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Silole-Containing Linear and Hyperbranched Polymers: Synthesis, Thermal Stability, Light Emission, Nano-Dimensional Aggregation, and Optical Power Limiting

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Summary: Linear polyacetylenes and hyperbranched polyphenylenes carrying 1,2,3,4,5-pentaphenylsilolyl (PS) pendants are designed and synthesized. Homopolymerization of $HC{\equiv}CPS$, $HC{\equiv}C(CH_2)_9OPS$, and $C_6H_5C{\equiv}C(CH_2)_9OPS$ and (co)polycyclotrimerization of $(HC{\equiv}C)_2PS$ with 1-octyne are effected by $NbCl_5$–, WCl_6–, $MoCl_5$–, and $TaCl_5$–based catalysts. High molecular weight linear (**1**–**3**) and hyperbranched polymers (**6**) are obtained in high yields (M_w up to ~70 × 10^3 and yield up to 85%). All the polymers are thermally stable, losing little weight when heated to 350 °C. Whereas all the polymers emit faint light when molecularly dissolved, polymers **2**, **3**, and **6** become emissive when aggregated in poor solvents or when cooled to low temperatures. Restricted intramolecular rotations of the phenyl rings upon the axes of the single bonds linked to the silole cores may be responsible for the aggregation- or cooling-induced emission. A multilayer electroluminescent device using **3** as an active layer emits a blue light of 496 nm with maximum brightness, current efficiency, and external quantum yield of 1118 cd/m^2, 1.45 cd/A, and 0.55%, respectively. Polymers **6** are non-linear optically active and strongly attenuate the optical power of intense laser pulses, whose optical limiting performances are superior to that of C_{60}, a best-known optical limiter.

Keywords: aggregation- and cooling-induced emission; hyperbranched polyphenylenes; light-emitting diode; optical limiting; organometallic polymers; polyacetylenes; polycyclotrimerization; siloles

Introduction

Siloles or silacyclopentadienes are a group of organometallic molecules that possess novel electronic and optical properties.[1],[2] We have recently observed a novel phenomenon of

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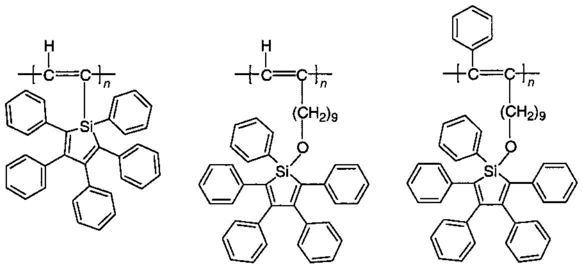
aggregation-induced emission (AIE) in this group of molecules: the siloles are practically nonluminescent when molecularly dissolved but become emissive when aggregated in poor solvents or fabricated into thin films.[3],[4] The photoluminescence (PL) quantum yield (Φ_{PL}) of the silole aggregates can differ from that of its molecularly dissolved species by two orders of magnitude (>300). Utilizing this AIE property, we have fabricated silole-based light-emitting diodes (LEDs), which exhibit outstanding electroluminescence (EL) performance. The highest external quantum efficiency is 8%,[5],[6] approaching the limit of the possible.[7],[8] Siloles are thus a group of excellent organometallic molecules for LED applications. Low molecular weight compounds, however, have to be fabricated into thin films by relatively expensive techniques. One way to overcome this processing disadvantage is to make high molecular weight polymers, which can be readily processed from their solutions into thin solid films over large areas by simple spin coating or doctor blade techniques. In this paper, we report our work on synthesizing silole polymers via transition metal-catalyzed metathesis and cyclotrimerization polymerizations of acetylenes and present the novel properties of the polymers originated from their unique molecular structures.

Results and Discussion

We prepared three acetylene-silole adducts by nucleophilic substitutions of 1-chloro-1,2,3,4,5-pentaphenylsilole with a Grignard reagent ethynylmagnesium bromide and alkynyl alcohols.[9] The polymerizations of the monomers were effected by $NbCl_5$–, WCl_6–, and $MoCl_5$–Ph_4Sn catalysts, producing polymers **1**–**3** (Figure 1) with high molecular weights in high yields (M_w up to ~70 × 10^3 and isolation yield up to 80%) (Table 1).



1 2 3

Figure 1. Linear polyacetylenes containing 1,2,3,4,5-pentaphenylsilolyl pendants.

