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Toward High Molecular Weight Triphenylamine-Based Hyperbranched Polymers

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ABSTRACT: Two kinds of triphenylamine-containing AB_2 monomers carrying or not carrying flexible alkyl chains were synthesized and fully characterized. One-pot Suzuki polycondensation (SPC) was applied to polymerize these monomers to prepare hyperbranched polymers. Hyperbranched polymers from AB_2 monomer not carrying alkyl chains exhibited poor solubility in common organic solvents such as THF, chloroform, toluene, etc. The poor solubility of the hyperbranched polymers hampered their applications and the further modification of the end groups. The introduction of difunctional core molecules, such as 9,9-dioctylfluorene and 9,9-dioctylfluorene trimer, in the polymerization process controlled the molecular weight and forced the hyperbranched copolymers soluble in common organic solvents mentioned above, but high molecular weight polymers could not be obtained. SPC of the AB_2 monomers carrying flexible alkyl chains afforded high molecular weight fluorene−triphenylamine (F−TPA) alternating hyperbranched copolymers, which are fully soluble in common organic solvents, and their peripheral bromo functional groups can be further modified. The structures of the hyperbranched polymers were fully characterized by NMR, GPC, and combustion analysis. Initial studies on the thermal and the optical properties of the hyperbranched polymers were also reported.

Introduction

Hyperbranched polymers have attracted increasing scientific and industrial attention in recent years due to their unusual chemical and physical properties such as compact three-dimensional structures, large numbers of terminal functional groups, and low intrinsic viscosities.[1,2] Network-free hyperbranched polymers are mainly prepared by one-pot polymerization of AB_x-type monomers. Many kinds of hyperbranched polymers are available now, and their syntheses and properties have been extensively reviewed.[1]

Polymeric and oligomeric materials based on triphenylamine (TPA) are a kind of important organic semiconductors used as hole transporting materials in thin layer electrooptical devices such as organic light-emitting diodes, solar cells, organic field effect transistors, two-photon micro- and nanolithography, and photorefractive holography.[3] Particular attention was paid to TPA-based star-shaped oligomers,[4] dendrimers,[5] linear oligomers,[6] copolymers,[7] and hyperbranched polymers.[8] In the literature, most hyperbranched TPA-containing polymers were prepared by the $A_2 + B_3$ route;[8] only in two papers was the AB_2 monomer route used.[9] In the first one, a Grignard reaction was used to prepare hyperbranched poly(triphenylamine);[9a] however, this method was proved unreproducible.[9b] In the second one, Wang et al. reported that they could prepare soluble hyperbranched TPA via Negishi coupling reaction. We noticed that the AB_2 monomers used in the two papers are moisture- and air-sensitive, and they were used as prepared without further characterization or checking their purities. The drawback obviously limited the application scope of these methods.

In this paper, we developed a more applicable methodology to prepare hyperbranched TPA homopolymers, fluorene (fluorene trimer) cored TPA copolymers, and TPA−fluorene alternating copolymers. AB_2 monomer 4-[bis(4-bromophenyl)amino]benzene-4-boronic pinacol ester (**1**) and 7-{4-[bis(4-bromophenyl)amino]phenyl}-9,9-dioctylfluorene-2-boronic pinacol ester (**7**) are very stable and can be easily purified by routine chromatography method. Suzuki polycondensation (SPC) was used for the polymerization.[10] Different from their result, we found that hyperbranched TPA homopolymers exhibited limited solubility in common organic solvents such as chloroform, THF, DMF, toluene, and CH_2Cl_2. The poor solubility hampered the further modification of their peripheral bromo functional groups. To get highly soluble hyperbranched polymers, we adopted two practical routes to improve their solubilities. One was using 9,9-dioctylfluorene (or trimer) diiodide as a core to copolymerize with the AB_2 monomer **1** to control the molecular weight. By this way, we obtained fully soluble (in THF) but lower molecular weight hyperbranched TPA copolymers. Another route was to introduce flexible alkyl chains onto each repeat unit to make the polymers soluble. For this purpose, monomer **7** carrying two flexible alkyl chains was prepared. As expected, one-pot SPC of monomer **7** afforded fully soluble hyperbranched polymers whose peripheral bromo functional groups could be further modified with fluorene monoboronic acid under the same reaction conditions. The hyperbranched polymers obtained were of extremely high molecular weight and fully soluble in common organic solvents such as THF, chloroform, CH_2Cl_2, toluene, etc.

Results and Discussion

Hyperbranched TPA Homopolymers. The synthesis of AB_2-type monomer **1** is outlined in Scheme 1. Treatment of the commercially available tris(4-bromophenyl)amine with 1.1 equiv of *n*-BuLi at −78 °C followed by quenching with 3-fold excess of $B(OCH_3)_3$ gave 4-[bis(4-bromophenyl)amino]benzeneboronic acid

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Scheme 1

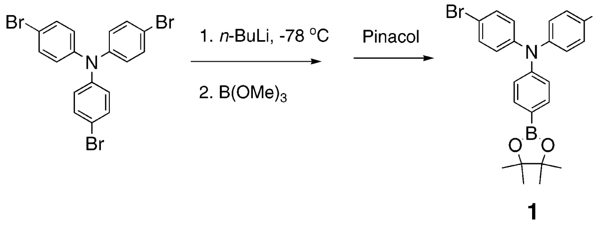


Table 1. Molecular Weight, Degrees of Polymerization, Polydispersity, and FL Quantum Yields (Φ_F) of the Hyperbranched Polymers 2, 4a, 4b, and 8

polymer	M_n	P_n	M_w	P_w	M_w/M_n	Φ_F
2	7300	23	9800	30	1.33	0.75
4a	4900	14	7400	22	1.50	0.75
4b	7900	21	9200	25	1.16	0.68
8	146000	143	169000	166	1.16	0.52

