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Graphical Abstract:



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Abstract:

A series of push-pull chromophoric extended styryls from 5,5'-(9-ethyl-9H-carbazole-3,6-diyl)bis(2-morpholinothiazole-4-carbaldehyde) were synthesized by Knoevenagal condensation reaction with active methylene compounds. The intermediate carbaldehyde was synthesized from carbazole through multistep reactions. The intramolecular charge transfer of synthesized highly conjugated symmetrical D- π -A (D- donor, A- acceptor) extended styryls with rigid structure have been investigated by means of photophysical properties. The photophysical properties like absorption, emission and quantum yield of styryl derivatives were evaluated in various solvents of different polarities. All these synthesized extended styryls have exhibited aggregation induced emission with enhanced fluorescence intensity. This series of compounds can also be used as fluorescence molecular rotors for viscosity sensing. The sensitivity of viscosity towards UV absorption as well as fluorescence emission has also been investigated.

Keywords: Extended styryl, Photophysical properties, Aggregation induced emission (AIE), Fluorescent Molecular Rotors (FMR).

1. Introduction:

The carbazole-based compounds are having respectable chemical and physical properties, such as highly emissive and electron conducting properties, chemical and thermal stability and also capability with various transformation, polymerization, metal catalyzed cross coupling reaction [1-3]. The carbazole containing compounds have many

applications in various fields like organic light emitting diodes (OLED) [4], dye-sensitized solar cells [5,6], non linear optics [7], photoconductors [8], solid state lasers [9], and bioimaging [10]. The carbazole derivatives are also appealing molecules because of their intense luminescence and electron efficiency [11].

Planar structure of the carbazole ring helps to maintain good conjugation within the molecule. The carbazole ring is having two electron rich active sites 3 and 6 positions with respect to the bridge nitrogen. The introduction of electron withdrawing groups at these position leads to intramolecular charge transfer [12]. The carbazole moiety being rigid with a donor-rigidised residue improves π -electron delocalization resulting in a better two-photon absorbing property [13]. The N-alkyl carbazole compounds show solid-state fluorescence with good photophysical properties, and electro-optical properties [12]. A wide variety of structural modifications on the donor, acceptor and π -conjugated moieties have been reported such as carbazole extended with thiazole or thiophene moieties [5].

The aggregation induced emission (AIE), first reported by Tang and co-workers in 2001 [14–19], has great importance due to its promising applications such as OLEDs [20–22], optoelectronic devices [23,24], biosensor [25–28], photo memory [29], and chemosensors [30,31]. The AIE phenomenon is mainly caused by restriction of intramolecular rotation [32] accompanied by restriction of intramolecular charge transfer [33], and twisted intramolecular charge transfer [34]. Many long conjugated molecules with twisted skeleton conformation have been established to show AIE phenomenon [18]. The restriction of the intramolecular rotation (RIR) and the non-planar configuration with π – π stacking interactions are mainly responsible for the AIE effect [35].

Much attention has also been paid to fluorescent molecular rotors (FMRs), which show solvent viscosity dependent fluorescence emission [36–39]. These rotors emit with low intensity in fluid solution (low viscosity) due to the free rotation of the C–C/C=C bonds in the excited state, which serves as an efficient overflow for the photo excited molecules [40].

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However, in a viscous environment the intramolecular rotation is restricted, and thus the emission is highly intensified [39].

In this paper, electron donating carbazole nucleus functionalized at 3 and 6 positions linked to the various acceptor residues originating from the active methylene compounds by Knoevenagel condensation to give extended styryls are reported. Photophysical properties of the synthesized compounds in several solvents have been studied.

2. Experimental :

2.1. Materials and equipment:

All the reagents and solvents were purchased from the S. D. Fine Chemicals Pvt. Ltd. and used without purification. All the solvents were used of spectroscopic grade. Melting points were recorded by open capillary on Sunder Industrial Product and are uncorrected. UV-Visible absorption measurements carried using Perkin Elmer were out spectrophotometer with 1 cm quartz cells. The excitation wavelength was taken as λ_{max} of compound. The scan range was 250 to 650 nm. Fluorescence emission measurements were recorded on Cary Eclipse fluorescence spectrophotometer (Varian, Australia) using 1 cm quartz cells. ¹H NMR and ¹³C NMR spectra were measured on an Agilent 500 MHz NMR spectrometer with tetramethylsilane as the internal standard.

2.2. Synthesis and characterization:

2.2.1. Preparation of 1,1'-(9-ethyl-9H-carbazole-3,6-diyl)bis(2-bromoethanone) 4:

N-Ethylcarbazole **2** (5.0 g, 25.6 mmol) was dissolved in dichloromethane (20 mL) and then AlCl₃ (8.5 g, 64.1 mmol) was added followed by drop wise addition of bromoacetyl bromide **3** (12.9g, 64.1 mmol, d = 2.3 g/mL) at 0 °C. The reaction mixture was stirred for 5-6 h at 0 °C and then poured over ice bath at 0-5 °C. The aqueous layer was extracted in dichloromethane. The organic layer was dried over anhydrous sodium sulphate and evaporated under vacuum. The precipitate was recrystallized from ethanol to obtained desired compound **2** as yellowish green crystal.

¹H-NMR(DMSO): 1.34 (t, 3H, CH₃), 4.5 (q, 16H), 5.01 (s, 4H), 7.81 (d, 2H, *J* = 8.6 Hz, ArH), 8.1 (d, 2H, *J* = 6.7 Hz), 9.1 (s, 2H).

