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Synthesis and characterization of triazine linked carbazole derivatives green-light-emitting molecules

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Abstract

Novel 2,4,6-triphenyl-1,3,5-triazine linked carbazole through olefin double bond star shape molecules with different linear and branched chain were synthesized and systematically investigated by aggregation induced emission (AIE) studies and electrochemical properties. These molecules are shows broad absorbance range with good intramolecular charge transfer character (ICT). These derivatives are exhibit positive solvatochromism effect and higher Stokes shift values in the range of 6819-1119 cm⁻¹. These derivatives are displayed aggregation-induced emission (AIE) property in THF-water mixture (TRZ-hexyl at 10/90%, TRZ-octyl at 30/70%, TRZ-branched at 50/50%). The electrochemical studies show that band gap of TRZ-hexyl, TRZ-octyl, and TRZ-branched at 1.87, 1.73 eV, and 1.86 eV respectively. All these derivatives are exhibit deep-lying highest occupied molecular orbital (HOMO) energy levels at ~ -5.04 eV and LUMO energy levels at ~ -3.20 eV. The proper AIE, HOMO, and LUMO energy level pave the way for their potential use in OLEDs and solar cell applications.

Key words: Triazine; Carbazole; Aggregation-induced emission (AIE); D-A type molecules; Fluorescence emission; OLED.

1. INTRODUCTION

In the past decades, organic π -conjugate materials are received more attention in potential applications of organic light-emitting diodes (OLEDs) and then organic solar cells because of their low cost, flexibility and easy to fabrication on the devices [1-5]. Presently, research groups were focused on three-arm based N-donor molecules due to their excellent electron donating strength, good thermal stability, photophysical properties and high fluorescence quantum yield [6-8]. The bipolar materials were used as an emitting layer for achieve high-performance full colour organic OLEDs device [9,10]. Further, bipolar materials can deliver high balanced carrier transportation ability and support to enhance the chance for carrier recombination. To improve the light emitting nature towards design Donor-Acceptor (D-A) type molecules, it's facilitated both electron and hole transporting property in the same molecules [11-13]. Triazine is one of the significant core centre to established wide range of optical and electrical applications, such as biomolecular labels, photosensitizers, sensors, solar cell, and OLEDs [14-17]. These molecules have higher electron affinity and symmetrical structure. Triazine molecules could be triply

functionalized with various electron-donating and electron-acceptors to given star-shaped architecture. Triazines are three-arm electron-deficient moiety, attached in a centre of electron rich moieties are certain attention since they are extended the π -conjugation from the heterocyclic triazine-core to the aromatic donor-substituents [18]. This π -conjugation of triazine centre widely employed different electron-donors such as carbazole, fluorene, diphenyl amine, and triphenyl amine moieties [19,20]. Among these, carbazole is more attractive electron-donors because of it could be easy way functionalized with various functional groups. In the presence of nitrogen moiety provides fully aromatic, high thermal and environmental stability [21-24].

When compared with linear and dendrite molecules, hyper-branched polymers are exhibit advantage for their process-ability into large-scale devices and simple synthetic access [25-27]. These hyper-branched molecules were compared with linear molecules, which exhibit unique advantages for their easy synthetic and large-scale device processability. Further, those hyperbranched molecules are having excellent properties, such as intramolecular charge transfer (ICT) (between donor and acceptor moiety), low viscosity and high solubility. These are key properties for the organic solar cells, two-photon absorption materials and organic light-emitting diodes applications [28,29]. The hyper-branched molecules have been proven the structure correlation effect which can help two-photon absorption due to their push-pull properties and co-planarity of the molecules. To improve the solution processability of the organic molecules, it's one of the important strategies attachments of (linear or branched) alkyl substituents on the molecule backbone [30]. Further, these substituent's affect molecular packing and effective charge transport properties. To compare linear with branched side chain contain molecule shown more π - π stacking, lamellar spacing and self-assembling properties in thin-film devices. Matulaitis and co-workers reported 2,4,6-triphenyl-1,3,5-triazine linked carbazole with different nitrogen position molecules used as the light emitting materials for OLEDs applications [31]. Kukhta et al., reported 2,4,6-triphenyl-1,3,5-triazine linked fluorene molecules showed high thermal stability with good hole transporting properties [21]. Reghu et al., reported triazine linked with different donor's molecules were showed good fluorescence quantum yield [32]. Recently, we are reported triazine linked carbazole based macromolecules were showed AIE property with good fluorescence quantum yield [33].

