

Supporting Information

Cationic Polyelectrolyte for Anionic Cyanines: An Efficient Way To Translate Molecular Properties into Material Properties

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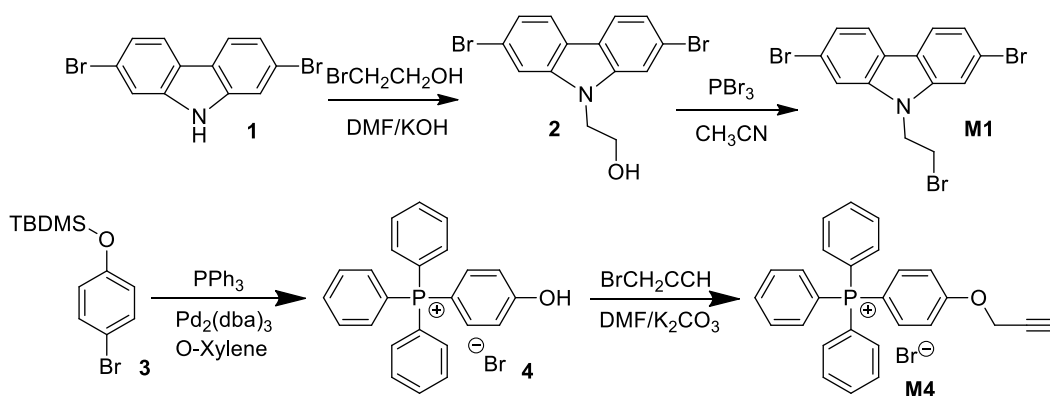
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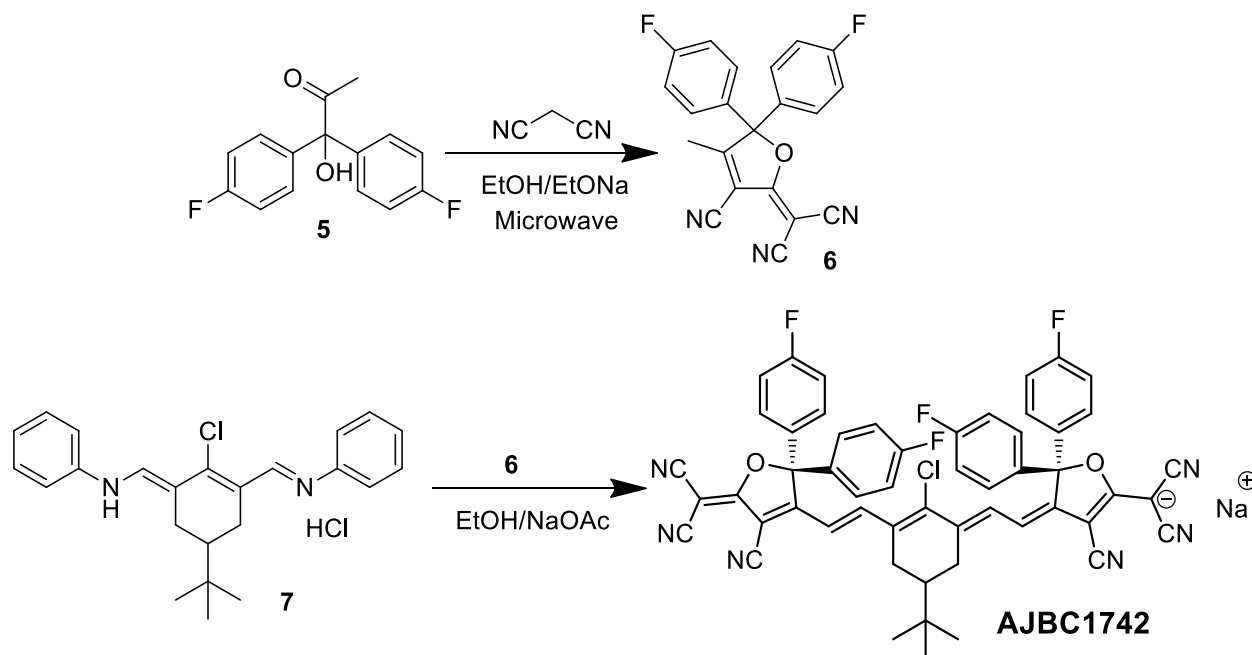
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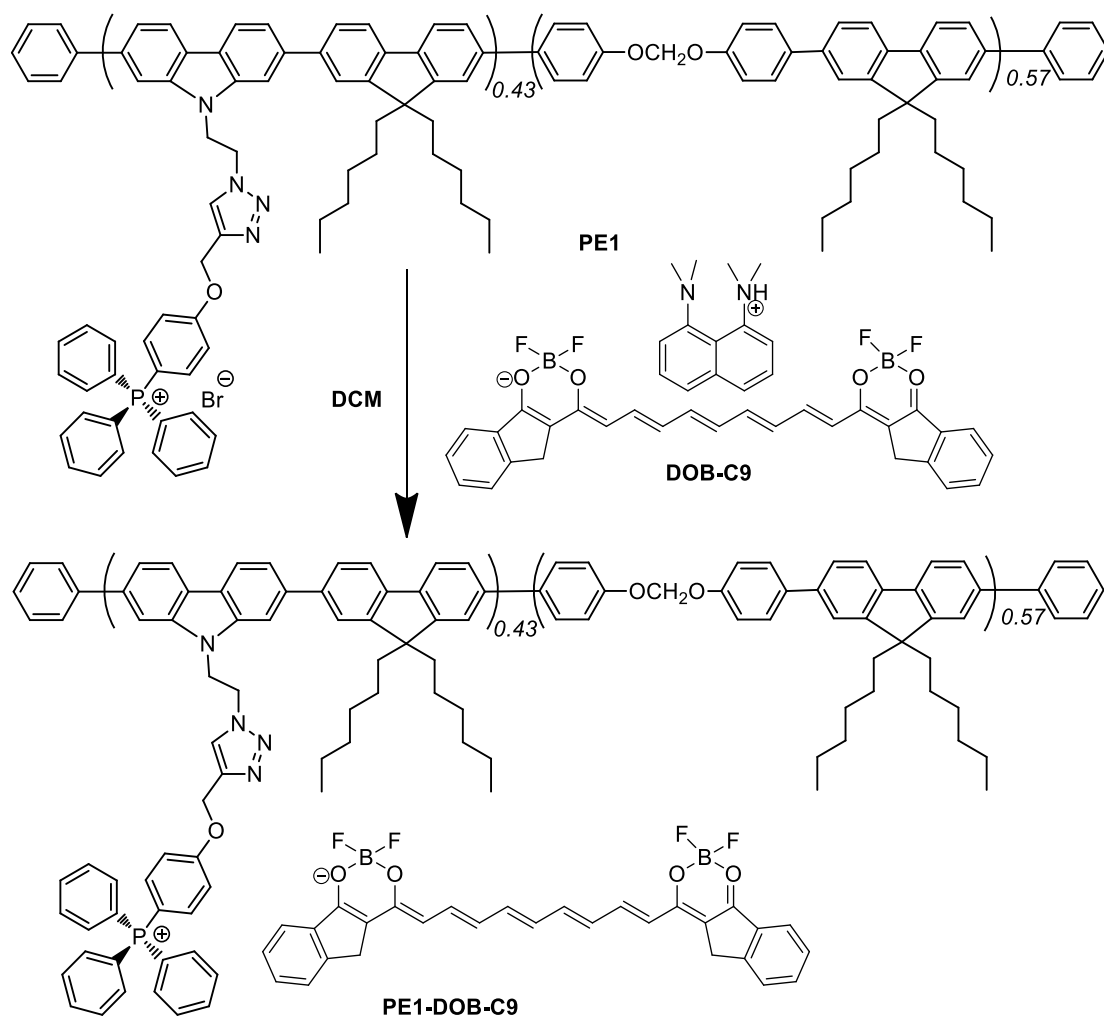
S1. Synthetic Details and Characterization Data



Scheme S1. The synthetic route of monomers **M1** and **M4** for preparing phosphonium-containing cationic polyelectrolyte (**PE1**).



Scheme S2. The synthetic route of anionic diaryl-TCF based heptamethine (**AJBC1742**).



Scheme S3. The synthetic route of polyelectrolyte-cyanine complex (**PE1-DOB-C9**).

Materials.

Anionic cyanines of **AJBC1720**, **AJBC1723** and **DOB-C9** were synthesized in our previous work.^{1,2} (4-Bromophenoxy)-tert-butyldimethylsilane (**3**),³ Bis(p-bromophenoxy)methane (**M2**),⁴ diaryl-TCF acceptor precursor (**5**)⁵ were prepared according to literature procedures. All other reagents were used as received.

Instrumentation.

¹H NMR and ¹³C NMR were measured using a Bruker 300 or 500 MHz instrument spectrometer. Mass spectroscopy (MS) was performed using a Bruker Esquire LC-Ion Trap at the Department of Chemistry Mass Spectrometry Facilities, University of Washington. Elemental analyses were performed by Intertek QTI Laboratory (Whitehouse, NJ). UV-Vis-IR spectra were measured using a Perkin-Elmer

Lambda-9 spectrophotometer. FT-IR spectra were collected using a Bruker Vector 33 Fourier Transform Infrared Spectrophotometer. Thermal transitions were measured on a TA Instruments Q20-1066 Differential Scanning Calorimeter with a heating rate of 10 °C min⁻¹ under nitrogen. The molecular weight was measured by a Waters 1515 gel permeation chromatography (GPC) with a refractive index detector at room temperature using THF as the eluent, and calibrated versus polystyrene standards.

Synthesis of N-ethanol-2,7-dibromo-carbazole (2).

2,7-Dibromocarbazole (**1**) (1.00 g, 3.1 mmol) was dissolved in DMF (6 mL) and then powdered potassium hydroxide (1.7 g, 30.0 mmol) was added. After the mixture was stirred for 1 hr., 2-bromoethanol (0.6 g, 6.0 mmol) was added slowly. After stirring for another 24 hrs at room temperature, the mixture was poured into ice brine (200 mL), then filtered and washed with water. The crude product was purified by recrystallization from ethanol/water to produce white powder **2** (0.90 g, 79.0%). ¹H NMR (CDCl₃, 300 MHz, 298 K) δ (ppm): 4.03 (t, J = 6.0 Hz, 2H, -CH₂OH), 4.36 (t, J = 6.0 Hz, 2H, -NCH₂-), 7.39 (dd, J = 1.5 Hz and 8.1 Hz, 2H, ArH), 7.61 (s, 2H, ArH), 7.86 (d, J = 8.1 Hz, 2H, ArH). ¹³C NMR (CDCl₃, 125 MHz, 298 K) δ (ppm): 45.7, 61.3, 112.3, 119.9, 121.5, 123.0, 141.7.

Synthesis of N-(2-bromoethyl)-2,7-dibromo-carbazole (M1).

Phosphorus tribromide (0.65 g, 2.4 mmol) was slowly dropped into a solution of N-ethanol-2,7-dibromo-carbazole (**2**) (0.80 g, 2.2 mmol) in anhydrous CH₃CN (5 mL), and this solution was stirred in a nitrogen atmosphere. The reaction mixture was stirred at 60 °C overnight, and then cooled to room temperature. Afterwards, the mixture was slowly poured into a diluted NaOH aqueous solution (2M, 200 mL), then filtered and washed with water. The crude product was purified by column chromatography on silica gel using DCM/hexane (1/1, V/V) as an eluent to produce white solid **M1** (0.80 g, 84.7%). ¹H NMR (CDCl₃, 300 MHz, 298 K) δ (ppm): 3.69 (t, J = 7.2 Hz, 2H, -CH₂Br), 4.64 (t, J = 7.2 Hz, 2H, -NCH₂-), 7.39 (dd, J = 1.5 Hz and 8.4 Hz, 2H, ArH), 7.39 (s, 2H, ArH), 7.90 (d, J = 8.4 Hz, 2H, ArH). ¹³C NMR (CDCl₃, 125 MHz, 298 K) δ (ppm): 27.7, 44.8, 111.9, 120.0, 121.6, 121.7, 123.4, 140.9. Anal. calcd for (%), found/calcd): C, 38.48/38.93; H, 2.12/2.33; N, 3.15/3.24.

