

Multi-Functional Hyperbranched Poly(vinylene sulfide)s Constructed via Spontaneous Thiol–Yne Click Polymerization

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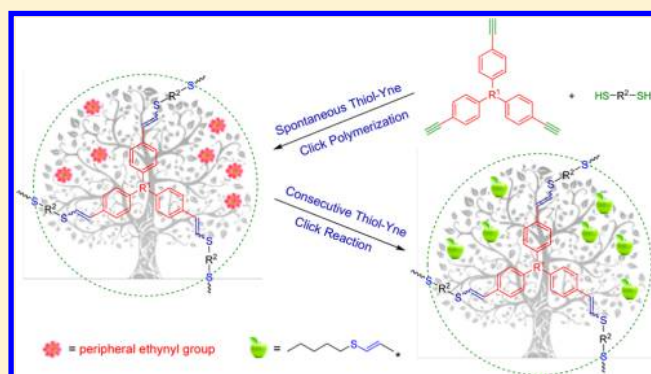
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Supporting Information

ABSTRACT: Multifunctional hyperbranched polymers have found wide applications in diverse areas. However, the preparation of these polymers is generally under harsh polymerization conditions with limited reactions. In this work, we prepared multifunctional hyperbranched poly(vinylene sulfide)s (*hb*-PVSSs) by our established efficient and spontaneous thiol–yne click polymerization for the first time. A series of *hb*-PVSSs with high molecular weights (M_w up to 63100) were obtained in high yields (up to 86%) from the polymerizations of monomers **1** and **2** with equivalent molar ratio in THF at 20 °C for 2 h. All the *hb*-PVSSs are regioregular, soluble, and thermally stable. Thanks to the unreacted ethynyl groups on their peripheries, the *hb*-PVSSs could be facily functionalized by consecutive thiol–yne click reactions. Moreover, the solid films of *hb*-PVSSs exhibit higher refractive index (RI) values ($n > 1.64$) than those of traditional optical plastics. The TPE-containing *hb*-PVSS shows unique aggregation-enhanced emission characteristic and its aggregates could be used to detect explosives with superamplification effect. Therefore, this work not only proves the universality of our developed spontaneous thiol–yne click polymerization but also provides a powerful and versatile platform for the preparation of multifunctional sulfur-containing polymers.



INTRODUCTION

Synthesis of functional polymers is an everlasting theme in polymer science because of their attractive properties and extensive applications. Generally, functional polymers were prepared by condensation, free radical, ionic, ring-opening, and coordination polymerizations, as well as postfunctionalization of preformed polymers.¹ However, most of them, if not all, were carried out under harsh conditions, which has greatly limited their applications in materials science etc. Delightfully, the concept of click chemistry proposed by Sharpless and co-workers in 2001 revolutionized the areas of synthetic chemistry including functional polymer synthesis due to its remarkable advantages, such as high efficiency, regioselectivity, mild reaction conditions, atom economy, and functionality tolerance.² Besides being applied in postfunctionalization of preformed polymers, the click reaction has been developed into a unique polymerization methodology, i.e., click polymerization, which has provided a versatile and powerful synthetic tool for the preparation of functional polymers.^{3–7}

Our groups have been engaged in the construction of functional polymers based on triple-bond building blocks.⁸ As a natural expansion, we embarked the research on alkyne-based

click polymerizations in 2006 and functional polymers were facily prepared by Cu(I)- and Ru(II)-catalyzed and metal-free azide–alkyne click polymerizations.^{9,10} Very recently, we also succeeded in establishing another alkyne-based click polymerization, i.e., catalyst-free thiol–yne click polymerization.¹¹ Simply mixing aromatic diynes and dithiols with equivalent molar ratio in THF at 30 °C readily produces linear poly(vinylene sulfide)s (PVSSs) with high molecular weights in excellent yields. Thanks to its radical reaction mechanism, this polymerization undergoes via a spontaneous fashion, which has remarkably simplified the reaction conditions and will facilitate the preparation of functional polymers.

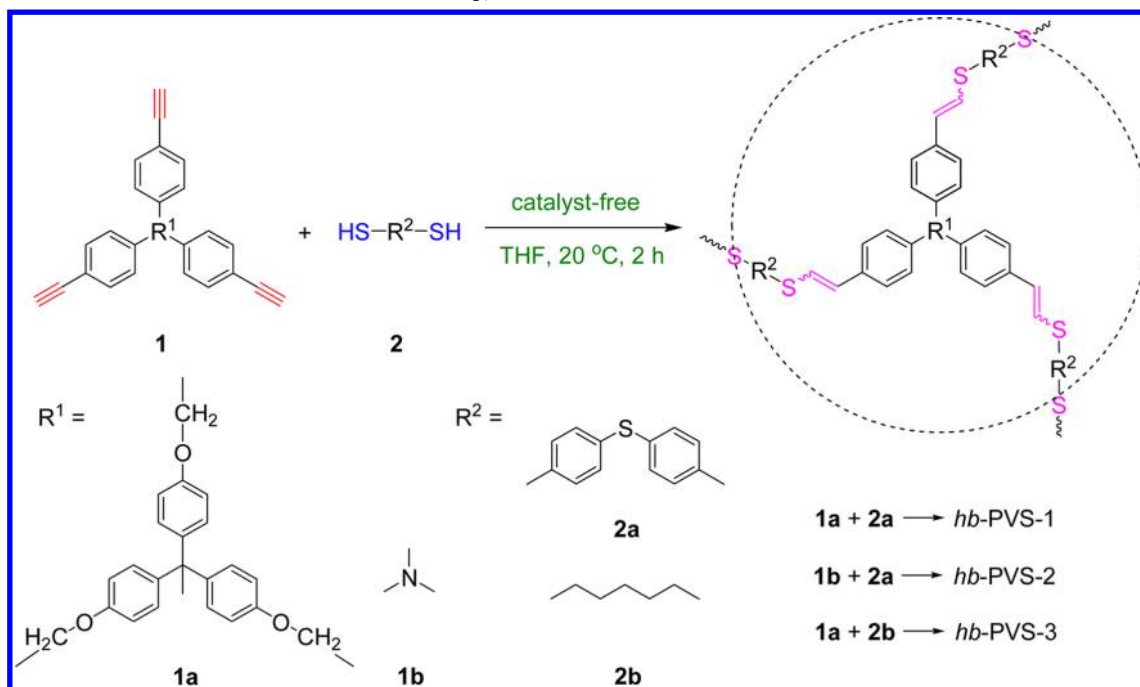
In this paper, we further demonstrated the efficiency of this spontaneous thiol–yne click polymerization and successfully applied it in the preparation of hyperbranched PVSSs (*hb*-PVSSs), which are expected to exhibit different properties with their linear counterparts due to their compact structures, tridimensional scaffold, multi end-functionalities, and internal space and

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Scheme 1. Syntheses of Hyperbranched Poly(vinylene sulfide)s by Spontaneous Thiol–Yne Click Polymerizations of Monomers 1 and 2 via $A_3 + B_2$ Co-Monomer Strategy



binding sites etc.¹² All the *hb*-PVSs with high molecular weights and regioregularity were obtained in high yields under the optimal polymerization conditions. They also enjoy good solubility and thermal stability, and exhibit multifunctional properties. Moreover, the ethynyl terminated *hb*-PVSs can be further functionalized via consecutive thiol–yne click reactions.

