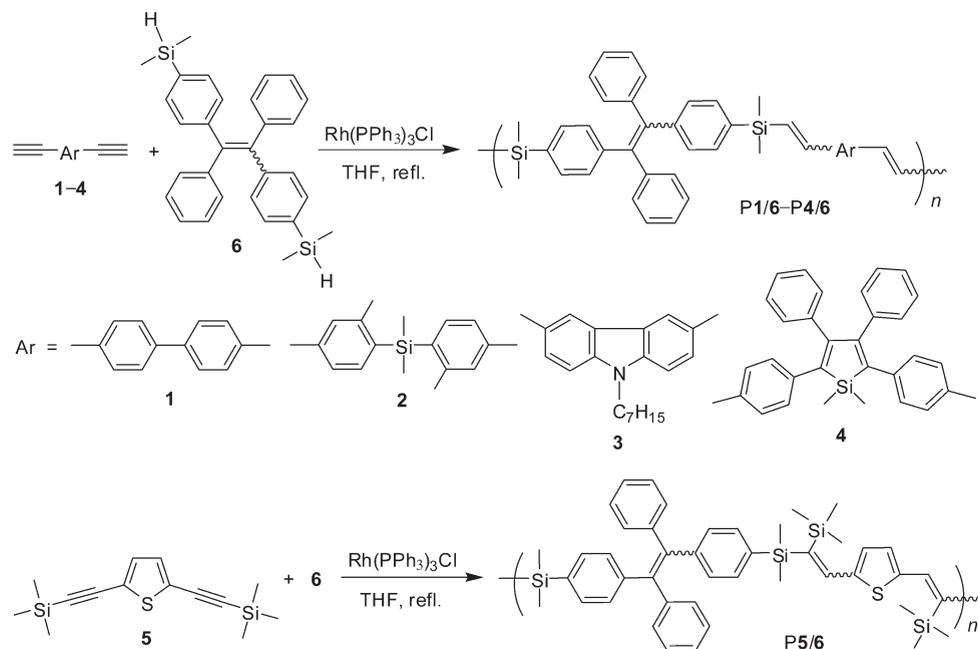


Scheme 1



Using Wilkinson's catalyst $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, Luh and co-workers had recently prepared some poly(silylenevinylene)s by hydrosilylations of diynes and disilanes.⁸ While the intrastrand chromophoric interactions in the polymers had been investigated, little efforts had been placed on the exploration of their practical applications. All the diynes used possessed terminal triple bonds at both ends. In contrast, those with internal acetylene functionalities were virtually not utilized as monomers for the polymerization.

Our group had been working on the development of conjugated polymers using acetylenes as building blocks. Employing monoynes, diynes, and triynes as monomers, we had successfully synthesized a large variety of polyacetylenes, polyarylenes, polydiynes, and polytriazoles with linear and hyperbranched architectures by metathesis, cyclotrimerization, coupling, and click polymerizations.⁹ Recently, we had developed a thiol-click polymerization technique for the synthesis of heteroatom-containing acetylenic polymers.¹⁰ The alkyne polyhydrothiolations of dithiols and bipropiolates proceeded smoothly in the presence of diphenylamine or rhodium complexes, producing sulfur-rich polymers with high molecular weights in high yields. Encouraged by such success, in this study, we widened the applicability of alkyne hydrosilylation to the construction of functional poly(silylenevinylene)s. We utilized tetraphenylethene (TPE)-containing disilane and terminal and internal diynes as monomers and succeeded in polymerizing them into high molecular weight polymers in satisfactory yields (Scheme 1). All the poly(silylenevinylene)s were soluble and film-forming. Thanks to the TPE unit, which exhibited a phenomenon of aggregation-induced emission,¹¹ all the polymers emitted intensely in the solid state though their solutions were only weakly emissive. Such effect had endowed the polymer nanoaggregates with a superamplification effect in the explosive detection process. UV irradiation of the thin films of the poly(silylenevinylene)s through copper masks photo-oxidized the exposed regions, generating fluorescent patterns. The polymers showed high

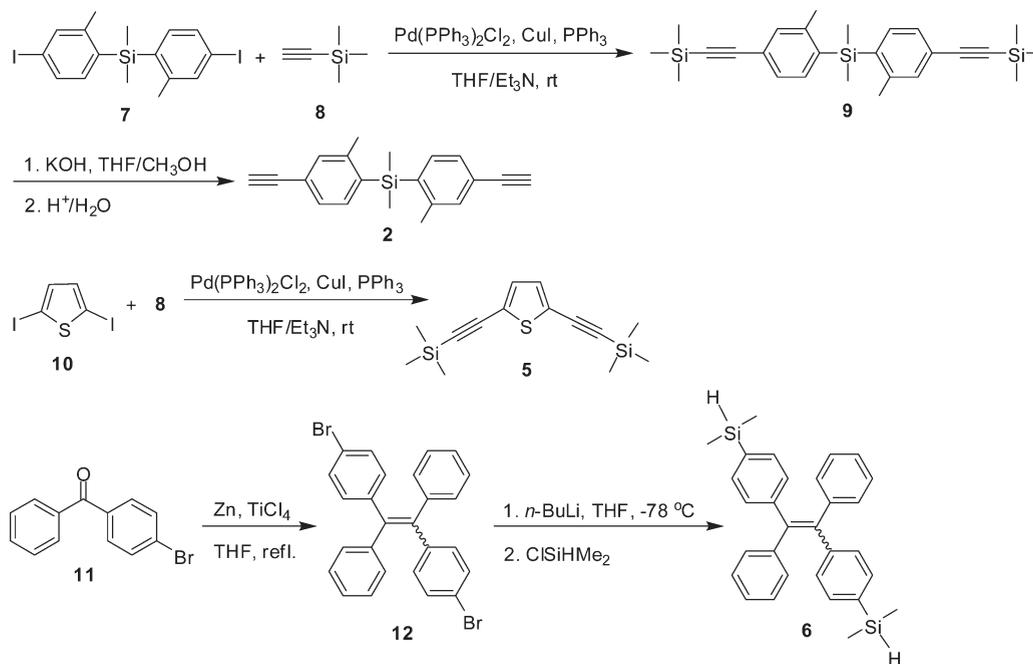
refractive indices in the wavelength region of 400–1700 nm, which could be tuned to a great extent by simple UV irradiation.

