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Benzyne–azide polycycloaddition: a facile route toward functional polybenzotriazoles†

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Benzyne, a highly reactive intermediate, has been used to synthesize various complex and diverse chemical entities, while benzyne-based polymerization has been rarely reported. In this work, three dibenzyne monomers, which were generated *in situ* from their precursors in the presence of CsF, were used to polymerize with diazides *via* a Huisgen 1,3-dipolar polycycloaddition, and soluble polybenzotriazoles with weight-average molecular weights (M_w) up to 13 000 were produced in moderate yields (up to 75%). All the resultant polymers show high thermal stability and good light refractivity. The tetraphenylethene-containing polybenzotriazoles exhibit the aggregation-induced emission or aggregation-enhanced emission characteristics. This benzyne–azide polycycloaddition will be a powerful tool for the preparation of functional polybenzotriazoles and be potentially applicable in materials and biological fields.

Introduction

Exploration of effective polymerization reactions is of vital significance for the construction of polymers with new structures and advanced functions due to their increasingly important roles played in academic and industrial fields.[1] The click polymerization, which exhibits the advantages of high efficiency, perfect selectivity, atom economy, mild reaction conditions, and so on, is a newly emerged polymerization methodology, which has been widely used in the preparation of functional polymers.[2–11] Among the developed click polymerizations, alkyne–azide polycycloaddition has been systematically studied.[12–15] As a result, transition-metal-catalysed alkyne–azide click polymerizations have been successfully developed, and 1,4- and 1,5-regioregular polytriazoles have been facilely prepared.[16–22] However, a major disadvantage of this click polymerization is that the metallic residuals in the resultant polymers are difficult to be completely removed due to the coordination effect between the metallic species and the

newly formed triazole rings, which greatly limits their applications in optoelectronic and biological areas.[23–26]

One of the solutions to address this difficulty is to develop click polymerization without using transition-metals, *i.e.*, metal-free alkyne–azide click polymerization (MFAACP). The key for realization of MFAACP is to use activated alkyne or azide monomers.[27] The general strategy to obtain activated monomers, such as activated alkynes, is to connect an electron-withdrawing group to the ethynyl group, which could lower their lowest unoccupied molecular orbital (LUMO) energy, thus facilitating the formation of triazoles.[28–31]

An alternative is to employ the ring strain of an alkyne to increase its activity,[32–34] which enables the strain-promoted alkyne–azide cycloaddition (SPAAC) to be performed under mild reaction conditions.[24,35–39] This SPAAC was also used to prepare functional polymers. For example, Adronov *et al.* prepared poly(ethylene glycol) (PEG) hydrogels with triazoles as linkers by the catalyst-free SPAAC polymerization of aza-dibenzocyclooctynes and diazides.[40] Recently, Zhang *et al.* developed a stoichiometric imbalance polymerization based on SPAAC, and polymers with high molecular weights up to 407 300 were obtained.[41] However, the SPAAC polymerization is still very rare, and the synthesis of the cyclooctyne monomers is not a trivial task.

To enrich the family of activated monomers and further develop the metal-free azide–alkyne polycycloaddition, another strain activated alkyne, *i.e.* benzyne, aroused our attention. Benzyne has a very simple structure and could be regarded as a benzene ring that two adjacent hydrogen atoms are replaced by a new carbon–carbon bond.[42–45] Experimental results and theoretical calculations indicate that benzyne could be described as an alkyne with a highly strained six-

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†Electronic supplementary information (ESI) available: Detailed synthetic routes to monomers, model compounds and polymers; ^{1}H and ^{13}C NMR, HRMS, and FT-IR spectra of **1**, **1a**, **2**, **1b**, **3**, **1c**, **4**, **2c**, **a**, **b**, **c**, **P1a2a**, **P1a2d**, **P1b2a**, **P1b2b**, **P1b2c**, **P1b2d**, and **P1c2c**. CCDC 1890990. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c9py00632j

membered carbon ring consisting of two C=C bonds and one C≡C bond.[42,46–49] The reactivity of benzyne was characterized by an unusually low-lying LUMO, and its alkyne-type feature could also be demonstrated by its reactivity pattern, such as Diels–Alder reaction and 1,3-dipolar cycloaddition.[50–53]

