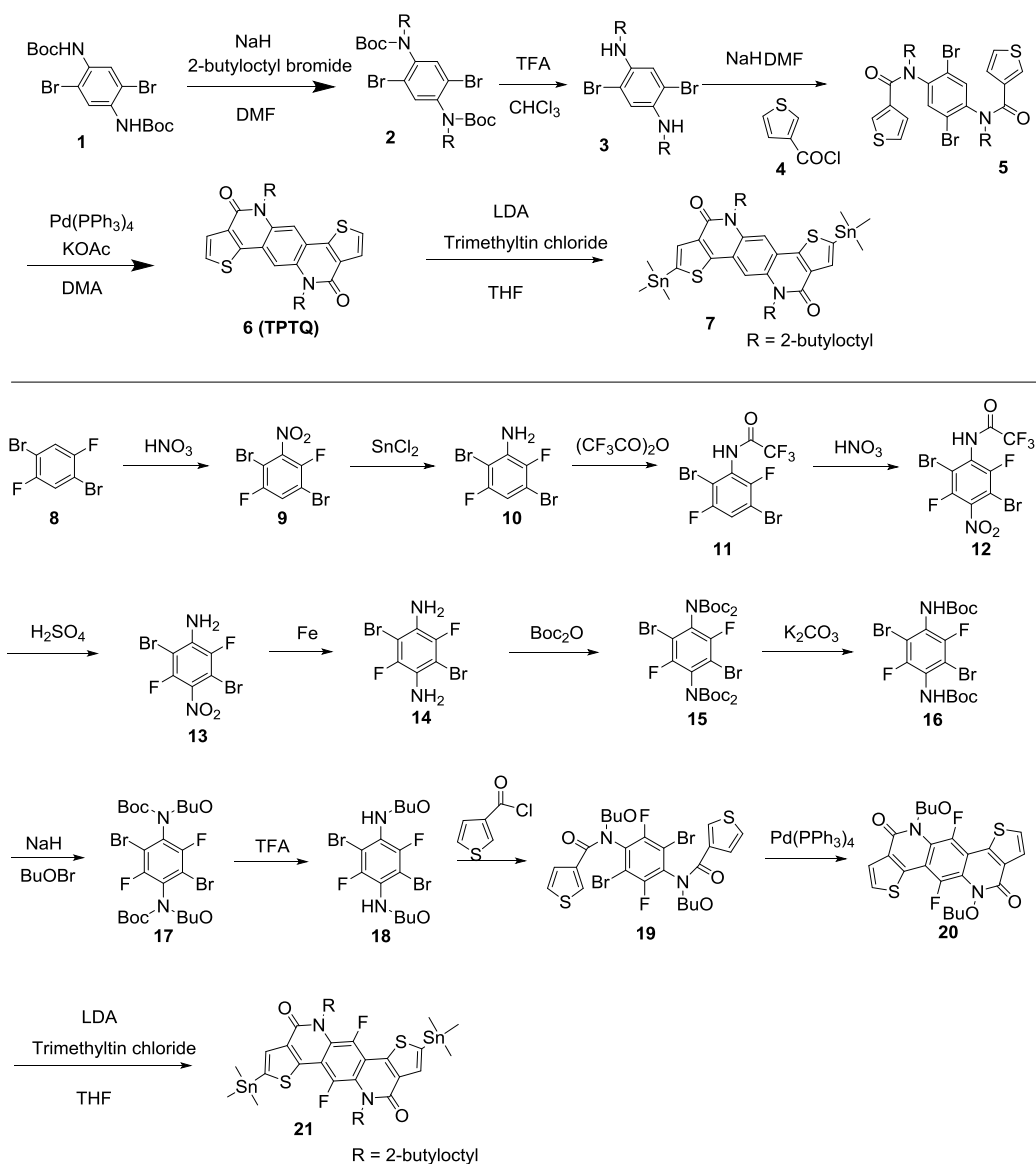


Supporting Information

Development and structure/property relationship of new electron accepting polymers based on thieno[2',3':4,5]pyrido[2,3-g]thieno[3,2-c]quinoline-4,10-dione for all-polymer solar cells

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Scheme S1. Synthesis of new monomers

Compound **2**: Sodium hydride (1.2 g, 30.0 mmol, 60 % dispersion in mineral oil) was suspended in dry DMF (30 ml). Compound **1** (4.66 g, 10.0 mmol) dissolved in DMF (50 ml) was added dropwise to the suspension of sodium hydride at 0°C. After 30 min, 2-butyloctyl bromide (7.5 g, 30.0 mmol) was slowly added to the mixture and the mixture was stirred at room temperature overnight. The mixture was poured into water (100 mL) and extracted with dichloromethane. The organic layer was washed three times with water and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (hexane: ethyl acetate = 30: 1 v/v) and dried

under vacuum to give product (6.2 g, 78%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.40 (s, 2H), 3.65 (s, 2H), 3.22 (s, 2H), 1.72 (m, 2H), 1.33 (s, 18H), 1.26 (m, 32H), 0.88 (m, 12H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 154.35, 149.03, 131.04, 128.95, 84.1, 53.42, 36.93, 31.95, 29.88, 28.57, 28.18, 26.33, 24.83, 23.23, 22.84, 14.25, 14.21. MS (MALDI-TOF) m/z 802.52 (M^+), calcd 802.80.

Compound 5: Compound **2** (5.6 g, 7.0 mmol) was dissolved in a mixture of CHCl_3 and TFA (30 ml, 1:2 v/v) and stirred at room temperature overnight. After extraction with dichloromethane, the organic layer was washed three times with water and dried over magnesium sulfate. After removal of the solvent under reduced pressure, the compound **3** was used directly for next step. A solution of thiophene-3-carboxylic acid (2.3 g, 17.9 mmol) in thionyl chloride (20 ml) was refluxed for 6 hours. The solvent was removed by reduced pressure to yield an acid chloride compound **4** as a yellow solid. After the acid chloride **4** was dissolved in dry DMF (20 mL), it was slowly added dropwise into a mixture of compound **3** and NaH (0.72 g, 17.9 mmol, 60 % dispersion in mineral oil) in dry DMF (30 mL) at 0 °C. The mixture was stirred at room temperature for 24 hours and poured into water (50 ml). The mixture was extracted with dichloromethane and washed three times with water. After drying over magnesium sulfate, the residue was purified by column chromatography on silica gel (hexane: ethyl acetate = 15: 1 v/v) and dried under vacuum to give product (2.9 g, 51 %). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.44 (d, 2H, $J = 2.8$ Hz), 7.13 (s, 2H), 7.04 (s&d, 4H), 4.09 (m, 2H), 3.37 (m, 2H), 1.56 (m, 2H), 1.23 (m, 32H), 0.86 (m, 12H). MS (MALDI-TOF) m/z 822.21 (M^+), calcd 822.84

