 3 at room temperature. The fluorescence quantum yields (Φ_F) were calculated relative to Fluorescein (Φ_F = 0.79 in 0.1 M H_2SO_4. Fluorescence life times were recorded on time correlated single photon counter (TCSPC). The neat solid films of compounds **1-5** were prepared by using spin coater (Holmarc HO-TH-05) at 1000 rpm for 2 min using ~6 mg/mL of sample in chloroform. Quartz substrate was used for neat solid film studies. Thermal studies were performed on Star^e system Mettler Toledo TGA 1 with a heating rate of 10 $^{\circ}$C/min under inert atmosphere.

Synthesis

*10-Methylacridone, (**6**).***10**-Methylacridone (**6**) was synthesized according to the reported procedures.[18a] To a mixture of 9(10H)-acridone (6.00 g, 30.7 mmol) in anhydrous DMF (240 mL) was added NaH (3.07 g, 60% oil dispersion, 76.7 mmol) at 0°C. The reaction temperature was raised slowly to room temperature and later mixture was stirred at 60 °C. After for 30 min, iodomethane (4.80 ml, 77.0 mmol) was added, and stirring was continued at 60 °C for 18 h. The reaction mixture was quenched by slow addition of H_2O. The resulting solid obtained by vacuum filtration was washed thoroughly with ethanol to give title compound **6** as light-yellow solid (5.77 g, 95%). M.P. 205 °C; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 3.82 (3H, s, CH_3), 7.24 (2H, t, *J = 7.1* Hz, aromatic), 7.47 (d, 2H, *J = 8.7*

*Hz,*aromatic), 7.67 (2H, d, *J = 8.7 Hz*, aromatic), 8.53 (2H, d, *J = 8.01 Hz,* aromatic); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 33.57, 114.73, 121.20, 122.42, 127.66, 133.76, 142.49, 178.04.

2,7-Dibromo-10-methylacridone, (7). Molecular bromine (31 g, 0.19 mol) was added drop-wise over 20 min to a solution of 10-methylacridone (5 g, 25.5 mmol) in acetic acid (45 ml). The solution was stirred continuously and heated at reflux temperature for 20 h, after which half of the solvent was removed by vacuum distillation. The reaction mixture was allowed to cool and then poured over crushed ice to obtain the yellow colored solid. The resulting solid was filtered and collected and washed with sodium bicarbonate solution and further treated with 20% aqueous solution of sodium bisulfate. The obtained solid was then dried under vacuum and purified using column chromatography to afford the title compound as yellow solid (7.85 g, 90%).^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 3.87 (3H, s, CH_3), 7.42 (2H, d, *J = 9.18 Hz*, aromatic), 7.80 (2H, d , *J = 9.15 Hz*, aromatic), 8.62 (2H, s, aromatic); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 34.02, 115.13, 116.91, 123.69, 130.22, 136.88, 141.20, 178.28.

General method for the synthesis of compound 1-5:

In a three necked round bottom flask equipped with reflux condenser and argon inlet and outlet ports, 2,7-dibromo-10-methylacridone (1.0 mmol) and diarylamine (2.2 mmol) were dissolved in anhydrous toluene (20 ml) under argon atmosphere. The palladium catalyst [$Pd_2(dba)_3$] (5-8 mol%), 2-dicyclohexylphoshpino-2′,6′-dimethylbiphenyl (SPhos) (10-15mol%) and sodium-t-butoxide (3.1 mol) were added to the reaction mixture. The reaction mixture was thoroughly stirred under argon atmosphere while the temperature was slowly raised to 100 ^{0}C. Reaction Mixture was stirred at this temperature for 12-24 hr. Reaction mixture was cooled to room temperature and extracted with chloroform (3 x 50 ml) followed by water wash (3 x 50 ml). All organic layers were combined and dried over anhydrous Na_2SO_4 and evaporated to get the crude product which was further purified by silica gel column chromatography.

