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Paper

Photophysical and thermal properties of novel solid state fluorescent benzoxazole based styryl dyes with DFT study

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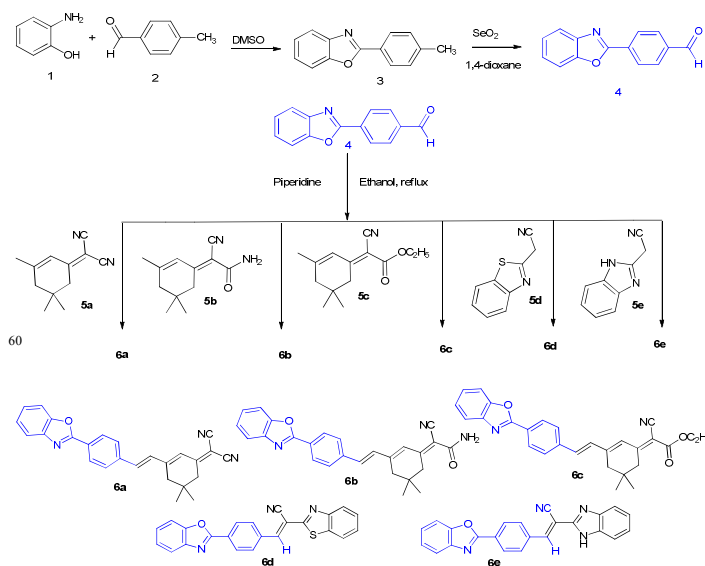
Novel benzoxazole styryl dyes **6a-6e** with donor(D)- $\pi(\pi)$ -acceptor(A) were synthesized and characterized. The spectral (absorption and emission) and thermogravimetric properties of the dyes were investigated. They were found to possess red-shifted absorption with high molar extinction coefficient when compared to their reported analogues. Compounds exhibited enhanced fluorescence emission in solid state (540-603 nm). They showed excellent thermal and photochemical stability. The effect of benzoxazole moiety on photophysical properties is explained by comparing with reported analogues and density functional theory (DFT) calculations. Thus investigations of photophysical properties provide important foundation for the molecular design and development of novel optoelectronic materials for OLED and NLO applications.

Introduction

Fluorescent styryl dyes have attracted researchers all over the globe for their applications in potentially interesting fields such as organic light-emitting diodes (OLEDs)¹, solar cells², fluorescent viscosity sensors³, molecular probes⁴, non-linear optics⁵, laser dyes⁶, fluorescent thermometer⁷, etc. They have great commercial demand since they are easily tailor-made depending on the requirements. Styryl dyes based on benzoxazole have been exploited for their excellent luminescent property. They have been known to exhibit strong photoluminescence (PL) in the blue region^{8,9}. Styryl dyes with benzoxazole as acceptor have been used as emitter material in organic electroluminescent (EL) devices¹⁰. Intramolecular exciplexes based on benzoxazole have been applied as fluorescent sensors for cations¹¹. Derivatives of 2-hydroxy phenyl benzoxazole form borate complexes (BODIPY) which are highly luminescent¹² and useful in monitoring of polymerization process¹³. Benzoxazole is widely employed as a key structure in many fields, i.e. ES IPT dyes^{14,15,16} or metal cation indicators¹⁷.

The reason for enhanced fluorescence on introduction of benzoxazolyl group in stilbene can be attributed to the decreased non-radiative processes due to the higher resistance to rotation offered by the bulky benzoxazolyl molecule while radiative process suffer competition from well-known *trans-cis* isomerisation¹⁸. Considering the effects of benzoxazole moiety on enhanced fluorescence of stilbenes, novel styryl dyes containing benzoxazole were synthesized (Scheme 1) and their photophysical properties both in the solution as well as in solid states were investigated. The effect of solvent polarity on the absorption and emission spectra were evaluated. Thermal stability of these synthesized dyes was also explored. The comparative

study of the photophysical properties of synthesized dyes with other reported analogues highlighted the superiority in optical properties. One of the added advantages of the system is the combination of a weak donor (benzoxazole) and a very strong acceptor (CN) end groups, which makes this type of compound suitable for non-linear optical applications owing to non-linear transparency¹⁹.



Scheme 1 Synthetic procedure for synthesis of benzoxazole based styryl dyes **6a-6e**.

