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### 1. Abstract

A set of three triphenylamine-bithiophene based Donor-Acceptor (D-A) molecules viz. **TPT**, **TPT-Ben** and **TPT-Ac** were designed, synthesized and studied for their photophysical properties. Systematic density functional theory (DFT) calculations have been performed on the molecules to gain insights into the structural, electronic and optical properties. The nanosecond transient absorption spectra showed broad absorption due to the presence of triphenylamine radical cation with an average time constant of 3.5  $\mu$ s. The molecules were found to emit in the Blue, Green and Orange-Red regions of the visible spectrum due to the differences in their Stokes shift values. A 3:2:1 mixture of **TPT**, **TPT-Ben** and **TPT-Ac** gave white light emission with a colour coordinate of (0.32, 0.36) even at an  $\mu$ M level concentration in both solution state (DMSO) as well as in the solid state (0.33, 0.37).

Keywords: Triphenylamine, Thiophene, Donor-acceptor, Stokes shift, White light emission.

### 2. Introduction

Developing red, green and blue (RGB) emitters with high luminescence efficiency is the most important aspect for generating white light emission. Different methods used so far for achieving white light emission include, mixing RGB emitters, [1,2] synthesizing white light emitting polymers with RGB monomers,[3] and using a single molecule as emitter with the aid of properties like ESIPT (excited state intramolecular proton transfer).[4,7] But still developing an efficient white organic light emission is an active area of research, mainly due to its applications in display and lighting. Donor-Acceptor systems based on triphenylamine have gained considerable interest over the period of time mainly due to their inherent properties like low-oxidation potential, propeller like geometry etc. They are widely used for applications towards 3D microfabrication, [8,9] two photon bioimaging, [10-12] organic photovoltaics, [13-15] optical data storage [16,17] and as hole transporting materials. [18-24] Besides this, another class of molecules that are extensively studied for their better photophysical properties are conjugated oligothiophenes. [25, 26] Though conjugated thiophenes are attractive for a wide range of applications including conductive layers in material applications, [27] photoactive layers in photovoltaics, [28] and in anti-static packaging, [29] their insolubility in organic

solvents limits their potential usage. [30] Herein, we report a set of three molecules, based on triphenylamine-bithiophene conjugate that proved to circumvent the problem of solubility of the latter without compromising on the electronic properties of both the components. The synthetic route for the construction of the molecules is depicted in Scheme 1. The basic molecule **TPT** was synthesised initially and was derivatised at its third position in order to get **TPT-Ben** and **TPT-Ac** (Figure 1). The 5' position of bithiophene in **TPT** was particularly chosen since this will mask the most reactive site of the thiophene moiety, subsequently making the molecule chemically and photochemically inert. [30]

In our set of systems, in the case of **TPT**, triphenylamine acted as a donor and bithiophene part served as an acceptor. In **TPT-Ben** the dibenzothiophene served the role of a second donor, whereas the acetophenone moiety acted as an acceptor in **TPT-Ac** (Figure 1). The selection of the substituents were made according to the electron donor and accepting property of the moieties.

The photophysical studies of the molecules indicated that, substitution on **TPT** with either donor or acceptor group would result in a red shift in its emission maxima. It was observed that while **TPT** showed emission in the blue region, it got shifted to the green region upon substitution with a donor unit (**TPT-Ben**), while the acceptor appended **TPT-Ac** showed a shift towards the red region of the visible light spectrum. Due to this observation of primary colour generation we examined the emission spectrum of a mixture of all the three compounds in solution state (in DMSO) at micromolar ( $\mu$ M) concentrations as well as in the solid state using PMMA matrix. The results showed that, at an optimum composition of 3:2:1 ratio of **TPT:TPT-Ben:TPT-Ac** (weight/ weight), the mixture gave rise to white light emission with a CIE colour coordinate of (0.32, 0.36) in the solution state and (0.33, 0.37) in the solid state.



Fig. 1. Triphenylamine-bithiophene derivatives a) TPT, b)TPT-Ben, c) TPT-Ac.

### 3. Experimental Section

#### 3.1 Methods

All the solvents were purchased from Merck Millipore. Boronic acids and 4bromotriphenylamine were purchased from Sigma Aldrich. The catalyst  $Pd(PPh_3)_4$  was purchased from Alfa Aesar and used without further purification. Reactions were carried out under inert atmosphere of argon in oven dried glasswares. Progress of the reaction was monitored using Silica Gel TLC plates (Merck-Millipore, 60 F254) and UV detection (254 nm and 365 nm). Column chromatography was done using activated aluminium oxide.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using Bruker NMR spectrometer (AV500) with working frequency of 500 MHz for <sup>1</sup>H NMR and 125 MHz for <sup>13</sup>C NMR. The chemical shifts were reported in  $\delta$  (ppm) relative to TMS as internal standard. Mass spectra were recorded using ESI/ HRMS at 60000 resolution (Thermo Scientific Exactive). Cyclic voltammetry experiments were carried out with a BAS 50W voltametric analyzer using three electrode cell assemblies. Pt wires were used as counter electrodes and quasi Ag/Ag<sup>+</sup> wires as reference electrode. Measurements were carried out with tetrabutylammonium hexafluorophosphate as a supporting electrolyte at a scan rate of 100 mVs<sup>-1</sup>. Oxidation potentials were determined using ferrocene as internal standard.

