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Synthesis and properties of hole-transporting triphenylamine-derived dendritic compounds



PIGMENTS

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ABSTRACT

Materials based on triphenylamino core linked with different alkoxyphenyl-substituents through olefinic spacers were synthesised, and their thermal, photophysical and photoelectrical properties were investigated. The synthesized compounds showed relatively good thermal stability. Derivatives containing shorter alkyl chains displayed glass-forming ability, while the compounds containing flexible alkyl termini demonstrated liquid-crystalline behaviour. Flexible alkyl substituents at the periphery of triphenylamine derivatives prevented the close packing of chromophores and hence, they showed relatively similar absorption and fluorescence in thin-films and solutions. Reduction in fluorescence quantum yield in thin-films upon decreasing the size of peripheral alkyl substituents confirmed enhanced intermolecular interactions and in turn, suggested migration-induced exciton quenching at nonradiative decay sites. Ionization potentials of thin solid layers estimated by photoelectron emission spectroscopy ranged from 5.21 to 5.47 eV. Hole-drift mobility of ethyl substituted triphenylamine measured using xerographic time-of-flight (XTOF) method was 1.3×10^{-3} cm² V⁻¹ s⁻¹ at an electric field of 10^{6} Vcm⁻¹.

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1. Introduction

In the last decades, the research and development of sustainable and renewable energy sources based on organic semiconductors like organic light emitting diodes (OLEDs), organic photovoltaic devices (OPVs) or organic field-effect transistors increased in greater scale due to the quest new technological approaches as well as new materials [1–5]. Solution processable dendritic materials are particularly interesting as charge-transporting and/or lightemitting materials in OLEDs and as light-harvesting antennae in OPVs [6–9].

Triphenylamine (TPA) based compounds are extensively investigated as hole-transporting organic semiconductors for organic electronics since they can form stable aminium radical cations upon oxidations [10-12]. TPA derived low-molar-mass, dendritic or hyper branched and polymeric materials have attracted enormous research interests in recent years because of their high holemobility, stable redox characteristics, electron-donating ability and/or interesting luminescence characteristics [13–18]. TPA is highly electron rich and possesses a propeller-like structure, which enables its derivatives to transport holes and to be solution processable. However, exploitation of low-molar-mass TPA compounds in cost-effective device fabrications is often limited because of their poor film forming property upon solution processing [19,20]. Hence, these materials must be deposited in optoelectronic devices by vacuum evaporation method, which is not beneficial for the commercial applications. Strategic design of electroactive compounds in the form of dendritic or star-shaped structures embedding flexible linkages represent a very convenient way to shift the processing technique in cost-effective way without much altering the intended decisive properties for application in organic electronics [21–24]. Though, TPA-based solution processable compounds possessing superior charge-transporting [23,25–27] and light harvesting/emitting properties [21,22,24] have been reported, they are still of interest in terms of competent and/or combined advanced properties. In this article, we report on the

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synthesis, thermal, photophysical and photoelectrical properties of a series of dendritic compounds containing triphenylamino group as a central core and electron-donating alkoxyphenyl-substituents as arms linked through olefinic spacers.

2. Experimental section

2.1. Materials

The starting compounds, i.e., triphenylamine, methyl-3,4,5trihydroxybenzoate and diethyl-4-methoxy benzyl phosphonate, were purchased from Sigma Aldrich and used as received. The reagents and the required materials, i.e., phosphoryl chloride, dimethyl formamide, 18-crown-6, iodoethane, 1-bromododecane, 1-bromodecane, lithium aluminium hydride (2 M solution in THF), phosphorous tribromide, triphenyl phosphine, potassium hydroxide, potassium carbonate, sodium sulphate, were also purchased from Sigma Aldrich and used as received.

2.2. General procedure for wittig reaction

5-(Bromomethyl)-1,2,3-tris (alkyloxy)benzene, 7, 8 and 9, (1.88 mmol) was dissolved in 35 mL of DMF and triphenyl phosphine (0.49 g, 1.88 mmol) was added into the obtained solution. It was refluxed for 12 h under nitrogen. DMF was evaporated at the reduced pressure and the crude product obtained was dissolved in 40 mL of dry THF. Then, the reaction mixture was cooled down to 0 °C. Potassium ter-butoxide (0.4 g, 3.6 mmol) followed by tris(4formylphenyl)amine (0.2 g. 0.6 mmol) were added under nitrogen. The reaction mixture was stirred at 0 °C for 1hr and then, allowed to warm to room temperature. It was further stirred for 6 h at room temperature under nitrogen. Water was added to the reaction mixture followed by ethyl acetate, and the organic layer was separated. The organic phase was washed with brine and dried over sodium sulphate before the solvent was evaporated. The crude product was purified by silica gel column chromatography using solvent mixtures of hexane/ethyl acetate (97/3) for 11, (95/5) for 12 and (8/2) for **13** as eluents. Compound **13** was further purified by recrystallisation from methanol.

