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Facile synthesis of poly(aroxycarbonyltriazole)s with aggregation-induced emission characteristics by metal-free click polymerization

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Regioselective 1,3-dipolar polycycloadditions of 4,4'-isopropylidenediphenyl dipropiolate (**1**) and tetraphenylethene (TPE)-containing diazides (**2**) are carried out in polar solvents such as DMF/toluene at a moderate temperature of 100 °C for 6 h, producing poly(aroxycarbonyltriazole)s (PACTs) **P3** with high molecular weights (M_w up to 23900) and regioregularities ($F_{1,4}$ up to ~90%) in high yields (up to ~99%). These metal-free click polymerizations can propagate smoothly in an open atmosphere without protection from oxygen and moisture. The obtained polymers are soluble in common organic solvents and thermally stable at temperatures up to 375 °C. Thanks to their contained TPE moieties, the PACTs show aggregation-induced emission and can serve as fluorescent chemosensors for superamplified detection of explosives.

aggregation-induced emission, metal-free click polymerization, propiolate, chemosensor

1 Introduction

The 1,3-dipolar cycloaddition of alkynes and azides, systematically investigated by Huisgen and coworkers in the 1960s, is an efficient route to generate 1,2,3-triazoles but has received little attention due to its low reaction efficiency [1, 2]. This reaction is vitalized by Sharpless' and Meldal's independent discoveries in 2002 that Cu(I)-species could significantly improve the reaction rate by seven orders higher in magnitude and furnish sole 1,4-disubstituted 1,2,3-triazoles [3, 4]. Since then, the Cu(I)-mediated alkyne-azide cycloaddition, dubbed "click chemistry" by Sharpless and coworkers, has attracted enormous interests due to its remarkable features such as high regioselectivity, high yield,

mild reaction conditions, functionality tolerance, and simple product isolation procedures etc [5, 6]. The click reaction has been actively utilized to synthesize bioconjugates and dendrimers, and to decorate surfaces and nanoparticles [7–10].

This reaction has also been used in polymer science, but mainly in the area of post-functionalization of preformed polymers [11–16]. Although some impressive advances have been achieved, the development of the click reaction into a polymerization technique for the synthesis linear and hyperbranched polymers is still challengeable [17–20]. The Cu(I)-mediated click polymerization generally suffers from the solubility problem, unless very long alkyl pendants or spacers are incorporated into the polymer structures [21–23]. Furthermore, the catalyst residues in polymers can deteriorate their photophysical properties, for example, their light emissions can be quenched by the metallic species. The

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development of the nonmetallic or metal-free click polymerization process is thus highly desired.

Our research groups have recently developed such a metal-free click polymerization. Bis(aryolacetylene)s can react with diazides in a polar solvent at a moderate temperature in a short reaction time, producing soluble and processable poly(aryoltriazole)s (PATAs) with high molecular weights and regioregularities in high yield (Scheme 1) [24, 25]. Thanks to the simple procedures and functionality tolerance of the polymerization, multi-faceted properties of PATAs, such as aggregation-induced emission (AIE), discovered by our group in 2001 [26, 27], have been realized.

As no metallic catalyst is used, such polymerization enjoys the advantages of being less toxic, environmentally friendly etc. Furthermore, the electronic and optical properties of PATAs are free from the detriment by the metallic catalyst residues. The preparation of aryolacetylene monomers requires many reaction steps and harsh reaction conditions. Furthermore, high reactive reagent and toxic heavy-metal oxidants such as MnO_2 or Jones reagent are involved during the experimental courses [28, 29], which will limit the application of such polymerization. It will be nice if the metal-free click polymerization starts from "simple" alkyne monomers, which can be readily prepared from commercially available reagents by simple reaction procedures in an environmentally benign fashion.

The structure key for aryolacetylene is that triple-bond is adjacent to an electron-withdrawing carbonyl group, which makes it more reactive. Propiolate derivatives, which are structurally similar to aryolacetylene, can be readily prepared from commercially available propiolic acid and aliphatic or aromatic diols via a simple esterification reaction. The activity of propiolate derivatives has been proven by their nonmetal-mediated polycyclotrimerization [30, 31]. It is thus envisioned that the metal-free click polymerization of propiolates and azides could furnish poly(aryoltriazole)s (PATAs) with high efficiency.

