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Polytriazoles with Aggregation-Induced Emission Characteristics: Synthesis by Click Polymerization and Application as Explosive Chemosensors

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The copper-catalyzed 1,3-dipolar cycloaddition of alkynes with azides is a typical example of "click" reaction.[1] Since the reaction enjoys the advantages of high efficiency and regioselectivity and requires mild reaction conditions and simple purification procedures, it has become a versatile synthetic tool with applicability in diverse areas including bioconjugation and surface modification.[2] The click reaction has also been utilized in polymer science with emphasis on the functionalization of preformed polymers through postpolymerization approaches.[3] The effort of developing the reaction into a new polymerization technique, however, has met with only limited success. The polymerization reactions of arylene diazides and arylene diynes catalyzed by copper(I) species were sluggish, taking as long as 7−10 days to finish.[4] The products often precipitated from the reaction mixtures even at the oligomer stage or became insoluble in common organic solvents after purification, unless very long alkyl chains, such as *n*-dodecyl groups, were attached to the arylene rings. The prepared polytrizoles were nonluminescent in the solid state, although their dilute solution emitted UV light, suggesting that the polymer emission has been quenched by the aggregate formation. If the polytriazoles are to be utilized as light-emitting materials, this issue must be properly tackled because luminophores are commonly used as solid films in their practical applications.[5]

We have recently discovered an intriguing phenomenon of aggregation-induced emission (AIE): a series of nonemissive molecules such as tetraphenylethene (TPE) and hexaphenylsilole as well as their derivatives are induced to emit efficiently by aggregate formation. The AIE effect greatly boosts the fluorescence quantum yields (Φ_F) of the molecules by up to 3 orders of magnitude, turning them from faint luminophores into strong emitters. Thanks to their unique AIE characteristics, the molecules have been found to serve as chemosensors, bioprobes, stimuli-responsive nanomaterials, and active layers in the construction of efficient organic light-emitting diodes.[6] Among the AIE luminophores, the TPE system has received much attention because of its facile preparation, ready functionalization, good photostability, and high photoluminescence (PL) efficiency.[7]

For practical applications, these low molecular weight luminophores have to be fabricated into solid films by expensive techniques such as vacuum vapor deposition processes, which are not well suited to the manufacture of large-area, flat-panel devices. One way to surmount this processing disadvantage is to synthesize high molecular weight polymers, which can be readily fabricated into large-area films by simple macroscopic processing techniques such as spin coating and static casting. However, polymers with efficient light emissions in the aggregate or solid state are rare because aggregation of the polymer chains commonly quenches light emission.[8,9] In this paper, we report a group of new TPE-containing polytriazoles (P**3**) synthesized from the click polymerization of diyne (**1**) with diazides (**2**; Scheme 1). The light emission of the polymers is dramatically enhanced, instead of being quenched, by aggregate formation.

Table 1. Click Polymerization of Diyne 1 with Diazides 2[a]

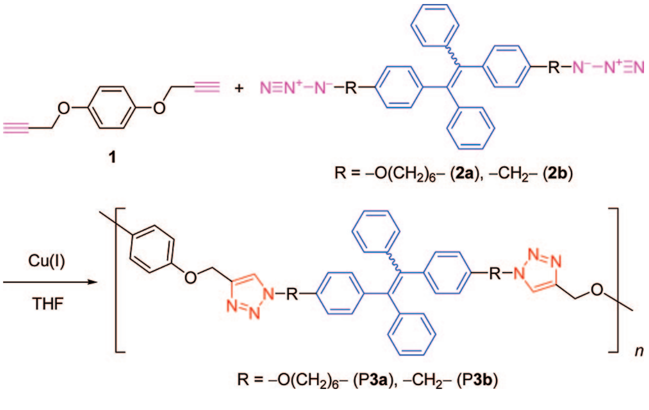
no.	monomer	polymer	catalyst	time (h)	M_w[b]	PDI[b]	yield (%)
1	**1** + **2a**		(catalyst-free)	110	1500	1.1	trace
2	**1** + **2a**		$CuSO_4$/SA[c]	1	insoluble	nd[d]	
3	**1** + **2a**	**P3a**	$Cu(PPh_3)_3Br$	12	36600	1.7	73.1
4	**1** + **2b**		$Cu(PPh_3)_3Br$	12	insoluble	nd[d]	
5	**1** + **2b**	**P3b**	$Cu(PPh_3)_3Br$	2.5	12100[e]	2.1[e]	71.8

[a] Carried out in THF at 60 °C under nitrogen unless otherwise specified; [**1**] = [**2**] = 0.1 M. [b] Weight-average molecular weight (M_w) and polydispersity index (PDI = M_w/M_n) estimated by gel permeation chromatography (GPC) in THF on the basis of a polystyrene calibration. [c] Carried out in a THF/water mixture (5:1, v/v); SA = sodium ascorbate. [d] nd = not determined. [e] Soluble fraction in THF. The polymer **P3b** is completely soluble in polar solvents such as DMF and DMSO.

