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Synthesis of Functional Hyperbranched Poly(methyltriazolylcarboxylate)s by Catalyst-free Click Polymerization of Butynoates and Azides

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Electronic Supplementary Information

Abstract Azide-alkyne click polymerization has become a powerful tool for polymer synthesis. However, the click polymerization between internal alkynes and azides is rarely utilized to prepare functional polymers. In this work, the polymerization reactions of activated internal alkyne monomers of tris(2-butynoate)s (**1**) with tetraphenylethene-containing diazides (**2**) were performed in dimethylformamide (DMF) under simple heating, affording four hyperbranched poly(methyltriazolylcarboxylate)s (*hb*-PMTCs) with high molecular weights (M_w up to 2.4×10^4) and regioregularities (up to 83.9%) in good yields. The *hb*-PMTCs are soluble in common organic solvents, and thermally stable with 5% weight loss temperatures up to 400 °C. They are non-emissive in dilute solution, but become highly emissive in aggregated state, exhibiting aggregation-induced emission characteristics. The polymers can generate fluorescent photopatterns with high resolution, and can work as fluorescent sensors to detect nitroaromatic explosive with high sensitivity.

Keywords Click polymerization; Hyperbranched polymer; Aggregation-induced emission; Explosive detection; Photopattern

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INTRODUCTION

Facile synthesis of polymers with new structures and functional properties is of great academic and industrial interest. Over the past decades, hyperbranched polymers have gained extensive attention because of their special physical and chemical properties, and great potential applications in coatings, catalysis, nanotechnology, supramolecular assembly, biomedical research, optoelectronic devices, and so on.^[1,2] With the sustained efforts by polymer chemists, a large number of hyperbranched polymers including polyethylenes,^[3] polyesters,^[4] polyglycerols,^[5] polyamides,^[6] polyphenylenes,^[7] and polyphosphates,^[8] have been prepared by various polymerization strategies.^[9–12] Among them, alkyne-based polymerization reactions, such as polycyclotrimerization, azide-alkyne and thiol-yne click polymerizations, have emerged as versatile synthetic tools for the construction of hyperbranched polymers.^[13–15]

In recent years, the Cu(I)-catalyzed and metal-free azide-alkyne

click polymerizations, derived from azide-alkyne cycloaddition reaction, have drawn much consideration owing to their advantageous characteristics, such as high efficiency, atom economy, regioselectivity, as well as mild reaction conditions.^[16–18] Actually, Voit *et al.* first attempted to prepare hyperbranched polytriazoles by polymerization of AB₂-type monomers carrying one azide group and two terminal alkyne groups using CuSO₄ and sodium ascorbate as catalysts in 2004, and only obtained insoluble products.^[19] After optimizing the reaction conditions, such as the solvents and catalyst system, a wide variety of soluble 1,4-regioregular hyperbranched polytriazoles with advanced functionalities were synthesized by the Cu(I)-catalyzed azide-alkyne click polymerization.^[15–18,20–22] Considering that copper catalysts may cause cytotoxicity and deteriorate the photoluminescence properties of the resulting polymers, our research group has developed metal-free click polymerizations of azide and activated terminal alkynes, and prepared a number of functional hyperbranched polytriazoles with high molecular weights and high 1,4-regioregularities.^[23,24] However, the alkyne monomers used in these click polymerizations are mainly terminal alkynes. The polymerization reactions between internal

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alkynes and azides are rarely utilized to prepare soluble hyperbranched polymers.^[25,26] In our previous work, we developed catalyst-free polycycloaddition reactions of azides and activated internal alkynes (phenylpropiolates and butynoates), and prepared a group of functional 1,4,5-trisubstituted polytriazoles.^[27–30] For instance, the polycycloadditions of dibutynoate with diazides proceeded smoothly at 100 °C under solvent- and catalyst-free conditions to give soluble poly(methyltriazolylcarboxylate)s (PMTCs) with high molecular weights (M_w up to 1.67×10^4) and satisfactory regioregularities in good yields.^[30] The simplicity and efficiency of this polymerization reaction encouraged us to explore its application in preparing functional hyperbranched polymers.

In this work, we prepared four hyperbranched PMTCs (*hb*-PMTCs) with high molecular weights and regioregularities in high yields by the catalyst-free butynoate-azide click polymerization. The *hb*-PMTCs enjoy good solubility and high thermal stability. Moreover, the polymers show aggregation-induced emission (AIE) features, which enable them to be utilized for detecting explosive and fabricating fluorescent patterns.