However, benzyne cannot be directly used due to its high reactivity and instability under ambient conditions. Thus, it must be generated *in situ* from its precursor. Indeed, by using suitable precursors, benzynes have been employed in the construction of functional products, such as polysubstituted aromatic derivatives and heterocyclic compounds.[46,54,55]

As far as we know, benzyne-based polymerization has been rarely reported. In 2005, Ihara *et al.* used the *in situ* generated benzyne to polymerize with pyridine and obtained novel copolymers bearing *o*-phenylene and 2,3-dihydropyridine units in the main chains.[56] Recently, Uchiyama *et al.* reported that the *in situ* generated benzyne could be homopolymerized in the presence of CuCN and a poly(*ortho*-phenylene) was yielded.[57] In these two reports, two carbon positions of the ethynyl group in benzyne were used, which might limit the derivation of the polymer structures.

By rational design of dibenzyne monomers, it is very likely to broaden the benzyne-based polymerizations to construct more functional polymers. Generally, a new polymerization is developed based on the elegant organic reaction. According to the literature, the reaction rate of a benzyne and an azide is very high, which meets the requirement for developing into an efficient polymerization.[58–63] Moreover, the generated functional benzotriazoles might potentially be applicable in optoelectronic and biological fields.[64–68]

Inspired by the reported efficient benzyne–azide reaction and based on our experience in alkyne–azide click polymerizations, we tried to develop a new metal-free polymerization of benzyne and azide monomers. Along this line, three new dibenzyne precursors **1** were designed and synthesized. The dibenzyne monomers generated *in situ* using CsF as the activator could readily polymerize with diazides to afford poly(benzotriazole)s (PBTAs) with high weight-average molecular weights (M_w up to 13 000) in moderate yields (up to 75%) (Scheme 1).
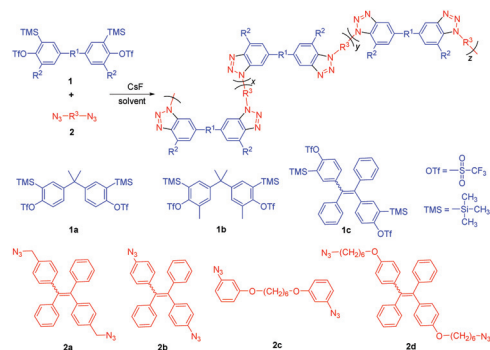
## Results and discussion

Precursor synthesis

The *in situ* generation of benzynes from their precursors has been well studied.[42,69] Herein, we used trimethylsilyl and triflate substituted benzene derivatives as precursors to generate benzyne monomers (Scheme 2 and S1–S3, ESI†).[70] The structures of the synthesized precursors were fully characterized by spectroscopic techniques (Fig. S1–S8, ESI†). Notably, a single crystal of **1c** (the *cis* conformation) was obtained, which was determined by single-crystal X-ray analysis (CCDC 1890990†) as shown in Scheme 2 and Table S1 (ESI†). These results unambiguously confirm their structures. Furthermore, diazides **2a**, **2b**, **2c**, and **2d** were synthesized according to reported procedures (Scheme S4, Fig. S9 and S10, ESI†).[23,71–74]
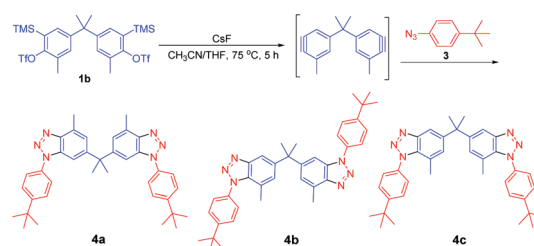
Model reaction

Before exploring the benzyne–azide polymerization, we tested whether the *in situ* generated benzyne from its precursor could react with azide in a cycloaddition fashion to produce corresponding benzotriazole. As illustrated in Scheme 3, benzyne could be readily generated from precursor **1b** in the presence of CsF at 75 °C in an acetonitrile/tetrahydrofuran (THF) mixture, which could immediately react with 1-azido-4-(*t*-butyl)benzene **3** (Scheme S5, ESI†) to generate the model compound **4** in a 92% yield in 5 h.

