Supporting information

Polymeric Near Infrared Emitters with Bay-Annulated Indigo Moieties

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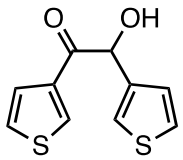
1) Detailed synthetic procedure and structural characterization of BAI containing polymers

1.1) Materials

All commercially available chemicals and solvents were used without further purification. Dry solvents were bought from Acros and stored over molecular sieve. All reactions were performed under argon atmosphere, if not specified otherwise. Degassing the solvents was performed using argon (12 hours) *via* Schlenk-technique.

1.2) Monomer synthesis



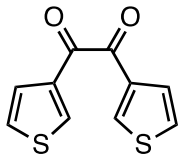
2-Hydroxy-1,2-di(thiophen-3-yl)ethanone (C1)

Thiophene-3-carbaldehyde (80.71 g, 719.01 mmol), 3-benzyl-5-(2-hydroxyethyl)-4-methyl-3-thiazoliumchloride (4.81 g, 17.81 mmol) and trimethylamine (24.01 g, 237.01 mmol) were dissolved in ethanol (202 mL). The reaction mixture was heated to 80°C and stirred for 3 hours. After cooling to room temperature, the solution was poured into iced water. The yellowish crude product was filtered off, washed with water, and recrystallized from ethanol to yield the desired white product (56.87 g, 70.1%).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 8.05 (dd, J = 2.9, 1.2 Hz, 1H, Ar-H), 7.51 (dd, J = 5.1, 1.3 Hz, 1H, Ar-H), 7.33 (dd, J = 2.8, 1.1 Hz, 1H, Ar-H), 7.30-7.27 (m, 2H, Ar-H), 7.00 (dd, J = 5.0, 1.3 Hz, 1H, Ar-H), 5.84 (d, J = 5.9 Hz, 1H, CH-OH), 4.33 (d, J = 6.0 Hz, 1H, OH).

^{13}C NMR (151 MHz, CDCl3) δ [ppm] = 192.6 (C=O), 140.1 (Ar-R), 138.1 (Ar-R), 134.3 (Ar-H), 127.4 (Ar-H), 127.2 (Ar-H), 126.7 (Ar-H), 126.4 (Ar-H), 124.3 (Ar-H), 72.6 (CH-OH).

GC-MS: m/z [M^+] = 224.0.



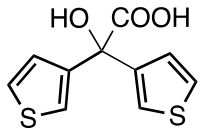
1,2-Di(thiophen-3-yl)ethane-1,2-dion (C2)

Copper(II)sulphate·$5H_2O$ (45.81 g, 182.99 mmol) was dissolved in a mixture of pyridine (75 mL) and water (40 mL) and heated to 60°C. 2-Hydroxy-1,2-di(thiophen-3-yl)ethanone (**C1**, 18.69 g, 83.01 mmol) was added in one portion. The solution was heated to 80°C for 1 h. At room temperature, 10% hydrochloric acid was added. After extraction with diethyl ether, the organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. 1,2-Di(thiophen-3-yl)ethane-1,2-dione, **C2**, was recrystallized from isopropanol to afford yellow crystals (15.95 g, 86.1%).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.30 (s, 2H, Ar-H), 7.63 (d, J = 4.7 Hz, 2H, Ar-H), 7.36 (dd, J = 4.9, 2.8 Hz, 2H, Ar-H).

^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 186.2 (C=O), 137.9 (Ar-H), 137.8 (Ar-R), 127.8 (Ar-H), 127.5 (Ar-H).

GC-MS: m/z [M^+] = 221.9.



2-Hydroxy-2,2-di(thiophen-3-yl)acetic acid (C3)

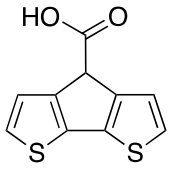
Potassium hydroxide (44.41 g, 790.98 mmol) was dissolved in a mixture of water (100 mL) and ethanol (100 mL). 1,2-Di(thiophen-3-yl)ethane-1,2-dione (**C2**, 51.71 g, 233.01 mmol) was added and the reaction mixture was dived into a 90°C hot oil bath. After 15 minutes the reaction mixture was cooled to 0°C. The pH was adjusted to 1 by adding concentrated hydrochloric acid. Ethanol was removed under reduced pressure. The remaining aqueous phase was extracted with diethyl ether and the combined organic phase was extracted with saturated sodium carbonate solution. The aqueous solution mixture was acidified with 10% hydrochloric acid which leads to a precipitate. The precipitate was filtered off and dissolved in diethyl ether, washed with water and dried over magnesium sulphate. The solvent was removed under reduced pressure. Crude,

beige 2-hydroxy-2,2-di(thiophen-3-yl)acetic acid (**C3**, 45.15 g, 81.1%) was used in the next step without further purification.

^{1}HNMR (400MHz, MeOD) δ[ppm]=7.36-7.32 (m, 4H, Ar-H), 7.17-7.13 (m, 2H, Ar-H), 4.89 (s, 2H, OH).

^{13}C NMR (101 MHz, MeOD) δ [ppm] = 175.9 (C=O), 145.4 (Ar-R), 128.3 (Ar-H), 126.3 (Ar-H), 123.6 (Ar-H), 77.9 (HO-C-COOH).

GC-MS: m/z [M-OH] = 224.0.



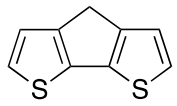
4-*H*-Cyclopenta[1,2-*b*:5,4-*b'*]dithiophene-4-carboxylic acid (C4)

2-Hydroxy-2,2-di(thiophen-3-yl)acetic acid (**C3**, 16.14 g, 67.21 mmol) was dissolved in benzene (175 mL) and cooled to 5°C. Aluminum trichloride (29.93 g, 223.99 mmol) was added to the reaction. The reaction solution was heated to 100°C and stirred for 30 minutes. After cooling the reaction mixture to room temperature, water and 4N aqueous hydrochloric acid were added and the mixture was extracted with diethyl ether. The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. 4*H*-Cyclopenta[1,2-*b*:5,4-*b*']dithiophene-4-carboxylic, **C4**, acid was purified by recrystallization from di-isopropyl ether to afford a slightly violet product (15.33 g, 95.1%).

