

Supporting Information

Mixed-halide triphenyl methyl radicals for site selective functionalization and polymerization

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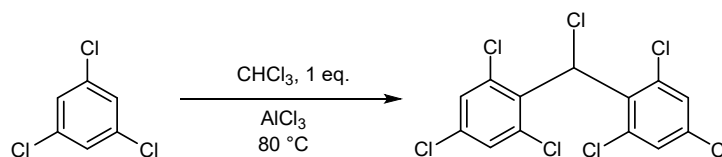
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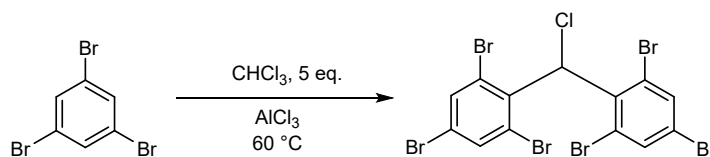
Synthetic procedures and compound data

Synthesis of 2,2'-(Chloromethylene)bis(1,3,5-trichlorobenzene):



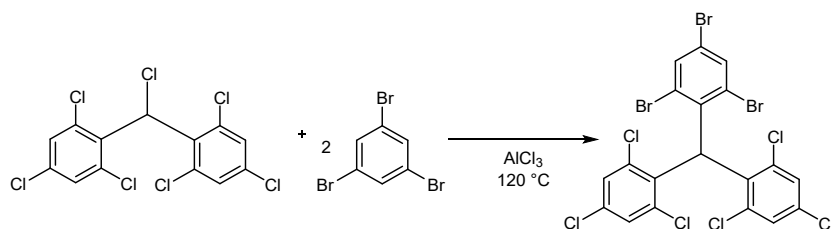
A 75 mL high-pressure reactor is charged with 1,3,5-trichlorobenzene (5.000 g, 27.56 mmol, 1 eq.), anhydrous chloroform (2.21 mL, 27.56 mmol, 1 eq.) and anhydrous aluminum chloride (3.674 g, 27.56 mmol, 1 eq.). The mixture is stirred for 2.5 h at 80°C . After cooling to room temperature, the reaction mixture is poured into 1 M hydrochloric acid (200 mL) and extracted with dichloromethane. After evaporation of the solvent the crude product is washed with cold dichloromethane to give the 2,2'-(chloromethylene)bis(1,3,5-trichlorobenzene) (5.200 g, 12.69 mmol, 92 %). The spectroscopic data is in accordance with that reported earlier.¹

Synthesis of 2,2'-(Chloromethylene)bis(1,3,5-tribromobenzene):



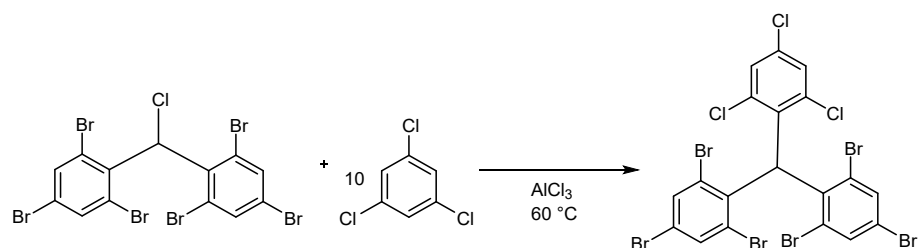
A 75 mL high-pressure reactor is charged with 1,3,5-trichlorobenzene (3.000 g, 9.53 mmol, 1 eq.) and dry chloroform (3.82 mL, 47.65 mmol, 5 eq.) and anhydrous aluminum chloride (0.381 g, 2.86 mmol, 0.3 eq.) is added. The resulting mixture is stirred for 17 h at 60°C . The mixture is poured into 1 M hydrochloric acid (200 mL) and extracted with dichloromethane. 2,2'-(chloromethylene)bis(1,3,5-tribromobenzene) (1.090 g, 1.61 mmol, 33 %) is obtained from the crude product after purification by silica gel column chromatography using hexane as eluent. The spectroscopic data is in accordance with literature.²

Synthesis of 2,2'-((2,4,6-Tribromophenyl)methylene)bis(1,3,5-trichlorobenzene) ($\text{HBr}_3\text{Cl}_6\text{M}$):



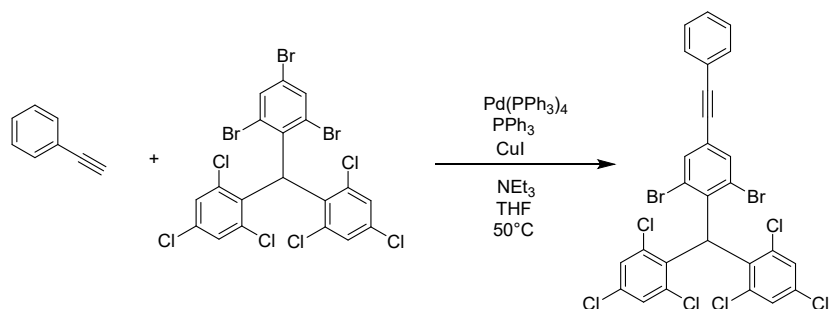
In a high-pressure reactor are added 2,2'-(chloromethylene)bis(1,3,5-trichlorobenzene) (500 mg, 1.22 mmol, 1 eq.), 1,3,5-tribromobenzene (769 mg, 2.44 mmol, 2 eq.) and anhydrous aluminum chloride (179 mg, 1.34 mmol, 1.1 eq.). The mixture is heated to 120°C for 1.5 h. After cooling to room temperature, 1 M hydrochloric acid (50 mL) is added and the mixture is extracted with dichloromethane. The crude product is purified by silica gel column chromatography using hexane as eluent followed by washing with cold dichloromethane. $\text{HBr}_3\text{Cl}_6\text{M}$ (390 mg, 0.56 mmol, 46 %) is obtained as a colorless solid. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ [ppm] = 7.74 (d, $J = 2.1$ Hz, 1 H), 7.65 (d, $J = 2.1$ Hz, 1 H), 7.37 (d, $J = 2.2$ Hz, 1 H), 7.36 (d, $J = 2.2$ Hz, 1 H), 7.24 (d, $J = 2.2$ Hz, 1 H), 7.22 (d, $J = 2.2$ Hz, 1 H), 6.60 (s, 1 H). $^{13}\text{C-NMR}$ (101 MHz, CDCl_3): δ [ppm] = 138.68 (s), 138.12 (s), 137.60 (s), 137.56 (s), 137.03 (s), 136.78 (s), 135.36 (s), 134.14 (s), 134.05 (s), 133.99 (s), 130.20 (s), 128.68 (s), 128.52 (s), 128.06 (s), 126.88 (s), 121.70 (s), 54.29 (s).

Synthesis of 2,2'-((2,4,6-Trichlorophenyl)methylene)bis(1,3,5-tribromobenzene) (HBr₆Cl₃M):



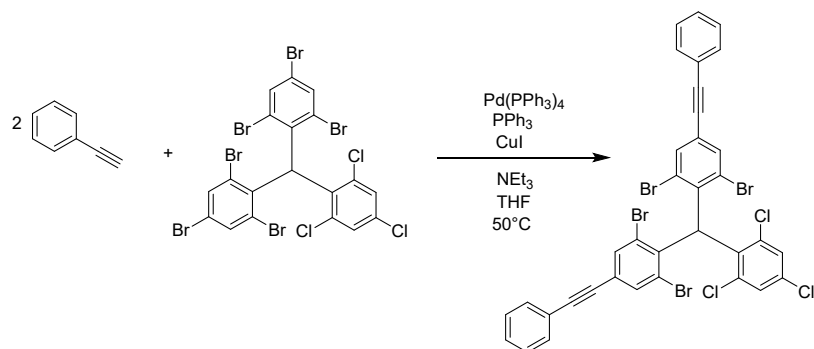
A high pressure vessel is charged with 2,2'-(chloromethylene)bis(1,3,5-tribromobenzene) (0.400 g, 0.59 mmol, 1 eq.), 1,3,5-trichlorobenzene (1.074 g, 5.92 mmol, 10 eq.) and anhydrous aluminum chloride (0.078 g, 0.65 mmol, 1.1 eq.). The mixture is stirred for 20 h at 60 °C, then poured into 1 M hydrochloric acid (100 mL) and extracted with dichloromethane. Unreacted reagent is separated by sublimation (1 mbar, 220 °C) to yield HBr₆Cl₃M (0.260 g 0.32 mmol, 54 %) as a colorless solid. **¹H-NMR** (400 MHz, CDCl₃): δ [ppm] = 7.75 (d, J = 2.1 Hz, 1 H), 7.74 (d, J = 2.1 Hz, 1 H), 7.65 (d, J = 2.1 Hz, 1 H), 7.64 (d, J = 2.1 Hz, 1 H), 7.37 (d, J = 2.2 Hz, 1 H), 7.22 (d, J = 2.2 Hz, 1 H), 6.52 (s, 1 H). **¹³C-NMR** (101 MHz, CDCl₃): δ [ppm] = 138.80 (s), 137.96 (s), 137.08 (s), 136.84 (s), 136.73 (s), 135.48 (s), 135.33 (s), 134.21 (s), 134.08 (s), 130.24 (s), 128.62 (s), 182.39 (s), 127.76 (s), 126.99 (s), 121.87 (s), 121.72 (s), 58.42 (s).

Synthesis of 2,2'-((2,6-dibromo-4-(phenylethynyl)phenyl)methylene)bis(1,3,5-trichlorobenzene):



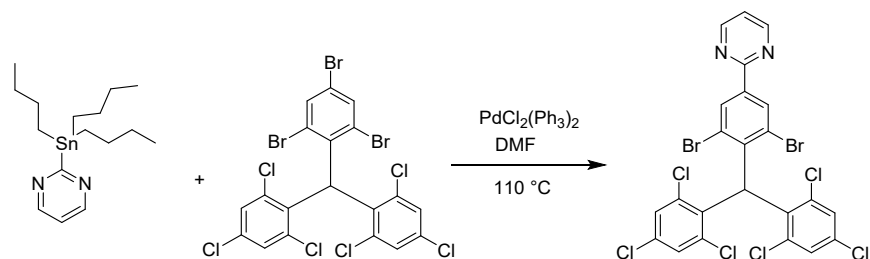
HBr₃Cl₆M (100 mg, 0.145 mmol, 1 eq) and phenylacetylene (45 mg, 0.436 mmol, 3 eq) are dissolved in anhydrous THF (9 mL) and triethylamine (3 mL). The solution is bubbled with argon. Pd(PPh₃)₄ (15 mg, 0.015 mmol, 0.1 eq), PPh₃ (8 mg, 0.029 mmol, 0.2 eq) and copper(I) iodide (3 mg, 0.015 mmol, 0.1 eq) are added. The solution is stirred under argon atmosphere for 24 h at 50 °C in the dark. The solvent is removed and the crude product is purified by column chromatography (DCM: hexane = 1:5). The product is obtained as a yellow solid (62.9 mg, 61.01 %). **¹H-NMR** (400 MHz, CDCl₃): δ [ppm] = 7.75 (d, J = 1.77 Hz, 1H), 7.66 (d, J = 1.76 Hz, 1H), 7.56-7.47 (m, 3H), 7.39-7.32 (m, 6H), 7.25 (d, J = 2.27 Hz, 1H), 7.23 (d, J = 2.27 Hz, 1H), 6.68 (s, 1H). **HRMS (MALDI)** (m/z): 707.74 [M]⁺.

Synthesis of 2,2'-(2,4,6-trichlorophenyl)methylenebis(1,3-dibromo-5-(phenylethynyl)benzene):



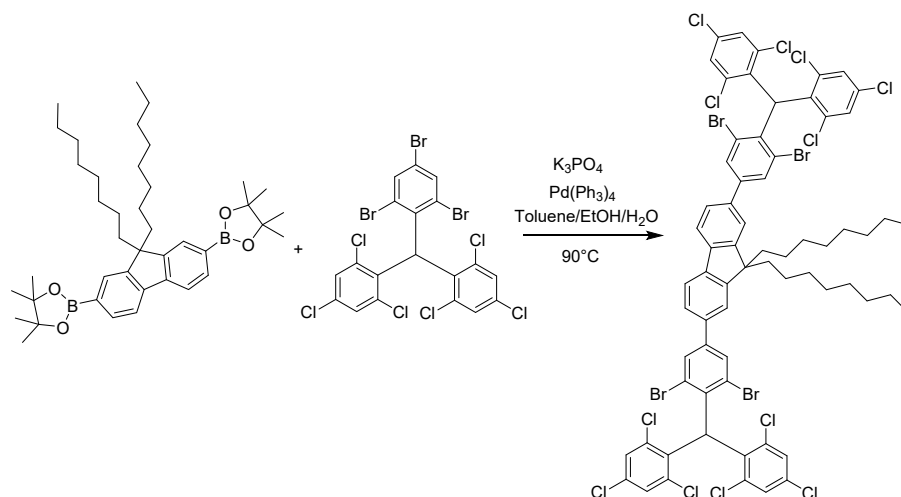
A mixture of $\text{HBr}_6\text{Cl}_3\text{M}$ (60 mg, 0.073 mmol, 1 eq) and phenylacetylene (45 mg, 0.438 mmol, 6 eq) is dissolved in triethylamine (4.5 mL) and anhydrous THF (12 mL). The solution is degassed with argon and the catalysts $\text{Pd}(\text{PPh}_3)_4$ (15 mg, 0.015 mmol, 0.2 eq), PPh_3 (8 mg, 0.029 mmol, 0.4 eq) and copper(I) iodide (3 mg, 0.015 mmol, 0.2 eq) are added. The reaction mixture is stirred under argon atmosphere for 24 h at 50 °C under exclusion of light. The crude product is purified by column chromatography (DCM: petroleum ether = 1:9). The product is obtained as a pale yellow product (21.6 mg, 34.23 %). **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ [ppm] = 7.77 (d, J = 1.76 Hz, 1H), 7.75 (d, J = 1.78 Hz, 1H), 7.67 (d, J = 1.77 Hz, 1H), 7.65 (d, J = 1.79 Hz, 1H), 7.54-7.47 (m, 4H), 7.40-7.31 (m, 7H), 7.24 (d, J = 2.22 Hz, 1H), 6.66 (s, 1H). **HRMS (MALDI)** (m/z): 863.71 [M] $^+$.

