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Synthesis and Optical Properties of Hyperbranched Polyarylenes and Linear Polyacetylenes

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Summary: New hyperbranched polyarylenes (HPAs) and linear polyacetylenes (LPAs) containing chromophoric moieties were synthesized in high yields (up to 97%) by coablt- and tantalum-catalyzed polycyclotrimerizations and tungsten-catalyzed metathesis polymerizations, respectively. The polymers possessed high molecular weights (M_w up to 113 000 Da) and were completely soluble in common organic solvents. The HPAs emitted strong UV light of 400 nm in high quantum yields (Φ_F up to 0.98) and limited intense laser pulses, whose limiting threshold and signal suppress power were better than those of C_{60}, a well-known optical limiter. The electroluminescence (EL) devices of the LPAs emitted blue light of ~460 nm and exhibited maximun brightness, current efficiency, and external quantum efficiency of 1118 cd/m^2, 1.53 cd/A, and 0.85%, respectively.

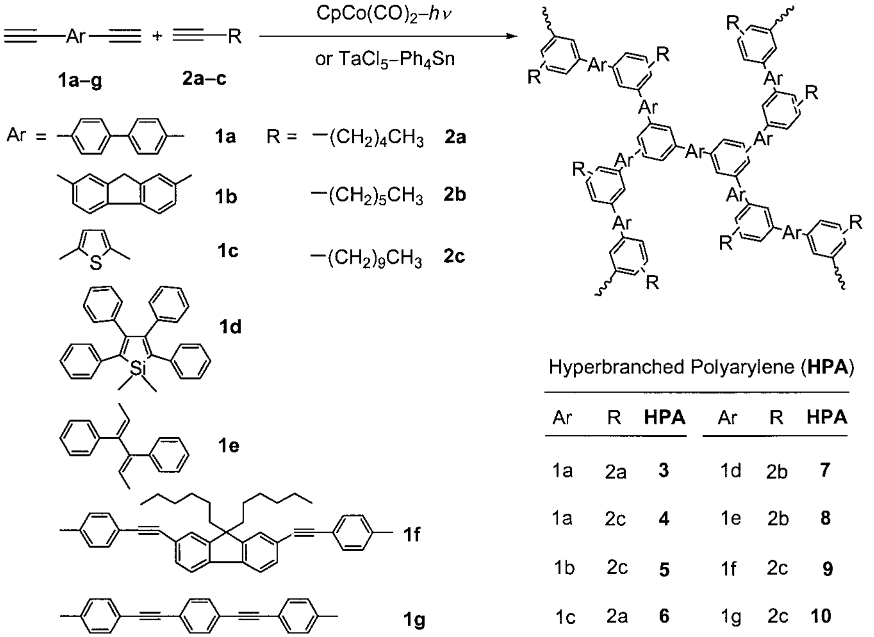
Keywords: hyperbranched polyarylenes; light-emitting diodes; optical limiting polyacetylenes; polycyclotrimerization

Introduction

Development of new conjugated polymers with novel structures and unique proerties has been the subject of intense research[1–3]. Our group has been working on the synthesis of linear and hyperbranched conjugative polymers via alkyne polymerizations catalyzed by transition metal complexes. Through systematic investigations, we have succeceded in generating a variety of HPAs[4–7] and LPAs[8–11] containing chromophoric moieties. In this paper, we report our recent work on the synthesis of new HPAs (Figure 1) and LPAs (Figure 2) and present the novel optical properties originating from their unique molecular structures.

Results and Discussion

We prepared the HPAs by copolycyclotrimerizations of diynes (**1**) with monoynes (**2**) using $CpCo(CO)_2$–$h\nu$ and $TaCl_5$–Ph_4Sn as catalysts (Figure 1). All the polymerization reactions proceeded smoothly and soluble polyarylenes with high molecular weights (M_w up to 7.2 x 10^4 Da) were obtained in high yields (up to 97.3%; Table 1). The HPAs were characterized by standard spectroscopic analyses, from which, satisfactory data corresponding to their expected structures were obtained.