^{1}H NMR (600 MHz, $(CD_3)_2CO$) δ [ppm] = 11.18 (s, 1H, COOH), 7.38 (d, J = 4.9 Hz, 2H, Ar-H), 7.26-7.25 (m, 2H, Ar-H), 4.76 (s, 2H, CH-COOH).

^{13}C NMR (151 MHz, $(CD_3)_2CO$) δ [ppm] = 170.0 (C=O), 149.1 (Ar-R), 139.0 (Ar-R), 126.2 (Ar-H), 124.6 (Ar-H), 49.9 (CH-COOH).

GC-MS: m/z [M-COOH] = 178.0.



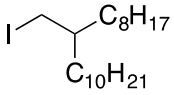
4-*H*-Cyclopenta[1,2-*b*:5,4-*b*']dithiophene (C5)

4*H*-Cyclopenta[1,2-*b*:5,4-*b*']dithiophene-4-carboxylic acid (**C4**, 7.68 g, 34.61 mmol) and copper (1.65 g, 25.89 mmol) were dissolved in freshly distilled quinoline (50 mL). The reaction mixture was heated to 245°C for 45 minutes. At room temperature, the suspension was poured into a mixture of ice and 4N aqueous hydrochloric acid. After adding diethyl ether, the mixture was filtered off and the filtrate washed with 10% aqueous hydrochloric acid, water, and aqueous sodium carbonate solution. The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. 4*H*-Cyclopenta[1,2- *b*:5,4-*b*']dithiophene, **C5**, was purified by silica gel column chromatography (eluent: hexane) to afford the greyish product (4.29 g, 69.6%).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] = 7.14 (d, J = 4.9 Hz, 2H, Ar-H), 7.05 (d, J = 4.9 Hz, 2H, Ar-H), 3.48 (s, 2H, Ar_2-CH_2).

^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ [ppm] = 150.1 (Ar-R), 138.8 (Ar-R), 125.0 (Ar-H), 123.4 (Ar-H), 32.2 (Ar_2-CH_2).

GC-MS: m/z [M^+] = 178.0.



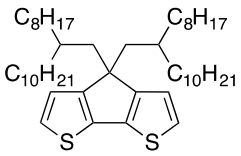
9-(Iodomethyl)nonadecane (C6)

2-Octyldodecan-1-ol (36.41 mL, 102.01 mmol), 1*H*-imidazole (8.35 g, 123.01 mmol), and triphenylphosphine (32.21 g, 123.01 mmol) were dissolved in methylene chloride (145 mL) and treated with iodine (31.09 g, 123.01 mmol) at 0°C. The reaction was stirred for 3 days at room temperature. Sodium sulphite solution was added and the organic phase was washed with water and brine. The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. The crude product, **C6**, was filtered over silica gel to afford the desired product (40.01 g, 95.9%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 3.27 (d, J = 4.6 Hz, 2H, I-CH_2), 1.39-1.17 (m, 32H, CH_2), 1.13-1.12 (m, 1H, CH), 0.89 (t, J = 6.8 Hz, 6H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 38.9 (CH), 34.6 (CH_2), 32.1 (CH_2), 32.1 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 26.7 (CH_2), 22.8 (CH_2), 16.8 (CH_2), 14.6 (CH_3).

GC-MS: m/z [M-IH] = 281.4.



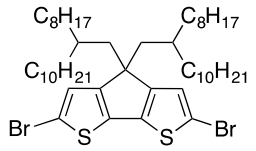
4,4-Bis(2-octyldodecyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophene (C7)

C5 (3.73 g, 20.91 mmol), potassium iodide (0.16 g, 0.94 mmol), and potassium hydroxide (4.72 g, 84.01 mmol) were dissolved in dimethyl sulfoxide (60 mL). The reaction solution was heated to 60°C. **C6** (18.33 g, 44.89 mmol) was added to the reaction mixture. The mixture was stirred at 60°C for 3 days. Water and brine were added, and the mixture was extracted with diethyl ether. The organic phase was dried over magnesium sulphate and the solvent was removed under reduced pressure. After a silica gel column chromatography (eluent: hexane) and repeated RP18-silica gel column chromatography (eluent: tetrahydrofuran/water 8/2) the product, **C7**, was isolated as brownish oil (12.19 g, 79.1%).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] = 7.03 (d, J = 4.9 Hz, 2H, Ar-H), 6.85 (d, J = 4.9 Hz, 2H, Ar-H), 1.78 (d, J = 5.0 Hz, 4H, C-(CH_2)$_2$), 1.28-0.98 (m, 44H, CH_2), 0.89 (m, 14H, CH_2), 0.84-0.74 (m, 22H, CH_3, CH_2), 0.62-0.49 (m, 2H, CH).

^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ [ppm] = 157.9 (Ar-R), 136.9 (Ar-R), 124.3 (Ar-H), 122.7 (Ar-H), 53.5 (C-(CH_2)$_2$), 44.0 (CH_2), 35.3 (CH_2), 33.8 (CH), 32.5 (CH_2), 32.2 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 26.6 (CH_2), 23.1 (CH_2), 23.0 (CH_2), 14.6 (CH_3).

FD-MS: m/z [M^+] = 739.3.



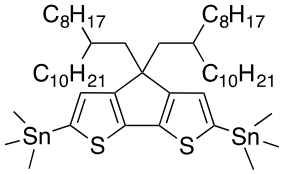
2,6-Dibromo-4,4-Bis(2-octyldodecyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophene (C8)

Benzyltrimethylammonium tribromide (4.11 g, 10.55 mmol) and zinc chloride (1.58 g, 11.60 mmol) were treated with **C7** (3.71 g, 5.02 mmol) in dimethylformamide (80 mL). The reaction mixture was stirred at 20°C for 2.5 hours. Water and an aqueous solution of 5% sodium bisulphate were added and the mixture was extracted with hexane. To obtain the desired brownish product, (3.91 g, 87.1%) several silica gel column chromatography runs (eluent: hexane) were necessary.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 6.88 (s, 2H, Ar-H), 1.73 (d, J = 5.1 Hz, 4H, C-$(CH_2)_2$), 1.32-1.02 (m, 44H, CH_2), 0.97-0.85 (m, 14H, CH_2), 0.82 (t, J = 7.2 Hz, 18H, CH_3), 0.53 (dt, J = 10.9, 5.4 Hz, 2H, CH).