Synthesis of (p-Hydroxyphenyl)triphenylphosphonium bromide (4).⁶

A mixture of (4-Bromophenoxy)-tert-butyldimethylsilane **3** (2.87 g, 10.0 mmol), triphenylphosphine (2.62 g, 10.0 mmol) and Pd₂(dba)₃ (92 mg, 0.1 mmol), anhydrous o-xylene (3.3 mL) was carefully degassed and charged with nitrogen. The reaction mixture was heated to reflux for 5 hrs. under nitrogen atmosphere. The phosphonium salts precipitated as the reaction proceeded. Afterwards, the reaction was cooled to room temperature, 30 mL of diethyl ether was added, and the resulting suspension was stirred at room temperature for 10 min. The precipitate was filtered and washed with 50 mL of diethyl ether. The crude product was purified by column chromatography on silica gel using DCM/MeOH (20/1, V/V) to produce pure white solid **4** (1.4 g, 40%). ¹H NMR (CDCl₃, 300 MHz, 298 K) δ (ppm): 7.25 (m, 2H, ArH), 7.5-7.8 (m, 14H, ArH), 7.86 (t, J = 7.2 Hz, 3H, ArH).⁶ Note: the TBDMS protective group has been removed during reaction possibly due to the high reaction temperature.

Synthesis of [(2-Propynyloxy)benzene]triphenylphosphonium bromide (M4).

Propargyl bromide (80wt% in Toluene, 0.40 g, 3.4 mmol) was added to a solution of (p-Hydroxyphenyl)triphenylphosphonium bromide **4** (0.49 g, 1.1 mmol) and anhydrous K₂CO₃ (0.49 g, 3.6 mmol) in DMF (5 mL). The reaction solution was stirred at 60 °C overnight. After cooling to room temperature, the solution was poured into an ice brine (100 mL) and then extracted with DCM. The crude product was purified by column chromatography on silica gel using DCM/MeOH (30/1, V/V) as an eluent to produce pure light yellow solid **M4** (0.50 g, 96.1%). ¹H NMR (CDCl₃, 500 MHz, 298 K) δ (ppm): 2.64 (dd, J = 2.5 Hz, 1H, -C \equiv CH), 4.91 (s, 2H, -OCH₂-), 7.39 (m, 2H, ArH), 7.52-7.66 (m, 8H, ArH), 7.77 (m, 6H, ArH), 7.9 (m, 3H, ArH). ¹³C NMR (CDCl₃, 125 MHz, 298 K) δ (ppm): 56.8, 107.3, 108.1, 117.5, 117.6, 117.7, 118.4, 130.7, 130.9, 134.3, 135.7, 136.4, 136.5, 163.3. ³¹P NMR (CDCl₃, 200 MHz, 298 K) δ (ppm): 22.5. MS (ESI): (M^+ = 393.2 (calcd for C₂₇H₂₂OP⁺, 393.4).

Synthesis of copolymer P-Br.

A mixture of N-(2-bromoethyl)-2,7-dibromo-carbazole **M1** (0.65 g, 1.50 mmol), Bis(p-bromophenoxy)methane **M2** (0.54 g, 1.5 mmol) and 9,9-Dihexylfluorene-2,7-bis (trimethyleneborate) **M3** (1.51 g, 3.0 mmol), K₂CO₃ (4.14 g, 30.0 mmol), THF (30 mL)/water (10 mL), and Pd(PPh₃)₄ (0.10

g, 0.086 mmol) was carefully degassed and charged with nitrogen. Then the reaction mixture was refluxed for 3 days. After the solution was cooled to room temperature, it was dropped into water (500 mL) to remove salt. The obtained solid was dissolved in THF, and the insoluble solid was filtered out. The filtrate was concentrated, precipitated into methanol (500 mL), and the obtained solid was then washed with 500 mL of methanol and acetone to produce a yellow polymer product (1.4 g, 81.9%). $M_w = 32500$ g/mol, PDI = 1.60 (GPC, THF, polystyrene calibration). ^1H NMR (CDCl_3 , 300 MHz, 298 K) δ (ppm): 0.6-1.0 (m, $-\text{CH}_3$ and $-\text{CH}_2-$), 1.0-1.3 (br, s, $-\text{CH}_2-$), 2.0-2.2 (br, s, $-\text{C}(\text{CH}_2)_2-$), 3.84 (s, $-\text{CH}_2\text{Br}$), 4.91 (s, $-\text{NCH}_2-$), 5.87 (s, $-\text{OCH}_2\text{O}-$), 7.5-8.0 (m, ArH), 8.23 (d, ArH).

Synthesis of copolymer P-N₃.

P-Br (0.50 g) was dissolved in THF (9 mL)/DMF (5 mL), and then sodium azide (0.32 g, 5.0 mmol) was added. The mixture was stirred at 60 °C for 3 days under an atmosphere of nitrogen. After the solution was cooled to room temperature, it was poured into water (200 mL) and then filtered. The obtained solid was dissolved in THF, dropped into 200 mL of methanol, then filtered and washed 200 mL of methanol. The resultant polymer was obtained as a gray powder (0.49 g, 100%). $M_w = 30400$ g/mol, PDI = 1.52 (GPC, THF, polystyrene calibration). ^1H NMR (CDCl_3 , 300 MHz, 298 K) δ (ppm): 0.6-1.0 (br, s, $-\text{CH}_3$ and $-\text{CH}_2-$), 1.0-1.3 (br, s, $-\text{CH}_2-$), 2.0-2.2 (br, s, $-\text{C}(\text{CH}_2)_2-$), 3.91 (s, $-\text{CH}_2\text{Br}$), 4.87 (s, $-\text{NCH}_2-$), 5.87 (s, $-\text{OCH}_2\text{O}-$), 7.5-8.0 (m, ArH), 8.23 (s, ArH).

Synthesis of phosphonium-based polyelectrolyte PE1.

A mixture of polymer P-N₃ (0.31 g), [(2-Propynyloxy)benzene]triphenylphosphonium bromide (**M4**) (124 mg, 0.26 mmol) and CuBr (37 mg, 0.26 mmol) was dissolved in THF (5 mL)/DMF (2.5 mL). Then *N,N,N,N,N*-pentamethyldiethylenetriamine (PMDETA) (45 mg, 0.26 mmol) was added and the reaction mixture was stirred at room temperature. The reaction progress was monitored by FT-IR spectra until the peak of azido group at 2096 cm^{-1} disappears. After 3 hrs., the reaction was stopped, and the solution was dropped into water (200 mL) to remove salt. The obtained solid was then dissolved in THF, and dropped into methanol (200 mL) to remove monomer, then filtered out and washed with methanol. The resulting polyelectrolyte **PE1** was obtained as yellow powder (0.40 g, 94.1%). $M_w =$

26200 g/mol, PDI = 1.48 (GPC, THF, polystyrene calibration).⁷ ¹H NMR (CDCl₃, 300 MHz, 298 K) δ (ppm): 0.5-0.8 (br, s, -CH₃ and -CH₂-), 0.9-1.2 (br, s, -CH₂-), 1.9-2.2 (br, s, -C(CH₂)₂-), 4.8-5.2 (br, s, -CH₂Br, -NCH₂- and -OCH₂C-), 5.85 (s, -OCH₂O-), 7.1 (s, -CH=C), 7.5-8.0 (m, ArH), 8.13 (s, ArH). ³¹P NMR (CDCl₃, 125 MHz, 298 K) δ (ppm): 22.5.

Synthesis of TCF end-group (6).

A mixture of compound **5** (656 mg, 2.5 mmol), malonitrile (330 mg, 5.0 mmol), sodium ethoxide (1 M, 0.15 mL), and absolute ethanol (200 Proof, 5 mL) in a 25 mL of flask with a magnetic bar was heated at 100 °C with microwave (30 W) for 30 min. After the solution was cooled to room temperature, ethanol was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using DCM as an eluent and further recrystallized from ethanol to produce a white solid **6** (410 mg, 45.6%). ¹H NMR (CDCl₃, 300 MHz, 298 K) δ (ppm): 2.43 (s, 3H, -CH₃), 7.19 (s, 4H, ArH), 7.21 (s, 4H, ArH). ¹³C NMR (CDCl₃, 125 MHz, 298 K) δ (ppm): 16.2, 60.2, 104.4, 106.7, 108.8, 109.9, 110.4, 116.7, 116.9, 129.4, 129.5, 130.7, 162.8, 164.8, 174.5, 178.9. MS (ESI): M-H⁺ = 358.0 (calcd for C₂₁H₁₁F₂N₃O, 359.3).

Synthesis of anionic TCF-heptamethine (AJBC1742).

Bridge **7** (208 mg, 0.5 mmol), diaryl TCF end groups **6** (359.3 mg, 1.0 mmol), and sodium acetate (84 mg, 1.0 mmol) were dissolved in 20 mL of absolute ethanol (200 Proof). The reaction mixture was refluxed for 6 hrs. under nitrogen. The ethanol was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using DCM/methanol (9:1) as an eluent to produce a green solid **AJBC1742** (235 mg, 50.3 %). ¹H NMR (Acetone-*d*₆, 500 MHz, 298 K) δ (ppm): 0.95 (s, 9H, -C(CH₃)₃), 1.38 (m, 1H, -CH-), 2.03 (m, 2H, -CH₂-), 2.74 (d, *J* = 15 Hz, -CH₂-), 6.32 (2H, *J* = 14 Hz, -CH=CH-), 7.26 (m, 8H, ArH), 7.48 (m, 8H, ArH), 7.70 (d, *J* = 14 Hz, -CH=CH-). ¹³C NMR (Acetone-*d*₆, 125 MHz, 298 K) δ (ppm): 26.6, 27.2, 31.9, 42.2, 47.4, 85.9, 99.4, 109.6, 113.2, 113.7, 114.4, 115.5, 115.7, 128.9, 130.4, 130.5, 130.6, 130.7, 134.7, 134.9, 141.1, 146.9, 162.1, 163.4, 164.1, 175.6. MS (ESI): M⁻ = 910.3 (calcd for C₅₄H₃₄ClF₄N₆O₂⁻, 910.3). Anal. calcd for (%), found/calcd): C, 69.93/69.49; H, 3.77/3.67; N, 8.59/9.00.

Synthesis of polyelectrolyte-cyanine complexes PE1-TCF1 and PE1-TCF2.

Polyelectrolyte **PE1** (1.0 equiv.) and anionic TCF-heptamethine **AJBC1720** or **AJBC1742** (~0.5 equiv.) were dissolved in DCM/DMSO (30/1, V/V). The mixture was stirred at room temperature for 3 hrs. Afterwards, the DCM was evaporated, the mixture was poured into 100 mL of methanol. The precipitated green solid was collected by filtration, and washed with 20 mL of water and 100 mL of methanol, respectively.

PE1-TCF1 (76 mg, 97.5%): **PE1** (60 mg, 0.08 mmol), **AJBC1720** (24 mg, 0.04 mmol). $M_w = 6100$ g/mol, PDI = 1.1 (GPC, THF, polystyrene calibration).⁷ ¹H NMR (CDCl₃, 300 MHz, 298 K) δ (ppm): 0.5-1.3 (br, m, -CH₃, -C(CH₃)₃ and -CH₂-), 1.9-2.2 (br, s, -C(CH₂)₂- and -CH-), 4.8-5.2 (br, s, -CH₂Br, -NCH₂- and -OCH₂C-), 5.85 (s, -OCH₂O-), 7.0 (s, -CH=C), 7.2-7.9 (m, ArH), 8.06 (s, ArH).

PE1-TCF2 (98 mg, 89.0 %): **PE1** (95 mg, 0.10 mmol), **AJBC1742** (43 mg, 0.05 mmol). $M_w = 7600$ g/mol, PDI = 1.08 (GPC, THF, polystyrene calibration).⁷ ¹H NMR (CDCl₃, 300 MHz, 298 K) δ (ppm): 0.4-1.2 (br, m, -CH₃, -C(CH₃)₃ and -CH₂-), 1.7-2.2 (br, s, -C(CH₂)₂- and -CH-), 2.2-2.6 (br, s, -CH₂-), 4.5-5.0 (br, s, -CH₂Br, -NCH₂- and -OCH₂C-), 5.6-5.8 (br, s, -OCH₂O-), 5.9-6.2 (-CH=CH-), 6.7-7.1 (br, s, ArH and -CH=C), 7.1-7.9 (m, ArH), 8.06 (s, ArH).

