



Dendritic polymers

Hyperbranched polyarylenes

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Abstract

Alkyne polycyclotrimerizations are effected by tantalum- and cobalt-based catalysts, giving soluble hyperbranched polyarylenes (HPAs) with high molecular weights (M_w up to $\sim 2 \times 10^5$) in high yields (up to 99.9%). All the HPAs exhibit excellent thermal stability, losing little of their weights when heated to > 400 °C. The HPAs graphitize when pyrolyzed at 800 °C in high yields (up to 86%). Upon photoexcitation, the HPAs efficiently emit strong deep-blue and blue-green light with fluorescence quantum yields up to 98%. The HPAs strongly attenuate intense laser pulses, with their limiting performances being superior to that of C_{60} , a well-known optical limiter. **To cite this article:** *M. Häußler, C. R. Chimie 6 (2003).*

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1. Introduction

Many potential optical and electronic applications have been proposed for conjugated polymers, which have stimulated dynamic research activities on polymers with extended π -conjugations [1,2]. The frontier of conjugated polymer research is moving from linear to dendritic or hyperbranched structures [3–7]. Compared to their dendritic congeners [8,9], hyperbranched polymers enjoy such advantages as ready preparations in large scales by one-pot, single-step reaction procedures [10–12].

Different synthetic strategies have been employed for the preparation of hyperbranched polymers

[10–12]. The most commonly adopted approach is self-condensations of AB_n -type monomers with $n \geq 2$ [13–16]. This type of polymerization can be carried out in a concurrent mode or by slow addition of the monomer or even in the presence of a core molecule of B_f ($f \geq 3$). Another approach is copolymerization of A_2 monomers with B_n comonomers ($n \geq 3$) [17–19]. The stoichiometric requirements between the pairs of the functional comonomers are, however, practically difficult to meet, which often limits the growth of propagating species, resulting in the formation of oligomeric products. If the condensation proceeds in an incomplete or imperfect fashion, polymers with low degrees of branching will be produced.

We are interested in synthesizing hyperbranched polymers by transition metal-catalyzed alkyne polycy-

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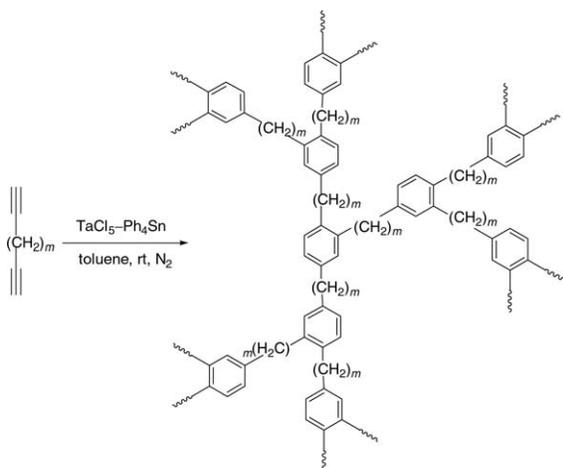


Fig. 1. Homopolycyclotrimerizations of aliphatic α,ω -diynes.

clotrimerizations [20,21]. This kind of [2 + 2 + 2] polycycloaddition reaction involves a single monomer species, suffers no stoichiometric constraints, and can thus potentially produce polymers with very high molecular weights. The resultant polymers should be highly branched because the polycyclotrimerization mechanism is intolerant of the formation of linear repeat units inside the hyperbranched cores. In our previous work, we have studied the homopolymerizations of *aliphatic* α,ω -diynes such as 1,8-nonadiyne and 1,9-decadiyne catalyzed with a binary mixture of TaCl_5 and Ph_4Sn [22, 23]. Under optimal polymerization conditions, completely soluble diyne homopolymers with high molecular weights (up to $\sim 1.4 \times 10^6$) and predominant 1,2,4-benzenetriyl core structures are obtained in high isolation yields (up to 93 wt%) [22–28]. The hyperbranched poly(alkenophenylene)s (HPAPs) show outstanding thermal stability and lose little of their weights at temperatures as high as $\sim 500^\circ\text{C}$, although the phenyl rings are separated by the alkyl chains (Fig. 1).