EXPERIMENTAL SECTION

Materials and Instrumentation. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use. Triethylamine was distilled and dried over potassium hydroxide. Other solvents of high purities were used without further purification. Bis(4-iodo-2-methylphenyl)dimethylsilane (7), trimethylsilylacetylene (8), 2,5-diiodothiophene (10), 4-bromobenzophenone (11), zinc dust, titanium(IV) chloride, chlorodimethylsilane, copper(I) iodide, triphenylphosphine, and dichlorobis(triphenylphosphine)palladium(II) were purchased from Aldrich and used as received. Chlorotris(triphenylphosphine)rhodium(I) was synthesized following the literature method.¹² Diyne monomers, named 4,4'-diethynylbiphenyl (1),¹³ 3,6-diethynyl-9-heptylcarbazole (3),¹⁴ and 1,1-dimethyl-2,5-bis(4-ethynylphenyl)-3,4-diphenylsilo (4),¹⁵ were synthesized according to our previous published procedures.

IR spectra were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. ¹H and ¹³C NMR spectra were measured on a Bruker ARX 300 spectrometer using chloroform-*d* as solvent and tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. Mass spectra (MS) were recorded on a GCT Premier CAB048 mass spectrometer operating in a TOF mode. UV-vis absorption spectra were measured on a Varian CARY 100 Bio spectrophotometer. Thermogravimetric analysis (TGA) of the polymers was evaluated on a TA TGA Q5000 instrument under nitrogen at a heating rate of 20 °C/min. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer. The PL quantum yields (Φ_F 's) were estimated using quinine sulfate ($\Phi_F = 54\%$ in 0.1 M sulfuric acid) as reference in THF. Weight- (M_w) and number-average (M_n) molecular weights and polydispersity indices (M_w/M_n) of the polymers were estimated by a Waters Associates gel permeation chromatography (GPC) system equipped with refractive index and UV detectors. THF was used as eluent at a flow rate of 1.0 mL/min. A set of monodisperse polystyrene standards covering molecular weight range of 10^3 – 10^7 was used for the molecular weight calibration.

Scheme 2



Refractive indices (RI's) of the polymers were measured on a J.A. Woollam variable angle ellipometry system with a wavelength tunability from 300 to 1700 nm. To fit the acquired Ψ and Δ curves with the data obtained from the three-layer optical model consisting of crystalline silicon substrate, 2 nm SiO_2 layer, and a uniform polymer film, the Levenberg–Marquardt regression algorithm was employed. The Cauchy dispersion law was applied to describe the polymer layer from the visible to IR spectral region.

Monomer Synthesis. Diyne **1**, **3**, and **4** were synthesized according to our previous published procedures, whereas compounds **2**, **5**, and **6** were prepared according to the synthetic routes shown in Scheme 2. Typical experimental procedures for their syntheses are shown below.

Preparation of Bis(4-ethynyl-2-methylphenyl)dimethylsilane (2). To a 500 mL round-bottom flask equipped with a septum and a stirring bar were added 2.3 g (8.0 mmol) of **7**, 28.1 mg (0.04 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 19 mg (0.1 mmol) of CuI , and 26 mg (0.1 mmol) of PPh_3 . Dry Et_3N (100 mL) and THF (100 mL) and 2.7 mL (1.9 g, 19.2 mmol) of **8** were then injected. After stirring for 12 h, the mixture was filtered and the precipitates were washed with diethyl ether. The filtrates were collected, and after solvent evaporation under reduced pressure, the crude product was purified by silica gel column chromatography using hexane/chloroform (1:1 v/v) as eluent. Compound **9** was then placed into a 500 mL round-bottom flask followed by addition of 200 mL of methanol and 1 g of KOH . After heating at 50°C for 3 h, the solution was concentrated and poured into 100 mL of 1 M HCl solution. The solution was extracted with chloroform four times. The organic layers were collected, dried over magnesium sulfate, and concentrated by a rotary evaporator. The obtained product was purified by silica gel column chromatography using hexane/chloroform (3:1 v/v) as eluent to give **2** as white solid in 86% yield (2.02 g). IR (KBr), ν (cm^{-1}): 3279 ($\equiv\text{C}-\text{H}$ stretching), 3049, 2955, 2955, 2108 ($\text{C}\equiv\text{C}$ stretching), 1905, 1783, 1589, 1533, 1446, 1382, 1252 ($\text{Si}-\text{CH}_3$ bending), 1130 ($\text{Si}-\text{Ph}$ stretching), 1064, 807 ($\text{Si}-\text{C}$ stretching). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 7.45 (s, 2H, Ar-H ortho to CH_3), 7.31 (d, 2H, Ar-H para to CH_3), 7.25 (s, 2H, Ar-H meta to CH_3), 3.08 (s, 2H, $\equiv\text{CH}$), 2.14 (s, 6H, CH_3), 0.59 [s, 6H, $\text{Si}(\text{CH}_3)_2$]. ^{13}C NMR (300 MHz, CDCl_3), δ (ppm): 144.51 (aromatic carbons

linked with CH_3), 138.76 [aromatic carbons linked with $\text{Si}(\text{CH}_3)_2$], 135.35 (aromatic carbons ortho to CH_3), 133.88 (aromatic carbons meta to CH_3), 129.36 (aromatic carbons para to CH_3), 123.71 (aromatic carbons linked with $\text{C}\equiv\text{CH}$), 84.38 ($\equiv\text{C}-\text{Ar}$), 78.32 ($\equiv\text{CH}$), 23.36, -0.45 [$\text{Si}(\text{CH}_3)_2$]. MS (TOF): m/z 289.14 [$(\text{M} + 1)^+$, calcd 289.13]. $\lambda_{\text{max}}/\epsilon_{\text{max}}$: 259 nm/ $1.64 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$.

2,5-Bis(2-trimethylsilylethynyl)thiophene (5). This compound was synthesized from 2.2 g (8.1 mmol) of **10**, 28.1 mg (0.04 mmol) of $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, 19 mg (0.1 mmol) of CuI , 26 mg (0.1 mmol) of PPh_3 , and 2.7 mL (1.9 g, 19.2 mmol) of **8** in dry $\text{THF}/\text{Et}_3\text{N}$ mixture (1:1 v/v). The procedure was similar to that for the synthesis of **9**. Brown powder; yield 95.3%. IR (KBr), ν (cm^{-1}): 2942, 2901, 2141 ($\text{C}\equiv\text{C}$ stretching), 1502, 1438, 1406, 1252, 1164 ($\text{Si}-\text{CH}_3$ bending), 848 ($\text{Si}-\text{C}$ stretching). ^1H NMR (300 MHz, CDCl_3), δ (TMS, ppm): 6.95 (s, 2H, thiophene protons), 0.08 [s, 18H, $\text{Si}(\text{CH}_3)_3$]. ^{13}C NMR (300 MHz, CDCl_3), δ (ppm): 133.0 (thiophene carbons at 3 and 4 positions), 125.2 (thiophene carbons at 2 and 5 positions), 100.6 ($\equiv\text{C}-\text{Ar}$), 97.6 [$\equiv\text{C}-\text{Si}(\text{CH}_3)_3$]. MS (TOF): m/z 276.08 (M^+ , calcd 276.08). $\lambda_{\text{max}}/\epsilon_{\text{max}}$: 316 nm/ $2.6 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$.

