

NMR studies of the reaction between amino-phenylene vinylene thiophene and tetracyanoethylene[☆]

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Abstract

Amino tricyanovinyl thiophene chromophores (A-TCVT) are prepared by a substitution reaction of amino-phenylene vinylene thiophene (A-PVT) with tetracyanoethylene (TCNE). This reaction does not occur directly. The vinylene double bond in the PVT unit first reacts rapidly with TCNE to form a [2+2] cycloaddition product. It is then reverted to PVT unit prior to the subsequent substitution at 50 °C. This reversible cycloaddition converts the cis-isomer of PVT units into the trans-counterparts, thus the final TCNE substituted products can be expected for a better performance as non-linear optical materials.

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Amino tricyanovinyl compounds with a phenylene vinylene thiophene fully conjugated bridge (A-TCVT) are an important class of non-linear optical chromophores due to their high performance and excellent stability.^{1–3} They are prepared by reacting amino-phenylene vinylene thiophene (A-PVT) with tetracyanoethylene (TCNE). This reaction could be performed through a lithiation reaction,¹ or by a nucleophilic substitution reaction.² The latter was intensively used for the preparation of A-TCVT containing polymers,³ where the lithiation reaction often results in damage to polymer structures due to the harsh reaction conditions.

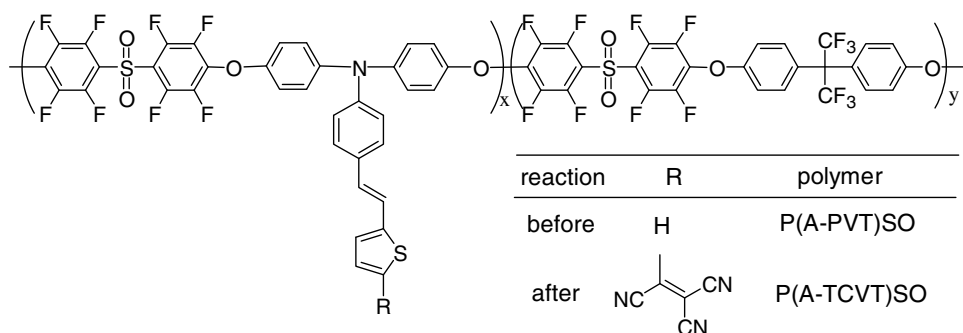
Recently we have successfully incorporated A-PVT units into fluorinated polyethersulfone by using a mild polycondensation reaction.⁴ The structure of the obtained polymer, P(A-PVT)SO is illustrated in [Scheme 1](#). A post polymerization substitution of this polymer with TCNE was tried in DMF at <70 °C to convert it into a non-linear optical polymer, P(A-TCVT)SO. However, a few initial trials of this substitution reaction with the use of a slight excess of

TCNE (molar ratio of [TCNE]/[A-PVT] = 1.1–1.2) following the reported procedure did not result in a quantitative conversion of the PVT group.³ It was found that the reaction could be easily completed at a lower reaction temperature (50 °C) when higher molar ratios (e.g., [TCNE]/[A-PVT] ~ 4.0) were used. Therefore, this reaction was carefully studied by ¹H NMR spectroscopy using 4.0 equiv TCNE in DMF-*d*₇, with the result shown in [Figure 1](#). In this experiment, the ¹H NMR spectrum of the starting polymer, P(A-PVT)SO, was collected first (0 min). TCNE was then added to the solution and the evolution of ¹H NMR spectra with reaction time was recorded at 23 °C. A clean spectrum was obtained in 240 min. No further changes were observed after this point, indicating that the reaction was complete at this time. However, a study of the 240 min spectrum revealed that the product was not consistent with the desired structure as shown in [Scheme 1](#). An unexpected pair of doublets appeared outside of the aromatic region at δ 5.53 and 5.98 ppm, indicating that the fully conjugated structure of the PVT unit had changed. The structure of the product, which was prepared from a scaled-up reaction under the same condition,⁵ was therefore carefully studied by 1D and 2D NMR techniques in acetone-*d*₆. The pair of doublets now appeared at δ 5.33

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Scheme 1. The structures of the polymers before and after reacting with TCNE. Reaction condition: 4.0 equiv TCNE in DMF at 50 °C for 24 h. $x/y = 2/1$.