Synthesis of polyelectrolyte- cyanine complex PE1-DOB-C9.

Polyelectrolyte **PE1** (45 mg, 0.06 mmol) was dissolved in 5 mL of DCM and then a solution of **DOB-C9** (22 mg, 0.03 mmol) dissolved in 2 mL of DMSO was added. The mixture was covered with foil and stirred at room temperature for 2 hrs. Afterwards, the DCM was evaporated and then 20 mL of acetonitrile was added. The precipitated polymer was collected by filtration, and washed with 20 mL of acetonitrile to produce green solid **PE1-DOB-C9** (50 mg, 87.7%). $M_w = 9800$ g/mol, PDI = 1.04 (GPC, THF, polystyrene calibration).⁷ ¹H NMR (CDCl₃, 300 MHz, 298 K) δ (ppm): 0.4-1.2 (m, -CH₃ and -CH₂-), 0.9-1.2 (br, s, -CH₂-), 1.7-2.2 (br, s, -C(CH₂)₂-), 2.9-3.2 (m, -CH₂-), 4.8-5.2 (br, s, -CH₂Br, -NCH₂- and -OCH₂C-), 5.6-6.0 (br, s, -OCH₂O- and -CH=CH-), 6.3-6.6 (br, s, -CH=CH-), 7.0 (s, -CH=C), 7.2-7.8 (m, ArH), 8.0 (s, ArH)

S2. Chart S1-S4

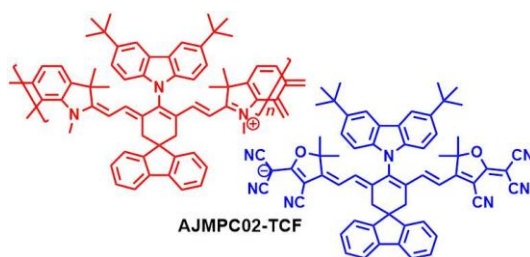


Chart S1. Structure of conjugated polycyanine-TCF heptamethine complex.⁸

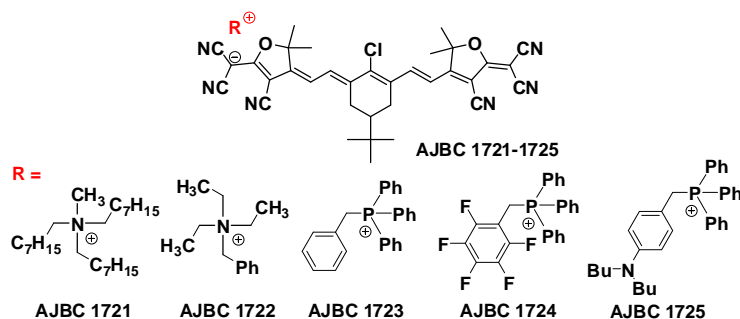


Chart S2. Structures of TCF heptamethines with different mono-cationic counterion.¹

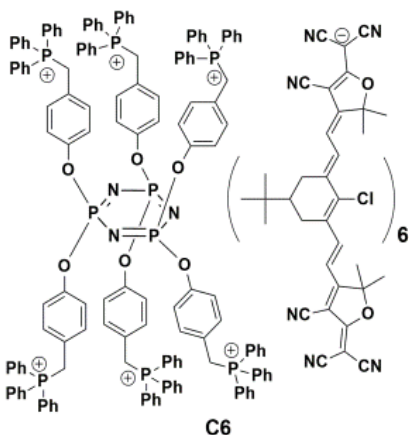


Chart S3. Structures of TCF-heptamethine salt complex (**C6**) with a counterion containing multiple charges.⁹

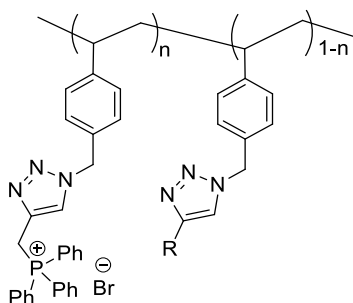


Chart S4. The structure of polystyrene based random polyelectrolyte.

S3. ^1H NMR and IR spectra of P-Br, P-N3 and PE1 and related discussion

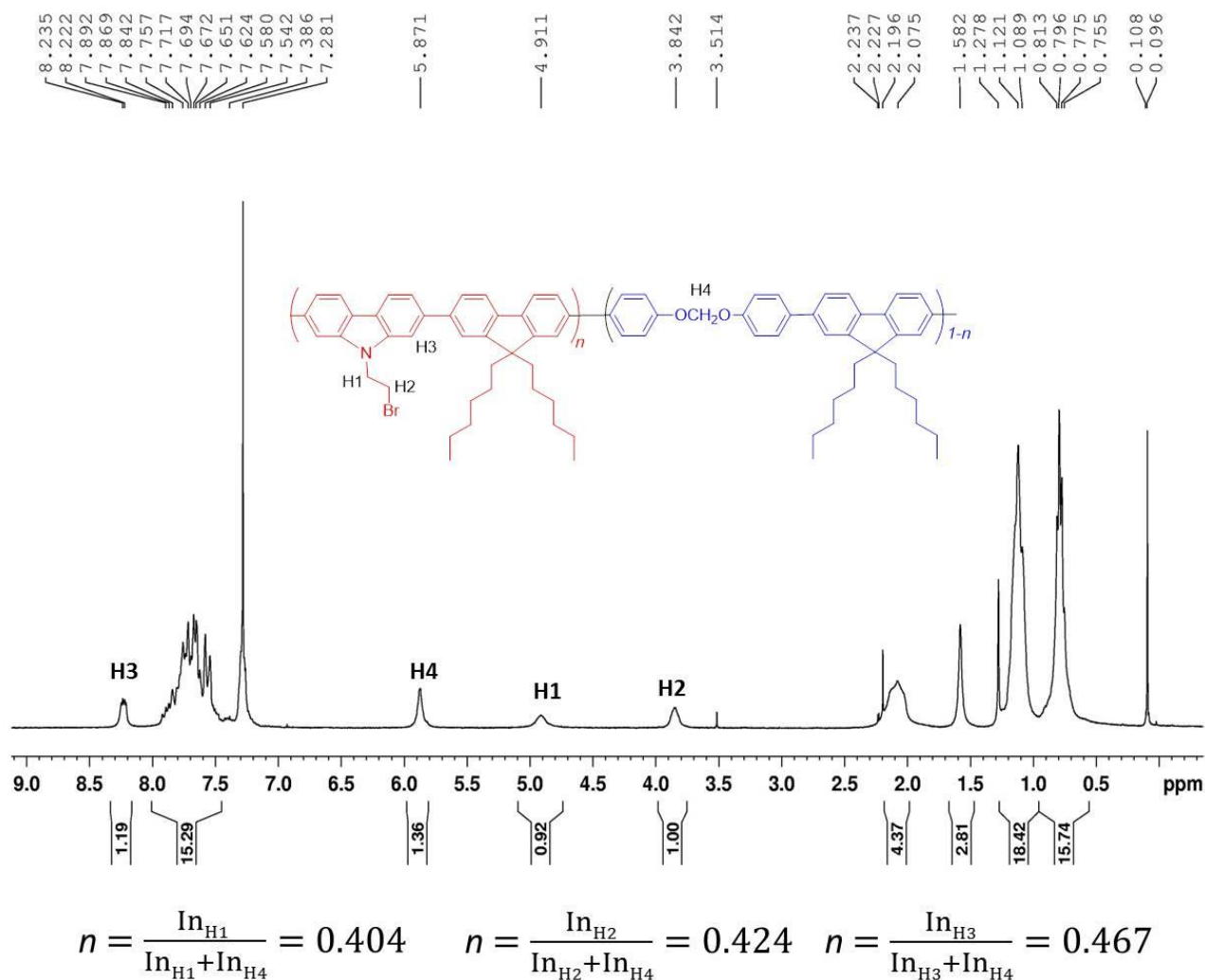


Figure S1. The ^1H NMR spectrum of **P-Br** conducted in chloroform-*d* at 298 K.

During Suzuki copolymerization reaction of **P-Br**, a relative molar ratio of 0.5 for the carbazole monomer (**M1**) was used. By comparing integration data of **H1-H4** from ^1H NMR spectrum of **PE1**, different values of the relative molar ratio for carbazole monomer (*n*) can be calculated by the relation contained in **Figure S1**, which gives an average *n* of 0.43.

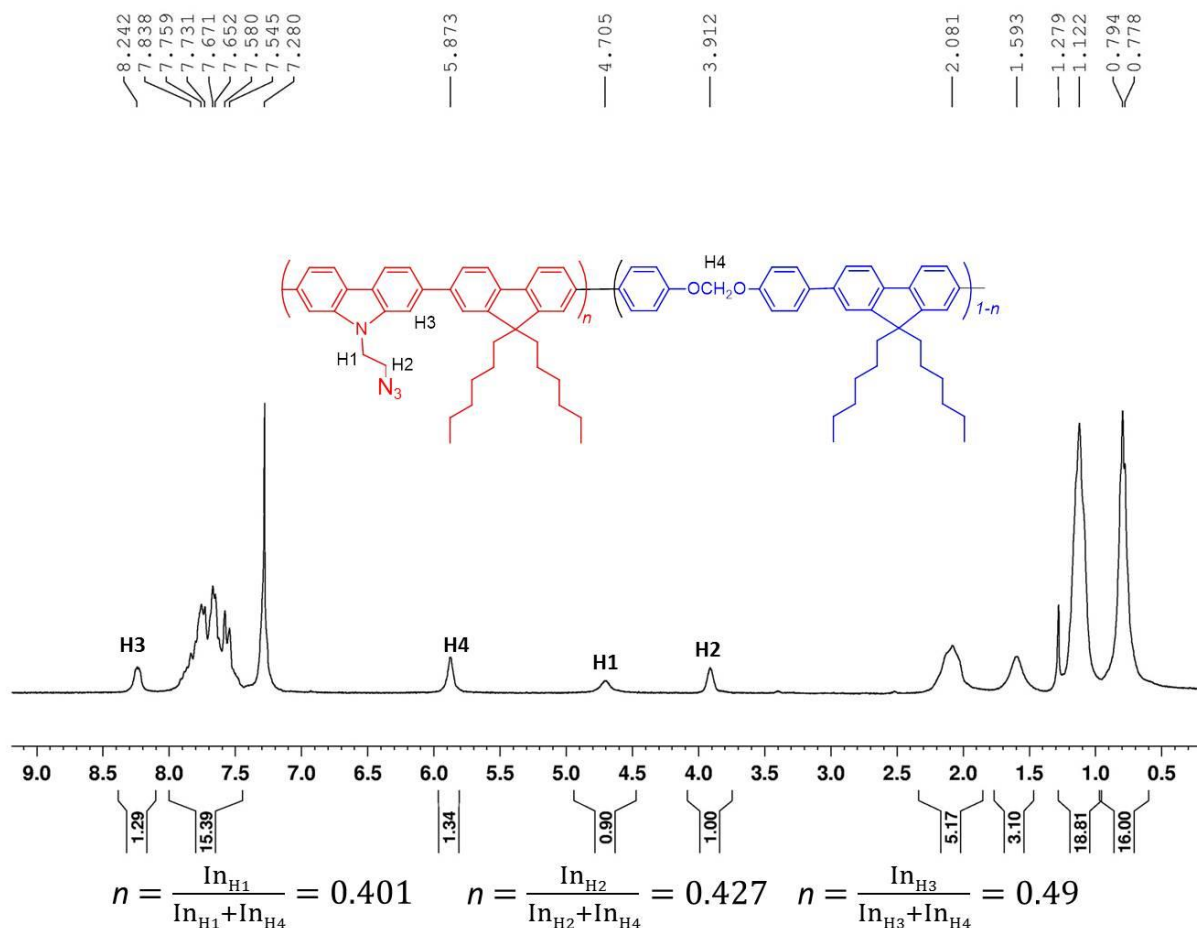


Figure S2. The ^1H NMR spectrum of **P-N3** conducted in chloroform-*d* at 298 K.