*2,7-Bis-(N,N-diphenylamino)-10-methylacridone, (**1**).* A mixture of 2,7-dibromo-10-methylacridone (0.37 g, 1 mmol) and diphenylamine (0.37 g, 2.2 mmol) were reacted in toluene as mentioned in general method. The crude solid thus obtained was purified by column chromatography using hexane / chloroform to obtain a bright yellow solid. Yield: 0.28 g (52%);mp 170°C; FTIR (KBr, ν/cm^{-1}): 692.79, 746.31, 1172.65, 1270.99, 1294.73, 1481.69, 1583.91, 3033.31:^{1}H-NMR (300 MHz, $CDCl_3$, δ ppm): 3.90 (3H, s,CH_3), 6.99 (4 H, t, *J = 6.1* Hz, aromatic), 7.07 (8H, d, *J= 7.0*Hz, aromatic), 7.23 (8H, t, *J= 6.1*Hz, aromatic), 7.45 (2H, d, *J = 7.7*Hz, aromatic), 7.53 (2H, d, *J = 5.35*Hz, aromatic), 8.23 (s, 2H, aromatic); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 30.90, 116.17, 121.79, 122.75, 123.05, 123.72, 126.17, 129.32, 130.23, 131.54, 141.60, 176.20; MALDI-TOF: Mass calcd for $C_{38}H_{29}N_3O$ [M$^+$]: 543.66; found: 543.75; Anal. Calcd. for$C_{38}H_{29}N_3O$: C, 83.95; H, 5.38, N, 7.73.Found : C, 84.28; H, 5.32; N, 7.68.

*2,7-Bis-(N-naphthyl-N-phenylamino)-10-methylacridone (**2**).* A mixture of 2,7-dibromo-10-methylacridone (0.36 g, 1 mmol) and N-naphthyl-N-phenyl amine (0.48 g, 2 mmol) were reacted in toluene as mentioned in general method. The crude solid thus obtained was purified by column chromatography using chloroform to obtain a bright yellow solid. Yield: 0.33 g (50%); M.P. 240°C; FTIR (KBr,ν/cm^{-1}): 693.71, 748.09, 1174.97, 1273.18, 1484.09, 1592.99, 2970.41, 3038.73; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 3.78 (3H, s, CH_3), 6.91

(2H, t, *J = 7.2*Hz, aromatic), 6.98 (4H, d, *J = 7.7*Hz, aromatic), 7.16 (4H, t, *J = 7.4*Hz, aromatic), 7.29-7.48 (14H, m, aromatic), 7.74 (2H, d, *J = 8.1* Hz, aromatic), 7.86 (2H, d, *J = 8.1* Hz, aromatic), 7.94 (2H, d, *J = 8.4* Hz, aromatic); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 29.70, 115.86, 119.19, 121.02, 121.53, 122.82, 124.12, 126.11, 126.38, 126.60, 127.14, 128.46, 129.19, 129.52, 131.10, 135.39, 137.87, 142.37, 143.27, 148.50, 176.70; MALDI-TOF: Mass calcd. for $C_{44}H_{33}N_3O$ [M^+]: 643.77; found: 644.11:Anal. Calcd. for$C_{44}H_{33}N_3O$: C, 85.82; H, 5.17; N, 6.53. Found : C, 86.12, H, 5.23, N, 6.49.

*2,7-Bis-(N,N-dianisylamino)-10-methylacridone, (**3**).* A mixture of 2,7-dibromo–10–methylacridone (0.36 g, 1 mmol) and 4,4`methoxydiphenyl amine (0.50 g, 2 mmol) were reacted in toluene as mentioned in general method. The crude solid thus obtained was purified by column chromatography using hexane / chloroform to obtain a bright orange solid. Yield: 0.38 g (58%); M.P. 178 °C; FTIR (KBr, ν/cm^{-1}:): 721.11, 808.08, 1029.65, 1172.27, 1234.21, 1499.72, 1593.89, 2832.08, 2928.79; ^{1}H-NMR (300 MHz, $CDCl_3$, δ, ppm): 3.77 (12H, s, OCH_3), 3.83 (3H, s, OCH_3), 6.79 (8H, d, *J = 8.7 Hz*, aromatic), 7.02 (8H, d, *J = 8.4 Hz*, aromatic), 7.34-7.42 (4H, m, aromatic), 8.04 (2H, s, aromatic); ^{13}C-NMR (75 MHz, $CDCl_3$, δ, ppm): 33.56, 55.51, 114.81, 115.63, 118.09, 127.76, 125.76, 129.00, 137.33, 141.12, 142.75, 155.65, 176.61; MALDI-TOF: Mass calcd for $C_{42}H_{37}N_3O_5$ [M^+]: 663.76; found: 663.79; Anal. Calcd. for$C_{42}H_{37}N_3O_5$: C, 76.00; H, 5.62; N, 6.33.Found: C, 76.33, H; 5.74; N, 6.43.

