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The synthesis and photo-physical properties of extended styryl fluorescent derivatives of *N*-ethyl carbazole

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ABSTRACT

The solvatochromic behavior of novel carbazole containing dyes obtained by the condensation of 9-ethyl-9*H*-carbazole-3-carboxaldehyde and 9-ethyl-9*H*-carbazole-3,6-dicarboxaldehyde with (1-phenyl-ethylidene) propanedinitrile and ethyl-2-cyano-3-phenyl-2-butenoate are described. The dyes were characterized by FT-IR, ¹H NMR, ¹³C NMR, Elemental analysis and Mass spectra. DSC–TGA analysis showed these dyes are thermally stable up to 300 °C. The UV–Vis absorption and fluorescence emission spectra of the dyes were studied in solvents of differing polarity; the dyes exhibited positive solvatochromism and solvatofluorism.

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1. Introduction

Carbazole compounds have been extensively investigated for electronic and photonic applications, such as fluorescent markers, charge transfer agents, solar energy collectors, nonlinear optical and two-photon absorbing materials [1-3]. Carbazole unit has an electron donating influence and carbazole containing dyes are known to have excellent photo-conductivity and relatively intense luminescence [4]. The thermal stability or the glass state durability of organic compounds can be greatly enhanced by the introduction of organic carbazole group in the core structure [5].

Carbazole is isoelectronic to diphenylamine, but it has a planar structure and it can be imagined as the bonded diphenylamine. The carbazole nucleus can be easily functionalized at 3-, 6-, 9-positions and covalently linked to other molecular groups [6,7]. A typical push–pull chromophore consist of a polar A– π –D system with a planar π -system end-capped by a strong electron donor (D) and a strong electron acceptor (A). The π -conjugated system ensuring intramolecular charge transfer (ICT) between the donor (D = *N*-alkyl group) and the acceptor (A = cyano group etc.) is the most

common of double and triple bonds in aromatic and heteroaromatic rings as well as their combinations [8,9]. Carbazole moiety being a rigid structure with a donor-rigidised residue improves π electron delocalization resulting in better two-photon absorbing property [3].

There has always been efforts to design and synthesize novel and well-defined organic push—pull system with prospective applications as chromophores for nonlinear optics (NLO), dyes electronic and photonic devices, organic light-emitting diodes (OLED) or functional polymers [10]. The *N*-alkyl carbazole compounds have shown excellent thermal and good electro-optical properties [11].

In this paper, we report synthesis of novel fluorescent extended styryl dyes containing *N*-ethyl carbazole moiety. The molecular structures are shown in Scheme 1. These dyes were obtained by condensation reaction between 9-ethyl-9*H*-carbazole-3-carbox-aldehyde and (1-phenylethylidene) propanedinitrile and ethyl-2-cyano-3-phenyl-2-butenoate. Their structures were determined by FT-IR, ¹H NMR, ¹³C NMR, Elemental analysis and Mass spectra. Also, their thermal stability and UV–Vis absorption and fluorescence emission characteristics were studied.

The fluorescence spectra were red shifted evidently in acetonitrile from dye 5b < 5a < 6b < 6a. The solvent effects on the fluorescence characteristics of the four compounds were studied,



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Scheme 1. Synthesis of extended styryl mono- and bis-styryl carbazole dyes 5a-b and 6a-b.

Table 1	
UV—Vis absorption and fluorescence emission maxima of 5a , 5b , 6a and 6b in various solv	ents.

Solvents	5a			5b			6a			6b		
	λmax	λem	Δλ									
Toluene	453	530	77	429	522	93	474	526	52	450	524	74
1,4-Dioxane	444	534	90	426	528	102	465	536	71	447	530	83
Ethyl acetate	447	548	101	426	534	108	468	550	82	448	546	98
Methanol	453	572	119	429	560	131	474	578	104	457	570	113
Acetone	450	558	108	429	548	119	474	568	94	451	552	101
Acetonitrile	450	570	120	429	560	131	471	578	107	450	572	122
DCM ^a	456	552	96	429	547	118	477	553	76	457	554	97
DMF ^b	457	574	117	430	560	130	484	584	100	459	574	115

 λ max and λ em were measured in nm.

^a Dichloromethane.

^b *N*,*N*-Dimethylformamide.

which indicate that the emission wavelength of the compounds has red shifted with the increase of solvent polarity.

2. Experimental

2.1. Materials and equipments

All commercial reagents and solvents were procured from s.d. fine chemicals (India). The reaction was monitored by TLC using on



Fig. 1. Effect of solvent polarity on UV-Vis absorption spectra of dye 5a.

