

Facile Synthesis of Functional Poly(methyltriazolylcarboxylate)s by Solvent- and Catalyst-free Butynoate-Azide Polycycloaddition

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Electronic Supplementary Information

Abstract The copper-catalyzed and metal-free azide-alkyne click polymerizations have become efficient tools for polymer synthesis. However, the 1,3-dipolar polycycloadditions between internal alkynes and azides are rarely employed to construct functional polymers. Herein, the polycycloadditions of dibutynoate (**1**) and tetraphenylethene-containing diazides (**2**) were carried out at 100 °C for 12 h under solvent- and catalyst-free conditions, producing soluble poly(methyltriazolylcarboxylate)s (PMTCs) with high molecular weights in high yields. The resultant polymers were thermally stable with 5% weight loss temperatures up to 377 °C. The PMTCs showed aggregation-induced emission (AIE) properties. They could work as fluorescent sensors for detecting explosive with high sensitivity, and generate two-dimensional fluorescent photopatterns with high resolution. Furthermore, their triazolium salts could be utilized for cell-imaging applications.

Keywords Solvent- and catalyst-free polycycloaddition; Aggregation-induced emission; Photopattern; Cell imaging

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INTRODUCTION

Development of facile and “green” polymerization methods for constructing functional polymers is an attractive research topic in polymer science. The new polymerization reactions based on the triple-bond building blocks have drawn much attention over the past few years.^[1,2] In general, most of the polymerization strategies are derived from the efficient organic reactions of small molecules. Thermal 1,3-dipolar alkyne-azide cycloaddition for synthesis of 1,2,3-triazoles was developed by Huisgen in the 1960s.^[3] Nevertheless, this reaction did not gain much interest due to its low regioselectivity and slow reaction rate. In 2002, the research groups of Meldal and Sharpless independently reported that Cu(I) catalysts could accelerate the reaction between azides and terminal alkynes to produce sole 1,4-disubstituted-1,2,3-triazoles.^[4,5] Since then, the Cu(I)-mediated azide-alkyne cycloaddition (CuAAC), regarded as an archetypal “click” reaction, has attracted considerable attention and

been widely used in bioconjugation, medicinal chemistry, and material science due to its advantageous properties, such as high atom economy, moderate reaction conditions, high yield, and high regioselectivity.^[6,7]

Thanks to the persistent efforts of polymer chemists, the CuAAC click reaction has been developed into an efficient polymerization methodology, click polymerization, for the preparation of linear and hyperbranched polytriazoles.^[8–11] However, the used copper catalysts during polymerization can form complexes with the resulting triazole rings, and are thus difficult to be completely removed from the polymeric products. The copper residues can cause biological toxicity and deteriorate the optoelectronic properties of the resultant polytriazoles, which limit the applications of such polymerization in constructing biomedical and optoelectronic polymeric materials.^[12,13] To circumvent this problem, exploration of catalyst- or metal-free polymerization processes is thus a promising way. Qin and Tang developed metal-free aryl-acetylene/propiolate-azide and activated azide-alkyne click polymerizations, and synthesized a series of linear and hyperbranched polytriazoles with advanced functional properties.^[14,15] Ma and coworkers reported a metal-free polycycloaddition of perfluorinated phenyl azide and alkyne facilitated by arene-perfluoroarene interactions.^[16,17] Sureshan and co-

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workers developed a topochemical azide-alkyne click polymerization without solvent and catalyst, and prepared a series of artificial biomacromolecules.^[18,19] However, the alkyne monomers used in the Cu(I)-catalyzed and metal-free click polymerizations are terminal alkynes. The polycycloadditions of azides and internal alkynes for the synthesis of functional polymers are rarely reported.^[20,21]

In recent years, our groups have developed metal-free polycycloadditions of azides and activated internal alkynes (benzoylthynylbenzenes and phenylpropiolates).^[22–25] For instance, the polymerization reactions of diphenylpropiolate with diazides were carried out in *N,N*-dimethylformamide (DMF) at 150 °C for 12 h, giving soluble poly(phenyltriazolylcarboxylate)s (PPTCs) with high molecular weights (M_w up to 26800) in high yields (up to 93.0%).^[23] In order to foster the internal alkyne-azide polycycloaddition an efficient tool for the construction of functional polymers, it is necessary to expand the ranges of internal alkyne monomers, and make the polymerization process more environmentally friendly.