In this work, we have reported carbazole and triazine containing star-shaped molecules with different side chains such as hexyl, octyl, and 2-ethyl hexyl. In the presences of the side chain on the AIE properties are great interest. We have investigated the results of optical properties, electrochemical properties, and AIE effect.



Scheme 1. Synthesis of triazine derivatives



Fig. 1. Structure of triazine derivatives

2. Experiments

2.1. Materials

p-Bromomethylbenzonitrile, trifluoromethanesulfonic acid, triethylphosphite, 18-crown-6, carbazole, 1-bromohexane, 2-ethyl hexyl bromide and 1-bromooctane were purchased from Sigma-Aldrich. Phosphoryl chloride (POCl₃), dry dimethylformamide (DMF), dichloromethane and chloroform solvent were obtained from SD Fine-Chem Limited. Potassium tert-butoxide (t-BuOK), sodium hydroxide (NaOH) and potassium hydroxide (KOH) were purchased from AVRA Company. Other solvents were purchased commercially as AR-grade quality and then used without further purification. Column chromatography was performed using silica gel Merck (60-120 mesh).

2.2. Instrumentation

IR Spectrum was recorded on SHIMADZU Infrared spectrophotometer (400-4000 cm⁻¹) with resolution IV. ¹H and ¹³C-NMR spectrum was carried using a Bruker 400 MHz spectrometer in CDCl₃ using tetramethylsilane as an internal standard. The UV-visible absorption spectrum was recorded with a JASCO V-670 spectrophotometer at room temperature. Fluorescence spectrum was recorded using Hitachi F-7000FL spectrometer. The cyclic voltammetry (CV) studies were carried out with (CH Instruments) at a scan rate of 100 mV/s. The surface morphology of the sample was investigated by scanning electron microscopy (Carl Zeiss EVO-185H, UK) equipped with an energy-dispersive X-ray spectrometer (EDX).

2.2.1. Synthesis of 2,4,6-tris [4-(diethylphosphonomethyl) phenyl]-1,3,5-triazine (TRZ)

The compound was synthesized according to our previous reported procedure method [34]. (2.45 g, yield: 92%). ¹H-NMR (CDCl₃, 400 MHz, ppm): 8.71-8.69 (d, 6H, J = 7.6 Hz), 7.51-7.49 (d, 6H, J = 7.2 Hz), 4.06-4.02 (t, 12H, J = 7.2 Hz), 3.30-3.25 (d, 6H, J = 22 Hz), 1.28-1.24 (t, 18H, J = 6.8 Hz). ¹³C-NMR: 171.51, 136.83, 136.74, 135.13, 135.09, 130.37, 130.30, 129.35, 62.58, 62.52, 34.97, 33.60, 16.63, 16.57.

2.2.2. Synthesis of 9-hexyl-9H-carbazole (R1)

Carbazole (3.30 g, 20 mmol), potassium hydroxide (2.96 g, 52.8 mmol) dissolved in DMF (40 mL) and then 1-bromohexane (3.30 g, 20 mmol) was added in dropwise. The reaction mixture was stirred at room temperature for 48 h. The reaction mixture was poured into water and extracted with chloroform and dried over anhydrous magnesium sulphate. The solvent was removed by rotary evaporator, the residue was re-crystallized in n-hexane to afford compound Ia (4.8 g, yield: 92%) as a white solid. ¹H-NMR (400 MHz, CDCl₃, ppm): 8.11–8.09 (d, 2H, J = 2.4 Hz), 7.46–7.42 (m, 2H), 7.42–7.39 (d, 2H, J = 8.4 Hz), 7.26–7.20 (m, 2H), 4.31–4.28 (t, 2H, J = 7.2 Hz), 1.88–1.85 (m, 2H), 1.41–1.37 (m, 6H), 0.86 (t, 3H).

2.2.3. Synthesis of 9-(2-ethylhexyl)-9H-carbazole (R3)

To the mixture of carbazole (5 g, 30 mmol) and sodium hydroxide (7.2 g, 185 mmol) were dissolved in 100 mL of DMSO and the reaction mixture was stirred at room temperature for 1 h. The 2-ethylhexyl bromide (6.9 g, 36 mmol) was added in a drop wise to the reaction mixture at room temperature for a period of 30 min. The resulting reaction mixture was further stirred for 24 h. After cool to room temperature, the mixture was poured into water and the organic layer was extracted with dichloromethane and dried over anhydrous magnesium sulphate. The crude product was further purified by column chromatography using hexane: ethyl acetate (9:1) as the eluent. Compound Ib (6.9 g, yield: 82 %, colourless oil). ¹H-NMR (400 MHz, CDCl₃, ppm): 8.23 (d, 2H), 7.57 (t, 2H), 7.51 (d, 2H), 7.36-7.33 (t, 2H), 4.25-4.22 (m, 2H), 2.33-2.15(m, 1H), 1.41-1.37 (m, 8H), 1.04 (m, 6H).

