

Electronic Supplementary Information (ESI)

for

Facile Synthesis of Telechelic Poly(phenylene sulfide)s by Means of Electron-deficient Aromatic Sulfonium Electrophiles

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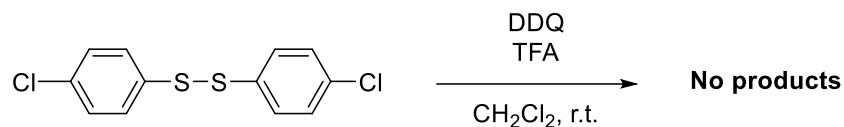
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1. Additional procedures and related information

1.1. Measurements

¹H NMR spectra (500 MHz) were recorded by JEOL JNM-ECX500. Chemical shifts were calibrated using tetramethylsilane as an internal standard. IR spectroscopy was conducted by JASCO FT/IR-6100. Size exclusion chromatography (SEC) was performed with SHIMADZU LC-20AD/CBM-20A using TOSOH TSKgel SuperHM-N column with SHIMADZU SPD-M20A UV detector (wavelength: 254 nm) (eluent: chloroform, flow rate: 0.3 mL min⁻¹, molecular weights were calibrated by polystyrene standards). Diffusion-ordered spectroscopy (DOSY) NMR spectra (600 MHz) were recorded by Bruker AVANCE 600 NEO (pulse sequence: ledbpgp2s). Cyclic voltammetry (CV) was conducted by BAS ALS 660D with a Pt wire, a Pt electrode (ϕ : 1.6 mm), and an Ag/AgCl electrode as a counter, a working, and a reference electrode, respectively, whose potential was corrected by ferrocene/ferrocenium redox couple ($E_{1/2} = 0.45$ V vs Ag/AgCl). Differential scanning calorimetry (DSC) was performed using TA Instruments Q200 (Scanning rate: 20 °C min⁻¹).

1.2. Oxidation of Cl-DPS with DDQ and TFA



Scheme S1

In a 10 mL flask, **Cl-DPS** (0.82 g, 2.9 mmol) was dissolved in dichloromethane (6 mL) and DDQ (0.623 g, 2.7 mmol) and TFA (383 μ L, 5 mmol) were added and stirred. Although the color of the solution turned deep green after starting the reaction (i.e., charge-transfer complexation of **Cl-DPS** and DDQ), no products were obtained 15 hours after the reaction owing to the presence of *p*-substituted units as well as the electron-withdrawing properties of chlorine groups that prevented electrophilic substitution reaction.

1.3. Reduction of Cl-Terminated PMPS for end structure detection

Disulfide-reduced Cl-terminated telechelic **PMPS (Red-Cl-PMPS)** was prepared with the procedure based on our previous report¹ with several modifications (Scheme 2 in the main text). In a two-necked 50 mL flask, **Cl-PMPS** (0.16 g) was dissolved in THF (5.4 mL). After adding sodium borohydride (0.15 g), methanol (0.6 mL) was added and stirred at 70 °C under reflux for 15 hours. After the reaction, the solution was precipitated in methanol containing 5vol% hydrochloric acid (200 mL), and the precipitate was collected by filtration, was washed with methanol and water, and was dried in vacuo to obtain **Red-Cl-PMPS** (0.15 g, Yield: 92%).

1.4. Determination procedure of end-functionalization degree

In this study, the degree of end-functionalization degree was determined as follows. First, M_n was calculated by both ^1H NMR (comparison of peak integrals for aromatic and methyl protons) and SEC in chloroform. As ^1H NMR can detect both proton/chlorine-terminated end groups including their numbers although SEC couldn't distinguish them, end-functionality was finally determined as equation (1) shown below.

$$\text{Degree of end functionalization} = \frac{M_n(\text{SEC})}{M_n(\text{NMR})} \quad \dots (1)$$

The degree of end-functionalization for **V-PMPS'** was also determined with a similar procedure (For **V-PMPS'**, M_n (NMR) was determined by comparing the integrals of vinyl and methyl protons).

1.5. Post-functionalization of Br-PMPS by Suzuki-Miyaura cross-coupling reaction

The reaction has been described in the upper part of Scheme 3 in the main text. To a 30 mL flask, **Br-PMPS** (Run 3, Table 2) (0.16 g, 40 μmol of Br), toluene (16 mL), $\text{Pd}(\text{PPh}_3)_4$ (46 mg, 40 μmol), cesium carbonate (37 mg, 112 μmol), 4-phenylboronic acid (15 mg, 100 μmol), and water (0.16 mL) were added stirred at 60 $^\circ\text{C}$ for 24 hours. The solution was precipitated in methanol containing 5vol% hydrochloric acid (300 mL), and the precipitation was collected (filtration), was washed with methanol and water, and was dried in vacuo to obtain **V-PMPS** as a brownish powder (69 mg, Yield: 42%, $M_n = 7.4 \times 10^3$, $M_w/M_n = 2.2$).