in a 46% yield on the 10 g scale. 4-[Bis(4-bromophenyl)-amino]benzeneboronic acid was converted to its corresponding boronic ester **1** by refluxing with pinacol in methylene chloride. Monomer **1** is a stable compound, which can be readily purified by normal silica gel column chromatography. The structure and high purity (>98%) of monomer **1** were unambiguously confirmed with ^{1}H and ^{13}C NMR spectroscopy and combustion analysis. The hyperbranched polymer **2** was prepared by Suzuki polycondensation (SPC) of AB$_2$-type monomer **1** (Scheme 2). One-pot SPC was performed in a biphasic mixture of THF and aqueous NaHCO$_3$ with Pd(PPh$_3$)$_4$ as a catalyst precursor.[10] Compared with normal SPC reactions, the polymerization of **1** went very quickly. During the reaction (about 1 day), a large amount of slightly yellowish hyperbranched TPA polymers precipitated from the reaction mixture. The polymers were obtained by simple filtration. The weight-average molar mass (M_w) of THF soluble fraction determined by gel permeation chromatography (GPC) calibrated with polystyrene standard was 9800 and the polydispersity (PD) 1.33 (monomodal). The results are summarized in Table 1. The GPC elution trace is shown in Figure 1. The hyperbranched TPA homopolymer **2** exhibited limited solubility in common organic solvents such as THF, chloroform, methylene chloride, acetone, DMF, toluene, and DMSO, but it was fully soluble in bromobenzene. Regarding the solubility of the hyperbranched TPA polymers, our result is different from what have been reported in the literature.[9] This was not surprising; the difference might be due to the following two reasons: (1) The molecular weight of the hyperbranched TPA obtained by SPC is much higher than that prepared by the Grignard reaction or the Negishi coupling reaction. (2) In our case, the starting material AB$_2$ monomer is analytically pure. The good solubility of hyperbranched polymer **2** in bromobenzene proved that it was of hyperbranched structure rather than cross-linked one. The poor solubility of hyperbranched homopolymers was probably due to their rigid conjugated structure and large number of peripheral bromo functional groups. Solubilities of hyperbranched polymer **2** in different types of solvents are summarized in Table 2.

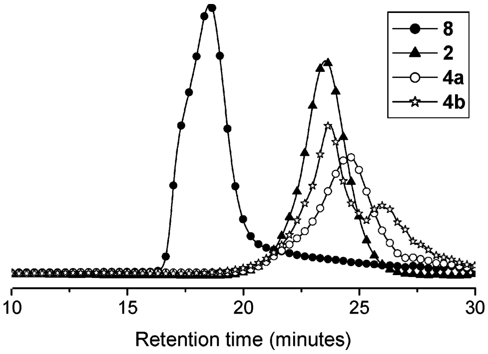


Figure 1. GPC elution traces of **8**, **2**, **4a**, and **4b**.

Hyperbranched TPA Copolymers. It has been proved recently by theoretical calculation,[11] computer simulation,[12] and experimental efforts that the introduction of multifunctional core molecules in the hyperbranched polymerization process can, to some extent, control the molecular weight and its distribution.[13] We use 2,7-diiodo-9,9-dioctylfluorene **(3a)** or its trimer **3b** as core molecules to copolymerize with the AB$_2$ monomer **1** to tailor the structures of the hyperbranched polymers (Scheme 3).

The fluorene unit(s) bearing alkyl chains should help to increase the solubility of the hyperbranched polymers in common organic solvents. Monomers **1**, **3a**, and **3b** are fully soluble in THF, and the polymerization was done with different feed ratios between **1** and **3a** (or **3b**)

Scheme 2

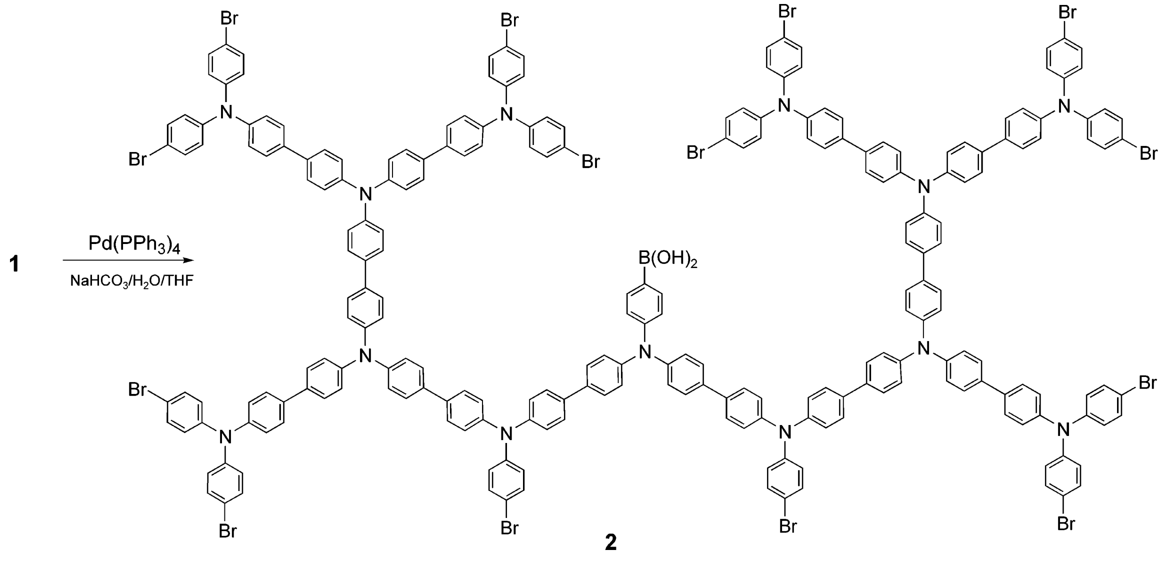
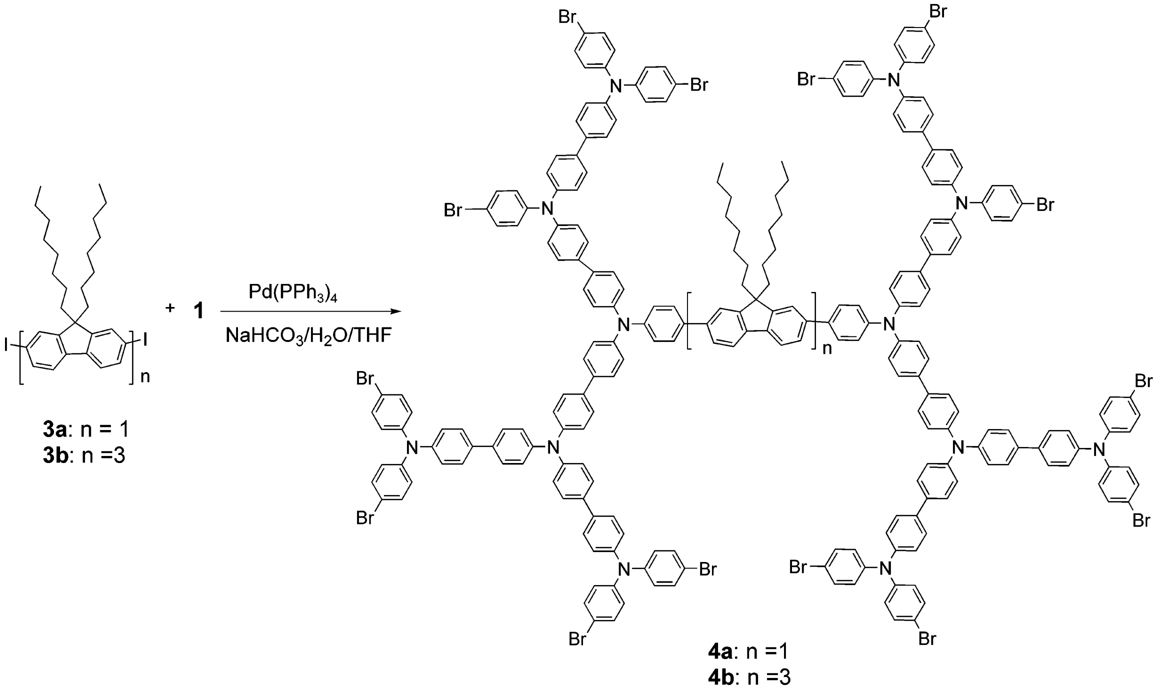