#### 3.2. General Procedure for the Suzuki-Miyaura Coupling [31]

The boronic acid (1 equivalent) and bromo compound (1 equivalent) were taken in reaction vessel along with  $Pd(PPh_3)_4$ . THF along with 2N Na<sub>2</sub>CO<sub>3</sub> dissolved in water (2:1) was added to

the reaction mixture. The reaction mixture was degassed with argon and allowed to stir at 65-70  $^{\circ}$ C for required time.

#### 3.2.1 Synthesis of 4-(2,2'-bithiophen-5-yl)-N,N diphenylaniline (TPT) [32]

4-bromotriphenylamine (500 mg, 0.002 mol) and 2,2'-bithiophen-5-ylboronic acid (0.3718 ml, 0.002 mol) were added to the Schlenk tube along with the  $Pd(PPh_3)_4$  as the catalyst. THF (2 mL) along with 2N Na<sub>2</sub>CO<sub>3</sub> (1 mL) dissolved in water (2:1 ratio) was added to the reaction mixture. The reaction mixture was degassed with argon and allowed to stir at 65-70 °C for 12 h. The extent of the reaction was monitored by the TLC and on completion, the reaction mixture was evaporated and the residue was subjected to column chromatography on activated aluminium oxide using hexane as eluent to afford the product in moderate yield.

#### **3.2.2 Spectral characterization of TPT**

Yield: 63% as a yellow crystal.

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.45 (d, 2H, *J* = 9 Hz), 7.29 (t, *J* = 7.5 Hz, 4H), (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 3.5 Hz, 1H), 7.12 (t, *J* = 5 Hz, 6H), 7.07-7.01 (m, 5H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 147.4, 147.3, 143.1, 137.6, 135.8, 129.3, 128.1, 127.8, 126.4, 124.6, 124.5, 124.2, 123.6, 123.4, 123.2, 122.8.

Mass Spectrometric Analysis: HRMS (ESI) m/z calculated for C<sub>26</sub>H<sub>19</sub>NS<sub>2</sub>, (M+H)<sup>+</sup>: 410.1037

Found: 410.1024

#### 3.2.3 Synthesis of 4-(5'-bromo-2,2'-bithiophen-5-yl)-N,N-diphenylaniline (TPT-Br) [32]

In the absence of light, a solution of NBS (220 mg, 0.00122 mol) in DMF (4 mL) was added drop wise to a solution of **TPT** (500 mg, 0.00122 mol) in DMF (10 mL) and cooled to 0 °C. The reaction was allowed to be stirred for 2 h at this temperature followed by 1 h at room temperature. After completion, 1 M aqueous solution of HCl was added to the reaction mixture (30 mL) and the product was extracted with dichloromethane (100 mL) and the resulting organic layer was washed with water (4 x 300 mL) and dried over  $Na_2SO_3$  and concentrated. The product was purified by column chromatography on activated aluminium oxide using hexane as the eluent.

## 3.2.4 Synthesis of 4-(5'-(dibenzo[b,d]thiophen-2-yl)-2,2'-bithiophen-5-yl)-N diphenylaniline (TPT-Ben)

4-(5<sup>-</sup>bromo-2,2<sup>-</sup>bithiophen-5-yl)-N,N-diphenylaniline and 4-dibenzothienyl boronic acid were added in a three necked round bottom flask along with the  $Pd(PPh_3)_4$  as the catalyst. The mixture was degassed with argon. THF along with 2N Na<sub>2</sub>CO<sub>3</sub> at a 2:1 ratio was added to the reaction mixture, again degassed with argon and allowed to stir at 65-70 °C for 12 h. The reaction mixture was evaporated and the residue was subjected to column chromatography on silica using ethyl acetate /hexane (1:4) mixture as eluent to afford the product in good yield.

#### 3.2.5 Spectral Characters of TPT-Ben

Yield: 73% as green solid.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.218-8.2 (m, 1H), 8.15 (d, J = 8Hz, 1H), 7.92-7.90 (m, 1H), 7.70 (d, J = 7 Hz, 1H), 7.58 (d, J = 3.5 Hz, 1H), 7.55 (d, J = 8 Hz, 1H), 7.527-7.492 (m, 4H), 7.30 (d, J = 8Hz, 4H), 7.23 (d, J = 3.5Hz, 1H), 7.18 (d, J = 3.5Hz, 1H), 7.15 (d, J = 8Hz, 4H), 7.10- 7.05 (m, 4H).

<sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>): δ (ppm) 147.5, 131.8, 130.9, 129.4, 128.0, 127.0, 126.4, 125.0, 124.9, 124.6, 123.6, 123.2, 121.8.

Mass Spectrometric Analysis: HRMS (ESI) m/z calculated for C<sub>38</sub>H<sub>25</sub>NS<sub>3</sub>, (M+H)<sup>+</sup>: 592.1227

Found: 592.1228

# **3.2.6** Synthesis of the compound 1-(4-(5'-(4-(diphenylamino)phenyl)-2,2'-bithiophen-5-yl)phenyl)ethanone (TPT-Ac)

4-(5<sup>'</sup>-bromo-2,2<sup>'</sup>-bithiophen-5-yl)-N,N-diphenylaniline and 4-acetylphenylboronic acid were added in a three necked round bottom flask along with the Pd(PPh<sub>3</sub>)<sub>4</sub> as the catalyst. The mixture was degassed with argon. THF along with 2N Na<sub>2</sub>CO<sub>3</sub> at a 2:1 ratio was added to the reaction mixture, again degassed with argon and allowed to stir at 65-70 °C for 12 h. The reaction mixture was evaporated and the residue was subjected to column chromatography on silica using ethyl acetate/hexane (1:5) mixture as eluent to afford the product in good yield.