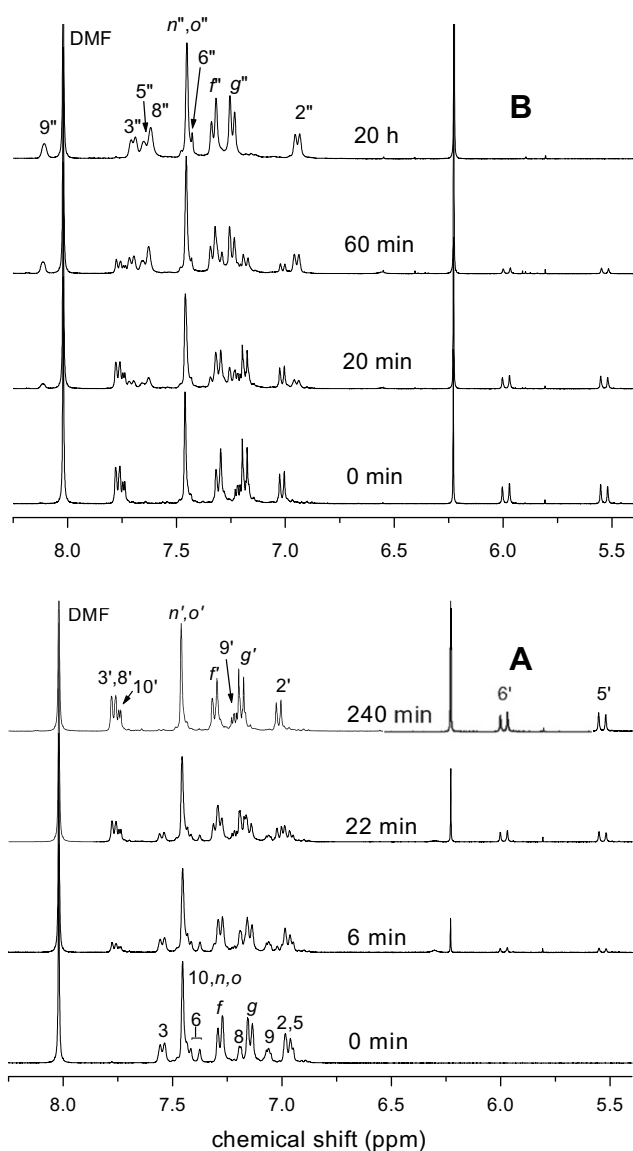


Fig. 1. ^1H NMR study of the reaction between P(A-PVT)SO and TCNE (4.0 equiv) in DMF- d_7 (A) at 23 °C and then (B) at 50 °C (see Scheme 2 for peak assignment).

and 5.74 ppm in the ^1H - ^{13}C heteronuclear correlation (2D-HMBC) NMR spectra due to the use of a different solvent. ^1H homonuclear decoupling showed that this pair of pro-

tons was 3-bond spin coupled with a large coupling constant ($^3J_{\text{H-H}} = 12.9$ Hz). Their chemical shift displacements in the olefinic region suggest that they might be on a double bond but different from the one in the highly conjugated PVT group. On the other hand, the one bond ^1H - ^{13}C correlation spectrum (2D-HSQC) indicated that these two hydrogen atoms were bound to two carbon atoms at low frequencies (δ 54.0 and 48.0 ppm), indicating the presence of two saturated tertiary carbon atoms rather than olefinic ones. The 2D-HMBC spectrum (Fig. 2) displays a large number of aromatic and aliphatic carbon atoms showing long-range couplings ($^2J_{\text{C-C-H}}$ and $^3J_{\text{C-C-H}}$) with these 2 protons. Totally seven ^1H - ^{13}C correlations per proton were found, including five in the aromatic region and two in the aliphatic region. Only the structure in the [2+2] cycloaddition product, P(A-TCNE)SO as shown in Scheme 2 can account for those specific aromatic and aliphatic 2- and 3-bond ^1H - ^{13}C couplings. These results clearly indicate that the PVT's vinylene moiety had undergone a [2+2] cycloaddition reaction with TCNE.