EXPERIMENTAL

Materials

Dichloromethane (DCM) was distilled under nitrogen in the presence of calcium hydride. DMF was of extra-dry quality and stored over molecular sieves from Aladdin Reagent Co., Ltd. (Shanghai, China). Tetrahydrofuran (THF) used in photoluminescence (PL) spectra measurements was spectral purity grade, and purchased from Aladdin Reagent Co., Ltd. 4,4',4''-Trihydroxytriphenylmethane was obtained from TCI Shanghai Chemical Reagent Co., Ltd. (China). 2-Butynoic acid was purchased from Shanghai D&B Biological Science and Technology Co., Ltd. (China). Other chemicals and solvents were obtained from Aladdin Reagent Co., Ltd. or Sinopharm Group Chemical Reagent Co., Ltd. (China), and used as received without further purification.

Instruments

¹H- and ¹³C-NMR spectra were recorded at room temperature on Varian Unity Inova 400 (400 MHz) or 600 (600 MHz) spectrometers. Fourier transform infrared (FTIR) spectroscopy was performed on a Bruker VERTEX 70v FTIR spectrophotometer with thin films on KBr pellets. UV spectra were measured on an Agilent Cary 5000 spectrophotometer. PL spectra were taken on an Edinburgh Instrument FLS 980 fluorospectrometer. Elemental analysis was performed on an Elementar Vario EL-III instrument. Thermo-gravimetric analysis (TGA) was performed on a Discovery TGA (METTLER TOLEDO instruments, Switzerland) under dry nitrogen at 10 °C·min⁻¹. Relative weight-average (M_w) molecular weights and polydispersity indices (PDI, M_w/M_n) of the polymers were determined by a PL GPC 50 integrated system, using a set of monodisperse linear polystyrene (PS) as calibration standards and THF as the eluent at a flow rate of 1.0 mL·min⁻¹. Thin solid films for photopattern fabrication were prepared by spin-coating the 1,2-dichloroethane solution of the polymers on silicon wafers and dried at room temperature overnight. The polymer films coated with copper photomasks were then irradiated using the 365 nm UV light with an intensity of 18.5 mW·cm⁻² as light source for 20 min in air at room

temperature. The photographs of the fluorescent photopatterns were taken on an Olympus BX 41 fluorescence optical microscope with a 330–385 wideband UV excitation.

Synthesis of Monomers

1,2-Bis(4-(4-azidobutoxy)phenyl)-1,2-diphenylethene (**2a**) and 1,2-bis(4-(6-azidoheptyloxy)phenyl)-1,2-diphenylethene (**2b**) were prepared according to our previous work.^[30] The tributynoate monomers of methanetriyltris(benzene-4,1-diyl) tris(2-butynoate) (**1a**) and propane-1,2,3-triyl tris(2-butynoate) (**1b**) were synthesized by a simple esterification reaction of 2-butynoic acid with 4,4',4''-trihydroxytriphenylmethane and glycerol, respectively. A detailed synthetic procedure for **1a** is shown below.

Into a 250 mL two-necked round-bottom flask were dissolved 2.28 g (7.8 mmol) of 4,4',4''-trihydroxytriphenylmethane, 7.24 g (35.1 mmol) of 1,3-dicyclohexylcarbodiimide (DCC), 0.57 g (4.7 mmol) of 4-dimethylaminopyridine (DMAP), and 0.89 g (4.7 mmol) of *p*-toluenesulfonic acid (*p*-TsOH) in 100 mL of distilled DCM under nitrogen. The solution was cooled to 0 °C with an ice-water bath, and 2.30 g (27.3 mmol) of 2-butynoic acid dissolved in 20 mL of DCM was added under stirring through a dropping funnel. The reaction mixture was stirred at room temperature overnight. After filtration and solvent evaporation, the crude product was purified by a silica gel column using petroleum ether/ethyl acetate (10/1, V/V) as eluent. Methanetriyltris(benzene-4,1-diyl) tris(2-butynoate) (**1a**) was obtained in 48.0% yield (1.82 g) as a pale yellow solid. FTIR (thin film, ν , cm⁻¹): 3034, 2969, 2919, 2278, 2231 (C≡C stretching), 1726 (C=O stretching), 1502, 1421, 1239, 1197, 1162, 1035. ¹H-NMR (400 MHz, CDCl₃, δ , TMS, ppm): 7.07 (s, 12H), 5.53 (s, 1H), 2.06 (s, 9H). ¹³C-NMR (150 MHz, CDCl₃, δ , TMS, ppm): 151.8, 148.6, 141.2, 130.4, 121.3, 88.1, 72.1, 55.0, 3.9. Elemental Anal. Calcd. for C₃₁H₂₂O₆: C, 75.91%; H, 4.52%; Found: C, 75.81%; H, 4.96%.

