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Comprehensive Report

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Functional Hyperbranched Polythioamides Synthesized from Catalyst-free Multicomponent Polymerization of Elemental Sulfur[†]

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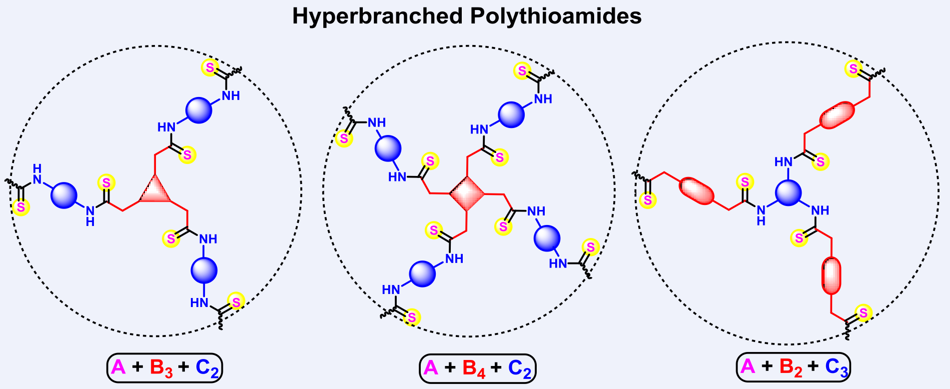
Comprehensive Summary

Hyperbranched polymers with unique topological structures, large number of branching sites and terminal groups have attracted much attention, and are expected to possess advanced functionalities compared with their linear polymer counterparts. The development of hyperbranched polymers ~~with unique structures~~ is hence highly desired but challenging, especially for sulfur-containing polymers which are attractive metal absorbents, optical materials, dielectric materials, and self-healing materials. In this work, six hyperbranched polythioamides with various topological structures, well-defined repeating units, satisfying yields (up to 99%), and high molecular weights (up to 101 400 g/mol) were successfully designed and synthesized from the catalyst-free multicomponent polymerization of elemental sulfur, aromatic alkynes and aliphatic amines, through different monomer combination strategies based on the designed three- or four-functional alkyne and amine monomers. The hyperbranched polythioamides possess unique luminescence property, and strong affinity toward Hg^{2+}, which can be utilized in the fluorescence detection of Hg^{2+}, as well as mercury removal from aqueous solutions with high ~~99.99%~~ efficiency, and low mercury residue of 0.1 ppb. Hyperbranched polythioamides with unique structures may be developed to a group of fascinating materials and find their potential applications as metal absorbents~~,~~ optoelectronic materials~~, and mechanically strong materials.~~



Keywords

Hyperbranched polymer | Polythioamide | Polymerization | Sulfur | Mercury

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Background and Originality Content

Hyperbranched polymers with unique three dimensional topological structures ~~and~~ large number of branching sites and terminal groups, generally show different solubility,[1] viscosity,[2] mechanical properties,[3] ionic conductivity,[4-5] and self-assembly properties,[6] compared with the corresponding linear polymers, and are of great potential in the applications such as coating, [7-8] lubricating,[9] light-harvesting,[10] drug sustained release agents and membranes,[11-14] polyelectrolytes,[4-5] and luminescent materials.[6,15-18] On the other hand, sulfur-containing polymers including polythioethers,[19-20] polythioesters,[21-22] poly(monothiocarbonate)s,[23] polytrithiocarbonates,[24] polythioureas,[25] polythioamides,[26] polythiophenes,[27] and others, which generally enjoy high refractive indices,[28] excellent metal coordination ability,[25,29-30] self-repairing performance,[31] electrical conductivity,[27,32-33] and degradability,[34-36] have attracted much attention as advanced materials in the applications including optical materials,[37] sewage treatment materials,[30,38] self-healing materials[31] and dielectric materials.[32,33] However, limited examples about sulfur-containing hyperbranched polymers such as disulfide-containing hyperbranched poly(amido amine)s with controllable bioreducibility and ~~stimuli-responsiveness~~ were developed,[39-44] due to the lack of efficient synthetic approaches, and current methods generally involve sulfur-bearing smelly and toxic monomers or byproducts.

Of all the sulfur-containing polymers, polythioamides with similar structures as the traditional high-performance polyamides such as ~~nylon~~ and Kevlar, were proved to possess high optical performance and metal coordination ability,[26,30] and ~~may~~ be promising engineering plastics. However, the reports about polythioamide structures and properties are still quite rare, because of the restriction of synthetic methods. For example, polythioamides were prepared through the conversion from polyamides with the utilization of malodorous Lawesson ~~reagents~~ in the risk of hydrolytic degradation;[45] polymerizations of dithiocarboxylic acid-*O*,*O*-diethyl esters or dithioesters with diamines, respectively, were also reported to prepare polythioamides, but with expensive monomers, harmful byproducts and long reaction time.[46-47]

