Polymer Chemistry

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Structure-dependent emission of polytriazoles†

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Aggregation-induced emission (AIE) and aggregation-enhanced emission (AEE) have recently been a hot research topic. Currently, efforts have been mostly made on low mass molecules. Their structure–property relationship has been well-established but no work on polymers has been reported, probably due to the harsh reaction conditions for most of the polymerization processes. We used the powerful and facile Cu(I)-catalysed click polymerization in this paper to synthesize four polytriazoles with small variation in either the backbones or the linking manner of the triazole. The results show that changing the hydrogen groups of the stilbene units of P**3b** and P**6b** to the phenyl rings of the tetraphenylethene moieties of P**3a** and P**6a** readily leads to distinctive differences in their photophysical properties. P**3a** and P**6a** are AEE-active, while P**3b** and P**6b** display a typical aggregation-caused quenching effect. Meanwhile, investigation on the linking manner of 1,4-positions of the triazole ring indicates that this variation exerts little influence on the emission properties. This work could thus serve as a guideline for the further design of luminogenic polymers for high-tech applications.

Introduction

The exploration of efficiently luminescent organic and polymeric materials has drawn increasing attention for their potential applications in a variety of areas, including organic light-emitting diodes, chemical sensors, biological probes and so on.[1–5] Many conventional fluorophores, however, suffer from the thorny problem of the aggregation-caused quenching (ACQ) effect due to energy transfer and the formation of excimers or exciplexes in the condensed phases.[6] As we know, most of the luminescent materials are generally used as solid films in their practical applications. Thus, the ACQ effect has greatly limited the scope of the application of fluorophores. To circumvent this problem and to prevent fluorophores from aggregation, lots of methods, such as chemical decoration and physical blending have been utilized.[7] These attempts, however, have met with only limited success.

Fluorophore aggregation is a natural process. If we could enable it to play a positive instead of negative role in applications, we could then generate more efficiently emissive molecules in the solid or condensed phases and broaden their high-tech applications. We have indeed observed such a phenomenon that the propeller-shaped siloles are weakly or not emissive when molecularly dissolved in good solvents, but are induced to emit strongly upon forming aggregates.[8] This unique phenomenon is exactly opposite to the ACQ effect and was termed "aggregation-induced emission" (AIE) in 2001. Experimental and theoretical studies have rationalized that the restriction of intramolecular rotation (RIR) is the main cause for the AIE effect.[9] When molecularly dissolved in a good solvent, the phenyl rings of a fluorophore can undergo dynamic rotation, which could quench the excited state energy non-radiatively, whereas in the aggregated state, dynamic rotation will be restricted, making the excited state energy decay through a radiative pathway, turning on the emission.[10]

According to the RIR mechanism, we have succeeded in transforming ACQ molecules, such as pyrene and triphenyamine, to AIE-active ones by covalently attaching AIE-active moieties, such as tetraphenylethene (TPE), on them, which greatly broadens the source for generating AIE-active molecules.[11] The studies of such a substituent effect are, however, performed on low mass molecules and no attempt on polymers has been made. The difficulty may lie in the polymerizations, which are generally carried out under harsh reaction conditions.[12] Another possibility may be the lack of suitable systems.

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† Electronic supplementary information (ESI) available: Monomer preparation, synthetic routes to **8**, **2a**, **2b**, **4**, **5a**, **5b** and **23**, TGA thermograms of the four polymers (Fig. S1), IR spectra of P**3b**, P**6a** and P**6b** and their monomers (Fig. S2–S4), ^{1}H NMR spectra of P**3b**, P**6a** and P**6b** and their monomers (Fig. S5–S7), UV spectra of M**1** and M**2** (Fig. S8), particle size analysis of P**3a** and P**3b** (Fig. S9), PL spectra of P**3a** and P**3b** in THF/methanol mixtures (Fig. S10 and S11), cyclic voltammograms of P**3a** and P**6a** (Fig. S12) and summary of theoretical and experimental HOMO and LUMO energy levels (Table S1). See DOI: 10.1039/c3py01387a

Thanks to their advantages, such as high efficiency, mild reaction conditions, and function tolerance, the Cu(I)-catalysed and metal-free azide–alkyne click polymerizations, which were developed based on the azide–alkyne click reactions,[13] have been established and recognized as facile alternatives for the preparation of functional polytriazoles with high molecular weight and in high yields.[14–16] Interestingly, the polytriazoles containing solely 1,4- or 1,5-disubstituted 1,2,3-triazole regioisomers display distinct emission behaviour.[17] However, no investigation on the linking manner of the triazole rings has been reported, which is pivotally important for understanding the relationship of the property and structure of polytriazoles.