2. Additional figures and tables

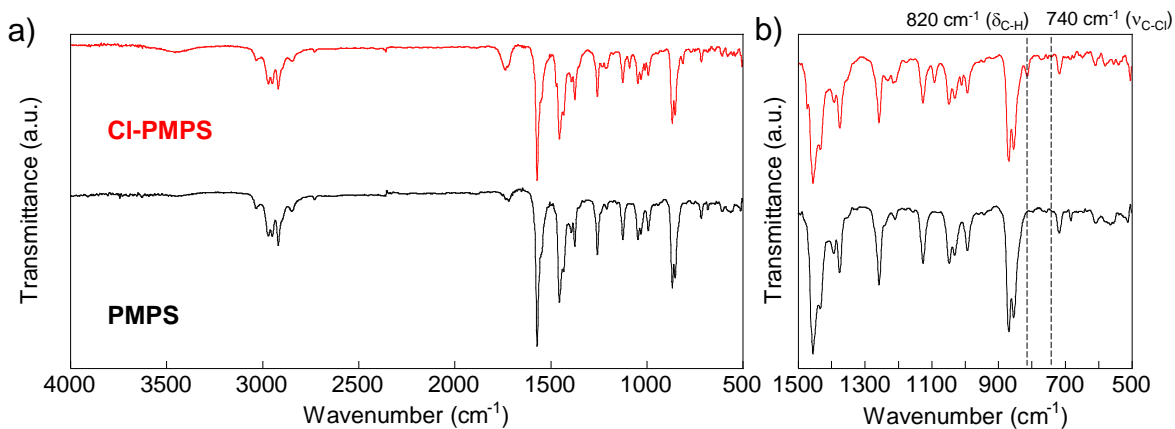


Fig. S1 IR spectra of CI-PMPS and PMPS: (a) Overall (4000-500 cm⁻¹) and (b) expanded (1500-500 cm⁻¹) spectra.

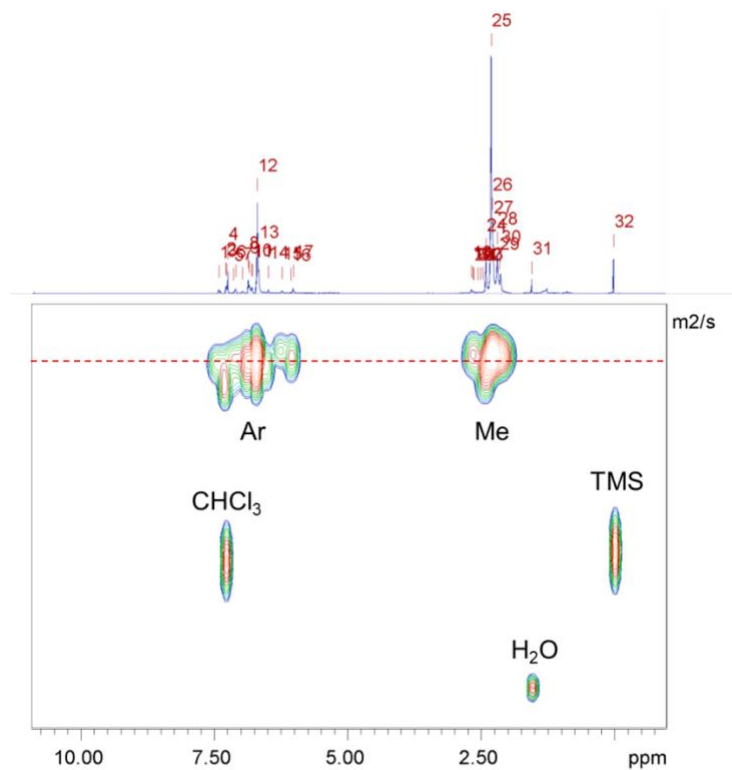


Fig. S2 DOSY-NMR spectrum of CI-PMPS in chloroform-*d*.