2.2.1. Tris(4-(3,4,5-tris(dodecyloxy)styryl)phenyl)amine (11)

Yield = 35% (0.46 g); Yellow solid (FW = 2210.66 g/mol). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.40 (d, J = 2.9 Hz, 6H), 7.10 (d, J = 2.9 Hz, 6H), 6.92 (s, 6H), 6.69–6.35 (m, 6H), 4.04–3.82 (m, 18H, OCH₂), 1.86–1.70 (m, 18H, CH₂), 1.50–1.26 (m, 162H, CH₂), 0.87 (t, J = 4.4 Hz, 27H, CH₃). ¹³C NMR (75.5 MHz, CDCl₃, δ ppm): 153.2, 152.7, 146.6, 132.6, 132.2, 127.7, 127.3, 124.2, 107.5, 105.1, 73.4, 69.0, 31.9, 30.3, 29.7, 29.7, 29.6, 29.4, 29.4, 29.3, 29.3, 26.1, 26.1, 22.7, 21.7, 14.1. IR (KBr, υ cm⁻¹): (aliphatic C–H) 2955, 2919, 2849; (Ar C= C) 1589, 1511; (C–N stretch) 1240; (C–O stretch) 1122. Anal. Calc. for C₁₅₀H₂₄₉NO₉: C 81.50; H, 11.35; N, 0.63; O, 6.51%. Found: C, 81.84; H, 11.79; N, 0.79%. MS (MALDI-TOF) *m/z* = 2208.38 (exact mass = 2208.91).

2.2.2. Tris(4-(3,4,5-tris(decyloxy)styryl)phenyl)amine (12)

Yield = 50% (0.58 g); Yellow semi-solid (FW = 1958.17 g/mol). ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.41–6.33 (m, 6H), 7.03–6.87 (m, 6H), 6.69–6.35 (m, 12H), 4.04–3.89 (m, 18H, OCH₂), 1.87–1.69 (m, 18H, CH₂), 1.51–1.27 (m, 126H, CH₂), 0.88 (t, J = 4.4 Hz, 27H, CH₃). ¹³C NMR (75.5 MHz, CDCl₃, δ ppm): 153.2, 152.8, 146.5, 132.8, 132.2, 127.6, 127.2, 124.2, 107.5, 105.0, 73.4, 69.1, 69.0, 68.8, 31.9, 31.9, 30.3, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 26.1, 26.1, 22.6, 21.7, 14.1 IR (KBr, υ cm⁻¹): (aliphatic C–H) 2954, 2924, 2853; (Ar C=C) 1589, 1507; (C–N stretch) 1235; (C–O stretch) 1117. Anal. Calc. for C₁₃₂H₂₁₃NO₉: C, 80.97; H, 10.96; N, 0.72; O, 7.35%. Found: C, 80.55;

H, 11.14; N, 0.68%. MS (MALDI-TOF) m/z = 1956.46 (exact mass = 1956.62).

2.2.3. Tris(4-(3,4,5-triethoxystyryl)phenyl)amine (13)

Yield = 31% (0.18 g); Yellow crystals (FW = 948.22 g/mol); m p.: 127–129 °C. ¹H NMR (300 MHz, CDCl₃), δ (ppm): 7.41 (d, J = 2.9 Hz, 6H), 7.11 (d, J = 2.9 Hz, 6H), 6.93 (s, 6H), 6.71 (s, 6H), 4.16–4.04 (m, 18H, OCH₂), 1.45 (t, J = 4.7 Hz, 18H, CH₃), 1.37 (t, J = 4.7 Hz, 9H, CH₃). ¹³C NMR (75.5 MHz, CDCl₃, δ ppm): 153.1, 146.5, 137.9, 132.8, 132.1, 127.5, 127.2, 127.1, 124.2, 105.2, 68.9, 64.7, 15.6, 15.0. IR (KBr, υ cm⁻¹): (aliphatic C–H) 2948, 2919, 2856; (Ar C=C) 1596, 1516; (C–N stretch) 1238; (C–O stretch) 1114. Anal. Calc. for C₆₀H₆₉NO₉: C, 76.00; H, 7.33; N, 1.48; O, 15.19%. Found: C, 75.88; H, 7.20; N, 1.52%. MS (EI) *m/z* = 949 [M + H]⁺.

