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Synthesis and photophysical properties of triphenylamine-based dendrimers with 1,3,5-triphenylbenzene cores

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Abstract—Two new conjugated dendrimers bearing a triphenylamine moiety as dendrons and 1,3,5-triphenylbenzene as a core have been synthesized through a convergent synthetic strategy. These conjugated dendrimers have high fluorescence quantum yields and exhibit similar absorption and emission behaviors in solutions and in solid films, which demonstrate that these dendrimers form good amorphous states.

In the past few decades, π-conjugated polymers have attracted considerable interest due to their potential applications in opto-electronic devices, such as organic light-emitting diodes (OLEDs),[1] photovoltaic cells,[2] optical power limiting,[3] and field-effect transistors.[4] However, the aggregation of π-conjugated skeletons often results in low quantum yields of luminescence.[5] Compared with the organic small molecules and polymers, π-conjugated dendritic systems with large branching building blocks can exhibit intrinsic two or three-dimensional architectures, which can overcome the quenching of luminescence. Furthermore, such large dendritic structures also efficiently improve the film formation ability. Therefore, they have become one of the most promising prospects among π-conjugated materials, and have been applied as active materials in electronic and photoelectronic devices.[6]

Triphenylamine (TPA) derivatives have been widely investigated for almost two decades because these compounds have showed excellent thermal and electrochemical stability, electron donating ability, and opto-electronic properties.[7] Considerable effort in synthetic chemistry, in particular by Shirota and co-workers, has led to the development of many classes of TPA-based compounds as hole-transporting or electroluminescent materials.[7a,b] To our knowledge, most of triphenylamine derivatives are connected by the N–C single bond and obtained either through palladium-catalyzed cross-coupling reactions requiring expensive and extremely air-sensitive palladium catalysts or through copper-catalyzed Ullmann condensations usually involving high temperatures and prolonged reaction times,[8] but few papers about triphenylamine derivatives connected by the C–C double bond were published.[9] In this Letter, therefore, we report the design, synthesis, characterization, and photophysical properties of two representative conjugated dendrimers having 1,3,5-triphenylbenzene as the core with three triphenylamine branches connected by phenylenevinylene units, which have the interesting photochemical and photophysical properties through Heck reaction and Horner–Wittig reaction. Heck reaction and Horner–Wittig reaction were extensively utilized to construct the trans double bond in each phenylenevinylene conjugation unit.[9a]

The synthetic routes to the first-generation dendrimer are shown in Scheme 1. The 1,3,5-tris-(4-methylphenyl)benzene (**1**) was synthesized in high yield via tetrachlorosilanemediated cyclotrimerization of 4-methylacetophenone under solvents of ethanol.[10] The bromination of **1** by employing *N*-bromosuccinimide (NBS) in benzene successfully afforded the desired **2**. Compound **3** can be easily prepared from **2** through the reaction with the triethyl phosphate under N_2.[11] The first-generation dendrimer TPB-TPA3 (**4**) was synthesized via the typical Wittig– Horner reaction between aldehyde **5** and the core tris(phosphonate) **3** in dry tetrahydrofuran, using potassium *tert*-butoxide as base.[12]

Keywords: Triphenylamine; Phenylenevinyl; Dendrimers; Fluorescence.