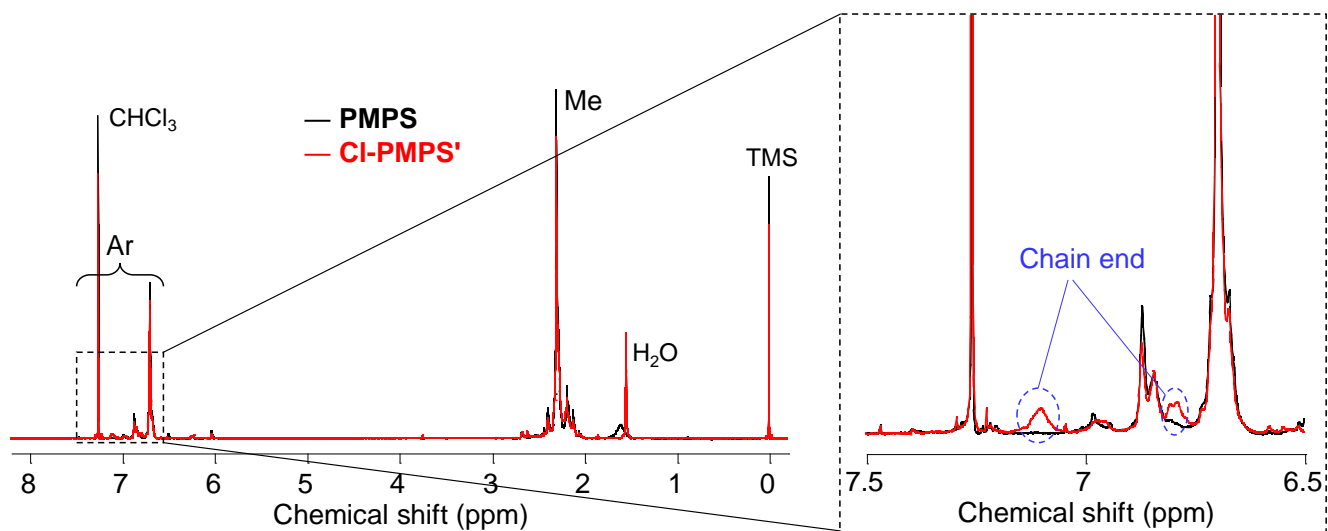


Fig. S3 Overall (left) and expanded (right) ^1H NMR spectra of **PMPS** and **Cl-PMPS'** in chloroform-*d*.

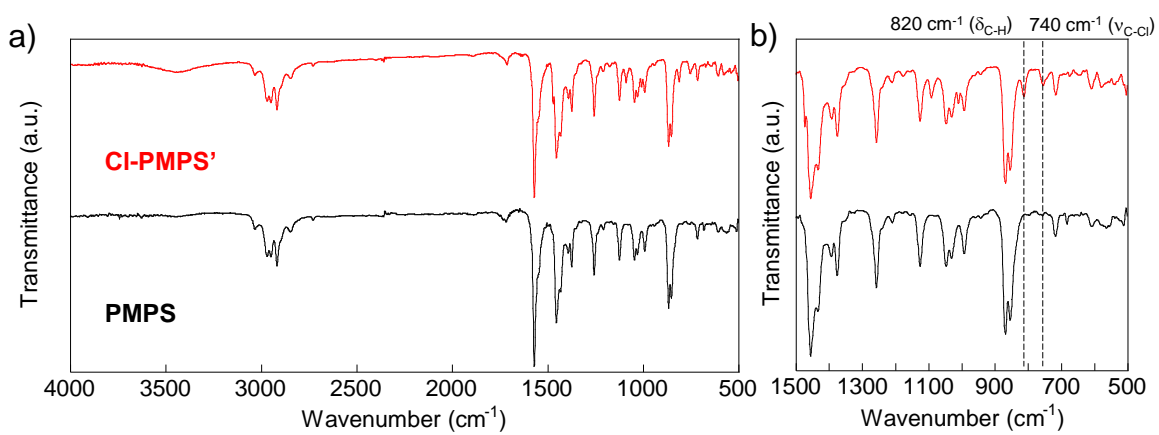


Fig. S4 IR spectra of **PMPS** and **Cl-PMPS'**: (a) Overall ($4000\text{-}500\text{ cm}^{-1}$) and (b) expanded ($1500\text{-}500\text{ cm}^{-1}$) spectra.

