Dyes and Pigments 97 (2013) 429-439

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments



journal homepage: www.elsevier.com/locate/dyepig

Red emitting solid state fluorescent triphenylamine dyes: Synthesis, photo-physical property and DFT study

Vinod D. Gupta, Abhinav B. Tathe, Vikas S. Padalkar, Prashant G. Umape, Nagaiyan Sekar*

Tinctorial Chemistry Group, Department of Dyestuff Technology, Institute of Chemical Technology, N. P. Marg, Matunga, Mumbai 400 019, Maharashtra, India

ARTICLE INFO

Article history: Received 7 September 2012 Received in revised form 13 December 2012 Accepted 21 December 2012 Available online 24 January 2013

Keywords: Red emitting dyes Solid state fluorescent dyes Triphenylamine Solvatochromism Thermally stable dyes Dipole moment

ABSTRACT

In this work, four red-emitting push–pull chromophoric dyes containing triphenylamine are reported. The synthesis and solvatochromic behavior of novel triphenylamine based Y-shaped dyes obtained by the condensation of 4-(diphenylamino) benzaldehyde and 4,4'-diformyltriphenylamine with (1-phenylethylidene) propanedinitrile and ethyl-2-cyano-3-phenyl-2-butenoate are reported. The UV–Visible absorption and fluorescence emission spectra of these dyes were studied in solvents of different polarities. The photophysical behavior and the relation between structure and properties of the chromophores were investigated experimentally. These dyes exhibited positive solvatochromism and solvatofluorism in solution. The dyes were characterized by FT-IR, ¹H NMR and Mass spectral analysis. Thermal analysis showed that, these dyes are thermally stable up to 300 °C. Density Functional Theory [B3LYP/6-31G(d)] computations have been used to have more understanding of structural, molecular, electronic and photophysical parameters of push–pull dyes. The absorption wavelength values are found to be in good agreement with the experimental results. Non-linear properties (β_0) were calculated by theoretical method and found in the range of 196.45 × 10⁻³⁰ to 222.18 × 10⁻³⁰ e.s.u.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

In the field of functional materials design and development of innovative molecules have been progressing remarkably in recent years due to their potential applications in the optoelectronic devices, such as electroluminescence devices [1], organic light emitting devices (OLED) [2], photoconductors [3], non-linear optics [4], thin film transistors [5], solid-state lasers [6], photovoltaics [7], and bio-sensing fluorescence technology [8].

Compounds having an intramolecular charge transfer properties are one of the most important materials. Such materials are usually functionalized by electron-donating (D) and electron-accepting (A) groups through a π -conjugated bridge which makes it possible to reduce the gap between HOMO and LUMO orbital of the molecule for broadening the range of absorption and to study the relationship between the variation of donor/acceptor chromophores and their corresponding photophysical and electrochemical properties [9].

The electron-rich triphenylamine unit is one of the promising donor moiety of donor-acceptor type of functional molecules because of its good electron-donating and high hole mobility properties [10]. Triphenylamine derivatives are important molecules in numerous dye-sensitized solar cells (DSSCs) due to the noncoplanarity of the three phenyl substituent's, strong electrondonating nature, high light-to-electrical energy-conversion efficiencies and good hole-transporting capability and organic electroluminescence materials [10b,11]. *p*-Aryl-substituted triphenylamine derivatives have also attracted considerable interest due to their wide range of applications in DSSCs, organic field-effect transistors, and organic light-emitting diodes (OLEDs), as well as second order nonlinear optical devices [12].

With these approach, to explore the relationship between chemical structures and various properties of these compounds, we have designed and synthesized a new series of twisted-intramolecular charge transfer (TICT) compounds by incorporating the triphenylamine moiety (electron donor) with multiple cyano groups (electron acceptor) for comparison (Fig. 1).

Properties of triphenylamine based derivatives were investigated using absorption and fluorescence spectroscopy, thermogravimetric analysis and density functional theory calculations. These dyes showed fluorescence in solution as well as in the solid state. The ground and excited electronic states of such chromophores can be shown by linear combinations of neutral and zwitterionic states (D-A) and (D^+-A^-) , respectively. These triphenylamine dyes have shown red-shifted absorption and emission properties in comparison with the carbazole based fluorescent dyes reported in the earlier paper [13]. The broader and red-shifted absorption and fluorescence

^{*} Corresponding author. Tel.: +91 22 3361 2707; fax: +91 22 3361 1020. *E-mail addresses*: n.sekar@ictmumbai.edu.in, nethi.sekar@gmail.com (N. Sekar).

^{0143-7208/\$ –} see front matter \odot 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.dyepig.2012.12.024



Fig. 1. Structures of the dyes TMS1, TMS2, TDS1 and TDS2.

bands with higher quantum yields is due to twisted-intramolecular charge transfer (TICT) bands which showed a positive solvatochromism and solvatofluorism by recording in different solvents. This combination of the non-planar triphenylamine core with a linear π -conjugated branch could lead to amorphous conjugated materials with good solution processability, decreasing the intermolecular π – π stacking and reducing luminance quenching by aggregation [12g,14].

Density functional theory computations [B3LYP/6-31G(d)] were carried out to study the geometrical and electronic properties of the synthesized molecules. The static first hyperpolarizability (β_0) and its related properties were calculated using B3LYP/6-31G(d) on the basis of the finite field approach [15].

2. Experimental section

2.1. Materials and equipments

All commercial reagents were purchased from Aldrich and Sd Fine Chemical Limited and used without purification and all solvents were reagent grade. The reaction was monitored by TLC using on 0.25 mm E-Merck silica gel 60 F₂₅₄ precoated plates, which were visualized with UV light. Melting points were measured on standard melting point apparatus from Sunder Industrial Product Mumbai and are uncorrected. The FT-IR spectra were recorded on a Jasco 4100 Fourier Transform IR instrument (ATR accessories). ¹H (300 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Varian Cary Eclipse Australia, 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 Spectronic Genesys 2 UV-visible spectrophotometer; fluorescence emission spectra were recorded on Varian Cary Eclipse fluorescence spectrophotometer using freshly prepared solutions at the concentration 1×10^{-6} mol L⁻¹ solution. DSC-TGA measurements were performed out on SDT Q600 v8.2 Build 100 model of TA instruments Waters (India) Pvt. Ltd. Fluorescence quantum yields were determined in different solvents by using Rhodamine B ($\phi = 0.97$ in ethanol) [16] as a reference standard using the comparative method. The emission spectra of the dyes and standard were measured at the absorbance below 0.05 to minimize the inner filter and re-absorption effect. Emission intensity values were plotted against absorbance values and linear plots were obtained. Gradients were calculated for each dye in each solvent and for the standard. All the measurements were done by keeping the parameters constant such as solvent and slit width constant. Relative quantum yields of the dyes in different solvents were calculated by using equation (1).

$$\Phi_{\rm X} = \Phi_{\rm Std} \left(\frac{{\rm Grad}_{\rm X}}{{\rm Grad}_{\rm Std}} \right) \left(\frac{\eta_{\rm X}^2}{\eta_{\rm Std}^2} \right)$$
(1)

Where,

 $\begin{array}{l} \Phi_X = \text{Quantum yield of dye sample} \\ \Phi_{Std} = \text{Quantum yield of standard sample} \\ \text{Grad}_X = \text{Gradient of dye sample} \\ \text{Grad}_{Std} = \text{Gradient of standard sample} \\ \eta_X = \text{Refractive index of solvent used for synthesized compound} \\ \eta_{Std} = \text{Refractive index of solvent used for standard sample} \end{array}$

2.2. Synthetic strategy

Four different kinds of red-emitting, solid state fluorescent push-pull D- π -A chromophoric dyes have been successfully synthesized. These dyes contain triphenylamine as an electron donor, cyano/carbethoxy group as electron acceptors conjugated through a π -bridge. They were synthesized by classical Knoevenagel condensation of 4-(diphenylamino)benzaldehyde **2a** and 4,4'-diformyltriphenylamine **2b** with active methylene compounds **3a** and **3b** as shown in Scheme 1. In the first step, triphenylamine **1** was mono or bis-formylated at 4 or 4 and 4' positions by Vilsmeier-Haack formylation reaction to obtain compounds **2a** and **2b** respectively. Finally, aldehyde **2a** or **2b** and suitable active methylene compound **3a** or **3b** were refluxed in absolute ethanol containing a catalytic amount of piperidine to yield desired fluorescent extended styryl dyes **TMS1**, **TMS2**, **TDS1** and **TDS2**.