2.2.4. Synthesis of 9-octyl-9H-carbazole (R2)

The compound R2 was synthesized by followed similar procedure for compound R3. Yellow liquid (yield: 85%). ¹H-NMR (CDCl₃, ppm): 8.18 (d, 2H, J = 7.60 Hz), 7.54–7.50 (m, 2H), 7.46 (d, 2H, J = 8.00 Hz), 7.31–7.27 (m, 2H), 4.34–4.31 (t, 2H, J = 7.20 Hz), 1.95–1.87 (m, 2H), 1.36–1.33 (m, 10H), 0.92 (t, 3H, J = 6.40 Hz).

2.2.5. Synthesis of 9-hexyl-9H-carbazole-3-carbaldehyde (Cz-hexyl)

POCl₃ (25 mL, 0.27 mole) was added drop wise to DMF (35 mL, 0.45 mole) for 30 min at 0 °C. Compound R1 (4.00 g, 16 mmol) or R2 or R3 in dichloromethane (20 mL) was added to the above solution at room temperature after that increase the temperature to 90 °C and stirred for 4 h. The reaction mixture was poured into ice-cubes and neutralized with NaOH solution. The solution was extracted three times with ethyl acetate and dried over anhydrous magnesium sulphate. The excess of dichloromethane was removed by vacuum distillation. The crude product was purified by column chromatography (eluent: hexane/ethyl acetate- 9:1) given the product as white colour solid compound (9-hexyl-9H-carbazole-3-carbaldehyde (Cz-hexyl), yield: 68%). ¹H-NMR (CDCl₃, ppm): 10.07 (s, 1H), 8.57 (s, 1H), 8.14–8.12 (d, 1H, J = 8 Hz), 8.00–7.98 (dd, 1H, J = 6.8 Hz), 7.55–7.51 (t, 1H, J = 8 Hz), 7.44–7.42 (d, 2H, J = 8.4 Hz), 7.33–7.30 (t, 1H, J = 7.2 Hz), 4.30–4.26 (t, 2H, J = 7.6 Hz), 1.90–1.82 (m, 2H), 1.31–1.28 (m, 6H), 0.87 (m, 3H).

Synthesis of Cz-octyl: The compound Cz-octyl was synthesized by followed similar procedure for compound Cz-hexyl. White colour solid (yield: 68%), ¹H-NMR (CDCl₃, ppm): 10.08 (s, 1H), 8.59 (s, 1H), 8.15-8.13 (d, 1H, J = 7.6 Hz), 8.01- 7.99 (dd, 1H, J = 8.8 Hz), 7.55-7.51 (t, 1H, J = 8 Hz), 7.46-7.44 (d, 2H, J = 8 Hz), 7.34-7.30 (t, 1H, J = 7.6 Hz), 4.32-4.29 (t, 2H, J = 7.2 Hz), 1.89-1.86 (m, 2H), 1.40-1.24 (m, 10H), 0.88 (m, 3H).

Synthesis of Cz-branched: The compound Cz-branched was synthesized by followed similar procedure for compound Cz-hexyl. colourless liquid (Cz-branched, yield: 68%), ¹H-NMR (CDCl₃, ppm): 10.09 (s, 1H), 8.60 (s, 1H), 8.16-8.14 (d, 1H, J = 8 Hz), 8.01- 7.98 (dd, 1H, J = 8.4 Hz), 7.54-7.50 (t, 1H, J = 8 Hz), 7.46-7.43 (m, 2H), 7.34-7.30 (t, 1H, J = 7.6 Hz), 4.21-4.19 (d, 2H, J = 7.6 Hz), 2.09-2.05 (m, 1H), 1.38-1.26 (m, 8H), 0.88 (m, 6H).

2.2.6. Synthesis of TRZ-hexyl, TRZ-octyl, TRZ-branched Common procedure:

To mixture of TRZ and Carbazole monomer in dry THF taken in 100 mL round bottom flask under N_2 atm. The potassium tert-butoxide and 18-crown-6 were added into the reaction mixture, stirred overnight after poured into water. The compound was extracted with DCM and washed with brine. The compound finally purified with column chromatography.

