

NJC

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis and Photophysical Properties of Triphenylamine-Based Multiply Conjugated Star Like Molecules

Rajendiran Balasaravanan,^a Kumaraguru Duraimurugan,^a Jayaraman Sivamani,^a Viruthachalam Thiagarajan^b and Ayyanar Siva^{a*}

Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX

DOI: 10.1039/b000000x

Novel triphenylamine-based star like molecules **11** were synthesized and characterized by FT-IR, ¹H, ¹³C, DEPT-135 NMR, and MALDI-TOF mass spectroscopy. The absorption and emission spectra of star like molecules were studied in different solvents. The effect of solvent polarity and aggregation studies on the absorption and emission spectra has also been studied. The new stars like molecules are found to exhibit broad absorption and emission band along with intramolecular charge transfer character. The fluorescence spectra of triphenylamine derivatives shift from blue to green wavelength on increasing the extended conjugation of the molecule. The experimental results indicate that there is cooperative enhancement originating from the inter-branch coupling and an increase of light-harvesting ability with increasing the conjugated molecule size.

Introduction

Dendrimers are a new class of polymers, exhibiting highly symmetric, globular, size mono disperse macro molecules with central core moiety, which have been extensively investigated over the past decades, because of their fascinating structure and attracting distinguished properties in organic, bioorganic and material chemistry.¹⁻³ The core is usually preferred as the emitting chromophore and the end groups are long chain charge transporting units which is increased the solubility⁴ of the dendrimers. Triphenylamine (TPA) is often used as a core moiety due to its electron richness and fluorescence properties. Further, TPA is a well-known compound to exhibit rigid plane, three dimensional steric, long conjugated length, amorphous nature, hole transporting properties⁵, good light harvesting properties⁶, and long life time. TPA related compounds are naturally used for 3D systems due to the non-coplanarity of three aromatic rings.^{7,8}

Recently, TPA related dendrimers have gained considerable attention due to their potential large two photon absorption cross sections, which is simultaneous absorption of two photons, enhanced non-linear responses, excellent electron donating ability, hole mobility,⁹ optoelectronic properties,¹⁰ thermal and electrochemical stability,¹¹ emitting fluorophore. They have found optical applications in optical power limiting properties¹², two photon fluorescence excitation microscopy,¹³ photodynamic therapy,¹⁴ large area displays,¹⁵ two dimensional (2D) light sources¹⁶ and three dimensional (3D) optical data storages.^{17, 18} They are also extensively used as hole transporting materials^{19, 20} in photo voltaic devices,²¹ field effect transistors,²² organic light emitting diodes²³, and dye sensitized solar cells.²⁴ Generally, simple strategy for obtaining longer wavelength emission is through donor-acceptor conjugation, such as donor-acceptor dipolar dyes, Donor- π -Donor, and donor-acceptor-donor quadrupolar dyes, which

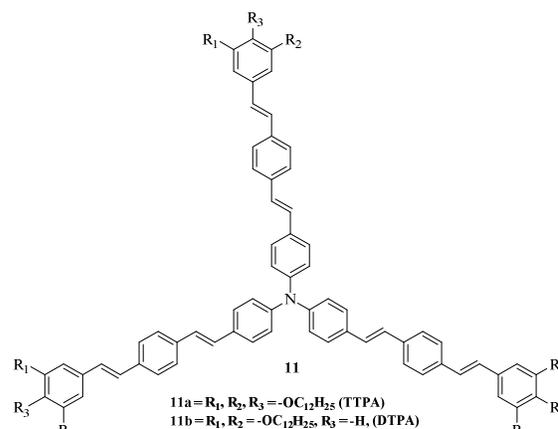


Fig. 1 Triphenylamine based D- π -D molecules.

shifts the fluorescence band to a longer wavelength and increases the Stokes shift. Further, all those molecules in polar solutions, the emission is quenched, which reduces fluorescent efficiency. This fluorescence quenching correlates with an increase in polarity, by which the transition from a local excited state to a highly polarized excited state, such as an intramolecular charge transfer state, is facilitated.^{25, 26} The polarized excited state is stabilized by solvation from polar solvent molecules, which leads to increased nonradiative deactivation.

In this work, we design a new synthetic procedure for the properties of phenylenevinylene based star like molecules which contain TPA as a central core and long alkyl chain as end groups (Figure 1) (tris(4-((E)-4-((E)-3,5-bis(dodecyloxy)styryl)styryl)phenyl)amine) (TTPA) and tris(4-((E)-4-((E)-3,4,5-tris(dodecyloxy)styryl)styryl)phenyl)amine) (DTPA). These star like molecules were prepared *via* a

^aDepartment of Inorganic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai-625 021, Tamilnadu, India. ^bDepartment of Chemistry, School of Chemistry, Bharathidasan University, Tiruchirappalli-620 024, Tamilnadu, India

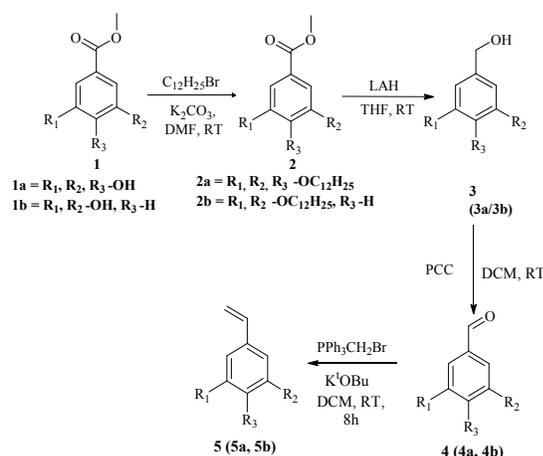
Corresponding author: (A.Siva) E.mail. drasiva@gmail.com