Compound 12: compound **12** was synthesized by a similar method with compound **5**.
Compound 10 was synthesized by the Boc deprotection of compound **9** (5.6 g, 7.0 mmol) and thiophene-3-carbonyl chloride was synthesized from thiophene-3-carboxylic acid (2.3 g, 17.9

mmol). To a solution of NaH (0.72 g, 17.9 mmol) and compound **10** was added thiophene-3-carbonyl chloride. The crude product was purified by column chromatography on silica gel (hexane: ethyl acetate = 15: 1 v/v) to give a white solid (2.9 g, 51 %). ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 7.44 (d, 2H, J = 2.8 Hz), 7.13 (s, 2H), 7.04 (s&d, 4H), 4.09 (m, 2H), 3.37 (m, 2H), 1.56 (m, 2H), 1.23 (m, 32H), 0.86 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 164.83, 142.96, 136.59, 135.42, 128.54, 127.93, 125.02, 122.77, 53.11, 36.50, 31.90, 31.26, 30.94 29.70. 28.56, 26.38, 23.02, 23.00, 14.25. MS (MALDI-TOF) *m/z* 822.21 (M⁺), calcd 822.84

Compound **6**: A solution of compound **5** (2.0 g, 2.4 mmol), Pd(PPh₃)₄ (115 mg, 0.1 mmol), and AcOK (70 mg, 7.2 mmol) in anhydrous DMA (150 mL) was degassed for 30 min using nitrogen gas and then stirred at 120 °C for 4 h. The mixture was extracted with dichloromethane and dried over magnesium sulfate. After solvent was evaporated under reduced pressure, the residue was chromatographed on a silica gel column with hexane/ethyl acetate (15:1 v/v) as eluent and recrystallized from dichloromethane/methanol to give a yellow product **6** (1.3g, 80%).

¹H-NMR (400 MHz, CDCl₃): δ (ppm) 7.76 (d, 2H, J = 5.2 Hz), 7.74 (s, 2H), 7.43 (d, 2H, J = 5.6 Hz), 4.40 (br, 4H), 2.02 (m, 2H), 1.24-1.34 (m, 32H), 0.82-0.91 (m, 12H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 158.81, 144.41, 132.31, 131.91, 127.52, 125.65, 119.43, 110.27, 46.16, 37.06, 31.96, 31.71, 29.89, 29.39, 27.17, 23.31, 22.77, 14.28, 14.22. MS (MALDI-TOF) *m/z* 661.41 (M⁺), calcd 661.01.

Compound **7**: LDA was prepared by adding *n*-BuLi (1.5 mL, 3.75 mmol, 2.5 M in hexanes) to a solution of diisopropylamine (0.40 g, 3.95 mmol) in 10 mL of THF, at -78 °C. The solution was stirred 30 min at 0 °C and then cooled again to -78 °C. The LDA was added dropwise to a solution of compound **6** (1.0 g, 1.51 mmol) in THF (250 mL) at -78 °C. The mixture was stirred at -78 °C for 2 hours and then 7.5 ml of trimethyltin chloride (1 M in hexanes) was

added dropwise. The reaction was allowed to warm to room temperature and stirred for 16 hours. The mixture was poured into water (200 mL) and extracted with diethyl ether. The organic layer was washed three times with water and dried over magnesium sulfate. After drying solvent, the residue was purified by recrystallization from isopropyl alcohol to give a yellow product **7** (1.0 g, 67%).

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.85 (s, 2H), 7.81 (s, 2H), 4.42 (br, 4H), 2.02 (m, 2H), 1.27-1.54 (m, 32H), 0.90 (m, 12H), 0.46 (s, 18H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 159.23, 149.51, 140.20, 135.44, 132.83, 131.98, 119.39, 110.71, 46.06, 37.18, 32.14, 32.07, 31.87, 29.95, 29.65, 27.39, 23.38, 22.80, 14.40, 14.24, -8.00. MS (MALDI-TOF) m/z 986.30 (M^+), calcd 986.63.

1,4-dibromo-2,5-difluoro-3-nitrobenzene (**9**): To a solution of 1,4-dibromo-2,5-difluorobenzene **8** (50g, 184mmol) in 100ml conc. H_2SO_4 , fuming nitric acid (19ml) was added drop wise through addition funnel. The mixture was stirred overnight. After the reaction is done, the mixture was poured onto ice, extracted with ethyl acetate. After evaporation of solvent, the brown oil (39.33g, 124mmol, 67% yield) was carried on to next step without purification. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.552 (1H, m)

2,5-dibromo-3,6-difluoroaniline (**10**): 1,4-dibromo-2,5-difluoro-3-nitrobenzene **9** (83g, 260mmol) and SnCl_2 (200g, 1050mmol) were stirred in 1740ml ethanol and 440ml conc. hydrochloric acid. The mixture was heated at 85°C overnight. After removal of ethanol by evaporation, mixture was neutralized by conc. potassium carbonate solution, and then extracted by ethyl acetate. Organic layer was washed by water. Compound **10** (48g, 167mmol, 64% yield) was carried on to next step without purification.

N-(2,5-dibromo-3,6-difluorophenyl)-2,2,2-trifluoroacetamide (11): 2,5-dibromo-3,6-difluoroaniline **10** (30g, 104mmol) was dissolved in 1.5L chloroform, then 90mL trifluoroacetic anhydride was added drop wise at room temperature. The reaction was stirred at room temperature overnight, neutralized with saturated NaHCO₃ solution, extracted with dichloromethane. The organic layer was washed water twice. After removal of solvent, the brown solid was further purified by column chromatography with hexane/dichloromethane=3/2. Compound **4** was obtained as white solid (22g, 55%).

N-(2,5-dibromo-3,6-difluoro-4-nitrophenyl)-2,2,2-trifluoroacetamide (12): Compound **11** was prepared with similar condition of (9). The crude product was further purified by column chromatography (hexane/dichloromethane=3/1). Pure **12** was obtained as white solid (36%).
¹H-NMR (400 MHz, CDCl₃): δ (ppm) 8.21(s, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 155.17, 154.77, 152.94, 150.39, 149.37, 146.80, 125.22, 125.05, 116.69, 113.83, 110.51, 110.29, 103.33, 103.06

2,5-dibromo-3,6-difluoro-4-nitroaniline (13)

To 0.21g(0.5mmol) of compound **12**, 5ml water and 1.5ml conc. H₂SO₄ was added. The reaction was heated to reflux for 3h. After cool down to room temperature, aqueous KOH solution then K₂CO₃ solution was added to adjust pH to 8. The mixture was then extracted with ethyl acetate. Organic layer was washed with water. Crude **13** (0.16g, 98%) was obtained as yellow oil after evaporation of solvent. ¹H-NMR (400 MHz, DMSO): δ (ppm) 3.66 (2H, s), ¹³C-NMR (100 MHz, DMSO): δ (ppm) 152.35, 149.86, 144.97, 142.58, 141.77, 141.60, 128.20, 103.47, 103.22, 94.99, 94.75

2,5-dibromo-3,6-difluorobenzene-1,4-diamine (14): Compound **14** was prepared with similar condition of (10). Crude product was further purified by recrystallization from hexane. **14** was white, needle like crystal (yield: 62%). ¹H-NMR (400 MHz, DMSO): δ (ppm) 3.64 (s, 4H),

^{13}C -NMR (100 MHz, DMSO): δ (ppm) 146.43, 144.10, 126.67, 126.52, 97.98, 97.70
m/z=301.91 found 302.69.