Herein, we developed a solvent- and catalyst-free butynoate-azide polycycloaddition, and synthesized PMTCs with high molecular weights and satisfactory regioregularities by the polymerizations of di(2-butynoate) and tetraphenylethene (TPE)-containing diazides. The PMTCs exhibit good solubility, high thermal stability, and AIE features. They can function as chemosensors to detect explosive of picric acid (PA), and generate fluorescent photopatterns with high resolution. Moreover, their 1,2,3-triazolium salts show good water dispersibility and great potential for biological imaging.

EXPERIMENTAL

Materials

Dichloromethane (DCM) was dried by calcium hydride, and then distilled under reduced pressure. 2-Butynoic acid was obtained from Shanghai D&B Biological Science and Technology Co., Ltd. (China). Neopentyl glycol was purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd. (China). Dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), and *p*-toluenesulfonic acid monohydrate (*p*-TsOH) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). All other chemicals were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (China), Chinasun Specialty Products Co., Ltd. (Jiangsu, China), or Energy Chemical. (Shanghai, China) and used without further purification.

Instruments

IR spectra were recorded on a Bruker VERTEX 70v FTIR spectrophotometer. ¹H- and ¹³C-NMR spectra were taken on Varian Unity Inova 400 (400 MHz) or 600 (600 MHz) spectrometers in DMSO-*d*₆ or CDCl₃ using tetramethylsilane (TMS) as internal reference at room temperature. Elemental analysis was performed on an Elementar Vario EL-III instrument. Thermogravimetric analysis (TGA) measurements were carried out using a Discovery TGA instrument (METTLER TOLEDO instruments, Switzerland) under dry nitrogen at 10 °C·min^{−1}. Relative weight-average (M_w) and number-average (M_n) molecular weights of the polymers and their polydispersity indices (M_w/M_n , PDI) were measured by a PL GPC 50 gel permeation chromatography (GPC) system equipped with an interferometric refractometer detector, using

a set of monodisperse polystyrene (PS) as calibration standards and THF as the eluent at a flow rate of 1.0 mL·min^{−1}. Photoluminescence (PL) spectra were obtained from an Edinburgh Instrument FLS 980 fluorospectrometer.

Synthesis of Monomers

1,2-Bis(4-(4-azidobutoxy)phenyl)-1,2-diphenylethene (**2a**) and 1,2-bis(4-((6-azidoheptyl)oxy)phenyl)-1,2-diphenylethene (**2b**) were synthesized according to our previous paper.^[23] 2,2-Dimethylpropane-1,3-diyl bisbutynoate (**1**) was synthesized by a simple DCC-mediated esterification between neopentyl glycol and 2-butynoic acid. The detailed synthetic procedure is described below.

Into a 250 mL two-necked flask were placed neopentyl glycol (1.04 g, 10 mmol), DCC (6.18 g, 30 mmol), DMAP (0.49 g, 4 mmol), and *p*-TsOH (0.76 g, 4 mmol). DCM (100 mL) was injected to dissolve the solids and the solution was cooled to 0 °C with an ice-water bath. Then, 2-butynoic acid (1.93 g, 23 mmol) dissolved in DCM (20 mL) was added dropwise by a dropping funnel, and the solution was stirred overnight at room temperature. After filtering off the insoluble substance, the solution was concentrated by rotary evaporation. The crude product was purified by a silica gel column using petroleum ether/ethyl acetate (100/1, V/V) as eluent. 2,2-Dimethylpropane-1,3-diyl bisbutynoate (**1**) was obtained in 53.0% yield (1.25 g) as a white solid. FTIR (thin film, ν , cm^{−1}): 2976, 2331, 2248 (C≡C stretching), 1712 (C=O stretching), 1479, 1375, 1263, 1070. ¹H-NMR (400 MHz, DMSO-*d*₆, δ , TMS, ppm): 3.92 (s, 4H), 2.04 (s, 6H), 0.92 (s, 6H). ¹³C-NMR (150 MHz, CDCl₃, δ , TMS, ppm): 153.7, 85.9, 72.3, 70.1, 34.7, 21.6, 3.8. Elemental Anal. Calcd. for C₁₃H₁₆O₄: C, 66.09; H, 6.83; Found: C, 65.99; H, 6.93.