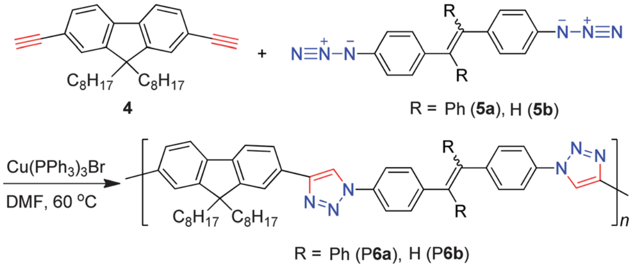
In this paper, we selected TPE and stilbene, in which, four and two rotary phenyl rings were attached on a vinyl group, respectively, as the emissive species and fluorenyl groups as the repeating units of polytriazoles, because they are easily functionalized with azide and alkyne groups. The TPE and stilbene moieties enabled us to understand the effect of the subtle change of the substituent on the photoproperty of the polytriazoles.

Thanks to the high efficiency of the Cu(PPh$_3$)$_3$Br-catalyzed click polymerizations, all the polymers (**P3a**, **P3b**, **P6a** and **P6b**) have high molecular weights and a relatively narrow polydispersity and were obtained in high yields (Schemes 1 and 2). The resulting polytriazoles could be readily dissolved in common organic solvents and show good thermal stability. Photoluminescence (PL) investigation shows that **P3a** and **P6a** feature the aggregation-enhanced emission (AEE) characteristics, but **P3b** and **P6b** are typical ACQ polymers, suggesting that a subtle change of the substitution from a hydrogen to phenyl group in the polymer backbones could cause a dramatic change in the emission profiles. Moreover, from comparison of the emission features of **P3a** with **P6a** or **P3b** with **P6b**, we can conclude that changing the linking manner of the triazole rings shows little influence on the polymer emission properties.

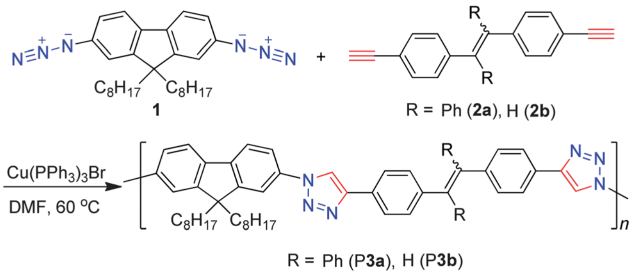
Experimental section

General information

Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl in an atmosphere of nitrogen immediately prior to use. *N*,*N*-Dimethylformamide (DMF) was pre-dried over calcium hydride, distilled under reduced pressure, and kept under nitrogen. Other solvents were purified by standard methods. All other chemicals were purchased from Acros or Aldrich and used as received without further purification.



Scheme 2 Synthesis of polytriazoles P6 by the click polymerization of fluorenyl diyne **4** and diphenylvinyl-based diazides **5**.



Scheme 1 Synthesis of polytriazoles P3 by the click polymerization of fluorenyl diazide **1** and diphenylvinyl-based diynes **2**.

Infrared (IR) spectra were taken on a Bruker Vector 22 spectrometer as thin films on KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on Bruker ADVANCE2B 400 NMR or Bruker DMX 500 NMR spectrometers in CDCl$_3$ using tetramethylsilane (TMS; $\delta = 0$) as the internal reference. The UV-vis spectra were measured on a Varian VARY 100 Bio UV-vis spectrophotometer. PL spectra were recorded on an RF-5301PC SERIES spectrofluorometer. Fluorescence quantum yields (Φ_F) were estimated using quinine sulfate in 0.1 N H$_2$SO$_4$ (Φ_F = 54.6%) as standard, and the absorbance of the solutions was kept around 0.05 to avoid the internal filter effect. Element analysis was conducted on a Thermo Finnigan Flash EA1112 system. Thermogravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer TGA 7 under dry nitrogen at 20 °C min^{-1}. Relative weight-average (M_w) and number-average (M_n) molecular weights of the polymers and their polydispersity indices (PDI, M_w/M_n) were estimated by a Waters 1515 gel permeation chromatography (GPC) system equipped with an interferometric refractometer detector, using a set of monodispersed linear polystyrenes (PS) as calibration standards and THF as the eluent at a flow rate of 1.0 mL min^{-1}. Particle size analysis was determined at room temperature by a Zeta Potential Analyzer (ZetaPALS, Zeta Potential Analyzer Utilizing Phase Analysis Light Scattering; Brookhaven Instruments Corporation, USA). The cyclic voltammetry (CV) analysis was conducted in an electrolyte of 0.1 M [(*n*-Bu)$_4$N]PF$_4$ in DCM at a scan rate of 100 mV s^{-1} at room temperature using a conventional three-electrode configuration. The working electrode was a platinum circular electrode. A Pt wire was used as the counter

