Journal of Fluorescence
https://doi.org/10.1007/s10895-020-02516-z

ORIGINAL ARTICLE

Donor-Pi-Acceptor Fluorene Conjugates, Based on Chalcone and Pyrimidine Derivatives: an Insight into Structure-Property Relationship, Photophysical and Electrochemical Properties

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Received: 16 January 2020 / Accepted: 14 February 2020

Abstract

A small set of four new fluorenyl chromophores (**5-5a-c**) was accomplished by stepwise nucleophilic substitution, Friedel-Crafts acylation, Ullman coupling, aldol condensation and cyclization reactions. The fluorene moiety was substituted at 2,7,9 and 9′ positions with diverse groups. The synthesized derivatives were characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. The optical properties were evaluated by by UV-VIS absorption and Fluorescence studies. HOMO and LUMO energy levels were evaluated by electrochemical studies and were found at −5.37-5.83 eV and − 2.47-2.94 eV respectively with band gap energy values 2.88 to 2.91 eV. The band gap energy values suggested that these synthesized molecules can be manipulated in the designing of blue and green OLEDS.

Keywords Fluorene conjugates · OLEDS · Optoelectronic properties · HOMO and LUMO · Band gap energy

Introduction

Fluorene derivatives have observed unprecedented privilege in the field of optoelectronics and organic electronics [1]. Conjugated fluorene small organic molecules play pivotal role in designing of organic light emitting diodes (OLEDs) [2]. Investigation of structure-property relationship in fluorene derivatives serves as guideline for the designing efficient light emitting materials [3]. The ease of modification in fluorene moiety paves the way for synthesis of new molecules having distinct optical characteristics. The rigidly planar biphenyl unit of fluorene provides the prospect for designing controlled organic electronic devices [4]. The aromatic rings of fluorene are electron rich and play key role in the enhancement of

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Jamaluddin Mahar and Ghulam Shabir both are first authors.

Research Highlights
- Facile synthesis of Pyrimidine derivatives of Fluorene chromophore by multistep strategy.
- Large stokes shift values and high fluorescence quantum yields.
- Chromophores exhibiting oxidation potential.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10895-020-02516-z) contains supplementary material, which is available to authorized users.

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absorption properties and lowering the oxidation potential [5–7]. The 2, 7 and 9 positions of fluorene ring are activated and can be readily functionalized to introduce desired motifs [8].

The judicious choice of heterocycles stimulate manipulation of HOMO-LUMO levels and emission colors in organic molecule seems to be attractive strategy [9, 10]. In the regard pyrimidine derivatives have observed resurgence in the past decade as efficient electron accepting chromophores. Pyrimidine, a six membered highly pi-deficient heterocyclic unit, has the ability to accept electrons and this feature makes pyrimidine a suitable architect for designing of fluorene-based materials with desirable push-pull properties [11, 12]. To explore the effect of electron donating groups linked with pyrimidine ring, we incorporated NH_2, SH and OH as electron donor moieties (Fig. 1). Fluorene nucleus is locked with thiophene ring which greatly influences the optoelectronic properties because it assists in reducing the band gap and tunes the colour in device [13–15]. Charge separation in these compounds can be controlled by modifying the chemical structure, i.e., extending the π-conjugation path or alternating the strength of donating and accepting substances. In order to undermine the effect of various electron donating and electron withdrawing groups attached to fluorene nucleus, we have carried out UV-visible studies, Fluorescence studies and electrochemical studies.

Experimental

Materials

Fluorene, iodine, hexylbromide, acetic acid, sulphuric acid, tetrahydrofuran, thiophene-2-carbaldehyde, diphenylamine, tetrabutylammonium bromide (TBAB), urea, thiourea, and guanidine hydrochloride were purchased from Sigma-Aldrich. Dimethylformamide (DMF) and Potassium hydroxide (KOH), were commercial products from Daejing, Korea. Solvents such as ethanol, ethyl acetate, and methanol were common laboratory grade chemicals.

Methods

All the chemicals used for analysis were of 99–100% purity. ^{1}HNMR spectra of all the compounds were conducted using a 300 MHz Bruker NMR spectrometer in $CDCl_3$ 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 δ (ppm). The FTIR spectra were taken in the single beam Nicolet FTR 100. Ultraviolet-visible (UV-VIS) spectroscopic studies were done by a double beam Cecil UV-VIS spectrophotometer 7400 series. Molar extinction coefficients of the compounds were obtained from (UV-VIS) spectroscopic data. Purification of the compounds was carried out by silica gel column chromatography. Electrochemical study was made by Electrochemical Analyzer CH1830C. Fluorescence quantum yields were determined using reference fluorescein having quantum yield 95% in water.