FT-IR (cm⁻¹): 1663 (-C=O); 1489 (-Ar); 824 (-C-Br).

Mass: 438 (m+1).

2.2.2. Preparation of 4,4'-(5,5'-(9-ethyl-9H-carbazole-3,6-diyl)bis(thiazole-5,2diyl))dimorpholine **6**:

Bis-haloacetyl *N*-ethylcarbazole **4** (5.0 g, 0.011 mmol) was heated with substituted thiourea **5** (3.6g, 0.025 mmol) in ethanol (25 mL) at 80 $^{\circ}$ C for 4 h. The reaction mixture was poured over ice-cold water. A pale yellow solid **6** was obtained, filtered and recrystallized using ethanol.

Yield: 72%; M.P.: 220-222 °C.

¹H-NMR (DMSO): 1.3 (t, 3H), 3.7 (m, 16H), 4.4 (q, 2H), 7.2 (s, 2H), 7.5 (d, 2H, *J* = 8.4 Hz), 7.9 (d, 2H, *J* = 8.5 Hz), 8.6 (s, 2H).

FT-IR (cm⁻¹): 1531 (-C=N); 1475 (-Ar); 1112 (-C-O); 699 (C-S).

Mass: 532 (m+1).

2.2.3. Preparation of 5,5'-(9-ethyl-9H-carbazole-3,6-diyl)bis(2-morpholinothiazole-4-carbaldehyde 7:

POCl₃ (4.3 g, 28.0 mmol, d=1.64g/mL) was added drop wise at 0 °C DMF (2.3g 28.0 mmol, D = 0.9 g/mL) followed by the addition of the compound **6** (5.0 g, 9.4 mmol) in DMF at 0 °C. The reaction mixture was stirred for 30 min at room temperature and heated to 70 °C for 5-6 h. Water (100 mL) was added into the reaction mixture and neutralized by 2N (25 mL \times 3) sodium bicarbonate solution. A green solid was obtained, filtered and purified by column chromatography on silica with dichloromethane/methanol as eluent. Yield: 68%; M.P.: >300°C;

¹H-NMR (CDCl₃): 1.43 (t, 3H), 3.7 (m, 16H), 4.38 (q, 2H), 7.4 (s, 2H, *J* = 6.42 Hz), 7.8 (d, 2H, *J* = 1.72 Hz), 8.4 (s, 2H), 9.7 (s, 2H).

FT-IR (cm⁻¹): 2969 (-C-H stretch, Ald), 1737 (-C=O), 1513 (-C=N), 1445 (-Ar), 1114 (-C-O), 697 (-C-S).

Mass: 589 (M+1).

2.2.4. Preparation of extended styryls 9a-9d:

The carbaldehyde **7** (0.2 g, 0.33 mmol) was stirred with various active methylene compounds **8a-8d** (0.74 mmol) in ethanol. Then piperidine was added in catalytic amount (0.1 mL) and the reaction mixture was refluxed for 24 h. After cooling the precipitated solid was filtered and purified by column chromatography on silica with n-hexane/ethyl acetate as eluent.

2.2.4.1. 2,2'-((5,5'-(9-Ethyl-9*H*-carbazole-3,6-diyl)bis(2-morpholinothiazole-5,4-diyl))bis(methanylylidene))dimalononitrile **9a**:

Color: Orange; Yield: 66%; M.P.: >300°C.

¹H-NMR (CDCl₃): 1.52 (t, 3H), 3.8 (m, 16H), 4.5 (q, 2H), 7.57 (d, 2H, *J* = 8 Hz), 7.72 (d, 2H, *J* = 9 Hz), 7.6 (s, 2H), 8.35 (s, 2H).

¹³C NMR (CDCl₃, δ): 13.8, 30.9, 66.0, 109.5, 114.8, 115.9, 122.8, 123.2, 124.5, 128.4, 141.8,150.1, 169.3, 173.4

FT-IR (cm⁻¹): 2206 (-CN), 1533 (C=N), 1425 (-Ar), 1105 (-C-O), 1025 (-C-N).

Mass: 684 (M+1).

HRMS: Calculated for $C_{36}H_{29}N_9O_2S_2Na [M+Na]^+$ 706.1783, found 706.1717.

2.2.4.2. (2Z,2'Z)-Diethyl 3,3'-(5,5'-(9-ethyl-9*H*-carbazole-3,6-diyl)bis(2-morpholinothiazole-5,4-diyl))bis(2-methylacrylate) **9b**:

Color: Yellow; Yield: 59%; M.P.: >212°C.

¹H-NMR: 1.31 (t, 6H), 1.47 (t, 3H), 3.80 (m, 16H), 4.20 (q, 4H), 4.40 (q, 2H), 7.52 (d, 2H, J

= 8.5 Hz), 7.78 (d, 2H, *J* = 7.5 Hz), 8.39 (s, 2H). 8.45 (s, 2H).

¹³C NMR (CDCl₃, δ): 13.8, 38.0, 48.5, 61.7, 66.1, 91.2, 108.8, 115.6, 117.5, 122.8, 123.2,

124.9, 128.1, 141.5, 147.3, 165.6, 168.1, 173.0, 183.0.