Table 2. Solubility of Hyperbranched Polymers 2, 4a, 4b, and 8 in Different Types of Solvents

	solvent[a]							
	THF	toluene	CH_2Cl_2	$CHCl_3$	DMF	DMSO	1,2-dichlorobenzene	bromobenzene
2	+ −	+ −	− −	− −	+ −	+ −	+ −	+ +
4a	+ +	+ +	+ −	+ +	+ −	+ −	+ +	+ +
4b	+ +	+ +	+ +	+ +	+ −	+ −	+ +	+ +
8	++	++	++	++	+ −	+ −	+ +	+ +

[a] Solubility: fully soluble at room temperature (+ +); partially soluble at room temperature (+ −); insoluble at room temperature (− −).

Scheme 3

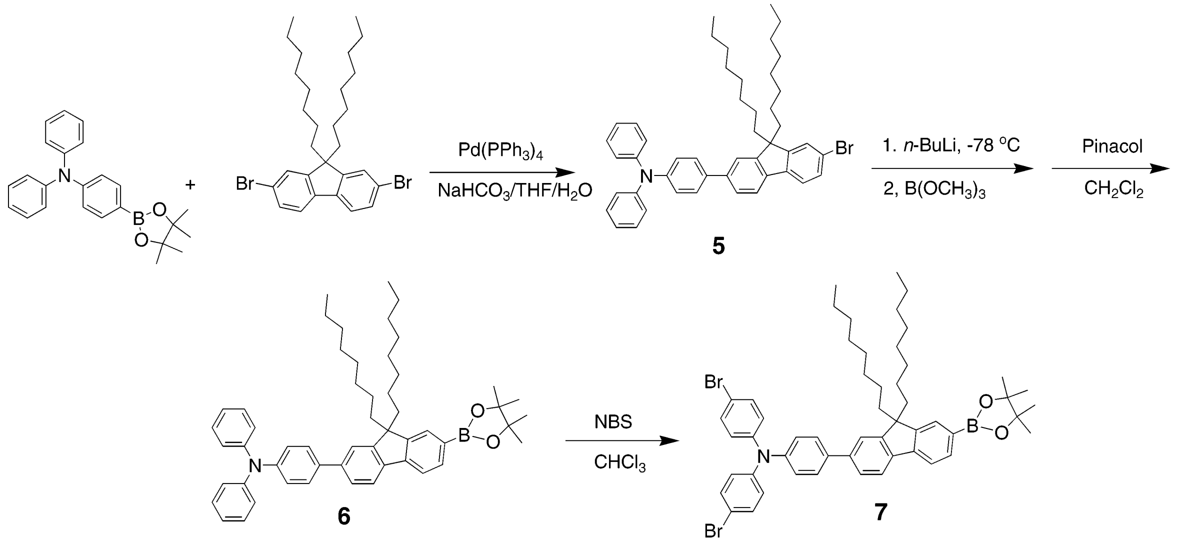


under standard SPC conditions. It is well-known that the reaction of arylboronic acid (or ester) proceeds at a higher rate with iodo aromatics than with bromo aromatics and also under especially mild conditions.[2j,14] Ideally at 45 °C, only iodo aromatics undergo reaction. The reaction procedure was therefore set as follows: first stirred at 45 °C for 1 day and then refluxed for 1 day. The polymerization should proceed in a core-first fashion. Standard workup afforded amorphous, slightly yellow solids. As expected, the hyperbranched copolymers **4a** and **4b** exhibited good solubility in common organic solvents such as THF, acetone, chloroform, benzene, and methylene chloride. Number-average molar mass (M_n) of **4a** and **4b** determined by GPC calibrated with polystyrene standard was 4900 and 7900, respectively. The GPC elution traces are shown in Figure 1. The molecular weight values should be treated as rough estimates due to the big differences in hydrodynamic radius between the hyperbranched polymers and the polystyrene standard. The results are summarized in Table 1. The good solubility of the hyperbranched copolymers made the characterization with solution ^1H and ^{13}C NMR spectroscopy possible. Compared with the hyperbranched TPA homopolymers, the molecular weights of the fluorene-cored, hyperbranched polymers **4a** and **4b** were apparently lower, but their solubilities in THF increased significantly. Solubilities of hyperbranched polymers **4a** and **4b** in different types of solvents are summarized in Table 2.