General Procedure for the Synthesis of Fluorene Dyes 5-5a-c

Synthesis of fluorene derivatives was accomplished through five step procedure which is as follows:

a) Preparation of monoiodoflourene (1)

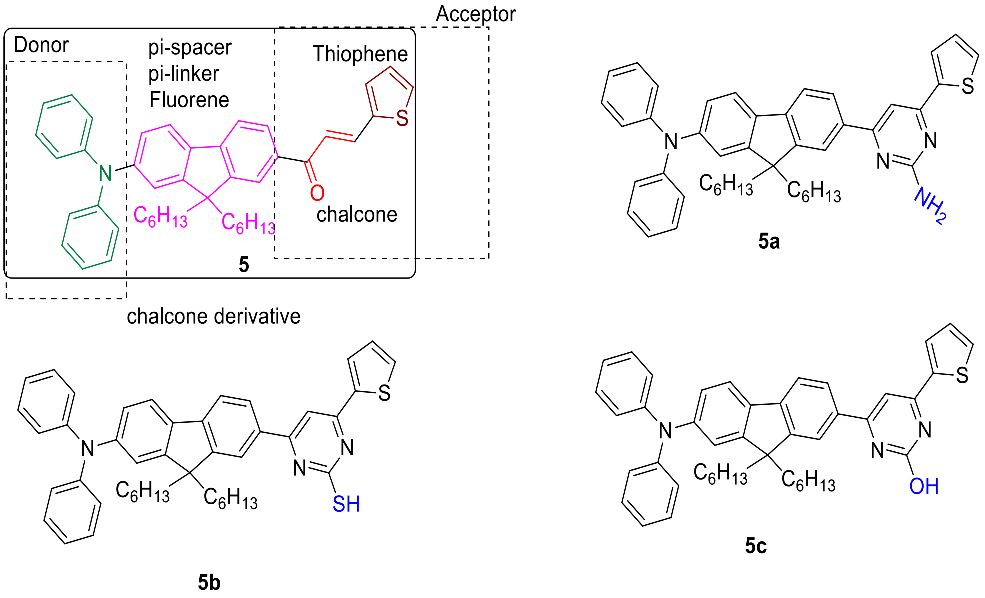
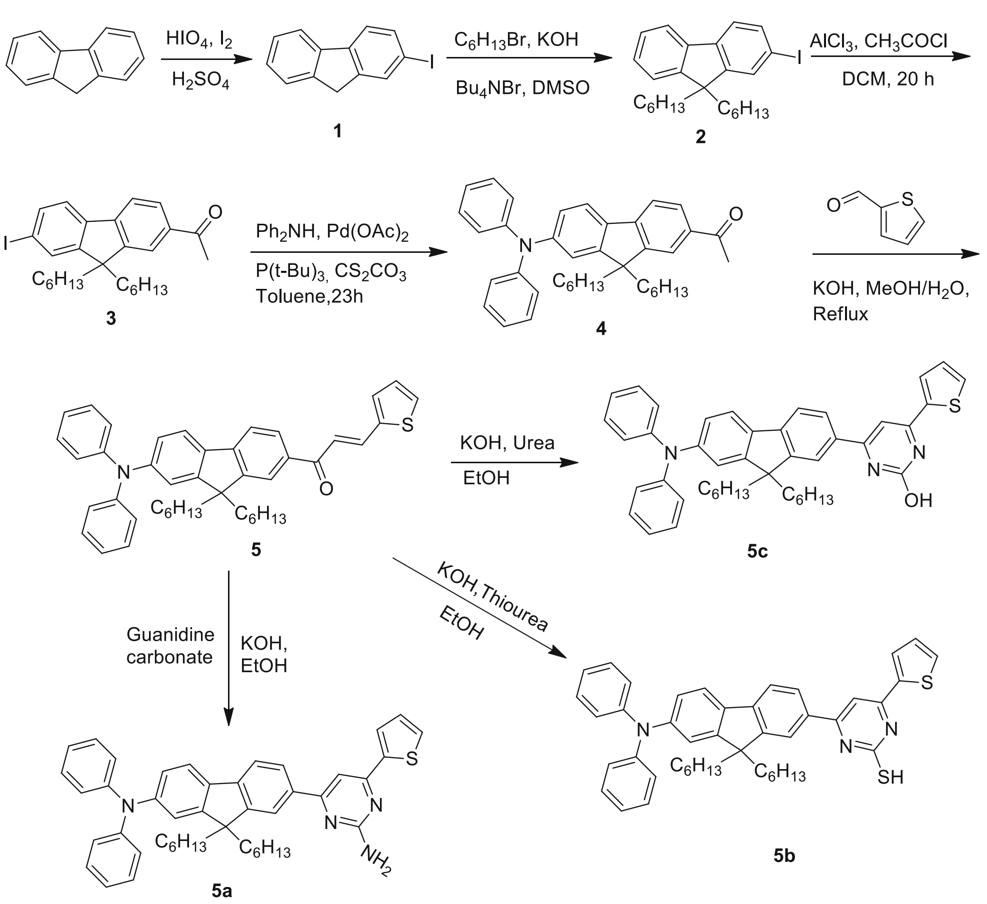


