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A facile convergent procedure for the preparation of triphenylamine-based dendrimers with truxene cores

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ABSTRACT

A simple convergent procedure has been developed for the preparation of triphenylamine dendrons containing an alkene at the center, which can be coupled in a single step to give dendrimers that contain truxene for the core without any protection–deprotection chemistry. These conjugated dendrimers exhibit similar absorption and emission behaviors in solutions and in thin films, which are indicative of the high isolation effect of well-organized three-dimensional dendrimers. They also have high fluorescence quantum yields and high glass transition temperatures, which indicate that these dendrimers are candidates for the application in OLED as light emitting materials.

1. Introduction

In the past few decades, π-conjugated dendrimers have been extensively studied because of their unusual molecular structures and the potential of acting as the active chemical components, such as organic light emitting diodes (OLEDs),[1] photovoltaic cells,[2] optical power limiting,[3] and field-effect transistors.[4] One of the important challenging goals of dendritic materials chemistry is to develop new families of π-conjugated dendritic molecules with novel branches and cores, to investigate their physical and chemical properties, as well as to understand the structure–property relationship within such structures. Compared with π-conjugated polymers, π-conjugated dendritic systems possessing well-defined conjugation lengths and structural models are characterized by the uniformity, absence of chain defects, and ease of purification and characterization, which make them superior to π-conjugated polymers for systematic investigation of the structure–property relationships. Further more, π-conjugated dendritic systems with large branching building blocks can exhibit intrinsic two- or three-dimensional architectures, which can overcome the quenching of luminescence, and such large dendritic structures also efficiently improve the film formation ability.[5]

Triphenylamine (TPA) derivatives have been widely investigated for almost two decades because these compounds have shown excellent thermal and electrochemical stability, electron donating ability, and optoelectronic properties.[6] 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.[6a–c] 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 time, but few papers about triphenylamine derivatives connected by the C–C double bond were published.[7] The triphenylamine derivatives connected by the C–C double bond can be easily synthesized by Heck reaction and Wittig–Horner reaction without air-sensitive catalysts or high temperatures and prolonged reaction time, and the structure similar to the *p*-phenylene vinylene moiety has the interesting photochemical and photophysical properties. Our group has previously reported triphenylamine-based dendrimers with 1,3,5-triphenylbenzene cores connected by the C–C double bond.[7c]

10,15-Dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (truxene), a polycyclic aromatic system with C_3 symmetry,[8] has been recognized as a potential starting material for the construction of bowl-shaped fragments of the fullerenes,[9] C_3 tripodal materials in chiral recognition,[10] and liquid crystalline compounds.[11,12] Some *syn*-trialkylated truxenes (monoalkylated at each CH_2 group) have been shown to self-associate in solution through arene–arene interactions.[13] Recently, Pei and co-workers have successfully introduced oligothiophene arms and oligophenylene to the truxene core[14a,b] and developed novel π-conjugated dendrimers based on

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truxene from the viewpoint of fundamental chemistry as well as practical applicants in organic optics and electronics.[14] Furthermore, Skabara and co-workers reported on employing the truxene core for the construction of virtually 'no-core' star-shaped oligofluorene architectures.[15]

In this paper, therefore, we report the design, synthesis, characterization, and photophysical properties of two representative conjugated dendrimers having truxene as the core with three triphenylamine branches through a simple convergent procedure without any protection–deprotection chemistry. These conjugated dendrimers are readily soluble in common organic solvents, exhibiting good film forming properties. They exhibit similar absorption and emission behaviors in solutions and in thin films, which are indicative of the high isolation effect of well-organized three-dimensional dendrimers. They also have high fluorescence quantum yield and high glass transition temperatures, which indicate that these dendrimers are candidates for the application in OLED as light emitting materials.