Synthesis of PMTCs

The polymerization reactions between bisbutynoate and diazides were carried out under nitrogen atmosphere using the standard Schlenk technique in a vacuum line system, unless otherwise stated. The experimental procedures for the polycycloaddition of **1** and **2a** are given below.

In a 10 mL Schlenk tube with a stopcock in the side arm was placed **1** (70.8 mg, 0.3 mmol) and **2a** (167.5 mg, 0.3 mmol). The tube was evacuated and refilled with dry nitrogen three times through the side arm. After stirring at 100 °C for 12 h, the mixture was dissolved with 5 mL of chloroform, and added dropwise into 200 mL of hexane through a cotton filter under vigorous stirring. After standing overnight, the precipitate was collected by filtration, then washed by hexane, and dried to a constant weight at ambient atmosphere.

Characterization data for **P3a**: White powder; 85.4% yield. M_w 1.05 × 10⁴; M_w/M_n 1.72 (GPC, determined in THF using PS as calibration). FTIR (thin film, ν , cm^{−1}): 3032, 2958, 2875, 2243 (C≡C stretching), 2096 (N₃ stretching), 1719 (C=O stretching), 1508, 1473, 1242. ¹H-NMR (400 MHz, DMSO-*d*₆, δ , TMS, ppm): 7.04, 6.90, 6.80, 6.62, 4.60, 4.34, 4.14, 3.86, 1.86, 1.63, 1.04. ¹³C-NMR (150 MHz, CDCl₃, δ , TMS, ppm): 161.1, 156.2, 143.7, 139.3, 137.4, 136.2, 132.3, 130.9, 127.3, 125.7, 113.0, 68.6, 66.3, 47.2, 34.8, 25.7, 21.6, 12.4, 8.4, 3.4.

Characterization data for **P3b**: White powder; 89.6% yield. M_w 1.67 × 10⁴; M_w/M_n 1.77 (GPC, determined in THF using PS as calibration). FTIR (thin film, ν , cm^{−1}): 3052, 3032, 2935, 2860, 2243 (C≡C stretching), 2094 (N₃ stretching), 1714 (C=O stretching).

ching), 1606, 1571, 1508, 1442, 1382, 1241. $^1\text{H-NMR}$ (400 MHz, DMSO-d_6 , δ , TMS, ppm): 7.05, 6.91, 6.81, 6.62, 4.55, 4.28, 4.16, 3.80, 1.74, 1.61, 1.36, 1.06. $^{13}\text{C-NMR}$ (150 MHz, CDCl_3 , δ , TMS, ppm): 161.7, 157.4, 143.9, 139.2, 137.3, 136.1, 132.2, 131.9, 127.6, 125.6, 113.5, 69.6, 67.3, 50.8, 47.7, 35.0, 31.6, 29.2, 26.3, 25.6, 22.7, 22.1, 13.7, 9.1.

RESULTS AND DISCUSSION

The dibutynoate monomer **1** was facily synthesized in one step through a DCC-mediated esterification reaction of commercially available 2-butyric acid and neopentyl glycol. The TPE-containing diazide monomers (**2a** and **2b**) were prepared following our previously reported procedures. All the obtained monomers were characterized by spectroscopic techniques, and satisfactory analysis data corresponding to their expected molecular structures were obtained (see the Experimental section for details).