0.25 mm E-Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light. Melting points were measured on standard melting point apparatus from Sunder industrial product Mumbai, and are uncorrected. The FT-IR spectra were recorded on a Perkins-Elmer Spectrum 100 FT-IR Spectrometer using KBr discs. ¹H NMR and ¹³C NMR spectra were recorded on VXR 400 MHz and 75 MHz instrument respectively using TMS as an internal standard. Hareus Rapid analyser was used for Elemental analysis. The visible absorption spectra of the compounds were recorded on a Spectronic Genesys 2 UV–Visible spectrophotometer. Simultaneous DSC–TGA measurements were performed out on SDT Q600 v8.2 Build 100 model of TA instruments Waters (India) Pvt. Ltd.

2.2. Synthesis and characterization

2.2.1. Synthesis of 9-ethyl-9H-carbazole **2**, 9-ethyl-9H-carbazole-3carboxaldehyde **3a** and 9-ethyl-9H-carbazole-3,6-dicarboxaldehyde **(3b)**

2, 3a and 3b were prepared using the reported method [12].

2.2.2. Synthesis of 3-(4-(1,1-dicyano-2-phenyl)buta-1,3-dienyl)-9ethyl-9H-carbazole (5a)

9-Ethyl-9*H*-carbazole-3-carboxaldehyde (1.12 g, 5 mmol) **3a** and (1-phenylethylidene) propanedinitrile (0.84 g, 5 mmol) **4a** were



Fig. 2. Effect of solvent polarity on fluorescence emission spectra of dye 5a.

dissolved in absolute ethanol (12 mL). Piperidine (0.1 mL) was added to the ensuing solution which was refluxed for 5 h. The red crystals thus obtained were filtered, washed with ethanol. The dye **5a** obtained was purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

Yield: 89%, Melting point = 208-210 °C.

¹H NMR (CDCl₃, 400 MHz): δ 1.46 (t, 3H, 7.3 Hz), 4.38 (q, 2H, 7.3 Hz), 7.07 (d, 1H, *J* = 15.2 Hz), 7.67 (d, 1H, *J* = 15.2 Hz), 8.20 (s, 1H), 8.10 (d, 1H), 7.53 (d, 1H), 7.72 (d, 1H), 7.50 (d, 1H), 7.59 (m, 2H), 7.29–7.20 (m, 5H) ppm.

¹³C NMR (CDCl₃, 75 MHz): δ 13.93, 37.98, 79.38, 109.22, 109.35, 113.67, 114.17, 120.31, 120.83, 121.44, 122.81, 122.92, 123.79, 125.58, 126.58, 126.78, 129.01, 130.94, 133.94, 140.61, 142.21, 151.16 ppm. Mass: *m/z* 374 (M + 1).

Anal. Calcd. for C₂₆H₁₉N₃: C, 83.62; H, 5.13; N, 11.25. Found; C, 83.59; H, 5.14; N, 11.21%.

FT-IR (KBr, cm⁻¹): 2217 (CN), 1584 (Ar), 1232 (C–N).

2.2.3. Synthesis of ethyl-2-cyano-5-(9-ethyl-9H-carbazol-3-yl)-3-phenylpenta-2,4-dienoate (5b)

9-Ethyl-9*H*-carbazole-3-carboxaldehyde (1.12 g, 5 mmol) **3a** and ethyl-2-cyano-3-phenyl-2-butenoate (1.08 g, 5 mmol) **4b** were dissolved in absolute ethanol (12 mL). Piperidine (0.1 mL) was added and the reaction mixture was refluxed for 5 h. The solvent was removed under reduced pressure. The orange colored dye **5b** obtained was purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

Yield: 68%, Melting point: 64-66 °C.

¹H NMR (CDCl₃, 400 MHz): δ 1.15 (t, 3H, 7.3 Hz), 1.45 (t, 3H, 7.3 Hz), 4.09 (q, 2H, 7.3 Hz), 4.39 (q, 2H, 7.3 Hz), 6.85 (d, 1H, J = 15.7 Hz), 8.76 (d, 1H, J = 15.7 Hz), 8.15 (s, 1H), 8.07 (d, 1H), 7.70 (d, 1H), 7.68 (d, 1H), 7.48 (m, 2H), 7.25–7.42 (m, 5H) ppm.

 13 C NMR (CDCl₃, 75 MHz): δ 13.82, 14.24, 37.79, 61.73, 101.12, 108.96, 117.49, 119.83, 122.12, 122.23, 122.52, 122.80, 123.49, 123.68, 126.37, 126.79, 128.08, 128.55, 128.95, 129.66, 140.41, 141.56, 149.16, 149.64, 163.14, 168.52 ppm.