Fig. 1 Design of donor-pi-acceptor Fluorene-pyrimidine conjugates

Scheme 1 Synthetic route for the targeted Fluorene derivatives (**5**, **5a-c**)



Fluorene (4 g, 23.6 mmol) was dissolved in acetic acid (AcOH) at 40 °C in a 100 mL two neck round bottom flask. In the reaction mixture sulphuric acid (H_2SO_4, 2.6 mL, 4.2 mmol) and iodine (2.52 g, 1.0 mmol) were added followed by iodic acid (1.4 g, 0.8 mmol) aqueous solution (5 mL). Continued heating at 70 °C for 1 h. On completion of the reaction, the mixture after cooling to room temperature was poured into ice cold water (250 ml), and the precipitates were obtained which were separated and neutralized by washing with 2% sodium bicarbonate solution ($NaHCO_3$). Precipitates were dried in vacuum desiccator. Purified compound was obtained by recrystallization of crude product in methanol.

b) Preparation of 9,9'-dihexyl monoiodoflourene (2)

Table 1 Wavelength of maximum absorption λ_{max} of D-π-A fluorene dyes in DCM (**5, 5a-5c**)

Dye	λ_{max} (nm)
5	430
5a	428
5b	428
5c	426

Dihexyliodo Fluorene (3.0 g, 6.3 mmol), Potassium hydroxide (KOH)(0.353 g, 6.3 mmol), and a catalytic amount of tetrabutylammonium bromide (0.20 g, 0.62 mmol) were added to a flask. The flask was degassed three times by applying freeze-thaw cycles. With the help of syringe n-Hexyl bromide (8.32 g, 7.07 mL, 50.4 mmol) was added (degassed) which was followed by the addition of DMSO. This mixture

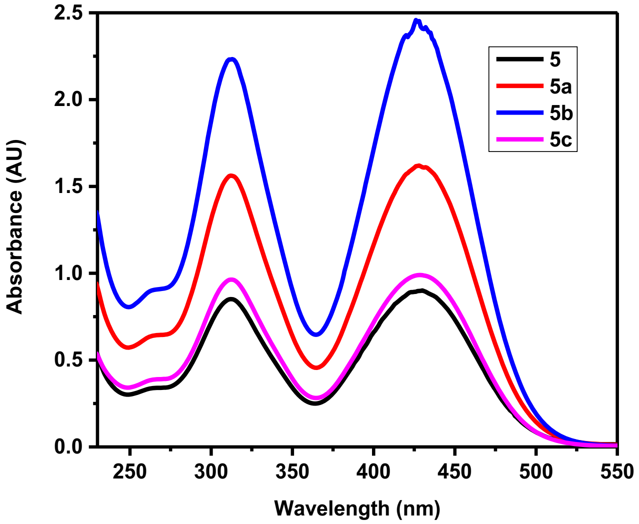


Fig. 2 UV-Visible spectrum of fluorene Dyes **5**, **5a-c**

stirred continuously for 24 h. The product was purified by silica gel column chromatography using a mixture of ethyl acetate: hexane (1:4) to afford the product as a white solid.

c) Synthesis of 2-Iodo-9,9-dihexyl-9*H*-fluoren-7-yl)-ethanone (3).

