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

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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} cm^2 V^{-1} s^{-1} at an electric field of 10^6 Vcm^{-1}.

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 light-emitting 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 hole-mobility, 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-3,4,5-trihydroxybenzoate 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(4-formylphenyl)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). ^{1}H NMR (300 MHz, $CDCl_3$), 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, OCH_2), 1.86–1.70 (m, 18H, CH_2), 1.50–1.26 (m, 162H, CH_2), 0.87 (t, J = 4.4 Hz, 27H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$, 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, 29.7, 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 $C_{150}H_{249}NO_9$: 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). ^{1}H NMR (300 MHz, $CDCl_3$), 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, OCH_2), 1.87–1.69 (m, 18H, CH_2), 1.51–1.27 (m, 126H, CH_2), 0.88 (t, J = 4.4 Hz, 27H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$, 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 $C_{132}H_{213}NO_9$: 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. ^{1}H NMR (300 MHz, $CDCl_3$), 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, OCH_2), 1.45 (t, J = 4.7 Hz, 18H, CH_3), 1.37 (t, J = 4.7 Hz, 9H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$, 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 $C_{60}H_{69}NO_9$: 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 °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. ^{1}H NMR (300 MHz, $CDCl_3$, 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, OCH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$, 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 $C_{45}H_{39}NO_3$: 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 ^{1}H and ^{13}C nuclei respectively. All the data are given as chemical shifts δ (ppm) downfield from TMS. IR-spectroscopy 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 higher-molecular-weight compounds were determined by MALDI-TOF using Shimadzu Biotech Axima Performance system and 2, 5-dihydroxybenzoic 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 θ–θ goniometer, and Anton-Paar TTK low temperature chamber. The goniometer was equipped with a curved graphite diffracted-beam monochromator, receiving (0.03°), incident and