Synthesis of 2-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dibromophenyl)pyrimidine:



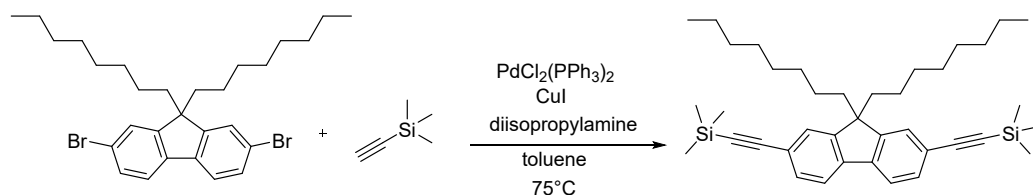
To a solution of 2-(tributylstannyl)pyrimidine (0.08 mL, 0.25 mmol, 1.2 eq.) in 3 mL dry DMF are added $\text{HBr}_3\text{Cl}_6\text{M}$ (145 mg, 0.21 mmol, 1 eq.) and bis(triphenylphosphine)palladium(II) chloride (15 mg, 0.02 mmol, 0.1 eq.) under nitrogen atmosphere. The solution is stirred for 18 h at 110 °C. The solvent is removed and the crude product is purified by silica gel column chromatography (petroleum ether:DCM = 5:1). 2-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dibromophenyl)pyrimidine (50 mg, 0.07 mmol, 31 %) is obtained as a colorless solid. **$^1\text{H-NMR}$** (400 MHz, CDCl_3): δ [ppm] = 8.81 (d, J = 4.9 Hz, 2 H), 8.68 (d, J = 1.8 Hz, 1 H), 8.59 (d, J = 1.8 Hz, 1 H), 7.38 – 7.36 (m, 2 H), 7.30 – 7.15 (m, 3 H), 6.74 (s, 1 H). **$^{13}\text{C-NMR}$** (101 MHz, CDCl_3): δ [ppm] = 162.00 (s), 157.52 (s), 139.68 (s), 138.78 (s), 138.34 (s), 137.72 (s), 134.47 (s), 134.41 (s), 134.21 (s), 134.00 (s), 133.89 (s), 130.18 (s), 130.15 (s), 128.66 (s), 128.48 (s), 128.18 (s), 126.78 (s), 120.06 (s), 54.29 (s). **HRMS (MALDI)**: m/z = 686.7361 [$\text{M}+\text{H}$] $^+$.

Synthesis of 2,7-bis(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dibromophenyl)-9,9-dioctyl-9H-fluorene



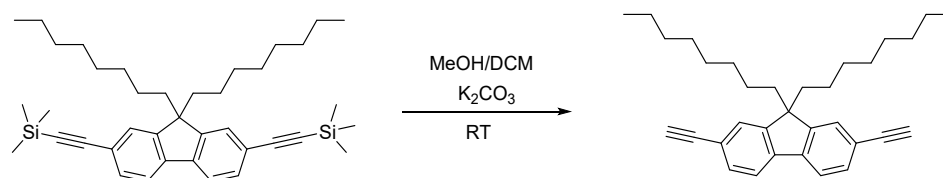
A mixture of 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (50 mg, 0.078 mmol, 1.1 eq) and $\text{HBr}_3\text{Cl}_6\text{M}$ (97 mg, 0.141 mmol, 2 eq) is dissolved in ethanol (0.5 mL)/ toluene (1.5 mL) and an aqueous solution of potassium phosphate (2M, 0.9 mL) is added. The mixture is degassed with argon. Then $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 0.008 mmol, 0.11 eq) is added under argon atmosphere and the reaction mixture is stirred at 50 °C in the dark for 46 h. After cooling to room temperature, the reaction is quenched with 5 % hydrochloric acid and extracted with dichloromethane. The combined organic phases are washed with water and brine and dried over sodium sulfate. The solvent is removed under vacuum and the crude product is purified by column chromatography (DCM:hexane = 1:8). The bromine atoms of the product are partly substituted with hydrogens and the mixture thereof could not be completely separated. Only the product with no bromine atoms left could be obtained as a pure compound in form of a white solid (40.6 mg). **¹H-NMR** (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 70°C): δ [ppm] = 7.78 (d, J = 7.8 Hz, 2H), 7.67-7.58 (m, 10H), 7.40 (s, 8H), 7.19-7.08 (br, 4H), 6.60 (s, 2H), 2.10-2.00 (m, 4H), 1.24-1.01 (m, 24H), 0.8 (t, J = 7.11 Hz, 6H). **HRMS (MALDI)** (m/z): 1288.07 [$\text{M}-4\text{Br}+4\text{H}$]⁺. The remaining mixture of product is also obtained as a white solid (33.2 mg). **HRMS (MALDI)** (m/z): 1445.89 [$\text{M}-2\text{Br}+2\text{H}$]⁺, 1365.99 [$\text{M}-3\text{Br}+3\text{H}$]⁺, 1288.07 [$\text{M}-4\text{Br}+4\text{H}$]⁺

Synthesis of (9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(trimethylsilane):



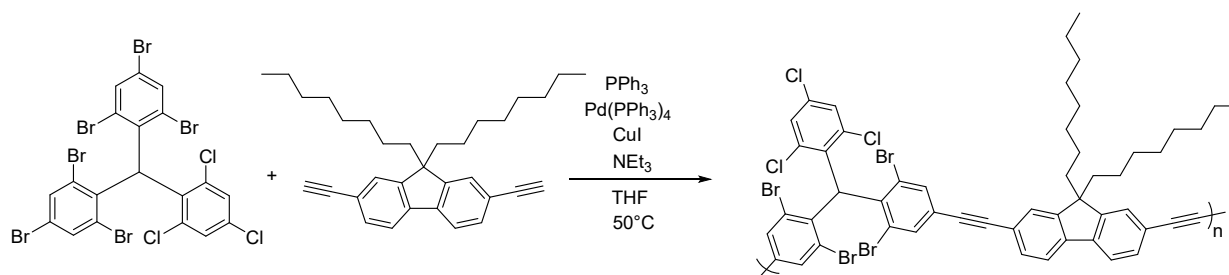
The compound is prepared according to a modified version of a literature known protocol.³ A flask is charged with 2,7-dibromo-9,9-dioctyl-9H-fluorene (548 mg, 1 mmol, 1 eq), $\text{PdCl}_2(\text{PPh}_3)_2$ (23.9 mg, 0.034 mmol, 0.03 eq) and CuI (3 mg, 0.014 mmol, 0.01 eq). Anhydrous toluene (10 mL) is added, and the reaction mixture is degassed with argon. Diisopropylamine (3.5 mL) is also degassed with argon and added to the flask. In a separate vial trimethylsilyl acetylene (304 μL , 2.2 mmol, 2.2 eq) is dissolved in diisopropylamine (1.1 mL) and degassed with argon before being added to the reaction mixture. The resulting reaction mixture is stirred at 75°C for 21 h. After cooling to room temperature, the reaction mixture is filtered over celite. The filtrate is concentrated under reduced pressure and purified by column chromatography (petroleum ether). The product is obtained as a yellow solid (248 mg, 44%). **¹H-NMR** (400 MHz, CDCl_3): δ [ppm] = 7.59 (d, J = 7.8 Hz, 2H), 7.45 (dd, J = 7.8, 1.4 Hz, 2H), 7.42 (d, J = 1.4 Hz, 2H), 2.07 – 1.85 (m, 4H), 1.25 – 0.99 (m, 24H), 0.83 (t, J = 7.1 Hz, 6H), 0.29 (s, 18H).

Synthesis of 2,7-diethynyl-9,9-dioctyl-9H-fluorene:



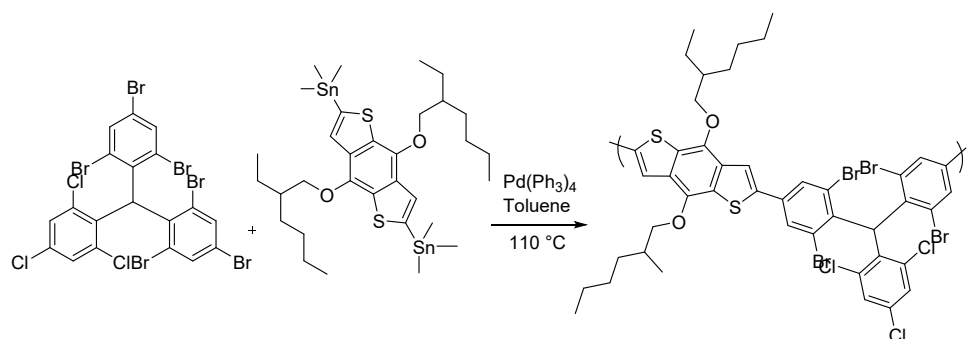
The compound is prepared according to a modified version of a literature known protocol.³ (9,9-Dioctyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(trimethylsilane) (120 mg, 0.206 mmol, 1 eq) is dissolved in methanol (5 mL) and DCM (5 mL). K_2CO_3 (11.4 mg, 0.082 mmol, 0.4 eq) is added and the reaction mixture is degassed with argon and stirred at room temperature for 7 h. The mixture is filtered, and the filtrate is concentrated under reduced pressure to yield the desired product as a brown solid (81 mg, 90%). **¹H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.63 (dd, J = 7.8, 0.7 Hz, 2 H), 7.48 (dd, J = 7.8, 1.4 Hz, 2 H), 7.45 (d, J = 1.3 Hz, 2 H), 3.15 (s, 2 H), 1.99 – 1.88 (m, 4 H), 1.30 – 0.97 (m, 24 H), 0.82 (t, J = 7.1 Hz, 6 H).

Polymerization by Sonogashira coupling:



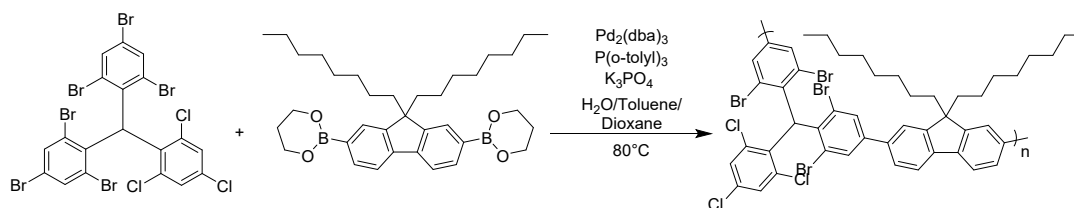
2,7-diethynyl-9,9-dioctyl-9H-fluorene (28 mg, 0.064 mmol, 1.1 eq) and HBr_6Cl_3M (80 mg, 0.097 mmol, 1 eq) are dissolved in anhydrous THF (6 mL) and triethylamine (4 mL) and the solution is bubbled with argon. $Pd(PPh_3)_4$ (13 mg, 0.012 mmol, 0.2 eq), PPh_3 (6 mg, 0.024 mmol, 0.4 eq) and CuI (2 mg, 0.012 mmol, 0.2 eq) are added. The reaction mixture is stirred under exclusion of light at 50 °C for 48 h. The polymers are end-capped by addition of bromobenzene (3 μ L, 0.03 mmol, 0.5 eq) and phenylacetylene (3 μ L, 0.03 mmol, 0.5 eq), each stirring for 2 h at 50 °C. After cooling to room temperature, the mixture is filtrated over celite. The solvent is removed under reduced pressure and the remaining solid is dissolved in DCM. An aqueous solution of KCN (3 mg) is added to the solution and the mixture is stirred for 30 min at room temperature. The mixture is subsequently extracted three times with dichloromethane and the combined organic phases are washed with water and brine, dried over sodium sulfate and concentrated under reduced pressure. For purification, the obtained brownish oil is dissolved in dichloromethane and precipitated in methanol. The solid is washed with methanol and dried, delivering the product as a yellow solid (51 mg, 76 %). **¹H-NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.83-7.74 (broad m, 2 H), 7.73-7.63 (broad m, 4 H), 7.54-7.47 (broad m, 4 H), 7.4-7.33 (broad m, 2 H), 6.67 (s, 1H), 1.97 (broad s, 4 H), 1.17-0.99 (broad m, 20 H), 0.85-0.77 (broad m, 6 H), 0.59 (broad s, 4 H). **GPC**: M_n = 9955 g/mol, M_w = 16695 g/mol, PDI = 1.7.

Polymerization by Stille coupling:



HBr₃Cl₆M (60 mg, 0.07 mmol, 1.0 eq.), (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (56 mg, 0.07 mmol, 1.0 eq.) and Tetrakis(triphenylphosphine)palladium(0) (8 mg, 0.01 mmol, 0.1 eq.) are dissolved in 1 mL dry Toluene under nitrogen atmosphere and the solution is stirred for 36 h at 110 °C. After cooling to room temperature the reaction mixture is poured into methanol and the precipitate is washed with methanol and acetone. **¹H-NMR** (400 MHz, CDCl₃): δ [ppm] = 8.23–7.36 (broad m, 8 H), 6.75 (broad s, 1 H), 4.23 (broad s, 1 H), 2.02–1.57 (broad m, 10 H), 1.50–0.73 (broad m, 18 H). **GPC**: M_n = 8400 g/mol, M_w = 16500 g/mol, PDI = 2.0.

