

## Supporting Information

# Pyridinium-activated alkyne-based spontaneous amino-yne click polymerization toward n- $\pi$ conjugated polyelectrolytes

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**Materials.** 2,6-Diethynylpyridine and diamines were purchased from Bidepharm, methyl trifluoromethanesulfonate was purchased from Energy, and ultra-dry solvents were purchased from Energy. All commercial reagents are of the highest purity. Unless otherwise specified, they were used without further purification.

**Instruments.** The weight-average molecular weights ( $M_w$ ) and polydispersities ( $M_w/M_n$ ) were measured by a Waters 1515 Gel Permeation Chromatography (GPC) system equipped with refractive index detector. A set of monodispersed polymethyl methacrylate (PMMA) standards covering the molecular weight range from  $10^3$  to  $10^7$  were utilized as standards and DMF containing 0.05 M LiBr was used as the eluent in a flow rate of 1.0 mL/min. Fourier transform infrared (FT-IR) spectra were measured on a PerkinElmer Spectrum 3 FT-IR Spectrometer (KBr disk).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were conducted on a Bruker Advance 400 or 500 MHz NMR spectrometer using DMSO as solvent. Thermogravimetric analysis (TGA) was carried out on a TA TGA Q5000 at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$  under nitrogen. Differential scanning calorimetry (DSC) analysis was performed on a DSC Q1000 under dry nitrogen at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . UV-vis spectra were measured on a Shimadzu UV-2600 spectrophotometer with bandwidth of 1 nm, medium scanning rate, and quartz cuvettes of 1 cm path length. Photoluminescence (PL) spectra were measured on a Horiba Fluoromax-4 spectrofluorometer.

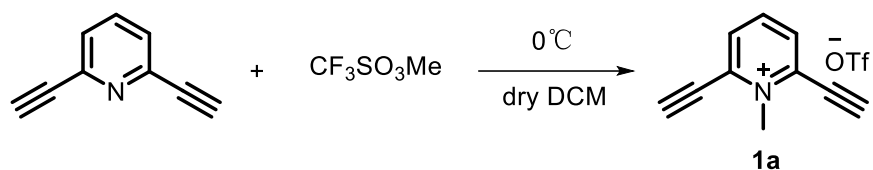
### **Monomer synthesis.**

#### **Synthesis of 2,6-diethynyl-1-methylpyridin-1-ium trifluoromethanesulfonate (1a).**

The detailed synthetic route to **1a** is illustrated in Scheme S1.<sup>1</sup> Into a 250 mL flame-dried two-necked round-bottom flask equipped with a stir bar were added 2,6-diethynylpyridine (1.27 g, 10.00 mmol). After purging with dry nitrogen for 3 times, 15 mL of DCM and methyl trifluoromethanesulfonate (1.64 g, 10.00 mmol) were injected into the flask by a hypodermic syringe under an ice bath. Afterward, the mixture was allowed to react at room temperature, using

TLC to monitor the complete of the reaction. Then, the system was added cold ether and filtrated. The obtained powders were washed with cold ether and dichloromethane for three times to obtain beige solid **1a** (2.85 g, 98% yield). FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3200, 2107, 1596, 1569, 1478, 1263, 1157, 1026, 818, 637, 517.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta$  8.55 (t,  $J = 8.1$  Hz, 1H), 8.34 (d,  $J = 8.1$  Hz, 2H), 5.90 (s, 2H), 4.41 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  145.1, 138.3, 132.4, 125.0, 122.4, 119.8, 117.3, 98.9, 75.0, 46.1.

**Scheme S1. Synthetic Route to Monomer 1a.**



**Synthesis of *N*-(4-aminophenyl)-*N*-phenylbenzene-1,4-diamine (**2b**).**

**2b** was synthesized according to previous work.<sup>2</sup> FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3423, 3338, 3028, 1620, 1591, 1505, 1328, 1264, 827, 756, 696, 570, 515.  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.14 (t,  $J = 7.7$  Hz, 2H), 7.04 – 6.72 (m, 7H), 6.62 (d,  $J = 8.2$  Hz, 4H).

