Recyclable terthiophenes for synthesizing precision conjugated oligomers

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Supplemental Information

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General Considerations

All reagents were used as received unless otherwise noted. Dichloromethane (DCM), N-bromosuccinimide (NBS), N, N-dimethylformamide (DMF), dichloro(1,2-bis(diphenylphosphino)ethane)nickel (Ni(dppe)Cl_2), tetra-n-butylammonium fluoride (1.0 M, solution in THF), 2-bromo-3-hexylthiophene, lithium diisopropylamide (LDA) (2.0 M, THF/heptane/ethylbenzene), and butylated hydroxytoluene (BHT) were purchased from Sigma-Aldrich. Synthesis of cis-[1,2-bis(diphenylphosphino)ethane](2-methylphenyl)nickel chloride was carried out following previously reported procedures with all characterization in agreement with previous reports. [1] Unstabilized tetrahydrofuran (THF) was purchased from Fisher Scientific, purified using a solvent purification system (SPS), and stored in a Schlenk flask containing activated 4 Å molecular sieves.

General Procedure of Temperature-Controlled Oligomerization

Preparation of BHT Solution and Diluted LDA Solution

BHT (2.99 g, 13.6 mmol) was added to 80 mL THF. The mixture was stirred for 10 min. The concentration of the BHT solution was approximately 0.17 M. This stock solution was remade once per half year.

LDA (2.0 M in THF, 1.2 mL) was added to 18.8 mL THF. The concentration of the LDA solution was approximately 0.12 M. This solution was prepared every time before use and disposed of at the end of the day.

Synthetic Procedures

Reactions were typically performed on 0.4 or 0.05 mmol scale of nickel(II) external initiator.

1. The reaction vessel was charged with the nickel(II) external initiator, and thiophene/terthiophene was inserted into the acetone/dry ice cooling bath (-78 °C).
2. After 5 min, diluted LDA solution (1.2 eq of the nickel(II) external initiator) was added dropwise to activate thiophene/terthiophene.
3. A negligible amount of the reaction mixture was withdrawn, protonated by HCl, and extracted with water and chloroform. The organic phase was further diluted by chloroform and transferred to a 0.5 D vial.
4. The diluted mixture was then analyzed by the MALDI-TOF-MS to monitor the composition of growing chains.
    a. If the signal of the growing chain with minus one repeating unit remains in the MALDI spectrum (Figure S1a-b), add another 0.1 mL diluted LDA and repeat steps 3-5.
    b. If the signal of the growing chain with plus one repeating unit shows in the MALDI spectrum (Figure S1c-d), 0.2 mL BHT was added to quench residual activated thiophene/terthiophene for 1 min (Figure S1e). The mixture was warmed to room temperature for 3 min and cooled to -78 °C for another 3 min. Repeat steps 2-5.
5. Hydrochloric acid (5 M) was added at the end of the oligomerization to quench the growing chain.

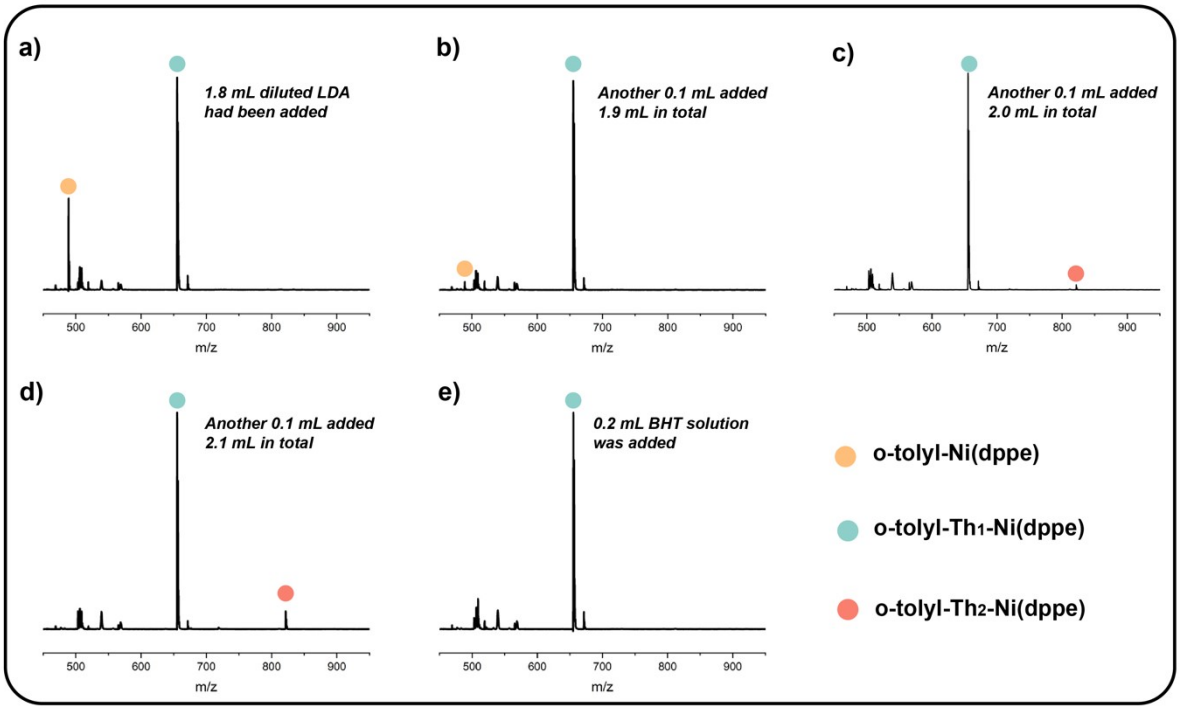


Figure S1. Examples of monitoring the composition of growing chains using MALDI-TOF-MS.

Instrumentation

MALDI-TOF mass spectrometry

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained using a Bruker AutoFlex Speed MALDI-TOF mass spectrometer from a matrix of trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (250:1 matrix-to-polymer ratio) cast from chloroform. Scan mode: reflector; ion mode: positive; solvent: chloroform. Monoisotopic peaks are reported as observed $[M+H]^+$ m/z values in the figure captions.

NMR spectrometry

^1H, ^{13}C, and ^{31}P NMR spectra were recorded using a Varian Mercury 400 spectrometer (400 MHz) or a Bruker Avance III 400 spectrometer (400 MHz). Chemical shifts are reported in ppm at ambient temperature. ^1H chemical shifts are referenced to the residual protonated chloroform peak at 7.26 ppm. 85% phosphoric acid was used as the external standard to collect ^{31}P NMR spectra.