Polymerization by Suzuki coupling:

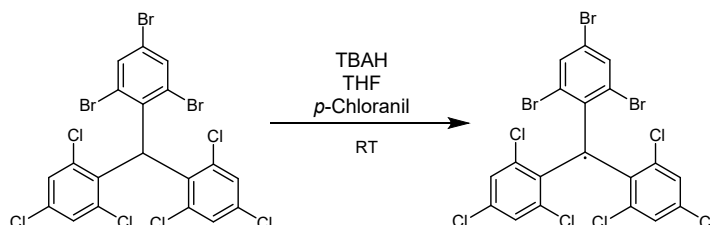


9,9-Dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester (54 mg, 0.097 mmol, 1 eq), HBr₆Cl₃M (80 mg, 0.097 mmol, 1 eq), Tris(dibenzylideneacetone)dipalladium(0) (3 mg, 0.003 mmol, 0.03 eq) and Tris(*o*-tolyl)phosphine (4 mg, 0.012 mmol, 0.12 eq) are dissolved in toluene (2.5 mL) and dioxane (9 mL). The solution is purged with argon. Potassium phosphate (141 mg, 0.195 mmol, 2 eq) is dissolved in water (2 mL) and added. The reaction mixture is stirred at 80 °C under argon atmosphere for 46 h. The polymers are end-capped by addition of bromobenzene (6 mg, 0.049 mmol, 0.5 eq) and phenyl boronic acid (8 mg, 0.049 mmol, 0.5 eq) dissolved in toluene (0.5 mL), each stirring for 2 h at 80 °C. After cooling to room temperature, the reaction mixture is filtered and the filtrate is extracted with dichloromethane. The combined organic phases are washed with water and brine and subsequently dried over sodium sulfate. The solvent is removed under reduced pressure. For purification, the remaining solid is dissolved in toluene and precipitated in methanol. The solid is centrifuged and the supernatant is disposed. This procedure is repeated for three times. The product is obtained as a white-brown solid (46.2 mg, 45 %). **¹H-NMR** (400 MHz, CDCl₃): δ [ppm] = 8.02–6.88 (broad m, 12 H), 6.66 (s, 1H), 2.22–1.78 (broad m, 4 H), 1.24–0.93 (broad m, 20 H), 0.88–0.52 (broad m, 10 H). **GPC**: M_n = 5386 g/mol, M_w = 14078 g/mol, PDI = 2.6.

General procedure to synthesize radicals from H compounds

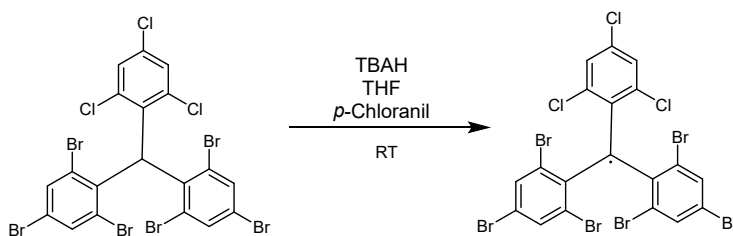
The H compound (1 eq) is dissolved in as little dry THF as possible and purged with argon. Then tetrabutylammonium hydroxide in methanol (1M, 2 eq) is added, which caused an immediate color change. The solution is stirred for 3-5 h under argon atmosphere and in the dark at room temperature. *p*-chloranil (5 eq) is added subsequently and the solution is stirred for another hour. After the reaction is finished, the solvent is removed under reduced pressure.

2,2'-((2,6-Dichloro-4-fluorophenyl)methylene)bis(1,3,5-trichloro-benzene) radical (TBr₃Cl₆M)



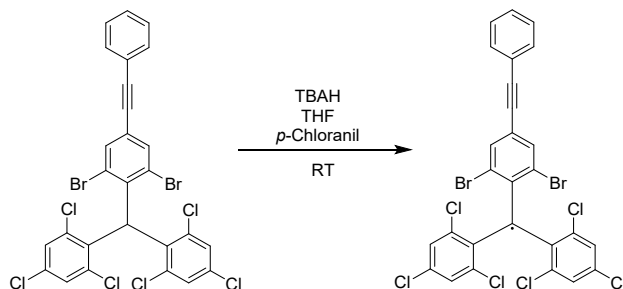
The crude product is purified by column chromatography using hexane as eluent. The product is obtained as a red solid. **HRMS (MALDI):** $m/z = 686.6096$ [M]⁺. **IR:** see Figure S1b.

2,2'-((2,4,6-Trichlorophenyl)methylene)bis(1,3,5-tribromobenzene) radical (TBr₆Cl₃M)



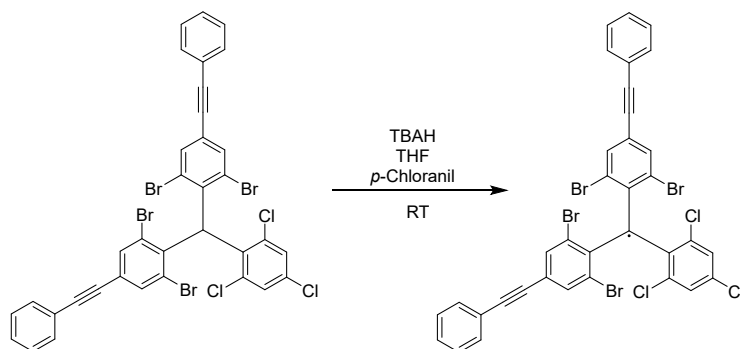
TBr₆Cl₃M is synthesized by the general procedure while for the deprotonation step the reaction mixture is warmed to 60 °C due to solubility reasons. After column chromatography using hexane as eluent, the product is obtained as a deep red solid. **HRMS (MALDI):** $m/z = 820.4563$ [M]⁺. **IR:** see Figure S1c.

2,2'-((2,6-dibromo-4-(phenylethynyl)phenyl)methylene)bis(1,3,5-trichlorobenzene) radical



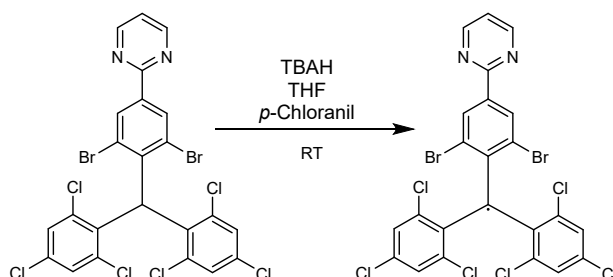
The crude product is purified by column chromatography (DCM:hexane = 1:5). The product is obtained as a green solid. **HRMS (MALDI):** (m/z): 706.73 [M]⁺. **IR:** see Figure S1e.

2,2'-((2,4,6-trichlorophenyl)methylene)bis(1,3-dibromo-5-(phenylethynyl)benzene)



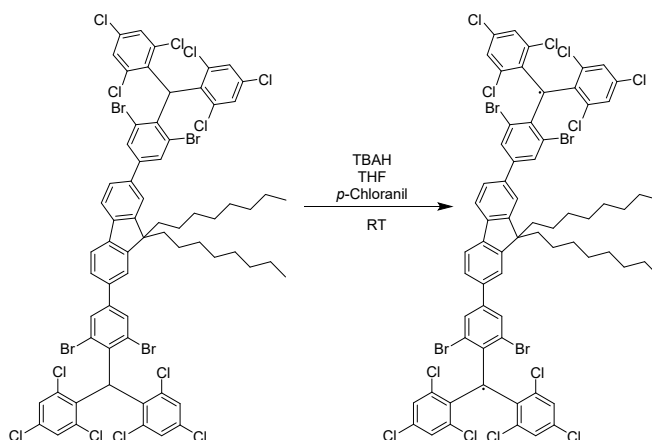
The crude product is purified by column chromatography (DCM:hexane = 1:9). The product is obtained as a green solid. **HRMS (MALDI)** (m/z): 862.70 [M]⁻. **IR**: see Figure S1f.

2-(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dibromophenyl)pyrimidine radical



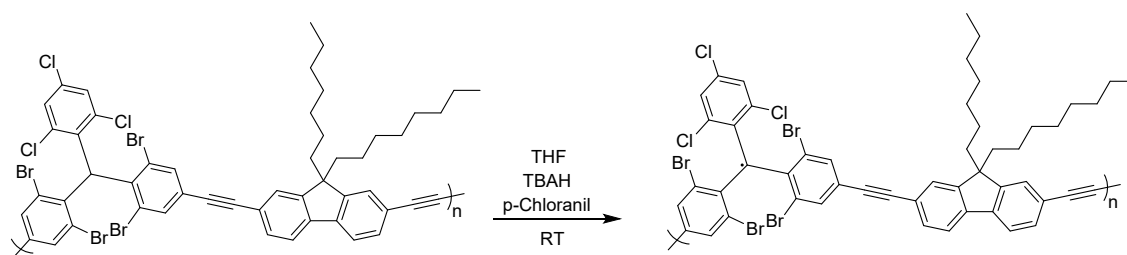
Deprotonation step is performed at 60 °C due to solubility reasons. After chromatographic purification (petroleum ether:DCM = 1:1) the product is obtained as a red solid. **HRMS (MALDI)**: m/z = 684.7211 [M]⁺. **IR**: see Figure S1g.

2,7-bis(4-(bis(2,4,6-trichlorophenyl)methyl)-3,5-dibromophenyl)-9,9-dioctyl-9H-fluorene radical



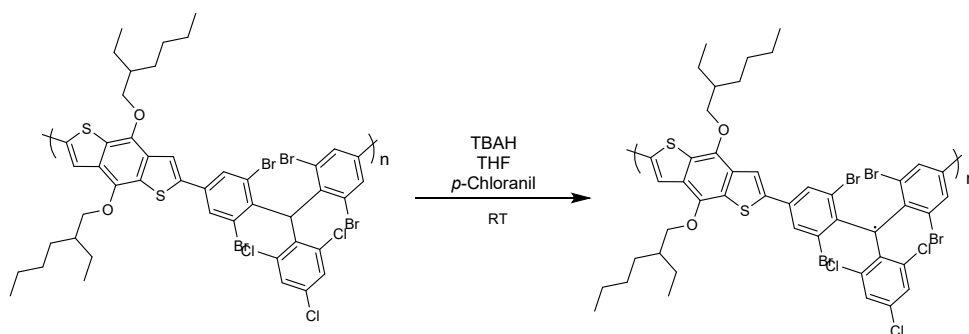
The crude product is purified by column chromatography (DCM:hexane = 1:3). The product is obtained as a green solid. **HRMS (MALDI)** (m/z): 1445.91 [M-2Br+2H]⁺, 1366.00 [M-3Br+3H]⁺, 1288.10 [M-4Br+4H]⁺. **IR**: see Figure S1h.

Sonogashira-polymer radical



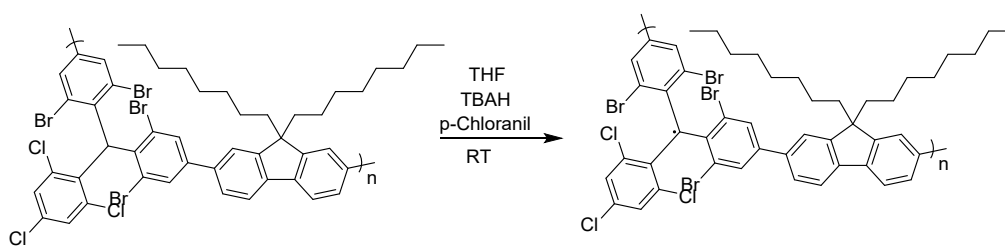
The crude product is dispersed in acetone. The dark dispersion is centrifuged for 5 minutes at 3900 rpm and the supernatant is disposed. The procedure is repeated for 3 times. After drying, the product is obtained as a dark brown powder. **IR:** see Figure S1i. **MALDI-TOF:** see Figure S2.

