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An Investigation of the effect of conjugation on fluorene based chromophores; Optoelectronic and electrochemical behavior

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Graphical Abstract

An Investigation of the effect of conjugation on fluorene based chromophores; Optoelectronic and electrochemical behavior

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The band gap energy values for newly synthesized fluorine derivatives suggest that these molecules can be employed in the design of blue and green OLEDS.



Abstract

The requisition of small light emitting organic molecules is on the rise in the field of organic electronics. This study is aimed at synthesis of fluorene based chromophores which possess promising optoelectronic properties. The characterization of synthesized derivatives was carried out by spectroscopy (¹H-NMR and ¹³C-NMR) and spectrometry (EI-MS). The optical properties evaluated by using UV-Vis spectroscopy, were from 394-420 nm, Fluorescence ranged 48 nm-113 nm, HOMO energy levels are -6.75 eV to -7.15 eV LUMO -4.08 to -4.52eV with a band gap energy values 2.63 to 2.67 eV. The band gap energy values suggest that these synthesized molecules can be manipulated in the designing of blue and green OLEDS.

Keywords: fluorene based chromophores; Stoke's shift; optical properties; electrochemical behavior; band gap;

1. Introduction

The wide band gap for blue OLEDS (organic light emitting diodes) is the major cause behind their low commercial success rate [1-3]. The quest to develop and explore efficient small organic molecules for the display devices such as OLEDS is in the continuous process of development since last two decades. To achieve high external quantum efficiencies (EQE) is considered as a daunting task in case of deep-blue OLEDS [4-6]. Materials with strong push-pull aptitude along with efficient hole transporting ability can certainly balance the charges in emitting layers and consequently can improve the performance of OLEDS. However, to achieve materials with high band energy value and blue emission is still a work in progress.

Fluorene is blessed with enriched organic electronic properties such as high thermal and photophysical stabilities along with high emission quantum yields [7]. Fluorene represents the class of polycyclic aromatic hydrocarbon (PAH) and serve as an essential structural unit in the field of organic electronics [8-10]. Fluorene apart from extended utility in organic electronics also exhibits applications in the synthesis of peptides, pharmaceuticals and dyes. Fluorene generally possess three reactive positions 2, 7 and 9 [11,12]. The derivatization at 2 and 7 positions allows adjusting electronic groups. Fluorene serve as π spacer who paves the way for fine tuning of electronic groups at 2 and 7 positions [13]. Herein, we explore the structure-property relationship (SPR) of electron deficient and electron rich groups attached at 2 and 7 position of fluorine. We have synthesized three A- π -A molecules and one A- π -D compound to evaluate their photophysical properties and electrochemical behavior. In the course of current study, fluorine moiety was locked with electron accepting motif of benzo[*d*]thiazole (Figure 1).



Figure 1. Design of A- π -A and A- π -D fluorene based molecules for applicability in blue OLEDS

1,3-diketone linked with electron withdrawing group CF_3 (6) served as a platform to carry out synthetic transformations to obtain various group bearing fluorine derivatives (9, 10 and 11). The SPR revealed that incorporating the 1,3-diketone played the role of accepting electrons. While in case of compound 9 which possessed extended conjugation having para *N*,*N*-dimethylstyryl moiety as an electron donating group. Compound 10 and 11 bear electron deficient moiety which also enhanced the extended conjugation in the system. The structure-property relationship played pivotal role in determining the photo physical and electrochemical behavior. The results of fluorescence, UV-Vis and cyclic voltammetry showed variation in nature of photo physical and electrochemical properties. The band gap energy values were found to lie in the region of bluegreen OLEDS.

2. Experimental

2.1. Materials

Fluorene, ethyl bromide, iodine, tetrabutyl ammonium bromide (TBAB) were purchased from Fluka. Aluminum chloride, acetyl chloride, 2-(tributylstannyl)benzo[*d*]thiazole were obtained from Sigma-Aldrich. Tetrakis(triphenylphosphine)palladium(0), potassium tertiary butoxide, 4-(dimethylamino)benzaldehyde, hydrazine hydrate, pyrene-1-carbaldehyde, piperidine, Acetonitrile (AcCN), dichloromethane (DCM), ethyl 2,2,2-trifluoroacetate (CF₃COOC₂H₅) were purchased from Sigma-Aldrich. Purification of the reagents was carried wherever necessary.