RESULTS AND DISCUSSION

Monomer Preparation. In order to obtain *hb*-PVSs, A_3 (1a and 1b) + B_2 (2a and 2b) or A_4 (1c) + B_2 (2a and 2b) comonomer strategies were used (A and B refer to the alkyne and thiol monomers, respectively, Schemes 1 and 2) Monomers 1a and 2a were used as model monomers to optimize the polymerization conditions, and monomers 1b, 1c, and 2b were applied to prove the universality of this powerful spontaneous thiol–yne click polymerization and to prepare multifunctional polymers.

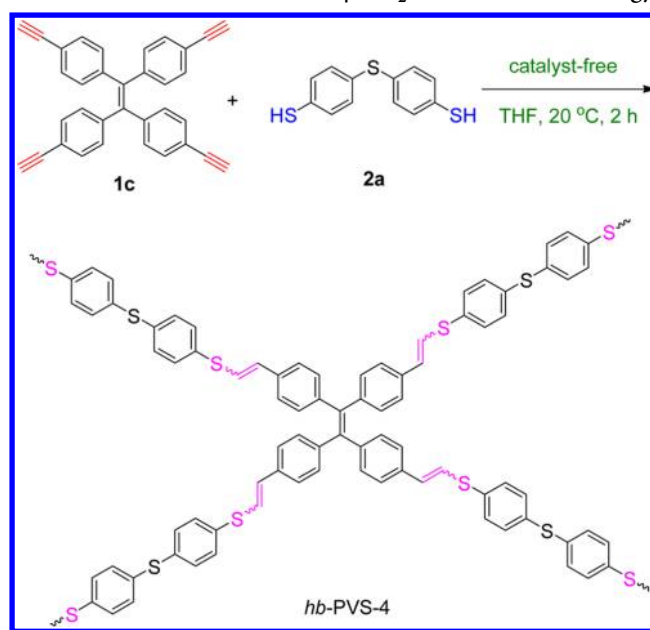
Click Polymerization. An ineluctable problem for the preparation of hyperbranched polymers via A_n ($n = 3$ or 4) + B_2 comonomer strategy is the gelation during the polymerization. One of the solutions is to quench the polymerization reaction before the gel point.¹³ From the textbook of polymer chemistry, it is known that the gel point can be calculated from the Flory Statistics.¹⁴ Generally, for an $A_2 + B_2 + A_f$ ($f > 2$) monomers system, the Flory statistics can be simplified into eq 1:

$$(p_A)_c = \frac{1}{[r + r\rho(f - 2)]^{1/2}} \quad (1)$$

where $(p_A)_c$ is the critical reaction extent of group A, r is the mole ratio of group B and A, and ρ is the percentage of group A from monomer A_f . Specifically, in our $A_3 + B_2$ comonomer system, eq 1 can be further simplified into eq 2:

$$(p_A)_c = \frac{1}{(2r)^{1/2}} \quad (2)$$

Scheme 2. Syntheses of Hyperbranched Poly(vinylene sulfide)s by Spontaneous Thiol–Yne Click Polymerizations of Monomers 1c and 2a via $A_4 + B_2$ Co-Monomer Strategy



Therefore, the gel point is determined by the mole ratio of the monomers. If equal molar concentration of A_3 and B_2 was used, the gel point $(p_A)_c$ calculated would be 0.866. However, in this case, group B would be consumed completely and the maximal reaction extent of group A is 0.667, which is far less than $(p_A)_c$. Similarly, for $A_4 + B_2$ comonomer system, the $(p_A)_c$ was deduced to be 81.6%, whereas, the maximal reaction extent of group A is 0.50 if equal molar concentration of the monomers were used. Thus, we can overcome the problem of gelation by using equal mole ratio of alkyne and thiol monomers.

To substantiate the theoretical calculation, we carried out the polymerization of **1a** (A_3) and **2a** (B_2) with equal molar concentration (Scheme 1). As expected, no gelation occurred when the polymerization was carried out in THF at 20 °C under nitrogen for 2 h, and soluble *hb*-PVS-1 with M_w of 69 000 was obtained in 84% yield (Table 1). It is worth noting

Table 1. Effect of Monomer Mole Ratio on the Thiol–Yne Click Polymerization of **1a and **2a**^a**

entry	[1a] (mM)	[2a] (mM)	yield (%)	S ^b	M _w ^c	PDI ^c
1	50	75		gelled		
2	50	50	84	√	69 000	5.86

^aCarried out in THF at 20 °C under nitrogen for 2 h. ^bSolubility (S) tested in common used organic solvents such as THF and chloroform: √ = completely soluble. ^cEstimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; PDI = M_w/M_n ; M_n = number-average molecular weight.

that no gelation was observed even the reaction time was further prolonged to 20 h. On the contrary, severe gelation took place during reaction when the mole ratio of **1a** and **2a** was adjusted to be 2:3 (equal molar concentration of functional groups) under the same polymerization conditions. Therefore, equal molar concentration of monomers instead of functional groups was adopted in following polymerizations in this paper.

Encouraged by these preliminary results, we further optimized the polymerization conditions. Table 2 shows the

Table 2. Effect of Temperature on the Thiol–Yne Click Polymerization of **1a and **2a**^a**

entry	T (°C)	yield (%)	S ^b	M _w ^c	PDI ^c
1	0	75	√	16 200	2.38
2	20	86	√	66 900	5.34
3	40	85	√	72 800	7.11
4	60	87	Δ	86 500	9.42

^aCarried out in THF under nitrogen for 2 h; [**1a**] = [**2a**] = 50 mM. ^bSolubility (S) tested in common used organic solvents such as THF and chloroform: √ = completely soluble; Δ = partially soluble. ^cEstimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; PDI = M_w/M_n ; M_n = number-average molecular weight.

effect of temperature on the polymerization of **1a** and **2a**. The M_w and polydispersity (PDI) values of the yielded polymers increased slowly when the reaction temperature was enhanced from 20 to 60 °C while the yields remained almost unchanged (~86%). Surprisingly, the polymer with M_w of 16 200 and PDI of 2.38 could be obtained in 75% yield even when the reaction was conducted at 0 °C, indicative of the high efficiency of this polymerization. Taking the solubility and energy-saving concern into account, we chose 20 °C as the preferable polymerization temperature. Then, we sought for the most effective solvent of the polymerization. Although the PDI is a little broader, the highest M_w and yield could be obtained when the reaction was carried out in THF. Thus, we can conclude that THF is the ideal solvent (Table 3). Next, we followed the time course of the polymerization (Table 4 and Figure S1). The M_w and PDI values of the polymers increased rapidly before 2 h, and remained almost unchanged afterward due to the complete consumption of thiol groups. We thus assigned 2 h as our optimal reaction time. Finally, we investigated the effect of

Table 3. Effect of Solvent on the Thiol–Yne Click Polymerization of **1a and **2a**^a**

entry	solvent	yield (%)	S ^b	M _w ^c	PDI ^c
1	toluene	56	√	12 900	2.28
2	1,4-dioxane	82	Δ	51 200	6.73
3	chloroform	84	√	32 200	3.87
4	THF	85	√	69 700	5.84
5	DMF	62	√	5300	2.29

^aCarried out at 20 °C under nitrogen for 2 h; [**1a**] = [**2a**] = 50 mM. ^bSolubility (S) tested in common organic solvents such as THF and chloroform: √ = completely soluble; Δ = partially soluble. ^cEstimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; PDI = M_w/M_n ; M_n = number-average molecular weight.