2,5-dibromo-3,6-difluoro-N,N,N',N'-tetra-(tert-butoxycarbonyl)-p-phenylenediamine (15):
Compound **14** (130mg, 0.43mmol), Boc_2O (563mg, 2.58mmol) and DMAP (1.5mg, 3%mol)
was dissolved in 3ml THF. The mixture was refluxed for 2.5h then cooled back to rt. After
rotovapting the solvent, solid mixture was purified by column chromatography (hexane/ethyl
acetate=6/1) to yield **15** (162mg, 53%) as a white solid. ^1H -NMR (400 MHz, CDCl_3): δ (ppm)
1.376(s, 12H), ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 153.077, 151.094, 148.658, 128.472,
110.507, 84.162, 27.812 M/z=702, found 725.1(+ Na^+)

2,5-dibromo-3,6-difluoro- N,N'-di-(tert-butoxycarbonyl)-p-phenylenediamine (16)

A suspension of **15** (5.1g, 7.26mmol) and K_2CO_3 (6g, 43.6mmol) in methanol was refluxed
overnight. After cooled to room temperature, the mixture was extracted with dichloromethane.
Organic layer was washed by water, dried over sodium sulfate. After removing the solvent,
the crude solid was recrystallized from hexane. Pure product obtained as white powder (3.15g,
86%). ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 9.226(2H, s), 1.471 (18H, s), ^{13}C -NMR (100
MHz, CDCl_3): δ (ppm) 153.529, 153.335, 151.583, 125.482, 111.093, 80.520, 28.4654
m/z=638.55 found 638.84

2,5-dibromo-3,6-difluoro-N,N'-dibutyloctyl-N,N'-di-(tert-butoxycarbonyl)-p-

phenylenediamine (17): A suspension of sodium hydride (0.96g, 60%, 24mmol) in anhydrous
DMF 200ml was cooled to 0°C. Compound **16** (3.0g, 6mmol) suspended in another 20ml
DMF was added drop wise to sodium hydride suspension at 0°C. After addition, the
suspension was warmed up to room temperature and stirred for 1 hour. The suspension was
then cooled to 0°C again, butyloctyl bromide was added drop wise. After addition, the
reaction was left to warm back to room temperature, and stirred overnight. After reaction is

done, the mixture is cooled to 0°C, water was added slowly to quench excess sodium hydride. The mixture was extracted by dichloromethane. The organic layer was washed with water, then dried over sodium sulfate. After removing the solvent, the crude product was purified by column chromatography (hexane/ethyl acetate=24/1) to yield **17** as a colorless oil (4.0g, 80%).
¹H-NMR (400 MHz, CDCl₃): δ (ppm) 3.322-3.621 (4H, m) 1.249-1.592 (52H, m) 0.842-0.870 (12H, m), ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 154.32, 153.42, 151.85, 130.49, 111.12, 80.96, 52.42, 52.17, 37.68, 37.53, 31.73, 31.43, 31.29, 31.07, 30.94, 29.66, 29.62, 28.72, 28.48, 27.86, 27.83, 26.53, 26.26, 26.23, 23.01, 22.98, 22.63, 14.06, 14.05
m/z=838.78 found 727.844 losing 2 t-Bu groups

2,5-dibromo-3,6-difluoro-N,N'-di-butyloctyl -p-phenylenediamine (**18**): Solution of **17** (4g, 4.8mmol) in dichloromethane was cooled to 0°C. 15ml of trifluoroacetic acid was added drop wise. The reaction was then warmed up to room temperature then stirred overnight. The mixture was then poured into 500ml water, extracted with dichloromethane. The organic layer was washed with saturated NaHCO₃ solution then water, dried over Na₂SO₄. After removing the solvent, crude product was purified by column chromatography (hexane/dichloromethane=5/1) to yield clear oil **18** (2.5g, 82%yield). ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 3.608(s, 1H) 3.140 (d, 2H) 1.524 (s, 1H) 1.271(s, 16H) 0.886(m, 6H), ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 147.87, 145.48, 128.73, 102.43, 50.82, 38.57, 31.87, 31.72, 29.68, 28.80, 26.55, 23.06, 22.66, 14.10. m/z=638.55 found 639.26

2,5-dibromo-3,6-difluoro-N,N'-di-butyloctyl-N,N'-di-(thiophene-3-carbonyl) -p-phenylenediamine (**19**): Compound **18** (2.5g, 3.9mmol) and N,N-diisopropylethylamine (5.4ml, 31.2mmol) was dissolved in 15ml dichloromethane. The solution was stirred at room temperature for 40min, and then cooled to 0C. A solution of thiophene-3-carbonyl chloride (3.0g, 23.4mmol) in 6ml dichloromethane was added drop wise at 0C. After addition, reaction

was warmed up to room temperature and stirred overnight. Reaction was poured into water and extracted with dichloromethane. Organic layer was washed with water twice, dried with Na₂SO₄. After evaporated solvent, crude product was purified by column chromatography (hexane/ethyl acetate=40/3). Product 19 was obtained as pale yellow oil (1.2g, 36%). Also, the mono-carbonyl product was isolated (1.8g, 61%). ¹H rotamers 2/1 ratio. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 7.233(0.33H, dd, J₁=2.8, J₂=1.2) 7.157(0.67H, dd, J₁=4.8, J₂=3.2) 7.083(0.33H, dd, J₁=5.2, J₂=1.2) 7.058(0.67H, dd, J₁=3.2, J₂=1.2) 7.016(0.67H, dd, J₁=5.2, J₂=1.2) 6.979(0.33H, d, J=4.8) 4.11-4.13, 3.33-3.45(m, 4H) 1.16-1.59(34H, m) 0.82-0.906(12H, m), ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 165.54, 165.33, 154.45, 151.96, 136.05, 135.90, 132.31, 132.13, 127.19, 127.08, 126.77, 125.45, 125.20, 111.76, 111.58, 52.28, 51.91, 37.26, 37.24, 31.94, 31.86, 31.71, 31.65, 31.50, 31.31, 29.60, 29.53, 29.50, 28.94, 28.76, 28.56, 26.76, 26.53, 26.35, 22.85, 22.95, 14.02. m/z=858.82 found 858.81