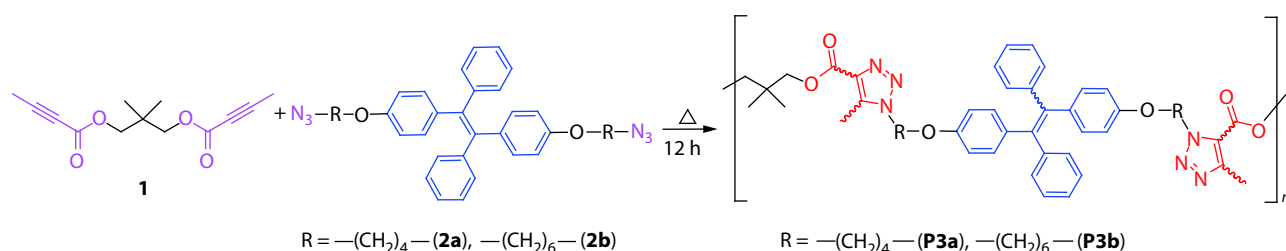
In our previous work, the metal-free polycycloadditions of diphenylpropiolates and diazides were performed in DMF at 150 °C, affording soluble PPTCs with high molecular weights in high yields.^[23] The molecular weights of the resultant polymers increased with increasing the monomer concentrations. This indicates that the polymerization reaction is promising to be performed in bulk state. Furthermore, the regioselectivities of aliphatic phenylpropiolate-azide polycycloaddition were higher than those of aromatic phenylpropiolate-azide polycycloaddition. In this work, we selected 2-butyrate as the activated internal alkyne monomer, and tried to conduct the solvent- and catalyst-free butynoate-azide polycycloaddition. Delightfully, polymerizations of 2,2-dimethylpropane-1,3-diyl bis(but-2-ynoate) (**1**) and TPE-containing diazides (**2a** and **2b**) proceeded smoothly in bulk at 100 °C for 12 h to afford the corresponding PMTCs **P3a** and **P3b** with high molecular weights (M_w up to 1.67×10^4) in good yields (up to 89.6%) (Scheme 1 and Table 1). Furthermore, the polymerization could be performed in an open atmosphere without the protection of oxygen and moisture (cf. No. 3 in Table 1), which simplified the reaction procedures. The resultant PMTCs possessed good solubility in common organic solvents such as dichloromethane, chloroform, THF, DMF, and DMSO. They

were also thermally stable with 5% weight loss temperatures higher than 361 °C (Fig. S1 in the electronic supplementary information, ESI).

P3a and **P3b** were characterized by FTIR and NMR techniques, and satisfactory analysis data were obtained (see the Experimental section for details). The FTIR and NMR spectra of **P3a** and its corresponding monomers **1** and **2a** are given as examples. As shown in Fig. S2 (in ESI), the stretching vibration bands of $\text{C}\equiv\text{C}$ at 2248 cm^{-1} and N_3 at 2095 cm^{-1} in the FTIR spectra of **1** and **2a**, respectively, become much weaker in the spectrum of **P3a**. This indicates that most of the alkynyl and azido groups in the monomers have been consumed by the polycycloaddition and transformed to the triazole rings in the polymer. The spectrum profiles of **P3b** are similar to those of **P3a** (Fig. S3 in ESI).

Since the $^1\text{H-NMR}$ spectra of **P3** have better resolution in DMSO-d_6 than in CDCl_3 , we thus provide the $^1\text{H-NMR}$ spectra of **P3a** and its corresponding monomers in DMSO-d_6 (Fig. 1) for discussion. The methylene protons adjacent to the azido groups of **2a** resonate at $\delta = 3.36$, which overlap with the water signal. Two new signals at $\delta = 4.34$ (signal a) and $\delta = 4.60$ (signal b) are observed in the spectrum of **P3a**. According to our previous work,^[23] the signal resonating at $\delta = 4.34$ is associated with the proton resonance of methylene groups neighboring triazole rings in structure α , while the signal at $\delta = 4.60$ is ascribed to that in structure β . This demonstrates that most of the acetylene and azide groups in the monomers have been transformed to the triazole rings in **P3a** by the polymerization. Moreover, since the resonance signals at $\delta = 4.34$ (signal a) and $\delta = 4.60$ (signal b) are well separated, we can employ their integrals to calculate the fraction of structure α in **P3a**, which is 71.4%. Similar phenomena can be observed in the spectrum of **P3b** (Fig. S4 in ESI). The fraction of structure α in **P3b** was calculated to be 70.8%. These regioregularities are higher than those of TPE-containing PPTCs (67.6% and 66.9%) obtained by the phenylpropiolate-azide polycycloaddition.^[23]