Propane-1,2,3-triyl tris(2-butynoate) (**1b**) was prepared by the reaction of glycerol and 2-butynoic acid. White solid; yield 48.3% (1.40 g). FTIR (thin film, ν , cm⁻¹): 2972, 2923, 2317, 2246 (C≡C stretching), 1719 (C=O stretching), 1492, 1456, 1373, 1324, 1246, 1073. ¹H-NMR (400 MHz, CDCl₃, δ , TMS, ppm): 5.33 (s, 1H), 4.35 (d, 4H), 2.01 (s, 9H). ¹³C-NMR (150 MHz, CDCl₃, δ , TMS, ppm): 152.9, 152.4, 87.5, 87.1, 71.7, 69.7, 62.8, 3.9. Elemental Anal. Calcd. for C₁₅H₁₄O₆: C, 62.07%; H, 4.86%; Found: C, 62.26%; H, 5.32%.

Synthesis of Polymers

All the polymerization reactions were conducted under nitrogen using a standard Schlenk technique. A typical experimental procedure for polymerization of **1a** and **2a** for *hb*-P1 is shown below as an example.

Into a 10 mL Schlenk tube equipped with a magnetic stir bar were placed **1a** (49.0 mg, 0.10 mmol) and **2a** (83.7 mg, 0.15 mmol). The tube was evacuated and refilled with nitrogen (three times) for 0.5 h, and DMF (0.25 mL) was injected to dissolve the solids. The reaction mixture was then stirred at 100 °C for 11 h. After being cooled down to room temperature, the solution was diluted with 5 mL of chloroform and added dropwise into 200 mL of petroleum ether through a cotton filter under strong stirring. The precipitates were allowed to stand overnight and collected by filtration. The polymer was washed with petroleum ether and dried to a constant weight at ambient conditions.

Characterization data of **hb-P1**. White powder; 80.6% yield. M_w 2.4×10^4 ; M_w/M_n 3.69 (GPC, PS calibration). FTIR (thin film, ν , cm^{-1}): 3044, 2946, 2873, 2275, 2231 ($\text{C}\equiv\text{C}$ stretching), 2096 (N_3 stretching), 1733 ($\text{C}=\text{O}$ stretching), 1603, 1505, 1358, 1240, 1204, 1173. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.16, 7.03, 6.92, 6.64, 5.59, 4.77, 4.40, 3.92, 3.34, 2.58, 2.08, 1.81. $^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , δ , TMS, ppm): 160.3, 157.3, 151.9, 148.7, 144.1, 141.2, 139.7, 138.9, 136.3, 132.5, 131.3, 130.4, 127.6, 126.2, 121.6, 113.5, 88.1, 72.1, 66.8, 55.1, 51.0, 47.8, 26.9, 25.8, 9.1, 4.0.

hb-P2. The polymer was prepared by the polymerization of methanetriyltris(benzene-4,1-diyl) tris(2-butynoate) (**1a**) and 1,2-bis(4-(6-azidohexyloxy)phenyl)-1,2-diphenylethene (**2b**) at 100 °C for 11 h. White powder; 78.0% yield. M_w 1.41×10^4 ; M_w/M_n 2.61 (GPC, PS calibration). FTIR (thin film, ν , cm^{-1}): 3044, 2938, 2864, 2276, 2232 ($\text{C}\equiv\text{C}$ stretching), 2095 (N_3 stretching), 1732 ($\text{C}=\text{O}$ stretching), 1604, 1505, 1357, 1240, 1203, 1173. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.16, 7.06, 6.91, 6.59, 5.59, 4.72, 4.33, 3.87, 4.27, 2.61, 2.06, 1.86, 1.74, 1.62, 1.48. $^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , δ , TMS, ppm): 160.3, 157.4, 151.9, 148.8, 144.2, 141.1, 139.6, 138.9, 136.3, 135.7, 132.5, 131.3, 130.4, 127.6, 126.1, 121.6, 113.5, 67.4, 55.1, 51.4, 48.0, 29.4, 26.0, 9.1, 4.0.

hb-P3. The polymer was synthesized by the polymerization of propane-1,2,3-triyl tris(2-butynoate) (**1b**) and 1,2-bis(4-(4-azidobutoxy)phenyl)-1,2-diphenylethene (**2a**) at 100 °C for 16 h. White powder; 79.5% yield. M_w 1.03×10^4 ; M_w/M_n 2.44 (GPC, PS calibration). FTIR (thin film, ν , cm^{-1}): 3047, 2950, 2873, 2241 ($\text{C}\equiv\text{C}$ stretching), 2097 (N_3 stretching), 1726 ($\text{C}=\text{O}$ stretching), 1604, 1506, 1366, 1242, 1177. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.03, 6.91, 6.60, 5.57, 4.63, 4.48, 4.38, 3.91, 3.34, 2.51, 2.05, 1.74, 1.67. $^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , δ , TMS, ppm): 161.1, 157.2, 144.1, 139.6, 136.5, 136.3, 135.8, 132.5, 131.3, 127.6, 126.2, 113.5, 66.8, 51.2, 47.7, 26.4, 9.1, 3.8.