Though propiolates have been subjected to prepare polymers via 1,3-dipolar cycloaddition with azide, no reaction condition optimization, structure characterization and

regioselectivity are available, which are very important parameters for the development of a simple synthetic strategy for accessing PACTs [32, 33]. In this paper, we will present our endeavors in construction of AIE-active PACTs by metal-free click polymerization of propiolates and azides.

2 Experimental

2.1 Materials

The chemicals in this work were all purchased from Acros or Alfa. THF and toluene were distilled from sodium benzophenone ketyl under nitrogen immediately prior to use. DMF was pre-dried over CaH_2 and distilled under reduced pressure. Other solvents were purified by standard methods. 4,4'-Isopropylidenediphenyl dipropiolate (**1**), 1,2-bis[4-(azidomethyl)phenyl]-1,2-diphenylethene (**2a**), and 1,2-bis[4-(6-azidohexyloxy)phenyl]-1,2-diphenylethene (**2b**) were prepared according to our previous papers [24, 31].

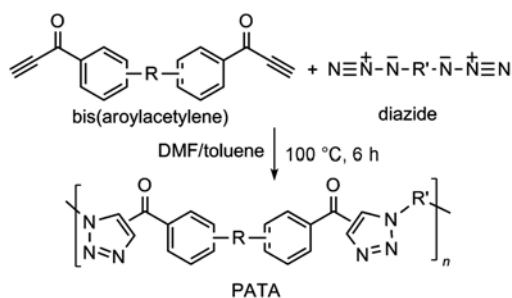
2.2 Instruments

The ^1H and ^{13}C NMR spectra were recorded on a Bruker ADVANCE2B 400 NMR spectrometer in $\text{DMSO-}d_6$ using tetramethylsilane ($\delta=0$) as internal reference. Infrared (IR) spectra were measured on a Bruker Vector 22 spectrometer. UV spectra were recorded on a Varian VARY 100 Bio UV-visible spectrophotometer. Photoluminescence (PL) spectra were measured on a Perkin-Elmer LS 55 spectrofluorometer. Thermal stabilities were evaluated by measuring thermogravimetric analysis (TGA) thermograms on a Perkin-Elmer TGA 7 under dry nitrogen at $20\text{ }^\circ\text{C}/\text{min}$. Molecular weights (M_w and M_n) and polydispersity indices (M_w/M_n , PDI) of the polymers were estimated by a Waters 1515 gel permeation chromatography (GPC) system equipped with an interferometric refractometer detector, using a set of monodisperse polystyrenes as calibration standards and THF as the eluent at a flow rate of $1.0\text{ mL}/\text{min}$.

2.3 Polymerization

Unless otherwise stated, the polymerizations of dipropiolate and diazides were carried out under nitrogen using Schlenk techniques in a vacuum line system. The purification of the products was, however, performed in an open atmosphere. General experimental procedures for the polymerization of dipropiolate and diazides are given as follows.

In a 15 mL Schlenk tube with a stopcock in the side arm was added dipropiolate (0.1 mmol) and diazide (0.1 mmol). The tube was evacuated and refilled with dry nitrogen three times through the side arm. Freshly distilled DMF (0.3 mL) and toluene (0.3 mL) were injected into the tube. The solution was reacted at $100\text{ }^\circ\text{C}$ for 6 h, then diluted with 5 mL of chloroform and added dropwise into 200 mL of hexane/chloroform mixture (10:1 v/v) through a cotton filter under



Scheme 1 Synthesis of poly(aryoltriazole) (PATA) via regioselective metal-free diyne-diazide click polymerization. DMF = *N,N*-dimethyl formamide.

vigorous stirring. After standing overnight, the precipitate was collected by filtration and dried to a constant weight at ambient atmosphere.

