CHEMISTRY OF MATERIALS
Article
pubs.acs.org/cm

Unique Photoluminescence of Diacetylene Containing Dendrimer Self-Assemblies: Application in Positive and Negative Luminescence Patterning

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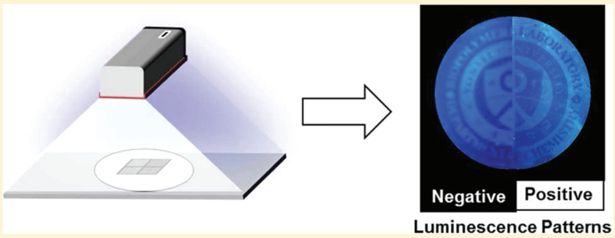
Supporting Information



ABSTRACT: A series of poly(benzyl ether) dendrimers with two benzene-1,3,5-tricarboxamide (BTA) units bridged by diacetylene were synthesized. The formation of hydrogen bonds between BTA units to form the supramolecular self-assembly was confirmed by FT-IR and AFM measurements. When the dendrimers in CH_2Cl_2 was excited with 280 nm irradiation, the dendrimers exhibited an unexpected strong photoluminescence (PL) around 450 nm in addition to 310 nm fluorescence upon excitation at 280 nm. The PL intensity of each dendrimers has shown generation dependency. With the continuous irradiation of 280 nm UV light, dendrimers exhibited decreased PL emission at both 310 and 450 nm by photopolymerization of diaceytlene units. A poly(vinylidene fluoride) (PVDF) membrane saturated with dendrimer solution were prepared to obtain a patterned PL image. Utilizing a photomask, a negative PL pattern was successfully obtained. When the membrane was annealed to 100 °C, new anomalous PL was generated and opposite type PL-patterned image could be obtained.

KEYWORDS: *supramolecular polymer, dendrimer, topochemical porlymerizatin, polydiacetylene, fluorescence pattern*

INTRODUCTION

Dendrimers are regularly branched macromolecules with well-predictable three-dimensional morphology that are used as building blocks for the construction of organized functional materials in a wide range of materials chemistry applications.[1] The solution properties of dendrimers depend primarily on their peripheral functionality, and the core structure is substantially insulated from the outer environment. Therefore, three-dimensional warping of functional systems using dendrimer frameworks has great potential to provide very interesting properties.[2] For example, three-dimensional warping of conjugated polymers by the poly(benzyl ether) dendritic framework provided high fluorescence emission by excitation energy transfer from dendritic wedges to the polymer backbone.[3] Such excitation energy transfer phenomena provide a motivation in the design of novel photofunctional materials.[4] Polydiacetylenes (PDA) are conjugated polymers with alternating ene-yne backbone structures, which can be prepared by topochemical polymerization of diacetylene monomers.[5] It is noteworthy that well-organized self-assembly of diacetylene monomers is essential for topological polymerization.[6] It is desirable to utilize sufficiently strong and directional interactions for the design of such well-ordered structure. Benzene-1,3,5-tricarboxamide (BTA) is a potential scaffold for the construction of self-assembled structures, since the three amide units can provide strong hydrogen bonding interactions.[7] Based on the above considerations, we synthesized a series of poly(benzyl ether) dendrimers with two BTA units bridged by diacetylene. Interestingly, these dendrimers exhibited unique photoluminescence (PL) from BTA units.[8] Herein, we report the topochemical polymerization of a luminescent supramolecular assembly of diacetylene-containing dendrimers for dual patterned PL imaging through two-step excitation energy transfer process from dendritic wedges to the core structure.

EXPERIMENTAL SECTION

Materials and Measurements. All commercially available reagents were reagent grade and used without further purification. Dichloromethane, n-hexane, tetrahydrofuran (THF), and ethyl acetate were freshly distilled before each use. Recycling GPC was carried out on a JAI model LC-9201 equipped with JAIGEL-2H and JAIGEL-3H column using THF as eluent. UV–vis, FT-IR, and PL emission spectra were recorded using a JASCO model V-660, JASCO model FT-IR 430 spectrometer, and JASCO model FP-6300, respectively. The solid phase fluorescence measurement was carried out using below-400 nm-cut off filter over detector. ^1H NMR spectra were recorded using a Bruker DPX 400 (400 MHz) spectrometer. Analytical GPC was carried out on a Younglin model Acme 9000 HPLC equipped with PLgel PL1110–650d column. MALDI-TOF MS measurements were performed on a Bruker model LRF20 using dithranol as a matrix. Atomic force microscopy (AFM) was performed using VEECO model Multimode, where the sample was prepared by spin-coating of a toluene solution of **1-G3** (1.0×10^{-4} M) onto freshly cleaved mica surface at 2000 rpm for 1 min.

Received: March 9, 2012
Revised: May 18, 2012
Published: May 24, 2012

Bulk Polymerization. For the bulk polymerization of dendrimers, 1.0 mg of **1-G3**, **1-G2**, and **1-G1** were placed onto clean quartz plates, and small amount of toluene was dropped to the dendrimers until the diameter of solution become about 10 mm. After the evaporation of toluene, UV-irradiation was carried out by mercury lamp for determined intervals (1, 2, 3, 5, and 10 min). After UV irradiation, the polymers were treated with various organic solvents. The only soluble portion of **1-G1** in CH_2Cl_2 was subjected to analytical GPC.

Fabrications of PL Patterns. PVDF membrane filter (Gelman Science FP-450) was put into the toluene solution of **1-G3** (0.5 mM). After the saturation of **1-G3**, the PVDF membrane was dried under dark condition. Two different types of photomask were utilized for the fabrications of PL patterns. Printed image onto polyethylene was utilized for the UV irradiation by Handy-UV lamp (ex: 254 nm, VILBER LOURMAT, VL-4LC). Heating processes were carried out as putting the membrane into an oven with temperature setting at 100 °C. For the UV irradiation in mercury lamp, thermally stable metal photomask have been utilized. PL images were captured under irradiation of 254 nm UV light by handy-UV lamp.

Quantum Yields. The quantum yield can be calculated from followed equation:

$$\Phi_f^i = \frac{F^i f_s n_i^2}{F^s f_i n_s^2} \Phi_f^s$$

where Φ_f^i and Φ_f^s are the photoluminescence QY of the sample and that of the standard, respectively. The subscript f is used because in most cases one is dealing with fluorescence. F^i and F^s are the integrated intensities (areas) of sample and standard spectra, respectively (in units of photons). f_x is the absorption factor (also known under the obsolete term "absorptance"), the fraction of the light impinging on the sample that is absorbed ($f_x = 1 - 10^{-A_x}$, where A = absorbance).[12] As a reference compound, naphthalene (7×10^{-5} M) was utilized (ex:270 nm, Φ = 0.23 in benzene).