In this work, we have extended our research efforts to the polycyclotrimerizations of *aromatic* diynes. In this account, we will briefly summarize our results on the homopolycyclotrimerizations of organic and organometallic diynes (Fig. 2) and their copolycyclotrimerizations with aromatic and aliphatic monoynes (Fig. 3). Different from the isolated benzene rings in the HPAPs discussed above, here the ‘new’ benzene rings formed by cyclotrimerization and the ‘old’ aromatic moieties from the monomers are interconnected

in the hyperbranched polyarylenes (HPAs). This enhances the electronic communications in the HPAs and endows them with efficient light-emitting and excellent optical-limiting properties.

2. Synthesis

We designed and synthesized a number of organic and organometallic diynes (**1–29**) and monoynes (**I–VII**) with varying aromatic rings and functional groups [29–39]. Most of the monomers are prepared in high isolation yields by palladium-catalyzed coupling reactions of silylacetylenes with dihaloarenes followed by base-catalyzed desilylations. We first checked the homopolymerization behaviors of the diynes. As can be seen from Table 1, the diynes containing carbazole functional groups (**1–4**) can be homopolymerized with the cobalt catalyst under UV irradiation into their corresponding HPAs (**P1–P4**) in high isolation yields (up to 99.9 wt %). The metallole-containing organometallic diynes (**5** and **6**) can be polymerized with $\text{TaCl}_5\text{–Ph}_4\text{Sn}$ at room temperature (Table 1, Nos. 5 and 6). The polymerizations of the silyldiynes are effected by TaBr_5 , giving HPAs **P7–P11** with high molecular weights (M_w up to $\sim 2.1 \times 10^5$; noting that the M_w here is calibrated by polystyrene standards and that the real absolute value can be much higher than the underestimated relative value [22]). The homopolymerizations of aromatic diynes **12–29** all proceeded rapidly but the resultant polymeric products are partially or completely insoluble due to the involved crosslinking reactions. The large free volumes and the irregular molecular structures created by the nonlinear carbazolyl, metallolyl, and silyl groups may have conferred the excellent solubility on homo-HPAs **P1–P11**.

To suppress the crosslinking reactions and to improve the polymer solubility, we copolymerized the aromatic diynes with monoynes. All the copolycyclotrimerizations underwent smoothly, giving completely soluble co-HPAs of high molecular weights (M_w up to $\sim 1.8 \times 10^5$) in high yields (up to 99.7%). 1-Alkynes (**I–IV**) are generally better comonomers than 1-arylacetylenes (**V–VII**) when the molecular weights of the HPAs are concerned. For example, when 4,4'-biphenyldiyne (**19**) copolymerizes with 1-octyne (**II**) in the presence of $\text{TaCl}_5\text{–Ph}_4\text{Sn}$, HPA **P19/II** of high molecular weight is produced (Table 2, No. 12). Similarly, a high molecular weight HPA (**P19/IV**) is ob-