By comparing integration data of **H1-H4**, different values can be calculated by the relation in **Figure S2**, which gives an average n of 0.439. Moreover, by comparing **Figure S1** and **S2**, the proton peak assigned to **H2** for **P-N3** has a shift from 3.84 to 3.91 ppm after converting from bromo-ethyl to azido-ethyl groups, suggesting the success of a complete reaction.

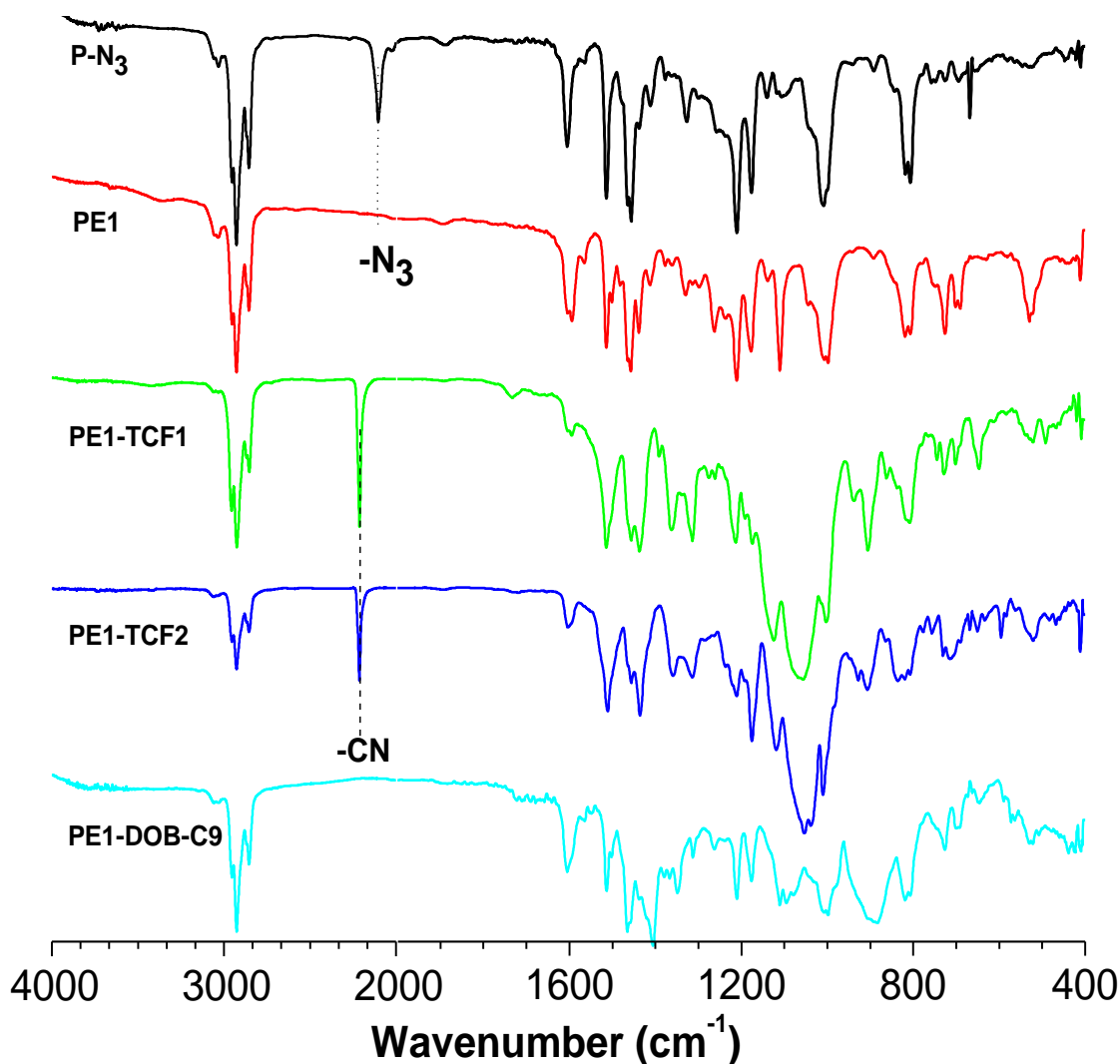


Figure S3. FT-IR spectra of polymer films on KBr pellets.

By comparing the IR spectra between **P-N3** and **PE1** in **Figure S3**, it was observed that after the click reaction the absorption band of the azido groups of P-N3 centered at 2096 cm^{-1} has disappeared, indicating the complete conversion of azido groups into triazole rings. Moreover, in the spectra of **PE1-TCF1** and **PE2-TCF2**, the appearance of the peak at 2208 cm^{-1} is attributed to cyanide groups in TCF end groups.

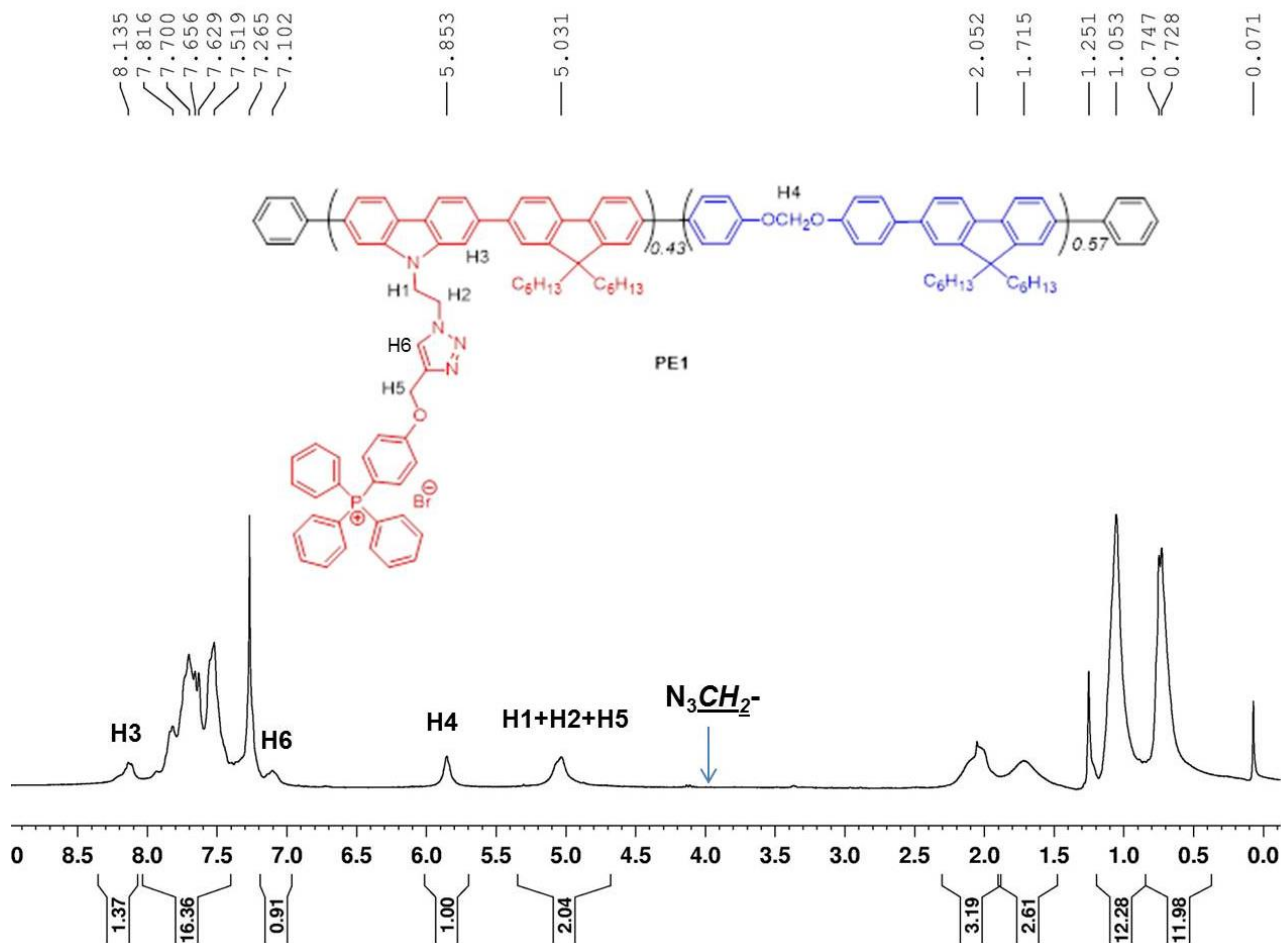


Figure S4. The ^1H NMR spectrum of **PE1** conducted in chloroform-*d* at 298 K.

By comparing **Figure S2** and **S4**, the proton peak at 3.9 ppm assigned to the methylene groups linked with the azido groups ($-\text{CH}_2\text{N}_3$) of **P-N3** has disappeared completely and shifted to 4.96 ppm after forming a triazole ring, suggesting the success of “Click chemistry” postfunctionalization. Moreover, the integration data is also consistent with those obtained in **Figure S1** and **S2** as shown below:

$$n = 1 - \frac{\frac{\text{In}_{\text{H4}}}{2}}{\frac{\text{In}_{\text{H3}} + \text{In}_{\text{H3}} + \text{In}_{\text{H3}} + \frac{\text{In}_{\text{H4}}}{2}}{6}} = 0.405$$

S4. Thermal and linear optical properties.

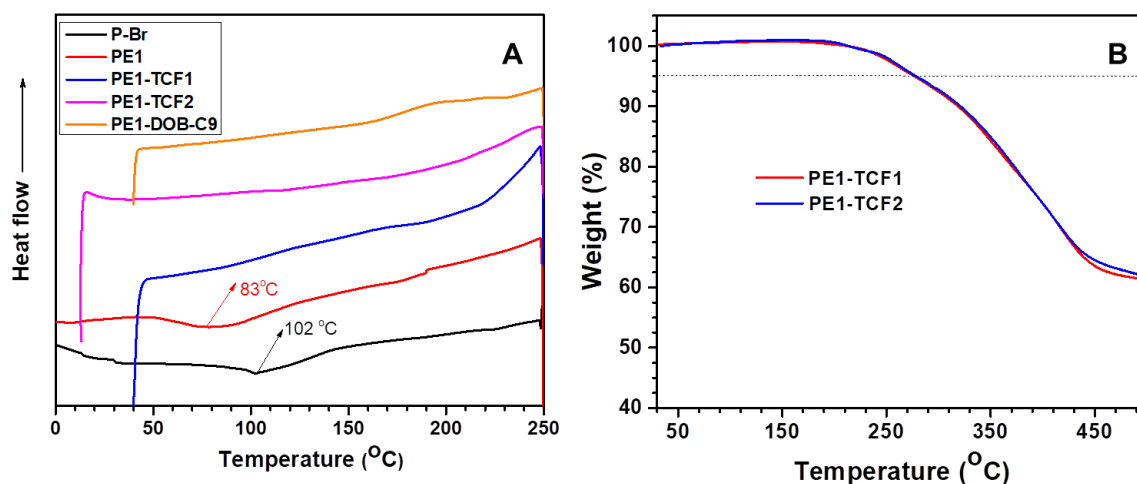


Figure S5. The DSC curves (A) and TGA curves (B) of polymers measured under nitrogen at a heating rate of 10 °C/min.

As shown in **Figure S5A**, the glass transition temperature of **P-Br** and **P-N3** was found to be 102 °C and 83 °C, respectively; however, no clear glass transition temperature was observed after forming the polyelectrolyte-cyanine complexes. As shown in **Figure S5B**, the thermal stabilities of **PE1-TCF1** and **PE1-TCF2** were also measured, and almost the same onset thermal decomposition temperatures (T_{ds}), corresponding to a 5% weight loss, are obtained as 277 °C.