2.3. Tris(4-(4-methoxystyryl)phenyl)amine (14)

Diethyl-4-methoxy benzyl phosphonate (0.48 g, 1.88 mmol) and tris(4-formylphenyl)amine (0.2 g, 0.6 mmol) were dissolved in 30 mL of dry THF and cooled to 0 °C. Potassium ter-butoxide (0.4 g, 3.6 mmol) was added into the solution. It was stirred at 0 $^\circ$ C for 1 h under nitrogen. Then, it was allowed to warm to room temperature and stirred for additional 4 h under nitrogen. Water was added to the reaction mixture followed by ethyl acetate, and the organic layer was separated. The organic phase was washed with brine and dried over sodium sulphate before the solvent was evaporated. The crude product was purified by silica gel column chromatography using hexane/ethyl acetate (8/2) solvent mixture as an eluent. Yield = 72% (0.28 g): Yellow crystals (FW = 641.82 g/mol): m p.: 199–201 °C. ¹H NMR (300 MHz, CDCl₃, δ ppm): 7.45 (d, J = 2.9 Hz, 6H), 7.39 (d, J = 2.9 Hz, 6H), 7.10 (d, J = 2.9 Hz, 6H), 6.96–6.87 (m, 12H), 3.82 (s, 9H, OCH₃). ¹³C NMR (75.5 MHz, CDCl₃, δ ppm): 159.1, 146.4, 132.4, 130.3, 127.5, 127.1, 126.9, 126.0, 124.2, 114.1, 55.3. IR (KBr, υ cm⁻¹): (arene C–H) 3024; (aliphatic C–H) 2951, 2927, 2851; (Ar C=C) 1605, 1511; (C-N stretch) 1249; (C-O stretch) 1173. Anal. Calc. for C₄₅H₃₉NO₃: C, 84.21; H, 6.12; N, 2.18; O, 7.48%. Found: C, 84.64; H, 5.89; N, 2.28%. MS (EI) $m/z = 642 [M + H]^+$.

2.4. Instrumentation

Nuclear magnetic resonance spectra were obtained in deuterated chloroform with a Varian Unity Inova spectrometer operating at 300 MHz and 75.5 MHz for ¹H and ¹³C nuclei respectively. All the data are given as chemical shifts δ (ppm) downfield from TMS. IRspectroscopy measurements were performed on a Perkin Elmer Spectrum GX spectrophotometer, using KBr pellets. Mass spectra of intermediates and low-molar mass target materials were obtained on a Waters ZQ 2000 spectrometer. The mass spectra of highermolecular-weight compounds were determined by MALDI-TOF using Shimadzu Biotech Axima Performance system and 2, 5dihydroxybenzoic acid (DHB) as the matrix under reflector mode of operation.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin Elmer Pyris Diamond DSC apparatus at a heating/cooling rate of 10 °C min⁻¹ under nitrogen atmosphere. Thermogravimetric analysis (TGA) was executed on TA Instruments Q100 under nitrogen atmosphere at a heating rate of 20 °C min⁻¹.

The textures of the mesophases were observed with a polarising microscope (AXIOLAB Zeiss) equipped with a LINKAM THMS 600 hot stage connected to a TP-92 temperature control unit.

X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 diffractometer (Bragg-Brentano parafocusing geometry) with vertical $\theta - \theta$ goniometer, and Anton-Paar TTK low temperature chamber. The goniometer was equipped with a curved graphite diffracted-beam monochromator, receiving (0.03°), incident and

diffracted-beam Soller slits. The detector was a scintillation counter. The angular 2θ diffraction range was between 1 and 40°. Sample was placed on a low background Si(510) plate, which later was placed on the temperature chamber sample holder. The data were collected with an angular (0.03°) step with 3 s per step. The X-ray diffractometer operated at 40 kV and 30 mA to generate Cu K α radiation.