(2,4,6-*tris*(4-((*E*)-2-(9-*hexyl*-9*H*-*carbazol*-3-*yl*)*vinyl*)*phenyl*)-1,3,5-*triazine* (*TRZ*-*hexyl*): yield-35%, yellow powder. ¹H-NMR (CDCl₃, ppm): 8.7 (s, 2H), 8.25 (s, 1H), 8.14-8.12 (d, 1H, J = 7.6 Hz), 7.72-7.70 (d, 2H, J = 8 Hz), 7.69-7.50 (t, 1H, J = 5.2 Hz), 7.50-7.44 (d, 2H, J = 8.4 Hz), 7.40-7.34 (t, 1H, J = 8.4 Hz), 7.27-7.20 (s, 2H), 4.25-4.22 (t, 2H, J = 7.2 Hz), 1.89-1.82 (m, 2H), 1.36-1.26 (m, 6H), 0.87 (m, 3H). ¹³C-NMR- 171.00, 142.03, 140.87, 140.49, 134.87,131.60, 129.38, 128.19, 126.30, 125.84, 125.36, 124.67, 123.25, 122.90, 120.49.119.13, 108.95, 43.20, 31.59, 28.98,26.98, 22.52, 14.03.FT-IR (cm⁻¹): 2924 (CH₃ stretch), 2208 (C triple bond N stretch), 1581 (C-C stretch aromatic), 831 (alkyl halide). HRMS: Calculated for C₈₁H₇₈N₆, 1134.6288; found 1134.6286.

(2,4,6-tris(4-((*E*)-2-(9-octyl-9H-carbazol-3-yl)vinyl)phenyl)-1,3,5-triazine (*TRZ*-octyl): yield-25%, yellow powder. ¹H-NMR (CDCl₃, ppm): 8.77 (s, 2H), 8.29 (s, 1H), 8.15 (d, 1H, J = 4.8 Hz), 7.74-7.25 (d, 3H, J = 6.4 Hz), 7.48-7.28 (m, 3H), 7.26 (s, 2H), 4.30-4.26 (t, 2H, J = 10.8 Hz), 1.88-1.87 (d, 2H, J = 5.6 Hz), 1.35-1.25 (m, 12H), 0.87 (m, 3H). ¹³C-NMR-171.28, 142.29, 141.10, 140.78, 135.09,131.87, 129.65, 126.55, 126.10, 125.58, 124.90, 123.48, 123.11, 120.71, 120.51, 119.36, 109.19, 43.45, 32.04, 29.94, 29.62, 29. 43, 27.43, 22.85, 14.32. FT-IR (cm⁻¹): 2924 (CH₃ stretch), 2208 (C triple bond N stretch), 1581 (C-C stretch aromatic), 831 (alkyl halide). HRMS: Calculated for C₈₇H₉₀N₆, 1218.7227; found 1218.7225.

(2,4,6-tris(4-((E)-2-(9-(2-ethylhexyl)-9H-carbazol-3-yl)vinyl)phenyl)-1,3,5-triazine (*TRZ-branched*): yield- 30%, yellow powder. ¹H-NMR (CDCl₃, ppm): 8.79 (m, 2H), 8.29-8.28 (d, 1H, J = 5.6 Hz), 8.14 (s, 1H), 7.72-7.20 (d, 2H, J = 8 Hz), 7.52-7.48 (d, 2H, J = 7.6 Hz), 7.48-7.30 (m, 2H), 7.28-7.24 (m, 2H), 4.16-4.05 (t, 2H, J = 8 Hz), 2.09-2.04 (m, 1H), 1.36-1.25 (m, 8H), 0.91 (m, 6H). ¹³C-NMR- 171.11, 142.11, 141.40, 141.05, 134.94,131.69, 129.42, 128.22, 126.34, 125.86, 124.67, 123.28, 122.92, 120.43, 119.42, 119.07, 109.28, 47.59, 39.46, 29.72, 28.85, 24.47, 23.08, 14.02,10.93. FT-IR (cm⁻¹): 2924 (CH₃ stretch), 2208 (C triple bond N stretch),

1581 (C-C stretch aromatic), 831 (alkyl halide). HRMS: Calculated for $C_{87}H_{90}N_6$, 1218.7227; found 1218.7226.

