Hyperbranched Poly(fluorenevinylene)s Obtained from Self-Polymerization of 2,4,7-Tris(bromomethyl)-9,9-dihexylfluorene

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ABSTRACT: Hyperbranched poly(fluorenevinylene)s (**HF0.04**−**HF0.17** and **HF0.08-cap**) were prepared from 2,4,7-tris(bromomethyl)-9,9-dihexylfluorene (**A**) by the Gilch reaction (the numbers represent monomer concentration in mmol/mL; **cap:** end-capped by benzyl bromide). The structural analysis of the hyperbranched products was obtained from their ^{1}H NMR spectra, from which an almost linear relationship between degree of branching (DB) and monomer concentration has been correlated. The absorption peaks blue-shifts significantly from 430 nm for linear **LF0.17-cap** counterpart, which was prepared from 2,7-bis(bromomethyl)-9,9-dihexylfluorene (**A′**), to 372 nm for the hyperbranched poly(fluorenevinylene)s which degenerates further at higher degree of branching. However, the photoluminescence spectra of the **HF** films show peaks at ca. 467−468 nm, which is close to that of the **LF0.17-cap** film (473 nm), suggesting effective photoexcited energy transfer occurs between segments in the **HF** samples. The maximal luminance (2180 cd/m^2) and maximal luminance efficiency (0.89 cd/A) of the electroluminescent device using end-capped hyperbranched poly(fluorenevinylene) as emitting layer (ITO/PEDOT/**HF0.08-cap**/Ca/Al) are superior to those from the **LF0.17-cap** (1452 cd/m^2, 0.47 cd/A) and other hyperbranched polymers without end-capping (184−26 cd/m^2, 0.01−0.09 cd/A). Current results indicate that both hyperbranched structure and end-capping contribute to enhanced optoelectronic performance in the poly(fluorenevinylene)s.

Introduction

Electroluminescent (EL) polymers have been extensively studied recently due to their tunable emission color through molecular design, good film-forming property, and easy fabrication via spin-coating or ink-jetting, which make them excellent candidates for both single-layer and multilayer polymer light-emitting diodes (PLEDs).[1] The most widely investigated EL polymers are the linear conjugated ones, such as poly(*p*-phenylenevinylene) (PPV),[1] polyfluorene (PF),[2] and their derivatives.[3] Polyfluorenes (PFs)[2] are promising materials for blue-light-emitting devices because of their high photoluminescence (PL) and electroluminescence (EL) efficiencies.[4] However, there are still some drawbacks that hamper their potential applicability, such as the undesired green emission that appears upon thermal annealing or device operation.[5] This low-energy emission band was attributed to interchain interaction (formation of excimers or aggregates)[6] in the solid state and/or ketone defects.[7,8] Several attempts have been made to minimize the interchain interaction, such as incorporation of longer and branched side chains or bulky substituents,[9] copolymerization technique,[10] dendrimer and hyperbranch attachment,[10,11] end-capping of PFs with bulky groups,[12] cross-linking of PFs,[13] and oligomer approach.[10,14]

Hyperbranched polymers have drawn considerable attention recently as a means of diminishing formation of interchain interaction due to their highly branched and globular molecular structures.[15] Therefore, hyperbranched electroluminescent polymers have become of current interest in terms of developing efficient light-emitting and other optoelectronic devices.[16] Halim et al. reported high-quality amorphous films formed by three-dimensional EL polymers which revealed improved thermal stability and emission efficiency.[17] Compared with dendritic polymers,[18] hyperbranched polymers not only are easier to synthesize but also exhibit comparable properties. The hyperbranched structure is of greater advantage than its linear counterpart in high solubility, improved processability, and minimized unfavorable intermolecular interactions and crystallization.[19] Besides, hyperbranched polymers prefer to form a globular structure with generations if they contain many peripheral chromophores.[20] Therefore, it is possible to endow these hyperbranched architectures with functions by controlling the nature of the end groups, such as enhanced adhesion and energy harvesting as well as optoelectronic characteristics.

Furthermore, the hyperbranched polymers generally possess low polydispersity and high degree of branching (DB) (DB = 0 for linear polymer and DB = 1 for dendrimer), i.e., hyperbranched structures that resemble perfect dendrimers.[21] The DB is commonly determined by NMR spectroscopy of the hyperbranched molecules, from which the degree of branching is readily calculated using the following equation:[21]

$$\mathrm{DB} = \frac{D+T}{D+L+T} \qquad (1)$$

in which *D*, *T*, and *L* are the fractions of dendritic, terminal, and linear monomer units, respectively, incorporated into the hyperbranched structures. Furthermore, an expression for DB in hyperbranched polymers based on AB$_m$ monomers was derived by Frey:[21]

$$\mathrm{DB} = \left(\frac{m-1}{m}\right)^{m-1} \qquad (2)$$

From a statistical point of view, DB may not exceed 0.5 in hyperbranched polymers based on AB$_2$ systems and 0.44 in AB$_3$ systems. Later, Frey proposed three different possible ways to enhance DB beyond the limiting value of a random polycondensation of AB$_m$ monomer:[22] (a) enhanced reactivity of linear vs terminal units, (b) polymerization of prefabricated perfect dendritic units, and (c) slow addition technique.

In this work, we employed a trifunctional derivative of fluorene [**A**: 2,4,7-tris(bromomethyl)-9,9-dihexylfluorene] as a branch unit to prepare hyperbranched polymers (**HF0.04**−**HF0.17** and **HF0.08-cap**) by the Gilch reaction.[23] The numbers in the polymer name represent the feed monomer concentration (0.04−0.17 mmol/mL), and the suffix "**cap**" means the terminal bromomethyl groups have been end-capped by reacting with benzyl bromide. The structure of monomer **A** has been confirmed by NMR and NOESY spectra as 2,4,7-tris(bromomethyl)-9,9-dihexylfluorene previously.[24] Although hyperbranched