Characterization data for P3a: the polymer was prepared from the click polymerization of 4,4'-isopropylidenediphenyl dipropiolate (**1**) and 1,2-bis[4-(azidomethyl)phenyl]-1,2-diphenylethene (**2a**). White powder; 98.7% yield. M_w 15400; M_w/M_n 1.5 (GPC, polystyrene calibration). $F_{1,4}$: 89.3%. IR (thin film), ν (cm^{-1}): 3136, 3050, 2966, 2884, 2098 (N_3 and $\text{C}\equiv\text{C}$ stretching), 1751 ($\text{C}=\text{O}$ stretching), 1502, 1207, 1048. ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 8.98, 8.52, 7.30, 7.18, 7.09, 6.96, 5.83, 5.61, 1.66. ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 163.0, 159.5, 148.5, 143.8, 143.5, 141.1, 138.9, 134.2, 131.7, 131.3, 130.8, 128.6, 128.3, 128.2, 127.3, 122.0, 53.6, 42.8, 31.5.

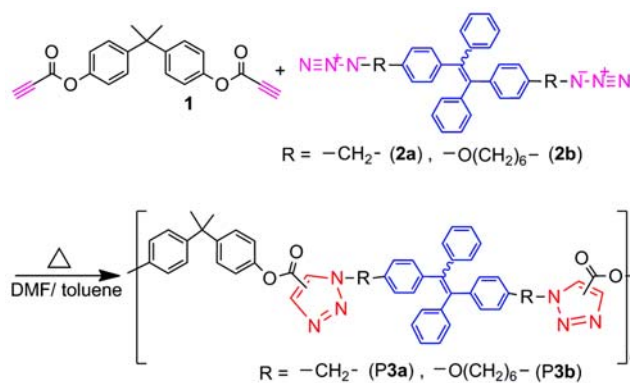
P3b: the polymer was prepared from the click polymerization of 4,4'-isopropylidenediphenyl dipropiolate (**1**) and 1,2-bis[4-(6-azido-hexyloxy)phenyl]-1,2-diphenylethene (**2b**). White powder, 98.9% yield. M_w 15100, M_w/M_n 1.4 (GPC, polystyrene calibration). $F_{1,4}$: 88.5%. IR (thin film), ν (cm^{-1}): 3137, 3045, 2939, 2858, 2095 (N_3 and $\text{C}\equiv\text{C}$ stretching), 1749 ($\text{C}=\text{O}$ stretching), 1505, 1240, 1207, 1043. ^1H NMR (400 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 8.96, 8.46, 7.29, 7.16, 7.05, 6.92, 6.80, 6.62, 4.65, 4.43, 3.81, 3.27, 1.86, 1.66, 1.50, 1.37, 1.26. ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$), δ (TMS, ppm): 159.7, 157.9, 148.7, 148.6, 144.5, 140.0, 138.6, 136.4, 132.6, 131.4, 130.7, 128.4, 128.3, 127.0, 121.9, 114.4, 67.8, 50.5, 42.6, 31.2, 30.1, 29.0, 26.1, 25.6.

3 Results and discussion

As propiolates are structurally similar to arylacetylenes, the optimal experimental conditions for the metal-free click polymerization of bis(arylacetylene)s and diazides were used in this work. The click polymerizations of dipropiolate **1** and diazides **2** propagate smoothly and furnish PACTs **P3a** and **P3b** with high molecular weights (up to 23900) and high regioregularities ($F_{1,4}$ up to 89.3%) in high yields (up to 98.9%) in 6 h (Scheme 2 and Table 1). Furthermore, oxygen and moisture exert little effect on the reaction: the polymer yields, molecular weights, and regioregularities of **P3(o)** [(o) means the reactions were carried out in open atmosphere] are almost identical to **P3** (Table 1). The results are comparable to those of PATAs [24, 25], indicating that such reaction can also be regarded as a kind of metal-free click polymerization. PACTs are readily soluble in common organic solvents such as THF, chloroform, DMF, DMSO but insoluble in water. They are also thermally stable: the 5% loses of their weights at a temperature as high as 375 °C.

P3a and **P3b** were characterized spectroscopically and satisfactory analysis data corresponding to their expected molecular structures are obtained. The ^1H NMR spectra of **P3a** are given in Figure 1 as an example.