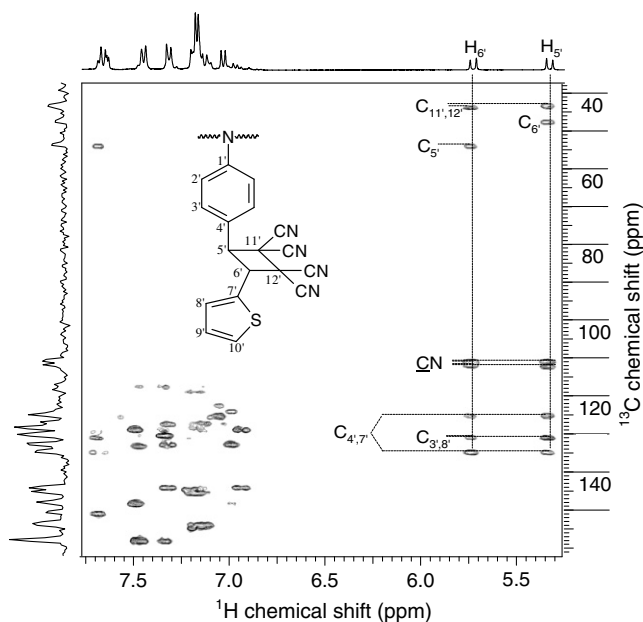
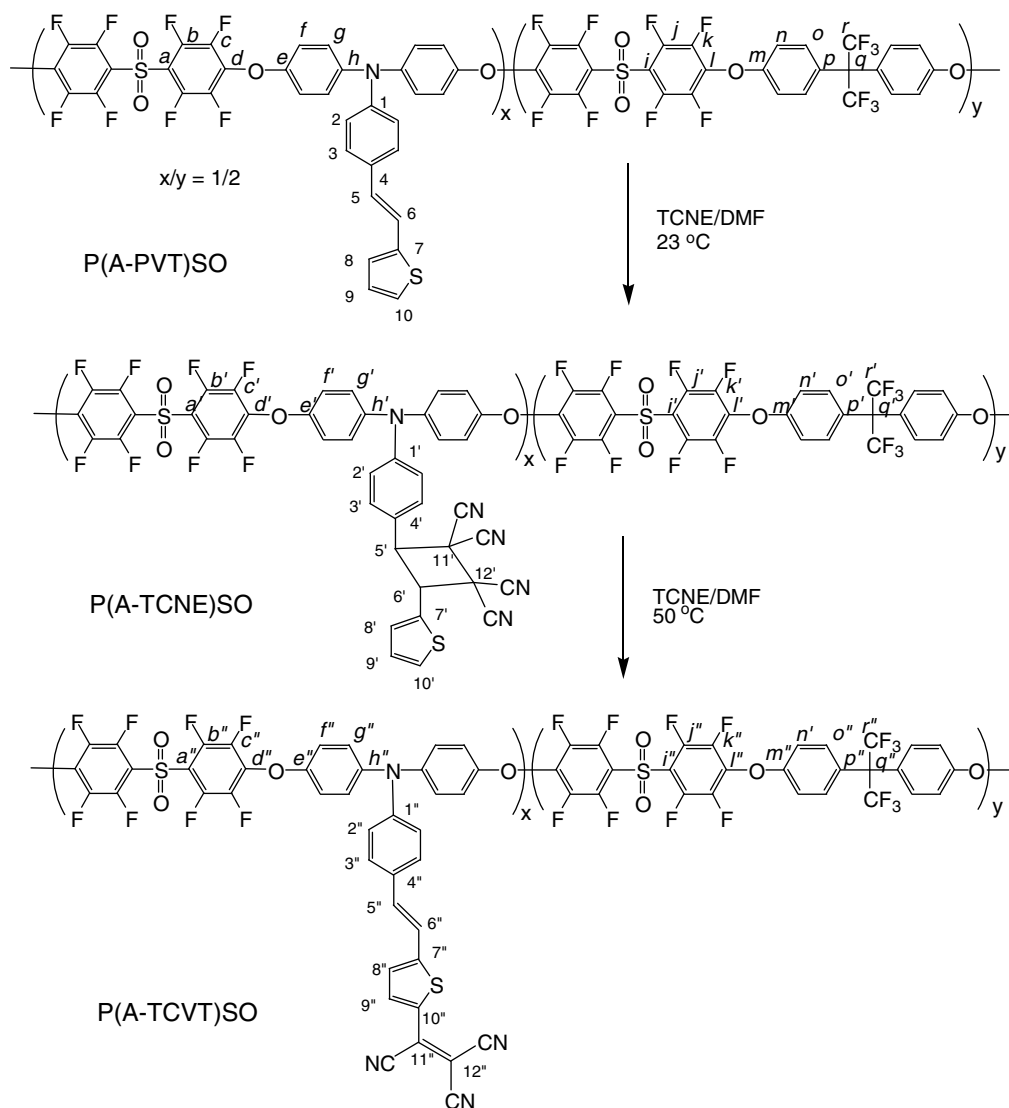