FTPTQ (20): Anhydrous DMAc was bubbled with nitrogen gas for 2 hours before reaction. To a round bottom flask, 12 (1.0g, 1.16mmol), KOAc (342mg, 3.48mmol) and Pd(PPh₃)₄ (134mg, 0.12mmol) were added. Then 100ml degased DMAc was added. The mixture was further bubbled with nitrogen for 1 hour before heated at 80C for 1.5h. After cooled to room temperature, the mixture was poured into water, extracted with dichloromethane. The organic layer was washed with water, and then dried over Na₂SO₄. After evaporating the solvent, product was purified by column chromatography (hexane/ethyl acetate=10/1). Product 20 was obtained as yellow powder (0.44g, 54%). ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 7.820 (2H, d, J=5.2) 7.594(2H, d, J=5.6) 4.625(4H, s) 1.885 (2H, s) 1.180-1.245(32H, m) 0.826(12H, m), ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 158.86, 142.63, 140.20, 137.47, 132.01, 128.68, 126.41, 120.78, 110.67, 48.78, 37.81, 31.77, 31.26, 31.00, 29.65, 28.63, 26.39, 23.03, 22.61, 14.08, 14.05
m/z=697.0 found 697.201

FTPTQ-ditin (21): Compound 21 is synthesized with the same procedure as compound 6.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.900(2H,s) 4.625(4H,s) 1.183-1.889(34H,m) 0.808-0.824(12H,m) 0.490(18H, s), $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 159.28, 143.36, 142.83, 142.66, 140.33, 134.16, 132.74, 120.32, 110.69, 48.63, 37.70, 31.81, 29.60, 28.72, 26.45, 23.01, 22.58, 14.10, -8.14. $m/z = 1022.29$ found 1022.395

Synthesis of Polymer

PQP: A mixture of compound **7** (0.120 g, 0.121 mmol), dibromo perylene diimide (PDI) (0.148 g, 0.121 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (7 mg, 5 mol%), tetrakis(triphenylphosphine)palladium, was dissolved in 2 ml of toluene/DMF (4:1 v/v). The mixture was degassed for 30 min and then heated at 120 °C for 24 h. After cooling to room temperature, the mixture was added to methanol. The precipitate was dissolved in chloroform and filtered with Celite to remove the metal catalyst. The polymer fibers were washed by Soxhlet extraction with methanol, acetone and chloroform. The final polymer was obtained after reprecipitation with methanol, yielding 175 mg (83%). $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.84 (s, 2H), 8.44 (m, 4H), 8.06 (s, 2H), 7.77 (m, 2H), 4.49 (br, 4H), 4.14 (br, 4H), 2.07 (m, 4H), 1.27 (m, 112H), 0.86 (br, 12H), 0.73 (br, 12H). Anal. calcd. for $[\text{C}_{112}\text{H}_{158}\text{N}_4\text{O}_6\text{S}_2]_n$: C, 78.18; H, 9.26; N, 3.26; O, 5.58; S, 3.73. Found: C, 77.30; H, 9.54; N, 3.18.