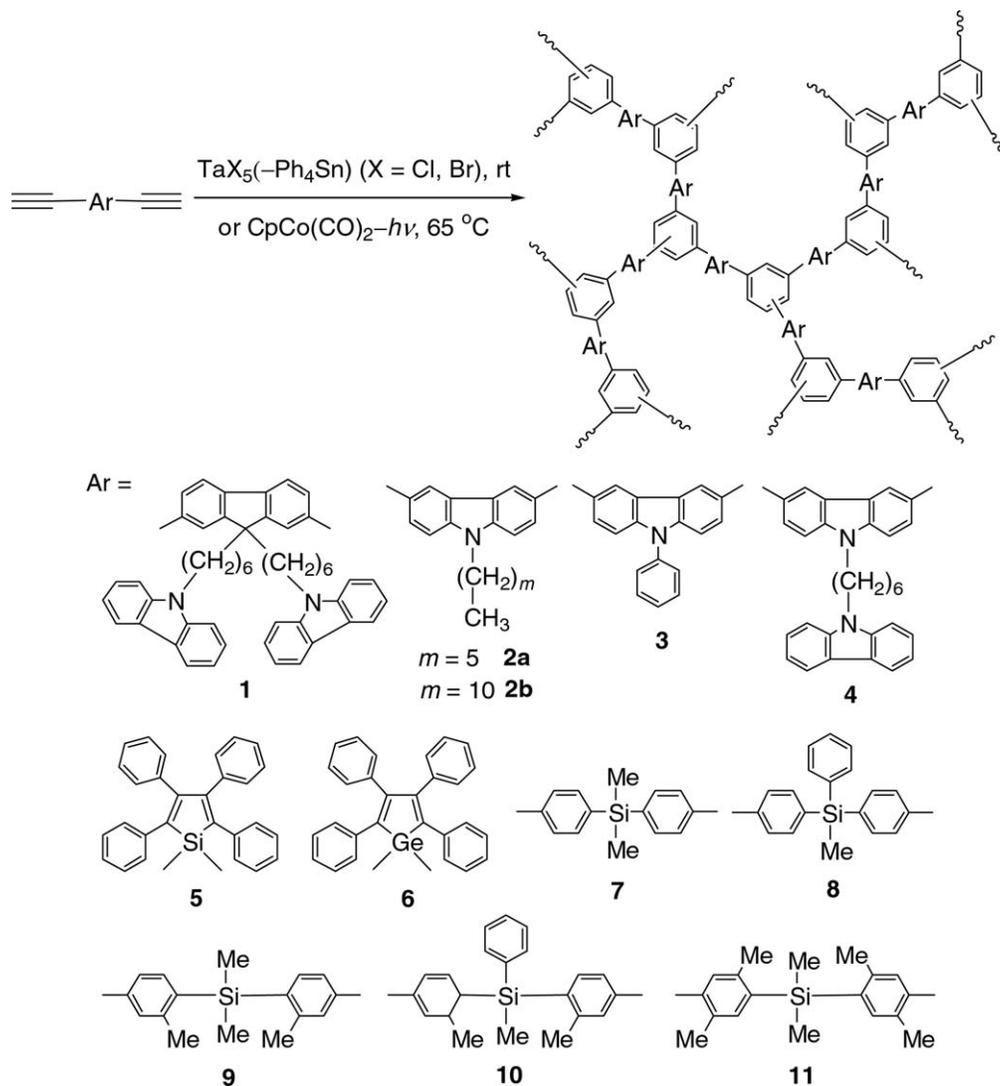


Fig. 2. Homopolycyclotrimerizations of aromatic diynes.

tained from the cobalt-catalyzed copolymerization of **19** with **IV**, a liquid crystalline 1-alkyne [39]. On the other hand, none of the copolymerizations of **19** (an aromatic diyne) with aromatic monoynes **V–VII** results in the formation of high molecular weight HPAs (Table 2, Nos. 14–16). This is possibly due to the electronic effects in the copolycyclotrimerization reactions. The electron-donating alkyl groups make the triple bonds of 1-alkynes electronically rich, which are likely to favorably interact with the electron-poor aromatic diynes [40], thus promoting the formation of high molecular weight HPA products.

