



Carbazole-containing push–pull chromophore with viscosity and polarity sensitive emissions: Synthesis and photophysical properties



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ABSTRACT

Carbazole based D- π -A extended styryl dyes with intramolecular charge transfer characteristics were synthesized. The intramolecular charge transfers of these D- π -A extended styryls have been examined with the study of photophysical properties like absorption, emission and quantum yield in various solvents of different polarities. All the dyes demonstrated positive solvatochromism. They showed largely improved photophysical properties and large Stokes shifts due to twist geometry. Oscillator strengths and transition state dipole moments have been studied to understand charge transfer within the molecules. The fluorescence molecular rotors properties of the series of extended styryls have been evaluated. The dyes having good charge transfer characteristics showed better FMR properties. Sensitivity of the fluorescence emission towards solvent polarity and viscosity has been investigated using fluorescence emission spectra.

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1. Introduction

Carbazole-based heteroatomic moieties have been extensively studied for their unique photophysics and photochemistry [1–6]. Carbazole core containing colorants are very useful in optoelectronic and electroluminescence devices [1], material chemistry [7], organic light emitting device [8], photoconductors [9,10], non liner optics [11], thin film transistors [12], photovoltaics [13], metal sensors [14], and dye sensitized solar cells [15].

Some conjugated carbazole derivatives are largely typical push–pull, D- π -A systems in which a strong electron donor (D) is linked to the strong acceptor (A) through a planar π system [16–18]. A system containing N-substituted carbazole acts as a donor and withdrawing groups present at 2-, 3-, 6 and 7 positions of carbazole are responsible for the intramolecular charge transfer (ICT). This type of π -conjugated system shows ICT characteristics [19]. The ICT molecules exhibit multi functionality such as multiple electroactivity or photoactivity with applications in organic electronics [11,20]. The organic conjugated molecules with large π -conjugated system generally exhibit two-photon absorption (TPA) with ICT [21].

The thermal stability and photophysical properties of π -conjugated system are enhanced by the introduction of carbazole moiety [22]. The stable π -conjugated chromophores show positive solvatochromism in various solvents inducing a red shift with the increase in polarity [23]. The positive solvatochromism results from the stabilization of the ground and excited states of the fluorophores in the solvent with change in polarity [24]. The molecular and optical properties of π -conjugated carbazole system can be altered by structural modification at 2-, 3-, 6-, 7- and 9- positions [25–27]. Triphenylamine based fluorescent styryls show emission in the red region due to the twisted-intramolecular charge transfer phenomenon (TICT) [28].

Recently, much attention has been paid to viscosity sensitive emission along with the charge transfer emission, viscosity has a great influence on the fluorescence intensity [29,30]. In low viscous solution, the intramolecular rotation is the predominant in excitation pathway, whereas in the high-viscous solutions, the intramolecular rotation is hindered, and fluorescence emission intensity increases as the intramolecular rotation decreases [31–34]. The fluorophores emit with low intensity in low viscosity solvents due to the free rotation of the C–C and C=C bonds in the excited state. Such system with low emission intensity emits with higher intensity in higher viscosity solvents or mixture of high viscosity solvents. p-(Dialkylamino)benzylidene malononitriles showed most predominant fluorescent molecular rotor (FMR) properties, with donor–acceptor relation through π -conjugation [31,32,35].

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In this work we have synthesized *N*-phenylcarbazole based extended styryls with red shifted emissions than the corresponding *N*-ethylcarbazole analogs. The extended styryl has twist geometry due to the presence of *N*-phenyl group at 9-position of carbazole. The extended styryl of *N*-phenylcarbazole exhibit the substitutionally tunable features of these simple twisted π -conjugated systems. The extended styryl of *N*-phenylcarbazole behaves differently as viscosity sensitive emitters. *N*-Phenylcarbazole was formylated by Vilsmeier–Haack reaction and condensed with two different active methylene compounds having electron withdrawing capacity to give range of extended styryls. Study of photophysical properties of synthesized extended styryls in different solvents has been carried out.