Mass: *m*/*z* 422 (M + 1).



Fig. 3. The UV–Vis absorption and fluorescence emission photographs of dye 5a in various solvents.



Fig. 4. The UV-Vis absorption and fluorescence emission photographs of dye 6a in various solvent.

FT-IR (KBr, cm⁻¹): 2211 (CN), 1713 (C=O), 1586 (Ar), 1232 (C–N), 1122 (C–O).

Anal. Calcd. for C₂₈H₂₄N₂O₂: C, 79.98; H, 5.75; N, 6.66. Found; C, 80.01; H, 5.72; N, 6.62%.

2.2.4. Synthesis of 3,6-Bis(4-(1,1-dicyano-2-phenyl)buta-1,3dienyl)-9-ethyl-9H-carbazole (**6a**)

9-Ethyl-9*H*-carbazole-3,6-dicarboxaldehyde (1.26 g, 5 mmol) **3b** and (1-phenylethylidene) propanedinitrile (1.68 g, 10 mmol) **4a** were dissolved in absolute ethanol (15 mL). Piperidine (0.1 mL) was added and the reaction mixture was refluxed for 8 h. The bright red crystals thus obtained were filtered, washed with ethanol. The dye **6a** obtained was purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

Yield: 74%, Melting point: 312–314 °C.

¹H NMR (CDCl₃, 400 MHz): δ 1.48 (t, 3H, 7.3 Hz), 4.40 (q, 2H, 7.3 Hz), 7.07 (d, 2H, J = 15.2 Hz), 7.65 (d, 2H, J = 15.2 Hz), 8.21 (s, 2H), 7.76 (d, 2H), 7.57 (d, 2H), 7.12–7.40 (m, 10H) ppm.

¹³C NMR (CDCl₃, 75 MHz): δ 14.02, 38.37, 80.32, 109.29, 110.03, 113.48, 113.91, 122.36, 122.94, 123.55, 126.85, 127.31, 128.94, 129.12, 131.15, 133.40, 142.62, 150.32 ppm.

Mass: *m*/*z* 552 (M + 1).

FT-IR (KBr, cm⁻¹): 2216 (CN), 1583 (Ar), 1234 (C–N).



Fig. 5. Daylight and in UV light (366 nm) photograph of dye 5a and 6a in solid state.



Fig. 6. Thermogravimetric analysis overlay graph of dyes 5a-b and 6a-b.

Anal. Calcd. for C₃₈H₂₅N₅: C, 82.74; H, 4.57; N, 12.70. Found; C, 82.69; H, 4.51; N, 12.67%.

2.2.5. Synthesis of 3,6-Bis(5-(ethyl-2-cyano-3-phenyl)penta-2,4dienoate)-9-ethyl-9H-carbazole (**6b**)

9-Ethyl-9*H*-carbazole-3,6-dicarboxaldehyde (1.26 g, 5 mmol) **3b** and ethyl-2-cyano-3-phenyl-2-butenoate (2.16 g, 10 mmol) **4b** were dissolved in absolute ethanol (15 mL). Piperidine (0.1 mL) was added and the reaction mixture was refluxed for 8 h. The bright red crystals thus obtained were filtered, washed with ethanol. The dye **6b** obtained was purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

Yield: 80%, Melting point: 250–252 °C.

¹H NMR (CDCl₃, 400 MHz): δ 1.15 (t, 6H, 7.3 Hz), 1.43 (t, 6H, 7.3 Hz), 4.09 (q, 4H, 7.3 Hz), 4.40 (q, 4H, 7.3 Hz), 6.85 (d, 2H, J = 15.7 Hz), 8.75 (d, 2H, J = 15.7 Hz), 8.14 (s, 2H), 7.70 (d, 2H), 7.54 (d, 2H), 7.35–7.50 (m, 10H) ppm.

¹³C NMR (CDCl₃, 75 MHz): δ 13.88, 14.24, 38.13, 61.82, 100.63, 109.5, 117.32, 122.29, 123.29, 1263.85, 127.63, 127.95, 128.16, 128.63, 128.89, 129.79, 141.92, 149.01, 163.03, 168.41 ppm.

Mass: *m*/*z* 622 (M + 1).

FT-IR (KBr, cm⁻¹): 2209 (CN), 1712 (C=O), 1588 (Ar), 1234 (C–N), 1118 (C–O).

Anal. Calcd. for $C_{42}H_{35}N_3O_4$: C, 78.12; H, 5.46; N, 6.51. Found; C, 78.08; H, 5.41; N, 6.48%.