^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 155.8 (Ar-R), 136.8 (Ar-R), 125.7 (Ar-H), 110.9 (Ar-Br), 55.3 (C-$(CH_2)_2$), 43.7 (CH_2), 35.4 (CH_2), 33.9 (CH), 32.3 (CH_2), 32.2 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 23.1 (CH_2), 14.6 (CH_3).

APCI-MS: m/z [M^+] = 896.5.



4,4-Bis(2-octyldodecyl)-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[1,2-*b*:5,4-*b*']dithiophene (C9)

C8 (2.33 g, 2.59 mmol) was dissolved in dry tetrahydrofuran (44 mL) and *N,N,N',N'*-tetramethylethylenediamine (1.4 mL, 10.37 mmol) was added. The solution was cooled to –78°C. *n*-Butyl lithium (4.3 mL, 10.37 mmol, 2.4 M) was added and the mixture was stirred for 60 minutes at –78°C. After reacting the mixture at 20°C for 60 minutes, the mixture was cooled to –78°C again. Trimethyltin chloride (10.4 mL, 10.37 mmol, 1 M) was added in one shot. The reaction mixture was allowed to warm up to room temperature overnight, poured into saturated aqueous ammonium chloride solution and extracted with

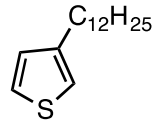
diethyl ether. After drying over magnesium sulphate, the solvent was removed under reduced pressure. The red-brownish oil (2.27 g, 82.1%) was used without further purification.

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] = 6.94 (s, 2H, Ar-H), 1.85 (d, J = 4.7 Hz, 4H, C-$(CH_2)_2$), 1.38-1.07 (m, 50H, CH_2), 0.96-0.86 (m, 26H, CH_2, CH_3), 0.65-0.56 (m, 2H, CH), 0.37 (s, 18H, CH_3).

^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ [ppm] = 160.0 (Ar-R), 142.8 (Ar-Sn), 136.3 (Ar-R), 130.6 (Ar-H), 52.5 (C-$(CH_2)_2$), 43.9 (CH_2), 35.8 (CH_2), 34.0 (CH), 32.2 (CH_2), 32.2 (CH_2), 30.2 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 29.7 (CH_2), 26.9 (CH_2), 23.0 (CH_2), 14.6 (CH_3), -7.8 (CH_3).

^{119}Sn NMR (149 MHz, $C_2D_2Cl_4$) δ [ppm] = –28.5.

FD-MS: m/z [M^+] = 1064.8.



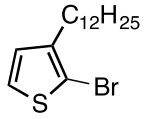
3-Dodecylthiophene
T1

3-Bromothiophene (10.98 g, 67.30 mmol) and [1,3-bis(diphenylphosphino)-propane]dichloronickel(II) (0.37 g, 0.67 mmol) were dissolved in heptane (100 mL) and tetrahydrofuran (60 mL) and cooled to 0°C. Dodecylmagnesium bromide (94.0 ml, 94.01 mmol, 1 M) was added dropwise to the cold solution. The reaction mixture was heated for 12 hours at 85°C. After cooling the reaction mixture to 20°C, 1N aqueous hydrochloric acid was added and the mixture was washed with water. The organic phase was dried over magnesium sulphate and the solvent removed under reduced pressure. The brown oil was precleaned by silica gel filtration (eluent: hexane). The following distillation afforded a yellowish oil (13.52 g, 80.1%).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] = 7.21 (dd, J = 4.9, 2.9 Hz, 1H, Ar-H), 6.92 (m, 2H, Ar-H), 2.61 (t, J = 7.5 Hz, 2H, Ar-CH_2), 1.68-1.53 (m, 2H, ArCH_2-CH_2), 1.31-1.27 (m, 18H, CH_2), 0.90 (t, J = 6.7 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ [ppm] = 143.6 (Ar-alkyl), 128.7 (Ar-H), 125.4 (Ar-H), 120.1 (Ar-H), 32.8 (Ar-CH_2), 30.9 (ArCH_2-CH_2), 30.6 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 23.1 (CH_2), 14.5 (CH_3).

GC-MS: m/z [M^+] = 252.2.



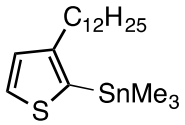
2-Bromo-3-dodecylthiophene
T2

T1 (5.01 g, 19.81 mmol) was dissolved in chloroform (30 mL) and acetic acid (30 mL). In portions, 1-bromopyrrolidine-2,5-dione (3.53 g, 19.81 mmol) was added. In the absence of light, the reaction mixture was stirred for 2 hours. The solution was treated with water, extracted with chloroform and washed with 2N aqueous sodium hydroxide solution. The organic phase was dried over magnesium sulphate and concentrated under reduced pressure. The crude orange oil was purified by silica gel flash chromatography (eluent: hexane). 2-Bromo-3-dodecylthiophene was obtained as yellowish oil (5.59 g, 85.1%).

^{1}H NMR (400 MHz, $C_2D_2Cl_4$) δ [ppm] = 7.13 (d, J = 5.6 Hz, 1H, Ar-H), 6.74 (d, J = 5.6 Hz, 1H, Ar-H), 2.49 (t, J = 7.4 Hz, 2H, Ar-CH_2), 1.15 (m, 2H, ArCH_2-CH_2), 1.25-1.20 (m, 18H, CH_2), 0.82 (t, J = 6.8 Hz, 3H, CH_3).