2. Experimental section

2.1. Materials and equipments

All the reagents and solvents were purchased from Sd Fine Chemicals Pvt. Ltd. and used without purification. All the solvents used were of spectroscopic grade. Melting point was recorded by open capillary on Sunder Industrial Product and is uncorrected. The reactions were monitored using pre-coated silica gel aluminum backed TLC plates; Kiesel gel 60 F₂₅₄ Merck (Germany). The FT-IR spectra were recorded on a Jasco 4100 Fourier Transform IR instrument (ATR accessories). ¹H and ¹³C NMR spectra were recorded on a 500 MHz Varian, USA instrument using TMS as an internal standard. Mass spectra were recorded on Finnigan Mass spectrometer. The absorption spectra of the compounds were recorded on a Perkin Elmer Lambda 25 UV–visible spectrophotometer; fluorescence emission spectra were recorded on Varian Cary Eclipse fluorescence spectrophotometer using freshly prepared solutions at the concentration of 1×10^{-6} mol L⁻¹. Fluorescence quantum yield were measured by using fluorescein as reference standard (in 0.1 M NaOH) [36].

2.2. Synthesis

2.2.1. Synthesis of 3-formyl-9-phenylcarbazole **4**, *N*-(4-formylphenyl)carbazole **4a** and 9-phenyl-9*H*-carbazole-3,6-dicarbaldehyde **4b**

The compounds **4**, **4a** and **4b** were prepared by the reported methods [37,38].

2.2.2. Synthesis of (1-phenylethylidene) propanedinitrile **5** and ethyl-2-cyano-3-phenyl-2-butenate **7**

The compounds **5** and **7** were prepared by the reported method [39].

2.2.3. General procedure for synthesis of extended styryls **6**, **8**–**12**

The carbaldehyde (**4**, **4a** and **4b** 1 eq.) and different active methylene compound (**5** and **7**; 1.2 eq.) were dissolved in absolute ethanol (10 mL). Piperidine was added in catalytic amount (0.1 mL) and the reaction mixture was refluxed for 4 h. The corresponding extended styryls (**6**, **8**, **9**, **10**, **11** and **12**) were obtained, filtered and recrystallized from methanol.

2.2.3.1. Synthesis of 2-(1-phenyl-3-(9-phenyl-9*H*-carbazol-3-yl)allylidene)malanonitrile **6**. Color: Orange; Yield: 68%; M.P.: 208–210 °C.

FT-IR: 2215 (–CN), 1584 (–C=C–), 1497(–Ar).

CHN Analysis: Found C = 85.41; H = 4.49; N = 9.91. Calculated for C₃₀H₁₉N₃ C = 85.47; H = 4.54; N = 9.97%.

Mass: Calculated 421.1 for C₃₀H₁₉N₃ found 422.2 (M+1).

¹H NMR (DMSO, δ): 7.10 (d, 1H, *J* = 15.4 Hz), 7.35 (m, 3H), 7.46 (t, 1H), 7.45 (m, 2H), 7.58 (d, 1H, *J* = 7.4 Hz), 7.63 (m, 6H), 7.69 (t, 2H), 7.82 (d, 1H, *J* = 8.8 Hz), 8.32 (d, 1H, *J* = 7.8 Hz), 8.64 (s, 1H) ppm.

¹³C NMR (DMSO, δ): 79.46, 110.62, 111.10, 113.99, 114.79, 121.54, 121.64, 122.04, 123.05, 124.18, 126.92, 127.23, 129.42, 129.50, 130.79, 131.44, 133.88, 136.49, 141.35, 142.57, 151.01, 171.84 ppm.

2.2.3.2. Synthesis of Ethyl 2-cyano-3-phenyl-5-(9-phenyl-9*H*-carbazol-3-yl)pent-2,4-dienoate **8**. Color: Yellow; Yield: 79%; M.P.: 186–188 °C.

FT-IR: 2209 (–CN), 1715 (–C=O), 1592 (–C=C–), 1485(–Ar), 1131(–C–O).

CHN Analysis: Found C = 81.99; H = 5.11; N = 5.92. Calculated for C₃₂H₂₄N₂O₂ C = 82.03; H = 5.16; N = 5.98%.

Mass: Calculated 468.1 for C₃₂H₂₄N₂O₂ found 469.2 (M+1).

¹H NMR (DMSO, δ): 1.33 (t, 3H), 4.34 (q, 2H), 6.82 (d, 1H, *J* = 15.89 Hz), 7.32 (m, 2H), 7.39 (d, 1H, *J* = 8.6 Hz), 7.44 (m, 3H), 7.60 (m, 6H), 7.70 (m, 3H), 8.27 (d, 1H, *J* = 7.9 Hz), 8.41 (s, 1H), 8.61 (d, 1H, *J* = 15.8 Hz) ppm.