The resonances of the acetylene protons of **1** and the methylene protons adjacent to the azido group of **2a** at δ 4.84 and 4.36, respectively, greatly weakened in the spectrum of **P3a**. New peaks resonated at δ 8.98, 8.52, 5.83, and 5.61 were, however, observed. The strong peaks at δ 8.98 and 5.61 are associated with the resonances of the protons in triazole rings (c) and methylene group (a) of 1,4-isomeric units, whereas, the weak signals at δ 8.52 (d) and 5.83 (b) are stemmed from those in 1,5-isomeric units. The results reveal that most of the acetylene and azido groups of the



Scheme 2 Synthetic routes to PACTs via metal-free click polymerization of dipropiolate **1** and diazides **2**.

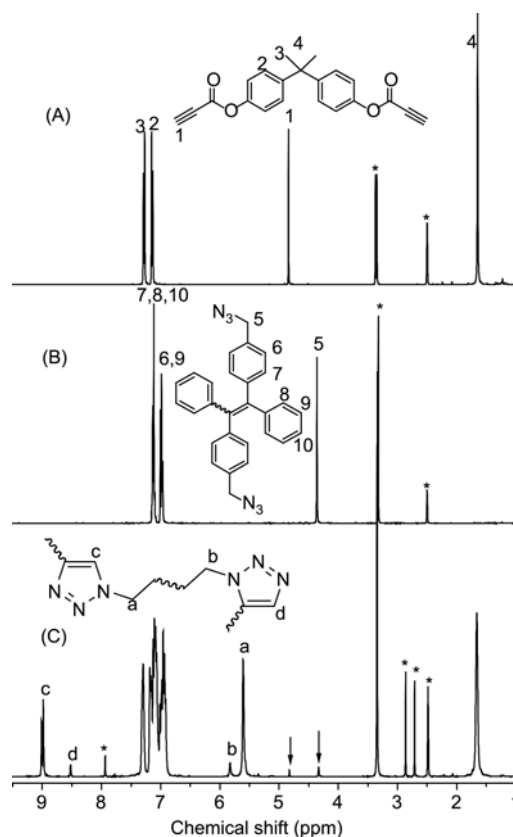


Figure 1 ^1H NMR spectra of monomers **1** (A), **2a** (B) and their polymer **P3a** (C) in $\text{DMSO-}d_6$. The solvents and water peaks are marked with asterisks.

Table 1 Click polymerization of dipropiolate **1** with diazides **2**^{a)}

No.	Monomer	Polymer	Yield (%)	M_w ^{b)}	M_w/M_n ^{b)}	$F_{1,4}$ (%) ^{c)}	T_d (°C) ^{d)}
1	1+2a	P3a	98.7	15400	1.5	89.3	366
2 ^{e)}	1+2a	P3a(o)	96.3	15300	1.5	88.5	375
3	1+2b	P3b	98.9	15100	1.4	88.5	365
4 ^{e)}	1+2b	P3b(o)	95.8	23900	1.6	88.5	367

a) Carried out in a DMF/toluene mixture (1:1 v/v) at 100 °C under nitrogen in 6 h; $[1]=[2]=0.167$ M. b) Determined by GPC in THF on the basis of a polystyrene calibration. c) Ratio of 1,4-regioisomer in the reaction products calculated from ¹H NMR spectra. d) Temperature for 5% weight loss. e) Carried out in open atmosphere.

monomers have been transformed to the triazole rings of the polymers by the click polymerization. The well separated resonances of peaks at 5.83 and 5.61 enable us to calculate the 1,4-regioisomeric ratio ($F_{1,4}$) value from their integrals in **P3a** (Figure 1(C)). The $F_{1,4}$ value was then calculated to be as high as 89.3%.