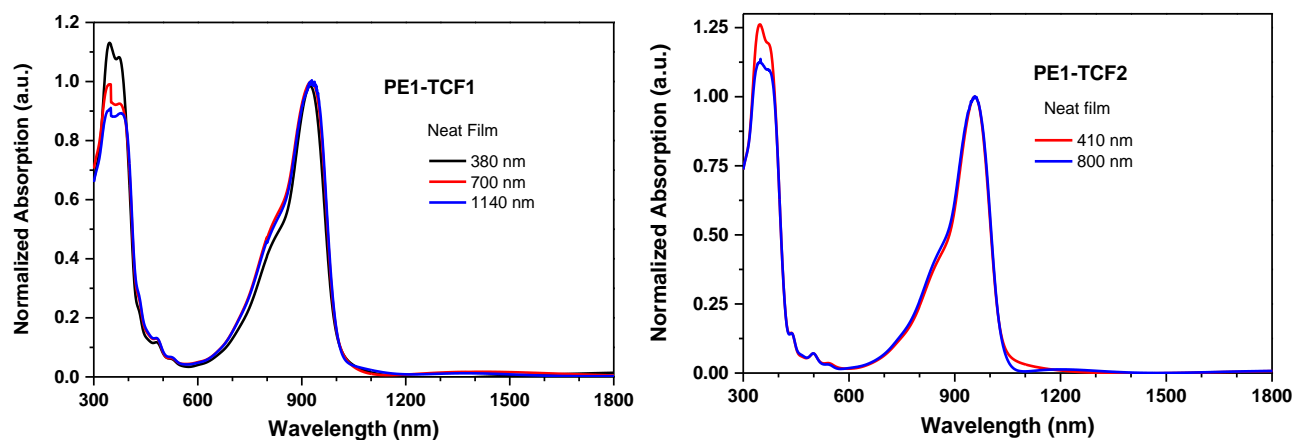


Figure S6. The normalized absorption spectra of neat films of **PE1-TCF1** and **PE1-TCF2** at different thicknesses.

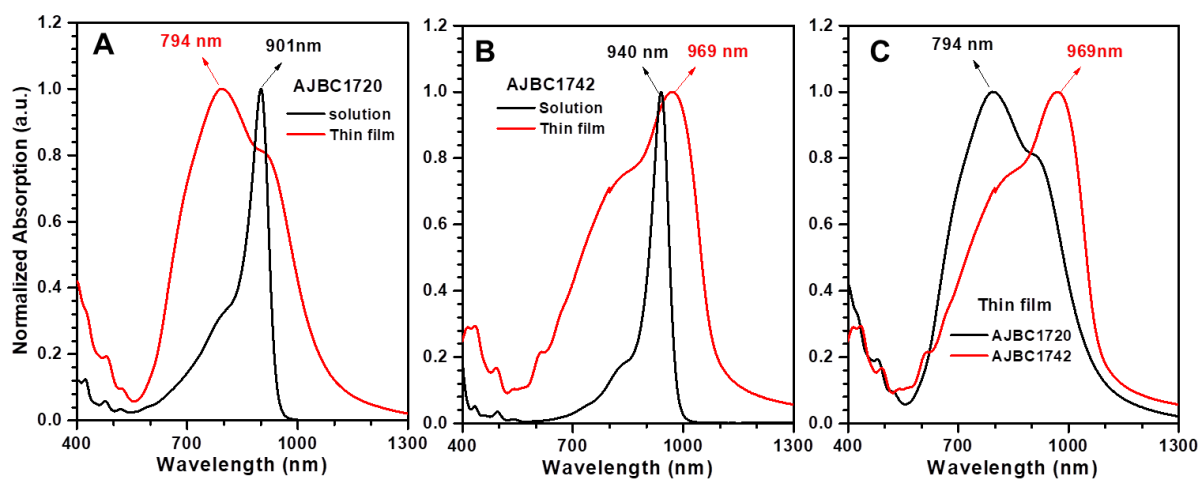


Figure S7. Absorption spectra of AJBC1720 and AJBC1742 in mixed DCM/methanol solutions (30/1, v/v) and thin films.

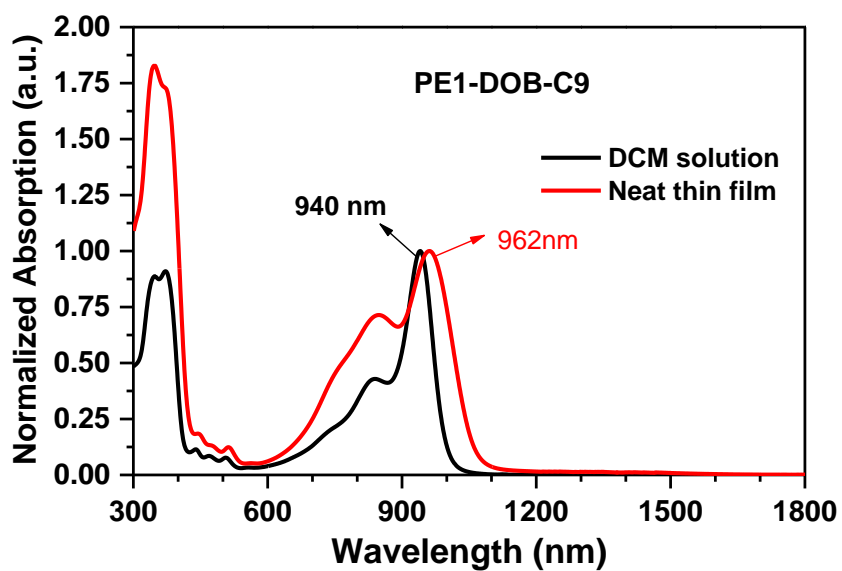


Figure S8. A: The absorption spectra of PE1-DOB-C9 in DCM solution and as a neat thin film.

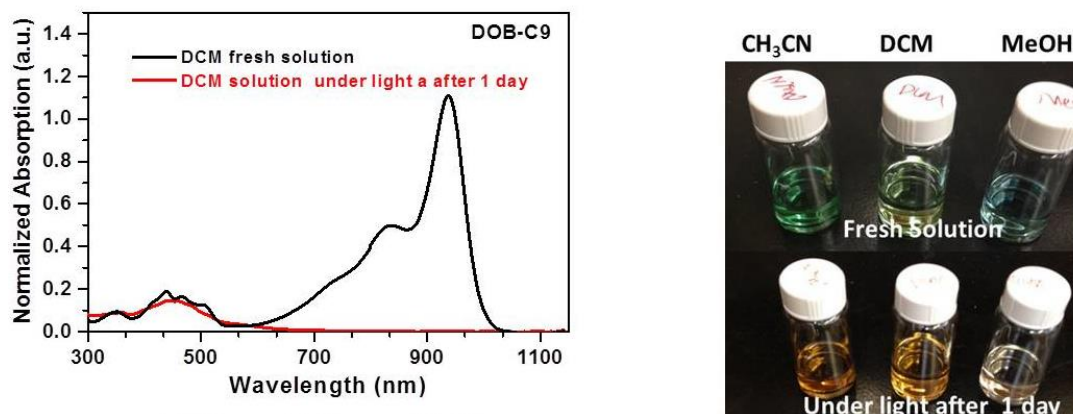


Figure S9. Left: The absorption spectra (left) and photographs (right) of **DOB-C9** in DCM solutions with and without exposure to light for 1 day.

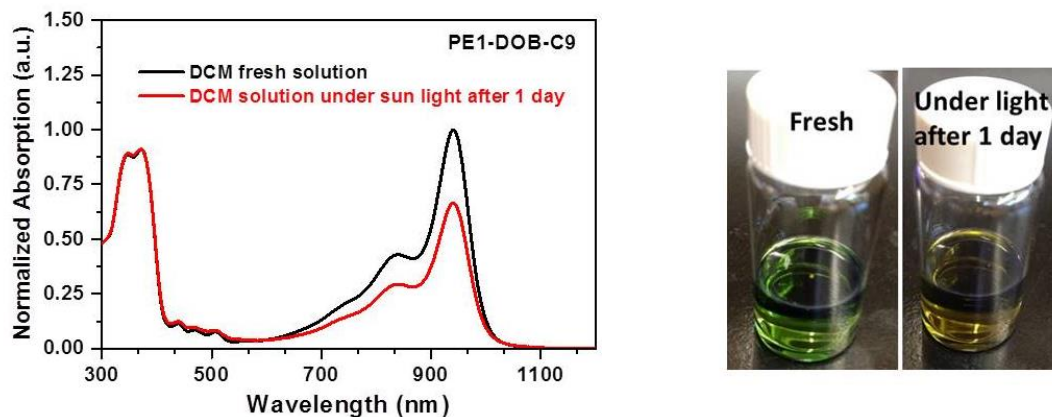


Figure S10. Left: The absorption spectra (left) and photographs (right) of **PE1-DOB-C9** in DCM solutions with and without exposure to light for 1 day.

S5. Third-order NLO properties characterization method and data

The recently developed dual-arm (DA) Z-scan technique has been used to study low concentration solutions, in which the small signal of interest, i.e. n_2 and α_2 from the solute, can be extracted from the large solvent background signals.¹⁰ In DA Z-scan, two arms containing the solution and solvent are concurrently scanned with precisely equalized irradiance distributions and sample Z-positions. Thus the subtraction of the signals from the two arms eliminates the solvent background, allowing direct determination of solute nonlinearities. The signal-to-noise ratio for the DA Z-scans is significantly

improved over that for a single-arm Z-scan (unless there is an identical reference arm), as the correlated beam noise sources (i.e. energy, pulsewidth, beam pointing fluctuations, etc.) are suppressed in real time. The DA Z-Scan was first calibrated by scanning the fused silica simultaneously in both the arms to obtain a flat resultant differential Z-Scan trace. The focal spot size and the pulse durations are estimated by performing Z-Scans of GaAs (open aperture) and fused silica (closed aperture) as reference samples at 1.3 μm and 1.55 μm . Based on the same methodology, the nonlinear signal of a thin film can be distinguished from that of the substrate it was deposited by simultaneously scanning a film-coated substrate and a blank substrate of identical thickness. However, in thin film measurements, large low-energy background signals are observed due to film inhomogeneities, which have to be subtracted to obtain corrected Z-scan signals.

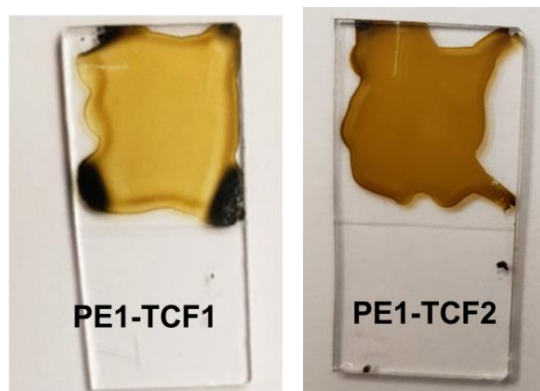


Figure S11. Photos of **PE1-TCF1** and **PE1-TCF2** films onto 1 mm thick quartz substrates.

PE1-TCF1 and **PE1-TCF2** are measured in both solutions and thin films, where the solution samples are in 1 mm optical pathlength quartz cuvettes, and the thin films are coated on 1 mm thick quartz substrates (**Figure S11**). DA Z-scans at wavelengths of 1.3 μm and 1.55 μm use the beams generated from an optical parametric amplifier (Light Conversion, TOPAS-C) pumped by a Ti:sapphire amplified laser system (Clark-MXR, CPA 2010) producing ~ 1 mJ, ~ 140 fs (FWHM) pulses at a repetition rate of 1 kHz. A 1 mm quartz cuvette filled with dichloromethane (Sigma-Aldrich, 650463, 99.9%) and a 1 mm thick blank quartz substrate is used in the reference arm for solution and thin film measurements, respectively. **PE1-DOB-C9** coated on a 1 mm thick quartz substrate is measured at 1.55 μm , which is

generated from another optical parametric amplifier (TOPAS-HE) pumped using ~ 10 mJ, ~ 35 fs (FWHM) pulses at a 1 kHz repetition rate from a Ti:Sapphire amplified laser system (Coherent, Legend Elite Duo HE+).

