J. Chem. Sci. © Indian Academy of Sciences.
DOI 10.1007/s12039-015-0973-0

Synthesis, photophysical, electrochemical and thermal investigation of Triarylamines based on 9*H*-Xanthen-9-one: Yellow–green fluorescent materials

BHARAT K SHARMA, AZAM M SHAIKH and RAJESH M KAMBLE*
Department of Chemistry, University of Mumbai, Santacruz (East), Mumbai 400 098, India
e-mail: kamblerm@chem.mu.ac.in

MS received 14 April 2015; revised 7 September 2015; accepted 18 September 2015

Abstract. Triarylamines containing 9*H*−Xanthen−9−one core and aromatic units such as phenyl, naphthyl and p−methoxyphenyl were synthesized by employing palladium catalyzed C−N bond forming amination reaction in good yields. The photophysical studies revealed that the absorption and emission spectra are influenced by the nature of the peripheral amines. The photoemission spectra can be readily tuned in the range 483–532 nm (solution) and 525–576 nm (film) displaying green or yellow emission (film) depending on the nature of the amine segment with optical band gaps in the range 2.52–2.75 eV (film). The ionization potential and electron affinity were found to be in the range 5.332–5.686 eV and 2.705–2.776 eV, respectively. Thermal studies revealed that the synthesized compounds have good thermal stability with 5% and 10% weight loss at temperature ranging from 260–330°C and 340–370°C, respectively.

Keywords. Triarylamines; 9*H*−Xanthen−9−one; Palladium−catalyzed aryl amination; Yellow−Green florescent materials.

1. Introduction

Organic semiconductors have received considerable attention during the last few decades because of fundamental curiosity about their electro-optical properties and technological applications. Organic π−conjugated molecules have been explored for their application as organic light emitting diodes (OLEDs),[1] organic field effect transistors (OFETs)[2] and dye-sensitized solar cells.[3] Since the breakthrough work by Tang and VanSlyke[4] in 1987, OLEDs appear to be the display devices in future. Donor−acceptor (D−A) molecules have recently attracted considerable attention as electroluminescent multifunctional materials for OLEDs.[5] Molecules containing electron−donating amino groups have been found to exhibit interesting charge−transporting properties in electroluminescent devices.[6] Triarylamines-based rigid polyaromatic chromophores such as anthracene,[7] fluorene,[8] pyrene,[9] carbazole,[10] dibenzothiophene,[11] etc., have been utilized in electronic devices with dual functions, i.e., hole transporting and fluorescent characteristics especially in OLEDs.

The electroluminescence (EL) from such D−A molecules can originate from locally excited states of the D or A moiety, or from intramolecular charge transfer (ICT) excited states[12] or even from intermolecular excimers or exciplexes.[13] Thus, a judicious choice of the D/A units could allow the simultaneous control of the HOMO/LUMO levels and the emission color of the D−A molecule. EL colors spanning the visible region, including blue,[14] green,[15] yellow,[16] and red[17] have been achieved from OLEDs based on D−A molecules.

Further, the incorporation of polyaromatic groups in the triarylamine core extends the conjugation in the molecular structure and has been found to be highly beneficial by effectively enhancing the optical properties such as absorption, emission as well as thermal stability.[10,18] Additionally, the presence of bulky groups around the trigonal amine nitrogen often hinders the aggregation of molecules in the solid state. The colour of the emission in such compounds was tuned by the electronic nature of the aromatic group. For instance, the anthracene,[7] fluorene,[8] pyrene[9] and perylene-based[19] triarylamines usually display blue emission, while the triarylamines derived from carbazole[10] and fluoranthene[20] emit either green or yellow photons.

However, triarylamines derived from electron–deficient units such as quinoxaline/pyrazine,[21] and oxadiazole[22] exhibit balanced charge–transporting

---

*For correspondence

properties which are important for the performance of electronic devices particularly in OLEDs. Similarly, 9*H*−Xanthen−9−one (Xanthone), a heteroaromatic molecule contains carbonyl group due to which it has high electron affinity and also possesses planar structure due to which the molecular overlap and intermolecular electron migration occurs easily with high efficiency in solid state.[23]

Keeping the above mentioned donor−acceptor architecture with the benefits of functional triarylamines in mind, we report the synthesis of novel donor−acceptor compounds featuring xanthone as core unit (acceptor) and various diarylamines (donors) derived from phenyl, naphthyl and p−methoxy−phenyl groups by employing palladium−catalyzed C−N bond forming amination reaction and their optical, electrochemical and thermal properties.

2. Experimental

2.1 *Materials and Methods*

2.1a *Chemicals and Instruments*: All the starting materials and reagents were purchased from commercial source (Sigma Aldrich and Alfa Aesar) and were used without any further treatment and purifications unless otherwise noted. The organic solvents were of HPLC and spectroscopic grade and were dried and freshly distilled using the standard procedures and handled in moisture free atmosphere.

Investigation and confirmation of chemical structures of all the synthesized materials were done using FT−IR, ^{1}H NMR, ^{13}C NMR and high resolution mass spectroscopy (HRMS). ^{1}H NMR spectra and ^{13}C NMR spectra were recorded using $CDCl_3$ on a Bruker 300 Ultrashield spectrometer with Tetramethylsilane (TMS) as internal reference at a working frequency of 300 MHz and 75 MHz, respectively. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier 91579. High resolution Mass spectrometric measurements were recorded on Tof Micromass YA−105 HR−MS system. Melting points of the products were determined by open capillary method. The thermogravimetric analysis (TGA) was performed using Perkin Elmer Pyris Diamond TG/DTA under nitrogen atmosphere.

