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**Synthesis of [1]benzothieno[3,2-*b*][1]benzothiophene pendant and norbornene
random co-polymers *via* ring opening metathesis.**

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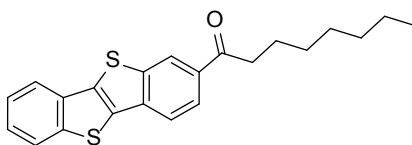
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Electronic Supplementary Information (ESI)

General Methods. All chemicals were purchased from commercial suppliers unless otherwise specified. ¹H NMR and ¹³C NMR spectra were recorded on a BRUKER 400 spectrometer in CDCl₃ solution at 298 K. Number average (*M_n*) and weight-average (*M_w*) were determined by Agilent Technologies 1200 series GPC running in chlorobenzene at 80 °C, using two PL mixed B columns in series, and calibrated against narrow polydispersity polystyrene standards. Electrospray mass spectrometry was performed with a Thermo Electron Corporation DSQII mass spectrometer. UV-vis spectra were recorded on a UV-1601 Shimadzu UV-vis spectrometer. Column chromatography was carried out on silica gel (for flash chromatography, VWR). BTBT was synthesised following literature procedures [14].

[1]Benzothieno[3,2-*b*][1]benzothiophene-2-octan-1-one.



[1]Benzothieno[3,2-*b*][1]benzothiophene (4 g, 16.64 mmol) was dissolved in dry dichloromethane (200 mL), under argon, followed by the addition of aluminum chloride (5.55 g, 41.6 mmol) at -10 °C. The solution was cooled to -78 °C and octyl

acid chloride (3.04 ml, 18.31 mmol) was added dropwise, and the mixture was stirred for 1h at the same temperature. The reaction mixture was allowed to stand without cooling and stirred for 3 h at rt. The reaction mixture was cooled to 0 °C, quenched with ice water (10 mL), and diluted with methanol to give a precipitate. The precipitate was filtered and washed with water (2 x 50 mL) and methanol (2 x 50 mL), then dried *in vacuo* to give [1]benzothieno[3,2-*b*][1]benzothiophene-2-octan-1-one (6 g, 16.37 mmol, 98 % yield) as white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, J = 0.8 Hz, 1H), 8.06 (dd, J = 8.3, 1.4 Hz, 1H), 7.99 - 7.87 (m, 3H), 7.49 (pd, J = 7.1, 1.2 Hz, 2H), 3.08 (t, J = 7.4 Hz, 2H), 1.88 - 1.76 (q, J = 7.4 Hz, 2H), 1.51 - 1.26 (m, 8H), 0.93 (t, J = 6.8 Hz, 3H).

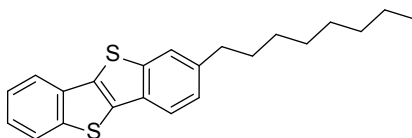
¹³C NMR (101 MHz, CDCl₃) δ 199.60, 142.81, 142.24, 136.93, 136.24, 133.63, 132.98, 132.77, 125.84, 125.14, 124.71, 124.53, 124.16, 122.07, 121.37, 38.83, 31.76, 29.41, 29.21, 24.56, 22.67, 14.13.

FT-IR (ν/cm⁻¹): 2956, 2919, 2852, 1677 (strong, C=O), 1586, 1463, 1426, 1385, 1342, 1321, 1295, 1275, 1252, 1226, 1191, 984, 952, 900, 811, 770.

MS (EI) m/z = 366 (M).

M.P. = 163 °C.

2-Octyl-[1]benzothieno[3,2-*b*][1]benzothiophene.