Absorption spectra of the dilute solutions were recorded by UV-Vis-NIR spectrophotometer Lambda 950 (Perkin Elmer). Photoluminescence (PL) of the solutions and thin films was excited by 365-nm wavelength light emitting diode (Nichia NSHU590-B) and measured using back-thinned CCD spectrometer (Hamamatsu PMA-11). For these measurements dilute solutions of the investigated compounds were prepared by dissolving them in spectral grade tetrahydrofuran (THF) at 1×10^{-5} M concentration. The neat films of the investigated compounds were prepared from the 1×10^{-3} M THF solutions on the glass substrates by drop-casting technique. Fluorescence quantum yield (Φ_F) of the samples was estimated by utilizing integrating sphere (Sphere Optics) coupled to the CCD spectrometer using an optical fibre. Fluorescence transients were recorded using time-correlated single photon counting system PicoHarp 300 (PicoQuant GmbH). Pulsed excitation at 1 MHz repetition rate was provided by the picosecond diode laser with the pulse duration of 70 ps and the emission wavelength of 375 nm.

The ionization potentials (I_p) were measured by photoelectron spectroscopy in air as described earlier [28]. The materials were dissolved in chloroform and coated onto Al plates pre-coated with



Scheme 1. Synthetic route for the preparation of dendritic compounds 11-14.

~0.5 μ m thick methylmethacrylate and methacrylic acid copolymer (MKM) adhesive layer. The function of MKM layer is not only to improve adhesion, but also to eliminate the electron photoemission from Al layer. In addition, this layer is conductive enough to avoid charge accumulation on it during the measurements.

Hole-drift mobility of compound 13 was estimated by xerographic time-of-flight method [29,30]. The sample for the measurement was prepared by drop casting of the THF solution of compound **13** onto a polyester film with Al layer. After coating the sample was heated at 70 °C for 1 h. Thus the charge-transporting layer of the sample was prepared. The thickness of the transporting layer was ca. 5 μ m. Hole drift-mobility (μ) was measured by time-of-flight technique in the xerographic mode. The electric field was created by positive corona charging. The charge carriers were generated at the layer surface by illumination with pulses of nitrogen laser (pulse duration was 1 ns, wavelength 337 nm). As a result of pulsed illumination the layer surface potential decreased down to 2-5% of the initial potential. The capacitance probe connected to the wide frequency band electrometer measured the rate of the surface potential decrease dU/dt. The transit time t_t for the samples with the transporting material was determined from the kink of the curve of the dU/dt transient in log-log scale. The holedrift mobility was calculated by using the formula $\mu = d^2/U_0 t_t$, where d is the layer thickness, and U₀ the surface potential at the moment of illumination.

3. Results and discussion

3.1. Synthesis and characterisation

Synthesis of triphenylamine-based compounds ramified with alkoxyphenyl-substituents is shown in Scheme 1. Tris(4formylphenyl)amine (10) was synthesized from triphenylamine by Vilsmeier–Haack reaction using the known procedure [31]. For the preparation of alkoxyphenyl-intermediates (1, 2 and 3), firstly, methyl-3,4,5-trihydroxybenzoate was O-alkylated in acetone using potassium carbonate and corresponding bromo or iodo alkanes, i.e. 1-bromododecane for 1, 1-bromodecane for 2, iodoethane for 3, respectively, in the presence of catalytic amount of 18-crown-6 [32,33]. In the next reaction, the ester functional groups of compounds **1**, **2** and **3** were reduced using lithium aluminium hydride in THF to prepare (3,4,5-tris(alkyloxy)phenyl)methanols 4, 5 and 6, respectively [32,33]. These derivatives were brominated in the next step using phosphorous tribromide to synthesize the respective bromo compounds 7, 8 and 9 [32]. The Wittig reagent (phosphonium ylide) was prepared in situ from the bromine-containing compounds 7, 8 and 9 by refluxing with one equivalent of triphenyl phosphine in DMF. Wittig reactions of compound **10** with the corresponding alkoxyphenyl derivatives yielded the dendritic compounds 11-13. Compound 14 was prepared from diethyl-4methoxy benzyl phosphonate and compound 10 using the modified Wittig conditions.

Dendritic compounds **11–13** were found to be soluble in common organic solvents like dichloromethane, chloroform, toluene or THF, which was benefited from the alkyl-substituents and the olefin spacer. Characterization of these materials by mass spectrometry, elemental analysis, IR spectroscopy and ¹H and ¹³C NMR spectroscopy was therefore easily accomplished. The characterization data were in good agreement with the chemical structures of the synthesised compounds **11–14**.