Column chromatography was carried out using SD−Fine silica gel (60–120 mesh), eluting with n−hexane and chloroform. The progress of reaction and the purity of the compound were checked by thin layer chromatography (TLC) on silica gel coated glass plates, in which the spots were visualized with UV light (λ 254–365 nm) and in iodine chamber.

2.1b *Redox and Spectroscopic properties*: Cyclic voltammetry studies were carried out on a computer controlled AUTOLAB PGSTATE 30 electrochemical analyzer equipped with USB electrochemical interface using GPES software version 4.9.005. 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 was employed. The measurements were carried at room temperature in anhydrous acetonitrile with tetrabutyl ammonium hexafluorophosphate solution (0.1 M) as supporting electrolyte at a scan rate of 100 mVs^{-1}. The potential of Ag/AgCl reference electrode was calibrated by using ferrocene/ferrocenium redox couple whose known oxidation potential is + 4.8 eV.

The HOMO energy values were estimated from the peak potentials (E_{ox}) of the oxidation event according to the equation (1).[24]

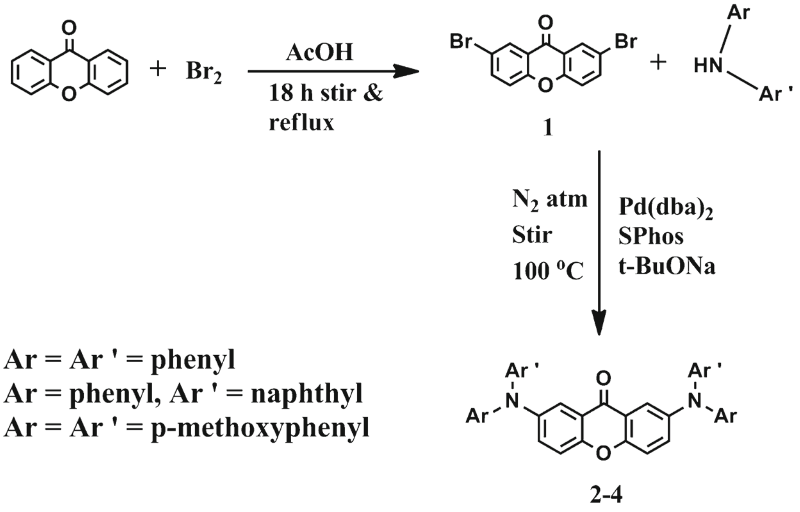
$$E_{HOMO} = -[E_{ox}^{peak} - E_{ox}(Fc/Fc^+) + 4.8]\ eV \qquad (1)$$

Where E_{ox} (Fc/Fc^+) is the peak potential of Fc/Fc^+ couple against the Ag/AgCl electrode and E_{ox}^{peak} is oxidation peak potential for the derivatives.

UV−Visible spectra were recorded for 10^{-5} M toluene solutions in a 1 cm path length quartz cuvette and for thermally deposited thin solid films, on SHIMADZU UV–2401PC at room temperature. The excitation and emission spectra were carried out on a Perkin Elmer LS 55 Fluorescence spectrophotometer. The fluorescence quantum yields (ϕ_F) were calculated relative to Alq_3 in benzene ($\phi_F = 0.16$)[25] as a standard for green emitting materials.

2.2 *Synthesis of materials (**2–4**)*

The detailed synthetic route adopted for the synthesis of triarylamines based on xanthone **2–4** is depicted in scheme 1 and the molecular structures of the synthesized derivatives are illustrated in chart 1. The starting bromo derivative, 2,7−Dibromoxanthen−9−one (**1**) required for the present study was synthesized according to the reported procedure[26] and the bromo precursor was conveniently converted to the triarylaminated derivatives **2–4** by treating it with the corresponding diarylamine using palladium catalyzed Buchwald−Hartwig amination reaction[27] utilizing palladium−bis(dibenzylideneacetone) [$Pd(dba)_2$] as a catalyst, 2−dicyclohexylphoshpino−2′,6′−dimethylbiphenyl (SPhos) as a ligand and sodium *tert*−butoxide as a base, under nitrogen atmosphere for 12–24 h at 100°C, giving derivatives **2–4** with yield more than 50%.



Scheme 1. Synthesis of **2–4**.

The C–N bond formation can be verified by the presence of peak at 1235–1303 cm^{-1} in FT–IR Spectra, corresponding to the stretching frequency of C–N bond (figure S1, see Supporting Information). Further, the weak C–H stretching was observed for all the molecules which may be due to the pseudosymmetry in these molecules. Substitution of xanthone with arylamine affords the corresponding triarylamine derivatives **2–4** as yellow to orange coloured solid soluble in common organic solvents including dichloromethane, toluene, chloroform, acetonitrile etc. However, they are sparingly soluble in alcohols and insoluble in water.

2.2a *2,7–Dibromoxanthen–9–one (**1**)*: Bromination of xanthone was done by the reported method which utilizes the following steps to get the desired product 2,7–Dibromoxanthen–9–one (**1**). Bromine (10 mL) was added dropwise over 20 min to a solution of xanthone (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 off–white solid. The resulting solid was filtered and collected and washed with sodium bicarbonate to neutralize the acetic acid and further treated with 20% aqueous solution of sodium bisulfate to remove excess bromine. The obtained solid was then dried under vacuum and purified using column chromatography (eluent: n–hexane) to afford (6.7 g, 52.4%) pure white crystalline solid desired product (**1**) M.p.: 211°C; Lit. M.p.: 211–212°C.[28]