2.2. Methods

All the chemicals used for analysis were of 99–100% purity. ¹H-NMR spectra of all the compounds were conducted on a 300 MHz Bruker NMR spectrometer in DMSO solvent. Splitting patterns were as follows: s (singlet), d (doublet), dd, (double doublet), t (triplet), m (multiplet) and br (broad). Chemical shifts were represented in d (ppm). The FTIR spectra were taken in the single beam Nicolet FT-IR 100. Ultraviolet-visible (UV-vis) spectra were recorded on a double beam Perkin-Elmer Lambda 900 UV-vis-NIR spectrophotometer. The data were used to calculate the molar extinction coefficients for the compounds. TLC plate Silica Gel 60 F_{254} was utilized to test the progress of fluorene chromophore. Mobile phase for TLC was n-hexane: ethyl acetate 5:2 ratio. Electrochemical analysis was made by Electrochemical Analyzer CH1830C. Fluorescence quantum yields were determined using reference fluorescein having quantum yield 94% in DCM.

Preparation of monoiodofluorene (1)



Fluorene (**5.0** g., 0.30 mole) was treated with iodic acid. The mixture was poured into water, and the product was filtered off, washed with water, and

dried (8.1 g.). A portion (1.02 g.) was chromatographed on silica gel in cyclohexane, giving almost colourless 2-iodofluorene (0.73 g., 65%), m.p. 127-128 [14].

1-(6-(benzo[d]thiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)-4,4,4-trifluorobutane-1,3-dione (06)



Synthesis of 1-(6-(benzo[*d*]thiazol-2-yl)-9,9-diethyl-9*H*-fluoren-2-yl)-4,4,4-trifluorobutane-1,3-dione was achieved by condensation of 1-(6-(benzo[*d*]thiazol-2-

yl)-9,9-diethyl-9*H*-fluoren-2-yl)ethanone (3.97 g, 10 mmol), with ethyl 2,2,2-trifluoroacetate $(CF_3COOC_2H_5)(2.84 \text{ g}, 0.02 \text{ mol})$ and potassium tertiary butoxide $(t-C_4H_9OK)(1.46 \text{ g}, 12 \text{ mmol})$ for 6 h in toluene. The mixture was neutralized by diluted hydrochloric acid and extracted with toluene. The solvent was evaporated under vacuum and pure product was obtained by recrystallization from ethanol.

Dark red solid; Yield: 73%; R_f: 0.49; m.p.165-167°C; FTIR (Neat, cm⁻¹) \tilde{v}_{max} : 3102(C=C-H), 2956(C-H_{str}), 2837 (C-H_{str}), 1727 (CF₃-C=O) 1698 (Ar-C=O), 1615, 1573, 1501 (Aromatic, C=C_{str}), 1452 (CH_{2bend}), 1372 (CH₃), 1628 (C=N),941 (C-S), 1246 (C-F).

¹H-NMR (300 MHz, CDCl₃) δ 8.24-8.03 (m, 4H), 7.92 (dd, *J* = 7.5, 6.9 Hz, 1H), 7.59-7.40 (m, 5H), 3.71 (s, 2H), 1.89 (q, *J* = 6.7 Hz, 4H), 1.00 (t, *J* = 6.7 Hz, 6H). ¹³C-NMR (75 MHz, CDCl₃) δ 194.8, 182.0, 162.6, 153.9, 152.5, 150.4, 142.7, 139.7, 139.2, 138.2, 136.3, 126.9, 126.0, 125.6, 125.5, 125.3, 123.7, 123.7, 122.7, 122.4, 121.8, 121.0, 55.0, ,32.2, 7.9; MS (m/z, APCI): calcd 493.13(M⁺), found 494.13[M+H]⁺.

General procedure for the Knoevenagel condensation of 1-(6-(benzo[*d*]thiazol-2-yl)-9,9diethyl-9*H*-fluoren-2-yl)-4,4,4-trifluorobutane-1,3-dione with aromatic aldehydes

Knoevenagel condensation [15] were achieved by using equivalent ratio of 1-(6-(benzo[d]thiazol -2-yl)-9,9-diethyl-9H-fluoren-2-yl)-4,4,4-trifluorobutane-1,3-dione and aromatic aldehydes in EtOH (25 mL). Piperidine (0.5 mL) was added slowly through a syringe with stirring, the reaction mixture was refluxed for 72 h. Purification of the products was obtained through a silica gel column using hexanes/ethyl acetate (5/2) as eluent.