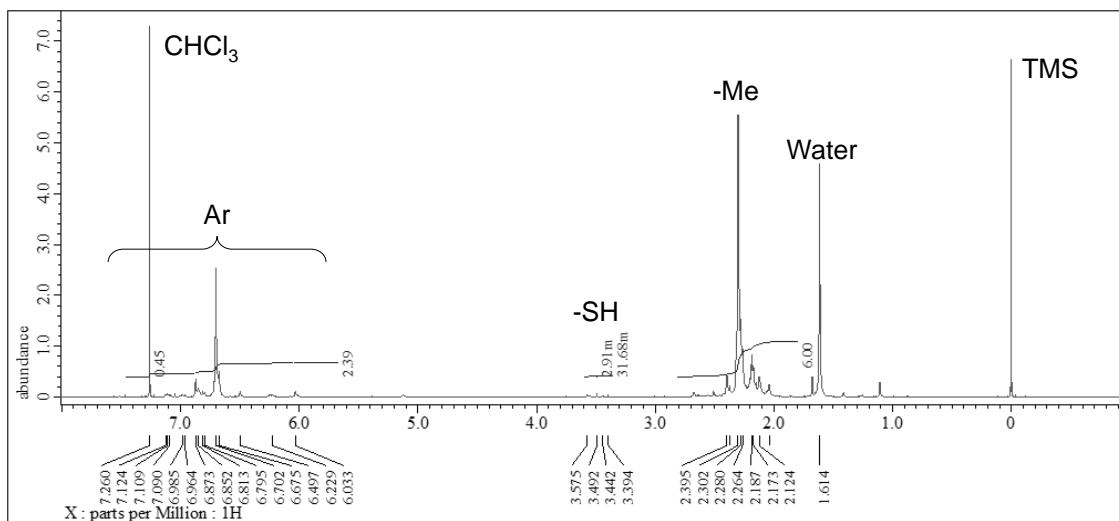


Fig. S5 ^1H NMR spectrum of Red-CI-PMPS in chloroform-*d*.

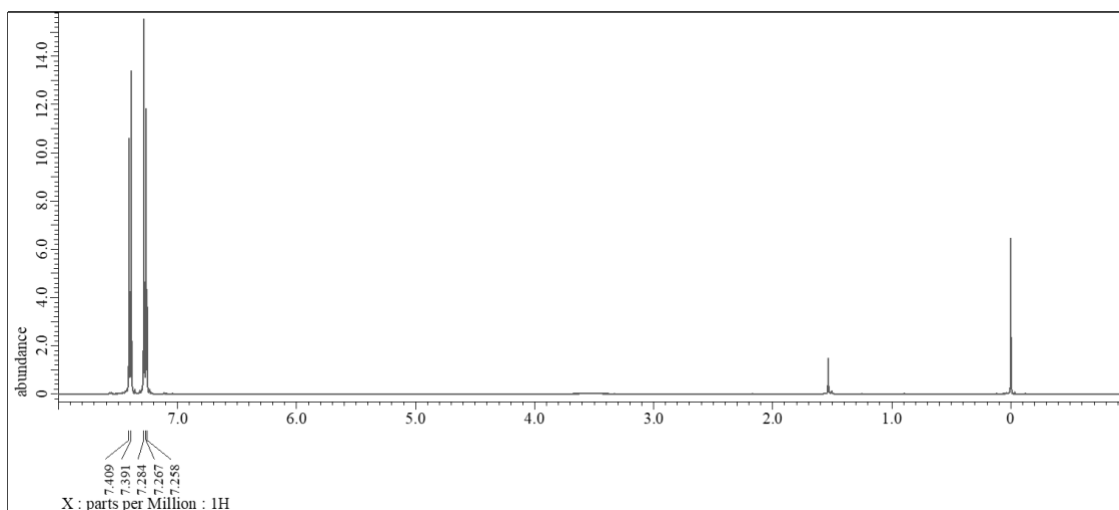


Fig. S6 ^1H NMR spectrum of CI-DPS in chloroform-*d*.

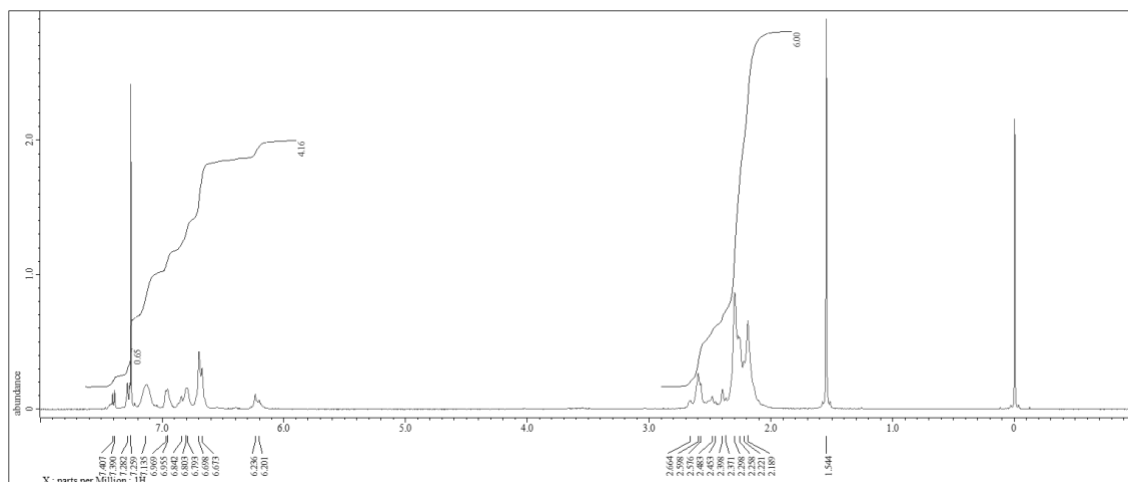


Fig. S7 ^1H NMR spectrum of **Cl-PMPS'** (Run 4 in Table 1) in chloroform- d .