The structures of the dyes were confirmed by FT-IR, ¹H NMR, and Mass spectral analysis. The ¹H NMR spectra of dye **TMS1** showed doublet peaks at δ 6.78 and 7.42 having trans vicinal coupling constant (J = 15.4 Hz) which indicates the ethylenic protons at styryl group are in transform and also showed a strong peak in FTIR at 980 cm⁻¹ (C–H trans vicinal). Similarly, the geometry of other three dyes were also confirmed by the presence of trans vicinal coupling in NMR spectra for ethylenic protons on π -bridge. The FT-IR spectra of these dyes showed presence of cyano and carbonyl ester group stretching near about 2210 and 1710 cm⁻¹ respectively.

Absorption and emission spectra were measured to investigate its photophysical properties and also the solvatochromism and solvatofluorism behaviors of the molecule were studied by measuring electronic absorption and emission spectra in solvents. Solvatochromic data was used to determine the ground and excited state dipole



Scheme 1. Synthesis of extended styryl mono- and bis-styryl triphenylamine dyes TMS1, TMS2, TDS1 and TDS2.

moments of the synthesized dyes by using Lippert–Mataga, Bakhshiev and Kawski–Chamma–Viallet correlations.

2.3. Computational methods

All computations were performed using the Gaussian 09 package [17]. The ground state (S₀) geometry of the synthesized dyes in their C₁ symmetry was optimized in the gas phase using DFT [18]. The functional used was B3LYP. The B3LYP method combines Becke's three parameter exchange functional (B3)[19] with the nonlocal correlation functional by Lee, Yang and Parr (LYP) [20]. The basis set used for all atoms was 6-31G(d). The vibrational analysis was performed using the same method to verify that the optimized structures correspond to local minima on the energy surface. The vertical excitation energies and oscillator strengths were obtained for the lowest 10 singlet—singlet transitions at the optimized ground state equilibrium geometries by using TDDFT at the same hybrid functional and basis set [21].

The low-lying first singlet excited states (S_1) of only one dye **TMS1** was relaxed using TDDFT to obtain its minimum energy geometry. The difference between the energies of the optimized geometries at first singlet excited state and ground state was used to calculate the emission [22]. Frequency computations were also carried out on Frank–Condon excited state of the dyes. All the computations in solvents of different polarities were carried out using the Self-Consistent Reaction Field (SCRF) under the Polarizable Continuum Model (PCM) [23]. Vertical electronic excitation spectra, including wavelengths, oscillators strengths, and main configuration assignment, were systematically investigated using TDDFT with PCM model on the basis of the optimized ground state structures.

2.4. Synthesis and characterization

2.4.1. Synthesis of 4-(diphenylamino)benzaldehyde (**2a**) and 4,4'-diformyltriphenylamine (**2b**)

The compounds **2a** and **2b** were prepared by the reported method [24].

2.4.2. Synthesis of (1-phenylethylidene) propanedinitrile (**3a**) and ethyl-2-cyano-3-phenyl-2-butenoate (**3b**)

The compounds **3a** and **3b** were prepared by the reported method [25].

2.4.3. Synthesis of 4-[4-(1,1-dicyano-2-phenyl)buta-1,3-dienyl] tri-phenylamine (**TMS1**)

4-(Diphenylamino)benzaldehyde (1.092 g, 4 mmol) **2a** and (1-phenylethylidene) propanedinitrile (0.672 g, 4 mmol) **3a** were

dissolved in absolute ethanol (25 mL). Piperidine was added in catalytic amount (0.1 mL) and the reaction mixture was refluxed for 6 h. The bright red crystals obtained were filtered, washed with ethanol. The dye **TMS1** obtained was purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

Yield: 68%, Melting point = $222-224 \circ C$.

¹H NMR (CDCl₃, 300 MHz): δ 6.78 (d, J = 15.4 Hz, 1H), 7.42 (d, J = 15.4 Hz, 1H), 6.95 (d, J = 8.8 Hz, 2H), 7.32–7.34 (m, 6H), 7.48–7.59 (m, 5H), 7.37 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.7 Hz, 2H), 7.13 (t, J = 8.1 Hz, 2H) ppm.

¹³C NMR (CDCl₃, 100 MHz): 79.5, 113.4, 114.0, 120.5, 121.5, 124.9, 125.9, 126.8, 128.9, 129.6, 130.4, 130.8, 133.5, 146.2, 148.9, 151.3, 171.3 ppm.

Mass: *m/z* 424.2 (M + 1).

FT-IR (cm⁻¹): 2214 (C≡N), 1574 (Ar), 1280 (C−N), 980 (C−H trans-vicinal).

2.4.4. Synthesis of ethyl-2-cyano-5-(4-triphenylamino)-3-phenylpenta-2,4-dienoate (**TMS2**)

4-(Diphenylamino)benzaldehyde (1.092 g, 4 mmol) **2a** and ethyl-2-cyano-3-phenyl-2-butenoate (0.864 g, 4 mmol) **3b** were dissolved in absolute ethanol (25 mL). Piperidine was added in catalytic amount (0.1 mL) and the reaction mixture was refluxed for 6 h. The solvent was removed under reduced pressure. The red colored dye **TMS2** obtained was purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

Yield: 56%, Melting point: 104–106 °C.

¹H NMR (CDCl₃, 300 MHz): δ 6.58 (d, *J* = 15.8 Hz, 1H), 8.54 (d, *J* = 15.8 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 8H), 7.32 (t, *J* = 8.7 Hz, 4H), 7.44–7.52, (m, 5H), 1.39 (t, *J* = 7.3 Hz, 3H), 4.35 (q, *J* = 7.3 Hz, 2H) ppm.

¹³C NMR (CDCl₃, 100 MHz): 14.2, 61.7, 100.5, 117.3, 121.3, 123.3, 124.4, 125.5, 128.0, 128.5, 128.9, 129.5, 129.7, 129.9, 136.7, 146.6, 147.4, 150.3, 162.9, 168.1 ppm.

Mass: *m*/*z* 471.1 (M + 1).

FT-IR (cm⁻¹): 2211 (C≡N), 1709 (C=O), 1579 (Ar), 1279 (C−N), 1232 (C−O), 970 (C−H trans-vicinal).

2.4.5. Synthesis of 4,4'-bis[4-(1,1-dicyano-2-phenyl)buta-1,3-dienyl] triphenylamine (**TDS1**)

4,4'-Diformyltriphenylamine (0.602 g, 2 mmol) **2b** and (1-phenylethylidene) propanedinitrile (0.84 g, 5 mmol) **3a** were dissolved in absolute ethanol (30 mL). Piperidine was added in catalytic amount (0.1 mL) and the reaction mixture was refluxed for 8 h. The dark red product thus obtained was filtered, washed

with ethanol. The dye **TDS1** obtained was purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

Yield: 52%, Melting point: 268–270 °C.

¹H NMR (CDCl₃, 300 MHz): δ 6.80 (d, J = 15.4 Hz, 2H), 7.48 (d, J = 15.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 4H), 7.13 (d, J = 8.4 Hz, 4H), 7.21 (d, J = 9.2 Hz, 2H), 7.34 (t, J = 9.2 Hz, 4H), 7.40 (d, J = 8.8 Hz, 6H), 7.55 (t, J = 7.3 Hz, 3H) ppm.

¹³C NMR (CDCl₃, 100 MHz): 80.9, 113.1, 113.7, 122.9, 123.2, 126.0, 126.6, 128.9, 129.0, 130.0, 130.3, 131.0, 133.3, 145.4, 148.2, 149.7, 171.1 ppm.

Mass: *m*/*z* 602.2 (M + 1).

FT-IR (cm⁻¹): 2217 (C≡N), 1578 (Ar), 1261 (C−N), 971 (C−H trans-vicinal).