3. Structure

All the HPAs give analytic data satisfactorily corresponding to their expected molecular structures [32,35,41–56]. Fig. 4 shows an example of the IR spectrum of co-HPA **P16/V**; the data for one of its monomers, i.e., **16**, is also given in the same figure for the purpose of comparison. The $\equiv\text{C-H}$ and $\text{C}\equiv\text{C}$ stretching vibrations of **16** occur at 3270 and 2100 cm^{-1} , respectively (Fig. 4A); these peaks are completely disappeared in the spectrum of its polymer (Fig. 4B). The absorption peaks associated with the

Table 1
Homopolycyclotrimerizations of aromatic diynes^a

No.	HPA	Catalyst	Yield (wt %)	M_w^b	M_w/M_n^b
1	P1	CpCo(CO) ₂ – <i>hν</i>	70.1	7800	3.8
2	P2a	CpCo(CO) ₂ – <i>hν</i>	71.3	5000	1.8
3	P3	CpCo(CO) ₂ – <i>hν</i>	99.9	2700	3.9
4	P4	CpCo(CO) ₂ – <i>hν</i>	83.7	4000	2.9
5	P5	TaCl ₅ –Ph ₄ Sn	83.0	5300	1.6
6	P6	TaCl ₅ –Ph ₄ Sn	47.0	5200	1.8
7	P7^c	CpCo(CO) ₂ – <i>hν</i>	28.1	11 800	1.4
8	P7^c	TaBr ₅	83.6	44 600	4.2
9	P8	TaBr ₅	80.3	42 200	3.5
10	P9	TaBr ₅	94.1	47 300	4.2
11	P10	TaBr ₅	81.2	209 400	10.7
12	P11	TaBr ₅	39.4	15 100	2.2

^a Carried out in toluene in an atmosphere of dry nitrogen for 12 h at 65 °C (for the Co catalyst) or room temperature (for the Ta catalysts); [diyne] = 0.1 M, [catalyst] = 10 mM.

^b Determined by GPC in THF on the basis of a polystyrene calibration.

^c Referred to as **P7–Co** or **P7–Ta** in the discussions in the text.

Table 2
Copolycyclotrimerizations of diynes with monoynes^a

No.	HPA	Catalyst	Yield (wt %)	M_w^b	M_w/M_n^c
1	P1/II	TaBr ₅ –Ph ₄ Sn	84.6	163 400	3.0
2	P2a/II	TaBr ₅ –Ph ₄ Sn	88.3	13 200	3.7
3	P3/II	TaCl ₅ –Ph ₄ Sn	84.4	28 700	7.0
4	P4/II	TaCl ₅ –Ph ₄ Sn	96.6	6800	3.8
5	P5/II	TaCl ₅ –Ph ₄ Sn	85.3	5800	1.7
6	P6/II	TaCl ₅ –Ph ₄ Sn	41.0	4500	8.5
7	P12/III	TaCl ₅ –Ph ₄ Sn	76.1	67 200	9.6
8	P13/I	TaCl ₅ –Ph ₄ Sn	94.7	97 300	3.5
9	P14/I	TaCl ₅ –Ph ₄ Sn	86.6	37 410	3.7
10	P16/V	TaBr ₅ –Ph ₄ Sn	75.4	21 000	3.1
11	P18/II	TaCl ₅ –Ph ₄ Sn	65.5	33 500	8.1
12	P19/II	TaCl ₅ –Ph ₄ Sn	68.9	183 100	5.6
13	P19/IV	CpCo(CO) ₂ – <i>hν</i>	84.9	28 600	5.8
14	P19/V	CpCo(CO) ₂ – <i>hν</i>	73.6	4300	1.6
15	P19/VI	TaCl ₅ –Ph ₄ Sn	31.3	7000	3.8
16	P19/VII	TaCl ₅ –Ph ₄ Sn	72.5	9900	6.0
17	P20/III	CpCo(CO) ₂ – <i>hν</i>	42.0	12 200	3.7
18	P21/V	TaBr ₅ –Ph ₄ Sn	98.1	10 500	3.1
19	P22/II	TaCl ₅ –Ph ₄ Sn	60.0	32 700	6.7
20	P23/II	TaCl ₅ –Ph ₄ Sn	97.0	28 600	1.7
21	P24/III	CpCo(CO) ₂ – <i>hν</i>	97.3	27 200	3.8
22	P25/II	CpCo(CO) ₂ – <i>hν</i>	62.7	15 300	2.6
23	P26/III	TaCl ₅ –Ph ₄ Sn	70.1	72 300	5.7
24	P27/III	TaCl ₅ –Ph ₄ Sn	74.1	93 400	8.7
25	P28/II	TaBr ₅ –Ph ₄ Sn	99.7	28 100	5.0
26	P29/III	CpCo(CO) ₂ – <i>hν</i>	79.6	14 100	2.7

^a Carried out in toluene under nitrogen for 12 h at room temperature (for the Ta catalysts) or 65 °C (for the Co catalyst); [diyne] = 0.1 M, [monoynne] = 0.09–0.31 M, [catalyst] = 10–20 mM.