Table 1 Cu(PPh$_3$)$_3$Br-catalyzed click polymerizations of dizides and diynes[a]

Polymer	Monomer	*t* (h)	Color	Yield (%)	M_w[b]	PDI[b]
P3a	**1** + **2a**	11	LY[c]	70.4	19 100	3.40
P3b	**1** + **2b**	12	DR[d]	81.1	20 800	2.60
P6a	**4** + **5a**	14	LY[c]	77.7	9600	2.17
P6b	**4** + **5b**	12	DR[d]	77.6	13 500	1.95

[a] Carried out at 60 °C under nitrogen; monomer concentration: 0.1 M. [b] M_w and PDI (M_w/M_n) were estimated by GPC in THF on the basis of a linear polystyrene calibration. [c] LY = light yellow. [d] DR = dark red.

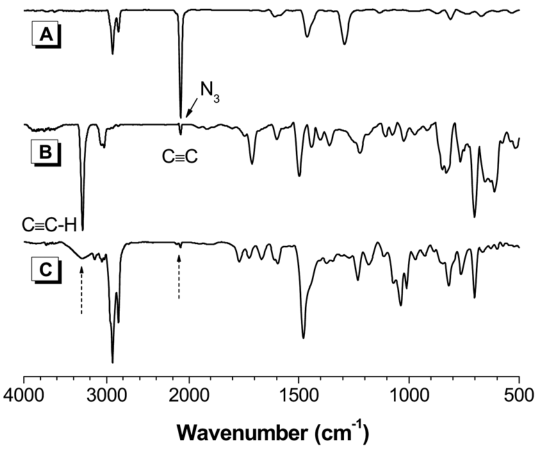
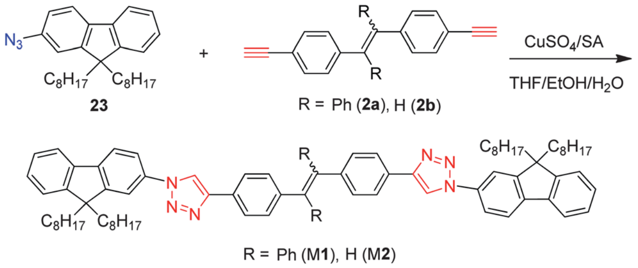


Fig. 1 IR spectra of monomers (A) **1** and (B) **2a**, and polymer (C) P**3a**.



Scheme 3 Synthesis of model compounds by the click reaction of fluorenyl azide **23** and diazides **2a** and **2b**.

electrode and an Ag/AgNO$_3$ electrode was used as the reference electrode.

Calculation details

Geometry optimizations and energy evaluations were carried out using the density functional theory (DFT) method at the B3LYP/6-31G(d) level, which has been successfully applied in previous studies on conjugated polymers.[18] To save computational time, three repeating units (**P3a**-M and **P6a**-M) and the octyl groups in the fluorenyl units of **P3a** and **P6a** were simplified to methyl groups due to the fact that the geometries and energies negligibly depended on the alkyl groups.[18] All the calculations were performed using the Gaussian 03 program.[19]

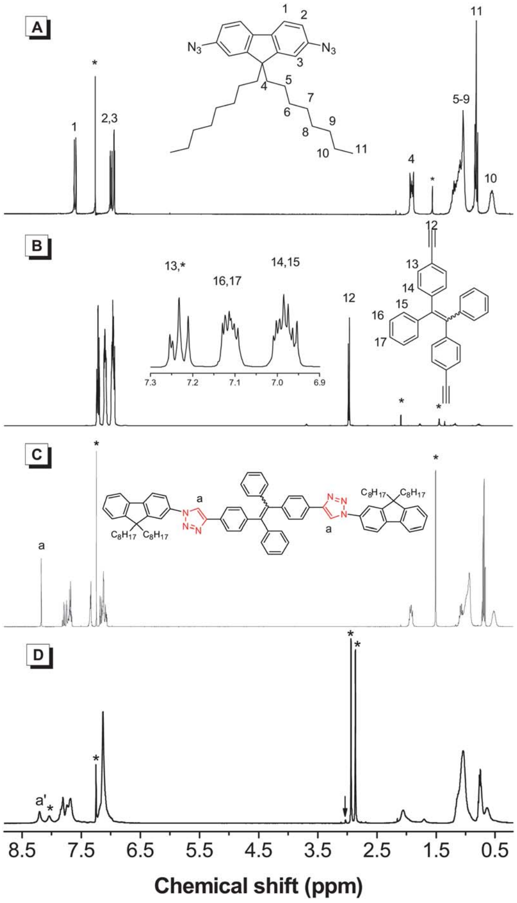


Fig. 2 ^{1}H NMR spectra of (A) monomers **1**, (B) **2a**, (C) model compound M**1** and (D) polymer P**3a** in CDCl$_3$. The solvent and water peaks are marked with asterisks.