3. Results and discussion

3.1. Synthesis and characterization of dyes

The four novel fluorescent extended styryl carbazole dyes were prepared by classical Knoevenagel condensation of *N*-ethyl-3-formylcarbazole **3a** and *N*-ethyl-3,6-biformylcarbazole **3b** with active



Fig. 7. Differential scanning calorimetric analysis (DSC) overlay graph of dyes 5a-b and 6a-b.

methylene compounds **4a** and **4b** as shown in Scheme 1. In the first step, the 9*H*-carbazole **1** was *N*-ethylated using diethyl sulphate which was further mono- and bis-formylated at 3- and 3,6-position by Vilsmeier–Haack formylation reaction to obtain compounds **3a** and **3b** respectively. Finally aldehyde **3a** or **3b** and suitable active methylene compound **4a**–**b** were refluxed in absolute ethanol containing a catalytic amount of piperidine to yield desired styryl carbazole dyes **5a**–**b** and **6a**–**b**. The structures of the dyes were confirmed by FT-IR, ¹H NMR, ¹³C NMR, Elemental analysis and Mass spectra. The ¹H NMR spectra of dye **5a** showed doublet peaks at δ 7.07 and 7.67 having trans vicinal coupling (*J* = 15.2 Hz) which indicates the ethylenic protons at styryl group are in trans form. The elemental analysis of these samples showed that they are pure and values were consistent with the calculated values.

3.2. Photo-physical properties

The UV–Vis absorption and fluorescence emission spectra of 1×10^{-6} mol L⁻¹ solution of dyes **5a–b** and **6a–b** were measured in different solvent of varying polarity, absorption and emission maxima are also reported in the Table 1. These dyes with A– π –D (**5a** and **6a**) and A– π –D– π –A (**5b** and **6b**) structure consist of an electron-donating *N*-ethyl carbazolyl unit and electron-with-drawing cyano or carboethoxy group. The results showed that these dyes exhibited strong solvatofluoric properties. The introduction of electron accepting groups in the positions induced intramolecular charge transfer and mesomeric dipole moment. Depending upon the electron affinity of acceptor groups, the CT band was red shifted as shown in Table 1. The absorption and emission spectra of dye **5a**, in several solvents having different polarities shown in Figs. 1 and 2.

The absorption maxima showed red shift with the increase in the solvent polarity which extended from 444 nm to 457 nm for dye **5a**, 426 nm to 430 nm for dye **5b**, 465 nm to 484 nm for dye **6a** and 447 nm to 459 nm for dye **6b** (Table 1). The only dye **5b** showed less shift in the absorption maxima.

The fluorescence emission spectra also exhibited a strong solvent effect. The emission maxima showed shift with solvent polarity which extended from 530 nm to 574 nm for dye **5a**, 522 nm to 560 nm for dye **5b**, 526 nm to 584 nm for dye **6a** and 524 nm to 574 nm for dye **6b**.

In highly polar solvent such as DMF the emissive S_1 state of intramolecular charge transfer (ICT) character is strongly solvated and its energy is hence dramatically lowered. As a consequence, the energy gap ΔE (S_1, S_2) is enlarged so that the coupling of the S_1 state directly to the ground state stays opened and the intersystem crossing from S_1 to T state is enhanced. The high electron-donating character of carbazole moiety leads to a red shift (lower energy) of the emission relative to the absorption is caused by energy losses due to dissipation of vibrational energy during the decay and is influenced by interaction between the fluorophore and the solvent molecules around the excited dipole, hydrogen bonding and formation of charge complexes.

The dipolar materials are bright orange to red in color and soluble in most of organic solvents. In less polar solvents such as toluene, all the compounds emit green light of moderate intensity. On increasing the solvent polarity the emission band also shifts bathochromatically and in DMF it emits orange light. Fig. 3 and Fig. 4 shows that the UV–Vis absorption and fluorescence emission photographs of dye **5a** and **6a** in various solvents, dye **5a** and **6a** in various solvents, dye **5a** and **6a** in various solvent with different color and fluorescence emission can be easily observed by naked eyes. Synthesized dyes **5a**–**b** and **6a**–**b** also showed solid-state fluorescence under UV light at 366 nm as shown in Fig. 5.