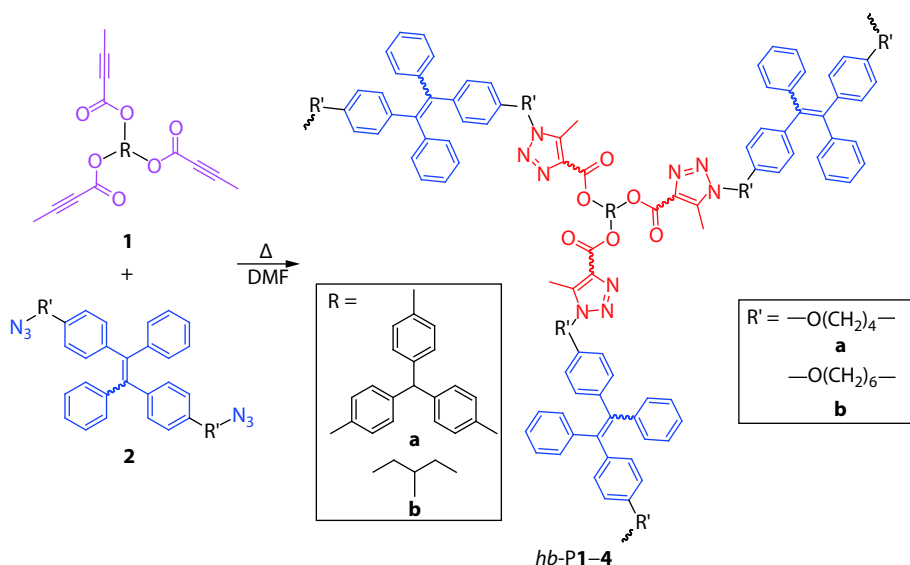
hb-P4. The polymer was prepared by the polymerization of propane-1,2,3-triyl tris(2-butynoate) (**1b**) and 1,2-bis(4-(6-azidohexyloxy)phenyl)-1,2-diphenylethene (**2b**) at 100 °C for 16 h. White powder; 86.8% yield. M_w 8500; M_w/M_n 2.07 (GPC,

PS calibration). FTIR (thin film, ν , cm^{-1}): 3044, 2935, 2862, 2240 ($\text{C}\equiv\text{C}$ stretching), 2094 (N_3 stretching), 1722 ($\text{C}=\text{O}$ stretching), 1604, 1507, 1385, 1242, 1173. $^1\text{H-NMR}$ (400 MHz, CDCl_3 , δ , TMS, ppm): 7.04, 1.97, 1.88, 1.71, 1.62, 1.44. $^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , δ , TMS, ppm): 161.1, 157.4, 145.7, 144.2, 139.6, 136.1, 132.5, 131.4, 127.6, 126.1, 113.5, 67.4, 51.1, 47.9, 31.6, 29.3, 26.0, 14.1, 9.1, 3.8.

RESULTS AND DISCUSSION

The tributynoate monomers **1a** and **1b** were synthesized by a one-pot and one-step DCC-mediated esterification of commercially available 2-butynoic acid and triols (Scheme S1, in the electronic supplementary information, ESI). The tetraphenylethene (TPE)-containing diazide monomers, **2a** and **2b**, were prepared following our previous reported procedures.^[30] All the monomers were characterized by FTIR, NMR spectroscopy, and elemental analysis, and satisfactory analysis data were obtained (see Experimental section for details).

