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## ARTICLE

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# Spontaneous amino-yne click polymerization enabled by pyridinium-activated alkynes toward p- $\pi$ conjugated ionic polymers

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The p- $\pi$  conjugated polymers have garnered considerable interests owing to their distinctive electronic structures, which arise from the interaction between p orbitals and  $\pi$  electrons. Currently, the p- $\pi$  conjugated polymers with charged side chains have been extensively studied, those featuring charged backbones are rare due to the synthetic difficulties. In this work, we developed a spontaneous amino-yne click polymerization utilizing pyridinium-activated alkyne and aromatic primary amine monomers, enabling the efficient synthesis of p- $\pi$  conjugated ionic polymers with high weight-average molecular weights ( $M_w$ , up to 44100) and excellent yields (up to 98%). The resultant polymers are emissive, but demonstrate remarkable photothermal properties. Upon irradiation with an 808 nm laser (1.0 W/cm<sup>2</sup>), the polymer powders rapidly reach temperatures as high as 310 °C within 20 s, the highest reported value for polymeric photothermal materials while maintaining outstanding photostability. Additionally, these polymers function as effective electrode materials via a four-electron-transfer process, retaining 85.2% of their capacity after 100 charge-discharge cycles. This work not only establishes a novel pyridinium-activated alkyne-based spontaneous amino-yne click polymerization but also provides a versatile strategy for designing p- $\pi$  conjugated ionic polymers with broad application potentials.

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## ARTICLE

## Introduction

Ionic polymers, that contain ionized moieties in their repeating units, play essential roles in various biological processes, including DNA transcription, protein folding, and cell signaling,<sup>1,2</sup> and other applications, such as dynamic ionic interactions, excellent water solubility, enhanced mobility, high electrical conductivity, and structural and functional flexibility.<sup>3,4</sup> Among them, the multifunctional ionic polymers possessing conjugated structures, have garnered much attention because of their diverse applications.<sup>5-15</sup>

The researchers have been extensively working on the design and synthesis of multifunctional ionic polymers featuring conjugated backbone and ionized side chains.<sup>16</sup> There are mainly two synthetic strategies for the synthesis of these polymers. The first approach involves the direct polymerization of functional monomers with ionic side-chains by oxidative polymerization, Wessling precursor route, Gilch synthesis, topological polymerization, and transition metal-catalysed Suzuki, Heck, Sonogashira, and Wittig polycouplings.<sup>17-24</sup> However, these polymerizations suffer from the monomer limitation, complex product purification, low reaction efficiency, poor atom economy, toxic by-products, and challenges in completely removing metal residues from the products, which hinder their applications in the optoelectronic and biologic fields.<sup>25,26</sup> The alternative is to firstly generate neutral polymers with ionization sites in their side chains, and followed by the introduction of ionic species through post-modification. This approach has been utilized to prepare polyelectrolytes from heteroaromatic polymers, such as polybenzimidazoles, with charged main-chains.<sup>27</sup> However, achieving complete conversion by this method is challenging, leading to unionized portions that are difficult to remove and purify from the polymers. Therefore, the development of new synthetic technique toward facile preparation of functional ionic polymers is highly demanded. Moreover, the research on facilely synthesizing ionic polymers with charged main chains is also limited.

Click polymerization, enjoying the distinct advantages of mild reaction conditions, excellent selectivity, atom economy, and functional group tolerance, has emerged as a powerful tool for preparing polymers with novel structures and multifunctional properties.<sup>28-30</sup> Among them, the alkyne-based click polymerizations have been well established and used for the synthesis of functional polymers. Attracted by these merits, we and others have established several efficient alkyne-based click polymerizations, including Cu(I)-catalysed azide-alkyne, catalyst-free thiol-yne, organobase-catalysed hydroxyl-yne, and spontaneous amino-yne click polymerizations, etc.<sup>31-37</sup> Notably,

the connection of electron-withdrawing groups, such as carbonyl, ester, sulfonyl ones with the ethynyl groups significantly enhances the reactivity of the latter for the click reactions.<sup>38-41</sup> Consequently, many of these polymerizations can proceed smoothly under mild reaction conditions, and some can even occur spontaneously under ambient conditions, thus, we coined these click polymerizations as X-yne click polymerization.<sup>42,43</sup> which has been widely and directly used by others.<sup>44-48</sup>

While the alkyne-based click polymerizations have been developed to prepare a variety of polymers, they have largely been used to synthesize non-conjugated polymers. To achieve the facile and efficient synthesis of functional main-chain conjugated polymers using readily available monomers, it is imperative to design and synthesis of new activated alkyne monomers.