**Synthesis of Model Compound.** To facilitate the structural characterization of polymers, the model compound of 2,2'-((9,9-dioctyl-9H-fluorene-2,7-diyl)bis(azanediyl))bis(ethene-2,1-diyl)bis(1-methylpyridin-1-ium) trifluoromethanesulfonate (**M1**) was prepared. Into a 10 mL Schlenk tube with a magnetic stirrer were added 2-ethynyl-1-methylpyridin-1-ium trifluoromethanesulfonate (133.5 mg, 0.5 mmol), and 9,9-dioctyl-9H-fluorene-2,7-diamine (210.4 mg, 0.5 mmol). Then, 10 mL of MeOH was injected into the tube by hypodermic syringes. The resulting mixture was stirred at  $25^\circ\text{C}$  for 2 h. Then, the reaction solution was concentrated and recrystallized twice with ether and DCM to give a brick red product **M1** in 76.5% yield (263 mg). FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3296, 3211, 2932, 2853, 1637, 1610, 1546, 1467, 1261, 1166, 1103,

1027, 960, 811, 637, 572, 516.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  10.68 (d,  $J = 12.7$  Hz, 2H), 8.62 (t,  $J = 12.7$  Hz, 2H), 8.43 (d,  $J = 6.4$  Hz, 2H), 8.38 (d,  $J = 8.8$  Hz, 2H), 8.04 (t,  $J = 8.0$  Hz, 2H), 7.72 (d,  $J = 8.1$  Hz, 2H), 7.45 (d,  $J = 2.1$  Hz, 2H), 7.35 – 7.19 (m, 4H), 5.93 (d,  $J = 12.5$  Hz, 2H), 3.98 (s, 6H), 2.15 – 1.92 (m, 4H), 1.02 (s, 24H), 0.74 (t,  $J = 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  (TMS, ppm) 150.2, 146.5, 130.5, 118.3, 112.5, 108.4, 53.6, 40.5, 31.2, 29.6, 28.9, 28.7, 23.6, 22.0, 13.9. HRMS  $m/z$  328.2421, calcd. for  $\text{C}_{45}\text{H}_{60}\text{N}_4^{2+}$  328.2404.

**Polymerization.** All the polymerizations were carried out in air. A typical procedure for the polymerization of **1** and **2a** is given below as an example. Into a 10 mL Schlenk tube equipped with a magnetic stirrer were added diyne (**1**, 93.2 mg, 0.2 mmol) and diamine (**2a**, 13.2 mg, 0.2 mmol). Then, 1.0 mL of DMSO was injected into it by a hypodermic syringe. After being stirred for 12 h, 5 mL of DCM was added to dilute the system, and the resultant solution was added dropwise into 200 mL of diethyl ether/ethyl acetate (5/1) via a cotton filter with vigorous stirring. The precipitates were filtered and washed with diethyl ether and then dried to a constant weight.

*Characterization Data for P1a2a.* Red powder, yield 98%;  $M_w$  (soluble part): 22 200, PDI: 1.81. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3296, 3211, 2926, 2847, 1637, 1545, 1466, 1254, 1162, 1028, 958, 811, 638, 571, 516.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (TMS, ppm) 10.89, 10.20, 8.71, 8.40, 8.30, 8.05 – 6.87, 6.65, 5.98, 4.05, 3.86, 2.03, 1.04, 0.77.

*Characterization Data for P1a2b.* Black powder, yield 91%;  $M_w$  (soluble part): 5700, PDI: 1.16. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 3022, 1629, 1549, 1482, 1264, 1228, 1164, 1024, 956, 822, 637, 512.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  (TMS, ppm) 10.83, 10.09, 8.16, 7.72, 7.51 – 6.47, 6.03 – 5.70, 4.01, 3.81.

