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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.

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; Kisel gel 60 F_{254} Merck (Germany). The FT-IR spectra were recorded on a Jasco 4100 Fourier Transform IR instrument (ATR accessories). ^{1}H and ^{13}C 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 ware 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-9H-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-butenoate **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-9H-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 $C_{30}H_{19}N_3$ C = 85.47; H = 4.54; N = 9.97%.

Mass: Calculated 421.1 for $C_{30}H_{19}N_3$ found 422.2 (M+1).

^{1}H 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.

^{13}C 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-9H-carbazol-3-yl)penta-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 $C_{32}H_{24}N_2O_2$ C = 82.03; H = 5.16; N = 5.98%.

Mass: Calculated 468.1 for $C_{32}H_{24}N_2O_2$ found 469.2 (M+1).

^{1}H 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.

^{13}C 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-(9H-carbazol-9-yl)phenyl)-1-phenylallylidene)malononitrile ***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 $C_{30}H_{19}N_3$ C = 85.49; H = 4.54; N = 9.97%.

Mass: Calculated 421.1 for $C_{30}H_{19}N_3$ found 422.2 (M+1).

^{1}H 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.

^{13}C 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-(9H-carbazol-9-yl)phenyl)-2-cyano-3-phenylpenta-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 $C_{32}H_{24}N_2O_2$ C = 82.03; H = 5.12; N = 5.93%.

Mass: Calculated 468.1 for $C_{32}H_{24}N_2O_2$ found 469.2 (M+1).

^{1}H NMR ($CDCl_3$, 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.

^{13}C NMR ($CDCl_3$, 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-9H-carbazole-3,6-diyl)bis(1-phenylprop-2-en-3-yl-1-ylidene)dimalononitrile ***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 $C_{32}H_{24}N_2O_2$ C = 84.12; H = 4.20; N = 11.68%.

Mass: Calculated 622.2 for $C_{42}H_{45}N_5Na$ found 623.4 (M+1).

^{1}H 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.

^{13}C NMR (DMSO, δ): 80.02, 111.59, 113.87, 113.86, 123.86, 124.18, 127.22, 127.39, 127.77, 127.95, 128.46, 129.24, 129.48, 130.88, 131.45, 133.81, 135.86, 143.22, 150.62, 171.74 ppm.

2.2.3.6. Synthesis of diethyl 5,5′-(9-phenyl-9H-carbazole-3,6-diyl) bis(2-cyano-3-phenylpenta-2,4-dienoate) ***12***. Color: Yellow; Yield: 45%; M.P.: 220–222 °C.

FT-IR: 2221 (−CN), 1721 (−C=O), 1594 (−C=C), 1432(−Ar), 1122 (−C−O).

CHN Analysis: Found C = 79.58; H = 5.02; N = 6.01. Calculated for $C_{32}H_{24}N_2O_2$ C = 79.63; H = 5.08; N = 6.06%.

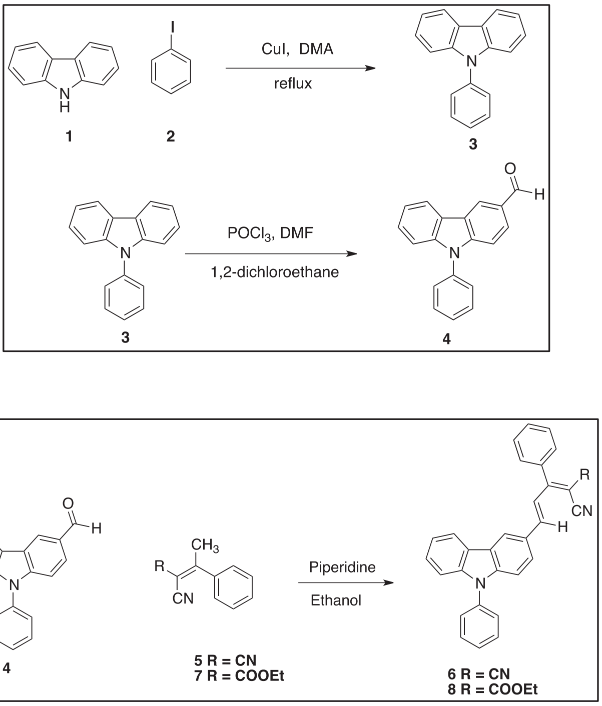
Mass: Calculated 693.2 for $C_{46}H_{35}N_3O_4$ found 693.