Figure S12 gives an example of a DA Z-scan signal of a $1.4\ \mu\text{m}$ thick **PE1-DOB-C9** neat film at a wavelength of $1.55\ \mu\text{m}$ after substrate and low-energy background subtractions, including open-aperture (OA), closed-aperture (CA), and their division (CA/OA). The minimum beam waist w_0 and pulsewidth τ are determined by OA and CA Z-scans of well-studied reference materials to determine each, respectively. Thus, OA Z-scans of GaAs and CA Z-scans of fused silica gave $w_0 = 28\ \mu\text{m}$ ($\text{HW1/e}^2\text{ M}$) and $\tau = 70$ fs (FWHM). The three OA scans taken at different pulse energies in **Figure S12** (a) are fit using $\alpha_2 = (4.8 \pm 1)\ \text{cm/GW}$, and the fit of CA and CA/OA signal in **Figure S12** (b) corresponds to $n_2 = -(310 \pm 60) \times 10^{-15}\ \text{cm}^2/\text{W}$. As stated in the main text, by using Eqns. (1-4) found in our previous work,⁸ the real and imaginary components of $\chi^{(3)}$ and γ are calculated from the measured quantities n_2 and α_2 , respectively, which is how the values in **Table 3** and **Table S2** are formulated.

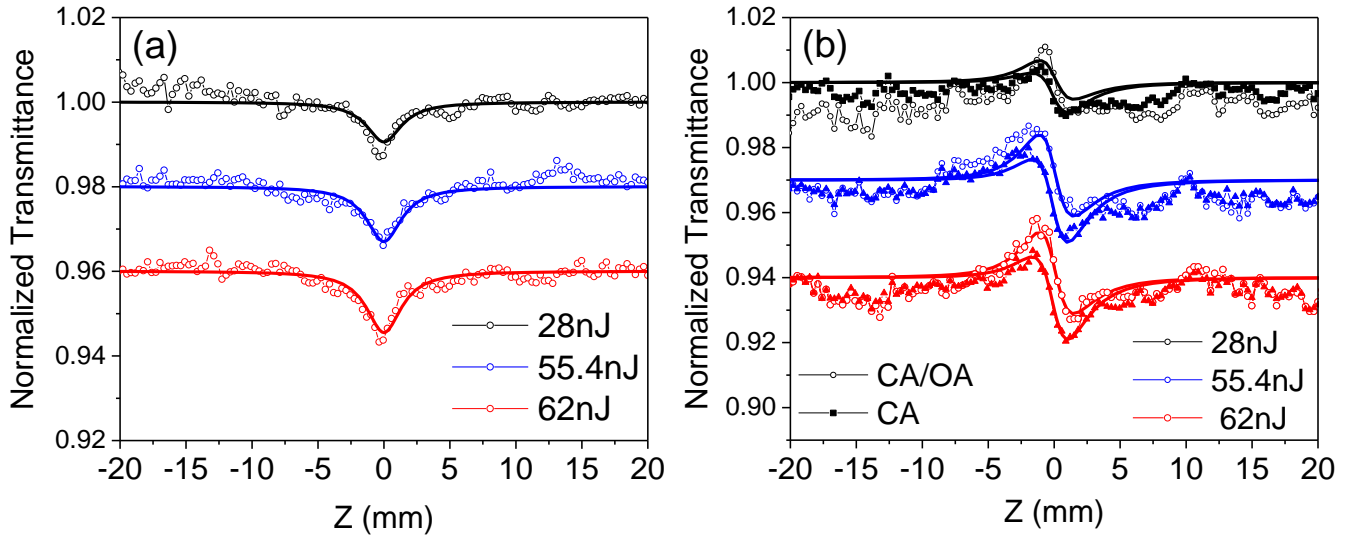


Figure S12. a: OA dual-arm (DA) Z-scans of a $1.4\ \mu\text{m}$ thick **PE1-DOB-C9** neat film using three different pulse energies each offset for clarity; b: CA DA Z-scans along with the divided result of the CA signal by the OA signal with three different pulse energy measurements (each offset for clarity) at a wavelength of $1.55\ \mu\text{m}$. The solid lines in (a) and (b) are theoretical fit using the Z-scan theory.¹⁰

Table S1. The Comparison of $|\text{Re}\chi^{(3)}|$ values in various materials.

no.	$ \text{Re}\chi^{(3)} $ (10^{-11} esu)	
	1.3 μm	1.5 μm
GaAs ^a	0.59	2.9
Silicon (110) ^b	0.81	1.3
As ₂ Se ₃ ^c	N/A	1.1
PE1-TCF1	1.6	2.8
PE1-TCF2	N/A	15.5

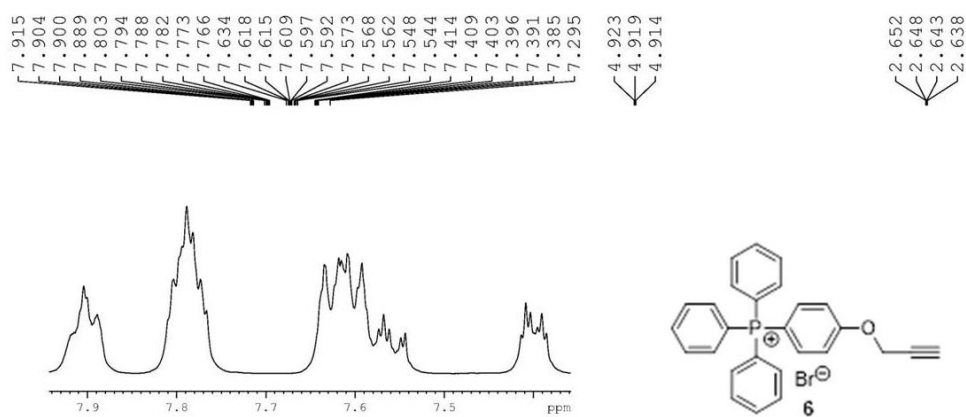
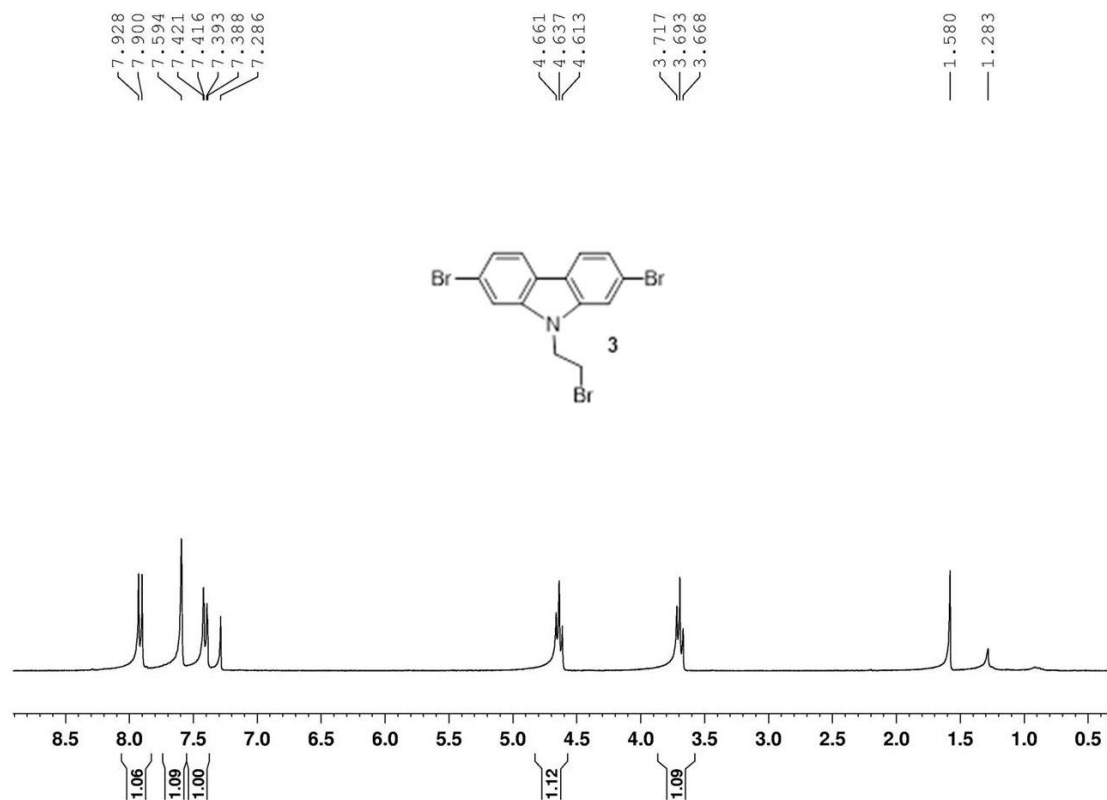
^a Values obtained and measured by Z-scan technique with bulk sample by CREOL authors; ^b From Reference 11, and actual measurements taken at 1274 nm and 1540 nm; ^c From Reference 12.

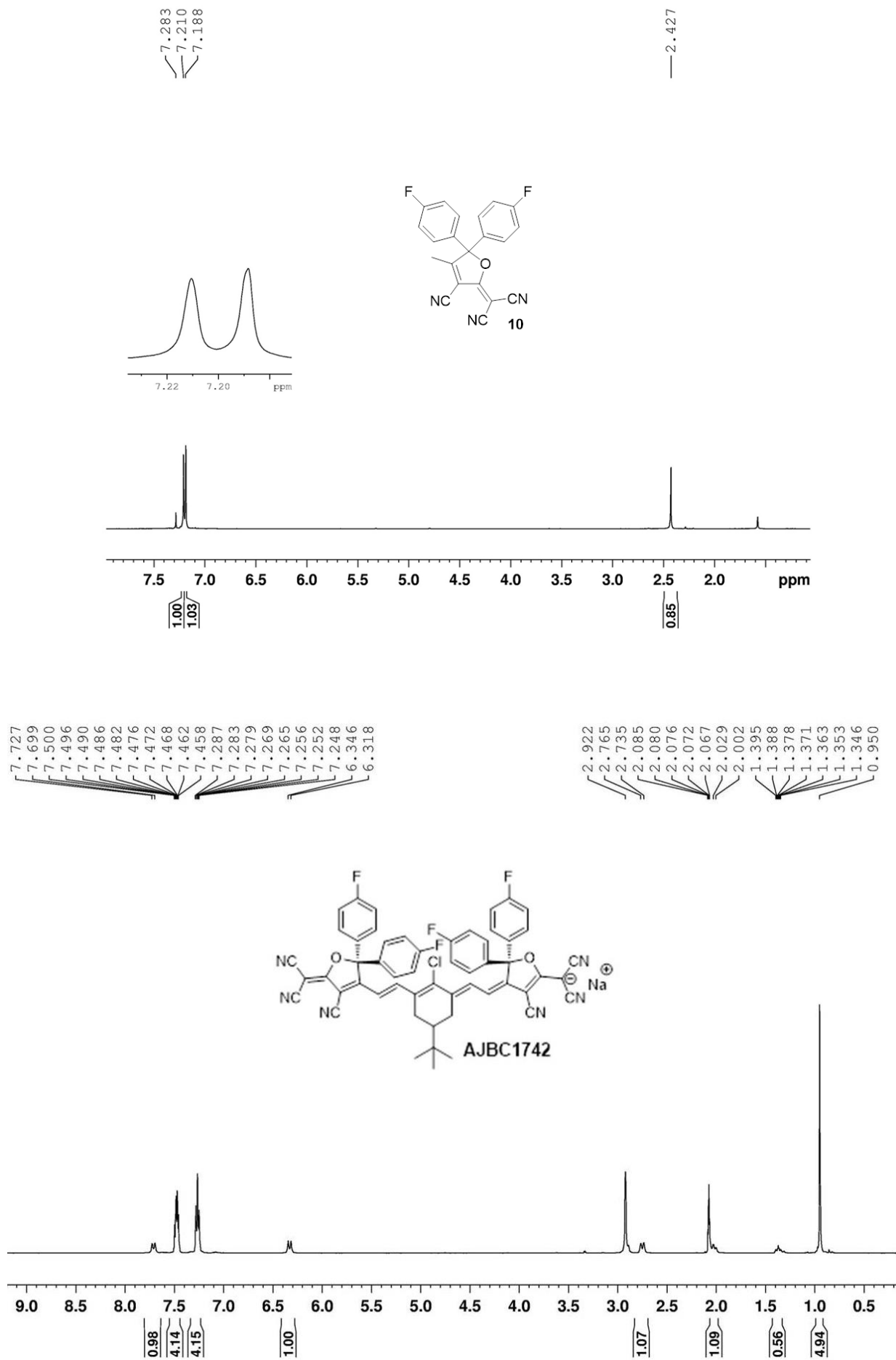
Table S2. The extrapolated γ values based on measured $\chi^{(3)}$ values at 1.3 and 1.55 μm .