Stille-polymer radical



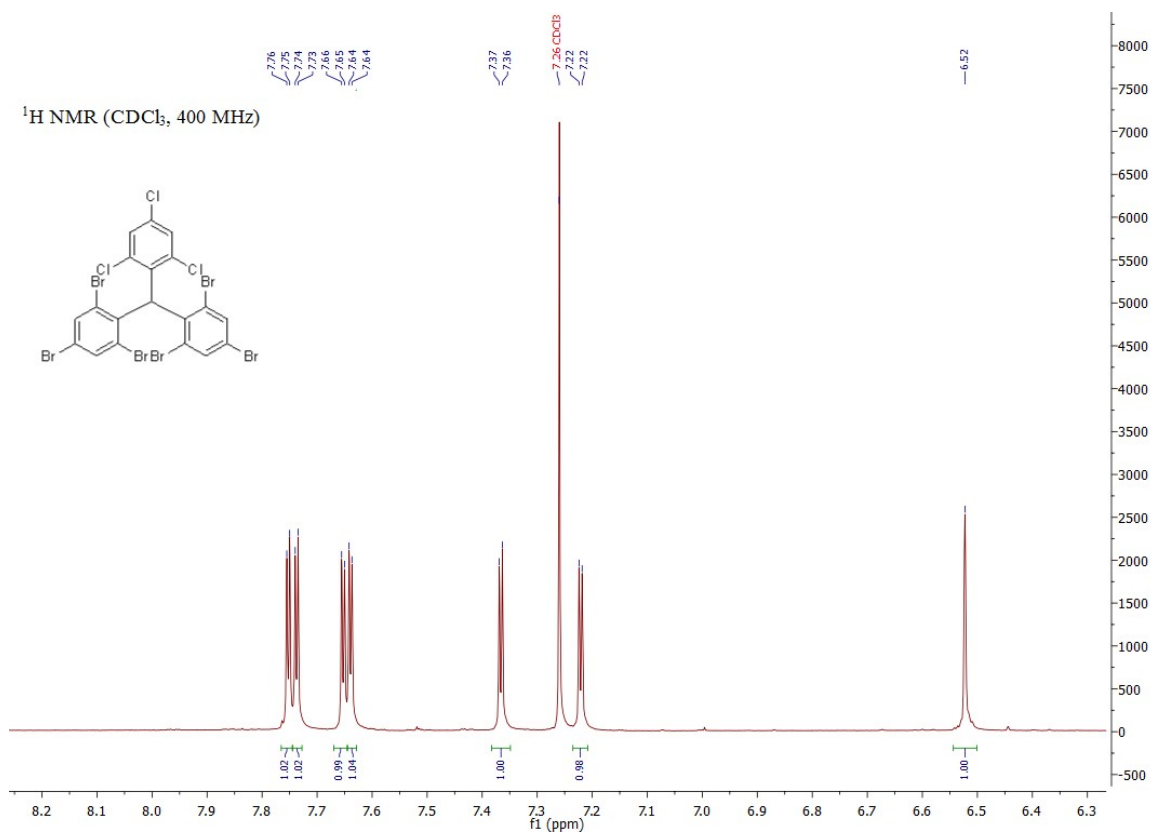
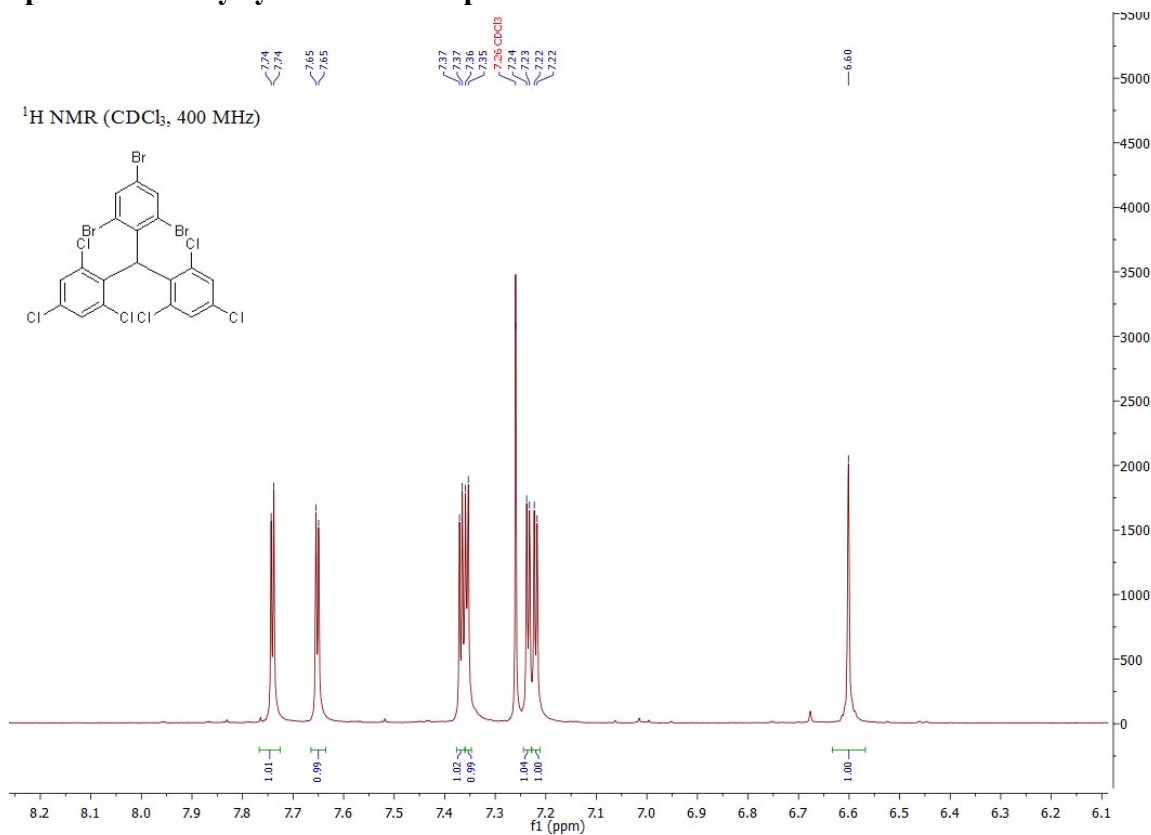
The crude product is dispersed in acetone. The dispersion is centrifuged for 5 minutes at 3900 rpm and the supernatant is disposed. The procedure is repeated for 3 times. After drying, the product is obtained as a yellow powder. **IR:** see Figure S1j.

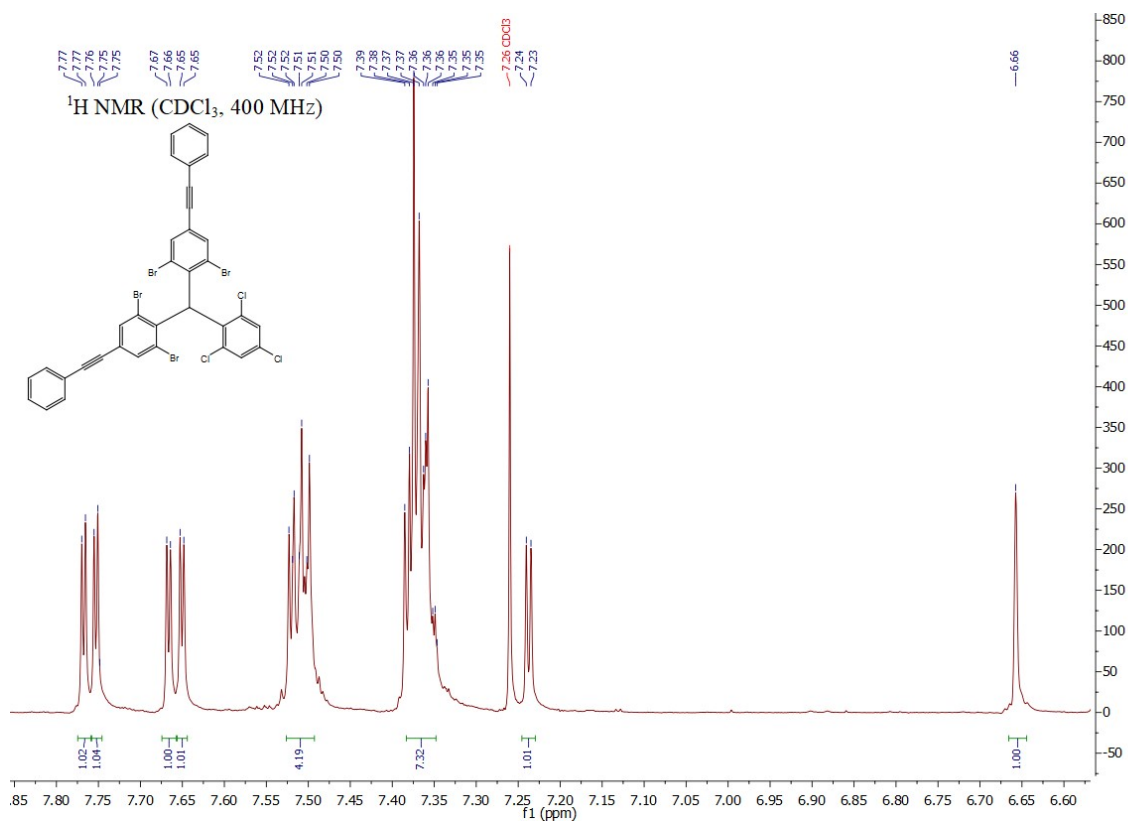
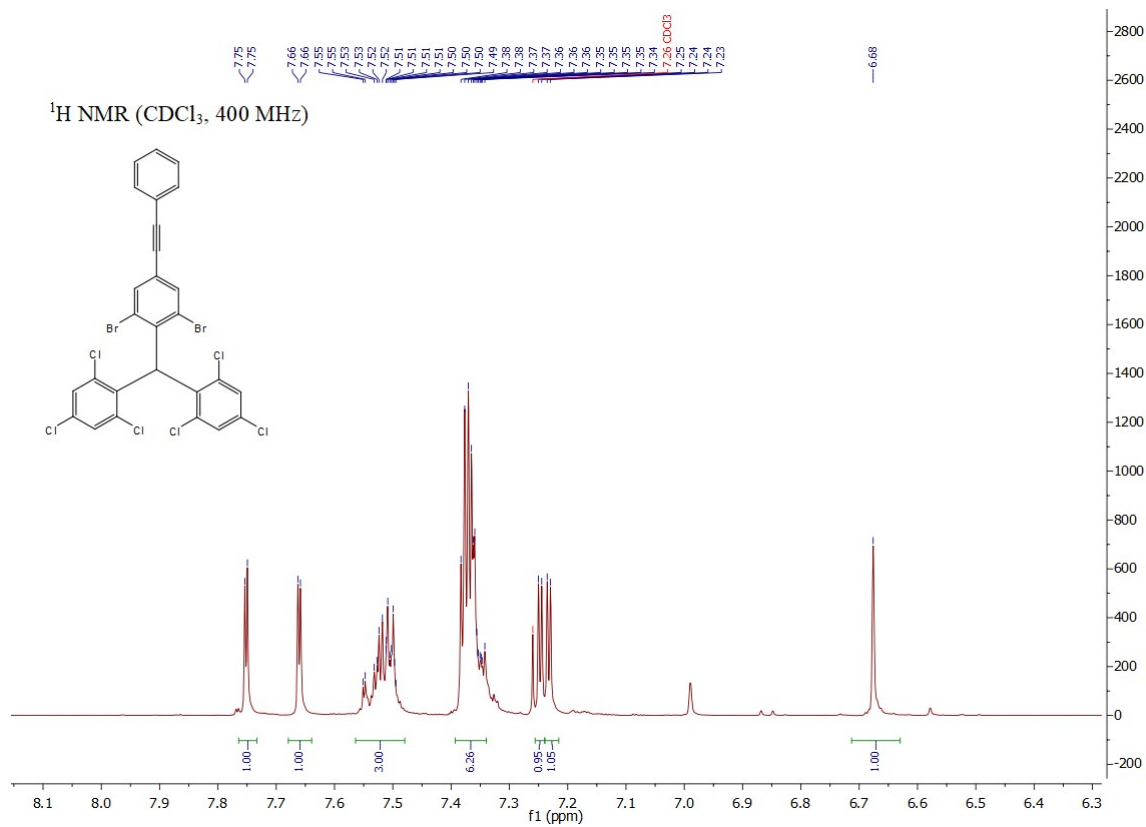
Suzuki-polymer radical