Fig. 2. ^1H - ^{13}C HMBC spectrum (acetone- d_6) of P(A-TCNE)SO showing the multiple carbon correlations originated from the cyclobutane protons.



Scheme 2. Reaction scheme of P(A-PVT)SO with TCNE in DMF at 23 °C and then at 50 °C.

The reaction solution for the NMR test at 23 °C depicted in Figure 1A was then heated to 50 °C and further monitored by NMR. Figure 1B shows that most signals shifted to higher frequencies, indicating that a new reaction was occurring with a strong electron withdrawing group attaching to the aromatic structure. At the same time, the pair of doublets at 5.53 and 5.98 ppm from the cyclobutane unit gradually decreased in intensity, indicating that this unit had dissociated. A clean ^1H NMR spectrum was obtained in 20 h. It matches perfectly the expected substitution product, P(A-TCVT)SO. Therefore it can be concluded that the nucleophilic substitution of the A-PVT group with TCNE does not directly occur as a one-step reaction. The double bond of the A-PVT group reacted first with TCNE at room temperature to form a [2+2] cycloaddition product, which further converted to the substitution product at 50 °C.⁶

The process at 50 °C for the formation of the substitution product actually involved two reactions, that is, the dissociation of the cyclobutane unit and the substitution

with TCNE. These two reactions might occur simultaneously or one after another. The double bond in the PVT unit will allow the rich amine electrons to delocalize all the way to the thiophene ring to promote the nucleophilic substitution. Therefore, the PVT units should have higher reactivity for this reaction than the cyclobutane derivatives, and it is more likely that the substitution occurred after the cyclobutane unit was reverted to the PVT unit. A UV spectroscopy study of the purified [2+2] cycloaddition product showed that it was reverted to the original PVT polymer at 22 °C in two days. It is believed that this cycloreversion should be faster in the reaction at 50 °C. However, the ^1H NMR spectra in Figure 1B showed no signals associated with the cycloreversion product, PVT polymer, formed during the reaction. It may indicate that the recovered PVT unit can react with TCNE immediately to form the substitution product. This assumption was checked using ^1H NMR to monitor the behaviors of the purified cycloaddition product in dried and in untreated $\text{DMF-}d_7$ at 50 °C. The results showed a nearly quantitative

conversion to the final substitution product in the dried solvent in 24 h. However, about 90% of cycloaddition product was reverted to PVT polymer in the wet solvent, with the formation of a new peak at ~ 6.23 ppm, attributing to HCN, a hydrolysis product of TCNE. This result indicates that the cycloreversion occurred first to recover PVT units and TCNE, then the recovered TCNE reacted with the formed PVT unit for substitution in dry solvent, or TCNE was scavenged by the trace of water in the wet solvent due to hydrolysis,⁸ so that its substitution on the PVT unit was prevented. This result confirms that the cycloreversion occurred prior to the substitution.

The effect of the [2+2] cycloaddition on the subsequent substitution was further examined using a model compound (PVT-BPE) as shown in Scheme 3. In this compound, two ethylene linkages instead of two phenylene moieties were attached to the amino group in order to simplify the spectrum in the aromatic region. Figure 3 illustrates the changes in the NMR spectra during the reaction. As soon as TCNE (4.0 equiv) was added into the PVT-BPE solution in DMF-*d*₇ at 23 °C, a clean, stable but completely different spectrum was observed in 2 min with two new doublets at δ 5.50 and 6.07 ppm, which is attributed to the formation of the cyclobutane unit by the [2+2] cycloaddition reaction of PVT-BPE with TCNE as discussed above, indicating that the cycloaddition of this model compound is very fast. A [2+2] cycloaddition reaction can be initiated photochemically or thermally. The combination of an electron-rich alkene and an electron-deficient one (nitro- or polycyano-alkene) as the reactants will facilitate the thermal process.⁹ It might explain that the cycloaddition of A-PVT with TCNE could be conducted at such unusually low temperature in dark.