Table 4. Time Course on the Thiol–Yne Click Polymerization of **1a and **2a**^a**

entry	t (h)	yield (%)	S ^b	M _w ^c	PDI ^c
1	0.5	68	√	8900	1.94
2	1.0	73	√	22 400	3.15
3	1.5	85	√	56 500	5.62
4	2.0	85	√	63 400	6.16
5	3.0	84	√	64 900	6.21
6	4.0	87	√	72 900	6.40
7	6.0	88	Δ	78 300	7.98

^aCarried out in THF at 20 °C under nitrogen; [**1a**] = [**2a**] = 50 mM. ^bSolubility (S) tested in common organic solvents such as THF and chloroform: √ = completely soluble; Δ = partially soluble. ^cEstimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; PDI = M_w/M_n ; M_n = number-average molecular weight.

monomer concentration on the polymerization. The M_w and yields of the products generally increased with enhancing the monomer concentration. The M_w probably became too large to be fully soluble in commonly used organic solvents when the concentration was enhanced to be 75 mM due to the high efficiency of this polymerization (Table 5). Thus, the monomer concentration of 50 mM was used for following polymerizations.

Table 5. Effect of Monomer Concentration on the Thiol–Yne Click Polymerization of **1a and **2a**^a**

entry	[1a] (mM)	yield (%)	S ^b	M _w ^c	PDI ^c
1	25	85	√	18 800	3.05
2	50	86	√	63 100	6.35
3	75	90	Δ	48 400	6.60

^aCarried out in THF at 20 °C under nitrogen for 2 h; [**1a**] = [**2a**]. ^bSolubility (S) tested in common organic solvents such as THF and chloroform: √ = completely soluble; Δ = partially soluble. ^cEstimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration; M_w = weight-average molecular weight; PDI = M_w/M_n ; M_n = number-average molecular weight.

With the optimal reaction conditions in hand, we polymerized other alkyne and thiol monomers to demonstrate the universality of this efficient thiol–yne polymerization and to prepare functional polymers (Schemes 1 and 2, Table 6). All the polymerizations propagated smoothly in a spontaneous fashion, and hyperbranched polymers of *hb*-PVS-2, *hb*-PVS-3, and *hb*-PVS-4 with high M_w (up to 61 000) were obtained in

Table 6. Spontaneous Click Polymerizations of Monomers **1** and **2**^a

entry	monomers	polymer	yield (%)	M_w^b	PDI ^b	$M_{w,a}^c$
1	1a + 2a	<i>hb</i> -PVS-1	86	63 100	6.35	1 679 000
2	1b + 2a	<i>hb</i> -PVS-2	84	59 900	6.26	4 753 000
3	1a + 2b	<i>hb</i> -PVS-3	79	10 300	2.64	117 900
4	1c + 2a	<i>hb</i> -PVS-4	86	61 000	4.96	2 435 000

^aCarried out in THF at 20 °C under nitrogen for 2 h; $[1] = [2] = 50$ mM. The polymers were precipitated in hexane/chloroform mixture (5:1 by volume). ^bEstimated by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration: M_w = weight-average molecular weight; M_w/M_n = polydispersity index (PDI); M_n = number-average molecular weight. ^cMeasured by LLS technique in THF.

good yields (up to 86%). It should be noted that GPC calibrated by linear polystyrene standards generally underestimates the molecular weights of hyperbranched polymers due to their globular architectures.¹⁵ We thus measured the absolute molecular weight ($M_{w,a}$) of the *hb*-PVSs with laser light scattering (LLS) technique (Table 6). The results show that the $M_{w,a}$ values of resultant *hb*-PVSs are 10–80-fold higher than their relative ones, which are consistent with our previous experiments.¹⁶

Structural Characterizations. Thanks to their good solubility in commonly used organic solvents, the structures of *hb*-PVSs were characterized by standard spectroscopic methods and satisfactory results corresponding to their structures were obtained. The IR spectra of *hb*-PVS-1 and its monomers **1a** and **2a** are shown in Figure 1 and discussed as an

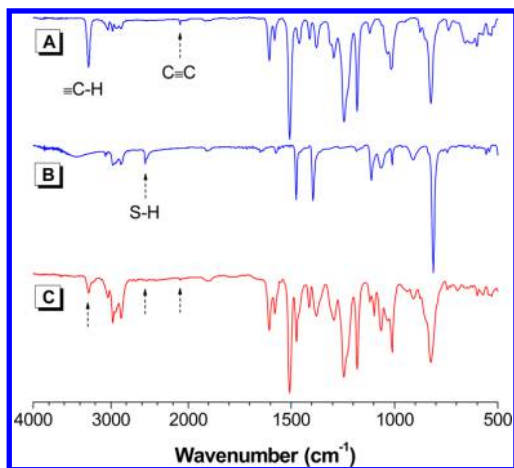


Figure 1. FT-IR spectra of monomers (A) **1a** and (B) **2a** and (C) polymer *hb*-PVS-1.

example. The S–H vibration of **2a** is observed at 2555 cm^{-1} , which disappears completely in the spectrum of *hb*-PVS-1. Meanwhile, the strong $\equiv\text{C}-\text{H}$ vibration band of **1a** locating at 3288 cm^{-1} weakened after polymerization. These results indicate that the ethynyl groups of **1a** and the mercapto groups of **2a** have been reacted by the polymerization, and the resultant polymer is rich in ethynyl groups on its periphery.

Figure 2 shows the ^1H NMR spectra of *hb*-PVS-1, its monomers **1a** and **2a**, and model compound **M1**, which was synthesized according to the procedures provided in Scheme S1. The peak at δ 3.07 in **1a** is assigned to the resonance of its ethynyl protons, which becomes weaker after polymerization. The mercapto protons of **2a** resonated at δ 3.46 are absent in the spectrum of *hb*-PVS-1. Meanwhile, new peaks assigned to the resonances of the vinylenes appeared at δ 6.45–6.76, further substantiating the conclusion drawn from the IR analysis. Moreover, by comparison with the spectrum of **M1**,

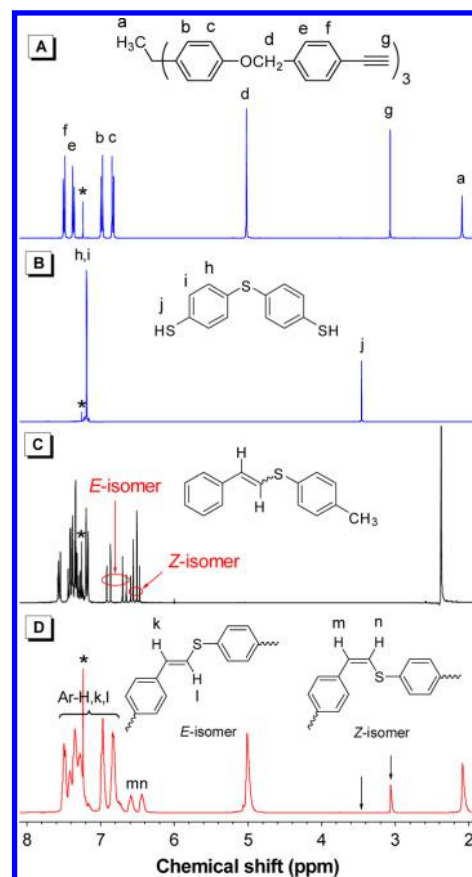


Figure 2. ^1H NMR spectra of monomers (A) **1a** and (B) **2a**, (C) model compound **M1**, and (D) polymer *hb*-PVS-1 in CDCl_3 . The solvent peaks are marked with asterisks.

we could readily assign the peaks of vinylenes protons to *E*- or *Z*-isomers. The resonance peaks at δ 6.45 and 6.60 in the spectrum of *hb*-PVS-1 are assigned to its containing *Z*-isomers, whereas, the peaks (overlapped with the aryl proton ones) around δ 6.76 are assigned to the *E*-isomers. The *E/Z* ratio of *hb*-PVS-1 is thus known as 34/66 from their integrals. It is noteworthy that no Markovnikov or double addition products were found, manifesting that the polymerization is regioselective and the formed vinyl groups are stable.