2.4.6. Synthesis of 4-[5-(ethyl-2-cyano-3-phenyl) penta-2,4-dienoate] triphenylamine (**TDS2**)

4,4'-Diformyltriphenylamine (1.26 g, 5 mmol) **2b** and ethyl-2cyano-3-phenyl-2-butenoate (2.16 g, 10 mmol) **4b** were dissolved in absolute ethanol (15 mL). Piperidine was added in catalytic amount (0.1 mL) and the reaction mixture was refluxed for 8 h. The bright red crystals thus obtained were filtered, washed with ethanol. The dye **TDS2** obtained was purified by column chromatography using silica gel 100–200 mesh and toluene as eluent system.

Yield: 45%, Melting point: 140-142 °C.

¹H NMR (CDCl₃, 300 MHz): δ 6.58 (d, J = 15.8 Hz, 2H), 8.57 (d, J = 15.8 Hz, 2H), 7.00 (d, J = 8.8 Hz, 4H), 7.09 (d, J = 7.3 Hz, 4H), 7.16 (t, J = 7.0 Hz, 2H), 7.32 (m, 8H), 7.48 (t, J = 6.6 Hz, 5H), 1.39 (t, J = 7.3 Hz, 6H), 4.35 (q, J = 7.3 Hz, 4H) ppm.

¹³C NMR (CDCl₃, 100 MHz): 14.2, 61.8, 101.3, 117.1, 123.2, 124.3, 126.2, 127.9, 128.1, 128.6, 128.9, 129.8, 129.9, 136.5, 145.9, 146.5, 146.8, 149.0, 162.8, 167.8 ppm.

Mass: m/z 718.4 (M + Na⁺).

FT-IR (cm⁻¹): 2209 (C≡N), 1712 (C=O), 1588 (Ar), 1268 (C−N), 1232 (C−O), 970 (C−H trans-vicinal).

3. Results and discussion

3.1. Photo-physical properties

The UV–Vis absorption and fluorescence emission spectra of extended styryl triphenylamine dyes **TMS1**, **TMS2**, **TDS1** and **TDS2** in solvents of varying polarities are reported in Table 1. These triphenylamine dyes have shown red-shifted absorption maxima (about 40 nm shift) as compared to its styryl analogues reported in literature [26]. These newly synthesized triphenylamine derivatives with $D-\pi-A$ (**TMS1** and **TMS2**) and $A-\pi-D-\pi-A$ (**TDS1** and **TDS2**) system consist of an electron-donating triphenylamine unit and electron-withdrawing cyano or carbethoxy groups conjugated

through π -bonding exhibited strong red-shifted absorption in wavelength ranging from 300 to 550 nm in solution as shown in Fig. 2. These red-shifted absorptions are due to the extended π -conjugation framework present in these dyes. The first peak near 300 nm is due to the π - π * transition of the dye and the second peak near 500 nm due to the twisted-intramolecular charge transfer transition (TICT) between donor group and acceptor mojety.

The absorption spectra of dye TMS1 showed red shift with the increase in the solvent polarity and showed shorter wavelength absorption maxima in ethyl acetate at 478 nm and longer wavelength in chloroform at 502 nm (Table 1 and Fig. 2). Similarly, dyes TMS2 and TDS1 showed short wavelength absorption maxima in ethyl acetate and dichloromethane at 454 and 505 nm and long wavelength absorption band in chloroform at 475 and 523 nm (Table 1 and Fig. 2). TDS2 showed short wavelength absorption maxima in 1,4-dioxane at 474 nm and long wavelength absorption in chloroform at 502 nm (Table 1 and Fig. 2). Both the dyes TMS1 and TMS2 have shown maximum 21 nm shift in the absorption maxima when measured in different solvents of varying polarities. In comparison with TMS1 (502 nm), the absorption maxima of TMS2 is at 475 nm in chloroform. The red shift of TICT band of TMS1 indicates that dicyanovinyl moiety present in TMS1 has stronger electron withdrawing effect than cyano carbethoxy vinyl unit (present in TMS2) increasing the charge transfer between donors and acceptors. Bis-styryl dyes (TDS1 and TDS2) have shown redshifted absorption bands when compared to mono-styryl dves (TMS1 and TMS2). Red-shifted absorption is due to presence of one additional electron withdrawing group present in the bis-styryl molecules which leads to decrease in the band gap energy.

In the previous report, the four dyes contain carbazole unit in place of triphenylamine (Fig. 3) as reported in this paper [13]. Triphenylamine dyes were found to have red-shifted absorption as compared to each of the corresponding system similar to carbazole (Table 2). **TMS1** and **TMS2** have 36 nm shift in comparison with carbazole dyes (**5a** and **5b** respectively) whereas the dyes **TDS1** and **TDS2** have 42 and 40 nm longer absorption as compared to dyes **6a** and **6b** of carbazole dyes. Unlike triphenylamine, carbazole system is rigid and the two phenyl rings are fused to a middle pyrrole ring whereas triphenylamine contains three phenyl rings attached to a single nitrogen atom. These phenyl rings present on triphenylamine can freely rotate and alter the optical properties of the triphenylamine derivatives.

A strong solvatofluorism was shown by triphenylamine dyes and they emit in the red region (Table 1 and Fig. 4, S1–S4) (see electronic supplementary material). These four dyes showed a blue-shifted fluorescence emission maxima in non-polar solvent (toluene) and red-shifted longer fluorescence emission maxima in polar solvent (acetonitrile and DMF) indicating that the charge

Table 1

Absorption maxima wavelength (λ_{abs} , nm), molar extinction coefficient (ε M⁻¹ cm⁻¹), fluorescence emission maxima wavelength (λ_{ems} , nm); fluorescence quantum yield (Φ_f) and Stokes shift (cm⁻¹) of extended styryl triphenylamine dyes in different solvents.

Solvent	TMS1			TMS2			TDS1			TDS2		
	$\lambda_{abs}\left(\epsilon ight)$	$\lambda_{ems}\left(\Phi_{f}\right)$	Stokes shift	$\lambda_{abs}\left(\epsilon ight)$	$\lambda_{ems} \left(\Phi_{f} \right)$	Stokes shift	$\lambda_{abs}\left(\epsilon ight)$	$\lambda_{ems}\left(\Phi_{f}\right)$	Stokes shift	$\lambda_{abs}\left(\epsilon ight)$	$\lambda_{ems}\left(\Phi_{f}\right)$	Stokes shift
Toluene	487 (24859)	574 (0.1322)	3112	463 (25457)	560 (0.0218)	3741	508 (50000)	570 (0.3730)	2141	490 (49545)	562 (0.4296)	2615
1,4-Dioxane	480 (31932)	610 (0.1050)	4440	459 (30116)	590 (0.0299)	4837	507 (44886)	601 (0.3347)	3085	474 (52606)	589 (0.5263)	4119
DCM	481 (35108)	599 (0.0644)	4096	454 (29975)	581 (0.0270)	4815	505 (41517)	588 (0.1453)	2795	481 (61304)	577 (0.3285)	3459
Chloroform	502 (33795)	619 (0.2063)	3765	475 (29645)	608 (0.0383)	4605	523 (43863)	604 (0.4419)	2564	502 (55668)	604 (0.5663)	3364
Ethyl acetate	478 (38242)	620 (0.0878)	4791	454 (28845)	599 (0.0262)	5332	505 (43923)	615 (0.1174)	3542	481 (52398)	602 (0.3368)	4179
Acetone	481(44129)	652 (0.0031)	5453	457 (46162)	630 (0.0065)	6009	508 (43021)	643 (0.0023)	4133	484 (53859)	634 (0.0301)	4888
Methanol	484 (35701)	631 (0.0008)	4813	463 (44703)	625 (0.0014)	5598	511 (8363)	627 (0.0005)	3621	493 (55877)	628 (0.0085)	4360
Ethanol	490 (41503)	630 (0.0035)	4535	466 (35245)	619 (0.0041)	5304	514 (7461)	633 (0.0028)	3657	493 (56781)	619 (0.0355)	4129
Acetonitrile	481 (50312)	659 (0.0006)	5616	457 (36139)	644 (0.0011)	6354	508 (39712)	652 (0.0001)	4348	487 (52398)	643 (0.0082)	4982
DMF	490 (36294)	654 (0.0016)	5118	466 (25646)	642 (0.0026)	5883	520 (37004)	653 (0.0021)	3917	496 (52954)	640 (0.0129)	4536



Fig. 2. Absorption spectra of dyes TMS1, TMS2, TDS1 and TDS2 (in DMF).

separation increases in the excited state which results in a larger dipole moment than that in the ground state and explains the sensitivity of the fluorescence emission spectra of these push—pull dipolar dyes to solvent polarities. The effect of solvent polarities on emission behavior of the dye **TMS1** is shown in Fig. 5 and S1. Also, dye **TMS1** showed higher fluorescence intensity in non-polar solvents and less in the polar solvents (Fig. S1). Similarly, red shift of 84, 83 and 81 nm for the dyes **TMS2**, **TDS1** and **TDS2** respectively as the solvent polarity increases from non-polar to polar medium (Table 1 and Figs. S2–S4).