^b Determined by GPC in THF on the basis of a polystyrene calibration.

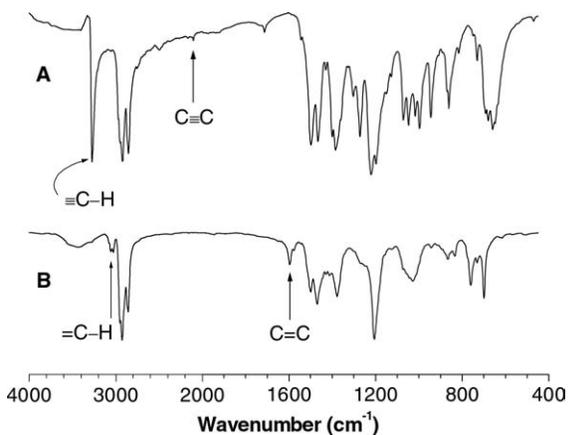


Fig. 4. IR spectra of (A) diyne **16** and (B) co-HPA **P16/V**.

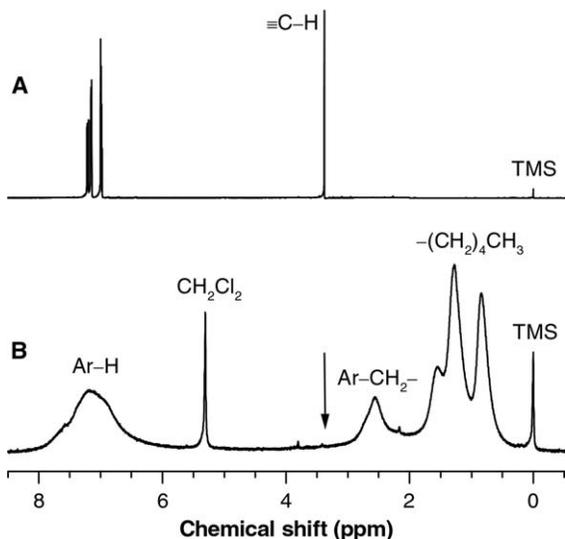


Fig. 5. ^1H NMR spectra of (A) diyne **18** in chloroform- d and (B) HPA **P18/II** in dichloromethane- d_2 .

HPA possesses an irregular stereostructure. Accompanying the polycyclotrimerization, the propargyl protons of monoyne **II** are transformed to the benzyl ones, whose absorption is observed at δ 2.55. The absorption peaks at δ 2–0.5 are unambiguously due to the resonance of the aliphatic protons of the pentyl group originally from the monoyne **II**.

An example of the ^{13}C NMR spectrum of co-HPA **P12/V**, along with that of one of its monomers (**12**), is shown in Fig. 6. The acetylenic carbons of **12** absorb at δ 83.7 and 79.8 (Fig. 6A), while those of **V** resonate at δ 80.7 and 70.5. However, no acetylenic absorption peak is observed in the spectrum of **P12/V** (Fig. 6B).