To a stirred suspension of aluminium chloride (4.55 g, 34.1 mmol) in dry diethyl ether (50 mL), under argon, was added lithium aluminium hydride, 1 M solution in Et₂O (34.1 ml, 34.1 mmol) dropwise. To the resulting reaction mixture, a solution of [1]benzothieno[3,2-*b*][1]benzothiophene-2-octan-1-one (5 g, 13.64 mmol) in dry dichloromethane (300 mL) was slowly added dropwise and was stirred at room temperature overnight. The reaction was quenched by cooling to 0 °C and adding ice water, then 2 M HCl was added until acidic pH was achieved. The reaction was extracted with dichloromethane (2 × 100 mL), the combined organic phases were washed with sat. aq. NaCl (2 x 100 mL), water (100 mL), dried over MgSO₄, and concentrated *in vacuo* to give 2-octyl-[1]benzothieno[3,2-*b*][1]benzothiophene (4.8 g, 13.61 mmol, 100 % yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.93 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.89 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.74 (d, 1.4 Hz, 1H), 7.47 (td, *J* = 7.5, 1.1 Hz, 1H), 7.40 (td, *J* = 7.4, 1.1 Hz, 1H), 7.31 (dd, *J* = 8.1, 1.4 Hz, 1H), 2.81 - 2.76 (t, *J* = 7.8 Hz, 2H), 1.72 (dt, *J* = 15.3, 7.7 Hz, 2H), 1.39 - 1.28 (m, 10H), 0.91 (t, *J* = 6.9 Hz, 3H).

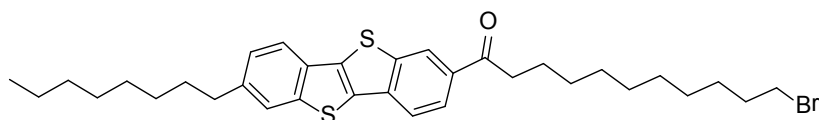
¹³C NMR (101 MHz, CDCl₃) δ 142.60, 142.10, 140.42, 133.41, 133.29, 132.60, 131.03, 125.92, 124.82, 124.71, 124.00, 123.37, 121.42, 121.27, 36.15, 31.90, 31.71, 29.50, 29.33, 29.27, 22.68, 14.12.

FT-IR (ν/cm⁻¹): 3049, 2958, 2919, 2874, 2850, 1677 (weak), 1590, 1551, 1465, 1450, 1429, 1411, 1379, 1336, 1299, 1269, 1254, 1228, 1193, 1165, 1126, 1070, 1057, 1016, 986, 952, 932, 891.

MS (EI) *m/z* = 352 (M).

M.P. = 112 °C.

2-Octyl-7-(11-bromoundecan-1-one)[1]benzothieno[3,2-*b*][1]benzothiophene.



11-Bromoundecanoic acid (0.752 g, 2.84 mmol) was dissolved in dry dichloromethane (200 mL), under argon, followed by the addition of oxalyl chloride (0.336 ml, 3.97 mmol). Four drops of dry DMF were added and the mixture was stirred for one hour until the evolution of gas ceased. The reaction mixture was concentrated *in vacuo* to remove the solvents and excess oxalyl chloride before taking onto the next step. 2-Octyl-[1]benzothieno[3,2-*b*][1]benzothiophene (1 g, 2.84 mmol) was dissolved in dry dichloromethane (200 mL), under argon, followed by the addition of aluminium chloride (0.378 g, 2.84 mmol) at -10 °C. The solution was cooled to -78 °C and 11-bromoundecanoic acid chloride (0.805 g, 2.84 mmol) was added drop-wise, and the mixture was stirred for 1 h at the same temperature. The reaction mixture was allowed to stand without cooling and stirred for 3 h at rt. The reaction mixture was cooled to 0 °C, quenched with ice water (10 mL), and diluted with methanol to give a precipitate. The precipitate was filtered and washed with water (2 x 50 mL) and methanol (2 x 50 mL), then dried *in vacuo* to give 2-octyl-7-(11-bromoundecan-1-one)[1]benzothieno[3,2-*b*][1]benzothiophene (1.5 g, 2.501 mmol, 88 % yield) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 8.56 (d, $J = 1.0$ Hz, 1H), 8.07 (dd, $J = 8.4, 1.5$ Hz, 1H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.2$ Hz, 1H), 7.76 (d, $J = 0.6$ Hz, 1H), 7.33 (dd, $J = 8.2, 1.4$ Hz, 1H), 3.43 (t, $J = 6.9$ Hz, 2H), 3.08 (t, $J = 7.4$ Hz, 2H), 2.80 (t, $J = 7.3$ Hz, 2H), 1.92 - 1.68 (m, 6H), 1.46 - 1.26 (m, 23H), 0.91 (t, $J = 6.9$ Hz, 3H).