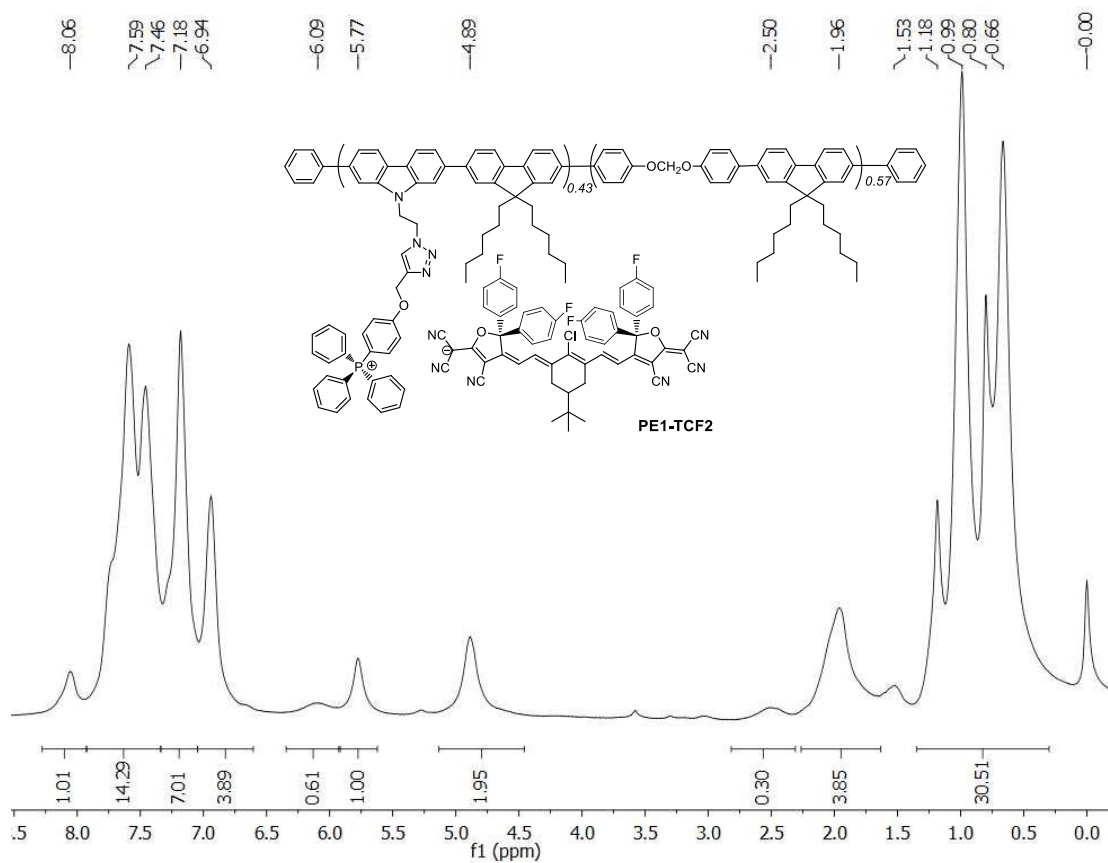
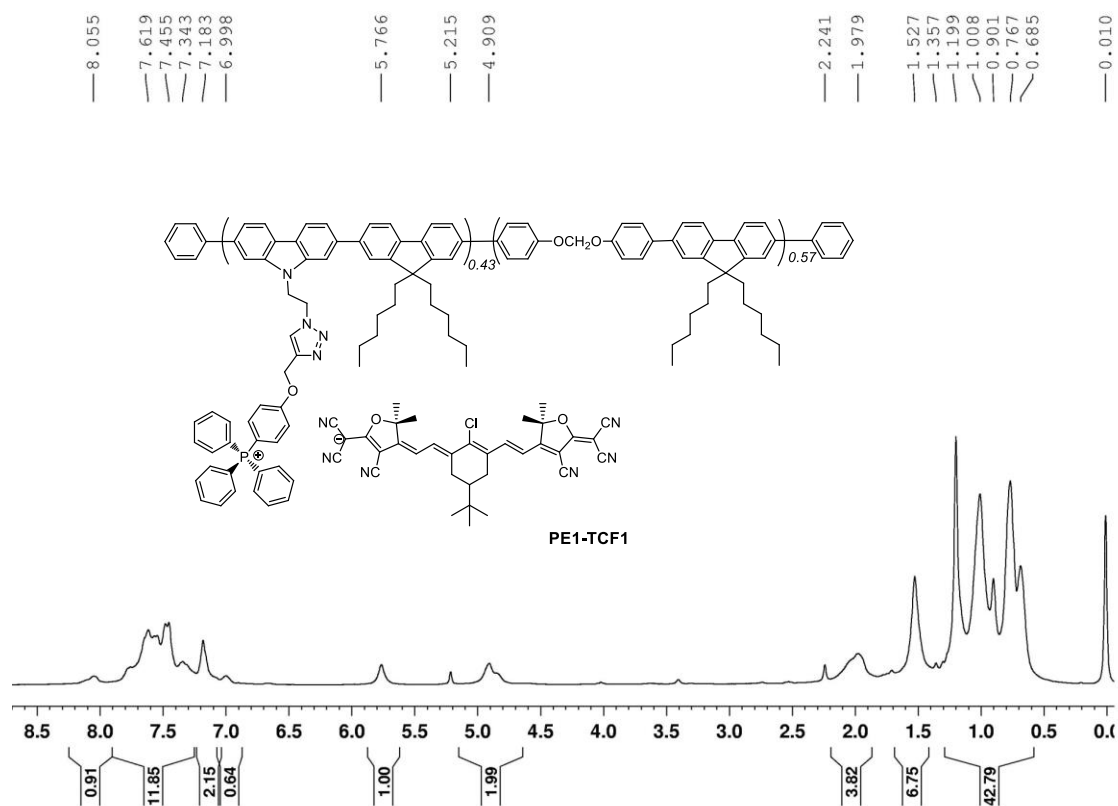
Sample (Thickness)	Wavelength (μm)	Cal. $\text{Re}(\gamma)$ (10^{-33} esu) ^a	Cal. $\text{Im}(\gamma)$ (10^{-33} esu) ^a
PE1-TCF1 (1.14 μm)	1.3	-4.3	0.21
	1.55	-7.9	0.86
PE1-TCF2 (2.3 μm)	1.55	-51	6.9

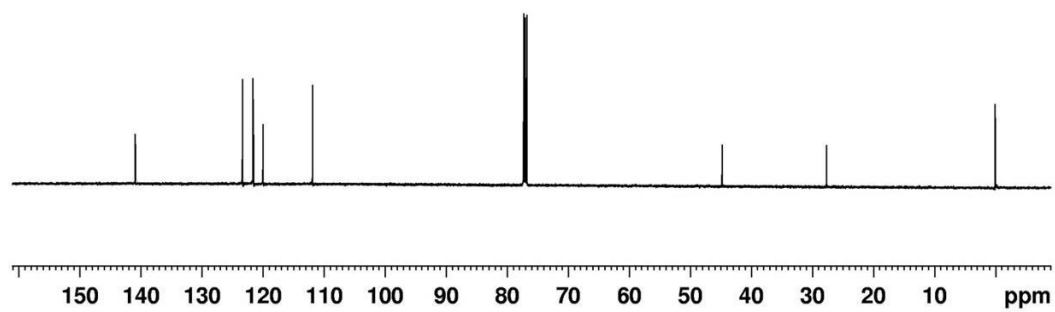
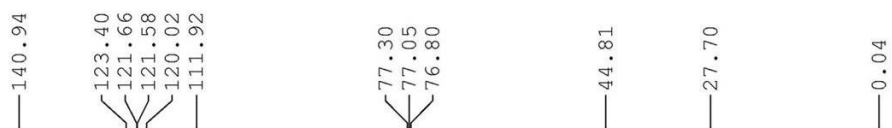
^a Extrapolated neat values were determined using equation of $\chi_{esu}^{(3)} = \epsilon_0^{-1} N f^{(3)} \gamma_{esu}$,¹³ where ϵ_0 is the vacuum permittivity, N is the number density of molecules, and $f^{(3)}$ is the third-order local field correction defined as $(n_0^2 + 2)^4/81$, where n_0 is the linear refractive index. The values of $\chi^{(3)}$ were taken from **Table 3**.

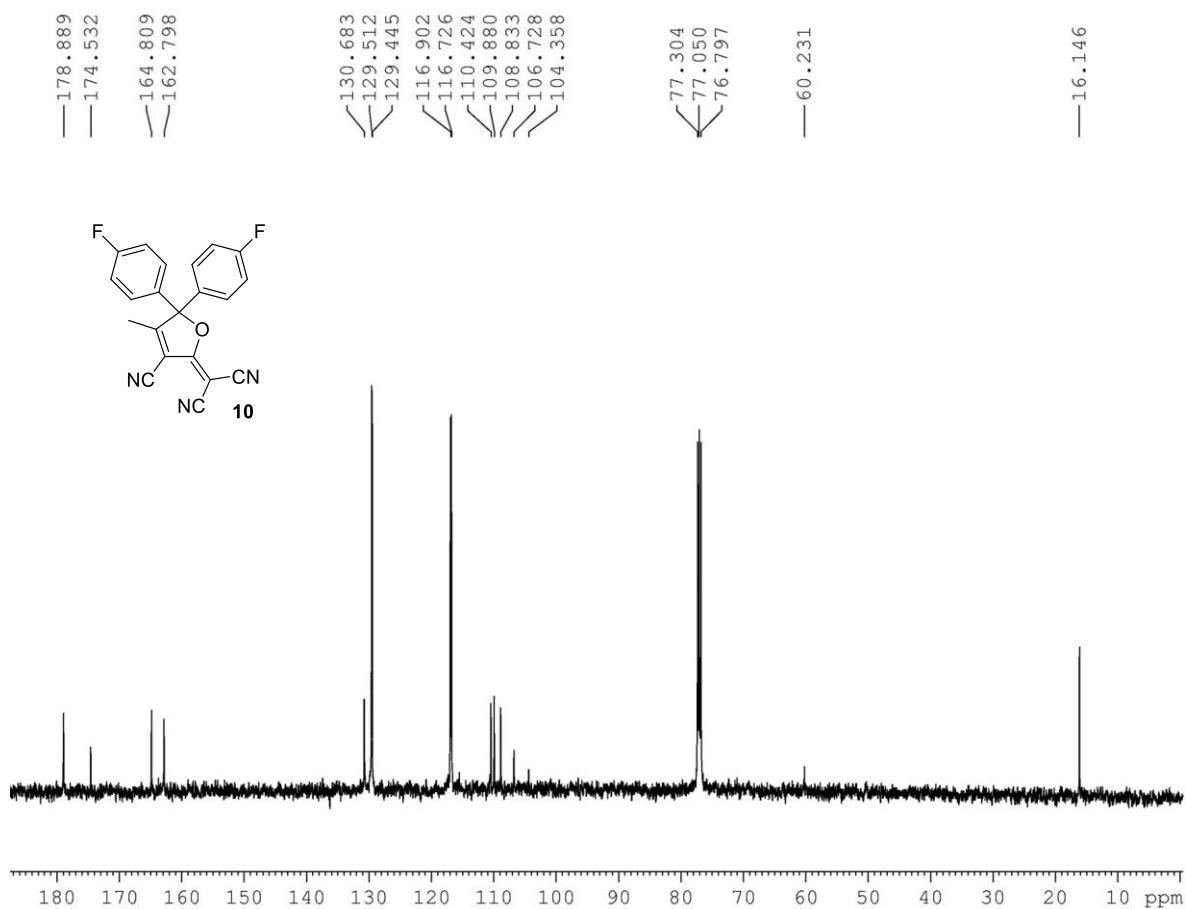
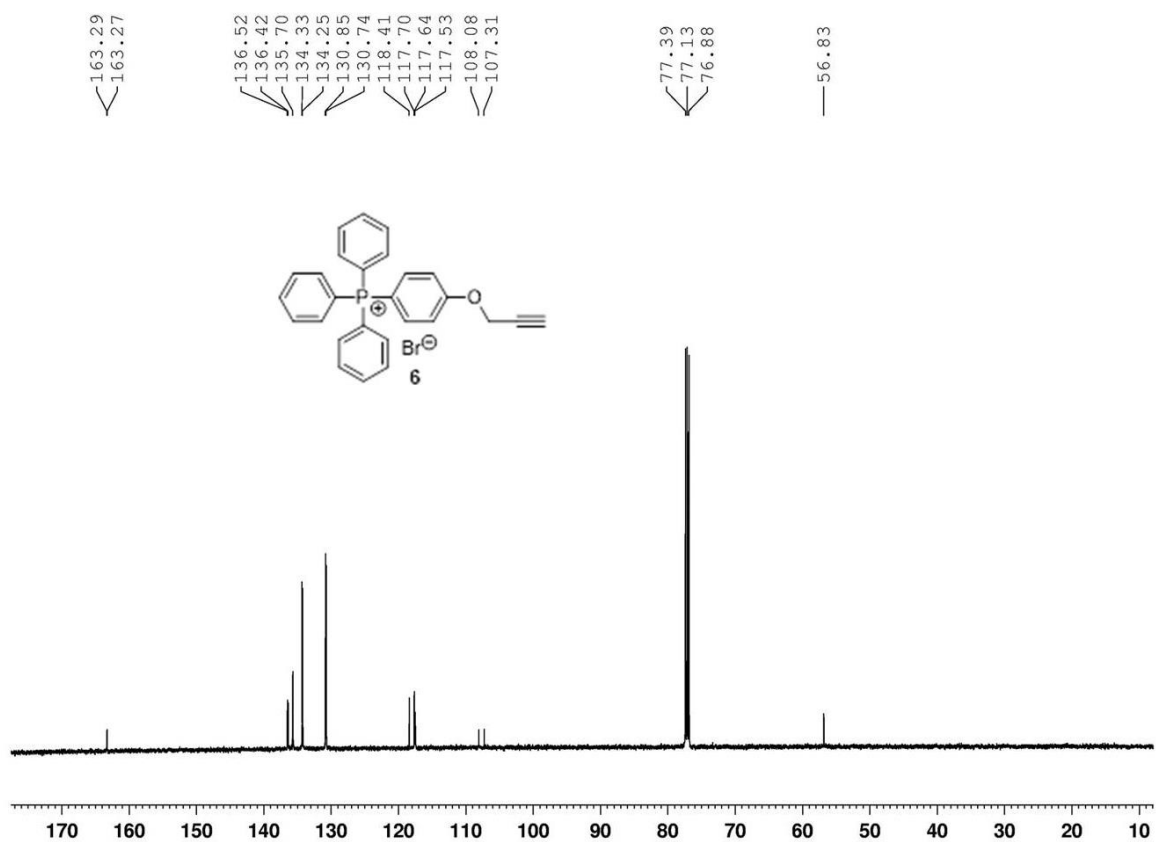
S6. NMR spectra