^{1}H NMR (CDCl$_3$, δ): 1.41 (t, 3H), 4.37 (q, 2H), 6.84 (d, 1H, J = 16.1 Hz), 7.37 (m, 7H), 7.59 (m, 9H), 7.62 (m, 4H), 7.98 (s, 1H), 8.16 (s, 1H), 8.71 (d, 1H, 15.5 Hz).

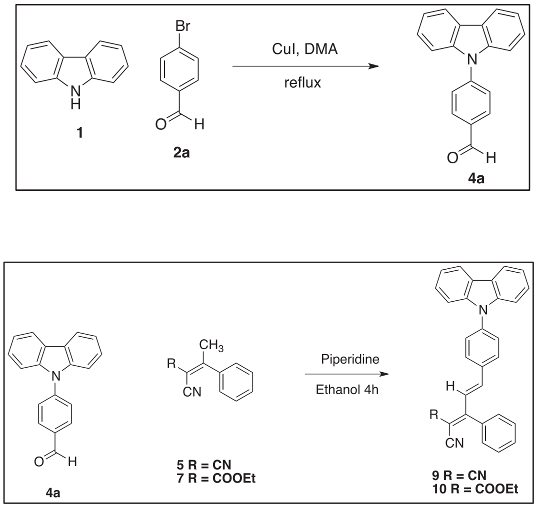
^{13}C NMR (CDCl$_3$, δ): 14.24, 61.76, 100.50, 110.30, 117.36, 120.59, 122.07, 123.18, 123.87, 123.37, 123.18, 127.90, 128.02,128.11, 128.59, 128.94, 129.69, 130.00, 134.54, 136.83, 137, 04, 140.20, 142.62, 149.32, 163.09, 168.41.

3. Results and discussions

All the extended styryls were synthesized from carbazole **1**. *N*-Substitution of carbazole followed by Vilsmeier–Haack reaction have been carried to afford 3-formyl-9-phenylcarbazole **4** (Scheme 1). 4-(9*H*-Carbazol-9-yl)benzaldehyde **4a** (Scheme 2) was synthesized by coupling 4-bromobenzaldehyde **2a** with carbazole **1** using Buchwald reaction. The crude compound was purified by column chromatography. 9-(4-Formylphenyl)-9*H*-carbazole-3-carbaldehyde **4b** (Scheme 3) was synthesized by bis-formylation of N-phenyl carbazole and purified by using column chromatography. The carbaldehydes (1 eq.) were heated with 2-(1-phenylethylidene)malononitrile **5** (1.2 eq.) and ethyl 2-cyano-3-phenylbut-2-enoate **7** (1.2 eq.) by Knoevenagel condensation to get the novel extended styryls.



Scheme 1.