#### **3.2.7 Spectral characterization of TPT-Ac**

Yield: 70% as orange solid.

<sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ: 7.98 (d, J = 8.5 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 5 Hz, 2H), 7.37 (d, J = 3.5 Hz, 1H), 7.30 (d, J = 7.5 Hz, 4H), 7.19 (d, J = 3.5 Hz, 3H), 7.20-7.13 (m, 5H), 7.09-7.05 (m, 4H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ: 197.3, 147.6, 147.4, 143.8, 141.1, 138.7, 138.5, 135.6, 135.2, 129.4, 129.2, 129.0, 127.7, 127.5, 126.6, 126.4, 125.5, 125.2, 125.0, 124.6, 124.4, 123.5, 123.3, 122.9, 26.6.

Mass Spectrometric Analysis: HRMS (ESI) m/z calculated for C<sub>34</sub>H<sub>25</sub>NOS<sub>2</sub>, (M+): 527.1377

Found: 527.1366

#### **3.3. Instrumentation**

Absorption spectra were recorded using a Shimadzu UV-2600 UV-Visible spectrophotometer. The optical diffuse reflectance spectra were measured for solid samples using the above mentioned spectrophotometer equipped with an integrating sphere. BaSO<sub>4</sub> was used as the reference material, and the solid samples were ground well before the measurement. The absorption (a/S) data were calculated from the reflectance spectra using the Kubelka–Munk function:  $\alpha$ /S = (1 - R) 2/2R, where R = reflectance at a given wavelength,  $\alpha$  = absorption coefficient, and S = scattering coefficient (practically wavelength independent when the particle size is larger than 5 mm). Steady-state fluorescence experiments were performed using FluoroLog-322 (Horiba) which was equipped with a 450 W Xe arc lamp by using optically dilute solutions. The fluorescence quantum yields in various solvents were determined by the relative method employing an optically matched solution of quinine sulphate in 0.1N sulphuric acid as the reference ( $\Phi_R = 0.54$ ). The following equation (1) was used for calculating the quantum yield, [33]

$$\Phi_{\rm S} = \frac{\rm Abs_R}{\rm Abs_S} \times \frac{\rm Area_S}{\rm Area_R} \times \frac{\rm nS^2}{\rm nR^2} \times \Phi_{\rm R}....(2)$$

where the subscript R and S refer to the reference and samples respectively. Abs, Area and n are the absorbance at the excitation wavelength, area under the fluorescence spectrum and refractive index of the solvent respectively. Time-resolved fluorescence spectra and lifetime experiments were performed by using an IBH picosecond single photon counting system employing the 375 nm nano LED as excitation sources and a Hamamatsu C4878-02 microchannel plate (MCP) detector. Decay in the fluorescence intensity (I) with time (t) was fitted either by a double/triple-exponential function:

 $I = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2}.$ (3)  $I = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau 2} + A_3 e^{-t/\tau 3}.$ (4)

where  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  are the lifetimes of different species, and  $A_1$ ,  $A_2$ , and  $A_3$  are their respective amplitudes. The weighted mean lifetime ( $\langle \tau \rangle$ ) was calculated according to equation (5):

The quality of the fits was checked by examining the residual distribution and the  $\chi^2$  value. The solid state samples were recorded with the front face mode. All the experiments were conducted at room temperature.

### 4. Results and discussions

#### 4.1. Synthesis of TPT, TPT-Ben, and TPT-Ac

**TPT** was synthesized from 4-bromotriphenylamine and 2,2'-bithiophen-5-ylboronic acid using THF/water system at 65-70 °C for 12 h. It was then subjected to a controlled NBS bromination to get **TPT-Br**. **TPT-Ben** was synthesized from **TPT-Br** and 4-dibenzothienyl boronic acid whereas **TPT-Ac** was synthesized from **TPT-Br** and 4-acetylphenylboronic acid using the same conditions employed for synthesis of TPT. (Scheme 1) All the compounds were characterized by <sup>1</sup>H and <sup>13</sup>C NMR and were further confirmed by mass spectrometric analyses.



**Scheme 1**. The synthetic route for the preparation of triphenylamine derivatives, **TPT,TPT-Ben**, and **TPT-Ac.** (a) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, THF-Water, 65-70 °C, 12 h, (b) N- bromo succinimide (recrystallized), 0 °C, DMF, dark, (c) Pd(PPh<sub>3</sub>)<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, THF-Water, 65-70 °C, 12 h.