Experimental Section

Materials and methods

All common reagent grade chemicals were procured from SD Fine Chemical Ltd. (Mumbai, India) and were used without further purification. The reactions were monitored by thin-layered chromatography (TLC) using 0.25 mm E-Merck silica gel 60 F₂₅₄ precoated plates, which were visualized with UV light. ¹H NMR spectra were recorded on a 400 MHz Varian mercury plus spectrometer. Chemical shifts were expressed in δ ppm using TMS as an internal standard. Mass spectra were obtained with a micromass-Q-TOF (YA105) spectrometer. All the DSC-TGA measurements were performed out on a SDT Q600 v8.2 Build 100 model of TA instruments Waters (India) Pvt. Ltd. Absorption spectra were recorded on a Perkin Elmer Lambda 25 UV-VIS Spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence Spectrophotometer using freshly prepared solutions of 1 x 10⁻⁵ M. Absorption and Emission spectra were performed using quartz cell of 1 cm path length. All compounds were excited at their maximum absorption values. All the experimental parameters were kept constant throughout in order to have precision and accuracy. Absorption and emission graphs were plotted using MATLAB R 2008a.ink software.

Synthesis of the dyes

General procedure for synthesis of 2-(*p*-tolyl)benzo[*d*]oxazole (3)

2-Aminophenol 1 (5 g, 0.0458 mol) and 4-methylbenzaldehyde 2 (5.5 g, 0.0458 mol) were added to DMSO (30 ml). The reaction mass was heated to 80 °C for 5-6 h. Then, the reaction mixture was cooled to room temperature and diluted with 50 ml cold water. The precipitate obtained was filtered and dried after repeated washing with water. Further, it was purified by recrystallization in ethanol and dried in oven at 50°C. Yield = 7.1 g, 69.6%, Melting Point: 114°C.

General procedure for synthesis of 4-(benzo[*d*]oxazol-2-yl)benzaldehyde (4)

Selenium dioxide (7.9 g, 0.0717 mol) was added to 1,4-dioxane (30 ml). The reaction mass was heated to 50 °C. 2-(*p*-Tolyl)benzo[*d*]oxazole (3, 5 g, 0.0240 mol) was added to reaction mass at 50 °C in portions. Then, the reaction temperature was raised to 90°C and maintained for 12 h. Reaction was monitored on TLC. After completion, reaction mass was filtered through celite. The filtrate was concentrated under vacuum on rotary evaporator. Solid obtained was purified by recrystallization from ethanol. Yield = 1.6 g, 30%.

Synthesis of (E)-2-(3-(4-(benzo[*d*]oxazol-2-yl)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile (6a)

4-(Benzo[*d*]oxazol-2-yl)benzaldehyde (4, 1.0 g, 4.5 mmol) and 2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)malononitrile (5a, 0.83g, 4.5 mmol) were dissolved in absolute ethanol (12 mL). Piperidine (0.1 mL) was added and the reaction mixture was refluxed for 9 h. The solvent was removed under reduced pressure. The orange color dye **6a** obtained was purified by

column chromatography using silica gel 100-200 mesh and hexane:ethylacetate (9:1) as eluent system. Yield: 62%. FT-IR (KBr, cm⁻¹): 2953 (C-H, Ar), 2217 (CN), 1560 (C=C). ¹H-NMR (DMSO-*d*₆, 400 MHz): δ=1.03 (s, 6H, -2CH₃), 2.58 (s, 2H, -CH₂), 2.64 (s, 2H, -CH₂), 6.98 (s, 1H, vinylic -H), 7.38 (d, *J* = 16.4 Hz, 1H), 7.44 (t, *J* = 6.0, 11.2 Hz, 2H), 7.62 (d, *J* = 16.0 Hz, 1H), 7.82 (t, *J* = 8.8, 16.8 Hz, 2H), 7.94 (d, *J* = 8.4 Hz, 2H), 8.22 (d, *J* = 8.4 Hz, 2H). ¹³C-NMR (CDCl₃, 126 MHz): δ= 28.0, 32.0, 39.2, 42.9, 79.6, 110.6, 112.4, 113.2, 120.1, 124.5, 124.7, 125.4, 127.8, 127.9, 128.1, 130.8, 135.5, 138.5, 142.1, 150.7, 153.0, 162.3, 168.9. HRMS (*m/z*): calcd for C₂₆H₂₁N₃O ([M + H])⁺ 392.1763, observed 392.1721.

Synthesis of (E)-2-(3-(E)-4-(benzo[*d*]oxazol-2-yl)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)-2-cyanoacetamide (6b)