To a solution of acetyl chloride (0.52 mL) in25mL of CH_2Cl_2 was added $AlCl_3$ (1.02 g, 7.67 mmol) under inert atmosphere at 0 °C. Followed by the addition of 2-iodo-9,9-dihexyl-9H-fluorene(3.09 g, 6.72 mmol) dissolved in 10 mL of CH_2Cl_2 at the same temperature. Then was stirred at ambient temperature for 20 h, the solution was treated with cold water. The organic phase was dried over $Na_2SO_4$and concentrated by rotary evaporator. The product was purified by silica gel column chromatography using a mixture of ethyl acetate: hexane (1:4). A white solid was obtained.

d) Synthesis of 1-(2-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-7-yl)ethanone (4).

In a reaction flask a mixture of diphenylamine (4.43 g, 26.20 mmol), 1-(2-iodo-9,9-dihexyl-9H-fluoren-7-yl)ethanonecarbaldehyde (2.4 g, 6.98 mmol), $P(tBu)_3$ (0.08 g, 0.42 mmol), Cs_2CO_3 (3.33 g, 10.22 mmol) and $Pd(OAc)_2$ (0.05 g, 0.24 mmol) in toluene (20 mL) was refluxed for 36 h. After that it was cooled to ambient temperature, the reaction mixture was filtered through a short plug (silica gel) and after was concentrated by rotary evaporated, a brownish yellow oil obtained.

e) Synthesis of (*E*)-3-(2-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-7-yl)-1-(thiophen-2-yl)prop-2-en-1-one (5).

Into the reaction mixture of 1-(2-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-7-yl)-ethanone (2 g, 3.68 mmol) was added the solution of KOH (0.25 g, 4.5 mmol) in 20 mL MeOH: H_2O (5:1). After mixing, Thiophene-2-carbaldehyde (0.41 g, 3.68 mmol) was added to the solution and refluxed for 48 h. Precipitated product was filtered, washed with n-hexane and dried in vacuum desiccator. Recrystallization was carried in n-hexane and yellow solid was obtained. In this way 5a-c fluorene derivatives were synthesized and characterization.

Table 2 Molar extinction coefficients of D-π-A fluorene dyes (**5, 5a-5c**)

Dyes	λ_{max}(nm)	A	ϵ_{max}(L mol^{-1} cm^{-1})
5	430	0.90101	18,020.2
5a	428	0.99082	19,816.4
5b	426	2.45808	49,161.6
5c	428	1.62007	32,401.4

Table 3 Fluorescence values of D-π-A fluorene dyes in DCM (**5, 5a-5c**)

Dye	λ_{ex} (nm)	λ_{em}(nm)	Stokes Shift (nm)	ϕ_f
5	430	645	215	13.3
5a	428	650	222	15.7
5b	426	657	231	14.5
5c	428	653	225	15.1

Results and Discussion

The synthesis of the different fluorene derivatives was executed as shown in Scheme 1. Mono iodination of fluorene was achieved by reacting it with stoichiometric amount of iodine in the presence of iodic acid [16, 17], then alkylation with n-hexyl bromide yielded compound **2** [18] which on Friedel-Crafts acylation provided the acetylated product 1-(9,9-dihexyl-7-iodo-9*H*-fluoren-2-yl)ethanone **3**. Arylamination of **3** was achieved by Buchwald-Hartwig amination coupling method to obtain acetophenone derivative **4** [19, 20]. The intermediate 4 on Claisen-Schmidt condensation with thiophene 2-carboxaldehyde furnished the chromophore (*E*)-1-(7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)-3-(thiophen-2-yl)prop-2-en-1-one **5** as a yellow solid. The synthesis of compounds **5a-c** was accomplished by condensation of compound **5** with urea, thiourea and guanidine in the presence of potassium hydroxide in ethanol at room temperature. The purified products were obtained after recrystallization from ethanol.

UV-Visible, FTIR and NMR Studies of Fluorene Dyes 5-5a-c

The structures of newly-synthesized fluorene derivatives were **5-5a-c** were investigated by UV-Visible, FTIR and NMR spectroscopy. The UV-visible absorption studies of the fluorene dyes were conducted in DCM solution (1×10^{-5} M) and the selected spectral data are summarized in Table 1, Fig. 2.