1,2-Bis(4-dimethylsilylphenyl)-1,2-diphenylethene (6). 4-Bromobenzophenone (**11**, 5 g, 19.2 mmol) and zinc dust (2.5 g, 38.2 mmol) were placed into a 250 mL two-necked round-bottom flask equipped with a reflux condenser. After evacuated under vacuum and flushed with dry nitrogen three times, 100 mL of THF was added. The mixture was cooled to -5 to 0°C , and 2.1 mL (19.2 mmol) of TiCl_4 was added slowly using a syringe. The mixture was slowly warmed to room temperature, and after stirring for 0.5 h, it was refluxed for 12 h. Compound **12** was isolated in 76% yield (3.6 g) after purification by silica gel column chromatography using hexane as eluent. Into another round-bottom flask was added dropwise 7.6 mL (12 mmol) of n -butyllithium (1.6 M in hexane) to a solution of **12** (1.5 g, 3 mmol) in THF at -78°C . After being stirred for 8 h, chlorodimethylsilane (1.32 mL, 12 mmol) was then injected slowly to the solution at -78°C . The solution was warmed gradually to room temperature and stirred overnight. The reaction was terminated by adding aqueous sodium hydrogen carbonate solution. The organic layer was extracted with petroleum ether and dried over anhydrous sodium sulfate. After

solvent evaporation under reduced pressure, the residue was purified by silica gel column chromatography using hexane as eluent. Yield 45% (0.62 g). IR (KBr), ν (cm^{-1}): 3055, 3006, 2958, 2109, 1593, 1494, 1438, 1382, 1252 (Si–CH₃ bending), 1115 (Si–Ph stretching), 872 (Si–C stretching), 767, 693. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.10 (d, 4H, Ar–H), 7.02 (m, 6H, Ar–H), 6.98 (m, 8H, Ar–H), 4.31 (q, 2H, Si–H), 0.28 [d, 12H, Si(CH₃)₂]. ¹³C NMR (75 MHz, CDCl₃), δ (ppm): 145.21, 144.3, 141.69, 135.9, 133.9, 132.0, 131.4, 128.4, 127.1, –3.15. MS (TOF): m/z 448.10 (M^+ , calcd 448.75). $\lambda_{\text{max}}/\epsilon_{\text{max}}$: 317 nm/ $1.90 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$.

Polymerization. All the polymerization reactions and manipulations were carried out under nitrogen, except for the purification of the polymers, which was done in open air. A typical experimental procedure for the polymerization of diyne **1** with disilane **6** is given below as an example. Into a baked 50 mL flask was added **1** (70.7 mg, 0.245 mmol), **6** (110 mg, 0.245 mmol), and 3.8 mg of Rh(PPh₃)Cl. The flask was evacuated under vacuum for half an hour and then flushed with nitrogen. Freshly distilled THF was injected into the tube to dissolve the monomers. After reflux under nitrogen for 24 h, the solution was cooled to room temperature, diluted with 3 mL of chloroform, and added dropwise to 150 mL of methanol through a cotton filter under stirring. The precipitate was allowed to stand overnight and filtered with a Gooch crucible. The polymer was washed with methanol and dried in a vacuum oven at 40 °C to a constant weight. Yield 71.2%. M_w 36 500; M_w/M_n 3.03 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3051, 2958, 2924, 2856, 1725, 1596, 1492, 1442, 1389, 1249 (Si–CH₃ bending), 1107, 987 (Si–Ph stretching), 817, (Si–C stretching), 774. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.59, 7.27, and 7.10 (Ar–H), 6.87 (*E*-ArCH=), 6.57 (*E*-SiCH=), 6.17 (*Z*-ArCH=), 5.98 (*Z*-SiCH=), 0.38 [Si(CH₃)₂]. ¹³C NMR (300 MHz, CDCl₃), δ (TMS, ppm): 144.63, 143.77, 141.16, 140.32, 137.43, 136.27, 133.29, 131.47, 130.74, 127.75, 127.05, 126.53, –2.41. $\lambda_{\text{max}}/\epsilon_{\text{max}}$: 318 nm/ $4.90 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$.

Other polymers were prepared by a similar procedure and their characterization data are given below.

P2/6: Yield 66.9%. M_w 25 000; M_w/M_n 2.52 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3063, 2958, 1592, 1446, 1382, 1252 (Si–CH₃ bending), 1107 (Si–Ph stretching), 808, (Si–C stretching), 693. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.47, 7.25, and 7.08 (Ar–H), 6.94 (*E*-ArCH=), 6.70 (*E*-SiCH=), 6.07 (*Z* olefin proton), 0.58, 0.41. ¹³C NMR (300 MHz, CDCl₃), δ (TMS, ppm): 145.73, 145.07, 144.76, 144.00, 141.73, 139.71, 137.95, 136.87, 135.91, 133.87, 132.04, 131.34, 128.52, 125.69, 123.93, –0.22, –0.57, –1.82. $\lambda_{\text{max}}/\epsilon_{\text{max}}$: 323 nm/ $1.87 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$.

P3/6: Yield 68.2%. M_w 20 600; M_w/M_n 2.29 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3063, 3014, 2958, 2862, 1600, 1487, 1389, 1252 (Si–CH₃ bending), 1107 (Si–Ph stretching), 816, (Si–C stretching), 703. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 8.25, 7.59, and 7.35 (Ar–H), 7.07 (Ar–H and *E*-ArCH=), 6.71 (*E*-SiCH=), 4.26, 1.85, 1.32, 0.86, 0.38. ¹³C NMR (300 MHz, CDCl₃), δ (TMS, ppm): 144.50, 145.00, 144.45, 141.76, 137.40, 135.91, 133.93, 132.09, 131.33, 128.34, 127.10, 125.74, 125.32, 124.52, 123.91, 119.40, 109.49, 43.98, 32.38, 30.40, 27.89, 27.10, 23.25, 14.73, –2.36. $\lambda_{\text{max}}/\epsilon_{\text{max}}$: 304 nm/ $5.1 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$.