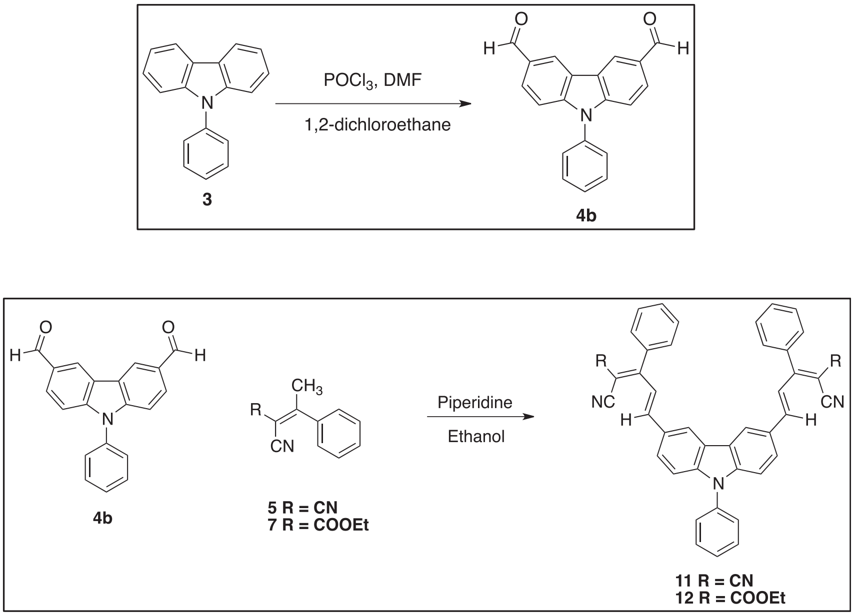


Scheme 2.

The compounds **6** and **8** were synthesized by the condensation of 9-phenyl-9*H*-carbazole-3-carbaldehyde **4** with methyl 2-(1-phenylethylidene)malononitrile **5** and ethyl 2-cyano-3-phenylbut-2-enoate **7** respectively by Knoevenagel condensation. Similarly **9** and **10** were synthesized by the condensation of 4-(9*H*-carbazol-9-yl)benzaldehyde **4a** with **5** and **7**. The compounds **11** and **12** were synthesized by condensation of 9-(4-formylphenyl)-9*H*-carbazole-3-carbaldehyde **4b** with **5** and **7** respectively. The styryl dyes were purified by crystallization in methanol. FT-IR, ^{1}H NMR, ^{13}C NMR and CHN spectral analysis were performed to confirm the structures of the extended styryls.

3.1. Photo-physical properties

The extended styryls can be divided in to two groups; one containing 2-(1-phenylethylidene)malononitrile as an acceptor unit (**6**, **9 and 11**), second containing 2-cyano-3-phenylbut-2-enoate as an acceptor unit (**8**, **10 and 12**). The UV–vis absorption and fluorescence emission spectra of the extended styryls in dichloromethane are shown in Figs. 1 and 2. The experimental absorption values and computed values of all the extended styryls in different solvents with varying polarities are tabulated in Table 1, S1–S5 and Figs. S1–S3. The extended styryls having D-π-A **(6, 8–10)** and A- π-D-π-A **(11, 12)** systems consist of an electron donating *N*-phenyl carbazole core and electron withdrawing dicyano vinylene and cyanoethoxy vinylene groups linked through π-bond. The absorption spectra of all the extended styryls showed two maxima. Shorter maxima was observed at around 300–350 nm due to the π–π* transition with low energy and longer maxima at around 350–450 nm due to ICT between the donor carbazole unit and the acceptor active methylene units. The presence of phenyl group on nitrogen atom in carbazole ring is responsible for more effective conjugation in the molecules. The molar extinction coefficients (ε) of the extended styryls **6**, **8**, **9** and **10** correspond to the ICT were in the range of 8800–44,800 Lmol^{-1} cm^{-1} while the extended styryls **11** and **12** observed much higher value of ε in the range of 32,000–60,000 Lmol^{-1} cm^{-1} in different solvents. These two extended styryls **11** and **12** observed shoulder peak, which may be due to conjugation from any one side of 3- and 6- position of carbazole.



Scheme 3.