$^{13}\text{C-NMR}$ spectroscopy generally gives more informative characterization data of polymers. The acetylene carbons of monomer **1** resonate at $\delta = 85.9$ and 72.3 , which disappear in the $^{13}\text{C-NMR}$ spectra of **P3a** and **P3b**. Meanwhile, new signals



Scheme 1 Synthesis of **P3a** and **P3b** by solvent- and catalyst-free polycycloaddition.

Table 1 Polycycloaddition of dibutynoate **1** and diazides **2**.^a

Run	Monomer	Polymer	$M_w^b \times 10^{-4}$	PDI ^b	Yield (%)	T_d^c (°C)
1	1 + 2a	P3a	1.05	1.72	85.4	367
2	1 + 2b	P3b	1.67	1.77	89.6	377
3 ^d	1 + 2b	P3b(o)	1.26	1.69	76.5	361

^a Performed at 100 °C for 12 h under nitrogen; ^b M_w and PDI of polymers estimated by GPC in THF using PS as calibration; ^c Temperature for 5% weight loss;

^d Performed in air at 100 °C for 12 h.

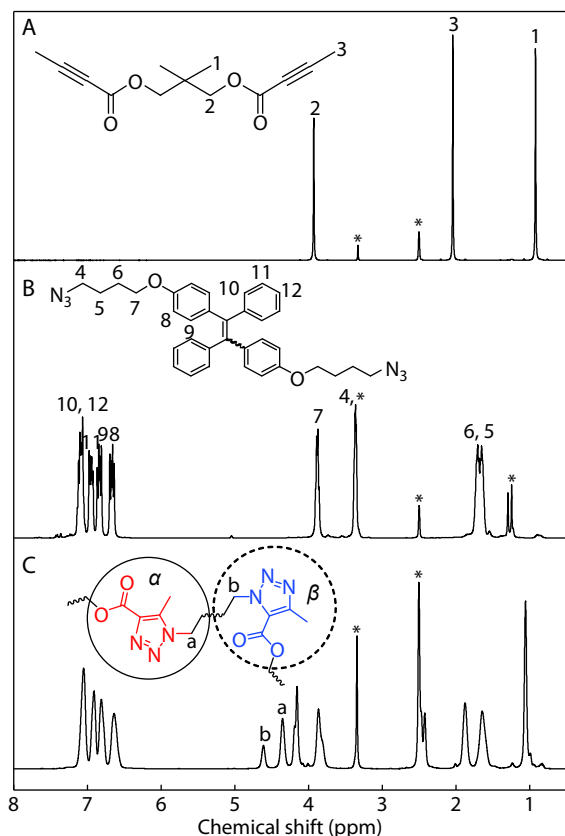


Fig. 1 ^1H -NMR spectra of (A) **1**, (B) **2a**, and (C) **P3a** in DMSO-d_6 . The solvents and water signals are marked with asterisks.

appear in the aromatic absorption region, which are stemmed from the resonances of carbon atoms of triazole rings (Figs. S5 and S6 in ESI). This once again proves that the polycycloaddition was realized through the transformation of alkyne and azide groups to the triazole rings.