(Z)-1-(7-(benzo[d]thiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)-2-(4-(dimethylamino)

benzylidene)-4,4,4-trifluorobutane-1,3-dione (09)



Reddish solid; Yield: 73%; R_f : 0.45; m.p.171-172°C; FTIR (Neat, cm⁻¹) \tilde{v}_{max} : 3095(C=C-H), 2930(C-H_{str}), 2851(C-H_{str}), 1714(CF₃-C=O), 1687(Ar-C=O), 1600, 1567, (Aromatic, C=C_{str}), 1448(CH₂bend), 1378(CH₃), 1624(C=N), 1325(C-N), 939(C-S), 1237(C-F). ¹H

NMR (300 MHz, CDCl₃) δ 8.87 (s, 1H), 8.79-7.74 (m, 8H), 7.81 (ddd, J = 7.5, 3.8, 1.4 Hz, 2H), 7.81 (ddd, J = 7.5, 3.8, 1.4 Hz, 2H), 7.58-7.33 (m, 3H), 7.33 (s, 1H), 6.72 (d, J = 7.5 Hz, 2H), 2.91 (s, 6H), 1.89 (q, J = 6.7 Hz, 4H), 1.01 (t, J = 6.7 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃ δ 192.2, 175.8, 175.6, 162.6, 153.9, 152.5, 151.0, 150.4, 142.7, 139.2, 138.9, 138.5, 136.3, 131.4, 128.5, 126.9, 126.5, 126.0, 125.5, 125.3, 123.7, 123.3, 122.7, 121.8, 121.1, 120.9, 118.0, 112.3, 54.4, 41.9, 32.2, 7.9; MS (m/z, APCI): calcd 624.21 (M⁺), found 626.21 [M+2H]⁺.

(Z)-1-(7-(benzo[d]thiazol-2-yl)-9,9-diethyl-9H-fluoren-2-yl)-4,4,4-trifluoro-2-(pyren-1-

methylene)butane-1,3-dione (10)



Reddish solid; Yield: 73%; R_f: 0.49; m.p.194-196°C; FTIR (Neat, cm⁻¹) \tilde{v}_{max} : 3090 (C=C-H), 2938 (C-H_{str}), 2856 (C-H_{str}), 1717 (CF₃-C=O) 1689 (Ar-C=O), 1601, 1565, (Aromatic, C=C_{str}), 1453 (CH₂bend), 1375 (CH₃), 1624 (C=N), 943 (C-S), 1237 (C-F); ¹H-NMR (300

MHz, CDCl₃): δ 9.26 (s, 1H), 8.34 (dd, J = 7.5, 1.4 Hz, 1H), 8.19-8.07 (m, 3H), 8.05-7.74 (m, 13H), 7.63-7.43 (m, 2H), 1.89 (q, J = 6.7 Hz, 4H), 0.98 (t, J = 6.7 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 192.2, 175.6, 162.6, 161.7, 153.9, 152.5, 150.4, 142.7, 139.2, 138.9, 138.5, 136.3, 131.8, 130.9, 130.3, 129.5, 129.0, 128.3, 128.2, 127.7, 127.2, 126.9, 126.5, 126.0, 125.7, 125.5, 125.3, 124.7, 123.8, 123.7, 123.3, 122.7, 121.8, 120.9, 118.0, 54.4, 32.2, 7.9; MS (m/z, APCI): calcd 705.19 (M⁺), found 706.30[M+H]⁺.

2-(9,9-diethyl-7-(5-(trifluoromethyl)-1H-pyrazol-3-yl)-9H-fluoren-2-yl)benzo[d]thiazole (11)



1-(6-(benzo[*d*]thiazol-2-yl)-9,9-diethyl-9*H*-fluoren-2yl)-4,4,4-trifluorobutane-1,3-dione (0.31g, 0.62 mmol) dropwise added into a flask containing hydrazine

hydrate (0.62 mmol) in EtOH (5 mL) catalytic amount of piperidine was added. The reaction proceeded at room temperature with continuous stirring for 6h, the solvent was diluted with 100 mL of ice cold distilled water and neutralized with dilute HCl at neutral pH crude product was precipitated. After recrystallization with the ethanol purified product was obtained. Light red solid; Yield: 84%; R_f: 0.65; m.p.141-142°C; FTIR (Neat, cm⁻¹) \tilde{v}_{max} : 3095(C=C-H), 2942(C-H_{str}), 2851 (C-H_{str}), 1670(C=N), 1620, 1570, (Aromatic, C=C_{str}), 1465 (CH_{2bend}), 1378 (CH₃), 942 (C-S), 1245 (C-F), 1112 (N-N); ¹H NMR (300 MHz, CDCl₃); δ 14.14 (s, 1H), 8.19 – 8.04 (m, 6H), 7.89 (d, *J* = 7.8 *Hz*, 1H), 7.59-7.36 (m, 3H), 2.15 (q, *J* = 7.2 *Hz*, 4H), 0.28 (t, *J* = 7.2 *Hz*, 6H); ¹³C NMR (75 MHz, CDCl₃); δ 168.1, 154.1, 151.6, 151.0, 144.8, 144.0, 142.3, 141.0, 134.9, 132.5, 128.2, 127.6, 127.2, 126.0, 125.2, 124.0, 123.2, 122.8, 121.8, 121.6, 121.6, 120.7, 120.5, 116.5, 101.8, 56.6, 32.2, 8.9; MS (m/z, APCI): calcd 489.15 (M⁺), found 490.01 [M+H]⁺.