Synthesis. **2**: Trimethyl benzene-1,3,5-tricarboxlate (3 g, 11.9 mmol) and NaOH (0.96 g, 23.9 mmol) were dissolved in MeOH (150 mL) and refluxed for 12 h. After that, the reaction mixture was evaporated and extracted with diethyl ether and water. The organic solvent was dried over anhydrous $MgSO_4$, and recrystallized with n-hexane to give **2** as a white powder (1.74 g) in 65% yield. ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 8.78 (d, 1 H; ArH), 8.76 (d, 2 H; ArH), 3.95 (s, 3 H; $-CO_2CH_3$).

3: To a mixture solution of hexa-2,4-diyne-1,6-diol (1.5 g, 13.6 mmol), PPh_3 (7.2 g, 27.2 mmol), and phthalimide (4.0 g, 27.2 mmol) in dry THF (30 mL) was slowly added diisopropylazodicarboxylate (DIAD; 14.3 mL, 1.9 M solution in toluene, 13.6 mmol), and the solution was stirred under N_2 for 3 h at 0 °C. The solution was filtered and residue was washed with THF to give **3** as a white powder (4.23 g, 84%). MALDI-TOF-MS: *m/z* calcd for $C_{22}H_{12}N_2O_4$, 391.07 $[M + Na]^+$; found, 391.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86−7.84 (m, 2 H; ArH in phthalimide), 7.75−7.71 (m, 2 H; ArH in phthalimide), 4.52 (s, 4 H; $-N-CH_2$).

4: 3 (2 g, 5.43 mmol) was dissolved in MeOH (40 mL) and hydrazine monohydrate (4 mL, excess) was added and refluxed for 1 h. The reaction mixture was filtered and filtrate was evaporated. The residue was dissolved in 1 N HCl/MeOH and recrystallized with water and THF to give **4** (133 mg) as crystalline solid in 13% yield. ^{1}H NMR (400 MHz, D_2O): δ = 3.92 (s).

5-G1: To a mixture solution of 1-bromododecane (10 g, 40.12 mmol) and 3,5-dihydroxybenzyl alcohol (2.74 g, 19.6 mmol) in dry acetone (50 mL) was added K_2CO_3 (10.8 g, 78.3 mmol), and the solution was refluxed under N_2 for 12 h. The solvent was evaporated and extracted with ethyl acetate and water. The organic layer was collected and dried over anhydrous $MgSO_4$. After silica column chromatography, **5-G1** (7.24 g) was obtained as colorless liquid in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51−7.36 (m, 3 H; ArH), 4.63 (d, 2 H; $-CH_2Ar$), 3.93 (t, 4 H; $-OCH_2$), 1.79 (m, 4 H; $-O-CH_2-CH_2$), 1.40−1.23 (m, 36 H; $-(CH_2)_9-$, 0.88 (t, 6 H; $-CH_3$).

6-G1: To mixture solution of **5-G1** (7.24 g, 15.19 mmol), PPh_3 (4.0 g, 15.19 mmol), and phthalimide (2.23 mg, 15.19 mmol) in dry THF (50 mL) was slowly added DIAD (8.0 mL, 1.9 M solution in toluene, 15.19 mmol), and the solution was stirred under N_2 for 3 h at 0 °C. The solvent was removed under reduced pressure, and residue was purified with column chromatography to give **6-G1** (7.42 g) as white solid in 80% yield. MALDI-TOF-MS: *m/z* calcd for $C_{39}H_{59}NO_4$, 606.44 $[M + H]^+$; found, 606.13. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82−7.80 (m, 2 H; ArH in phthalimide), 7.69−7.67 (m, 2 H; ArH in phthalimide), 6.54−6.33 (m, 3 H; ArH), 4.76 (s, 2 H; $N-CH_2$), 3.93 (t, 4 H; $-O-CH_2$), 1.79 (m, 4 H; $-O-CH_2-CH_2$), 1.40−1.23 (m, 36 H; $-(CH_2)_9-$), 0.88 (t, 6 H; $-CH_3$).

7-G1: To a solution of **6-G1** (2.29 g, 4.07 mmol) in THF/EtOH (20 mL, 1:1 v/v) was added hydrazine monohydrate (5 mL), and the solution was refluxed for 1 h. The solvent was evaporated and extracted with ethyl acetate and water. The organic layer was collected and dried to give **7-G1** (1.43 g) as colorless liquid in 80% yield. MALDI-TOF-MS: *m/z* calcd for $C_{31}H_{57}NO_2$, 476.44 $[M + H]^+$; found, 476.244. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.44−6.32 (m, 3 H; ArH), 3.93 (t, 4 H; $-O-CH_2$), 3.44 (s, 2 H; H_2N-CH_2), 1.76 (m, 4 H; $-O-CH_2$-CH_2), 1.40−1.23 (m, 36 H; $-(CH_2)_9-$), 0.88 (t, 6 H; $-CH_3$).