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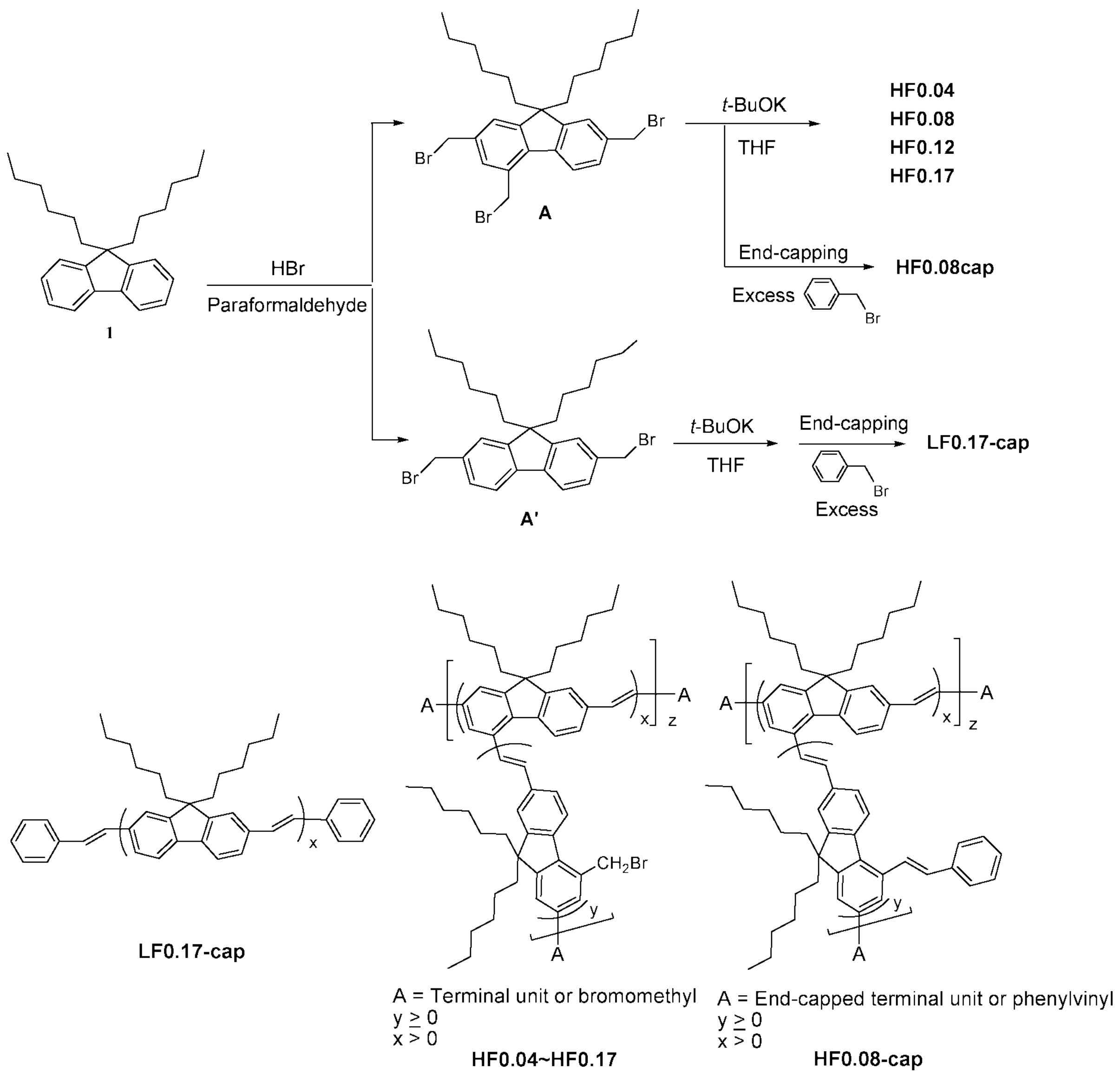
Scheme 1. Synthesis of Monomers (A, A′) and Polymers



polyfluorene derivatives were reported in the past,[25] this is the first report to prepare hyperbranched polyfluorenes using fluorene derivative (**A**) as both monomer and branch unit. A linear counterpart **LF0.17-cap** was also synthesized from 2,7-bis(bromomethyl)dihexylfluorene (**A′**) for comparative study. In order to confirm the relation between feed concentration and degree of branching (DB), the **HF0.04−HF0.17** were not end-capped so that the numbers of residual bromomethyl groups estimated from their ^{1}H NMR spectra could be used to calculate the *D*, *T*, *L*, and DB. Moreover, the optical, electrochemical, and preliminary electroluminescent properties of the hyperbranched polymers (**HF0.04−HF0.12** and **HF0.08-cap**) were investigated and compared with its corresponding linear polymer (**LF0.17-cap**).

Table 1. Polymerization Results and Characterization of the Poly(fluorenevinylene)s[a]

polymer	polym time[b] (h)	yield (%)	M_n[c] (×10^4)	M_w[c] (×10^4)	PDI[c]	monomer conc[d] (mmol/mL)
HF0.04	16	61	3.18	5.26	1.65	0.04
HF0.08	12	59	3.19	5.31	1.66	0.08
HF0.08-cap[e]	12	56	3.40	5.72	1.68	0.08
HF0.12	10	63	3.26	5.13	1.57	0.12
HF0.17	6	72	3.69	6.34	1.72	0.17
LF0.17-cap[e]	24	62	2.20	4.48	2.20	0.17

[a] The polymerization temperature was 25 °C (room temperature). [b] The polymerization times were chosen to avoid gelation. [c] M_n, M_w, and PDI were determined by gel permeation chromatography using polystyrene standards and $CHCl_3$ as eluent. [d] Monomer feed concentrations in THF. [e] End-capped by reacting with excess of benzyl bromide.

Experimental Section

Materials. The starting material 9,9-dihexylfluorene (**1**) and linear monomer 2,7-bis(bromomethyl)-9,9-dihexylfluorene (**A′**) were prepared according to published literature methods.[26] Hyperbranched (**HF0.04−HF0.17** and **HF0.08-cap**) and linear (**LF0.17-cap**) poly(fluorenevinylene)s were prepared by a modified Gilch reaction using *t*-BuOK as catalyst, as shown in Scheme 1.[24] Paraformaldehyde (Showa), hydrogen bromide solution (33 wt % in acetic acid) (Acros), benzyl bromide (TCI Co.), *t*-BuOK solution (1 M in THF, Aldrich Co.), tetrahydrofuran (THF, Tedia Co.), and other solvents were pure or HPLC-grade reagents. All reagents and solvents were used without further purification.

Instrumentation. All newly synthesized compounds were identified by ^{1}H NMR spectra and elemental analysis (EA). ^{1}H NMR spectra were obtained on a Bruker AVANCE-400 NMR spectrometer. The elemental analysis was carried out on a Heraus CHN-Rapid elemental analyzer. The FT-IR spectra were measured as KBr disk on a Fourier transform infrared spectrometer, model Valor III from Jasco. The molecular weights and molecular weight