3. Results and Discussions

3.1 Synthesis

Synthesis of the compound **06** (Figure 2) started with commercially available fluorene and iodine. Selective iodination of fluorene yields 2-Iodofluorene [14], alkylation of this 2-iodofluorene was carried out with bromoethane by using KOH as base, TBAB as phase transfer catalyst in DMSO at room temperature to give 2-Iodo-9,9-diethylfluorene This compound was subjected to Friedel-Crafts acylation reaction with acetyl chloride, which yields the ketone, 1-(9,9-diethyl-7-iodo-9*H*-fluoren-2-yl)ethanone after a simple recrystallization. 1-(9,9-diethyl-7-iodo-9*H*-fluoren-2-yl)ethanone and 2-(tributylstannyl)benzo[*d*]thiazole were subjected for C-C coupling by using renowned Stille coupling reaction to furnish 1-(6-(benzo[*d*]thiazol-2-yl)-9,9-diethyl-9*H*- fluoren-2-yl)ethanone [15].

The 1-(6-(benzo[*d*]thiazol-2-yl)-9,9-diethyl-9*H*-fluoren-2-yl)ethanone was treated with ethyl 2,2,2-trifluoroacetate by Claisen condensation method to yield 1-(6-(benzo[*d*]thiazol-2-yl)-9,9-diethyl-9*H*-fluoren-2-yl)-4,4,4-trifluorobutane-1,3-dione **06** [16]. Knoevenagel Condensation of **06** with 4-(dimethylamino)benzaldehyde using piperidine as base in acetonitrile afford excellent yield of (*Z*)-1-(7-(benzo[*d*]thiazol-2-yl)-9,9-diethyl-9*H*-fluoren-2-yl)-2-(4-(dimethylamino) benzylidene)-4,4,4-trifluoro butane-1,3-dione **09** [17,18]. By following same method when compound 0**6** was treated with pyrene-1-carbaldehyde offered (*Z*)-1-(7-(benzo[*d*]thiazol-2-yl)-

9,9-diethyl-9*H*-fluoren-2-yl)-4,4,4-trifluoro-2-(pyren-1-methylene)butane-1,3-dione **10** in good yield. When hydrazine hydrate was treated with compound **6** the cyclization of diketone occurred and product 2-(9,9-diethyl-7-(5-(trifluoromethyl)-1H-pyrazol-3-yl)-9H-fluoren-2-yl)benzo[*d*] thiazole**11**was obtained in good yield. (Scheme 1)



Figure 2. Synthesis of Fluorene based various π acceptor dyes (06, 09-11)

3.2 UV-Visible, FTIR and NMR studies of fluorene A- π -A dyes (06, 09-11)

The characterization of newly synthesized Fluorene derivatives was achieved by UV-Visible, FTIR and NMR spectroscopy. The UV-visible absorption spectra of these dyes were recorded in dichloromethane at room temperature using $(1 \times 10^{-7} \text{ M})$ solution (**Figure 3**). The selected spectral data are tabulated below in **Table 1**.



Figure 3. UV-Visible spectra of fluorene A- π -A chromophores (6, 9-11)

Table 1. Wavelength of maximum absorption λ_{max} of Fluorene A- π -A dyes in dichloromethane (6, 9-11)

Dye	λ_{\max} (nm)
06	362, 394
09	393, 420
10	391, 420



The absorption studies of fluorene acceptor- π -acceptor (A- π -A) dyes were investigated in dichloromethane solution. The solution displayed two band pattern absorption maxima (λ_{max}), first at 361-393 nm and the other at 394-420 nm, respectively. The high absorption λ_{max} for all the compounds at 397-420 nm are attributed to π - π * transition of the compounds. This transition is the characteristic of the C=C, of fluorene conjugated architecture. Absorption spectroscopic results of these derivatives showed that Knoevenagel reaction at the active methylene effect the absorption maxima and also the wavelength. The cyclisation of 1,3-diketone did not affect in a pronounced manner on the absorption.