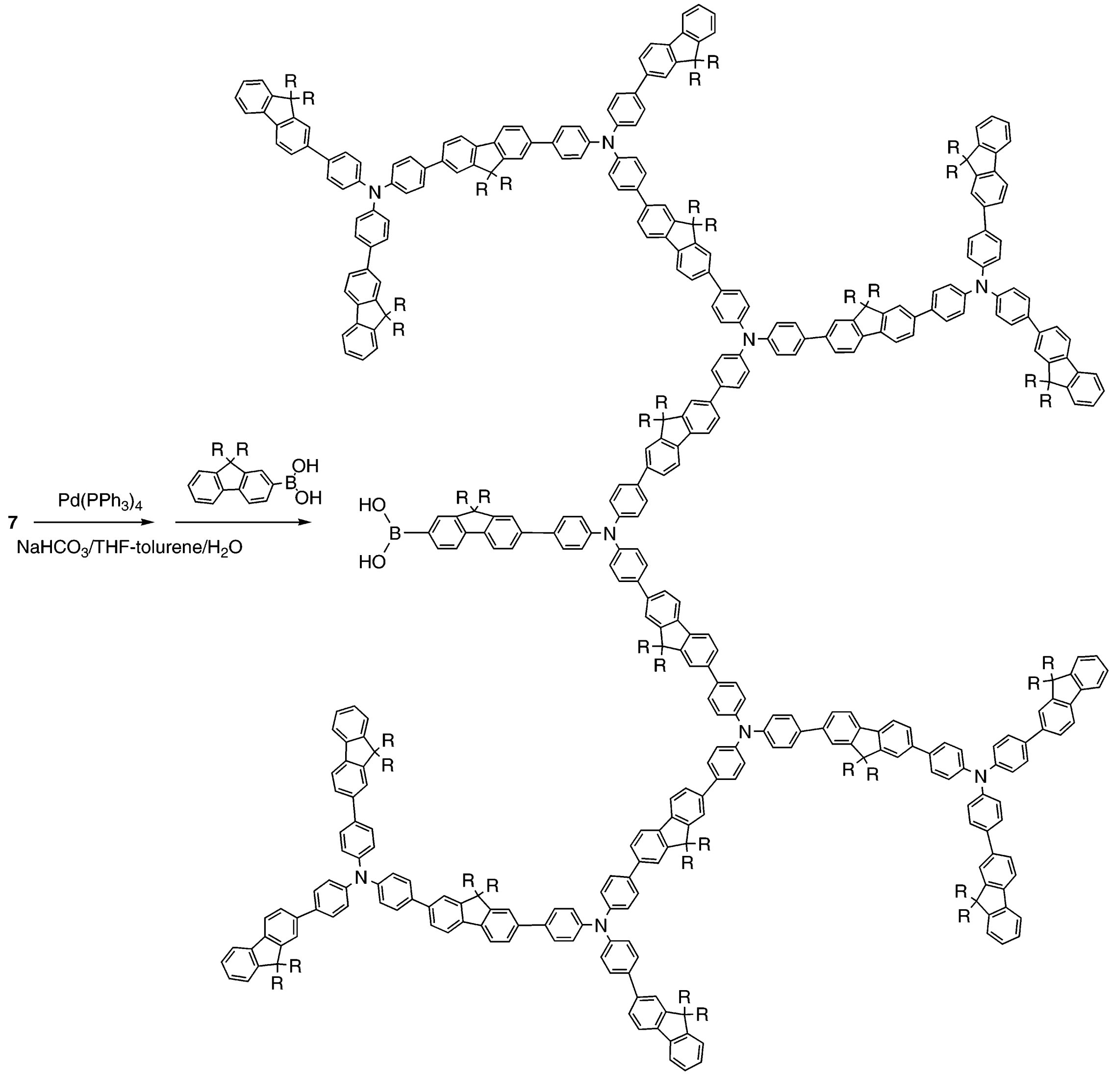
Hyperbranched Triphenylamine−Fluorene Alternating Copolymers. It is obvious that the poor solubility of the polymers in the solvents used for the reaction restricts the formation of high molecular weight hyperbranched polymers. Therefore, a novel AB_2 monomer **7** bearing two flexible alkyl chains were designed and synthesized, and a good solubility of hyperbranched polymers from **7** was anticipated. The synthetic route leading to **7** is outlined in Scheme 4. The reaction of TPA−monoboronic pinacol ester with 5-fold of 2,7-dibromo-9,9-dioctylfluorene under Suzuki cross-coupling conditions afforded monobromide **5** in a 76% yield. The treatment of **5** with 2.1-fold of *n*-BuLi at −78 °C, then its quenching with $B(OMe)_3$, and followed by refluxing with pinacol in CH_2Cl_2 afforded the corresponding boronic pinacol ester **6** in a 61% total yield. Bromination of **6** with NBS in $CHCl_3$ at room temperature afforded **7** in a quantitative yield. High purity of monomer **7** was unambiguously proved with ^1H and ^{13}C NMR spectroscopy and combustion analysis.