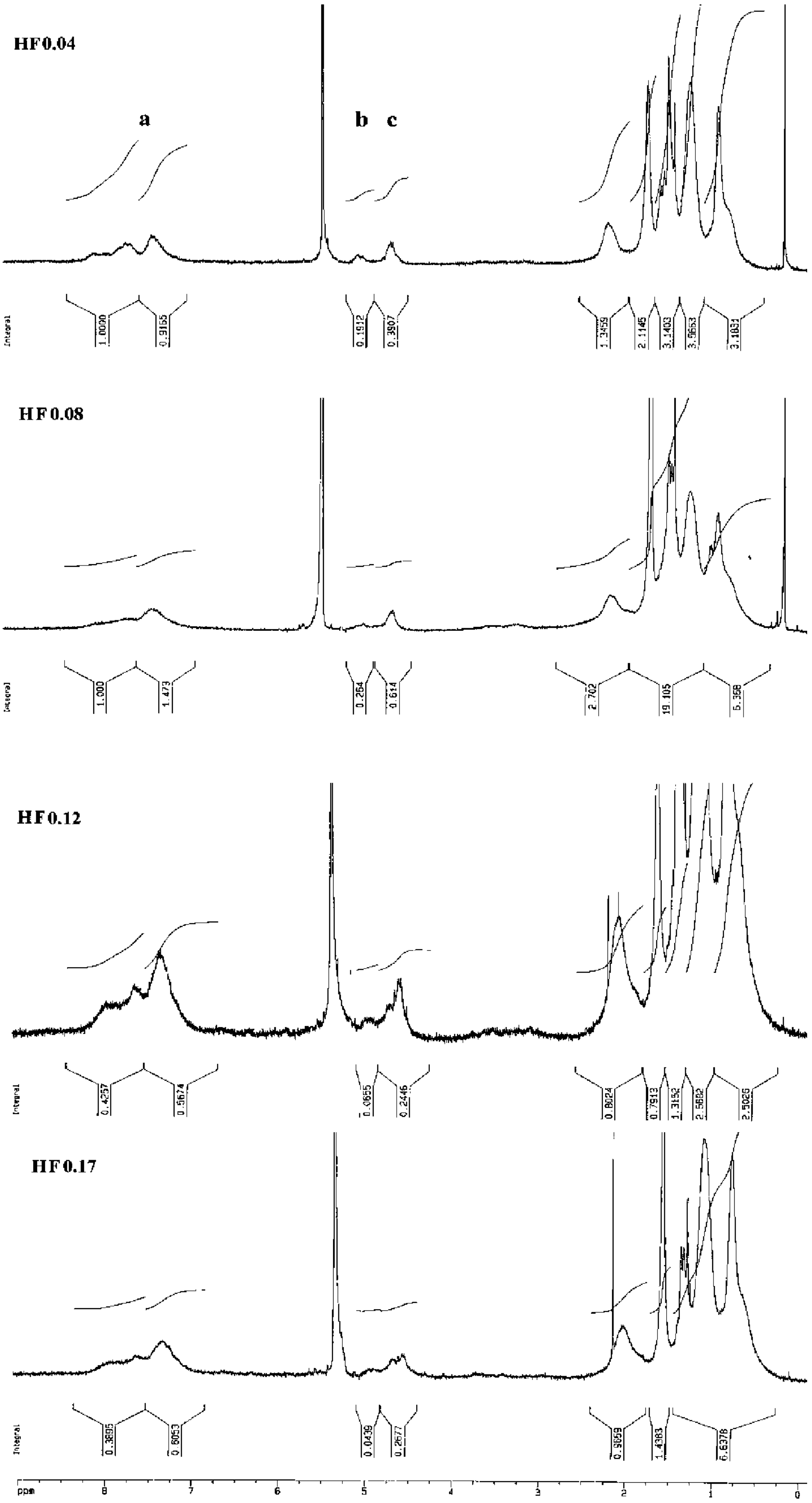
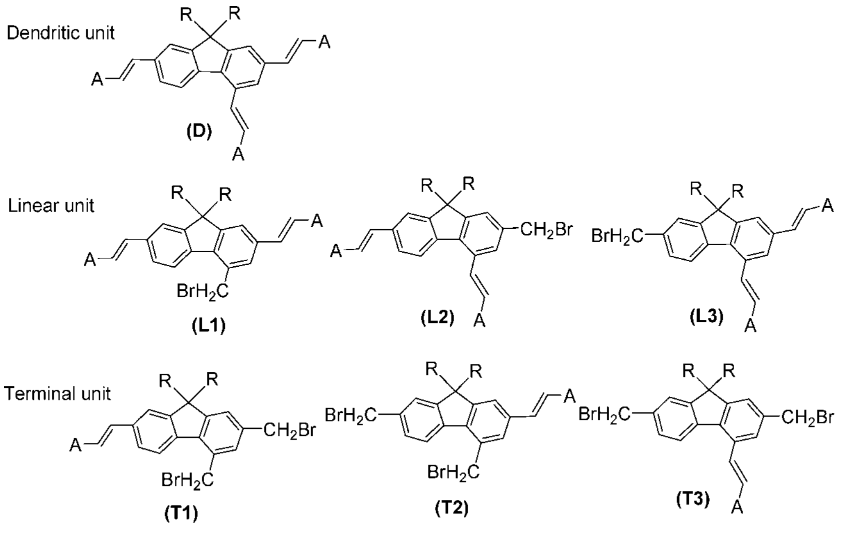


Figure 1. ^{1}H NMR spectra of **HF004−HF0.17** in CD_2Cl_2 (a: aromatic protons; b: protons at 4-bromomethyl groups; c: protons at 2- or 7-bromomethyl groups).

distributions were determined by a gel permeation chromatograph (GPC) using chloroform ($CHCl_3$) as eluent. Monodisperse polystyrene standards were employed for molecular weight calibration. UV/vis absorption spectra were measured with a Jasco V-550 spectrophotometer, and the photoluminescence (PL) spectra were obtained using a Hitachi F-4500 spectrofluorometer. The voltammograms of the polymers were measured with a cyclic voltammetric apparatus (model CV-50W from BAS) equipped with a three-

Chart 1. D, L, and T Units in Polymers



R= *n*-hexyl, A= reacted

electrode cell. The cell was made up of a polymer-coated glassy carbon as working electrode, a Ag/AgCl electrode as the reference electrode, and a platinum wire electrode as the auxiliary electrode. The electrodes were immersed in acetonitrile containing 0.1 M (n-Bu)$_4$NClO$_4$ as electrolytes. The energy levels were calculated by comparing with the ferrocene (FOC) value of −4.8 eV with respect to vacuum level, which is defined as zero.[27] Polymer light-emitting-diodes configured as ITO/PEDOT:PSS/**HF**s or **LF0.17-cap**/Ca/Al were fabricated by successive spin-coating; i.e., the hole-injection layer (PEDOT:PSS: Baytron P from Bayer) was first spin-coated onto cleaned ITO glass, followed with coating of emitting polymer layer. The film thickness of the emitting layer was about 60−100 nm as measured by an atomic force microscope (AFM). Finally, calcium and aluminum were deposited onto the polymeric film to form as the cathode via vacuum deposition under 2.0×10^{-6} Torr. The film thickness of calcium (aluminum) was about 50 (100) nm as measured by an AFM. The devices were fabricated in the ambient conditions and then their optoelectronic properties measured in a glovebox filled with nitrogen. Device performance and electroluminescence spectra were investigated and recorded using a combination of a Keithley power supply (model 2400) and an Ocean Optics usb2000 spectrofluorometer, respectively.

Synthesis of Monomer A and Polymers (HFs and LF0.17-cap) (Scheme 1). *2,4,7-Tris(bromomethyl)-9,9-dihexylfluorene (***A***).* To 100 mL HBr solution (33% in acetic acid) was added 9,9-dihexylfluorene (**1**: 3.41 g, 10 mmol) and paraformaldehyde (6.13 g, 200 mmol). The mixture was heated to 70 °C slowly and then stirred for 48 h. It was poured into 500 mL of cold water after cooling to room temperature. The mixture was extracted with CH_2Cl_2, and the extract was washed with saturated $NaCl_{(aq)}$. A sticky liquid was obtained after solvent removal of the organic portion. The liquid was further purified by column chromatography using silica as a stationary phase and a mixture of n-hexane and toluene (v/v = 10/1) as an eluent, resulting in 4.5 g of 2,4,7-tris(bromomethyl)-9,9-dihexylfluorene (**2**) (65.1%). ^{1}H NMR (400 Hz, $CDCl_3$): δ = 7.9 (d, 1H, Ar H, J = 7.90), 7.42−7.24 (m, 4H, Ar H), 4.82 (s, 2H, $-CH_2-$), 4.60 (s, 2H, $-CH_2-$), 4.54 (s, 2H, $-CH_2-$), 1.97−1.92 (m, 4H, $-CH_2-$), 1.26−0.74 (m, 16H, $-CH_2-$), 0.59 (m, 6H, $-CH_3$). Anal. Calcd for $C_{28}H_{37}Br_3$ (%): C, 54.83; H, 6.08. Found: C, 54.41; H, 6.01.

Table 2. Influence of Monomer Concentration on Molar Ratios of Individual Units and Degree of Branching (DB)

	molar ratios of individual units			
conc (mmol/L)[a]	D[b]	L[b]	T[b]	DB[c]
0.04	0.22	0.55	0.23	0.45
0.08	0.19	0.46	0.35	0.53
0.12	0.27	0.44	0.30	0.57
0.17	0.31	0.31	0.38	0.70

[a] Concentration of monomer in THF. [b] Molar ratios of dendritic (D), linear (L), and terminal units (T). [c] Degree of branching calculated by eq 1: DB = $(D + T)/(D + L + T)$.