P4/6: Yield 78.1%. M_w 11 300; M_w/M_n 2.34 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 3063, 3021, 2958, 1600, 1494, 1446, 1252 (Si–CH₃ bending), 1108 (Si–Ph stretching), 823 (Si–C stretching), 693. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.02 (Ar–H), 6.43 (*E* olefin proton), 5.90 (*Z* olefin proton), 0.36 (SiCH₃). ¹³C NMR (300 MHz, CDCl₃), δ (TMS, ppm): 145.55, 145.02, 144.35, 141.74, 139.67, 137.95, 136.96, 133.86, 133.11, 132.05, 131.33, 130.66, 130.09, 128.80, 129.00, 128.33, 127.12, –1.84, –3.10. $\lambda_{\text{max}}/\epsilon_{\text{max}}$: 310 nm/ $4.16 \times 10^4 \text{ mol}^{-1} \text{ L cm}^{-1}$.

P5/6: Yield 55.9%. M_w 14 900; M_w/M_n 2.39 (GPC, polystyrene calibration). IR (KBr), ν (cm^{-1}): 2958, 2901, 2149, 1511, 1442, 1414,

Table 1. Synthesis of Poly(silylenevinylene)s^a

no.	polymer	yield (%)	M_w^b	M_w/M_n^b
1	P1/6	71.2	36 500	3.03
2	P2/6	66.9	25 000	2.52
3	P3/6	68.2	20 600	2.29
4	P4/6	78.1	11 300	2.34
5	P5/6	55.9	14 900	2.39

^a Carried out in refluxed THF under nitrogen using Rh(PPh₃)₃Cl as catalyst. [**1–5**] = [**6**] = 0.05 M, [cat.] = 0.001 M. ^b Determined by GPC in THF on the basis of a polystyrene calibration.

1252 (Si–CH₃ bending), 1179 (Si–Ph stretching), 848, (Si–C stretching), 759. ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.04 and 6.90 (Ar–H), 6.45 (*E* olefin proton), 6.24 (*Z* olefin proton), 0.39 (SiCH₃). ¹³C NMR (300 MHz, CDCl₃), δ (TMS, ppm): 147.56, 145.74, 144.90, 144.24, 141.82, 138.26, 134.10, 132.06, 131.28, 128.33, 127.07, 2.36, –0.26. $\lambda_{\text{max}}/\epsilon_{\text{max}}$: 325 nm/ $4.2 \times 10^5 \text{ mol}^{-1} \text{ L cm}^{-1}$.

Fluorescent Photopatterning and RI Tuning. Photooxidation and RI tuning of the polymer films were conducted in air or nitrogen at room temperature using 365 nm light obtained from a Spectroline ENF-280C/F UV lamp (diameter = 5 cm) at a distance of 1 cm as light source. The intensity of the incident light was $\sim 18.5 \text{ mW/cm}^2$. The films were prepared by spin-coating the polymer solutions (5 mg/mL in 1,2-dichloroethane) at 1000 rpm for 1 min on silicon wafers. The films were dried in vacuum at 40 °C for 1 h. The photopatterns were generated on silicon wafers using Cu-negative masks. After UV exposure for 5 min, the images of the resultant patterns were taken on an Olympus BX41 fluorescence optical microscope.

RESULTS AND DISCUSSION

Monomer Synthesis. To explore the alkyne hydrosilylation, a versatile tool for the synthesis of poly(silylenevinylene)s with novel materials properties, we designed the molecular structures of a group of functional diynes (**1–5**) and disilane (**6**) as shown in Scheme 1. While some monomers (**1**, **3**, and **4**) were prepared according to our previous published papers,^{13–15} diyne **2** and **5** and disilane **6** were synthesized by the procedures given in Scheme 2. The Sonogashira coupling of **7** and **8** was catalyzed by Pd(PPh₃)₂Cl₂ and CuI in THF/Et₃N mixture, which gave compound **9** that converted into product **2** by base-catalyzed hydrolysis followed by acidification. Utilizing the same procedure, the Pd-catalyzed reaction of **10** with **8** furnished **5**. McMurry coupling of **11** in the presence of TiCl₄ and Zn dust produced **12**, whose lithiation with *n*-butyllithium followed by reaction with chlorodimethylsilane gave **6**. All the monomers were characterized by standard spectroscopic methods, from which satisfactory data corresponding to their molecular structures were obtained.

Polymerization. After obtaining the monomers, we then tried to polymerize them by Rh(PPh₃)₃Cl, a commonly used catalyst for alkyne hydrosilylation.⁸ Reaction of **1** with **6** in the presence of Rh(PPh₃)₃Cl in refluxed THF gave a high molecular weight polymer in a reasonably high yield (Table 1, no. 1). Under the same conditions, **6** reacted respectively with **2–5**, producing P2/6–P5/6 with M_n 's from 25 000 to 14 900 in 56–78% yields. Analysis of their filtrates by GPC showed that they were unreacted monomers and oligomeric species with molecular weights of several thousands.

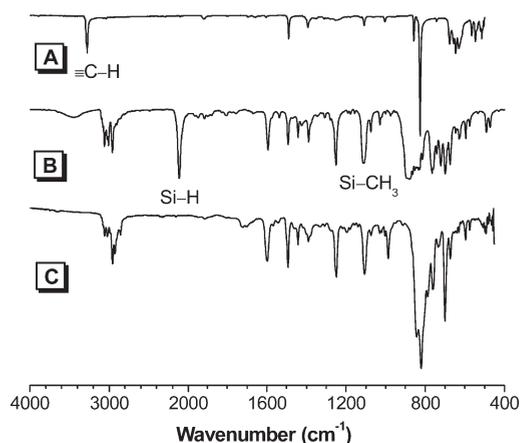


Figure 1. IR spectra of (A) **1**, (B) **6**, and (C) its polymer P1/6.

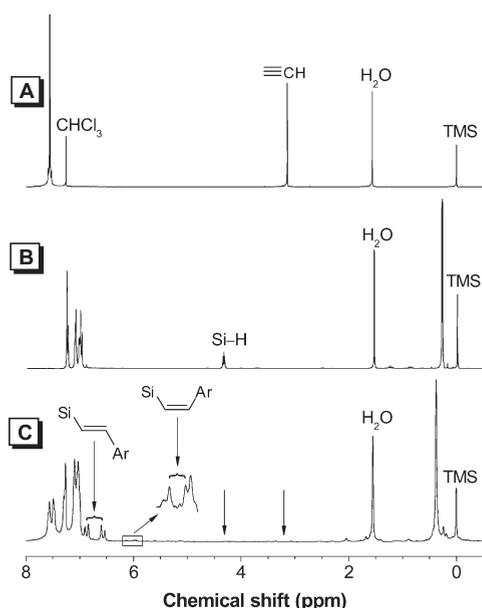


Figure 2. ^1H NMR spectra of (A) **1**, (B) **6**, and (C) its polymer P1/6 in chloroform-*d*.