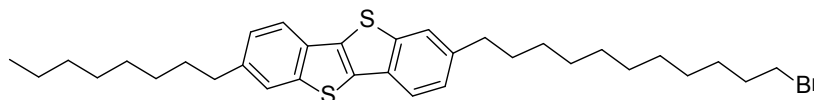
^{13}C NMR (101 MHz, CDCl_3) δ 199.08, 142.69, 141.57, 140.91 (2C), 135.97, 132.89, 131.67, 130.20, 125.70, 124.19, 124.02, 122.94, 121.24, 120.66, 38.26, 35.68, 33.51, 32.32, 31.36, 31.12, 29.19, 28.96, 28.92, 28.87, 28.80, 28.74, 28.24, 27.66, 24.04, 22.15, 13.58.

FT-IR (ν/cm^{-1}): 2960, 2917, 2850, 1679 (C=O strong), 1584, 1463, 1403, 1383, 1366, 1340, 1303, 1279, 1256, 1245, 1219, 1198, 1137, 1092, 1077, 1051, 1036, 1103, 978, 952, 906, 878, 825, 780, 710, 650.

MS (EI) $m/z = 599$ (M).

M.P. = 135 °C.

2-Octyl-7-(11-bromoundecane)[1]benzothieno[3,2-b][1]benzothiophene.



To a stirred suspension of aluminum chloride (0.834 g, 6.25 mmol) in dry diethyl ether (50 mL), under argon, was added lithium aluminium hydride, 1 M solution in Et₂O (6.25 ml, 6.25 mmol) dropwise. To the resulting reaction mixture, a solution of 2-octyl-7-(11-bromoundecan-1-one)[1]benzothieno[3,2-*b*][1]benzothiophene (1.5 g, 2.501 mmol) in dry dichloromethane (300 mL) was slowly added dropwise and was stirred at room temperature overnight. The reaction was quenched by cooling to 0 °C and adding ice water, then 2 M HCl was added until acidic pH was achieved. The reaction was extracted with dichloromethane (2 × 100 mL), the combined organic phases were washed with sat. aq. NaCl (2 x 100 mL), water (100 mL), dried over MgSO₄, and concentrated *in vacuo* to give 2-octyl-7-(11-bromoundecane)[1]benzothieno[3,2-*b*][1]benzothiophene (1.45 g, 2.475 mmol, 99 % yield) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 7.77 (d, J = 8.1 Hz, 2H), 7.71 (s, 2H), 7.28 (d, J = 8.6 Hz, 2H), 3.41 (t, J = 6.9 Hz, 2H), 2.77 (t, 7.8 Hz, 4H), 1.86 (dt, J = 15.2, 6.9 Hz, 2H), 1.71 (dt, J = 15.3, 7.7 Hz, 4H), 1.46 - 1.23 (m, 25H), 0.90 (t, J = 7.0 Hz, 3H).

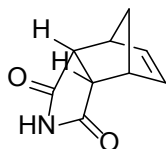
¹³C NMR (126 MHz, CDCl₃) δ 142.41, 140.09, 140.03, 132.55, 131.20, 125.83, 123.33, 121.07, 36.12, 34.03, 32.84, 31.89, 31.71, 31.67, 29.50, 29.41, 29.33, 29.26, 28.76, 28.18, 22.67, 14.10.

FT-IR (ν/cm⁻¹): 3050, 2960, 2919, 2850, 2731, 2650, 1597, 1549, 1461, 1441, 1407, 1336, 1305, 1286, 1262, 1236, 1210, 1187, 1135, 1092, 1055, 1016, 950, 874, 814, 792.

MS (EI) m/z = 585 (M).

M.P. = 72 °C.

Cis-5-norbornene-endo-2,3-dicarboxylic imide



A solution of *cis*-5-norbornene-*endo*-2,3-dicarboxylic anhydride (1 g, 6.09 mmol) and ammonium acetate (0.470 g, 6.09 mmol) in acetic acid (10 ml) was stirred at 140 °C for 16 hours. The reaction mixture was diluted with water (100 mL) and extracted with EtOAc (3 × 100 mL). The combined organic layers were dried (MgSO₄) and concentrated *in vacuo* to produce *cis*-5-norbornene-*endo*-2,3-dicarboxylic imide as a white solid.