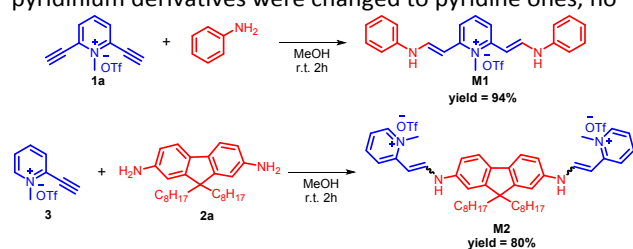
It is well-known that pyridinium is an electron-withdrawing group that can enhance the reactivity of terminal ethynyl group at the *para*-position. This activated ethynyl group can covalently react with cysteines.<sup>49,50</sup> In this study, by employing the pyridinium activated ethynyl monomers and aromatic primary amine monomers, we successfully developed a new type spontaneous amino-yne click polymerization, and the p- $\pi$  conjugated ionic polymers with high weight-average molecular weights ( $M_w$ , up to 44100) were generated in high yields (up to 98%). Thanks to its excellent functional group tolerance, fluorene, triphenylamine (TPA), and tetraphenylethene (TPE) groups could be facilely incorporated into the main-chains, and emissive ionic polymers were obtained with the quantum yields in the range of 0.2-3.5%. Notable, the resultant polymers also show high photothermal conversion, and the temperature of their powders could rapidly reach as high as 310 °C within 20 s upon irradiation with an 808 nm laser at 1.0 W/cm<sup>2</sup>. Additionally, they can be utilized as cathode materials for Li-ion batteries with high performance. Thus, this work not only designs and synthesizes a new type of activated alkyne monomers and established a new spontaneous amino-yne click polymerization, but also facilely generated a new kind of ionic main chains p- $\pi$  conjugated polymers with versatile properties.

## Results and Discussion

Before exploration of the pyridinium-activated alkyne-based amino-yne click polymerization, we first investigated the model reactions. As shown in Scheme 1, the 2,6-diethynylpyridinium **1a** spontaneously reacted with aniline in methanol at 25 °C, and model compound **M1** was obtained in 94% yield. Similarly, the reaction of 2-ethynylpyridinium **3** and aromatic diamine **2a**



could furnish **M2** in an 80% yield. As sharp contrast, when the pyridinium derivatives were changed to pyridine ones, no

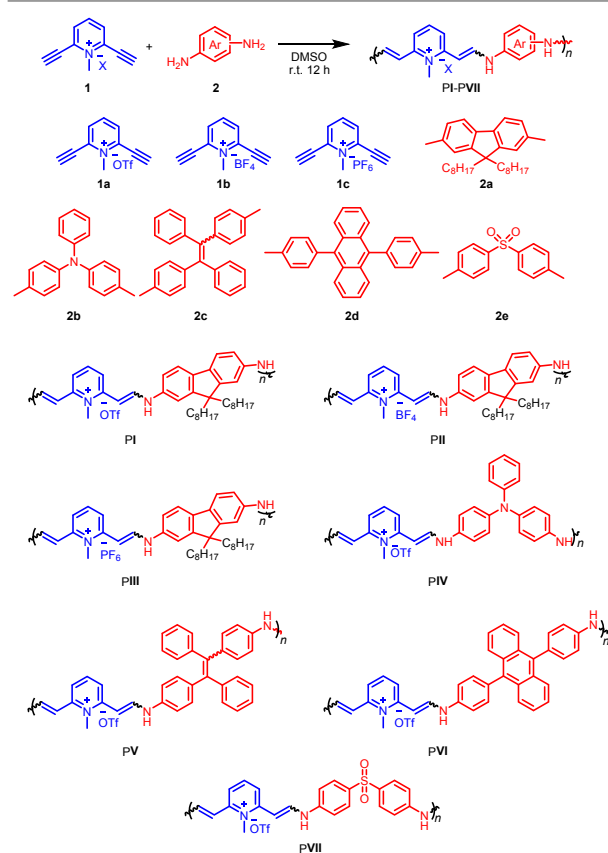


**Scheme 1.** The reaction results of pyridinium-activated alkynes and primary aromatic amines.

product was obtained under the same reaction conditions. These results unambiguously confirm that the activation of the ethynyl groups by the pyridinium salt is critical to facilitate the reaction.