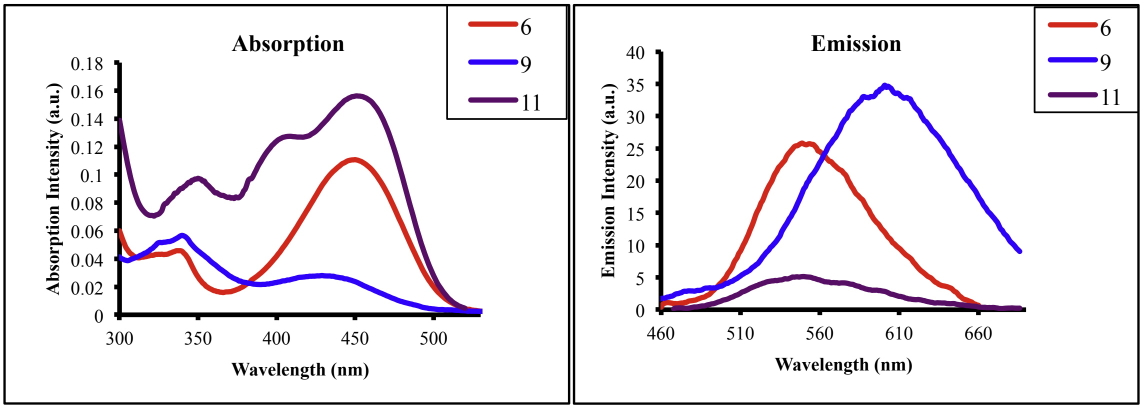


Fig. 1. Absorption and emission graph of compound **6**, **9**, and **11** in dichloromethane.

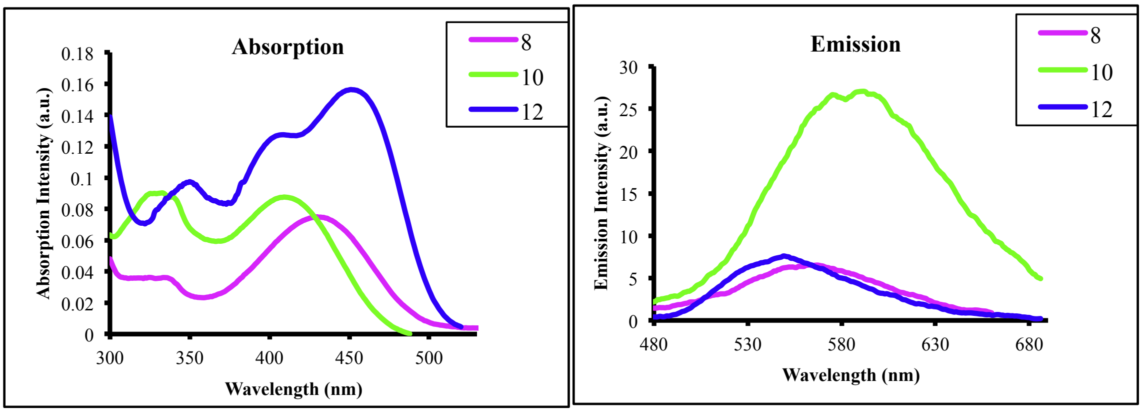


Fig. 2. Absorption and emission graph of compound **8**, **10**, and **12** in dichloromethane.

Table 1
Absorption maxima (λ_{abs}, nm), molar extinction coefficient (ε; $Lmol^{-1}$ cm^{-1}) of extended styryl **6** in different solvents.

Solvent	λ_{abs}[a]	FWHM	(ε) ($Lmol^{-1}$ cm^{-1})	f[b]
Toluene	446	63	31,200	0.288
1,4-Dioxane	450	63	44,000	0.264
DCM	453	183	44,800	0.476
Chloroform	438	188	40,400	0.521
Ethyl acetate	438	74	31,600	0.378
Acetone	441	150	37,200	0.363
Acetonitrile	439	176	35,200	0.359
DMF	447	72	26,800	0.279
DMSO	452	189	27,600	0.321

[a] Absorption maxima experimental.
[b] Oscillator strength experimental.

