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Anionic conjugated polytriazole: direct preparation, aggregation-enhanced emission, and highly efficient Al³⁺ sensing†

Wenhui Dong,[a] Haiqiang Wu,[a] Ming Chen,[a] Yang Shi,[a] Jingzhi Sun,[a] Anjun Qin*[a,b] and Ben Zhong Tang*[a,b,c]

The anionic polytriazole **PI** with a weight-average molecular weight of 190 300 was facilely and directly prepared in an excellent yield of 98.1% in 6 h by the well-established Cu(I)-catalyzed click polymerization of 4,4′-diazido-2,2′-stilbenedisulfonic acid disodium salt hydrate (**1**) and AIE-active tetraphenylethene (TPE)-containing diyne (**2**) under mild reaction conditions. **PI** is soluble in high polar solvents, and thermally stable with 5% loss of its weight at temperatures higher than 290 °C. The photo-physical property investigation showed that **PI** possesses the unique feature of aggregation-enhanced emission (AEE). By taking this feature, **PI** could be used for the specific detection of aluminum ions with a threshold as low as 31 ppb, which could potentially be used for strict drinking water purity control of the aluminum ion content.

Introduction

Conjugated polymers (CPs) have drawn much attention among scientists due to their remarkable features and wide applications.[1–6] The delocalized electrons migrating along the conjugated backbones result in amplification of fluorescence signals and consequent excellent performance in organic photoluminescence (PL) or electroluminescence devices.[7–10] While, for the application of CPs in chemo- and bio-sensors, they generally need to be decorated with ionic species to make them soluble in aqueous or alcohol solvents.

Currently, ionic conjugated polymers, *i.e.* conjugated poly-electrolytes (CPEs) have been widely applied in the opto-electronic field as interfacial materials and chemo-sensors as well as in biological areas.[11–19] However, most of the preparation routes for the CPEs are not straightforward and at least two steps are required: firstly, neutral CPs were prepared *via* polymerizations such as Suzuki, Yamamoto, and Sonogashira poly-couplings, which must be carried out under harsh conditions and should carefully exclude oxygen and/or moisture. Secondly, post-ionized reactions of the neutral CPs, such as quaternization of their amino groups, and/or hydrolysis of ester groups should be performed. These routes are time-consuming and hard to obtain unity charged CPEs.

Moreover, the main-chains of CPEs are mainly based on polyfluorenes,[20–23] whose emission is efficient in their dilute solutions but weakened or quenched completely when they form aggregates or are fabricated into thin-solid films. This phenomenon is known as aggregation-caused quenching (ACQ). Although the CPEs with the ACQ effect have been widely utilized for practical applications, it is hard to explore their full potential in the solid states, which might limit their further applications.[24–27]

Our groups have been working on the development of new polymerization reactions based on triple-bond building blocks and construction of functional polymers with linear and hyper-branched structures.[28,29] In the past decade, we have succeeded in establishing Cu(I)-catalyzed and metal-free click polymerizations of azides and alkynes.[30–33] These polymerizations enjoy the advantages of high efficiency, regioselectivity, easy access to the monomers, mild reaction conditions, *etc*. Thus, we envisioned that ionic polytriazoles (PTAs), which are rarely reported, could be directly prepared *via* this powerful click polymerization from ionic monomers.

ᵃMOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: qinaj@zju.edu.cn, msqinaj@scut.edu.cn
ᵇGuangdong Innovative Research Team, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China
ᶜDepartment of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk
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Moreover, thanks to its excellent tolerance to functional groups, the click polymerization could produce linear and hyperbranched polytriazoles (PTAs) with multifaceted functions, such as aggregation-induced emission (AIE).[34] The AIE is a new concept coined by Tang in 2001 and refers to a unique phenomenon that some non-planar luminogens emit faintly in their solutions but strongly in their aggregate and/or film states.[35–37]

By combining the advantages of orthogonal and robust click polymerization and the unique AIE feature, in this paper, we directly prepared an ionic conjugated PTA from the commercially available ionic diazide 4,4′-diazido-2,2′-stilbenedisulfonic acid disodium salt hydrate (1) and AIE-active tetraphenylethene (TPE)-containing diyne (2)[38,39] under mild reaction conditions. The resulting PTA already emits weakly when dissolved in its good solvent but efficiently upon aggregation, demonstrating a typical phenomenon of aggregation-enhanced emission (AEE). By taking advantage of the AEE, this polymer could be used as a chemo-sensor to sensitively and selectively detect Al^{3+}.