Structural Characterization. The polymeric products were characterized by IR and NMR spectroscopies, and all gave satisfactory analysis data corresponding to their expected molecular structures. An IR spectrum of P1/6 is shown in Figure 1 as an example; for comparison, the spectra of its monomer **1** and **6** are also provided in the same figure. The $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$ stretching vibrations of **1** occur at 3274 and 2100 cm^{-1} , respectively, which are not observed in P1/6. The spectrum of P1/6 also displays no Si-H stretching vibration of **6** at 2117 cm^{-1} . Meanwhile, the peak at 1600 cm^{-1} associated with $\text{C}=\text{C}$ stretching vibration becomes broader and stronger after the polymerization, suggesting that the triple bonds of **1** and the dimethylsilyl groups of **6** have been transformed into vinyl silylene units in P1/6.

Similar results were obtained from the NMR analyses. Figure 2 shows the ^1H NMR spectra of P1/6 and its monomer **1** and **6**. The spectrum of P1/6 shows no acetylene and Si-H proton resonances of **1** and **6** at δ 3.9 and 4.7, respectively. On the other hand, new peaks assigned to the proton absorptions of the linear

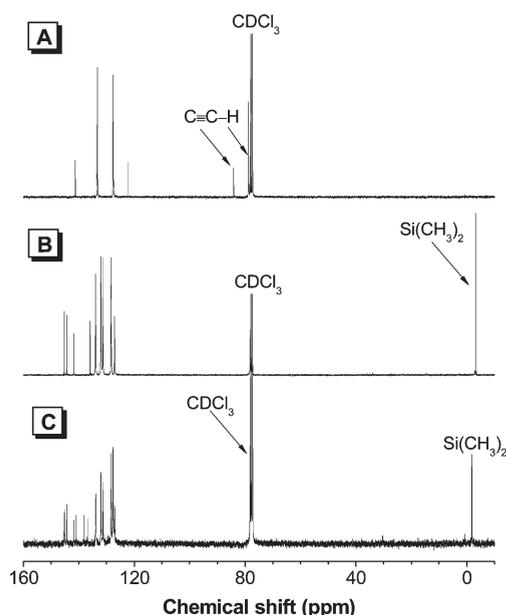


Figure 3. ^{13}C NMR spectra of (A) **1**, (B) **6**, and (C) its polymer P1/6 in chloroform-*d*.

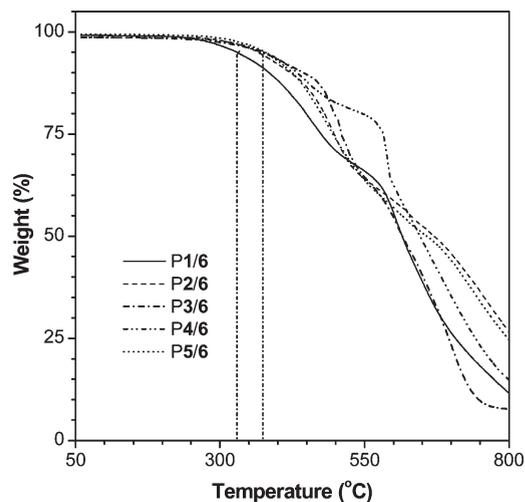


Figure 4. TGA thermograms of P1/6–P5/6 recorded under nitrogen at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$.

E-vinylene structure are observed at δ 6.57 and 6.87. The associated absorptions of the *Z*-vinylene protons are observed at 6.17 and 5.98, but their intensities are much weaker. Using their integrals, an *E/Z* ratio of 91/9 is calculated. No unexpected peaks are found, and all the peaks can be readily assigned. Thus, the polymeric product is indeed P1/6 with a molecular structure as shown in Scheme 1. Similar observations were found in the spectra of P2/6–P5/6, and their *E* contents are calculated to be 77.1, 100, 75, and 50%, respectively.

The ^{13}C NMR spectra of P1/6, **1**, and **6** are shown in Figure 3. The acetylene carbon atoms of **1** resonate at δ 84.07 and 78.8, which are absent in the spectrum of P1/6. The transformation of the dimethylsilyl group of **6** to vinyl silylene units in P1/6 by the polymerization has downfield shifted the methyl carbon resonance, which is now observed at δ -2.41 . The absorptions of the

olefin carbons of the vinylene structures of P1/6 are hard to distinguish, presumably due to their overlapping with those of the aromatic carbons.

Thermal Stability. The thermal stability of the polymers was evaluated by TGA analysis. As shown in Figure 4, all the polymers are thermally stable, losing 5% of their weights (T_d) at 330–378 °C (Table 1). The high T_d values of the polymers are understandable because they are constructed from aromatic rings, which possess a high resistance to thermolysis.

Absorption and Emission. Figure 5 shows the UV spectra of the poly(silylenevinylene)s in their dilute solutions in THF. The polymers exhibit absorption peaks inherent to their monomers. Their maxima are, however, located at longer wavelengths. For example, P2/6 absorbs at 270 and 330 nm, which are red-shifted from those of **2** and **6** by 11 and 13 nm, respectively. This indicates a more extended electronic conjugation in the polymer system, thanks to the electronic communication between the TPE and the aromatic chromophoric units.

All the poly(silylenevinylene)s were weakly emissive when molecularly dissolved in the solutions but became strong emitters when aggregated in poor solvents or fabricated as thin films

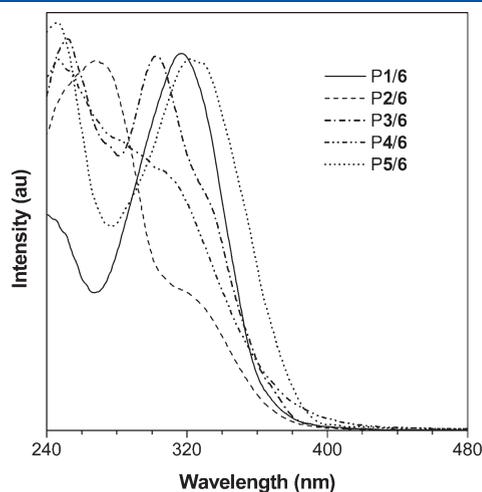


Figure 5. Absorption spectra of THF solutions of P1/6–P5/6. Concentration: 10^{-5} M.

in the solid state. The photoluminescence (PL) spectra of P1/6 in THF and THF/water mixture are given in Figure 6 as an example. In THF, P1/6 emits faintly at 452 nm. Addition of water into its THF solution has enhanced its PL accompanying with a red shift in the peak maximum. The higher the water content, the stronger is the light emission. From the molecular solution in THF to the aggregate state in 90% aqueous solution, the emission intensity of P1/6 has increased by 15-fold (Figure 6B). Since P1/6 is not soluble in water, its chains thus must have aggregated in THF/water mixtures with high water contents. Clearly, the PL of P1/6 is enhanced by aggregate formation, demonstrating a phenomenon of aggregation-enhanced emission (AEE). The AEE effect was not an isolated case observed only in P1/6 but was also found in other polymers. As shown in Figure S1–S4, all the polymers are AEE-active although their emissions vary with their molecular structures.