3.2. Thermal properties

The thermal behaviour of compounds **11–14** under heat was investigated by DSC and TGA under a nitrogen atmosphere. The DSC

curves of compounds **11** and **14** are shown in Fig. 1. The data are summarized in Table 1.

During the first heating scan, compound 14 exhibited a sharp endotherm at 204 °C corresponding to the melting point. However, when the sample of compound **14** was cooled from the melt, it showed a glass transition at 91 °C demonstrating the formation of amorphous phase. During the second heating scan, compound 14 displayed not only the same glass transition observed upon cooling but also a temptation towards melting. This could be attributed to the comparatively lower stability of its glassy state [34]. Compound 13 containing ethyl chains demonstrated a glass transition at 107 °C during the first heating scan. On further heating above glass transition, compound 13 displayed two endothermic phase transitions at 130 and 168 °C, respectively (Table 1). The first endotherm at 130 °C suggested the solid-solid phase transition, where one crystal form apparently was transformed into another crystal form. The endothermic peak at 168 °C corroborates the melting of the second crystal structure to give an isotropic phase [34]. However, the cooling scan and the second heating scan of compound 13 did not show any thermal transitions which suggested that it can be transformed into amorphous (glassy) phase when cooled from the melt [34].

Different thermal behaviour was observed for compounds possessing flexible alkyl chains at the TPA rim. These compounds did not show any glass transitions. For compound **11** containing dodecyl alkyl chains, both the first and the second DSC heating cycles showed multiple endotherms apparently suggesting the occurrence of a liquid crystalline-like phase transitions. Upon first



Fig. 1. DSC thermograms of **11** and **14** recorded at a heating/cooling rate of 10 °C min⁻¹ under nitrogen.

 Table 1

 Thermal characteristic of compounds 11–14.

Compound	$T_{\mathbf{g}} \circ \mathbf{C}^{\mathbf{a}}$	$T_{\mathbf{c}} \circ \mathbf{C}^{\mathbf{b}}$	$T_{\rm m} \circ {\rm C}^{\rm c}$	$T_{\rm ID} ^{\circ}{\rm C}^{\rm d}$
11	_	2	37	369
12	_	-13	15	320
13	107	_	130, 168	387
14	91	-	204	417

^a Glass transition temperature.

^b Crystallization temperature.

^c Melting temperature.

^d 5% weight loss temperature.

heating, endothermic thermal transitions were observed at 24 °C and 37 °C with the enthalpy values of $\Delta H = 14.5$ kJ/mol and $\Delta H = 105.3$ kJ/mol, respectively. Cooling from the melt displayed only an exotherm corroborating the crystallization at 2 °C $(\Delta H = 115.6 \text{ kJ/mol})$. However, during the second heating cycle, the endothermic transitions reappeared at 24 °C ($\Delta H = 46.3$ kJ/mol) and 35 °C ($\Delta H = 32.4$ kJ/mol), respectively. Therefore, a liquidcrystalline phase was presumably formed on heating and existed between a short temperature range of 24 °C and 35 °C. The formed mesophase was found to be monotropic towards heating direction since, on cooling, the isotropic melt found to be merely solidified through a unique exotherm to acquire a crystalline phase. This observation was in concordance with the data of polarized optical microscopy (POM) measurements. The similar thermal transitions were also observed for compound 12 containing decyl chains; however, the mesophase was found to be less stable under heating and became isotropic liquid below room temperature.

Fig. 2 demonstrates the POM photographs of the mesophase of compound **11** during the heating of the sample. Upon heating to 24 °C, a viscous anisotropic liquid was formed with a rapid change in birefringence suggesting the formation of mesophase. At temperatures above 35 °C, the formed mesophase became a low-viscosity (free-flowing) isotropic fluid. The cooling of this isotropic melt did not again lead to the mesophase and the melt remained isotropic up to the room temperature. Nevertheless, the sample was found to be crystalline after storage at *ca*. 20 h at the ambient temperature. Hence, in conclusion, compound **11** could exist in liquid crystal form (monotropic) over the short range of temperatures between 24 °C and 35 °C.

Representative X-ray diffraction (XRD) patterns of compound **11** in the crystalline and the liquid crystalline phase are depicted in



Fig. 3. Absorption and fluorescence spectra of the TPA derivatives (a) **11**, (b) **12**, (c) **13** and (d) **14** in 10^{-5} M THF solutions (dashed lines) and neat films (solid lines). Fluorescence quantum yield values are indicated.