A slightly modified SPC condition was applied to polymerize AB_2-type monomer **7** (Scheme 5). The alternating copolymer **8** was prepared in a biphasic system THF−toluene (1:1, v:v)/aqueous $NaHCO_3$ with $Pd(PPh_3)_4$ as a catalyst precursor. The reaction was stirred at reflux for 36 h under nitrogen, then fluorene−monoboronic acid was added, and the mixture was refluxed for a further 24 h. During the reaction, no precipitation was observed. Standard workup afforded the alternating hyperbranched polymer **8** as a slightly yellow solid. The yield was up to 98%. The molecular weight and polydispersity of **8** were characterized with GPC using polystyrene as reference standards and THF

Scheme 4



Scheme 5



8
(R= n-octyl)

as an eluent. The results are summarized in Table 1. The elution curve of **8** is also shown in Figure 1 for a comparison with **2**, **4a**, and **4b**. It is amazing that the introduction of flexible alkyl chains in AB_2 monomer **7** significantly increased the solubility of the hyperbranched polymers. The good solubility of bromo-ended

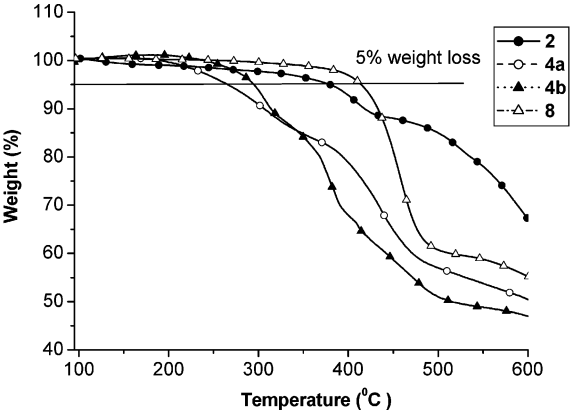


Figure 2. TGA traces of hyperbranched polymers **2, 4a**, **4b**, and **8**.

hyperbranched polymers made the further modification of terminal functional groups possible. The end-capping of the bromo end groups with 9,9-dioctylfluorene-2-boronic acid was quite successful, and the bromo content of **8** was below the detection limit (<0.3%). The weight-average molar mass (M_w) determined by gel permeation chromatography (GPC) calibrated with polystyrene standard was 169 000 and the polydispersity (PD) 1.16 (monomodal). The results are also summarized in Table 1. Alternating hyperbranched polymer **8** exhibited excellent solubility in common organic solvents, such as THF, chloroform, methylene chloride, and toluene. The enhanced solubility of **8** is probably attributed to the introduction of flexible alkyl chain in each repeat unit and being free of large numbers of bromo end groups. Solubilities of **8** in different solvents are also summarized in Table 2.

The thermal properties of the hyperbranched polymers **2**, **4a**, **4b**, and **8** were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The fluorene-capped hyperbranched polymer **8** was the most stable one among these polymers; it showed 5% decomposition at about 416 °C under nitrogen (Figure 2). Compared with **8**, the hyperbranched polymers with bromo end groups were less stable. Hyperbranched polymers **2**, **4a**, and **4b** lost 5% of their weight at 378, 264, and 295 °C, respectively. All the hyperbranched polymers did not exhibit any glass transition in the DSC trace of second heating (10 °C/min).

Optical Properties. The absorption and emission spectra of **1**, **2**, **4a, 4b**, **7**, and **8** in dilute THF solution are shown in Figure 3. Monomers **1** and **7** had absorption peaks at about 315 and 349 nm, respectively. Compared with the absorption spectrum of **1**, the red shift of **7** was attributed to the conjugation of the TPA unit with the fluorene unit. Hyperbranched polymers **2**, **4a**, and **4b** exhibited similar absorption spectra that were very broad, unsymmetrical, and peaked at around 370 nm. Compared with polymers **2**, **4a,** and **4b**, the absorption spectrum of hyperbranched polymer **8** was broader and red-shifted with a peak at 383 nm and a shoulder at 290 nm. In the solution photoluminescence spectrum, monomers **1** and **7** emitted in the ultraviolet region, while the hyperbranched polymers **2**, **4a**, **4b**, and **8** emitted in the blue region. Monomer **1** had an emission peak at 396 nm and a shoulder at around 414 nm, and hyperbranched polymer **2** exhibited an emission peak at 420 nm and a small shoulder at about 440 nm. Compared with the hyperbranched homopolymer **2**, the hyperbranched copolymers **4a** and **4b** showed broader and red-shifted emission spectra with the maxima at around 435 nm. Apparently the emission in the long wavelength region was due to the existence of the fluorene and the trifluorene cores. Monomer **7** had a broad emission band ranging from 380 to 500 nm, while polymer **8** exhibited a narrower emission band peaked at 436 nm. The quantum efficient yields of the hyperbranched polymers in toluene solution were measured using a dilute solution of 9,10-diphenylanthracene in toluene ($\Phi_F = 1.0$) as the standard. All polymers exhibited moderate quantum efficient yields in solution, and the results are summarized in Table 1.

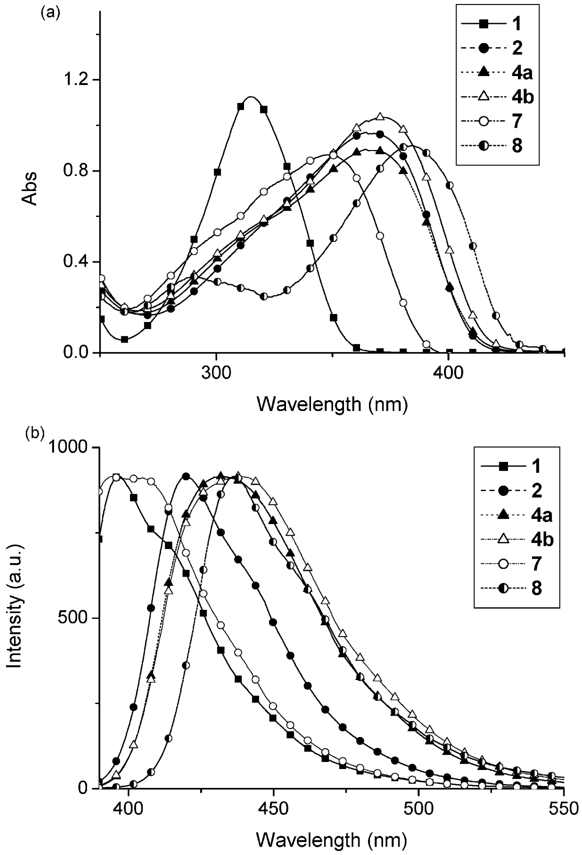


Figure 3. UV–vis absorption (a) and emission (b) spectra of **1**, **2**, **4a**, **4b**, **7**, and **8** in THF solution.