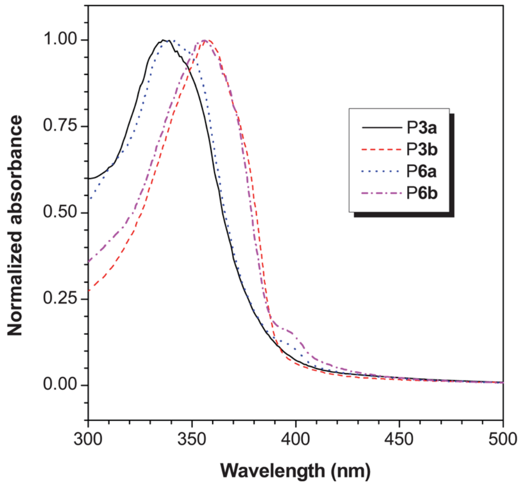


Fig. 3 Normalized UV absorption spectra of P**3a**, P**3b**, P**6a** and P**6b** in THF solutions. Concentration: 10 μM.

Polymer synthesis

Polymer preparation. Into a 10 mL Schlenk tube with a stopcock were added diyne monomer (0.1 mmol), diazide monomer (0.1 mmol), and 1.8 mg (0.002 mmol) of Cu(PPh$_3$)$_3$Br. The tube was evacuated and reflushed with dry nitrogen three times. Then freshly distilled DMF (1 mL) was injected to dissolve the monomers. After stirring at 60 °C for a certain amount of time, the reaction mixture was diluted with 5 mL of chloroform and then added dropwise to 200 mL of the hexane and chloroform mixture (10/1, V/V) through a cotton filter under stirring. The precipitates were allowed to stand overnight and collected by filtration. The polymer was washed with hexane several times and dried to a constant weight at ambient atmosphere.

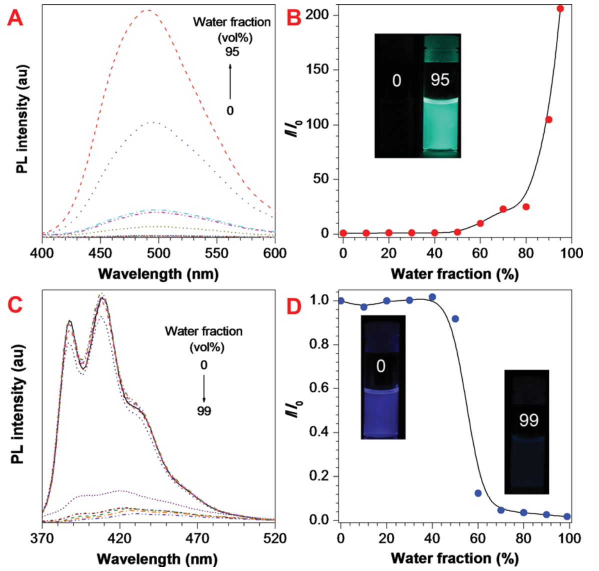


Fig. 4 PL spectra of (A) M1 and (C) M2 in THF/water mixtures with different water fractions; the excitation wavelengths for P3a and P3b are 318 and 354 nm, respectively; concentration: 10 μM. Plots of the fluorescence changes in (B) M1 and (D) M2 *versus* the water fraction in the THF/water mixtures. The insets are photographs taken under the illumination of a handheld UV lamp.

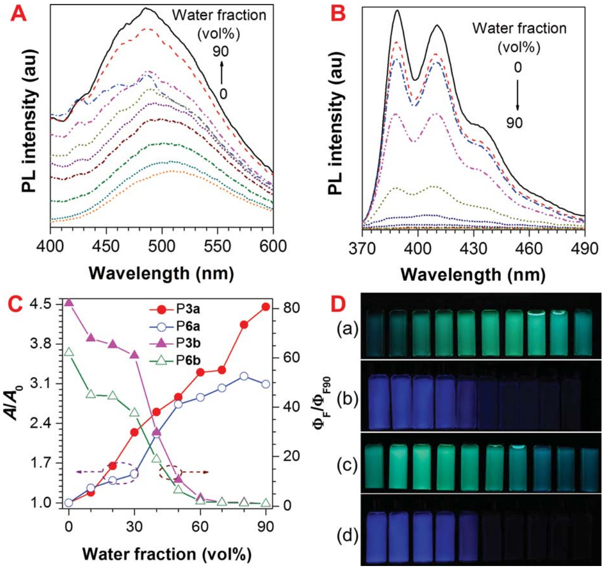


Fig. 5 PL spectra of (A) P3a and (B) P3b in THF/water mixtures with different water fractions; the excitation wavelengths for P3a and P3b are 337 and 358 nm, respectively; polymer concentration: 10 μM. (C) Plots of relative emission integral areas (P3a and P6a) and quantum yields (P3b and P6b) *versus* the water fraction in the THF/water mixtures. *A* is the integration area. (D) Solutions of (a) P3a, (b) P3b, (c) P6a, and (d) P6b in the THF/water mixtures with water fractions from 0–90%; the photographs were taken under the illumination of a handheld UV lamp.