In comparison with the carbazole dyes (**5a**, **5b**, **6a** and **6b**), triphenylamine dyes have shown red-shifted fluorescence maxima (Table 2). **TMS1** (652 nm) and **TMS2** (644 nm) have shown 94 and 84 nm shift in fluorescence maxima comparison with respect to carbazole dyes (**5a** (558 nm) and **5b** (560 nm) respectively) whereas the dyes **TDS1** and **TDS2** have 75 and 82 nm longer absorption as compared to dyes **6a** and **6b**. Here, triphenylamine extends the conjugation and acts a strong electron donor, thus results in longer absorption and emission than that of carbazole dyes.

The Stokes shift increases with the increase in the solvent polarity which indicates an extensive structural re-organization in the excited state [27]. This shows that these dyes have polar excited state and it is more stabilized in the polar solvent. This confirms the twisted intramolecular charge transfer characteristics of these push-pull dyes. Compared with fluorescence spectra in solution, four dyes in solid state have a slight red-shifted fluorescence band revealing intermolecular π - π interaction and aggregation in the solid state. **TMS1**, **TMS2**, **TDS1** and **TDS2** showed solid state fluorescence maxima at 630, 625, 665 and 649 nm (Figs. 4 and 6). Bright red fluorescence shown by dye **TDS2** in solid state powder form (Figure S5).

3.2. Quantum yields of the dyes

The fluorescence quantum yields of the synthesized dyes were determined in different solvents and tabulated in Table 1. The fluorescence quantum yields of the dyes largely depend on both the nature of the substituent and the solvent polarity. Here, decrease in the solvent polarity strongly enhances the fluorescence quantum yields of TMS1, TMS2, TDS1 and TDS2 as shown in Table 1. The four dyes showed higher quantum efficiencies in non-polar solvents whereas in polar solvents the quantum yield values were invariably found to be very low. These dyes showed highest quantum yield in chloroform in the increasing order: TMS2 (0.0383) < TMS1 (0.2063) < **TDS1** (0.4419) < **TDS2** (0.5663). The quantum yield values were the lowest in acetonitrile in the decreasing order: TDS2 (0.0082) > TMS2 (0.0011) > TMS1 (0.0006) > TDS1 (0.0001). These dyes showed very less emission intensity in acetonitrile and DMF showing an obvious positive solvatokinetic behavior suggesting that a highly polar excited-state population charge transfer state and a non-radiative decay was prominent in these dyes [28].

These fluorescent materials are bright red to dark red in color and soluble in most of the organic solvents. In less polar solvents such as toluene, all the dyes emit orange to yellow light of moderate intensity. On increasing the solvent polarity the emission band also shifts bathochromatically and in DMF it emits red light. Fig. S5 that the daylight and fluorescence emission photographs of dye **TMS1** in different solvents and the difference in the emission color can be easily observed by naked eyes. These dyes showed very less emission intensity in acetonitrile and DMF solvents, which is in accordance with the low fluorescence quantum yield observed (Table 1). Push-pull charge transfer mechanism in D $-\pi$ -A type chromophore is illustrated in Fig. S8 and A $-\pi$ -D $-\pi$ -A type chromophore in Fig. S9.

3.3. Thermal stability of dyes

The dye molecules should have strong intermolecular interactions and form compact aggregates to possess high thermal stability [29]. In order to give more insight into the thermal properties of the dyes **TMS1**, **TMS2**, **TDS1** and **TDS2**, the thermal studies



Fig. 3. Structures of previously reported dyes 5a, 5b, 6a and 6b [13].

Table	2
-------	---

Comparative photo-physical properties of the triphenylamine and carbazole (given in bracket) based dyes in different solvents.

Solvent	TMS1 (5a)		TMS2 (5b)		TDS1 (6a)		TDS2 (6b)	
	λ _{abs} , nm	λ _{ems} , nm	λ _{abs} , nm	λ _{ems} , nm	λ _{abs} , nm	λ _{ems} , nm	λ _{abs} , nm	λ _{ems} , nm
Toluene	487 (453)	574 (530)	463 (429)	560 (522)	508 (474)	570 (526)	490 (450)	562 (524)
1,4-Dioxane	480 (444)	610 (534)	459 (426)	590 (528)	507 (465)	601 (536)	474 (447)	589 (530)
DCM	481 (456)	599 (552)	454 (429)	581 (547)	505 (477)	588 (553)	481 (457)	577 (554)
Chloroform	502 (-)	619 (-)	475 (-)	608 (-)	523 (-)	604 (-)	502 (-)	604 (-)
Ethyl acetate	478 (447)	620 (548)	454 (426)	599 (534)	505 (468)	615 (550)	481 (448)	602 (546)
Acetone	481(450)	652 (558)	457 (429)	630 (548)	508 (474)	643 (568)	484 (451)	634 (552)
Methanol	484 (453)	631 (572)	463 (429)	625 (560)	511 (474)	627 (578)	493 (457)	628 (570)
Ethanol	490 (-)	630 (-)	466 (-)	619 (-)	514 (-)	633 (-)	493 (-)	619 (-)
Acetonitrile	481 (450)	659 (570)	457 (429)	644 (560)	508 (471)	652 (578)	487 (450)	643 (572)
DMF	490 (457)	654 (574)	466 (430)	642 (560)	520 (484)	653 (584)	496 (459)	640 (574)

*(-) indicated not reported.

have been carried out using thermal gravimetric techniques (TGA). The thermogravimetric studies have been carried out in the temperature range 50–600 °C under nitrogen gas at a heating rate of 10 °C min⁻¹. The TGA results indicated that the synthesized dyes are stable up to 300 °C which indicates that the presence of triphenylamine conjugated framework imparts thermal stability. TGA revealed the onset decomposition temperature (T_d) of dyes **TMS1**, **TMS2**, **TDS1** and **TDS2** are 306 °C (93%), 323 °C (96%), 324 °C (93%) and 328 °C (96%), respectively (Fig. S7) which indicate that the decomposition temperatures increase with the increase of conjugation length and electron rich substituent effect.

In general the backbones of these dyes are stable up to 300 °C and above 300 °C the thermogravimetric curve of these dyes showed a major loss in weight. The comparisons of the T_d (decomposition temperature) show that the thermal stability of the **TMS1**, **TMS2**, **TDS1** and **TDS2** decreases in the order **TDS2** > **TDS1** > **TMS2** > **TMS1**. The results showed that synthesized dyes have good thermal stability. Dyes **TMS1** and **TMS2** showed a sharp decomposition after temperature 306 °C and 323 °C respectively and completely decomposed beyond 550 °C. However, dyes **TDS1** and **TDS2** showed sluggish decomposition characteristics and completely decomposed beyond 600 °C. The high molecular weight and polar substituents of the synthesized dyes are beneficial for intermolecular interactions, such as van der Waals force and dipole–dipole interaction to increase the thermal stability.

3.4. Optimized geometries of dyes TMS1, TMS2, TDS1 and TDS2

Ground state geometries of the dyes were having planar arrangement with one of the phenyl ring present on the triphenylamine moiety, π -bridge and acceptor cyano or carbethoxy group



Fig. 4. Fluorescence emission spectra of dyes TMS1, TMS2, TDS1 and TDS2 (in DMF).

present at the end. The resulting optimized geometry of dye **TMS1** is such that it has a small twist dihedral angle along $C_6-C_1-C_{39}-N_{52}$ is 13.1° (Fig. 7) but bis-styryl dye **TDS1** showed little lower twist of 15.3° (Fig. S10). Dye **TDS1** did not possess a vertical plane of symmetry (C_S) in the molecule. Therefore, bonds of either-side of middle triphenylamine moiety have different bonds lengths.