^{13}C NMR (101 MHz, $C_2D_2Cl_4$) δ [ppm] = 142.4 (Ar-alkyl), 128.7 (Ar-H), 125.6 (Ar-H), 109.0 (Ar-Br), 32.2 (Ar-CH_2), 30.0 (ArCH_2-CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 23.1 (CH_2), 14.6 (CH_3).

GC-MS: m/z [M^+] = 332.1.



2-(Trimethylstannyl)-3-dodecylthiophene
T3

T2 (7.04 g, 21.25 mmol) and N,N,N',N'-tetramethylethylenediamine (3.3 mL, 21.87 mmol) were dissolved in tetrahydrofuran (700 mL). The solution was cooled to –78°C

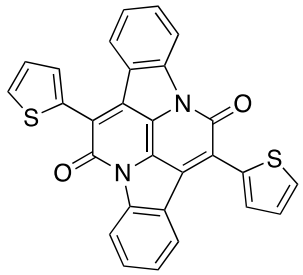
and *n*-butyl lithium (8.9 ml, 21.25 mmol, 2.8 M) was added dropwise. The solution was stirred for another hour at –78°C, followed by adding trimethyltin chloride (27.6 ml, 27.60 mmol, 1 M) in one shot. The reaction was allowed to warm up to room temperature overnight. Saturated aqueous ammonium chloride solution was added, and the solution was extracted three times with diethyl ether. The combined organic phase was dried over magnesium sulphate. 2-(Trimethylstannyl)-3-dodecylthiophene was obtained after removing the solvent under reduced pressure and heating at 50°C under high vacuum as a yellowish oil (8.69 g, 99.0%).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 7.55-7.52 (m, 1H, Ar-H), 7.14-7.10 (m, 1H, Ar-H), 2.68-2.61 (m, 2H, Ar-CH_2), 1.70-1.56 (m, 2H, ArCH_2-CH_2), 1.43-1.22 (m, 18H, CH_2), 0.92 (m, 3H, CH_3), 0.41 (s, 9H, CH_3).

^{13}CNMR (151MHz, $C_2D_2Cl_4$) δ[ppm]=151.2 (Ar-alkyl), 131.6 (Ar-Sn), 130.8 (Ar-H), 129.8 (Ar-H), 32.9 (Ar-CH_2), 32.5 (Ar-CH_2CH_2), 32.3 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 30.0 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.7 (CH_2), 23.1 (CH_2), 14.5 (CH_3), -7.5 (Sn-CH_3).

^{119}Sn NMR (149 MHz, $C_2D_2Cl_4$) δ [ppm] = –36.6.

FD-MS: m/z [M+] = 416.9.



7,14-Di(thiophen-2-yl)diindolo[3,2,1-de:3',2',1'-ij][1,5]naphthyridine-6,13-dione (BAI1)

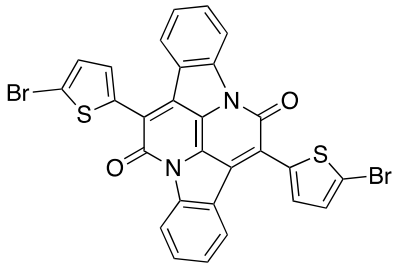
(*E*)-[2,2'-Biindolinylidene]-3,3'-dione (Indigo, 12.23 g, 46.60 mmol) was dissolved in xylene (606 ml) and heated to 145°C. 2-(Thiophen-2-yl)acetyl chloride (23.0 ml, 187.01 mmol) was dissolved in xylene (60 ml) and added during 30 minutes to the indigo solution. The reaction was monitored by TLC and was allowed to stir for 48 hours. The dark red solid was filtered off and rinsed with tetrahydrofuran. The product (8.53 g, 38.5%) was used for the next step without further purification.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.51 (d, J = 7.8 Hz, Ar-H), 8.05 (d, J = 7.7 Hz, Ar-H), 7.71-7.66 (m, Ar-H), 7.64-7.64 (m, Ar-H), 7.55-7.52 (m, Ar-H), 7.27-7.21 (m, Ar-H).

^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 158.9 (C=O), 144.5 (Ar-R), 134.9 (Ar-R), 132.4 (Ar-H), 130.4 (Ar-H), 130.1 (Ar-R), 130.1 (Ar-H), 126.8 (Ar-H), 126.4 (Ar-H), 125.8 (Ar-R), 125.4 (Ar-H), 125.0 (Ar-R), 122.3 (Ar-R), 118.0 (Ar-H).

MALDI-MS: m/z [M^+] = 475.1.

FT-IR (ATR): υ [cm^{-1}] = 3102, 3073, 1625, 1413, 955, 859, 834, 763, 740, 708, 701, 692.



7,14-Bis(5-bromothiophen-2-yl)diindolo[3,2,1-de:3',2',1'-ij][1,5]naphthyridine-6,13-dione (BAI2)

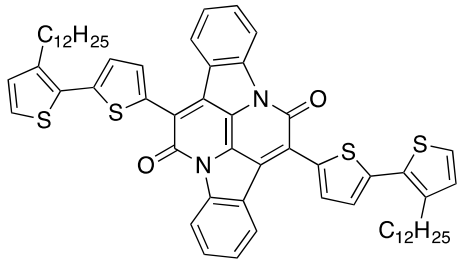
BAI1 (9.20 g, 19.41 mmol) was suspended in chloroform (700 ml). 1-Bromopyrrolidine-2,5-dione (3.45 g, 19.41 mmol) was added in portions. After 15 hours, the reaction solution was filtered off and washed with water, acetone, and chloroform. The obtained reddish black product (8.54 g, 69.7%) was used without further purification.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.53 (d, J = 7.8 Hz, Ar-H), 8.14 (d, J = 7.7 Hz, Ar-H), 7.59-7.56 (m, Ar-H), 7.50 (d, J = 3.72 Hz, Ar-H), 7.32-7.29 (m, Ar-H), 7.21 (d, J=3.8Hz, Ar-H).