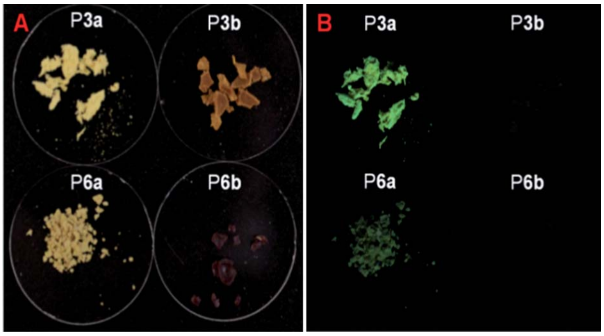


Fig. 6 Photographs of the solid powders of P3a, P3b, P6a and P6b taken under (A) normal lighting and (B) UV illumination.

Characterization. P3a: light yellow powder; 70.4% yield. M_w 19 100; M_w/M_n 3.41. ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.20, 7.81, 7.68, 7.13, 3.15, 2.05, 1.70, 1.04, 0.78, 0.77, 0.75, 0.74, 0.64. ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 152.9, 143.9, 143.3, 140.8, 140.2, 136.6, 131.9, 131.4, 127.8, 127.7, 126.6, 126.7, 125.3, 125.1, 121.0, 119.4, 115.2, 56.1, 40.2, 31.6, 29.8, 29.1, 23.7, 22.4, 13.9.

P3b: dark red powder; 81.1% yield. M_w 20 800; M_w/M_n 2.60. ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.29, 7.96, 7.87, 7.78, 7.66, 7.63, 7.61, 7.49, 7.22, 7.15, 3.14, 2.16, 2.10, 1.25, 1.08, 0.87, 0.78, 0.68.

P6a: light yellow powder; 77.7% yield. M_w 9600; M_w/M_n 2.17. ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.22, 7.94, 7.83, 7.76, 7.61, 7.48, 7.17, 3.15, 2.06, 1.75, 1.03, 0.76, 0.65. ^{13}C NMR (125 MHz, $CDCl_3$), δ (TMS, ppm): 151.8, 148.8, 144.0, 142.6, 141.0, 140.6, 135.2, 132.6, 131.2, 129.0, 128.3, 127.9, 127.2, 124.6, 120.1, 119.7, 117.4, 55.4, 40.4, 40.2, 31.6, 29.9, 29.1, 23.7, 22.4, 13.9.

P6b: dark red powder; 77.6% yield. M_w 13 500; M_w/M_n 1.95. ^1H NMR (400 MHz, $CDCl_3$), δ (TMS, ppm): 8.29, 7.85, 7.70, 7.49, 7.12, 7.05, 3.16, 2.11, 2.03, 1.26, 1.06, 0.88, 0.78, 0.65.

Results and discussions

Monomer synthesis

The diazide monomer **1** was prepared according to the route shown in Scheme S2 (ESI†). The iodination and alkylation of fluorine at its 2,7- and 9-positions, respectively, readily provided the intermediate of **11**. The substitution reaction of **11** with the azide derivative **8** (Scheme S1, ESI†) in the presence of *n*-butyllithium gave the compound **1** in moderate yield. The diyne monomer **4** was prepared by the Sonogashira coupling reaction between the fluorene derivative **11** and trimethylsilyl acetylene, followed by deprotection (Scheme S5, ESI†). The TPE/stilbene containing diynes **2a** (ref. 16b) and **2b**, and diazides **5a** (ref. 16a) and **5b** were synthesized according to our reported procedures (Schemes S3, S4, S6 and S7, ESI†). Monoazide **23** was synthesized in a similar way to monomer **1** (Scheme S8†). The detailed synthesis procedures of the monomers are given in the ESI.† All the monomers were carefully purified and characterized by spectroscopic methods, from which satisfactory analysis data corresponding to their structures were obtained (see ESI† for the details).