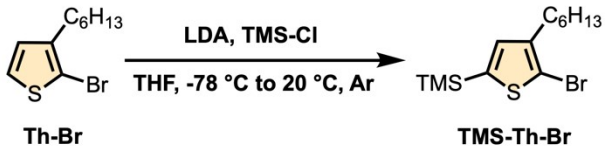
Direct real-time mass spectroscopy (DART-MS)

Direct real-time mass spectra were obtained using a JEOL JMS-T100LP-4G spectrometer. The compounds were dissolved in dichloromethane and probed under positive mode. Positive ion species observed are typically $[M+H]^+$ and $[M+NH_4]^+$.

Ultraviolet/visible light spectrometry (UV/vis)

UV-Vis absorption measurements were obtained using a Agilent Cary 5000 UV-Vis Spectrometer. All samples were dissolved in chloroform (~ 0.18 M) and measurements were taken in a 1 cm quartz cuvette. Beer-Lambert law was used to calculate the extinction coefficient.

Synthesis of TMS-Th-Br



Scheme S1. Synthesis of TMS-Th-Br.

2-bromo-3-hexylthiophene (Th-Br) (1.65 g, 6.68 mmol, 1.0 eq) was dissolved in 22 mL anhydrous tetrahydrofuran (THF) in an oven-dried 50 mL Schlenk flask filled with argon. The mixture was cooled down to -78 °C. Lithium diisopropylamide (LDA) (2M, 4 mL, 8.0 mmol, 1.2 eq) was added dropwise, and the color of the mixture turned to orange/yellow. After 10 min, trimethylsilyl chloride (TMS-Cl) (1.3 mL, 10.3 mmol, 1.5 eq) was added dropwise, and the color of the mixture turned bright yellow. After 1.5 h, the mixture was warmed up to 20 °C. After 30 min, the solvent was removed under a high vacuum. The crude product was extracted with dichloromethane (DCM) and brine. The organic phase was concentrated, dried over $MgSO_4$, filtered, and dried in vacuo to yield TMS-Th-Br as a yellow oil (1.91g, 90 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (s, 1H), 2.57 (t, 2H), 1.59-1.34 (m, 8H), 0.91 (t, 3H), 0.30 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.26, 140.72, 135.03, 113.60, 31.65, 29.85, 29.38, 29.07, 22.64, 14.11, -0.21.

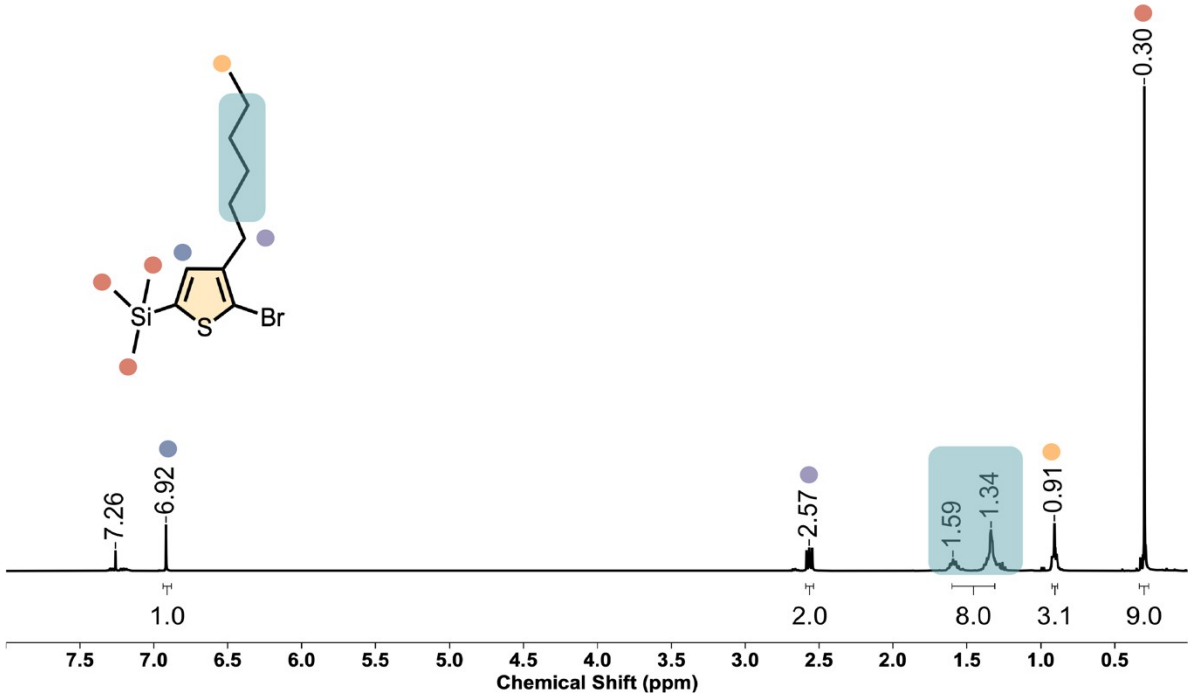


Figure S2. ^{1}H NMR spectrum of 2-bromo-3-hexyl-5-trimethylsilylthiophene (TMS-Th-Br).

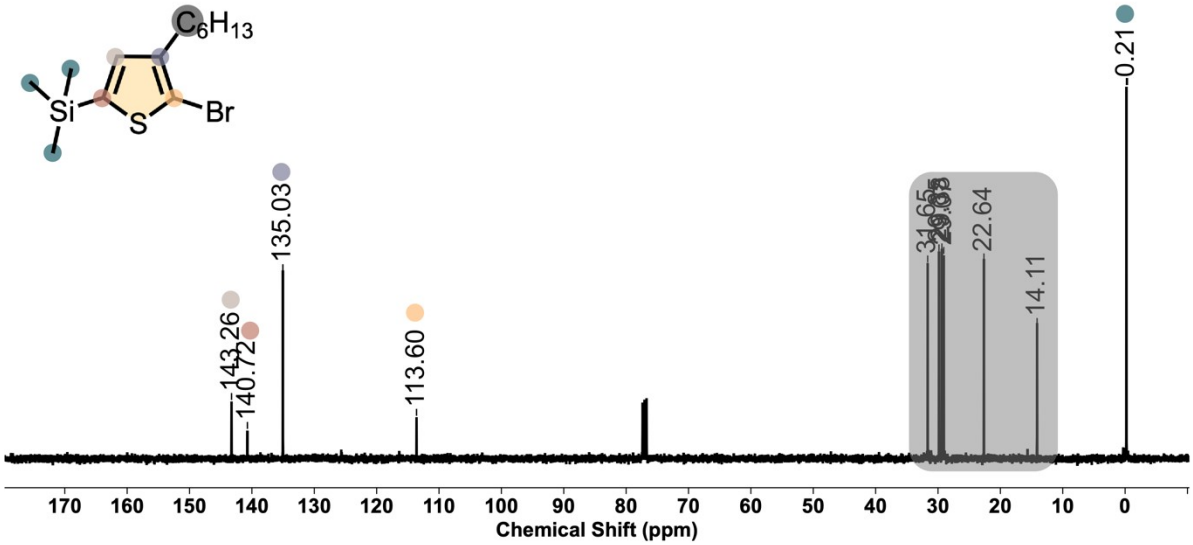
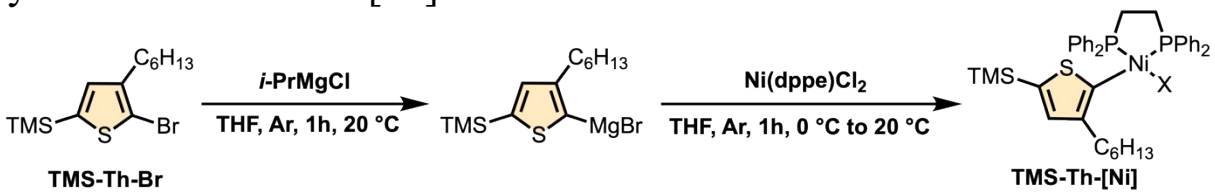