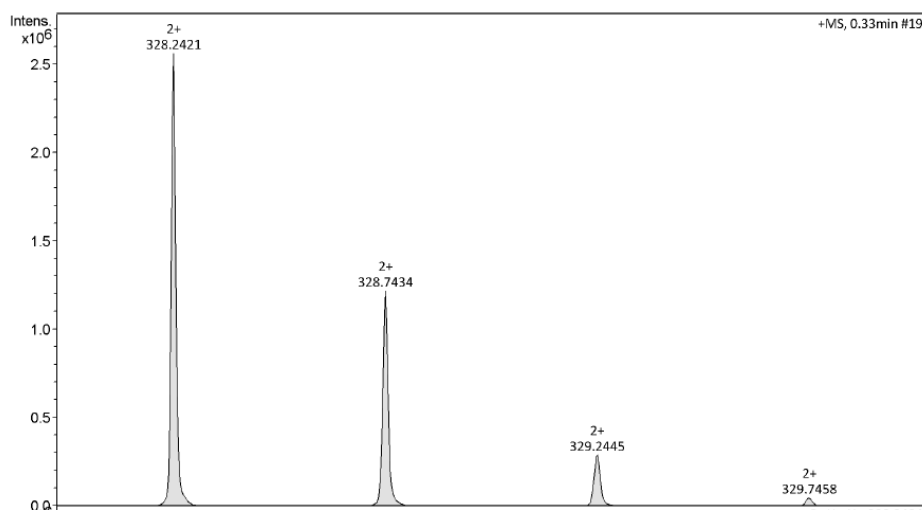
*Characterization Data for P1a2c.* Yellow powder, yield 88%;  $M_w$  (soluble part): 3600, PDI: 1.06. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 1628, 1549, 1480, 1344, 1258, 1165, 1027, 962, 816, 751, 638,

516.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (TMS, ppm) 9.45, 8.41 – 8.20, 8.04, 7.83, 7.54 – 7.31, 7.12, 7.08 – 6.94, 6.82, 6.67 – 6.53, 6.16, 3.85.

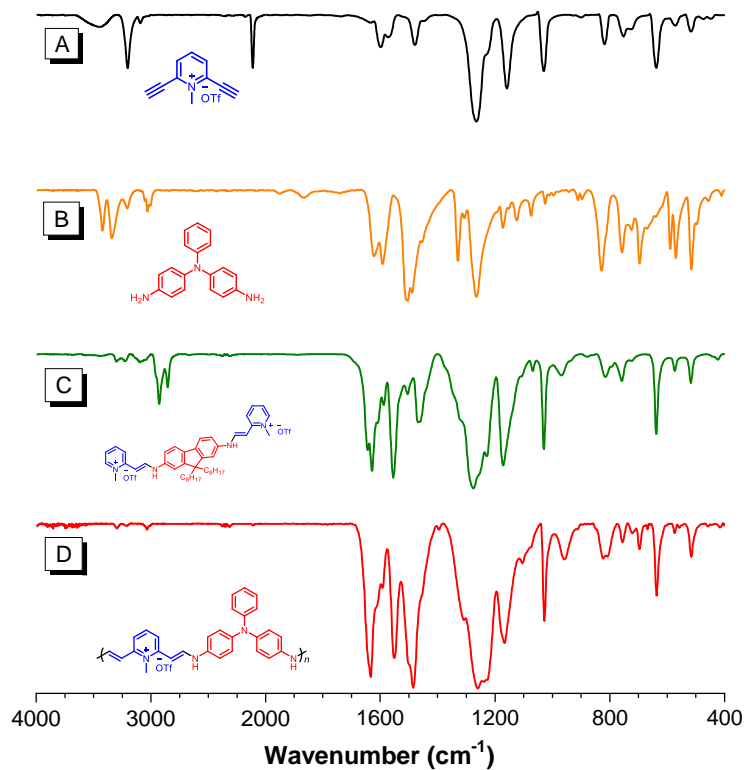
*Characterization Data for P1a2e.* Dark red powder, yield 98%;  $M_w$  (soluble part): 14 500, PDI: 1.45. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 1637, 1604, 1550, 1486, 1261, 1165, 1024, 961, 809, 759, 700, 636, 570, 511.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (TMS, ppm) 10.72, 10.03, 8.56, 8.35, 7.90, 7.71, 7.54, 7.34 – 6.71, 6.68 – 6.48, 6.31, 6.14 – 5.77, 4.01.

*Characterization Data for P1a2f.* Dark red powder, yield 93%;  $M_w$  (soluble part): 8600, PDI: 1.35. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 1638, 1607, 1550, 1513, 1482, 1391, 1263, 1164, 1024, 942, 815, 765, 633, 570, 515.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (TMS, ppm) 11.02, 10.36, 8.83, 8.50, 8.42, 8.00, 7.89, 7.81 – 7.21, 7.15, 6.94, 6.09, 4.11, 3.95.