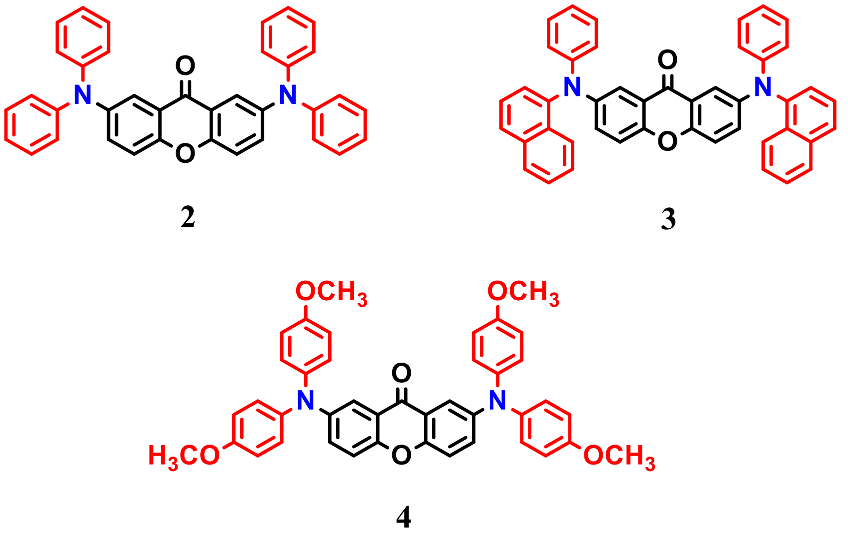


Chart 1. Structure of synthesized Compounds **2–4**.

2.2b *2,7−Bis(N−phenylanilino)xanthen−9−one (**2**)*: A mixture of 2,7−Dibromoxanthone (**1**) (354 mg, 1 mmol) and diphenylamine (530 mg, 2 mmol) was dissolved in anhydrous toluene (20 mL). To this solution, palladium bis(dibenzylideneacetone) [Pd (dba)$_2$] (30 mg, 5.21×10^{-5} mol), 2−dicyclohexylphoshpino−2′, 6′−dimethylbiphenyl (SPhos) (45 mg, 11×10^{-5} mol) and sodium *tert*–butoxide (300 mg, 3.1 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100°C for 12 h. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n−hexane: chloroform ratio as 80:20) to obtain a bright yellow solid. Yield: 63.4%; M.p.: 173°C; IR (KBr) ν/cm^{-1} 1264 (C–N str), 1654 (C=O str), 1073 (–O– str); HR–MS m/z calcd for [M$^+$] $C_{37}H_{27}N_2O_2$ 531.2073; found m/z: 531.2071; ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 6.998–7.093 (m, 12H, ArH) 7.219–7.394 (m, 8H, ArH), 7.465 (d, 2H, $J_1 = 2.7$ Hz), 7.495 (d, 2H, $J_1 = 2.7$ Hz) 7.96 (d, 2H, $J = 2.7$ Hz); ^{13}C NMR (75MHz, CDCl$_3$, δ, ppm): 119.00, 120.07, 122.16, 123.17, 124.06, 129.45, 131.66, 144.11, 147.48, 152, 176.27; Anal. Calcd. (%) For $C_{37}H_{27}N_2O_2$: C-83.59, H-5.11, N-5.27; Found (%): C-83.64, H-5.15, N-5.18.

2.2c *Synthesis of 2,7−Bis(N−naphthylanilino)xanthen−9−one (**3**)*: A mixture of 2,7−Dibromoxanthone (354 mg, 1 mmol) and N−naphthylphenylamine (530 mg, 2 mmol) was dissolved in anhydrous toluene (20 mL). To this solution, palladium bis(dibenzylideneacetone) [Pd(dba)$_2$] (30 mg, 5.21×10^{-5} mol), 2−dicyclohexylphoshpino−2′, 6′−dimethylbiphenyl (SPhos) (45 mg, 11×10^{-5} mol) and sodium *tert*–butoxide (300 mg, 3.1 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100°C for 24 h. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n−hexane: chloroform ratio as 80:20) to obtain a bright yellow solid. Yield: 340 mg, 54.0%; M.p.: 265°C; IR (KBr) ν/cm^{-1} 1303 (C– N str), 1648 (C=O str), 1143 (–O– str); HR–MS m/z calcd for [M$^+$] $C_{45}H_{31}N_2O_2$ 631.2386; found m/z: 631.2402. ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 6.91–7.016 (m, 10H, ArH,), 7.145–7.399 (m, 14H, ArH) 7.760 (d, 2H, $J = 8.1$ Hz), 7.863 (d 2H, $J = 9.3$ Hz, ArH,) 7.903 (d, 2H, $J = 8.4$ Hz, ArH); ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm) 117.35, 118.85, 121.59, 121.94, 122.10, 123.97, 126.20, 126.35, 126.50, 126.80, 127.16, 128.51, 129.29, 129.62, 130.96, 135.38, 143.06, 144.67, 148.18, 151.48, 176.43. Anal. For $C_{45}H_{31}N_2O_2$, Calcd.(%): C-85.55, H-4.94, N-4.43; Found (%): C-85.58, H-4.88, N-4.47.