Click polymerization

In our previous work we used the efficient organosoluble $Cu(PPh_3)_3Br$-catalyzed azide–alkyne click polymerizations to

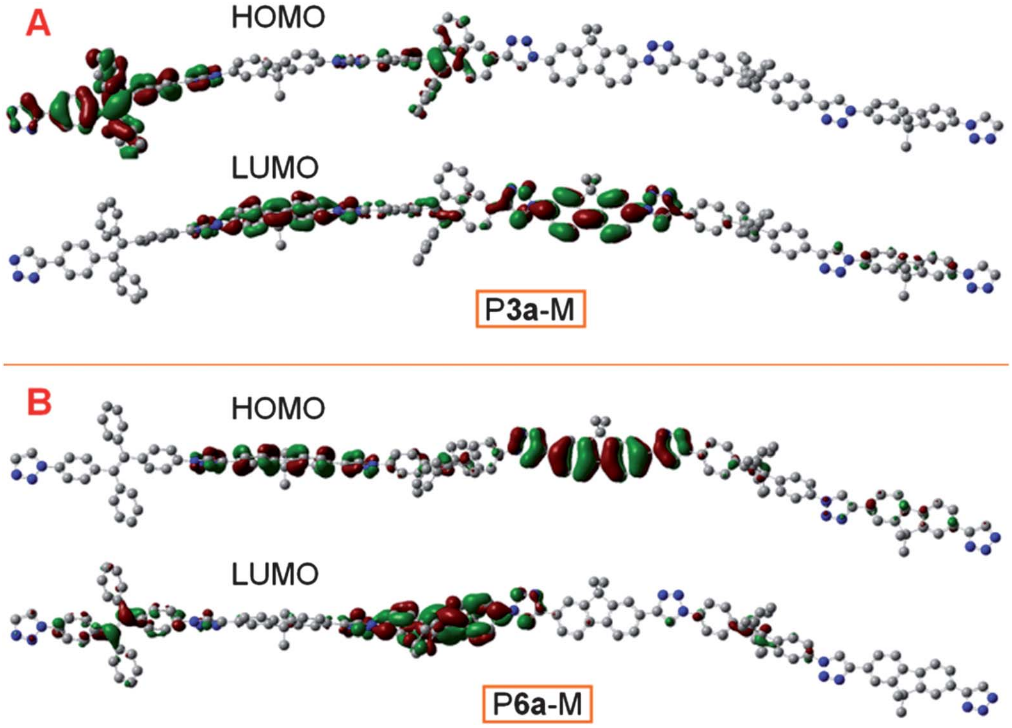


Fig. 7 Optimized molecular structures and molecular amplitude plots of the HOMO and LUMO of the models (trimers) of P**3a** and P**6a**. To facilitate the calculation, the octyl groups in the fluorenyl units were simplified to methyl groups.

prepare soluble polytriazoles with linear and hyperbranched structures.[16] The polymerization could readily be carried out at 60 °C and functional polytriazoles could be obtained with high molecular weights in high yields within a short period of reaction time. Encouraged by such a highly efficient click polymerization, we tried to utilize it to polymerize diazide **1** and diyne **2a** (Scheme 1). We first performed the polymerization reaction in DMF at 60 °C for 8 h, which produced soluble polymer P**3a** with a relatively low M_w (8600) in a low yield (17.8%). Increasing the reaction time to 11 h enhanced both the M_w (19 100) and the yield (70.4%) (Table 1). We then employed this reaction time to polymerize other monomers. For the polymerization of **1** and **2b**, and **4** and **5b**, we found the reaction time of 12 h was the best and could obtain P**3b** and P**6b** with high M_w of 20 800 and 13 500 in high yields of 81.1 and 77.6%, respectively. Meanwhile, prolonging the reaction time from 11 to 14 h, the yield and M_w of P**6a** could be enhanced from 42.6% and 7000 to 77.7% and 9600, respectively.

All the obtained polytriazoles are soluble in commonly used organic solvents, such as THF, DCM and chloroform, demonstrating that they are solution-processable. The polymers are also thermally stable. The temperatures for 5% weight loss are higher than 345 °C under nitrogen (Fig. S1†), revealing their strong resistance to thermolysis at elevated temperatures.

Structural characterization

All the polymers were characterized by standard spectroscopic methods, and satisfactory results corresponding to their structures were obtained. Since the IR spectral profiles of P**3b**, P**6a** and P**6b** are similar to that of P**3a** (Fig. S2–S4, ESI†), the spectra of the latter and its monomers are shown in Fig. 1 as an example. Monomer **1** exhibits a strong absorption band at 2104 cm^{-1} due to the stretching vibration of the azide groups. **2a** absorbs at 3288 and 2103 cm^{-1}, which are assignable to the stretching vibrations of ≡C–H and C≡C, respectively. All these bands become much weaker in the spectrum of P**3a**, indicating that most of the azido and ethynyl groups of the monomers have been transformed to the triazole rings of the polymer by the click polymerization.

