Electronic Supplementary Information

Incorporating trifunctional 1,6-heptadiyne moiety into polyacetylene ionomer for improving its physical and conductive properties

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Synthesis of TDPAA

TDPAA was synthesized by the reaction of **TAPA** with propargyl bromide (Scheme 1). The structure of **TDPAA** was characterized by ¹H NMR, ¹³C NMR, and FT-IR spectroscopy. In the ¹H NMR spectrum (Fig. S1a), the peak signals at 3.18, 4.08, and 6.87 ppm belonged to the acetylenyl, methylene, and aromatic ring protons, respectively. The three peaks area ratios matched well with 1:2:2. Moreover, the absence of amino proton signal in the ¹H NMR spectrum demonstrated that the reaction was conducted completely. Besides, in the ¹³C NMR spectrum of **TDPAA** (Fig. S1b), the peak signal at 80.40 ppm was attributed to the acetylenic carbon, and the peak signals at 143.82, 139.57, and 124.33 ppm were assigned to the carbonyl carbon in the phenyl ring. In the FT-IR spectrum of **TDPAA** (Fig. S2a) it was clear to see the acetylenic hydrogen stretching (3301 cm⁻¹) and the phenyl ring stretching (1520 cm⁻¹), while the amino hydrogen stretching was not yet appeared in the FT-IR spectrum. The molecular weight and chemical elemental composition of **TDPAA** measured by MS analysis and elemental analysis matched well with the calculated values. Apparently, all these points confirmed the successful preparation of **TDPAA**.





Fig. S2 IR spectra of (a) TDPAA, (b) poly[MDTA]⁺[TFSI]⁻, and (c) poly(TDPAA-[MDTA]⁺[TFSI]⁻).

[TDPAA]:[MDTA] ⁺ [TFSI] ⁻	diethyl eher	acetone	DCM	THF	DMF
25:0	-	-	-	-	-
0:75	-	++	++	++	++
1:75	-	++	++	++	++
3:75	-	+	+	+	+
6:75	-	-	-	+	+
9:75	-	-	-	-	-
15:75	-	-	-	-	-

Table S1 Solubility of different polymers in various solvents at room temperature

*1 mg of matter in 1 mL of solvent;

- : insoluble; + : soluble; ++ : good soluble.



Fig. S3 Photographs of viscous semi-solid poly([**MDTA**]⁺[**TFSI**]⁻) (a), sticky soft solid poly(**TDPAA**₁-[**MDTA**]⁺[**TFSI**]⁻₇₅) (b), flexible solid and free-standing film poly(**TDPAA**₆-[**MDTA**]⁺[**TFSI**]⁻₇₅) (c), and insoluble hard solid poly(**TDPAA**₁₅-[**MDTA**]⁺[**TFSI**]⁻₇₅) (d).



Fig. S4 GPC traces of polymers with different feed ratios of TDPAA to [MDTA]⁺[TFSI]⁻.

Characterization of copolymers

The NMR spectroscopy was used to characterize the structure of polymers, and the representative NMR spectra of poly(**TDPAA**₁-[**MDTA**]⁺[**TFSI**]₇₅) were shown in Fig. 1. In the ¹H NMR spectrum of poly(**TDPAA**₁-[**MDTA**]⁺[**TFSI**]⁻₇₅) (Fig. 1a), the acetylenic proton signal peak of monomer [MDTA]⁺[TFSI]⁻ at 2.05 ppm disappeared after MCP, and the new signal peak appeared at 6.90 ppm could be assigned to the protons (H_a) of conjugated double bonds on poly(TDPAA-[MDTA]+[TFSI]-) backbone, which indicated that the monomer was transformed into polymer. However, the proton signals (H_o, H_n) of **TDPAA** moiety was very weak and indistinguishable from those of poly([MDTA]⁺[TFSI]⁻) in the ¹H NMR spectrum (Fig. 1a), because these signals overlapped with each other and also the amount of **TDPAA** was quite small. Therefore, the ¹³C NMR spectroscopy was performed to demonstrated the copolymerization of TDPAA and [MDTA]⁺[TFSI]⁻, as shown in Fig. 1b. The acetylenic carbon signals of TDPAA at 80.40 and 116.86 ppm, as well as the acetylenic carbon signals of [MDTA]⁺[TFSI]⁻ at 80.91 and 70.45 ppm disappeared. The peak signal at 139.84 ppm was assigned to the carbon atoms (C_a) of the new generated conjugated double bonds, and the peak signals of carbon atoms on phenyl group in TDPAA at 143.82 and 139.57 ppm shifted to 147.20 ppm in poly(TDPAA₁-[MDTA]⁺[TFSI]₇₅) (Fig. 1b), meaning that the monomers were converted into polymer