2.2d *Synthesis of 2,7−Bis(4,4′ −methoxydiphenylamine)xanthen−9−one (**4**)*: A mixture of 2,7−Dibromoxanthone (354 mg, 1 mmol) and 4,4’methoxydiphenyl amine (530 mg, 2 mmol) was dissolved in anhydrous toluene (20 mL). To this solution, palladiumbis (dibenzylideneacetone) [Pd(dba)$_2$] (30 mg, 6×10^{-5} mol), 2–dicyclohexylphoshpino−2′, 6′−dimethylbiphenyl (SPhos) (45 mg, 11×10^{-5} mol) and sodium *tert*–butoxide (300 mg, 3.1 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100°C for 16 h. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n−hexane: chloroform ratio as 80:20) to obtain a bright orange solid. Yield: 338 mg, 52.16 %; M.p.: 195°C. IR (KBr) ν/cm^{-1} 1235 (C–N str), 1656 (C=O str), 1035 (–O– str); HR–MS m/z calcd for [M$^+$] $C_{41}H_{35}N_2O_6$ 651.2495; found m/z: 651.2474; ^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 3.768 (s, 12H, $-OCH_3$), 6.810 (d, 8H, $J = 9.0$ Hz, ArH), 7.024 (d, 8H, $J = 8.7$ Hz, ArH), 7.245 (d, 2H, $J = 2.7$ Hz, ArH,), 7.326 (d, 2H, $J = 2.7$ Hz ArH), 7.356 (d, 2H, $J = 2.7$ Hz, ArH,); ^{13}C NMR (75 MHz, CDCl$_3$, δ, ppm): 55.466, 114.47, 114.89, 116.11, 118.558, 121.858, 124.16, 126.12, 128.86, 140.78, 144.96, 150.95, 155.96, 176.41; Anal. For $C_{41}H_{35}N_2O_6$ Calcd. (%): C-75.55, H-5.41, N-4.29; Found (%): C-75.59, H-5.44, N-4.23.

3. Results and Discussion

3.1 *Photophysical properties*

In order to realize the functioning of organic materials in device applications, studying their photophysical properties is important. The photophysical properties of the synthesized molecules are greatly influenced by the nature of peripheral amines. The photophysical studies were performed on the 10^{-5} M solution of **2–4** in various solvents as well as thin solid film using UV–Vis absorption and fluorescence spectroscopy. The pertinent data are summarized in table 1 and table S1 (see Supporting Information) and the spectra are displayed in figures 1 and 2.

The synthesized molecules show similar UV−Vis absorption spectra in solution and thin solid film (figure 1). However, parent molecule xanthone shows two absorption peaks at 285 and 338 nm arising due to

Table 1. Photophysical data of the synthesized compounds **2–4**.

	Toluene					Thin Film			
Compounds	λ_{max}[a], /nm (ε_{max}/$M^{-1}cm^{-1} \times 10^3$)[b]	λ_{em}[c], /nm	Stokes shift[d], /cm^{-1}	E_g^{opt} [e] /eV	ϕ_F [f]	λ_{max}[a],/nm	λ_{em}[c], /nm	Stokes shift[d], /cm^{-1}	E_g^{opt} [e] /eV
2	306 (99.93), 327 (107.47), 400 (10.42)	493	4716	2.71	0.14	307, 328, 413	527	5237	2.52
3	286 (55.80), 318 (68.39), 352 (28.06), 398 (10.03)	483	4421	2.75	0.22	265, 318, 357, 413	525	5165	2.75
4	299 (74.29), 325 (70.88), 425 (7.47)	532	4732	2.56	0.22	301, 328, 430	576	5894	2.56

[a] Absortion spectra recorded in toluene 10^{-5} mol L^{-1} and for thin solid film form.
[b] Extinction coefficient (/M^{-1} cm^{-1} × 10^3) measured in toluene.
[c] Emission spectra recorded in toluene 10^{-5} mol L^{-1} and for thin solid film form.
[d] Stokes shift calculated from charge transfer absorption and emission maxima observed in solution and thin solid film form.
[e] Optical bandgap estimated using emission and excitation spectra in toluene and thin solid film form.
$E_g^{opt} = (1240/\lambda_{opt})$ eV. λ_{opt} /nm values are 457 (**2**), 450 (**3**), 484 (**4**)
[f] Quantum yield relative to Alq_3 ($\phi_F = 0.16$ in benzene).[25]

π –π^* and n–π^* transition. Upon substituting the electron donating amine groups at the 2nd and 7th position of xanthone, the absorption maxima are found to be blue shifted in all the derivatives. The absorption spectra of the compounds **2–4** (figure 1) exhibit a well-resolved absorption profile in the range of 286–425 nm. Among these transitions, the higher energy absorption between 286–352 nm is probably originating from the π–π^* and n–π^* transition located within the arylamine units and the xanthone core while the lower energy band between 398–425 nm is attributed to the charge transfer transition between the electron–donating diphenylamine and the electron–accepting 9*H*−xanthen−9−one core.

In addition, the absorption spectrum of the derivative **3** is found with a shoulder peak at 352 nm which may be due the π–π^* transition overlapping with lower energy charge transfer transition (figure 1). The λ_{max} in absorption for all the derivatives as thin films are found to be nearly same order relative to the solution spectra.

The compounds **2** and **3** emit green light with λ_{max} at 493 and 483 nm (figure 2a) upon excitation at their corresponding absorption maxima in toluene with a bathochromic shift of 34 nm and 42 nm in thin solid film, respectively (figure 2b), while the compound **4** shows green emission with λ_{max} at 532 nm in toluene (figure 2a) and a significantly (44 nm) red−shifted yellow emission at λ_{max} 576 nm as thin film due to the auxochromic effect of electron−donating p−methoxy groups at phenyl rings of amine (figure 2b). The emission peaks of the dyes **2–4** in the toluene are in the range 483–532 nm with a bathochromic shift as the thin film ranging from 525–576 nm which may be due to the intermolecular aggregations[29] in the solid state (table 1).