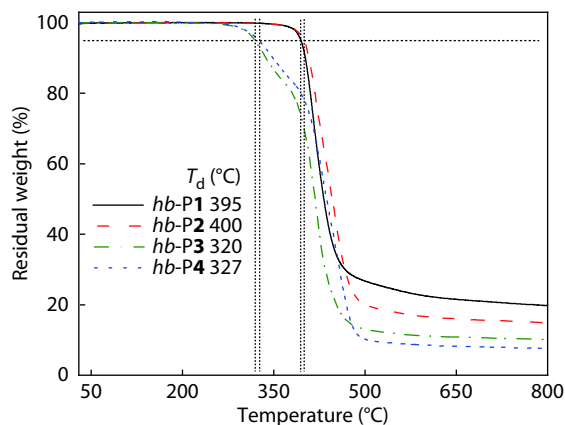
In our previous work, the polycycloadditions of dibutynoate and TPE-containing diazides were performed at 100 °C for 12 h under solvent- and catalyst-free conditions to give linear PMTCs with high molecular weights in high yields.^[30] Herein, we first explored the solvent- and catalyst-free polycycloaddition to prepare **hb-PMTCs**. Unfortunately, only insoluble gels were obtained in a short reaction time. We then adopted the reaction conditions of metal-free polycycloaddition of triphenylpropiolates and azides.^[28] The polymerizations of **1a** and **1b** with **2a** were carried out in DMF at 100 °C for 12 and 17 h, respectively, yielding insoluble gels. We thus shortened the reaction time. The polycycloaddition reactions of **1a** and **1b** with **2a** and **2b** proceeded smoothly at 100 °C in DMF for 11 and 16 h, respectively, producing the corresponding **hb-PMTCs**, **hb-P1–4**, with high molecular weights in good yields (Scheme 1, Table 1). It should be noted that the M_w and M_n values of hyperbranched polymers determined by GPC on the basis of linear polymer calibration are usually underestimated because of their globular architectures.^[31]



Scheme 1 Synthesis of **hb-P1–4** by click polymerizations of tributynoates **1** and diazides **2**.

Table 1 Click polymerizations of tributynoates **1** and diazides **2**.^a

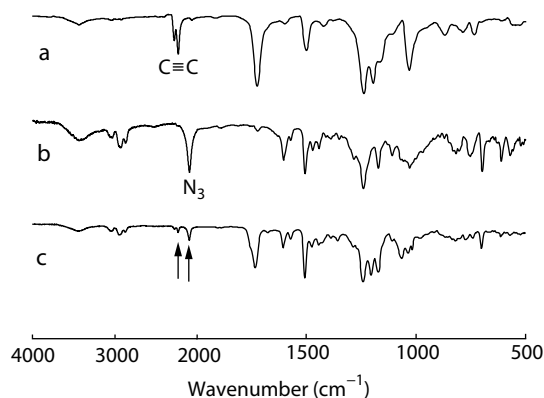
<i>hb</i> -PMTC	Monomer	Time (h)	M_w^b	PDI ^b	Yield (%)	F_a^c (%)
<i>hb</i> -P1	1a+2a	11	2.4×10^4	3.69	80.6	82.6
<i>hb</i> -P2	1a+2b	11	1.41×10^4	2.61	78.0	83.9
<i>hb</i> -P3	1b+2a	16	1.03×10^4	2.44	79.5	81.1
<i>hb</i> -P4	1b+2b	16	8.5×10^3	2.07	86.8	78.4

^a Carried out in DMF under N₂ at 100 °C, [1]/[2] = 2/3, [1] = 0.4 mol·L⁻¹.^b Estimated by GPC in THF using PS as calibration. ^c Fraction of *a*-isomer determined by ¹H-NMR.**Fig. 1** TGA thermograms of *hb*-P1–4 recorded under nitrogen at a heating rate of 10 °C·min⁻¹.

The obtained *hb*-PMTCs are soluble in commonly used organic solvents such as chloroform, DCM, THF, DMF, and DMSO. Moreover, they can be readily fabricated into thin solid film through a spin-coating technique, showing good solution processability. *hb*-P1–4 also possess high thermal stability with 5% weight loss temperatures of 395, 400, 320, and 327 °C, respectively (Fig. 1).

The *hb*-PMTCs have been characterized by FTIR, ¹H-NMR, and ¹³C-NMR spectroscopic techniques, from which satisfactory results were obtained. The FTIR as well as ¹H- and ¹³C-NMR spectra of *hb*-P1 and its corresponding monomers **1a** and **2a** were provided as examples. As given in Fig. 2, monomers **1a** and **2a** show the stretching vibration bands of C≡C and N₃ at 2231 and 2096 cm⁻¹, respectively, which become much weaker in the spectrum of *hb*-P1. This indicates that most of the ethynyl and azido groups in the monomers have been consumed by the polymerization. The spectral profiles of *hb*-P2–4 are similar to that of *hb*-P1 (Figs. S1–S3 in ESI).