2. Results and discussion

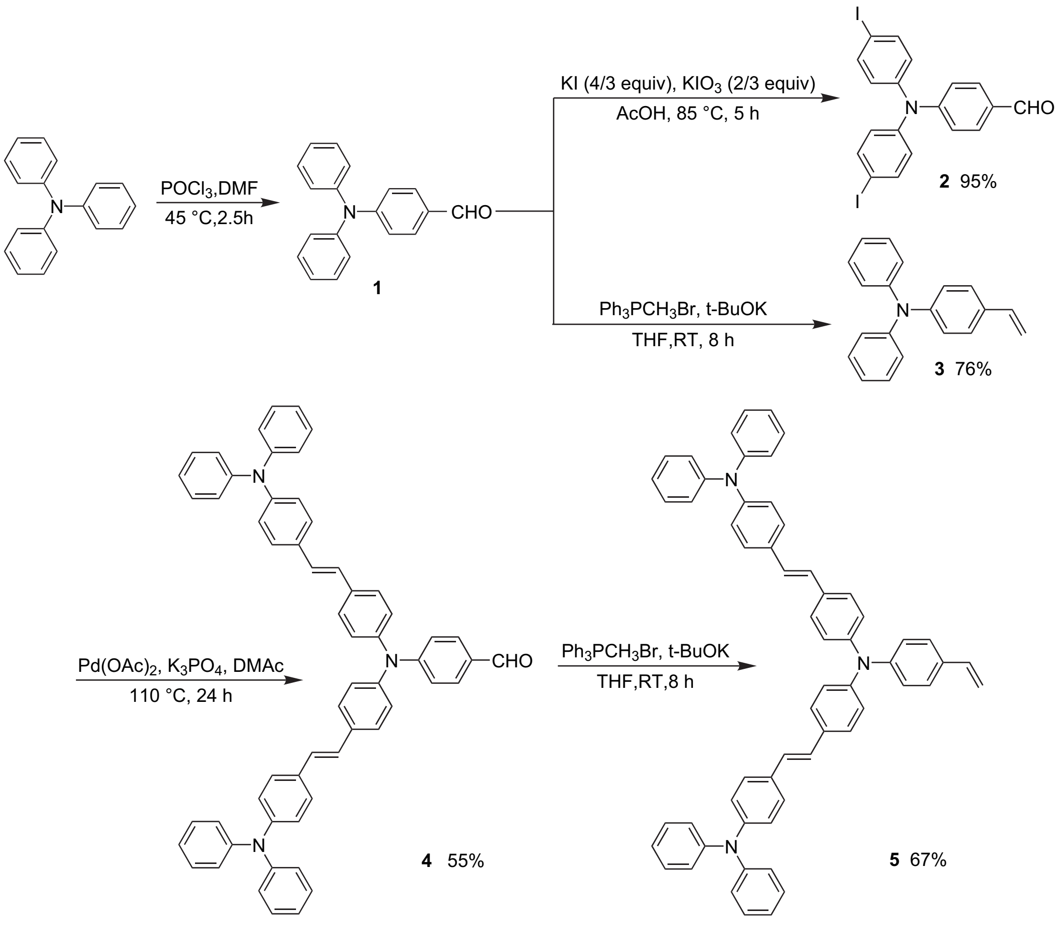
2.1. Synthesis of the triphenylamine-based dendrons

The strategy as reported by our group[7c] for the alkene-focused dendron synthesis was illustrated in Scheme 1. The formation of a dendron with an alkene at its center involves a Heck coupling followed by a simple Wittig reaction. First, 4-(diphenylamino)-benzaldehyde **1** was readily obtained from triphenylamine through a Vilsmeier reaction in a yield of 79%. Iodination of **1** with KI/KIO_3 in AcOH at 85 °C provided compound **2** in a yield of 95%,[16] an important intermediate for the synthesis of larger triphenylamine dendrons. The first generation alkene-focused dendron **3** was prepared in an 88% yield from the reaction of 4-(diphenylamino)-benzaldehyde **1** with the methyltriphenylphosphonium bromide.[17] The first step in the procedure was the formation of the aldehyde **4**, which was prepared in an 88% yield from the coupling of **3** with **2** by the Heck reaction.[18] The second step in the first cycle of the procedure was the reaction of aldehyde **4** with methyltriphenylphosphonium bromide to give the second generation alkene-focused dendron **5**.