The diyne and diazide monomers, namely 1,4-bis(propargyloxy)benzene (**1**), 1,2-bis[4-(azidohexyloxy)phenyl]-1,2-diphenylethene (**2a**), and 1,2-bis[(4-azidomethyl)phenyl]-1,2-diphenylethene (**2b**), were synthesized according to Scheme S1.[10] The reactions proceeded smoothly, and the desired monomers were obtained in good yields. The monomer structures were confirmed by spectroscopic analyses (see Supporting Information for detailed characterization data).[10]

We attempted to transform the monomers to their polymers by 1,3-dipolar polycycloaddition. We have previously succeeded in the catalyst-free polycycloaddition of bis(aroylacetylene)s with diazides by simple heating.[11] No high molecular weight polymers, however, were obtained when **1** and **2** were refluxed in THF for 110 h (Table 1, no. 1). This is due to the low reactivity of diyne **1** because it contains no election-withdrawing groups.[11,12] Although the monomers could be polymerized by

Scheme 1. Synthetic Route to Polytriazoles P3 via Click Polymerization of Diyne 1 with Diazides 2



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using $CuSO_4$/sodium ascorbate (SA) in a THF/water mixture under "standard" click reaction conditions,[1] the resultant polymer was insoluble. The insolubility is possibly caused by the low solvating power of the aqueous mixture to the resultant polytriazole as well as the formation of polymer complexes due to the coordination of the Cu ions with the nitrogen-rich heteroatom rings.[13,14]

We then investigated the click polymerization in organic media using an organosoluble catalyst of $Cu(PPh_3)_3Br$.[14,15] Delightfully, polymerization of **1** and **2a** in THF at 60 °C for 12 h produced P**3a** with a high molecular weight in a high yield (Table 1, no. 3). Under the same reaction conditions, the click polymerization of **1** and **2b** gave insoluble P**3b**, probably due to the higher activity of **2b**. Shortening the reaction time helped to solve the problem and enabled us to obtain soluble P**3b** in a high yield. Thus, $Cu(PPh_3)_3Br$ in THF works much better than $CuSO_4$/SA in THF/water mixture for the diyne−diazide click polymerization. Moreover, as $Cu(PPh_3)_3Br$ is less likely to dissociate in the organic media, cross-linking reaction and hence the solubility problem associated with polymer complex formation can be overcome. P**3a** is soluble in common organic solvents such as THF, chloroform, DMF, etc. Its cousin with shorter methylene spacer (P**3b**) is partially soluble in THF but can be completely dissolved in polar solvents such as DMF and DMSO.

P**3** and P**3b** were characterized spectroscopically, and both the polymers gave satisfactory analysis data corresponding to their expected molecular structures (see Supporting Information for details).[10] Our previous studies have revealed that the ^1H NMR spectra of polytriazoles in DMSO-d_6 are better resolved than those in $CDCl_3$.[11,14] We thus measured the spectra of P**3** in DMSO-d_6 (Figures S1 and S2).[10] The resonances of the ethynyl protons of diyne **1** and the methylene protons adjacent to the azido group of diazide **2b** occur at δ 3.62 and 4.46, respectively, which almost disappeared in the polymer spectrum, indicative of the high molecular weight of the polymer. A new peak associated with the resonance of the proton of the 1,4-triazole unit appears at δ 8.26. These results testify that **1** has indeed undergone click polymerization with **2** and that its acetylenic triple bonds have been transformed to the triazole rings of P**3** by the cycloaddition with the azide groups of **2**. The ^{13}C NMR spectra (Figures S3 and S4)[10] of the monomers and polymers substantiate the conclusions drawn from the ^1H NMR spectra: the alkyne and azide units have been transformed to triazole rings. All the polytriazoles are thermally stable. As can be seen from the thermogravimeteric analysis curves shown in Figure S5,[10] P**3a** and P**3b** lose 5% of their weights at temperatures of 363 and 343 °C, respectively, indicative of their high resistance to thermolysis.