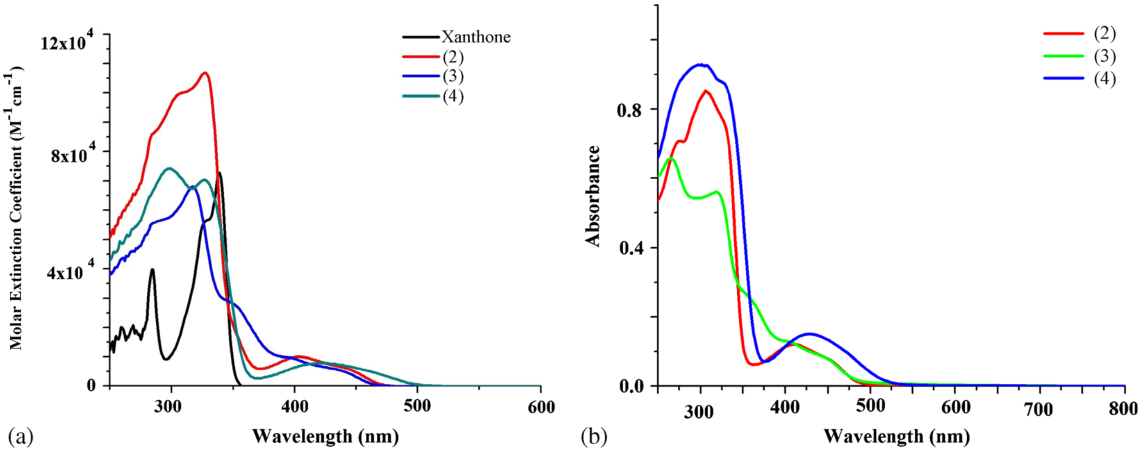


Figure 1. UV−Vis absorption spectra of compounds **2–4** and xanthone in toluene solution (**a**), and thin solid film (**b**).

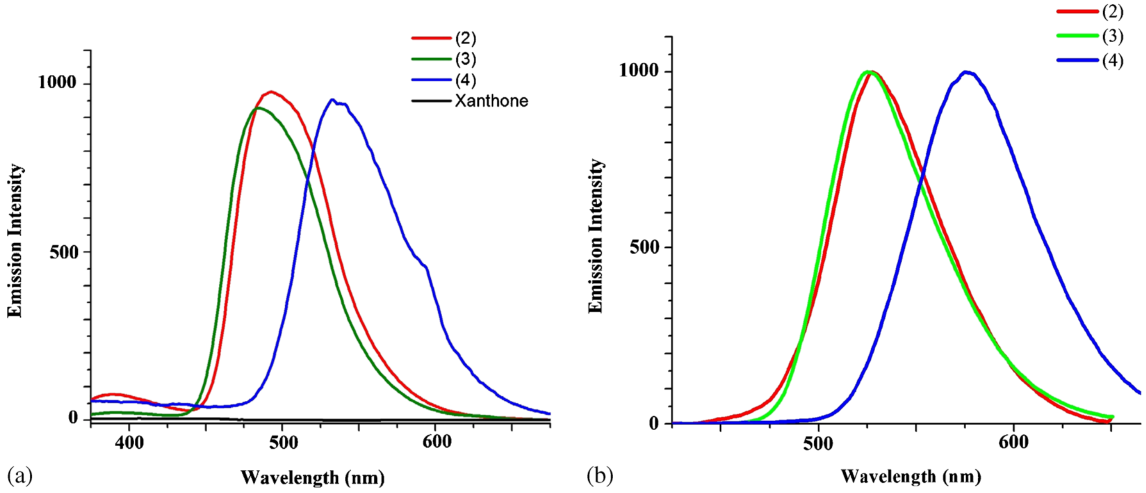


Figure 2. Emission spectra of the compounds **2–4** and xanthone in toluene solution (**a**), and thin solid film (**b**).

Further, the absorption and emission behavior of the synthesized derivatives were recorded in two other solvents, chloroform and acetonitrile (figure S5) and it was observed that the absorption spectra for all the derivatives was of the same order while the emission spectra were found to be red shifted by 36–39 nm for compound **2** in chloroform and acetonitrile and 43 nm for compound **3** in chloroform 30 nm blue shift for compound **3** in acetonitrile was observed as compared with the emission of the dyes in toluene. The emission intensity of the derivative **4** was quenched in polar solvents like chloroform and acetonitrile (table S1). The shifts only in the emission spectra with change in polarity of the solvent indicate that the ground state geometry of the derivatives is not affected by the polarity of solvent however excited state geometry of the compounds is greatly affected by the nature and polarity of the solvent.

Optical band gap (E_g^{opt}) for the derivatives in toluene and thin film were calculated using emission and excitation spectra (figure S7) and are in the range 2.56–2.75 eV and 2.52–2.75 eV respectively (table 1). Molar extinction coefficients (ε) of **2-4** are high in solution which indicate that the long wavelength band in the absorption spectra is a charge transfer band through the π–π^* transition.

The Stokes shifts of molecules **2–4** were high, 4421–4732 cm^{-1} in toluene and 5165–5894 cm^{-1} in thin films ensuring that there is no re−absorption of the emitted radiation. The fluorescence quantum yield of **2–4** were calculated using tris(8−hydroxyquinolinato) aluminium(III) (Alq$_3$) (ϕ_F = 0.16 in benzene)[25] as standard. The quantum yields of the derivatives are in the range 0.14–0.22 in toluene (table 1) (for chloroform and acetonitrile see table S1 in Supporting Information). Material performance of the synthesized molecules **2–4** for electroluminescent application is evaluated by Commission International de I'Eclairage (CIE) coordinates. The (CIE) coordinates of compound **2–4** are determined by using photoluminescence spectra in thin solid film. The obtained CIE are located in yellow−green region (see Supporting Information).

Table 2. Electrochemical and thermal data for compounds **2–4**.