The electronic transitions in dyes **5-5a-c** in DCM provided two absorption bands with maxima at 310-315 nm and 426-430 nm respectively (Fig. 1). The λ_{max} for all the compounds at 426-430 nm is the result of π-π* transition of the compounds due to the presence of C=C, which is the characteristic of fluorine conjugated motif. From UV results, it is revealed that all fluorene derivatives show approximately identical λ_{max}. This evidence indicates that cyclization at α,β unsaturated position of D-π-A fluorene dyes does not affect much the λ_{max} of dyes [21].

The FTIR spectra of fluorene chromophores provided absorption bands due to C=C-H, C-H, S-H, α, β-unsaturated C=O, Aromatic C=C, C=N, CH_2, (C-N_{str}), C-S, Ar-H. In case of compound **5** characteristic IR absorption band at 1680/cm

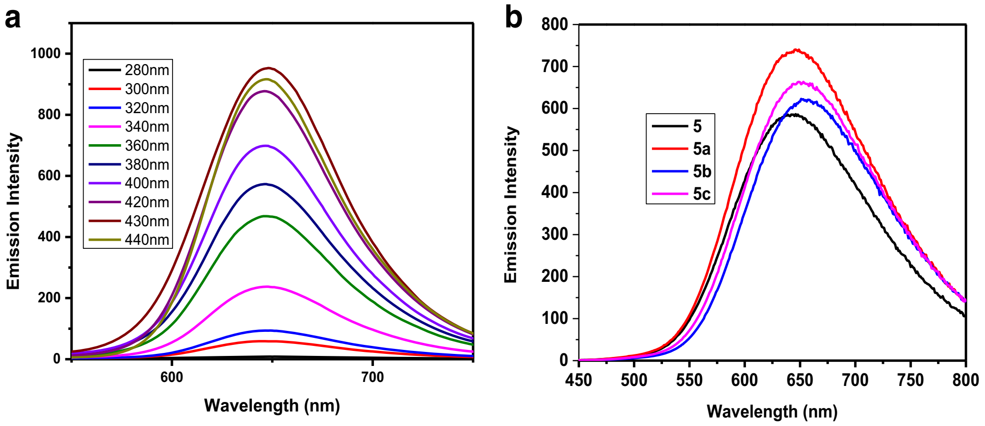


Fig. 3 **a** Excitation spectrum of fluorene dye **5**, (**b**) Emission spectrum of D-π-A fluorene dyes **5**, **5a-c**

is due to α,β-unsaturated C=O moiety developed as a result of reaction between intermediate **4** and thiophene-1-aldehyde. Cyclization at α,β-unsaturated C=O position of compound **5** resulted in synthesis of different derivatives which were confirmed by disappearance of carbonyl band and appearance of C=N band in range from 1490 to 1495/cm. The substitution on pyrimidine ring "common in all derivatives" has been confirmed by the bands of different auxochromes like OH at 3490/cm, two bands of NH_2 at 3350, 3310/cm and SH at 2515/cm. All these stretching and bending absorption bands identify the fluorene derivatives (**5-5a-c**).

The ^{1}H NMR spectrum of compound **5** exhibited a triplet peak due to CH_3 group at 0.79 ppm, a multiplet due to methylene envelope in the region of 1.39–1.25 ppm and a multiplet at 1.99–1.88 ppm due to methylene envelope at 9,9′-position of fluorine (Figure S1). Similarly, in the aromatic region signals due to different protons occupy the region 7.94–7.05 ppm, common in all compounds. The ^{13}C NMR spectrum of compound **5** showed signals for thirty different carbons which are at 182.1, 153.0, 151.4, 148.1, 147.8, 145.9, 145.0, 144.0, 135.0, 133.0, 132.7, 131.6, 129.3, 129.2, 129.1, 124.2, 123.2, 122.9, 122.8, 121.0, 120.1, 119.5, 118.8, 55.1, 40.2, 31.5, 29.6, 23.8, 22.6, 14.1 ppm values. The carbonyl group is evidenced from its signal at 182.1 ppm while alkyl chains at 9,9′-positon of fluorine are confirmed by the signals at 40.2, 31.5, 29.6, 23.8, 22.6 and 14.1 ppm and methine carbon of fluorine is at 55.11 ppm (Figure S2). The other derivatives of fluorene, **5a-c** have been identified from their respective ^{1}H NMR and ^{13}C NMR spectra.