3. Results and discussion

3.1. Synthesis

The synthetic scheme of TRZ derivatives are shown in Scheme 1, names are 2,4,6-tris(4-((E)-2-(9-hexyl-9H-carbazol-3-yl)vinyl)phenyl)-1,3,5-triazine (TRZ-hexyl), 2,4,6-tris(4-((E)-2-(9-octyl-9H-carbazol-3-yl)vinyl)phenyl)-1,3,5-triazine (TRZ-octyl) and 2,4,6-tris(4-((E)-2-(9-(2-ethylhexyl)-9H-carbazol-3-yl)vinyl)phenyl)-1,3,5-triazine (TRZ-branched). Its important key step of this synthesis is Witting-Horner coupling reaction between carbazole aldehyde and TRZ monomer. Those synthesized compounds were confirmed by FT-IR, ¹H, ¹³C-NMR, and HRMS (Fig S1-S20).

3.2. Photophysical properties

The solvatochromism effect of TRZ derivatives were examined in seven different solvents with 1×10^{-5} M. The absorption, excitation and emission spectra of TRZ derivatives are illustrated in Fig. 2, 3 (TRZ-hexyl), Fig. 4, 5 (TRZ-octyl), and Fig. 6, 7 (TRZ-branched). These corresponding data were summarized in Table 1. From UV-visible spectra of TRZ derivatives observed absorption (λ_{max}) with wavelength ranging from 280 nm to 460 nm. The three derivatives have shown very close absorption maximum at 403 nm. The solvent polarity of the TRZ derivatives have shown negligible shift for ground state. The emission studies of TRZ derivatives are more sensitive towards solvent polarity, its exhibit broad red-shift emission for increasing solvents polarity. The emission shift moved in the solvent from cyclohexane to DMF it's quite interesting. As per emission maxima was disturbed, while increasing solvent polarity cyclohexane to DMF solvent, a red shift of 116 nm. The TRZ derivatives shows a structured emission in non-polar solvent like cyclohexane, whereas in all other solvents it shows moderate to high polarity with a broad and structureless emission [35]. In the case of TRZ hexyl in cyclohexane solvent two emission bands were observed at 434 nm and 464 nm. The 434 nm peak assigned to emission from the local excited state of the TRZ-hexyl and the band at 464 nm to ICT from the carbazole group to triazine moiety [36]. The three TRZ derivatives are shown a large bathochromic shift because lack of solvent induced interactions in excited state. Generally, donor-acceptor kind pattern molecules were attributed charge transfer induced effect. Particularly, we have observed more stock shift respect to TRZ-hexyl in solution of ACN (FL $\lambda_{emi} = 550 \text{ nm}, \Delta ss = 6571 \text{ cm}^{-1}$). Similarly, we have observed TRZ-branched blue (FL $\lambda_{emi} = 433$ nm, $\Delta ss = 1119 \text{ cm}^{-1}$) to red shift emission with a large stokes shifts (FL $\lambda_{emi} = 547 \text{ nm}$, $\Delta ss = 1000 \text{ cm}^{-1}$) to red shift emission with a large stokes shifts (FL $\lambda_{emi} = 547 \text{ nm}$, $\Delta ss = 1000 \text{ cm}^{-1}$) to red shift emission with a large stokes shifts (FL $\lambda_{emi} = 547 \text{ nm}$, $\Delta ss = 1000 \text{ cm}^{-1}$) to red shift emission with a large stokes shifts (FL $\lambda_{emi} = 547 \text{ nm}$, $\Delta ss = 1000 \text{ cm}^{-1}$) to red shift emission with a large stokes shifts (FL $\lambda_{emi} = 547 \text{ nm}$, $\Delta ss = 1000 \text{ cm}^{-1}$) to red shift emission with a large stokes shifts (FL $\lambda_{emi} = 547 \text{ nm}$, $\Delta ss = 1000 \text{ cm}^{-1}$) to red shift emission with a large stokes shifts (FL $\lambda_{emi} = 547 \text{ nm}$). 6160 cm⁻¹). In particular, octyl containing molecules have shown more stokes shift (FL λ_{emi} = 550 nm, $\Delta ss = 6819 \text{ cm}^{-1}$) compare with others derivatives. These effects suggest that possibility