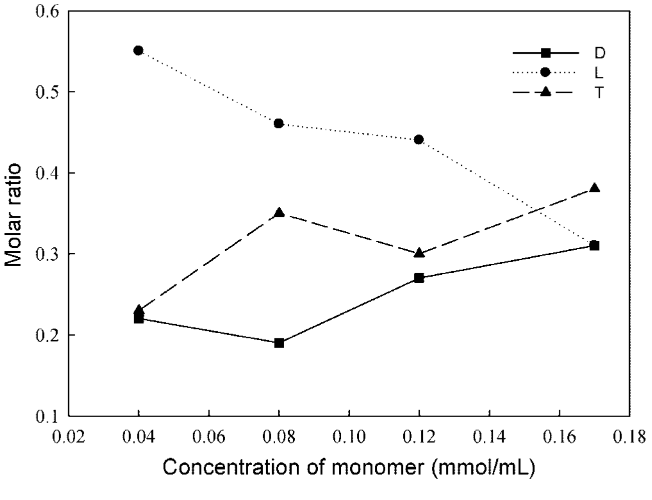


Figure 2. Influence of monomer concentration on molar ratios of D (dendritic), L (linear), and T (terminal) units in the resulting hyperbranched polymers.

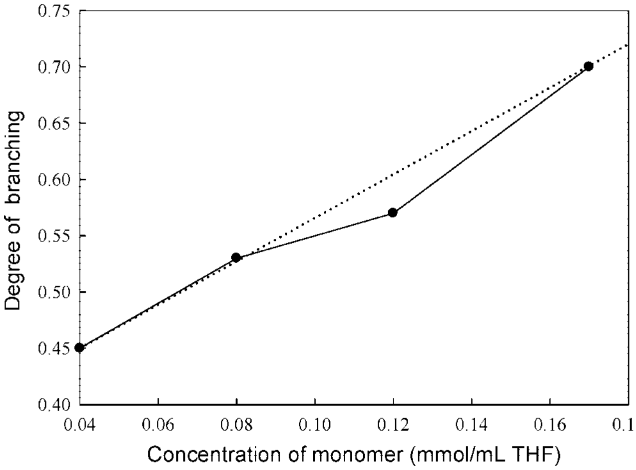


Figure 3. Degree of branching (DB) vs concentration of monomer.

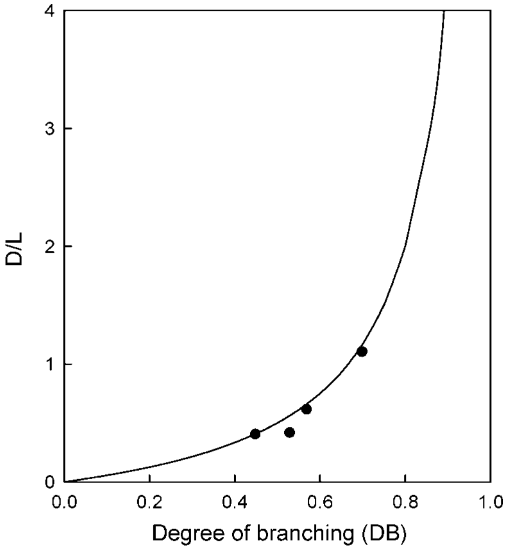


Figure 4. Ratios of dendritic to linear units (*D*/*L*) vs DB for hyperbranched **HF004−HF0.17**: ideal (—) and actual (●).

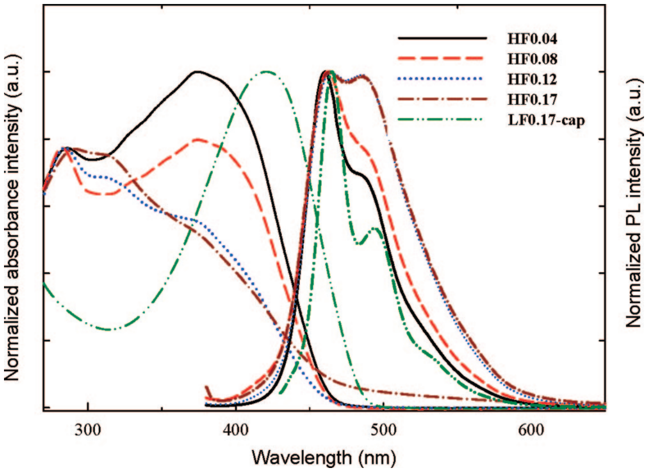


Figure 5. Absorption and photoluminescence spectra of **HF004−HF0.17** and **LF0.17-cap** in $CHCl_3$ (1×10^{-6} g/mL). Excitation: 380 and 424 nm for **HF0.04−HF0.17** and **LF0.17-cap**, respectively.

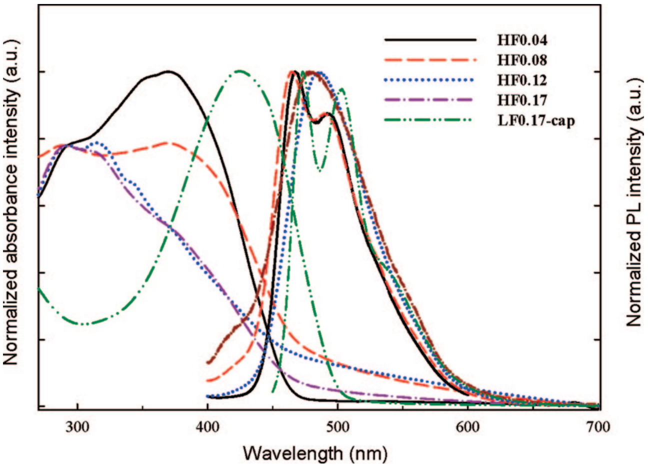


Figure 6. Absorption and photoluminescence spectra of **HF004−HF0.17** and **HF0.17-cap** films coated on quartz plate. Excitation: 380 and 426 nm for **HF0.04−HF0.17** and **LF0.17-cap**, respectively.

Table 3. Optical Properties of the Hyperbranched and Linear Poly(fluorenevinylene)s

polymer	UV−vis λ_{max}[a] solution (nm)	UV−vis λ_{max} film (nm)	PL λ_{max}[a] solution (nm)	PL λ_{max} film (nm)
HF0.04	286, 372	286, 372	465, 486[b]	467, 492[b]
HF0.08	286, 372	286, 372	464, 488[b]	467, 493[b]
HF0.08-cap	286, 314, 374	286, 314, 375	464, 488[b]	468, 496[b]
HF0.12	286, 315, 372	286, 315, 372	465, 485[b]	468, 496[b]
HF0.17	286, 315, 372	286, 315, 372	464, 486[b]	468, 496[b]
LF0.17-cap	424	430	465, 494[b]	473, 503[b]

[a] Concentration: 1×10^{-5} M in $CHCl_3$. [b] Wavelength of the shoulder.

Synthesis of Hyperbranched (HF0.04−HF0.17 and HF0.08-cap) and Linear Poly(fluorenevinylene)s (LF0.17-cap). The general synthetic procedures for the poly(fluorenevinylene)s are described as follows: To a two-necked 10 mL glass reactor containing the monomer (**A** or **A′**) and dry THF was added with *t*-BuOK solution (1 M in THF), and the feed molar concentration was adjusted between 0.04 and 0.17 mmol/mL. The solution was then stirred at room temperature for a predetermined time interval under a nitrogen atmosphere (Table 1). The mixture was poured into methanol before gelation, and the appearing precipitates were collected by filtration. The products were further purified by extracting with methanol using a Soxhlet apparatus to remove oligomers and other residual catalysts, followed by drying under vacuum at room temperature.