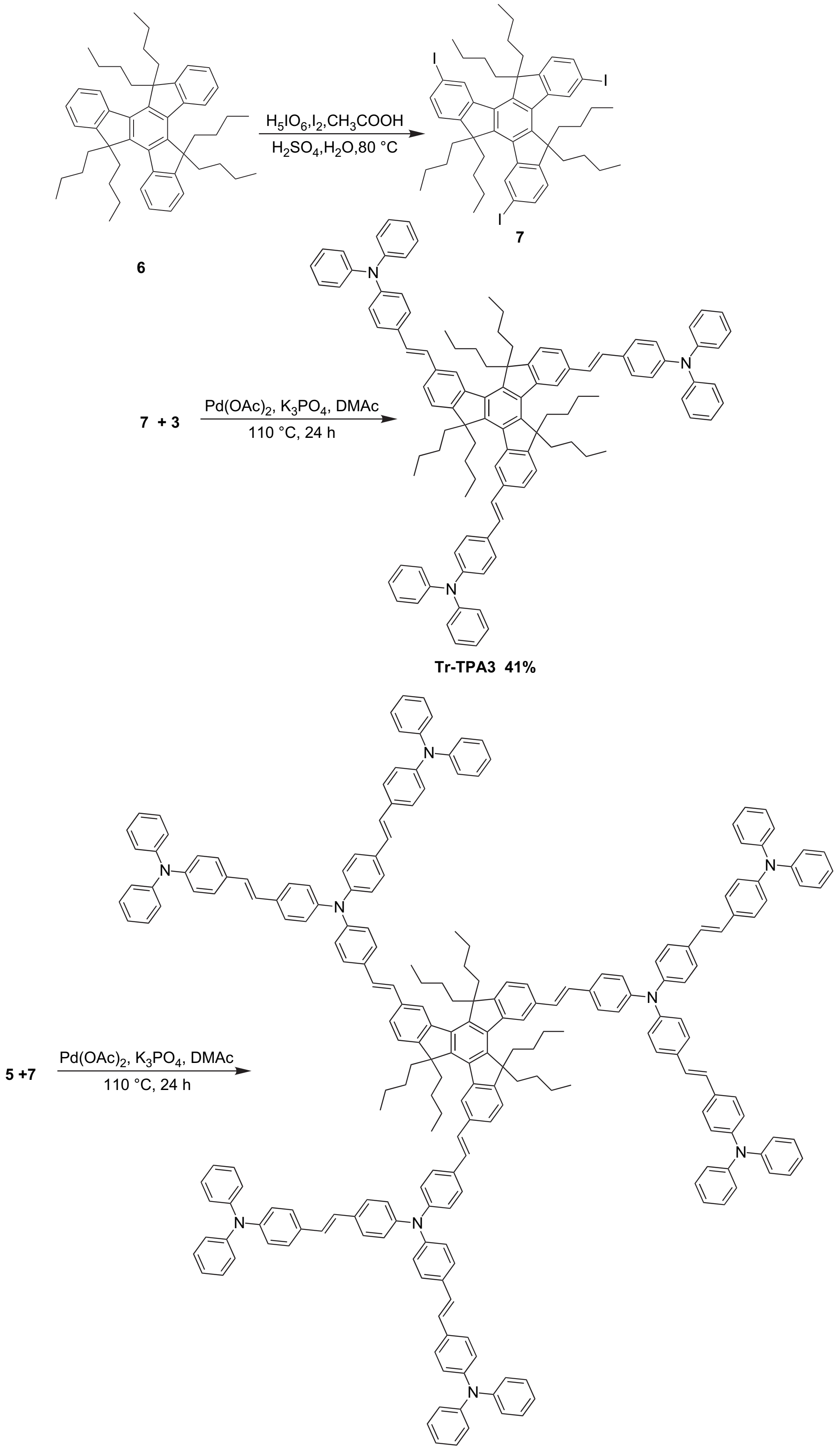
2.2. Synthesis of the dendrimers

The synthesis of dendritic triphenylamine-based truxene is shown in Scheme 2. Firstly, truxene was alkylated to give readily soluble hexabutylated truxene, which was subsequently converted to hexabutylated truxene triiodide **7** in high yield by electrophilic iodination as reported by Pei co-workers.[14d] The obtained alkenes **3** and **5** were converted into the corresponding dendritic truxenes Tr-TPA3 and Tr-TPA9 with **7** by Heck reaction.[18]

The dendrimers are soluble in common organic solvents such as chloroform, dichloromethane, 1,2-dichloroethane, and THF, which are helpful for separation and purification. All dendrons and dendrimers were characterized by FTIR, elemental analysis, ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, and MALDI-TOF mass spectrometry. Both dendrons **3** and **5** possess a proton chemical shift at 5.77 ppm and 5.80 ppm and have the coupling constant ($J\sim16.5$ Hz), respectively, which prove to be the trans alkene



Scheme 1. Synthesis of triphenylamine dendrons **3** and **5**.