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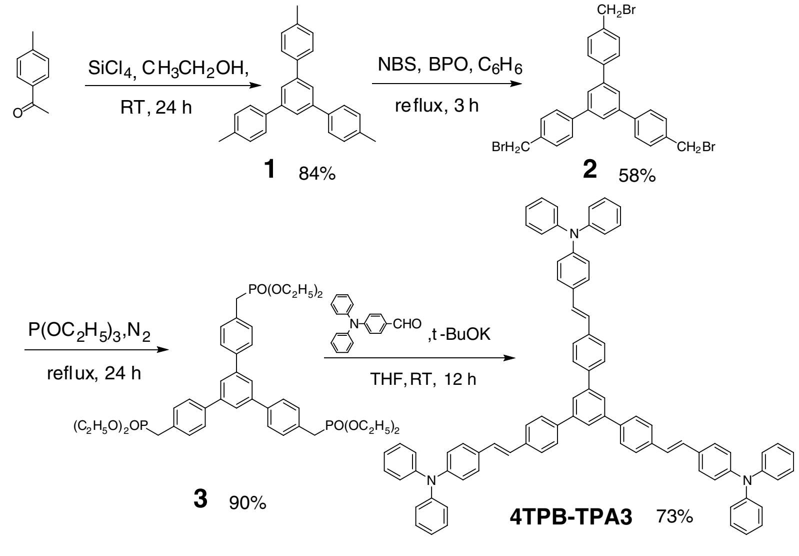
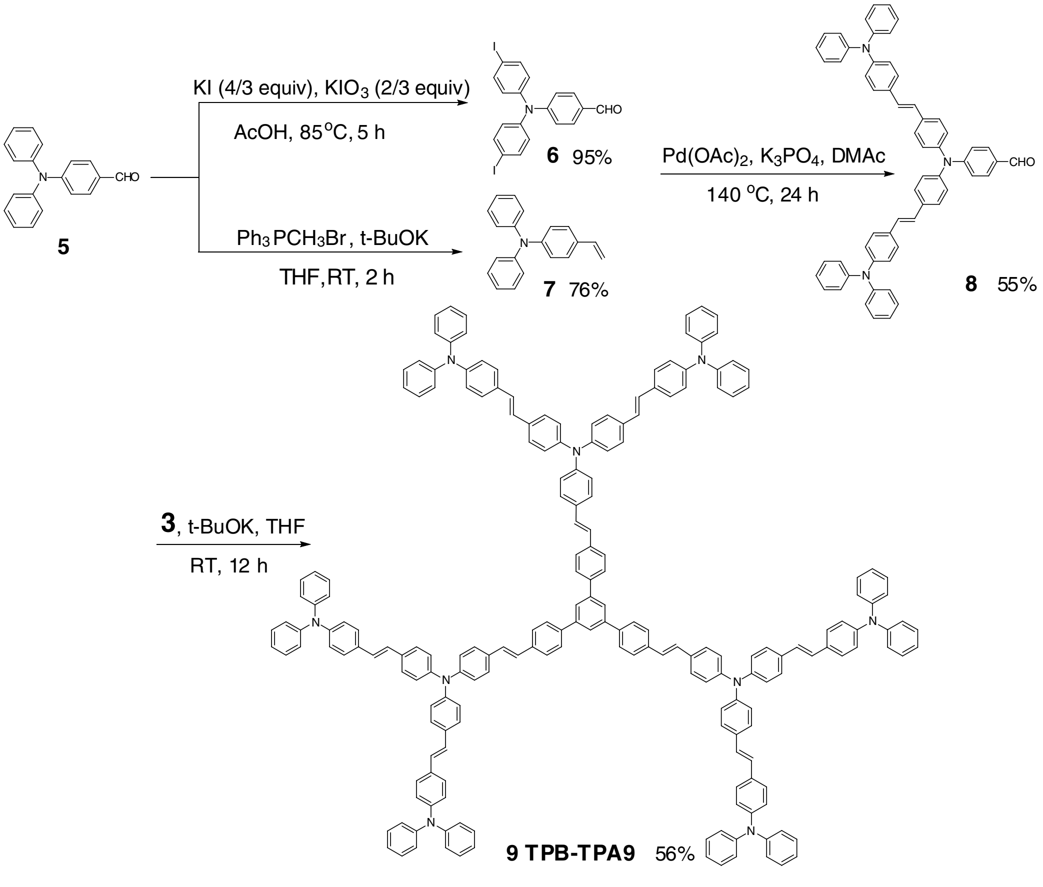


Scheme 1. Synthesis of the first-generation dendrimer **4**.