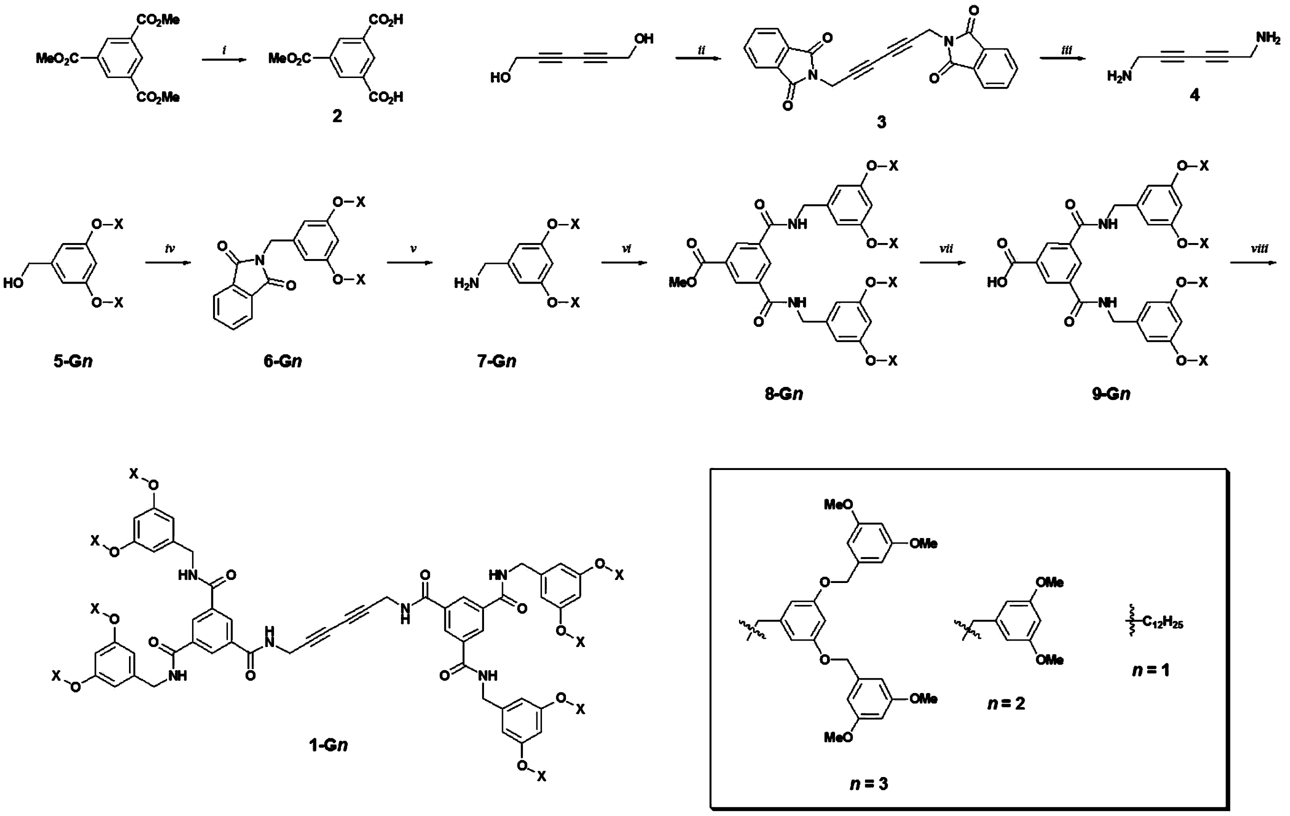
8-G1: To a mixture solution of **7-G1** (1.43 g, 3.01 mmol), **2** (268 mg, 1.20 mmol), EDC (634 mg, 3.31 mmol), and HOBt (447 mg, 3.31 mmol) in CH_2Cl_2 (30 mL) was added TEA (2 mL), and the solution was stirred for 24 h at 25 °C. The reaction mixture was poured into distilled water and extracted with ethyl acetate. The combined extracts were evaporated to dryness and purified with column chromatography. After freeze-drying, **8-G1** (1.16 g) was obtained as white powder in 85% yield. MALDI-TOF-MS: *m/z* calcd. for $C_{72}H_{118}N_2O_8$: 1161.88 $[M + Na]^+$; found: 1158.63. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 2 H; ArH), 8.42 (s, 1 H; ArH), 6.70 (t, 2 H; $-NH$), 6.44−6.34 (m, 6 H; *o*, *p*-H in ArH), 4.54 (d, 4 H; $-NH-CH_2$), 3.93 (m, 11 H; $-O-CH_2$ and $-CO_2CH_3$), 1.79 (m, 8 H; $-O-CH_2-CH_2$), 1.40−1.23 (m, 72 H; $-(CH_2)_9-$), 0.88 (t, 12 H; $-CH_3$).

9-G1: To a solution of **8-G1** (1.16 mg, 1.02 mmol) in THF (20 mL) was added 3 M NaOH solution (20 mL), and the solution refluxed for 12 h. The reaction mixture was poured into 0.2 N HCl aqueous solution (100 mL) and extracted with ethyl acetate (100 mL). The combined extracts were dried over anhydrous $MgSO_4$ and freeze-dried from benzene to give **9-G1** (1.12 g) as white powder in 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 2 H; ArH), 8.47 (s, 1 H; ArH), 6.42−6.36 (m, 6 H; *o*, *p*-H in ArH), 4.54 (d, 4 H; $-NH-CH_2$), 3.93 (t, 8 H; $-O-CH_2$), 1.79 (m, 8 H; $-O-CH_2-CH_2$), 1.40−1.23 (m, 72 H; $-(CH_2)_9-$), 0.88 (t, 12 H; $-CH_3$).

1-G1: To a mixture solution of **9-G1** (465 mg, 0.413 mmol), **4** (34 mg, 0.19 mmol), EDC (108 mg, 0.57 mmol), and HOBt (76 mg, 0.57 mmol) in CH_2Cl_2 (10 mL) was added TEA (1.5 mL), and the solution was stirred 24 h at 25 °C. The solvent was evaporated and purified with column chromatography and recycling GPC. After freeze-drying, **3** (283 mg) was obtained as white powder in 65% yield. MALDI-TOF-MS: *m/z* calcd. for $C_{148}H_{236}N_6O_{14}$: 2345.79 $[M + Na]^+$; found: 2345.546. Elemental Anal. Calcd: C, 76.50; H, 10.24; N, 3.62. Found: C, 76.48; H, 10.37; N, 3.61. ^{1}H NMR (400 MHz, DMSO-*d6*): δ = 9.17 (b, 6 H; -NH), 8.51 (s, 4 H; ArH), 8.47 (s, 2 H; ArH), 6.42−6.36 (m, 12 H; *o*, *p*-H in ArH), 4.54 (d, 8 H; $-NH-CH_2$), 3.93 (t, 16 H; $-O-CH_2$), 3.41 (s, 4 H; $\equiv C-CH_2$), 1.79 (m, 16 H; $-O-CH_2-CH_2$), 1.40−1.23 (m, 144 H; $-(CH_2)_9-$), 0.88 (t, 24 H; $-CH_3$).

6-G2: To a mixture solution of **5-G2** (2 g, 4.45 mmol), PPh_3 (1.16 g, 4.45 mmol), and phthalimide (654 mg, 4.45 mmol) in dry THF (10 mL) was slowly added DIAD (2.34 mL, 1.9 M solution in toluene, 4.45 mmol), and the solution was stirred under N_2 for 3 h at 0 °C. The reaction mixture was evaporated in reduced pressure and purified with column chromatography. After freeze-drying from benzene **6-G2** (3.38 g) was obtained as white powder in 99% yield. MALDI-TOF-MS: *m/z* calcd. for $C_{33}H_{31}NO_8$: 608.17 $[M + K]^+$; found: 608.78. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82−7.80 (m, 2 H; ArH in phthalimide), 7.69−7.67 (m, 2 H; ArH in phthalimide), 6.64−6.39 (m, 9 H; *o*, *p*-H in ArH), 4.93 (s, 4 H; $-O-CH_2$), 4.76 (s, 2 H; $-N-CH_2$), 3.76 (s, 12 H; -OCH_3).