The ^{13}C NMR spectrum of *hb*-PVS-1 also displays obvious resonance peaks of the ethynyl carbon atoms at δ 83.4 and 77.4 (Figure 3), indicating that some ethynyl groups are remained in *hb*-PVS-1. This result is consistent with those obtained from the IR and ^1H NMR analyses. Similar results are observed for *hb*-PVS-2, *hb*-PVS-3, and *hb*-PVS-4 as well (Figures S2–S10).

Additionally, the degree of branching (DB) is one of the most important parameters for hyperbranched polymers, which is usually calculated from ^1H NMR spectrum. However, we

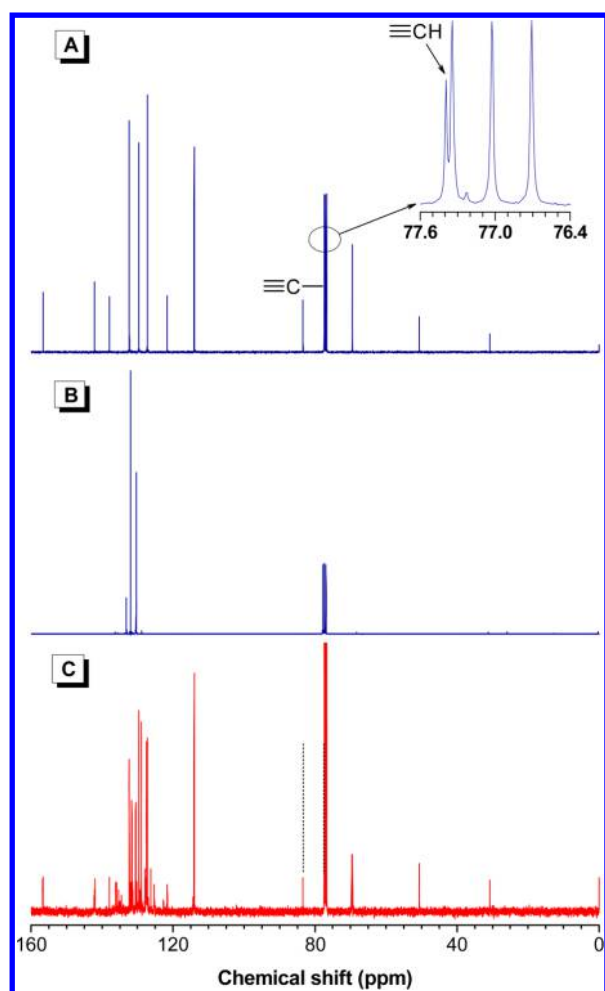


Figure 3. ^{13}C NMR spectra of monomers (A) **1a** and (B) **2a** and (C) polymer *hb*-PVS-1 in CDCl_3 .

cannot assess the DB values of *hb*-PVSs because of the poor resolution of related resonances in the ^1H NMR spectra.

Thermal Stability. The thermal properties of *hb*-PVSs were evaluated by thermogravimetric analysis (TGA) under nitrogen. As shown in **Figure 4**, all the *hb*-PVSs possess excellent thermal

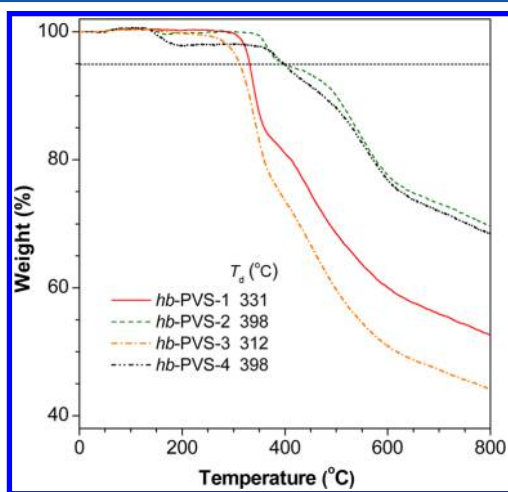


Figure 4. TGA thermograms of *hb*-PVSs. T_d represents the temperature of 5% weight loss.

stability, with temperatures for 5% weight loss higher than 310 °C. However, an obvious weight loss was found from 140 to 200 °C in the TGA curve of *hb*-PVS-4, which could be ascribed to its absorbed organic solvents probably due to its porous 3D scaffold. To verify this assumption, the N_2 absorption experiment was carried out and the surface area of *hb*-PVS-4 was calculated to be $99.33 \text{ m}^2/\text{g}$, confirming *hb*-PVS-4 possesses porous structure. In addition, the char yields of *hb*-PVS-2 and *hb*-PVS-4 are as high as 70% due to their containing aromatic conjugated structures and readily cross-linked double and triple bonds, which might be potentially used as sources to generate carbon materials with different morphologies.

Light Refractivity. Since the synthesized *hb*-PVSs are rich in aromatic rings and sulfur atoms, they are expected to possess high refractive index (RI) values (n).^{6a,17} Wavelength-dependent refractivity measurement revealed that the RI values of *hb*-PVSs are higher than 1.60 in the wavelength region of 400–1600 nm (**Figure 5**). It is worth noting that these values are

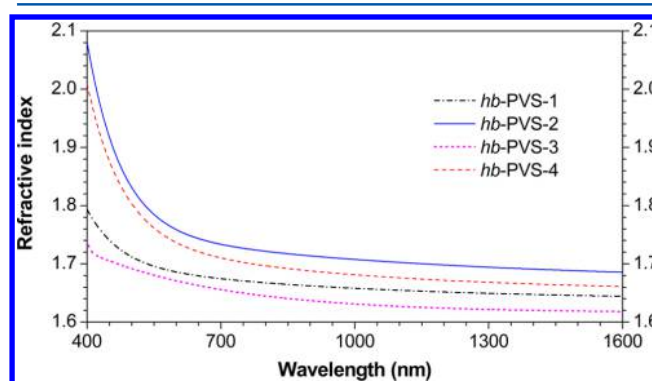


Figure 5. Light refraction spectra of thin solid films of *hb*-PVSs.

much higher than those of commercially important optical plastics. For example, the RI values of poly(methyl methacrylate), polycarbonate, and polystyrene at 589.3 nm are 1.491, 1.581, and 1.590, respectively,¹⁸ whereas, those of *hb*-PVS-1, *hb*-PVS-2, *hb*-PVS-3, and *hb*-PVS-4 at the same wavelength are 1.688, 1.763, 1.673, and 1.741, respectively. Moreover, among the *hb*-PVSs, *hb*-PVS-2 shows the best light refractivity due to its higher content of polarizable aromatic rings and hetero atoms. The high RI values of these *hb*-PVSs might enable them to find broad applications in the areas of organic optical materials.