FT-IR (cm⁻¹): 2203 (-CN), 1701 (-C=O), 1521 (-C=N), 1435 (-Ar), 1113 (-C-O), 1014 (-C-N).

Mass: 778 (M+1).

HRMS: Calculated for $C_{40}H_{39}N_7O_6S_2Na$ [M⁺] 778.2481, found 778.2410.

2.2.4.3. (2Z,2'Z)-3,3'-(5,5'-(9-Ethyl-9H-carbazole-3,6-diyl)bis(2-morpholinothiazole-5,4-

diyl))bis(2-(benzo[*d*]thiazol-2-yl)acrylonitrile) **9c**:

Color: Red; Yield: 48%; M.P.: >300°C.

¹H-NMR: 4.87 (q, 2H), 7.29 (t, 2H), 7.39 (t, 2H), 7.6 (d, 2H, *J* = 8.3Hz), 7.7 (d, 2H, *J* = 7.5

Hz), 7.84 (d, 2H, *J* = 6.7Hz), 7.89 (d, 2H, *J* = 7.8Hz), 8.39 (s, 2H).

¹³C NMR (CDCl₃, δ): 13.9, 30.9, 48.4, 66.0, 96.4, 109.1, 116.3, 117.7, 121.3 122.8, 123.4,

124.9, 125.5, 126.4, 128.4, 134.5, 139.6, 141.4, 153.9, 164.2, 165.6, 172.1.

FT-IR: 2201 (-CN), 1525 (-C=N), 1425 (-Ar), 1112 (-C-O), 1027 (-C-N);

Mass: 900(M+1).

HRMS: Calculated for C₄₈H₃₈N₉O₂S₄ [M⁺] 900.1265, found 900.1082.

2.2.4.4. (2Z,2'Z)-3,3'-(5,5'-(9-Ethyl-9H-carbazole-3,6-diyl)bis(2-morpholinothiazole-5,4-

diyl))bis(2-(1*H*-benzo[*d*]imidazol-2-yl)acrylonitrile) **9d**:

Color: Yellow; Yield: 51%; M.P.: Decompose 260°C.

¹H-NMR (DMSO δ): 1.39 (t, 3), 3.65 (m, 16H), 4.59 (q, 2H), 7.08 (m, 4H), 7.32 (d, 2H, *J* = 6.67 Hz), 7.42 (d, 2H, *J* = 6.65 Hz), 7.82 (m, 4H), 8.24 (s, 2H), 8.58 (s, 2H), 12.69 (s, 2H).

¹³C NMR (DMSO, δ): 14.4, 48.5, 65.8, 92.6, 110.1, 111.6, 115.6, 118.0, 118.7, 122.9, 123.5,

125.5, 128.7, 135.4, 138.2, 141.2, 143.9, 148.9, 164.4, 171.2.

FT-IR: 2207 (-CN), 1524 (-C=N), 1418 (-Ar), 1120 (-C-O), 1024 (-C-N).

Mass: 867 (M+1).

HRMS: Calculated for $C_{48}H_{40}N_{11}O_2S_2 [M+H]^+$ 866.0258, found 866.1890.

3. Results and Discussion:

3.1. Design of extended styryl:

<< Please insert Figure 1: Design of extended styryl.>>

In continuation of our previous work [12], we planned to synthesize novel highly conjugated symmetrical D- π -A (D- donor, A- acceptor) extended styryls with rigid structure exhibiting intramolecular charge transfer. Design of such extended styryls with introduction of the thiazole ring between the acceptor and donor for rigidity may lead to enhancement of photophysical properties (**Figure 1**). The thiazole ring is responsible for restriction of cistrans polarization of extended double bond, which may improve the fluorescence. The thiazole bridge also gives rigidity to double bond due to which the terminal cyano groups rotate spontaneously which leads to the Fluorescent Molecular Rotors (FMR). At the same time thiazole ring gives more planarity to the molecules that may lead to Aggregation Induced Emission (AIE) phenomenon.

3.2. Synthesis of carbaldehyde 7 and extended styryls 9a-9d:

We first synthesized the carbaldehyde **7** by multistep reactions on carbazole **1** (Scheme 1). The 9H-carbazole **1** was *N*-ethylated using diethyl sulphate, which was further bis-acetylated using bromo acetyl bromide at 3,6-position by Friedel-Craft reaction to obtain the compound **4**. The compound **4** was condensed with morpholine-substituted thiourea **5** to give the intermediate **6**. This intermediate **6** was formylated by Vilsmeier-Haack reaction to give the carbaldehyde **7**.

All the extended styryls were synthesized by simple classical Knoevenagel condensation of the carbaldehyde **7** with the active methylene compounds **8a-8d** as shown in **Scheme 2**. The carbaldehyde **7** and the various active methylene compounds **8a-8d** were refluxed in absolute ethanol containing a catalytic amount of piperidine (2 drops) to yield the desired extended styryls **9a-9d** linked through morpholine-thiazole to the carbazole core. The carbaldehyde **7** and the extended styryls **9a-9d** were purified by column

chromatography and confirmed by FT-IR, mass spectrometry, ¹H-NMR spectroscopy.