#### 4.2. Photophysical Characterization



Figure 2 depicts the absorption and emission profiles of **TPT**, **TPT-Ben** and **TPT-Ac** in DMSO. **TPT** showed an absorption maximum at 383 nm while **TPT-Ben** and **TPT-Ac** exhibited the same at 411 nm and 425 nm respectively. The high energy absorption band at -300 nm can be attributed to the  $n-\pi^*$  transition of the triphenylamine core [34] and the broad structure-less

absorption can be assigned to the CT band. [32] The molar extinction coefficients ( $\varepsilon$ ) of the low energy bands of the three molecules were calculated as 38,000 M<sup>-1</sup> cm<sup>-1</sup>, 48,000 M<sup>-1</sup> cm<sup>-1</sup>, 20,000 M<sup>-1</sup> cm<sup>-1</sup> for **TPT**, **TPT-Ben**, **TPT-Ac** respectively (Supporting information, Figure S10). Studies indicated that, the dependence of the absorption spectra of the molecules on the polarity of the different solvents used for the experiment like toluene, THF, ethyl acetate, 1, 4 dioxane, methanol, acetonitrile and DMSO are negligible ( $\leq 11$  nm) (Supporting information, Figure S10). The molecules **TPT**, **TPT-Ben and TPT-Ac** showed emission maxima at 481 nm (blue), 541 nm (green) and at 617 nm (orange-red) respectively. Unlike solvent independent absorption profile, all the three molecules showed an emission maximum that are greatly influenced by the polarity of the solvent. In DMSO, the Stoke shift values for **TPT**, **TPT-Ben** and **TPT-Ac** were calculated as 5319.64 cm<sup>-1</sup>, 5846.61 cm<sup>-1</sup> and 7321.96 cm<sup>-1</sup> respectively. In figure 3b the Stokes shifts (in wavenumber) are plotted vs. solvent orientation polarizability ( $\Delta f$ ),  $\Delta f = (\varepsilon - 1)/(2\varepsilon + 1)$ - (n<sup>2</sup> -1)/(2n<sup>2</sup> + 1), where  $\varepsilon$  is the dielectric constant and n is the refractive index). [35–37] It shows a nonlinear relationship indicating the presence of an intramolecular charge transfer state in the molecules. [38]



Fig. 3. a) The change in the emission spectra of TPT, TPT-Ben and TPT-Ac with respect to different solvents and their polarity.  $\lambda_{exc}$  TPT = 380 nm, TPT-Ben = 410 nm, TPT-Ac = 420 nm. (b) Relationship between solvent orientation polarizability ( $\Delta f$ ) and Stokes shift (in wavenumber).

The formation of aggregates of the derivatives was observed in the THF/water mixture as shown in supporting information, Figure S12 and S13. In the case of **TPT**, an increase of fluorescence intensity was found with an increase in concentration of water up to 80%. But further increase in the concentration of water decreased the emission intensity tremendously and similar observations were found in the case of **TPT-Ben** also. But in the case of **TPT-Ac** the emission intensity was found to decrease with respect to the concentration of water.

Quantum yield ( $\Phi$ ) of the triphenylamine derivatives **TPT**, **TPT-Ben** and **TPT-Ac** were measured in different solvents and was found to increase with an increase in the solvent polarity. All the three derivatives showed highest quantum yield in DMSO. The fluorescence lifetime of the derivatives were measured in different solvents using time correlated single photon counting spectrometer by exciting at 375 nm using a nano second LED source. The results are depicted in Table 1. The radiative and ( $k_r$ ) non-radiative ( $k_{nr}$ ) rate constants were also calculated using fluorescence lifetime and quantum yield according to the equation 1 and the results are included in Table 1.

$$k_r = \frac{\Phi}{\langle \tau \rangle} k_{nr} = \frac{1}{\langle \tau \rangle} - k_{nr}$$
 (1)

Where the  $k_r$  and  $k_{nr}$  are the radiative and non radiative rate constants respectively,  $\Phi$  is the quantum yield and  $\langle \tau \rangle$  is the fluorescence lifetime.

The PL studies on the molecules were extended to the solid state also. Both the three molecules showed good emission in their solid state also. The solid state spectrum is provided in the supporting information, Figure S14. The solid state excitation and absorption of the molecules were also measured and given in supporting information, Figure S15.

Compound	Solvent	Dielectric Constant E	λ max (Abs) (nm)	λ max (Emis) (nm)	Stokes Shift (cm <sup>-1</sup> )	Φ	τ (ns)	k <sub>r</sub>	k <sub>nr</sub>
ТРТ	Toluene	2.25	380	440	3589	0.14	0.3	0.47	2.9
	Dioxane	2.38	380	437	3432	0.14	0.3	0.47	2.9
	THF	7.58	383	455	4132	0.18	0.5	0.36	1.64

	DMSO	46.7	383	481	5320	0.44	0.9	0.52	0.65
TPT-Ben	Dioxane	2.25	400	476,500	$4508^*$	0.15#	0.6	0.25	1.4
	Toluene	2.38	400	475,503	$4508^*$	0.15#	0.4	0.38	2.13
	THF	7.58	402	506	5113	0.16	0.5	0.32	1.7
TPT-Ac	DMSO	46.7	411	541	5847	0.29	0.5	0.58	1.4
	Dioxane	2.25	417	519	4713	0.16	0.6	0.27	1.4
	Toluene	2.38	418	501,525	4430 <sup>*</sup>	0.13#	0.45	0.29	1.9
	THF	7.58	420	552	5694	0.36	0.9	0.40	0.71
	DMSO	46.7	425	617	7322	0.48	1.5	0.32	0.34