Elemental sulfur, as the main byproduct from petroleum industry,[48] is an ideal sulfur source for the preparation of sulfur-containing polymers, considering its economic and environmental benefits.[26] Of all the recently developed synthetic methodologies for the direct utilization of elemental sulfur,[28,49] multicomponent polymerizations (MCPs) featured with attractive characteristics such as great structural diversity, high efficiency, mild condition, high atom economy, and simple operation, have ~~proved~~ to be advantageous for the preparation of sulfur-containing polymer materials, and especially for the synthesis of polythioamides. For example, we have developed the catalyst-free MCPs of elemental sulfur, aromatic diynes, and aliphatic diamines at 100 °C with mild condition to afford linear polythioamides with well-defined structures.[48] We have also reported the scalable MCPs of elemental sulfur, dicarboxylic acids and diamines at 100 °C without catalyst, or with base in the case of aromatic diamines, affording linear polythioamides with a great diversity of polymer structures, and proving their potential in metal ion extractions.[26] Similar MCPs of elemental sulfur, aliphatic diamines, and aromatic dialdehydes,[50] or polymerization of sulfur and benzyl diamines were also reported to produce linear polythioamides.[51] Most recently, polyethyleneimine (PEI) was used as reactant to be crosslinked by sulfur and 1,4-diethynylbenzene to afford polymer materials with potential application in mercury adsorption, but the structures are not well-defined because of the irregular structure of PEI, potential cross-linking, and poor solubility of the product.[52]

In this work, ~~by~~ taking advantage of the unique designability of MCP on its monomer structures and the various monomer combinations, a series of hyperbranched polythioamides with diversified topological structures, well-characterized chemical structures, and good solubility were successfully synthesized from the MCP of elemental sulfur, aromatic alkynes and aliphatic amines. A group of diynes, triyne, tetrayne, diamines, and triamine monomers were designed and synthesized, and various monomer combinations including A + B_3 + C_2, A + B_4 + C_2, and A + B_2 + C_3 were adopted for the catalyst-free MCP, which ~~is~~ more convenient and efficient in terms of monomer synthesis and storage compared with AB_n-type monomer strategy with two or more kinds of reactive sites in a single molecule.[53] Six hyperbranched polythioamides were produced with different topological structures, structural diversity, satisfied yields and molecular weights (M_ws), and good solubility. To the best of our knowledge, there has been neither report about hyperbranched polythioamide structures with well-defined repeating unit ~~structure~~, nor report about hyperbranched polythioamide synthesized ~~directly~~ from small molecular monomers. These hyperbranched polythioamides enjoy good solubility, unique luminescence, and mercury affinity, which could be applied in the fluorescence detection and removal of Hg^{2+}.

Results and Discussion

Synthesis of trithioamides and tetrathioamide model compounds

Three small molecular model compounds were first designed and synthesized. Triphenylamine (TPA)-containing triyne **2a** and tetraphenylethene (TPE)-containing tetrayne **2b** were used to synthesize trithioamide **4** and tetrathioamide **5**, respectively, with S_8 and benzylamine **3e** in pyridine at 100 °C. Alternatively, triamine **3d** could also undergo the same reaction with S_8 and phenylacetylene **2e** to afford trithioamide **6** (Scheme 1). Although there were three or four reaction sites, satisfying isolated yields of 60%—72% can be obtained for these model compounds. Their structures were characterized by the standard spectroscopy analysis which will be discussed below.

Synthesis of hyperbranched polythioamides from the mc~~ps~~ of sulfur, amines and alkynes

A series of diyne, triyne, tetrayne, diamine, and triamine monomers **2a**—**2d** and **3a**—**3d** were purchased or prepared according to the literatures.[54-56] Three groups of hyperbranched polythioamides with each of their structure moieties corresponding to the above-mentioned three model compound structures, respectively, were then designed and synthesized from the MCPs of sulfur, alkynes, and amines with different monomer combination strategies (Scheme 2 and Figure 1).

Through A + B_3 + C_2 monomer combination with TPA-containing triyne **2a**, *para*- or ~~*meso*~~-dibenzylamines **3a**/**3b**, and sulfur as the monomers, hyperbranched polymers *hb*-P**1** and *hb*-P**2** were both afforded from the MCP with the high concentration of diamines of 0.5 mol/L at 100 °C in 99% yield and high ~~molecular weights (~~M_ws~~)~~ of 44 500 and 40 800 g/mol, respectively, suggesting the high polymerization efficiency of electron-rich aromatic alkyne monomer with benzylamine monomers (Scheme 2A and Figure S1). When triyne monomer **2a** was replaced by tetrayne **2b** in the MCP with sulfur and benzylamine, *hb*-P**3** with a M_w of 38 900 g/mol could be afforded in 74% yield through the A + B_4 + C_2 monomer combination (Scheme 2B). If the *para*-benzylamine **3a** was replaced by ~~dihexyl~~amin~~e~~ **3c**, *hb*-P**4** with similar M_w of 36 100 g/mol but decreased yield was obtained, suggesting that benzylamine showed higher reactivity compared with alkylamine monomer. When aliphatic triamine **3d** was adopted for A + B_2 + C_3 monomer combination with sulfur and aromatic diyne monomers **2c** with the loading ratio of 1/8[S_8] : ~~[~~**2c**~~/~~**2d**~~]~~ : [**3d**] = 6.0 : 1.5 : 1.0,