3.3. Thermal stability of dyes

In order to give more insight into the dyes **5a**, **5b**, **6a** and **6b** the thermal studies of the compounds have been carried out using thermal gravimetric techniques (DSC-TGA). The thermogravimetric studies have been carried out in the temperature range 50–600 °C under nitrogen gas at a heating rate of 10 °C min⁻¹. The DSC-TGA results indicated that the due to presence of carbazole frame work of the synthesized dyes are stable up to 300 °C. TGA revealed the onset decomposition temperature (T_d) of compounds 5a, 5b, 6a and 6b at 306 °C, 300 °C, 340 °C and 320 °C, respectively as shown in Fig. 6. Above 300 °C the thermogravimetric curve of the synthesized compounds show a major loss in weight. The comparisons of the T_d (decomposition temperature) show that the thermal stability of the 5a, 5b, 6a and 6b decreases in the order **6a > 6b > 5a > 5b**. The results showed that synthesized dyes have good thermal stability. Dye 5a, 5b showed sharp decomposition at 306 and 300 °C respectively and completely decomposed beyond 550 °C. However dyes 6a and 6b showed two step decomposition behaviors and completely decomposed beyond 600 °C. Differential scanning calorimetric (DSC) analysis of target molecules show exothermal peak at 387 °C, 376 °C, 383 °C and 372 °C, respectively as shown in Fig. 7. Except dye 5a, other dyes 5a, 6a, 6b showed melting point behavior.

4. Conclusions

In summary, we have developed an efficient and simple protocol for the synthesis of fluorescent extended mono- and bis-styrylated chromophores containing both carbazole and electron withdrawing cyano/carboethoxy moieties. The synthesized compounds were confirmed by FT-IR, ¹H NMR, ¹³C NMR, Elemental analysis and Mass spectra. From the emissive properties, it was concluded that the electronic coupling between D and A was sufficient to allow charge transfer (CT) in their molecules. The ICT maximal emission displayed a large wavelength shifted and Stokes shift increased in response to the increase of the solvent polarity. The DSC–TGA results show that they are having good thermal stability and hence these dyes may have various applications in nonlinear optics (NLO), electronic and photonic devices, organic light-emitting diodes.

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References

- Chang C, Kuo I, Lin J, Lub Y, Chen C, Back H, et al. A novel carbazole derivative, BMVC: a potential antitumor agent and fluorescence marker of cancer cells. Chemistry & Biodiversity 2004;1:1377–84.
- [2] Qian Y, Xiao G, Wang G, Sun Y, Cui Y, Yuan C. Synthesis and third-order optical nonlinearity in two-dimensional A-π-D-π-A carbazole-cored chromophores. Dyes and Pigments 2006;71:109–17.
- [3] Fitilis I, Fakis M, Polyzos I, Giannetas V, Persephonis P, Vellis P, et al. A twophoton absorption study of fluorene and carbazole derivatives. The role of the central core and the solvent polarity. Chemical Physics Letters 2007;447: 300-4.
- [4] Li H, Zhang Y, Hu Y, Ma D, Wang L, Jing X, et al. Novel soluble N-phenylcarbazole-containing PPVs for light-emitting devices: synthesis electrochemical, optical, and electroluminescent properties. Macromolecular Chemistry and Physics 2004;205:247–55.
- [5] Thomas K, Lin J, Tao Y, Ko C. Novel green light-emitting carbazole derivatives: potential electroluminescent materials. Advanced Materials 2000;12: 1949–51.
- [6] Wada T, Zhang Y, Choi YS, Sasabe H. Photoconductive crystals for nonlinear optics: molecular design and crystal structure. Journal of Physics D: Applied Physics 1993;26:B221–4.

- [7] Wada T, Zhang Y, Yamakado M, Sasabe H. Linear and nonlinear optical properties of carbazole-containing polymers. Molecular Crystals and Liquid Crystals 1993;227:85–92.
- [8] Fu H, Wu H, Hou X, Xiao F, Shao B. N-Aryl carbazole derivatives for non-doped red OLEDs. Synthetic Metals 2006;156:809–14.
- [9] Zhu W, Meng X, Yang Y, Zhang Q, Xie Y, Tian H. Bisthienylethenes containing a benzothiadiazole unit as a bridge: photochromic performance dependence on substitution position. Chemistry: a Europian Journal 2010;16: 899–906.
- [10] Xia ZY, Zhang ZY, Su JH, Zhang Q, Fung KM, Lam MK, et al. Robust and highly efficient blue light-emitting hosts based on indene-substituted anthracene. Journal of Materials Chemistry 2010;20:3768–74.
- [11] Kuo W, Hsiue, Jeng R. Synthesis and macroscopic second-order nonlinear optical properties of poly(ether imide)s containing a novel two-dimensional carbazole chromophore with nitro acceptors. Journal of Materials Chemistry 2002;12:868–78.
- [12] Bai G, Li J, Li D, Dong C, Han X, Lin P. Synthesis and spectrum characteristic of four new organic fluorescent dyes of pyrazoline compounds. Dyes and Pigments 2007;75:93–8.