Encouraged by these exciting results, we tried to develop this spontaneous reaction into a powerful polymerization. The monomers of pyridinium-activated diynes **1** and aromatic primary diamines **2** were prepared and the synthetic details are shown in supplementary information (Schemes S1-S3). Notably, the aromatic primary diamines are essential building blocks in the synthesis of p- $\pi$  conjugated polymers due to their containing lone pairs.

In general, systematic optimization of reaction conditions is essential for establishing an effective polymerization. Therefore, the diyne **1a** and diamine **2a** were used a representative monomers to optize the polymerization conditions.



**Scheme 2.** Spontaneous Click Polymerization of Diynes **1** and Diamines **2**.

First, the effect of solvent on the polymerization results was studied. As shown in Table S1, highly polar solvents were found to be more favourable for the polymerization, likely due to better solubility of **1a**. Although the reaction in methanol gave the highest yield (81%), the product is partially soluble. Delightfully, the polymerization in DMSO produced soluble polymer with the highest  $M_w$  value of 17900. Therefore, DMSO was selected as the optimal solvent.

Next, the reaction temperature was screened (Table S2). Elevating the temperature from 25 to 40 °C generally enhanced the yields of the products. However, the products became partially soluble when the temperatures higher than 25 °C, although the  $M_w$  values of soluble parts are higher than that generated at 25 °C. To obtain a fully soluble polymer, 25 °C was selected for following experiments.

Third, the monomer concentration was optimized (Table S3). Increasing the monomer concentrations from 0.1 to 0.5 M generally furnished products with enhanced  $M_w$  values and yields. However, the products became partially soluble when the concentrations are higher than 0.4 M. When taking the product solubility, the  $M_w$  and yield into account, 0.3 M was used for further study.

Forth, the effect of reaction time on the polymerization results was investigated. As listed in Table S4, the highest yield (90%) and  $M_w$  value (44100) of product was obtained when the reaction time is 12 h. Notable, the product is also soluble. Therefore, 12 h was chosen as the optimal reaction time.

**Table 1.** Spontaneous Click Polymerization of Diynes **1** and Diamines **2**.<sup>a</sup>

| Enter          | Monomer               | Polymer | Yield (%) | $M_w^b$           | $\bar{D}^b$ | $S^c$ |
|----------------|-----------------------|---------|-----------|-------------------|-------------|-------|
| 1              | <b>1a</b> + <b>2a</b> | PI      | 90        | 44100             | 2.00        | √     |
| 2              | <b>1b</b> + <b>2a</b> | PII     | 90        | 9100              | 1.53        | √     |
| 3              | <b>1c</b> + <b>2a</b> | PIII    | 93        | 27000             | 2.89        | √     |
| 4 <sup>d</sup> | <b>1a</b> + <b>2b</b> | PIV     | 92        | 4500 <sup>f</sup> | 1.13        | Δ     |
| 5 <sup>d</sup> | <b>1a</b> + <b>2c</b> | PV      | 91        | 7400 <sup>f</sup> | 1.48        | Δ     |
| 6 <sup>d</sup> | <b>1a</b> + <b>2d</b> | PVI     | 95        | 6900 <sup>f</sup> | 1.36        | Δ     |
| 7 <sup>e</sup> | <b>1a</b> + <b>2e</b> | PVII    | 98        | 17000             | 1.95        | √     |

<sup>a</sup> Carried out at 25 °C under  $N_2$  for 12 h.  $[1] = [2] = 0.30$  M. <sup>b</sup> Determined by gel-permeation chromatography (GPC) using DMF containing 0.05% LiBr as the eluent based on a linear poly(methyl methacrylate) (PMMA) calibration.  $M_w$  = weight average molecular weight; dispersity ( $\bar{D}$ ) =  $M_w/M_n$ ;  $M_n$  = number-average molecular weight. <sup>c</sup> Solubility (S) tested in DMF and DMSO; Δ = partially soluble, √ = completely soluble. <sup>d</sup> The reaction time is 8 h. <sup>e</sup> The reaction time is 6 h. <sup>f</sup> Soluble part.