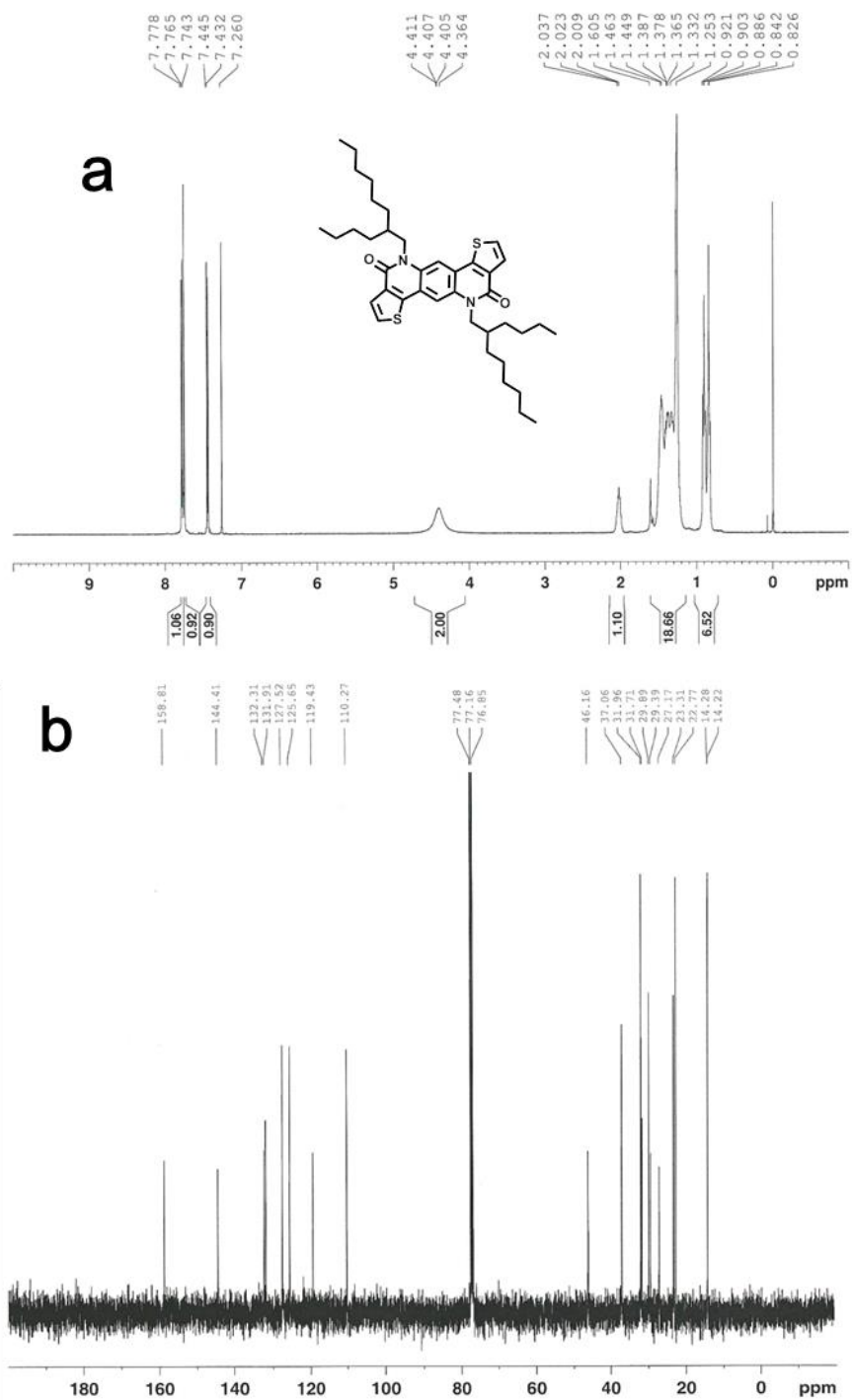


Figure S1. (a) ^1H NMR and (b) ^{13}C NMR of Compound **6**

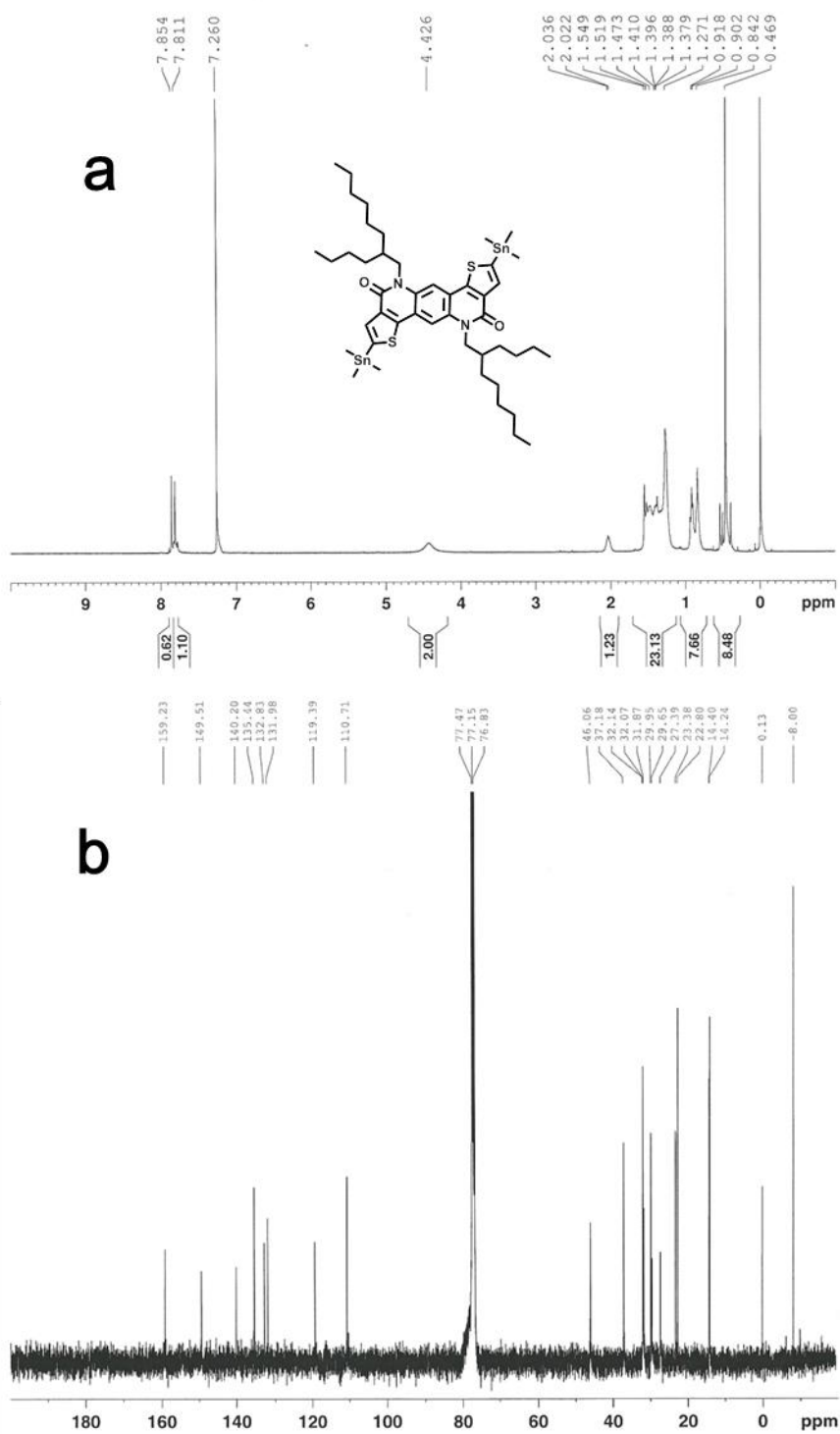