The optimized geometry of dye **TMS2** is such that it has also a small twist dihedral angle of 15.3° along $C_6-C_1-C_{39}-O_{54}$ angle between the phenyl ring of triphenylamine and terminal carbethoxy units (Fig. S11). The dye **TDS2** showed highest twist angle among the four dyes of angle 23.5° (Fig. S12). Also one of the two carbonyl groups is facing away from triphenylamine ring whereas second carbonyl ring is pointing inwards. But, in dye **TMS2**, carbonyl group is pointing towards triphenylamine ring. The pending phenyl ring on C₃₀ atom of π -bridge was twisted with a dihedral angle 57.4°, 64.4° for the dyes **TMS1** and **TMS2** and in case of dyes **TDS1** and **TDS2**, it is 57.3° and 61.8° on one side of extended conjugation and for other side it is 57.0° and 65.2°.

Dye TMS1 was optimized in the excited state and major bond lengthening was observed between the bonds C₄-N₃₃, C₂₂-N₃₃, C₁₁-N₃₃, C₃₄-C₃₅, C₃₅-C₃₈, C₃₈-C₃₉, C₃₉-C₅₃, C₃₉-C₅₁, C₅₁-N₅₂ and C₅₃-N₄₄ by 0.054, 0.031, 0.031, 0.017, 0.010, 0.040, 0.012, 0.012, 0.006 and 0.006 Å and bond length shortened for the bonds C₂₉-C₃₀, C₃₁-C₃₂, C₃₁-C₃₃ with 0.012, 0.011, 0.023 Å (Fig. 7 and S13). Also, the three phenyl ring present on triphenylamine are orthogonal to each other by -62.9 and -64.6° and more twisting is being observed in the excited state as shown in Fig. 7 and S13. Also the bond angles between three rings on triphenylamine are not same and decreases from 121.1 to 118.5° along the angle $C_4 - N_{33}$ - C_{11} and 121.2 to 118.6° along the bond angle $C_4{-}N_{33}{-}C_{22}$ whereas bond angle increases from 117.7 to 122.9° along the bond angle C₁₁-N₃₃-C₂₂. Such lengthening and shortening of the bonds i.e. the bond length alteration were due to the effect of donor and acceptor groups present in the molecules. Similarly for dyes



Fig. 5. Normalized fluorescence emission spectra of dye TMS1 in different solvents.



Fig. 6. Solid-state fluorescence spectra (normalized) of dyes TMS1, TMS2, TDS1 and TDS2 in powder form.

TMS2, **TDS1** and **TDS2** the ground state geometry is shown in the Figs. S11–S13.

The Mulliken charge distribution in ground state (DMF solvent) on selected atoms of the dyes TMS1, TMS2, TDS1 and TDS2 are shown in Table 3 and Fig. 8 and S14-S17. In the excited state, the dye **TMS1** showed increase in the positive charge on atom C₂₂ and C_{11} ; and decrease on C_4 which suggest charge delocalization in the molecule from triphenylamine donor moiety to dicyanovinyl acceptor moiety. These atoms are also engaged in bond lengthening at the excited state. The charge on nitrogen atom present as a central atom in the triphenylamine moiety did not show any change in the charge (Fig. S14). The charge on the C₄ atom was found to be nearly same in dyes TMS2, TDS1 and TDS2 in the ground state. The atom C_{39} (in dyes **TMS1** and **TMS2**) and C_{38} (in dyes TDS1 and TDS2) to which cyano and carbethoxy groups are attached possess positive charge 0.020 and 0.028 in the dyes TMS1 and TDS1 whereas it is negative -0.043 and -0.038 in the dyes TMS2 and TDS2 (Table 3). Fig. 8 and S13-S16 represent Mulliken charge distribution on atoms in the molecule. Structures indicating charge distribution on the dyes were visualized using GaussView 5.0 software [30].

Table 3

Mulliken charge (e) distribution for dyes **TMS1**, **TMS2**, **TDS1** and **TDS2** in the ground state (GS) optimized geometry [excited state (ES) for **TMS1**] in DMF.

Atom no.	TMS1		TMS2	Atom no.	TDS1	TDS2
	GS	ES				
N33	-0.644	-0.644	-0.645	N33	-0.642	-0.643
C ₄	0.336	0.212	0.331	C ₄	0.311	0.307
C ₁₁	0.252	0.300	0.253	C ₁₁	0.309	0.305
C ₂₂	0.253	0.303	0.256	C ₂₁	0.232	0.238
C ₁	0.160	0.169	0.161	C ₁	0.163	0.165
C ₃₄	-0.175	-0.166	-0.178	C ₃₃	-0.172	-0.177
C ₃₅	-0.208	-0.202	-0.199	C ₃₄	-0.201	-0.193
C ₃₈	0.165	0.176	0.103	C ₃₇	0.166	0.102
C ₃₉	0.020	0.025	-0.043	C ₃₈	0.028	-0.038
C ₅₁	0.300	0.301	0.26	C ₅₀	0.304	0.264
C ₅₃	0.286	0.293	0.664	C_{52}/C_{81}	0.291	0.667
N ₅₂	-0.545	-0.543	-0.559	N_{51}/N_{52}	-0.540	-0.555
N ₅₄ /O ₅₄	-0.541	-0.540	-0.534	N ₅₃ /O ₈₂	-0.537	-0.531
H ₃₆	0.174	0.185	0.168	H ₃₅	0.178	0.171
H ₃₇	0.167	0.172	0.187	H ₃₆	0.171	0.191
0 ₅₅	-	-	-0.489	0 ₈₃	-	-0.487

3.5. Electronic vertical excitation spectra (TDDFT)

Electronic vertical excitations were calculated using TD-B3LYP/ 6-31G(d) method. Computed vertical excitation spectra associated with their oscillator strengths, composition, and their assignments of the chromophores as well as corresponding experimental absorption wavelengths of the dyes TMS1, TMS2, TDS1 and TDS2 are reported in supporting material in Tables S1-S4. As discussed earlier in the Section 3.1, absorption maxima did not show much solvatochromism, while Stokes shift increases progressively with the increase in solvent polarity for all four dyes. These observations are in accordance with the higher stabilization in increasingly polar solvents. The absorption band occurring with higher oscillator strength at lower energy is due to intramolecular charge transfer (ICT) characteristic of donor- π -acceptor push-pull dyes (Tables S1–S4). These ICT bands for all four dyes were mainly due to the electronic transition from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO).



Fig. 7. Optimized geometry parameters of dye TMS1 in DMF solvent in the ground state and excited state (bond length are in Å, dihedral angles are in degree).



Fig. 8. Graph of Mulliken charge distribution on the dye **TMS1** in the ground and excited state optimized geometry in DMF.

Dye **TMS1** showed the lower experimental absorption maxima in 1,4-dioxane (480 nm) and red-sifted absorption band in DMF (490 nm). The computed vertical excitations for dye **TMS1** were found low in 1,4-dioxane (516 nm) and high in chloroform (502 nm). Similar, solvatochromism results were obtained for the other three dyes **TMS2**, **TDS1** and **TDS2**. The largest wavelength difference between the experimental absorption maxima and computed vertical excitation is 45 nm (DCM) for dye **TMS1**. On moving from toluene to DMF, 13 nm shift in the absorption band was observed for dye **TMS1** and similar 14 nm shift was observed in the computed vertical excitation spectra. The largest wavelength difference between experimental absorption maxima and computed vertical excitation was 65 (acetone), 78 and 87 nm (DCM) for dyes **TMS2**, **TDS1** and **TDS2**.

TMS1 was optimized in the first excited state to calculate the fluorescence. Experimentally obtained fluorescence emission spectral data and emission computed from TD-B3LYP/6-31G(d) computations are shown in Table 4. The computational results obtained by using TD-B3LYP/6-31G(d) were not able to reproduce the solvatofluorism behavior of the dye **TMS1** and shown almost nearly same value of emission energy. The experimental emission wavelength and emission computed by TD-B3LYP/6-31G(d) showed a largest difference of 58 nm in toluene and showed a closest difference of 4 and 5 nm in methanol and ethanol. A graph plotted (Fig. S18) represents correlation between experimentally recorded emissions against the emissions computed from TD-B3LYP/6-31G(d) for the dye **TMS1**.