Finally, under above optimised reaction conditions, we studied the universality of this polymerization by using other pyridinium-activated diynes **1** and diamine monomers **2b-2e** (Scheme 2). As shown in Table 1, all the polymerizations performed spontaneously and smoothly, and produced products with  $M_w$  values up to 44100 in the yields up to 98%, confirming the robustness of this polymerization. However, the structure of diamines significantly influence the polymerization results. For example, the polymerizations of diyne **1a** with **2b**, **2c**, and **2e** without long alkyl chains resulted in partially soluble products and the  $M_w$  values of soluble parts are relatively low although their yields are very high. Thanks to the flexibility and



polarity of sulfonyl group, soluble PVII with excellent yield and high  $M_w$  value was obtained.

The resultant polymers are insoluble in most low polar solvents such as dichloromethane (DCM), tetrahydrofuran (THF), and ethyl acetate (EA), due to their ionic main chains. Delightfully, they could be mostly dissolved in high polar solvents such as DMSO, facilitating their further applications. The polymers are thermally stable. As shown in Fig. S1, the thermogravimetric analysis (TGA) indicates that the temperatures for 5% weight loss are in the range between 294 and 367 °C, which are much higher than that of previously prepared unconjugated polymers via X-yne click polymerizations.<sup>38</sup>

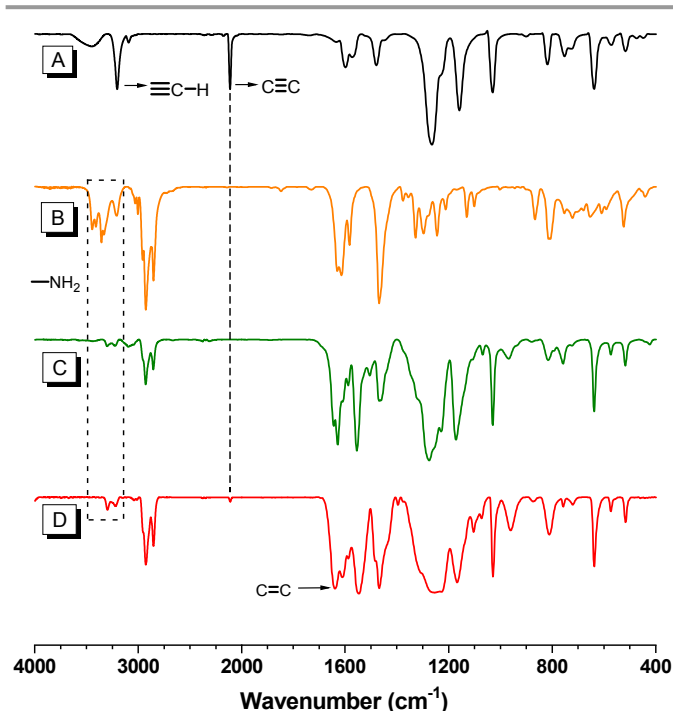


Fig. 1. FT-IR spectra of **1a** (A), **2a** (B), model compound **2** (C), and PI (D).

All polymers were characterized using standard spectroscopic techniques, consisting of Fourier transform infrared (FT-IR), and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies. To accurately characterize the polymer structures, model compound **M2** was synthesized and used for comparison. Although the reaction of **3** and **2a** furnished **M2** with *E* and *Z* isomers in the ratio of 5:2, pure *E*-**M2** could be obtained by recrystallization. Fig. 1 shows an example of FT-IR spectra of monomers **1a** and **2a**, model molecule *E*-**M2** and polymer PI. The vibration peaks of ethynyl groups at 3200 and 2098  $\text{cm}^{-1}$  of **1a** disappeared in the spectra of *E*-**M2** and PI. Meanwhile, a new vibration peak of PI at 1639  $\text{cm}^{-1}$  assignable to the vinyl group, was observed, which was formed by the reaction of **1a** and **2a**. Meanwhile, the stretching vibration peak of **2a** at 3444-3209  $\text{cm}^{-1}$  could not be observed in the spectra of *E*-**M2** and PI. These results confirm the occurrence of the polymerizations. Similar results are found for other polymers (Figures. S2–S7).