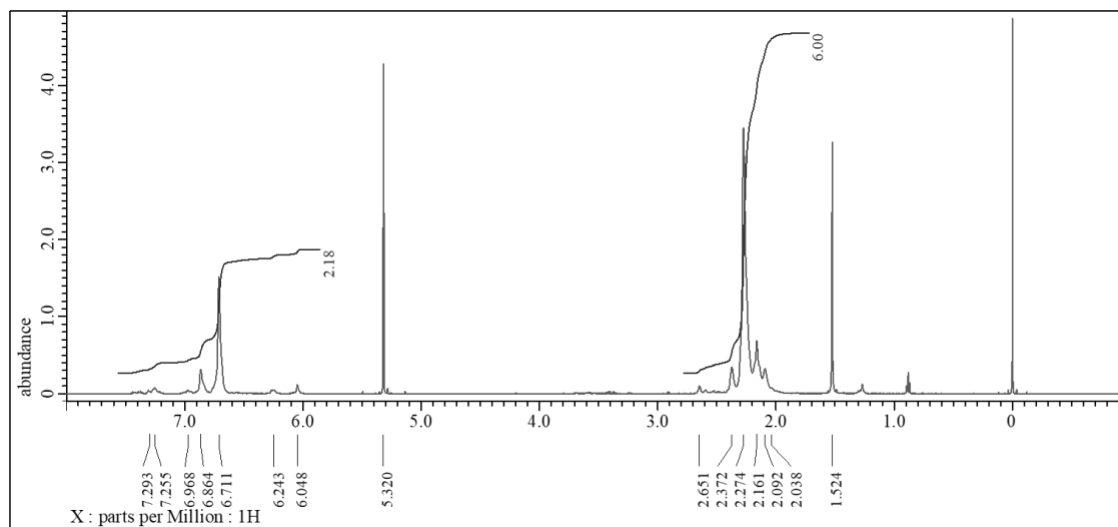


Fig. S8 ^1H NMR spectrum of **Br-PMPS** (Run 4 in Table 2) in dichloromethane- d_2 .

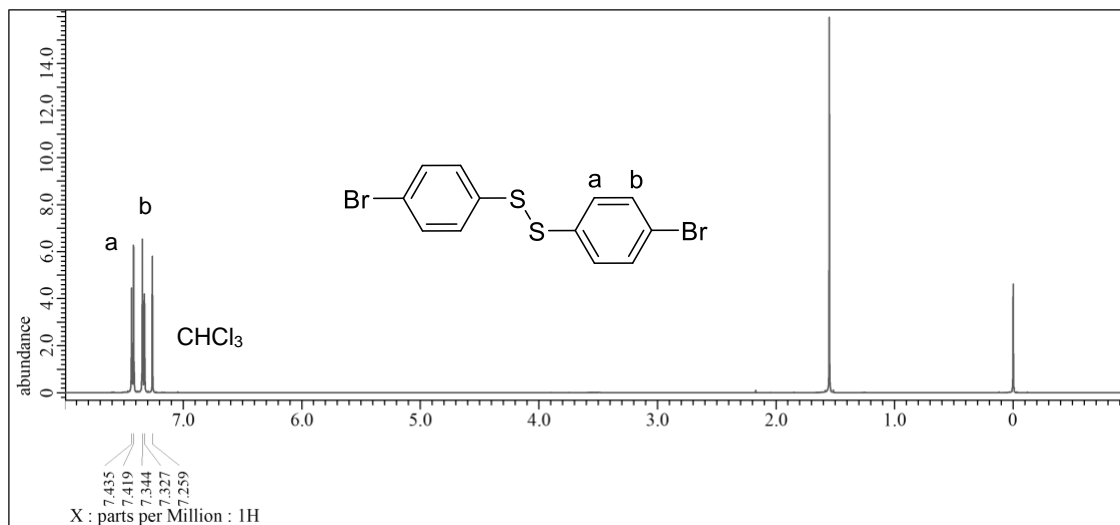


Fig. S9 ^1H NMR spectrum of **Br-DPS** in chloroform-*d*.