¹H-NMR spectroscopy can provide more detailed structural information about the polymers. Fig. 3 shows the ¹H-NMR spectra of *hb*-P1 and its monomers **1a** and **2a**. The resonance of methylene protons adjacent to the azido groups of **2a** at δ 3.34 becomes weaker in the spectrum of *hb*-P1. Meanwhile, two new signals resonating at δ 4.40 (a) and 4.77 (b) are observed. The signal at δ 4.40 (a) is assigned to the proton resonance of methylene group adjacent to triazole rings in structure *a*, while the signal at δ 4.77 (b) is attributed to that in structure *β* (Fig. 3C).^[28,30] The results demonstrate that most of carbon-carbon triple bonds and azido groups of the monomers have been transformed into the triazole rings of the *hb*-PMTC by the polymerization. Moreover, the integrals of the signals at δ 4.40 and 4.77 enable us to calculate the fraction of

**Fig. 2** FTIR spectra of monomer **1a** (a), **2a** (b), and their polymer *hb*-P1 (c).

the structure *a* (F_a) in *hb*-P1, which is 82.6%. Similar results were drawn from the analysis of the ¹H-NMR spectra of *hb*-P2–4 and their monomers as presented in Figs. S4–S6 (in ESI). The fractions of the structure *a* in *hb*-P2–4 are calculated to be 83.9%, 81.1%, and 78.4%, respectively (Table 1). It is worth noting that the F_a values of *hb*-PMTCs are higher than those of the linear analogues (71.4% and 70.8%).^[30] This may be caused by the stronger steric hindrance due to the branched structures of *hb*-PMTCs. These advantages of high regioselectivities and atom efficiency as well as mild reaction conditions make the catalyst-free butynoate-azide polycycloaddition a click polymerization reaction.

The ¹³C-NMR spectra of *hb*-P1 and its monomers are given in Fig. S7 (in ESI). The ethynyl carbon atoms of monomer **1a** show resonance signals at δ 88.1 and 72.1, which become much weaker in the spectrum of *hb*-P1. Meanwhile, new signals resonating at δ 139.7, 136.5, 47.8, and 9.0 are observed. The signals at δ 139.7 and 136.5 are associated with the resonances of carbon atoms of triazole rings, and the signals at δ 47.8 and 9.0 are stemmed from the carbon resonances of methylene and methyl groups adjacent to triazole rings in the polymer. These results further prove that the ethynyl and azido groups have been transformed to triazole rings by the polymerization. Similar phenomena are observed in the ¹³C-NMR spectra of *hb*-P2–4 (Figs. S8–S10, in ESI). In addition, degrees of branching of *hb*-P1–4, as one of the most important intrinsic parameters of hyperbranched polymer, are hardly evaluated due to the poor resolution of related resonances in their NMR spectra.

Aggregation-induced emission (AIE) is an unusual photo-physical phenomenon: a series of π -conjugated molecules with propeller-shaped structures, such as TPE, hexaphenylsilole, distyrylanthracene, tetraphenylpyrazine, and their derivatives, are weakly or non-emissive in dilute solutions, but emit intensively in aggregate and solid states.^[32] During the past decade, luminescent materials with AIE characteristics have been a hot research topic for their wide applications in optoelectronics, chemosensing, and biomedical field.^[33–36] However, AIE-active hyperbranched polymers have been less reported so far.^[37–39]

Since TPE is a typical AIE molecule, TPE-containing *hb*-P1–4 with flexible linkers are anticipated to possess AIE activities. We thus explore their luminescence behaviors in solution and

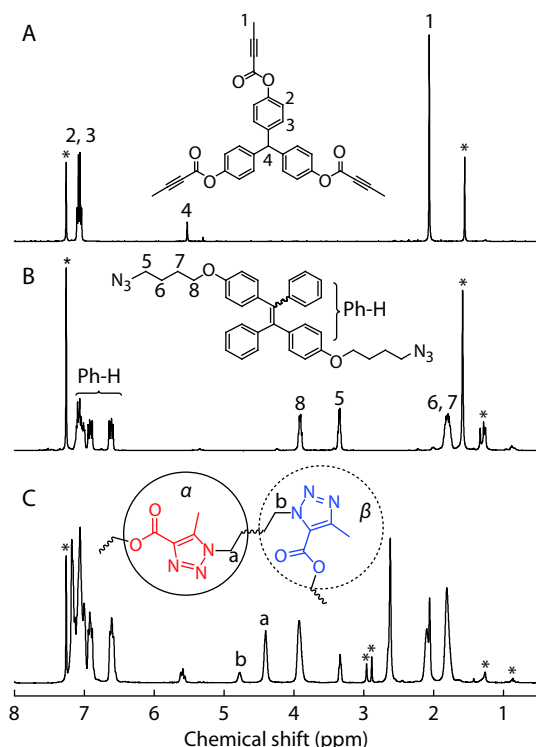


Fig. 3 ^1H -NMR spectra of monomer **1a** (A) and **2a** (B) and their polymer **hb-P1** (C) in CDCl_3 . The solvent and water signals are marked with asterisks.

aggregated states. As shown in Fig. 4(a), the PL curves of **hb-P1** in THF and THF-water mixtures with water fraction (f_w) lower than 20% runs nearly parallel to the abscissa. This suggests that it is non-emissive when molecularly dissolved in good solvents. Upon progressive addition of water as the poor solvent into its THF solution, the luminescence intensity of **hb-P1** increases gradually and reaches the maximum value at f_w of 90%. Other **hb**-PMTCs have similar fluorescence behaviors. The maximum luminescence intensities of **hb-P1–4** are 247-fold, 319-fold, 214-fold, and 251-fold, respectively, higher than those in THF solution (Fig. 4b). Obviously, the **hb**-PMTCs are AIE active. It is worth noting that the degrees of enhancement in fluorescence intensities of **hb-P2** and **hb-P4** with long alkyl spacers are higher than those of **hb-P1** and **hb-P3** with short alkyl spacers.