Theoretically, there will be three isomers of the model compound **4**. Due to their different polarities, the isomers of **4** could be separated *via* column chromatography with ease. All the isomers were characterized by ¹H and ¹³C NMR and high-resolution mass spectrometry (HRMS) (Fig. 1 and S11–S21, ESI†), and satisfactory results corresponding to their structures were obtained.
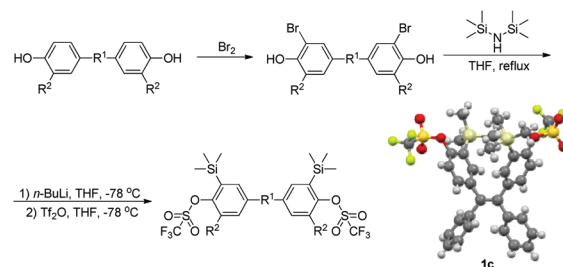
Scheme 2 General synthetic routes to benzyne precursors **1** and the single crystal structure of monomer **1c**.

Scheme 1 Synthesis of polybenzotriazoles by benzyne–azide polycycloaddition.

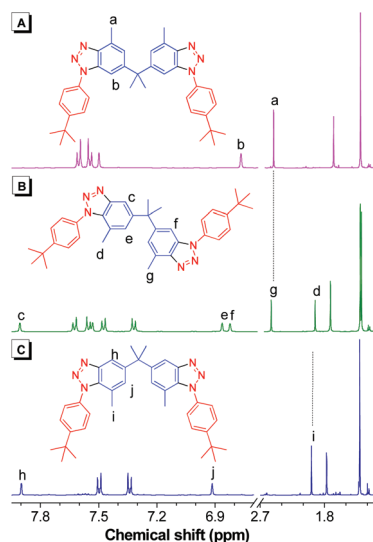**Scheme 3** Model reaction of **1b** and 1-azido-4-(*t*-butyl)benzene **3**.

Fig. 1 ^{1}H NMR spectra of regioisomers **4a** (A), **4b** (B) and **4c** (C) in CD$_2$Cl$_2$.

Polymerization

The high yield of the model reaction and well defined structures of the model compound encouraged us to try the polymerization of dibenzynes and diazides. Considering the accessibility of monomers and the solubility of corresponding polymers, dibenzyne precursor **1a** and diazide **2a** were used as the model monomers to optimize the polymerization conditions and the results are shown in Table 1.

According to the reports, the benzyne–azide cycloaddition could be efficiently carried out in several F$^-$/solvent systems.[58–62] However, the conditions of organic reactions are not fully suitable for the polymerizations. Thus, five F$^-$/solvent systems were screened to achieve the most suitable condition for the polymerization. When CsF was selected as the fluoride

source and CH$_3$CN as the solvent, the polymerization furnished a partially soluble product in 5 h, and the M_w of the soluble part was measured to be 6100, suggesting that this polymerization is highly efficient (entry 1, Table 1). As a comparison, when the polymerizations were carried out with other systems as listed in entries 2, 3 and 4 of Table 1, products with low M_w were obtained in poor yields even after 12 h. Delightfully, when the polymerization was performed with the system listed in entry 5, Table 1, the polymer with the highest M_w could be obtained in a moderate yield. Thus, we chose CsF as the fluoride source, and the CH$_3$CN/THF (v/v, 1/1) mixture as the solvent for the following polymerization.

Then, the polymerization temperature and time were studied. When the polymerization was conducted at 45 °C, it furnished a product with a low M_w of 4100 in 35% yield (entry 6, Table 1). On elevating the temperature to 75 °C, the M_w of the product increased to 12 400, and its yield was also improved (entry 7, Table 1). Thus, 75 °C was chosen as the optimal temperature. Afterward, we screened the reaction time. When the reaction was carried out for 4 h, the M_w of the product could reach 8000, while the yield was slightly low (53%) (entry 8, Table 1). Prolonging the reaction time could further enhance the M_w and improve the yield of the product. When the polymerization was performed for 10 h, the best yield, M_w and polydispersity index of the polymer were obtained. We thus adopted 10 h as the optimal reaction time.