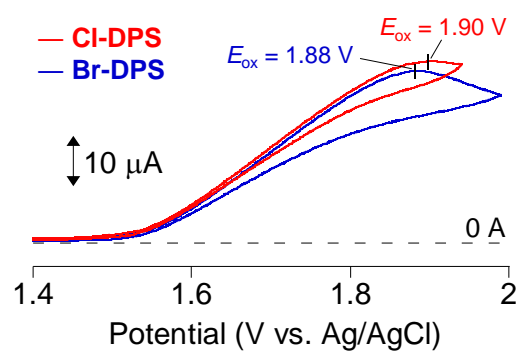


Fig. S10 Cyclic voltammograms of **Cl-DPS** and **Br-DPS** in 0.1 M TBABF₄ dichloromethane solution (monomer concn.: 10 mM, scan rate: 10 mV s⁻¹). *p*-Halogenated **DPS** had higher oxidation potentials compared with **3,5-DPS** (1.65 V).²

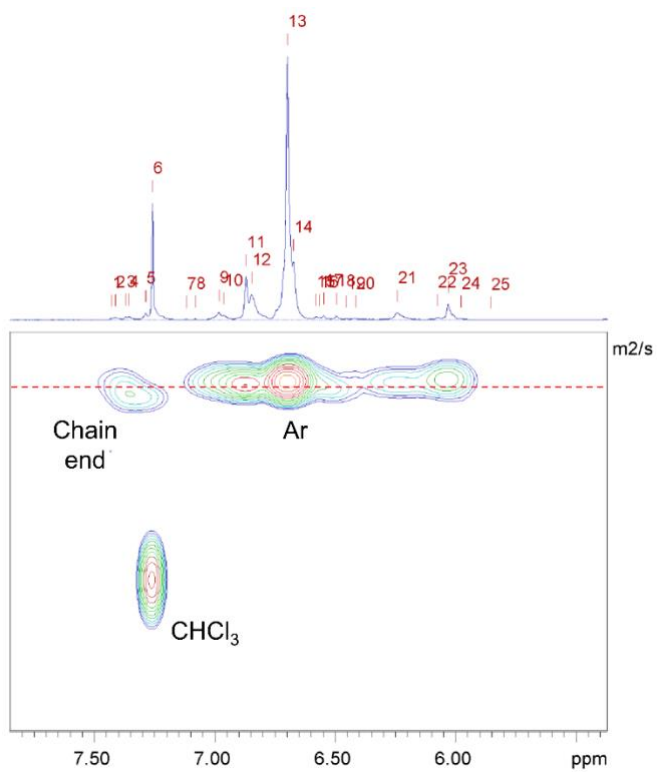


Fig. S11 DOSY-NMR spectrum of **Br-PMPS** in chloroform-*d*.

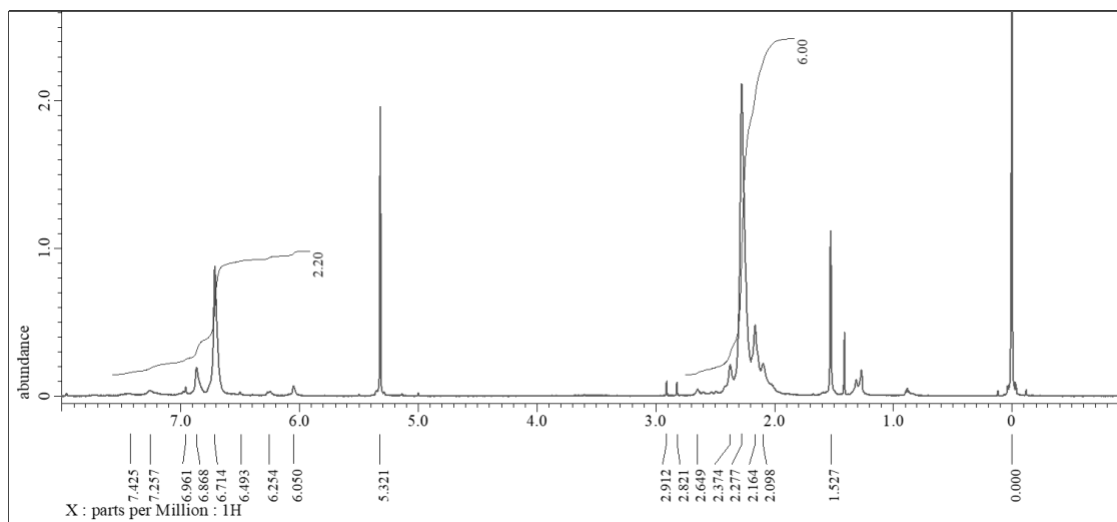


Fig. S12 ¹H NMR spectrum of **V-PMPS** in dichloromethane-*d*₂.