<< Please insert Reaction Scheme 1: Synthesis of 5,5'-(9-ethyl-9H-carbazole-3,6-

diyl)bis(2-morpholinothiazole-4-carbaldehyde 7 >>

<< Please insert Reaction Scheme 2: Synthesis of extended styryls (9a-9d) >>

3.3. Effect of solvent polarity on photophysical properties of carbaldehyde 7 and extended styryls **9a-9d**:

All the compounds show fluorescence in various solvents under irradiation of UV light except the carbaldehyde **7**. The carbaldehyde **7** has less solubility in organic solvents and hence fluoresces only in highly polar aprotic solvents, DMF and DMSO (**Figure 2**). The carbaldehyde **7** showed slight red shift in the absorption as well as in the emission from DMF to DMSO (**Table 1**). In the case of DMF, the carbaldehyde **7** showed a triple absorption but in DMSO it showed single absorption. A study of the photophysical properties of the carbaldehyde **7** in the different mixtures of DMSO and DMF has also been carried out to understand the effect of change in solvent polarity. There was no extreme change observed in the absorption and emission values at various compositions of solvent mixtures (**Table S1**).

<< Please insert Figure 2: Effect of solvent polarity on photophysical properties of

carbaldehyde 7.>>

<< Please insert Table 1: Effect of solvent polarity on photophysical properties of

carbaldehyde 7. >>

To evaluate the effect of the solvent polarity on the photophysical properties of the extended styryls **9a-9d**, the absorption and emission properties of all the extended styryls were measured in different solvents of differing polarities. All the analyses were carried out at room temperature and concentrations of solutions were 1×10^{-6} M. The photophysical data of the extended styryls **9a-9d** were given in (**Figure 3a-3d**), (**Tables 2 and S2-S5**).

All the extended styryls **9a-9d** (A- π -D- π -A) were having *N*-ethylcarbazole unit as the electron donor and cyano group as the electron acceptor. Due to the presence of electron accepting group, these extended styryls show intramolecular charge transfer. Thus photophysical properties of these extended styryls were highly influenced by the solvent polarity against the parent carbaldehyde **7**.

<< Please insert Figure 3a: Effect of solvent polarity on photophysical properties of extended styryl 9a. >>

<< Please insert Figure 3b: Effect of solvent polarity on photophysical properties of extended styryl 9b. >>

<< Please insert Figure 3c: Effect of solvent polarity on photophysical properties of extended styryl 9c. >>

<< Please insert Figure 3d: Effect of solvent polarity on photophysical properties of extended styryl 9d. >>

<< Please insert Table 2: Effect of solvent polarity on photophysical properties of

extended styryl 9a. >>

All the extended styryls **9a-9d** showed a broad absorption band in all the solvents. The short-wavelength absorption at around 380 nm can be attributed to the π - π * transitions from the carbazole core to the morpholine-thiazole moiety. This large absorption band in the visible region was corresponding to ICT transition from the central electron donating N-ethylcarbazole unit to both the electron accepting cyano groups at the terminal via the morpholine-thiazole moiety. The absorption maxima of all the extended styryls **9a-9d** varied in different solvents but independent of solvent polarity. The absorption band observed was from 443 nm to 452 nm for **9a**, from 433 nm to 446 nm for **9b**. **9a** showed little bathochromic shift than the **9b** as **9a** having malanonitrile group which is more electron withdrawing as compared to ethylcyanoacetate in **9b**. Similar trend was observed in the case of **9c** and **9d**; the absorption band observed was from 471 nm to 482 nm for **9c**,

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from 450 nm to 463 nm for **9d**. **9c** showed bathochromic shift as compared to the **9d** due to the vacant d-orbital of benzothiazole sulfur atom, which exhibits strong electron withdrawing effect than the benzimidazole unit. The absorbance values of extended styryls **9a-9d** were higher in chlorinated solvents.

The fluorescence emission wavelength of the synthesized extended styryls **9a-9d** is independent on solvent polarity. The dye **9b** observed a red shift in chlorinated solvents like DCM and chloroform as compared to the other solvents. The quantum yield of all the extended styryls **9a-9d** also varied in different solvents, but it was independent of the solvent polarity. The **9a** showed the highest quantum yield in 1,4-dioxane and lowered in toluene. The **9b** and **9c** showed the highest quantum yield in DMSO and lower in acetone and acetonitrile respectively. While **9d** observed the highest quantum yield in DCM and lowered in DMF.

The main curiosity of this work is to enhance the photophysical properties of previously reported extended styryls [12]. Cis-trans polarization may possible across the double bond of previously synthesized molecules as shown in **Figure 4a**. Introduction of the thiazole ring gives more stability as well as restricts cis-trans polarization in double bond. Also introduction of morpholine ring at terminal position plays an important role to enhance color and stability of compounds [41] but failed to give an enhancement in the photophysical properties (**Figure 4b**). Selection of morpholine moiety is due to its donating ability intermediate between dimethylamino and diethylamino groups.

The morpholine moiety presented at the thiazole ring has the donating ability, which may disturb the main conjugation between the donor carbazole to the acceptor cyano groups. Due to the two donors present in the system, there is competition between two types of conjugation, conjugation from donor carbazole to acceptor cyano and other from morpholine nitrogen to acceptor cyano moiety (**Figure 4b**).