3.2. Fluorescence emission

The extended styryls were having similar properties as compared to the known styryl [16]. All the extended styryls **6**, **8–12** observed red shift in emission maxima from non-polar solvent toluene to polar solvent DMSO Figs. S1–S3. The compounds **6**, **9** and **11** containing two powerful electron withdrawing cyano groups emit orange light in solid state as well as in solution whereas the compounds **8**, **10** and **12** containing one powerful electron withdrawing cyano group and one weak electron withdrawing carboethoxy group were yellow fluorescent in solid as well as in solution.

The excited states of these molecules in polar solvents are more stable which might be due to the charge separation in the molecules at the excited state. These red shifts for extended styryls from non-polar to polar solvents in **6, 8–12** were found to be 80 nm, 77 nm, 43 nm, 52 nm, 79 nm and 74 nm respectively. It was observed that the extended styryls **9** and **10** showed lower shift as they have less donor effect from *N*-phenyl substituted carbazole moiety. This underlines that extension of conjugation due to the presence of strong electron donating group at 3- and 6- positions on the carbazole moiety have good effect on the emission values. In the case of extended styryls **9** and **10**, fluorescence quantum yield decreases with increasing solvent polarity, which is caused by the radical ion formation in aromatic hydrocarbons with increasing solvent polarity [40–42] (Table S7–S8).

The fluorescence quantum yields of these molecules are good in non-polar solvents. The extended styryl **6** showed $\phi = 0.14$ and $\phi = 0.12$ fluorescence quantum yields in toluene and 1,4-dioxane respectively. Similar results were obtained in the case of **8**, which showed higher fluorescence quantum yield in non-polar solvents like toluene ($\phi = 0.14$), 1,4-dioxane ($\phi = 0.11$), dichloromethane ($\phi = 0.14$) and chloroform ($\phi = 0.15$). In the case of **9**, the highest fluorescence quantum yield was observed in chloroform ($\phi = 0.42$) while the extended styryls **11** and **12** showed the highest fluorescence quantum yields in polar solvents like DMSO ($\phi = 0.16$) (Table 2 S6–S10). The lower values of fluorescence quantum yields due to the rotation barriers of the cis–trans isomerization at terminal C=C bond and the internal rotations around C–C bond at 3-, 6- and 9- position of carbazole that decreases the band gap in ground (S_0) and excited state (S_1) and may quenches the fluorescence quantum yield [43,44].

Table 2
Fluorescence emission maxima (λ_{em}, nm), fluorescence quantum yield (ϕ_f) and Stokes shift (cm^{-1}) of extended styryl **6** in different solvents.

Solvent	λ_{em}	Stokes shift (cm^{-1})	$f(\phi)$
Toluene	515	3004.0	0.14
1,4-Dioxane	490	2422.8	0.12
DCM	549	4007.2	0.035
Chloroform	542	3624.8	0.027
Ethyl acetate	497	2710.3	0.095
Acetone	511	3106.2	0.12
Acetonitrile	515	3361.5	0.16
DMF	570	4827.5	0.05
DMSO	521	2930.03	0.03

The extended styryls **11** and **12** showed positive fluorescence solvatochromism with the increase in solvent polarity (Fig. S3). These molecules have more conjugation from involvements of both the sides of 3- and 6- positions on the carbazole, which is responsible for higher extinction coefficient, positive solvatochromism, higher Stokes shift and good quantum yield. In these compounds fluorescence was enhanced due to intramolecular charge transfer from carbazole to electron withdrawing group present at 3- and 6- positions on carbazole.

3.3. Emission in the solid-state

The solid-state emission of all the extended styryls in the range of 508–597 nm as shown in Fig. 3. The extended styryl **6** containing cyano group observed a blue shift as compared to its analog **8** having 1- cyano-1-thoxy carbonyl vinylene group. While the extended styryls **9** and **11** containing more polar dicyanovinylene group showed red shift as compared to their respective analogs **10** and **12**. Dicyanovinylene extended styryl dyes **6**, **9 and 11** showed better emission intensity as related to their analogs **8, 10 and 12** containing ethoxycarbonylcyano vinylene group. Extended styryl dyes **11** and **12** observed less emission intensity as they contained two-acceptor unit and one donor. Two acceptor units may quench the fluorescence. These extended styryls may lead to H-type of aggregation that shows blue shift while mono substituted styryls **6**, **8–10** shows J-type of aggregation with red shift [45].