HF0.04: monomer **A** (0.170 g, 0.277 mmol), *t*-BuOK solution (2 mL), and dry THF (4 mL). Yield: 61%. IR (KBr pellet): ν 3056, 2955 (C−H stretching vibrations of aliphatic), 1670, 1592 (−C=C− stretching), 962 cm^{-1} (trans −C=C−). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.10−7.00 (m, Ar−H and −CH=), 4.75−5.00 (m, 2H, $-CH_2-$ at 4-position), 4.75−4.25 (m, 2H, $-CH_2-$ at 2- or 7-position), 1.97−1.92 (m, 4H, $-CH_2-$), 1.40−0.90 (m, 16H, $-CH_2-$), 0.75 (m, 6H, $-CH_3$). Anal. Found for **HF0.04** (%): C, 83.64; H, 9.77.

HF0.08: monomer **A** (0.153 g, 0.249 mmol), *t*-BuOK solution (1 mL), and dry THF (2 mL). Yield: 59%. IR (KBr pellet): ν 3056, 2955 (C−H stretching vibrations of aliphatic), 1670, 1592 (−C=C− stretching), 962 cm^{-1} (trans −C=C−). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.10−7.00 (m, Ar−H and −CH=), 4.75−5.00 (m, 2H, $-CH_2-$ at 4-position), 4.75−4.25 (m, 2H, $-CH_2-$ at 2- or 7-position), 1.97−1.92 (m, 4H, $-CH_2-$), 1.40−0.90 (m, 16H, $-CH_2-$), 0.75 (m, 6H, $-CH_3$). Anal. Found for **HF0.08** (%): C, 82.01; H, 9.36.

HF0.08-cap: monomer **A** (0.153 g, 0.249 mmol), *t*-BuOK solution (1 mL), and dry THF (2 mL). After polymerization for 12 h, the terminal bromomethyl groups were end-capped by reacting with excess benzyl bromide (0.469 g, 2.74 mmol) at 60 °C for 24 h. Yield: 56%. IR (KBr pellet): ν 3056, 2955 (C−H stretching vibrations of aliphatic), 1670, 1592 (−C=C− stretching), 962 cm^{-1} (trans −C=C−). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.10−7.00 (m, Ar−H and −CH=), 1.97−1.92 (m, 4H, $-CH_2-$), 1.40−0.90

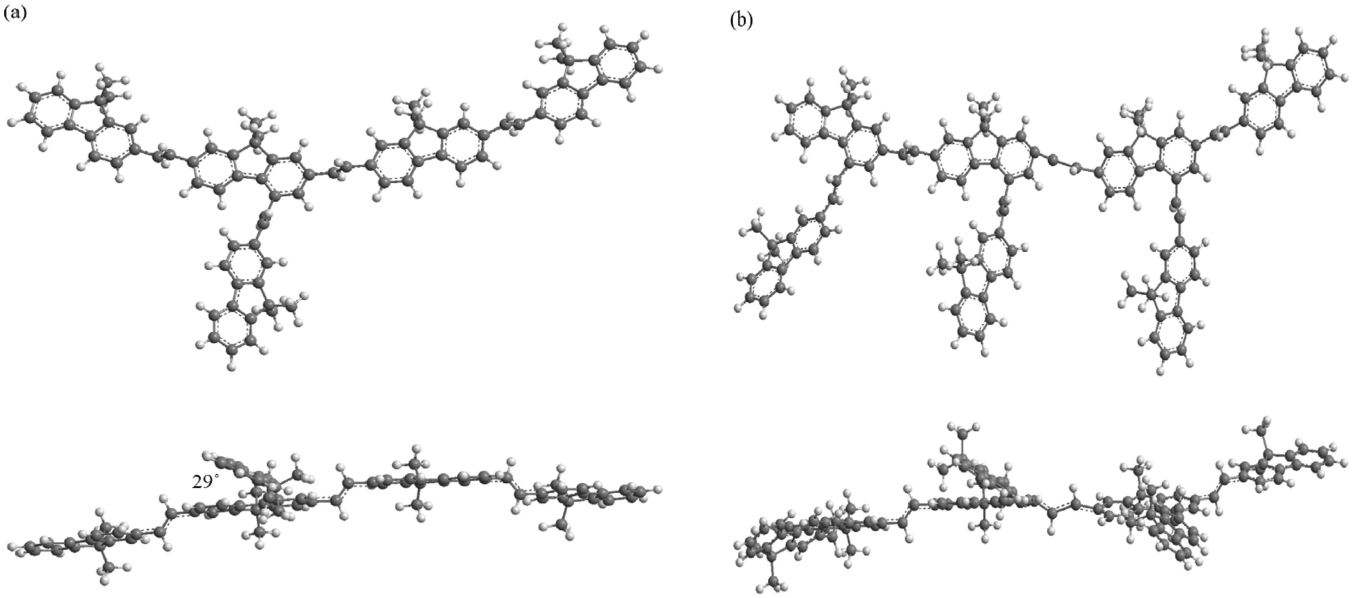


Figure 7. Optimized geometries and side view of lightly branched model (a) and highly branched model (b) obtained from semiempirical MNDO calculation.

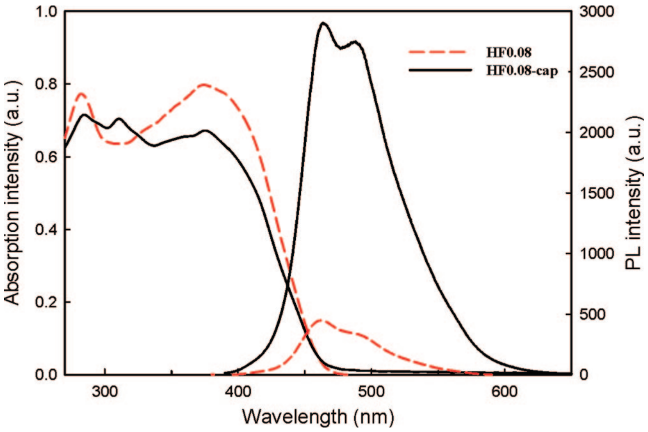


Figure 8. Absorption and photoluminescence spectra of the **HF008** and **HF0.08-cap** in $CHCl_3$ (10^{-5} M). Excitation: 380 nm.

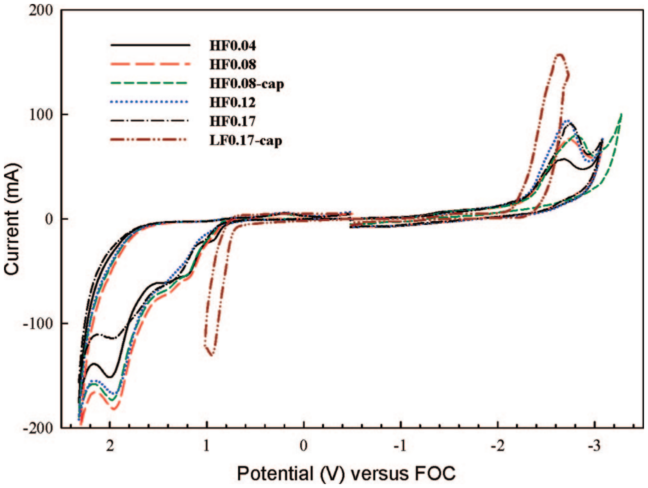


Figure 9. Cyclic voltammograms of polymer films coated on glassy carbon electrode. Scan rate: 50 mV/s.