Table 1: Summary of photophysical characterization of the molecules. \* The low energy emission maximum is used for the Stokes shift value calculations. # Two peaks are not separated for QY calculation

#### 4.3. Computational details

Density functional theory (DFT) at the B3LYP/6-31G\* level was carried out to gain a better insight on the nature of the electronic transition and frontier molecular orbital (FMO) distributions. [39] The calculated FMO (frontier molecular orbitals) distributions of model systems are presented in the Figure 4. It is evident from the figure that, in all the model systems studied, the HOMO is delocalized on the TPA (triphenyalmine) and thiophene moieties. On the other hand LUMO is delocalized over thiophene and acceptor units. This feature confirms that, there is an intramolecular charge transfer (ICT) transition between the TPA and end acceptor groups. It is evident from the figure 4 that substituting -Ac moiety on the 5'-postion of bithiophene in **TPT** core leads to a clear charge separated state when compared to substitution by the -Ben unit at the same position. Hence the molecule **TPT-Ac** exhibited red shift in the absorption spectrum when compared to **TPT-Ben**. Comparing the molecules **TPT** and **TPT-Ben**, the degree of charge transfer is almost the same which indicates that charge transfer state of these molecules is primarily determined by the **TPT** and the bithiophene moieties. Moreover, there is no significant effect of the secondary donor (-Ben moiety) unit on the charge transfer state. TD-DFT calculations were also performed to find out the orbitals involved in the dominant excited state electronic transitions and their corresponding energies and oscillator strength. It was found that for the all the molecules the ICT peaks arised from the HOMO to LUMO transition.



**Fig. 4**. Contour plots (isosurface value= 0.025 au) of the HOMO and LUMO levels of the derivatives at B3LYP/6-31G\* level. The hydrogen atoms are omitted for clarity.

The excited and ground state geometries were also computed using B3LYP/6-31G\* level. It was found that **TPT-Ben** and **TPT-Ac** showed a twist on excitation from ground to excited state. They tend to be more planar in their  $S_1$  state. Figure 5 shows the ground and excited state geometries of the molecules. The emission spectrum of **TPT-Ac** was getting broad in polar solvents, this observation may be addressed with this conformation change from ground to excited state. In the case of **TPT-Ac** twist angle between the thiophene and phenylacetlene is  $21.1^{\circ}$ , which become 0° in the exited state. **TPT-Ben** was nearly perpendicular in the ground sate with a twist angle of 87.6°. In the exited state the calculated angle between thiophene and dibenzothiophene was  $37.7^{\circ}$ .



Fig.5. Optimized molecular structures in ground and excited singlet states at B3LYP/6-31G\* level of theory.

#### 4.4. Thermal and electrochemical studies

Thermal stability of a molecule is an important parameter when it comes to DSSC, OLED or any other optoelectronic applications. The temperature stability of the molecules was tested using Thermogravimetric (TG) as well as Differential Scanning Calorimetric (DSC) analysis. Among the three synthesized derivatives **TPT-Ben** showed maximum temperature stability while **TPT** showed the minimum. The decomposition temperature for **TPT-Ben** was found to be 444 °C. **TPT** showed a decomposition temperature of about 268 °C and **TPT- Ac** showed an initial loss at around 420 °C but a complete decomposition occurs only at a temperature near 460 °C. supporting information, Figure S16 and supporting information, Figure S17 shows the TG and DSC curves for the molecules. The CV curve of all the three molecules showed two oxidation potentials that can be assigned to the triphenyalamine radicals supporting information, Figure S18.[40] The HOMO values for the molecules were calculated from the oxidation potentials and was found to be 5.26 eV, 5.29 eV and 5.14 eV respectively for **TPT. Ben** and **TPT-Ac**. The LUMO values for the molecules were derived from the HOMO and the optical band gap obtained from solid state absorption profile. LUMO value for **TPT had** been calculated as 2.52 eV, for **TPT-Ben** as 2.62 eV and for **TPT-Ac** 2.61 eV supporting information, Figure S19. The

compiled results for electrochemical and thermal analysis of the molecules were given in Table 2.

Compound	HOMO	Optical	LUMO	Melting	Td.( °C)
	(eV)	band gap (eV)	(eV)	points(°C)	
ТРТ	5.26	2.6	2.66	161	268
TPT-Ben	5.29	2.5	2.79	169	444
TPT-Ac	5.14	2.2	2.94	214	420

 Table 2: Summary of electrochemical and thermal analysis on the triphenylamine derivatives TPT, TPT-Ben and TPT-Ac

 synthesized.

#### 4.5. Nanosecond transient absorption spectra

To get an insight about the excited state properties of the molecules nanosecond transient absorption studies were carried out. Figure 6 shows the nanosecond transient absorption spectra of triphenylamine derivatives, **TPT**, **TPT-Ben and TPT-Ac**, in Ar saturated THF obtained by exciting at 355 nm using nanosecond laser flash photolysis. It shows a broad transient absorption maximum around 600 nm. The first negative signal near 400 nm in the transient absorption spectrum of the derivatives corresponds to the ground state bleach. In the presence of oxygen there is no significant change in the spectral dynamics. The time constant of the transient maximum around 600 nm for **TPT**, **TPT-Ben** and **TPT-Ac** was estimated be around 3.5, 4.88 and 2.9 µs respectively. Based on the literature [41-43] and on the fact that there is no significant change in the time constant in the oxygen medium, the transient maximum are attributed to formation of the radical cation of the triphenylamine core.