Ar	R	**HPA**	Ar	R	**HPA**
1a	2a	**3**	1d	2b	**7**
1a	2c	**4**	1e	2b	**8**
1b	2c	**5**	1f	2c	**9**
1c	2a	**6**	1g	2c	**10**

Figure 1. Synthesis of hyperbranched polyarylenes containing chromophoric moieties by alkyne copolycyclotrimerizations catalyzed by cobalt- and tantalum-based complexes.

Table 1. Synthesis[a] and optical properties[b] of hyperbranched polyarylenes (HPAs)

HPA	catalyst[c]	yield wt %	M_w[d]	M_w/M_n[d]	λ_{max} nm	Φ_F	F_L mJ/cm^2	$F_{t,m}/F_{i,m}$
3	A	76.0	20350	2.24	398	0.49	343	0.21
5	B	70.1	72270	5.70	400	0.98	509	0.11
6	B	65.5	33500	8.10	486	0.14	802	0.13
9	A	97.3	27157	3.78	399	0.15	155	0.08
10	A	42.0	12150	3.67	399	0.46	260	0.11

[a] Carried out in toluene under N$_2$ at 65 °C for 6 h; [**1**] = 0.1 M, [**2**] = 0.09–0.31 M, [cat.] = 10 mM.
[b] Abbriviations: λ_{max} = emission maximum (in dichloromethane), Φ_F = fluorescence quantum yield, F_L = optical limiting threshold, $F_{t,m}/F_{i,m}$ = signal suppression.
[c] Catalyst A = CpCo(CO)$_2$–hv, catalyst B = TaCl$_5$–Ph$_4$Sn.
[d] By GPC in THF (polystyrene calibration).

Figure 3A shows the photoluminescence (PL) spectra of **3** and **5** in dichloromethane. Upon excitation, **3** and **5** emitted intense UV light of 400 nm, whose emission efficiencies were 1.1- and 2.3-folds higher that of PPO (0.43), a well-known highly luminescent disubstituted polyacetylene. Although the emission efficiency varied with the type of diynes (Table 1), all the HPAs except **6** emitted intensely in the UV spectral region.

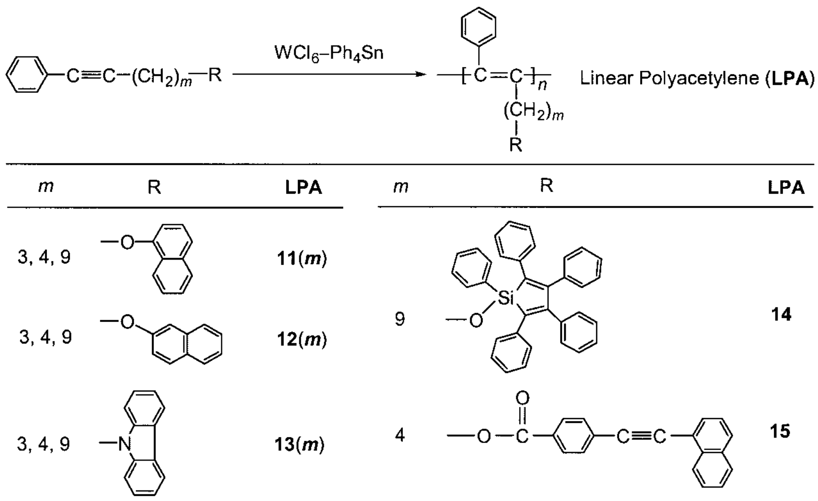


Figure 2. Synthesis of linear poly(1-phenyl-1-alkynes) containing chromophoric pendnats by metathesis polymerizations catalyzed by tungsten-based initiators.