3.4. Dipole moment changes of the extended styryls on photoexcitation

The ICT feature of the extended styryls can be evaluated by a Lippert–Mataga plot [Eq. (1)] [46–48]. The common solvent effects on the molecules were described solvatochromism properties by Lippert–Mataga Eq. (1). Lippert–Mataga equation is used to estimate change in dipole moment on photoexcitation as a function of the solvent polarity.

$$\Delta\nu = \frac{2\Delta f}{4\pi\varepsilon_0 \hbar c a^3}\left(\mu_e - \mu_g\right)^2 + b \qquad (1)$$

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$
where,

$\Delta\nu = \nu_{abs} - \nu_{em}$ stands for Stokes shift,
ν_{abs} and ν_{em} = absorption and emission (cm^{-1}),
$\hbar$ = Planck's constant,
c = velocity of light in vacuum,
a = Onsager cavity radius,
b = constant,
Δf = orientation polarizability,
μ_g = ground-state dipole in the ground-state geometry,
μ_e = excited-state dipole in the excited-state geometry,
ε_0 = permittivity of the vacuum,
$(\mu_e - \mu_g)^2$ = proportional to the slope of the Lippert–Mataga plot.

The Lippert–Mataga plots of the Stokes shift of the extended styryl dyes **6**, **8**, **11 and 12** against orientation polarizability showed very good linearity as shown by regression coefficient close to unity (Fig. S4). In case of extended styryl dyes **9 and 10**, Lippert–Mataga

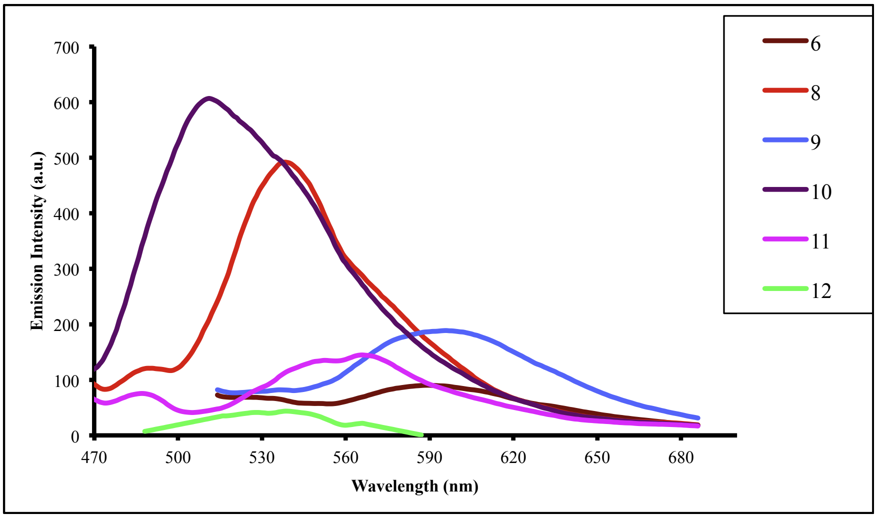


Fig. 3. Solid-state emission spectra of extended styryls.

plots were non linear with low regression factor, which concluded that fluorescence quenching occurred in polar solvents. However, in case of the extended π-conjugation framework such as **11 and 12**, the dipole moment changes were much better with the solvent polarity (up to 8 D). The higher dipole moment changes in these compounds infer that the ICT feature in the extended styryls was more significant. These results are attributed to the di-substitution on the carbazole ring at 3- and 6-positions. Similar observation is encountered in case of the extended styryls **6** and **8**, the dipole moment differences were up to 6 D due to only mono substitution on carbazole ring at 3-position.