The FTIR spectra of fluorene A- π -A dyes afforded absorption bands due to C=C-H, C-H, S-H, Aromatic C=C, α , β -unsaturated C=O, C=N, (C-N_{str}), CH₂, C-S, C-F, Ar-H. Compound **11** showed the characteristic IR absorption band at v_{max} 1497-1501 cm⁻¹ is due to C=N moiety. This compound was synthesized by the reaction of compound **06** with hydrazine hydrate, cyclisation with hydrazine was confirmed by the disappearance of both carbonyl peaks \tilde{v} 1701-1738 cm⁻¹ from the synthesized compound. Along this appearance of C=N band in range, from \tilde{v} 1497-1501 cm⁻¹. The peak obtained at \tilde{v} 1246, 1237, 1052 and 1050 cm⁻¹ showed the existence of C-F stretching. The FTIR data of stretching and bending absorption bands recognize the Fluorene A- π -A dyes (**06, 09-11**). The ¹H-NMR spectrum of compound **11** exhibited a high field triplet peak due to CH₃ group at 0.28 ppm, a triplet due to methylene proton at 2.15. The protons of the aromatic region of are observed from 8.13-7.36 ppm, and singlet at 14.0 ppm due to N-H of pyrazole ring. ¹³C-NMR spectra of compound **11** there are signals for twenty eight different carbon peak at 56.6 is due to the alkylation at 9-position of fluorene, methylene carbon absorbed at 32.2 and methyl carbon at 8.9 ppm. The disappearance of carbonyl group peaks from 194.8 and 182.0 and the appearance of the peaks at 168.1, 154.1 are confirming the cyclization of the compound and evidence for the confirmation of dye **11**. While the peaks at 56.6 ppm is for methine carbon of fluorene and other two peaks at δ 32.2 ppm and 8.9 ppm, confirmed the alkylation at 9,9'-position of fluorene. The other synthesized compounds of fluorene A- π -A dyes have been characterized by using the same techniques.

3.3 Optical properties

3.3.1 Maximum extinction coefficients (ϵ_{max})

It is an essential property which depends upon the path length (l) absorbance (A) and concentration (c), of the species (Beer-Lambert law) i.e., $A = \epsilon_{max}$ Cl. Molar extinction coefficient of fluorene A- π -A dyes are presented in **Table 2**

Dyes	$\lambda_{max}(nm)$	Α	$\epsilon_{\max}(L \text{ mol}^{-1} \text{ cm}^{-1})$
06	394	0.68400	136800.0
09	420	0.616240	123248.0
10	420	1.490332	298066.4
11	395	0.868987	173797.4

Table 2 Molar extinction coefficients of fluorene A- π -A dyes (06, 09-11)

Absorption spectra of these dyes showed that compound **09** and **11** showed almost same absorption pattern and absorption maxima but there is an increase in the molar extinction coefficient of **11** which indicated that after socialization there is little difference in conjugation but a huge increase in stability. Whereas the compound **09** showed bathochromic shift and hyperchromic shift in UV-visible absorption of the compound, it revealed that the introduction of

4-(dimethylamino)benzaldehyde at the active methylene of compound **06** had effected the band I and increases the molar extinction coefficient, due to this enhancement it would be more beneficial than parent compound **06**. Following the same procedure the compound **06** was coupled with pyrene-1-carboxaldehyude this compound showed same bathochromic shift as shown by **09** but a drastic enhancement in molar extinction coefficient observed this indicated that coupling at the active methylene of compound **06** is more beneficial for the optoelectronic properties of the compound and therefore compound **06** and **10** had shown a high effect in this regard.

3.3 Fluorescence examination

Fluorescence Spectra of fluorene A- π -A dyes (06, 09-11) in dichloromethane solution were recorded. These dyes 06, 09, 10 and 11 emit maximum at λ_{max} 422, 527, 533 and 443 nm respectively. Compounds 09 and 10 showed higher emission value due to coupling of conjugated aldehyde at active methylene and in case of 10 it also showed a broad range which indicated that the pyrene group at the active methylene had great influence in electronic transition and bear the more importance in organic electronics. While compound 06 and 11 showed almost similar behavior which indicated that the cyclization at 1,3-dicarbonyl carbons did not affect the electronic transformation in good extent, fluorescence and Stoke's shift are compared to literature value which reveals that these compounds are the best candidates for the blue OLEDS [19] Figure 4 and Table 3.



Figure 4 Fluorescence spectra of fluorene A- π -A dyes in dichloromethane (06, 09-11)

Table 3 Fluorescence values of fluorene A	$-\pi$ -A dyes in dichloromethane (06, 09-11)
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Excitation	Emission	Emission	Stoke Shift
wavelength (nm)	wavelength (nm)	Height	(nm)
394	422	25391.3	049
420	527	14755.9	107
420	533	17393.8	113
395	443	27239.2	048
	Excitation wavelength (nm) 394 420 420 395	ExcitationEmissionwavelength (nm)wavelength (nm)394422420527420533395443	Excitation Emission Emission wavelength (nm) wavelength (nm) Height 394 422 25391.3 420 527 14755.9 420 533 17393.8 395 443 27239.2

Singlet Energies (E_s)

Singlet energies were calculated by using the same procedure reported above. The data is represented in **Table 4**