Fig. 2. Photographs showing optical textures of compound 11 taken at 32 (a) and 34 °C (b) during heating of the sample. (c) XRD patterns of 11 in the crystalline phase at 15 °C and N_D mesophase at 33 °C.

Fig. 2c. The XRD profile of compound **11** recorded at 15 °C showed a number of sharp diffractions suggesting the occurrence of a crystalline phase at this temperature. In the pattern recorded at 33 °C, a broad diffraction appeared at $2\theta = 20.4^{\circ}$ (4.3 Å). This diffraction could be attributed to the planar distance between discotic molecules. Moreover, a broad diffraction of low intensity also emerged at $2\theta = 2.1^{\circ}$ (42 Å), which apparently indicated the existence of a short-range columnar order in the mesophase. Therefore, compound **11** could be recognized as monotropic nematic discotic (N_D) mesophase with a short-range of columnar organization between 24 °C and 35 °C.

Compounds **11–14** found to be thermally stable without showing any decomposition under heating below *ca*. 320 °C. The onsets of thermal decompositions (at 5% weight loss) of compounds **11–14** were in the range of 320–417 °C. Such thermal stability allows their thermal treatment in a wide temperature range. Compound **13** containing ethyl substituents showed comparatively higher thermal stability with respect to that of its closer analogues **11** and **12**. Higher thermal stability of **13** could apparently be attributed to its more rigid structure. Interestingly, a similar trend was observed for compound **14** containing even shorter methyl substituents.

3.3. Photophysical properties

Absorption and fluorescence spectra of the dendritic TPA derivatives **11**, **12**, **13** and **14** are displayed in Fig. 3. The obtained optical properties of the derivatives are summarized in Table 2.

All the studied compounds exhibit similar absorption spectra in 10^{-5} M THF solutions, which are typical of phenylethenylsubstituted TPA derivatives [25,26]. Since the compounds have identical backbone and different (yet non-conjugated) alkoxy endgroups, the lowest energy absorption band maxima is located at similar wavelengths, 392–393 nm. The higher energy absorption band with half the intensity of the former and peaking at 302–311 nm can be attributed to the local excitation of a single TPA moiety [25]. Owing to highly twisted and labile molecular structure of the TPA compounds **11–14**, they demonstrate unstructured fluorescence spectra in THF solutions with the band maxima peaked at around 455 nm. As it was expected, fluorescence quantum yield (Φ_F) of the compounds in dilute solutions was estimated to be almost independent on the alkoxy end-groups and ranged from 49% to 52% (see Table 2).

Table 2	Tal	bl	е	2
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Photophysical	properties	of the	TPA	derivatives	11–14
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	Solution			Film						
	λ ^{max a} abs	λ _{FL} ^{max b}	$\Phi_{\rm F}{}^{\rm C}$	$\boldsymbol{\tau^d}$	λ ^{max a} abs	λ _{FL} maxb	$\Phi_{\rm F}{}^{\rm C}$	$\tau^{\mathbf{d}}$	f ^e	$\tau_{\text{avg}}{}^{f}$
Compound	nm	nm	%	ns	nm	nm	%	ns	%	ns
	311				319			0.25	25	
11	392	456	52	1.9	391	453	33	1.01	51	1.12
								2.27	24	
	311				316			0.20	36	
12	392	456	50	1.8	394	456	20	0.79	48	0.84
								2.45	16	
	311							0.20	50	
13	393	457	49	1.8	398	477	8	1.12	17	4.46
								12.6	33	
	302					460		0.02	74	
14	393	453	49	1.7	396	555	4	1.05	14	0.63
								3.93	12	

^a Absorption band maximum.

^b Fluorescence band maximum.

^c Fluorescence quantum yield ($\Phi_{\rm F}$) determined by integrating sphere method.

^d Fluorescence lifetime measured at. λ_{FL}^{max} .

^e Fractional contribution to the total fluorescence intensity.

^f Average fluorescence lifetime calculated by $\tau_{avg} = \sum \tau_i \bullet f_i$.