Next, the effect of the amount of CsF on the polymerization was studied. According to the benzyne generation mechanism, the benzyne precursor was activated by F$^-$, thus, the rate and yield of benzyne generation would be affected by the amount of CsF. As shown in entries 11 and 12 of Table 1, when 2 equivalents of CsF toward **1a** were used, the polymerization could furnish a product with a M_w of 6600, however, the yield was very low. By increasing the amount of CsF to 4 equiv., the M_w of the polymer could reach the maximum, while a further

Table 1 Polymerization of dibenzyne precursor **1a** and diazide **2a** under various conditions[a]

Entry	F$^-$/solvent systems	T (°C)	t (h)	[CsF][b] (equiv.)	c (M)	Yield (%)	M_w[c]	Đ[c]
1[d]	CsF/CH$_3$CN	60	5	4	0.10	41	6100	1.57
2[e]	TBAF/THF	60	12	—	0.10	27	5800	1.48
3[f]	KF/18-crown-6/THF	60	12	—	0.10	40	5400	1.23
4[g]	CsF/18-crown-6/THF	60	12	—	0.10	45	4300	1.37
5	CsF/CH$_3$CN/THF	60	12	4	0.10	64	8400	1.52
6	CsF/CH$_3$CN/THF	45	12	4	0.10	46	6000	1.25
7	CsF/CH$_3$CN/THF	75	12	4	0.10	65	12 400	2.01
8	CsF/CH$_3$CN/THF	75	4	4	0.10	53	8000	1.41
9	CsF/CH$_3$CN/THF	75	6	4	0.10	66	10 200	1.84
10	CsF/CH$_3$CN/THF	75	10	4	0.10	73	11 900	1.80
11	CsF/CH$_3$CN/THF	75	10	2	0.10	35	6600	1.27
12	CsF/CH$_3$CN/THF	75	10	5	0.10	75	11 200	1.67
13	CsF/CH$_3$CN/THF	75	10	4	0.05	43	8500	1.54
14	CsF/CH$_3$CN/THF	75	10	4	0.15	75	12 100	1.78
15	CsF/CH$_3$CN/THF	75	10	4	0.20	65	12 300	2.05

[a] Carried out in F$^-$/solvent systems under nitrogen. [**1**] = [**2**]. CH$_3$CN/THF (v/v, 1/1). [b] Equivalent to [**1a**]. [c] Estimated by GPC using THF as an eluent on the basis of a polystyrene calibration; M_w = weight-average molecular weight; polydispersity index ($Đ$) = M_w/M_n; M_n = number-average molecular weight. [d] The polymerization afforded a partially soluble product; the yield was calculated from the soluble polymer. [e] [TBAF] = 4[**1a**]. [f] [KF] = [18-crown-6] = 4[**1a**]. [g] [CsF] = [18-crown-6] = 4[**1a**].

increase of the amount of CsF, *i.e.* 5 equiv., exerted little effect on the M_w and yields of the products. Thus, [CsF]/[monomer] = 4 was the optimized condition.

Lastly, the effect of monomer concentration on the polymerization was studied (entries 13–15, Table 1). Low concentrations of the monomers decreased the M_w and yields of the products. Increasing the monomer concentrations generally enhanced the M_w and yields of the products. However, when the polymerization was carried out at a monomer concentration beyond 0.15 M, the M_w of the product was nearly unchanged, while the yield slightly decreased. We thus used the monomer concentration of 0.15 M for the following polymerization.

By using the optimized conditions, we investigated the scope of benzyne precursors and azide monomers for the polycycloaddition (Table 2). Three benzyne precursors **1a**, **1b**, and **1c** were used to polymerize with two aliphatic and two aromatic azides (their structures are given in Scheme 1). The results showed that all the polymerizations proceeded smoothly, and the corresponding polymers with good M_w (8300 to 13 000) were produced in moderate yields. These results manifest the universality of this benzyne–azide polycycloaddition.

The resultant polymers exhibit high thermal stability as shown in Fig. 2. The thermogravimetric analysis (TGA) measurement indicates that the decomposition temperatures

of the polymers with 5% weight loss are in the range of 331 to 398 °C under nitrogen. The high thermal stabilities make them suitable for general applications.

