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Spontaneous amino–yne click polymerization enabled by pyridinium-activated alkynes toward p– π conjugated ionic polymers

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The p– π conjugated polymers have garnered considerable interest owing to their distinctive electronic structures, which arise from the interaction between p orbitals and π electrons. Currently, the p– π 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– π conjugated ionic polymers with high weight-average molecular weights (M_w , up to 44 100) 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⁻²), 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– π conjugated ionic polymers with broad application potentials.

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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,^{1,2} and other applications, such as dynamic ionic interactions, excellent water solubility, enhanced mobility, high electrical conductivity, and structural and functional flexibility.^{3,4} Among them, the multifunctional ionic polymers possessing conjugated structures have garnered much attention because of their diverse applications.^{5–15}

Researchers have been extensively working on the design and synthesis of multifunctional ionic polymers featuring conjugated backbones and ionized side chains.¹⁶ 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 polycondensations.^{17–24} 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 biological fields.^{25,26} The alternative is to firstly generate neutral polymers with ionization sites in their side chains, 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 mainchains.²⁷ 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 techniques 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,^a has emerged as a powerful tool

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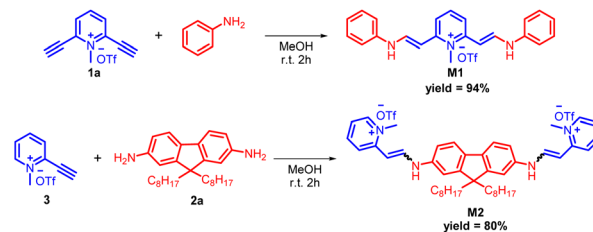
for preparing polymers with novel structures and multifunctional properties.^{28–30} Among them, the alkyne-based click polymerizations have been well established and used for the synthesis of functional polymers. Attracted by these merits, we and others have established several efficient alkyne-based click polymerizations, including Cu(I)-catalysed azide–alkyne, catalyst-free thiol–yne, organobase-catalysed hydroxyl–yne, and spontaneous amino–yne click polymerizations *etc.*^{31–37} 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.^{38–41} 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,^{42,43} which has been widely and directly used by others.^{44–48}

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 synthesize new activated alkyne monomers.

It is well known that pyridinium is an electron-withdrawing group that can enhance the reactivity of the terminal ethynyl group at the *para*-position. This activated ethynyl group can covalently react with cysteines.^{49,50} In this study, by employing the pyridinium activated ethynyl monomers and aromatic primary amine monomers, we successfully developed a new type of spontaneous amino–yne click polymerization, and *p*– π conjugated ionic polymers with high weight-average molecular weights (M_w , up to 44 100) 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%. Notably, 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⁻². 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 generates a new kind of ionic main chain *p*– π 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. In



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

a sharp contrast, when the pyridinium derivatives were changed to pyridine ones, no 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 SI (Schemes S1–S3). Notably, the aromatic primary diamines are essential building blocks in the synthesis of *p*– π conjugated polymers as they contain 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 as representative monomers to optimize the polymerization conditions.

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 the 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 a soluble polymer with the highest M_w value of 17 900. 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, M_w and yield into account, 0.3 M was used for further study.

Fourth, the effect of reaction time on the polymerization results was investigated. As listed in Table S4, the highest yield (90%) and M_w value (44 100) of product were obtained when the reaction time was 12 h. Notably, the product was also soluble. Therefore, 12 h was chosen as the optimal reaction time.