Figure S3. ^{13}C NMR spectrum of 2-bromo-3-hexyl-5-trimethylsilylthiophene (TMS-Th-Br).

Synthesis of TMS-Th-[Ni]



Scheme S2. Synthesis of TMS-Th-[Ni].

TMS-Th-Br (1.0 g, 3.13 mmol, 1.0 eq) was dissolved in 7 mL anhydrous tetrahydrofuran (THF) in an oven-dried 25 mL Schlenk flask filled with argon at 20 °C. Isopropylmagensium chloride solution (2M, 1.65 mL, 3.29 mmol, 1.0 eq) was added dropwise into the flask to activate the thiophene. Meanwhile, [1,3-bis(diphenylphosphine)propane] dichloro nickel (II) (1.37 g, 2.6 mmol, 0.83 eq) was dissolved in 70 mL anhydrous THF in an oven-dried 100 mL Schlenk flask filled with argon at 0 °C. After one h, when the activation of thiophene reached complete conversion, the activated thiophene solution was transferred dropwise into the 100 mL Schlenk flask. The 100 mL flask was kept at 0 °C for 30 min and warmed to 20 °C for another 30 min. The crude product was filtered, dried under a high vacuum, and washed with cold methanol to yield an orange suspension. This suspension was vacuum filtered and dried in vacuo to yield TMS-Th-[Ni] as an orange/yellow solid (840 mg, 36%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (3H), 7.69-7.28 (13H), 7.08 (2H), 6.82 (2H), 6.63 (s, 1H), 2.52-2.13 (5H), 1.66-1.55 (3H), 1.19 (8H), 0.88 (t, 3H), 0.11 (s, 9H) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ 57.26 (d, J = 32.4 Hz), 53.99 (d, J = 33.7 Hz), 42.02 (d, J = 32.4 Hz), 39.19 (d, J = 33.7 Hz) ppm.

MALDI-TOF-MS: TMS-Th-(dppe) m/z: 657.8 (cal. 637.6). TMS-Th-(dppe)O m/z: 653.6 (cal. 653.5).

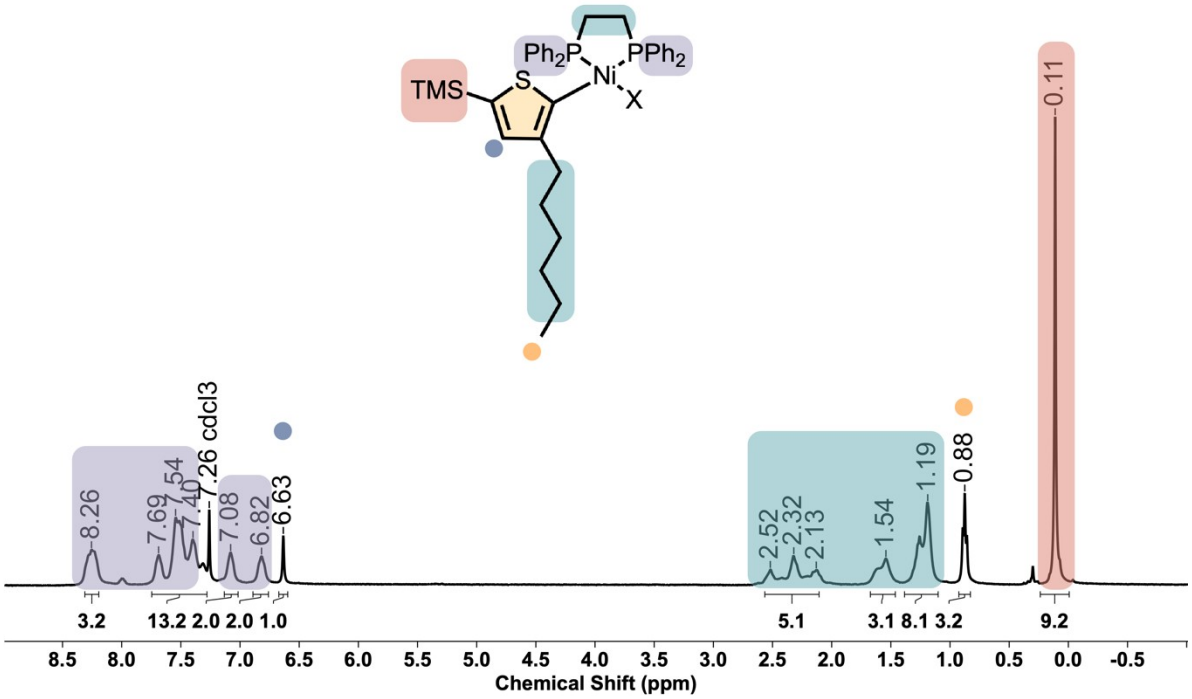


Figure S4. ^{1}H NMR spectrum of TMS-Th-[Ni].