Tetraphenylethene (TPE) possesses AIE feature: it is nonemissive when molecularly dissolved but induced to emit intensively by aggregate formation [26, 34, 35]. To check whether the PACTs are endowed with the same AIE characteristics by incorporation of TPE moieties, we then investigated the PL spectra of **P3a** and **P3b** in THF/water mixtures with different water fractions (f_w). When excited at 322 nm, the PL curve of **P3a** in THF solution exhibits almost a flat line parallel to the abscissa (Figure 2(A)), indicating that the polymer is nonemissive when molecularly dissolved. In contrast, when water is added into its THF solution, the emission peaked at 468 nm is gradually intensified and increased swiftly when f_w is larger than 50% due to the nanoaggregate formation, indicative of the AIE feature of **P3a**. Similar AIE behaviors are observed in the **P3b**.

The changes in the Φ_F values of **P3a** and **P3b** further verify their AIE activities. As can be seen from Figure 2(B), both **P3a** and **P3b** show very small Φ_F values (0.62% and

0.38%, respectively) in pure THF. The Φ_F values of polymers increase gradually afterwards, and reach the highest ones (24.8 and 21.5%, respectively) at the f_w of 90%, which are 40- and 57-fold higher than those in pure THF. It is worth pointing out that the Φ_F values of polymers are much higher than those of their monomers in the THF/water mixtures with high f_w under the same experimental conditions.

Thus, even though the TPE units are knitted in the PACTs backbone, their peripheral phenyl rings can still rotate against the central olefinic double bonds in solution, making the polymers nonemissive. The intramolecular rotations of the polymers in the aggregates are probably restricted more deeply than that of TPE molecules, which may turn on and intensify their luminescence [36, 37].

The unique AIE features of **P3a** and **P3b** prompt to explore their potential application, such as chemosensors to detect explosives [38]. We employed 2,4,6-trinitrophenol (picric acid, PA) among the explosive nitroaromatic compounds as the model because it is commercially available. Due to their highest emission intensities, PACT aggregates in THF/water mixtures with f_w of 90% were used as the fluorescent sensors. Figure 3(A) shows the PL behaviors of **P3a** upon addition of PA as an example. With gradual addition of PA into the aggregate suspension, the PL intensities

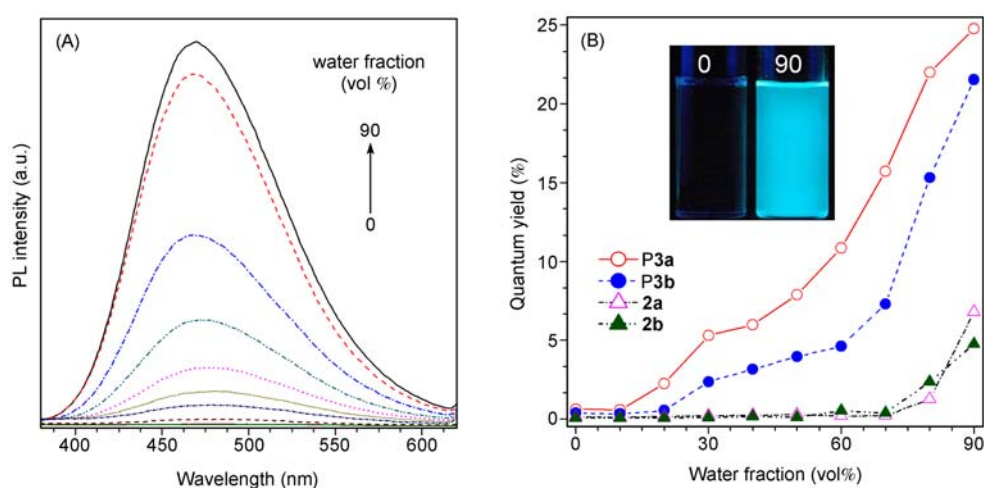


Figure 2 (A) PL spectra of **P3a** in THF and THF/water mixtures. Concentration: 10 μ M; λ_{ex} : 322 nm. (B) Variation in the quantum yields (Φ_F) of **P3a**, **P3b** and their monomers **2a** and **2b** in THF/water mixtures with different water fraction. The Φ_F values were estimated using quinine sulfate in 0.1 M H_2SO_4 ($\Phi_F = 54.6\%$) as standard. Inset: Photographs taken under illumination of a hand-held UV lamp.