We also prepared a diacetylene (**4**; Figure 2) by reacting 1,1-dichloro-2,3,4,5-tetraphenylsilole with ethynylmagnesium bromide.[10] Homo- and copolycyclotrimerizations of **4** with 1-octyne **5** were effected with $TaCl_5$–Ph_4Sn in toluene at room temperature, which gave completely soluble hyperbranched poly(phenylenesilolenes) **6** in high yields (Table 2). All the polymers were characterized by standard spectroscopic methods and satisfactory analysis data corresponding to their molecular structures were obtained.

Table 1. Synthesis of poly(silolylacetylenes)[a]

no.	catalyst	solvent	temp (°C)	yield (%)	M_w[b]	M_w/M_n[b]
		Poly(1,2,3,4,5-pentaphenysilolylacetylene) (1)				
1	$NbCl_5$–Ph_4Sn	toluene	60	60.0	46 400	1.7
2	$NbCl_5$–Ph_4Sn	toluene	80	78.0	68 800	1.8
		Poly{11-[(1,2,3,4,5-pentaphenylsilolyl)oxy]-1-undecyne} (2)				
3	WCl_6–Ph_4Sn	toluene	60	60.3	11 500	3.5
4	WCl_6–Ph_4Sn	dioxane	60	29.0	33 900	2.6
5	$MoCl_5$–Ph_4Sn	toluene	60	11.7	10 600	3.4
		Poly{11-[(1,2,3,4,5-pentaphenylsilolyl)oxy]-1-phenyl-1-undecyne} (3)				
6	WCl_6–Ph_4Sn	toluene	60	80.5	33 400	2.2

[a] Carried out under nitrogen for 24 h; $[M]_0 = 0.1$ M, [cat.] = [cocat.] = 10 mM.
[b] Estimated by GPC in THF on the basis of a polystyrene calibration.

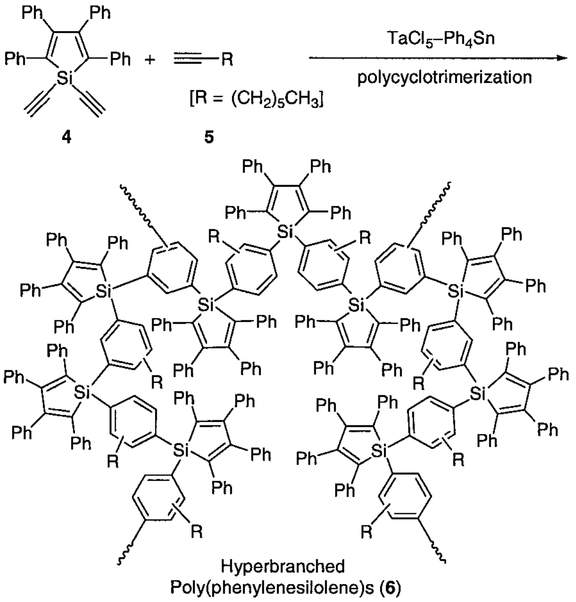


Figure 2. Synthesis of hyperbranched poly(phenylenesilolenes) by polycyclotrimerizations of alkynes catalyzed by tantalum-based initiator.

Table 2. Synthesis[a] and Properties of Hyperbranched Poly(phenylenesilolenes)

no.	feed ratio [**5**]/[**4**][b]	polymer yield (%)	M_w[c] (Da)	M_w/M_n[c]	T_d[d] (°C)	F_L[e] (mJ/cm^2)	$F_{t,m}/F_{i,m}$[f]	λ_{em}[g] (nm)	Φ_F[h]
1	0	83.0 (**6a**)	5 320	1.6	395	185	0.19	505	0.01
2	0.5	85.3 (**6b**)	5 820	1.7	378	182	0.24	493	0.01
3	1.0	67.6 (**6c**)	3 610	1.4	355	190	0.28	504	0.01
4	1.5	34.0 (**6d**)	3 530	1.4	343	1 140	0.32	499	0.01

[a] By homopolymerization of diyne **4** or copolymerizations of **4** with 1-octyne **5** catalyzed with $TaCl_5$–Ph_4Sn in toluene at room temperature under nitrogen for 24 h; [**4**] = 0.072 M, [$TaCl_5$] = [Ph_4Sn] = 20 mM.

[b] Molar ratio.