Synthesis of TMS-Th_3 using pristine Th-Br

TMS-Th-[Ni] (264 mg, 0.36 mmol, 1.0 eq) and 2-bromo-3-hexylthiophene (278 mg, 1.13 mmol, 3.1 eq) were dissolved in 15 mL anhydrous tetrahydrofuran in an oven-dried 25 mL Schlenk flask filled with argon. The reaction vessel was inserted into the acetone/dry ice cooling bath. Follow the general procedure of temperature-controlled oligomerization (page S3). At the end of the oligomerization, hydrochloric acid (5 M, 5 mL) was added to quench the growing chain for 10 min. THF was removed in a high vacuum. The product was extracted with chloroform and brine. The organic phase was dried over $MgSO_4$, filtered, and dried in vacuo. The silica column chromatography was carried out using hexanes as the eluent to separate unreacted 2-bromo-3-hexylthiophene, butylated hydroxytoluene (BHT), and TMS-Th_3. 72% of unreacted 2-bromo-3-hexylthiophene (73 mg) was recycled as the first fraction of eluent, and the purity was evidenced by ^{1}H NMR (Figure 3c). BHT was separated as the second fraction, and the target compound TMS-Th_3 was the last. The solution of the last fraction was finally dried in vacuo to yield yellow oil (130 mg, 63%). The silica column was slightly yellow after the workup, indicating that some TMS-Th_3 was captured by the column. Therefore, although all TMS-Th-[Ni] was converted to TMS-Th_3, the final yield of TMS-Th_3 was 63%. This issue could be fixed by using other solvents as eluents and optimizing the silica packing.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (s, 1H), 6.96 (1H), 6.94 (s, 1H), 6.89 (1H), 2.75 (m, 4H), 2.59 (t, 2H), 1.71-1.24 (m, 24H), 0.89 (t, 9H), 0.32 (s, 9H) ppm.

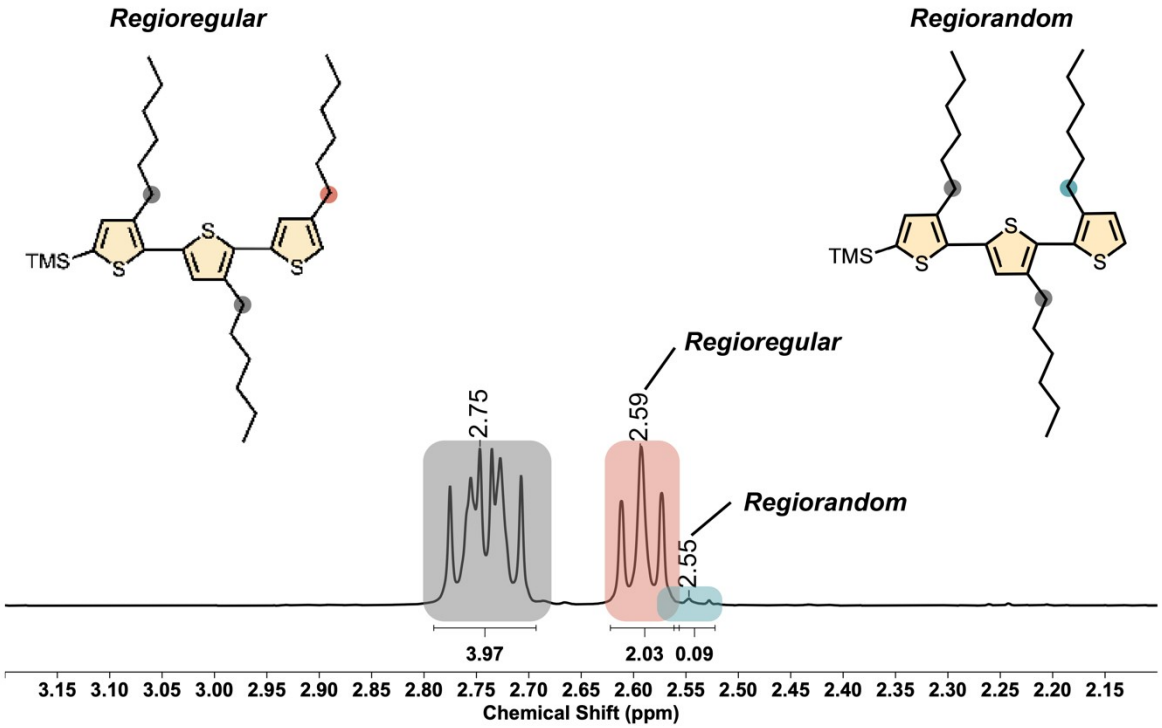


Figure S5. Regioregularity analysis of TMS-Th_3 by ^{1}H NMR.

MALDI-TOF-MS: m/z: 571.2 (cal. 571.4).

Calculation of the yield of recovered Th-Br

0.36 mmol (1.0 eq) external initiator and 1.13 mmol (3.1 eq) Th-Br were added to the reaction flask. 2.0 eq Th-Br was consumed to afford TMS-Th_3.

The theoretical moles of unreacted Th-Br is:

$$1.13 - 2\times0.36 = 0.41 \text{ mmol}$$

The theoretical mass of unreacted Th-Br is:

$$0.41 \text{ mmol} \times 247 = 101.27 \text{ mg}$$

The experimental mass of recovered Th-Br is 73 mg.

Therefore, the recycling yield is:

$$73 \div 101.27 = 72.3\%$$

Synthesis of TMS-Th_3 using recycled Th-Br

TMS-Th-[Ni] (55 mg, 0.075 mmol, 1.0 eq) and recycled Th-Br (71 mg, 0.29 mmol, 3.87 eq) were dissolved in 3 mL anhydrous tetrahydrofuran in an oven-dried 10 mL Schlenk flask filled with argon. The synthetic and purification procedure was the same as the synthesis of TMS-Th_3 using pristine Th-Br, yielding a yellow oil (24 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (s, 1H), 6.96 (1H), 6.94 (s, 1H), 6.89 (1H), 2.74 (m, 4H), 2.60 (t, 2H), 1.70-1.23 (m, 24H), 0.89 (t, 9H), 0.32 (s, 9H) ppm.

MALDI-TOF-MS: m/z: 571.3 (cal. 571.4).

Bromination of o-tolyl-penta(3-hexylthiophene) (o-tolyl-Th_5)

o-tolyl-penta(3-hexylthiophene) (o-tolyl-Th_5) was synthesized following the previous procedure. [1] Th_5 (34.5 mg, 0.037 mol, 1.0 eq) and NBS (6.8 mg, 0.038 mmol, 1.03 eq) were dissolved in 2 mL DMF and stirred at 20 °C in the darkness overnight. The mixture was extracted with DCM and brine. The organic phase was dried over $MgSO_4$, filtered, and dried in vacuo to yield o-tolyl-Th_5-Br as a yellow oil (30.3 mg, 82 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.41 (m, 1H), 7.25-7.21 (m, 3H), 6.97 (4H), 6.91 (s, 2H), 2.61 (t, 10H), 2.49 (s, 3H), 1.70-0.90 (57H).

MALDI m/z: 1000.9 (cal. 1000.8) assigned to o-tolyl-Th_5-Br; 1080.4 (cal. 1080.7) assigned to o-tolyl-Th_5-Br_2.