The synthetic routes to the second-generation dendrimer are shown in Scheme 2. Iodination of **5** with KI/KIO_3 in AcOH at 85 °C provided compound **6** in a yield of 95%,[13] an important intermediate for the synthesis of larger triphenylamine dendrons. *N*,*N*-Diphenyl-4-vinylbenzenamine **7** was prepared with **5** by the Wittig reaction with methyltriphenylphosphonium bromide in a good yield.[14] Triphenylamine dendron **8** was obtained by the Heck reaction[15] between **6** and **7**. The synthetic method of the second-generation dendrimer TPB-TPA9 (**9**) was similar to that of TPB-TPA3.[12]

Dendrimers are soluble in common organic solvents such as chloroform, dichloromethane, 1,2-dichloroeth-



Scheme 2. Synthesis of the second-generation dendrimer **9**.

ane, and THF, which are helpful for separation and purification. All intermediates and final products were characterized by FT-IR, ^{1}H NMR spectroscopy, ^{13}C NMR spectroscopy, and MALDI-TOF mass spectrometry. The ^{1}H NMR spectra ($CDCl_3$) of TPB-TPA3 and TPB-TPA9 showed sharp and well resolved signals at room temperature. The coupling constant ($J \sim 16.5$ Hz) of olefinic protons in the TPB-TPA3 and TPB-TPA9 indicates that Heck reaction and Wittig–Horner reaction afforded the pure all-trans isomers. The pure all-trans isomers of TPB-TPA3 and TPB-TPA9 were further confirmed by the characterization of vibration band of trans double bond at 962 cm^{-1} and 659 cm^{-1} in FT-IR spectra, respectively.[16]

In order to investigate their photophysical properties, the absorption and the photoluminescent (PL) spectra of TPB-TPA3 and TPB-TPA9 both in dilute chloroform solutions and in the solid films were recorded. Figure 1 illustrates the absorption and PL spectra of TPB-TPA3 and TPB-TPA9 in dilute chloroform solutions. For the UV–vis absorption spectrum in chloroform solutions, TPB-TPA3 displayed two absorption peaks at 304 nm and 384 nm, which were ascribed to the absorption of the triphenylamine moiety and π–π^* transition, respectively. It was also observed that TPB-TPA9 displayed two absorption peaks at 305 nm and 411 nm, which exhibited behaviors similar to that of TPB-TPA3. Nonetheless, the intensity of the peak at about 304 nm of TPB-TPA9 decreased in comparison with that of TPB-TPA3, because the relative number of triphenylamine in TPB-TPA9 was reduced. For the emission spectra in dilute chloroform solutions, TPB-TPA3 and TPB-TPA9 also displayed similar behaviors. The emission peaks of compounds TPB-TPA3 and TPB-TPA9 are located at 456 nm and 490 nm, respectively. The emission peak of TPB-TPA9 was red shifted 34 nm from that of TPB-TPA3, which showed that there was obvious π–π^* delocalization with the increase of the generation of dendrimers. These results also demonstrated that the effective conjugation length significantly improved with the increasing generation of the dendrimers.[17] The fluorescence quantum yields (φ_f) of TPB-TPA3 and TPB-TPA9 in dilute chloroform solutions were measured to be 100% by using quinine sulfate as a standard. The fluorescence life time of TPB-TPA3 (0.38 ns) is longer than that of TPB-TPA9 (0.16 ns) due to the stronger core–core interactions in TPB-TPA3 because of the absence of the second dendron.[18]