Scheme 1. Synthesis of Diacetylene-Containing Dendrimers[a]



[a]Reagents and conditions: (i) NaOH, MeOH, reflux, 12 h; (ii) PPh_3, phthalimide, DIAD, THF, 0 °C, 3 h; (iii) $H_2NNH_2 \cdot H_2O$, MeOH, reflux, 1 h; (iv) PPh_3, phthalimide, DIAD, THF, 0 °C, 3 h; (v) $H_2NNH_2 \cdot H_2O$, THF/EtOH (1/1), reflux, 1 h; (vi) **2**, EDC, HOBt, TEA, CH_2Cl_2, 25 °C, 24 h; (vii) THF, NaOHaq, reflux, 12 h; (viii) **4**, EDC, HOBt, TEA, CH_2Cl_2, 25 °C, 12 h.

7-G2: To a solution of **6-G2** (2 g, 3.509 mmol) in THF/EtOH (30 mL, 1:1 v/v) was added hydrazine monohydrate (7 mL), and the solution was refluxed for 1 h. The solvent was evaporated and extracted with ethyl acetate and water. The organic layer was freeze-dried from benzene to give **7-G2** (1.042 g) as white powder in 68% yield. MALDI-TOF-MS: *m*/*z* calcd. for $C_{25}H_{29}NO_6$: 440.20 $[M + H]^+$; found: 439.902. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.58-6.40$ (m, 9 H; *o*, *p*-H in ArH), 4.97 (s, 4 H; $-O-CH_2$), 3.78 (s, 14 H; $-OCH_3$, NH_2-CH_2).

8-G2: To a mixture solution of **7-G2** (1.04 g, 2.366 mmol), **2** (259 mg, 1.154 mmol), EDC (487 mg, 2.54 mmol), and HOBt (343 mg, 2.54 mmol) in CH_2Cl_2 (10 mL) was added TEA (2 mL), and the solution as stirred for 24 h at 25 °C. The reaction mixture was poured into distilled water and extracted with ethyl acetate. The combined extracts were evaporated to dryness and purified with column chromatography. After freeze-drying, **8-G2** (724 mg) was obtained as white powder in 59% yield. MALDI-TOF-MS: *m*/*z* calcd. for $C_{60}H_{62}N_2O_{16}$: 1067.42 $[M + H]^+$; found: 1067.09. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.54$ (s, 2 H; ArH), 8.42 (s, 1 H; ArH), 6.62−6.19 (m, 18 H; *o*, *p*-H in ArH), 4.93 (s, 8 H; $-O-CH_2$), 4.57 (d, 4 H; $-N-CH_2$), 3.90 (s, 3 H; $-CO_2CH_3$), 3.78 (s, 24 H; $-OCH_3$).

9-G2: To a solution of **8-G2** (724 mg, 0.68 mmol) in THF (7 mL) was added 5 M NaOH aqueous solution (2 mL) and MeOH (5 mL), and the mixture was stirred for 12 h at 25 °C. The reaction mixture was poured into 0.2 N HCl aqueous solution (100 mL) and extracted with ethyl acetate (100 mL). The combined extracts were dried over anhydrous $MgSO_4$ and freeze-dried from benzene to give **9-G2** (548 mg) as white powder in 77% yield. MALDI-TOF-MS: *m*/*z* calcd for $C_{59}H_{60}N_2O_{16}$: 1075.38 $[M + Na]^+$; found: 1076.029. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.51$ (s, 2 H; ArH), 8.47 (s, 1 H; ArH), 6.61−6.36 (m, 18 H; *o*, *p*-H in ArH), 4.90 (s, 24 H; $-O-CH_2$), 4.52 (s, 4 H; $-N-CH_2$), 3.74 (s, 24 H; $-OCH_3$).

1-G2: To a mixture solution of **9-G2** (300 mg, 0.29 mmol), **4** (25.2 mg, 0.14 mmol), EDC (59 mg, 0.31 mmol), and HOBt (41 mg, 0.31 mmol) in CH_2Cl_2 (10 mL) was added TEA (1.5 mL), and the solution was stirred 24 h at 25 °C. The solvent was evaporated and purified with column chromatography and recycling GPC. After freeze-drying, **1-G2** (297 mg) was abtained as white powder in 47% yield. MALDI-TOF-MS: *m*/*z* calcd. for $C_{124}H_{124}N_6O_{30}$: 2200.83 $[M + Na]^+$; found: 2200.39. Elemental Anal. Calcd: C, 68.37; H, 5.74; N, 3.86, found: C, 68.39; H, 5.66; N, 3.74. ^1H NMR (400 MHz, DMSO-*d6*): $\delta = 9.17$ (b, 6 H; -NH), 8.51 (s, 2 H; ArH), 8.45 (s, 4 H; ArH), 6.73−6.39 (m, 36 H; *o*, *p*-H in ArH), 4.94 (s, 24 H; $-O-CH_2$), 4.40 (d, 8 H; $-N-CH_2$), 3.41 (s, 4 H; $\equiv C-CH_2$) 3.74 (s, 48 H; $-OCH_3$).

6-G3: To a mixture solution of **5-G3** (3 g, 3.04 mmol), PPh_3 (798 mg, 3.04 mmol), and phthalimide (448 mg, 3.04 mmol) in dry THF (15 mL) was slowly added DIAD (1.6 mL, 1.9 M solution in toluene, 3.04 mmol), and the solution was stirred under N_2 for 3 h at 0 °C. The reaction mixture was poured into distilled water and extracted with CH_2Cl_2. The organic layer was evaporated under reduced pressure, and the residue was purified with column chromatography to give **6-G3** (3.38 g) in 99% yield. MALDI-TOF-MS: *m*/*z* calcd for $C_{65}H_{63}NO_{16}$, 1136.40 $[M + Na]^+$; found, 1138.19. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.82-7.80$ (m, 2 H; ArH in phthalimide), 7.69−7.67 (m, 2 H; ArH in phthalimide), 6.64−6.39 (m, 21 H; *o*, *p*-H in ArH), 4.93 (s, 12 H; $-O-CH_2$), 4.76 (s, 2 H; $-N-CH_2$), 3.76 (s, 24 H; $-OCH_3$).