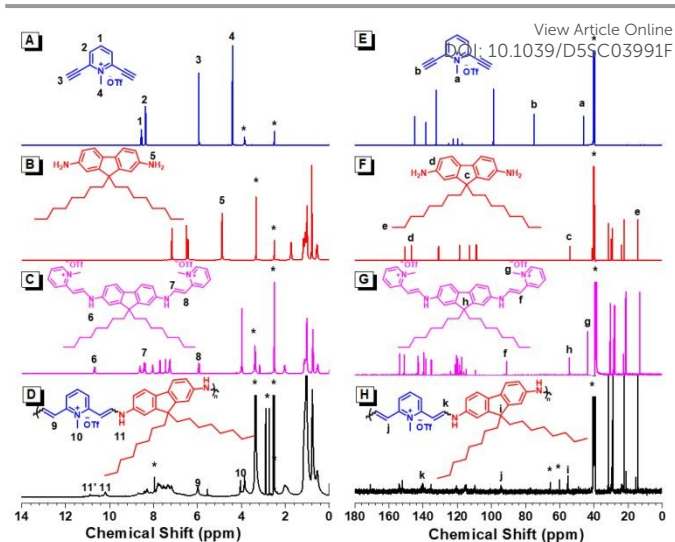


Fig. 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1a** (A) and (E), **2a** (B) and (F), model compound *E*-**M2** (C) and (G), and PI (D) and (H) in  $\text{DMSO}-d_6$ , respectively. The solvent peaks are marked with asterisks.

More detailed information about the polymer structures could be obtained from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The  $^1\text{H}$  NMR spectra of **1a**, **2a**, *E*-**M2** and PI are shown in Fig. 2A-2D as an example. The ethynyl proton resonance of **1a** is observed at  $\delta$  5.90 and that of amino group of **2a** at  $\delta$  4.88. These peaks are almost disappeared in the spectra of *E*-**M2** and PI. In the spectrum of *E*-**M2**, the proton resonance peak at  $\delta$  5.93 represents the vinyl group with *E* conformation. Different from *E*-**M2**, in the spectrum of PI, besides the peaks at  $\delta$  8.30 and 5.98, there is a resonance at  $\delta$  6.65, suggesting the formation of the *Z*-isomeric units. Moreover, different from the amino proton resonance of **2a** at  $\delta$  4.88, two resonances peaks of PI at  $\delta$  10.89 and 10.20 were found, further confirming the existing of the isomeric units.

The  $^{13}\text{C}$  NMR spectra further confirmed the conclusions drawn from the  $^1\text{H}$  NMR spectral analysis (Fig. 2E-2H). The resonance peaks of the ethynyl carbons of **1a** at  $\delta$  74.56 and 98.44 disappeared in the spectrum of PI. Meanwhile, new peaks at  $\delta$  140.16 and 109.76, representing the resonance of vinyl carbons, appeared in the spectrum of PI. Similar results were found for the polymers PII-PVII (Fig. S8–S13). Above spectral results indicate the success of the polymerization.

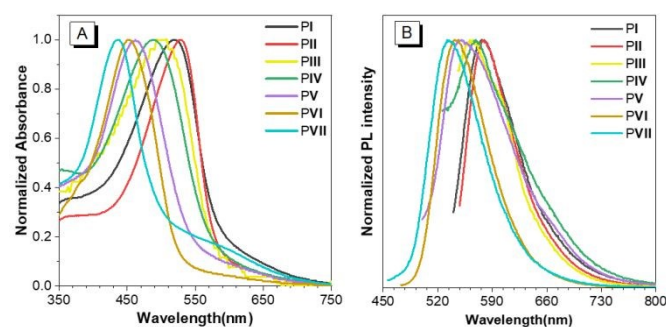
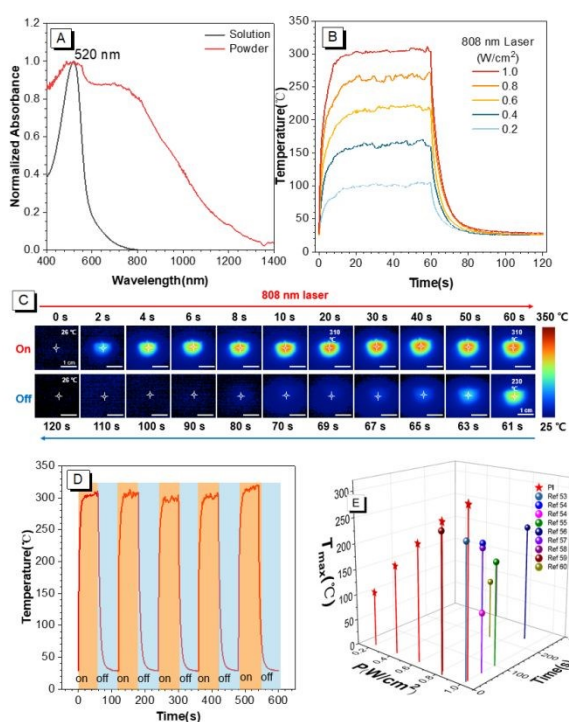