3.5. *Oscillator strength and transition state dipole moment*

Oscillator strength is dimensionless quantity that expresses the probability of absorption and emission properties in energy levels, which helps to understand charge transfer within the molecules. It simply describes number of electron transition from the ground to the excited states. Oscillator strength (*f*) can be calculated using the following Eq. (2) [49]. Where ε is the extinction coefficient (Lmol^{-1} cm^{-1}), and ν represents the wavenumber (cm^{-1}). From this equation we have calculated oscillator strength for extended styryls and tabulated in Table S11.

$$f = 4.32 \times 10^{-9} \int \varepsilon(\nu)\, d\nu \tag{2}$$

By using the value of *f*, we have calculated transition dipole moment that was the differences in electric charge distribution between the ground and excited state of the molecule. The transition dipole moment for absorption (μ_a) is a measure of the probability of radiative transitions which have been calculated for the extended styryls in different solvent environments using the Eq. (3) [50]. The transition dipole moment increased with increase in the oscillator strength.

$$\mu_a^2 = \frac{f}{4.72 \times 10^{-7} \times \nu} \tag{3}$$

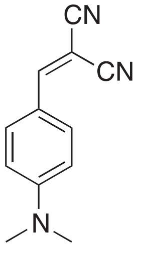
where,

μ_a is transition dipole moment (D),
f is oscillator strength,
ν is wavenumber (cm^{-1}).

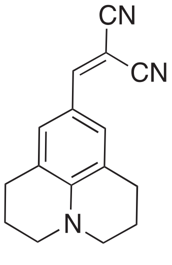
The extended styryls **6** (5.0–6.9 D), **8** (3.3–4.9 D), **11** (5.3–8.6 D) and **12** (6.1–7.9) have significant transition dipole moment as compared to **9** (2.3–3.1 D) and **10** (3.1–4.5 D) due to lack of charge transfer. Observed results conclude that the conjugation of 3- and 6- position of carbazole gave better charge transfer than the substitution at the 9- position of carbazole.

3.6. *Relation between fluorescent molecular rotor (FMR) and intramolecular charge transfer*

The emission intensity of the synthesized extended styryls increased with increasing solvent viscosity. The compounds **6**, **8**, **11** and **12** showed good FMR properties than the remaining extended styryls **9** and **10**. These diverse results may be due to the intramolecular charge transfer (ICT) between the acceptor and donor. The extended styryls **6**, **8**, **11** and **12** have better ICT than **9** and **10**. ICT was disturbed due to the radical ion formation in aromatic hydrocarbons, which quenched the fluorescence with increasing solvent polarity. Similar results are observed in case of fluorescence quantum yield. In highly polar solvents fluorescence of extended styryl dyes **9** and **10** diminishes. These results prove that lack of ICT is observed in these molecules. Hence it has been concluded that extended styryl dyes **9** and **10** were inactive as FMRs. The rotors **6**, **8**, **11** and **12** were compared with the traditionally reported rotors **A** and **B**. The emission maxima of extended styryl dyes **6**, **8**, **11** and **12** which can act as FMRs was observed to have a red shift of 30–60 nm as compared to the rotor **A** (λ_{em} = 470 nm in toluene). The ICT is more favorable at 3- and 6- positions of carbazole as compared to 9-phenyl carbazole.