4-(Benzo[*d*]oxazol-2-yl)benzaldehyde (4, 1.0 g, 4.5 mmol) and (E)-2-cyano-2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)acetamide (5c, 0.92 g, 4.5 mmol) were dissolved in absolute ethanol (15 mL). Piperidine (0.1 mL) was added and the reaction mixture was refluxed for 14 h. The solvent was removed under reduced pressure. The orange color dye **6b** obtained was purified by column chromatography using silica gel 100-200 mesh and hexane:ethylacetate (8:2) as eluent system. Yield: 67%. FT-IR (KBr, cm⁻¹): 3461, 3334 (NH₂), 3155, 2960, 2343 (CN), 1662 (C=O), 1514 (C-O), 1401 (C-N). ¹H-NMR (DMSO-*d*₆, 400 MHz): δ= 0.98 (s, 6H, -2CH₃), 2.51 (s, 2H, -CH₂), 2.60 (s, 2H, -CH₂), 6.84 (s, 1H), 7.11 (d, *J* = 16.4 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 16.4 Hz, 1H), 7.67 (s, 1H), 7.79-7.84 (m, 4H, ArH), 7.88 (d, *J* = 8.4 Hz, 2H), 8.18 (d, *J* = 8.4 Hz, 2H). ¹³C-NMR (DMSO-*d*₆, 100 MHz): δ= 27.8, 30.77, 31.06, 104.5, 110.8, 116.71, 119.7, 124.9, 125.27, 125.58, 125.8, 126.2, 127.5, 127.9, 128.17, 128.8, 131.9, 132.4, 139.8, 141.5, 148.4, 150.1, 157.5, 161.9, 163.4. HRMS (*m/z*): calcd for C₂₆H₂₃N₃O₂ ([M + H])⁺ 410.1869, observed 410.1861.

Synthesis of (E)-2-(1H-benzo[*d*]imidazol-2-yl)-2-(3-(E)-4-(benzo[*d*]oxazol-2-yl)styryl)-5,5-dimethylcyclohex-2-en-1-ylidene)acetonitrile (6c)

4-(Benzo[*d*]oxazol-2-yl)benzaldehyde (4, 1.0 g, 4.5 mmol) and (E)-ethyl 2-cyano-2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)acetate (5d, 1.0 g, 4.5 mmol) were dissolved in absolute ethanol (15 mL). Piperidine (0.1 mL) was added and the reaction mixture was refluxed for 14 h. The solvent was removed under reduced pressure. The orange color dye **6c** obtained was purified by column chromatography using silica gel 100-200 mesh and hexane:ethyl acetate (8:2) as eluent system. Yield: 48%. FT-IR (KBr, cm⁻¹): 2960, 2343, 2209 (CN), 1712(C=O), 1526 (C=C), 1232 (C-O). ¹H-NMR (DMSO-*d*₆, 400 MHz): δ= 1.03 (s, 6H, -2CH₃), 1.28 (t, 3H, -CH₃), 2.61 (s, 2H, -CH₂), 2.94 (s, 2H, -CH₂), 4.25 (q, 2H, -CH₂), 6.96 (s, 1H, vinylic -H), 7.26 (d, *J* = 16.0 Hz, 1H), 7.36-7.45 (m, 3H, ArH), 7.52 (d, *J* = 16.0 Hz, 1H), 7.81 (t, *J* = 8.8, 17.6 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 2H), 8.19 (d, *J* = 8.4 Hz, 2H). ¹³C-NMR (DMSO-*d*₆, 100 MHz): δ= 13.9, 14.0, 27.6, 27.8, 30.6, 31.0, 31.4, 61.2, 110.9, 115.9, 119.8, 124.6, 124.9, 125.6, 126.2, 126.6, 127.6, 128.2, 132.1, 132.4, 133.9, 134.1, 141.5, 150.2, 152.1, 152.9, 161.8, 162.2. HRMS (*m/z*): calcd for C₂₈H₂₆N₂O₃ ([M + H])⁺ 439.2022, observed 439.1988.

Synthesis of 2-(1H-benzo[d]thiazol-2-yl)-3-(4-(benzo[d]oxazol-2-yl)phenyl)acrylonitrile (6d)

4-(Benzo[d]oxazol-2-yl)benzaldehyde (4, 1.0 g, 4.5 mmol) and 2-(1H-benzo[d]thiazol-2-yl)acetonitrile (5e, 0.70 g, 4.5 mmol) were dissolved in absolute ethanol (15 mL). Piperidine (0.1 mL) was added and the reaction mixture was refluxed for 7 h. The solvent was removed under reduced pressure. The yellow color dye **6d** obtained was purified by column chromatography using silica gel 100-200 mesh and hexane:ethylacetate (8:2) as eluent system. Yield: 59%. FT-IR (KBr, cm^{-1}): 3047 (C-H, Ar), 2343 (CN), 1681 (C=O), 1450 (C-N), 1241, 1059, 759, 743. ^1H NMR (500 MHz, CDCl_3) 7.36 – 7.44 (m, 2H), 7.46 (t, $J = 7.1$ Hz, 1H), 7.56 (t, $J = 8.2$ Hz, 1H), 7.60 – 7.69 (m, 1H), 7.79 – 7.85 (m, 1H), 7.94 (dd, $J = 8.0, 0.5$ Hz, 1H), 8.11 (dd, $J = 8.2, 0.5$ Hz, 1H), 8.18 (d, $J = 8.7$ Hz, 2H), 8.29 (s, 1H), δ 8.39 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (126 MHz, CDCl_3) 106.94, 110.81, 116.24, 120.39, 121.74, 123.77, 124.95, 125.86, 126.26, 127.10, 128.18, 130.04, 130.76, 134.85, 135.08, 142.05, 145.22, 150.87, 153.59, 161.69, δ 162.27. HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{13}\text{N}_3\text{OS}$ ($[\text{M} + \text{H}]^+$) 380.0858, observed 380.0826.