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 44 100 in the yields up to 98%, confirming the robustness of this polymerization. However, the structure of diamines significantly influences 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 the 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.³⁸

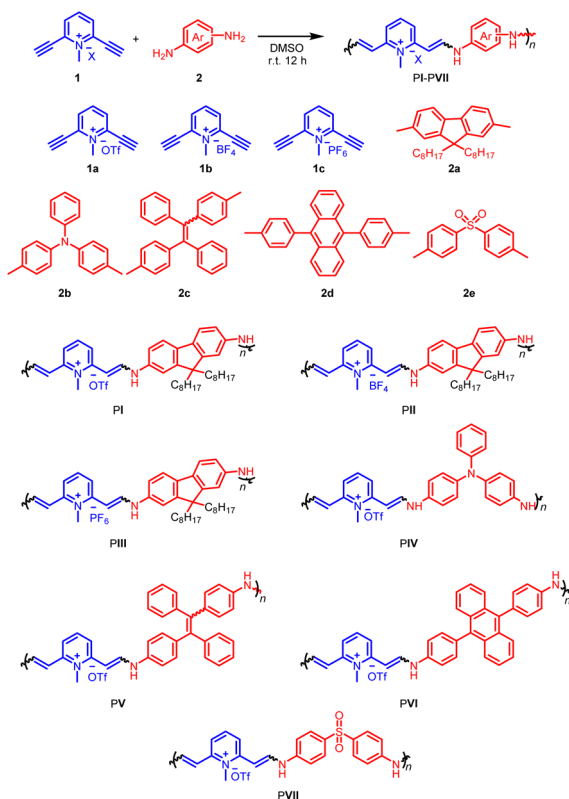
All polymers were characterized using standard spectroscopic techniques, consisting of Fourier transform infrared (FT-IR), and ¹H and ¹³C NMR spectroscopies. To accurately characterize the polymer structures, model compound **M2** was synthesized and used for comparison. Although the reaction of

Table 1 Spontaneous click polymerization of Diynes **1** and Diamines **2^a**

Enter	Monomer	Polymer	Yield (%)	M_w^b	D^b	S^c
1	1a + 2a	PI	90	44 100	2.00	✓
2	1b + 2a	PII	90	9100	1.53	✓
3	1c + 2a	PIII	93	27 000	2.89	✓
4 ^d	1a + 2b	PIV	92	4500 ^f	1.13	Δ
5 ^d	1a + 2c	PV	91	7400 ^f	1.48	Δ
6 ^d	1a + 2d	PVI	95	6900 ^f	1.36	Δ
7 ^e	1a + 2e	PVII	98	17 000	1.95	✓

^a Carried out at 25 °C under N₂ for 12 h. [1] = [2] = 0.30 M. ^b 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 (D) = M_w/M_n ; M_n = number-average molecular weight. ^c Solubility (S) tested in DMF and DMSO; Δ = partially soluble, ✓ = completely soluble. ^d The reaction time is 8 h. ^e The reaction time is 6 h. ^f Soluble part.

3 and **2a** furnished **M2** with *E* and *Z* isomers in the ratio of 5 : 2, pure *E*-**M2** could be obtained by re-crystallization. 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 cm⁻¹ of **1a** disappeared in the spectra of *E*-**M2** and **PI**. Meanwhile, a new vibration peak of **PI** at 1639 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 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 (Fig. S2–S7).



Scheme 2 Spontaneous click polymerization of diynes **1** and diamines **2**.

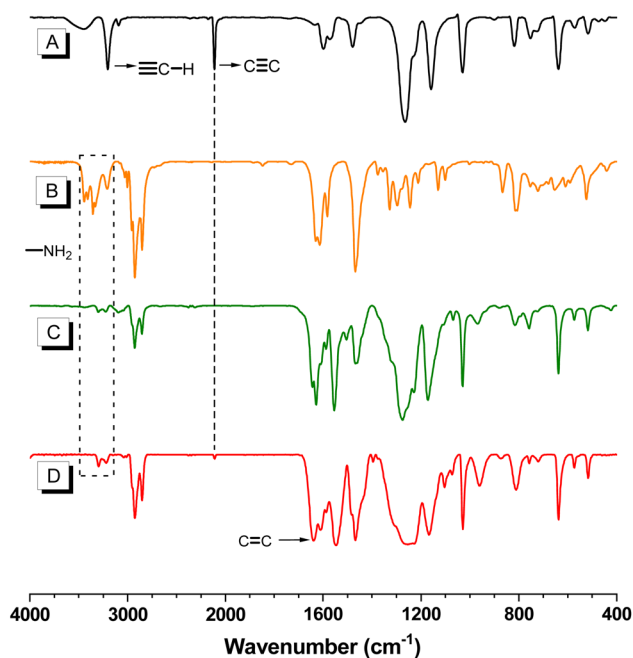


Fig. 1 FT-IR spectra of **1a** (A), **2a** (B), model compound *E*-**M2** (C), and **PI** (D).