Scheme 2. Synthesis of the dendrimers Tr-TPA3 and Tr-TPA9.

hydrogen. The coupling constant ($J\sim16.5$ Hz) of olefinic protons in Tr-TPA3 and Tr-TPA9 indicates that Heck reaction afforded the pure all-trans isomer. The pure all-trans isomers of Tr-TPA3 and Tr-TPA9 were further confirmed by the characterization of vibration band of trans double bond at 958 $\mathrm{cm}^{-1}$and 960 cm^{-1} in FTIR spectra, respectively.[19] Additional definitive evidence for the dendrimer molecular structures was obtained from MALDI-TOF mass spectra. The deviation between the calculated and experimentally measured m/z values was no more than one mass unit. For example, the molecular formula of Tr-TPA9 is $C_{231}H_{209}N_9$. The calculated average for the peak of the molecular ion [M+H] is 3100.6 and we obtained the value 3101.4. The MALDI-TOF mass spectrometry of Tr-TPA3 and Tr-TPA9 are shown in Supplementary data.

2.3. Photophysical properties

In order to investigate their photophysical properties, the absorption and the photoluminescent (PL) spectra of Tr-TPA3 and Tr-TPA9 both in dilute chloroform solutions and in the solid films were recorded. Figure 1 illustrates the absorption and PL spectra of Tr-TPA3 and Tr-TPA9 in dilute chloroform solutions. For the UV–vis absorption spectrum in chloroform solution, Tr-TPA3 displays two absorption peaks at 311 nm and 392 nm, which are ascribed to the absorption of triphenylamine moiety and π–π* transition, respectively. It is also observed that Tr-TPA9 displays two absorption peaks at 310 nm and 413 nm, which exhibits similar behaviors to Tr-TPA3. Nevertheless, the intensity of the peak at about 310 nm of Tr-TPA9 decreases in comparison with that of Tr-TPA3, because the relative number of triphenylamine compared to the number of π–π* transition in Tr-TPA9 is reduced. For the emission spectra in dilute chloroform solutions, Tr-TPA3 and Tr-TPA9 also display similar behaviors. The emission peaks of compounds Tr-TPA3 and Tr-TPA9 locate at 445 nm (465 nm) and 476 nm, respectively. The emission peak of Tr-TPA9 is red-shifted 31 nm from that of Tr-TPA3, which shows that there is obvious π–π* delocalization with the increase of the generation of dendrimers. These results also demonstrate that the effective conjugation length significantly improves with the increasing generation of the dendrimers.[20] The fluorescence quantum yields (φ_f) of Tr-TPA3 and Tr-TPA9 in dilute chloroform solution are measured to be 100% and 84.7%, by using quinine sulfate as a standard, respectively. It is intelligible that the Tr-TPA9, the multibranched molecules with higher generation, has lower quantum yields than the Tr-TPA3 with lower generation, since multibranched configuration shows more tendency toward the twisted geometry on the excited state, which might consume the excited energy and reduce their quantum yield.

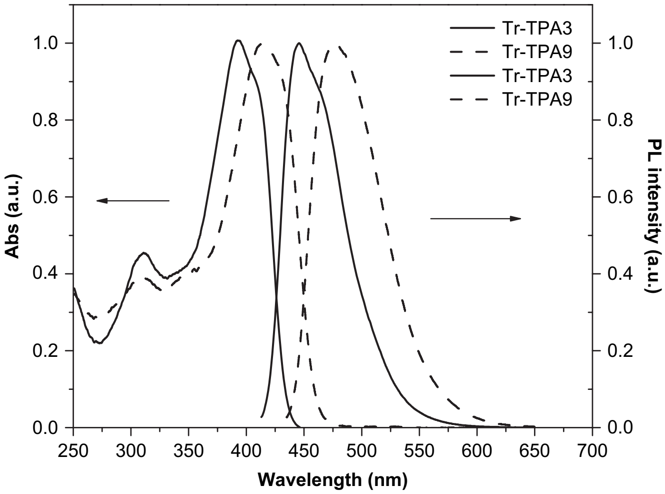


Figure 1. Normalized absorption (left) and fluorescence spectra (right) of novel conjugated dendrimers in dilute chloroform solution (1×10^{-6} M). Emission spectra were obtained upon excitation at the absorption maximum.