**Fig. 6.** a) Nanosecond transient absorption spectra of **TPT** derivatives obtained by laser flash photolysis at 355 nm excitation in Ar saturated THF b) Corresponding decay kinetics.



4.6. Generation of white light using the triphenylamine derivatives

**Fig. 7.** Pictorial representation of the generation of white light using a 3:2:1 combination of the synthesised triphenylamine derivatives **TPT**, **TPT-Ben and TPT-Ac**.

Generating white light is always fascinating due to its applications in solid state lighting and displays. An interesting observation made after the photoluminascent studies of the molecules was that, the molecules emitted in blue, green and orange regions and also the Stokes shift values for the derivatives increased from the blue emitter to the orange-red emitter. As a result the molecules can be excited using same excitation wavelength. Based on this observation we examined the emission of a mixture of the three triphenylamine-bithiophene derivatives in solution state (DMSO) as well as in the solid state. In both the cases, the mixture showed white light emission with a colour coordinate of (0.32, 0.36) and (0.33, 0.37) respectively. The mixture of TPT, TPT-Ben, and TPT-Ac was excited at a 400 nm and they gave white light for different permutations of concentrations i.e. the white light generation is independent of the slight variations in concentration. The best colour coordinate of the white light emission in solution state was obtained at 400 nm excitation with a ratio of 3:2:1 for TPT, TPT-Ben and TPT-Ac (Figure 8). The colour coordinates obtained for different permutation combinations of concentration are given in supporting information. The emission of the mixture of three molecules in solid state was also checked on a PMMA matrix. The ratio between the three was kept the same as that used for the solution state studies is 3:2:1 for TPT, TPT-Ben and TPT-Ac.



Fig. 8. a) Fluorescence emission profile for the mixture of **TPT**, **TPT-Ben** and **TPT-Ac** in solution state and in film state at micromolar concentration ( $\lambda_{exc}$ = 400 nm). Inset shows the photograph of solid state emission for the mixture at the  $\mu$ M concentration and at 3:2:1 ratio of triphenylamine derivatives under 365 nm excitation b) The CIE colour coordinate for the white light emission in solid state and in solution state.

### 5. Summary

In summary, we demonstrated the synthesis and characterisation of a set of three triphenylaminebithiophene based donor-acceptor molecules **TPT**, **TPT-Ben**, and **TPT-Ac**. The emission from these set of molecules was successfully tuned from blue to orange red. A 3: 2: 1 mixture of the molecules produced white light emission in both solid and solution state employing the near lying absorption maxima. We strongly believe that these triphenylamine based donor-acceptor systems can find applications in the field of white light emitting diodes. Our future work in this area will focus on the more suitable functionalization of the triphenylamine-bithiophene core for better photophysical applications.

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#### References

- [1] Sun, N.; Wang, Q.; Zhao, Y.; Chen, Y.; Yang, D.; Zhao, F.; Chen, J.; Ma, D. High-performance hybrid white organic light-emitting devices without interlayer between fluorescent and phosphorescent emissive regions. *Adv. Mater.* **2014**, *26* (10), 1617–1621.
- [2] Farinola, G. M.; Ragni, R. Electroluminescent materials for white organic light emitting diodes. *Chem. Soc. Rev.* 2011, 40 (7), 3467–3482.
- [3] Reineke, S.; Thomschke, M.; Lussem, B.; Leo, K. White organic light-emitting diodes: status and perspective. *Rev. Mod. Phys.* **2013**, *85* (3), 1245–1293.
- [4] Tang, K.-C.; Chang, M.-J.; Lin, T.-Y.; Pan, H.-A.; Fang, T.-C.; Chen, K.-Y.; Hung, W.-Y.; Hsu, Y.-H.; Chou, P.-T. Fine tuning the energetics of excited-state intramolecular proton transfer (ESIPT): white light generation in a single ESIPT system. *J. Am. Chem. Soc.* 2011, *133* (44), 17738–17745.