Synthesis of 2-(1H-benzo[d]imidazol-2-yl)-3-(4-(benzo[d]oxazol-2-yl)phenyl)acrylonitrile (6e)

4-(Benzo[d]oxazol-2-yl)benzaldehyde (4, 1.0 g, 4.5 mmol) and 2-(benzo[d]imidazol-2-yl)acetonitrile (5e, 0.78g, 4.5 mmol) were dissolved in absolute ethanol (15 mL). Piperidine (0.1 mL) was added and the reaction mixture was refluxed for 6 h. The solvent was removed under reduced pressure. The yellow color dye **6e** obtained was purified by column chromatography using silica gel 100-200 mesh and hexane:ethylacetate (9:1) as eluent system. Yield: 64%. FT-IR (KBr, cm^{-1}): 3285 (NH), 3051 (C-H, Ar), 2237 (CN), 1594, 1416 (C-N), 1314, 1243, 1057, 740. ^1H -NMR (DMSO- d_6 , 400 MHz): δ = 7.27-7.32 (m, 2H), 7.37-7.45 (m, 2H), 7.63-7.68 (m, 2H), 7.77-7.81 (m, 2H), 8.17 (d, 2H, $J = 8.4$ Hz), 8.38 (d, 2H, $J = 8.4$ Hz), 8.48 (s, 1H). ^{13}C -NMR (DMSO- d_6 , 126 MHz): δ = 104.4, 111.5, 116.3, 120.5, 125.5, 126.5, 128.3, 128.9, 130.7, 136.0, 141.9, 144.3, 147.6, 150.8, 161.8. HRMS (m/z): calcd for $\text{C}_{23}\text{H}_{14}\text{N}_4\text{O}$ ($[\text{M} + \text{H}]^+$) 363.1203, observed 363.1181.

Results and discussion

Synthetic strategy of dyes 6a-6e

Dyes **6a-6e** were synthesized by classical Knoevenagel condensation of 4-(benzo[d]oxazol-2-yl)benzaldehyde with different acceptor chromophoric systems based on substituted isophorone, benzthiazole and benzimidazole. (Benzo[d]oxazol-2-yl)benzaldehyde (**4**) was prepared by oxidation (selenium dioxide in dioxane) of 2-(*p*-tolyl)benzo[d]oxazole (**3**), obtained by condensation of *ortho*-aminophenol (**1**) with tolualdehyde (**2**). The aldehyde (**4**) after conventional condensation with different active methylenes (**5a-5e**) in ethanol-piperidine gave the target styryl dyes (**6a-6e**). The structures and purities of the prepared compounds were confirmed using FTIR, ^1H NMR, ESI-MS spectrometry and thin layer chromatography. The spectral data are in good agreement with the expected structure of the compounds and the data of analysis is provided in the experimental section. It is noteworthy that the ^1H NMR spectra of

dyes **6a-6e**, bearing vinyl hydrogens display two characteristic doublets localized at chemical shifts in the range of 6-8 ppm.

Based on the large coupling values (J) of 16-17 Hz for the olefinic protons it is established that these dyes exist in *trans*-conformation in the ground state.

UV-vis absorption and emission of dyes 6a-6e

The photophysical properties of the dye were investigated in DMSO solvent (Figure 1 and Figure 2). All the dyes displayed an intramolecular charge transfer (ICT) band arising due to the presence of benzoxazole moiety as donor in the presence of strong acceptor system (CN) which is in agreement with DFT study. Inspection of absorption spectra reveals that the intensity and position of charge transfer (CT) band is dependent on the type of acceptor heterocyclic system. Dyes **6a**, **6b** and **6c** showed an absorbance band at 415 nm, 387 nm and 407 nm respectively. The hypsochromic shift of **6b** is due to weaker pulling strength of acceptor cyano-acetamide as compared with malononitrile (**6a**) and ethylcyanoacetate (**6c**). Compounds **6d** and **6e** absorbed at 383 nm and 377 nm respectively. Thus a "blue-shift" is observed in absorption spectra of compounds on going from **6a-6e**, due to weaker push-pull effect.