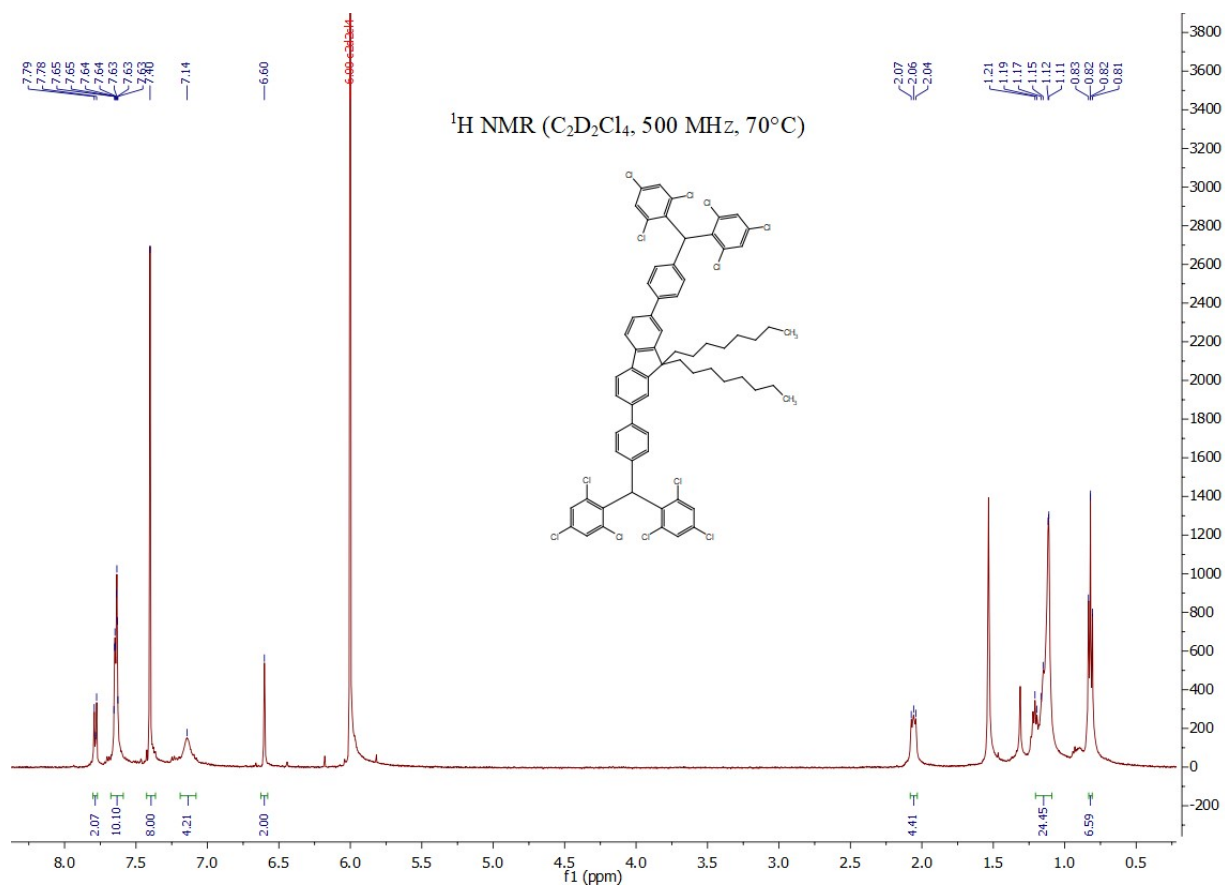
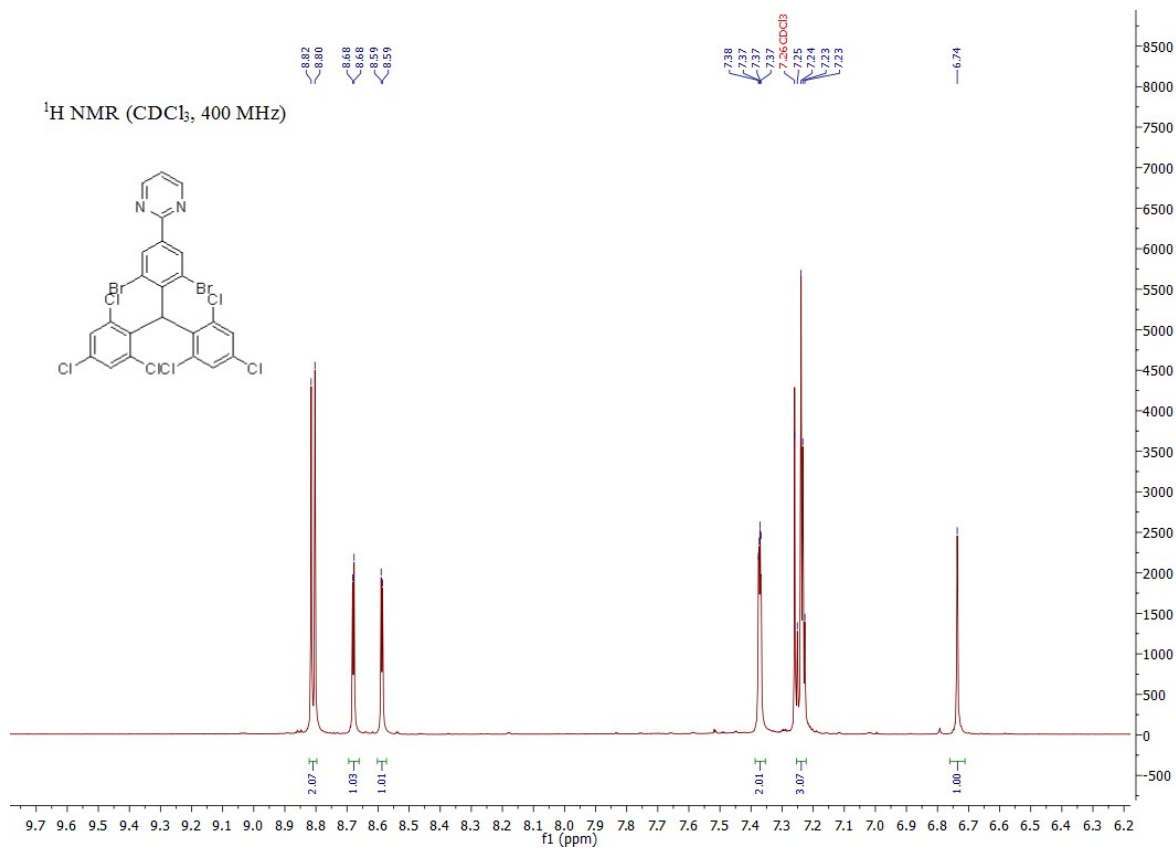


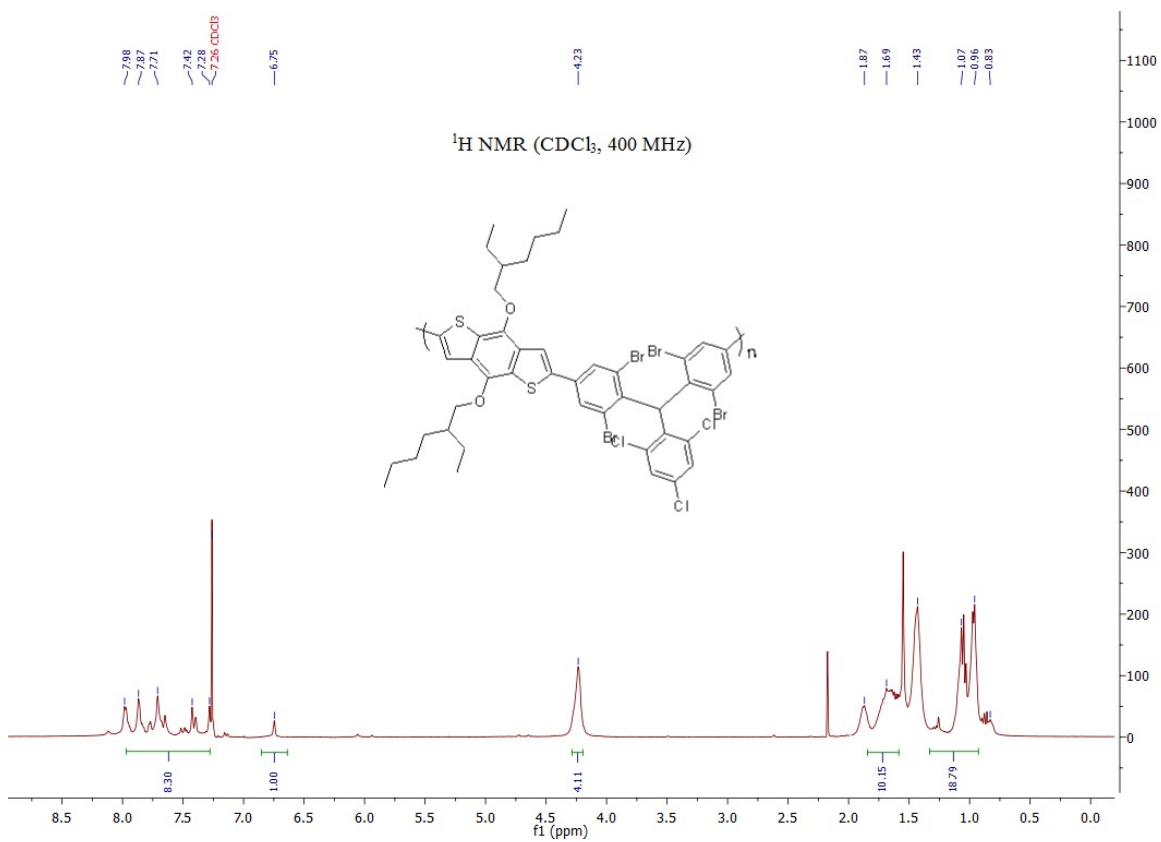
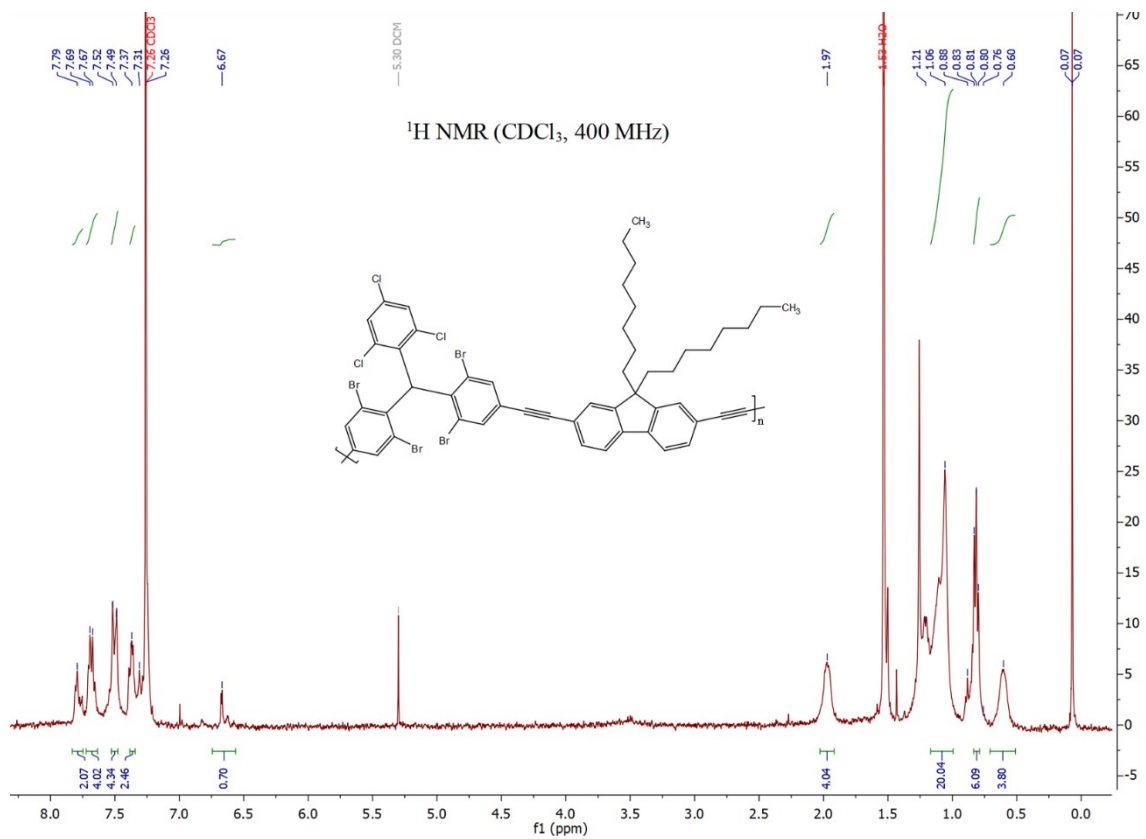
The crude product is dispersed in acetone. The dark dispersion is centrifuged for 5 minutes at 3900 rpm and the supernatant is disposed. The procedure is repeated for 3 times. After drying, the product is obtained as a dark green powder. **IR:** see Figure S1k.

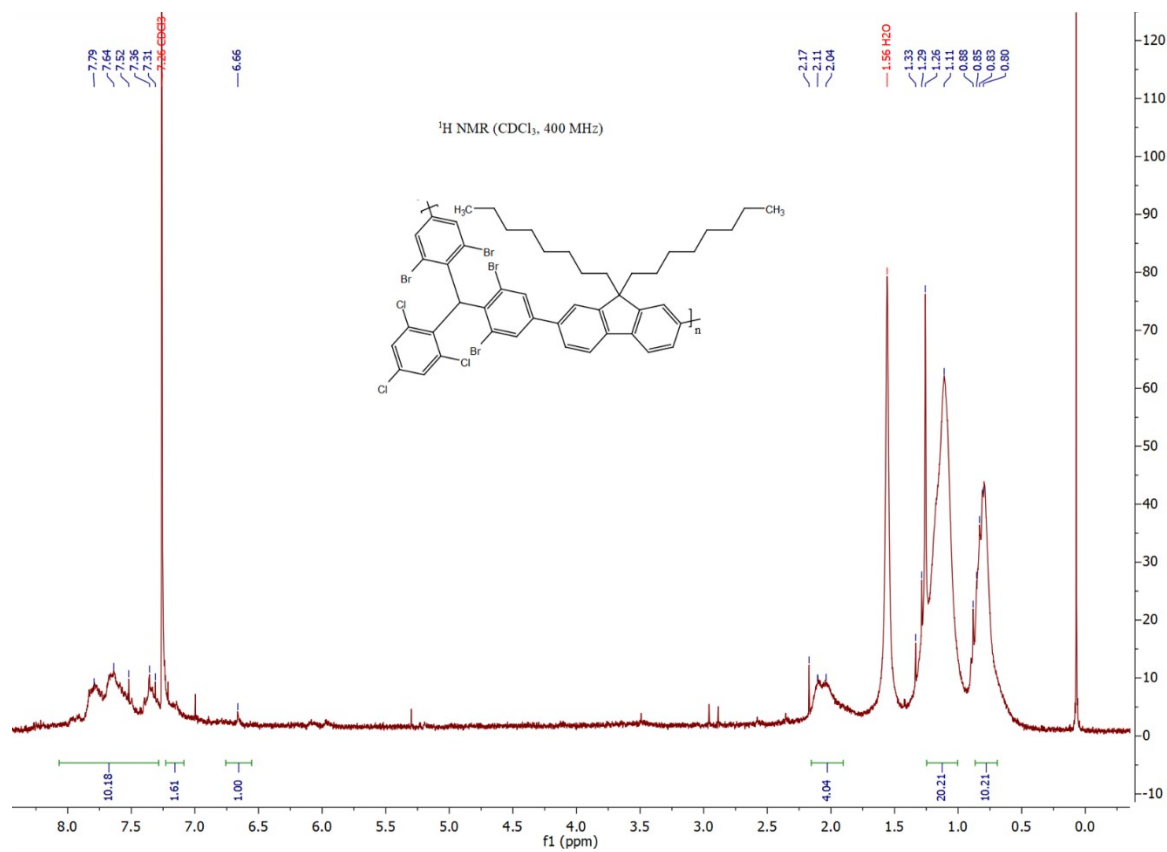
NMR spectra of newly synthesized compounds