Cite this: DOI: 10.1039/c0xx00000x

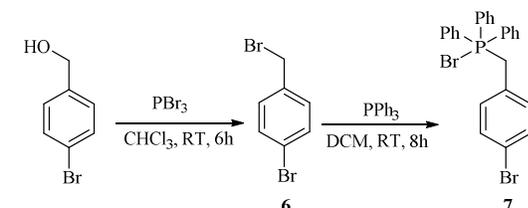
www.rsc.org/xxxxxx

ARTICLE TYPE

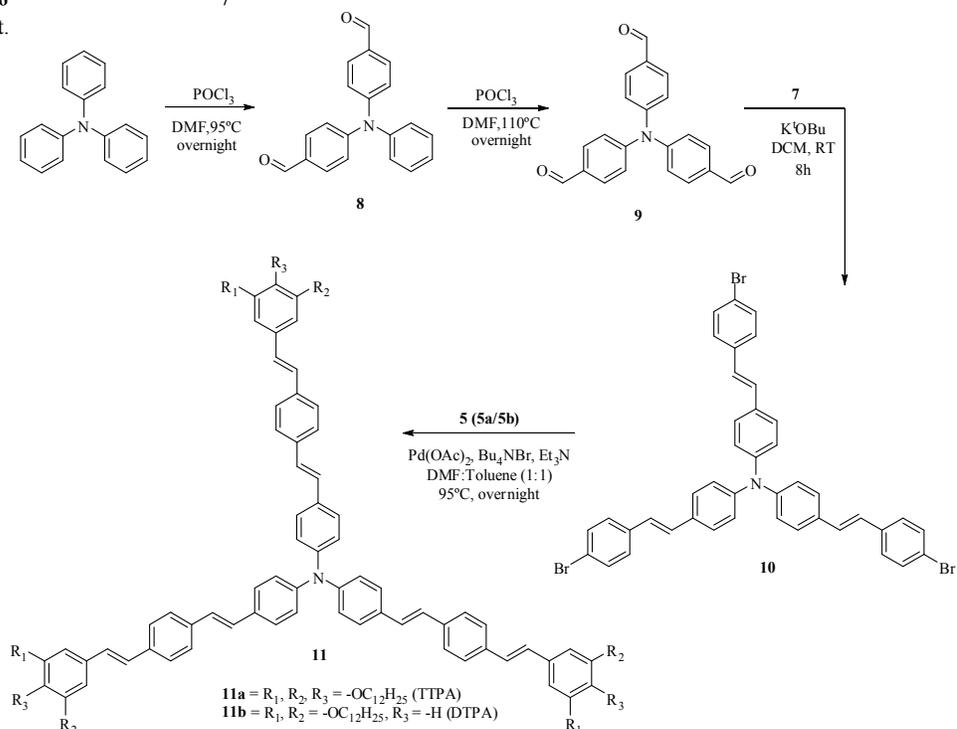
convergent synthetic approach by Wittig reaction and followed by triple site Heck coupling reaction. These TPA derivatives with Donor – π conjugation – Donor (D- π -D) structures have a lower band gap due to the intramolecular charge transfer between donor and donor through conjugation and it may enhance the two photon absorption properties of TPA derivatives. The three dimensional structure of these star like molecules can improve the carrier and charge transport to provide favourable electronic properties. Therefore, these star like molecules contain symmetrical D- π -D structure with TPA as a core and long alkyl group as periphery. Furthermore, the phenylene vinylene groups enhanced the conjugation, and broaden the absorption band of these compounds when compared with inter mediate compound of **10**. These conjugated star like molecules have good solubility in all common organic solvents and they have very good ICT properties. Using cyclic voltammogram, these star like molecules exhibit lower HOMO and LUMO energy band gap.



Step 1 Synthesis of Vinylated aromatic compounds.



Step 2 Synthesis of Wittig salt.

Scheme 1. Schematic representation for the synthesis of star like molecules (**11**).

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Experimental Section

Materials and Methods

All the chemicals and reagents were used in this work as an analytical grade. Methyl 3, 4, 5-trihydroxy benzoate, methyl 3, 5-dihydroxy benzoate, 1-bromododecane, LAH, PCC, PBr₃, (4-bromophenyl) methanol, POCl₃, K^tOBu, Pd(OAc)₂ were obtained from Sigma Aldrich. DMF, toluene, DCM, CHCl₃ were obtained from Merck and all the solvents were obtained from laboratory grade.

The ¹H and ¹³C NMR and DEPT-135 NMR spectra were recorded on a Bruker (Avance) 300 & 400 MHz NMR instrument using TMS as an internal standard, CDCl₃ and DMSO as solvent. Standard Bruker software was used throughout. Chemical shifts are given in parts per million (δ-scale) and the coupling constants are given in Hertz. Silica gel-G plates (Merck) were used for TLC analysis with a mixture of pet.ether and ethylacetate as an eluent. Column chromatography was carried out in silica gel (60-120 mesh) using pet.ether and ethylacetate as an eluent. UV visible absorption spectra were recorded on JASCO V630 Spectrophotometer. Photoluminescence were recorded on Agilent 8000. Life time measured in Time Correlated Single Photon Counting (TCSPC). Electrochemical measurements were recorded in CH instruments model 680 Amp Booster. Thermal analyses were recorded on TGA Q50 V20. 13 Build 39. Mass spectra were analysed by Voyager DE PRO Biospectrometry Workstation (Applied Biosystems) matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy (MS) instrument. A pulsed nitrogen laser of 337 nm was used, and the TOF was operated in the delayed extraction mode.

General procedure A for alkylation (2)²⁰

Methyl hydroxy benzoate **1** (5g, 0.027 mmol) dissolved in a dry DMF (75ml) under nitrogen atmosphere and it cooled to 0°C, K₂CO₃ (22.5g, 0.163mmol) was added to the above solution and followed by 1-bromo dodecane (22.3mL, 0.090 mmol), after addition the suspension was allowed to warm and stirred until the reaction was complete. Then the reaction mixture was poured into ice-water and extracted with Ethyl acetate, combined organic layers was washed with brine solution, dried over Na₂SO₄ and evaporated, The crude product was purified by silica gel (60-120 mesh) column chromatography using petroleum ether as an eluent. The pure product is a colorless solid.

Methyl 3,4,5-tris(dodecyloxy)benzoate (2a)

Synthesized according to general procedure A using methyl 3,4,5-trihydroxy benzoate **1a** and 1-bromo dodecane. Yield is 90%, FT-IR (cm⁻¹) 1082, 1630, 1725; ¹H NMR (300MHz, CDCl₃) δ_H 7.30 (d, 2H), 4.03-3.99 (t, 6H), 3.89 (s, 3H), 1.86-1.69 (m, 6H), 1.47-1.44 (m, 6H), 1.37-1.17 (m, 54H), 0.94-0.86 (t, 9H); ¹³C NMR (75MHz, CDCl₃) δ_C 166.84, 152.91, 142.48, 124.72, 107.88, 73.58, 69.11, 52.03, 31.86, 30.85, 30.26, 29.63, 29.57, 29.33, 26.02, 22.63, 14.04

Methyl 3, 5-bis(dodecyloxy)benzoate (2b)

Synthesized according to general procedure A using methyl 3,5-dihydroxy benzoate **1b** and 1-bromo dodecane. Yield is 90%, FT-IR (cm⁻¹) 1076, 1635, 1720; ¹H NMR (300 MHz, CDCl₃) δ_H 7.15 (d, *J* = 2.1 Hz, 2H), 6.63 (t, *J* = 2.2 Hz, 1H), 3.96 (t, *J* = 6.5 Hz, 4H), 3.89 (s, 3H), 1.86 – 1.69 (m, 5H), 1.43 (d, *J* = 7.5 Hz, 6H), 1.26 (s, 36H), 0.88 (t, *J* = 6.6 Hz, 7H); ¹³C NMR (75 MHz, CDCl₃) δ_C 167.38, 160.56, 132.20, 108.02, 106.97, 68.70, 52.53, 33.33, 30.07, 30.04, 30.00, 29.77, 26.42, 23.09, 14.50.