In dilute solutions, the polymer chains of **hb**-PMTCs are fully stretched due to the twisted TPE moieties and flexible spacers contained. The phenyl rings of TPE units in the **hb**-PMTCs can rotate and vibrate actively, which consumes the excited energy and thus makes the polymers non-emissive in solution. With a large amount of nonsolvent of water added into their THF solutions, the **hb**-PMTCs form nanoaggregates. The intramolecular motions of TPE moieties are greatly suppressed, making the polymers highly emissive.^[32] Furthermore, the polymers bearing long flexible spacers are more soluble in solutions, resulting in a greater enhancement in emission intensity from solution to aggregate state.^[40]

Sensitive detection of explosives is of great importance for civilian and national security. In recent years, AIE-active polymers have been widely used as fluorescent sensors for

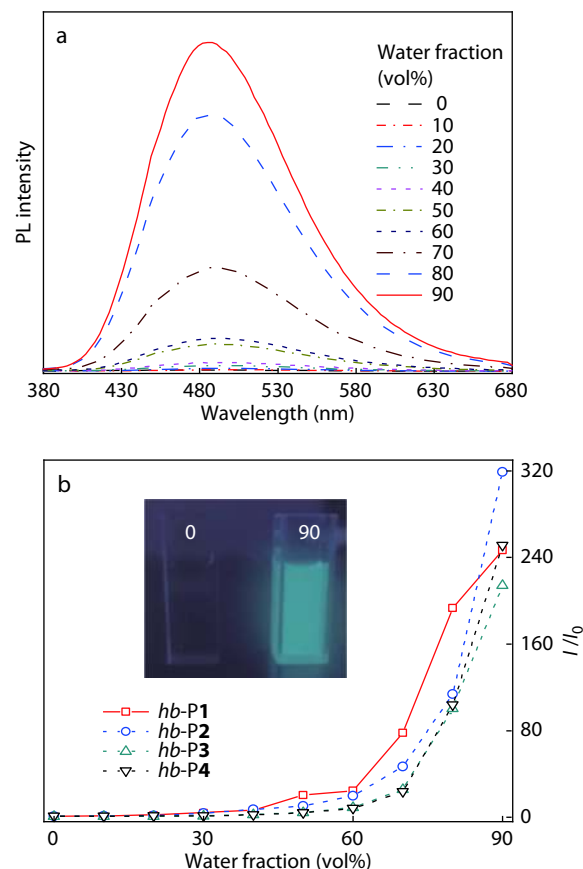


Fig. 4 PL spectra of **hb-P1** in THF/water mixtures with different water fractions (f_w). Concentration: $10\ \mu\text{mol}\cdot\text{L}^{-1}$; λ_{ex} : 332 nm (a). Plots of relative emission peak intensity (I/I_0) of **hb-P1–4** versus f_w of their THF/water mixtures. Inset: photographs of **hb-P1** in THF/water mixtures with f_w of 0 and 90% taken under UV illumination (b).

explosive detection due to their good processability and super-amplification quenching effect.^[41–44] The AIE properties of **hb**-PMTCs enable us to explore their application in detecting explosives. We employed picric acid (PA) as a model compound of nitroaromatic explosive owing to its commercial availability, and the aggregates of **hb**-PMTCs in THF/water mixtures with f_w of 90% due to their maximum luminescence intensities.

As can be seen in Fig. 5(a), the PL intensity of **hb-P1** aggregates decreases progressively with gradual addition of PA, and the luminescence quenching could be identified at a PA concentration of $0.2\ \mu\text{g}\cdot\text{mL}^{-1}$. Similar PL behaviors are observed in the aggregates of **hb-P2–4**. The Stern-Volmer plots of **hb-P1–4** are almost linearly correlated with PA concentration below $20\ \mu\text{g}\cdot\text{mL}^{-1}$ (Fig. 5b), giving the quenching constants of 14290, 14300, 24670, and $11900\ \text{L}\cdot\text{mol}^{-1}$, respectively, which are comparable to those of TPE-containing hyperbranched polymers synthesized by the phenylpropiolate-azide polycycloaddition.^[28] At PA concentration above $20\ \mu\text{g}\cdot\text{mL}^{-1}$, the curves bend upward, manifesting a superamplified fluorescence quenching effect.^[44] This may be ascribed to the triazole rings and branched structures of the **hb**-PMTCs, which interact with more PA molecules and provide more channels for exciton diffusion.