(m, 16H, $-CH_2-$), 0.75 (m, 6H, $-CH_3$). Anal. Found for **HF0.08-cap** (%): C, 88.45; H, 9.77.

HF0.12: monomer **A** (0.312 g, 0.508 mmol), *t*-BuOK solution (1.3 mL), and dry THF (2.6 mL). Yield: 63%. IR (KBr pellet): ν 3056, 2955 (C−H stretching vibrations of aliphatic), 1670, 1592 ($-C{=}C-$ stretching), 962 cm^{-1} (trans $-C{=}C-$). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.10−7.00 (m, Ar−H and $-CH{=}$), 4.75−5.00 (m, 2H, $-CH_2-$ at 4-position), 4.75−4.25 (m, 2H, $-CH_2-$ at 2- or 7-position), 1.97−1.92 (m, 4H, $-CH_2-$), 1.40−0.90 (m, 16H, $-CH_2-$), 0.75 (m, 6H, $-CH_3$). Anal. Found (%) for **HF0.12**: C, 79.37; H, 8.95.

HF0.17: monomer **A** (0.351 g, 0.572 mmol), *t*-BuOK solution (1 mL), and dry THF (2 mL). Yield: 63%. IR (KBr pellet): ν 3056, 2955 (C−H stretching vibrations of aliphatic), 1670, 1592 ($-C{=}C-$ stretching), 962 cm^{-1} (trans $-C{=}C-$). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.10−7.00 (m, Ar−H and $-CH{=}$), 4.75−5.00 (m, 2H, $-CH_2-$ at 4-position), 4.75−4.25 (m, 2H, $-CH_2-$ at 2- or 7-position), 1.97−1.92 (m, 4H, $-CH_2-$), 1.40−0.90 (m, 16H, $-CH_2-$), 0.75 (m, 6H, $-CH_3$). Anal. Found for **HF0.17** (%): C, 79.28; H, 8.74.

LF0.17-cap: monomer **A′** (0.24 g, 0.461 mmol), *t*-BuOK solution (0.8 mL), and dry THF (1.6 mL). After polymerization for 24 h, the trace terminal bromomethyl groups were end-capped by reacting with excess benzyl bromide (0.469 g, 2.74 mmol) at 60 °C for 24 h. Yield: 62%. IR (KBr pellet): ν 3056, 2955 (C−H stretching vibrations of aliphatic), 1670, 1592 ($-C{=}C-$ stretching), 962 cm^{-1} (trans $-C{=}C-$). ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 8.10−7.00 (m, Ar−H and $-CH{=}$), 1.97−1.92 (m, 4H, $-CH_2-$), 1.40−0.90 (m, 16H, $-CH_2-$), 0.75 (m, 6H, $-CH_3$). Anal. Found for **LF0.17-cap** (%): C, 89.45; H, 9.88.

Results and Discussion

Synthesis and Characterization. In general, polymerization of a trifunctional monomer results in fast gelation due to formation of three-dimensional networks. Therefore, the degree of conversion (polymerization time) should be strictly controlled to prevent undesirable gelation. The syntheses of the monomer **A** and polymers (**HF0.04−0.17**, **LF0.17-cap**) are outlined in Scheme 1. The "polymerization time" was chosen arbitrarily as 2 h before the "gelation", which was determined by the appearance of precipitates under the same polymerization conditions. The polymers obtained under this condition (before gelation) were still soluble in common organic solvents such as $CHCl_3$ and CH_2Cl_2. However, the product precipitated from the reaction mixture was insoluble in common organic solvents due to its cross-linked structure. As shown in Table 1, the number-average (M_n) and weight-average molecular weights (M_w) of the poly(fluorenevinylene)s, determined by gel permeation chromatography using monodisperse polystyrene as cali-

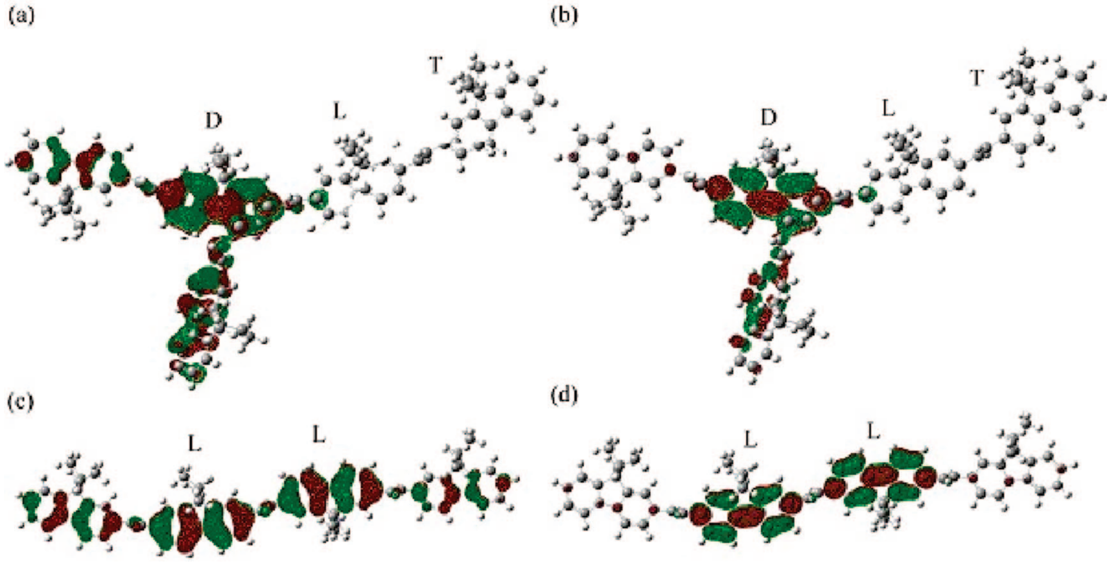


Figure 10. Optimized geometries and molecular orbital of branched model (a: HOMO; b: LUMO) and linear model (c: HOMO; d: LUMO) using semiempirical MNDO calculation.

Table 4. Electrochemical Data of the Hyperbranched and Linear Poly(fluorenevinylene)s

polymer	$E_{\mathrm{onset(ox)}}$ (V) vs FOC[a]	$E_{\mathrm{onset(red)}}$ (V) vs FOC[a]	E_{LUMO} (eV)[b]	E_{HOMO} (eV)[c]	E_g^{el} (eV)[d]	E_g^{opt} (eV)[e]
HF0.04	0.80	−2.26	−2.54	−5.60	3.06	2.69
HF0.08	0.81	−2.28	−2.52	−5.61	3.09	2.63
HF0.08-cap	0.81	−2.28	−2.52	−5.61	3.09	2.63
HF0.12	0.82	−2.28	−2.52	−5.62	3.10	2.67
HF0.17	0.84	−2.28	−2.52	−5.64	3.12	2.65
LF0.17-cap	0.73	−2.06	−2.74	−5.53	2.79	2.46

[a] $E_{\mathrm{FOC}} = 0.48$V vs Ag/AgCl. [b] $E_{\mathrm{LUMO}} = -e(E_{\mathrm{onset(red),\ FOC}} + 4.8)$ V. [c] $E_{\mathrm{HOMO}} = -e(E_{\mathrm{onset(ox),\ FOC}} + 4.8)$ V. [d] Band gaps estimated from electrochemical data ($E_g^{\mathrm{el}} = |\mathrm{LUMO} - \mathrm{HOMO}|$). [e] Band gaps estimated from onset absorption ($E_g^{\mathrm{opt}} = hc/\lambda_{\mathrm{onset}}$).