NMR spectroscopy could provide more detailed information on the polymer structures. To facilitate the structural characterization of the obtained polymers, model compounds **M1** and **M2** were designed and synthesized by the click reaction of **2a**/**2b** and 2-azido-9,9-dioctyl-fluorene (**23**) under the same reaction conditions, respectively (Scheme 3). Fig. 2 shows the ^{1}H NMR spectra of polymer P**3a** and its monomers (**1** and **2a**), as well as its model compound **M1** in $CDCl_3$. The ethynyl protons of **2a** resonate at δ 3.03 (Fig. 2A), which almost disappeared in the spectrum of P**3a** (Fig. 2D), indicating that the ethynyl groups were mostly consumed after polymerization. By comparing with the ^{1}H NMR spectrum of **M1**, the peak at δ 8.02 (a′) in the spectrum of P**3a** could be readily assigned to the resonances of the protons of the formed 1,4-disubstitued 1,2,3-triazole rings (Fig. 2C). These results along with the IR analysis demonstrate that most of the ethynyl and azido groups of **1** and **2a** have been consumed by the click polymerization and converted to the triazole rings of P**3a**. Similar phenomena are observed in the ^{1}H NMR spectra of P**3b**, P**6a** and P**6b** (Fig. S5–S7, ESI†).

UV absorption

On the basis of full characterization of the structures of the resulting model compounds and polytriazoles, we studied their photophysical properties. Firstly, we measured the UV-vis spectra of the model compounds (Fig. S8†). **M1** and **M2** showed absorption maxima ($\lambda_{\mathrm{ab,max}}$) at 318 and 354 nm, respectively. In comparison, **P3a** and **P3b** showed $\lambda_{\mathrm{ab,max}}$ at 337 and 358 nm, respectively (Fig. 3), suggesting an increase in the conjugation length. Changing the hydrogen (**P3b**) to a phenyl group (**P3a**) blue-shifted their $\lambda_{\mathrm{ab,max}}$ by *ca.* 20 nm. This may appear to be abnormal at first glance, since the phenyl group should increase the conjugation, leading to a longer absorption wavelength. But if we take a closer inspection to the conformation of the polymer, this blue-shift is reasonable. In **P3b**, the stilbene takes an almost planar conformation, making the polymer chain more conjugated, whereas, in **P3a**, the phenyl rings in TPE increased the steric hindrance, turning them out of plane, and thus the conjugation becomes shorter. The absorption of **P6a** peaked at 340 nm, which is quite close to that of **P3a**, indicating that swapping the substituents at the 1,4-positions of the 1,2,3-triazole has little influence on the absorbance on the polymer. Similar to **P3b**, **P6b** exhibits an absorption maximum at 358 nm, 18 nm longer than that of **P6a**. This may also be explained by the aforementioned conjugation effects.

Emission characteristics

The substitution of phenyl rings in **M1**, **P3a** and **P6a** from hydrogen groups in **M2**, **P3b** and **P6b** blue-shifted their absorption. What are the emission behaviours of these model compounds and polytriazoles? Furthermore, the TPE unit is AIE-active, are the model compounds and polytriazoles also AIE-active? To answer these questions we thus measured their PL spectra.

We first studied the emission behaviour of the model compounds. The dilute THF solution of **M1** is non-emissive (Fig. 4A). The emission spectra did not change much until 60% water was added. Further increase in the water fraction led to a swift increase in emission intensity (Fig. 4B). In the THF–water mixture with a water fraction of 95%, the emission was 206-fold higher than that in pure THF solution, demonstrating a typical AIE characteristic. Differently to **M1**, the dilute THF solution of **M2** showed a strong purple emission (Fig. 4C). Increasing the water fraction does not affect its emission until 60%, above which, the emission of **M2** dramatically dropped, indicating that **M2** is a typical ACQ molecule (Fig. 4D).

Next, we investigated the PL spectra of the polymers. Fig. 5A shows the PL spectra of **P3a** in the THF/water mixtures with different water fractions. In pure THF solution, **P3a** emits a weak greenish blue light with a maximum peak at 511 nm. With gradual increasing the water fraction, the emission intensity was enhanced accordingly, demonstrating that **P3a** possesses the AEE feature. Differently from **M1**, the rotation of the phenyl rings of **P3a** in THF solution was already restricted to some extent due to the steric hindrance, enabling it to emit weakly. Increasing the water fraction will decrease the solvation power, and make the polymer chains aggregated, which was confirmed by the DLS particle size measurement (Fig. S9A†). According to the RIR mechanism, the aggregates further restricted the rotation of the phenyl rings and intensified the emission. In addition, the AEE effect was also observed in the THF/methanol mixtures (Fig. S10†), suggesting that this effect is poor solvent independent.