[c] Estimated by GPC in THF on the basis of a polystyrene calibration.

[d] Temperature for 5% weight loss (TGA, under nitrogen, heating rate: 20 °C/min).

[e] Optical limiting threshold (incident fluence at which the nonlinear transmittance is 50% of the linear one).

[f] Signal suppression (ratio of the saturated transmitted fluence to the maximum incident fluence).

[g] Emission maximum (in THF).

[h] Quantum yield of fluorescence (using 9,10-diphenylanthracene as standard).

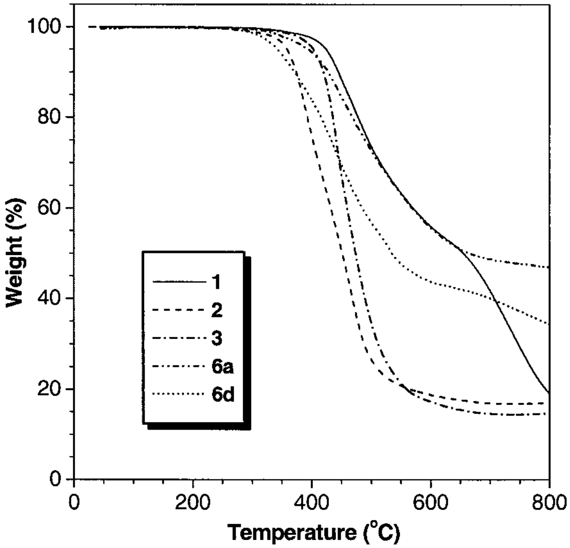


Figure 3. TGA thermograms of silole-containing linear polyacetylenes and hyperbranched polyarylenes recorded under nitrogen at a heating rate of 20 °C/min.

Figure 3 shows the TGA thermograms of the polymers. All the polymers were thermally stable and lost little of their weights at a temperature as high as ~350 °C. The degradation temperatures of polysilolyloxyacetylenes **2** and **3** were much higher than those of their structural congeners, poly(dimethylalkoxysilylacetylene)s $-\{HC{=}C[Si(CH_3)_2OC_mH_{2m+1}]\}_n-$ (m = 2, 3),[11] probably due to the "jacket effect"[12],[13] of the bulky silolyl pendants. Wrapping of the polyacetylene backbone in the stable silole rings may have shielded the double bonds from the harsh chemical and thermal attacks. Polymer **6a** showed higher thermal stability than that of **6d**. This is easy to understand: **6a** is an all-aromatic homopolymer, which should be thermally very stable; the incorporation of the weak aliphatic (hexyl) moiety into **6d** should increase its thermolytic susceptibility, and the copolymer should thus start to decompose at a relatively low temperature.

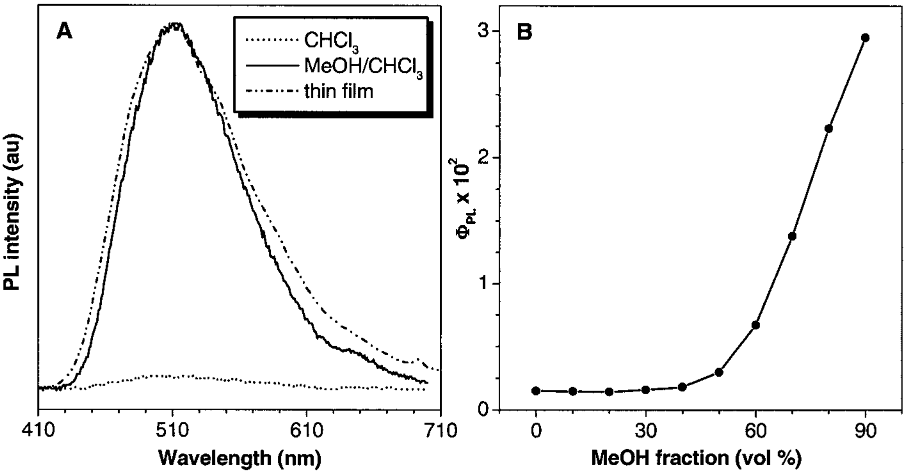


Figure 4. (A) Photoluminescence spectra of **2** in chloroform solution, methanol/chloroform mixture (9:1 by volume), and solid state (thin film); concentration of **2** in the solution and the mixture: 10 μM; excitation wavelength (nm): 400 (solution/mixture), 325 (thin film). (B) Quantum yield (Φ_{PL}) of **2** *vs.* solvent composition of methanol/chloroform mixture.