Compound	$E_{ox}^{peak\ a}$ (V)	$E_{red}^{peak\ b}$ (V)	HOMO[c]	LUMO[d]	E_g^{cv}	T$_d$ (°C)[f]	T$_{max}$ (°C)[g]	T$_m$ (°C)[h]
2	1.218	−1.658	−5.686	−2.724	2.962	280 (340)	410	173
3	1.129	−1.677	−5.597	−2.705	2.892	330 (360)	450	265
4	0.864 (1.315)	−1.612	−5.332	−2.776	2.556	260 (370)	563	195

[a] E_{ox}^{peak} oxidation peak potential Vs Fc/Fc$^+$.
[b] E_{red}^{peak} reduction peak potential Vs Fc/Fc$^+$.
[c] HOMO energy level calculated from $E_{HOMO} = -[E_{ox}^{peak} - E_{ox}(Fc/Fc^+) + 4.8\,]$ eV.
[d] LUMO energy calculated from $E_{LUMO} = -[E_{red}^{peak} - E_{red}(Fc/Fc^+) + 4.8\,]$ eV.
[e] $\mathbf{E_g^{cv}}$ calculated from $\mathbf{E_g^{cv}}$ = (HOMO−LUMO) eV.
[f] $\mathbf{T_d}$ Decomposition temperature at 5% and 10% (in parentheses) and weight loss derived by TGA.
[g] $\mathbf{T_{max}}$ Derivative weight loss
[h] $\mathbf{T_m}$ Melting point.

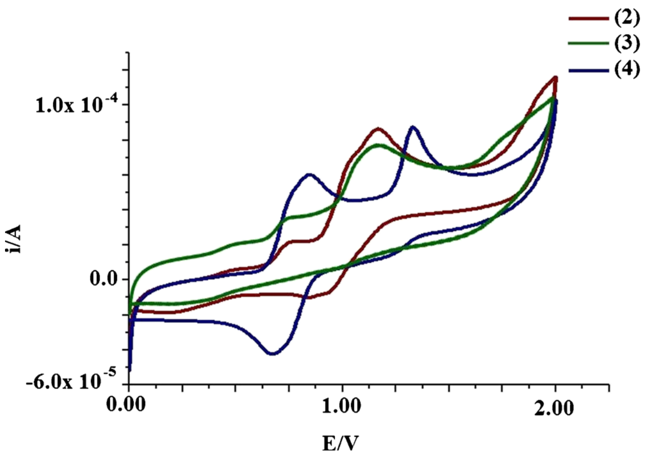


Figure 3. The cyclic voltammograms of compounds **2–4** measured in acetonitrile solution against ferrocenium/ferrocene, at 100 mV/sec.

3.2 *Electrochemical properties*

The charge transport capability of a molecular material can be identified from its propensity to stabilize both its cation and anion. Electrochemical measurements can be used to estimate the capability of the dye to produce and stabilize the cation and anion. We studied **2–4** by cyclic voltammetric measurements using ferrocene as an internal standard to calibrate the redox potentials. The observed parameters are reported in table 2. The cyclic voltammograms are displayed in figure 3.

On anodic sweeps, no oxidation wave was observed for the parent xanthone core (see figure S8 in SI). However, irreversible wave was presented by all of the dyes due the oxidation processes at relatively low oxidation potentials at 1.129–1.315 V. It is attributable to the oxidation of the peripheral amines[30] at the 2nd and 7th position of xanthone core. The oxidation potentials increased in the following order **4**<**3**<**2**. This trend is attributed to the electronic nature of the aryl substituents attached to the amine nitrogen. An additional reversible oxidation couple at low positive potential at 0.864 V is also observed for compound **4** which probably may arise from the oxidation of p−methoxy segment.[30]

On cathodic sweep, parent xanthone molecule exhibits two steps of reductions (figure S8 in SI). The first quasi-reversible peak occurs at −1.78 V and another irreversible reduction peak at −2.27 V due to the double reduction of carbonyl group forming dianion. **2–4** show only one irreversible reduction peak between −1.612 to −1.677 V at lower potential compared to xanthone due to the presence of terminal electron donor diarylamine groups thus suggesting formation of radical anion.

The HOMO energy levels of the synthesized materials **2–4** are in range of −5.332 to −5.686 eV which are similar to or slightly higher than that of most widely used hole transporting material 4,4′−bis(1−naphthylphenylamino)biphenyl (NPB) (HOMO = −5.20 eV and LUMO = −2.4 eV) and thus might be beneficial for the hole−injection and transport properties.[31] The LUMO energy levels are in the range of −2.705 to −2.776 eV. The energy band gaps determined from the cyclic voltammetry measurements are in range of 2.556–2.962 eV and are comparable with the optically calculated band gaps.

3.3 *Thermal properties*

The thermal stability of the synthesized molecules was determined by TGA and DTA in the temperature range of 30–1000°C at a constant heating rate of 10°C min^{-1} under nitrogen atmosphere. The observed TGA parameters are reported in table 2 and displayed in figure 4. TGA plots of compounds **2–4** indicate that the derivatives have high thermal stability with the