Most of the “traditional” luminophores are highly emissive

in solution, but become weakly or non-emissive in aggregated state, showing an aggregation-caused quenching effect. Exactly opposite to the effect, the luminophores with AIE characteristics, such as TPE, silole, and their derivatives, are non-emissive in their dilute solutions, but emit efficiently through aggregate formation.^[26,27] Such unique photophysical behavior makes the AIE luminogens find applications in organic light-emitting diodes, chemical sensing, and biological probes.^[26–33]

Considering TPE is a typical AIE-active molecule, the TPE-containing PMTCs, **P3a** and **P3b**, are expected to possess AIE activity. We thus investigated their emission spectra in solution and aggregated state. As shown in Fig. 2(a), the PL spectra of **P3a** in THF solution and THF-water mixtures with water fractions (f_w) lower than 30% give flat lines nearly parallel to the abscissa. This suggests that the polymer was almost non-emissive when it was molecularly dissolved. With increasing the water fractions ($f_w > 30\%$), the emission of **P3a** in THF-water mixtures is enhanced gradually. The maximum PL intensity of **P3a** is recorded at f_w of 90%, which is about 220 times higher than that in THF solution (Fig. 2b). The similar emission behaviors are also observed for **P3b**. Since water is a poor solvent for PMTCs, aggregates of the polymers must be formed in the THF-water mixtures with high f_w . **P3a** and **P3b** were induced to emit fluorescence upon aggregation, that is to say, they were AIE-active.

As is known, detection of explosives is vitally important for national security and civilian safety. In recent years, AIE-active polymers have drawn much attention in the field of explosive detection due to their advantageous characteristics such as super-amplification quenching effect and facile device fabrication.^[34] Motivated by the AIE properties of **P3a** and **P3b**, we utilized them as fluorescent sensors for the detection of explosive nitro-aromatic compounds. Thanks to its commercial availability, picric acid (PA) was used as a model explosive. Fig. 3(a) shows the PL spectra of **P3a** in the THF-water mixtures with f_w of 90% containing different amounts of PA. The PL intensities of **P3a** progressively decreased with gradual

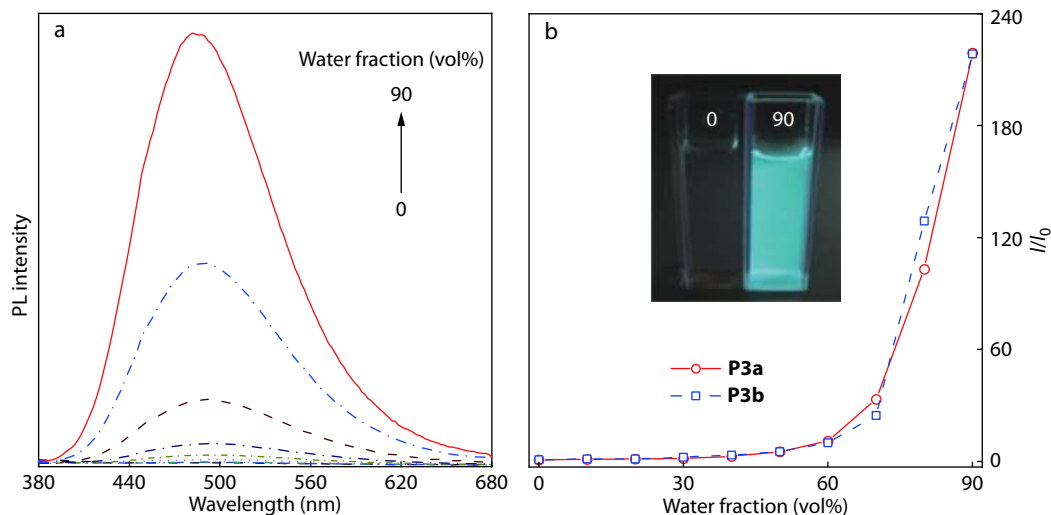


Fig. 2 (a) PL spectra of **P3a** in THF-water mixtures with different water fractions (f_w). Concentration: $10 \mu\text{mol}\cdot\text{L}^{-1}$; $\lambda_{\text{ex}} = 320 \text{ nm}$. (b) Plots of relative emission peak intensity (I/I_0) of **P3a** and **P3b** at 485 and 490 nm, respectively, versus f_w of their THF-water mixtures. Inset: Photographs of **P3a** in THF-water mixtures with f_w of 0% and 90% taken under 365 nm UV illumination.