Silole's emission is characterized by its AIE feature. Do the silole polymers behave in a similar way? The answer to this question is yes or no, depending on the molecular structure of the polymer. No emission from the silole pendants was observed when the chloroform solution of **1** was photoexcited. Even when we added methanol into chloroform (while keeping the solution concentrations unchanged), hardly could the light emission of **1** be enhanced by the addition of the poor solvent. The rigid polyacetylene backbone of **1** may not allow its directly attached silole pendants to pack well in the aggregation state, thus making the polymer AIE-inactive. Thanks to the decoupling effect of the long nonanyloxy chain, polymers **2** and **3**, on the other hand, exhibited a pronounced AIE effect. As shown in Figure 4, the PL spectrum of the chloroform solution of **2** was almost a flat line with a Φ_{PL} value as low as 0.15%. The Φ_{PL} value started to swiftly increase when more than 40% of methanol was added into the mixture. When the methanol fraction was increased to 90%, Φ_{PL} rose to 2.95%, which is ~20 times higher than the solution value. Polymer **3** showed similar behavior but its Φ_{PL} in a mixture with 90% methanol was higher (9.3%), probably due to the additional contribution of its backbone emission: its poly(1-phenyl-1-alkyne) main chain is known to luminesce in the similar spectral region.[14],[15] Similar to polymer **1**, all the hyperbranched poly(phenylenesilolenes) were AIE-inactive, possibly owing to the rigid hyperbranched polyphenylene sphere, which hampers the packing of the silole pendants.

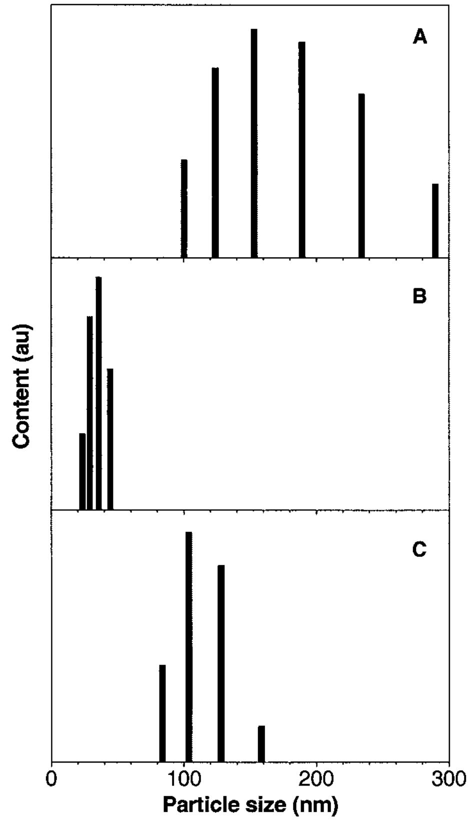


Figure 5. Particle size distributions of polymers (A) **1**, (B) **2**, and (C) **3** in methanol/ chloroform mixtures (9:1 by volume); concentration of polymers: 10 μM.

We carried out particle size analysis, which proved that the polymers did form nanoaggregates in the methanol/chloroform mixtures. Examples of the particle size histograms are shown in Figure 5. The size distribution and average size varied with polymer because of the difference in the polymer solubility in the solvent mixture. Polymer **1** is very hydrophobic and rigid and will easily associate into large nanoaggregates in the polar mixture. Polymer **2** possesses polar siloxy moieties with a better miscibility with the polar solvent and hence forms smaller aggregates under comparable conditions. Polymer **3** is a disubstituted polyacetylene with a more rigid backbone structure and its aggregates are thus understandably bigger than those of **2**.

Aggregation normally quenches light emission;[16],[17] what is the cause for this "abnormal" AIE phenomenon? To address this mechanistic question, we designed and carried out more experiments. When a dilute dioxane solution of **3** (10 μM) was cooled, the intensity of its PL spectrum was progressively increased in a nonlinear fashion (Figure 6A). When cooled from room temperature to below the mp (11.8 °C) of the solvent, the liquid solution changed to a solid "glass". The intramolecular rotations of the peripheral phenyl rings upon the axes of the single bonds linked to the central silacyclopentadiene cores may be physically restricted by the solid environmental surroundings. This restricted rotation in some sense rigidifies the chromophoric molecule as a whole, thus making the silole pendant more emissive.