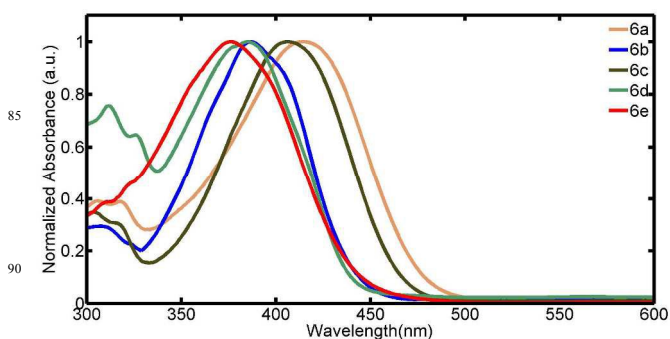


Fig. 1. Uv-vis absorption spectra of dyes **6a-6e** in dimethylsulfoxide (DMSO) at 293 K.

The fluorescence emissions of the compounds were studied (Figure 2). Dye **6a** exhibited good Stokes shift of 123 nm followed by **6e** (116nm), **6d** (84 nm) while **6b** and **6c** gave similar shift of 55 nm.

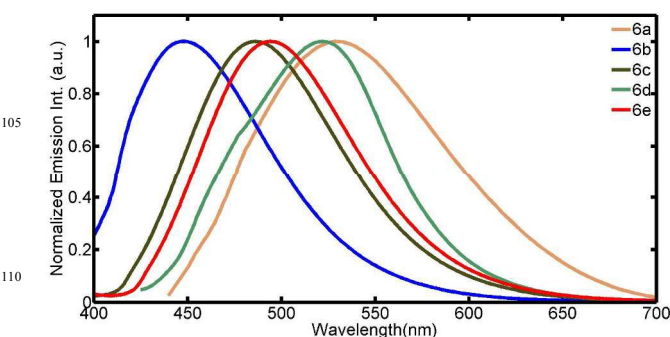


Fig. 2. Fluorescence spectra of dyes **6a-6e** in dimethylsulfoxide (DMSO) at 293 K.

The UV-vis absorption and emission of the compounds were studied in solvents of varying polarity, dielectric constant and refractive index as listed in Table 1. Molecules with π -electron system exhibit different charge distribution in the electronic ground state and in excited state and hence show solvatochromism, which is very-well established experimentally. All the dyes exhibited single broad absorption profile in the range of 300-600 nm. Thus, for the tested organic styryl dyes only a comparatively less solvent dependence is observed in UV-vis absorption spectra, while considerable effect is seen over fluorescence spectra. For dye **6a** (Figure S1) with an isophorone-malononitrile acceptor system, a single broad absorption maxima at 407 nm in toluene was observed which varied to 415 nm in DMSO. Furthermore, a red-shift was observed in fluorescence spectra with maxima changing from 502 nm in toluene to 530 nm in DMSO. Thus, a remarkable solvatofluorism was observed for dye **6a** with weak emission intensity which is attributed to the stabilization of excited state by solvent molecules. On excitation, intra molecular charge transfer (ICT) occurs, and the excited state gets much more dipolar than ground state. Stabilization of this dipolar state by differential solvation results in lowering of band gap giving rise to red-shifted emission²⁰.

For dyes **6b** and **6c** bearing an isophorone-cyanoacetamide and isophorone-ethylcyanoacetate based acceptor system respectively (Figure S2 and Figure S3), different absorption maxima were observed. In case of dye **6b**, a hypsochromic shift was observed in both absorption and emission spectra. The absorption shifted from 396 nm in toluene to 387 nm in DMSO whereas emission value varied from 461 nm to 447 nm in DMSO. Dye **6c** showed solvatofluorism with increase in solvent polarity from toluene (461 nm) to DMSO (486 nm).

Dyes **6d** and **6e** (Figure S4 and Figure S5) with benzthiazole and benzimidazole as acceptors, were found to show positive solvatofluorism. The emission changed from 460 nm (toluene) to

523 nm (DMSO) for dye **6d** and 477 nm (toluene) to 494 nm (DMSO) for dye **6e**. The progressive bathochromic shift of charge-transfer band with increase in the polarity of the solvent depicts that the fluorescence originates from a highly polar state. Dye **6d** was found to fluoresce intensely in DMSO indicating greater stabilization of excited state. The increase in emission intensity for dye **6d** is tentatively assigned to decrease non-radiative decay channel which is enhanced by high polarity.