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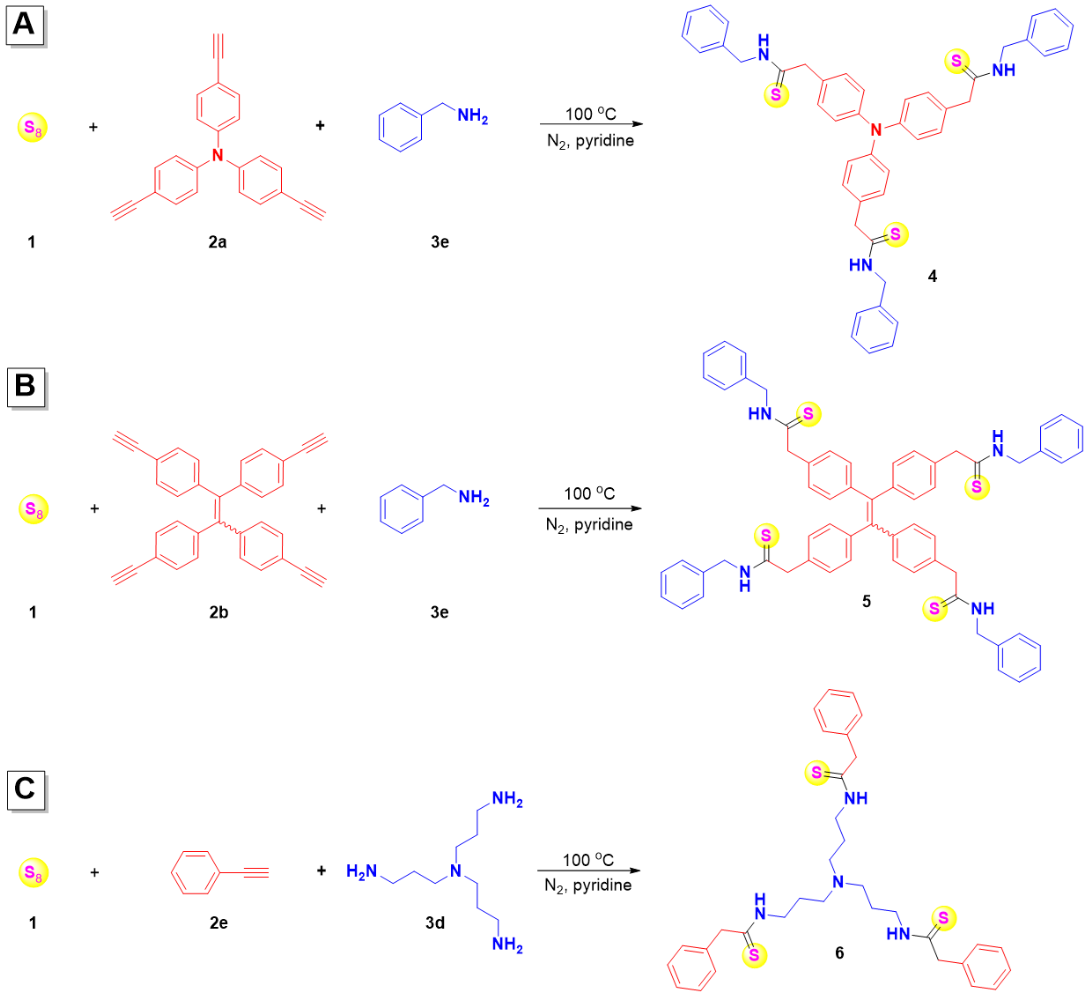
Scheme 1 The synthesis ~~route~~ of model compounds **4**, **5** and **6**



hb-P**5** with high M_w of 101 400 g/mol could be obtained (Scheme 2C). Similarly, the MCP of sulfur, **3d**, and TPE-containing diyne **2d** ~~can~~ generate *hb*-P**6** with a large M_w of 71 200 g/mol. Of all the three monomer combination strategies, the highest yields could be afforded ~~in~~ the A + B_3 + C_2 manner, and the highest M_ws could be produced ~~in~~ the A + B_2 + C_3 manner.

Even though there are abundant thioamide groups with potential intra- and intermolecular hydrogen bonds existing in the structures, the hyperbranched polythioamides generally possess satisfying solubility in polar solvents such as DMSO and DMF with sonication, which were also partially soluble in THF, except *hb*-P**5** with large M_w and prepared from phenyldiacetylene monomer **2c** with poor solubility. The successful synthesis of *hb*-P**1**—**6** suggested the general applicability of various monomers with multiple functional groups, and the high yields and large M_ws of the polymer products proved the high efficiency of this MCP of sulfur, alkyne, and amine.

Structural characterization of hyperbranched polythioamides

The chemical structures of the hyperbranched polythioamides *hb*-P**1**—**6** were confirmed by their IR, ^{1}H and ^{13}C NMR spectra, together with the comparison with those spectra of the corresponding monomers and model compounds. Taking *hb*-P**1** for an example, in the ^{1}H NMR spectra of *hb*-P**1** and its model compound **4** with similar structural unit, the terminal alkyne proton resonance at δ 4.13 ~~of monomer **2a**~~ has disappeared, and the NH_2 peak from the benzyl (di)amine at δ 1.67 has shifted to δ 10.61 (**4**) and 10.66 (*hb*-P**1**), respectively, representing their characteristic thioamide proton resonance. Meanwhile, the -CH_2- proton peak from benzyl amine reactants has shifted from δ 3.68 to 4.75, and ~~a~~ new ~~single peak~~ emerged at δ 3.92 in the spectrum of *hb*-P**1**, representing the -CH_2- protons produced from alkyne groups, which are in good correspondence with these -CH_2- peaks of **4** at δ 4.78 and 3.91, respectively, confirming the formation of thioamide groups in the hyperbranched polymer (Figures 2A—2D). Similarly, in the ^{1}H NMR spectrum of *hb*-P**2**, the three characteristic peaks also emerged at δ 10.64, 4.75 and 3.93 (Figure S2), and the characteristic peaks of -NH- protons on the thioamide groups appeared at δ 10.10—10.58 in the ^{1}H NMR spectra of *hb*-P**2**—*hb*-P**6**, proving their ~~well-defined~~ hyperbranched polythioamide structures (Figure S3—S6).