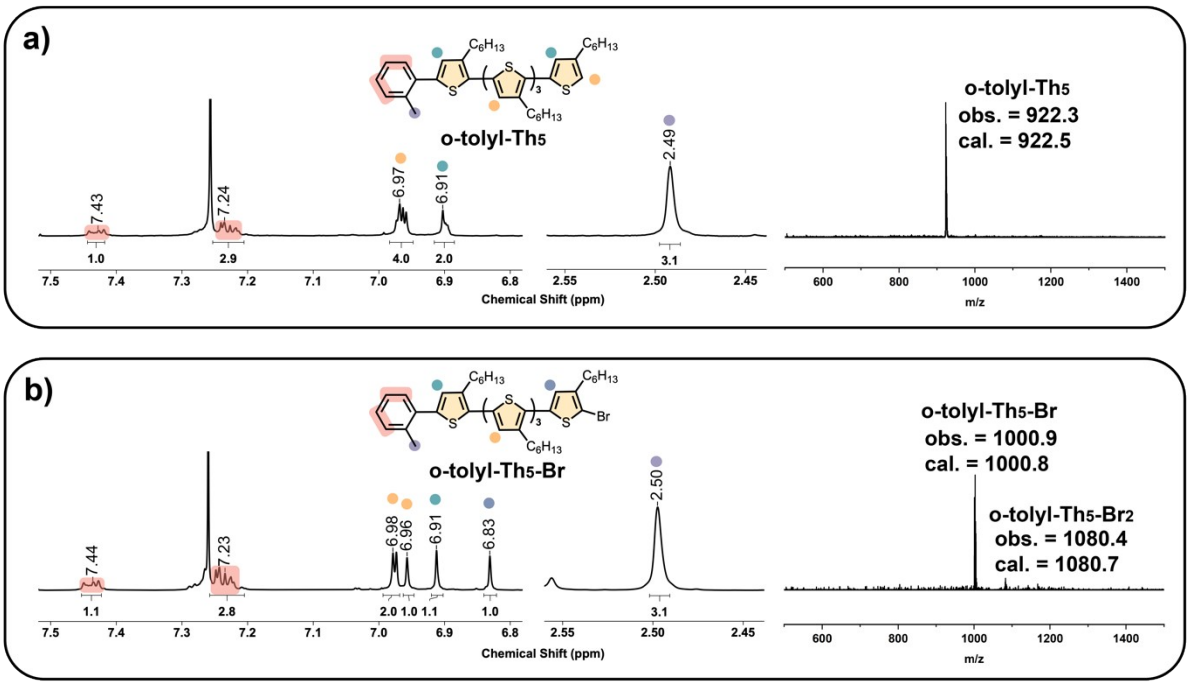


Figure S6. ^{1}H NMR and MALDI-TOF-MS spectra of a) o-Th_5 and b) o-Th_5-Br.

Synthesis of TMS-Th_3-Br and Th_3-Br

Synthesis of TMS-Th_3-Br by brominating TMS-Th_3

TMS-Th_3 (130 mg, 0.23 mmol, 1.0 eq) and NBS (42.2 mg, 0.24 mmol, 1.03 eq) were dissolved in 2 mL DMF in a 200 mL scintillation vial charged with a stir bar. The mixture was stirred overnight in darkness at 20 °C. The crude product was extracted with DCM and brine. The organic phase was dried over $MgSO_4$, filtered, and dried in vacuo to yield a yellow oil (110 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (s, 1H), 6.93 (1H), 6.81 (s, 1H), 2.75 (m, 4H), 2.59 (t, 2H), 1.68-1.21 (m, 24H), 0.82 (t, 9H), 0.32 (s, 9H) ppm. Unassigned signals at 6.88 and 6.86 ppm indicate the product was not pure TMS-Th_3-Br.

MALDI-TOF-MS: m/z: 651.6 (cal. 651.3).

Synthesis of Th_3-Br by desilylating TMS-Th_3-Br

TMS-Th_3-Br (110 mg, 0.19 mmol, 1.0 eq) was dissolved in 3 mL anhydrous THF in an oven-dried 10 mL Schlenk flask filled with argon. TBAF (0.95 mL, 0.95 mmol) was added dropwise into the flask, and the color of the reaction mixture turned from yellow to orange immediately. The mixture was stirred at 20 °C overnight. The crude product was extracted with DCM and brine. The organic phase was dried over $MgSO_4$, filtered, and dried in vacuo to yield an orange/yellow oil (75 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, 1H), 6.93-6.92 (2H), 6.81 (1H), 2.74 (m, 4H), 2.59 (t, 2H), 1.71-1.22 (m, 24H), 0.83 (t, 9H) ppm. Unassigned signals at 6.88 and 6.86 ppm indicate the product was not pure Th_3-Br.

MALDI-TOF-MS: m/z: 500.3 (cal. 500.6) assigned to Th_3. m/z: 580.3 (cal. 580.2) assigned to Th_3-Br. m/z: 658.1 (cal. 658.4) assigned to Br-Th_3-Br.

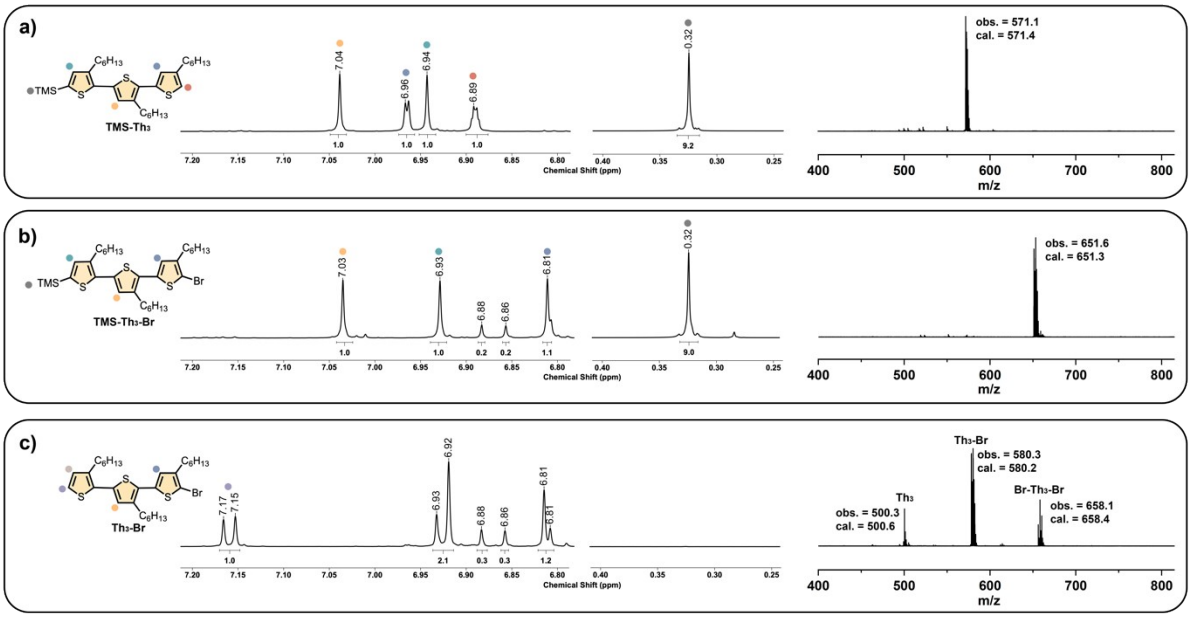


Figure S7. ^{1}H NMR spectroscopy and MALDI-TOF-MS characterization of a) TMS-Th_3, b) TMS-Th_3-Br, c) Th_3-Br obtained by desilylating TMS-Th_3-Br.