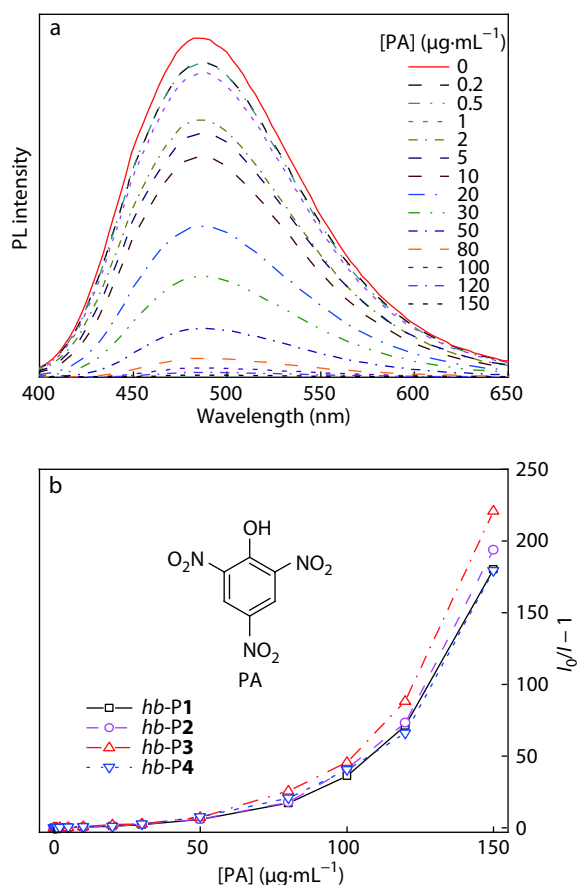


Fig. 5 PL spectra of *hb*-P1 in THF/water mixtures (1/9, V/V) with different amounts of PA. Concentration: $10 \mu\text{mol}\cdot\text{L}^{-1}$; λ_{ex} : 332 nm (a). Plots of $I_0/I - 1$ of *hb*-P1–4 versus PA concentration, where I = peak intensity, and I_0 = peak intensity at $[\text{PA}] = 0 \mu\text{g}\cdot\text{mL}^{-1}$. Inset: chemical structure of PA (b).

The efficient solid-state emission and good film-forming ability of the *hb*-PMTCs make them promising for the fabrication of fluorescent patterns.^[45] This is the case. Thin solid films of *hb*-P1–4 were easily prepared by spin-coating on silicon wafers, and then irradiated under a UV light through a copper photomask. The fluorescence of the exposed area is quenched by a UV-induced oxidation process, while the unexposed area remains emissive. Two-dimensional fluorescent patterns with sharp line edges are readily generated without going through further development process (Fig. 6 and Figs. S11–S13 in ESI). These properties make the *hb*-

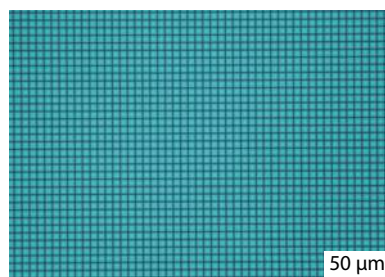


Fig. 6 Two-dimensional fluorescent pattern of *hb*-P1. The photograph was taken under UV irradiation.

PMTCs promising candidates for the fabrication of large-scale flexible photonic devices through photolithography techniques.

CONCLUSIONS

In summary, four functional TPE-containing *hb*-PMTCs have been readily synthesized by the catalyst-free butynoate-azide click polymerization. The polymerizations of tributynoates (**1**) with TPE-containing diazides (**2**) proceeded smoothly in DMF at 100 °C for 11 and 16 h, respectively, giving *hb*-P1–4 with high molecular weights (M_w up to 2.4×10^4) and regioregularities (up to 83.9%) in good yields (up to 86.8%). The resultant *hb*-PMTCs have good solubility in common organic solvents, good film-forming ability, and thermal stability. Thanks to the TPE moieties contained, *hb*-P1–4 are AIE active. Their nanoaggregates can be utilized as chemosensors for detecting explosive of PA with a superamplification fluorescence quenching effect. Moreover, their films could generate fluorescent photopatterns with high resolution after UV irradiation through a photomask. These properties make the *hb*-PMTCs good candidate materials for high-tech applications.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2421-y>.

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