General procedure B for reduction (3)²⁷

The ester **2** (1 eq) in THF was added to a suspension of lithium aluminium hydride (1.5 eq) in THF at 0°C. The suspension was allowed to warm at room temperature and stirred until the reaction was complete. After completion of the reaction, the mixture was quenched by 2N HCl and filtered through celite. The filtrate was extracted with EtOAc and washed with brine solution. The combined organic layers were dried over anhydrous Na₂SO₄ and purified by column chromatography using petroleum ether / ethyl acetate (4:1) as an eluent, to afford target compound.

3, 4, 5-tris(dodecyloxy)phenyl)methanol (3a)

Synthesized according to general procedure B using methyl 3,4,5-tris(dodecyloxy)benzoate **2a** (4 g, 0.8 mmol). Yield is 94%, FT-IR (cm⁻¹) 1080, 1650, 3435; ¹H NMR(300MHz, CDCl₃) δ_H 6.56 (s,2H), 4.59 (s, 2H), 3.99-3.91 (m, 6H), 1.82-1.69 (m, 6H), 1.59-1.46 (m, 6H), 1.43-1.11 (m, 54H), 0.90-0.86 (t,9H); ¹³C NMR (75MHz, CDCl₃) δ_C 153.21,137.79, 136.15, 105.34, 73.41, 69.17, 65.58, 31.90, 30.29, 29.68, 29.64, 29.59, 29.40, 29.29, 26.08, 22.62, 14.09.

3, 5-bis(dodecyloxy)phenyl)methanol (3b)

Synthesized according to general procedure B using methyl 3, 5-di(dodecyloxy)benzoate **2b** (5 g, 0.71 mmol). Yield is 91%. FT-IR (cm⁻¹) 1075, 1638, 3450; ¹H NMR (300 MHz, CDCl₃) δ_H 6.49 (s, 2H), 6.37 (d, *J* = 1.8 Hz, 1H), 4.61 (s, 2H), 3.93 (t, *J* = 5.8 Hz, 4H), 1.84 – 1.71 (m, 4H), 1.42 (d, *J* = 6.8 Hz, 4H), 1.26 (s, 32H), 0.88 (t, *J* = 5.7 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ_C 100.95, 143.59, 105.46, 100.97, 68.48, 65.88, 32.33, 30.04, 30.01, 29.76, 26.45, 23.09, 14.52.

General procedure C for aldehyde (4)²⁸

PCC (1.5 eq) added to the solution of alcohol **3** (1 eq) in CH₂Cl₂ at 0 °C under nitrogen atmosphere. The reaction was allowed to room temperature and stirred until reaction was complete. After completion of the reaction the mixture was quenched by 2N HCl and filtered through celite bed. The filtrate was extracted with EtOAc and washed with brine solution. The combined organic layers were dried over anhydrous Na₂SO₄ and purified by column chromatography using petroleum ether / ethyl acetate (97:3) as an eluent, to afford target compound.

3, 4, 5-tris(dodecyloxy)benzaldehyde (4a)

Synthesized according to general procedure C using 3, 4, 5-tris(dodecyloxy)phenyl)methanol **3a** (2.2, 0.33 mmol). Yield is 85%, FT-IR (cm⁻¹) 1075, 1642, 1705; ¹H NMR(300MHz, CDCl₃) δ_H 9.83 (s, 1H), 7.19 (s, 2H), 4.08-4.01 (m, 6H), 1.88-1.80 (m, 6H), 1.48-1.42 (m,6H), 1.40-1.20 (m, 54H), 0.94-0.86 (t, 9H); ¹³C NMR(75MHz, CDCl₃) δ_C 191.22, 153.47, 143.76, 131.40, 107.75, 73.57, 69.15, 31.89, 30.31, 29.66, 29.63, 29.60, 29.51, 29.34, 29.21, 26.03, 22.66, 14.07.

3, 5-bis(dodecyloxy)benzaldehyde (4b)

Synthesized according to general procedure C using 3, 5-di(dodecyloxy)phenyl)methanol **3b** (3.6 g, 0.76 mmol). Yield is 88%, FT-IR (cm⁻¹) 1060, 1645, 1710; ¹H NMR (300 MHz, CDCl₃) δ_H 9.89 (s, 1H), 6.98 (s, 2H), 6.69 (d, *J* = 1.6 Hz, 1H), 3.98 (t, *J* = 6.4 Hz, 4H), 1.84 – 1.73 (m, 4H), 1.44 (d, *J* = 7.0 Hz, 4H), 1.27 (s, 32H), 0.88 (t, *J* = 6.2 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ_C 192.49, 161.17, 138.72, 108.42, 107.99, 68.84, 32.32, 30.04, 29.99, 29.75, 29.53, 26.40, 23.09, 14.51.

10 General procedure D for styrene (5)²⁹

Methyltriphenylphosphonium iodide (1.2 eq) and aldehyde **4** (1 eq) was dissolved in 10ml of DCM under nitrogen atmosphere and then K^tOBu (2 eq) was added slowly. The mixture was stirred for about 8 h. After completion of the reaction, the mixture was poured into 100 ml water. The crude product was extracted with EtOAc and washed with brine. The combined organic layers were dried over anhydrous Na₂SO₄. The crude material was purified by column chromatography using petroleum ether / ethyl acetate (99:1) as an eluent, to afford white solid as a product.

1, 2, 3-tris(dodecyloxy)-5-vinylbenzene (5a)

Synthesized according to general procedure D using 3, 4, 5- tris(dodecyloxy)benzaldehyde **4a** (2.84g, 0.44 mmol) and methyltriphenylphosphonium iodide (2.1g, 0.52 mmol). Yield is 73%, FT-IR (cm⁻¹) 1075, 1620, 1690; ¹H NMR (300MHz, CDCl₃) δ_H 6.60 (s, 2H), 6.64-6.55 (m, 1H), 5.61 (d, *J* = 17.5 Hz, 1H), 5.17 (d, *J* = 10.8 Hz, 1H), 4.00-3.92 (m, 6H), 1.84-1.79 (m, 6H), 1.47-1.41 (m, 6H), 1.40-1.26 (m, 54H), 0.90-0.86 (t, 9H); ¹³C NMR (75MHz, CDCl₃) δ_C 153.19, 138.41, 136.95, 132.77, 112.68, 104.96, 73.49, 69.15, 31.92, 30.33, 29.75, 2970, 29.65, 29.42, 29.36, 26.10, 22.69, 14.10.

1, 3-bis(dodecyloxy)-5-vinylbenzene (5b)

Synthesized according to general procedure D using 3, 5-di(dodecyloxy)benzaldehyde **4b** (1g, 0.21 mmol) and Methyltriphenylphosphonium iodide (0.9g, 0.25 mmol). Yield is 75%, FT-IR (cm⁻¹) 1070, 1623, 1685; ¹H NMR (300 MHz, CDCl₃) δ_H 6.75 – 6.63 (m, 1H), 6.60 (s, 2H), 6.43 (s, 1H), 5.76 (d, *J* = 17.5 Hz, 1H), 5.27 (d, *J* = 10.8 Hz, 1H), 3.98 (t, *J* = 6.4 Hz, 5H), 1.93–1.76 (m, 5H), 1.50 (d, *J* = 6.0 Hz, 6H), 1.34 (s, 39H), 0.95 (t, *J* = 6.1 Hz, 7H); ¹³C NMR (75 MHz, CDCl₃) δ_C 160.40, 139.40, 137.01, 113.85, 104.78, 100.93, 67.93, 31.94, 29.69, 29.66, 29.63, 29.42, 2938, 29.30, 26.08, 22.69, 14.08.