Interestingly, a blue-shift of the emission peaks was observed for **M1** and **P3a** with the addition of water. Taking **P3a** for example, at a 90% water fraction, the PL peaked at around 485 nm, 26 nm shorter than that in pure THF. This may probably be explained as the polymer aggregates could force the TPE units to take a more twisted conformation, thus in turn jeopardizing the conjugation of the polymer chains.

P3b exhibits a distinctively different PL behaviour from **P3a**. When dissolved in THF, **P3b** emits a strong blue light, which was gradually quenched by the addition of water (Fig. 5B). When the water fraction was up to 60%, the emission from **P3b** was almost completely quenched due to the aggregation (Fig. S9B†), indicating that **P3b** is a typical ACQ polymer. Repeating the experiment in THF/methanol mixtures showed similar results (Fig. S11†).

The only difference between **P3a** and **P3b** is that the hydrogen atoms of the stilbene units in **P3b** were replaced by the phenyl rings of the TPE units in **P3a**, but the change in PL properties is dramatic. In **P3b**, the molecule takes a planar conformation, which may favour the π–π interactions, thus the emission will be quenched in an aggregated state. In **P3a**, however, the additional steric hindrance brought by the phenyl rings will force the TPE unit to take a twisted conformation, preventing the π–π interaction and making it emit strongly in the aggregated state. Thus, a subtle change in the molecular structure will dramatically affect the emission characteristics.

P6a shows a similar emission behaviour to **P3a** and is AEE-active, whereas, the emission profile of **P6b** is similar to that of **P3b**. The plots of intensities of **P3a** and **P6a**, and the quantum yields of **P3b** and **P6b** *versus* the water fraction share the same trends (Fig. 5C), suggesting that exchanging the substituents on the 1,4-positions of the triazole ring has a negligible influence on the emission.

For a direct view of the emission behaviours of these polymers, their emission photographs in THF/water mixtures with different water fractions were taken (Fig. 5D, from left to right, the water fraction increased from 0 to 90%). Furthermore, the photographs of their emission in the solid state are provided in Fig. 6. The appearance of **P3a** and **P6a** under daylight is a yellow powder, while **P3b** and **P6b** are deep brown and dark red powders, respectively. Under the illumination of UV light, **P3a** and **P6a** emit green light, while no emission could be observed from **P3b** and **P6b**. From the photographs, we can easily conclude that **P3a** and **P6a** are AEE-active, whereas, **P3b** and **P6b** are typical ACQ polymers.

When carrying out a detailed inspection of the PL spectra of **P3a** and **P3b**, we could find that the emission peak of the latter red-shifted, although its absorption blue-shifted, indicating that the phenyl rings of TPE play positive roles for the polymer emission, but negative roles for its absorption.

Theoretical calculation

Although the linking manner of P3**a** and P6**a**, as well as P3**b** and P6**b** on the triazole is different, they display similar photophysical behaviours. To gain insight into this photophysical process of these polymers, theoretical simulations of P3**a** and P6**a** were performed. Geometry optimizations and energy evaluations were carried out using the density functional theory (DFT) method at the B3LYP/6-31G(d) level. To facilitate the calculation, we took three repeating units (named P3**a**-M and P6**a**-M), and the octyl groups in the fluorenyl units were simplified to methyl groups. The HOMO and LUMO energy levels for P3**a** (−5.21 and −1.78 eV) and P3**b** (−5.30 and −1.83 eV) were obtained, which agreed well with the experimental results deduced from the CV measurements (Fig. S12†), indicating the applicability of the calculation. As shown in Fig. 7, the HOMO and LUMO in P3**a**-M and P6**a**-M are basically located in one repeat unit, suggesting that the triazole ring can serve as a conjugation unit to link the TPE and fluorene units. Since the conjugation length is basically not changed, it's reasonable to observe similar absorption and emission behaviours.

Conclusions

In summary, four soluble and thermally stable polytriazoles were facilely synthesized by the $Cu(PPh_3)_3Br$-catalyzed azide–alkyne click polymerization. The photophysical property investigation disclosed that a small variation in the substituent groups of the polytriazole backbones from P3**a** and P6**a** to P3**b** and P6**b** can lead to completely different absorption and emission behaviours. P3**a** and P6**a** are AEE-active, whereas, P3**b** and P6**b** exhibit typical ACQ phenomena. Thus, for the first time we presented that a subtle change on the substituents can greatly affect the emission properties of polymers. We also proved experimentally and theoretically that exchanging the substituents on the 1,4-positions of the triazole ring shows little influence on the emission profile of the polytriazoles. This kind of research will serve as a guideline for the design of new luminescent polymers.

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