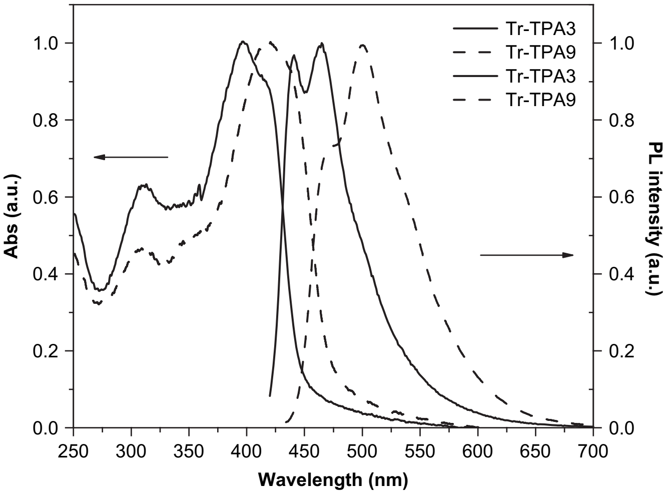


Figure 2. Normalized absorption (left) and fluorescence spectra (right) of novel conjugated dendrimers in the solid films. Emission spectra were obtained upon excitation at the absorption maximum.

Table 1
Photophysical properties of Tr-TPA3 and Tr-TPA9

	λ_{abs}/nm	λ_{em}/nm	φ_f[a]/%	λ_{abs}/nm	λ_{em}/nm
	Sol	Sol	Sol	Films	Films
Tr-TPA3	392	445(465)	100	396	467(441)
Tr-TPA9	413	476	84.7	414	500

[a] Quinine sulfate was used as a standard (λ_{exc}=365 nm; φ_f=0.546 in H_2O).

The absorption and emission spectra of Tr-TPA3 and Tr-TPA9 in the solid films are presented in Figure 2. The absorption behaviors of Tr-TPA3 and Tr-TPA9 in the solid films are quite similar to those in solution. The absorption maxima of Tr-TPA3 and Tr-TPA9 in films are red-shifted in relation to those in solution, due to the aggregation effect, with the degree of red-shift depending on the generation number of the dendrimer. The absorption maxima of Tr-TPA3 and Tr-TPA9 in films, for example, are red-shifted by 4 nm and 1 nm, respectively, or in other words, the higher the generation, the smaller the red-shift in the absorption. These results indicate the absence of aggregation in the dendrimers because of such large sizes of the molecules with six butyl substituents in truxene and lots of the noncoplanar triphenylamines. There is no significant ordering of the dendrimers either from aggregation or crystallization, and hence the dendrimers films are in a good amorphous state,[21] which are very important for the application of materials in optical and electronic devices such as OLEDs. The emission peaks of Tr-TPA3 and Tr-TPA9 in the solid films are red-shifted in comparison with those in solutions. Moreover, the molecular vibronic features disappeared for compound Tr-TPA9, gave out bright blue emission with high quantum efficiency. The photophysical properties of Tr-TPA3 and Tr-TPA9 are summarized in Table 1.