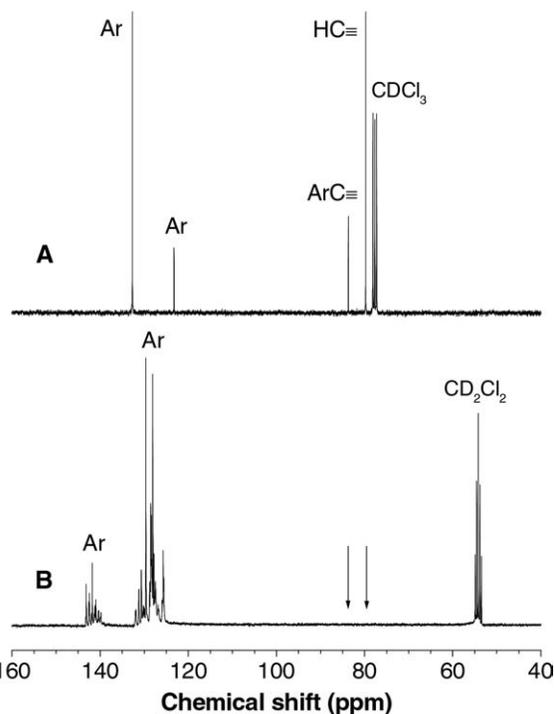


Fig. 6. ^{13}C NMR spectra of (A) diyne **12** in chloroform- d and (B) HPA **P12/V** in dichloromethane- d_2 .

On the other hand, many peaks are seen in the spectral region of aromatic carbon absorptions. These resonance peaks are the sum of the absorptions of aromatic carbons of the ‘old’ phenyl ring of monomer **12** and the ‘new’ ones of co-HPA **P12/V** formed by alkyne polycyclotrimerization.

4. Properties

The thermal stabilities of the HPAs are evaluated by thermogravimetric analysis (TGA). Fig. 7 shows a few examples of their TGA thermograms and Table 3 summarizes their thermal analysis data. The HPAs are thermally very stable: for instance, **P7-Co** loses merely 5% of its weight at a temperature as high as 595 °C. All the polymers, except for **P1/II** and **P18/II**, graphitize in > 50% yields upon pyrolysis at 800 °C, with **P19/I** carbonized in a yield as high as 86 wt % (Table 3, No. 11). The thermal stabilities of the HPAs are similar to that of poly(*p*-phenylene) (PPP) but different from those of polyacetylenes such as poly(1-

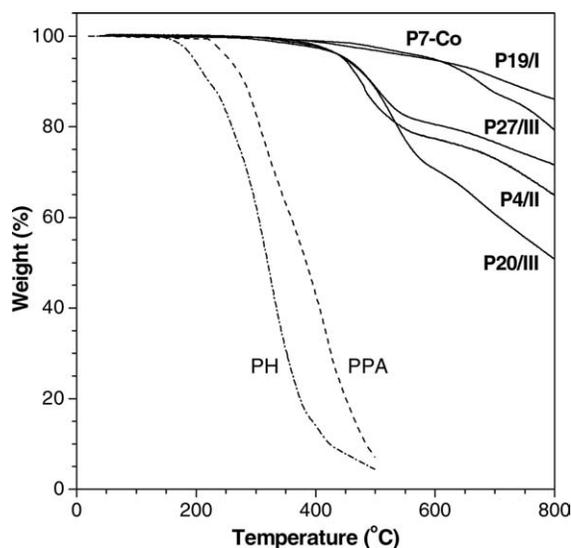


Fig. 7. TGA thermograms of hyperbranched polyarylenes; the data for linear poly(1-hexyne) (PH) and poly(phenylacetylene) (PPA) are shown for comparison.

hexyne) (PH) and poly(phenylacetylene) (PPA; a linear polymer of monoyne **V**): PPP is stable up to ~550 °C [3–7], whereas PPA and PH start to decompose at temperatures as low as 220 and 150 °C, respectively [57]. PPP is made of thermally stable aromatic rings, but PPA and PH consist of labile polyene chains. The excellent thermal stabilities of the HPAs verify that they are composed of aromatic rings instead of polyene chains.