The high molar extinction coefficients values (2.48 - 6.93×10^4 L mol⁻¹ cm⁻¹) of dyes **6a-6e** is due to the S₀→ CT band transitions. The intramolecular charge transfer takes place through D- π -A system involving the electron flow from benzoxazole moiety towards CN groups resulting in decrease of energy gap between HOMO and LUMO. All the dyes exhibited large Stokes shift in the range of 3.25×10^3 - 6.58×10^3 cm⁻¹. The large bathochromic shifts of the emission bands with the solvent polarity indicate greater stabilization of the excited singlet state in polar solvents. It is the characteristic for molecules which have enlarged dipoles and charge transfer (CT) characters in their excited singlet states²¹. The relative fluorescence quantum yields of the dyes **6a-6e** are listed in Table 2. Anthracene was used as standard for the measurement of the fluorescence quantum yield ($\Phi_f = 0.27$ in ethanol). Dyes **6d** and **6e** displayed high quantum yield value. In addition, benzoxazolyl containing styryl dyes have higher quantum yield as compare to previously reported compound²². A comparative study of synthesized dye molecules with reported analogues was done. It is interesting to note that the absorption and emission wavelengths of these dyes are significantly red-shifted when compared to reported analogues as listed in Table 3. The red-shifted emission is attributed to the decreased non-radiative decay processes in the excited state. The thermal stability of these compounds was remarkably higher as compared to their analogues.

Table 1. Photo-physical properties of the dyes **6a-6e** in different solvents.

Solvents	6a				6b				6c			
	λ_{abs} , nm ($\epsilon \times 10^4$)	λ_{ems} , nm	λ_{exct} , nm	$\Delta\lambda$, cm ⁻¹	λ_{abs} , nm ($\epsilon \times 10^4$)	λ_{ems} , nm	λ_{exct} , nm	$\Delta\lambda$, cm ⁻¹	λ_{abs} , nm ($\epsilon \times 10^4$)	λ_{ems} , nm	λ_{exct} , nm	$\Delta\lambda$, cm ⁻¹
Toluene	407 (6.26)	502	406	4650	396 (3.37)	461	398	3561	401 (5.05)	461	405	3246
EDC	408 (6.27)	515	409	5092	394 (3.92)	485	395	4762	403 (5.32)	495	404	4612
THF	405 (6.43)	520	411	5461	388 (3.70)	453	388	3698	397 (5.53)	450	397	2967
Acetone	403 (5.90)	527	404	5839	383 (2.84)	456	385	4180	395 (4.81)	464	398	3765
Ethanol	404 (6.02)	465	409	3247	382 (3.69)	450	383	3956	396 (5.63)	457	398	3371
ACN	402 (6.53)	525	407	5828	382 (2.84)	446	384	3756	394 (5.50)	500	395	5381
DMF	409 (5.33)	538	412	5863	383 (2.39)	463	385	4511	402 (5.12)	508	402	5191
DMSO	415 (4.73)	530	418	5193	387 (3.63)	447	387	3568	407 (5.26)	486	409	3994

Molar absorptivity (ϵ) in M⁻¹ cm⁻¹. The concentration of dyes used for recording absorbance and emission spectra was 1×10^{-5} mol L⁻¹.

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Solvents	6d				6e			
	λ_{abs} , nm ($\epsilon \times 10^4$)	λ_{ems} , nm	λ_{exct} , nm	$\Delta\lambda$, cm^{-1}	λ_{abs} , nm ($\epsilon \times 10^4$)	λ_{ems} , nm	λ_{exct} , nm	$\Delta\lambda$, cm^{-1}
Toluene	387 (4.04)	460	388	4101	386 (2.36)	477	388	4942
EDC	383 (4.50)	506	385	6347	412 (1.97)	500	412	4272
THF	377 (3.19)	450	378	4303	376 (3.19)	477	378	5631
Acetone	376 (2.98)	464	378	5044	374 (3.62)	479	372	5861
Ethanol	377 (3.74)	452	377	4401	363 (3.08)	477	365	6584
ACN	377 (2.57)	480	379	5692	374 (4.14)	482	375	5991
DMF	384 (4.16)	472	385	4855	378 (3.72)	490	380	6047
DMSO	383 (1.63)	523	385	6989	377 (3.04)	494	378	6282

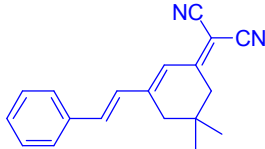
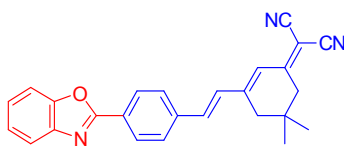
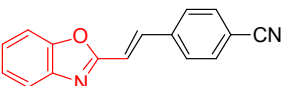
Molar absorptivity (ϵ) in $M^{-1} cm^{-1}$. The concentration of dyes used for recording absorbance and emission spectra was $1 \times 10^{-5} mol L^{-1}$.

Table 2. Relative quantum yield of dyes **6a-6e**.