Structural characterization

The resultant polymers are soluble in chloroform, THF and *N,N*-dimethylformamide (DMF), but insoluble in dimethylsulfoxide (DMSO), enabling us to characterize their structures by spectroscopic methods such as FT-IR and ^{1}H and ^{13}C NMR. Fig. 3 shows the FT-IR spectra of monomers **1b** and **2a**, their model compound **4b** and polymer **P1b2a** as an example. The $-N_3$ stretching vibration absorption of **2a** was observed at 2087 cm^{-1}, which became much weaker in the spectrum of the polymer. According to the reaction mechanism, it is proposed that the polymers tend to be terminated by the azide groups due to the high activity of benzyne intermediates. In the spectrum of **P1b2a**, a new strong stretching vibration peak of the benzotriazole ring appeared at 1600 cm^{-1}, suggestive of the occurrence of the polymerization. Similar results were obtained for other polymers (Fig. S22, ESI†).

The NMR spectra of polymers could provide detailed structural information. The ^{1}H NMR spectra of monomers **1b** and **2a**, and their model compound **4b** and polymer **P1b2a** are given in Fig. 4. The resonant peak of methyl protons in the benzene rings of **1b** was observed at δ 2.34 (b), while the corresponding proton signal of **P1b2a** was shifted to δ 2.60 (o) and 2.27 (k), which are in good agreement with that of the model compound **4b**. The resonance of the methylene group adjacent to the azide group in **2a** was recorded at δ 4.23, which was shifted down-field at δ 5.86 (j) and 5.67 (q), suggestive of the formation of electron-withdrawing benzotriazole rings. Furthermore, the newly appeared peak at δ 7.89 (l) was readily assignable to the resonance of protons in the benzotriazole rings of the polymer when comparing with its model compound. These results unambiguously confirm the occurrence of the polymerization and the formation of the expected structures. Since the peaks (o and k) of methyl protons on the benzotriazole rings are well-separated, they could be used to calculate the ratio of the isomers in the polymer, which was deduced to be 62 : 38. This result is in accordance with the model reaction shown in Scheme 3.

Table 2 Monomer scope of the benzyne–azide polymerization[a]

Entry	Monomer	Polymer[b]	Yield (%)	M_w[b]	$Đ$[b]
1	**1a** + **2a**	**P1a2a**	75	12 100	1.78
2	**1a** + **2d**	**P1a2d**	66	8300	1.52
3	**1b** + **2a**	**P1b2a**	70	13 000	1.80
4	**1b** + **2b**	**P1b2b**	59	12 300	1.98
5	**1b** + **2c**	**P1b2c**	69	9700	1.59
6	**1b** + **2d**	**P1b2d**	69	10 200	1.71
7	**1c** + **2c**	**P1c2c**	55	9000	1.57

[a] Carried out in CH$_3$CN/THF (v/v, 1/1) under nitrogen in the presence of CsF for 10 h at 75 °C. [**1**] = [**2**]. [CsF] = 4[**1**]. [b] Estimated by GPC using THF as an eluent on the basis of a PS calibration; M_w = weight-average molecular weight; polydispersity index ($Đ$) = M_w/M_n; M_n = number-average molecular weight.
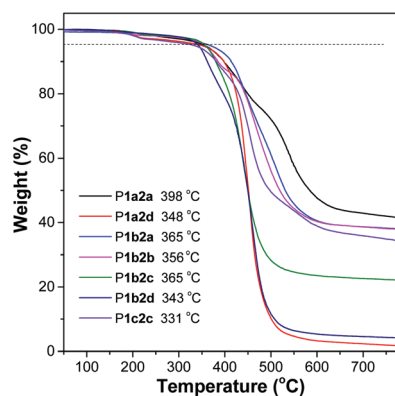

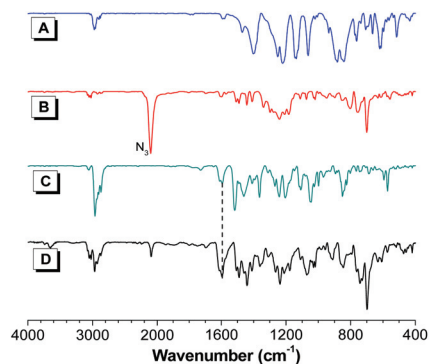**Fig. 2** TGA thermograms of the poly(benzotriazole)s.