Most importantly, in the ^{13}C NMR spectra of **4** and *hb*-P**1**, the characteristic carbon resonances of thioamide groups have emerged at δ 201.70 and 200.36, respectively, proving the formation of the HN-C=S groups in the hyperbranched polymer. Meanwhile, two -CH_2- carbon resonances emerged at δ 51.01 and 43.83 in the spectrum of *hb*-P**1**, corresponding to the peaks at δ 50.71 and 48.60 in the spectrum of **4**, representing the methylene groups on each side of the thioamide moiety (Figure 2E—2H). A small peak at δ 83.42 could still be observed in the spectrum of *hb*-P**1**, which was probably associated with the unreacted terminal alkyne moieties. In addition, the characteristic ^{13}C NMR peak for the thioamide groups in *hb*-P**5** was also found at the same

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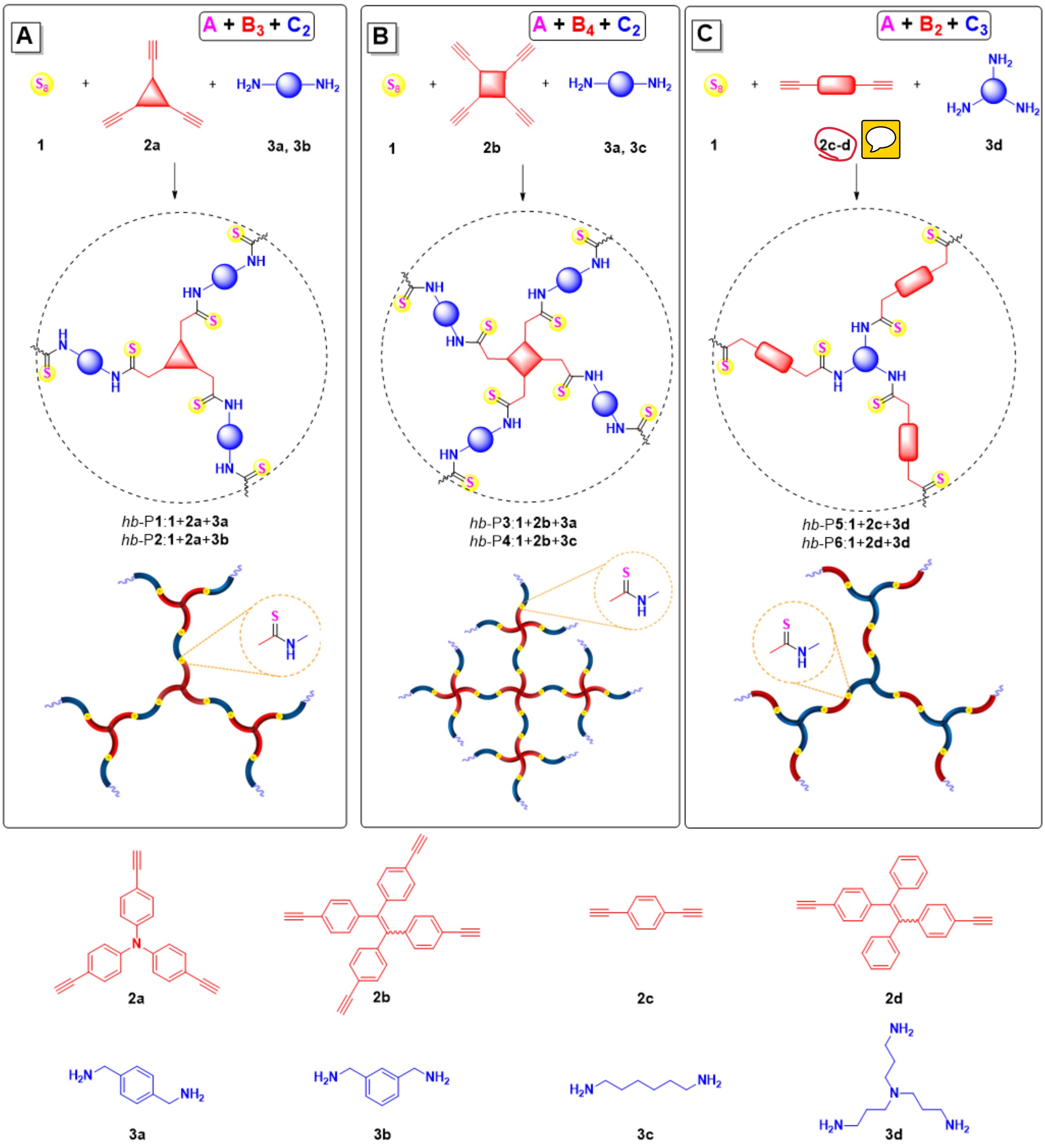
Scheme 2 Multicomponent po~~lymerization~~ of sulfur **1**, alkynes **2a—2d** and amines **3a—3d** through (A) A + B_3 + C_2, (B) A + B_4 + C_2 and (C) A + B_2 + C_3 methods



region at *δ* 200.33.