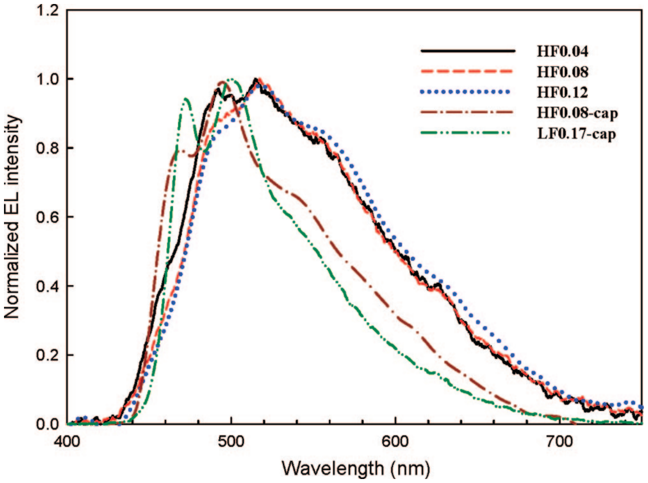


Figure 11. EL spectra of **HF004−HF0.12**, **HF0.08-cap**, and **LF0.17-cap** devices (ITO/PEDOT:PSS/polymer/Ca/Al).

Table 5. Electroluminescence Data of the EL Devices (ITO/PEDOT:PSS/Polymer/Ca/Al)

polymer	turn-on voltage (V)	$L_{\max}$[a] (cd/m^2)	LE[b] (cd/A)	bias[c] (V)	current density[c] (mA/cm^2)	CIE coordinates[c] (x, y)
HF0.04	20	184	0.09	27	203	(0.31, 0.40)
HF0.08	21	125	0.05	24	270	(0.32, 0.42)
HF0.12	19	26	0.01	25	192	(0.33, 0.43)
HF0.08-cap	17	2180	0.89	21	244	(0.24, 0.41)
LF0.17-cap	13	1452	0.47	19	312	(0.24, 0.37)

[a] $L_{\max}$: maximal luminance. [b] LE: luminance efficiency at maximal luminance. [c] The values at maximal luminance.

bration standard, are in the ranges of (2.20−3.69) × 10^4 and (4.48−6.34) × 10^4 g/mol, respectively, with polydispersity indexes (PDI) being in the range of 1.57−2.20.

In general, the determination of degree of branching requires the synthesis of model compounds which mimic exactly the units present in the hyperbranched polymer. By comparing the NMR spectra of those model compounds to that of polymers the individual units *D*, *L*, and *T* can be assigned in the hyperbranched polymer. On the basis of this assignment, mole fractions in percentage of individual units were calculated and used for the degree of branching determination. However, in our polymers the chemical shifts of protons at 4- (b: ~4.9 ppm) and 2,7-bromomethyl groups (c: ~4.6 ppm) show little overlap as shown in Figure 1, which can be conveniently applied to the estimation of contents of individual units. Therefore, in order to estimate the degree of branching (DB) from residual bromomethyl groups, the hyperbranched poly(fluorenevinylene)s (**HF0.04−HF0.17**) were not end-capped by reacting with benzyl bromide, except **HF0.08cap**. The relative peak areas of protons at a, b, and c positions in Figure 1 are attributed to the protons situated at benzene rings, 4-bromomethyl, and 2,7-bromomethyl groups, respectively. In Chart 1 among the seven possible linkages of monomer units in the hyperbranched polymers we assumed that L1 = L2 ≫ L3 and T1 = T2. On the basis of this assumption and the relative peak areas of the protons in Figure 1, the molar ratios of dendritic (D), linear (L), and terminal (T) units of the **HF0.04−HF0.17** were estimated, and their relation with feed monomer concentration is plotted as shown in Figure 2 and Table 2. The molar ratios of L units decrease gradually from 0.55 to 0.31 with an increase in monomer concentration (from 0.04 to 0.17 mmol/L), whereas those of D units show the opposite trend, suggesting that an increase in monomer concentration leads to more complete reaction of bromomethyl groups in monomer **A**. The degree of branching (DB) can be readily estimated from eq 1 and summarized in Table 2; the plot of DB vs monomer concentration is shown in Figure 3.

Interestingly, an almost linear relationship between DB and monomer concentration can be correlated. This is the first report about the interesting phenomenon in hyperbranched polyfluorenes. Therefore, the DB of a hyperbranched poly(fluorenevinylene) can be estimated from its feed concentration using the linear plot in Figure 3.

Previous literature mentioned that for an AB_2 system the DB can be expressed as[21]

$$\mathrm{DB} = \frac{2D}{2D + L} \tag{3}$$

According to eq 3, the ratio of D and L units in a hyperbranched polymer can be written as a function of DB, resulting in the equation[21]

$$\frac{D}{L} = \frac{\mathrm{DB}}{2(1 - \mathrm{DB})} \tag{4}$$

The plot of eq 4 for polymer obtained from ideal AB_2-type monomer is shown in Figure 4 as a solid curve. The data estimated from the hyperbranched **HF0.04**−**HF0.17** fit in well with the theoretical curve, indicating that the three substituted 2,4,7-tris(bromomethyl)-9,9-dihexylfluorene (**A**) can be virtually viewed as an AB_2-type monomer. The reactivity of the bromomethyl groups at the 4-position is very different from those at 2- and 7-positions.

Optical Properties. The optical characteristics of the poly(fluorenevinylene)s, both in $CHCl_3$ and as cast thin films, were investigated with a spectrophotometer and a spectrofluorometer. Their absorption and photoluminescence (PL) spectra in $CHCl_3$ and in the film state are shown in Figures 5 and 6, respectively, with the corresponding spectral maxima summarized in Table 3. The linear **LF0.17-cap** shows absorption peak at 424 nm in $CHCl_3$ and 430 nm in the film state. However, the absorption peak shifts hypsochromically to ca. 372 nm for the hyperbranched **HF0.04** and **HF0.08** and degenerates further to become as a shoulder for **HF0.12** and **HF0.17** with increased degree of branching. According to previous literature,[28] the absorption wavelength of the **HF0.04**−**HF0.17** ($\lambda_{\max} \approx 372$ nm) corresponds to linear oligo(fluorenevinylene) with about two repeat units ($\lambda_{\max} = 376$ nm). In general, hyperbranched structure leads to reduction in π-conjugation length, as compared with its linear counterpart, due to possible interruption of the conjugation at branch unit.[29] Figure 7a,b depicts the optimized geometries of lightly and highly branched structures obtained from a semiempirical MNDO calculation.[30] In Figure 7a, branching at the 4-position results in a twist angle of 29° between the two bridged fluorene units, indicating that effective conjugation length of poly(fluorenevinylene) is reduced. Accordingly, the effective conjugation length in the **HF0.04** is only about two repeat units ($\lambda_{\max} \approx 372$ nm), which is much smaller than that of linear **LF0.17-cap** ($\lambda_{\max} = 424$ nm). Moreover, as shown in Figure 7b, the high degree of branching results in more severely twisted structures in polymer backbone that further reduces the conjugation length.