^{13}CNMR (151MHz, $C_2D_2Cl_4$) δ[ppm]=158.2 (C=O), 144.3 (Ar-R), 136.8 (Ar-R), 132.7 (Ar-H), 130.3 (Ar-H), 130.0 (Ar-R), 129.6 (Ar-H), 126.7 (Ar-H), 125.7 (Ar-R), 125.3 (Ar-H), 124.3 (Ar-R), 122.4 (Ar-R), 118.4 (Ar-Br), 118.2 (Ar-H).

MALDI- MS: m/z [M^+] = 631.8.

FT-IR (ATR): υ [cm^{-1}] = 3102, 3073, 1765, 1704, 1624, 1413, 1252, 1074, 955, 859, 834, 802, 775, 763, 742, 701, 690.



7,14-Bis(3'-dodecyl-[2,2'-bithiophene]-5-yl)diindolo[3,2,1-de:3',2',1'- ij][1,5]naphthyridine-6,13-dione (BAI3)

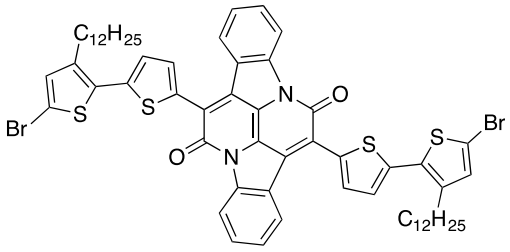
Tri-*o*-tolylphosphine (0.66 g, 2.17 mmol), tetrakis(triphenylphosphane)palladium(0) (0.63 g, 0.54 mmol), **BAI2** (11.41 g, 18.04 mmol), and **T3** (17.98 g, 43.31 mmol) were dissolved in toluene (225 mL) and heated to 100°C for 4 days. After concentration of the resulting solution, repeated silica gel column chromatography (eluent: hexane/chloroform 1/1 and 5.5/4.5) was applied to purify the purple product (0.27 g, 1.5% yield).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.57 (d, J = 7.7 Hz, 2H, Ar-H), 8.24 (d, J = 7.3 Hz, 2H, Ar-H), 7.76-7.63 (m, 4H, Ar-H), 7.61-7.51 (m, 2H, Ar-H), 7.35-7.26 (m, 2H, Ar-H), 7.22 (d, J = 5.1 Hz, 2H, Ar-H), 6.97 (d, J = 5.1 Hz, 2H, Ar-H), 2.88-2.86 (m, 2H, Ar-CH_2), 2.62-2.60 (m, 2H, CH_2), 1.98-0.86 (m, 40H, CH_2), 0.95-0.78 (m, 6H, CH_3).

^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 158.7 (C=O), 132.7 (Ar-H), 132.6 (Ar-R), 132.5 (Ar-R), 131.3 (Ar-R), 130.5 (Ar-H), 129.0 (Ar-H), 126.3 (Ar-H), 125.3 (Ar-H), 124.7 (Ar-H), 120.4 (Ar-H), 118.0 (Ar-H), 32.1 (CH_2), 30.7 (CH_2), 30.7 (CH_2), 30.5 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 22.8 (CH_2), 14.1 (CH_3).

MALDI-MS: m/z [M^+] = 973.3.

FT-IR (ATR): υ [cm^{-1}] = 3073, 2952, 2915, 2848, 1727, 1624, 1573, 1457, 1435, 1412, 1379, 1279, 1254, 1159, 1119, 1075, 956, 816, 802, 774, 761, 720, 692.



7,14-Bis(5'-bromo-3'-dodecyl-[2,2'-bithiophene]-5-yl)diindolo[3,2,1-de:3',2',1'- ij][1,5]naphthyridine-6,13-dione (BAI4)

BAI3 (0.27 g, 0.28 mmol) was dissolved in chloroform (28 mL) and cooled to 0°C. 1-Bromopyrrolidine-2,5-dione (0.10 g, 0.57 mmol) was added in portions. The reaction was

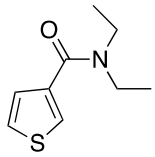
stirred 12 hours at 20°C, followed by washing with water and brine. After the solvent was removed under reduced pressure, 7,14-bis(5'-bromo-3'-dodecyl-[2,2'-bithiophene]-5-yl)diindolo[3,2,1-*de*:3',2',1'-*ij*][1,5]naphthyridine-6,13-dione (0.27 g, 87.1%) was obtained as a purple solid.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.46-8.42 (m, 2H, Ar-H), 8.18-8.17 (m, 2H, Ar-H), 7.66-7.63 (m, 2H, Ar-H), 7.53-7.46 (m, 2H, Ar-H), 7.30-7.25 (m, 2H, Ar-H), 7.19-7.17 (m, 2H, Ar-H), 6.92 (s, 2H, Ar-H), 2.78-2.76 (m, 2H, Ar-CH_2), 2.51-2.49 (m, 2H, CH_2), 1.64-1.55 (m, 4H, CH_2), 1.36-1.09 (m, 36H, CH_2), 0.82-0.77 (m, 6H, CH_3).

^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 158.7 (Ar-R), 144.8 (Ar-R), 144.2 (Ar-R), 140.8 (Ar-R), 134.8 (Ar-R), 132.2 (Ar-H), 131.3 (Ar-R), 131.0 (Ar-R), 130.5 (Ar-H), 129.7 (Ar-R), 126.5 (Ar-H), 126.1 (Ar-H), 125.5 (Ar-H), 124.7 (Ar-R), 123.1 (Ar-H), 120.5 (Ar-R), 118.1 (Ar-H), 111.7 (Ar-Br), 32.1 (Ar-CH_2), 30.7 (ArCH_2-CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

MALDI-MS: m/z [M+] = 1133.2.

FT-IR (ATR): υ [cm^{-1}] = 3061, 2952, 2919, 2849, 1721, 1624, 1602, 1432, 1414, 1382, 1291, 1249, 1079, 1061, 962, 839, 792, 751, 720.