Unlike in dilute solutions the absorption spectra of the TPA derivatives in the neat films continuously red-shifted and broaden with decreasing the size of alkoxy chains. For the compounds with long decyloxy and dodecyloxy chains (compounds **11** and **12**) absorption spectra closely resemble those of dilute solutions. Obviously, bunches of long alkoxy chains prevent close packing of the molecules, thus weakening their intermolecular interactions in the solid state. On the other hand, short ethoxy groups (compound **13**) are unable to suppress this interaction resulting in broadened and red-shifted (by 5 nm) absorption spectrum with respect to that of solution. Upon replacement of the long tris(alkoxy) end-moieties with single methoxy groups at the *para* positions of the phenyls (compound **14**) intermolecular interactions are enhanced even more causing much stronger broadening of the band (see Fig. 3).



Fig. 4. Fluorescence transients of the TPA derivatives (a) **11**, (b) **12**, (c) **13** and (d) **14** in 10^{-5} M THF solutions (grey points) and neat films (black points). Lines mark exponential fits to the experimental data. Instrument response function (IRF) and fluorescence lifetimes are indicated.

Similar to the absorption spectra of neat films of compounds 11–14, fluorescence spectra also showed constant red shift as the size of alkoxy chains is being reduced. Due to the weak intermolecular interaction caused by sufficiently long alkoxy end-groups fluorescence spectra of the neat films of compounds 11 and 12 demonstrate negligible red shift as compared to those of solutions. Interestingly, vibronic structure in the spectra of **11** and **12** can be noticed, which might suggest molecular ordering in the films caused by the formation of liquid-crystalline phase at room temperature as disclosed by DSC and XRD measurements. The relatively short ethoxy groups (compound 13) already cause noticeable red shift of the fluorescence spectrum (by 20 nm) as compared to that in solution. Since the fluorescence spectrum of neat film of 13 contains no traces of vibronic replica and maintains the shape alike in solutions, it is likely dominated by amorphous character. Fluorescence spectrum of the neat film of compound 14 is found to be radically different in respect to those of the rest TPA derivatives. The methoxy groups are too small to impede tight molecule packing inducing excimer state formation via enhanced intermolecular forces. Thus, a new significantly red-shifted (by 74 nm) and unstructured band at 555 nm due to the excimer states is formed. Interestingly, a small band at the shorter wavelengths (~460 nm) similar to those observed in the neat films of compounds 11-13 can be also detected, which likely originates from the areas featuring weakly interacting molecule species.

 $\Phi_{\rm F}$ of the neat films of the synthesized compound was found to be considerably reduced (down to an order of magnitude) as compared to those of solutions. $\Phi_{\rm F}$ of 33%, 20%, 8% and 4% were obtained for the compounds 11, 12, 13 and 14, respectively. The most pronounced reduction of $\Phi_{\rm F}$ occurred for the TPA compounds with shorter alkoxy end-groups, what corresponded well to the stronger redshift of absorption and fluorescence spectra in the neat solid films. This reduction in $\Phi_{\rm F}$ confirmed enhanced intermolecular interactions, and moreover, suggested migration-induced exciton quenching at nonradiative decay sites to be the main excited-state deactivation channel [27]. Our previous studies indicated that exciton diffusion can be very efficient in tris(phenylethenyl)-substituted TPA films [27]. Hence, emission quenching facilitated by exciton diffusion is indeed probable in these compounds. Additionally, the significant reduction of $\Phi_{\rm F}$, which is particularly well pronounced in compound 14 and partly also in compound 13, can be attributed to the appearance of longlived excimer states. This is because long-lived states are naturally more susceptible to trapping by quenching sites such as lattice distortions, impurity traps and other defects.



Fig. 5. Photoelectron spectra and ionization potentials of the thin films of 11-14.

Fluorescence transients of the TPA derivatives **11–14** in dilute solutions demonstrate single exponential decay profiles with fluorescence lifetime (τ) varying from 1.7 ns to 1.9 ns (Fig. 4). Very similar τ of the compounds perfectly correlates with the similar fluorescence quantum yield data. Unlike in solutions, fluorescence transients in the compound neat films are clearly nonexponential indicating dispersive exciton hopping through the localized states in the disordered media [35]. Each transient consists of the very fast (sub-nanosecond) and slower nanosecond-time-scale components, which contributes unequally to the overall excited-state decay. The slower component ($\tau > 1$ ns) dominates in compounds **11** and **12** featuring long alkoxy end-groups, whereas the fast one prevails in compounds 13 and 14 with much shorter end-moieties. Since the latter two compounds suffer from strong emission quenching in the neat films (stronger than observed in compounds 11 and 12) due to exciton migration-facilitated nonradiative decay, it is natural to associate the initial fast decay in the transients to migrationinduced exciton quenching [25,36,37]. Thus, the transients of the neat films directly support $\Phi_{\rm F}$ data and unambiguously indicate the importance of the long alkoxy chains for suppressing exciton migration to nonradiative decay sites. The long peripheral moieties are assumed to prevent molecule agglomeration in the solid state due to steric hindrance effects. Much slower decay components $(\tau > 4 \text{ ns})$ present only in the transients of compounds **13** and **14** can be explained by long-lived excimer states revealed in the fluorescence spectra of the compound neat films.