Aggregation-Enhanced Emission (AEE). Among the synthesized *hb*-PVSs, *hb*-PVS-4 contains the unique repeating unit of tetraphenylethene (TPE), which is an archetypal moiety featured the aggregation-induced emission (AIE) characteristics.^{19,20} To check whether *hb*-PVS-4 is also AIE-active, we measured its photophysical property.

Figure 6A shows the photoluminescence (PL) spectra of *hb*-PVS-4 in THF and THF/water mixtures with different water fractions (f_w). When excited at its maximum absorption wavelength of 330 nm, the diluted THF solution of *hb*-PVS-4 emits weak light at 530 nm, which is red-shifted from that of TPE by $\sim 60 \text{ nm}$ due to the extended conjugation. The emission is progressively enhanced with its emission profiles unchanged upon gradual addition of poor solvent of water into its THF solution, manifesting the typical effect of AEE. The PL enhanced process is shown visually in the inset of **Figure 6B**.

The variation of fluorescence quantum yields (Φ_F) of *hb*-PVS-4 in the THF and THF/water mixtures was measured

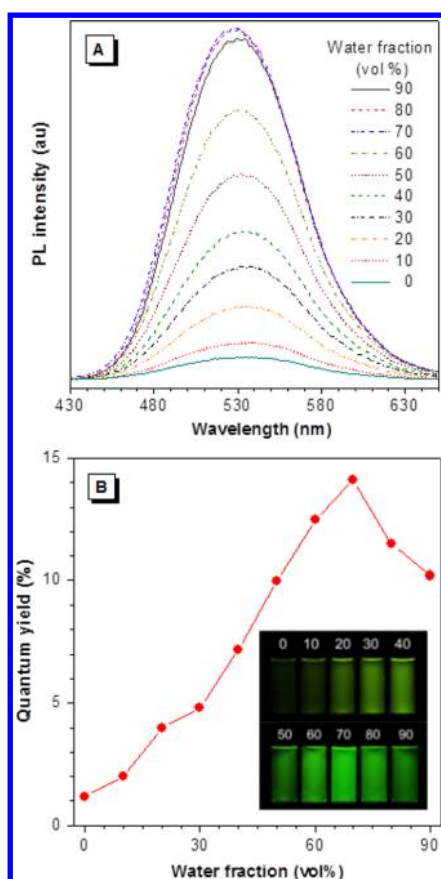


Figure 6. (A) PL spectra of *hb*-PVS-4 in THF and THF/water mixtures. Polymer concentration: 10 μ M. λ_{ex} = 330 nm. (B) Changes of quantum yields of *hb*-PVS-4 versus water fraction in THF/water mixtures. Quinine sulfate in 0.1 N H_2SO_4 (Φ_{F} = 54.6%) was used as standard. Inset: fluorescent images of *hb*-PVS-4 in THF and THF/water fractions taken under a hand-held UV lamp.

(Figure 6B) to further confirm its AEE feature. Because of its rigid structure, the Φ_{F} of *hb*-PVS-4 in pure THF is 1.19%, and increases linearly with gradual addition of water. The highest Φ_{F} value of 14.13% was obtained in the THF/water mixtures with f_{w} of 70%, which is 12-fold higher than that in pure THF. Moreover, the Φ_{F} values in the THF/water mixtures with f_{w} of 80% and 90% decrease to 11.49 and 10.20%, respectively, probably due to the precipitation of large aggregates.

Explosive Detection. As aforementioned, the AEE-active *hb*-PVS-4 is potentially useful as a chemo-sensor. Therefore, we attempted to explore the application of *hb*-PVS-4 as a fluorescence probe in sensitive detection of explosives, which is of vital importance for public security.²¹ Because of its commercial availability, 2,4,6-trinitrophenol (picric acid, PA) was used as a model explosive, and the aggregates of *hb*-PVS-4 in THF/water mixture with f_{w} of 90% were utilized as fluorescent probe. Figure 7A shows the PL spectra of polymer aggregates containing different amounts of PA. As a result, the emission decreased gradually but with the spectral profiles unchanged upon addition of PA, suggesting that this polymer could indeed be used to detect explosives.

The Stern–Volmer plots of relative fluorescence intensity of the polymer aggregates versus the concentration of PA could provide more detailed information about this chemo-responsive process. As shown in Figure 7B, when the concentration of PA was below 0.1 mM, linear curve with quenching constant of 22

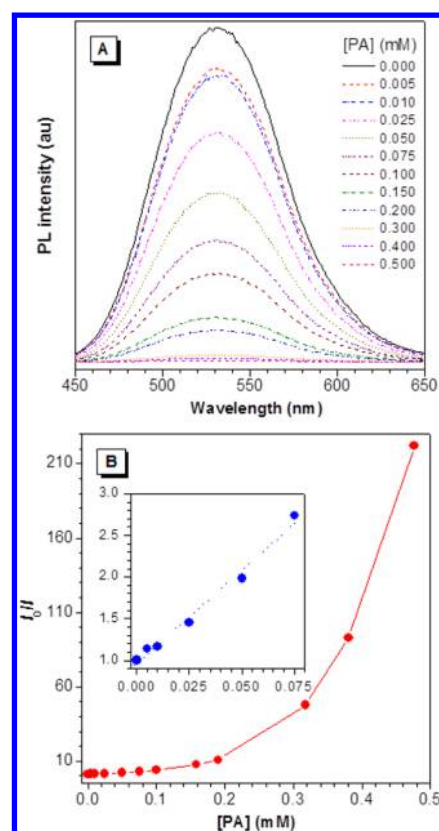
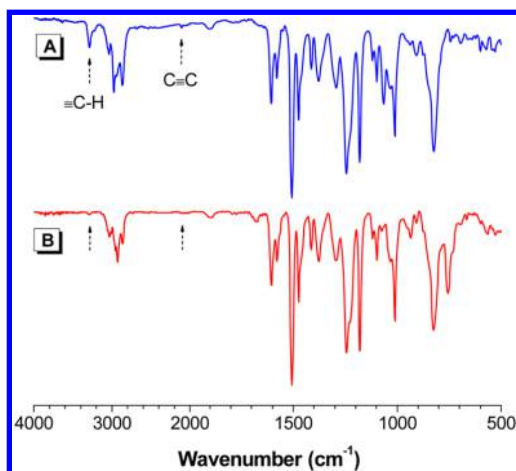
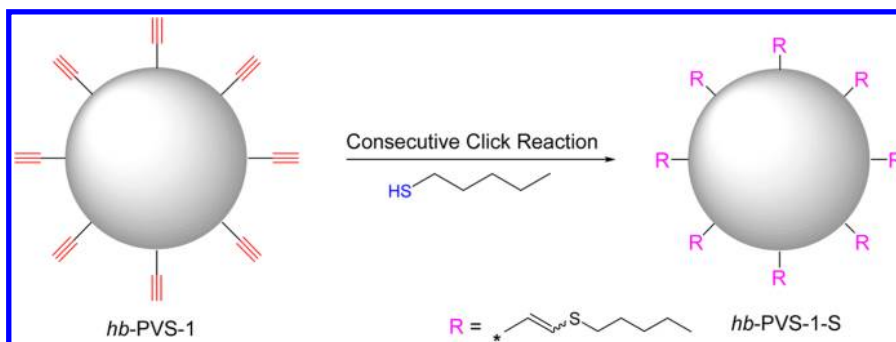


Figure 7. (A) PL spectra of *hb*-PVS-4 in THF/water mixture (1:9 v/v) containing different amounts of PA. Polymer concentration: 10 μ M. Excitation wavelength: 330 nm. (B) Stern–Volmer plots of I_0/I versus [PA] in THF/water mixture with f_{w} = 90%. I = peak intensity and I_0 = peak intensity at [PA] = 0 mM.