<< Please insert Figure 4a: Possible cis-trans polarization between -C=C- of previously

reported extended styryl. >>

<< Please insert Figure 4b: Restricted cis-trans polarization due to presence of thiazole

ring. >>

3.3.1. Solvent polarity function plots:

Effects of solvent polarity on the synthesized molecules were also studied with the help of Lippert-Mataga plots [42]. Lippert-Mataga equation (eq. 1) is used to estimate change in dipole moment on photoexcitation as a function of the solvent polarity. Lippert-Mataga plot generally shows specific solvent effect such as dipole moment changes of the dyes with photoexcitation and this clarifies that the solvent effect such as hydrogen bonding may lead to quench the fluorescence [43,44].

$$\Delta \nu = \frac{2\Delta f}{4\pi\varepsilon_0 \hbar c a^3} (\mu_{e-}\mu_g)^2 + b$$

(1)

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

Where, $\Delta v = v_{abs} - v_{em}$ stands for Stokes shift,

 v_{abs} and v_{em} are 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.

Lippert-Mataga plots were constructed for all the extended styryls 9a-9d, which concluded that there was no specific solvent effect exists (Figure S1). Slope of 9c was much smaller than other extended styryls, which concluded that 9c has smaller dipole moment changes on photoexcitation.

The Wellers plots [45] can be used to study ICT. These plots of emission wave numbers of emission versus the respective polarity functions were screened for the linearity (**figure S2**). The polar solvents were used to plot these functions and linear plots were obtained which concluded that these extended styryls **9a-9d** observed good charge transfers within the molecules at the excited state.

3.3.2. 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 ground to excited state. Oscillator strength (*f*) can be calculated using the following Equation 2 [46]. Where ε is the extinction coefficient (Lmol⁻¹cm⁻¹), and ν represents the wavenumber (cm⁻¹). From this equation we have calculated oscillator strength for extended styryls and tabulated in **Table 3**.

$$f = \int 4.42 \times 10^{-9} \int \varepsilon(\nu) \, d\nu \tag{2}$$

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 equation 3 [46]. The transition dipole moment increased with increase in the oscillator strength.

$$\mu_a^2 = \frac{f}{2.13 \times 10^{-30} \times \nu}$$
3

Where,

 $\mu_{\rm a}$ is transition dipole moment (D),

f is oscillator strength,

 ν is wavenumber (cm⁻¹).

The extended styryls **9a** (4.6-5.9 D), **9b** (6.5-9.8 D), **9c** (7.3-8.2 D) and **9d** (6.2-7.4) have significant transition dipole moment. Observed results were concluded that the conjugation of 3- and 6- position of carbazole gave better charge transfer through the carbazole to cyano groups.

<< Please insert Table 3: Oscillator strength (*f*) and Transition dipole moments (TDM)

obtained from absorption properties of extended styryls in various solvents.>>

3.3.3. Solid state fluorescence:

The carbaldehyde **7** and all the extended styryls **9a-9d** showed solid state fluorescence under long UV (365 nm). The carbaldehyde **7** was excited at 340 nm while the extended styryls **9a-9d** were excited at 400 nm keeping all the parameters constant such as source of light, slit width, sample holder. The carbaldehyde **7** showed emission maxima at 486 nm while the extended styryls **9a-9d** showed emission maxima at 540 nm, 541 nm, 612 nm, 539 nm respectively (**Figure 5**). All the extended styryls **9a-9d** observed a bathochromic shift as compared to the carbaldehyde **7**. The extended styryl **9c** showed solid state fluorescence in NIR region with the highest red shift.

<< Please insert Figure 5: Solid state fluorescence spectra for carbaldehyde 7 and

extended styryls 9a-9d.>>

Solid state fluorescence emissions of all the synthesized styryls except **9d** were observed red shift as compared to the corresponding emission in solutions. This may be due to molecular staking in the solid state. This red shift was also depending upon presence of neighboring polar substituents. The extent of red shift in carbaldehyde **7** (4 nm/170.75cm⁻¹) was smaller compared to extended styryls **9a-9c** since these styryls contained more polar groups such as malanonitrile, ethylcyanoacetate and benzthiazolylacetonitrile respectively. The red shift was large in the case of the extended styryls **9a** (28 nm/1012.73 cm⁻¹), **9b** (28 nm/1008.83cm⁻¹), **9c** (49 nm/1422.12 cm⁻¹). The extended styryl **9c** showed the highest red

shift at 612 nm (16339.86 cm⁻¹) may due to the presence of empty d-orbital of sulphur of benzothiazole ring. These groups may responsible for different types of aggregations. Carbaldehyde **7** and extended styryls **9a-9c** were undergo J-aggregation in solid state resulting in red shift whereas **9d** was formed H-aggregates with blue shift.

3.4. Aggregation-induced emission (AIE):

The study of AIE of the extended styryls **9a-9d** has been carried out in the mixture of DMF and water. Different amount of water has been added to the pure solution of DMF to get 10-90% volume of water-DMF solution. The absorption and emission spectra have been recorded immediately after the sample preparation (**Figure S3-S6**).

When water was added, absorption maxima of synthesized extended styryls **9a-9d** remained unchanged but a dramatic change was observed in the emission maxima. These extended styryls showed almost similar absorption maxima in different combination of water-DMF solutions at around 448 nm, 443 nm, 474 nm and 479 nm respectively.