As shown in Table 3, the PL peaks of the poly(fluorenevinylene)s in $CHCl_3$ are concentrated at 464−465 nm, indicating that the conjugation lengths of the emitting species are almost the same. This should be attributed to effective excitation energy transfer from the short conjugated oligo(fluorenevinylene) segments to the longer ones which are the main emitting species. In the film state the PL peaks of the **HF0.04**−**HF0.17** red-shift slightly (2−4 nm) in comparison to those in $CHCl_3$. The red shifts of the hyperbranched **HF0.04**−**HF0.17** are smaller than that of the linear **LF0.17-cap** (8 nm), indicating that the hyperbranched structure is able to suppress the aggregation. The influence of end-capping of the terminal $-CH_2Br$ groups after polymerization was evaluated by comparing the optical properties of the **HF0.08** with **HF0.08cap**. As shown in Figure 8, in $CHCl_3$ the absorption spectra of **HF0.08** and **HF0.08-cap** are similar both in feature and intensity, suggesting the resemblance in their main chain structures and conjugation lengths. But the PL spectral intensity of **HF0.08** is significantly lower than that of **HF0.08-cap**. In considering their structural difference, this is presumably due to the heavy atom effect caused by the remaining $-CH_2Br$ groups in **HF0.08**. The presence of heavy atoms, either as substituent or in the environment, greatly increases the rate of spin-forbidden processes, which is due to an increase in spin−orbit coupling. Typically, the presence of heavy atoms decreases the fluorescence efficiency.[31]

Electrochemical Properties. Cyclic voltammetry (CV) has been employed and is considered to be an effective tool in investigating the electrochemical properties of conjugated compounds. The oxidation and reduction potentials revealed in cyclic voltammograms show the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels, which correspond to ionization potentials (IP) and electron affinities (EA), respectively. The polymer films coated on a glassy carbon working electrode, supported in 0.1 M tetra-*n*-butylammonium perchlorate (Bu_4NClO_4) in anhydrous acetonitrile, were measured at a scanning rate of 50 mV/s. The cyclic voltammograms are shown in Figure 9; the corresponding electrochemical data are summarized in Table 4. The onset oxidation (p-doping) and reduction potentials (n-doping) of the linear **LF0.17-cap** are located at 0.73 and −2.06 V, respectively, whereas those of the hyperbranched **HF0.04**−**HF0.17** and **HF0.08-cap** are shifted to 0.80−0.84 V and −2.26 to −2.28 V. It is noteworthy that the hyperbranched poly(fluorenevinylene)s possess very similar onset reduction potentials, suggesting that the reduction starts from the same segments. To elucidate this possibility, optimized geometries and molecular orbital of branched and linear fluorene−vinylene segments were simulated using a semiempirical calculation. As shown in Figure 10, the LUMO of the branched model is confined exclusively to D unit, while that of linear one spreads over at least two L units. These findings are in good agreement with the electrochemical results. The estimated HOMO and LUMO energy levels of the **HF0.04**−**HF0.17** are situated at −5.60 to −5.64 eV and −2.52 to −2.54 eV, respectively, which are slightly different from those of the **LF0.17-cap** at −5.53 eV and −2.74 eV. On the basis of the HOMO and LUMO energy levels, the band gaps (E_g^{el}) of the **HF0.04**−**HF0.17** are estimated to be 3.06−3.12 eV. The optical band gaps (E_g^{opt}) of the **HF0.04**−**HF0.17** calculated from the onset absorption in thin film state are 2.63−2.69 eV, which is much smaller than those obtained from the CV measurements. This is probably due to different mechanisms involved in the two measurements. The onset absorption is mostly contributed by the inner parts of the hyperbranched globules, while the oxidation and reduction processes in the CV measurements are mainly happened on the periphery groups.

Electroluminescence Properties. Double-layer electroluminescent devices using the poly(fluorenevinylene)s as emitting materials [ITO/PEDOT:PSS/polymer/Ca(50 nm)/Al(100 nm)] were fabricated to investigate their optoelectronic characteristics. As shown in Figure 11, the EL spectra of the **LF0.17-cap** and **HF0.08-cap** are similar to their PL spectra (Figures 6 and 8), suggesting that the emitting species are the same under photo- and electroexcitation. For the **HP0.08-cap**, electroexcited energy transfers readily from the periphery groups to the inner, longer conjugated oligo(fluorenevinylene) segments under a potential bias. The EL spectra of the **HF0.04**, **HF0.08**, and **HF0.12** reveal a new peak at 516 nm with much broader emission in the longer wavelength region, which is presumably due to external heavy atom effect on the singlet−triplet transitions.[31] The EL performances of the devices are shown in Table 5. The maximal luminance (L_{max}) and maximal luminance efficiency (LE) of the **HF0.04−HF0.12** devices are 26−184 cd/m^2 and 0.01−0.09 cd/A, respectively. Clearly, the device performance decreases smoothly (L_{max}: 184 cd/m^2 → 26 cd/m^2; LE: 0.09 cd/A → 0.01 cd/A) with an increase in degree of branching (DB). This is due to aggravated heavy atom effect because the content of $-CH_2Br$ groups is greater at higher DB. In addition, the turn-on voltages are quite high (19−20 V) as compared with conventional EL devices. The poor performance of the poly(fluorenevinylene)s without end-capping are believed to be due to heavy atom effect on the singlet−triplet transitions. However, the influence of film morphology on the device performance cannot be excluded. The poor PLED performance and high turn-on voltage might partially be due to the poor film quality. The maximal luminance of the **HF0.08-cap** device was 2180 cd/m^2 at a current density of 244 mA/cm^2 (bias: 21 V), and the CIE coordinate of the emission light was (0.24, 0.41). The maximal luminance of the **LF0.17-cap** is 1452 cd/m^2 at a current density of 312 mA/cm^2, which is comparable to the EL performance of previously reported oligo(fluorenevinylene) with nine repeat units (885 cd/m^2 and 0.25 cd/A).[28] In addition, luminance efficiency of the **HF0.08-cap** (0.89 cd/A) is about 2 times that of the **LF0.17-cap** (0.47 cd/A). Evidently, the EL performance of the **HF0.08-cap** device is superior to that from the linear **LF0.17-cap** although both polymers are end-capped. In general, hyperbranched polymers exhibit higher fluorescence quantum yield than linear counterpart.[25,29] Current results suggests that hyperbranched structure and end-capping in the poly(fluorenevinylene)s leads to enhanced optoelectronic performance.

Conclusion

We have successfully prepared hyperbranched (**HF0.04−HF0.17** and **HF0.08-cap**) and linear (**LF0.17-cap**) poly(fluorenevinylene)s using the Gilch reaction from an A_3-type (**A**) and an A_2-type (**A′**) monomers, respectively. These hyperbranched polymers are soluble in common organic solvents, and their weight-average molecular weights (M_w) were (4.48−6.34) × 10^4 g/mol with polydispersity indexes (PDI) being in the range of 1.57−2.20. An almost linear relationship between degree of branching (DB) and monomer feed concentration has been correlated. Therefore, the DB of a hyperbranched poly(fluorenevinylene) can be estimated from its monomer concentration using the linear plot. The three substituted 2,4,7-tris(bromomethyl)-9,9-dihexylfluorene (**A**) has been confirmed as an AB_2-type monomer; the reactivity of the bromomethyl groups at the 4-position is very different from those at 2- and 7-positions. Two-layer PLED devices (ITO/PEDOT:PSS/**HF0.08-cap**/Ca/Al) exhibit maximal luminance and maximal luminance efficiency of 2180 cd/m^2 and 0.89 cd/A, respectively, which are superior to those from the linear **LF0.17-cap** (1452 cd/m^2, 0.47 cd/A) and other hyperbranched **HF0.04−HF0.12** without end-capping (26−184 cd/m^2, 0.01−0.09 cd/A). The lower luminance efficiency of the **HF0.04−HF0.12** devices has been attributed to the heavy atom effect.

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