3.4. Photoelectrical properties

lonization potentials (I_p) of thin solid layers of the synthesized compounds **11–14** were estimated by photoelectron emission spectroscopy. Photoelectron emission spectra of **11–14** are shown in Fig. 5. The intersection points of the linear parts of the photoelectron spectra drawn with the abscissa axis give the ionization potential values. I_p values of triphenylamine derivatives **11–14** were comparable and ranged from 5.21 eV to 5.47 eV. It was found that the extracted photocurrent from the thin films of compounds **11** and **12** was comparatively lower with respect to that extracted from the solid layers of **13** and **14**. This observation can apparently be attributed to the relatively lower amount of chromophores per unit area of thin films of compounds **11** and **12**. I_p values of the thin layers of compounds**11–14** are rather close to that of commonly used anode materials in electroluminescent devices, for example, indium–tin oxide (ITO) [**38**].

Room temperature hole-drift mobility of a thin layer of compound **13** was measured by xerographic time-of-flight (XTOF) method. Fig. 6 demonstrates representative dU/dt hole-transients for the thin film of compound **13**. It exhibited a dispersive holetransport; which along with the strong electric-field mobility dependence suggested the trap-dominant charge transport in this material. Nevertheless, well-defined transit times (t_t) established from the intersection points of two asymptotes of doublelogarithmic plots provided hole-drift mobility at respective applied fields.

The electric field dependency of hole-drift mobilities of the thin film of **13** is shown in Fig. 7. Hole-drift mobility of 1.3×10^{-3} cm² V⁻¹ s⁻¹ was observed in the amorphous layer of compound **13** at an electric field of 10^6 Vcm⁻¹ at 25 °C. Due to the formation of crystallites in the thin film after solution casting onto Al substrate, we were not able to measure the charge carrier mobility in the layer of compound **14**. Compounds **11** and **12** did not show any significant photosignal of hole-transport in the thin layers. In the case of compounds **11** and **12**, the presence of longer but flexible alkyl chains increases the distance between electrophores. The increased distance between the electrophores restrict



Fig. 6. XTOF transients for the thin film of compound 13. The arrow mark indicates transit time of holes at respective surface voltage.



Fig. 7. Electric field dependence of hole-drift mobility for the layer of 13.

the tunnelling between conducting segments that are separated by less conducting regions such as long and flexible alkyl chains [39].

4. Conclusion

Triphenylamine derivatives possessing distinct peripheral alkyl substituents were synthesised by employing Wittig reaction protocols. Peripheral alkyl substitutions in synthesised materials were found to be largely affected their thermal, photophysical and photoelectrical properties. As the alkyl chain length decreased, increase in thermal stability was observed. Glass-forming ability was observed for the compounds possessing shorter alkyl substituents, whereas liquid-crystalline-like phase transitions were noted for compounds containing flexible chains. Comparatively lower intermolecular interactions in solid layers of triphenylamine derivatives containing flexible alkyl chains were quite obvious from their photophysical and photoelectrical properties. Typical redshift and no signature of vibronic replica in the spectra of thinfilms of triphenylamine derivatives containing shorter alkyl chains revealed their prominence in intermolecular interactions. Single exponential fluorescence lifetime decay profiles well correlating with relatively similar fluorescence quantum yields in dilute solutions of triphenylamine derivatives suggested the negligible contribution of their non-conjugated alkyl substitutions. However, non-exponential fluorescence transients and associated large variation in fluorescence quantum yields in their neat films clearly owed towards the considerable influence of alkyl chains in the solid-state molecular packing. Difference in the extracted photocurrent and variations in the ionization potential values of thin solid layers of synthesized compounds also confirmed their alkyl substitution influenced molecular packing levels. Hole-drift mobility of ethyl substituted triphenylamine exceeded 1.3×10^{-3} cm² V⁻¹ s⁻¹ at an electric field of 10^6 Vcm⁻¹ as measured by Xerographic time-of-flight (XTOF) method.

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