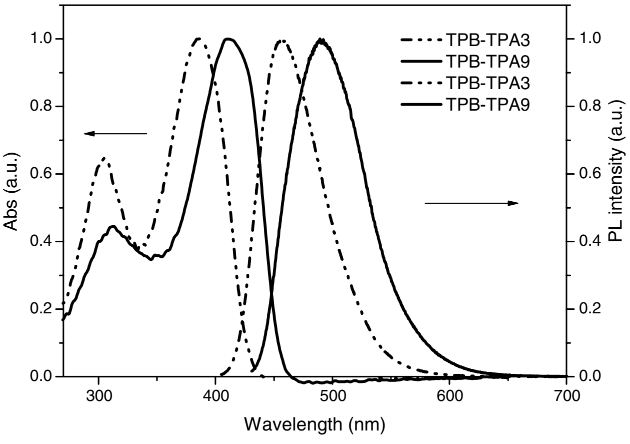


Figure 1. Normalized absorption (left) and fluorescence spectra (right) of novel conjugated dendrimers in dilute chloroform solution (1×10^{-6} M). Emission spectra were obtained upon excitation at the absorption maximum.

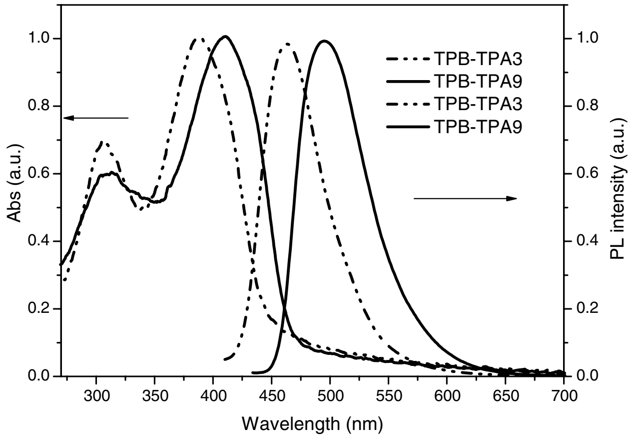


Figure 2. Normalized absorption (left) and fluorescence spectra (right) of novel conjugated dendrimers in the solid films. Emission spectra were obtained upon excitation at the absorption maximum.

Figure 2 outlines the absorption and emission spectra of TPB-TPA3 and TPB-TPA9 in the solid films. The absorption behaviors of TPB-TPA3 and TPB-TPA9 in the solid films were quite similar to those in solutions. The absorption maximum of TPB-TPA3 and TPB-TPA9 in films were red shifted in relation to those in solutions, due to the aggregation effect, with the degree of red shift depending on the generation number of the dendrimers. The absorption maximum of TPB-TPA3 and TPB-TPA9 in films, for example, were red shifted by 3 nm and 1 nm, respectively, or in other words, the higher the generation, the smaller the red shift in the absorption.[19] These results indicated the absence of aggregation in the dendrimers, because of large branches and lots of the noncoplanarity of triphenylamine. There is no significant ordering of the dendrimers either from aggregation or crystallization, and hence the dendrimer films are in a good amorphous state,[20] which is very important for the application of materials in optical and electronic devices such as OLEDs. The emission peaks of the first-generation dendrimer TPB-TPA3 and the second-generation dendrimer TPB-TPA9 in the solid films were red shifted 10 nm and 1 nm from those in solutions, respectively. The results indicated that the emission peak of the higher-generation dendrimer had a smaller shift than that of the lower one, indicative to a certain extent of a site isolation or dendron dilution effect, reducing the extent or possibility of aggregation of the triphenylbenzene core. The films were fabricated by spin casting onto quartz plates from their solutions in chloroform. The quantum efficiencies of the films are 17.2% and 5.2% for TPB-TPA3 and TPB-TPA9 relative to 100% in solutions, respectively. The much-reduced fluorescence quantum yields in films compared to solutions result from the intermolecular

Table 1. Photophysical properties of TPB-TPA3 and TPB-TPA9

	λabs/nm sol	λem/nm sol	τ/ns[a] sol	φ_f [b] sol (%)	λabs/nm films	λem/nm films	φ_{fl}[c] (%) films
TPB-TPA3	384	456	0.38	100	387	465	17.2
TPB-TPA9	411	490	0.16	100	412	491	5.2

[a] Double-exponential decay.