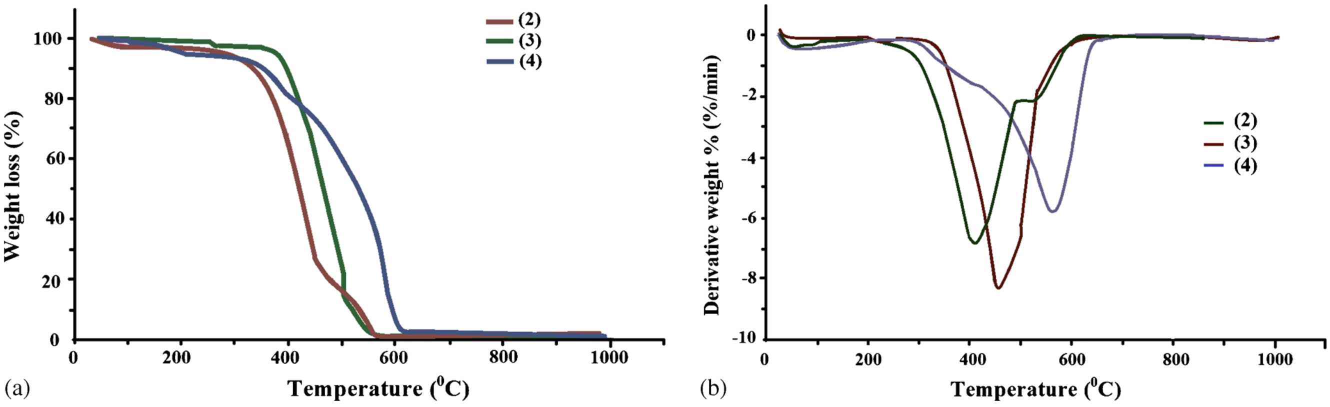


Figure 4. TGA thermograms (**a**) and derivative weight loss (**b**) of compounds **2–4** under nitrogen atmosphere at normal pressure. Heating rate, 10°C/min.

decomposition temperature corresponding 5% and 10% weight loss in the range of 260–330°C and 340–370°C respectively (figure 4(a)) and are comparable with the previously reported hole−transporting materials such as 9,10−bis(diphenylamino) anthracene (PPA), 9,10−bis(1−napthylphenylamino)anthracene (NPA), 1,4−bis(phenyl−m−tolylamino) biphenyl (TPD), 4, 4′−bis(1−naphthylphenylamino)biphenyl (NPB) with stability in range 185–382°C.[7c,31a] The order of thermal stability among the diarylamine derivatives is **4**<**2**<**3** (table 2).

The derivative weight loss plot figure 4(b) shows a narrow derivative peak with high decomposition temperature with T_{max} in the range of 410–563°C (table 2). The DTA plots of synthesized compounds **2–4** (see Supporting Information) show sharp endothermic peaks which are attributed to the corresponding melting points of compounds and exothermic peaks were observed above 350°C indicating that no crystallization takes place below 350°C. Melting points of the derivatives **2–4** are in the range of 173–265°C.

4. Conclusions

The triarylamines containing 9*H*−Xanthen−9−one have been synthesized via palladium−catalyzed C−N bond forming reaction in good yields. The compounds were thoroughly analyzed by routine spectroscopic methods and subjected to photophysical, electrochemical and thermal studies. The absorption, emission, electrochemical and thermal properties of the dyes are significantly influenced by the nature of peripheral amine segments attached to the xanthone core. The emission colour of these materials varied from green to yellow by changing the nature of the amine. The electrochemical investigation of the compounds showed that the ionization potentials and electron affinities are in a good range, comparable with the most commonly used hole−transporting materials. Thermal properties revealed that the derivatives have a high melting point and good thermal stability. The results indicate that the molecules are promising candidates for electroluminescent device applications.

Supplementary Information

All the additional details pertaining to the characterization of the compounds **2**–**4** using FT-IR (figures S1), ^{1}H NMR (figure S2), ^{13}C NMR (figure S3), HRMS spectra (figure S4), UV-Vis absorption and emission spectra (figure S5), Absorption and Emission Properties of compound **2–4** in solvents of varying polarity and their CIE Coordinates as thin solid film (table S1), Emission and Excitation Spectra (figure S7), complete scan Cyclic Voltammograms (figure S8), Derivative weight loss and DTA plots (figure S9), CIE coordinates (figure S10) and Photograph of compounds in solution form (figure S11) are given in the Supporting Information. Supplementary Information is available at www.ias.ac.in/chemsci.

Acknowledgments

We thank the Micro-Analytical Laboratory, Department of Chemistry, University of Mumbai for providing Instrumentation facility. We also thank the Department of Chemistry IIT-Mumbai for providing HR-MS Spectra.

References

1. (a) Friend R H, Gymer R W, Holmes A B, Burroughes J H, Marks R N, Taliani C, Bradley D D C, dos Santos D A, Bredas J L, Lögdlund M and Salaneck W R 1999 *Nature* **397** 121; (b) Baldo M A, Thompson M E and Forrest S R 2000 *Nature* **403** 750
2. Anthony J E 2008 *Angew. Chem. Int. Ed.* **47** 452
3. (a) Imahori H, Umeyama T and Ito S 2009 *Acc. Chem. Res.* **42** 1809; (b) Ning Z and Tian H 2009 *Chem. Commun.* 5483; (c) Grätzel M 2009 *Acc. Chem. Res.* **42** 1788
4. Tang C W and VanSlyke S A 1987 *Appl. Phys. Lett.* **51** 913
5. (a) Kulkarni A P, Tonzola C J, Babel A and Jenekhe S A 2004 *Chem. Mater.* **16** 4556; (b) Jenekhe S A, Liangde Lu and Maksudul M A **2001** *Macromolecule* **34** 7315; (c) Furuta P T, Deng L, Garon S, Thompson M E and Frechet J M J 2004 *J. Am. Chem. Soc.* **126** 15388; (d) Kulkarni A P, Wu P-T, Kwon T W and Jenekhe S A 2005 *J. Phys. Chem. B.* **109** 19584; (d) Chiang C-L, Wu M-F, Dai D-C, Wen Y-S, Wang J-K and Chen C-T 2005 *Adv. Funct. Mater.* **15** 231
6. Shirota Y J J 2000 *Mat. Chem.* **1** 1
7. (a) Kim S K, Yang B, Park Y I, Ma Y, Lee J-Y and Kim H-J 2009 *Org. Electron.* **10** 822; (b) Yang B, Kim S K, Xu H, Park Y-I, Zhang H-Y, Gu C, Shen F Z, Wang C L, Liu D D, Liu X D, Hanif M, Tang S, Li W J, Li F, Shen J C, Park J W and Ma Y-G 2008 *Chem. Phys. Chem.* **9** 2601; (c) Yu M X, Duan J P, Lin C H, Cheng C H and Tao Y T 2002 *Chem. Mater.* **14** 3958; (d) Danel K, Huang T-H, Lin J T, Tao Y-T and Chuen C-H 2002 *Chem. Mater.* **14** 3860
8. (a) Noine K, Pu Y-J, Nakayama and Kido K-I 2010 *Org. Electron.* **11** 717; (b) Kwon Y S, Lee K H, Young K G, Seo J H, Kim Y K and Yoont S S 2009 *J. Nanosci. Nanotechnol.* **9** 7056; (c) Jiang Z, Liu Z, Yang C, Zhong C, Qin J, Yu G and Liu Y 2009 *Adv. Funct. Mater.* **19** 987; (d) Lai M Y, Chen C H, Huang W S, Lin J T, Ke T H, Chen L Y, Tsai M H and Wu C C 2008 *Angew. Chem. Int. Ed.* **47** 581