Figure S2. (a) ^1H NMR and (b) ^{13}C NMR of Compound 7

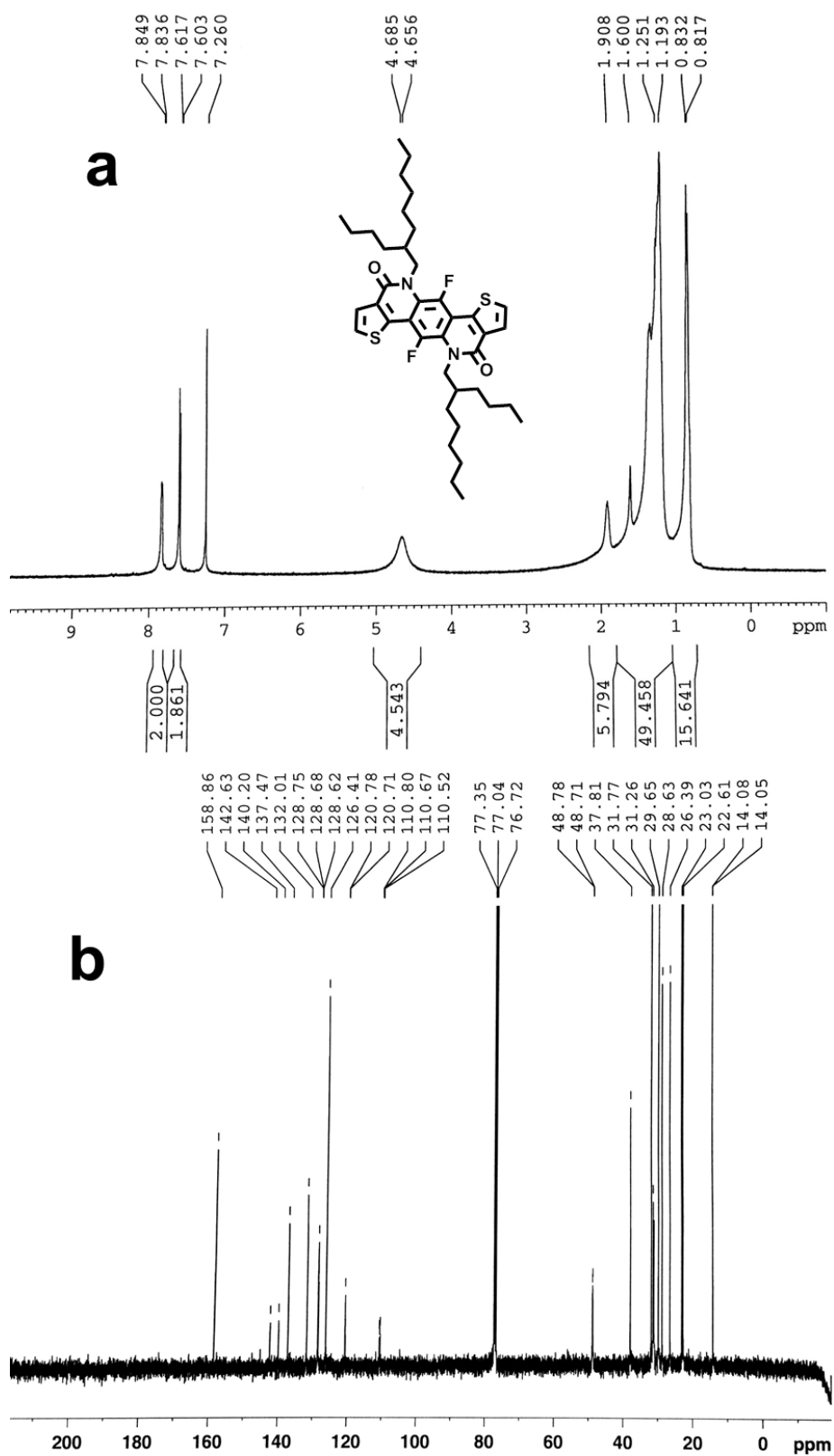
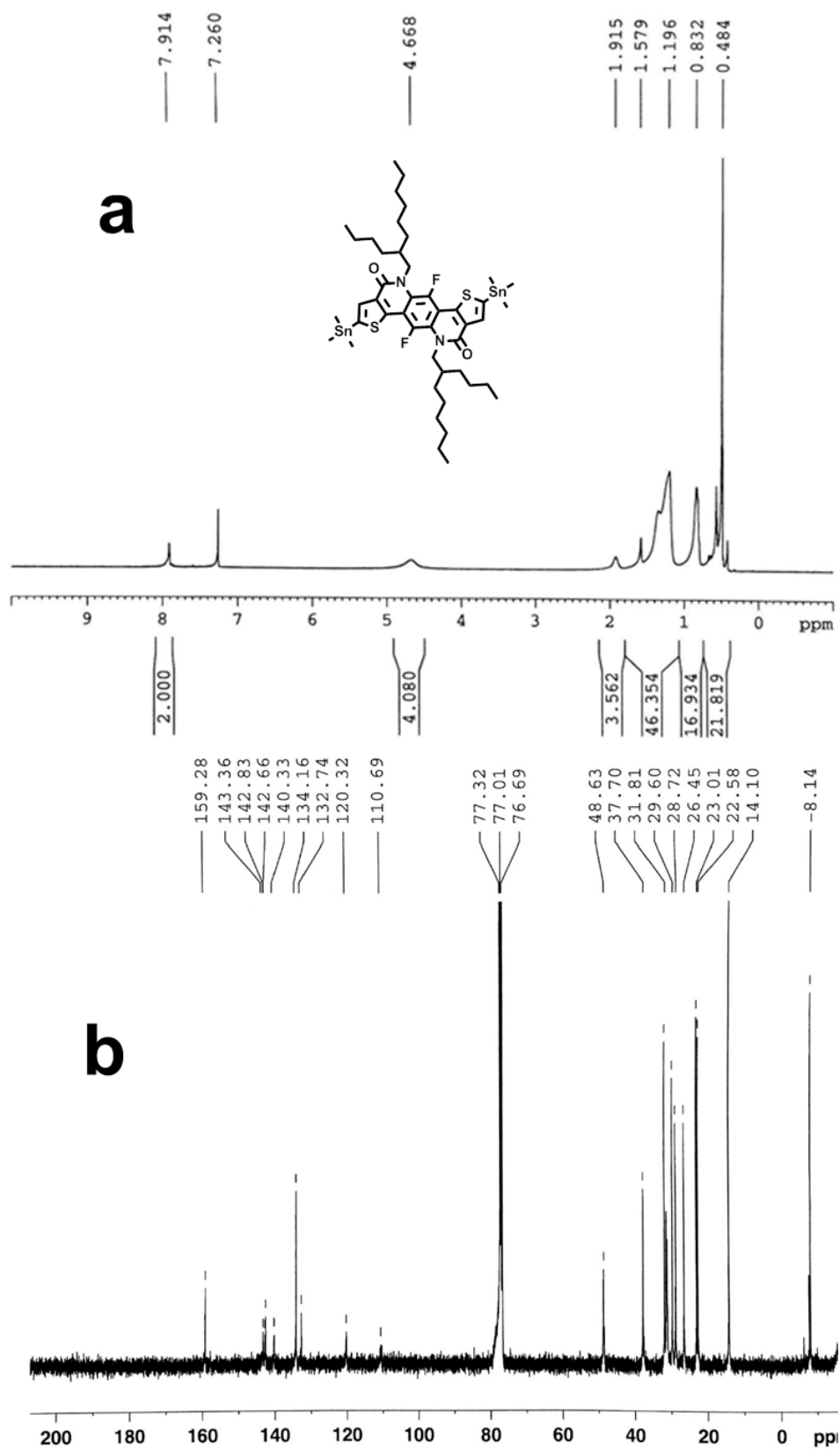