The IR spectra of *hb*-P**1** and **4** were also studied (~~**Figure S7**~~). The stretching vibration of ≡C-H and C≡C bonds of **2a** located at 3266 and 2101 cm^{-1}, respectively, have disappeared in the spectrum of model compound **4**, and have significantly decreased in the spectrum of *hb*-P**1**. The stretching vibration of -NH_2 of **3a** at 3309 cm^{-1} has converted to the –NH- stretching vibration at 3176 (**4**) and 3279 nm (*hb*-P**1**), respectively. Most importantly, the strong absorption bands both at 1504 cm^{-1} in the spectra of **4** and *hb*-P**1** are associated with the C=S stretching vibration of the thioamide groups.[26] Similarly, these strong resonances appeared at 1538 and 1531 cm^{-1} in the spectra of model compound **6** and *hb*-P**5** (~~**Figure S8**~~), representing their thioamide moieties.

To prove the existence form of sulfur in the polymer structures, X-ray photoelectron spectroscopy was measured (~~**Figure S9**~~). The binding energies of S 2p were observed at 162.13/163.33 eV (**4**) and 162.15/163.32 eV (*hb*-P**1**), which were different from those of elemental sulfur at 164.23/165.42 eV, proving that sulfur has all converted to thioamide moieties in the hyperbranched polymer.

Photophysical properties of hyperbranched polythioamides

The photophysical properties of the hyperbranched polythioamides *hb*-P**1** and *hb*-P**4** prepared from the chromophore-

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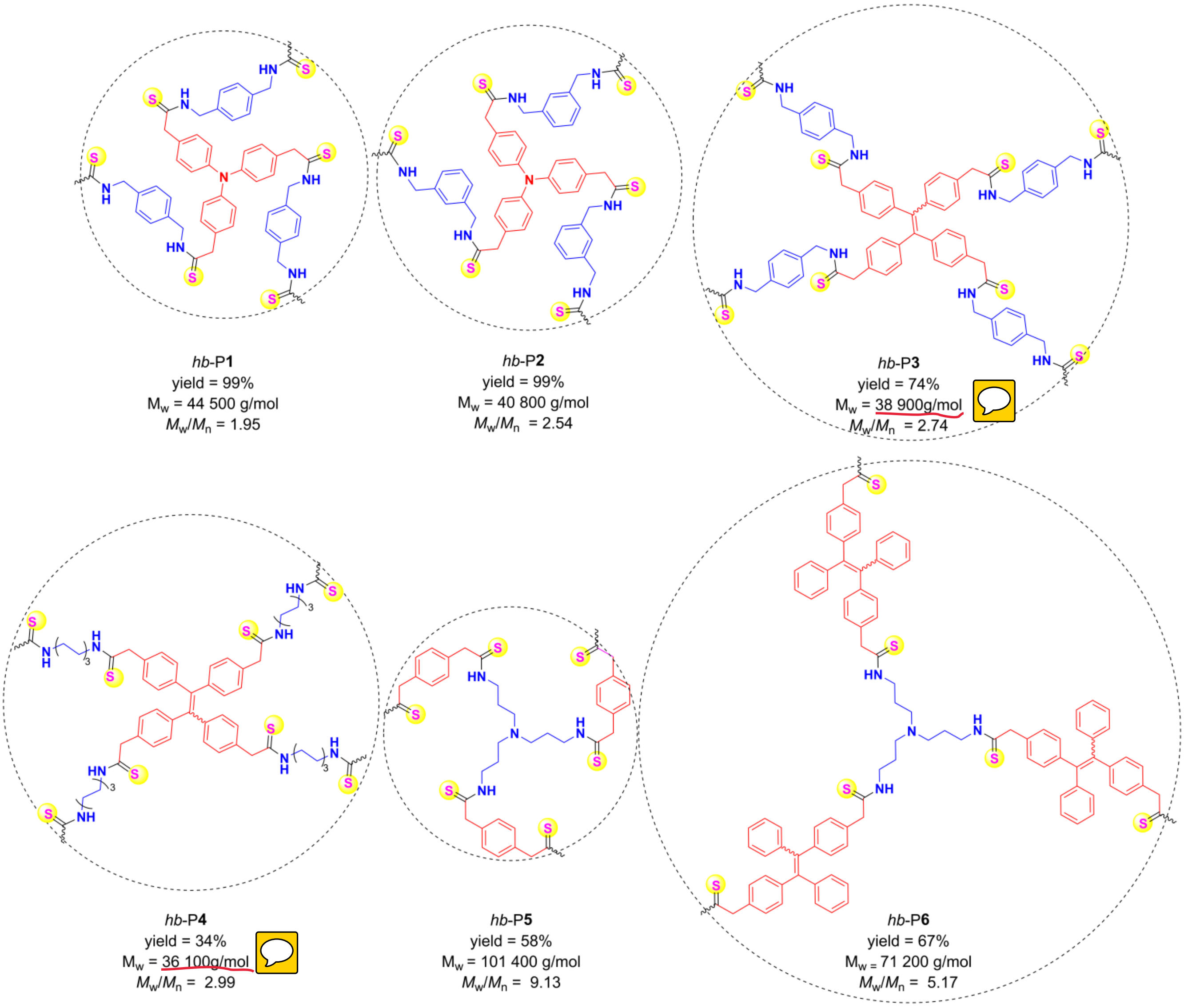

hb-P**1**
yield = 99%
M_w = 44 500 g/mol
M_w/M_n = 1.95

hb-P**2**
yield = 99%
M_w = 40 800 g/mol
M_w/M_n = 2.54

hb-P**3**
yield = 74%
M_w = 38 900g/mol
M_w/M_n = 2.74

hb-P**4**
yield = 34%
M_w = 36 100g/mol
M_w/M_n = 2.99

hb-P**5**
yield = 58%
M_w = 101 400 g/mol
M_w/M_n = 9.13

hb-P**6**
yield = 67%
M_w = 71 200 g/mol
M_w/M_n = 5.17

Figure 1 Chemical structures, yields, and molecular weights of hyperbranched polythioamides *hb*-P**1**—**6**.