¹³C NMR (DMSO, δ): 14.53, 62.16, 100.80, 110.53, 111.10, 117.53, 121.38, 121.48, 123.01, 123.48, 123.65, 123.83, 126.27, 127.2, 127.45, 127.78, 128.66, 129.1, 129.31, 130.25, 130.76, 136.62, 136.94, 141.26, 142.03, 162.68, 167.88 ppm.

2.2.3.3. Synthesis of 2-(3-(4-(9*H*-carbazol-9-yl)phenyl)-1-phenylallylidene)malanonitrile **9**. Color: Orange; Yield: 61%; M.P.: 170–172 °C.

FT-IR: 2213 (–CN), 1592 (–C=C–), 1448(–Ar).

CHN Analysis: Found C = 85.51; H = 5.51; N = 9.91. Calculated for C₃₀H₁₉N₃ C = 85.49; H = 4.54; N = 9.97%.

Mass: Calculated 421.1 for C₃₀H₁₉N₃ found 422.2 (M+1).

¹H NMR (DMSO, δ): 6.9 (d, 1H, *J* = 15.6 Hz), 7.32 (t, 2H), 7.44 (m, 6H), 7.60 (m, 3H), 7.67 (m, 3H), 7.77 (d, 2H, *J* = 8.4 Hz), 8.14 (d, 2H, *J* = 7.8 Hz) ppm.

¹³C NMR (DMSO, δ): 82.78, 109.72, 112.78, 113.30, 120.49, 120.66, 123.86, 124.98, 120.21, 127.09, 128.91, 129.12, 130.29, 131.29, 132.86, 133.00, 140.10, 140.79, 147.82, 170.89 ppm.

2.2.3.4. Synthesis of Ethyl 5-(4-(9*H*-carbazol-9-yl)phenyl)-2-cyano-3-phenylpent-2,4-dienoate **10**. Color: Yellow; Yield: 71%; M.P.: 188–190 °C.

FT-IR: 2214 (–CN), 1717 (–C=O), 1596 (–C=C), 1447(–Ar), 1118 (–C–O).

CHN Analysis: Found C = 82.04; H = 5.12; N = 5.93. Calculated for C₃₂H₂₄N₂O₂ C = 82.03; H = 5.12; N = 5.93%.

Mass: Calculated 468.1 for C₃₂H₂₄N₂O₂ found 469.2 (M+1).

¹H NMR (CDCl₃, δ): 1.43 (t, 3H), 4.41 (q, 2H), 6.74 (d, 1H, *J* = 15.7 Hz), 7.30 (t, 2H), 7.42 (m, 6H), 7.55 (m, 3H), 7.59 (d, 2H, *J* = 8.4), 7.73 (d, 2H, *J* = 8.4), 8.13 (d, 2H, *J* = 7.7 Hz), 8.75 (d, 1H, *J* = 16.4 Hz) ppm.

¹³C NMR (CDCl₃, δ): 14.19, 62.12, 102.89, 109.72, 116.76, 120.41, 123.70, 126.10, 126.35, 127.03, 128.72, 128.96, 129.91, 134.25, 136.24, 139.68, 140.33, 145.99, 162.53, 167.42 ppm.

2.2.3.5. Synthesis of 2,2'-(9-phenyl-9*H*-carbazole-3,6-diyl)bis(1-phenylprop-2-en-3-yl-1-ylidene)dimalanonitrile **11**. Color: Red; Yield: 48%; M.P.: 190–192 °C.

FT-IR: 2219 (–CN), 1589 (–C=C), 1441(–Ar).

CHN Analysis: Found C = 84.06; H = 4.15; N = 11.63. Calculated for C₃₂H₂₄N₂O₂ C = 84.12; H = 4.20; N = 11.68%.

Mass: Calculated 622.2 for C₄₂H₄₅N₅Na found 623.4 (M+1).

¹H NMR: 7.03 (d, 2H, *J* = 15.5 Hz), 7.37 (d, 2H, *J* = 9 Hz), 7.63 (m, 16H), 7.99 (d, 2H, *J* = 8.5 Hz), 8.70 (s, 1H) ppm.

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