2.4. Thermal analysis

For the photoelectronic applications, the thermal stability of organic materials is critical for device stability and lifetime because during the electroluminescent process, heat is generated that can affect the material morphology and the device performance, finally leading to the degradation of OLEDs. Hence, the relatively high T_g is essential for materials used as emissive materials for optoelectronic applications. We found that the two dendrimers were amorphous

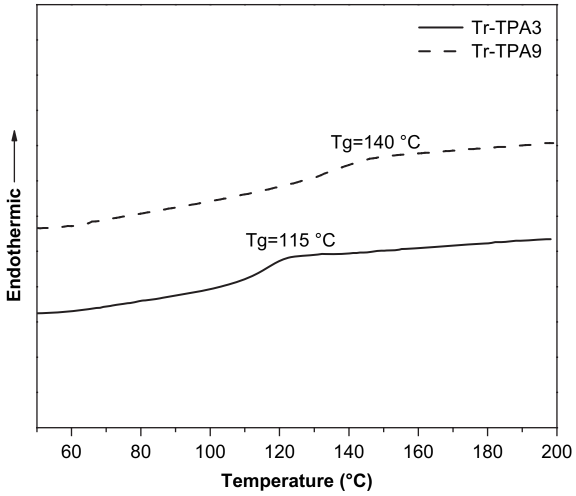


Figure 3. DSC curves (second run) of compounds Tr-TPA3 and Tr-TPA9.

at room temperature. The glass transition temperatures (T_g) of the dendrimers increased from 115 °C to 140 °C with the increase of the generation of dendrimers because the multibranched molecules with higher generation tend to hinder translational, rotational, and vibrational motions of the molecule and result in T_g enhancement. Furthermore, no transitions related to crystalline structures were observed for the two dendrimers and upon cooling, the materials stay in an amorphous glassy phase. The differential scanning calorimetric thermogram of compounds Tr-TPA3 and Tr-TPA9 is shown in Figure 3.

3. Conclusion

In conclusion, we have synthesized two new conjugated dendrimers bearing triphenylamine moiety as dendrons and truxene as a core through a convergent synthetic strategy without any protection–deprotection chemistry. These conjugated dendrimers exhibit similar absorption and emission behaviors in solutions and in thin films, which demonstrate that these dendrimers form amorphous states. They also have high fluorescence quantum yields and high glass transition temperatures, 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.

4. Experimental section

4.1. Experimental

All chemicals, reagents, and solvents were used as received from commercial sources without further purification. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and distilled. ^{1}H NMR and ^{13}C NMR spectra were recorded on an AVANCE 500 spectrometer and a Varian Mercury-300 NMR, respectively, with tetramethylsilane (TMS) as the standard. The compounds were characterized by Flash EA 1112, CHNS-O elemental analysis instrument. The FTIR spectra were recorded via the KBr pellet method by using a Nicolet Impact 410 FTIR spectrophotometer. The mass spectra were recorded on a Kratos MALDI TOF mass system, and the spectrum was recorded in the linear or reflect mode with anthracene-1,8,9-triol as the matrix. UV–vis absorption spectra were measured using a Shimadzu UV-3100 spectrophotometer. The photoluminescence were recorded on Shimadzu RF-5301PC fluorescence spectrophotometer. The DSC analysis was determined using a NETZSCH (DSC-204) instrument at 10 °C min^{-1} under nitrogen. Compounds of **1**–**3** were readily obtained according to the literature procedures.[16,17]

4.2. Compound 2

4-(*N*,*N*-Diphenylamino)benzaldehyde (14.00 g, 51.28 mmol), potassium iodide (11.43 g, 68.85 mmol), and acetic acid (210 mL) were heated to 85 °C, and the solution was allowed to cool. Then the potassium iodate (10.97 g, 51.26 mmol) was added and the reaction mixture was heated at 85 °C for 5 h. The solution was allowed to cool to room temperature and poured into ice-water under stirring. The yellow precipitated solid was collected by filtration, and the collected solid was poured into 5% $NaHSO_3$ (100 mL) to clear I_2 and KIO_3. The final filtrated yellow solid was pure compound **2**. Mp: 142–143°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1H, CHO), 7.71 (d, J=8.5 Hz, 2H, Ar), 7.63 (d, J=8.5 Hz, 4H, Ar), 7.05 (d, J=8.5 Hz, 2H, Ar), 6.89 (d, J=8.5 Hz, 4H, Ar).