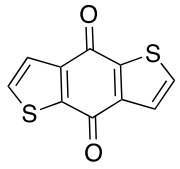
N,N-Diethylthiophene-3-carboxamide (BD1)

Thiophene-3-carboxylic acid (12.99 g, 101.01 mmol) was dissolved in methylene chloride (60mL) and cooled to 0°C. Oxalyl dichloride (17.4mL, 203.02mmol) was added dropwise followed by one drop of dimethylformamide and the solution was stirred for 12 hours at 20°C. Excessive oxalyl dichloride was removed under reduced pressure. The yellowish solid was dissolved in methylene chloride and added dropwise to a cold solution of diethylamine (21.2 mL, 203.01 mmol) in methylene chloride (60 mL). The solution was stirred for 30 minutes at room temperature. Water was added, and the aqueous solution was extracted with chloroform. The combined organic phase was washed with water, dried over magnesium sulphate and the solvent was removed under reduced pressure. No further purification was necessary to obtain the product as yellow oil (18.43 g, 99.1%).

^{1}HNMR (600MHz, $C_2D_2Cl_4$) δ[ppm]=7.41-7.36 (m, 1H, Ar-H), 7.25 (dd, J=4.8, 3.2 Hz, 1H, Ar-H), 7.11 (d, J = 5.0 Hz, 1H, Ar-H), 3.37 (q, J = 14.2, 7.0 Hz, 4H, CH_2), 1.12 (t, J = 7.2 Hz, 6H, CH_3).

^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 166.4 (C=O), 138.2 (Ar-R), 127.2 (Ar-H), 125.7 (Ar-H), 125.2 (Ar-H), 41.7 (N-CH_2), 13.8 (CH_2-CH_3).

GC-MS: m/z [M^+] = 183.1.



Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (BD2)

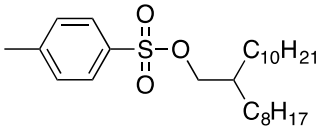
BD1 (8.01 g, 43.71 mmol) was dissolved in tetrahydrofuran (160 mL) and cooled to 0°C. Under cooling, *n*-butyl lithium (17.2 mL, 48.1 mmol) was added dropwise. After 12 hours of stirring at room temperature, water was added, and the dark yellow solid was filtered off. The solid was washed excessively with water, methanol, and hexane followed by recrystallization from glacial acetic acid to afford the yellow product (2.81 g, 58.3%).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 7.71 (d, J = 5.0 Hz, 1H, Ar-H), 7.67 (d, J = 5.0 Hz, 1H, Ar-H).

^{13}C NMR (151 MHz, $CDCl_3$) δ [ppm] = 174.7 (C=O), 145.1 (Ar-R), 143.0 (Ar-R), 133.7 (Ar-H), 126.8 (Ar-H).

GC-MS: m/z[M^+]=219.9.

FT-IR (ATR): υ[cm^{-1}]=3272, 3094, 3077, 1643, 1621, 1492, 1382, 1281, 1199, 1095, 1007, 919, 547, 831, 764, 754, 724, 694.



2-Octyldodecyl-4-methylbenzenesulfonate (BD3)

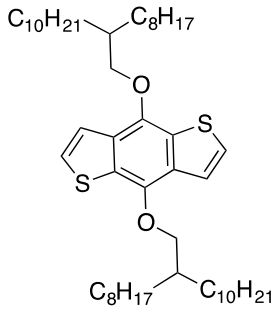
2-Octyldodecan-1-ol (10.15 g, 34.01 mmol) was dissolved in pyridine (27.1 mL, 334.01 mmol) and dry methylene chloride (100 mL) and cooled to 0°C. 4-Methylbenzene-1-sulfonyl chloride (6.41 g, 33.61 mmol) was dissolved in dry methylene chloride (70 mL) and added dropwise to the cold solution. The reaction mixture was stirred for 24 hours at 20°C and poured into chloroform. The organic phase was washed with 2N hydrochloric

acid and brine, dried over magnesium sulphate and the solvent was removed under reduced pressure. To afford the product as colorless oil (11.86 g, 77.1%) a silica gel column chromatography was performed (eluent: hexane/ethyl acetate 9.75/0.25).

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.78 (d, J = 8.3 Hz, 2H, Ar-H), 7.33 (d, J = 8.0 Hz, 2H, Ar-H), 3.91 (d, J = 5.4 Hz, 2H, O-CH_2), 2.44 (s, 3H, Ar-CH_3), 1.63-1.52 (m, 1H, CH), 1.36-1.03 (m, 32H, CH_2), 0.88 (t, J = 6.9 Hz, 6H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 144.7 (Ar-S), 133.4 (Ar-R), 129.8 (Ar-H), 128.1 (Ar-H), 73.0 (O-CH_2), 37.7 (CH-(CH_2)$_2$), 32.0 (CH_2), 32.0 (CH_2), 30.1 (CH_2), 30.0 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 26.5 (CH_2), 29.4 (CH_2), 26.6 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 21.7 (CH_3), 14.2 (CH_3).

LC-MS: m/z [M-IH] = 280.3.



4,8-Bis((2-octyldodecyl)oxy)benzo[1,2-b:4,5-b']dithiophene (BD4)

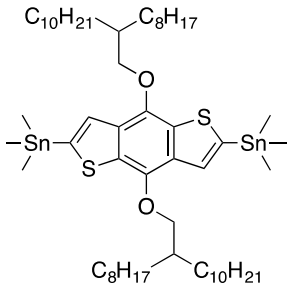
BD2 (0.51 g, 2.31 mmol) and zinc (0.33 g, 5.01 mmol) were dissolved in a solution of sodium hydroxide (3.85 g, 96.01 mmol) in water (23 mL). The dark red solution was heated to 100°C for 1 hour. **BD3** (3.26 g, 7.21 mmol) and tetrabutylammonium bromide (0.25 g, 0.77 mmol) were added. Next, another portion of zinc (0.81 g, 12.38 mmol) was added. The reaction solution was poured into water, extracted several times with diethyl ether and the organic phase dried over magnesium sulphate. The organic solvent was removed under reduced pressure. The brown oil was purified by silica gel and repeated flash column chromatography (eluent for both: chloroform/hexane 9/1) to afford the purified product (1.07 g, 59.5%).