Table 4

Experimental UV–Visible emission and computed emission from TD-B3LYP/6-31G(d) computations for dye **TMS1** in different solvents.

Solvents	Experimental ^a λ _{ems} (nm)	TD-B3LYP/6-31G(d) emission (nm) ^b
1,4-Dioxane	574	632
Toluene	610	632
Ethyl acetate	620	633
DCM	599	633
Chloroform	619	633
Acetone	652	635
Methanol	631	635
Ethanol	630	635
Acetonitrile	659	635
DMF	654	636

^a Experimentally recorded emission maxima.

^b Emission computed using TD-B3LYP/6-31G(d) level.

3.6. Frontier molecular orbitals

The different frontier molecular orbitals were studied to understand the electronic transition and charge delocalization within these push-pull chromophores. The comparative increase and decrease in the energy of the occupied (HOMO's) and virtual orbitals (LUMO's) gives a qualitative idea of the excitation properties and the ability of hole or electron injection. First allowed and the strongest electron transitions with largest oscillator strength usually correspond almost exclusively to the transfer of an electron from HOMO \rightarrow LUMO. Table S5 shows the energies of different molecular orbitals involved in the electronic transitions of these push-pull dyes in different solvents. It was observed that electronic transition in each case included HOMO \rightarrow LUMO transition.

In the case of mono-styryl D $-\pi$ –A dye **TMS1**, the energy gap of HOMO and LUMO orbitals were lowered as the solvent polarity was increased. But the extent of decrease in energy levels was found to be more in the case of LUMO by 0.057 eV and the increase in HOMO by 0.019 eV as we move from 1,4-dioxane to DMF. This indicates that the LUMO is more relaxed in the polar solvent (Table S5). Whereas in case of **TMS2**, both HOMO and LUMO were relaxed as the solvent polarity was increased. The extent of decrease of LUMO (0.128 eV) was greater than HOMO (0.042 eV).

But, in case of bis-styryl $A-\pi-D-\pi-A$ dye **TDS1**, energy of both the orbitals was increased as a function of solvent polarity. The energy of HOMO was highly increased by 0.124 eV, while the energy of LUMO was increased to lesser extent by 0.026 eV (Table S6). For the dye **TDS2**, energy of HOMO was increased by 0.058 eV and that of LUMO was lowered by 0.051 eV as the solvent polarity increased. Normally, all these dyes have shown decrease in the band gap (HOMO–LUMO) as polarity of the solvent increased.

Molecular orbital plots for these dyes are shown in Figs. 9 and 10. From the pictorial diagram, it was found that HOMO and LUMO orbitals of the dyes are fully delocalized on the donor triphenylamine moiety, phenyl ring and acceptor cyano or carbethoxy group through π -bond conjugation. Electron densities in the HO-MOs of all these four dyes were largely located on donor triphenylamine moiety, and electron densities on the LUMOs were found localized on acceptor through π -bridge. The excitation from HOMO to LUMO mostly consists of charge transfer from triphenylamine moiety on the donor to the acceptor end. Energy gap of HOMO \rightarrow LUMO explains the charge transfer interactions within the dye, which also influences non-linear properties of dyes. Fig. 9 contains FMO of dye TMS1 in the excited state, which shows that electron densities are located on the donor triphenylamine moiety in the HOMO and these electron densities were fully transferred on the acceptor moiety in the LUMO.

3.7. Static second-order nonlinear optical (NLO) properties

Push-pull chromophores are likely to have good non-linear properties and their first hyperpolarizability (β_0) value can be enhanced due to their relative orientation. Thus, push-pull chromophores have been studied due to their good linear and nonlinear optical properties.

Second-order NLO properties of the triphenylamine $D-\pi-A$ and $A-\pi-D-\pi-A$ chromophores were calculated by using density functional theory (DFT). The static first hyperpolarizability (β_0) and its related properties for dyes **TMS1**, **TMS2**, **TDS1** and **TDS2** were calculated using B3LYP/6-31G(d) on the basis of the finite field approach [15].

The computed β -tensors are given in Table 5. The computed first hyperpolarizability β_{0} , of dyes was found to be ranging from 196.45, 222.18, 216.24 and 221.65 \times 10⁻³⁰ e.s.u. for dyes **TMS1**, **TMS2**, **TDS1** and **TDS2** respectively. These values are greater than urea (0.38 \times

436



Fig. 9. Frontier molecular orbitals of dye TMS1 in the ground and excited state.



Fig. 10. Frontier molecular orbitals of dyes TMS2, TDS1 and TDS2 in the ground state.

 10^{-30} e.s.u.) by 516, 583, 568 and 582 times. As expected, these dyes have shown a large hyperpolarizability, suggesting considerable charge transfer characteristics of the first excited state which is further supported by the large difference in the dipole moments

between the ground and excited states from the solvatochromism studies. These dyes can be used as a promising candidate in the field of non-linear optics.

Table 5

Static first hyperpolarizability and its β -components of dyes **TMS1**, **TMS2**, **TDS1** and **TDS2** (all values in e.s.u.).

β -tensors	TMS1	TMS2	TDS1	TDS2
β_{xxx}	-1.03×10^{-28}	2.30×10^{-28}	1.25×10^{-29}	$-5.76 imes 10^{-29}$
β_{xxy}	-2.86×10^{-30}	$-2.15 imes 10^{-29}$	-2.04×10^{-28}	$-2.04 imes 10^{-28}$
β_{xyy}	8.06×10^{-31}	$-7.46 imes 10^{-30}$	-2.52×10^{-29}	$2.14 imes 10^{-29}$
β_{yyy}	1.10×10^{-31}	6.67×10^{-30}	$-1.23 imes 10^{-29}$	$-1.58 imes 10^{-29}$
β_{xxz}	-8.26×10^{-29}	-5.66×10^{-32}	-1.26×10^{-29}	$-4.04 imes 10^{-30}$
β_{yyz}	9.52×10^{-31}	-3.95×10^{-31}	-2.58×10^{-30}	$-3.38 imes 10^{-30}$
β_{xzz}	-5.72×10^{-29}	-5.75×10^{-31}	-4.18×10^{-31}	$5.76 imes 10^{-31}$
β_{yzz}	$1.52 imes 10^{-30}$	-6.21×10^{-32}	9.22×10^{-31}	$1.32 imes 10^{-30}$
β_{zzz}	-3.36×10^{-29}	$-5.00 imes 10^{-32}$	6.13×10^{-31}	$-4.37 imes 10^{-31}$
β_{o}	196.45×10^{-30}	222.18×10^{-30}	216.24×10^{-30}	221.65×10^{-30}

4. Conclusion

In this paper, we have developed push–pull chromophores of $A-\pi-D$ and $A-\pi-D-\pi-A$ types containing triphenylamine as electron donor and electron withdrawing cyano/carbethoxy moieties. Triphenylamine moiety was introduced to the make the system non-planar. These synthesized fluorophores were confirmed by FT-IR, ¹H NMR and Mass spectral analysis. The optical properties of these dyes were studied in solvents of different polarities. The resultant solvatochromism data showed that these dyes have a high Stokes shift ranging from 2141 to 6354 cm⁻¹ which increases with the solvent polarity. Solvatochromism studies have shown large increase in the dipole moment in the first excited

state suggesting a pronounced charge delocalization in the first excited state. From the fluorescence properties, it was concluded that the electronic coupling between donor and acceptor was sufficient to allow the intramolecular charge transfer in these molecules which is responsible for the Stokes shift increments in response to the increase in the solvent polarity. The quantum yield was observed to be low in polar solvent whereas in non-polar solvent they exhibit comparative higher quantum yield.

Triphenylamine dyes were optimized at B3LYP/6-31G(d) level in the ground state geometry. The geometrical parameter and charge distribution analysis were discussed. Vertical excitations and emissions were computed and compared with the experimental values. The computed absorption and emission wavelengths are in good agreement with the experimental results. These dyes have shown a prominent absorption at the longer wavelength due to HOMO \rightarrow LUMO transition with high oscillator strength. Frontier molecular orbital plots have displayed that majority of electron density resided on the chromophores and mostly on donor triphenylamine moiety. First hyperpolarizability was calculated at B3LYP/6-31G(d) level using finite field approach and found that these dyes possess a large second-order nonlinear property and this is mainly due to the strong donor- π -acceptor conjugation which is attributed to the excited state intramolecular charge transfer. The TGA results show that they possess a good thermal stability.