In 40-50% of water-DMF solution, emission wavelength of **9a** was observed a red shift from 606 nm to 612 nm with enhanced fluorescence due to the presence of two cyano groups, which act as strong electron withdrawing groups. In the case of **9b** anomalous results were obtained. In 40-50% water-DMF solution, emission of **9b** showed hypsochromic shift from 567 nm to 547 nm. This hypsochromic shift may due to the presence of the ester group, which acts as a weak withdrawing group. A large red shift was observed in the case of **9c** in 30-40% water-DMF solution from 560 nm to 605 nm. Similarly **9d** showed a red shift in 50-60% water-DMF solution from 580 nm to 602 nm. The Stokes shift also increases with increasing water content. The shift observed in emission peak of these extended styryls **9a-9d** with increasing water content may due to the strong electronic interaction through the π -stacking in aggregate that present at carbazole and thiazole unit. All these synthesized extended styryls **9a-9d** showed aggregation induced emission with enhanced fluorescence intensity. The quantum efficiency of extended styryls

9a-9d increases with increasing water fraction, indicating that the aggregated state has higher quantum yield as compared to the non-aggregated state. The aggregates formed with 40 to 50% of water fraction showed the highest quantum yield (**Figure S10**).

The change in dipole moment at excited state and ground state can be explained by using Bilot-Kawski function (eq. 4) that give the ratio of ground state and excited state dipole moment (**Figure S7**). Ratio of excited state and ground state dipole moment drastically increases in **9a** (19 fold) and **9d** (32 fold). These results concluded that dipole moment increases in excited state and unaffected in ground state.

$$\vartheta_{a-}\vartheta_f = \frac{(\mu_e - \mu_g)^2}{\pi \varepsilon h c a^3} \Delta f_{BK} + \text{ constant}$$

$$\Delta f_{BK} = \frac{2n^2 + 1}{n^2 + 2} \left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \right)$$

3.5. Fluorescent Molecular Rotors (FMR):

FMR needs good intramolecular charge transfer (ICT) within the molecule, which also requires planarity with rigidity. Keeping this concept in mind, previously reported extended styryls [14] has been modified by introduction of morpholine-thiazole moiety to avoid cis-trans polarization which responsible for fluorescence quenching.

The carbaldehyde **7** showed absorption around 330 nm and extended styryl **9a-9d** having ICT showed absorption in the range of 450-480 nm. This proves that molecules showed good charge transfer from carbazole to acceptor cyano moiety. According to the concept of FMR, polarity dependent emission molecules are FMR inactive. Emissions of synthesized extended styryls **9a-9d** are independent on solvent polarity, which can be used as FMR.

Effects of viscosity on emission properties of synthesized molecules **9a-9d** have also been studied to check compatibility as FMR. These synthesized molecules **9a-9d** have less solubility in the mixture of ethylene glycol and glycerol. Thus, these synthesized molecules

9a-9d have been solubilized in highly polar aprotic solvent DMF and increased their viscosity using glycerol (**Figure S8**). Similar study has been carried out in non-polar solvent DCM and increased their polarity with PEG-400 (**Figure S9**). The pattern of increase in emission intensity was the same in both the studies. This result proved that the change in emission intensity was due to the change in viscosity and not because of polarity. Thus synthesized molecules **9a-9d** are good candidates for FMR.

 $\log I = C + x \log \eta$

The emission intensity of FMR and viscosity of the solvent was described by using Förster– Hoffmann equation (5), in which η is viscosity of the solvents, *I* is the emission intensity of the rotors, *C* is a constant on temperature and *x* is the viscosity sensitivity of the rotors. The higher the *x* value proves that emission intensities are more sensitive towards the viscosity change. The *x* values of the rotors **9a-9d** in DMF-Glycerol system were 0.35, 0.35, 0.37 and 0.54 respectively, while *x* values of the rotors **9a-9d** in DCM: PEG-400 system was 0.42, 0.52, 0.67, and 0.64 respectively. Rotors **9c** and **9d** in DCM: PEG-400 system showed better *x* value as compared to the historical rotor 4-(dicyanovinyl)julolidine (*x* values is 0.6) [39]. The higher values of *x* in DCM: PEG-400 may due to the effect of solvent polarity on the transition from the local excited state to the intramolecular charge transfer (ICT) state.

4. Conclusion:

In this paper, we have extended our previous work and succeeded to synthesize four extended styryls containing carbazole core as a donor and electron withdrawing cyano moiety linked through π bridge of morpholine-thiazole moiety with intramolecular charge transfer. All synthesized extended styryls were showed solid state fluorescence. The aim was to observe bathochromic shift in photophysical properties as compared to previously reported extended styryls by introduction of more conjugation and rigidity via thiazole ring. But anomalous results were obtained. Morpholine ring presented on thiazole moiety may disturb the conjugation. Photophysical properties of all synthesized extended styryls were in

good agreement and independent on solvent polarity. Morpholine-thiazole moiety presented in extended styryls were provided rigidity which responsible to act as FMRs. All these extended styryls were also showed aggregation induced emission (AIE) with enhanced fluorescence intensity.

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List of figures captions:

Figure 1: Design of extended styryl.

Reaction Scheme 1: Synthesis of 5,5'-(9-ethyl-9H-carbazole-3,6-diyl)bis(2-morpholinothiazole-4-carbaldehyde **7.**

Reaction Scheme 2: Synthesis of extended styryls (9a-9d).

Figure 2: Effect of solvent polarity on photophysical properties of carbaldehyde 7.

Figure 3a: Effect of solvent polarity on photophysical properties of extended styryl 9a.

Figure 3b: Effect of solvent polarity on photophysical properties of extended styryl 9b.