400 M^{-1} was recorded. In this stage, PA molecules prefer to interact with the peripheral excitons of *hb*-PVS-4 aggregates. However, with the addition of more PA, the excess portion would penetrate into small cavities which were generated from the 3D structures of the aggregates. These cavities provide massive channels for the excitons to migrate, thus accelerate the quenching by the explosives. Consequently, the Stern–Volmer plots bend upward remarkably after 0.2 mM, showing superamplification effect.^{9f} Actually, the electron-rich sulfur atoms in *hb*-PVS-4 contribute to the high quenching constant as well, due to the strong electrostatic interaction with the electron-deficient PA molecules.

Consecutive Click Reaction. According to our previous structural characterizations, the *hb*-PVSs are end-capped by ethynyl groups on their peripheries, which provide an opportunity for further functionalization of them by efficient polymer reactions, such as azide–alkyne and thiol–yne click reactions.^{9c} Since the thiol–click reactions have drawn special attention from biochemists,²² we used pentanethiol as a representative thiol compound for the consecutive click modification of *hb*-PVS-1.

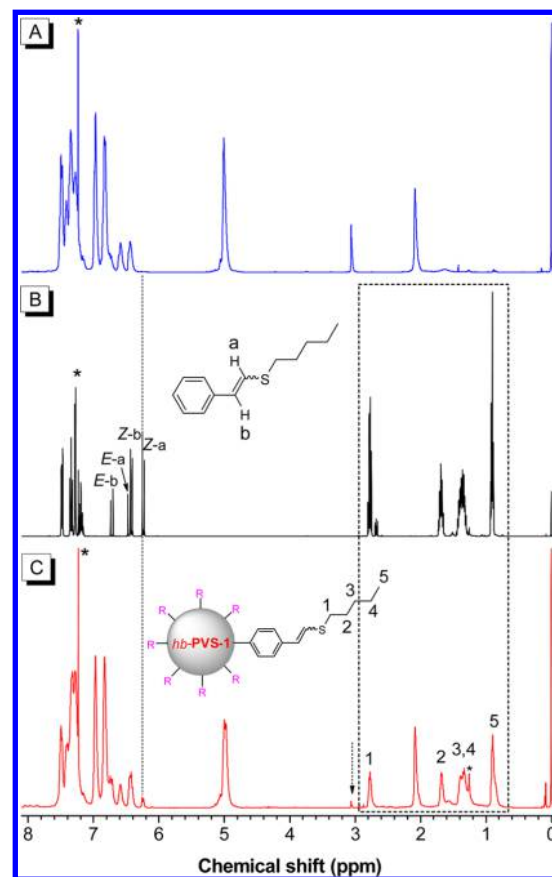
The alkyl sulfide end-capped polymer, *hb*-PVS-1-S, could be obtained by simply mixing *hb*-PVS-1 and pentanethiol in THF at room-temperature for 12 h (Scheme 3). As indicated by the GPC measurement, the M_{w} of *hb*-PVS-1-S (40100) was enhanced compared with that of *hb*-PVS-1 (18800), suggesting the success of the consecutive thiol–yne reaction. The conclusion could also be drawn by the structural analysis (Figure 8). The vibration of $\equiv\text{C}-\text{H}$ in *hb*-PVS-1 is disappeared

Scheme 3. Consecutive Thiol–Yne Click Reaction of *hb*-PVS-1Figure 8. IR spectra of polymers (A) *hb*-PVS-1 and (B) *hb*-PVS-1-S.

in the IR spectrum of *hb*-PVS-1-S. Similarly, in the ^1H NMR spectrum of *hb*-PVS-1-S (Figure 9C), we can hardly observe the resonance peak of the ethynyl protons, which appears at δ 3.07 in the spectrum of *hb*-PVS-1. Meanwhile, after comparing with the synthesized model compound of **M2** (Scheme S2), we can readily assign the new emerged peaks at δ 2.77–0.89 to the resonances of alkyl protons. These results suggest that pentanethiol has been grafted onto the periphery of *hb*-PVS-1 successfully.

CONCLUSION

In this paper, multifunctional *hb*-PVSs were prepared by our established spontaneous catalyst-free thiol–yne click polymerization. Under the optimized reaction conditions, the polymerizations of **1** and **2** with equivalent molar ratio propagated smoothly without any gelation, producing regioregular *hb*-PVSs with high absolute molecular weights ($M_{w,a}$ up to 4.753×10^6) in excellent yields (up to 86%). The *hb*-PVSs are thermally stable and soluble in commonly used organic solvents like THF and chloroform etc. Furthermore, they possess good film-forming ability and exhibit higher RI values ($n > 1.60$) than that of traditional optical plastics. The TPE-containing *hb*-PVS-4 shows the unique AEE effect and its aggregates could be used to detect explosive with superamplification effect. Finally, by taking advantage of the abundant ethynyl groups on their peripheries, *hb*-PVSs could be facilely functionalized by consecutive efficient polymer reaction, such as thiol–yne click reaction. Thanks to their multifunctionality, our prepared *hb*-PVSs are envisioned to find broad applications in biological and optoelectronic fields.

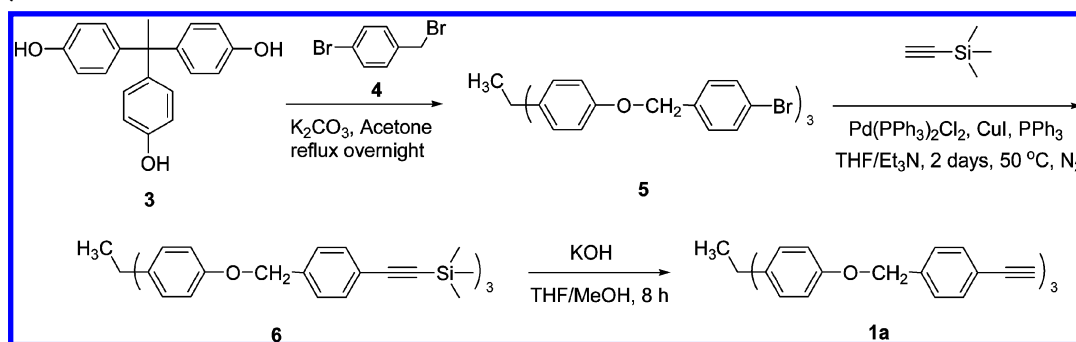
Figure 9. ^1H NMR spectra of (A) polymer *hb*-PVS-1, (B) model compound **M2**, and (C) polymer *hb*-PVS-1-S in CDCl_3 . The solvent peaks are marked with asterisks.

EXPERIMENTAL SECTION

Materials. 4,4'-Thiobisbenzenethiol, 1,5-pentanedithiol, 1,1,1-tris-(4-hydroxyphenyl)ethane, phenylacetylene, *p*-thiocresol, 1-pentane-thiol, picric acid, etc. were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification. Tetrahydrofuran (THF), toluene, and 1,4-dioxane were distilled under nitrogen under normal pressure from sodium benzophenone ketyl immediately prior to use. Triethylamine (Et_3N) was distilled and dried over potassium hydroxide. *N,N*-Dimethylformamide (DMF) was extra-dry grade.