successfully. Moreover, the peak signal of methylene carbon in **TDPAA** shifted from 75.64 ppm to 99.74 ppm after cyclization, and the peak signals of carbon atoms on the phenyl group in **TDPAA** at 143.82 and 139.57 ppm shifted to 147.70 and 145.85 ppm in the ¹³C NMR spectrum of poly(**TDPAA**₆-[**MDTA**]⁺[**TFSI**]⁻⁷⁵) (Fig. S5b). In addition, FT-IR spectroscopy was another technique to identify the structure of polymers. Compared with the IR spectrum of **TDPAA** (Fig. S2a), the absence of acetylenic hydrogen stretching (3286 cm⁻¹) and the disappearance of carbon-carbon triple bond stretching (2114 cm⁻¹) of copolymer in Fig S2c indicated the transformation of alkynyl to conjugated double bonds. Besides, two new absorption peaks appeared at 1581 cm⁻¹ and 3121 cm⁻¹, which were assigned to the phenyl ring and triazolium group, meaning the copolymerization of **TDPAA** with [**MDTA**]⁺[**TFSI**]⁻ occurred. All the changes illustrated the successful synthesis of poly(**TDPAA-[MDTA**]⁺[**TFSI**]⁻).





Fig. S5 ¹H (a) and ¹³C (b) NMR spectra of poly(TDPAA₆-[MDTA]⁺[TFSI]⁻75) in DMSO-d₆.

The UV-vis absorption spectra of TDPAA and polymers were illustrated as Fig. S6. TDPAA exhibited a single absorption peak with the maximum absorption wavelength (λ_{max}) at 328 nm, while poly([MDTA]⁺[TFSI]⁻) displayed two λ_{max} peaks at 541 nm (0-1) transition) and 580 nm (0-0 transition). Obviously, poly(TDPAA-[MDTA]+[TFSI]-) presented a characteristic absorption of conjugated poly([MDTA]+[TFSI]-) backbone at 400-700 nm and an enhanced absorption strength of TDPAA moiety at 330-390 nm as increasing the amount of TDPAA, likely due to the interaction between triphenylamine group and the conjugated skeleton, which was different from the absorption curve of TDPAA/poly([MDTA]+[TFSI]-) blend, wherein the mixture of **TDPAA**/poly([**MDTA**]⁺[**TFSI**]⁻) performed two independent absorption ranges for the two components. These observations demonstrated that the TDPAA moiety was indeed incorporated into the copolymer.



Fig. S6 UV-vis spectra of TDPPA and polymers at the concentration of 0.01 mg mL⁻¹ in acetone.



Fig. S7 DSC (in the second heating process) (a) and TGA (b) curves of polymers.

[bmim] ⁺ [TFSI] ⁻ : LiTFSI ^a	$R^{b}\left(\Omega ight)$	σ_{i} (S cm ⁻¹)
5:1	100	5.0×10 ⁻⁴
5:2	50	1.0×10 ⁻³
5:3	32	1.6×10-3
5:4	13	3.7×10 ⁻³
5:5	28	1.8×10-3

^aThe mass ratio of [bmim]⁺[TFSI]⁻ to LiTFSI. ^bThe intrinsic resistance obtained by EIS at 30 °C.



Fig. S8 Linear sweep voltammogram of poly(**TDPAA**₆-[**MDTA**]⁺[**TFSI**]⁻₇₅) doped with LiTFSI at a scan rate of 0.5 mV s⁻¹ (stainless steel as the working electrode, and Li foil as the counter and reference electrodes).



Fig. S9 The stress-strain curve of poly(TDPAA₆-[MDTA]⁺[TFSI]⁻75) film.