4.3. Compound 3

4-(*N*,*N*-Diphenylamino)benzaldehyde **1** (5.46 g, 20 mmol) and methyltriphenylphosphonium bromide (8.57 g, 24 mmol) were dissolved in 100 mL of dry THF. *t*-BuOK (3.36 g, 30 mmol) in 30 mL of dry THF was added dropwise slowly to the resulting solution at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 for 12 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3×60 mL). The combined organic extracts were washed with brine, dried (Mg_2SO_4), and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether/CH_2Cl_2=4:1) to give 4.12 g (76%) of product **3** as a white solid. Mp: 91–92°C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J=8.5 Hz, 2H, Ar), 7.23–7.26 (m, 4H, Ar), 7.09 (d, J=8.0 Hz, 4H, Ar), 6.98–7.03 (m, 4H, Ar), 6.63–6.69 (m, 1H, CH), 6.63 (d, J=16.5 Hz, 1H, $CH{=}CH_2$), 5.15 (d, J=8.5 Hz, 1H, $CH{=}CH_2$).

4.4. Compound 4

A round-bottomed flask (250 mL) was oven dried and cooled under N_2 atmosphere. 4-[*N*,*N*-Di(4-iodophenyl)amino]benzaldehyde **2** (5.25 g, 10 mmol), compound **3** (7.0 g, 26 mmol), K_3PO_4 (6.5 g, 30 mmol), and 10 mg $Pd(OAc)_2$ were dissolved in dry DMAc (50 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h at this temperature. After being cooled to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine, dried (Mg_2SO_4), and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether/CH_2Cl_2=1:1) to give 4.47 g (55%) of product **4** as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.83 (s, 1H, CHO), 7.71 (d, J=8.5 Hz, 2H, Ar), 7.45 (d, J=8.5 Hz, 4H, Ar), 7.38 (d, J=8.5 Hz, 4H, Ar), 7.25–7.28 (m, 12H, Ar), 7.10–7.15 (m, 12H, Ar), 7.00–7.06 (m, 8H, Ar), 6.96 (d, J=16.5 Hz, 2H, Ar). MALDI/TOFMS: calcd for $C_{59}H_{45}N_3O$: 812.0, found: 812.9. Anal. Calcd for $C_{59}H_{45}N_3O$: C, 87.27; H, 5.59; N, 5.17. Found: C, 87.15; H, 5.70; N, 5.09.

4.5. Compound 5

Compound **4** (2.02 g, 2.5 mmol) and methyltriphenylphosphonium bromide (1.1 g, 3 mmol) were dissolved in 50 mL of dry THF. BuOK (0.45 mg, 4 mmol) in 10 mL of dry THF was added dropwise slowly to the resulting solution at 0 °C, then the reaction mixture was warmed to room temperature and stirred under N_2 for 12 h. The reaction mixture was poured into water and extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine, dried (Mg_2SO_4), and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether/CH_2Cl_2=4:1) to give 1.36 g (67%) of product **5** as a yellow solid.

^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.39 (m, 12H, Ar), 7.10–7.27 (m, 12H, Ar), 7.01–7.09 (m, 20H, Ar), 6.65–6.71 (m, 1H, CH), 6.70 (d, *J*=17.5 Hz, 1H, CH=CH_2), 5.18(d, *J*=11.0 Hz, 1H, CH=CH_2). MALDI/TOFMS: calcd for $C_{60}H_{47}N_3$: 809.4, found: 811.4. Anal. Calcd for $C_{60}H_{47}N_3$: C, 88.96; H, 5.85; N, 5.19. Found: C, 88.85; H, 6.01; N, 5.07.

4.6. Compound 7

A mixture of compound **6** (2.00 g, 2.96 mmol) and 10 mL of solvent mixture ($CH_3COOH/H_2SO_4/H_2O$=100:40:3) was heated to 60 °C with vigorous stirring, followed by addition of 3 mL of $CHCl_3$, H_5IO_6 (0.58 g, 2.45 mmol), and I_2 (1.25 g, 4.93 mmol). The mixture was stirred at 80 °C under nitrogen atmosphere for 3 days. The mixture was cooled to room temperature, and 100 mL of water was added. The brown precipitate was filtered and purified by recrystallization three times from ethanol to afford **7** (1.93 g, 61.8%) as a white solid.

^1H NMR (500 MHz, $CDCl_3$) δ 7.92–8.14 (3H, d, *J*=12 Hz), 7.72–7.80 (3H, s), 7.64–7.72 (3H, d, *J*=12 Hz), 2.72–2.98 (6H, m), 1.88–2.16 (6H, m), 0.76–1.08 (36H, m), 0.59–0.76 (18H, t, *J*=9.0 Hz), 0.29–0.58 (12H, m).