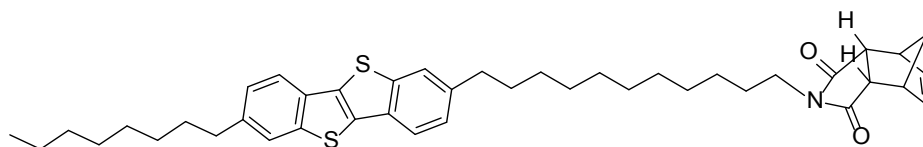
¹H NMR (400 MHz, CDCl₃) δ 7.92 (bs, 1H), 6.31 (t, J = 1.8 Hz, 2H), 3.33 (m, 2H), 2.76 (d, J = 1.4 Hz, 2H), 1.60 (ddt, J = 9.8, 2.9, 1.4 Hz, 1H), 1.49 (ddt, J = 9.8, 2.9, 1.4 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 177.29, 137.27, 48.65, 44.69, 42.44.

FT-IR (ν/cm⁻¹): 3165, 3143, 3072, 2999, 2973, 2949, 1759, 1715, 1685, 1422, 1388, 1336, 1182, 978, 924, 898, 854.

MS (EI) m/z = 163 (M).

2-Octyl-7-(11-(*cis*-5-norbornene-*endo*-2,3-dicarboxylicimide)undecane)
[1]benzothienopheno[3,2-*b*] benzothienophene.



2-Octyl-7-(11-bromoundecane)[1]benzothieno[3,2-*b*][1]benzothiophene (0.5 g, 0.854 mmol), *cis*-5-norbornene-*endo*-2,3-dicarboxylic imide (0.209 g, 1.280 mmol) and potassium carbonate (0.177 g, 1.280 mmol), in dry DMF (50 ml) and dry THF (50.0 ml), were refluxed overnight under N₂. The reaction mixture was cooled to room temperature and the THF was removed *in vacuo*. Water (50 mL) was added to the reaction mixture and the precipitate was filtered, washed with water (50 mL) and methanol (50 mL), then dried *in vacuo* to give 2-octyl-7-(11-(*cis*-5-norbornene-*endo*-2,3-dicarboxylicimide)undecane) [1]benzothienopheno[3,2-*b*] benzothienophene (560 mg, 0.838 mmol, 98 % yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 8.1 Hz, 2H), 7.73 (d, 1.3 Hz, 2H), 7.29 (dd, J = 8.1, 1.3 Hz, 2H), 6.30 (t, J = 1.7 Hz, 2H), 3.47 (t, 2H), 3.47 (t, J = 7.5 Hz, 2H), 2.77 (t, J = 7.6 Hz, 2H), 2.68 (d, J = 1.0 Hz, 2H), 1.71 (dd, J = 14.2, 7.0 Hz, 2H), 1.64 - 1.47 (m, 3H), 1.47 - 1.13 (m, 26H), 0.91 (t, J = 6.9 Hz, 3H).

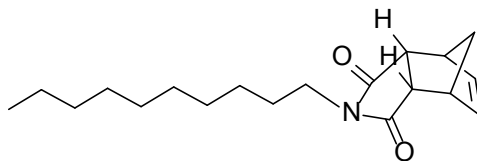
¹³C NMR (101 MHz, CDCl₃) δ 177.62, 141.89, 139.56, 137.33, 132.03, 130.68, 125.33, 122.83, 120.57, 47.30, 44.66, 42.21, 38.26, 35.63, 31.40, 31.23, 29.00, 28.92, 28.83, 28.78, 28.63, 27.28, 26.46, 22.18, 13.63.

FT-IR (ν/cm⁻¹): 2921, 2852, 1769, 1694, 1599, 1562, 1461, 14611396, 1366, 1338, 1305, 1286, 1256, 1286, 1256, 1208, 1169, 1141, 1101, 1073, 1055, 1036, 1014, 950, 880.

MS (EI) m/z = 668.3567 (M).

M.P. = 69 °C.