of strong ICT interactions between carbazole donors to triazine acceptors. Moreover, the hexyl and branched alkyl chain containing TRZ derivatives have exhibited similar behaviour, whereas octyl chain containing carbazole acts as a donor and triazine moiety act as an acceptor with better ICT. Further, we have investigated solid absorption and emission spectra were obtained shown in Fig. 8 and Fig. 9. In solid UV spectra were displayed negligible difference with same absorption pattern was observed. The solid emission maximum of TRZ-hexyl, TRZ-octyl and TRZbranched was observed 539, 556, and 548 nm, respectively. The emission maximum difference of TRZ-hexyl to TRZ-octyl was observed 17 nm a red shift. The fluorescence quantum yields $(\Phi_{\rm F})$ for TRZ derivatives are 0.30, 0.31, 0.30 in chloroform solution used as a reference to riboflavin ($\Phi_{\rm F} = 0.36$ in ethanol). To understand the mechanism behind excited state properties, we have measured fluorescence lifetime in low polar cyclohexane to high polar ACN excitation state at 398 to 413 nm using the time-correlated single-photon-counting technique and the obtained data's are shown in Fig. 10, 11 and Fig. 12. The curve shows low to high polar solvents increasing with a lifetime of two to three folds. The lifetime at maximum TRZ-hexyl, TRZ-octyl, and TRZ-branched molecules in DMF solvent of 4.7×10^{-08} sec, 5.0×10^{-08} sec, and 1.5×10^{-08} sec, respectively. The lifetime was significantly affected varying the alkyl chain length also we have observed good lifetime in TRZ-Octyl compound for all the solvents.



Fig. 2. (a) Solvatochromism UV-visible and (b) excitation spectra of TRZ-hexyl measured in different solvents



Fig. 3. Solvatochromism emission spectra of TRZ-hexyl measured in different solvent



Fig. 4. (a) Solvatochromism UV-visible and (b) excitation spectra of TRZ-octyl measured in different solvents



Fig. 5. Solvatochromism emission spectra of TRZ-octyl measured in different solvent



Fig. 6. (a) Solvatochromism UV-visible and (b) excitation spectra of TRZ-branched measured in different solvents



Fig. 7. Solvatochromism emission spectra of TRZ-branched measured in different solvent



Fig. 8. Solid state UV-visible spectra of TRZ derivatives



Fig. 9. Solid state FL emission spectra of TRZ derivatives



Fig. 10. Lifetime decay curve of TRZ-hexyl



Fig. 11. Lifetime decay curve of TRZ-octyl



Fig. 12. Lifetime decay curve of TRZ-branched

Solvents	TRZ-Hexyl					TRZ-Octyl				TRZ-Branched					
	λ _{abs} (UV)	λ _{emi} (FL)	Φ_{F}	$\Delta_{\rm ss}$ (cm ⁻¹)	τ (ns)	λ _{abs} (UV)	λ _{emi} (FL)	$\Phi_{ m F}$	$\Delta_{\rm ss}$ (cm ⁻¹)	τ (ns)	λ _{abs} (UV)	λ _{emi} (FL)	$\Phi_{\rm F}$	Δ_{ss} (cm ⁻¹)	τ (ns)
Cyclo	393,	434,	1.00	2474	6.3	393,	434,	1.6	2379	5.6	394,	433,	0.2	1119	2.8
-hexane	413	464				413	458				413	459			
Toluene	398	464	1.07	3574	2.3	399	462	0.9	3417	2.4	399	460	1.5	3190	1.0
CHCl ₃	403	504	0.30	4972	3.1	401	504	0.3	5096	3.0	403	503	0.3	4933	3.0
THF	407	508	0.89	4808	3.5	401	508	0.7	5175	3.5	409	505	1.9	4569	3.5
Acetone	400	538	0.35	6413	3.1	402	534	0.5	6149	2.2	403	534	0.6	6087	2.6
ACN	404	550	0.04	6571	4.3	400	550	0.1	6819	3.3	403	547	0.1	6532	2.7
DMF	410	550	0.10	6209	0.4	407	550	0.1	6389	0.5	409	547	0.1	6160	0.1

3.3Aggregation Induced Emission (AIE)

All the TRZ derivatives are insoluble in water but soluble in organic solvents, we have observed that THF/H₂O fractions significantly effect of UV-vis and emission intensity. In UV-vis spectra had shown increasing percentage of water fraction as well as slowly increase the FL emission intensity also with a small red shift. Fig. 13-15 has shown emission spectra of TRZ-octyl, TRZ-branched in different percentage of THF/H₂O mixtures. Emission spectra had shown when added a large amount of water in THF solution absorption gradually increases reached maxima absorption of TRZ-hexyl at 10/90%, TRZ-octyl at 30/70%, TRZ-branched at 50/50%