Synthesis of Th_3 and Th_3-Br

Synthesis of Th_3 by desilylating TMS-Th_3

TMS-Th_3 (150 mg, 0.26 mmol, 1.0 eq) was dissolved in 4 mL anhydrous THF in an oven-dried 10 mL Schlenk flask filled with argon. TBAF (1.3 mL, 1.3 mmol) was added dropwise into the flask, and the color of the reaction mixture turned from yellow to orange immediately. The mixture was stirred at 20 °C overnight. The crude product was extracted with DCM and brine. The organic phase was dried over $MgSO_4$, filtered, and dried in vacuo to yield a yellow oil (122 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, 1H, J = 8.0 Hz), 7.04 (s, 1H), 6.97 (1H), 6.89 (1H), 6.81 (d, 1H, J = 8.0 Hz), 2.74 (m, 4H), 2.60 (t, 2H), 1.72-1.24 (24H), 0.89 (t, 9H) ppm.

MALDI-TOF-MS: m/z: 500.3 (cal. 500.6).

Synthesis of Th_3-Br by brominating Th_3

Th_3 (122 mg, 0.24 mmol, 1.0 eq) was dissolved in chloroform (2.5 mL)/acetic acid (0.5 mL) mixture in a 20 mL Scintillation vial charged with a stir bar. NBS (42.7 mg, 0.24 mmol, 1.0 eq) was dissolved in the same solvent mixture and added into an addition funnel. NBS solution was added dropwise to the vial. The reaction mixture in the vial was stirred at 20 °C overnight. The crude product was extracted with DCM and brine. The organic phase was dried over $MgSO_4$, filtered, and dried in vacuo to yield a yellow oil (117 mg, 94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, 1H, J = 7.2 Hz), 7.04 (s, 1H), 6.84 (1H), 6.81 (d, 1H, J = 7.2 Hz), 2.74 (m, 4H), 2.59 (t, 2H), 1.73-1.25 (24H), 0.89 (t, 9H) ppm.

MALDI-TOF-MS: m/z: 580.1 (cal. 580.2).

Synthesis of o-tolyl-Th_{12} using pristine Th_3-Br

o-tolyl-Ni(dppe)Br (50 mg, 0.086 mmol, 1.0 eq) and Th_3-Br (250 mg, 0.43 mmol, 5.0 eq) were dissolved in 3 mL anhydrous tetrahydrofuran in an oven-dried 10 mL Schlenk flask filled with argon. The reaction vessel was inserted into the acetone/dry ice cooling bath. Follow the general procedure of temperature-controlled oligomerization. At the end of the oligomerization, hydrochloric acid (5 M, 4 mL) was added to quench the growing chain for 10 min. THF was removed in a high vacuum. The product was extracted with chloroform and brine. The organic phase was dried over $MgSO_4$, filtered, and dried in vacuo. The silica column chromatography was carried out using gradient eluent (hexanes to dichloromethane) to separate unreacted Th_3-Br, butylated hydroxytoluene (BHT), and o-tolyl-Th_{12}. BHT was the first fraction. 89% of unreacted Th_3-Br (44.5 mg) was recycled as the second fraction, exhibiting blue photoluminescence upon irradiation with a 365 nm UV lamp. The purity was evidenced by ^{1}H NMR (Figure 5f). Finally, the target compound o-tolyl-Th_{12} was the last to come out of the column, exhibiting yellow photoluminescence upon illumination under a 365 nm UV lamp. The solution of the last fraction was finally dried in vacuo to yield an orange/brown solid (140 mg, 84%).

Recovered Th_3-Br

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (d, 1H, J = 7.2 Hz), 7.04 (s, 1H), 6.84 (1H), 6.81 (d, 1H, J = 7.2 Hz), 2.74 (m, 4H), 2.60 (t, 2H), 1.72-1.25 (24H), 0.88 (t, 9H) ppm.

MALDI-TOF-MS: m/z: 580.2 (cal. 580.2).

o-tolyl-Th_{12}

MALDI-TOF-MS: m/z: 2086.2 (cal. 2086.3).