7-G3: To a solution of **6-G3** (1.5 g, 1.347 mmol) in THF/EtOH (20 mL, 1:1 v/v), hydrazine monohydrate (7 mL) was added and refluxed for 1 h. The solvent was evaporated and extracted with ethyl acetate and water. The organic layer was freeze-dried from benzene to give **7-G3** (846 mg) as white powder in 64% yield. MALDI-TOF-MS: *m*/*z* calcd for $C_{57}H_{61}NO_{14}$, 984.41 $[M + H]^+$; found, 984.739. ^1H

NMR (400 MHz, $CDCl_3$): δ = 6.67−6.40 (m, 21 H; *o*, *p*-H in ArH), 4.97 (s, 12 H; $-O-CH_2$), 3.78 (s, 26 H; $-OCH_3$, NH_2-CH_2).

8-G3: To a mixture solution of **7-G3** (845 mg, 0.86 mmol), **2** (94 mg, 0.42 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC; 177 mg, 0.92 mmol), and 1-hydroxy benzotriazole (HOBt; 125 mg, 0 92 mmol) in CH_2Cl_2 (7 mL) was added triethylamine (TEA; 2 mL), and the solution was stirred for 24 h at 25 °C. The reaction mixture was poured into distilled water and extracted with ethyl acetate. The combined extracts were dried over anhydrous $MgSO_4$ and purified with column chromatography. After freeze-drying form benzene, **8-G3** (666 mg) was obtained as white powder in 74% yield. MALDI-TOF-MS: *m*/*z* calcd for $C_{124}H_{126}N_2O_{32}$, 2178.82 $[M + Na]^+$; found, 2280.34. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 2 H; ArH), 8.42 (s, 1 H; ArH), 6.62−6.37 (m, 42 H; *o*, *p*-H in ArH), 4.93 (s, 24 H; $-O-CH_2$), 4.52 (d, 4 H; $-N-CH_2$), 3.90 (s, 3 H; $-CO_2CH_3$), 3.78 (s, 48 H; $-OCH_3$).

9-G3: To a solution of **8-G3** (666 mg, 0.31 mmol) in THF (7 mL) were added 5 M NaOH aqueous solution (2 mL) and MeOH (5 mL), and the solution was stirred for 12 h at 25 °C. The reaction mixture was poured into 0.2 M HCl aqueous solution (100 mL) and extracted with ethyl acetate (100 mL). The combined extracts were dried over anhydrous $MgSO_4$ and freeze-dried from benzene to give **9-G3** (630 mg) as white powder in 95% yield. MALDI-TOF-MS: *m*/*z* calcd for $C_{123}H_{124}N_2O_{32}$, 2164.81 $[M + Na]^+$; found, 2165.620. ^1H NMR (250 MHz, $CDCl_3$): δ = 8.51 (s, 2 H; ArH), 8.47 (s, 1 H; ArH), 6.61−6.36 (m, 42 H; *o*, *p*-H in ArH), 4.90 (s, 24 H; $-O-CH_2$), 4.52 (s, 4 H; $-N-CH_2$), 3.74 (s, 48 H; $-OCH_3$).

1-G3: To a mixture solution of **9-G3** (300 mg, 0.14 mmol), **4** (12.4 mg, 0.068 mmol), EDC (29 mg, 0.15 mmol), and HOBt (20 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was added TEA (1.5 mL), and the solution was stirred 24 h at 25 °C. The reaction mixture was evaporated and purified with column chromatography and recycling GPC. After freeze-drying form benzene, **1-G3** (72 mg) was obtained as white powder in 24% yield. MALDI-TOF-MS: *m*/*z* calcd for $C_{252}H_{252}N_6O_{62}$, 4395.65 $[M + K]^+$; found, 4395.533. Elemental Anal. Calcd: C, 69.47; H, 5.83; N, 1.93. Found: C, 69.49; H, 5.78; N, 1.81. ^1H NMR (400 MHz, DMSO-*d6*): δ = 9.17 (b, 6 H; $-NH$), 8.51 (s, 2 H; ArH), 8.45 (s, 4 H; ArH), 6.73−6.39 (m, 84 H; *o*, *p*-H in ArH), 4.94 (s, 48 H; $-OCH_2$), 4.40 (d, 8 H; $-N-CH_2$), 3.41 (s, 4 H; $\equiv C-CH_2$) 3.74 (s, 96 H; $--OCH_3$).

■ RESULTS AND DISCUSSION

A series of poly(benzyl ether) dendrimers (**1-G*n*,** *n* = *n*th generation; Scheme 1), with two BTA units bridged by diacetylene, were synthesized and characterized by ^1H NMR and MALDI-TOF-MS analysis. All of the dendrimers were highly soluble in various organic solvents such as $CHCl_3$, CH_2Cl_2, DMSO, and toluene. Although the dendrimers were highly soluble in $CDCl_3$, the ^1H NMR spectra displayed slightly complex peak patterns, which simplified to sharp peaks after the addition of a drop of CF_3CO_2H (see Figure S1 in the Supporting Infomraiton). These results suggest the formation of a molecular assembly via hydrogen bonding and that CF_3CO_2H promotes dissociation of the self-assembled dendrimer structures.[7a]

The formation of hydrogen bondings was confirmed by FT-IR analysis. FT-IR spectra in solid state displayed relatively broad absorption bands at 3320 cm^{-1} and sharp bands at 1653 and 1530 cm^{-1}, characteristic stretching vibrations for the N−H, and amide I and II, respectively (see Figure S3 in the Supporting Information). Although the FT-IR absorption bands deviated slightly from the typical C_3 symmetric helical arrangement of BTA, the values were in good agreement with previously reported values of an octyl substituted BTA, which indicate the formation of hydrogen bonds between BTA units to form the supramolecular self-assembly even in solution state.[9] In fact, a toluene solution of **1-G3** (1.0×10^{-4} M) spin-coated on a mica substrate was observed by AFM to have a fibrous network structure of regular thickness (ca. 2 nm) (Figure 1).

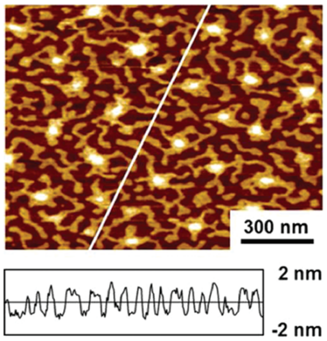


Figure 1. AFM image of **1-G3** on mica (1.0×10^{-4} M).