[b] Quinine sulfate was used as a standard (λexc = 365 nm; $\varphi_f = 0.546$ in H_2O).

[c] Determined by using an integrating sphere.

interactions such as aggregates, which can be caused by the relatively dense packing of dendrimer units in films. The photophysical properties of TPB-TPA3 and TPB-TPA9 are summarized in Table 1.

In conclusion, we have synthesized two new conjugated dendrimers bearing a triphenylamine moiety as dendrons and 1,3,5-triphenylbenzene as a core through a convergent synthetic strategy. These conjugated dendrimers exhibit similar absorption and emission behaviors in solutions and in solid films, which demonstrate that these dendrimers form amorphous states. They also have high fluorescence quantum yields, which indicate that these dendrimers are candidates for the application in OLED as light emitting materials. We are currently investigating the electroluminescent properties of these dendrimers.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.06.052.

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12. The general procedure used for the Wittig–Horner reaction: 546 mg (2.0 mmol) of 4-(diphenylamino)benzaldehyde and 378 mg (0.5 mmol) of **3** were dissolved in 20 ml of dry THF. The resulting solution was added dropwise slowly to 280 mg (2.5 mmol) of *t*-BuOK in 20 ml of dry THF at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 overnight. The mixture was poured into water and extracted with dichloromethane. The organic phase was washed with water, brine, and dried over $MgSO_4$. After removing the solvent, the product was purified by column chromatography using dichloromethane/petroleum ether (1/4) gave **5** (406 mg, 73%) as a yellow solid.
    ^1H NMR (500 MHz $CDCl_3$) δ 7.02–7.08 (m, 15H, Ar), 7.12–7.15 (m, 15H, Ar), 7.25–7.28 (m, 12H, Ar), 7.42 (d, $J = 8.5$ Hz, 6H, Ar), 7.61 (d, $J = 8.0$ Hz, 6H, Ar), 7.70 (d, $J = 8.5$ Hz, 6H, Ar), 7.81 (s, 3H, Ar) ^{13}C NMR (75 MHz $CDCl_3$) 123.06, 123.53, 124.51, 126.40, 126.79, 127.39, 127.54, 128.39, 129.28, 131.39, 137.01, 139.84, 141.93, 147.42, 147.50. MALDI/TOF MS: Calcd for $C_{84}H_{63}N_3$: 1113.5, Found: 1114.3. Anal. Calcd for $C_{84}H_{63}N_3$: C, 90.53; H, 5.70; N, 3.77. Found: C, 90.31; H, 5.82; N, 3.58. The same procedure was used to prepare the dendrimer **TPB-TPA9**: Compound **9**: ^1H NMR (500 MHz $CDCl_3$) δ 6.96–7.05 (m, 36H, Ar), 7.08–7.15 (m, 48H, Ar), 7.24–7.29 (m, 30H, Ar), 7.36–7.40 (m, 18H, Ar), 7.43 (d, $J = 8.0$ Hz, 6H, Ar), 7.60 (d, $J = 8.0$ Hz, 6H, Ar), 7.69 (d, $J = 7.5$ Hz, 6H, Ar), 7.80 (s, 3H, Ar) ^{13}C NMR (75 MHz $CDCl_3$) 122.95, 123.64, 124.04, 124.33, 124.41, 124.63, 126.40, 126.67, 126.84, 126.90, 127.16, 127.22, 127.48, 127.56, 128.32, 129.25, 131.73, 131.84, 132.51, 136.95, 139.86, 141.94, 146.33, 146.68, 147.10, 147.54. MALDI/TOF MS: Calcd for $C_{204}H_{153}N_9$ 2728.2, Found: 2729.4. Anal. Calcd for $C_{204}H_{153}N_9$: C, 89.74; H, 5.65; N, 4.62. Found: C, 89.54; H, 5.81; N, 4.48.
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