Figure S3. (a) ^1H NMR and (b) ^{13}C NMR of Compound **20**



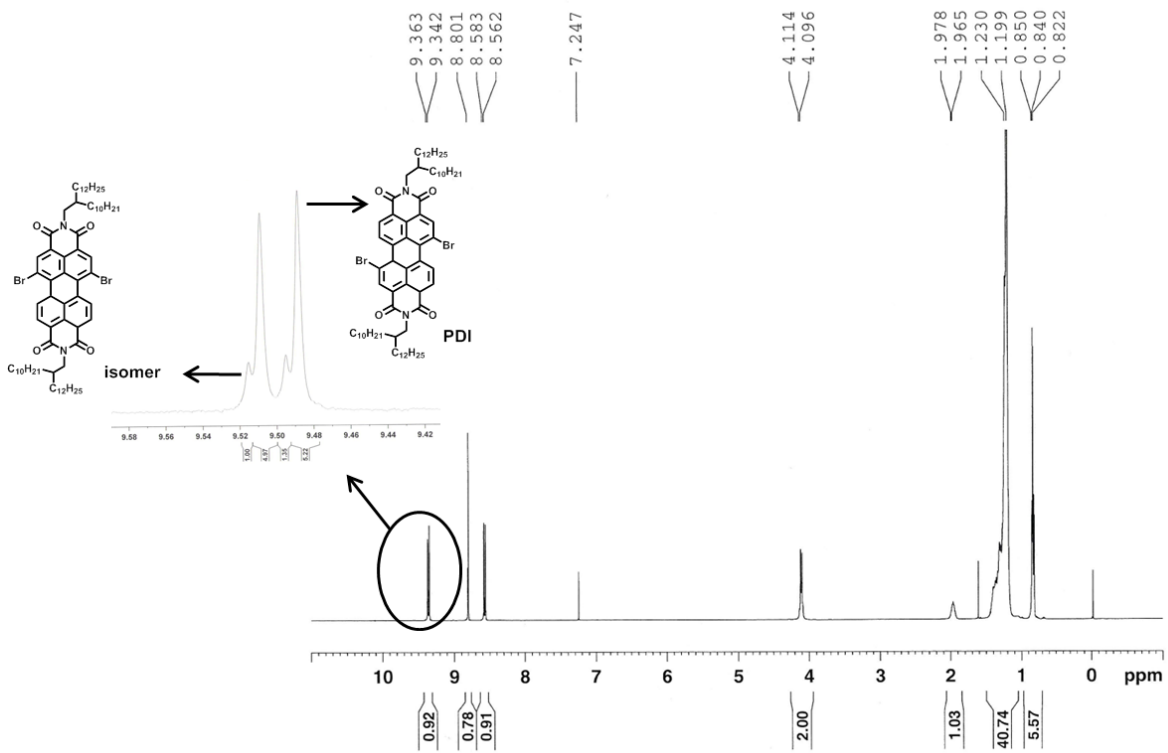


Figure S5. Two isomers of PDI dibromide monomer

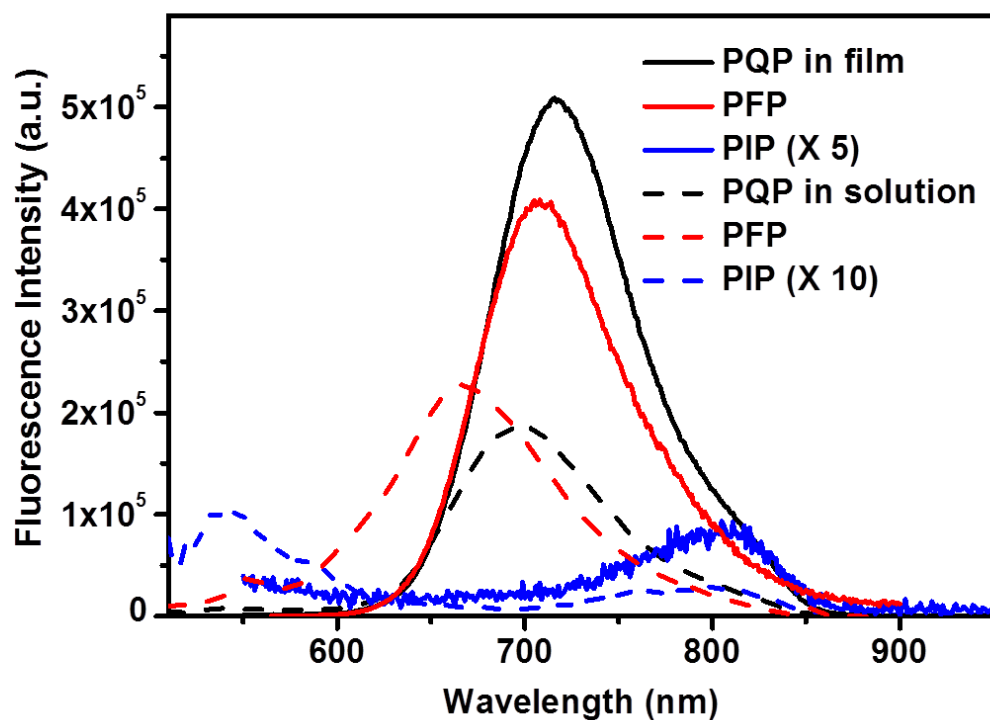


Figure S6. fluorescence spectra of the polymers excited at 507 nm for **PIP** and 509 nm for **PQP** and **PFP** in CF solution after the absorption intensity in chloroform solution was adjusted as 0.04, and in film after spin-coating from chloroform solution (1.0 w%) by 1500 rpm

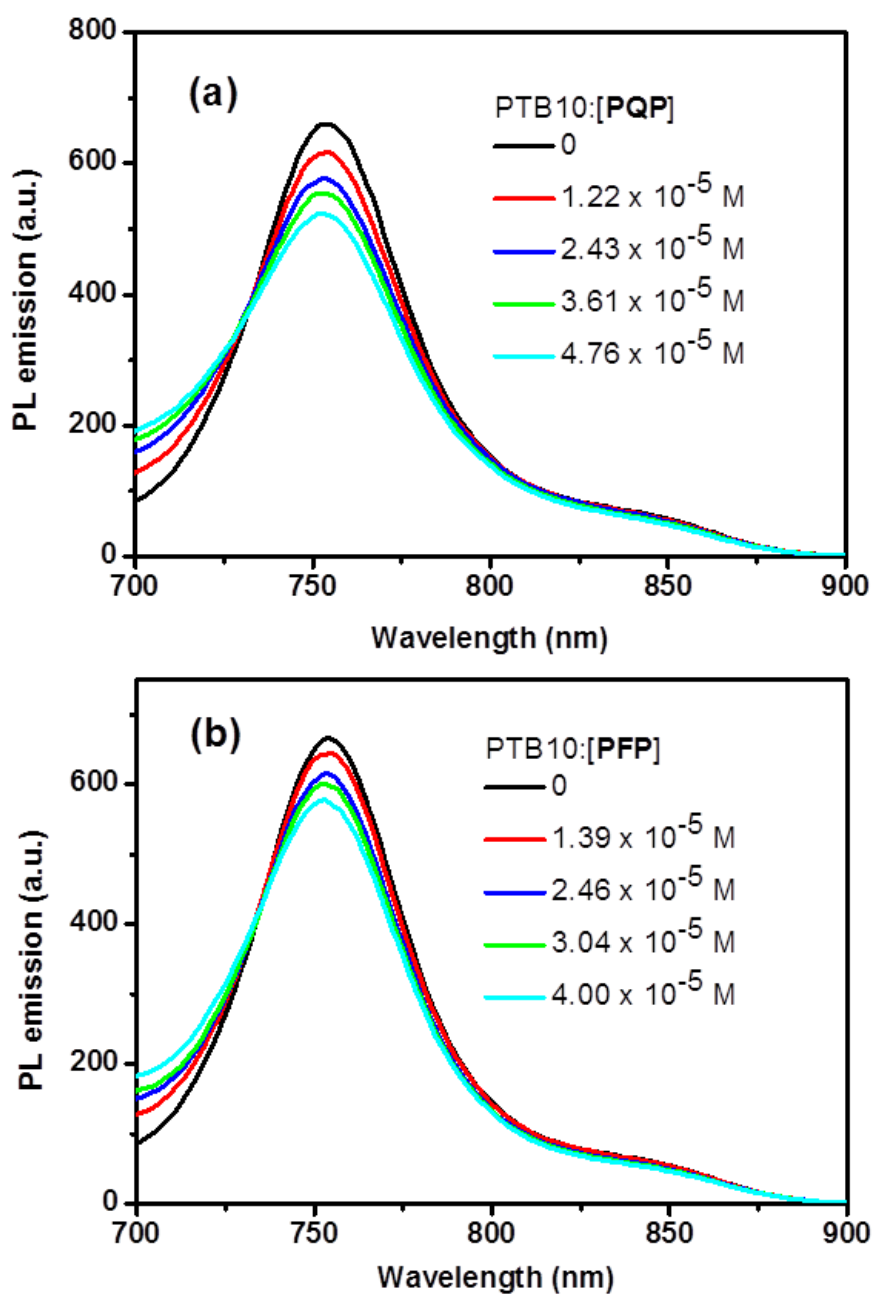


Figure S7. PL quenching of (a) PTB7-Th:PQP and (b) PTB7-Th:PFP in blend solution (1,2-dichlorobenzene) with increasing molar concentration of electron acceptors.