4-Bromobenzyl bromide (6)³⁰

PBr₃ (1.5 ml, 1.6 mmol) was dropwise added to (4-bromophenyl) methanol (1 g, 0.53 mmol) in CHCl₃ was stirred at 0 °C under nitrogen. The resulting mixture was stirred for 6 h. After completion of the reaction, the mixture was quenched with iced water and neutralized with NaHCO₃ (aq). Then the solution was extracted with EtOAc, washed with water and brine, dried over anhydrous Na₂SO₄ to afford white needle as a product without further purification. Yield is 91%. ¹H NMR (300 MHz, CDCl₃) δ_H 7.40 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 4.37 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ_C 136.76, 131.94, 130.65, 122.44, 32.40.

55 4-Bromobenzyl bromide Wittig salt (7)³⁰

4-Bromobenzylbromide (0.5g, 0.2 mmol), triphenylphosphine (0.58g, 0.22 mmol), in CH₂Cl₂ (5 ml) was stirred for about 8 h. After completion of the reaction the phosphonium salt was scratched with Et₂O. The crude product was diluted with CH₂Cl₂ and scratched with Et₂O, filtered and washed with Et₂O to afford target compound as a white solid, yield 98%. ¹H NMR (300 MHz, CDCl₃) δ_H 7.77 (dd, *J* = 13.3, 7.5 Hz, 9H), 7.68 – 7.56 (m, 6H), 7.22 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 5.55 (d, *J* = 14.6 Hz, 2H); ¹³C NMR (75 MHz,

CDCl₃) δ_C 134.97, 134.21, 133.13, 131.62, 130.11, 126.34, 122.49, 117.89, 116.75, 30.05.

Bis-(4-formylphenyl)-amine (8)²⁰

To a mixture of phosphoryl chloride (12.4ml, 13.3 mmol) and dimethylformamide (12 ml, 17.4 mmol) at 0°C was dropwise added triphenylamine (2 g, 0.66 mmol) in THF (10 ml) while stirring. The resulting mixture was stirred at 95°C under nitrogen for overnight. The mixture was then cooled to room temperature, poured into ice-water (300 ml), and neutralized with 40% aq. NaOH. The brown colour solution was extracted with EtOAc, washed with water and the combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and concentrated it. The crude product was purified by column chromatography with petroleum ether/ethyl acetate as an eluent (10:1). Pale yellow solid, yield is 70%, ¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 2H), 7.78 (d, *J* = 7.9 Hz, 4H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ_C 190.57, 152.02, 145.51, 131.34, 131.27, 130.19, 127.09, 126.30, 122.78.

Tris-(4-formylphenyl)-amine (9)²⁰

To a mixture of phosphoryl chloride (12.4ml, 13.3 mmol) and dimethylformamide (12 ml, 17.4 mmol) at 0°C was dropwise added Bis-(4-formylphenyl)-amine **8** (2 g, 0.66 mmol) in THF (10 ml) while stirring. The resulting mixture was stirred at 110°C under nitrogen for overnight. The mixture was then cooled to room temperature, poured into ice-water (300 ml), and neutralized with 40% aq. NaOH. The brown color solution was extracted with EtOAc, washed with water and the combined organic layer was washed with brine, dried over anhydrous Na₂SO₄ and concentrated it. The crude product was purified by column chromatography with petroleum ether/ethyl acetate as an eluent (4:1). Pale yellow solid, yield is 22.7%. ¹H NMR (400 MHz, CDCl₃) δ_H 9.95 (s, 3H), 7.85 (d, *J* = 8.3 Hz, 6H), 7.26 (d, *J* = 8.3 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ_C 190.54, 151.21, 132.59, 131.53, 124.56.

100 Tris-(4-((E)-4-bromostyryl)phenyl)amine (10)³¹

The Phosphonium salt **7** (1.86g, 0.36 mmol) and Tris-(4-formylphenyl)-amine **9** (0.4g, 0.12 mmol) was dissolved in CH₂Cl₂ (10 ml) under nitrogen atmosphere, K^tOBu (0.82g, 0.73 mmol) was added to portion wise at 0°C. After addition, the mixture stirred for 8 h at room temperature. Then the reaction mixture was poured into 100ml water. The crude product was extracted with EtOAc and washed with brine. The combined organic layers were dried over anhydrous Na₂SO₄. Purification was operated by column chromatography by eluting with petroleum ether / ethyl acetate (99:1) to afford green solid as a product, yield 42%. FT-IR (cm⁻¹) 1060 (trans olefinic bond), 1624 (C=C, aromatic Stretch), 1322 (C-N Stretch for TPA). ¹H NMR (300 MHz, CDCl₃) δ_H 7.39 (d, *J* = 8.4 Hz, 6H), 7.33 (d, *J* = 8.6 Hz, 6H), 7.28 (d, *J* = 8.5 Hz, 6H), 7.03 (d, *J* = 8.5 Hz, 6H), 6.97 (d, *J* = 9.3 Hz, 3H), 6.87 (d, *J* = 16.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ_C 146.84, 136.52, 131.79, 130.44, 128.76, 127.82, 127.58, 126.28, 124.33, 121.08.

General procedure E for Heck coupling reaction (11)

Tris-(4-((E)-4-bromostyryl)phenyl)amine (1eq), vinyllated aromatic compound (3 eq), Bu₄NBr (6 eq), Pd(OAc)₂ (8 mol%) were dissolved in dry DMF/ toluene (1:1) mixture. The resulting solution was purged under nitrogen for half an hour, then triethylamine (0.23 mmol) was added as a base and heated the reaction mixture to 95°C and maintained for overnight. After completion of reaction, the resulting mixture was passed through celite bed and washed with ethyl acetate. The organic layer further washed with saturated brine solution and dried over anhydrous Na₂SO₄. The crude material was purified by column

chromatography using petroleum ether / ethyl acetate (97:3) as a eluent, to afford greenish semi solid as a product.