The reaction temperature was then raised to 50 °C and NMR spectra recorded at 2.5, 16, and 24 h are displayed in Figure 3. The reaction resulted in a gradual change in the ¹H NMR spectra within 24 h. During this period, the two doublets at δ 5.44 and 6.00 ppm from the cyclobutane unit decreased in intensity while accompanied by the formation of two new coupled doublets at δ 7.60 and 7.70 ppm with a much larger coupling constant. This is in

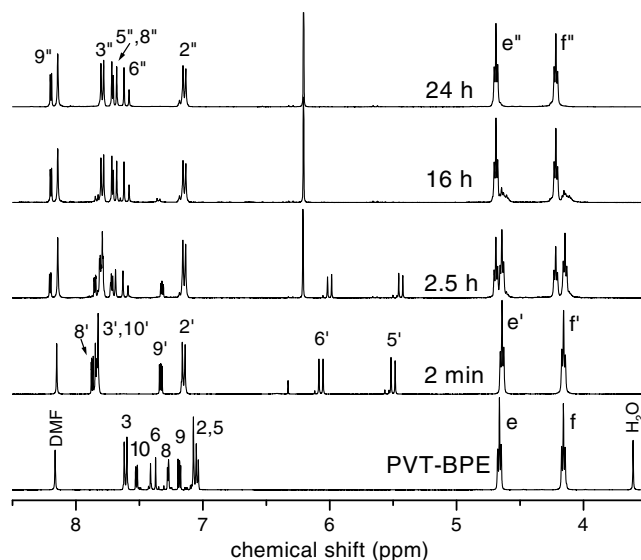
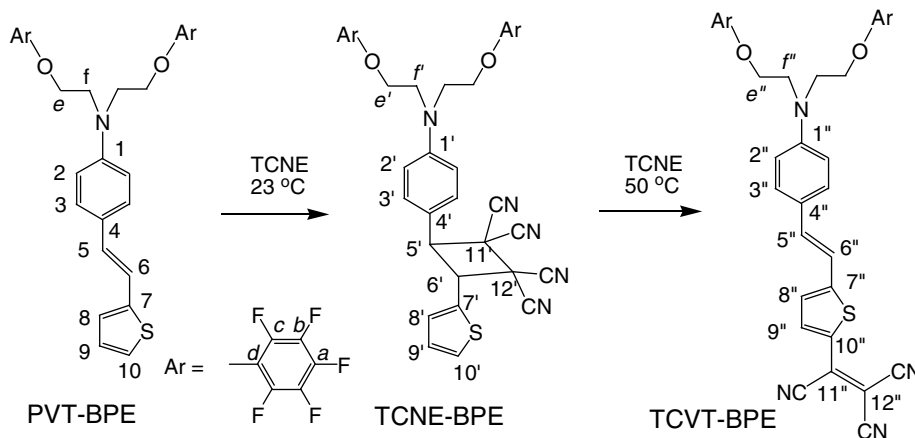


Fig. 3. ¹H NMR spectra of PVT-BPE and its reaction solution in DMF-*d*₇ in the presence of TCNE (4.0 equiv) at 23 °C for 2 min, and then at 50 °C for 2.5, 16, and 24 h (see Scheme 3 for peak assignment).

good agreement with the formation of a highly conjugated double bond, further confirming that the cyclobutane unit was dissociated. On the other hand, the spectrum of the cycloaddition product (2 min) showed three thiophene proton peaks (two *d*-lets and one *dd*-let), which were easily identified due to their smaller coupling constants. During the reaction, the *dd*-let gradually disappeared, while the two *d*-lets shifted to much higher frequencies, indicating a strong electron-withdrawing group attached to C-10 of the PVT unit. The IR spectra of the TCNE substituted products displayed two new peaks at 1588 and 1422 cm⁻¹ corresponding to the formation of disubstituted thiophene ring.¹⁰