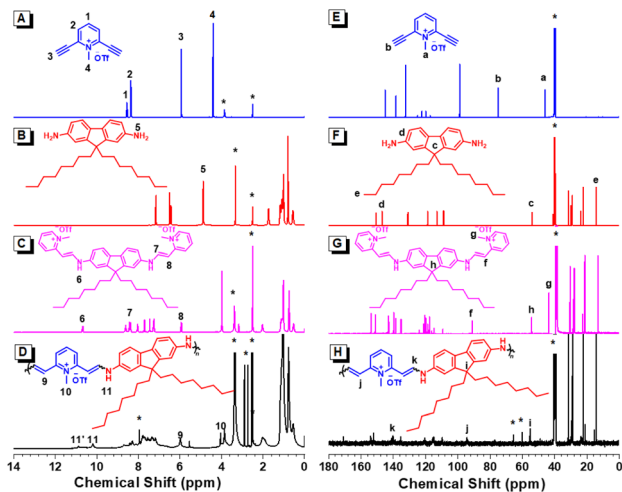


Fig. 2 ^1H and ^{13}C NMR spectra of **1a** (A) and (E), **2a** (B) and (F), model compound *E-M2* (C) and (G), and **PI** (D) and (H) in $\text{DMSO}-d_6$, respectively. The solvent peaks are marked with asterisks.

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

The ^{13}C NMR spectra further confirmed the conclusions drawn from the ^1H NMR spectral analysis (Fig. 2E–H). The resonance peaks of the ethynyl carbons of **1a** at δ 74.56 and 98.44 disappeared in the spectrum of **PI**. Meanwhile, new peaks at δ 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.

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 in the range of 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.

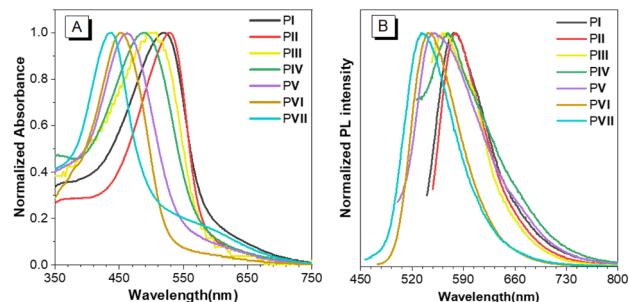


Fig. 3 (A) Absorption and (B) photoluminescence spectra of **PI–PVII** in DMSO . Concentration: 10^{-5} M; the emission was excited at the maximum absorption wavelength.

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,^{51–53} we thus investigated its photothermal properties.

As shown in Fig. 4B and C, upon irradiation of the **PI** powders (15 mg) with an 808 nm laser at 1.0 W cm^{-2} , the