Optical Properties

Maximum Extinction Coefficients (⊠$_{max}$)

The measurement of how strongly a chemical species absorbs light at a particular wavelength depending upon the absence or presence of certain functionalities in the molecule is known as maximum extinction coefficient. It is fundamental property which depends upon the actual the concentration (c), absorbance (A) and path length (l) of the species (Beer-Lambert law) i.e., $A = \epsilon_{max}$ cl. Molar extinction coefficient of fluorene dyes is presented in Table 2.

Absorption in UV-visible region by **5-5a-c** fluorene dyes is higher for those dyes which have pyrimidine ring instead of alpha- beta- unsaturated carbonyl. Dyes with SH auxochromes showed higher value of molar extinction coefficients and high absorption intensity. It can be generalized that fluorene containing pyrimidine derivative instead of α, β-unsaturated ketone have higher molar extinction coefficient. Compounds containing mercapto and amino group have large influence in molar extinction coefficients than hydroxyl as it is evidenced from high molar extinction coefficients of **5b** and **5c** as compared to **5a**.

Fluorescence Examination

Fluorescence studies of dyes **5-5a-c** were conducted to observe their emission position and intensity. Fluorescence data recorded for 1×10^{-5}M solution of these dyes in DCM are summarized in Table 3.

Table 4 Singlet energies of D-π-A fluorene dyes **(5, 5a-5c)**

Dye	λ_{max}(Å)	E_s (kcal/mol)
5	4300	66.51
5a	4280	66.82
5b	4260	67.14
5c	4280	66.82

Table 5 Oscillator strengths of D-π-A fluorene dyes **(5, 5a-5c)**

Dye	$\Delta V_{1/2}$ (cm^{-1})	ϵ_{max} (L mol^{-1} cm^{-1})	Oscillator strengths (f)
5	5039.19	18,020.2	0.392
5a	4946.59	19,816.4	0.423
5b	4697.43	49,161.6	0.998
5c	4810.49	32,401.4	0.673

Table 6 Theoretical radiative lifetime of D-π-A fluorene dyes **(5, 5a-5c)**

Dye	$\Delta V_{1/2}$(cm^{-1})	ϵ_{max} (L mol^{-1} cm^{-1})	V_{max} (cm^{-1})	T_o(ns)
5	5039.19	18,020.2	23,255.81	7.13
5a	4946.59	19,816.4	23,364.48	6.54
5b	4697.43	49,161.6	23,474.17	2.75
5c	4810.49	32,401.4	23,364.48	4.11

Excitation wavelengths were found at 426–430 nm (Fig. 3a). The emission spectra of these dyes show only one emission band with maxima at 645-657 nm, after excitation at different wavelengths (Fig. 3b). All dyes displayed very similar emission spectrum, which showed the minor effect of auxochrome on emission intensity which is seen in small extension of emission wavelength in dyes **5a-c** bearing OH, SH and NH_2 groups. Fluorescence peak of high intensity at 645-657 nm for diverse dyes corresponds to absorption peak in the range of 426–430 nm [22, 23].

Singlet Energies (E_s)

Singlet energies were calculated by using the equation, $\mathbf{E_s = 2.86 \times 10^5/ \lambda_{max}}$ [24] and observed data is summarized Table 4.

It is concluded from this study, that there is little bit change in the singlet energies of fluorene dyes. Singlet energy is dependent on wavelength of maximum absorption, which is almost constant. In order to obtain noticeable changes in wavelength of maximum absorption there must be conjugation extension through alternate single and double bonds.

Oscillator strengths were calculated by the reported procedure using the equation, $f = 4.32 \times 10^{-9}\ \Delta V_{1/2}\ \epsilon_{max}$ [25]. The results are shown in Table 5. It is observed that oscillator strength varied from 0.392 to 0.998 and is highest for **5b**, having sulphur atom outside of pyrimidine ring. In compound **5b**, the molar extinction coefficient is higher than other derivatives, therefore its oscillator strength is high. This can be generalized that oscillator strength is dependent upon the molar extinction coefficient (Table 5).