1-Decyl(*cis*-5-norbornene-*endo*-2,3-dicarboxylic) imide



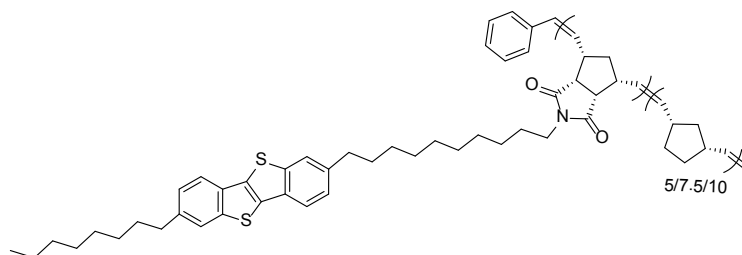
Cis-5-norbornene-*endo*-2,3-dicarboxylic anhydride (1 g, 6.09 mmol), 1-decylamine (1.218 ml, 6.09 mmol), and triethylamine (1.202 ml, 6.09 mmol) were refluxed in dry toluene (50 ml), under argon, for 16 h with a Dean-Stark apparatus. The reaction mixture was cooled, concentrated *in vacuo*, and dissolved in dichloromethane (100 mL). This was washed with 0.1 M HCl (4 x 50 mL), brine (50 mL), and water (50 mL), dried (MgSO₄), and concentrated *in vacuo*. The material was purified *via* flash column chromatography (silica gel, 1% triethylamine - 20% ethyl acetate in hexane) and concentrated *in vacuo* to give 1-decyl(*cis*-5-norbornene-*endo*-2,3-dicarboxylic) imide (1.6 g, 5.27 mmol, 87 % yield) as a clear colourless oil. Values consistent with literature values [23](#).

¹H NMR (400 MHz, CDCl₃) δ 6.30 (t, J = 1.8 Hz, 2H), 3.47 (t, J = 7.5 Hz, 2H), 3.31 - 3.26 (m, 2H), 2.68 (d, J = 1.2 Hz, 2H), 1.54 (m, 3H), 1.35 - 1.20 (m, 15H), 0.90 (t, J = 6.9 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 178.07, 137.83, 47.79, 45.16, 42.70, 38.76, 31.86, 29.48, 29.43, 29.24, 29.13, 27.76, 26.95, 22.65, 14.08.

MS (EI) m/z = 303.2191 (M).

Procedure for the ROMP of p-BTBT1,2, and 3:



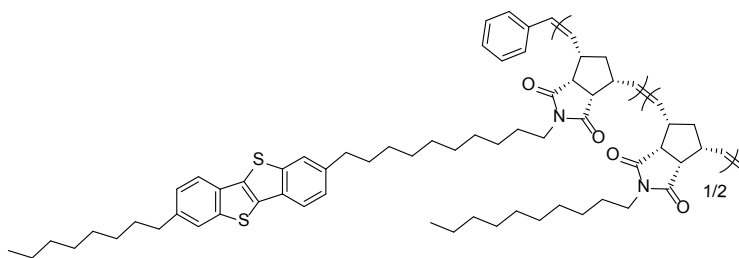
To a solution of 2-octyl-7-(11-(cis-5-norbornene-endo-2,3-dicarboxylicimide)undecane) [1]benzothienopheno [3,2-b]benzothienophene (100 mg, 0.150 mmol) and bicyclo[2.2.1]hept-2-ene (5 eq, 70.5 mg, 0.748 mmol/ 7.5 eq, 106 mg, 1.123 mmol/ 10 eq, 141 mg, 1.497 mmol) in dry, de-gassed (Ar), chlorobenzene (2 ml), stirring at 1000 rpm under argon at 0 °C, was rapidly injected dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidasolidinylidene](benzylidene)bis(3-bromopyridine)ruthenium(II) (3.97 mg, 4.49 μmol) in chlorobenzene (0.1 mL). The mixture was allowed to stir for 30 min. The polymerisation was irreversibly terminated by the addition of ethyl vinyl ether (1 mL), and the volatiles were removed under vacuum using a rotary evaporator. The polymer was precipitated twice from CH₂Cl₂ (10 mL) with pentane (10 mL) and washed with hot methanol *via* Soxhlet extraction, and finally dried under vacuum to yield a white polymer.

p-BTBT1: ¹H NMR (400 MHz, CDCl₃) δ 7.73 (m, 4H), 7.28 (m, 2H), 5.75 – 5.23 (m, 16H), 3.44 (m, 2H), 3.04 – 2.68 (m, 8H), 2.46 (m, 2H), 2.06 – 1.06 (m, 50H), 0.90 (m, 3H). GPC : $M_n = 1.3 \times 10^4 \text{ g mol}^{-1}$ / $M_w = 4.9 \times 10^4 \text{ g mol}^{-1}$, mp = 110 °C, 40 mg (23.5 %). $tM_n = ((668.01 \times 1) + (94.15 \times 5)) / 0.03 = 25 \text{ kg/mol}$.