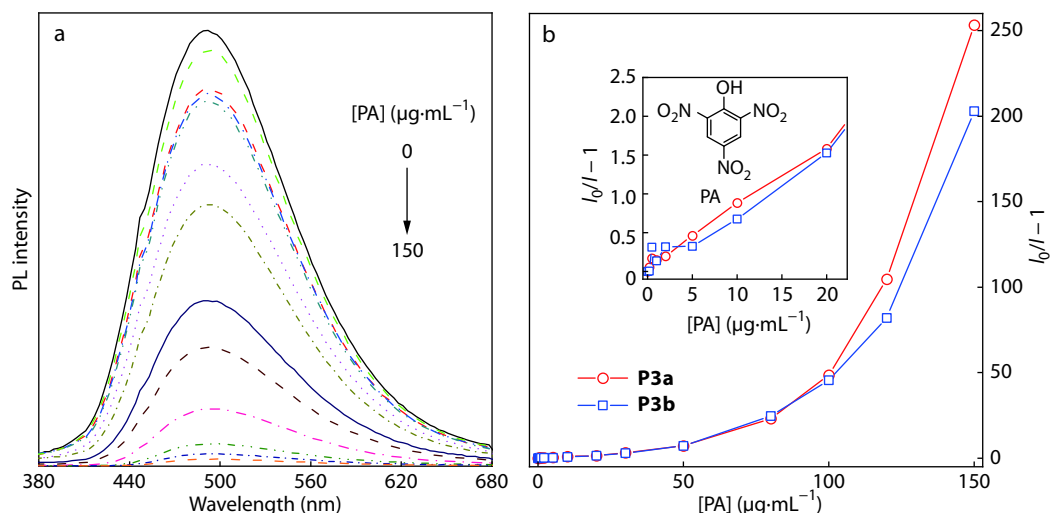


Fig. 3 (a) PL spectra of **P3a** in THF-water mixtures (1/9, V/V) containing different amounts of picric acid (PA). Concentration of **P3a**: $10 \mu\text{mol}\cdot\text{L}^{-1}$. (b) Plots of $I_0/I - 1$ of **P3a** and **P3b** versus PA concentration, where I = peak intensity, and I_0 = peak intensity at $[\text{PA}] = 0 \mu\text{g}\cdot\text{mL}^{-1}$. Inset: chemical structure of PA and plots of $I_0/I - 1$ of **P3** versus PA concentration.

addition of PA. The similar luminescence behaviors were also observed for **P3b**. Their detection limits were $0.2 \mu\text{g}\cdot\text{mL}^{-1}$, which is comparable to those of TPE-containing PPTCs in our previous work.^[23–25] In addition, when the PA concentrations are below $20 \mu\text{g}\cdot\text{mL}^{-1}$, the Stern-Volmer plots of **P3a** and **P3b** show linear relation and give the quenching constants of 17700 and $15920 \text{ L}\cdot\text{mol}^{-1}$, respectively. Afterward, the curves of **P3a** and **P3b** bend upward, exhibiting a super-amplification fluorescence quenching effect by the explosive of PA (Fig. 3b). This may be due to the triazole ring structures and the formed cavities in the nanoaggregates of PMTCs, which can interact with more PA molecules and provide more pathways for exciton diffusion.^[34]

The efficient solid-state luminescence and good film-forming properties of PMTCs enable them to be employed to produce fluorescent patterns. The thin solid films of **P3a** and **P3b** fabricated by spin-coating technique were subjected UV irradiation for 20 min through copper photomasks. The fluorescence of the exposed area was quenched by UV-induced oxidation process, while the unexposed area remained emissive. Two dimensional luminescent images with clear edges were

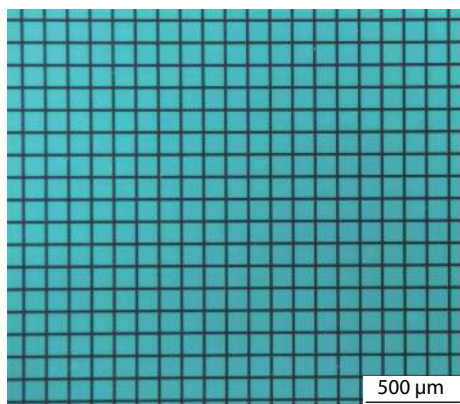


Fig. 4 Two-dimensional fluorescent pattern of **P3a** taken under UV irradiation.