IR spectra of synthesized radicals

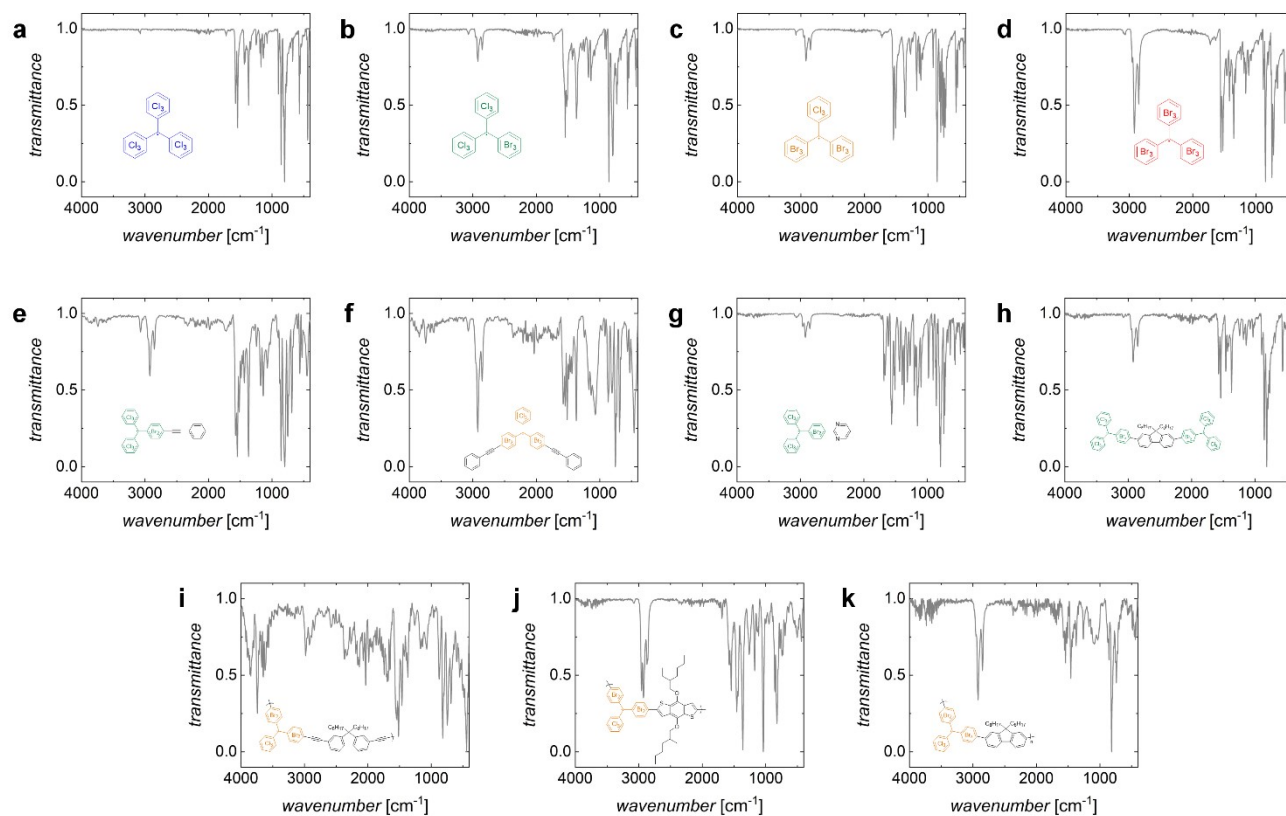


Figure S1: IR spectra of all synthesized open shell molecules with corresponding chemical structure.

MALDI-TOF spectrum of Sonogashira-polymer radical

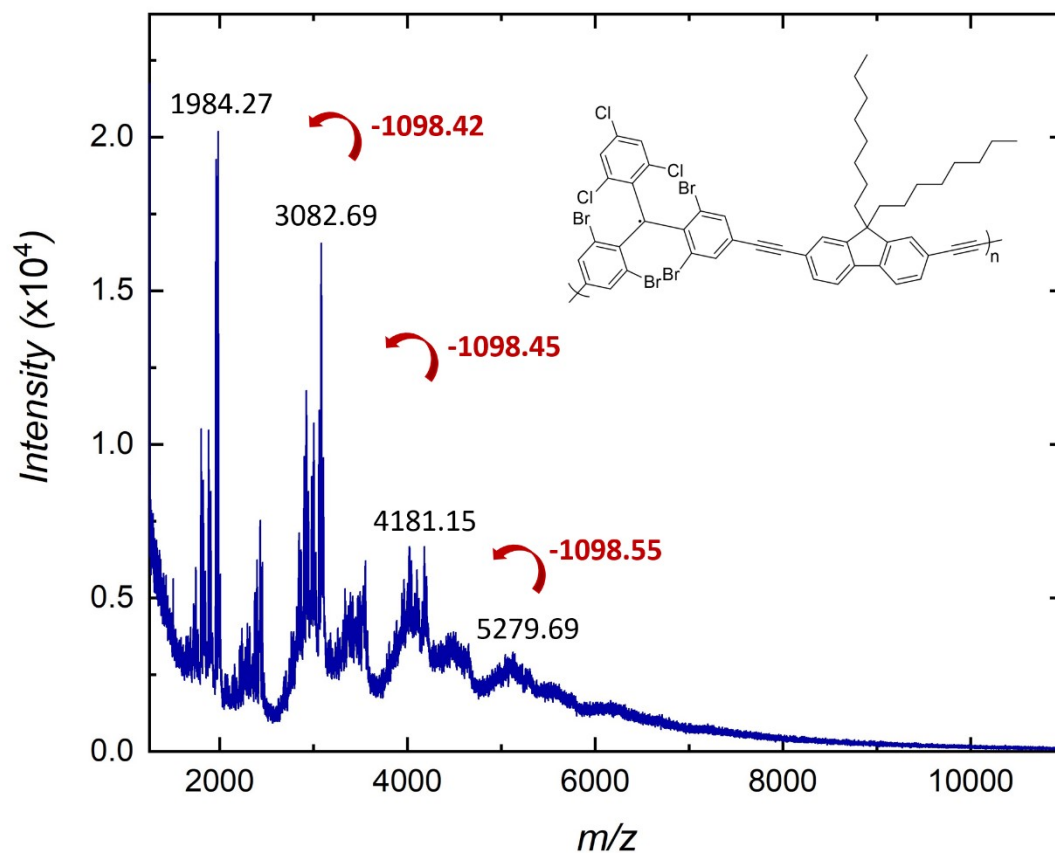


Figure S2: MALDI-TOF spectrum of Sonogashira-polymer radical using DCTB as matrix. The fragmentation pattern shows that the repetition unit of the polymer has a molecular weight of 1098.5 g/mol. This is in accordance with the chemical structure that we proposed for our radical, which is also shown in the figure.

DFT calculations of mixed halide radicals

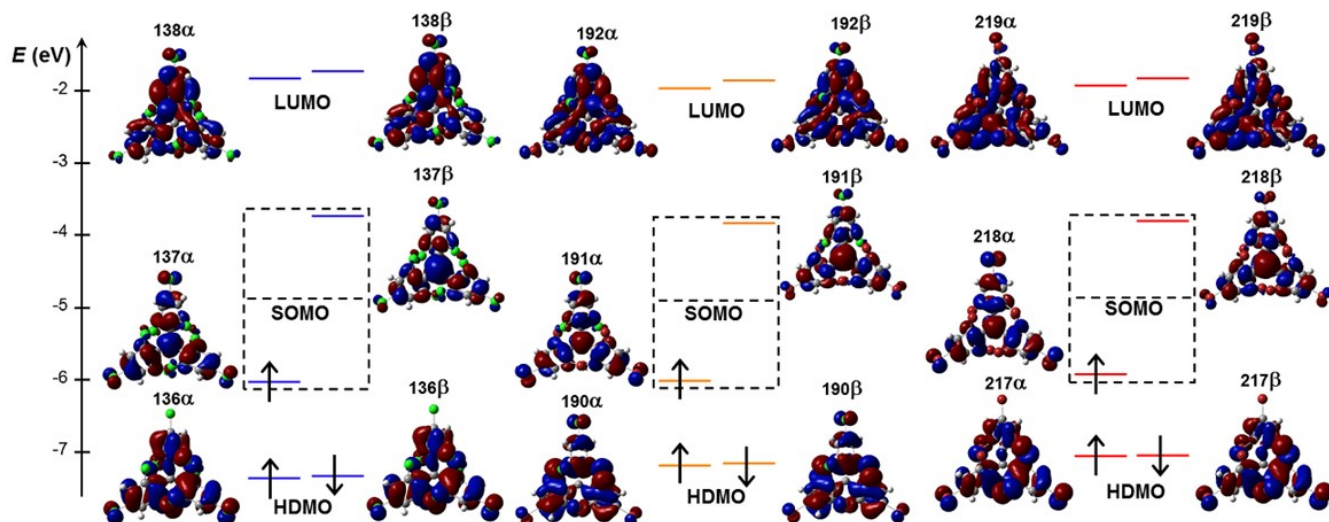


Figure S3: Frontier molecular orbitals and energy diagrams for the electronic ground state of TTM (left), TBr₆Cl₃M (middle) and TTBrM (right) radicals obtained by DFT calculations using U-B3LYP/6-31+G(d).

Table S1: Energies E and oscillator strengths f of the vertical $D_1 \rightarrow D_0$ transitions of the TTXM radicals.

Compound	TTM	TBr ₃ Cl ₆ M	TBr ₆ Cl ₃ M	TTBrM
$E(D_1 \rightarrow D_0)$ [eV]	2.22	2.14	1.96	1.84
$f(D_1 \rightarrow D_0)$	0.026	0.028	0.025	0.022

Table S2: Cartesian coordinates of the TTXM radicals in their optimizes ground (D_0) and first excited state (D_1) geometry, calculated by (TD-)DFT (U-B3LYP(6-31+G(d))).

		Coordinates (D_0) [Å]			Coordinates (D_1) [Å]		
		X	Y	Z	X	Y	Z
TTM	C	-0.493807	-3.686538	0.907287	-0.868932	-3.604616	0.866117
	C	-0.598194	-2.298615	0.898040	-0.847914	-2.226599	0.880274
	C	0.123628	-1.469136	-0.000151	-0.002178	-1.419639	0.000239
	C	0.973915	-2.166420	-0.898260	0.840951	-2.229129	-0.879998
	C	1.102893	-3.552280	-0.907381	0.857430	-3.607219	-0.866296
	C	0.362156	-4.304116	-0.000010	-0.006914	-4.301927	-0.000224
	Cl	0.508841	-6.047189	0.000110	-0.009831	-6.038094	-0.000514
	Cl	-1.620513	-1.609426	2.145841	-1.842867	-1.433479	2.068188
	Cl	1.866856	-1.316200	-2.146027	1.838652	-1.438849	-2.067480

	C	0.000019	0.000087	-0.000142	0.000104	0.029470	0.000276
	C	1.210578	0.841755	-0.000070	1.264350	0.753069	0.004552
	C	-1.334198	0.627551	-0.000089	-1.261968	0.756966	-0.004263
	C	2.289924	0.631173	0.897974	2.366584	0.359173	0.824001
	C	3.439723	1.415510	0.907273	3.604812	0.989872	0.838219
	C	3.546502	2.465769	0.000177	3.787526	2.111650	0.034450
	C	2.524919	2.731584	-0.907011	2.756213	2.570554	-0.787488
	C	1.389195	1.926989	-0.897948	1.540815	1.896908	-0.802781
	C	-2.363054	0.239865	-0.898378	-2.365129	0.366499	-0.824013
	C	-3.627806	0.820928	-0.907516	-3.601371	1.001084	-0.838613
	C	-3.908761	1.838125	0.000041	-3.780835	2.123396	-0.034856
	C	-2.946083	2.270561	0.907529	-2.748381	2.579057	0.787420
	C	-1.691824	1.667184	0.898271	-1.535094	1.901601	0.803042
	Cl	4.982734	3.464302	0.000314	5.323376	2.950915	0.047225
	Cl	0.206281	2.275533	-2.145496	0.369639	2.469960	-1.978118
	Cl	2.204303	-0.599126	2.145430	2.164666	-0.981947	1.939028
	Cl	-5.491731	2.582462	0.000129	-5.314074	2.967436	-0.048104
	Cl	-2.072763	-0.958182	-2.146385	-2.167089	-0.975309	-1.938932
	Cl	-0.583901	2.207854	2.146185	-0.362472	2.470945	1.978749
	H	-1.056766	-4.269801	1.626146	-1.514972	-4.146510	1.547248
	H	1.755446	-4.033343	-1.626150	1.501715	-4.151020	-1.547567
	H	4.226399	1.219426	1.626000	4.395252	0.634594	1.488779
	H	2.615202	3.537400	-1.625609	2.909770	3.423926	-1.437668
	H	-4.370568	0.496405	-1.626451	-4.392723	0.648295	-1.489419
	H	-3.169889	3.049573	1.626504	-2.899467	3.432889	1.437573
TTM-Br₃Cl₆	C	1.570831	3.423386	1.338948	1.450076	3.492551	1.250052
	C	2.628659	3.730724	0.488325	2.581087	3.773725	0.489302
	C	3.017911	2.846792	-0.514395	3.060583	2.846053	-0.437158
	C	2.327967	1.647879	-0.661049	2.402197	1.632704	-0.595203
	C	1.240975	1.267363	0.170145	1.252277	1.255502	0.160552
	C	0.899440	2.216456	1.170194	0.835173	2.257109	1.089595
	C	0.513929	0.000021	0.000041	0.536193	-0.000000	0.000028
	C	-0.961529	0.000048	0.000031	-0.913680	-0.000024	0.000015
	C	1.240926	-1.267336	-0.170096	1.252317	-1.255482	-0.160522
	C	2.327837	-1.648007	0.661145	2.402228	-1.632677	0.595247
	C	3.017695	-2.846961	0.514435	3.060654	-2.846002	0.437175
	C	2.628454	-3.730776	-0.488393	2.581208	-3.773650	-0.489332
	C	1.570710	-3.423286	-1.339063	1.450211	-3.492478	-1.250103
	C	0.899394	-2.216323	-1.170251	0.835266	-2.257060	-1.089612
	Cl	-0.346004	1.877293	2.358160	-0.517566	1.919138	2.158567
	Cl	2.812908	0.658726	-2.025674	2.990219	0.610766	-1.895227
	Cl	3.486037	5.242284	0.686565	3.402181	5.307986	0.684254
	Cl	2.812714	-0.659081	2.025957	2.990186	-0.610774	1.895329
	Cl	-0.345939	-1.876970	-2.358278	-0.517455	-1.919086	-2.158609
	Cl	3.485725	-5.242389	-0.686690	3.402348	-5.307882	-0.684323
	C	-1.724560	0.870059	-0.816570	-1.718407	0.929360	-0.783674
	C	-3.114755	0.888210	-0.820987	-3.095939	0.945676	-0.771735
	C	-3.801062	0.000047	0.000025	-3.790296	-0.000042	-0.000031
	C	-3.114758	-0.888117	0.821037	-3.095940	-0.945749	0.771698
	C	-1.724564	-0.869964	0.816622	-1.718410	-0.929417	0.783680
	Br	-0.893149	2.042628	-2.068034	-0.858428	2.125510	-1.968833
	Br	-0.893133	-2.042635	2.067980	-0.858464	-2.125539	1.968896