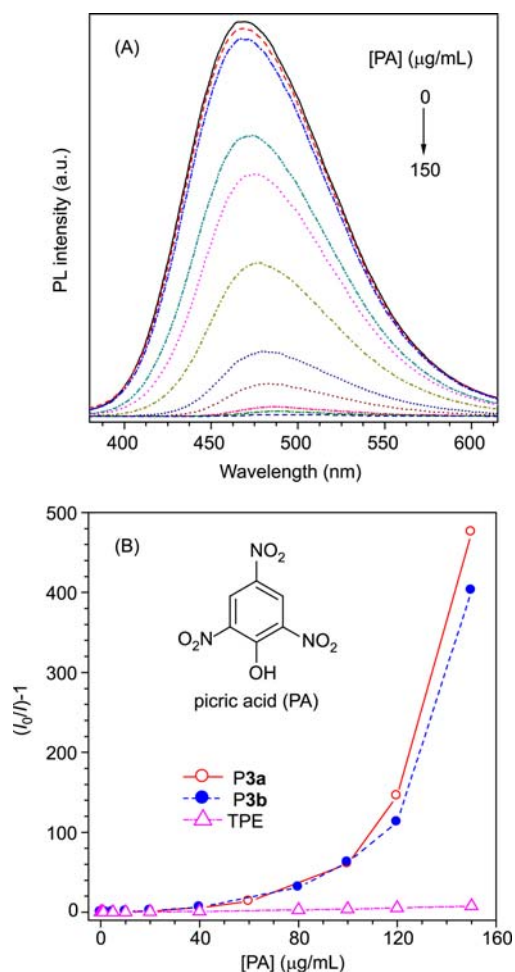


Figure 3 (A) PL spectra of **P3a** in THF/water mixtures (f_w : 90%) containing different amounts of picric acid (PA). Concentration: 10 μM ; λ_{ex} : 322 nm. (B) Stern–Volmer plots of $I_0/I-1$ of **P3a**, **P3b**, and TPE versus PA concentration, where I = peak intensity and I_0 = peak intensity at $[\text{PA}] = 0$ $\mu\text{g/mL}$.

of **P3a** become progressively weakened. The fluorescence quenching can be clearly detected at a PA concentration as low as 1 $\mu\text{g/mL}$ or 1 ppm. Similar PL behaviors are observed in the **P3b**. For comparison, the quenching behavior of TPE aggregates upon addition of PA was also investigated. The PL of TPE in THF/water mixtures with f_w of 90% also becomes weaker in the presence of PA. The Stern–Volmer plot is almost linear with a constant of 10700. Whereas, the plots of **P3a** and **P3b** display a linear relation and give higher quenching constants (18800 and 22000 M^{-1} , respectively) when the PA concentrations are below 20 $\mu\text{g/mL}$ (Figure 3(B)). Afterwards, the curves of polymers bend upward, indicating that the quenching becomes superamplified. These results are quite similar to our previous paper [25], indicative of their similar quenching mechanism. Besides the energy transfer between the PA and TPE moiety/ molecule, the formed cavities in the aggregates of the polymers can also bind with more PA molecules and provide additional interbranched diffusion pathways for exci-

tons to migrate, making the polymer more sensitive than the TPE molecules [39, 40].

4 Conclusions

In summary, we have succeeded in extending the alkyne monomers used for metal-free click polymerization from arylacetylenes to propiolates. The latter can be readily prepared by the one-step and one-pot esterification procedure in ambient conditions. The polymerizations of dipropiolate with TPE-containing diazides propagate smoothly and produce soluble PACTs with high molecular weights and high regioregularities in high yields.

The PACTs show unique AIE characteristics and their nanoaggregates can function as sensitive fluorescent chemosensors for the detection of explosives. It is anticipated that further optimization of polymerization conditions will make the metal-free click polymerization of propiolates and azides an even more efficient and versatile synthetic tool for the generation of PACTs with new topological structures and advanced functional properties. The chemo- and bio-degradability of the contained ester groups in PACTs are currently under exploration in our laboratories.

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