(THF/H₂O) respectively. The fluorescence emission spectra of TRZ derivatives in the THF/H₂O different mixtures of water content are shown in Fig. 13. The triazine derivatives are shown good AIE property due to the retraction of intramolecular rotations. The THF solvent used as organic phase, as THF slowly evaporates the triazine derivatives are transferred into aqueous phase with the formation of nanoparticle via aggregation of triazine molecules. The TRZ-hexyl FL spectra had showed emission at 510 nm, when excitation have performed at 407 nm. The addition of water ration into TRZ-hexyl in THF solution, the FL emission intensity was significantly increased with a slight red-shift, with colour change from green (0% H₂O) to yellow (90% H₂O) and then maximum intensity was observed at 90% H₂O. Depending upon increased the water ratio, TRZ-hexyl has shown linear plot with 3.34-fold increases of emission intensity at 514 nm. Another reason for why we could believe aqueous media restricted intramolecular rotation because of the formation of nano-aggregates and the number of emissive molecules per unit volume also decreased. In case of TRZ-octyl compound maximum emission intensity was observed for 70% H_2O . Further addition of water higher than 70%, the emission intensity was decreased, due to the low solubility of the compound. The water fraction of 70% has shown 6 nm a red shift or higher intensities at 268 nm with a 2.85-fold increases. The colour changes with a change in water volume were from green (0% water) to greenish yellow (70% water). Similarly, the TRZ-branched molecule has shown maximum emission intensity at 50% H_2O ratio with 13 nm a red shift emission of 5.31-fold increases. The increase water ratio into TRZ-branched the emission intensity was moderated increase at 10%, 20% H₂O ratio. The 30%, 40% H₂O water the emission intensity was sudden increases observed and the maximum was reached at 50% H₂O ratio. The alkyl chain length hexyl, 2-ethyl hexyl to octyl the peak emission intensity increases of AIE state 3.34, 5.32, and 2.85 folds respectively. These are recognised to the fact that a long alkyl chain hinders intermolecular tight stacking. In the different number of alkyl chains are controlling the nature of the molecular packing and fluorescence properties. Branched alkyl side chains have shown more AIE properties compared with linear alkyl side chains due to the more π - π stacking and fusible packing capability. The AIE properties are mainly alkyl lengthdependent fluorescence properties, those conjugated molecules with twisted backbone conformations and these molecules usually have shown aggregation-induced emission (AIE) and the mechano-chromic luminescence phenomenon [37,38].



Fig. 13. (a) Emission spectra of TRZ-hexyl in aqueous THF with different water ratios and (b) FL intensity of TRZ-hexyl with different water fractions mixture



Fig.14. (a) Emission spectra of TRZ-octyl in aqueous THF with different water ratios and (b) FL intensity of TRZ-octyl with different water fractions mixture



Fig. 15. (a) Emission spectra of TRZ-branched in aqueous THF with different water ratios and (b) FL intensity of TRZ-branched with different water fractions mixture

In additional, solvatochromism effect of the molecules correlated with Stokes shift against Lippert–Mataga and Reichardt–Dimorth's $E_T(30)$ parameters are shown in Fig. 16, 17 [30,39]. The TRZ derivatives displayed reasonable linear relationship demonstrating the presence of general solvent effects. Furthermore, these TRZ derivatives are showed moderate quantum yield in non-polar solvent as cyclohexane to polar ACN. It was significantly increased by the increasing solvent polarity.



Fig. 16. Lippert-Mataga plot of TRZ derivatives



Fig. 17. Plot of E_T (30) Vs Stokes shift of TRZ derivatives

3.4 DFT calculation

In theoretical studies of the density functional theoretical (DFT) study, further identification of geometry of these molecules and photophysical studies. The obtained geometry of HOMO and LUMO of the TRZ derivatives are shown in Fig. 18. In the carbazole moiety a large contribution in HOMO energy level due to the electron-donating property. Whereas the LUMO energy levels mainly focused on the triazine core, and then slight contribution from the double bond linkage. Further, it is interesting to note that the molecules look like star shape due to their contribution of all the molecules. The HOMO and LUMO energy levels are -4.97 eV and -1.79 eV, respectively. The HOMO and LUMO energy level of TRZ derivatives displayed almost identical.