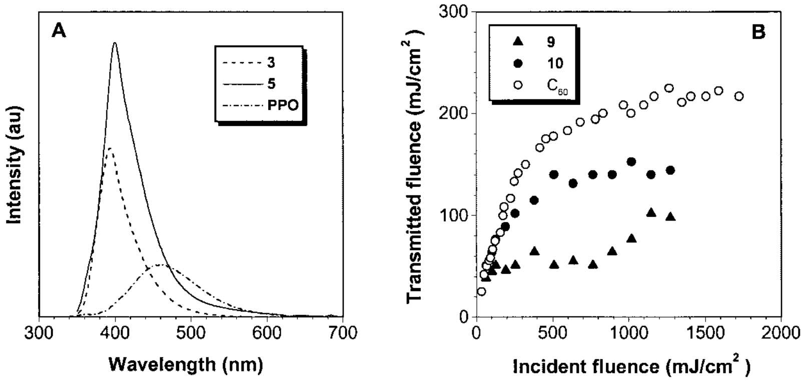


Figure 3. (A) Emission spectra of **3** and **5** (in dichloromethane). λ_{ex} (nm): 398 (**3**) and 400 (**5**). Polymer concentration: 2 mM. Data for poly(1-phenyl-1-octyne) (PPO) is shown for comparison. (B) Optical responses to 8 ns, 10 Hz pulses of 532 nm laser light, of dichloromethane solutions (0.86 mg/mL) of **9** and **10**. Data for C_{60} is shown for comparison.

The HPAs consist of clusters of aromatic rings and may exhibit optical limiting properties. This proved to be the case. As shown in Figure 3B, the transmitted fluence of **9** increased initially with the incident fluence but started to deviate from linearity when the incident fluence exceeded 155 mJ/cm^2. The signal suppression (0.08) was 1.6 times better than that achievable by C_{60}[12–14] under comparable conditions; that is, **9** is a better optical limiter than C_{60}. The optical limiting performance of **10** was poorer than **9** but still better than C_{60}. The signal suppressions of other HPAs were all fairly low (Table 1). Clearly, the HPAs are a group of strong optical limiters.

Table 2. Synthesis[a] and optical properties[b] of linear polyacetylenes (LPAs)

LPA	yield	M_w[c]	λ_{PL}	Φ_F	λ_{EL}	V_{on}	L	CE	PE	η_{EL}
	wt %	kDa	nm		nm	V	cd/m^2	cd/A	lm/W	%
11(3)	91.2	112.7	452	0.68	468	12	955	0.83	0.18	0.53
11(4)	90.2	29.8	452	0.52	464	12	1019	0.83	0.20	0.61
12(3)	83.9	68.2	452	0.37	460	8	511	1.01	0.27	0.75
12(4)	90.0	38.4	452	0.76	460	8	1065	1.23	0.30	0.85
13(3)	79.3	43.0	454	0.29	460	9	72	0.76	0.23	0.63
14	80.5	33.4	506	0.32	496	13	1118	1.53	0.29	0.55
15	37.9	21.9	452	0.26	460	9	908	0.95	0.28	0.65

[a] By WCl_6–Ph_4Sn in toluene under N_2 at 60 °C for 24 h; $[M]_0 = 0.2$ M; [cat.] = [cocat.] = 10 mM.
[b] Abbreviations: λ_{PL} = emission maximum (PL; film), Φ_F = fluorescence quantum yield, λ_{EL} = emission maximum (EL), V_{on} = turn-on voltage, L = maximum brightness, CE = maximum current efficiency, PE = maximum power efficiency, η_{EL} = maximum external quantum efficiency.
[c] by GPC in THF; $M_w/M_n = 1.6$–3.0 (polystyrene calibration).

We synthesized the light-emitting LPAs by W-catalyzed acetylene polymerizations (Figure 2). Overcoming the involved synthetic difficulties, we succeeced in synthesizing the functional disubstituted polyacetylenes containing naphthalene, carbazole, silole, and naphthylethynylphenyl pendants in high yields (up to 91%; Table 2).