Solvent	6a (Φ_f)	6b (Φ_f)	6c (Φ_f)	6d (Φ_f)	6e (Φ_f)
THF	0.0444	0.0436	0.0303	0.0783	0.2400
EDC	0.0242	0.02102	0.0177	0.0285	0.1704
Ethanol	0.0977	0.0153	0.0115	0.0426	0.1152
DMF	0.02154	0.01755	0.01097	0.1036	0.2149

The concentration of dye (C) used for calculation of quantum yield is $1 \times 10^{-5} mol L^{-1}$.

Table 3. Comparative study with reported analogues.

Sr.no.	Reported Dyes	Synthesized dye	Ref.
1.	 <p>E)-2-(5,5-dimethyl-3-styrylcyclohex-2-en-1-ylidene)malononitrile (S) λ_{abs} : 393 nm, λ_{ems} : 480 nm (Ethanol) $\Delta\lambda = 4872 cm^{-1}$, M.P. 167-169°C</p>	 <p>λ_{abs} : 404 nm, λ_{ems} : 542 nm (Ethanol) $\Delta\lambda$: 6364 cm^{-1} M.P. >200 °C</p>	[23,24]
2.	 <p>λ_{abs} : 329 nm, λ_{ems} : 403 nm</p>	<p>Dyes: 6a-6e λ_{abs} : 325-420 nm, λ_{ems} : 413-540 nm</p>	[25]

Solid state fluorescence

It was found that the dyes **6a-6e** are highly fluorescent in solid state (Figure 3). Intense yellowish emissions were observed upon illumination of the solid dye under UV lamp (365 nm). Materials showing fluorescence in solid state have potential application as electroluminescence devices. The solid state fluorescence emission maxima for the compounds were recorded on Varian

15 Cary Eclipse Fluorescence Spectrophotometer. Dyes **6a-6e** exhibited yellow fluorescence in solid state and their emission maxima are shown in figure 3. The results suggest that these solid state yellow luminescent dyes could possibly be used in electroluminescence devices, as phosphor and in organic light emitting diodes.

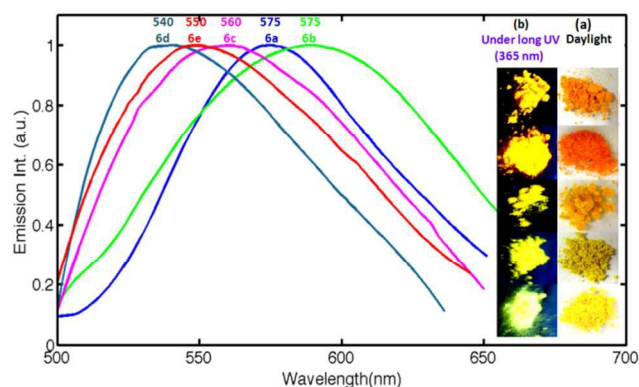


Fig. 3. Normalized solid state fluorescence plots for dyes **6a-6e**. Inset showing photograph of solid dyes under UV light and daylight.

Theoretical results

The ground state geometry of the compounds **6a-6e** was optimized in vacuum using Density Functional Theory (DFT).

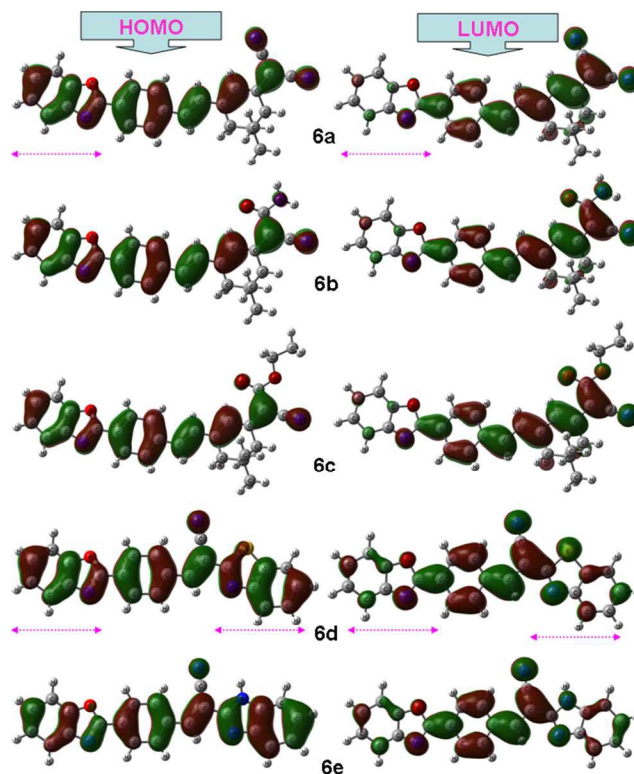


Fig. 4. DFT computed HOMO and LUMO diagrams of the dyes **6a-6e** at the B3LYP/6-31G(d,p) level.