Synthesis of TTPA (11a)

Synthesized according to general procedure E using Tris-(4-((E)-4-bromostyryl)phenyl)amine **10** (0.13g, 0.016 mmol) and 1, 2, 3-tris(dodecyloxy)-5-vinylbenzene **5a** (0.32g, 0.05 mmol). Yield is 64%, FT-IR (cm⁻¹) 3026 (C-H Stretch), 1658 (C=C olefin), 1594 (C=C, aromatic Stretch), 1120 (C-O Stretch), 1054 (*trans* olefinic bond), 1322 (C-N Stretch for TPA). ¹H NMR (400 MHz, CDCl₃) δ 7.49 (d, *J* = 3.9 Hz, 2H), 7.45 (d, *J* = 6.8 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.08 (s, 1H), 7.04 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 16.2 Hz, 1H), 6.74 (s, 1H), 4.03 (dt, *J* = 17.4, 6.5 Hz, 3H), 1.88 – 1.77 (m, 3H), 1.54 – 1.47 (m, 3H), 1.30 (s, 27H), 0.91 (t, *J* = 6.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 153.28, 146.80, 138.35, 136.42, 132.39, 131.73, 128.68, 127.76, 127.52, 127.45, 126.67, 126.64, 126.07, 124.36, 124.17, 120.98, 105.19, 73.52, 69.16, 31.91, 29.74, 29.72, 29.69, 29.65, 29.60, 29.44, 29.42, 29.37, 29.35, 26.11, 22.67, 14.09; MS (MALDI-TOF): *m/z* calcd for C₁₇₄H₂₆₇NO₉: 2515.04; found 2516.99.

Synthesis of DTPA (11b)

Synthesized according to general procedure E using Tris-(4-((E)-4-bromostyryl)phenyl)amine **10** (0.3g, 0.038 mmol) and 1,3-bis(dodecyloxy)-5-vinylbenzene **5b** (0.54g, 0.12 mmol). Yield is 65%, FT-IR (cm⁻¹) 3026 (C-H Stretch), 1662 (C=C olefin), 1590 (C=C, aromatic Stretch), 1122 (C-O Stretch), 1058 (*trans* olefinic bond), 1322 (C-N Stretch for TPA). ¹H NMR (300 MHz, CDCl₃) δ 7.50 (s, 6H), 7.45 (d, *J* = 9.9 Hz, 6H), 7.42 – 7.32 (m, 6H), 7.12 (d, *J* = 8.6 Hz, 6H), 7.10 – 7.03 (m, 9H), 6.96 (d, *J* = 16.2 Hz, 3H), 6.69 (s, 6H), 6.42 (s, 3H), 4.00 (t, *J* = 6.4 Hz, 12H), 1.84 – 1.79 (m, 12H), 1.48 (d, *J* = 7.5 Hz, 12H), 1.30 (s, 96H), 0.91 (t, *J* = 6.2 Hz, 18H). ¹³C NMR (75 MHz, CDCl₃) δ 160.47, 146.80, 139.15, 136.87, 136.43, 135.15, 131.72, 130.37, 128.51, 127.75, 127.50, 126.84, 126.63, 126.07, 124.16, 120.98, 105.09, 100.94, 68.05, 31.88, 29.63, 29.60, 29.57, 29.37, 29.31, 29.27, 26.04, 22.64, 14.07; MS (MALDI-TOF): *m/z* calcd for C₁₃₈H₁₉₅NO₆: 1962.49; found 1964.04.

Results and Discussion

Synthesis and Characterization of star like molecules

The initial focus of our systematic approach was on the synthesis of triphenyl amine based star like molecules with optical properties. The synthetic routes of two star like molecules (TTPA and DTPA) are depicted in Scheme 1. These star like molecules were synthesized *via* convergent synthetic approach. Briefly, the important intermediate **10** was synthesized by the Wittig reaction between the 4-bromobenzyl bromide Wittig salt (**7**) and tris-(4-formylphenyl)-amine (**9**) in DCM using K^tOBu as a base. Compound **9** was prepared according to previous reported procedure²⁰ and Compound **8** was reacted with POCl₃ and DMF at 110°C. Another key reactant **5** was obtained by stepwise reaction. First, the alkylation carried out between methyl hydroxy benzoate **1** and 1-bromo dodecane in DMF under nitrogen atmosphere while K₂CO₃ as a base, the alkylated product was reduced from ester to alcohol **3**, using LAH in THF at 0°C. Then the alcohol was oxidised with PCC in DCM at 0°C to afford corresponding aldehyde **4**. Finally, the vinylated product **5** was obtained by Wittig reaction between aldehyde and methyltriphenylphosphonium iodide in DCM under nitrogen atmosphere, by using K^tOBu as a base. The triple site Heck coupling reaction of intermediate **10** and vinylated compound **5**

catalyzed by Pd(OAc)₂ in ligand TBAB and basic media gives the desirable star like molecules of DTPA and TTPA. All the compounds were unambiguously characterized by ¹H, ¹³C, DEPT 135 NMR and mass spectra and all spectral data are given in supporting information.

Photophysical studies

The photophysical studies of TTPA (11a) and DTPA (11b) in a series of protic and aprotic solvents have been carried out. Table 2 show the absorption and fluorescence data of **11a** and **11b** in different solvents. The absorption and emission spectra of triphenylamine based molecules and their intermediate **10** in THF are depicted in Figure 2. The absorption spectrum of intermediate compound **10** displayed at 390 nm and the DTPA and TTPA in THF display two absorption peaks centred around 350 and 420 nm. These bands are attributed to the localised aromatic π-π* transition. The first absorption band in the shorter wavelength region between 250-390 nm is attributed to the triphenylamine moiety. The longer wavelength absorption band between 390 to 420 nm is ascribed to the bromophenylene and alkoxyatedvinylene modified TPA. The emission spectra of TPA derivatives were recorded by exciting at its longer wavelength absorption maximum. The observed red shift in the absorption and emission maximum of DTPA and TTPA as compared with the triphenylamine core containing bromophenylene reflects there is an obvious increase in π-π* delocalization with the increase of the generation of star like molecules as the whole molecule has acted as electron rich molecules (ie. D-π-D). In solution the vibronic splitting is very less obviously because the individual components are broadened. These results are also demonstrated that the effective conjugation length improves with the increasing generation of the star like molecules. Further, we compared both the star like compounds behaviour in solid thin film. The absorption and emission characteristics of DTPA and TTPA were presented in Figure S3. From the thin film coated absorption spectra of all TPA derivatives shows broad band compared to solution state which might be contribute to the enhanced photoactivity under visible light. The edge of TTPA compound shows a remarkable shift to the visible range compared to DTPA compound, a broad absorption covering the range of 300-550 nm (UV to visible) for TTPA and a broad band of DTPA compound appeared between the ranges of 320-500 nm. This may be attributed to the absorption tendency of conjugated triphenylamine moieties. We assume that the main contribution to absorption in the spectral region from 300-500 nm to 300-550 nm is due to the monomer form rather than due to the aggregated form of the TPA derivatives. This behaviour is confirms the low tendency of conjugated molecules to form aggregates in the solid state. Similar behaviour is also found in emission spectra.

Table 1 Photo physical properties of DTPA and TTPA in THF.