thus readily generated without further processing procedures (Fig. 4 and Fig. S7 in ESI). This makes the PMTCs promising materials for the fabrication of large-scale thin-film optoelectronics through photolithography techniques.^[35,36]

Poly(1,2,3-triazolium)s are a type of polymer electrolytes developed recently.^[37,38] Much effort has been devoted to their synthesis; nevertheless, their biomedical applications have been rarely reported.^[39,40] As no catalyst is used in the butyrate-azide polycycloaddition, PMTC for the biological applications can be free from the toxic catalyst residues. We thus prepared the PMTC-based poly(1,2,3-triazolium)s and explored their application in cell-imaging. **P3a** and **P3b** were quat-

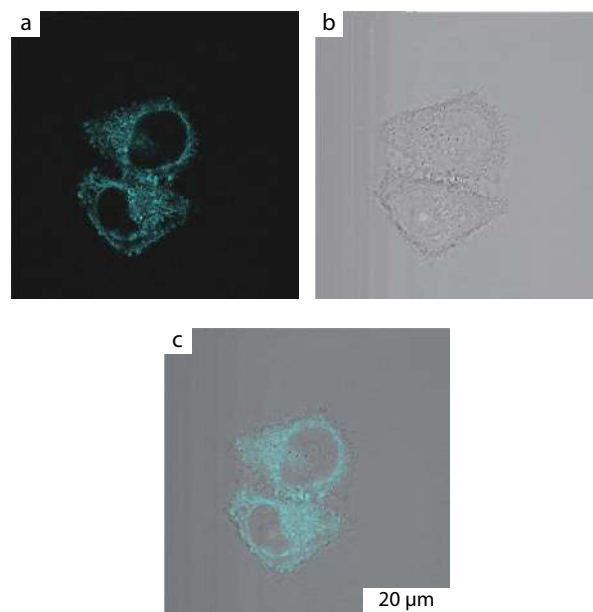


Fig. 5 (a) Laser scanning confocal microscopy, (b) bright-field, and (c) merged images of HeLa cells stained with the triazolium salts of **P3a** ($6.4 \mu\text{mol}\cdot\text{L}^{-1}$) for 3 h at room temperature ($\lambda_{\text{ex}} = 405 \text{ nm}$, $\lambda_{\text{em}} = 431\text{--}585 \text{ nm}$).

ernized with methyl iodide to give the poly(1,2,3-triazolium)s (^1H - and ^{13}C -NMR spectra see Figs. S8 and S9 in ESI) according to the reported procedure.^[40] The obtained triazolium salts showed good water dispersibility, which endows them with potential applications in biomedical fields. The cell imaging experiment on HeLa cells was performed. After incubating with the triazolium salts of **P3a** and **P3b** for 3 h at room temperature without washing process, a bright luminescence was observed for the HeLa cells (Fig. 5 and Fig. S10 in ESI). The results suggest that the poly(1,2,3-triazolium)s can be up-taken by HeLa cells.

CONCLUSIONS

In summary, we have successfully prepared TPE-containing PMTCs with satisfactory molecular weights (M_w up to 1.67×10^4) and regioregularities (up to 71.4%) in good yields (up to 89.6%) by the solvent- and catalyst-free butynoate-azide polycycloaddition. The polymerization could be performed in an open atmosphere. The resultant polymers possessed good solubility in common organic solvents and high thermal stability. They were non-emissive in dilute solution, but became strongly emissive in aggregated state, exhibiting AIE characteristics. The PMTCs could work as chemosensors to detect explosive of PA with a super-amplification fluorescence quenching effect, and generate luminescent photopatterns with high resolution. Furthermore, their triazolium salts showed great potential for biological imaging. It is anticipated that the butynoate-azide polycycloaddition could be developed into a more powerful tool for constructing functional PMTCs with higher regioregularities and new topological structures through further optimization of the polymerization conditions.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2316-y>.

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