In summary, this paper describes the synthesis, characterization, photo-physical, thermal properties and DFT study of these twisted push—pull styryl dyes. In conclusion, these dyes can be used promising candidate for various applications in nonlinear optics (NLO), electronic and photonic devices, and organic light – emitting diodes.

Acknowledgements

Vinod Gupta is greatly thankful to University Grant Commission (UGC), New Delhi, India for providing financial support. Abhinav Tathe is grateful to UGC for research support under Major Research Project as well as UGC-CSIR fellowship. Vikas Padalkar is thankful for postdoctoral fellowship from the Principal Scientific Adviser (PSA), Govt. of India. Prashant Umape is thankful to UGC-CAS for providing research fellowship under Special Assistance Programme (SAP).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2012.12.024.

References

- Lai RY, Fabrizio EF, Lu L, Jenekhe SA, Bard AJ. Synthesis cyclic voltammetric studies and electrogenerated chemiluminescence of a new donor acceptor molecule: 3,7-[bis[4-phenyl-2-quinolyl]]-10-methylphenothiazine. J Am Chem Soc 2001;123:9112–8.
- [2] (a) Tang CW, VanSlyke SA, Chen CH. Electroluminescence of doped organic thin films. J Appl Phys 1989;65:3610–6;

(b) Chen CH, Shi J, Tang CW, Klubek KP. Recent developments in the synthesis of red dopants for Alq₃ hosted electroluminescence. Thin Solid Films 2000; 363:327–31;

(c) Tao XT, Miyata S, Sasabe H, Zhang GJ, Wada T, Jiang MH. Efficient organic red electroluminescent device with narrow emission peak. Appl Phys Lett 2001;78:279–81;

(d) Zhang XH, Chen BJ, Lin XQ, Wong OY, Lee CS, Kwong HL, et al. A new family of red dopants based on chromene-containing compounds for organic electroluminescent devices. Chem Mater 2001;13:1565–9;

(e) Li J, Liu D, Hong ZR, Tong SW, Wang PF, Ma CW, et al. A new family of isophorone-based dopants for red organic electroluminescent devices. Chem Mater 2003;15:1486–90.

- [3] (a) Pacansky J, Waltman RJ. X-ray photoelectron and optical absorption spectroscopic studies on the dye chlorodiane blue, used as a carrier generation molecule in organic photoconductors. J Am Chem Soc 1992;114:5813–9;
 (b) Law KY. Organic photoconductive materials: recent trends and developments. Chem Rev 1993;93:449–86;
 (c) Lambert C, Schelter J, Fiebig T, Mank D, Trifonov A. Photoinduced charge transfer processes along triarylamine redox cascades. J Am Chem Soc 2005; 127:10600–10.
- [4] (a) Reinhardt BA, Brott LL, Clarson SJ, Dillard AG, Bhatt JC, Kannan R, et al. Highly active two-photon dyes: design, synthesis, and characterization toward application. Chem Mater 1998;10:1863–74;
 (b) Staub K, Levina GA, Barlow S, Kowalczyk TC, Lackritz HS, Barzoukas M, et al. Synthesis and stability studies of conformationally locked 4-(diarylamino)aryl- and 4-(dialkylamino)phenyl-substituted second-order nonlinear

optical polyene chromophores. J Mater Chem 2003;13:825–33; (c) Albota M, Beljonne D, Bredas JL, Ehrlich JE, Fu JY, Heikal AA, et al. Design of organic molecules with large two-photon absorption cross sections. Science 1998:281:1653–6:

(d) Abbotto A, Beverina L, Bozio R, Facchetti A, Ferrante C, Pagani GA, et al. Novel heteroaromatic-based multi-branched dyes with enhanced two-photon absorption activity. Chem Commun 2003:2144–5.

[5] (a) Song Y, Di C, Yang X, Li S, Xu W, Liu Y, et al. A cyclic triphenylamine dimer for organic field-effect transistors with high performance. J Am Chem Soc 2006;128:15940–1;

(b) Tsai J, Chueh C, Lai M, Wang C, Chen W, Ko B, et al. Synthesis of new indolocarbazole-acceptor alternating conjugated copolymers and their applications to thin film transistors and photovoltaic cells. Macromolecules 2009;42:1897–905;

(c) Wang C, Dong H, Hu W, Liu Y, Zhu D. Semiconducting π -conjugated systems in field-effect transistors: a material Odyssey of organic electronics. Chem Rev 2012;112:2208–67.

 [6] (a) Garcia-Moreno I, Costela A, Martin V, Pintado-Sierra M, Sastre R. Materials for a reliable solid-state dye laser at the red spectral edge. Adv Funct Mater 2009;19:2547–52;
 (b) Furumi S, Tamaoki N. Glass-forming cholesteric liquid crystal oligomers for

(b) rating of analysis of assessment of the constraint of the cons

efficiency Förster resonance energy transfer in solid-state dye sensitized solar cells. Nano Lett 2010;10:2387–94.

- [7] (a) Wong MS, Li ZH, Tao Y, D'Iorio M. Synthesis and functional properties of donor-acceptor π-conjugated oligomers. Chem Mater 2003;15:1198–203;
 (b) Loi MA, Denk P, Hoppe H, Neugebauer H, Winder C, Meissner D, et al. Long-lived photoinduced charge separation for solar cell applications in phthalocyanine–fulleropyrrolidine dyad thin films. J Mater Chem 2003;13:700–4.
- [8] Jiao GS, Thoresen LH, Burgess K. Fluorescent, through-bond energy transfer cassettes for labeling multiple biological molecules in one experiment. J Am Chem Soc 2003;125:14668–9.
- [9] (a) Li YW, Guo Q, Li ZF, Pei JN, Tian WJ. Solution processable D–A small molecules for bulk-heterojunction solar cells. Energy Environ Sci 2010;3: 1427–36;

(b) Walker B, Kim C, Nguyen TQ. Small molecule solution-processed bulk heterojunction solar cells. Chem Mater 2011;23:470–82.

 [10] (a) Shirota Y. Organic materials for electronic and optoelectronic devices. J Mater Chem 2000;31:1–25;
 (b) Roquet S, Cravino A, Leriche P, Alévêque O, Frère P, Roncali J. Triphenyl-

amine-thienylenevino A, teriche P, Aleveque O, Frete P, Kohcali J, Thiphenylamine-thienylenevinylene hybrid systems with internal charge transfer as donor materials for heterojunction solar cells. J Am Chem Soc 2006;128: 3459–66;

(c) Ning ZJ, Tian H. Triarylamine: a promising core unit for efficient photovoltaic materials. Chem Commun 2009;37:5483–95.

[11] (a) Thomas KRJ, Hsu Y-C, Lin JT, Lee K-M, Ho K-C, Lai C-H, et al. 2,3-Disubstituted thiophene-based organic dyes for solar cells. Chem Mater 2008;20:1830–40;

(b) Tian H-N, Yang X-C, Pan J-X, Chen R-K, Liu M, Zhang Q-Y, et al. A triphenylamine dye model for the study of intramolecular energy transfer and charge transfer in dye-sensitized solar cells. Adv Funct Mater 2008;18: 3461–8;

(c) Liu H, Lin HW, Wu C-C, Chou S-H, Chen S-H. Organic dyes containing coplanar diphenyl-substituted dithienosilole core for efficient dye-sensitized solar cells. J Org Chem 2010;75:4778–85.