Figure 3c: Effect of solvent polarity on photophysical properties of extended styryl 9c.

Figure 3d: Effect of solvent polarity on photophysical properties of extended styryl 9d.

Figure 4a: Possible cis-trans polarization between -C=C- of previously reported extended styryl.

Figure 4b: Restricted cis-trans polarization due to presence of thiazole ring.

Figure 5: Solid state fluorescence spectra for carbaldehyde 7 and extended styryls 9a-9d.

7 nm FWHM cm ⁻¹ ϵ (X 10 ⁴) nm cm (I mol ⁻¹ cm ⁻¹)	n ⁻¹ φ nm cm	-1
(Linoi cin)		-
307 63 32573.2 4.2	41 6 0 10 1 66 114	22
DMF 4/3 2114 338 44 29585.7 3.8	+1.6 0.10 166 114	32
DMSO 340 78 29411.7 3.7 482 2074	46.8 0.12 142 866	55

Table 1: Effect of solvent polarity on photophysical properties of carbaldehyde 7.

Table 2: Effect of solvent polarity on photophysical properties of extended styryl 9a.

		Abs	sorption (λ_a	bs)	E	mission (λ _e	Stokes shift		
9a	nm	FWHM	cm ⁻¹	$\epsilon (X 10^4)$ (Lmol ⁻¹ cm ⁻¹)	nm	cm ⁻¹	ф	nm	cm ⁻¹
Toluene	451	73	22172.9	2.3	508	19685.0	0.001	57	2487.9
Dioxane	445	69	22371.3	3.1	515	19417.4	0.1	68	2953.9
DCM	447	71	22421.5	2.2	512	19531.2	0.009	66	2890.3
CHCl ₃	446	71	22573.3	1.5	508	19685.0	0.004	65	2888.3
EtOAc	443	68	22471.9	2.2	507	19723.8	0.005	62	2748.1
Acetone	445	76	22471.9	2.1	522	19157.0	0.003	77	3314.9
ACN	445	80	22471.9	2.4	516	19379.8	0.009	71	3092.1
DMF	448	88	22321.4	0.8	524	19083.9	0.004	76	3237.5
DMSO	451	88	22123.8	1.8	522	19157.0	0.047	70	2966.8

	9a		9	b	9	с	9c	
	f	TDM	f	TDM	f	TDM	f	TDM
Toluene	0.368	5.95	0.438	6.41	0.574	7.63	0.390	6.20
Dioxane	0.324	5.54	0.933	9.35	0.534	7.35	0.460	6.70
DCM	0.472	6.71	0.970	9.55	0.651	8.10	0.565	7.45
CHCl3	0.338	5.67	1.001	9.61	0.579	7.62	0.404	6.25
EA	0.225	4.61	0.454	6.51	0.563	7.53	0.411	6.34
Acetone	0.334	5.62	0.459	6.53	0.624	7.92	0.429	6.44
ACN	0.377	5.97	0.987	9.59	0.530	7.28	0.380	6.03
DMF	0.142	3.68	1.022	9.82	0.616	7.93	0.413	6.33
DMSO	0.291	5.29	0.427	6.37	0.663	8.24	0.451	6.65

 Table 3: Oscillator strength (f) and Transition dipole moments (TDM) obtained from absorption properties of extended styryls in various solvents.

0.427

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Figure 1: Design of extended styryl.



Reaction Scheme 1: Synthesis of 5,5'-(9-ethyl-9H-carbazole-3,6-diyl)bis(2-morpholinothiazole-

4-carbaldehyde 7.





Reaction Scheme 2: Synthesis of extended styryls (9a-9d).

Figure 2: Effect of solvent polarity on photophysical properties of carbaldehyde 7.





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Figure 3b: Effect of solvent polarity on photophysical properties of extended styryl 9b.









Figure 3d: Effect of solvent polarity on photophysical properties of extended styryl 9d.

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Figure 4b: Restricted cis-trans polarization due to presence of thiazole ring.





Figure 5: Solid state fluorescence spectra for carbaldehyde 7 and extended styryls 9a-9d.

Highlights

- > Synthesis and characterization of carbazole based extended styryl with morpholine thiazole as π -conjugated bridge.
- Photophysical properties of extended styryls have been studied extensively by using spectroscopic methods.
- Synthesized extended styryls showed aggregation induced emission and viscosity sensitive emission.
- The aggregation induced emission and viscosity sensitive emission were carried out using spectroscopic methods.

Supporting information

Figure

Figure S1: Lippert-Mataga plots for extended styryls 9a-9d.

Figure S2: Weller plots for extended styryls 9a-9d.

Figure S3: Aggregation induced emission of extended styryl 9a.

Figure S4: Aggregation induced emission of extended styryl 9b.

Figure S5: Aggregation induced emission of extended styryl dye 9c.

Figure S6: Aggregation induced emission of extended styryl dye 9d.

Figure S7: Bilot-Kawski plots for extended styryls 9a-9d.

Figure S8: Fluroscent Molecular Rotor of styryl 9a in DMF: Glycerol system.

Figure S9: Fluroscent Molecular Rotor of styryl 9a in DCM: PEG-400 system.

Figure S10: Quantum yield extended styryl 9a-9d in aggregation state.

Table

Table S1: Effect of binary mixtures on photophysical properties of carbaldehyde 7.
Table S2: Effect of solvent polarity on photophysical properties of extended styryl 9b.
Table S3: Effect of solvent polarity on photophysical properties of extended styryl 9c.
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Figure S2: Weller plots for extended styryls 9a-9d.