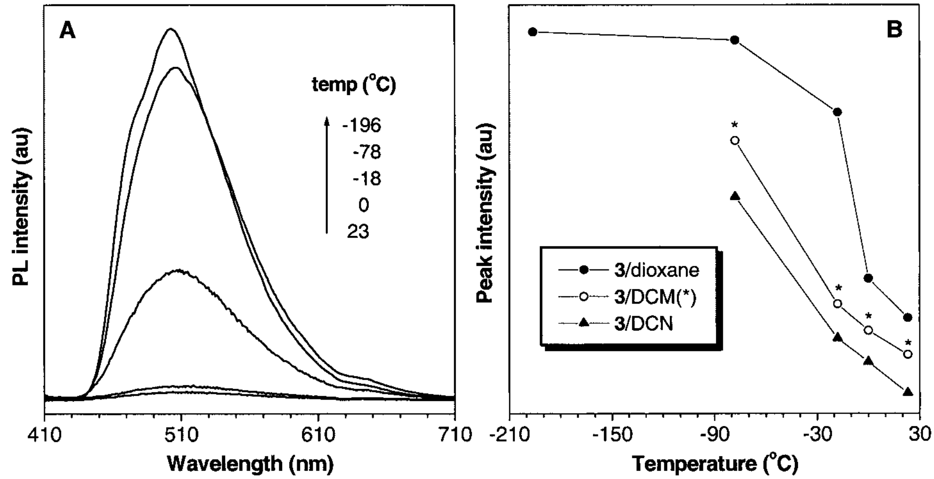


Figure 6. (A) Photoluminescence spectra of a dioxane solution of **3** at different temperatures and (B) effect of temperature on the peak intensity of the photoluminescence spectra of **3** in dioxane and DCM. All the solutions have a concentration of 10 μM except for the one marked with (*), whose concentration is 20 μM. Excitation wavelength: 407 nm.

To separate the cooling effect from the "glass" effect, we chose dichloromethane (DCM), a liquid with much lower melting point, for the PL measurement. The PL intensity of the solution increased with a decrease in temperature in a nearly "linear" fashion (Figure 6B). This enhancement in emission must be due to the restricted intramolecular rotation caused by cooling-induced conformation freezing because the melting point of the solvent (–95 °C) is lower than the lowest temperature we tested for this solution (–78 °C). We doubled the solution concentration to 20 μM and found that the emission enhancements were also roughly doubled at all the temperatures. This once again proves that the solute has indeed remained molecularly dissolved at the low temperatures because if the solute aggregates, it should evoke a clear "nonlinear" response to the concentration change. Similar to polymer **3**, polymers **2** and **6** also showed much stronger emission when their solutions were cooled.

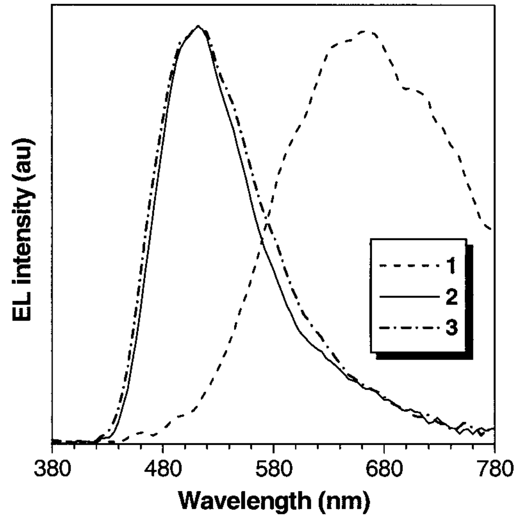


Figure 7. Electroluminescence spectra of single-layer devices of **1**, **2**, and **3** with a device configuration of ITO/polymer/LiF/Al.