The TPE unit is AIE active.[7] Will the AIE effect be preserved in the polymers containing the TPE moieties? To answer this question, we investigated the PL behaviors of P**3a** and P**3b** in the solution and aggregate states. The PL spectrum of a diluted THF solution of P**3a** is almost a flat line parallel to the abscissa (Figure 1A); that is, the polymer is virtually nonluminescent when molecularly dissolved in its good solvent. However, when large amounts of water (>60 vol %) are added into the solution, strong PL peaks are observed at 480.5 nm under identical measurement conditions. As water is a nonsolvent of P**3a**, the polymer chains must have aggregated in the solvent mixtures with high water contents. P**3a** is thus induced to emit by aggregation; in other words, it is AIE active. The similar phenomenon is observed in the P**3b** system: its dilute solution in DMF is nonemissive, but its aggregates in the DMF/water mixtures are highly luminescent (Figure S6).[10] Less amount of water (~10 vol %) is needed to cause the aggregate formation of P**3b** and to activate its AIE process (Figure 1B), owing to the lower solubility of P**3b** associated with its more hydrophobic and rigid molecular structure.

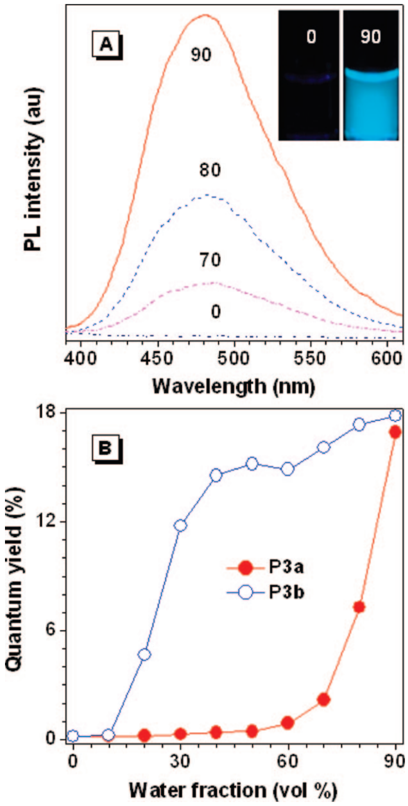

Figure 1. (A) PL spectra of P**3a** in the THF/water mixtures with different water fractions. Polymer concentration: 10 μM; excitation wavelength: 326 nm. (B) Variation in the quantum yields (Φ_F) of P**3a** and P**3b** with water fraction in the THF/water mixture. The Φ_F values were estimated using quinine sulfate in 0.1 N H_2SO_4 ($\Phi_F = 54.6\%$) as standard.

Thus, even after the TPE units have been knitted together by the triazole units in P**3**, their peripheral phenyl rings can still actively rotate in the solution state, making the polymers nonemissive. In the aggregate state, the intramolecular rotation is restricted, which blocks the nonradiative channel and turns on the light emission of the polymers.[6,16] The aqueous mixtures are macroscopically homogeneous and visually transparent with no precipitates, suggesting that the polymer aggregates suspended in the mixture are in nano size.[8] This is confirmed by particle size measurements (Figure S7).[10] No signals are recorded for the P**3** solutions in the pure solvents, proving that the polymers are genuinely dissolved. However, particles with sizes of ~15−605 nm, with most being in the range of ~62−241 nm, are detected in the THF/water and DMF/water mixtures of P**3a** and P**3b** with various water contents, verifying the formation of nanosized aggregates in the aqueous mixtures.

The changes in the Φ_F values of P**3** in the aqueous mixtures with different water fractions further confirm the AIE characteristics of the polymers. In the pure solvents, both P**3a** and P**3b** give negligibly small Φ_F values (0.18% and 0.16%, respectively). The Φ_F value of P**3a** remains almost unchanged until ca. 50% of water is added, while P**3b** starts to aggregate at a water fraction of 10%, as manifested by the sudden rise in the Φ_F value in the aqueous mixture due to its poorer solubility (Figure 1B). At the water fraction of 90%, the Φ_F values of