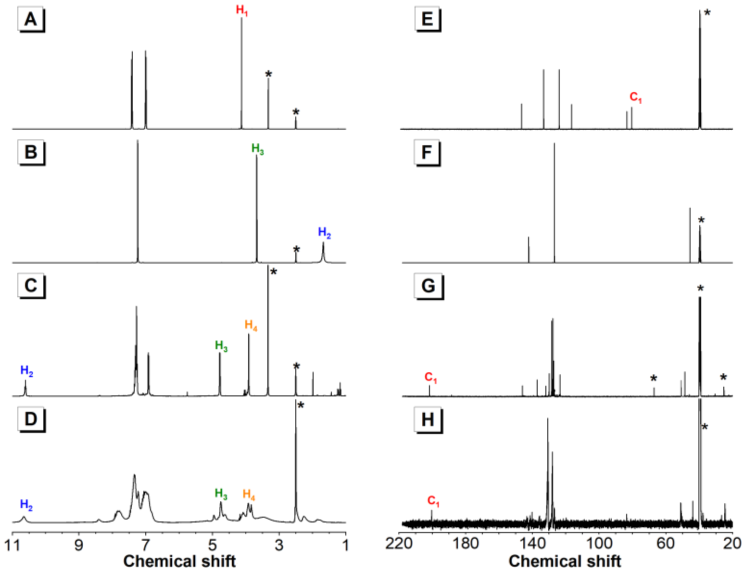

Figure 2 ^{1}H NMR spectra of (A) **2a**, (B) **3a**, (C) **4**, (D) *hb*-P**1**. ^{13}C NMR spectra of (E) **2a**, (F) **3a**, (G) **4**, (H) *hb*-P**1** in DMSO-d_6. The solvent peaks were marked with asterisks.

containing monomers were investigated as examples. In the UV-vis spectra of their dilute DMF solutions, TPA-containing *hb*-P**1** possessed absorption ~~maxima~~ at 314 nm, while the TPE-containing *hb*-P**4** possessed redshifted absorption ~~maxima~~ at 329 nm (Figure S10). The photoluminescence spectra of these hyperbranched polythioamides were then measured in DMF solutions and DMF/water mixtures. The emission maxima of their DMF solutions were located at 483 (h*b*-P**1**) and 486 nm (*hb*-P**4**), respectively. When poor solvent~~,~~ water~~,~~ was gradually added into their DMF solutions, the emission of TPA-containing *hb*-P**1** was significantly quenched (Figure 3A), and the emission intensity of TPE-containing *hb*-P**4** was gradually increased with the emission peak slightly redshifted to 509 nm, demonstrating the aggregation-enhanced emission property of *hb*-P**4** (Figure 3B). When poor solvent water was added to make the molecules aggregate, the intramolecular and intermolecular hydrogen bonds among the thioamide moieties might form to restrict the free rotation of phenyl rings on TPE moieties and enhance the emission. The photoluminescence spectra of the corresponding model compounds **4** and **5** in DMF/water mixtures also suggested similar phenomena (Figure S11).

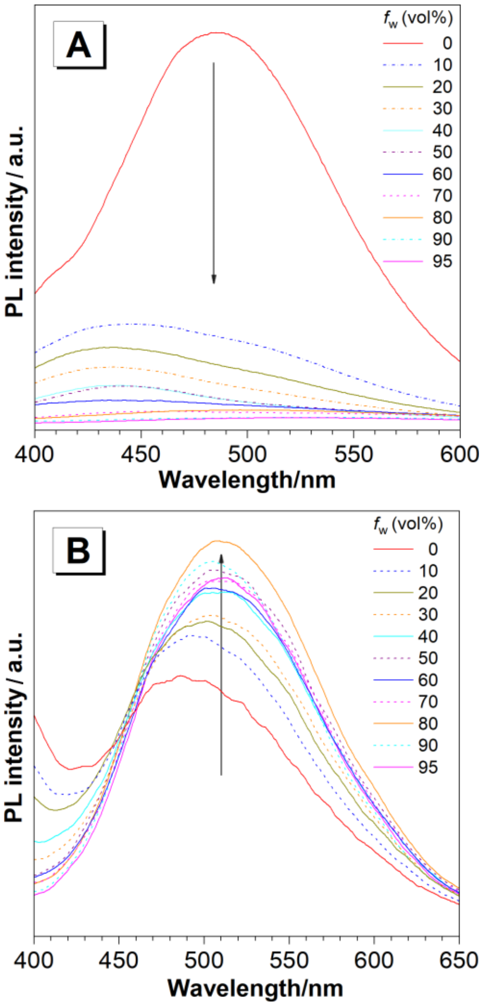

Figure 3 PL spectra of (A) *hb*-P**1**~~,~~ (B) *hb*-P**4** in DMF/water mixtures with different water fractions (f_w)~~,~~ ~~concentration:~~ 10 µmol/L. ~~Excitation wavelength: 330 nm.~~ Calculated by the repeating units of the hyperbranched polythioamides~~.~~