- [5] Park, S.; Ji, E. K.; Se, H. K.; Seo, J.; Chung, K.; Park, S. Y.; Jang, D. J.; Medina, B. M.; Gierschner, J.; Soo, Y. P. A white-light-emitting molecule: frustrated energy transfer between constituent emitting centers. *J. Am. Chem. Soc.* **2009**, *131* (39), 14043–14049.
- [6] Nandhikonda, P.; Heagy, M. D. An organic white light-emitting dye: very small molecular architecture displays panchromatic emission. *Chem. Commun. (Camb).* 2010, 46 (42), 8002–8004.
- [7] Zhao, J.; Ji, S.; Chen, Y.; Guo, H.; Yang, P. Excited state intramolecular proton transfer (ESIPT): from principal photophysics to the development of new chromophores and applications in fluorescent molecular probes and luminescent materials. *Phys. Chem. Chem. Phys.* 2012, *14* (25), 8803–8817.
- [8] Wenhui, Z.; Stephen, M. K.; Kevin, L. B.; Tianyue, Y.; Kevin, C. J.; Christopher, K. O.; Joseph, W. P.; Seth, R. M. An efficient two-photon-generated photoacid applied to positive-ton 3D microfabrication. *Science*. **2002**, *296*, 1106–1109.
- [9] Lafratta, C. N.; Fourkas, J. T.; Baldacchini, T.; Farrer, R. A. Multiphoton fabrication. Angew. Chemie - Int. Ed. 2007, 46, 6238–6258.
- [10] Chennoufi, R.; Bougherara, H.; Gagey-Eilstein, N.; Dumat, B.; Henry, E.; Subra,
  F.; Bury-Moné, S.; Mahuteau-Betzer, F.; Tauc, P.; Teulade-Fichou, M. P.; Deprez, E.
  Mitochondria-targeted triphenylamine derivatives activatable by two-photon excitation for triggering and imaging cell apoptosis. *Sci. Rep.* 2016, 6 (21458), 1–12.
- [11] Allain, C.; Schmidt, F.; Lartia, R.; Bordeau, G.; Fiorini-Debuisschert, C.; Charra, F.; Tauc, P.; Teulade-Fichou, M. P. Vinyl-Pyridinium Triphenylamines : Novel far- red emitters with high photostability and two- photon absorption properties for staining DNA. *ChemBioChem* 2007, *8*, 424–433.
- Gan, X.; Wang, Y.; Ge, X.; Li, W.; Zhang, X.; Zhu, W.; Zhou, H.; Wu, J.; Tian,
   Y. Triphenylamine Isophorone Derivatives with Two Photon Absorption: Photo-Physical
   Property, DFT Study and Bio-Imaging; *Dye. Pigment.* 2015; 120, 65-73.
- [13] Echeverry, C. A.; Cotta, R.; Insuasty, A.; Ortíz, A.; Martín, N.; Echegoyen, L.; Insuasty, B. Synthesis of novel light harvesters based on perylene imides linked to triphenylamines for dyes sensitized solar cells. *Dye. Pigment.* **2018**, *153*, 182–188.

- [14] Surya, P. S.; M, S. R.; Thomas, K. R. J.; Balaiah, S.; Bhanuprakash, K.; Sharma, G. D. New triphenylamine-based organic dyes with different numbers of anchoring groups for dye-sensitized solar cells. *J. Phys. Chem. C* 2012, *116*, 5941–5960.
- [15] Xu, W.; Peng, B.; Chen, J.; Liang, M.; Cai, F. New triphenylamine-based dyes for dye-sensitized solar cells. J. Phys. Chem. C 2008, 112 (3), 874–880.
- [16] Jiang, Y.; Wang, Y.; Yang, J.; Hua, J.; Wang, B.; Qian, S.; Tian, H. Synthesis, two-photon absorption, and optical power limiting of new linear and hyperbranched conjugated polyynes based on bithiazole and triphenylamine. *J. Polym. Sci. Part A Polym. Chem.* **2011**, 49 (8), 1830–1839.
- [17] Morel, Y.; Baldeck, P. L.; Paci, B.; Kretsch, K.; Nunzi, J.; Andraud, C.; Proprie, L. Optical limiting in the visible range : molecular engineering around. *J. Mater. Chem.* 2003, *13*, 2157–2163.
- [18] Kawasumi, K.; Wu, T.; Zhu, T.; Chae, H. S.; Van Voorhis, T.; Baldo, M. A.; Swager, T. M. Thermally activated delayed fluorescence materials based on homoconjugation effect of donor-acceptor triptycenes. *J. Am. Chem. Soc.* **2015**, *137* (37), 11908–11911.
- [19] Hontz, E.; Chang, W.; Congreve, D. N.; Bulović, V.; Baldo, M. A.; Van Voorhis,
   T. The role of electron-hole separation in thermally activated delayed fluorescence in donor-acceptor blends. *J. Phys. Chem. C* 2015, *119* (45), 25591–25597.
- [20] Zhou, C.; Zhang, T.; Zhang, S.; Liu, H.; Gao, Y.; Su, Q.; Wu, Q.; Li, W.; Chen, J.; Yang, B. Isomerization effect of triphenylamine-acridine derivatives on excited-state modification, photophysical property and electroluminescence performance. *Dye. Pigment.* 2017, *146*, 558–566.
- [21] Rybakiewicz, R.; Zagorska, M.; Pron, A. Triphenylamine-based electroactive compounds: synthesis, properties and application to organic electronics. *Chem. Pap.* 2017, 71 (2), 243–268.
- [22] Agarwala, P.; Kabra, D. A review on triphenylamine (tpa) based organic hole transport materials (htms) for dye sensitized solar cells (dsscs) and perovskite solar cells (pscs): evolution and molecular engineering. *J. Mater. Chem. A* **2017**, *5* (4), 1348–1373.
- [23] Tao, Y.; Yang, C.; Qin, J. Organic host materials for phosphorescent organic light-emitting diodes. *Chem. Soc. Rev.* 2011, 40 (5), 2943–2970.