Fig. 3 FT-IR spectra of **1b** (A), **2a** (B), **4b** (C) and **P1b2a** (D).

Fig. 4 ^{1}H NMR spectra of **1b** (A), **2a** (B), **4b** (C) and P**1b2a** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.
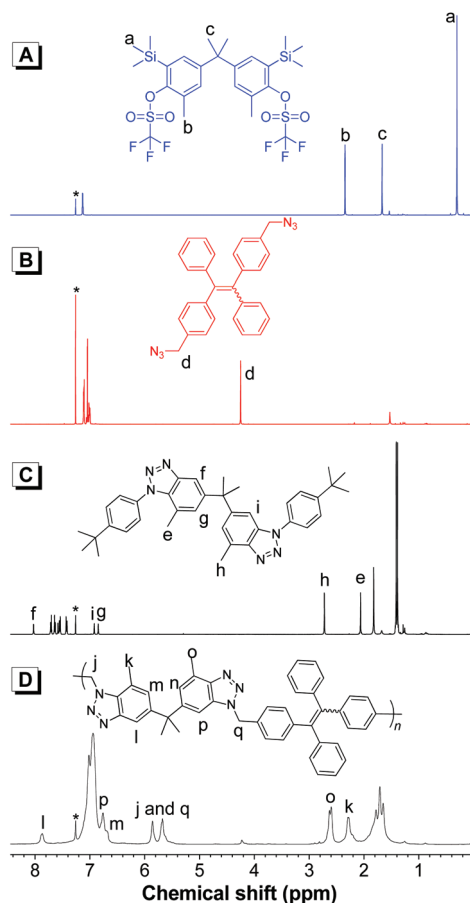

Fig. 5 ^{13}C NMR spectra of **1b** (A), **2a** (B), **4b** (C) and P**1b2a** (D) in CDCl$_3$. The solvent peaks are marked with asterisks.

The conclusion drawn from the ^{1}H NMR analysis was also substantiated by the ^{13}C NMR spectra of monomers, model compound and polymers. As shown in Fig. 5, the methyl group on the benzene ring of **1b** resonated at δ 17.48 (d), which disappeared and two new methyl resonant peaks emerged at δ 18.54 (m) and 16.89 (k). In addition, the peaks at δ 104.27 (l) and 113.73 (n) are also the characteristic carbon resonance of the benzotriazole rings. Similar results were also obtained from the ^{1}H and ^{13}C NMR spectra of other polymers (Fig. S23–S34, ESI†), manifesting the robustness of our developed polycycloaddition.

Light refraction

The refractive index (RI) is one of the key factors to be considered in the design and application of photonic materials. Generally, the introduction of aromatic rings, polarizable π-conjugated units and heteroatoms into the polymers is beneficial for the improvement of RI values.[75] Our resultant PBTAs possess highly polarized benzotriazole rings in their main-chains, and are supposed to exhibit high RI values. Thus, we investigated the light refraction properties of these polymers. As shown in Fig. 6, their RI values at 632.8 nm are in the range of 1.6545 to 1.5866. Notably, the highest RI value was recorded in P**1c2c** because its conjugation is better than the others.
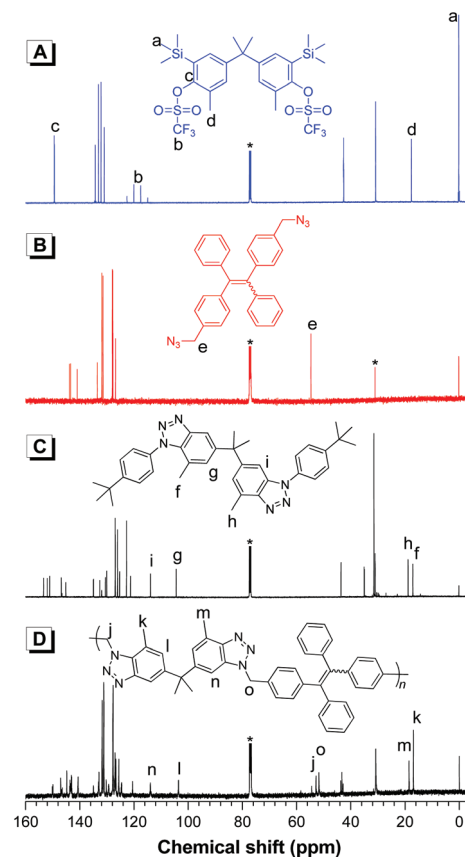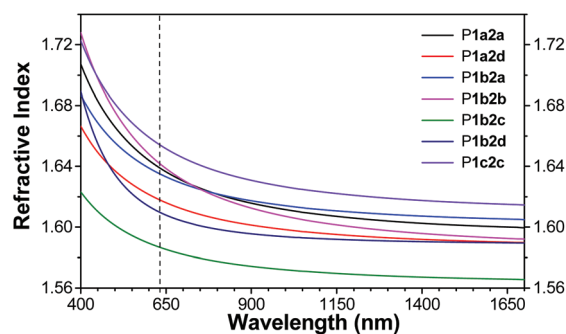