Mercury detection and removal with hyperbranched polythioamides

Mercury pollution in water could cause serious environmental and health problems because of the toxicity of mercury species to respiratory and nerve systems,[57] the detection and removal of mercury ion are hence important and have been widely investigated with the mercury absorbents including biomaterials,[58] covalent organic frameworks,[59] traditional diatomite,[60] chitosan,[61] or modified activated carbon.[62] Linear or hyperbranched polymers with abundant thioamide moieties as well-known ligands for Hg^{2+}, could hence be developed as Hg^{2+} absorbents,[30,38] and *hb*-P**1**, *hb*-P**5** and *hb*-P**6** were studied as examples.

The fluorescence intensity of the DMF solution of *hb*-P**1** was gradually decreased in the presence of increasing ~~concentration~~ of Hg^{2+} (Figure 4), which was decreased by half with 8 mg/L Hg^{2+}, and to ~~20%~~ with 16 mg/L Hg^{2+}. A linear relationship between the fluorescence quenching ratio I/I_0 and the $[Hg^{2+}]$ can be found within the measured concentration range. The *in situ* fluorescence quenching of *hb*-P**1** by Hg^{2+} may endow the possibility of mercury removal with real time monitoring. To investigate the selectivity of the hyperbranched polythioamides among metal ions, solid powder of *hb*-P**1** was added into aqueous solutions of different metal ions including Na^+, K^+, Pb^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Cr^{3+}, Cr^{2+} and Hg^{2+}, respectively (Figure S12), suggesting high selectivity towards Hg^{2+}.

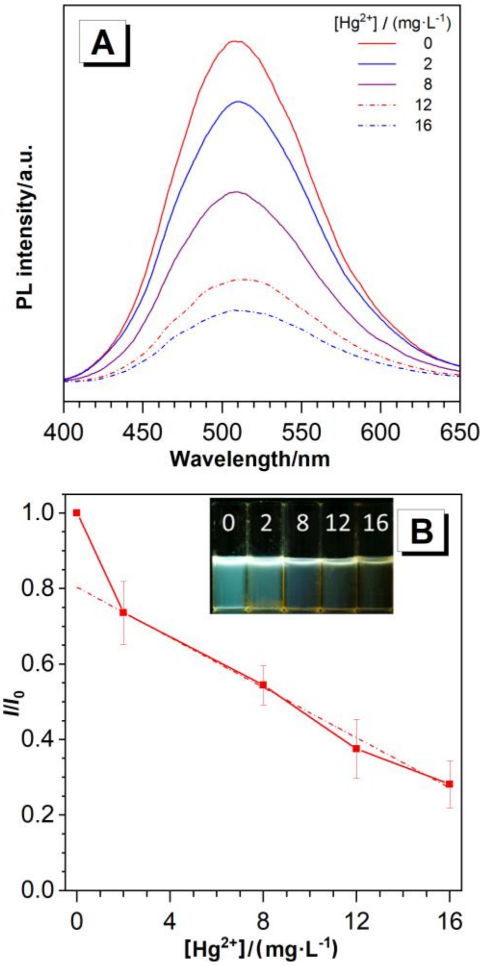

Figure 4 (A) Fluorescence of hyperbranched polythioamide *hb*-P**1** ~~with Hg^{2+} solution ranging from 2 to 16 mg/L in DMF solution~~, [Polymer] = 40 mg/L. (B) The plot of relative emission intensity (I/I_0) versus $[Hg^{2+}]$ ~~when DMF solution of *hb*-P**1** was added with $HgCl_2$, *i.e.*, $[Hg^{2+}]_0$ in DMF solutions ranging from 0 to 16 mg/~~L. I_0 = PL intensity in the absence of Hg^{2+}. Inset: fluorescence photographs of the resultant solutions taken upon UV irradiation.

Moreover, solid powders of the hyperbranched polymers were respectively added into 10 mL of aqueous solution of $HgCl_2$. After stirring and centrifugation, the insoluble solid was removed by filtration, and the remaining concentration [Hg^{2+}] in the resulting supernatant was measured by Atomic Absorption Spectroscopy. With a constant ratio of m_P/m_{Hg2+} and the initial concentration [Hg^{2+}]$_0$ range of 5 to 100 mg/L, the removal efficiencies of *hb*-P**1** were generally measured to be above 99.92%, and the remaining [Hg^{2+}] could be decreased to as low as 0.10 μg/L, which was below the limit of drinking water standards of WHO (6 μg/L), U.S. (2 μg/L), China and EU (1 μg/L) (Figure 5 and Table S1).[63-64] Similarly, *hb*-P**5** and *hb*-P**6** also show high removal efficiency, and slightly decreased efficiency with low [Hg^{2+}]$_0$ compared with *hb*-P**1**, maybe due to the relatively flexible structures ~~compared with *hb*-P**1**~~.