[12] (a) Kuwabara Y, Ogawa H, Inada H, Noma N, Shirota Y. Thermally stable multilayered organic electroluminescent devices using novel starburst molecules, 4,4',4"-tri(N-carbazolyl) triphenylamine (TCTA) and 4,4',4"-Tris(3methylphenylphenylamino)triphenylamine (*m*-MTDATA), as hole-transport materials. Adv Mater 1994;6:677–9;

(b) Song Y, Di C, Yang X, Li S, Xu W, Liu Y, et al. Cyclic triphenylamine dimer for organic field-effect transistors with high performance. J Am Chem Soc 2006;128:15940–1;

(c) Tao YT, Wang Q, Ao L, Zhong C, Yang CL, Qin JG, et al. Highly efficient phosphorescent organic light-emitting diodes hosted by 1,2,4-triazole-cored triphenylamine derivatives: relationship between structure and optoelectronic properties. J Phys Chem C 2010;114:601–9;

(d) Lambert C, Schelter J, Fiebig T, Mank D, Trifonov A. Photoinduced charge transfer processes along triarylamine redox cascades. J Am Chem Soc 2005; 127:10600–10;

(e) Faccini M, Balakrishnan M, Diemeer MBJ, Hu Z, Clays K, Asselberghs I, et al. Enhanced poling efficiency in highly thermal and photostable nonlinear optical chromophores. J Mater Chem 2008;18:2141–9;

(f) Cravino A, Leriche P, Aleveque O, Roquet S, Roncali J. Light-emitting organic solar cells based on a 3D conjugated system with internal charge transfer. Adv Mater 2006;18:3033–7;

(g) He C, He QG, Yi YP, Wu GL, Bai FL, Shuai ZG, et al. Improving the efficiency of solution processable organic photovoltaic devices by a star-shaped molecular geometry. J Mater Chem 2008;18:4085–90;

(h) Wu G, Zhao G, He C, Zhang J, He Q, Chen X, et al. Synthesis and photovoltaic properties of a star-shaped molecule with triphenylamine as core and benzo [1,2,5]thiadiazol vinylene as arms. Sol Energy Mater Sol Cells 2009;93:108–13; (i) Zhao G, Wu G, He C, Bai F, Xi H, Zhang H, et al. Solution-processable multi-armed organic molecules containing triphenylamine and DCM moieties: synthesis and photovoltaic properties. J Phys Chem C 2009;113:2636–42;

(j) Horiuchi T, Miura H, Sumioka K, Uchida S. J Am Chem Soc 2004;126: 12218–9;

(k) Ito S, Zakeeruddin S, Humphry-Baker R, Liska P, Charvet R, Comte P, et al. High-efficiency organic-dye-sensitized solar cells controlled by nanocrystalline-TiO₂ electrode thickness. Adv Mater 2006;18:1202–5;

(l) Ito S, Miura H, Uchida S, Takata M, Sumioka K, Liska P, et al. High-conversion-efficiency organic dye-sensitized solar cells with a novel indoline dye. Chem Commun 2008:5194–6;

(m) Qin P, Yang X, Chen R, Sun LC, Marinado T, Edvinsson T, et al. Influence of π -conjugation units in organic dyes for dye-sensitized solar cells. J Phys Chem C 2007;111:1853–60;

(n) Hagberg DP, Marinado T, Karlsson KM, Nonomura K, Qin P, Boschloo G, et al. Tuning the HOMO and LUMO energy levels of organic chromophores for dye sensitized solar cells. J Org Chem 2007;72:9550–6;

(o) Leriche P, Frere P, Cravino A, Aleveque O, Roncali J. Molecular engineering of the internal charge transfer in thiophene-triphenylamine hybrid π -conjugated systems. J Org Chem 2007;72:8332–6.

[13] Gupta VD, Padalkar VS, Phatangare KR, Patil VS, Umape PG, Sekar N. The synthesis and photo-physical properties of extended styryl fluorescent derivatives of N-ethyl carbazole. Dyes Pigm 2011;88:378–84.

[14] (a) Wu IY, Lin JT, Tao YT, Balasubramaniam E, Su YZ, Ko CW. Diphenylthienylamine-based star-shaped molecules for electroluminescence applications. Chem Mater 2001;13:2626–31;

(b) Katsuma K, Shirota Y. A novel class of π -electron dendrimers for thermally and morphologically stable amorphous molecular materials. Adv Mater 1998; 10:223–6;

(c) Shirota Y. Photo- and electroactive amorphous molecular materialsmolecular design, syntheses, reactions, properties, and applications. J Mater Chem 2005;15:75–93;

(d) Cravino A, Leriche P, Aleveque O, Roquet S, Roncali J. Light-emitting organic solar cells based on a 3D conjugated system with internal charge transfer. Adv Mater 2006;18:3033–7;

(e) Yang Y, Zhou Y, He Q, He C, Yang C, Bai F, et al. Solution-processable redemission organic materials containing triphenylamine and benzothiodiazole units: synthesis and applications in organic light-emitting diodes. J Phys Chem B 2009;113:7745–52.

[15] Vidya S, Ravikumar C, Hubert JI, Kumaradhas P, Devipriyac B, Raju K. Vibrational spectra and structural studies of nonlinear optical crystal ammonium D, L-tartrate: a density functional theoretical Approach. J Raman Spectrosc 2011;42:676–84.

- [16] Jose J, Burgess K. Syntheses and properties of water-soluble Nile red derivatives. J Org Chem 2006;71:7835–9.
- [17] Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09 revision C01. Wallingford CT: Gaussian Inc; 2010.
- [18] Treutler O, Ahlrichs R. Efficient molecular numerical integration schemes. J Chem Phys 1995;102:346–54.
- [19] Becke AD. A new mixing of Hartree–Fock and local density-functional theories. J Chem Phys 1993;98:1372–7.
- [20] Lee C, Yang W, Parr RG. Development of the Colle–Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 1988;37:785–9.
- [21] (a) Hehre WJ, Radom L, Schleyer PvR, Pople J. Ab initio molecular orbital theory. New York: Wiley; 1986;
 (b) Bauernschmitt R, Ahlrichs R. Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory. Chem Phys Lett 1996;256:454–64;
 (c) Furche F, Rappaport D. Density functional theory for excited states: equilibrium structure and electronic spectra. In: Olivucci M, editor. Computational Photochemistry, vol. 16. Amsterdam: Elsevier; 2005 [Chapter 3].
- [22] Valeur B. Molecular fluorescence: principles and applications. Weinheim: Wiley-VCH Verlag; 2001.
- [23] (a) Cossi M, Barone V, Cammi R, Tomasi J. Ab initio study of solvated molecules: a new implementation of the polarizable continuum model. Chem Phys Lett 1996;255:327–35;
 (b) Tomasi J, Mennucci B, Cammi R. Quantum mechanical continuum solva-

(b) Tomasi J, Mennucci B, Cammi R. Quantum mechanical continuum solvation models. Chem Rev 2005;105:2999–3094.

- [24] Lee HJ, Sohn J, Hwang J, Park SY. Triphenylamine-cored bifunctional organic molecules for two-photon absorption and photorefraction. Chem Mater 2004; 16:456–65.
- [25] Mowry DT. New compounds: 1-phenylethylidenemalonitrile. J Am Chem Soc 1943;65:991.
- [26] (a) Hoyle VA. Preparation of disperse methine dye compounds; 1975. US3917604A;

(b) Diebert CE, Fisher JG. Methine textile dyes; 1975. GB1412324A;
(c) Lartia R, Allain C, Bordeau G, Schmidt F, Fiorini-Debuisschert C, Charra F, et al. Synthetic strategies to derivatizable triphenylamines displaying high two-photon absorption. J Org Chem 2008;73:1732–44.

- [27] Detert H, Schmitt V. Acidochromism of stilbenoid chromophores with a paminoaniline centre. J Phys Org Chem 2006;19:603-7.
- [28] Lakowicz JR. Principles of fluorescence spectroscopy. 2nd ed. New York: Kluwer Academic; 1999.
- [29] (a) Giles CH, Duff DG, Sinclair RS. The relationship between dye structure and fastness properties. Rev Prog Color Relat Top 1982;12:58-65;
 (b) Chunlong Z, Nianchun M, Liyun L. An investigation of the thermal stability of some yellow and red azo pigments. Dyes Pigm 1993;23:13-23;
 (c) Das S, Basu R, Minch M, Nandy P. Heat-induced structural changes in merocyanine dyes: X-ray and thermal studies. Dyes Pigm 1995;29:191-201;
 (d) Kim YD, Kim JP, Kwon OS, Cho IH. The synthesis and application of thermally stable dyes for ink-jet printed LCD color filters. Dyes Pigm 2009; 81:45-52.
- [30] Dennington R, Keith T, Millam J. Gaussview version 5.0. Shawnee Mission KS: Semichem Inc; 2009.