	Br	-5.698689	0.000037	0.000013	-5.673604	-0.000061	-0.000051
	H	1.281377	4.100413	2.133731	1.078305	4.200960	1.980923
	H	3.829140	3.093741	-1.188812	3.919908	3.079534	-1.054974
	H	3.828846	-3.094039	1.188899	3.919970	-3.079482	1.055004
	H	1.281262	-4.100224	-2.133925	1.078480	-4.200868	-1.981012
	H	-3.650063	1.570406	-1.469666	-3.639278	1.659269	-1.379560
	H	-3.650067	-1.570332	1.469697	-3.639289	-1.659344	1.379514
TTXM-Br ₆ Cl ₃	C	3.595712	-0.692319	0.620403	3.575666	-0.696266	0.623698
	C	3.704825	-1.744520	-0.282643	3.677459	-1.774163	-0.273138
	C	2.636681	-2.095257	-1.100814	2.586064	-2.157748	-1.055064
	C	1.450463	-1.377381	-1.003432	1.406875	-1.443825	-0.960769
	C	1.266958	-0.298766	-0.102369	1.207403	-0.316237	-0.054087
	C	2.396150	0.003953	0.699472	2.387993	-0.006898	0.732184
	C	-0.000007	0.441503	-0.000017	-0.026992	0.444165	0.007762
	C	-0.000038	1.908922	-0.000009	0.028900	1.900603	-0.006348
	C	-1.266945	-0.298814	0.102344	-1.290471	-0.249104	0.092590
	C	-1.450394	-1.377446	1.003396	-1.451329	-1.441654	0.863451
	C	-2.636587	-2.095361	1.100796	-2.619251	-2.182750	0.967704
	C	-3.704761	-1.744644	0.282655	-3.750764	-1.717592	0.307946
	C	-3.595703	-0.692425	-0.620377	-3.683314	-0.562356	-0.474822
	C	-2.396163	0.003884	-0.699464	-2.487939	0.133995	-0.581310
	Br	2.325545	1.339638	2.057355	2.289822	1.314643	2.085242
	Br	0.104239	-1.878069	-2.255421	0.023432	-1.916714	-2.151288
	Br	5.336171	-2.704916	-0.406956	5.305979	-2.716959	-0.406144
	Br	-0.104119	-1.878110	2.255340	0.032996	-2.050230	1.888331
	Br	-2.325632	1.339606	-2.057315	-2.482678	1.561925	-1.844216
	Br	-5.336076	-2.705090	0.406995	-5.387997	-2.665408	0.451333
	C	0.774772	2.676129	-0.910896	0.889056	2.624009	-0.878693
	C	0.784024	4.066376	-0.922405	0.995927	4.008709	-0.909014
	C	-0.000084	4.753453	0.000021	0.192941	4.755640	-0.051594
	C	-0.784173	4.066330	0.922430	-0.680501	4.124777	0.831893
	C	-0.774882	2.676084	0.910887	-0.740817	2.736117	0.852272
	Cl	1.699671	1.908352	-2.188576	1.844637	1.748593	-2.069138
	Cl	-1.699769	1.908247	2.188539	-1.772478	2.038763	2.091991
	Cl	-0.000110	6.502263	0.000044	0.285544	6.505609	-0.080056
	H	4.424635	-0.427397	1.264932	4.421430	-0.424597	1.244173
	H	2.729940	-2.901200	-1.818052	2.671823	-2.980279	-1.754916
	H	-2.729804	-2.901318	1.818024	-2.656571	-3.078274	1.576058
	H	-4.424651	-0.427516	-1.264880	-4.554162	-0.225888	-1.024656
	H	1.377180	4.600793	-1.654810	1.666436	4.493295	-1.608874
	H	-1.377350	4.600712	1.654844	-1.285713	4.704813	1.518677
TTXM-Br ₉	C	3.695798	0.382602	0.872724	-0.858645	-3.587787	0.864148
	C	2.379240	-0.059149	0.860690	-0.853389	-2.208523	0.864412
	C	1.387754	0.476389	0.000051	-0.000365	-1.403730	0.000008
	C	1.841648	1.507862	-0.860516	0.851952	-2.209351	-0.864344
	C	3.152104	1.967402	-0.872516	0.856124	-3.588622	-0.863800
	C	4.072912	1.397640	0.000108	-0.001507	-4.279500	0.000266
	Br	5.866785	2.013077	0.000100	-0.002298	-6.166812	0.000393
	Br	1.956347	-1.360979	2.184340	-1.932470	-1.351987	2.155764
	Br	0.708595	2.276063	-2.184086	1.931373	-1.354011	-2.156213
	C	0.000025	0.000142	-0.000069	0.000137	0.047378	-0.000026

C	-1.106340	0.963760	-0.000216	1.259744	0.761424	0.005004
C	-0.281358	-1.439824	-0.000035	-1.259037	0.762204	-0.005014
C	-1.138471	2.090308	0.860244	2.370798	0.332431	0.783855
C	-2.179584	3.009305	0.872348	3.609225	0.954316	0.820272
C	-3.247232	2.827996	-0.000146	3.789340	2.103034	0.056962
C	-3.280019	1.745619	-0.872699	2.754765	2.591008	-0.739969
C	-2.226612	0.840740	-0.860673	1.535921	1.927803	-0.763249
C	0.385208	-2.348599	-0.860477	-2.370212	0.334048	-0.784134
C	0.128065	-3.713278	-0.872545	-3.608259	0.956683	-0.820630
C	-0.825801	-4.225937	-0.000023	-3.787830	2.105322	-0.057077
C	-1.516453	-3.391903	0.872534	-2.753116	2.592488	0.740160
C	-1.240968	-2.030812	0.860449	-1.534666	1.928560	0.763500
Br	-4.677550	4.073340	-0.000031	5.459260	3.005255	0.090303
Br	-2.325291	-0.524906	-2.183937	0.267095	2.588852	-2.019662
Br	0.200733	2.375686	2.183497	2.140406	-1.167666	1.936897
Br	-1.189578	-6.087203	-0.000002	-5.457222	3.008523	-0.090478
Br	1.617423	-1.751351	-2.183676	-2.140481	-1.165850	-1.937584
Br	-2.157445	-1.013758	2.183926	-0.265825	2.588468	2.020516
H	4.410026	-0.046492	1.564400	-1.505070	-4.130105	1.543728
H	3.452484	2.744623	-1.564150	1.502028	-4.131579	-1.543363
H	-2.165234	3.842466	1.563941	4.405559	0.570834	1.446437
H	-4.103342	1.616852	-1.564231	2.907042	3.466730	-1.359185
H	0.651146	-4.361976	-1.564095	-4.404702	0.573836	-1.447045
H	-2.245211	-3.795966	1.564127	-2.905006	3.468120	1.359598

Transient photoluminescence profile of mixed halide radicals

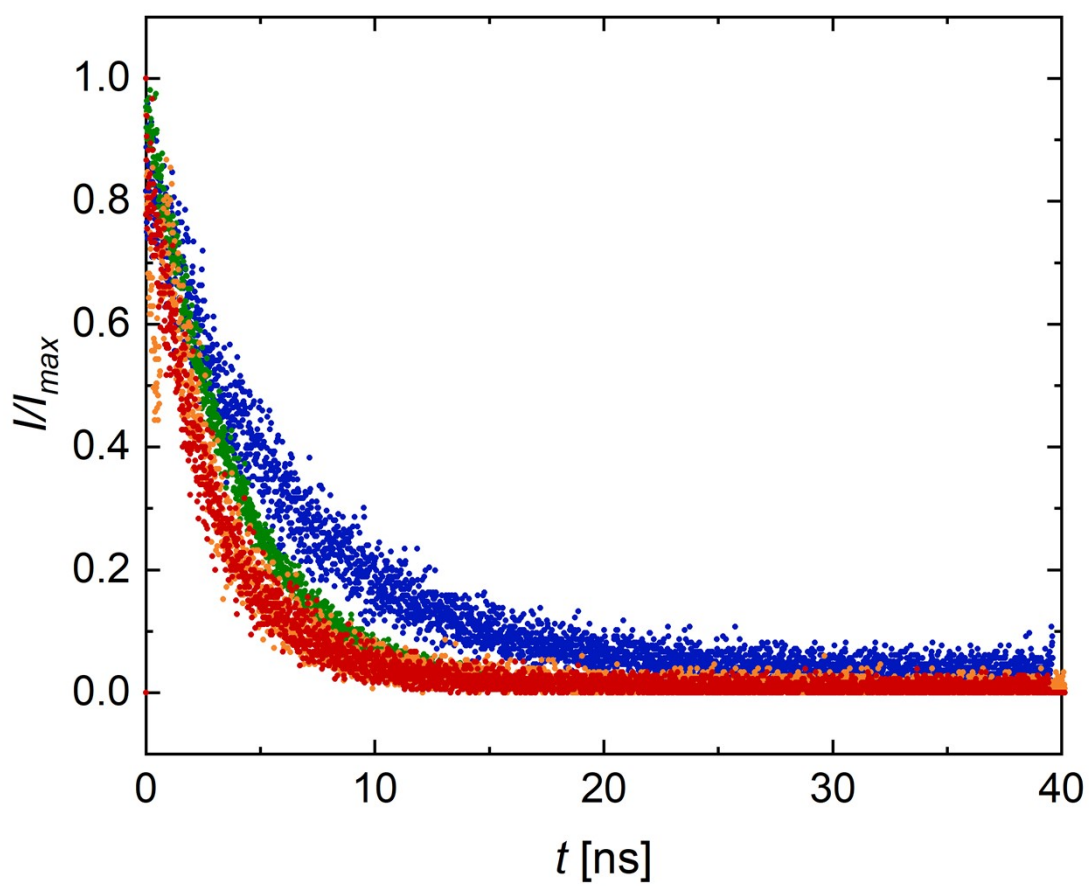


Figure S4: Normalized transient photoluminescence spectra of degassed DCM solutions of TTM (●), TTBr₃Cl₆M (●), TBr₆Cl₃M (●) and TBrM (●).

Optical characterization of coupling products

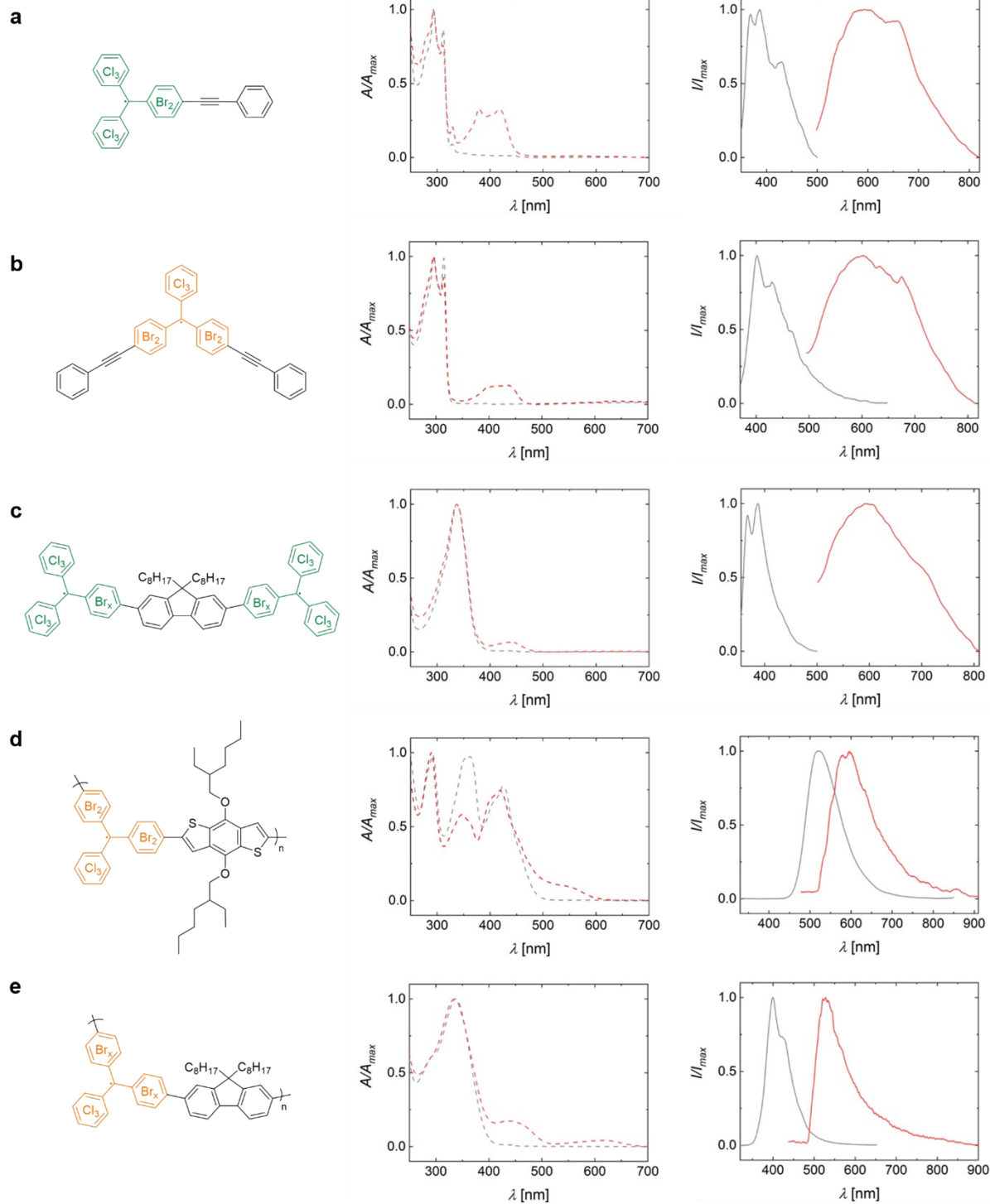


Figure S5: (a)-(e) Normalized absorption (dotted lines) and PL (straight lines) spectra of newly formed radicals (—) and their corresponding precursors (---). The photoluminescence spectra of the radicals are obtained by excitation into the absorption signal assumably deriving from the HDMO→SOMO transition.