Dye	λ _{max} (Å)	E _s (kcal/mol)
06	3940	72.58
09	4200	68.09
10	4200	68.09
11	3950	72.40

Table 4 Singlet energies of fluorene A- π -A dyes in dichloromethane (06, 09-11)

The calculated singlet energy of these compounds obtained from the calculations showed that there is no change in between compound **06** and **11** for compound **09** and **10** both displayed the same maximum absorption therefore there singlet energy is same. From these results it was noticed that the change occur in the absorption wavelength when the coupling occurs at active methylene center of the precursor and cyclization didn't showed this effect, but it was also noted that as the compound have two bands pattern, it reflected that after the coupling at active center it increase the absorption wavelength in some extent in **09** and **10**. But there was a promising change in molar absorptivity, as singlet energy is related to maximum absorption, so therefore compound **09** and **10** had same singlet energy. From these results it is observed that the enhanced delocalization couldn't effect in large extent.

3.4 Oscillator strengths of fluorene A- π -A dyes in dichloromethane (06, 09-11)

Already documented method was used for the calculation of oscillator strengths. The obtained results of oscillator strength of these dyes are tabulated below in **table 5.** The range is in between 0.304 to 1.174, compound **06** which contain two carbonyl moieties in the structure showed the minimum oscillator strength substitution at active methylene, it increased the oscillator strength of the molecule with increase in conjugation at active methylene center and an increased in

oscillator strength, were observed. The increase in oscillator strength was also observed when the cyclisation was carried out with hydrazine at carbonyl moieties. From this it can be suggested that the increase in conjugation by coupling at active nuclei or cyclization will increase the oscillator strength. Compound **10** showed the highest value of oscillator strength, which could be due to strong π - π * transition, **Table 5**.

Dye	$\Delta V_{1/2} \text{ (cm}^{-1}\text{)}$	ϵ_{\max} (L mol ⁻¹ cm ⁻¹)	Oscillator strengths f
06	515.40	136800.0	0.304
09	683.65	123248.0	0.364
10	911.70	298066.4	1.174
11	515.40	173797.4	0.387

Table 5 Oscillator strengths of fluorene A- π -A dyes in dichloromethane (06, 09-11)

3.5 Theoretical Radiative Lifetimes (T_o)

The theoretical radiative life time of these dyes was from 2.75 to 7.13 (ns). Compound **10** has higher ϵ_{max} value and smaller values of the radiative lifetime (T_o). Results of spectroscopic data showed that those compounds having larger absorptions in UV-visible region exhibited radiative lifetime (T_o) value lower. Calculated theoretical radiative lifetimes are listed in **table 6**.

Table 6 Theoretical radiative lifet v_{max} of fluorene A- π -A dyes (06, 09-11)

Dyes	$\Delta V_{1/2} (cm^{-1})$	ϵ_{\max} (L mol ⁻¹ cm ⁻¹)	v_{max} (cm ⁻¹)	T _o (ns)
06	515.4	136800.0	25380.71	7.71
09	683.65	123248.0	23890.52	7.28
10	911.70	298066.4	23890.52	2.26

11	515.4	173797.4	25319.46	6.09

3.6 Fluorescence Rate constant (k_f) and theoretical fluorescence lifetime (T_f)

The fluorescence rate constants of these dyes were in range from varied from $1.30 \times 10^8 \text{ s}^{-1}$ to $4.42 \times 10^8 \text{ s}^{-1}$ and theoretical fluorescence lifetime obtained was 0.972 to 4.872. Compound **10** displayed highest fluorescence rate constant value. This compound was obtained by the coupling of pyrene-1-carboxaldehyde with compound **06** at the active methylene whereas the radiative life time of the same compound is very low. High fluorescence rate constant of **10** is due to large size of pyrene ring and extended conjugation due to which increase in the fluorescence rate constant and decrease in radiative lifetime is observed. The compound **11** also showed the same effect, but in little extent because here conjugation increased due to cyclization, but this conjugation is not prominent therefore small effect observed are documented in **Table 7**.