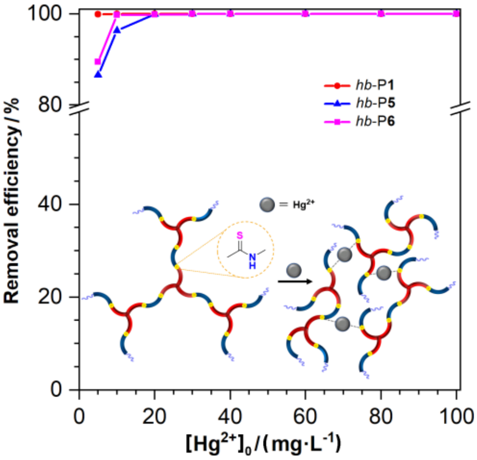

Figure 5 Extraction efficiency of hyperbranched polythioamides with different initial ~~concentration~~ of Hg^{2+}.

Conclusions

Herein, a series of hyperbranched polythioamides with diverse topological structures and well-defined repeating units were facilely synthesized through a catalyst-free multicomponent polymerization of elemental sulfur, aromatic alkynes and aliphatic amines. Based on a group of monomers with double or multiple functional groups such as diynes, triyne, tetrayne, diamines, and triamine, various $A + B_3 + C_2$, $A + B_4 + C_2$, and $A + B_2 + C_3$ monomer combination strategies were adopted to afford six hyperbranched polythioamides with satisfying yields (up to 99%) and molecular weights (up to 101 400 g/mol), whose well-defined structures were fully characterized through ^1H, ^{13}C NMR and IR spectra. The luminescence property of the hyperbranched polythioamides with TPA and TPE units in the polymer chain was compared, revealing that the TPA-containing hyperbranched polythioamide showed aggregation-caused fluorescence quenching, and the TPE-containing polythioamides showed aggregation-enhanced fluorescence. Meanwhile, the fluorescence of the polythioamide solution could be quenched by Hg^{2+} with a linear relationship in the measured concentration range, which ~~may~~ be used for the fluorescence detection of Hg^{2+} concentration. Moreover, with the abundant thioamide groups in the three dimensional hyperbranched structures and the strong affinity of the thioamide groups with Hg^{2+}, even the solid powder of the hyperbranched polymers could be used to extract Hg^{2+} conveniently with >99.99% efficiency, and low Hg^{2+} residue (as low as 0.1 ppb), demonstrating their potential application in the treatment of mercury pollution as mercury absorbents, which may be further combined with the unique fluorescence of the polymer for the real-time monitoring of the mercury removal process. This work demonstrated the straightforward synthesis from industrial sulfur waste to hyperbranched polythioamides with a one-step multicomponent polymerization of sulfur, alkynes, and amines, directly converting sulfur waste to profitable functional polymer materials with potential application in the treatment of environmental pollution, which provides a great opportunity for the resource utilization.

Experimental

The experimental details of this report are recorded in the Supporting Information of this report.

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.202100498.

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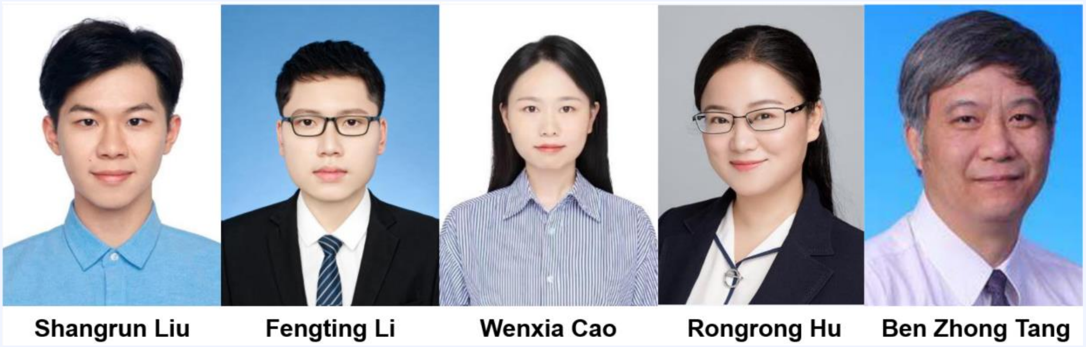

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Functional Hyperbranched Polythioamides Synthesized from Catalyst-free Multicomponent Polymerization of Elemental Sulfur

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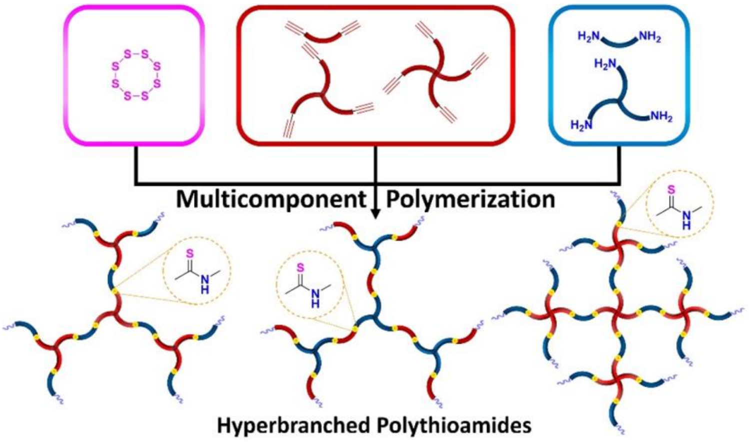

A series of functional hyperbranched polythioamides were synthesized through the multicomponent polymerization of elemental sulfur, alkynes and amines through A + B_3 + C_2, A + B_4 + C_2 or A + B_2 + C_3 monomer combinations.