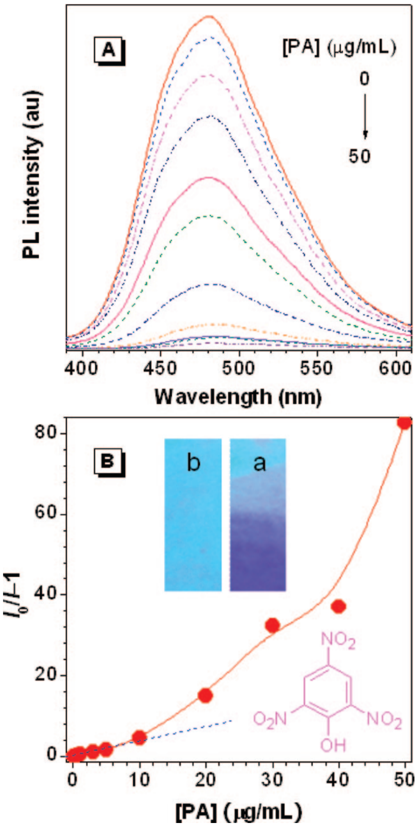

Figure 2. (A) PL spectra of P**3a** in the THF/water mixture (1:9 v/v) containing different amounts of picric acid (PA). Polymer concentration: 10 μM; excitation wavelength: 326 nm. (B) Plot of $I_0/I - 1$ versus PA concentration, where I = peak intensity and I_0 = peak intensity at [PA] = 0 μg/mL. Inset: chemical structure of PA and fluorescence images of P**3a** samples adsorbed in the filter papers before (b) and after (a) being partially dipped into a toluene solution of PA (50 μg/mL).

P**3a** and P**3b** reach ~16.9 and 17.8%, which are about 94- and 110-fold higher than those in the pure solvents, respectively.

The efficient emissions of P**3** in the aggregate state prompted us to explore their potential applications as chemosensors. Nitroaromatics such as 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and picric acid (PA; or 2,4,6-trinitrophenol) are warfare explosives, sensitive detection of which has antiterrorism and homeland-security implications. Because of the commercial unavailability of DNT and TNT, we used PA as a model explosive in this work.[17] The nanoaggregates of P**3a** and P**3b** in the THF/water and DMF/water mixtures with 90% water contents were used as explosive probes, respectively. The emissions of the nanoaggregates are weakened when PA is added (Figures 2A and S8[10]). The emission quenching is observed at a concentration as low as 0.1 μg/mL or 0.1 ppm. When the concentrations of PA are below 10 and 30 μg/mL, the Stern−Volmer plots of P**3a** and P**3b** are linear and give quenching constants of 0.987 × 10^5 and 1.10 × 10^5 M^{-1}, respectively (Figures 2B and S8[10]).[18] When the PA concentration is further increased, the curves deviate from linearity and bend upward.

To gain an insight into the quenching mechanism, we measured the absorption spectrum of PA. The spectrum overlaps with the PL spectra of the polymer aggregates in wavelength region of ~385−485 nm (Figure S9).[10] This facilitates the energy transfer from the excited states of the polymers to the ground-state of PA, thus resulting in the fluorescence quenching.[19] The self-absorption in the concentrated PA solutions have probably contributed to the "super-quenching" effect observed in the high concentration region. In addition to the "wet" measurements, we tested whether the PA detection could also work in the solid state. The polymers were adsorbed onto filter papers.[20] The paper films were then dipped into a toluene solution of PA (50 μg/mL) as well as pure toluene, which is a nonsolvent for both P**3a** and P**3b**. As shown in the inset of Figure 2B, the film of P**3a** displays strong PL upon photoexcitation, which becomes nonemissive after dipping into the PA solution. This demonstrates a prototype device using the AIE polymers for detecting explosives in real-world applications.

In summary, we successfully synthesized TPE-containing polytriazoles with high molecular weights in high yields by the Cu(I)-catalyzed click polymerization. The polymers are soluble and thermally stable ($T_d \geq 340$ °C). Utilizing the novel AIE effect, the polytriazoles are used as chemosensors for the detection of explosives in the aggregate and solid states. This work offers a new synthetic route to functional polymers with "abnormal" but useful optical properties. The possibility of using these AIE-active polymers for other high-tech applications is currently under exploration in our laboratories.

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Supporting Information Available: Text describing the experimental procedures and giving the characterization data; ^{1}H and ^{13}C NMR spectra of monomers **1** and **2** and polymers P**3a** and P**3b**; TGA thermograms of P**3**; PL spectra of P**3b** in the absence and presence of PA in the DMF and DMF/water mixtures; histogram showing the particle size distributions of the polymer aggregates in the THF/water and DMF/water mixtures; and absorption spectrum of PA and emission spectra of P**3** in the THF/water and DMF/water mixtures with 90% water fraction. This material is available free of charge via the Internet at http://pubs.acs.org.

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