Table 7 Fluorescence rate constant and theoretical fluorescence lifetime of fluorene A- π -A dyes(06, 09-11)

Dye	T _o (ns)	$k_{f} (10^{8}/s)$	φ _f	T _f (ns)
06	7.71	1.30	0.63	4.857
09	7.28	1.37	0.60	4.368
10	2.26	4.42	0.43	0.972
11	6.09	1.64	0.80	4.872

3.7 By conventional method the florescence life time of the dyes also confirmed by time domain using,

Steady-state and Time-resolved Photoluminescence

Steady-state and time-resolved photoluminescence (PL) of the samples were carried out by using standard instrument, Flau Time 300 (FT-300) steady state and life-time spectrometer, PicoQuant GmbH, Germany. The PL was measured following pulsed LED laser excitation source, PLS-300, centered at 305 nm with full width half maximum (FWHM) of ~416 ps and pulse energy 0.077 pJ. (**Figure 5**)



Figure 5 Steady-State florescence life time of fluorene A- π -A dyes

3.8 Thermal properties fluorene A- π -A dyes

These derivatives possess good thermal stability with thermal decomposition temperature around >220°C, determined by TGA under nitrogen measured from 50-750°C at a heating rate of 20 °C/min. . (Figure 6). The results indicate that compound 10 has a highest thermal degradation temperature 282° C while compound 9 has second highest value 267° C, while compound 6 degraded at 222° C and compound 11 at 233° C. These results revealed that the substitution at the active methylene enhanced the stability of the compounds this is due to increase in conjugation of molecule and rigidity due to substitution with bulky group.



. (Figure 6) Thermal analysis of fluorene A- π -A dyes

3.7 Electrochemical Properties

3.7.1 Electrochemical studies fluorene A- π -A dyes (06, 09-11)

The electrochemical study of all compounds was carried by using cyclic voltammetry in dichloromethane solution in the presence of 0.1 M TBAPF_6 as a supporting electrolyte. From their cyclic voltamogram band gap energy, HOMO and LUMO energies were obtained. Combined cyclic voltamogram of these dyes are displayed in **Figure 7**, table 2.16.



Figure 7 Cyclic Voltammogram of fluorene A- π -A dyes (06, 09-11) in dichloromethane

Compounds	$E_{1/2}(V)$	LUMO (eV)	HOMO (eV)	E _g (V)
06	-0.712	-4.08	-6.75	2.67
09	-0.426	-4.37	-7.01	2.64
10	-0.277	-4.52	-7.15	2.63

	11	-0.642	-4.15	-6.81	2.66
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3.8 Band Gap Energy Values (Eg)

The span of energies between valence and conduction bands for semiconductors and insulators is known as band gap energy. Every material has its characteristic band gap energy. The formation of various materials is the results of this variation in band energy. For these dyes band gap energies were calculated by using the standard procedure [20]. The band gap energy of compounds is given in table 8. Compound **11** showed little difference in the band gap energy value compared to the compound **06**, which indicating that cyclization at 1,3-diketone position affect the band gap value but this effect was not significant. Compound **09** has exhibited comparatively higher value than **11** and slightly lower than **10**. These results infer that the coupling in active methylene center of compound **06** with extended conjugation either by bulky conjugated group or small group containing electron donating auxochrome will reduce the band gap energy.

3.9 Highest occupied molecular orbitals (HOMO)

Table 8 shows the highest occupied molecular orbital energy levels, varies from -4.08 to -4.52 eV for these dyes. The value varies with the conjugation with an increase in conjugation as results showed that compound **10** has greater conjugation compared to all other compounds therefore it displayed highest value of HOMO energy levels. It was concluded that HOMO energy levels can be altered only by increasing the delocalization of electrons through conjugation. It is due to the fact that as conjugation increases the energy difference will decrease and vice versa.

4. Conclusions

In summary, we have synthesized fluorene based chromophores (06, 09-11) by using a simple synthetic protocol. The synthesized compounds were subjected to photo physical studies such as; fluorescence, UV-visible spectroscopy and cyclic voltammetry. Compound 10 showed maximum absorption at 420nm with higher stoke shift value 113nm. Conducting behavior of the compound 10 was observed with highest occupied molecular orbital value with -7.15eV and lowest unoccupied molecular orbital value with -4.52eV having band gap energy value of 2.63eV. From the results of photo-electrochemical behavior we infer that compound 10 serve as a structural template for the designing of blue and green OLEDS.

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Conflict of interest

Authors declare no any conflict of interest

References

[1] Li C, Li Z, Yan X, Zhang Y, Zhang Z, Wang Y. Structurally simple non-doped sky-blue OLEDs with high luminance and efficiencies at low driving voltages. J Mater Chem C 2017; 5: 1973-80.

[2] Chen WC, Yuan Y, Ni SF, Zhu ZL, Zhang J, Jiang ZQ, Liao LS, Wong FL, Lee CS. Highly Efficient Deep-Blue Electroluminescence from a Charge-Transfer Emitter with Stable Donor Skeleton. ACS Appl Mater Interfaces 2017; 9: 7331-8.

[3] Shan T, Gao Z, Tang X, He X, Gao Y, Li J, Sun X, Liu Y, Liu H, Yang B, Lu P. Highly efficient and stable pure blue nondoped organic light-emitting diodes at high luminance based on phenanthroimidazole-pyrene derivative enabled by triplei-triplet annihilation. Dyes and Pigments. 2017;142:189-97.