We investigated the PL behaviors of the polymers in the solid state. Upon excitation at 325 nm, a strong blue light of 452 nm was emitted from **12**(4) (Figure 4A). We fabricated a multilayer EL device with a configuration of ITO/**12**(4):PVK (1:4)/bathocuproine/Alq_3/LiF/Al. The device emitted a blue light of 460 nm, which suggests that the PL and EL of **12**(4) originate from the radiative decay of similar singlet exciton species. Interestingly, the PL peak of **14** red-shifted by 46 nm from that of **12**(4). As the emission spectrum of the polyene backbone of

14 partly overlapped with the absorption spectrum of its silole pendants, the light emitted by the backbone might be absorbed by the pendants, which thus emitted at 506 nm. The EL of **14** also originated from the emission of the silole pendants and was peaked at 496 nm. It is noteworthy that the color emitted by the polymers can be turned by changing their pendant groups.

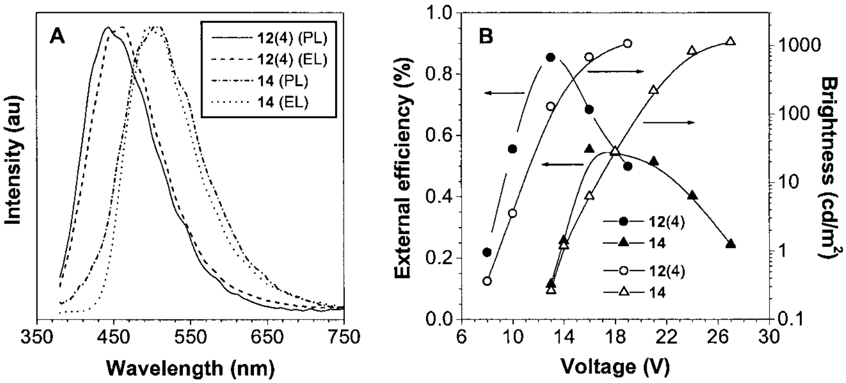


Figure 4. (A) Normalized PL (λ_{ex} = 337 nm) and EL spectra of the thin films of **12**(4) and **14**. (B) Dependence of external quantum efficiency and brightness on applied voltage in the EL devices of ITO/**12**(4) (or **14**):PVK (1:4)/bathocuproine/Alq$_3$/LiF/Al.

Figure 4B shows the changes of external quantum efficiency and emission brightness with driven voltage. The brightness of **12**(4) and **14** increased exponentially with the voltage. The maximum brightness of **12**(4) was 1065 cd/m2 at 19 V, while that of **14** was 1118 cd/m^2 at 27 V. The external quantum efficiencies of **12**(4) and **14** initially increased with voltage and reached their maximum values of 0.85% and 0.55% at 13 and 16 V, respectively. Afterwards, they dropped rapidly. The PL and EL results of other LPAs are given in Table 2. Upon photoexcitation, all the polymers emitted intensely with high efficiencies. Their EL profiles were similar to those of their PL spectra with slight red-shifts. Although the brightness varied with the spacer length and the chromophoric pendant, their power efficiencies and external quantum efficiencies were high (Table 2), being 20 times better than those of their structural congeres reported by Kobayashi and coworkers[15].

Conclusion

In this work, we succeeded in synthesizing soluble functional HPAs in high yields by alkyne polycyclotrimerizations initiated by CpCo(CO)$_2$-$h\nu$ and TaCl$_5$–Ph$_4$Sn catalysts. The HPAs are efficient UV emitters and excellent optical limiters. We prepared functional LPAs by WCl_6–Ph_4Sn catalyst. The LPAs are characterized by strong blue luminescence. Their multilayer EL devices emitted intensely and efficiently.

Acknowledgments

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