Careful examination of the TGA data in Table 3 reveals that the co-HPAs with shorter alkyl chains generally have better thermal stabilities. Thus, **P19/I**, a co-HPA of 4,4'-biphenyldiyne (**19**) with 1-heptyne (**I**; a monoyne with a short alkyl chain), is highly resistant to pyrolysis ($T_d = 585$ °C, $W_r = 86\%$), while its congener **P19/II**, a co-HPA of **19** with 1-octyne (**II**; a monoyne with a longer alkyl chain), shows lower T_d and W_r (Table 3, Nos. 11 and 12). **P19/IV** contains even longer alkyl chains and hence shows even lower T_d and W_r . Similar general trend is observed in the **P26/x** series with $x = \mathbf{I}$ (1-heptyne), **II** (1-octyne), and **III** (1-dodecyne) (Table 3, Nos. 16–18), although all

Table 3
Thermal and optical properties of hyperbranched polyarylenes

No.	HPA	T_d^a (°C)	W_r^b (wt %)	λ_{em}^c (nm)	Φ_F^d (%)	T (%)	F_L^e (mJ/cm ²)	$F_{i,m}/F_{i,m}^f$
1	P1/II	414	16	402	90	72	2300	0.63
2	P2a/I	487	58	400	7	84	1400	0.36
3	P2b/I	404	83	398	10	83	635	0.36
4	P2b/IV	474	64	399	20	83	577	0.35
5	P3/II	477	70	398	21	49	1034	0.19
6	P4/II	463	65	396	28	46	1050	0.17
7	P7-Ta	564	72	397	1	84	2500	0.40
8	P7-Co	595	79	402	1	85	1500	0.43
9	P12/II	452	71 ^g	400	94	59	1016	0.15
10	P18/II	440	0	486	14	48	802	0.13
11	P19/I	585	86	398	49	58	343	0.21
12	P19/II	463	66	400	74	69	1265	0.15
13	P19/IV	412	50	397	9	92	900	0.52
14	P20/III	449	51	399	46	64	260	0.11
15	P24/III	458	53	399	15	44	155	0.08
16	P26/I	467	75	400/31	66	126	0.11	
17	P26/II	451	70	400	86	48	1000	0.15
18	P26/III	459	65	400	98	65	509	0.11

^a Temperature for 5 % weight loss.

^b Weight of the residue left at 800 °C.

^c Peak of emission spectrum in dichloromethane solution.

^d Quantum efficiency using 9,10-diphenylanthracene ($\Phi_F = 90\%$ in cyclohexane) as a standard.

^e Optical limiting threshold (incident fluence at which nonlinear transmittance is 50% of initial linear one).

^f Signal suppression (ratio of saturated transmitted fluence to maximum incident fluence).

^g At 750 °C.

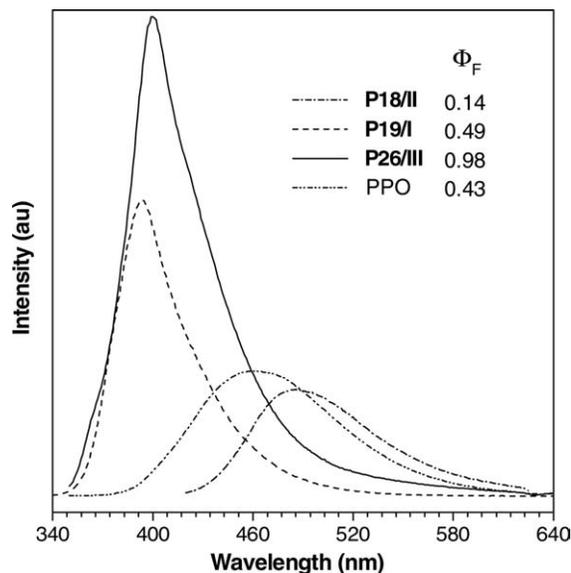


Fig. 8. Photoluminescence spectra of dichloromethane solutions of **P18/II**, **P19/I**, and **P26/III** and a THF solution of poly(1-phenyl-1-octyne) (PPO). Concentration: 2 mM; excitation wavelengths (nm): 345 (**P19/I** and **P26/III**), 355 (PPO), and 412 (**P18/II**).

the HPAs are thermally very stable, compared to ‘common’ organic polymers.