While the Φ_F values of the polymers in the solution state were low in absolute terms ($\Phi_F = 0.24$ – 3.17% , Table 2), in relative terms most of them were higher than that of TPE ($\Phi_F = 0.24\%$).¹⁶ In the solution of TPE, the active intramolecular rotations of its phenyl rings nonradiatively deactivate its excitons, making it weakly luminescent in the solution.¹⁷ The TPE units in poly(silylenevinylene)s are, however, knitted by covalent bond, which makes the phenyl blades less free to undergo intramolecular rotations, and as a result the polymers are somewhat luminescent in the solutions. The solid thin films of the polymers

Table 2. Thermal and Optical Properties of Poly(silylenevinylene)s^a

polymer	T_d (°C)	λ_{abs}	λ_{em}	Φ_{soln}	Φ_{film}
P1/6	330	318	452	3.17	31.0
P2/6	366	323	450	0.67	23.6
P3/6	372	304	450	0.79	24.1
P4/6	377	310	502	1.00	22.1
P5/6	378	325	495	0.24	13.1

^a Abbreviation: T_d = temperature for 5% weight loss, λ_{abs} = absorption maximum in THF, λ_{em} = emission maximum in THF, Φ_{soln} = quantum yield in THF using quinine sulfate as standard ($\Phi_{soln} = 54\%$ in 0.1 M sulphuric acid), Φ_{film} = quantum yield of the solid film measured by an calibrated integrating sphere.

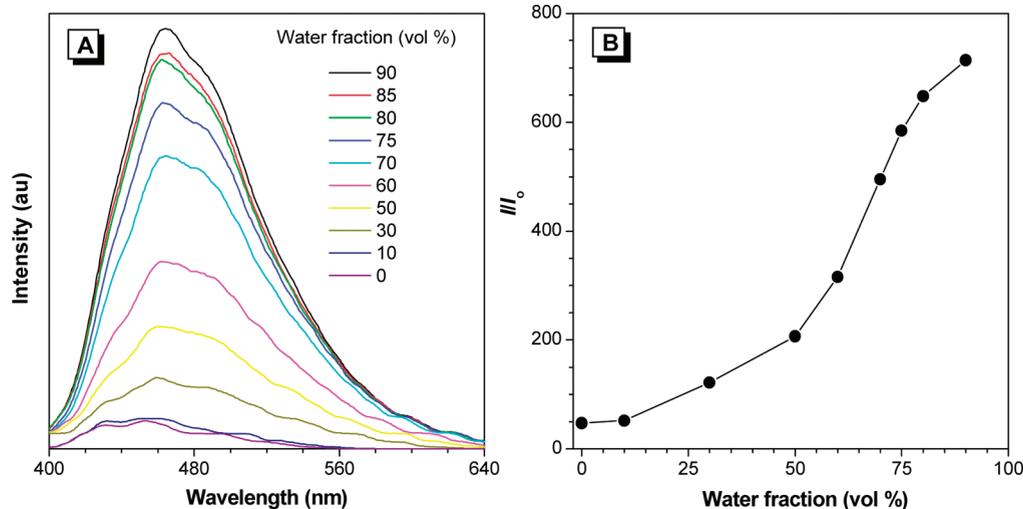


Figure 6. (A) PL spectra of P1/6 in THF and THF/water mixtures with different water fractions. (B) Change in the relative PL intensity (I/I_0) with the composition of the THF/water mixture. I_0 = PL intensity in pure THF solution. Concentration: 10^{-5} M; excitation wavelength: 340 nm.