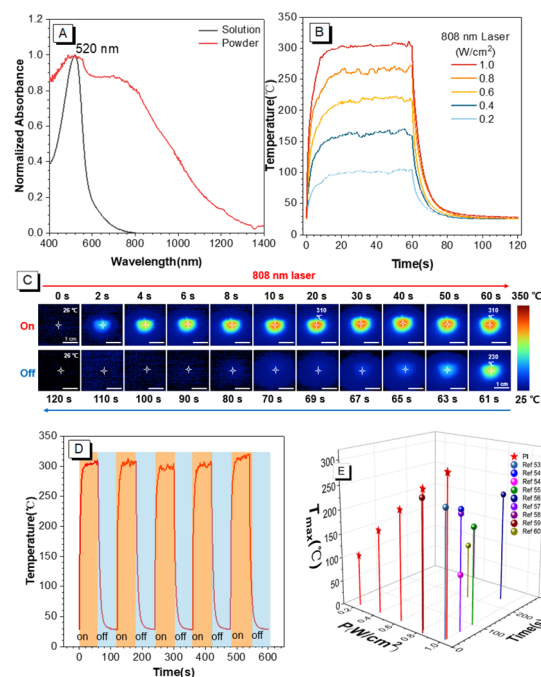


Fig. 4 (A) UV-vis-NIR spectra of **PI** in DMSO solution ($10 \mu\text{M}$) and in the powder state. (B) Heating and cooling characteristics of **PI** powder under 808 nm laser irradiation at various power densities (0.2 , 0.4 , 0.6 , 0.8 , and 1.0 W cm^{-2}). (C) Thermal IR images of **PI** powder (15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



photothermal temperature could be rapidly elevated to *ca.* 280 °C in 5 s and further reach equilibrium at 310 °C in 20 s. Since the temperature is lower than the T_d value, this photothermal behaviour 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).^{53–60} 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 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.⁵³

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.^{61–63} 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 batteries because of its high theoretical specific capacities of 189 mA h g^{−1} with a four-electron transfer process. As shown in Fig. 5A and B, the capacity retention of the cell reached as high as 85.2% after 100 cycles at 50 mA g^{−1}. Moreover, the charge storage mechanism of the **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 cm^{−1} became stronger when charged to 4.2 V and recovered when discharged to 2.5 V (Fig. 5C), which proves the loss (during charge) or gain (during discharge) of electrons on nitrogen atoms and redistribution of electrons.⁶⁴ The new vibrational absorption peak at 621 cm^{−1} was observed after charging, which belongs to Cl–O bonds from ClO₄[−], indicating the storage of anions.^{62,65,66} Meanwhile, the EPR signal was enhanced when charged to 4.2 V, suggesting the presence of

unpaired electrons, which was well in accordance with the 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- π conjugated polymers with high M_w values (up to 44 100) 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- π conjugation. Additionally, the polymers exhibit excellent photothermal conversion behaviour. 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^{−2} 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- π 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, and photothermal measurements, and prepared the SI. G. Zhang performed the electrochemical studies. H. Xu helped with photothermal measurements. L. Wei, W. Liu, and K. Zhang helped with synthesis and isolating some new compounds. C. Li, G. Zhang, C. Wang and A. Qin wrote the paper. C. Li, B. Wang, A. Qin, and B. Z. Tang conceived and designed the experiments and supervised the overall project. C. Li, G. Q. 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

Data available on request from the authors.

The synthetic details of monomers and polymers, the characterization of monomers, model compounds and polymers, and the photothermal properties of the polymers. See DOI: <https://doi.org/10.1039/d5sc03991f>.

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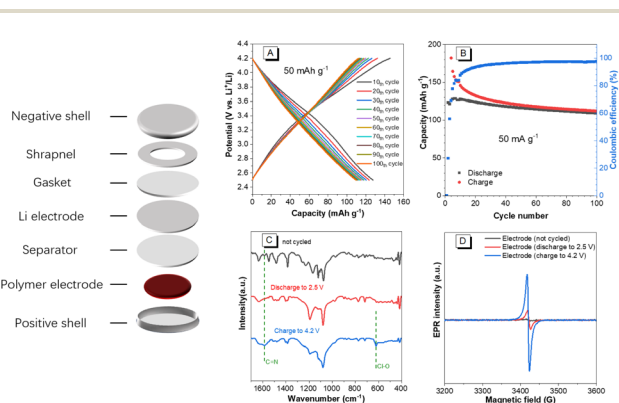


Fig. 5 Schematic illustration of the battery assembly (left) (A) the charge–discharge curves and (B) cycling stability at 50 mA h g^{−1} of PIV cathode, respectively. (C) FT-IR spectra and (D) electron paramagnetic resonance (EPR) spectra of the PIV cathode in different states, respectively.



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