- [24] Li, Z.; Wu, Z.; Fu, W.; Liu, P.; Jiao, B.; Wang, D.; Zhou, G.; Hou, X. Versatile fluorinated derivatives of triphenylamine as hole-transporters and blue-violet emitters in organic light-emitting devices. J. Phys. Chem. C 2012, 116 (38), 20504–20512.
- [25] Mazzeo, M.; Pisignano, D.; Favaretto, L.; Barbarella, G.; Cingolani, R.; Gigli, G.
   Bright oligothiophene-based light emitting diodes. In *Synthetic Metals*; 2003; Vol. 139, pp 671–673.
- [26] Zhu, X.-H.; Peng, J.; Cao, Y.; Roncali, J. Solution-processable single-material molecular emitters for organic light-emitting devices. *Chem. Soc. Rev.* 2011, 40 (7), 3509–3524.
- [27] Turkoglu, G., Cinar, M.E. & Ozturk, T. Top Curr Chem (Z) (2017) 375: 84.
- [28] Junwu, C. A.; Yong, C. Development of Novel conjugated donor polymers for high-efficiency bulk-heterojunction photovoltaic devices. Acc. Chem. Res. 2009, 42 (11), 1709–1718.
- [29] Persaud, K. C. Polymers for chemical sensing. *Mater. Today* **2005**, *8* (4), 38–44.
- [30] Bolduc, A.; Dong, Y.; Guérin, A.; Skene, W. G. Solvatochromic investigation of highly fluorescent 2-aminobithiophene derivatives. *Phys. Chem. Chem. Phys.* 2012, 14 (19), 6946.
- [31] Miyaura, N.; Suzuki, A. palladium-catalyzed cross-coupling reactions of organoboron compounds. *Chem. Rev.* 1995, 95 (7), 2457–2483.
- [32] Leliège, A.; Blanchard, P.; Rousseau, T.; Roncali, J. Triphenylamine/tetracyanobutadiene-based d-a-d π-conjugated systems as molecular donors for organic solar cells. *Org. Lett.* 2011, *13* (12), 3098–3101.
- [33] Brouwer, A. M. Standards for photoluminescence quantum yield measurements in solution (iupac technical report). *Pure Appl. Chem.* **2011**, *83* (12), 2213–2228.
- [34] Yang, X.; Huang, H.; Pan, B.; Aldred, M. P.; Zhuang, S.; Wang, L.; Chen, J.; Ma, D. Modified 4,4',4"-tri(n-carbazolyl)triphenylamine as a versatile bipolar host. J. Phys. Chem. C 2012, 116, 15041–15047.
- [35] Lippert, E. Dipolmoment und elektronenstruktur von angeregten molekülen. Zeitschrift fur Naturforsch. - Sect. A J. Phys. Sci. **1955**, 10 (7), 541–545.

- [36] Mataga, N.; Kaifu, Y.; Koizumi, M. The solvent effect on fluorescence spectrum, change of solute-solvent interaction during the lifetime of excited solute molecule. *Bull. Chem. Soc. Jpn.* **1955**, 28 (9), 690–691.
- [37] Mataga, N.; Kaifu, Y.; Koizumi, M. Solvent effects upon fluorescence spectra and the dipolemoments of excited molecules. *Bull. Chem. Soc. Jpn.* **1956**, *29* (4), 465–470.
- [38] Li, Y.; Li, Z.; Ablekim, T.; Ren, T.; Dong, W. Rational design of tetraphenylethylene-based luminescent down-shifting molecules: photophysical studies and photovoltaic applications in a cdte solar cell from small to large units. *Phys. Chem. Chem. Phys.* 2014, *16* (47), 26193–26202.
- [39] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.
- [40] Thangthong, A.; Prachumrak, N.; Tarsang, R.; Keawin, T.; Jungsuttiwong, S.; Sudyoadsuk, T.; Promarak, V. Blue light-emitting and hole-transporting materials based on 9,9-bis(4-diphenylaminophenyl)fluorenes for efficient electroluminescent devices. *J. Mater. Chem.* **2012**, 22 (14), 6869.
- [41] Bonvoisin, J.; Launay, J.-P.; Van Der Auweraer, M.; De Schryver, F. C. Organic mixed-valence systems: intervalence transition in partly oxidized aromatic polyamines. electrochemical and optical studies. J. Phys. Chem. A 1994, 98 (19), 5052–5057.
- [42] Lor, M.; Jordens, S.; De Belder, G.; Schweitzer, G.; Fron, E.; Viaene, L.; Cotlet, M.; Weil, T.; Mullen, K.; Verhoeven, J. W.; Van der Auweraer, M.; De Schryver, F. C.

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Direct proof of electron transfer in a rigid first generation triphenyl amine core dendrimer substituted with a peryleneimide acceptor. *Photochem. Photobiol. Sci.* **2003**, *2* (5), 501.

[43] Lor, M.; Thielemans, J.; Viaene, L.; Cotlet, M.; Hofkens, J.; Weil, T.; Hampel, C.; Müllen, K.; Verhoeven, J. W.; Van der Auweraer, M.; De Schryver, F. C. Photoinduced electron transfer in a rigid first generation triphenylamine core dendrimer substituted with a peryleneimide acceptor. *J. Am. Chem. Soc.* 2002, *124* (33), 9918–9925.

**Table of content** 



## Design, synthesis and photophysical investigation of triphenylamine-bithiophene dyes as RGB emitters for white light applications

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#### **<u>Highlight</u>**

- 1) A set of three triphenylamine thiophene derivatives were synthesized and charecterized
- 2) Their photophysical studies were carried out
- 3) The DFT calculations on the molecules were done to have an insight about their structural, electronic and optical properties
- 4) Transient absorption studies showed the presence of triphenylamine radical cations in the systems
- 5) A mixture of the three molecules in solution and solid state gave white light emission