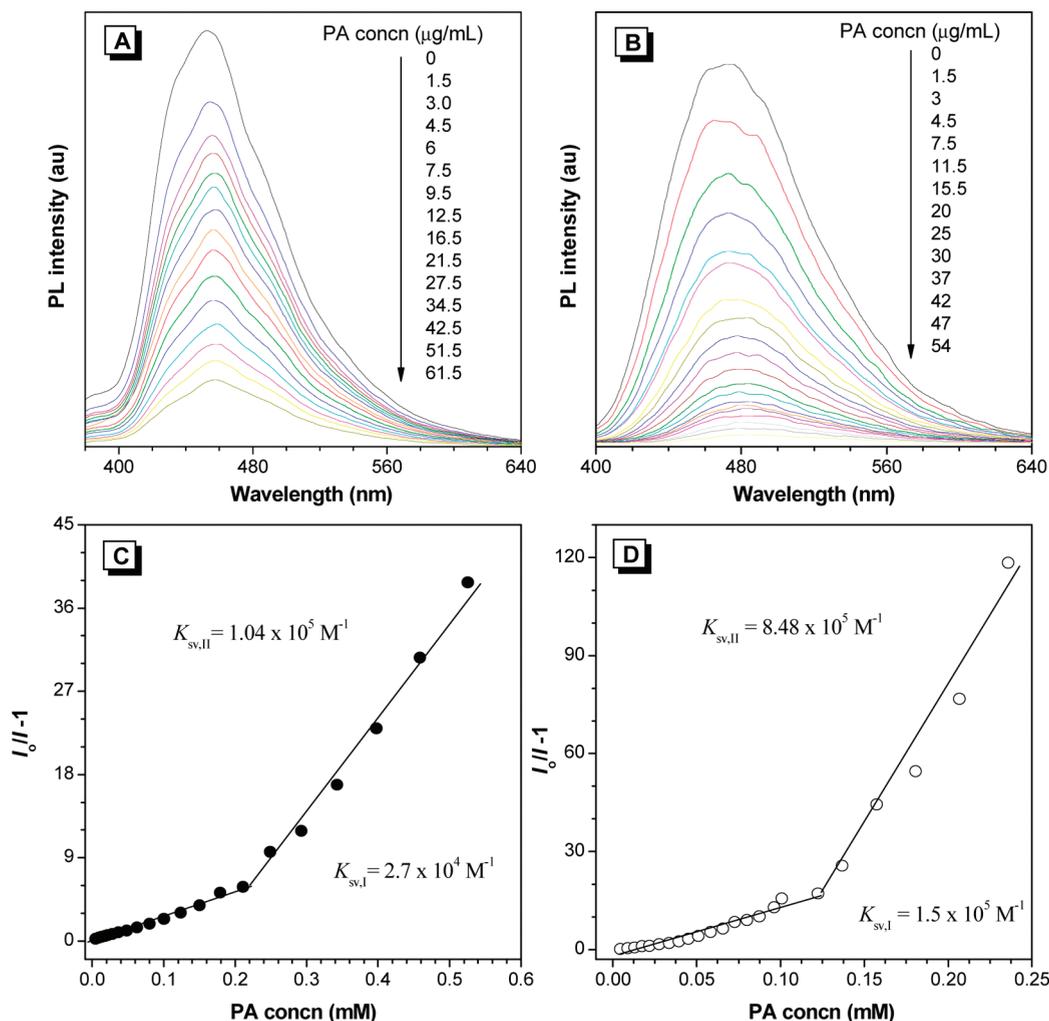


Figure 7. (A) Fluorescence quenching of P1/6 in (A) THF and (B) THF/water mixture (1:9 v/v) by picric acid (PA). Concentration of P1/6: 10^{-5} M; excitation wavelength: 345 nm. (C, D) Stern–Volmer plots for fluorescence quenching of P1/6 by PA in (C) THF and (D) THF/water mixture (1:9 v/v). I_0 = PL intensity in the absence of PA in THF or THF/water mixture (1:9 v/v).

emitted at wavelengths similar to those in the solutions with higher Φ_F values (13–31%), duly verifying their AEE features.

Explosive Detection. Fluorescent probes for explosive detection are in great demand because the threat from the increased use of explosives in terrorism acts has become a global concern.¹⁸ Promoted by the AEE characteristics of P1/6–P5/6, we explored their utility as chemosensors for sensitive detection of explosives. The nanoaggregates of the polymers in THF/water mixtures with 90% water contents were utilized as probes. For comparison, the detection was also carried out in pure THF solutions. Picric acid (PA) was employed as a model compound due to its commercial availability.

As shown in Figure 7, the PL spectrum of P1/6 is progressively weakened when an increasing amount of PA is added into its THF solution or nanoaggregates in the aqueous mixture. The PL quenching can be clearly discerned at a PA concentration as low as 1 ppm. The PL of the polymer aggregates drops at a much faster rate than that of its isolated species in THF. When the PA concentration is increased to 54 $\mu\text{g/mL}$, virtually no light is emitted from the polymer nanoaggregates in the 90% aqueous mixture. The Stern–Volmer plot for the emission quenching of isolated species of P1/6 in THF solution by PA is shown in

Figure 7C, from which the Stern–Volmer constant (K_{sv}) or quenching efficiency can be determined. Intriguingly, the plot is composed by two stages. In stage I or in the low PA concentration (≤ 0.2 mM), the plot is linear with a $K_{sv,I}$ value of $2.7 \times 10^4 \text{ M}^{-1}$. When the PA concentration is increased to >0.2 mM, the Stern–Volmer plot is deviated from the linear one for the low [PA] region and enters stage II, where the plot follows another linear relationship with a 3.8-fold higher quenching efficiency ($K_{sv,II} = 1.04 \times 10^5 \text{ M}^{-1}$). A similar curve was obtained for the polymer nanoaggregates suspended in 90% aqueous mixture. The $K_{sv,I}$ and $K_{sv,II}$ values are determined to be 1.5×10^5 and $8.48 \times 10^5 \text{ M}^{-1}$, which are 5.5- and 8.1-fold higher than those in pure THF. The quenching constants are also much higher than those of polysiloles and polygermoles reported previously (6710 – $11\,000 \text{ M}^{-1}$ in the concentration range of 0–0.2 mM), demonstrative of a superamplification effect in the emission quenching process.¹⁹ Generally, intrinsic autoaggregation of chains of fluorescent conjugated polymers and/or their analyte-induced aggregation cause self-quenching problems that greatly reduce the sensing performance. However, aggregation is beneficial to the PL of P1/6. Moreover, due to their three-dimensional topological structures, the nanoaggregates offer

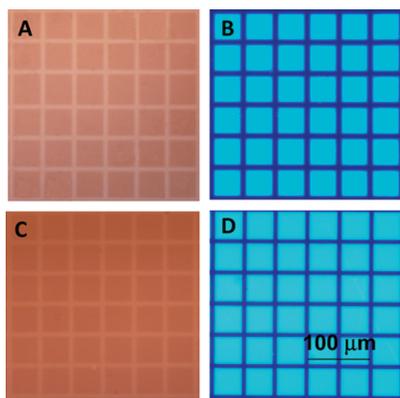


Figure 8. Two-dimensional photopatterns generated by photo-oxidation of (A, B) P1/6 and (C, D) P5/6 films in air at room temperature for 5 min. The photographs were taken under (A, C) normal room and (B, D) UV illumination.

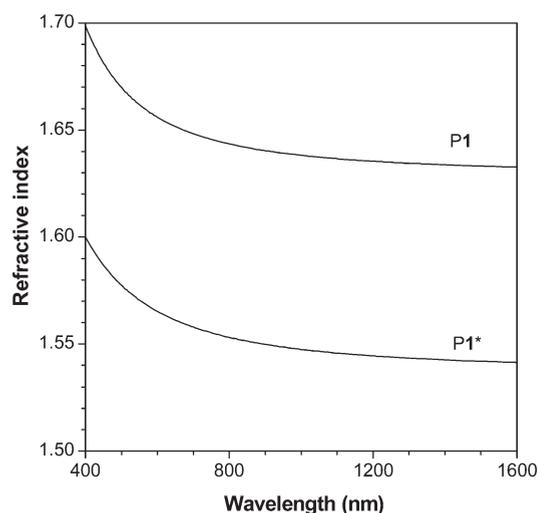


Figure 9. Wavelength dependence of refractive index of thin films of P1/6. Data for the thin film of P1/6 after UV irradiation under nitrogen for 15 min at room temperature are denoted as P1/6*.

many cavities to bind with the quencher molecules and provide additional interbranch diffusion pathways for excitons to migrate.²⁰ The PA molecules in the inner cores and on the outer shells of the aggregates work cooperatively to facilitate the PL annihilation via electron and/or energy transfers, thus resulting in the observed superquenching effect. The light emissions of other poly(silylenevinylene)s are also quenched efficiently by PA with large K_{sv} values (Figure S5–S8). Again, the nanoaggregates of the polymers work better as chemosensors than their isolated species for explosive detection.