Figure 3 also reveals a significant impact of the reversible [2+2] cycloaddition on the steric conformation of the PVT vinylene moiety of the final product. Several weak peaks can be seen in the aromatic region of the starting molecule, PVT-BPE. These peaks cannot be removed by a careful purification, meaning they are not attributed to



Scheme 3. Reaction scheme of PVT-BPE with TCNE in DMF-*d*₇ at 23 °C for 1 h and then at 50 °C for 24 h.

impurities. NMR analyses indicated that they were related to cis-isomer of PVT-BPE. The PVT unit was synthesized from the Wittig reaction. Accompanying the predominant trans-isomer, a small amount of the cis-isomer was also formed.¹¹ The content of the cis-isomer was estimated to be ~8% from the ¹H NMR analysis. If this cis-structure remained in the final TCNE substituted product, it would act as a bending linkage between the electron-donating and electron-accepting units, resulting in lower electro-optic efficiency than the linear trans-counterpart. The reversible process of the [2+2] cycloaddition has favorably converted all the cis-isomer into the trans-isomer, showing a similar effect as the iodine treatment.¹² This effect is evidenced by the absence of peaks from the cis-isomer in the NMR spectrum of the final product (24 h) in Figure 3.

It is worth to note that a new singlet appeared at δ 6.23 ppm in all of the spectra recorded from reaction solutions in DMF-*d*₇ except in carefully dried solvent. Its intensity increased gradually with reaction time. Some additional features of this peak are following: (1) It appeared immediately after the addition of TCNE and was accompanied with the shift or disappearance of the water signal at 3.61 ppm; (2) its maximum intensity was similar to the intensity of water signal in the PVT-BPE spectrum; (3) it was not found in the purified final product. ¹H and 2D NMR studies of TCNE in DMF-*d*₇ indicated that this peak is attributed to HCN formed from the hydrolysis of TCNE.⁷ This side reaction could compete with the substitution reaction by consuming extra TCNE, and it could be prevented when an anhydrous solvent was used.

In conclusion, the substitution reaction of PVT units in polymer and in a model compound with TCNE does not occur straightaway in DMF. TCNE first adds to the vinylene moiety in PVT to form a [2+2] cycloaddition product rapidly at room temperature. It is then reverted to PVT unit at 50 °C, and immediately followed by the substitution reaction. This reversible cycloaddition converts the cis-isomer of PVT units into the trans-counterparts. It is expected to produce better performance of the final TCNE substituted product as a non-linear optical material.