A



B

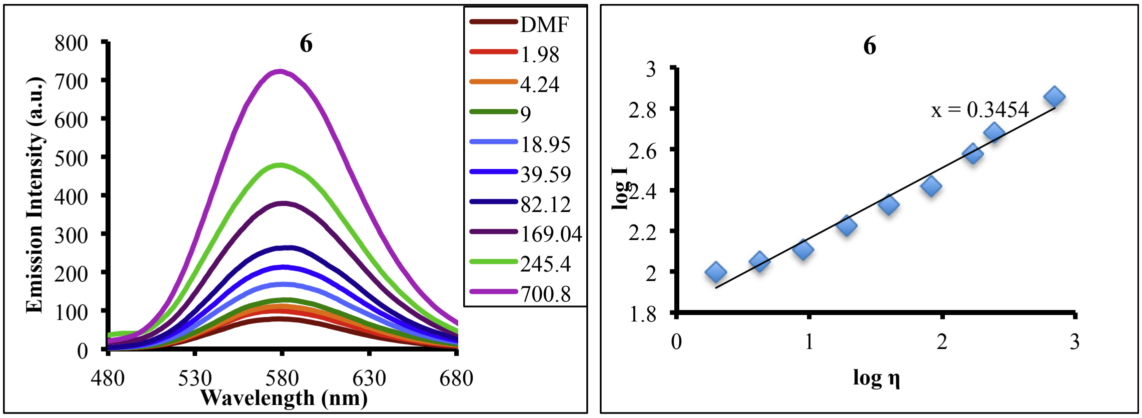


Fig. 4. Emission spectra of **6** in mixed solvents of DMF and glycerol, and emission intensity on the viscosity of the solvents.

3.7. *Sensitivity of emission to viscosity*

The effects of change in viscosity on emission of the synthesized FMRs **6, 8, 11** and **12** have been studied. The molecules **6**, **8**, **11** and **12** have less solubility in the mixture of ethylene glycol and glycerol. Thus, these molecules have been solubilized in highly polar aprotic solvent DMF and increased their viscosity using glycerol (Fig. 4). The emissions intensities of synthesized FMRs were increased with increase in solvent viscosity. But the emission intensities of extended styryl dyes **9** and **10** were decreased by increasing solvent polarity.

$$\log I = C + x \log \eta \tag{4}$$

The emission intensity of FMR and effect of viscosity of the solvent was described by using Förster–Hoffmann Eq. (4), in which η is viscosity of the solvents, I is the emission intensity of the rotors, C is a constant and x is the viscosity sensitivity of the rotors. The FMR **6** (x value 0.34) showed low value of x as compared to the FMR **8** (x value 0.49). The extended styryl dyes **9** and **10** show enhancement in emission intensity with the increasing viscosity. The FMR **9** showed x value 0.39 and **10** showed x value 0.47, which indicates that those molecules are low emissive in low viscous system can emit good in higher viscosity. Similar study has been carried out in DCM: PEG-400 system instead of DMF-Glycerol system, but such an observation was not evident. No enhancement on fluorescence of extended styryl dyes **9** and **10** has been observed. According to these two results compound **9** and **10** are FMR inactive. These results concluded that FMRs required good intramolecular charge transfer within the system. The FMR **11** (x value 0.1) showed a low value of x as compared to FMR **12** (x value 0.29) in DMF: Glycerol system. Same observation was observed in case of the FMR **6** and **8**. Same results were also observed in case of DCM:PEG-400 system, in this system FMR **11** (x value 0.23) showed low value of x as compared to FMR **12** (x value 0.37). The x value of dicyano vinylene containing FMRs **(6, 11)** are lower than that of cyano ethoxy crarobnyl vinylene FMRs (**8, 12**) in both the viscous system.

4. Conclusion

This paper reports synthesis of six carbazole based extended styryls with intramolecular charge transfer. Effect of extended conjugation at 3-, 6-, and 9-position on carbazole ring on the photophysical properties and viscosity sensitive emission are studied. The impact of intramolecular charge transfer on fluorescent molecular rotor was studied. In this study, we introduced new solvent system for viscosity dependent emission. Synthesized extended styryl dyes showed good photophysical properties with good intramolecular charge transfer. The strong π conjugation in the molecules leads FMRs, hence photophysical properties can be significantly enhanced. The ICT effect plays a key role in the viscosity sensitivity emission of the extended styryls. The absorption, emission, oscillator strength and charge distribution between acceptor and donor were discussed.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.02.012.

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