Results and discussion

Click polymerization and characterization of PI

The click polymerization was carried out in the presence of $CuSO_4$/sodium ascorbate, a typical catalytic system for the azide–alkyne click reaction[40] and dimethylformamide (DMF) was chosen as the solvent to ensure these two monomers to be completely dissolved (Scheme 1).

According to our experience gained during the development of click polymerization, the reaction time plays a crucial role for the solubility and molecular weight of the product. We thus followed the time course of the polymerization of 1 and 2 in DMF at 60 °C at the monomer concentration of 0.024 M and the Cu(I) concentration of 0.6 mM. As can be seen from Table 1, the weight-average molecular weight (M_w) of the product gradually increased with time. After 6 h, the M_w of the product reached 190 300, the polydispersity index was 2.06, and the yield was as high as 98.1% (Table 1 and Fig. S1, ESI†). Thanks to its conjugated aromatic structure, PI is thermally stable. As can be seen from the TGA curves (Fig. S2, ESI†), the
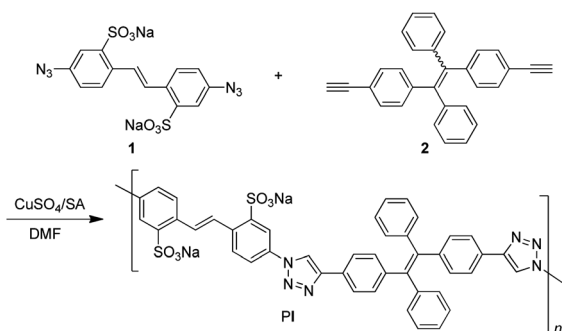
Table 1 Time courses of the click polymerization of 1 and 2 [a]

Entry	t (h)	Yield (%)	M_w [b]	PDI [b]
1	1	61.9	7400	1.47
2	2	69.3	7900	1.27
3	3	96.0	16 500	1.17
4	4	98.9	54 400	1.22
5	5	99.9	149 700	2.03
6	6	98.1	190 300	2.06

[a] Carried out in DMF at 60 °C, [1] = [2] = 0.024 M, [Cu(I)]/[1] = 2.5%. [b] Relative value estimated by GPC in DMF containing 0.05% LiBr using a set of monodisperse poly(methyl methacrylate) calibration, PDI = M_w/M_n.

temperatures for the 5% weight loss are 292 and 321 °C under nitrogen and in air, respectively, revealing its strong resistance to thermolysis and oxidation at elevated temperatures.

It is worth noting that the polymer product with rigid main-chains retains good solubility in DMF probably due to its sulfonic groups and propeller-shaped TPE units. Besides being dissolved in DMF, PI is also soluble in dimethyl sulfoxide (DMSO), partially soluble in water, and insoluble in tetrahydrofuran (THF). Thus, PI was fully characterized by spectroscopic methods, and satisfactory results corresponding to its expected molecular structure were obtained [see Experimental section and the ESI† for details].

To clearly illustrate the structure of PI, its model compound 3 was synthesized in 95.0% yield under similar reaction conditions from diazide 1 and TPE-containing monoyne 4 (Scheme S1, ESI†). From the ^{1}H NMR spectra of 3 and PI in deuterated DMSO, in which the spectral resolution is better than that in $CDCl_3$, we can easily identify that the peak at δ 9.24 belongs to the resonance of the proton of the 1,4-disubstituted 1,2,3-triazole moiety and no resonance ascribed to the 1,5-regioisomer could be observed, suggesting that regioregular PI was obtained (Fig. 1). A similar conclusion could also be drawn from the ^{13}C NMR spectrum of PI (Fig. S3, ESI†).

Photo-physical study and AEE property of PI

After characterizing the structure of PI, we investigated its photo-physical properties in the solution and aggregate states. We first recorded its absorption spectrum (Fig. S4, ESI†) in DMF. PI exhibits only one absorption peak at 356 nm. Furthermore, its maximum absorption is bathochromically shifted by 16 nm compared to our previously reported TPE-containing conjugated hyperbranched PTAs due to its better conjugation.[41]