However, in addition to 310 nm emission, an unexpected strong PL was observed around 450 nm (Figure 2b) upon excitation at 280 nm. Interestingly, this blue PL gradually decreased by successive addition of MeOH (Figure 3). Similarly, the blue PL was almost completely absent in DMSO. In sharp contrast, the anomalous PL around 450 nm became much stronger after the addition of a nonpolar solvent, *n*-hexane (Figure 3). Because hydrogen bonding interactions become more stable under nonpolar conditions, BTA core units readily self- assemble into hydrogen-bonded aggregate by the addition of *n*-hexane. Therefore, the anomalous PL can possibly be explained by aggregation-induced enhanced emission (AIEE).[10]

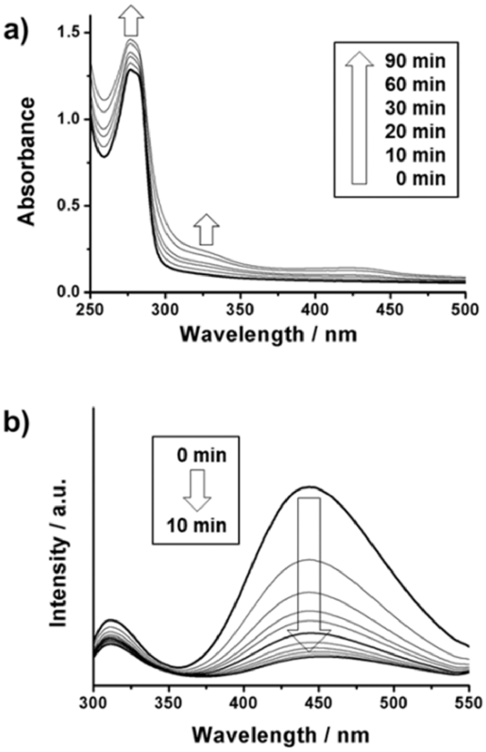


Figure 2. UV−vis absorption and PL emission of **1-G3** (0.125 mM, 1 mm path length) in CH_2Cl_2. (a) UV−vis absorption and (b) PL emission changes of **1-G3** upon 280 nm UV irradiation.

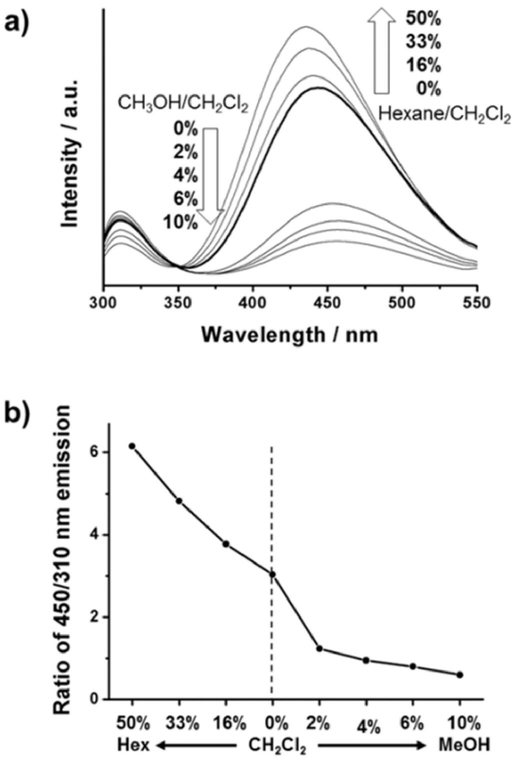


Figure 3. PL changes of **1-G3** in CH_2Cl_2 by addition of *n*-hexane and methanol. (a) PL emission spectra and (b) relative PL intensity between 450 and 310 nm.

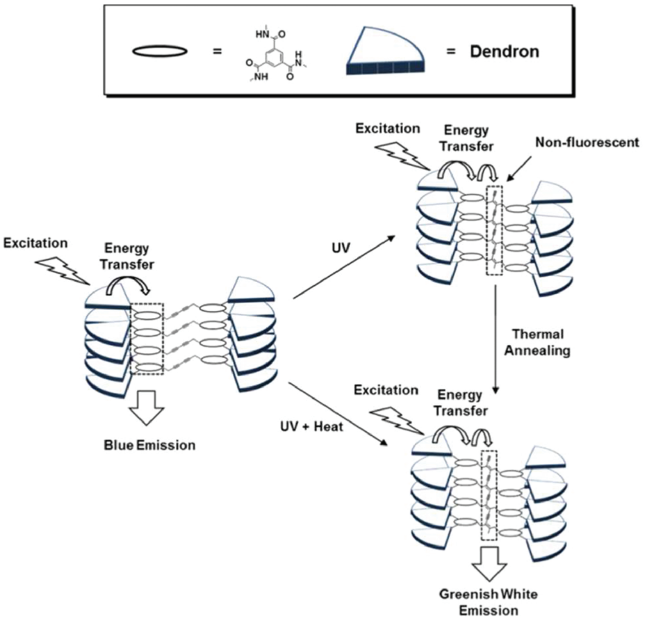
In relation with this fact, PL emission of structural fragments also has been measured. Dendrons without BTA core unit (**5-G3** and **5-G2**) exhibited PL emission only at 310 nm, but **8-G3** and **8-G2** having amide units emitted the anomalous PL around 450 nm (see Figure S4 in the Supporting Information), indicating the anomalous PL is emitted from amide bearing benzene moiety in core.

The PL intensity of each dendrimers has shown generation dependency. Large dendrimer emitted stronger PL than smaller ones at same concentration. In relation with this, quantum yield of each dendrimer was measured (see Figure S5 in the Supporting Information).[12] As a result, **1-G3** exhibited the highest quantum yield. Because the PL emission of dendrimers predominantly takes place from BTA units, the highest quantum yield can be explained by excitation energy transfer from benzene moieties to core BTA units. A large number of benzene moieties in dendritic wedges might efficiently absorb light energy so-called "antenna effect"[11] and transfer the excitation energy to the BTA core units. In addition to the generation dependency, the PL emission was gradually increased by the concentration increment of dendrimers, reinforcing the AIEE phenomena of dendrimers.