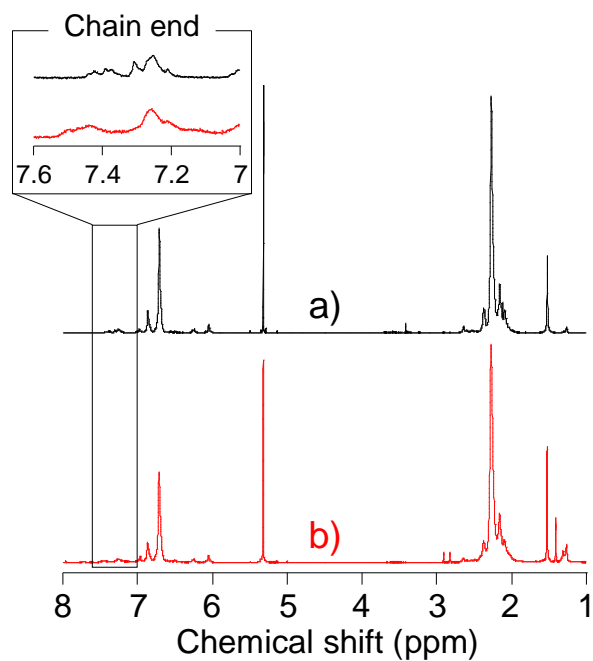


Fig. S13 ¹H NMR spectra of (a) **Br-PMPS** (Run 3 in Table 2) and (b) **V-PMPS** in dichloromethane-*d*₂.

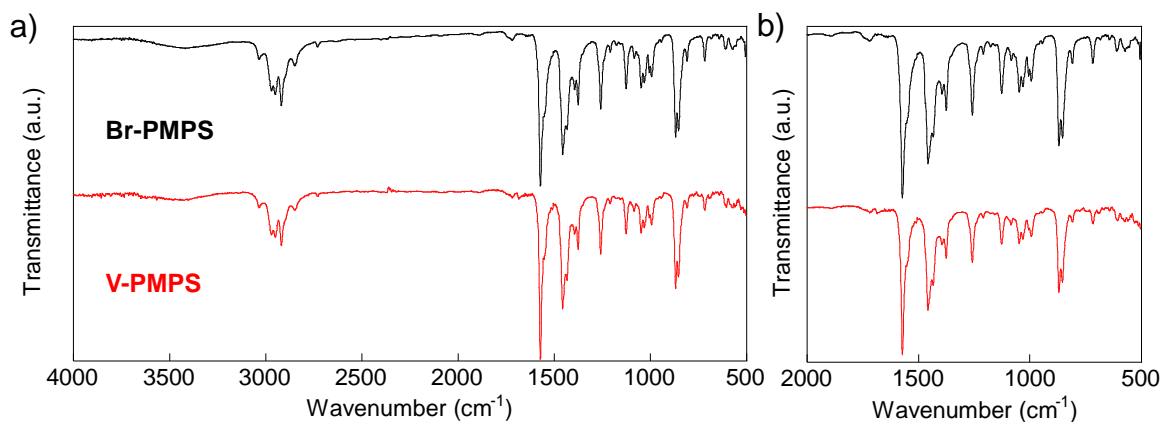


Fig. S14 IR spectra of **Br-PMPS** (Run 3 in Table 2) and **V-PMPS**: (a) Overall (4000-500 cm⁻¹) and (b) expanded (2000-500 cm⁻¹) spectra.