Solid films on quartz plates used for the UV–vis and photoluminescence measurements were prepared by spin-coating with 1% THF solution (for **1**, **7**, **4a**, **4b**, and **8**) or bromobenzene solution (for **2**) at 2000 rpm. All polymers formed homogeneous films. The UV–vis and photoluminescence spectra of **1**, **2**, **4a**, **4b, 7**, and **8** are shown in Figure 4. Compared with the corresponding solution absorption spectra, the film absorption spectra of **1**, **2**, **4a**, **4b**, and **7** were only slightly red-shifted; for polymer **8** in film, the absorption peak red-shifted to 415 nm (about 30 nm red shift) and a long wavelength tail (450–510 nm) appeared. In solid film, monomer **1** exhibited almost the same emission spectrum as in solution. The emission spectrum of hyperbranched homopolymer **2** was red-shifted by about 12 nm compared with the corresponding solution emission spectrum. The red shift was probably due to the aggregation of the polymer chains in the solid state. Compared with the corresponding solution spectra, hyperbranched copolymers **4a** and **4b** showed a narrower emission band with the maxima at around 440 nm. The shrink of emission

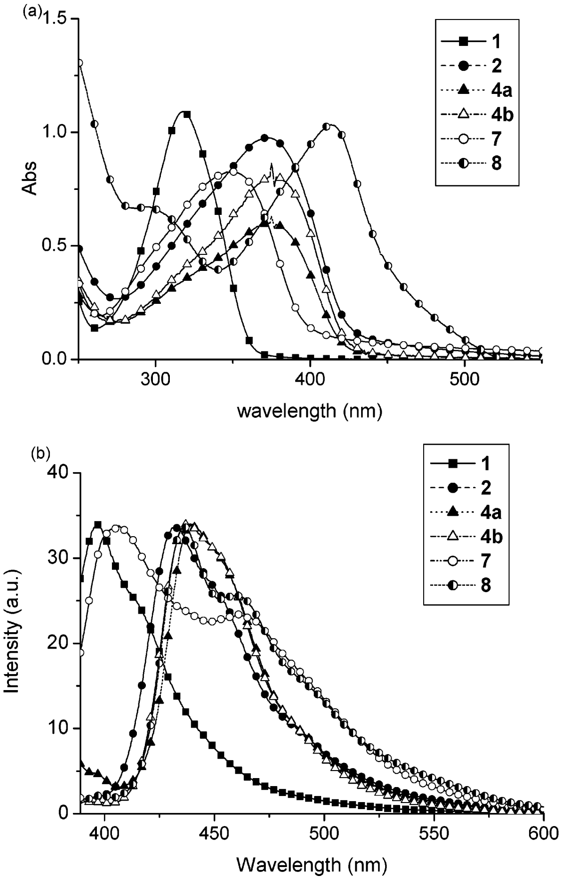


Figure 4. UV−vis absorption (a) and emission (b) spectra of **1**, **2**, **4a, 4b**, **7**, and **8** in films.

band in the short wavelength range might be due to the more efficient energy transfer in solid film than in solution. In the case of monomer **7** in film, its emission spectrum is extremely broad and red-shifted. The most significant difference was that in film monomer **7** exhibited an additional peak at 462 nm and a tail in the long wavelength range (440−600 nm), which did not exist in the corresponding solution absorption spectrum. As expected, polymer **8** also exhibited a red-shifted broader emission band (with an additional peak and a shoulder at around 462 and 493 nm, respectively) in film than in solution. The large red shift and the long wavelength tail were probably due to the formation of aggregation in solid film.

Experimental Section

All chemicals were purchased from Aldrich or Acros and used without further purification. 2,7-Diiodo-9,9-dioctylfluorene (**3a**),[15] 2,7-bis(2-iodo-9,9-dioctylfluoren-7-yl)-9,9-dioctylfluorene (**3b**),[16] 2,7-dibromo-9,9-dioctylfluorene,[17] 9,9-dioctylfluorene-2-boronic acid,[18] and [4-(diphenylamino)phenyl]boronic pinacol ester[19] were prepared according to literature procedures. The catalyst precursor $Pd(PPh_3)_4$ was prepared according to the literature[20] and stored in a Schlenk tube under nitrogen. Solvents were dried according to standard procedures. All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200−300 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker DM300, AV400, or AV600 spectrometer in $CDCl_3$ or 1,2-dichlorobenzene-d_4. The gel permeation chromatography (GPC) measurements were performed on a Waters chromatograph connected to a Waters 410 differential refractometer with THF as an eluent. Electronic absorption spectra were obtained on a Shimadzu UV−vis spectrometer model UV-1601PC. Fluorescence spectra were recorded on a Hitachi F-4500. Elemental analyses were performed on a Flash EA 1112 analyzer or Carlo Erba 1106 analyzer. TGA (Pyris 1 TGA) and DSC (TA2910) measurements were carried out under a nitrogen atmosphere at a heating rate of 10 °C/min to record the differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively.

Pinacol [4-(Bis(4-bromophenyl)amino)phenyl]boronate (1). To a stirred solution of tris(4-bromophenyl)amine (5.0 g, 10.4 mmol) in ether (75 mL) was added dropwise a solution of *n*-BuLi (4.0 mL, 11.4 mmol, 2.89 M in *n*-hexane) at −78 °C under nitrogen; the mixture was allowed to warm to −40 °C slowly, stirred for 1 h, and cooled to −78 °C again. Trimethyl borate (3.4 mL, 31.3 mmol) was then added dropwise, and the reaction was stirred overnight. The mixture was poured into water, the organic layer separated, the aqueous layer extracted with ether for three times, and the combined organic layer dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by chromatography on silica gel column eluting with CH_2Cl_2 increasing to CH_2Cl_2/ether (v:v, 7:3) to afford 4-(bis(4-bromophenyl)amino)phenylboronic acid as a white solid. A mixture of 4-(bis(4-bromophenyl)amino)phenylboronic acid (2.1 g, 4.7 mmol), pinacol (1.3 g, 10.9 mmol), and anhydrous CH_2Cl_2 (150 mL) was refluxed for 5 h with a Dean−Stark apparatus to remove the formed H_2O. After removal of the solvent, the residue was purified by chromatography on silica gel eluting with hexane/EtOAc (v/v, 5:1) to afford **1** as a white solid (2.5 g, 46%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, 2H), 7.37 (d, 4H), 7.02 (d, 2H), 6.96 (d, 4H), 1.34 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 146.1, 136.1, 132.4, 126.1, 122.4, 116.1, 83.7, 24.8. Anal. Calcd for $C_{24}H_{24}BBr_2NO_2$: C, 54.48; H, 4.57; N, 2.65. Found: C, 54.56; H, 4.58; N, 2.66.