Another interesting aspect of the dendrimers occurred with the continuous irradiation of 280 nm UV light. Under these conditions, dendrimers exhibited slightly increased absorption in $\lambda < 450$ nm (Figure 2a), which can be explained by photopolymerization of diacetylene units. Through the photopolymerization reaction, dendronized-polymers with PDA backbone can be obtained. Because the PDA backbone in polymers has elongated π-conjugation length, absorption in long wavelength region can be increased. The photopolymerization of dendrimers was also evidenced by ^{1}H NMR experiments. The ^{1}H NMR spectrum of **1-G3** in $CDCl_3$ (0.2 mM) displayed peak broadening after being subjected to continuous UV irradiation, indicating that polymerization of diacetylene units led to a restriction of conformation change for **1-G3**. In sharp contrast, the ^{1}H NMR spectrum of **1-G3** after the addition of a drop of CF_3CO_2H did not change during photoirradiation since the dendrimers did not have preorganized structure in the presence of CF_3CO_2H (see Figure S1 in the Supporting Information). As aforementioned, well-organized-structure is essential for topological polymerization of diacetylene monomers.[6] The supramolecular assembly formation of BTA units would provide an optimum geometry for topochemical polymerization of diacetylene units even under very dilute conditions.

In general, the pristine PDAs obtained by photopolymerization are nonfluorescent, but they often become fluorescent by the exposure to external stimulus, such as heat, pH change, and mechanical forces. Because our dendrimers exhibited unique PL emission, the PL emission change of **1-G3** was monitored upon continuous irradiation of 280 nm UV light. As a result, the PL emissions of **1-G3** at both 310 and 450 nm were gradually decreased by the photopolymerization (Figure 2b). The decrease of PL emission can be explained by an additional excitation energy transfer process. The elongation of π-conjugation length by photopolymerization lowers the HOMO−LUMO energy level of the PDA backbone, and additional excitation energy transfer pathway can be generated from dendritic wedges or self-assembled BTA units to the PDA backbone (Scheme 2).[13] Like other PDAs, the PDA backbone of polymerized **1-G3** would be nonfluorescent. Therefore, the additional energy transfer would eventually decrease the intensity of PL emission. Photopolymerization of dendrimers in cast film was also performed. For the photopolymerization of each dendrimer, a toluene solution was drop cast onto a quartz plate, and the PL changes were observed using a fluorescence spectrophotometer under continuous irradiation with 280 nm UV light. All of the solid films exhibited strong PL around 450 nm, which had a generation dependency with the highest generation dendrimer **1-G3** exhibiting the strongest PL

Scheme 2. Proposed Mechanism of PL Changes



emission (Figure 4). The PL intensity around 450 nm gradually decreased over time. To determine the degree of polymerization, we treated the polymerized film with various organic solvents, such as CH_2Cl_2, $CHCl_3$, ethyl acetate, THF, acetone, DMSO, and toluene. However, within 1 min of UV irradiation by mercury lamp, dendrimers **1-G3** and **1-G2** resulted in insoluble films with all of the tested solvents. Only **1-G1**, which had the smallest dendritic wedges and long alkyl chains, was partially soluble in CH_2Cl_2 after photopolymerization. The solution thus obtained was subjected to size exclusion chromatography to yield a new peak in the high molecular weight region in addition to the monomeric peak. The proportion of high molecular weight polymer gradually increased with UV exposure time. After 10 min of UV irradiation, more than 50% of monomeric **1-G1** was consumed to form polymer (Figure 5). It is noteworthy that **1-G1** also resulted in a partial insoluble mass, indicating the ratio of high molecular weight to monomeric compound was actually much greater than 50%.

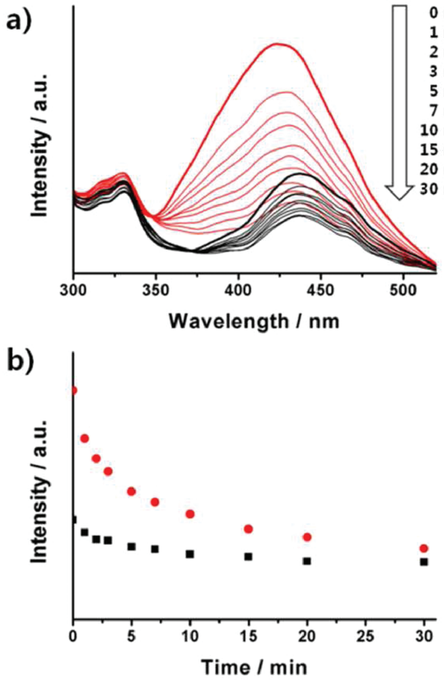


Figure 4. (a) PL changes of **1-G3** (red) and **1-G2** (black) in cast film upon 280 nm UV irradiation. (b) The maximum intensity of each spectrum.

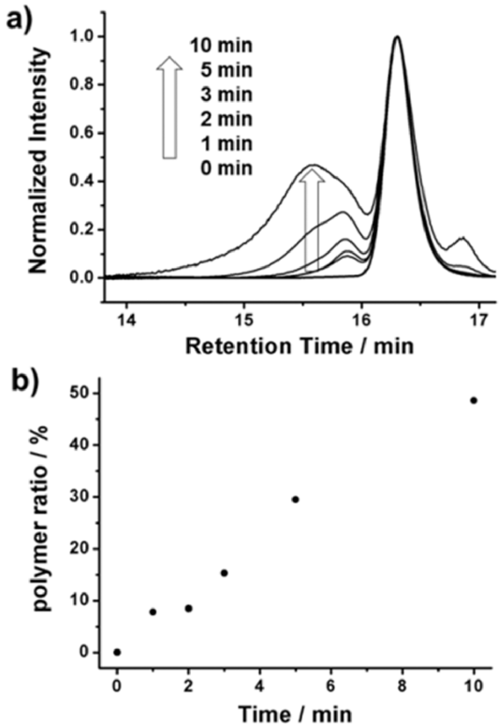


Figure 5. Photopolymerization of **1-G1** in cast film. (a) UV exposure time-dependent size exclusion chromatogram and (b) ratio of polymeric substances.

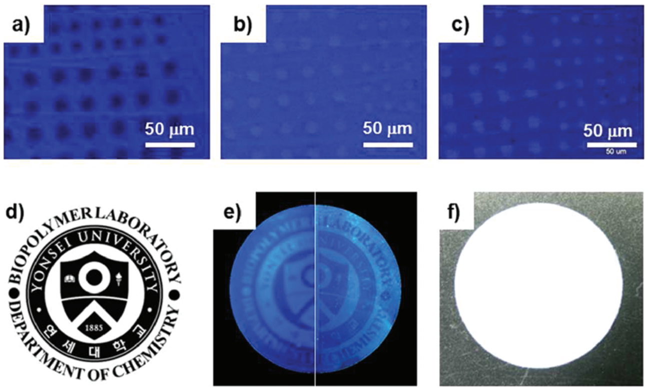


Figure 6. PL patterned images and PL changes of **1-G3**/PVDF. (a) Negative PL pattern obtained by 254 nm UV irradiation using metal photomask, (b) PL pattern obtained by UV irradiation for 3 min using a mercury lamp, (c) positive PL pattern obtained by 254 nm UV irradiation to a, (d) Image of photomask, (e) negative (left half) and positive (right half) PL pattern, (f) Bright field image of **1-G3**/PVDF film after photoirradiation.