[4] Udagawa K, Sasabe H, Igarashi F, Kido J. Simultaneous Realization of High EQE of 30%, Low Drive Voltage, and Low Efficiency Roll Off at High Brightness in Blue Phosphorescent OLEDs. Advanced Optical Materials. 2016;4:86-90.

[5] Zhan X, Wu Z, Lin Y, Xie Y, Peng Q, Li Q, Ma D, Li Z. Benzene-cored AIEgens for deepblue OLEDs: high performance without hole-transporting layers, and unexpected excellent host for orange emission as a side-effect. Chemical Science. 2016;7:4355-63.

[6] Cui LS, Kim JU, Nomura H, Nakanotani H, Adachi C. Benzimidazobenzothiazole Based Bipolar Hosts to Harvest Nearly All of the Excitons from Blue Delayed Fluorescence and Phosphorescent Organic Light Emitting Diodes. Angewandte Chemie International Edition. 2016;55:6864-8.

[7] Belfield KD, Ren X, Van Stryland EW, Hagan DJ, Dubikovsky V, Miesak EJ. Near-IR twophoton photoinitiated polymerization using a fluorone/amine initiating system. J Am Chem Soc 2000; 122:1217-8.

[8] Belfield KD, Schafer KJ, Mourad W, Reinhardt BA. Synthesis of new two-photon absorbing fluorene derivatives via Cu-mediated Ullmann condensations. J Org Chem 2000; 65:4475-81.

[9] Belfield KD, Morales AR, Kang BS, Hales JM, Hagan DJ, Van Stryland EW, Chapela VM, Percino J. Synthesis, characterization, and optical properties of new two-photon-absorbing fluorene derivatives. Chem Mater, 2004; 16:4634-41.

[10] Corredor CC, Huang ZL, Belfield KD, Morales AR, Bondar MV. Photochromic polymer composites for two-photon 3D optical data storage. Chem Mater 2007; 19:5165-73.

[11] Feng L, Zhang C, Bie H, Chen Z. Synthesis and photoluminescent properties of some novel fluorene derivatives. *Dyes Pigm* 2005; 31-4.

[12] Xu X, Ye S, He B, Chen B, Xiang J, Zhou J, Lu P, Zhao Z, Qiu H. Dimesitylborylfunctionalized fluorene derivatives: Promising luminophors with good electron-transporting ability for deep blue organic light-emitting diodes. Dyes Pigm 2014;101:136-41.

[13] Feng XJ, Chen SF, Ni Y, Wong MS, Lam MM, Cheah KW, Lai GQ. Fluorene derivatives for highly efficient non-doped single-layer blue organic light-emitting diodes. Organic Electronics 2014;15:57-64.

[14] Ogata Y, Urasaki I. Iodination of Acenaphthene and Fluorene with Iodine–Peracetic Acid. *Journal of the Chemical Society C: Organic*; 1970;12:1689-91.

[15] Zhao D, You J, Hu C. Recent progress in coupling of two heteroarenes. *Chemistry–A European Journal* 2011;17:5466-92.

[16] Liu SG, Su WY, Pan RK, Zhou XP. Red Emission of Eu (III) Complex Based on 1-(7-(tertbutyl)-9-ethyl-9*H*-carbazol-2-yl)-4, 4, 4-trifluorobutane-1, 3-dione Excited by Blue Light. *Chinese Journal of Chemical Physics* 2012; 25:697-702.

[17] Bogdał D. Coumarins: fast synthesis by Knoevenagel condensation under microwave irradiation. Journal of Chemical Research, Synopses. 1998;1:468-9.

[18] Texier-Boullet F, Foucaud A. Knoevenagel condensation catalysed by aluminium oxide.Tetrahedron Letters 1982;23:4927-8.

[19] Xu X, Ye S, He B, Chen B, Xiang J, Zhou J, Lu P, Zhao Z, Qiu H. Dimesitylborylfunctionalized fluorene derivatives: Promising luminophors with good electron-transporting ability for deep blue organic light-emitting diodes. Dyes and Pigments 2014;101:136-41.

[20] Ego C, Marsitzky D, Becker S, Zhang J, Grimsdale AC, Müllen K, Friend RH. Attaching perylene dyes to polyfluorene: three simple, efficient methods for facile color tuning of lightemitting polymers. *J Am Chem Soc* 2003;125:437-43. Highlights

- Synthesis of some novel fluorene based chromophores with promising optoelectronic properties was carried
- The UV-Vis absorption and fluorescence were in the range 394-420nm and 48nm-113nm, respectively.
- The band gap energy values 2.63 to 2.67 eV suggest the use of these compounds in blue and green OLEDS.

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