Fig. 6 Light refraction spectra of thin solid films of poly(benzotriazole)s.

Photophysical properties

As can be seen from Scheme 1, P**1b2a**, P**1b2d** and P**1c2c** contain tetraphenylethene (TPE) units, the typical luminogen featuring the aggregation-induced emission (AIE) characteristics.[76,77] We thus investigated their photoluminescence properties in THF/water mixtures with different water fractions (f_w). Due to its flexible structure, P**1b2d** displays a typical AIE behaviour. It is non-emissive in THF solution, but intense emission was observed in the THF/water mixture with a higher f_w and the highest emission intensity
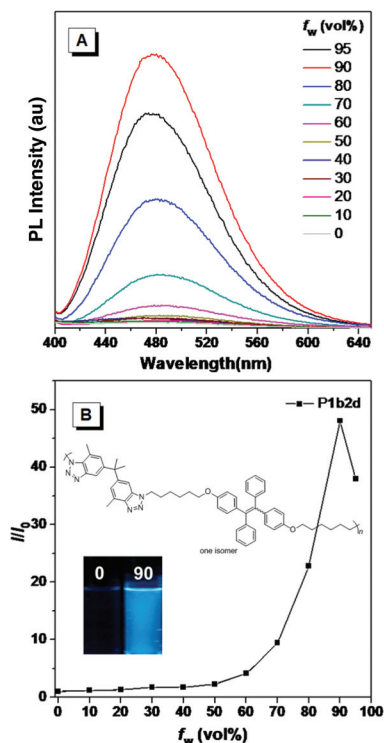
Fig. 7 (A) PL spectra of **P1b2d** in THF and THF/water mixtures with different water fractions (f_w). Concentration: 10 μM; excitation wavelength: 350 nm. (B) Plots of I/I_0 of **P1b2d** versus f_w, where I = peak intensity and I_0 = peak intensity at f_w = 0. Inset: photograph taken under the illumination of a hand-held UV lamp.

was recorded in the THF/water mixture with a f_w of 90%, which is nearly 50 times higher than that in THF solution (Fig. 7). However, because of the more rigid structures of **P1b2a** and **P1c2c** than that of **P1b2d**, they are already emissive when molecularly dissolved in THF, and their emission intensity could also be enhanced by increasing the f_w in the THF/water mixtures (Fig. S35 and S36, ESI†), demonstrating the unique aggregation-enhanced emission (AEE) characteristics.

Conclusions

In this work, a new benzyne–azide polycycloaddition was successfully established, in which the activated alkynes of benzyne monomers were generated *in situ* from their precursors in the presence of CsF. Soluble PBTAs with high M_w were obtained in moderate yields. These polymers possess high thermal stabilities and exhibit good light refractive properties. The TPE-containing PBTAs show the unique AIE or AEE features depending on the rigidity of their structures. Thus, this work not only generates new types of activated alkynes and establishes a new benzyne-based polycycloaddition, but also provides a facile route to construct functional PBTAs. Application of the resultant PBTAs and exploration of more benzyne monomers for the polymerization are in progress in our laboratory.

Conflicts of interest

There are no conflicts to declare.

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