9. (a) Thomas K R J, Velusamy M Lin J T, Chuen C H and Tao Y T 2005 *J. Mater. Chem.* **15** 4453; (b) Jia W-L McCormick T, Q-D, Liu H, Fukutani M, Motala R-Y, Wang Y, Tao S and Wang 2004 *J. Mater. Chem.* **14** 3344
10. (a) Shen J-Y Yang X-L, Huang T-H, Lin J T, Ke T-H, Chen L-Y, Wu C-C and Yeh M-C 2007 *Adv. Funct. Mater.* **17** 983; (b) Thomas K R J, Velusamy M, Lin J C T, Chuen C H and Tao Y T 2004 *Adv. Mater.* **14** 387
11. Haung T-H, Lin J T, Chen L-Y and Wu C-C 2006 *Adv. Mater.* **18** 602
12. (a) Grabowski Z R, Rotkiewicz K and Rettig W 2003 *Chem. Rev.* **103** 3899; (b) Yoshihara T, Druzhinin S I and Zachariasse K A 2004 *J. Am. Chem. Soc.* **126** 8535
13. (a) Förster T 1969 *Angew. Chem. Intl. Ed.* **8** 333; (b) Jenekhe S A and Osaheni J A 1994 *Science* **265** 765
14. (a) Hamada Y, Adachi C, Tsutsui T and Saito S J 1992 *J. Appl. Phys.* **31** 1812; (b) Goes M, Verhoeven J W, Hofstraat H and Brunner K 2003 *ChemPhysChem* **4** 349
15. (a) Thomas K R J, Lin J T, Tao Y-T and Chuen C-H 2002 *Chem. Mater.* **14** 3852; (b) Zhu W, Hu M, Yao R and Tian H 2003 *J. Photochem. Photobiol. A* **154** 169
16. Kelnhofer K, Knorr A, Tak Y-H and Bassler H 1997 *J. Daub. Acta Polym.* **48** 188
17. (a) Thomas K R J, Lin J T, Velusamy M, Tao Y-T and Chuen C-H 2004 *Adv. Funct. Mater.* **14** 83; (b) Chiang C-L, Wu M-F, Dai D-C, Wen Y-S, Wang J-K and Chen C-T 2005 *Adv. Funct. Mater.* **15** 231
18. Kapoor N and Thomas K R J 2010 *New J. Chem.* **34** 2739
19. (a) Shen W-J, Dodda R, Wu C-C, Wu F-I, Liu T-H, Chen H-H, Chen C-H and Shu C-F 2004 *Chem. Mater.* **16** 930; (b) Wu C C, Lin Y T, Chiang H H, Cho T Y, Chen C W, Wong K T, Liao Y L, Lee G H and Peng S M 2002 *Appl. Phys. Lett.* **81** 577
20. Xia Z Y, Su J H, Fan H H, Cheah K W, Tian H and Che C H 2010 *J. Phys. Chem. C* **114** 11602
21. Thomas K R J, Lin J T, Tao Y-T and Chuen C-H 2005 *Chem. Mater.* **17** 1860
22. Thomas K R J, Lin J T, Tao Y T and Chuen C-H 2004 *Chem. Mater.* **16** 5437
23. Horiuchi T, Kamatani J, Yamada N, Kishino K and Saitoh A *Japanese Patent* WO 2011/136156 A1
24. (a) Agarawal N, Nayak P K and Periasamy N 2008 *J. Chem. Sci.* **120** 355; (b) Shaikh A M, Sharma B K and Kamble R M 2015 *Can. Chem. Trans.* **3** 158
25. Katsuta S 1994 *Chem. Lett.* 1239
26. Coleman M P and Mary K B 2002 *J. Org. Chem.* **67** 7641
27. (a) Patt P F J and Hartwig J F 1994 *J. Am. Chem. Soc.* **116** 5969; (b) Guran A S and Buchwald S L 1994 *J. Am. Chem. Soc.* **116** 7901; (c) Hartwig J F, Shelgy Q and Kataoka N *Japanese Patent* WO 02/11883 A1
28. Faust J A and Sahyun M *US Patent.* 1962/3,042,674
29. (a) Ulla H, Garudachari B, Satyanarayan M N, Umesh G and Isloor A M 2014 *Optical Materials* **36** 704; (b) Jandke M, Stohriegl P, Berleb S, Werner E and Brutting W 1998 *Macromolecules* **31** 6434
30. Chiu K Y, Su T X, Li J H, Lin T-H, Liou G-S and Cheng S-H 2005 *J. Electroanal. Chem.* **575** 95
31. (a) Wu C, Djurovich P I and Thompson M E 2009 *Adv. Func. Mater.* **19** 3157; (b) Koene B E, Loy D E and Thompson M E 1998 *Chem. Mater.* **10** 2235