TPE is a typical AIEgen. Is the TPE-containing PI also AIE-active? To answer this question, we investigated its PL spectra in DMF/THF mixtures with different f_{THF} (Fig. 2). When excited at 356 nm, the DMF solution of PI emits at 492 nm but the intensity is quite low. The PL remains faint in the DMF/THF mixtures with the f_{THF} lower than 70%. Afterwards, it increased swiftly but the spectral profiles remained unchanged. The maximum intensity was recorded in the DMF/THF mixture with an f_{THF} of 90%, which is 5.8 times higher
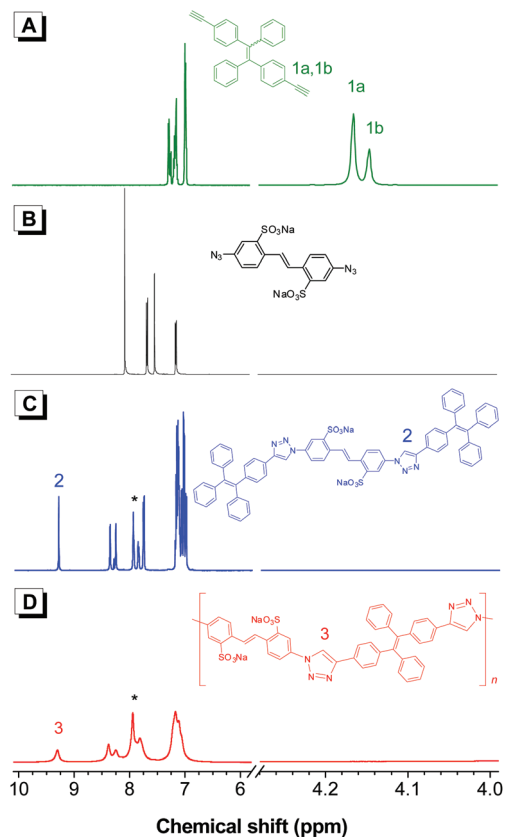

Scheme 1 Synthetic route to ionic conjugated polytriazole of PI.

Fig. 1 ^{1}H NMR spectra of monomers **2** (A) and **1** (B), model compound **3** (C), and **PI** (D) in DMSO-d_6. The solvents were marked as asterisks.
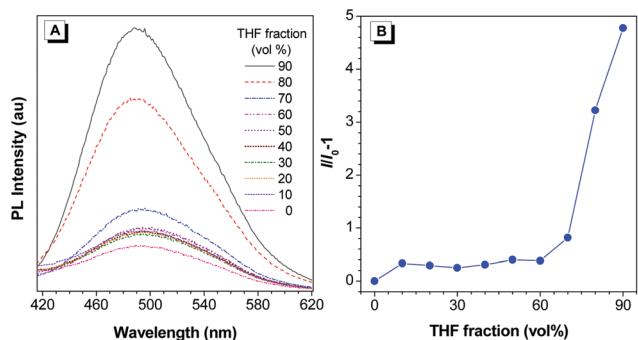

Fig. 2 (A) PL spectra of **PI** in DMF and DMF/THF mixtures. Concentration: 5 μM; λ_{ex}: 356 nm. (B) Plot of the relative PL intensity of **PI** versus the THF fraction (f_{THF}) in DMF/THF mixtures. I: PL intensity, I_0: PL intensity at f_{THF} = 0%.

than that in pure DMF. Moreover, the absolute quantum yield (Φ_F) measurement showed a similar trend. The Φ_F value of the **PI** aggregate in the DMF/THF mixture with an f_{THF} of 90% was recorded to be 11.7%, which is 19.5 times higher than that in pure DMF (0.6%), demonstrating a typical aggregation-enhanced emission (AEE) effect.

This AEE effect could be explained by the well-established restriction of intramolecular rotation (RIR) mechanism.[42–48]

When **PI** is dissolved in DMF, the rotation of phenyl rings of TPE units is slightly restricted, but could still consume the energy of its excited state. Whereas, in the aggregate state, the intramolecular rotation is greatly restricted, which effectively blocks the nonradiative energy dissipation channels of **PI** and turns on emission.

According to the RIR mechanism, if the rotation of the phenyl rings of TPE in **PI** is restricted by addition of an analyte, then we can develop efficient chemo- or bio-sensors. It is reported that the nitrogen of the triazole ring and the oxygen atom of the sulfonic group could coordinate with metal cations,[49–53] which will serve as a cross-linker of the polymer chains, trigger the RIR process, and turn on the emission of the polymer. Based on this understanding, we tried to use **PI** as a fluorescent probe to detect metal cations and develop efficient chemo-sensors.

Metal cation detection

Similar to the behavior in DMF, **PI** emits weakly in DMSO. Since our used cations (the counter anions are also nitrates) are water soluble, and DMSO is less toxic than DMF, we thus carried out the test in DMSO. 14 metal cations Na^+, K^+, Ag^+, Zn^{2+}, Mg^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, and Cr^{3+} were tried. Interestingly, only Al^{3+} could greatly boost the emission of **PI** in the DMSO/water mixture with a water fraction (f_w) of 0.5%, suggesting that **PI** could specifically detect Al^{3+} (Fig. 3).