Fig. 3. (A) Absorption and (B) photoluminescence spectra of PI-PVII in DMSO. The concentration:  $10^{-5}$  M; The emission was measured at the maximum absorption wavelength.





Since the polymers contain the emissive fluorene, TPA and TPE moieties, we thus investigated their photo-physical properties. As shown in Fig. 3, their absorption peaks are ranged in 436-528 nm and the photoluminescence (PL) peaks are between 534-578 nm. However, the resultant polymers show low PL quantum yields (0.2-3.5%, Table S5), which might be ascribed to their strong intramolecular charge transfer. It is worth noting that the PL of the resultant polymers is red-shifted compared with the previous reported polymers that generated from the X-yne click polymerizations. The red-shifted absorption and PL spectra of the polymers are attributed to the extended conjugation and donor-acceptor (D-A) structures in their backbones.

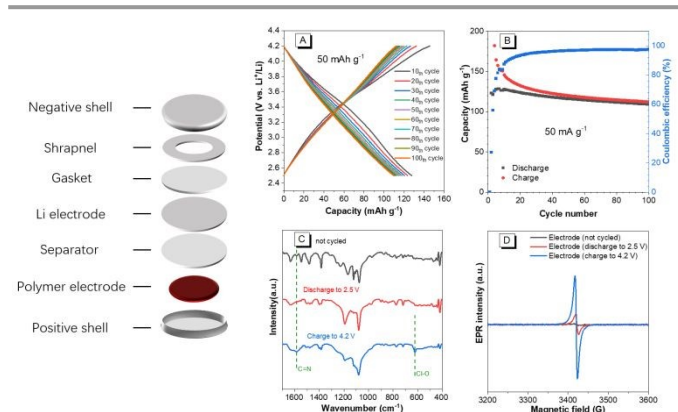


**Fig. 4.** (A) UV-vis-NIR spectra of PI in DMSO solution (10  $\mu$ M) and in powder state. (B) Heating and cooling characteristics of PI powder under 808 nm laser irradiation at various power densities (0.2, 0.4, 0.6, 0.8, and 1.0  $\text{W cm}^{-2}$ ). (C) Thermal IR images of PI powder (15 mg) under 808 nm laser irradiation at 1.0  $\text{W cm}^{-2}$ , followed by turning off the laser. (D) Reversibility of PI powder (15 mg) under 808 nm laser irradiation at 1.0  $\text{W cm}^{-2}$ . (E) The highest temperature and corresponding time of the reported polymer organic photothermal materials under 808 nm laser irradiation.

Interestingly, although the absorption peak of PI is located at 520 nm in solution, its powders are lasted to around 1400 nm (Fig. 4A). This might be attributed to the strong intermolecular interactions of the polymer chains. Based on our previous reports that the materials with near-infrared (NIR) absorption and low PL quantum yields might show remarkable photothermal conversion,<sup>51-53</sup> we thus investigated its photothermal properties.