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- Synthesis of P(A-TCNE)SO*: P(A-PVT)SO (0.109 g, 0.1 mmol of PVT unit) and TCNE (0.051 g, 0.4 mmol) were dissolved in 0.5 mL of anhydrous DMF at 0 °C. The solution was stirred at 0 °C for 3 h and then dropped into 10 mL of methanol to precipitate the polymer at 0 °C; the pale green powder was collected using centrifuge and washed with cold methanol 3 times and dried at room temperature under vacuum for 12 h (0.095 g, 78% yield). ¹H NMR (400 MHz, acetone-*d*₆): δ (ppm) 7.710–7.620 (m), 7.46 (d, *J* = 8.2 Hz), 7.330 (d, *J* = 8.58 Hz), 7.220–7.090 (m), 7.040 (d, *J* = 8.58 Hz), 7.010–6.930 (m), 5.737 (d, *J* = 12.8 Hz), 5.337 (d, *J* = 12.8 Hz); ¹³C NMR (100 MHz, acetone-*d*₆): δ (ppm) 157.7, 154.0, 153.4, 150.5, 148.1, 147.9, 145.5, 145.3, 145.1, 144.5, 144.0, 143.9, 141.4, 134.5, 132.9, 132.5, 130.4, 130.2, 129.9, 129.8, 128.9, 128.5, 128.3, 127.8, 126.9, 126.7, 125.1, 124.8, 123.7, 122.2, 121.4, 118.4, 118.3, 116.9, 111.9, 111.6, 110.62, 110.57, 53.9, 47.8, 43.9, 43.1. ¹⁹F NMR (376 MHz, acetone-*d*₆): δ (ppm) –63.80 (6F, m), –137.44 (4F, m), –137.65 (8F, m), –151.97 (4F, m), 152.46 (8F, m). IR (cm⁻¹): 2976, 2872, (CH stretching), 1637, 1604, 1501, 1491 (sh) (phenyl ring), 1389, 1319, 1295, 1260, 1197, 1177, 1097, 1065, 997, 829, 599. *M*_n: 19,000 Da. *M*_w/*M*_n: 1.8.
- Synthesis of P(A-TCVT)SO*: P(A-PVT)SO (0.1091 g, 0.1 mmol of PVT unit) and TCNE (0.051 g, 0.4 mmol) were dissolved in 0.5 mL of anhydrous DMF. The solution was stirred at 50 °C for 16 h and then dropped into 10 mL of methanol to precipitate the polymer; the deep blue powder was collected by centrifuge and was washed with methanol 3 times and dried at room temperature under vacuum for 12 h (0.090 g, 76% yield). ¹H NMR (400 MHz, acetone-*d*₆): δ (ppm) 8.090–7.940 (m), 7.650–7.380 (m), 7.36–6.84 (m); ¹³C NMR (100 MHz, acetone-*d*₆): δ (ppm) 159.4, 157.8, 154.2, 150.3, 148.1, 148.0, 145.5, 145.4, 145.2, 144.3, 144.0, 143.9, 142.7, 141.5, 140.6, 139.6, 137.3, 132.9, 132.3, 130.1, 129.9, 128.7, 128.1, 126.8, 126.5, 123.7, 121.7, 118.5, 117.8, 117.0, 114.0, 113.9, 81.6, 64.7 (m), 49.8; ¹⁹F NMR (376 MHz, acetone-*d*₆): δ (ppm) –63.80 (6F, m), –137.54 (4F, m), –137.96 (8F, m), –152.40 (4F, m), 152.92 (8F, m); IR (cm⁻¹): 2972, 2873, (CH stretching), 2218, 1637, 1604, 1588, 1499, 1492 (sh) (phenyl ring), 1422, 1391, 1321, 1296, 1261, 1183, 1168, 1097, 1075, 997, 824, 598. *T*_g: 217 °C. Mp: 20,100 Da.
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- Characterization of TCVT-BPE*: ¹H NMR (400 MHz, acetone-*d*₆): δ (ppm) 8.048 (1H, d, *J* = 4.4 Hz, H-9''), 7.622 (2H, d, *J* = 8.8 Hz, H-3''), 7.519 (1H, d, *J* = 16.0 Hz, H-5''), 7.506 (1H, d, *J* = 4.4 Hz, H-8''), 7.410 (1H, d, *J* = 16.0 Hz, H-6''), 6.968 (2H, d, *J* = 8.8 Hz, H-2''), 4.546 (4H, t, *J* = 5.6 Hz, H-e''), 4.098 (4H, t, *J* = 5.6 Hz, H-f''); ¹³C NMR (100 MHz, acetone-*d*₆): δ (ppm) 160.8 (s, C-7''), 150.1 (s, C-1''), 142.9 (s, C-9''), 142.7 (d, *J*_{C-F} = 238 Hz, C-b'' or C-c''), 139.0 (d, *J*_{C-F} = 238 Hz, C-b'' or C-c''), 138.8 (s, c-5''), 138.1 (d, *J*_{C-F} = 235 Hz, C-a''), 134.8 (m, C-d''), 132.5 (s, C-10''), 131.9 (s, C-11''), 130.8 (s, C-3''), 128.1 (s, C-8''), 125.3 (s, C-4''), 116.5 (s, C-6''), 114.2 (s, CNs), 113.5 (s, C-2''), 80.2 (s, C-12''), 74.2 (s, C-e''), 51.7 (s, C-f''). IR (cm⁻¹): 3062, 2972, 2875 (CH stretching), 2218, 1637, 1603 (sh), 1588, 1522 (sh), 1500, 1422, 1320, 1296, 1261, 1176, 1097, 1075, 998, 824, 673, 646, 598. *T*_m: 189.0 °C. MS: calcd for C₃₃H₁₆F₁₀N₄O₂S: 722.1; found *m/z*: 723.1 (M+1).
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