Besides the specificity, the sensitivity is also another important factor for a chemo-sensor. We thus investigated this parameter for the **PI** probe. The deduced results showed that the detection limit of **PI** for Al^{3+} is as low as 31 ppb (Fig. S5, ESI†). Moreover, the detection range is between 31 ppb and 1.85 ppm, which implies great potential for practical applications.[54–61] It is worthy of note that the detection limits for Al^{3+} in drinking water are 200 ppb and 0.2 mg L^{-1} (ca.
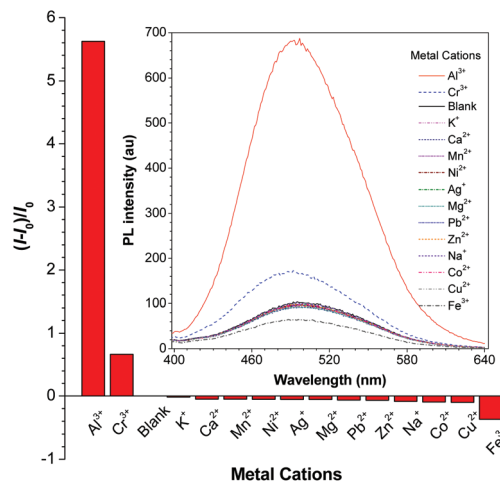

Fig. 3 The change of the relative PL intensity of **PI** upon addition of metal cations into the DMSO/water mixture with a water fraction (f_w) of 5%. Inset: the PL spectra of **PI** containing different metal cations in the DMSO/water mixture with an f_w of 5%.
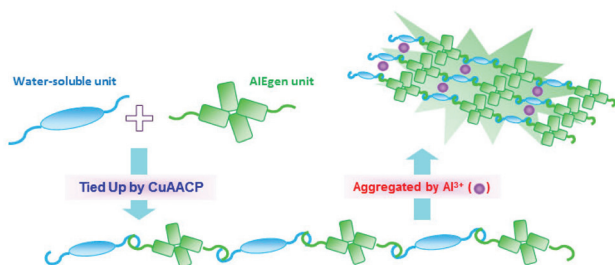
Fig. 4 Proposed schematic sensing mechanism of PI for Al^{3+}.

7.4 ppm according to the U.S. Environmental Protection Agency and the World Health Organization (WHO) regulations), respectively.[62] These requirements suggest that PI could be applied in more strict water purity control of the aluminum ion content. In addition, PI is also a real-time probe and its rapid response to Al^{3+} makes it more convenient to use (ESI Video†).

Generally, the predominant mechanisms for Al^{3+} detection are based on the excited-state intramolecular proton transfer (ESIPT)[63–66] and photo-induced electron transfer (PET),[67] does our developed probe PI follow these mechanisms? To answer this question, we also used the AIE-active model compound **3** to detect Al^{3+} as a control. Surprisingly, **3** has no fluorescence response upon addition of these 14 metal cations including Al^{3+} (Fig. S6, ESI†). Thus, it is suggested that the sensing ability of PI towards Al^{3+} is related to the polymer main-chains. Furthermore, the titration experiment showed that the PL of PI in DMSO gradually intensified upon addition of Al^{3+} and saturated at the molar ratio of Al^{3+} to PI of 2. Meanwhile, the ^{1}H NMR spectrum of PI in the presence of Al^{3+} showed that a new broad peak at δ 9.40 appeared, indicative of the strong interaction between the nitrogen atom of the triazole rings with Al^{3+} (Fig. S7, ESI†). Based on the coordination of Al^{3+} to the nitrogen atoms of triazole rings and the oxygen atoms of sulfonate,[49–53] we propose that one Al^{3+} probably coordinated with the sulfonic group in one polymer chain and nitrogen of the triazole ring at the 3-position in another polymer chain at the same time (Fig. 4). This interaction will draw two polymer chains closer, which have restricted the rotation of the phenyl rings of the TPE units, making the system emissive. Thus, our strategy greatly simplifies the probe design for Al^{3+} detection.

Conclusions

In summary, using the well-established Cu(I)-catalyzed azide–alkyne click polymerization of ionic diazide **1** and TPE-containing diyne **2**, AEE-active anionic polytriazole PI with a high M_w was obtained in excellent yield. PI is thermally stable and soluble in high polar solvents like DMF and DMSO but insoluble in THF. The synergic coordination effect of sulfonic and triazole groups of PI could be used to selectively and sensitively detect Al^{3+}, which could be potentially used for strict drinking water purity control of the aluminum ion content.

Acknowledgements

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