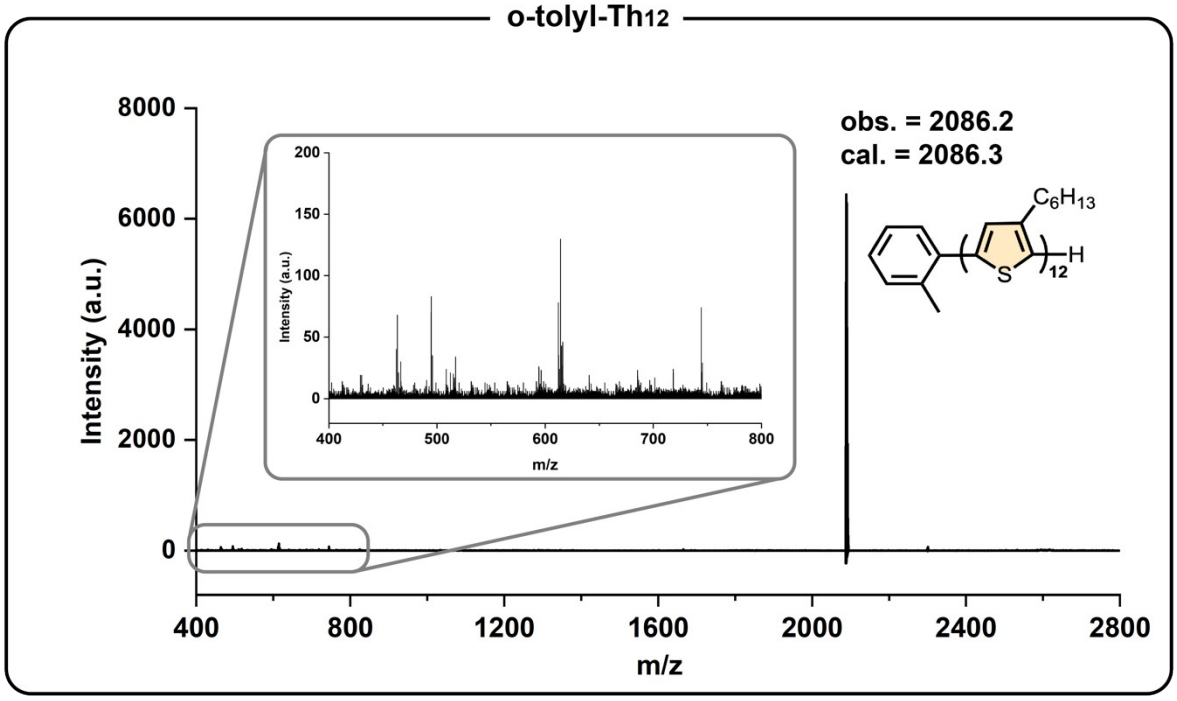


Figure S8. MALDI-TOF-MS characterization of end-capped 12-mer synthesized using pristine Th_3-Br, with an inset showing the pristine Th_3-Br is separated.

Calculation of the yield of recovered Th_3-Br

0.08 mmol (1.0 eq) external initiator and 0.43 mmol (5.0 eq) Th_3-Br were added to the reaction flask. 4.0 eq Th_3-Br was consumed to afford o-tolyl-Th_{12}.

The theoretical moles of unreacted Th_3-Br is:

$$0.43\text{-}4\times0.086 = 0.086 \text{ mmol}$$

The theoretical mass of unreacted Th_3-Br is:

$$0.086 \times 580 = 50 \text{ mg}$$

The experimental mass of recovered Th_3-Br is 44.5 mg.

Therefore, the recycling yield is:

$$44.5 \div 50 = 89\%$$

Synthesis of o-tolyl-Th_{12} using recycled Th_3-Br

o-tolyl-Ni(dppe)Br (10 mg, 0.017 mmol, 1.0 eq) and Th_3-Br (44.5 mg, 0.077 mmol, 4.5 eq) were dissolved in 2.5 mL anhydrous tetrahydrofuran in an oven-dried 10 mL Schlenk flask filled with argon. The reaction vessel was inserted into the acetone/dry ice cooling bath. The synthetic and purification procedure was the same as the synthesis of o-tolyl-Th_{12} using pristine Th_3-Br, yielding brown oil (27.3 mg, 77%).

o-tolyl-Th_{12} using recycled Th_3-Br

MALDI-TOF-MS: m/z: 2086.2 (cal. 2086.3).

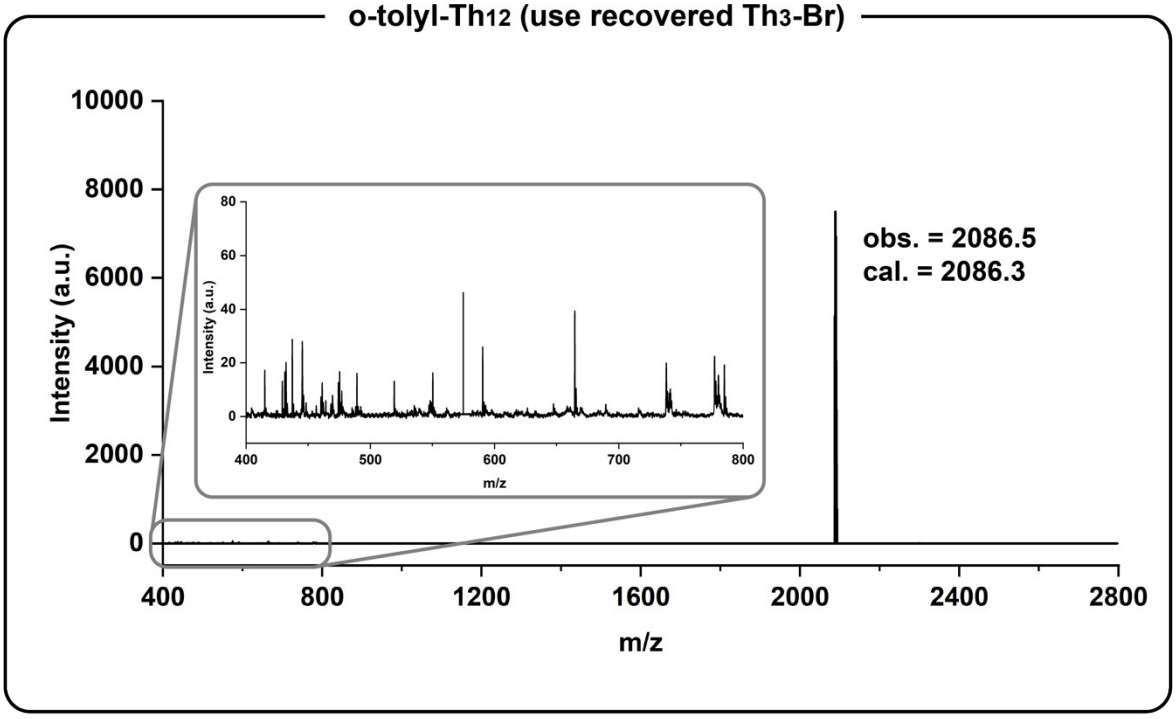


Figure S9. MALDI-TOF-MS characterization of end-capped 12-mer synthesized using recovered Th_3-Br, with an inset showing the recovered Th_3-Br is separated.

Lithiation and recovery of Th-Br and Th_3-Br

Th-Br trial

Pristine Th-Br (100 mg, 0.40 mmol, 1.0 eq) was dissolved in 3 mL anhydrous tetrahydrofuran in an oven-dried 10 mL Schlenk flask filled with argon. The flask was inserted into an acetone/dry ice cooling bath. After 5 min, diluted LDA solution (0.15 M, 2.8 mL, 1.05 eq) was added dropwise into the flask, and the reaction mixture changed from colorless to bright yellow. After 10 min, the reaction mixture was warmed to room temperature, and the mixture color eventually turned to purple. After 30 min, 1.5 mL methanol was added to neutralize the lithium centers, and the mixture was stirred for another 30 min. The solvent was removed in vacuo. The crude product was extracted by dichloromethane and water/brine. The organic layer was dried over $MgSO_4$, filtered, and dried in a high vacuum to yield brown oil (85 mg). The product was characterized by ^{1}H NMR and DART-MS.