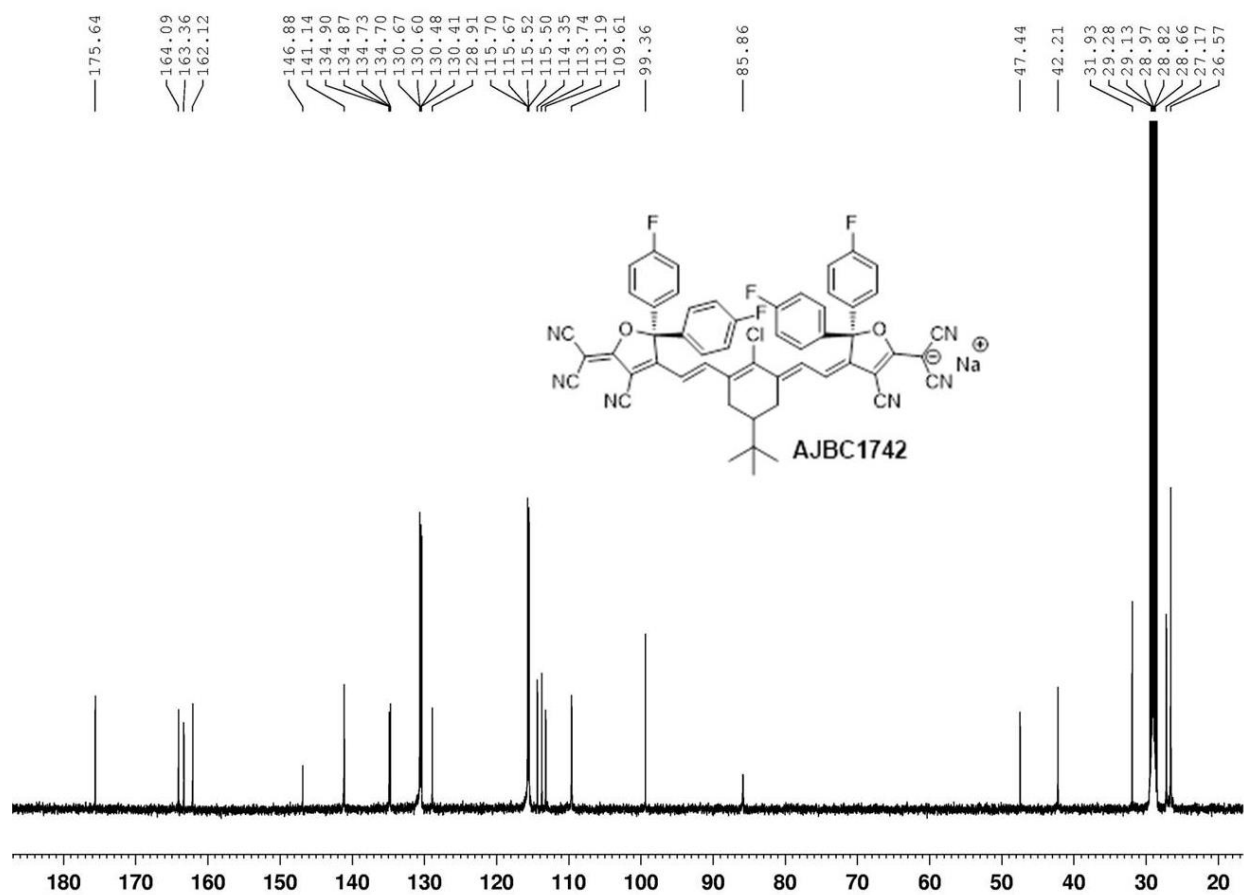


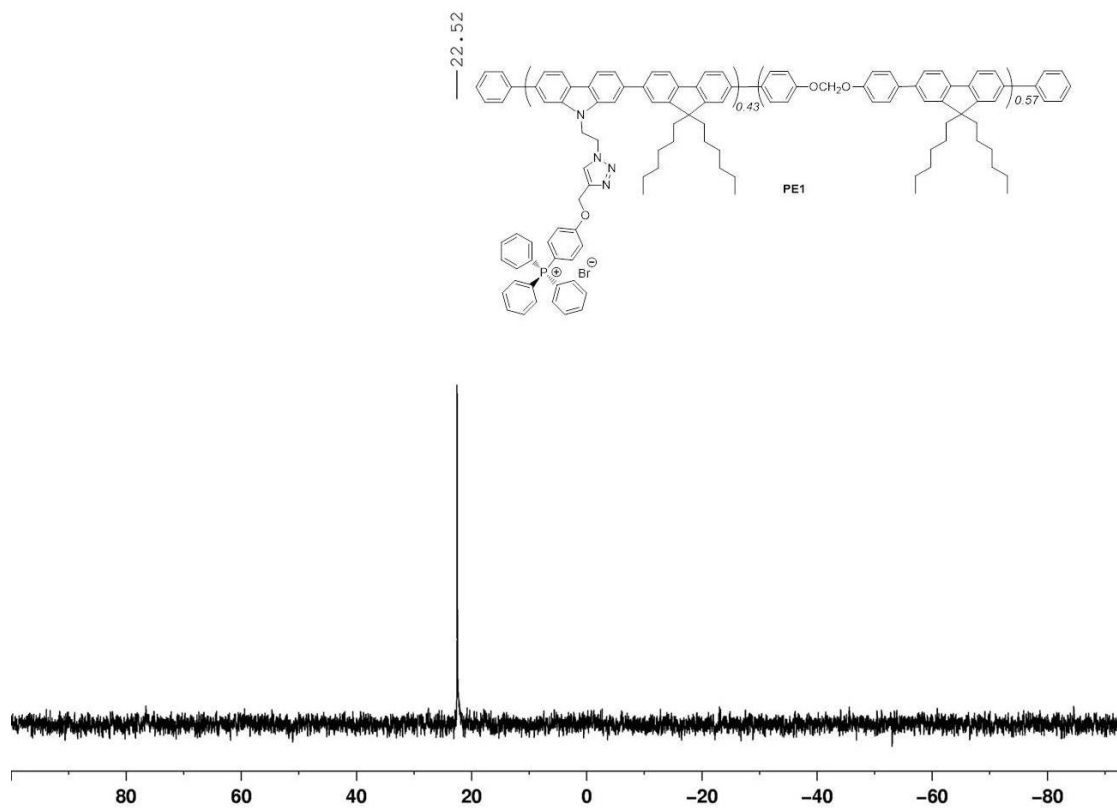
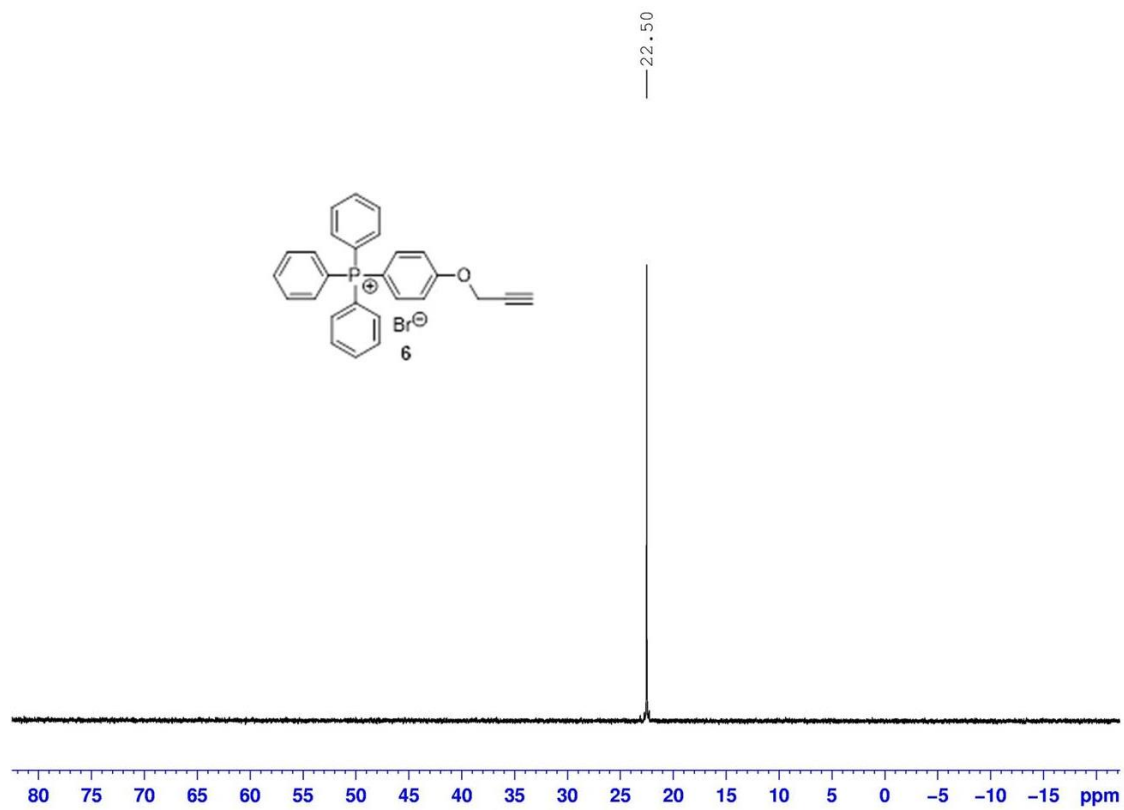












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