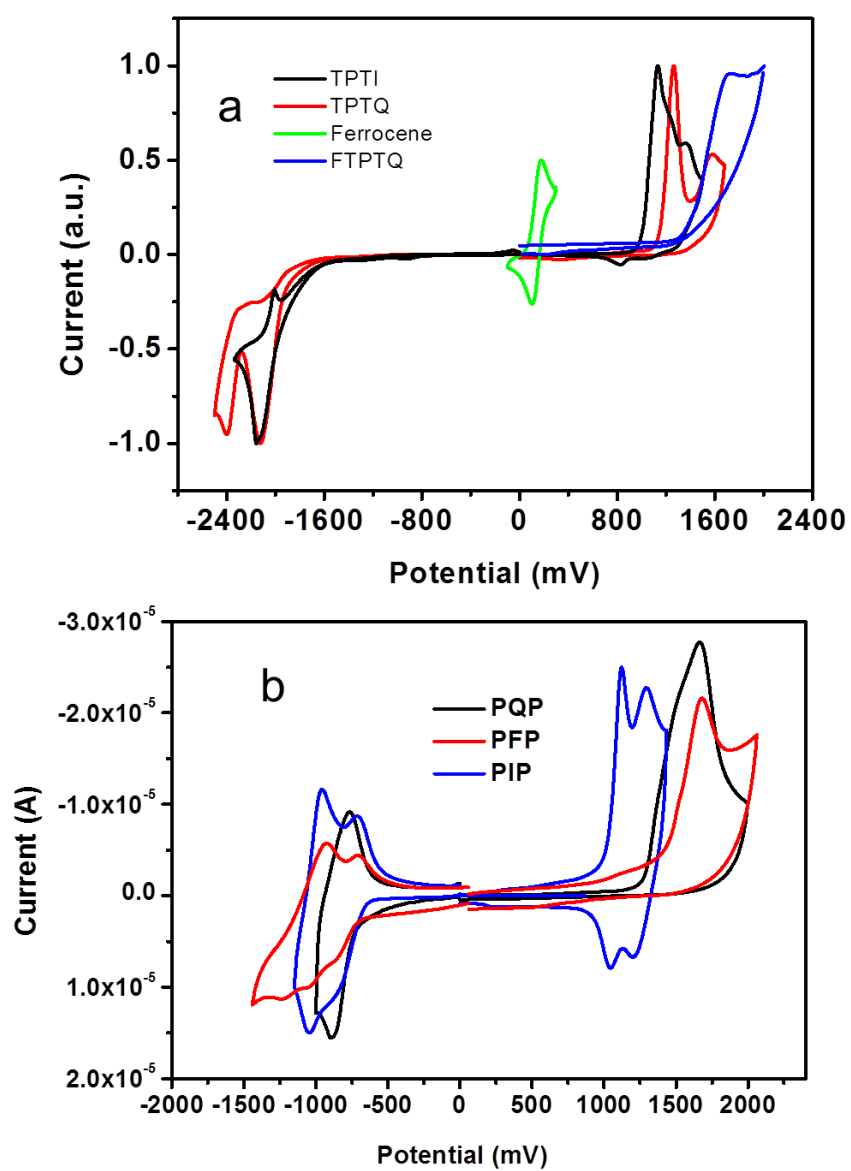


Figure S8. Cyclic voltammograms of the electron accepting (a) monomers and (b) polymers

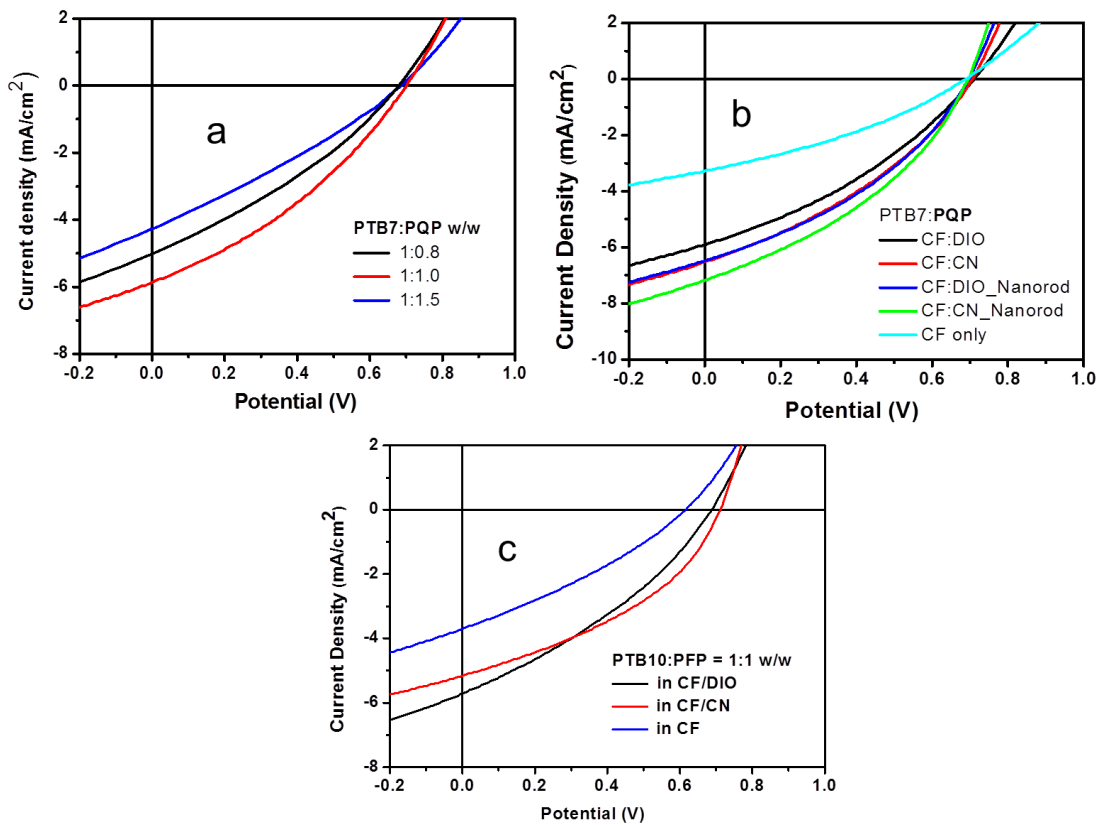


Figure S9. $J-V$ characteristics, under simulated AM 1.5 G solar irradiation, of PTB7:PQP blend films (a) with different blend ratios, (b) spin-coated by different solvent, (c) of PTB7-Th:PFP blend films by different solvents