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 7.47 (d, J = 5.5 Hz, 2H, Ar-H), 7.36 (d, J = 5.5 Hz, 2H, Ar-H), 4.17 (d, J = 5.1 Hz, 4H, O-CH_2), 1.91-1.86 (m, 2H, CH), 1.71-1.58 (m, 4H, CH_2), 1.57-1.19 (m, 56H, CH_2), 0.93-0.89 (m, 16H, CH_2, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 144.9 (Ar-R), 131.6 (Ar-R), 130.1 (Ar-R), 126.0 (Ar-H), 120.4 (Ar-H), 76.6 (CH_2), 39.4 (CH), 32.1 (CH_2), 32.1 (CH_2), 31.5 (CH_2), 30.2

(CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 27.2 (CH_2), 22.9 (CH_2), 14.3 (CH_3).

APCI-MS: m/z [M^+] = 783.6.



4,8-Bis((2-octyldodecyl)oxy)-2,6-bis(trimethylstannyl)benzo[1,2-b:4,5-b']-dithiophene (BD5)

BD4 (0.45 g, 0.58 mmol) was dissolved in dry tetrahydrofuran (6.2 mL) and cooled to –78°C. *n*-Butyl lithium (0.5 mL, 1.46mmol, 2.8M) was added dropwise and the solution was stirred at –78°C for 30 minutes, followed by stirring for 2 hours at 20°C. After the solution was again cooled to –78°C, trimethyltin chloride (1.8 mL, 1.8 mmol, 1 M) was added and the reaction mixture was allowed to warm up to room temperature overnight. The resulting solution was poured into saturated aqueous ammonium chloride solution and extracted with diethyl ether. After drying over magnesium sulphate, the solvent was removed under reduced pressure. The colorless solid (0.63 g, 98.1%) was used for the next step without further purification.

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 7.52 (s, 2H, Ar-H), 4.19 (d, J = 5.3 Hz, 4H, O-CH_2), 1.88-1.85 (m, 2H, CH), 1.69-1.64 (m, 4H, CH_2), 1.53-1.40 (m, 16H, CH_2), 1.39-1.28 (m, 44H, CH_2), 0.90-0.88 (m, 12H, CH_3), 0.45 (s, 18H, CH_2).

^{13}C NMR (151 MHz, $CDCl_3$) δ [ppm] = 143.4 (Ar-R), 140.5 (Ar-R), 134.0 (Ar-R), 133.1 (Ar-Sn), 128.2 (Ar-H), 76.1 (O-CH_2), 39.4 (CH-$(CH_2)_2$), 32.1 (CH_2), 32.1 (CH_2), 31.6 (CH_2), 30.5 (CH_2), 30.4 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 22.9 (CH_2), 14.3 (CH_3), -8.2 (Sn-CH_3).

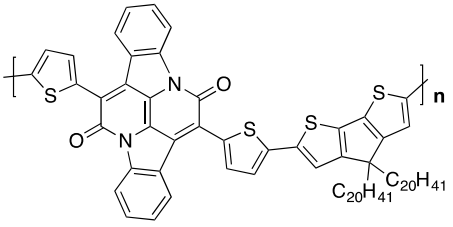
^{119}Sn NMR (224 MHz, $C_2D_2Cl_4$) δ [ppm] = -24.6.

FD-MS: m/z [M^+] = 1108.3.

1.3) Polymer synthesis

General procedure for Stille-type couplings

Tetrakis(triphenylphosphane)palladium(0) (0.1 eq.), dibromoaryl monomer (1 eq.), and bis(trialkylstannyl)aryl monomer (1 eq.) were evacuated for 1 hour at $1x10^{-3}$ mbar in a microwave tube. The solids were dissolved in tetrahydrofuran (15 mL) and the reaction was carried out in the microwave reactor at 125°C for 25 minutes, followed by stirring for 72 hours at 90°C. The polymer solution was poured into cold methanol resulting in polymer precipitation. The polymer was filtered off and washed with methanol and acetone in a Soxhlet tube. For extraction of the soluble polymer fractions the Soxhlet tube was extracted with solvents as hexane, ethyl acetate, methylene chloride, and chloroform. After drying under high vacuum, the polymer fractions were dried and characterized.



PBAIC-1

Following the general procedure of the Stille-type cross coupling, tetrakis(triphenylphosphane)palladium(0) (69 mg, 0.06 mmol), **BAI2** (376 mg, 0.59 mmol), and **C9** (633 mg, 0.59 mmol) were reacted. After Soxhlet extraction, 20 mg of a black solid (28.3% of yield) was obtained from the chloroform fraction by precipitation into methanol and drying.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.70-8.53 (m, 2H, Ar-H), 8.40-8.24 (m, 2H, Ar-H), 7.85-7.69 (m, 2H, Ar-H), 7.64-7.49 (m, 2H, Ar-H), 7.42-7.17 (m, 4H, Ar-H), 7.10-6.86 (m, 2H, Ar-H), 1.97-1.87 (m, 4H, C-$(CH_2)_2$), 1.37-0.55 (m, 78H, CH_3, CH_2).

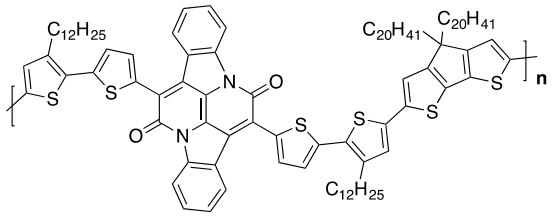
^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 159.7 (C=O), 144.1 (Ar-R), 137.8 (Ar-R), 137.5 (Ar-R), 131.9 (Ar-H), 131.6 (Ar-H), 126.5 (Ar-H), 126.3 (Ar-R), 125.6 (Ar-R), 125.1 (Ar-H), 124.4 (Ar-R), 122.8 (Ar-H), 122.5 (Ar-H), 120.3 (Ar-H), 118.1 (Ar-H), 54.7 (C-$(CH_2)_2$), 44.5 (CH_2), 35.6 (CH_2), 34.6 (CH), 32.1 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 26.8 (CH_2), 26.7 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 14.2 (CH_3).