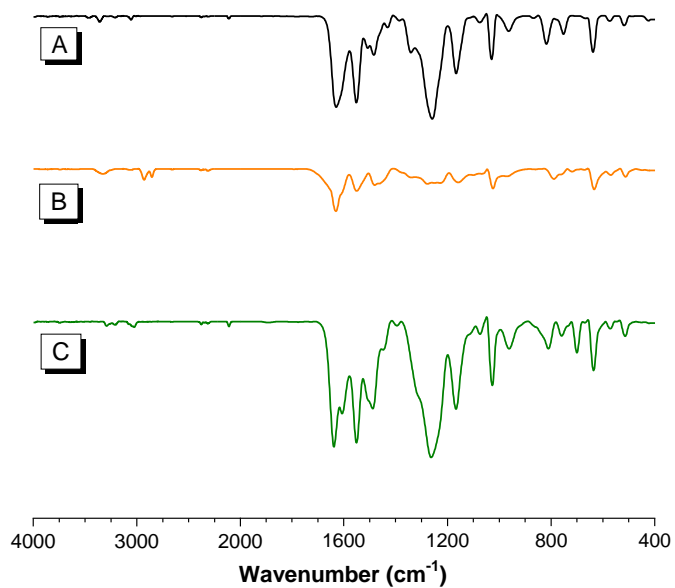
*Characterization Data for P1a2g.* Orange powder, yield 98%;  $M_w$  (soluble part): 4910, PDI: 1.13. FT-IR (KBr disk),  $\nu$  ( $\text{cm}^{-1}$ ): 1639, 1551, 1488, 1314, 1270, 1222, 1169, 1025, 960, 822, 636, 572, 512.  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  (TMS, ppm) 10.81, 10.07, 8.61, 8.37, 8.17, 7.92, 7.74 (s, 7H), 7.52, 7.39, 7.30 – 7.21, 7.09 – 6.78, 5.89, 4.02, 3.81.



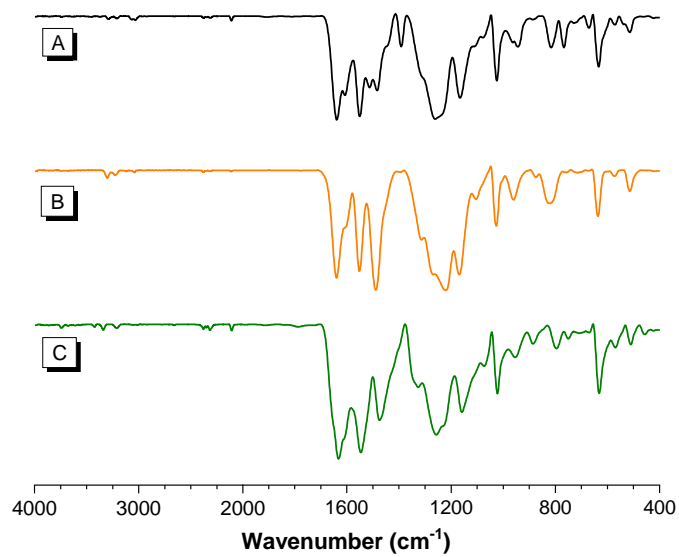
**Figure S1.** HRMS spectra of model compound M1.



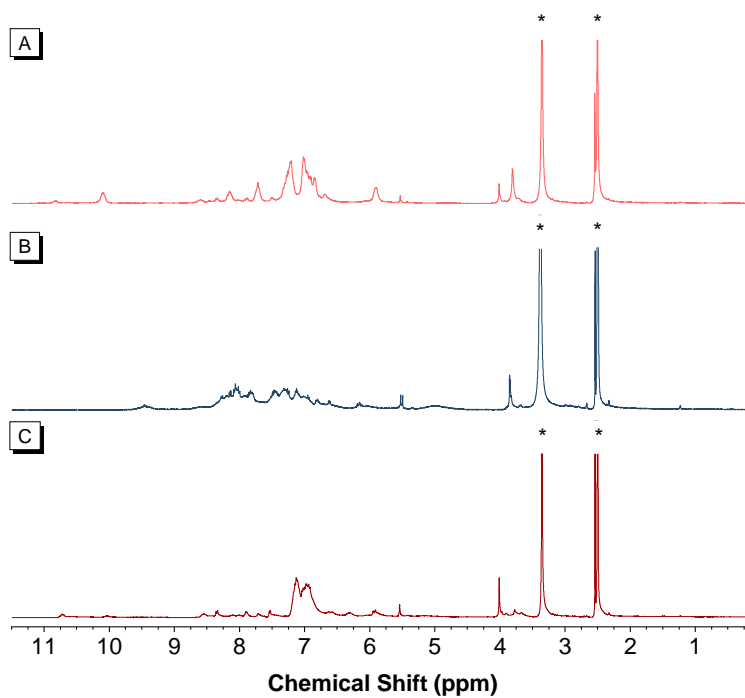
**Figure S2.** FT-IR spectra of **1a** (A), **2b** (B), **M1** (C) and **P1a2b** (D).