Fig. 18. Density functional theory calculation of LUMO and HOMO energy level diagram of TRZ derivatives

3.5 Electrochemical properties

The electrochemical properties of the TRZ derivatives were investigated using cyclic voltammetry using DCM solutions at 100 mV/s scan rate. The obtain CV spectra are shown in Fig. 19, and corresponding data's are summarized in Table 2. The onset oxidation potential was observed in the range of 1.35, 1.20 eV, and 1.43 eV for TRZ-hexyl, TRZ-octyl, and TRZ-branched, respectively. From these onset value, we have calculated the HOMO energy levels of - 5.48, -5.33 eV, and -5.48 eV for TRZ-hexyl, TRZ-octyl and TRZ-branched respectively. The onset reduction potential and LUMO were observed almost similar ~ -0.52 eV and ~ -3.61 eV for TRZ derivatives. The band gap of TRZ-hexyl, TRZ-octyl, and TRZ-branched molecules are 1.87, 1.73 eV, and 1.86 eV respectively. Among these three molecules, octyl chain containing molecule shows low HOMO and low band gap due to their side-chain interference and self-assembly of the molecular packing [33]. It suggested that the synthesized TRZ derivatives are good donor materials for organic solar cell applications [23,24].

HOMO and LUMO energy levels are calculated by following equations

HOMO= -eV (E_{ox}^{onset} - $E_{1/2}$ ferrocene + 4.4); **LUMO**= -eV (E_{red}^{onset} - $E_{1/2}$ ferrocene + 4.4)



Fig. 19. Cyclic voltammograms of TRZ derivatives in DCM at a scan rate of 100 mV s⁻¹

Table 2. Optical and electrochemical properties of TRZ derivatives

Sample	Optical p	properties (th	in film)	Electro chemical data (CV)					
	UV (nm)	PL (nm)	$\Delta_{\rm ss}~({\rm cm}^{-1})$	Eox onset / HOMO	Ered onset /LUMO	Band gap			
	X, í			(eV)	(eV)	(eV)			
TRZ-Hexyl	406	540	6112	1.30/ -5.08	-0.52/ -3.21	1.87			
TRZ-Octyl	401	554	6887	1.20/ -4.93	-0.53/ -3.20	1.73			
TRZ-	406	550	6449	1.43/ -5.08	-0.52/ -3.21	1.86			
Branched									

3.6 Morphology studies

The morphology of TRZ derivatives was analysed by Atomic force microscopy (AFM) and the obtained images are shown in Fig. 20. All the molecules are showed a smooth surface, which reveals that the molecule can easily make a good surface in the film. Furthermore, the molecules are investigated by scanning electron microscopy (SEM) and the images are shown in Fig. 21, 22, and 23 with and without water fractions respectively. The sample was prepared by using ITO coated plated. The SEM images of TRZ derivatives are shown different structures such as cactaceae chapati kalli (TRZ-hexyl), rocky mountain (TRZ-octyl) star shape (TRZ-branched) like structure morphology particle are agglomerate, after the presence of water show spherical structures for all the TRZ derivatives. This is due to the presence of molecules are absorption water to form mechanism.



Fig. 20. (a) AFM images of TRZ-hexyl, (b) TRZ-octyl and (c) TRZ-branched



Fig. 21. (a) SEM image of TRZ-hexyl and (b) TRZ-hexyl + H_2O



Fig. 22. (a) SEM image of TRZ-octyl and (b) TRZ-octyl + H_2O



Fig. 23. (a) SEM image of TRZ-branched and (b) TRZ-branched + H₂O

3. Conclusions

The novel three star shaped molecules containing triazine centre has been designed, synthesized, studied for fluorescence and AIE studies. The TRZ derivatives are displayed high optical properties in excitation states compare to ground. The emission spectra show large extent emission of non-polar to polar solvents in the range of 432 to 549 nm with high quantum yields. The DFT and the electrochemical band gap of TRZ derivatives showed ~1.80 eV suggested that good solar cell materials. The TRZ derivatives in organic solvents displayed less emission compared to aggregation state. The introduction of different side chains can enrich the flexibility of molecules, but not much difference in optical properties and electrochemical behaviour. The obtain results communicate that the presence of triazine with carbazole molecules showed efficient fluorescence and AIE properties and also provide useful information for the further design of OLEDs and solar cell materials.

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Justification

- Three novel star shaped molecules have been designed, synthesized, studied for fluorescence and AIE studies. •
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- The synthesized molecules are displayed high optical properties in excitation states compare to ground state. The electrochemical band gap of TRZ derivatives showed ~1.80 eV suggested that good donor materials for organic solar cell materials. The presence of different side chains can enrich the flexibility of molecules. These results conclude the molecules provided useful information for the further design of OLEDs and • solar cell materials.