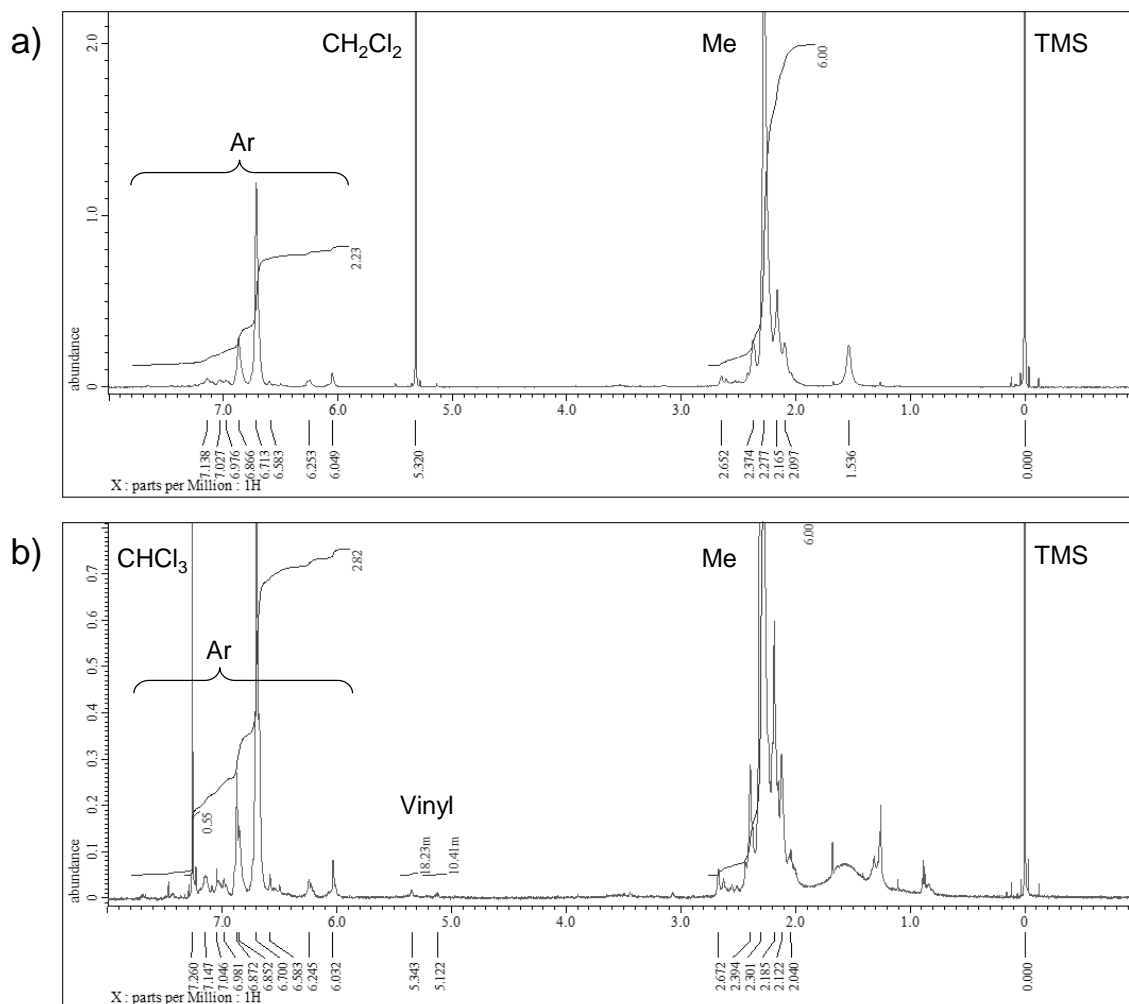


Fig. S15 ¹H NMR spectrum of V-PMPS' in (a) dichloromethane-*d*₂ and (b) chloroform-*d*.

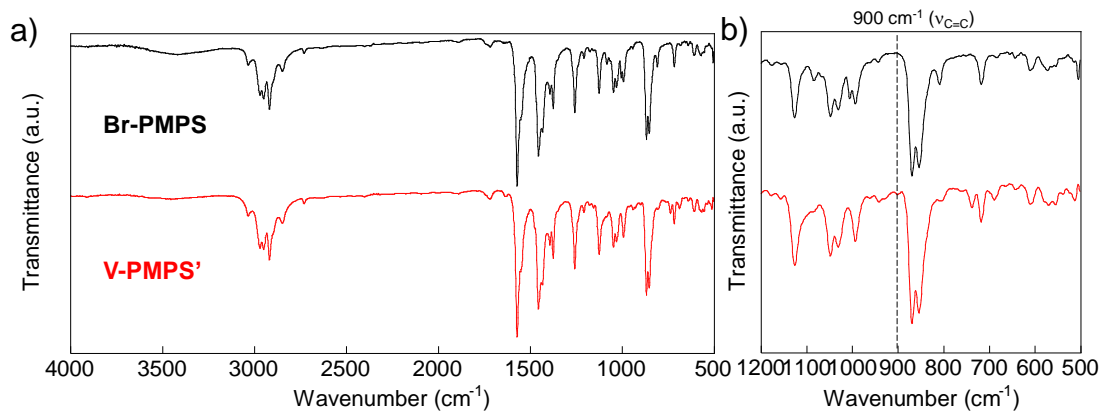


Fig. S16 IR spectra of **Br-PMPS** (Run 4 in Table 2) and **V-PMPS'**: (a) Overall (4000-500 cm⁻¹) and (b) expanded (1200-500 cm⁻¹) spectra.

Supplementary references

- 1 S. Watanabe and K. Oyaizu, *ACS Applied Polymer Materials*, 2021, **3**, 4495–4503.
- 2 K. Yamamoto, N. Iwasaki, H. Nishide and E. Tsuchida, *Eur. Polym. J.*, 1992, **28**, 341–346.