Electron paramagnetic resonance (EPR) spectra of coupling products

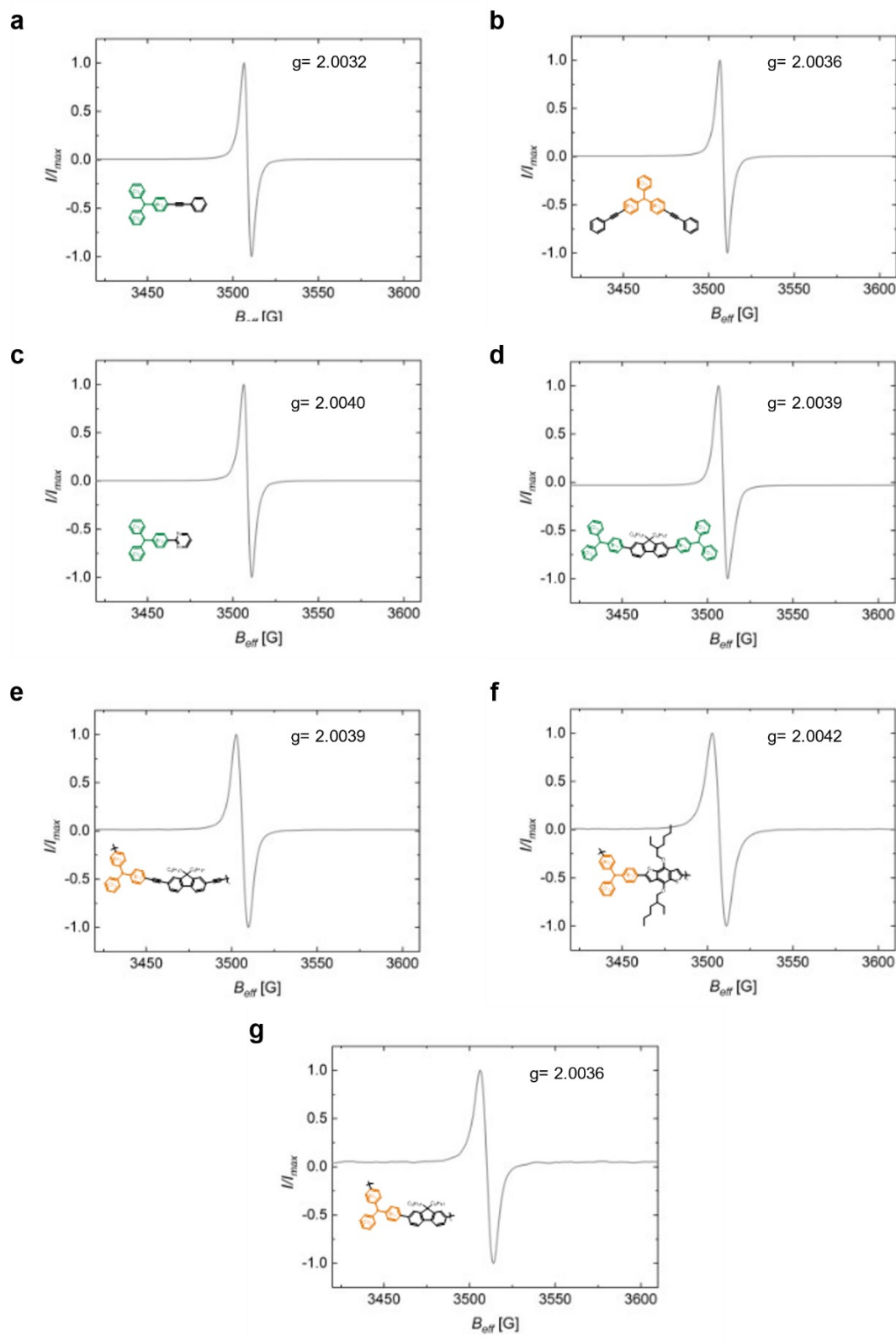
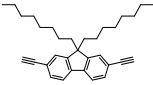
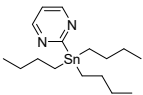
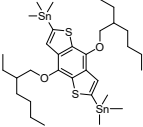
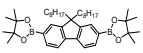
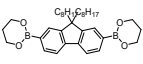
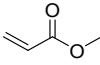
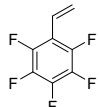


Figure S6: Normalized EPR spectra of coupling products measured in toluene with corresponding g-factors.

Overview of all cross-coupling reactions

Table S3: Performed cross-coupling reactions to test the reactivity of the mixed-halide triphenylmethyl motives including reaction conditions. A check (✓) indicates that the respective reaction has worked, while a cross (✗) implies that no conversion is achieved under the given conditions.

Reactant 1	Reactant 2	Coupling reaction	Catalyst	Base	Solvent	Temperature	Reaction time	
HBr ₃ Cl ₆		Sonogashira	Pd(PPh ₃) ₄ [10 mol%]/ PPh ₃ [20 mol%]/ CuI [10 mol%]	NEt ₃ [150 eq]	THF	50 °C	24 h	✓
HBr ₆ Cl ₃		Sonogashira	Pd(PPh ₃) ₄ [20 mol%]/ PPh ₃ [40 mol%]/ CuI [20 mol%]	NEt ₃ [300 eq]	THF	50 °C	24 h	✓
HBr ₆ Cl ₃		Sonogashira polymerization	Pd(PPh ₃) ₄ [20 mol%]/ PPh ₃ [40 mol%]/ CuI [20 mol%]	NEt ₃ [450 eq]	THF	50 °C	24 h	✓
HBr ₃ Cl ₆		Stille	PdCl ₂ (PPh ₃) ₂ [10 mol-%]		DMF	110 °C	18 h	✓
HBr ₆ Cl ₃		Stille polymerization	Pd(PPh ₃) ₄ [10 mol-%]		Toluene	110 °C	36 h	✓
HBr ₃ Cl ₆		Suzuki	Pd(PPh ₃) ₄ [10 mol%]	K ₃ PO ₄ [26 eq]	Toluene/ EtOH/ H ₂ O	90 °C	2-48 h	(✓) Br abstraction
HBr ₆ Cl ₃		Suzuki Polymerization	Pd ₂ (dba) ₃ [3 mol%]/ P(<i>o</i> -Tolyl) ₃ [12 mol%]	K ₃ PO ₄ [2 eq]	Toluene/ EtOH/ H ₂ O	80 °C	46 h	(✓) Br abstraction
HBr ₃ Cl ₆		Heck	Pd(OAc) ₂ [10 mol%]/ P(<i>o</i> -Tolyl) ₃ [50 mol%]	NEt ₃ [1 eq]	DMF	100 °C	24 h	✗

HBr ₃ Cl ₆		Heck	Pd(OAc) ₂ [2 mol%]/ PPh ₃ [6 mol%]	NEt ₃ [2 eq]	DMF	120 °C	24 h	✗
HBr ₃ Cl ₆		Heck	Pd(OAc) ₂ [2 mol%]/ PPh ₃ [6 mol%]	K ₂ CO ₃ [2 eq]	DMF	120 °C	24 h	✗
HBr ₃ Cl ₆		Heck	Pd(OAc) ₂ [5 mol%]/ PPh ₃ [15 mol%]	NEt ₃ [2 eq]	DMF	120 °C	24 h	✗
HBr ₃ Cl ₆		Heck	Pd(OAc) ₂ [5 mol%]/ P(<i>o</i> -Tol) ₃ [15 mol%]	NEt ₃ [2 eq]	DMF	120 °C	24 h	✗
HBr ₃ Cl ₆		Direct arylation	Pd(OAc) ₂ [5 mol%]/ (1-Ad) ₂ POH [10 mol%]	KHCO ₃ [2 eq]	DMF	120 °C	24 h	✗
HBr ₃ Cl ₆		Direct arylation	Pd(OAc) ₂ [5 mol%]/ (1-Ad) ₂ POH [10 mol%]	LiO ^t Bu [2 eq]	DMF	120 °C	24 h	✗
HBr ₃ Cl ₆	HBr ₃ Cl ₆	Yamamoto	Ni(cod) ₂ [163 mol%]	Bpy [1.63 eq]	DMF	80 °C	88 h	✗

IR spectroscopy of Stille-type radical polymer

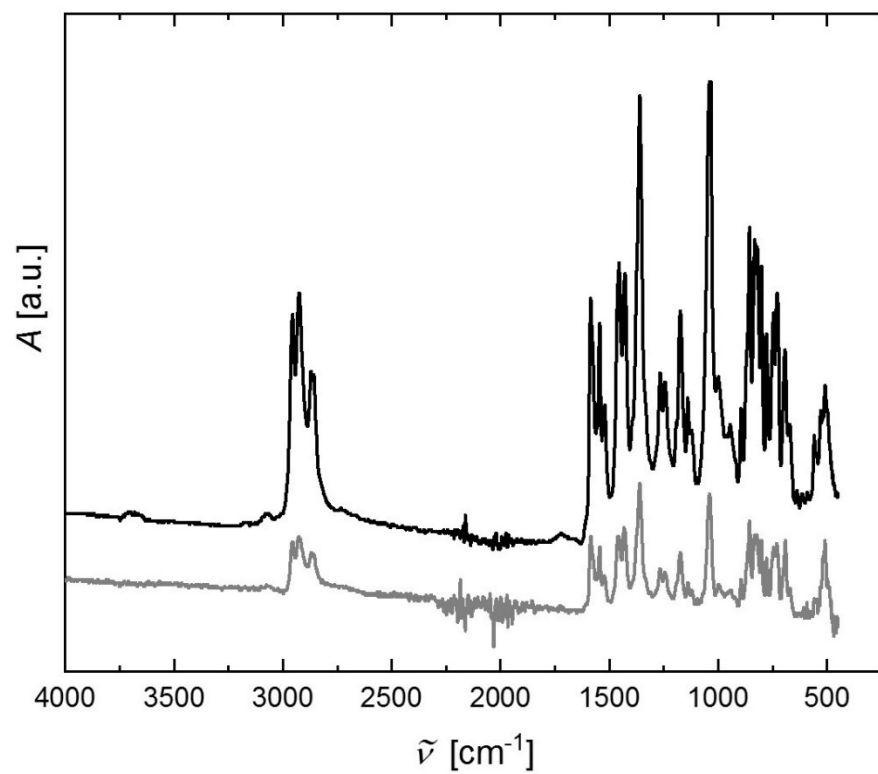


Figure S7: IR spectra of Stille-polymer before (—) and after (—) conversion to the radical.

Increasing radical conversion efficiency for the polymeric materials

Standard reaction conditions for the radical conversion of the precursor molecules include stirring of the H-compound with 2 equivalents of tetrabutylammonium hydroxide (TBAH) at room temperature and the subsequent addition of 5 equivalents of *p*-chloranil. However, these conditions only deliver very low yields for the radical conversion of the polymeric materials. By increasing the reaction temperature to 60°C and the base concentration to 3 equivalents, the radical transformation could be performed with higher yields. The ratio of transformed radicals is measured by EPR spectroscopy. Spin density is determined based on concentration dependent calibration with DPPH.

Table S4: Conversion of the polymers to the corresponding radicals depending on the reaction conditions.

	Sonogashira Polymer	Stille Polymer	Suzuki Polymer ¹
Ratio of transformed radicals (room temperature, 2 eq TBAH, 5 eq <i>p</i> -chloranil)	3 %	2 %	25 %
Ratio of transformed radicals (60°C, 3 eq TBAH, 5 eq <i>p</i> - chloranil)	41 %	22 %	28 %

¹ The value of the Suzuki Polymer could not be determined accurately, since the number of bromine atoms present at the trityl moiety is unknown. Depending on the degree of bromine-hydrogen substitution the value could be up to 6 % lower.

References

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