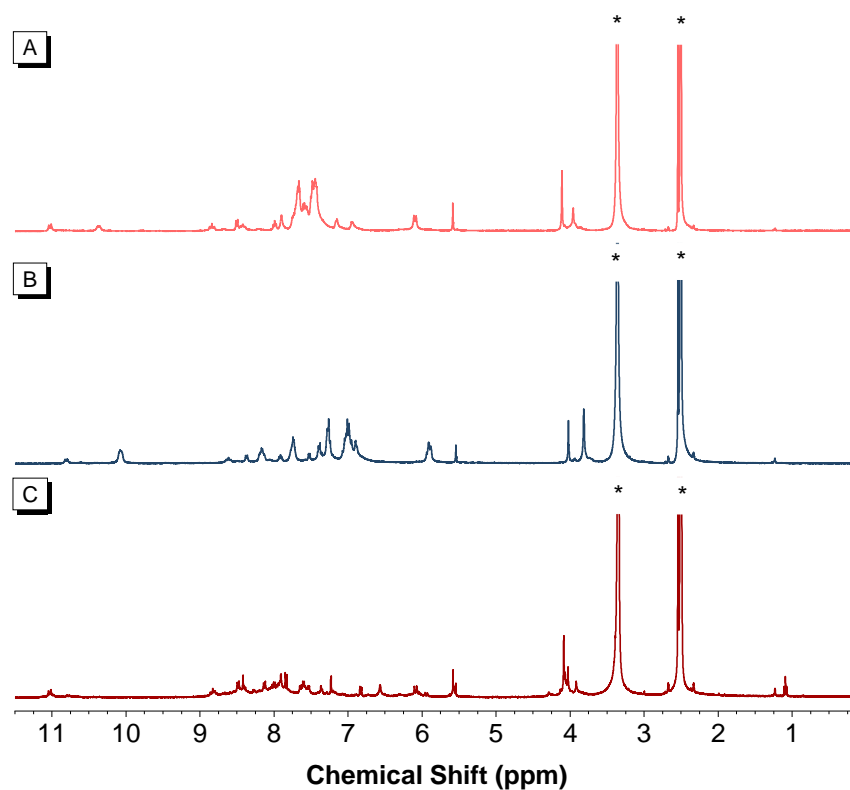
**Figure S3.** FT-IR spectra of **P1a2c** (A), **P1a2d** (B), and **P1a2e** (C).



**Figure S4.** FT-IR spectra of P1a2f (A), P1a2g (B), and P1a2h (C).



**Figure S5.** <sup>1</sup>H NMR spectra of P1a2b (A), P1a2c (B), and P1a2e (C) in DMSO-*d*<sub>6</sub>. The solvent peaks were marked with asterisks.



**Figure S6.**  $^1\text{H}$  NMR spectra of **P1a2f** (A), **P1a2g** (B), and **P1a2h** (C) in  $\text{DMSO-}d_6$ . The solvent peaks were marked with asterisks.

## Reference

- (1) Haindl, S.; Xu, J.; Freese, T.; Huebner, E. G.; Schmidt, A. The intersection of allenylidenes and mesomeric betaines. 1-Methylpyridinium-2-acetylde and its palladium complexes. *Tetrahedron* **2016**, 72, 7906-7911.
- (2) Basaki, N.; Kakanejadifard, A.; Faghihi, K. Preparation of new enforcement polyamide nanocomposite filled by ternary layer double hydroxide and investigation of electrochemical activity, optical and thermal properties. *Polym. Bull.* **2021**, 78, 6723-6741.