Th_3-Br trial

Pristine Th_3-Br (170 mg, 0.29 mmol, 1.0 eq) was dissolved in 3 mL anhydrous tetrahydrofuran in an oven-dried 10 mL Schlenk flask filled with argon. The flask was inserted into an acetone/dry ice cooling bath. After 5 min, diluted LDA solution (0.15 M, 2.0 mL, 1.03 eq) was added dropwise into the flask. The following treatment was the same as the Th-Br trial. The final product was a yellow/orange oil (142 mg). The product was characterized by ^{1}H NMR, DART-MS, and MALDI-TOF-MS.

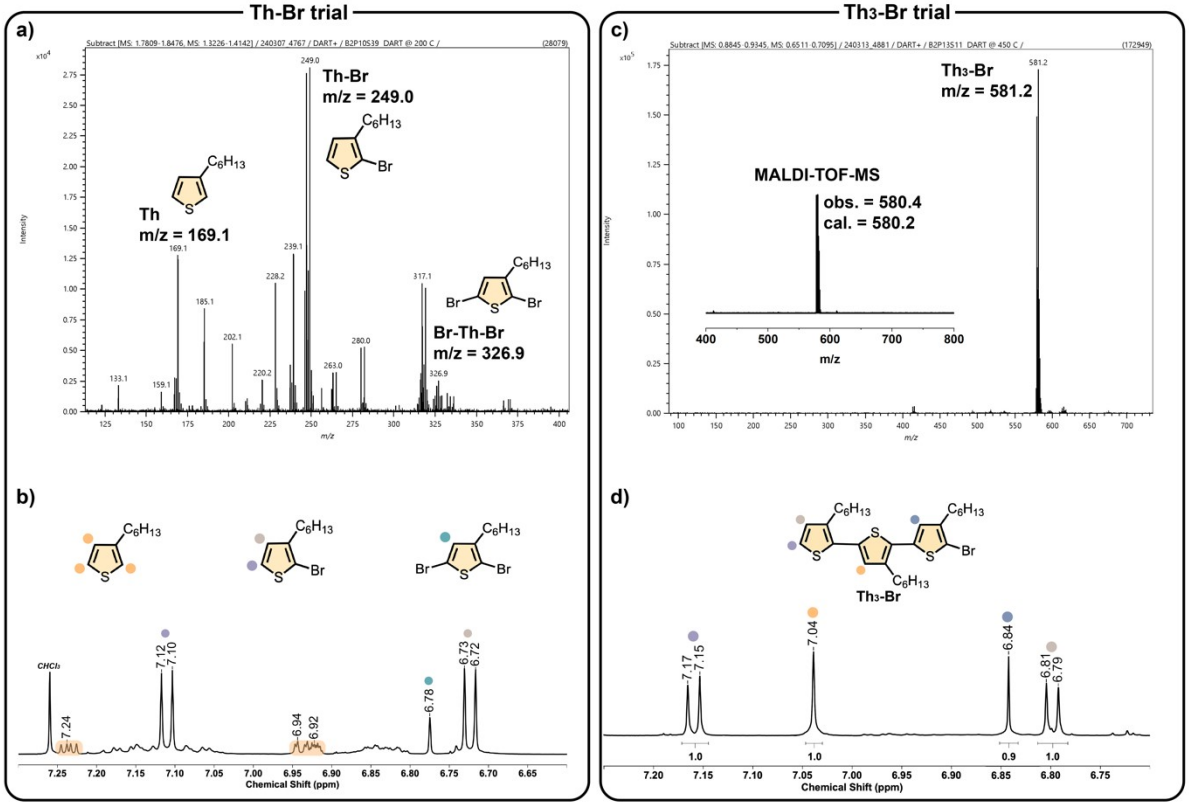
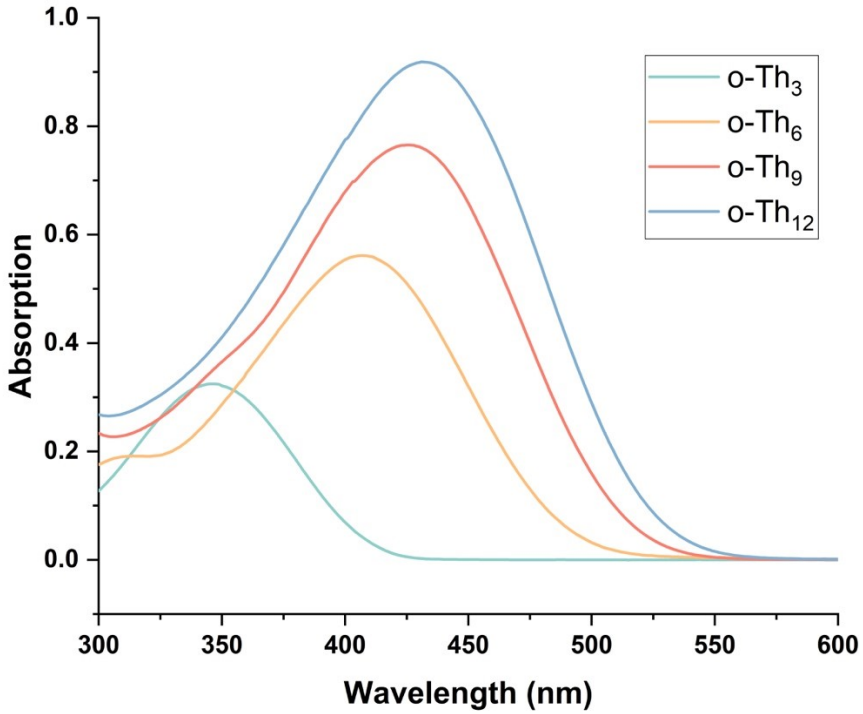


Figure S10. Direct analysis in real-time mass spectra of a) Th-Br trial and c) Th_3-Br trial (inset, MALDI-MS spectra). ^{1}H NMR spectra of b) Th-Br trial and d) Th_3-Br trial.

Note: There is a 1 Da difference between MALDI-MS and DART-MS results. MALDI-TOF-MS used the "Snap" peak detection method, which labels the signal with the lowest m/z value (only ^{12}C). DART-MS employed the "Centroid" peak detection method, which labels all signals and reports the most intense signal.

UV/vis absorption spectrometry



	λ_{max} (nm)	λ_{onset} (nm)	Extinction Coefficient (L mol^{-1} cm^{-1})
o-Th_3	346	427	18500
o-Th_6	408	498	32000
o-Th_9	425	524	45000
o-Th_{12}	432	532	57000

Figure S11. UV/vis absorption spectra of *o*-Th_3, *o*-Th_6, *o*-Th_9, and *o*-Th_{12} in chloroform (~ 0.18 M).

Reference

1. H. Xu, S. Ye, R. Zhao and D. S. Seferos, Homogeneous Synthesis of Monodisperse Sequence-Defined Conjugated Oligomers by Temperature Cycling, Angew. Chem. Int. Ed., 2022, 61, e202210340.