Instruments. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer as thin films on KBr pellets. ^1H and ^{13}C NMR spectra were measured on a Bruker AV 500, Bruker AV 400, or Varian NMR 300 spectrometer in chloroform-*d* using tetramethylsilane (TMS; $\delta = 0$) as internal reference. Elemental analysis was performed on a ThermoFinnigan Flash EA 1112. Relative molecular weights (M_w and

Scheme 4. Synthetic Route to Monomer 1a



M_n) and polydispersity indices (PDI, M_w/M_n) of the polymers were estimated by a Waters PL-GPC-50 gel permeation chromatography (GPC) system equipped with refractive index (RI) detector, using a set of monodisperse polystyrenes as calibration standards and THF as the eluent at a flow rate of 1.0 mL/min. Absolute molecular weights ($M_{w,abs}$) were measured by laser light scattering (LLS) technique on a Waters Alliance e2695 Separations Module equipped with Wyatt DAWN EOS laser light scattering detector, Wyatt ViscoStar viscosity detector, Waters 2414 Refractive index Detector, and Waters 2489 UV/Visible Detector using THF as the eluent. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer TGA 7 under dry nitrogen at a heating rate of 10 °C/min. N₂ absorption experiment was measured on a Quatachrome Autosorb-1-C and surface area was calculated from the Brunauer-Emmet-Teller (BET) formula. Refractive index (RI) values were determined on a Metricon Models 2010 and 2010/M prism coupler thin film thickness/refractive index measurement system. UV-vis spectra were measured on a Varian VARY 100 Bio UV-vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. Fluorescence quantum yields (Φ_F) were estimated using quinine sulfate in 0.1 N H₂SO₄ ($\Phi_F = 54.6\%$) as standard, and the absorbance of the solutions was kept around 0.05 to avoid internal filter effect.

Monomer Preparation. All the thiol monomers were purchased from commercial sources. The alkyne monomers **1b** and **1c** were prepared according to the experimental procedures in our previous work. Monomer **1a** was synthesized for the first time and the synthetic route is shown in Scheme 4. Detailed experimental procedures for the synthesis of **1a** are given below.

1,1,1-Tris[4-(4-bromobenzyloxy)phenyl]ethane (5). To a acetone solution (60 mL) of 1,1,1-tris(4-hydroxyphenyl)ethane (**3**) (1.532 g, 5.0 mmol) and 1-bromo-4-(bromomethyl)benzene (**4**) (4.123 g, 16.5 mmol) was added 2.590 g of potassium carbonate (18.8 mmol). The resulted suspension was refluxed overnight and then filtered before cooling. The filtrate was concentrated by a rotary evaporator under reduced pressure, and the crude product was purified by recrystallization in acetone. A white solid product **5** was obtained in 88% yield (3.563 g). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.50 (m, 6H, Ar-H), 7.29 (m, 6H, Ar-H), 6.99 (m, 6H, Ar-H), 6.83 (m, 6H, Ar-H), 4.99 (s, 6H, -CH₂O-), 2.11 (s, 3H, -CCH₃).

1,1,1-Tris[4-(4-(trimethylsilyl)ethynyl)benzyloxy]phenyl]ethane (6). Into a 250 mL round-bottom flask were added PdCl₂(PPh₃)₂ (160 mg, 0.228 mmol), CuI (87 mg, 0.456 mmol), PPh₃ (180 mg, 0.684 mmol), **5** (3.063 g, 3.8 mmol), and a mixture of THF/TEA (2:1 v/v) (60 mL) under nitrogen. After the catalysts were completely dissolved, 2.5 mL (17.1 mmol) of trimethylsilylacetylene was injected. The solution was stirred at 50 °C for 48 h, and then the formed precipitates were removed by filtration and washed with diethyl ether. The filtrate was concentrated by a rotary evaporator under reduced pressure and the crude product was purified by a silica gel column chromatography using PE/dichloromethane (DCM) (5:1 v/v) as eluent. White powder of **6** was obtained 87% yield (2.849 g). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.47 (m, 6H, Ar-H), 7.37 (m, 6H, Ar-H), 6.97 (m, 6H, Ar-H), 6.85 (m, 6H, Ar-H), 5.03 (s, 6H, -CH₂O-), 2.10 (s, 3H, -CCH₃), 0.26 [s, 27H, -Si(CH₃)₃].

1,1,1-Tris[4-(4-ethynylbenzyloxy)phenyl]ethane (1a). Into a 250 mL round-bottom flask was added **6** (2.827 g, 3.3 mmol) and THF (60 mL). Then KOH (2.200 g, 39 mmol) dissolved in methanol (80 mL) was added. The mixture was stirred at room temperature overnight. After most of the solvent was evaporated, 1 M HCl solution (50 mL) was added. The aqueous solution was extracted with DCM for three times. The organic phases were combined and washed with water and brine, and then dried over MgSO₄ for an hour. After filtration and solvent evaporation, the crude product was purified by a silica gel column chromatography using PE/DCM (2:1 v/v) as eluent. White powdery product of **1a** was obtained in 45% yield (0.958 g). IR (thin film), ν (cm⁻¹): 3290 (≡C-H stretching), 2109 (weak C≡C stretching). ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.48 (m, 6H, Ar-H), 7.38 (m, 6H, Ar-H), 6.98 (m, 6H, Ar-H), 6.84 (m, 6H, Ar-H), 5.02 (s, 6H, -CH₂O-), 3.07 (s, 3H, ≡CH), 2.09 (s, 3H, -CCH₃). ¹³C NMR (100 MHz, CDCl₃), δ (ppm): 156.6, 142.1, 137.9, 132.3, 129.6, 127.2, 121.6, 113.9, 83.4, 77.3, 69.4, 50.6, 30.7. Anal. Calcd for C₄₇H₃₆O₃: C, 87.01; H, 5.59. Found: C, 86.64; H, 5.53.

Preparation of Model Compounds. The synthetic routes to model compounds are shown in Supporting Information as Schemes S1 and S2.

M1 was prepared according to the procedure depicted in our previous work. A light yellow oil of **M1** was obtained in 89% yield (202 mg). ¹H NMR (300 MHz, CDCl₃), δ (TMS, ppm): 7.57–7.17 (Ar-H), 6.91 (d, $J = 15.3$ Hz, -CH=CH- from the *E*-vinylene unit), 6.70 (d, $J = 15.3$ Hz, -CH=CH- from the *E*-vinylene unit), 6.55 (d, $J = 10.8$ Hz, -CH=CH- from the *Z*-vinylene unit), 6.50 (d, $J = 10.8$ Hz, -CH=CH- from the *Z*-vinylene unit), 2.38 (s, CH₃).

M2 was prepared from the following procedure: Into a 10 mL Schlenk tube were placed phenylacetylene (**7**, 102 mg, 1.0 mmol) and 1-pentanethiol (**9**, 104 mg, 1.0 mmol) under nitrogen. THF (1.0 mL) was injected into the tube using a hypodermic syringe, and the mixture was stirred at room temperature for 12 h. After solvent evaporation, the crude product was purified by a silica gel column chromatography using PE as eluent. Colorless oil of **M2** was obtained in 61% yield (126 mg). ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 7.49 (m, Ar-H), 7.47 (m, Ar-H), 7.36–7.19 (m, Ar-H), 6.70 (d, $J = 15.6$ Hz, -CH=CH- from the *E*-vinylene unit), 6.47 (d, $J = 15.6$ Hz, -CH=CH- from the *E*-vinylene unit), 6.40 (d, $J = 10.8$ Hz, -CH=CH- from the *Z*-vinylene unit), 6.25 (d, $J = 10.8$ Hz, -CH=CH- from the *Z*-vinylene unit), 2.76 (m, 2H, -SCH₂-), 1.68 (m, 2H, -CH₂-), 1.35 (m, 4H, -CH₂-), 0.89 (m, 3H, -CH₃).