Because the PL emission gradually decreased with photoirradiation, the resulting dendrimers could be utilized for patterned PL imaging, an emerging technology in the areas of display, memory, sensors, and molecular switches.[14] In order to obtain a patterned PL image, a poly(vinylidene fluoride) (PVDF) membrane was immersed into a 0.5 mM solution of **1-G3** in toluene, followed by drying. The resulting **1-G3**-doped PVDF membrane (**1-G3**/PVDF) exhibited strong blue PL upon UV irradiation that gradually dissipated over time. Utilizing a photomask, a negative PL pattern was successfully obtained after 10 min of light irradiation at 254 nm with a UV handy lamp. As shown in Figure 6a and left half of e, the masked areas continued to emit a strong blue PL, but the UV-exposed areas have dark contrast. On the other hand, when the **1-G3**/PVDF membrane was exposed to a mercury lamp for 3 min, the UV-exposed areas exhibited positive contrast with a bright greenish white PL emission (Figure 6b). Because PDA is one of the representative polymers with stress-induced colorimetric and fluorescence transitions,[5] we hypothesized that thermal energy emitted from a mercury lamp could influence on the PL emission. Therefore, we investigated the influence of thermal annealing on the negative PL pattern obtained from UV handy lamp irradiation. Interestingly, after the PL patterned **1-G3**/PVDF membrane was annealed to 100 °C, the dark contrast areas again emitted a bright greenish white PL, indicating that **1-G3**/PVDF could provide dual patterned PL imaging. When the thermally annealed **1-G3**/

PVDF or the PL pattern obtained from mercury lamp irradiation (Figure 6b) were exposed to 254 nm UV light, the original PL disappeared and a perfect positive PL pattern resulted (Figure 6c and right half of e).

For precise observation of PL changes, the **1-G3**/PVDF membrane was placed on a fluorescence spectrophotometer, and PL emission around 450 nm was monitored upon continuous irradiation with 280 nm UV light. As a result, the PL emission around 450 nm was found to greatly decrease within 5 min (Figure 7a). When this **1-G3**/PVDF membrane material was then annealed at 100 °C for 5 min, PL was recovered with a slightly red-shifted emission (Figure 7b). The increase in PL emission occurred over the entire visible range. This observation indicates that the thermal energy reorganizes the core PDA backbone from a nonfluorescent state to a fluorescent state.[5]

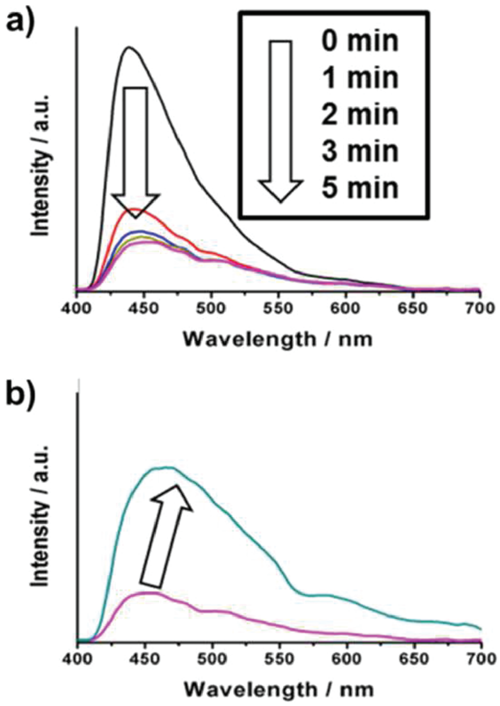


Figure 7. PL emission changes of **1-G3**/PVDF upon (a) continuous 280 nm UV irradiation and (b) successive thermal annealing.

The plausible mechanism of PL emission changes can be proposed as following (Scheme 2). (i) The self-assembled BTA core emits blue PL because a large number of benzene moieties in dendritic wedges absorb UV light and transfer their excitation energy to self-assembled BTA core. (ii) By the photopolymerization of diacetylene units, the excitation energy of BTA core again transfers to PDA backbone. In this stage, PDA backbone is nonfluorescent state. (iii) Nonfluorescent PDA backbone reorganized to fluorescent state by thermal annealing. The dendrimers emit strong greenish white PL through two-step energy transfer.

Generally, the polymerization of diacetylene monomers results in a new absorption band around 640 nm.[5] However, unlike typical diacetylene monomers, absorption changes of the dendrimers only occurred in invisible UV ranges (Figure 1a), whereas PL emission greatly changed, because the emission of dendrimers relies on the energy transfer mechanism. Hence, the **1-G3**/PVDF membrane maintained its original white color even after photopolymerization (Figure 6f). Because the two BTA units in dendrimer are possible to provide a preorganized structure for the diacetylene units, a much more dilute concentration can be utilized for diacetylene polymerization. In addition, because photopolymerization involves excitation energy transfer mechanism, light absorption predominantly occurs at the large number of benzene moieties in the dendritic wedges. This characteristic may be useful for unique applications such as security ink, which needs to be composed of invisible substances.[15] In addition, the patterned images would be impossible to photocopy and would be readable only under specific conditions. These new dendrimers satisfy all of the above criteria and may also provide dual patterned images, i.e., positive and negative PL patterning.

■ CONCLUSIONS

In summary, poly(benzyl ether) dendrimers with two BTA moieties bridged with diacetylene were designed to obtain π-conjugated polymeric materials through topochemical polymerization. The dendrimers emitted strong anomalous PL around 450 nm by energy transfer from the dendritic wedges to the self-assembled BTA units. Excitation energy transfer from the dendritic wedges induced photopolymerization of the diacetylene units. Polymerization of the diacetylene units resulted in a new energy transfer pathway with greatly decreased blue PL emission. Furthermore, the PDA backbone again emitted greenish white PL when it was thermally annealed. Using the unique optical properties of this material, we successfully generated dual-patterned PL images.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral date and quantum yields of each dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (2011-0001126). J.-H.K. and Y.-H.J. acknowledge fellowships from the BK21 program from the Ministry of Education, Science and Technology, Korea.

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