Compounds	λ_{abs} (nm)	λ_{em} (nm)	Stoke shift (cm ⁻¹)	ΦF
DTPA	406	500	4630	0.40
TTPA	404	492	4427	0.37

The absorption and emission spectra of TPA derivatives recorded in various solvents are shown in Figure 3 and Figure S1. The emission band is found to shift towards longer wavelengths with increasing solvent polarity; this shift is due to the stabilization of the charge-transfer transition in polar solvents. The observed higher value of stokes shift on moving from non-polar to polar solvents is an indicative of the fact that the intramolecular charge

transfer transition is more when compared to the ground state. Further, when increasing the solvent polarity, the emission spectra was increasing gradually, due to the charge separation upon excitation³², which is confirmed by Dimroth–Reichardt solvent polarity correlations³³ (Figure 4). Figure 5 shows the fluorescence decays of DTPA and TTPA in DMF monitored at 529 and 522 nm respectively. DTPA and TTPA exhibit a single exponential decay in DMF with a lifetime of 2.31 and 2.19 ns respectively. This confirms, both TPA derivatives exhibit single conformation in the excited state. Furthermore, we also investigated the PL quantum yields (Φ_F , Table 1) of the star like molecules **11**(**11a/11b**) by using quinine sulphate in 0.1(M) H₂SO₄ (refractive index $\eta=1.33$) as a standard one having quantum yield of 0.54³⁴, and the Φ_F values of TTPA and DTPA are 0.37 and 0.40 respectively. The quantum efficiency of the DTPA (**11b**) is slightly higher than the TTPA (**11a**) due to the lower energy of the emitting states, which may in turn facilitate the nonradiative pathways.³⁵

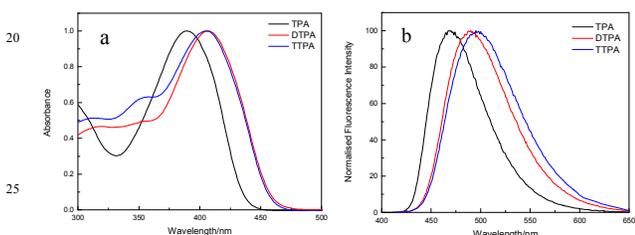


Fig. 2 Absorption and emission spectra of TPA derivatives in THF.

Table 2 Absorption and emission values of DTPA and TTPA in various organic solvents.

En try	Solvents	E_{T30}	DTPA			TTPA		
			λ_{abs} (nm)	λ_{em} (nm)	Stoke shift (cm^{-1})	λ_{abs} (nm)	λ_{em} (nm)	Stoke shift (cm^{-1})
1	Acetone ^a	42.2	404	514	5297	402	505	5074
2	Benzene ^b	34.3	410	468	3028	409	464	2898
3	DCM ^a	40.7	405	507	4967	407	499	4530
4	DMF ^a	43.2	406	528	5691	407	517	5227
5	DMSO ^a	45.1	407	534	5843	399	524	5978
6	MeOH ^c	55.4	388	509	6127	380	498	6235
7	THF ^a	37.4	406	500	4630	404	492	4427

^a polar aprotic, ^b non-polar aprotic, ^c polar protic.

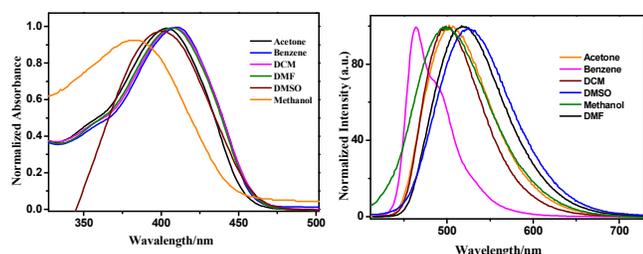


Fig. 3 Absorption and fluorescence spectra of TTPA in different solvents.

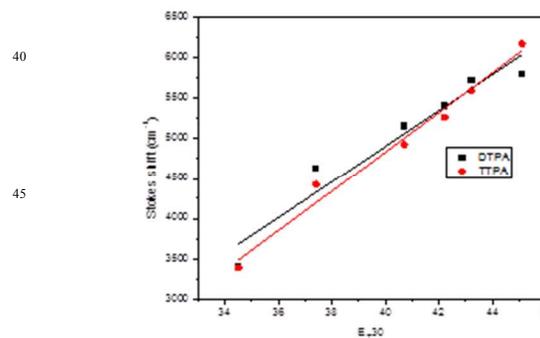


Fig. 4 Dimroth–Reichardt solvent polarity correlations for DTPA and TTPA.

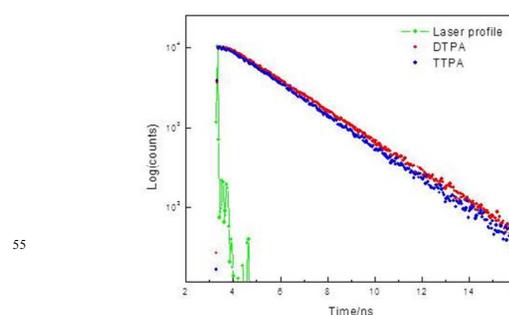


Fig. 5 Fluorescence decay profile of DTPA and TTPA in DMF solution.

Aggregation studies

In general, highly conjugated star like molecules show an aggregation induced fluorescence quenching/enhancement behaviour. Further, the solubility is fully depends on the side groups attached to the backbone that can facilitate good solubility of conjugated molecules in common organic solvents and also allow for easy processing due to their size and relative flexibility. However, conjugated star like molecules are able to aggregate to lower their energy due to the long alkyl chain present in the molecules. Hence we would like to study the aggregation induced fluorescence behaviour of TPA derivatives having highly branched conjugation and an alkyl chain in the terminals. Further we studied the absorption and emission behaviour of the aggregation process of TPA derivatives (**11**) by increasing the percentage of water in the THF solution. Figure 6 and Figure S2, shows the absorption and emission behaviour of TTPA in pure THF and in THF/water mixtures. Interestingly, the increasing of percentage of water has led to the decrease in absorbance along with clear isobestic point at 445 nm. Above 60% of water the precipitation of TPA derivatives leads to scattering in the absorption spectrum figure 6a. With gradual increase in percentage of water which leads to decrease in emission intensity as similar to absorption spectra figure 6b. The observed red shift in the emission spectra of TPA derivatives until 80% of water is due to the increase in polarity, and further increase in water fraction leads to blue shift. The blue shift is likely due to the formation of π -stacked aggregates with a *cis* to *trans* formation and also the scattering of the light due to the precipitation occurs.

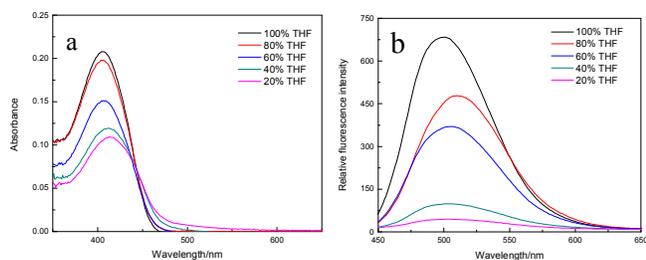


Fig. 6 Aggregation induced quenching of DTPA in THF/water system DTPA (a) absorption (b) emission spectra.