Hyperbranched TPA Homopolymer (2). A mixture of **1** (500 mg, 0.95 mmol), $NaHCO_3$ (0.8 g, 9.5 mmol), THF (20 mL), water (10 mL), and $Pd(PPh_3)_4$ (11 mg, 9.5 μmol) was carefully degassed and charged with nitrogen. The mixture was heated to reflux and stirred for 24 h. The formed yellow solids were filtered, washed with water and THF, and dried under vacuum to give **2** as a yellow solid (280 mg, 91.7%). ^1H NMR (300 MHz, 1,2-dichlorobenzene-d_4): δ 7.54−7.47 (broad), 7.28−7.25 (broad), 7.02−6.97 (broad). Anal. Calcd for $(C_{18}H_{12}BrN)_n$: C, 67.10; H, 3.75; N, 4.35. Found: C, 63.30; H, 3.75; N, 3.77.

Fluorene-Cored TPA Hyperbranched Copolymer (4a). A mixture of **1** (200 mg, 0.38 mmol), **3a** (30 mg, 0.048 mmol), $NaHCO_3$ (0.5 g, 6.0 mmol), THF (20 mL), water (5 mL), and $Pd(PPh_3)_4$ (4.4 mg, 3.8 μmol) was carefully degassed and charged with nitrogen. The mixture was first stirred at 45 °C for 12 h and then heated to reflux for a further 12 h. THF was added to dissolve the formed precipitate, the organic layer separated, dried over Na_2SO_4, and evaporated to dryness. The residue was dissolved in THF (15 mL) and precipitated into hexane (30 mL). Filtration and drying under vacuum gave **4a** as a slightly yellow solid (114 mg, 81.5%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.76−7.74 (broad, 2H), 7.60−7.55 (broad, 6H), 7.49−7.46 (broad, 24H), 7.37−7.35 (broad, 20H), 7.21−7.19 (broad, 6H), 7.17−7.15 (broad, 12H), 7.11−7.07 (broad, 6H), 7.05−7.02 (broad, 6H), 6.99−6.97 (broad, 12H), 2.02 (broad, 4H), 1.28−1.25 (broad, 12H), 1.18−1.05 (broad, 20H), 0.80−0.77 (broad, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.0, 132.0, 127.2, 125.2, 124.2, 115.3, 55.8, 40.1, 31.4, 29.7, 29.3, 28.8, 24.5, 24.2, 23.4, 22.2, 13.7.

Trifluorene-Cored TPA Hyperbranched Copolymer (4b). A mixture of **1** (200 mg, 0.38 mmol), **3b** (67 mg, 0.048 mmol), $NaHCO_3$ (0.5 g, 6.0 mmol), THF (20 mL), water (5 mL), and $Pd(PPh_3)_4$ (5.2 mg, 4.5 μmol) was carefully degassed and charged with nitrogen. The mixture was first stirred at 45 °C for 12 h and then heated to reflux for a further 12 h. THF was added to dissolve the formed precipitate, the organic layer separated, dried over Na_2SO_4, and evaporated to dryness. The residue was dissolved in THF (15 mL) and precipitated into hexane (30 mL). Filtration and drying under vacuum gave **4b** as a slightly yellow solid (121 mg, 68.6%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.89−7.82 (broad, 6H), 7.74−7.60 (broad, 18H), 7.56−7.52 (broad, 32H), 7.45−7.39 (broad, 24H), 7.28−7.25

(broad, 10H), 7.23−7.19 (broad, 16H), 7.16−7.13 (broad, 6H), 7.10−7.07 (broad, 8H), 7.04−7.01 (broad, 12H), 2.15−2.06 (broad, 16H), 1.32−1.22 (broad, 60H), 0.91−0.76 (broad, 30H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 132.4, 127.6, 126.1, 125.5, 124.5, 115.6, 55.3, 40.4, 31.7, 30.0, 29.2, 23.9, 22.6, 14.0.

4-(2-Bromo-9,9-dioctyl-fluoren-7-yl)-*N*,*N*-diphenylaniline (5). A mixture of pinacol [4-(diphenylamino)phenyl]boronate (0.66 g, 1.8 mmol), 2,7-dibromo-9,9-dioctylfluorene (5.0 g, 9.1 mmol), $NaHCO_3$ (2.0 g, 23.8 mmol), THF (60 mL), water (20 mL), and $Pd(PPh_3)_4$ (21.3 mg, 18.4 μmol) was carefully degassed and charged with nitrogen. The mixture was stirred and refluxed for 12 h and then poured into water. The organic layer was separated, the aqueous layer extracted with CH_2Cl_2 for three times, the combined organic layer dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (v/v, 1:10) to afford **5** as a colorless oil (0.96 g, 76%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.71−7.68 (d, 1H), 7.57−7.51 (m, 5H), 7.46−7.44 (d, 2H), 7.30−7.25 (m, 4H), 7.18−7.14 (m, 6H), 7.07−7.02 (t, 2H), 2.00−1.93 (m, 4H), 1.23−1.05 (m, 20H), 0.83−0.79 (t, 6H), 0.65−0.63 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 153.2, 151.0, 147.7, 147.2, 140.0, 139.9, 138.9, 135.4, 129.9, 129.3, 127.8, 126.1, 125.6, 124.4, 123.9, 123.0, 120.9, 120.0, 55.5, 40.3, 31.8, 29.9, 29.2, 23.7, 22.6, 14.0. Anal. Calcd for $C_{47}H_{54}BrN$: C, 79.19; H, 7.64; N, 1.96. Found: C, 79.29; H, 7.96; N, 2.01.