The HPAs luminesce when photoexcited, examples of their photoluminescence (PL) spectra being given in Fig. 8. The HPA carrying thienyl chromophores (**P18/II**) emits a blue-green light of 486 nm, while that with biphenyl ones (**P19/I**) emits a deep-blue light of 398 nm. More efficient PL is observed in **P26/III**, a co-HPA containing fluorenyl chromophores. The emission intensities of co-HPAs **P19/I** and **P26/III** are obviously higher than that of poly(1-phenyl-1-octyne), a well-known luminescent disubstituted polyacetylene [58,59]. The PL efficiencies of the HPAs change with their molecular structures, with **P1/II**, **P12/II**, **P19/II**, **P26/II**, and **P26/III** exhibiting fluorescence quantum yields (Φ_F) as high as > 70% (Table 3). The emission of **P26/III** is especially efficient, with a Φ_F value (98%) well approaching unity.

Molecules of fused aromatic rings may limit optical power [60–62]. The HPAs are aromatic macromolecules and are hence good optical limiters. As can be seen from the examples given in Fig. 9, the HPAs effectively attenuate the power of intense 532 nm laser pulses. The transmitted fluence of **P20/III** initially increases with incident fluence in a linear fashion. It commences to deviate from linearity at an incident

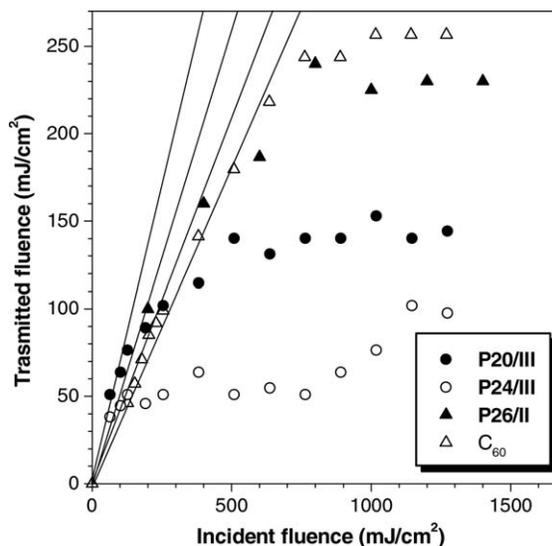


Fig. 9. Optical limiting responses to 8-ns, 532-nm optical pulses, of dichloromethane solutions of hyperbranched polyarylenes **P20/III**, **P24/III**, and **P26/II**; concentration: 0.86 mg ml⁻¹. Data for a toluene solution C₆₀ (0.16 mg ml⁻¹) is shown for comparison.

fluence of ~260 mJ cm⁻² and reaches a saturation plateau at 140 mJ cm⁻². Its optical limiting threshold (F_L) and signal suppression ($F_{t,m}/F_{i,m}$; Table 3, No. 14) are superior to those of C₆₀, a well-known optical limiter [63]. Compared to **P20/III**, **P24/III** is a better optical limiter but **P26/II** is poorer one. This indicates that the optical limiting performance of an HPA is sensitive to a change in its molecular structure, offering the opportunity to tune its optical limiting properties through molecular engineering endeavor.

5. Conclusion

New organic and organometallic HPAs are successfully synthesized in high isolation yields by one-pot, transition metal-catalyzed homopolycyclotrimerizations of functional aromatic diynes and their copolycyclotrimerizations with monoynes. All the homo- and co-HPAs are completely soluble in common organic solvents such as THF, dichloromethane, chloroform, and toluene. Thanks to their conjugated molecular structures, the HPAs are efficient light emitters. The aromatic polymers are both thermally and optically stable, losing little of their weights when heated to high temperatures and showing no signs of photodegrada-

tion when shot by intense optical pulses. These remarkable attributes make the HPAs promising materials for high-tech applications.

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