Photopatterning. Since the polymers are emissive in the solid state, we thus explored their potential use as fluorescent imaging materials. The polymers can form uniform, tough films by spin-coating their 1,2-dichloroethane solutions onto silicon wafers. Unlike previously prepared poly(vinylene sulfide)s,¹⁰ the poly(silylenevinylene)s render soluble even when they are exposed to UV light from a UV lamp in air at room temperature for 45 min. The polymers may be decomposed upon UV irradiation, but GPC analysis shows that the molecular weights of the polymers hardly change after the UV treatment. We speculate that the vinyl

Table 3. Refractive Indices and Chromatic Dispersions of Poly(silylenevinylene)s^a

polymer	$n_{632.8}$	ν_D	ν_D'	D	D'
P1/6	1.6530	30.51	150.31	0.0328	0.0067
P1/6* ^b	1.5625	29.68	336.95	0.0337	0.0030
P2/6	1.6196	23.89	2303.86	0.0419	0.0004
P2/6* ^b	1.5733	57.83	1896.67	0.0173	0.0005
P3/6	1.6383	18.36	119.61	0.0545	0.0084
P3/6* ^b	1.5994	33.08	131.45	0.0302	0.0076
P4/6	1.6798	35.83	142.97	0.0279	0.0070
P4/6* ^b	1.6265	47.86	191.66	0.0209	0.0052
P5/6	1.6275	33.08	131.63	0.0302	0.0076
P5/6* ^b	1.5385	28.42	112.36	0.0352	0.0089

^a All data taken from Figure 9 and Figures S9–S12, unless otherwise specified. Abbreviation: n = refractive index (at 632.8 nm), ν_D = Abbé number [defined as $(n_D - 1)/(n_F - n_C)$, where n_D , n_F , and n_C are the refractive indices at wavelengths of Fraunhofer D, F, and C spectral lines of 589.2, 486.1, and 656.3 nm, respectively], ν_D' = modified Abbé number [defined as $(n_{1319} - 1)/(n_{1064} - n_{1599})$, where n_{1319} , n_{1064} , and n_{1599} are the refractive indices at the nonabsorbing wavelengths at 1064, 1319, and 1550 nm], D' = optical dispersion = $1/\nu_D'$. ^b For the thin films of P1/6 and P5/6 after UV irradiation.

units of P1–P3 may be well shielded by the phenyl rings and the bulky dimethylsilyl groups, thus reducing the likelihood of the polymers to cross-link by UV-induced olefin polymerization. However, UV irradiation of the thin films of P1/6 and P5/6, for example, through copper masks quenches the light emissions of the exposed regions, while the unexposed squares remain emissive. Two-dimensional fluorescent patterns are thus generated without development (Figure 8).

Light Refraction. The poly(silylenevinylene)s are comprised of polarizable aromatic rings and heteroatoms and may show high refractive indices (RI). Indeed, as can be seen in Figure 9, P1/6 displays high RI values ($n = 1.6985$ – 1.6333) in a wide wavelength region (400–1600 nm). Others polymers show similarly high RI values (Figure S9–S12). The RI values of the polymers at 632.8 nm are 1.6196–1.6798 (Table 3), which are much higher than those of the commercially important optical plastics such as poly(methyl methacrylate) ($n \sim 1.49$), polycarbonate, and polystyrene (both $n \sim 1.589$).²¹ Thus, all the poly(silylenevinylene)s are highly refractive polymers, which may find high-tech applications as coating materials in the advanced display systems such as microlens components for charge-coupled devices and high performance CMOS image sensors.²²

The RI's of the poly(silylenevinylene)s can be tuned by UV irradiation. For example, upon exposure to UV light of 365 nm from a UV lamp under nitrogen for 15 min, the n values of P1/6 decrease dramatically. The difference in the refractivity is as large as 0.090, which is very unusual and very remarkable.

For a material to be useful for technological applications, its optical dispersion, which is a measure of variation in its RI value with wavelength, should be small.²³ To evaluate the application potential of an optical material, a modified Abbé number (ν_D'), using its RI values at the nonabsorbing wavelengths of 1064, 1319, and 1550 nm, has been proposed.²⁴ The first two wavelengths are chosen in view of the practical interest of commercial laser wavelengths (Nd:YAG), while the last one is the wavelength for telecommunication. The ν_D values of P1/6–P5/6 range

from 18.36 to 35.83, which are similar to those of conjugated polymers with absorptions in the visible spectral region (their ν_D values are in the range of 9–38, with majority being between 10 and 20).²⁵ Their ν_D' values are, however, much higher (119.61–2303.86), particularly for P2/6, which exhibits the highest ν_D' values and hence the lowest D' value of 0.0004. Although the Abbé numbers of the poly(silylenevinylene)s vary to different extents upon UV exposure, they still exhibit very low optical dispersions or chromatic aberrations.

CONCLUSION

In this work, functional poly(silylenevinylene)s were synthesized in satisfactory yields with high molecular weights by Rh-catalyzed alkyne polyhydrosilylations of disilane with diynes in refluxed THF. All the polymers were soluble and possessed high stereoregularity. They enjoyed high thermal stability, losing little of their weights when heated to ≥ 330 °C. The polymers were weakly emissive in the solutions but became strong emitters when aggregated in poor solvents and fabricated as thin films in the solid state, demonstrating a phenomenon of AEE. The emissions of the polymers could be quenched efficiently by picric acid with a superamplification effect, suggesting that they can be utilized as sensitive chemosensors for explosive detection. Thin solid films of the poly(silylenevinylene)s showed high refractive indices (RI = 1.7190–1.6102) in the wavelength region of 400–1700 nm, which could be tuned to a large extent ($\Delta n = 0.09$) by UV irradiation. UV irradiation of the thin films of the polymers through photomasks quenched the light emissions of the exposed regions, generating two-dimensional fluorescent images.

ASSOCIATED CONTENT

S Supporting Information. PL spectra of P2/6–P5/6 in THF and THF/water mixtures with different water fractions, fluorescence quenching of P2/6–P5/6 in THF and THF/water mixture (1:1 v/v) by picric acid, and wavelength dependence of refractive index of thin films of P2/6–P5/6 before and after UV irradiation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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