Electrochemical Experiments

Figure 7, shows the cyclic voltammetry (CV) diagrams of the two star like molecules of DTPA and TTPA in CH_2Cl_2 in the presence of $\text{Bu}_4\text{N}(\text{PO}_4)$ as the supporting electrolyte with glassy carbon working electrode, a platinum wire counter electrode and saturated calomel as a reference electrode at the scan rate of 100 mVs^{-1} . Figure 6 shows quasi reversible redox peaks of DTPA and TTPA. The oxidation peak potentials of DTPA and TTPA are 0.86 and 0.848 V, respectively, suggesting a successive formation of the cation radical should be attributed to the removal of electrons from the triphenylamine groups. On the basis of the roughly evaluated onset oxidation potentials, the HOMO energy levels of DTPA and TTPA are estimated as -5.274 and -5.27 eV, respectively ($\text{HOMO} = -e(E^{\text{onset}} + 4.6)$), which means that the electron donating ability of the TPA is enhanced (Figure 7). The LUMO energy levels of DTPA and TTPA are -2.194 and -2.16 eV, respectively, calculated from the HOMO energy level and energy band gap (E_g) determined from the UV-Vis absorption spectra ($\text{LUMO} = \text{HOMO} - E_g$). The energy level parameters and the electrochemical properties data are listed in Table 3. The calculated ground-state geometries demonstrate intramolecular charge transfer (ICT) occurs in both molecules during the procedure of charge excitation from HOMO to LUMO. Generally, high charge mobility containing molecules (D- π -D) having strong intra molecular charge transfer. Hence, the restrict charge conjugation through the π system of TPA derivatives and favour the charge delocalization by a “through space” mechanism. The experimental results indicate that there is cooperative enhancement originating from the inter-branch coupling and an increase of light-harvesting ability with increasing the conjugated molecule size.

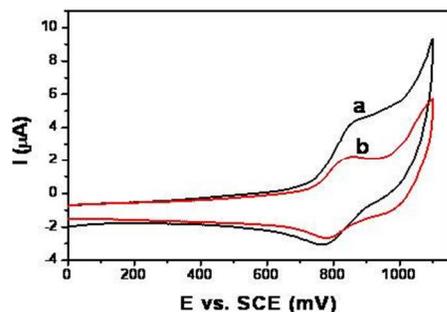


Fig. 7 Cyclic voltammograms of (a) DTPA and (b) TTPA in 0.1M $\text{Bu}_4\text{NPO}_4/\text{CH}_2\text{Cl}_2$, scan rate of 100 mVs^{-1} .

Table 3 The energy level parameters and the electrochemical properties of DTPA and TTPA.

11	E^{onset} (V)	$^a E_p^{\text{ox}}$ (V)	$^b \text{HOMO}$ (eV)	$^c \text{LUMO}$ (eV)	$^d E_g$ (eV)
DTPA	0.674	0.86	-5.274	-2.634	2.64
TTPA	0.67	0.848	-5.27	-2.60	2.67

^a Onset oxidation potential, ^b peak potential, ^c HOMO (eV) = $-e(E^{\text{onset}} + 4.6)$; LUMO = HOMO - E_g , ^d Determined from UV-Vis absorption spectra.

Thermogravimetric studies

The synthesized triphenylamine based star like molecules of TTPA and DTPA were investigated through thermogravimetric analysis (TGA) under nitrogen atmosphere and heating rate at $20 \text{ }^\circ\text{C min}^{-1}$. From the TGA curve (Figure S4) the TTPA based dendrimers initial decomposition temperature from $86.98 \text{ }^\circ\text{C}$ to $183.88 \text{ }^\circ\text{C}$ gradually increasing the weight losses of 0.05 to 2.5%. Similarly, DTPA having initial decomposing temperature at $80.88 \text{ }^\circ\text{C}$ then the decomposing temperature gradually increased to $365.40 \text{ }^\circ\text{C}$ and the weight losses is 0.3% ($80.88 \text{ }^\circ\text{C}$), 5.24% ($232.71 \text{ }^\circ\text{C}$) and 19.82% ($365.40 \text{ }^\circ\text{C}$) are respectively, these results exhibiting the more thermal stability of TPA derivatives. From the TGA results (Figure S4) we observed that the DTPA based star like molecule is more stable than the TTPA. Further, we measured the DSC (Figure S5) of DTPA and TTPA, it shows that the melting temperature of DTPA and TTPA is $162 \text{ }^\circ\text{C}$ and $113 \text{ }^\circ\text{C}$ respectively. The above results indicate that the melting temperature of TTPA is quit less compare to DTPA, due to the presence of increasing the number of alkoxy chain at the end of the peripheral. In addition to that, there is no glass transition temperature detected; the reason may be that the structure of DTPA and TTPA are so rigid.

Conclusion

To summarize, novel triphenylamine-based star like molecules have been synthesized and well characterised by various spectral data. The photophysical properties of newly synthesized star like molecules of DTPA and TTPA were carried out in various solvents. Comparing the two compounds such as DTPA and TTPA, both the compounds are similar photo behaviours and almost equal life time in the excited states. This may be due to the inter-branch coupling, as a result in cooperative enhancement. Furthermore, two newly synthesized molecules exhibit broad absorption range covering the whole visible spectral region in solution as well as solid thin film phase. Based on the thermogravimetric results DTPA is more stable than the TTPA. Hence, these photophysical and electrochemical properties call attention to that our materials are potential candidates as donor materials for solution-processable organic photovoltaic cells.

Acknowledgment

RB and AS acknowledge the financial support of the Department of Science and Technology, New Delhi, India (Grant No. SR/F/1584/2012-13), Council of Scientific and Industrial Research, New Delhi, India (Grant No. 01(2540)/11/EMR-II) and University Grants Commission, New Delhi, India (Grant No. UGC No.41-215/2012 (SR)). VT thanks to UGC-FRP (Grant No. F. 4-5(24-FRP)/2013(BSR)) for financial support.