*2,7-Bis-(N-(p-aminobenzene),N-phenylamino)-10-methylacridone (**4**).* A mixture of 2,7-dibromo-10-methylacridone (0.36 mg, 1 mmol) and N-phenyl-*p*-phenylenediamine (0.40 g, 2.2 mmol) were reacted in toluene as mentioned in general method. The crude solid thus obtained was purified by column chromatography using chloroform / ethylacetate as solvent to obtain a bright orange solid. Yield: 0.32 g (56%); M.P. 217 $^{\circ}$C; FTIR (KBr, ν/cm^{-1}): 690.67, 743.52, 804.56, 1175.16, 1224.62, 1286.89, 1489.49, 1519.86, 1589.36, 2922.97, 3022.18, 3289.46, 3391.34; ^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm): could not be obtained because of very poor solubility; MALDI-TOF: Mass calcd. for $C_{38}H_{31}N_5O$ [M$^+$]: 573.69; found: 573.78; Anal. Calcd. for$C_{38}H_{31}N_5O$: C, 79.56; H, 5.45; N, 12.21.Found: C, 79.83; H, 5.51; N, 12.31.

*2,7-Bis-(morpholino)-10-methylacridone, (**5**).* A mixture of 2,7-dibromo–10–methylacridone (0.36 g, 1 mmol) and morpholine (0.19 g, 2.2 mmol) were reacted in toluene as mentioned in general method. The crude solid thus obtained was purified by column chromatography using chloroform to obtain a bright yellow solid. Yield: 0.24 g (62%); M.P. 198 $^{\circ}$C; FTIR (KBr ν/cm^{-1}): 636.97, 726.17, 793.32, 908.81, 1114.03, 1210.84, 1264.28, 1495.94, 1586.24, 2855.94, 2964.48, 3055.22; ^{1}H-NMR (300 MHz, CDCl$_3$, δ, ppm): 3.25 (8H, t, J = *4.7*Hz, NCH$_2$), 3.86 (3H, s, CH$_3$), 3.91 (8H, t, J = *4.8 Hz,*OCH$_2$), 7.36-7.43 (4H, m, aromatic), 7.97 (2H, d, J = *2.7 Hz*, aromatic); ^{13}C-NMR (75 MHz, CDCl$_3$, δ, ppm): 33.44, 49.96, 66.91, 111.22, 115.82, 122.38, 124.41, 136.82, 145.50, 177.17; MALDI-TOF: Mass calcd for $C_{22}H_{25}N_3O_3$ [M$^+$]: 379.45; found: 379.54; Anal. Calcd. for$C_{22}H_{25}N_3O_3$: C, 69.64; H, 6.64; N, 11.07.Found: C, 69.95; H, 6.71; N, 10.92.

Supporting information: ^{1}H-NMR, ^{13}C-NMR, MALDI mass, FTIR, absorbance and emission spectra in different solvents, fluorescence life times and decay profiles, cyclic voltammograms, thermograms etc. are provided in supporting information.

Acknowledgement

BKS and AS thank the University Grant Commission, India for research fellowships. We thank the Micro-Analytical Laboratory, Department of Chemistry, University of Mumbai and UM-DAE, Centre for Excellence in Basic Sciences, Mumbai for providing instrumentation facility. We also thank the Bhabha Atomic Research Centre, Mumbai for TCSPC and Tata Institute of Fundamental Research, Mumbai for MALDI-TOF facilities.

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