Pinacol [7-(4-(Diphenylamino)phenyl)-9,9-dioctyl-fluoren-2-yl]boronate (6). To a stirred solution of **5** (0.96 g, 1.35 mmol) in ether (10 mL) and THF (10 mL) was added dropwise a solution of *n*-BuLi (1.0 mL, 2.9 mmol, 2.89 M in *n*-hexane) at −78 °C under nitrogen; the mixture was stirred for 1 h at −78 °C. Trimethyl borate (0.72 mL, 6.6 mmol) was then added dropwise, and the reaction was stirred overnight. The mixture was poured into water, the organic layer separated, the aqueous layer extracted with ether for three times, the combined organic layer dried over Na_2SO_4, and evaporated to dryness. The crude product was purified by chromatography on silica gel eluting with CH_2Cl_2 increasing to CH_2Cl_2/ether (v:v, 4:1) to afford 7-(4-(diphenylamino)phenyl)-9,9-dioctyl-fluoren-2-yl-2-boronic acid as a white solid. A mixture of 7-(4-(diphenylamino)phenyl)-9,9-dioctyl-fluoren-2-yl-2-boronic acid (0.57 g, 0.84 mmol), pinacol (0.18 g, 1.5 mmol), and anhydrous CH_2Cl_2 (50 mL) was refluxed for 5 h with a Dean−Stark apparatus to remove the formed H_2O. After removal of the solvent, the residue was purified by chromatography on silica gel eluting with hexane/EtOAc (v/v, 6:1) to afford **6** as a white solid (0.62 g, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83−7.80 (d, 1H), 7.76−7.69 (m, 3H), 7.57−7.54 (d, 4H), 7.30−7.25 (m, 4H), 7.18−7.14 (m, 6H), 7.06−7.01 (t, 2H), 2.03−1.98 (m, 4H), 1.40 (s, 12H), 1.25−1.03 (m, 20H), 0.82−0.77 (t, 6H), 0.64 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 150.1, 147.7, 147.1, 143.9, 140.0, 139.9, 135.7, 133.8, 129.3, 128.9, 127.8, 125.5, 124.4, 124.0, 122.9, 121.0, 120.4, 119.0, 83.7, 55.2, 40.3, 31.8, 30.0, 29.2, 25.0, 23.7, 22.6, 14.1. Anal. Calcd for $C_{53}H_{66}BO_2N$: C, 83.77; H, 8.75; N, 1.84. Found: C, 83.63; H, 8.79; N, 2.00.

Pinacol [[7-(4-Bis(4′-bromophenyl)phenylamino)-phenyl]-9,9-dioctyl-fluoren-2-yl]boronate (7). To a stirred solution of **6** (0.5 g, 0.66 mmol) in $CHCl_3$ (10 mL) was added NBS (0.3 g, 1.7 mmol) at 0 °C under nitrogen, and the mixture was stirred overnight at room temperature. After removal of the solvent, the crude production was purified by chromatography on silica gel eluting with hexane/EtOAc (v/v, 6:1) to afford **7** as a white solid (0.6 g, 99%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83−7.81 (d, 1H), 7.77−7.75 (d, 2H), 7.72−7.69 (d, 1H), 7.59−7.53 (t, 4H), 7.39−7.36 (d, 4H), 7.15−7.13 (d, 2H), 7.02−6.99 (d, 4H), 2.03−2.01 (m, 4H), 1.40 (s, 12H), 1.25−1.04 (m, 20H), 0.83−0.78 (t, 6H), 0.64 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.0, 151.0, 147.4, 144.6, 141.1, 140.5, 134.7, 133.2, 129.8, 129.1, 126.7, 125.5, 122.0, 121.3, 119.9, 116.6, 107.0, 84.7, 56.2, 41.3, 32.7, 30.9, 30.1, 25.7, 24.6, 23.5, 15.0. Anal. Calcd for $C_{53}H_{64}BBr_2O_2N$: C, 69.37; H, 7.03; N, 1.53. Found: C, 69.34; H, 7.15; N, 1.73.

Hyperbranched TPA−Fluorene Homopolymer (8). A mixture of **7** (200 mg, 0.22 mmol), $NaHCO_3$ (0.5 g, 6.0 mmol), THF (10 mL), toluene (10 mL), water (10 mL), and $Pd(PPh_3)_4$ (2.2 mg, 1.9 μmol) was carefully degassed and charged with nitrogen. The mixture was heated to reflux and stirred for 36 h. Then 9,9-dioctylfluorene-2-boronic acid (142 mg, 0.33 mmol) and additional $Pd(PPh_3)_4$ (2.2 mg, 1.9 μmol) were added, and the mixture was further stirred and refluxed for 24 h. CH_2Cl_2 was then added, and the organic layer was separated and dried over $MgSO_4$. After removal of the solvent, the residue was then dissolved in THF (5 mL) and precipitated into methanol (5 mL). The formed precipitate was recovered by filtration, taken up in benzene, and freeze-dried to afford **8** as a slightly yellow solid (218 mg, 98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75−7.59 (broad), 7.34−6.90 (broad), 2.15−2.00 (broad), 1.26−0.88 (broad), 0.81−0.60 (broad). ^{13}C NMR (150 MHz, $CDCl_3$): δ 151.7, 151.4, 151.0, 146.7, 141.0, 140.1, 140.0, 139.4, 136.1, 127.9, 126.9, 126.8, 125.5, 124.5, 122.9, 121.0, 119.9, 119.7, 55.3, 55.1, 40.4, 31.8, 30.0, 29.2, 23.8, 22.6, 14.1. Anal. Calcd for $(C_{76}H_{93}N)_n$: C, 89.44; H, 9.19; N, 1.37. Found: C, 88.90; H, 9.28; N, 1.03; Br <0.3%.

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