Table 4. TD-B3LYP/6-31G(d,p) in the gas phase

Dyes	$E_{\text{LUMO}};$ E_{HOMO}	ΔE^a (eV)	Dipole moment (Debye)	λ_{abs} , nm	Excitation energy (eV)	λ_{em} , nm
6a	-0.11255; -0.21839	0.10584	7.98	449 (1.54) ^b 365 (0.42)	2.7645 3.3969	495 (1.70) ^b
6b	-0.10014; -0.20918	0.10904	2.67	435 (1.74) 357 (0.27)	1.7361 0.2697	487 (1.90)

6c	-0.10264	0.10809	4.32	440 (1.73)	2.8185	492 (1.90)
	-0.21073			360 (0.27)	3.4408	
6d	-0.10404	0.11591	2.26	423 (1.53)	2.9347	485 (1.58)
	-0.21995			377 (0.03)	3.2875	
6e	-0.09995	0.11301	0.93	434 (1.31)	2.8541	508 (1.08)
	-0.21296			390 (0.14)	3.1739	

^a $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$

^b Oscillatory strength (*f*)

Thermal and photochemical stability study

The thermal degradation temperatures (T_d) of dyes 6a–6e were recorded by thermogravimetric analysis (Figure 5). The dyes were heated at the rate of 10°C/min from 30–600 °C under inert atmosphere of nitrogen gas. These novel colorants showed excellent thermal stability. The comparisons of the T_d (decomposition temperature) at 95% weight of the sample, show that the thermal stability of dyes decreases in the order **6d**(336°C)>**6e**(327°C)>**6c**(293°C)>**6a**(291°C)>**6b**(252°C).

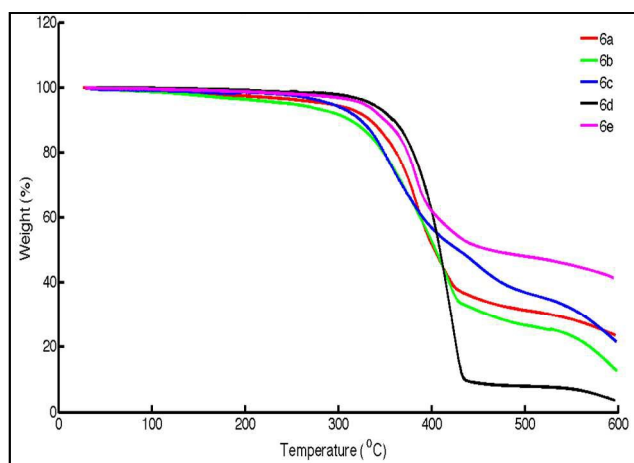


Fig. 5. TGA overlay graph for dyes **6a–6e**.

Photochemical stability was next investigated by irradiating the solution of dyes, in acetonitrile at room temperature in UV cabinets (at 254 nm, 0.15 mW/cm²) for a period of 6 h²⁶. In the photostability study, we have tried to discuss about the effect of UV irradiation on photostability of the dye molecules in terms of the absorption. No changes in absorbance intensity of the dyes were observed on plotting the absorbance versus duration of irradiation, which inferred that the dyes are extremely photochemically stable (Figure 6, S6). The photochemical stability was compared by carrying out a control experiment with similar molecule (**S**). It was observed that the absorbance intensity of **S** was comparable with synthesized molecule **6a** (Figure 6).

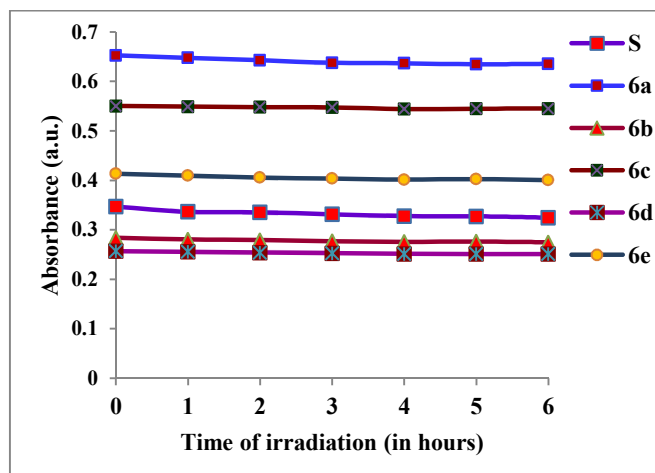


Fig. 6. Photochemical stability study for dyes **6a–6e**.

Conclusions

Novel dyes synthesized exhibited good thermal stability and solid state luminescence property. Their photophysical properties reveal that they can be potential candidates for OLED, NLO and polymeric security application. Emission spectra of these dyes were red shifted in solvents of varying polarity showing positive solvatofluorism. Comparison with reported analogues showed the advantage of synthesized dye in terms of photophysical and thermal properties.

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