4.7. Compound Tr-TPA3

A round-bottomed flask (25 mL) was oven dried and cooled under N_2 atmosphere. Compound **7** (0.21 g, 0.2 mmol), compound **3** (0.27 g, 1 mmol), K_3PO_4 (0.21 g, 1 mmol), and 0.5 mg $Pd(OAc)_2$ were dissolved in dry DMAc (10 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h at this temperature. After being cooled to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2 (3×40 mL). The combined organic extracts were washed with brine, dried (Mg_2SO_4), and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether/CH_2Cl_2=4:1) to give 0.122 g (41%) of product Tr-TPA3 as a yellow solid.

^1H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J*=8.0 Hz, 3H, Ar), 7.57 (d, *J*=9.0 Hz, 6H, Ar), 7.46 (d, *J*=8.0 Hz, 6H, Ar), 7.26–7.32 (m, 12H, Ar), 7.13–7.22 (m, 18H, Ar), 7.09 (d, *J*=8.5 Hz, 6H, Ar), 7.05 (t, *J*=7.5 Hz, 6H, Ar), 2.96–3.01 (m, 3H, CH_2), 2.11–3.16 (m, 3H, CH_2), 0.88–0.93 (m, 12H, CH_2), 0.49–0.59 (m, 12H, CH_2), 0.46 (t, *J*=7.5 Hz 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) 13.86, 22.90, 26.57, 36.81, 55.53,120.08, 122.86, 123.60, 124.50, 124.86, 127.32, 127.70, 129.28, 131.79, 135.70, 138.19, 139.84, 145.09, 147.24, 147.57, 154.17. MALDI/TOFMS: calcd for $C_{111}H_{111}N_3$: 1485.9, found: 1487.6. Anal. Calcd for $C_{111}H_{111}N_3$: C, 89.65; H, 7.52; N, 2.83. Found: C, 89.54; H, 7.75; N, 2.76.

4.8. Compound Tr-TPA9

A round-bottomed flask (25 mL) was oven dried and cooled under N_2 atmosphere. Compound **7** (0.21 g, 0.2 mmol), compound **5** (0.58 g, 0.72 mmol), K_3PO_4 (0.21 g, 1 mmol), and $Pd(OAc)_2$ were dissolved in dry DMAc (10 mL). The reaction mixture was heated to 110 °C in an oil bath and stirred for 24 h at this temperature. After being cooled to room temperature, the reaction mixture was poured into water and extracted with CH_2Cl_2 (3×40 mL). The combined organic extracts were washed with brine, dried (Mg_2SO_4), and concentrated to dryness under vacuum. The crude product was purified by flash column chromatography (petroleum ether/CH_2Cl_2=4:1) to give 0.149 g (24%) of product Tr-TPA9 as a yellow solid.

^1H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J*=7.0 Hz, 3H, Ar), 7.58 (d, *J*=9.0 Hz, 6H, Ar), 7.49 (d, *J*=8.0 Hz, 6H, Ar), 7.37–7.42 (m, 24H, Ar), 7.25–7.28 (m, 24H, Ar), 7.20 (d, *J*=8.0 Hz, 6H, Ar), 7.11–7.15 (m, 39H, Ar), 6.98–7.06 (m, 39H, Ar), 2.99 (br, 3H, CH_2), 2.14 (m, 3H, CH_2), 0.88–0.93 (m, 12H, CH_2), 0.58–0.64 (m, 12H, CH_2), 0.47 (t, *J*=7.0 Hz, 18H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) 13.87, 22.90, 26.57, 29.69, 55.54, 122.96, 123.67, 124.13, 124.42, 126.44, 126.90, 127.17, 127.32, 127.66, 129.26, 131.77, 132.49, 135.70, 138.20, 139.85, 145.10, 146.42, 147.12, 147.58, 154.18. MALDI/TOFMS: calcd for $C_{231}H_{209}N_9$: 3100.6, found: 3101.4. Anal. Calcd for $C_{231}H_{209}N_9$: C, 89.41; H, 6.53; N, 4.06. Found: C, 89.24; H, 6.72; N, 3.94.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.04.021.

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