Figure S3: Aggregation induced emission of extended styryl 9a.





Figure S4: Aggregation induced emission of extended styryl 9b.





Figure S6: Aggregation induced emission of extended styryl dye 9d.



Figure S7: Bilot-Kawski plots for extended styryls 9a-9d.



Figure S8: Fluroscent Molecular Rotor of styryl 9a in DMF: Glycerol system.



Figure S9: Fluroscent Molecular Rotor of styryl 9a in DCM: PEG-400 system.



Figure S10: Quantum yield extended styryl 9a-9d in aggregation state.



Tables:

	DMF - DMSO	Polarity	λ_{abs} in nm	λ_{em} in nm
	% composition	function	$(\varepsilon \times 10^4 \text{ in } \text{Lmol}^{-1} \text{ cm}^{-1})$	(Intensity in a.u.)
	100-0	0.47983871	307 (4.8)	464 (109.0)
7	80-20	0.480867347	307 (5.1)	467 (135.9)
	60-40	0.481796117	307 (5.1)	469 (122.0)
	40-60	0.482638889	308 (5.0)	467 (100)
	20-80	0.48340708	308 (5.1)	467 (110.2)
	0-100	0.484110169	331 (4.2)	471 (87.0)

Table S1: Effect of binary mixtures on photophysical properties of carbaldehyde 7.

		Ab	sorption (λ_a	bs)	Emission (λ_{emi})			Stokes shift	
9b	nm	FWHM	cm ⁻¹	ε (X 10 ⁴) (Lmol ⁻¹ cm ⁻¹)	nm	cm ⁻¹	φ	nm	cm ⁻¹
Toluene	440	72	22727.2	2.9	473	21141.6	0.047	33	1585.6
Dioxane	440	106	22727.2	6.5	515	19417.4	0.05	75	3309.7
DCM	441	114	22675.7	6.7	513	19493.1	0.053	72	3182.5
CHCl ₃	433	111	23094.6	3.2	476	21008.4	0.033	43	2086.2
EtOAc	438	118	22831.0	6.5	473	21141.6	0.048	35	1689.4
Acetone	436	123	22935.7	3.9	481	20790.0	0.025	45	2145.7
ACN	437	124	22883.2	6.5	483	20703.9	0.043	46	2179.3
DMF	443	116	22573.3	6.7	481	20790.0	0.049	38	1783.3
DMSO	446	113	22421.5	2.8	481	20746.8	0.059	35	1631.5

 Table S2: Effect of solvent polarity on photophysical properties of extended styryl 9b.

CERT

		Ab	sorption (λ_a	bs)	E	Emission (λ_{emi})			Stokes shift	
9c	nm	FWHM	cm ⁻¹	$\epsilon (X 10^4)$ (Lmol ⁻¹ cm ⁻¹)	nm	cm ⁻¹	φ	nm	cm ⁻¹	
Toluene	476	86	21008.4	4.7	561	17825.3	0.048	85	3183.0	
Dioxane	475	86	21052.6	5.4	563	17761.9	0.027	88	3290.6	
DCM	474	88	21097.0	4.7	563	17761.9	0.034	89	3335.0	
CHCl ₃	471	91	21231.4	4.8	557	17953.3	0.033	86	3278.1	
EtOAc	473	88	21141.6	4.6	556	17985.6	0.044	83	3156.0	
Acetone	473	91	21141.6	5.1	565	17699.1	0.034	92	3442.5	
ACN	471	90	21231.4	4.4	573	17452.0	0.022	102	3779.4	
DMF	478	92	20876.8	4.7	567	17636.6	0.050	88	3240.1	
DMSO	482	91	20746.8	5.0	567	17636.6	0.096	85	3110.2	

 Table S3: Effect of solvent polarity on photophysical properties of extended styryl 9c.

9d		Ab	sorption (λ_a	bs)	E	Emission (λ_e	Stokes shift		
	nm	FWHM	cm ⁻¹	$\epsilon (X 10^4)$ (Lmol ⁻¹ cm ⁻¹)	nm	cm ⁻¹	φ	nm	cm ⁻¹
Toluene	463	92	21598.2	3.7	550	18181.8	0.020	87	3416.4
Dioxane	458	85	21834.0	5.6	556	17985.6	0.040	98	3848.4
DCM	462	92	21645.0	3.9	562	17793.5	0.070	100	3851.5
CHCl ₃	454	91	22026.4	4.7	552	18115.9	0.047	98	3910.5
EtOAc	459	86	21786.4	4.9	551	18148.8	0.039	92	3637.6
Acetone	453	85	22075.0	5.0	548	18248.1	0.038	95	3826.9
ACN	450	89	22222.2	4.4	554	18050.5	0.037	104	4171.7
DMF	456	85	21929.8	4.6	553	18083.1	0.021	97	3846.7
DMSO	460	88	21739.1	4.6	554	18050.5	0.028	94	3688.6

Table S4: Effect of solvent polarity on photophysical properties of extended styryl 9d.

Spectral Data:

Mass spectrum of 4:



¹H NMR spectrum of 4:



Mass spectrum of 6:



Mass spectrum of 7:



HRMS spectrum of 9a



¹H NMR s spectrum of 9a



¹³C NMR spectrum of 9a