Table 7 Fluorescence rate constant and theoretical fluorescence life time of D-π-A fluorene dyes **(5, 5a-5c)**

Dye	T_o(ns)	k_f (10^8/s)	ϕ_f	$_f$(ns)
5	7.13	1.4	0.58	4.135
5a	6.54	1.53	0.66	4.316
5b	2.75	3.64	0.74	2.035
5c	4.11	2.43	0.62	2.548

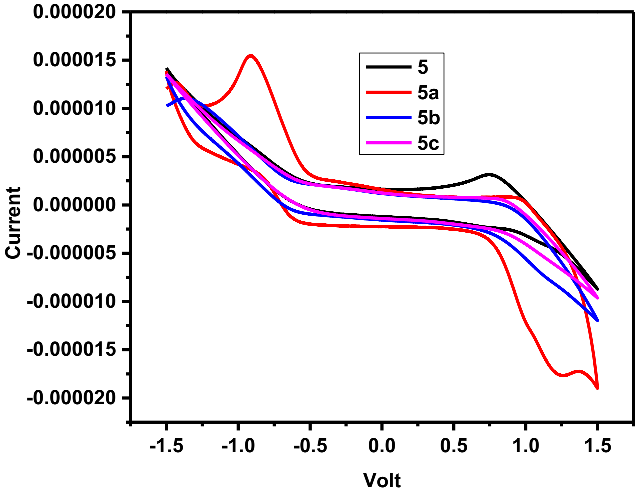


Fig. 4 Combined voltammogram of D-π-A fluorene dyes (**5, 5a-c**)

Theoretical Radiative Lifetimes (T_o)

Molar extinction coefficient (ϵ_{max}) is a fundamental entity for the theoretical radiative lifetimes (T_o) [26]. It is obtained from the half-width of the selected absorption ($\Delta V_{1/2}$) and mean frequency ($V^2{}_{max}$). Theoretical radiative lifetimes (T_o) of pyrimidine dyes is low and dependent on the auxochrome present on the pyrimidine ring and varies from 2.75 to 7.13 (ns) (Table 6). The compounds **5b** and **5c**, have smaller values of radiative lifetime (T_o) and larger ϵ_{max} value. From the data, it is observed that those fluorene derivatives which exhibit lower values of radiative lifetime (T_o), have larger absorptions intensity in UV-visible region. Calculated theoretical radiative lifetimes are given in Table 6.

Fluorescence Rate Constants (k_f)

The fluorescence rate constants of dyes are represented in Table 7. The k_f values for these dyes are ranging from 1.40 to 3.64×10^8 s^{-1} and the dye **5b** shows the highest value owing to mercapto group present on pyrimidine ring. The radiative life time of **5b** is very low which suggests its striking high value of fluorescence rate constant. This may also be credited to large size of sulphur "due to this its polarization factor" which increases the fluorescence rate constant and decreases the radiative life time. Same pattern is also shown

Table 8 Oxidation potential E_{ox}, LUMO, HOMO and band gap energy of molecular orbital's of D-π-A fluorene dyes **(5, 5a-5c)**

Dye.	E_{oxi} (V)	LUMO /eV	Eg/eV	HOMO/eV	λ $_{(nm)}$
5	1.391	−2.9073	2.8837	−5.791	430
5a	1.433	−2.9359	2.8971	−5.833	428
5b	1.330	−2.8193	2.9107	−5.366	426
5c	0.966	−2.4689	2.8971	−5.730	428

by **5c** which has next highest fluorescence rate constant in this sequence.

Electrochemical Properties

The electrochemical behaviour of dyes **5-5a-c** was investigated by cyclic voltammetry using DCM solution containing 0.1 M TBAPF6 as a supporting electrolyte (Fig. 4). All redox potentials, band gap energies (E_g), HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) were calculated using this technique.

Reduction potentials of reversible processes were calculated from Cyclic Voltammograms using published procedure $E_{1/2} = [E_{HOMO} + E_{LUMO}]/2$ [27, 28]. Results of redox potentials of dyes are shown in Table 8. Band gap energies of all dyes are very close to each other and all dyes seems to be equally proficient for OLEDs.

Conclusions

Synthesis of fluorene derivatives **5-5a-c** has been achieved through multistep procedure and their characterization has been made well through spectroscopic techniques. All these dyes are highly fluorescent having valuable quantum yields and exhibit absorptions and emissions in the range 426–430 and 645–657 nm respectively. These chromogens displayed the oxidation potential E_{ox} at 0.96 to 1.43 eV with LUMO and HOMO levels in the range − 2.41 to −4.93 and − 5.36 to −5.83 eV, respectively.

Acknowledgements We are thankful to PAK-USAID for financial assistance and also thankful to HEC Pakistan for funding.

Compliance with Ethical Standards

Conflict of Interest Authors declare no conflict of interest.

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