p-BTBT2: ¹H NMR (400 MHz, CDCl₃) δ 7.73 (m, 4H), 7.28 (m, 2H), 5.75 – 5.28 (m, 16H), 3.45 (m, 2H), 3.04 – 2.46 (m, 22H), 2.06 – 0.90 (m, 77H). GPC : $M_n = 9.7 \times 10^3 \text{ g mol}^{-1}$ / $M_w = 6.1 \times 10^4 \text{ g mol}^{-1}$, mp = 90 °C, 84 mg (41.6 %). $tM_n = ((668.01 \times 1) + (94.15 \times 7.5)) / 0.03 = 46 \text{ kg/mol}$.

p-BTBT3: ¹H NMR (400 MHz, CDCl₃) δ 7.73 (m, 4H), 7.28 (m, 2H), 5.75 – 5.28 (m, 22H), 3.45 (m, 2H), 3.03 – 2.46 (m, 28H), 2.04 – 0.90 (m, 95H). GPC : $M_n = 8.6 \times 10^3 \text{ g mol}^{-1}$ / $M_w = 4.4 \times 10^4 \text{ g mol}^{-1}$, mp = 80 °C, 79 mg (32.8 %). $tM_n = ((668.01 \times 1) + (94.15 \times 10)) / 0.03 = 54 \text{ kg/mol}$.

Procedure for the ROMP of p-BTBT-4 and 5:



To a solution of 2-octyl-7-(11-(cis-5-norbornene-endo-2,3-dicarboxylicimide)undecane) [1]benzothienopheno [3,2-b]benzothienophene (100 mg, 0.150 mmol) and 1-decyl(cis-5-norbornene-endo-2,3-dicarboxylic) (1 eq, 45.4 mg, 0.15 mmol / 2 eq, 91 mg, 0.30 mmol) in dry, de-gassed (Ar), chlorobenzene (2 ml), stirring at 1000 rpm under argon at 0 °C, was rapidly injected dichloro[1,3-bis(2,4,6-trimethylphenyl)-2-imidasolidinylidene] (benzylidene)bis(3-bromopyridine)ruthenium(II) (2 mg, 2.25 μmol / 1.3 mg, 1.50 μmol) in chlorobenzene (0.1 mL). The mixture was allowed to stir for 30 min. The polymerisation was irreversibly terminated by the addition of ethyl vinyl ether (1 mL), and the volatiles were removed under vacuum using a rotary evaporator. The polymer was precipitated twice from CH_2Cl_2 (10 mL) with pentane (10 mL) and washed with hot methanol *via* Soxhlet extraction, and finally dried under vacuum to yield a white polymer.

p-BTBT4: ^1H NMR (400 MHz, CDCl_3) δ 7.73 (m, 4H), 7.28 (m, 2H), 5.78 (m, 2H), 5.17 (m, 2H), 3.43 (m, 4H), 3.30 (m, 2H), 3.04 (m, 6H), 2.76 (m, 6H), 2.28 – 2.09 (m, 2H), 1.70 – 1.55 (m, 12H), 1.27 (m, 34H), 0.90 (m, 6H). GPC : $M_n = 6.9 \times 10^4 \text{ g mol}^{-1}$ / $M_w = 8.9 \times 10^4 \text{ g mol}^{-1}$, mp = 72 °C, 55 mg (36.8 %).
 $tM_n = ((668.01 \times 1) + (303.22 \times 1)) / 0.015 = 65 \text{ kg/mol}$.

p-BTBT5: ^1H NMR (400 MHz, CDCl_3) δ 7.73 (m, 4H), 7.28 (m, 2H), 5.78 (m, 3H), 5.17 (m, 3H), 3.43 (m, 6H), 3.30 (m, 2H), 3.04 (m, 9H), 2.76 (m, 6H), 2.28 – 2.10 (m, 3H), 1.70 – 1.55 (m, 18H), 1.27 (m, 46H), 0.90 (m, 9H). GPC : $M_n = 1.04 \times 10^5 \text{ g mol}^{-1}$ / $M_w = 1.6 \times 10^5 \text{ g mol}^{-1}$, mp = 62 °C, 107 mg (56.1 %).
 $tM_n = ((668.01 \times 1) + (303.22 \times 2)) / 0.01 = 127 \text{ kg/mol}$.