References

- 1 J. M. J. Frechet, *Dendrimers and supramolecular chemistry* PNAS, 2002, **99**, 4782-4787.
- 2 G. R. Newkome, C. N. Moorefield and F. Vogtle, *Dendritic Molecules: Concepts, Syntheses, Perspectives* (VCH, Weinheim, Germany), 1986.
- 3 (a) J. M. J. Frechet, and D. A. Tomalia, eds. *Dendrimers and Other Dendritic Polymers* (Wiley, Chichester, U.K.). 2001; (b) J. You, G. Li and Z. Wang, *Org. Biomol. Chem.*, 2012, **10**, 9481-9490; (c) J. You, G. Li, R. Wang, Q. Nie, Z. Wang and J. Li, *Phys. Chem. Chem. Phys.*, 2011, **13**, 17825-17830; (d) J. You, G. Li and Z. Wang, *RSC Adv.*, 2012, **2**, 9488-9494; (e) J. You, G. Li and Z. Wang, *Polymer*, 2012, **53**, 5116-5123.
- 4 J. Li and D. Liu, *J. Mater. Chem.*, 2009, **19**, 7584-7591.
- 5 J. Cremer and C.A. Briehn, *Chem Mater.*, 2007, **19**, 4155-4165.
- 6 K. R. J. Thomas, J. T. Lin, M. Velusamy, Y.T. Tao and C.H. Chuen, *Adv. Funct. Mater.*, 2004, **14**, 83-90.
- 7 J. M. Lupton, D.W. Samuel, R. Beavington, P.L. Burn and H. Bassler, *Adv. Mater.*, 2001, **13**, 258-261.
- 8 N. Satoh, J. S. Cho, M. Higuchi and K. Yamamoto, *J. Am. Chem. Soc.*, 2003, **125**, 8104-8105.
- 9 W. Denk, J. H. Strickler and W.W. Webb, *Science*, 1990, **248**, 73-76.
- 10 W. R. Zipfel, R.M. Williams and W.W. Webb, *Nat. Biotechnol.*, 2003, **21**, 1369-1377.
- 11 J. D. Bhawalkar, N. D. Kumar, C. F. Zhao and P.N. Prasad, *J. Clin. Lasers Med. Surg.*, 1997, **15**, 201-204.
- 12 A. Karotki, M. Kruk, M. Drobizhev, A. Rebane, E. Nickel and C.W. Spangler, *IEEE J. Sel. Top. Quantum Electron.*, 2001, **7**, 971-975.
- 13 Z. Fang, T. L. Teo, L. Cai, Y. H. Lai, A. Samoc, and M. Samoc, *Org. Lett.*, 2009, **11**, 1-14.
- 14 (a) J. E. Ehrlich, X. L. Wu, L. Y. S. Lee, Z. Y. Hu, H. Rockel, S. R. Marder and J. W. Perry, *Opt.Lett.*, 1997, **22**, 1843-1845; (b) J. D. Bhawalkar, G. S. He and P. N. Prasad, *Rep. Prog. Phys.*, 1996, **59**, 1041-1070.
- 15 D. A. Parthenopoulos and P. M. Rentzepis, *Science*, 1989, **245**, 843-845.
- 16 K. Li, J. Qu, B. Xu, Y. Zhou, L. Liu, P. Peng and W. Tian, *New J. Chem.*, 2009, **33**, 2120-2127.
- 17 S. Roquet, A. Cravino, P. Leriche, O. Aleveque, P. Frere and J. Roncali, *J. Am. Chem. Soc.*, 2006, **128**, 3459-3466.
- 18 Z. Yang, B. Xu, J. He, L. Xue, Q. Guo, H. Xia and W. Tian, *Organic Electronics*, 2009, **10**, 954-959.
- 19 (a) Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1; (b) Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, **107**, 953.
- 20 K. C. Majumdar, B. Chattopadhyay, P. K. Shyam and N. Pal, *Tetrahedron Letters*, 2009, **50**, 6901-6905.
- 21 T. C. Lin, Y. F. Chen, C. L. Hu and C. S. Hsu, *J. Mater. Chem.*, 2009, **19**, 7075-7080.
- 22 (a) A. R. Murphy and J. M. J. Frêche, *Chem. Rev.*, 2007, **107**, 1066-1096; (b) A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay and A. Salleo, *Chem. Rev.*, 2010, **110**, 3-24.
- 23 Y. Yang, J. Zhang, Y. Zhou, G. Zhao, C. He, Y. Li, M. Andersson, O. Inganäs and F. Zhang, *J. Phys. Chem. C*, 2010, **114**, 3701-3706.
- 24 P. Bonhôte, J. E. Moser, R. H. Baker, N. Vlachopoulos, S. M. Zakeeruddin, L. Walder and Grätzel, *J Am Chem Soc.*, 1999, **121**, 1324-1336.
- 25 (a) X. Q. Zhang, Z.G. Chi, B. J. Xu, H. Y. Li, Z. Y. Yang, X. F. Li, S. W. Liu, Y. Zhang and J. R. Xu, *Dyes Pigm.*, 2011, **89**, 56- 62; (b) W. Qin, D. Ding, J. Z. Liu, W. Z. Yuan, Y. Hu, B. Liu and B. Z. Tang, *Adv. Funct. Mater.*, 2012, **22**, 771- 779.
- 26 (a) B. R. Gao, H. Y. Wang, Y. W. Hao, L. M. Fu, H. H. Fang, Y. Jiang, L. Wang, Q. D. Chen, H. Xia, L. Y. Pan, Y. G. Ma and H. B. Sun, *J. Phys. Chem. B*, 2010, **114**, 128-134; (b) B.-R. Gao, H. Y. Wang, Z. Y. Yang, H. Wang, L. Wang, Y. Jiang, Y. W. Hao, Q. D. Chen, Y. P. Li, Y. G. Ma and H. B. Sun, *J. Phys. Chem. C*, 2011, **115**, 16150-16154.
- 27 D. Choi, J. H. Lee, K. H. Shin and E. J. Shin, *Bull. Korean Chem. Soc.*, 2007, **28**, 983-989.
- 28 V. R. Donuru, G. K. Vegesna, S. Velayudham, G. Meng and H. Liu, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2009, **47**, 5354-5366.
- 29 M. J. Park, J. Lee, I. H. Jung, J. H. Park, H. Kong, J. Y. Oh, D. H. Hwang and H. K. Shim, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2010, **48**, 82-90.
- 30 H. Hopf, J. Hucker, and L. Ernst, *Eur. J. Org. Chem.*, 2007, 1891-1904.
- 31 Z. Liu, X. Xiong, J. Qin, H. Gong and Q. Wang, *Journal of Molecular Structure*, 2009, **934**, 86-90.
- 32 (a) C. Katan, F. Terenziani, O. Mongin, M. H. V. Werts, L. Porrees, T. Pons, J. Mertz, S. Tretiak and M. Blanchard-Desce, *J. Phys. Chem. A*, 2005, **109**, 3024-3037; (b) G. Bordeau, R. Lartia, G. Metge, C. F. Debuisschert, F. Charra and M. P. Teulade-Fichou, *J. Am. Chem Soc.*, 2008, **130**, 16836-16837.
- 33 (a) C. Reichardt, *Chem. Rev.* 1994, **94**, 2319-2358; (b) S. Achelle, I. Nouira, B. Pfaffinger, Y. Ramondenc, N. Plé, J. Rodriguez-López. *J. Org. Chem* 2009, **74**, 3711-3717; (c) C. Katan, F. Terenziani, O. Mongin, M. H. Werts, L. Porrees, T. Pons, J. Mertz, S. Tretiak, M. Blanchard-Desce. *J Phys Chem A* 2005, **109**, 3024-3037.
- 34 S. Chandra, P. Patra, S. H. Pathan, S. Roy, S. Mitra, A. Layek, R. Bhar, P. Pramanik and A. Goswami, *J. Mater. Chem. B*, 2013, **1**, 2375-2382.
- 35 H. M. Kim, M. S. Seo, S. J. Jeon and B. R. Cho, *Chem. Commun.*, 2009, 7422-7424.