Spontaneous Thiol-Yne Click Polymerization. All the polymerizations were carried out under nitrogen atmosphere using a standard Schlenk technique. A typical procedure for the polymerization of **1a** and **2a** is given below as an example.

Into a 10 mL Schlenk tube were placed **1a** (32.4 mg, 0.05 mmol) and **2a** (12.5 mg, 0.05 mmol). After evacuated and refilled with nitrogen for three times, THF (1.0 mL) was injected into the tube to dissolve the monomers. The mixture was stirred at 20 °C for 2 h. Then, the resultant solution was diluted with THF (2.0 mL) and added dropwise into 300 mL of hexane/chloroform mixture (5:1 by volume) through a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The

polymer was washed with hexane and dried under normal pressure at room temperature to a constant weight.

Characterization Data of *hb-PVS-1*. White powder. Yield: 86%. M_w 63 100; M_w/M_n 6.35. IR (thin film), ν (cm^{-1}): 3285, 2975, 2107, 1605, 1577, 1505, 1475, 1413, 1378, 1293, 1243, 1180, 1098, 1066, 1012, 825. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.50–7.21 (Ar–H), 6.97 (Ar–H), 6.84 (Ar–H and $-\text{CH}=\text{CH}-$ from the *E*-vinylene unit), 6.59 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 6.44 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 5.01 ($-\text{CH}_2\text{O}-$), 3.06 (residual $\equiv\text{C}-\text{H}$), 2.09 ($-\text{CCH}_3$). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 156.7, 142.0, 137.9–121.5, 113.9, 83.4, 77.2, 69.4, 50.6, 30.7.

Characterization Data of *hb-PVS-2*. Pale yellow powder. Yield: 84%. M_w 59 900; M_w/M_n 6.26. IR (thin film), ν (cm^{-1}): 3290, 2972, 2101, 1597, 1503, 1475, 1323, 1282, 1176, 1098, 1066, 1012, 833, 563. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.34 (Ar–H), 7.02 (Ar–H and $-\text{CH}=\text{CH}-$ from the *E*-vinylene unit), 6.72 ($-\text{CH}=\text{CH}-$ from the *E*-vinylene unit), 6.53 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 6.35 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 3.03 (residual $\equiv\text{C}-\text{H}$). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 145.9, 133.2, 131.6, 130.3, 130.0, 124.2, 123.5, 116.3, 83.6, 77.2.

Characterization Data of *hb-PVS-3*. White powder. Yield: 79%. M_w 10 300; M_w/M_n 2.64. IR (thin film), ν (cm^{-1}): 3285, 2927, 1605, 1506, 1460, 1412, 1376, 1291, 1244, 1179, 1013, 826, 729. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.47 (Ar–H), 7.38–7.27 (Ar–H), 6.97 (Ar–H), 6.82 (Ar–H), 6.69 ($-\text{CH}=\text{CH}-$ from the *E*-vinylene unit), 6.41 ($-\text{CH}=\text{CH}-$ from the *E*- and *Z*-vinylene units), 6.21 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 5.00 ($-\text{CH}_2\text{O}-$), 3.07 (residual $\equiv\text{C}-\text{H}$), 2.78 ($-\text{SCH}_2-$), 2.08 ($-\text{CCH}_3$), 1.70 ($-\text{CH}_2-$), 1.55 ($-\text{CH}_2-$). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 156.8, 142.0, 132.3, 129.6, 128.8, 127.9, 127.4, 127.2, 125.6, 114.0, 83.4, 77.2, 69.7, 50.6, 35.6, 32.4, 30.7, 29.8.

Characterization Data of *hb-PVS-4*. Yellow powder. Yield: 86%. M_w 61 000; M_w/M_n 4.96. IR (thin film), ν (cm^{-1}): 3293, 2955, 2107, 1575, 1503, 1474, 1388, 1359, 1098, 1066, 1011, 838, 812. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.25 (Ar–H), 6.97 (Ar–H), 6.76 ($-\text{CH}=\text{CH}-$ from the *E*-vinylene unit), 6.63 ($-\text{CH}=\text{CH}-$ from the *E*-vinylene unit), 6.48 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 6.41 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 3.04 (residual $\equiv\text{C}-\text{H}$). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 134.8, 131.6, 131.3, 130.5, 128.4, 125.6, 120.5, 83.6, 77.7.

Consecutive Thiol–Yne Click Reaction. Into a 10 mL Schlenk tube was placed *hb-PVS-1* (44.9 mg, $M_w = 18\,800$, PDI = 3.11). After evacuated and refilled with nitrogen for three times, THF (2.0 mL) was injected into the tube to dissolve the parent polymer. Then 1-pentanethiol (12.4 μL , 10.4 mg, 0.1 mmol) was injected via a hypodermic syringe. The mixture was stirred at room temperature for 12 h. The resultant solution was diluted with THF (2.0 mL) and then added dropwise into 300 mL of hexane/chloroform mixture (5:1 by volume) through a cotton filter under stirring. The precipitate was allowed to stand overnight and then collected by filtration. The polymer was washed with hexane and dried under normal pressure at room temperature to a constant weight. White powder of *hb-PVS-1-S* (46.2 mg) was obtained.

Characterization Data of *hb-PVS-1-S*. White powder. M_w 40 100; M_w/M_n 4.43. IR (thin film), ν (cm^{-1}): 2926, 1605, 1577, 1506, 1473, 1413, 1377, 1294, 1244, 1178, 1098, 1009, 935, 824, 755. ^1H NMR (400 MHz, CDCl_3), δ (TMS, ppm): 7.49–7.28 (Ar–H), 6.97 (Ar–H), 6.83 (Ar–H), 6.74 ($-\text{CH}=\text{CH}-$ from the *E*-vinylene unit), 6.58 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 6.44 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 6.42 ($-\text{CH}=\text{CH}-$ from the *E*- and *Z*-vinylene units), 6.25 ($-\text{CH}=\text{CH}-$ from the *Z*-vinylene unit), 4.97 ($-\text{CH}_2\text{O}-$), 3.06 (residual $\equiv\text{C}-\text{H}$), 2.77 ($-\text{SCH}_2-$), 2.08 ($-\text{CCH}_3$), 1.67 ($-\text{CH}_2-$), 1.35 ($-\text{CH}_2-$), 0.89 ($-\text{CH}_3$).

Preparation of Polymer Aggregates. For the Aggregation enhanced emission (AEE) measurement, a stock solution of *hb-PVS-4* in THF (1×10^{-4} M) was first prepared. Aliquots of this stock solution were transferred into volumetric flasks (10 mL), into which appropriate volumes of THF and water were added dropwise under vigorous stirring to furnish 1×10^{-5} M solutions with different water

contents (0–90 vol %). UV and PL spectra were measured immediately after the solutions were prepared.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b01868.

Time course on the thiol–yne polymerization of **1a** and **2a**, detailed synthetic routes to model compounds **M1** and **M2**, FT-IR and ^1H and ^{13}C NMR spectra of *hb-PVS-2*, *hb-PVS-3*, and *hb-PVS-4*, and the BET plot of *hb-PVS-4* calculated from N_2 absorption (PDF)

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Notes

The authors declare no competing financial interest.

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