As shown in Figure 4B and 4C, upon irradiation of the PI powders (15 mg) with an 808 nm laser at 1.0  $\text{W cm}^{-2}$ , the photothermal temperature could be rapidly elevated to ca. 280  $^{\circ}\text{C}$  in 5 s and further reach equilibrium at 310  $^{\circ}\text{C}$  in 20 s. Since the temperature is lower than the  $T_d$  value, this

photothermal behaviours showed excellent reversibility (Fig. 4D). To the best of our knowledge, this value represents the highest photothermal temperature to date for organic polymeric materials (Fig. 4E).<sup>53-60</sup> Similar photothermal behaviors for PII-PVII were also observed although their temperatures are not higher than that of PI (Fig. S14-S19, and Table S6). The high photothermal temperature could be explained based on the Jablonski diagram. When the polymers absorb light to the excited state, most of the energy was decayed non-radiatively because of the radiative decay pathway is insufficient as indicated by their low PL quantum yields. Therefore, the non-radiative decay readily generates heat, from which elevated temperature was realized.<sup>53</sup>



**Fig. 5.** Schematic illustration of the battery assembly (Left) (A) The charge-discharge curves and (B) cycling stability at 50  $\text{mA g}^{-1}$  of PIV cathode, respectively. (C) FT-IR spectra and (D) electron paramagnetic resonance (EPR) spectra of PIV cathode in different states, respectively.

Meanwhile, the resultant polymers feature a positively charged backbone and abundant C-N and C=N bonds in their structures, which might enable them to exhibit electrochemical activity and high battery capacity.<sup>61-63</sup> Thus, the polymers were assembled into battery cells, and their electrochemical performance was evaluated. The results demonstrated that PIV exhibited excellent electrochemical performance as a cathode in Li ion battery because of its high theoretical specific capacities of 189  $\text{mAh g}^{-1}$  with a four-electron transfer process. As shown in Fig. 5A and 5B, the capacity retention of the cell reached as high as 85.2% after 100 cycles at 50  $\text{mA g}^{-1}$ . Moreover, the charge storage mechanism of PIV cathode was characterized by FT-IR and EPR. Owing to the reversible redox cycling of the pyridine rings during the charge-discharge process. The intensity of the stretching vibrational peaks of the C=N bonds at 1585  $\text{cm}^{-1}$  became stronger when charged to 4.2 V and recovered when discharged to 2.5 V (Fig. 5C), which proves that the loss (during charge) or gain (during discharge) of electrons on nitrogen atoms and redistribution of electrons.<sup>64</sup> The new vibrational absorption peak at 621  $\text{cm}^{-1}$  was observed after charging, which belongs to Cl-O bonds from  $\text{ClO}_4^-$ , indicating the storage of anions.<sup>62,65,66</sup> Meanwhile, the EPR signal was enhanced when charged to 4.2 V, suggesting the presence of unpaired electrons, which was coincident well with the about three-electron transfer calculated by the actual capacity (Fig. 5D).



## Conclusions

In this work, we successfully established a spontaneous amino-yne click polymerization based on pyridinium-activated alkynes, and thermally stable p- $\pi$  conjugated polymers with high  $M_w$  values (up to 44100) were obtained in high yields (up to 98%). Compared with the polymers generated from other X-yne click polymerizations, both the absorption and PL peaks of the resulting polymers are significantly red-shifted because of the p- $\pi$  conjugation. Additionally, the polymers exhibit excellent photothermal conversion behaviours. The powders of PI can reach a temperature as high as 310 °C under irradiation with an 808 nm laser at 1.0 W cm<sup>-2</sup> while maintaining outstanding reversibility. Furthermore, owing to its unique ionic structure, PIV could be used as battery cathode materials, retaining 85.2% capacity after 100 charge-discharge cycles. This study not only establishes a new type of X-yne click polymerization and provides a strategy to facilitate prepare p- $\pi$  conjugated polymers under mild conditions, but also addresses the gap in using click polymerization to synthesize conjugated polymers.

## Author contributions

C. Li performed the synthesis, structural characterization, thermal, photophysical measurements, photothermal measurements and prepared the ESI. G. Zhang performed the electrochemical studies. H. Xu helped with photothermal measurements. L. Wei, H. Liu, K. Zhang helped with synthesis and isolating the part of new compounds. C. Li, G. Zhang, C. Wang and A. Qin. wrote the paper. C. Li, B. Wang, A. Qin, and B. Z. T. conceived and designed the experiments and supervised the overall project. C. Li, G. Zhang, C. Wang and A. Qin. wrote and revised the paper with the contribution of all other authors.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The datasets supporting this article have been uploaded as the ESI. †

## Acknowledgements

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