Siloles are excellent materials for LED applications. How are their polymers? We checked the EL performances of polymers **1**–**3** using a single-layer device configuration. The EL spectrum of **1** peaked at 664 nm, while the emission maximums of **2** and **3** were at ~512 nm (Figure 7). All the EL devices exhibited similarly low current efficiencies: 0.014 (**1**), 0.013 (**2**), and 0.013 cd/A (**3**). This is not surprising because the injection and transportation of charges are generally not balanced in devices with a single-layer structure. We thus tried to modify the device configuration, using **3**, the most PL-active polymer, as the emitting material. We added poly(9-vinylcarbazole) (PVK) and tris(8-hydroxyquinolinato)aluminum (Alq_3) on the anode and cathode sides, respectively, to facilitate the charge injection and to enhance the charge transport efficiencies in the EL device. Between the PVK and Alq_3 layers, we also added a layer of bathocuproine (BCP) to prevent the holes from traveling through to reach the cathode. With these modifications, an EL device with a configuration of ITO/(**3**:PVK)(1:4)/BCP/Alq_3/LiF/Al was fabricated, which emitted a strong blue light of 496 nm with a maximum luminance of 1118 cd/m^2. The maximum current and external quantum efficiencies of the device were 1.45 cd/A and 0.55%, respectively, which are comparable to some of the best results reported by other research groups for blue-emitting LEDs.[18],[19]

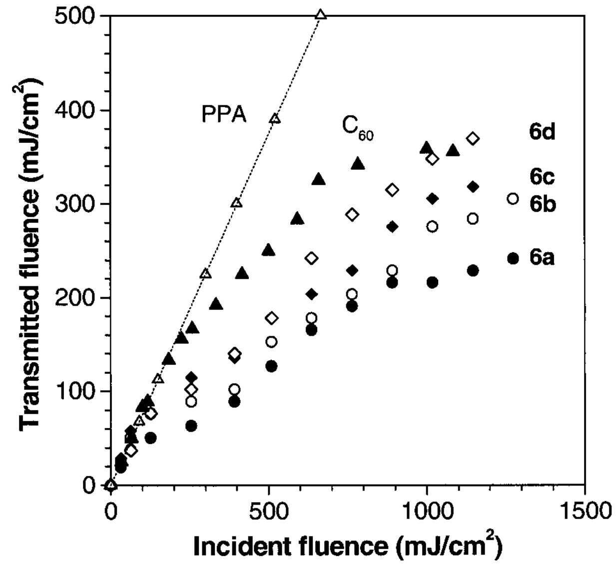


Figure 8. Optical responses to 8 ns, 10 Hz pulses of 532 nm laser light, of dichloromethane solutions (0.70 mg/mL) of hyperbranched poly(phenylenesilolene)s. Data for poly(phenylacetylene) (PPA) and C_{60} solutions are shown for comparison. Linear transmittance (%): 70 (**6a**), 80 (**6b**), 82 (**6c**), 85 (**6d**), 79 (C_{60}), 75 (PPA).

The hyperbranched polymers **6** were optically very stable. Figure 8 shows optical responses of the polymer solutions to 532 nm laser pulses, along with the data for the solutions of poly(phenylacetylene) (PPA)[20] and C_{60}.[21],[22] PPA photodegraded under the attack of harsh laser shots. The hyperbranched polyarylenes showed comparable linear transmittance in the low fluence region (T = 70–85%) but became opaque in the high fluence region. The polymers strongly attenuated the power of the intense laser pulses, whose optical limiting performances are superior to that of C_{60}, a best-known optical limiter.[21]–[23] Among the hyperbranched polymers, **6a** exhibited the best performance, which started to limit the optical power at a low threshold (185 mJ/cm^2) and suppressed the optical signals to a great extent (19%; Table 2, no. 1).

Conclusions

In this work, we succeeded in incorporating silole ring, an organometallic chromophore with novel luminescence properties, into linear polyacetylene and hyperbranched polyphenylene structures through the facile metathesis and cyclotrimerization polymerizations of alkynes catalyzed by transition-metal catalysts. All the polymerizations yielded completely soluble polymers of high thermal stability. While none of the polymers were strong luminophors when molecularly dissolved, polymers **2**, **3** and **6** became emissive when aggregated in poor solvents or when cooled to low temperatures. A multilayer EL device with a configuration of ITO/(**3**:PVK)(1:4)/BCP/Alq$_3$/ LiF/Al was fabricated, which emitted blue light of 496 nm and exhibited maximum luminance, current efficiency, and external quantum efficiency of 1118 cd/m^2, 1.45 cd/A, and 0.55%, respectively. The hyperbranched poly(phenylenesilolene)s strongly limited intense laser pulses, whose optical-limiting thresholds and signal-suppress power were better than those of C_{60}, a well-known optical limiter.

Acknowledgments

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