GPC: detected at 800 nm: M_n = 8,300 g·mol^{-1}, M_w = 11,500 g·mol^{-1}, PDI: 1.39.

HOMO: -5.03 eV. **LUMO**: -3.55 eV.

TGA: onset of decomposition: 350°C.

FT-IR (ATR): υ [cm^{-1}] = 3058, 2919, 2849, 1630, 1602, 1439, 1406, 1318, 1080, 754, 692.



PBAIC-2

According to the general procedure, tetrakis(triphenylphosphane)palladium(0) (37 mg, 0.03 mmol), **BAI4** (242mg, 0.21mmol), and **C9** (227 mg, 0.21 mmol) were reacted. After Soxhlet extraction of the raw polymer, the methylene chloride (206 mg, 56.2%) fraction (black solid) was collected by precipitation into methanol and drying.

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.69-8.55 (m, 2H, Ar-H), 8.36-8.19 (m, 2H, Ar-H), 7.83-7.68 (m, 2H, Ar-H), 7.65-7.52 (m, 2H, Ar-H), 7.41-7.16 (m, 5H, Ar-H), 7.11-6.94 (m, 3H, Ar-H), 2.99-2.73 (m, 4H, C-$(CH_2)_2$), 2.07-1.87 (m, 4H, C-$(CH_2CH_2)_2$), 1.77-1.68 (m, 4H, CH_2), 1.37-0.55 (m, 120H, CH_3, CH_2, CH).

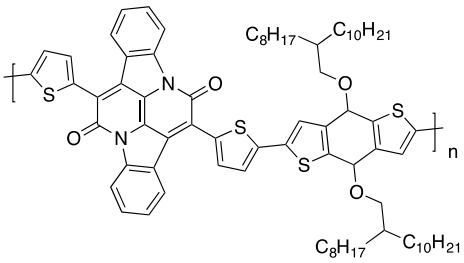
^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 158.8 (C=O), 144.4 (Ar-R), 141.7 (Ar-R), 140.6 (Ar-R), 137.4 (Ar-R), 135.0 (Ar-R), 132.1 (Ar-H), 131.5 (Ar-R), 131.1 (Ar-H), 129.8 (Ar-R), 129.5 (Ar-R), 127.8 (Ar-H), 126.4 (Ar-H), 126.2 (Ar-H), 125.2 (Ar-H), 124.5 (Ar-R), 123.2 (Ar-H), 122.4 (Ar-H), 118.1 (Ar-H), 54.7 (C-$(CH_2)_2$), 44.5 (CH_2), 35.8 (CH_2), 35.7 (CH_2), 34.7 (CH), 32.1 (CH_2), 32.0 (CH_2), 30.7 (CH_2), 30.6 (CH_2), 30.5 (CH_2), 30.1 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 22.8 (CH_2), 22.8 (CH_2), 14.1 (CH_3).

GPC: detected at 740 nm: M_n = 11,300 g/mol, M_w = 21,900 g/mol, PDI: 1.94.

HOMO: -5.07 eV. **LUMO**: -3.78 eV.

TGA: onset of decomposition: 360°C.

FT-IR (ATR): υ [cm^{-1}] = 3058, 2920, 2849, 1630, 1415, 1318, 1080, 961, 772, 754.



PBAIBD-1

BAI2 (276 mg, 0.42 mmol), **BD5** (468 mg, 0.42 mmol), tri-*o*-tolylphosphine (161 mg, 0.05mmol), and tris(dibenzylideneacetone)dipalladium(0) (15mg, 0.02mmol) were dissolved in toluene (72 mL) under inert conditions. The reaction mixture was heated to 100°C for 6 days. Next, the reaction mixture was poured into cold methanol to precipitate the polymer, which was filtered off and washed with methanol and acetone in a Soxhlet tube. For Soxhlet extraction, hexane and chloroform were used. By precipitation into methanol, the hexane fraction was collected and dried (149 mg, 28.1%).

^{1}H NMR (600 MHz, $C_2D_2Cl_4$) δ [ppm] = 8.77-8.50 (m, 2H, Ar-H), 8.45-8.19 (m, 2H, Ar-H), 8.00-7.72 (m, 2H, Ar-H), 7.66-7.53 (m, 2H, Ar-H), 7.45-7.21 (m, 6H, Ar-H), 4.23-4.00 (m, 4H, O-CH_2), 1.43-1.29 (m, 66H, CH_2), 1.04-0.67 (m, 12H, CH_3).

^{13}C NMR (151 MHz, $C_2D_2Cl_4$) δ [ppm] = 158.4 (C=O), 144.2 (Ar-R), 142.7 (Ar-R), 136.9 (Ar-R), 123.2 (Ar-H), 131.8 (Ar-R), 131.3 (Ar-H), 130.2 (Ar-R), 128.8 (Ar-R), 126.1 (Ar-H), 125.3 (Ar-H), 124.9 (Ar-H), 124.5 (Ar-R), 120.6 (Ar-H), 118.0 (Ar-H), 76.9 (O-CH_2), 39.8 (CH), 32.1 (CH_2), 31.9 (CH_2), 30.4 (CH_2), 30.3 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.4 (CH_2), 27.3 (CH_2), 22.7 (CH_2), 14.1 (CH_3).

GPC: detected at 760 nm: M_n = 8,400 g/mol, M_w = 11,200 g/mol, PDI: 1.33.

HOMO: -5.52 eV. **LUMO**: -3.98 eV.

TGA: onset of decomposition: 280°C.

FT-IR (ATR): υ [cm^{-1}] = 3066, 2919, 2849, 1629, 1601, 1454, 1415, 1358, 1080, 1030, 960, 799, 754, 721.

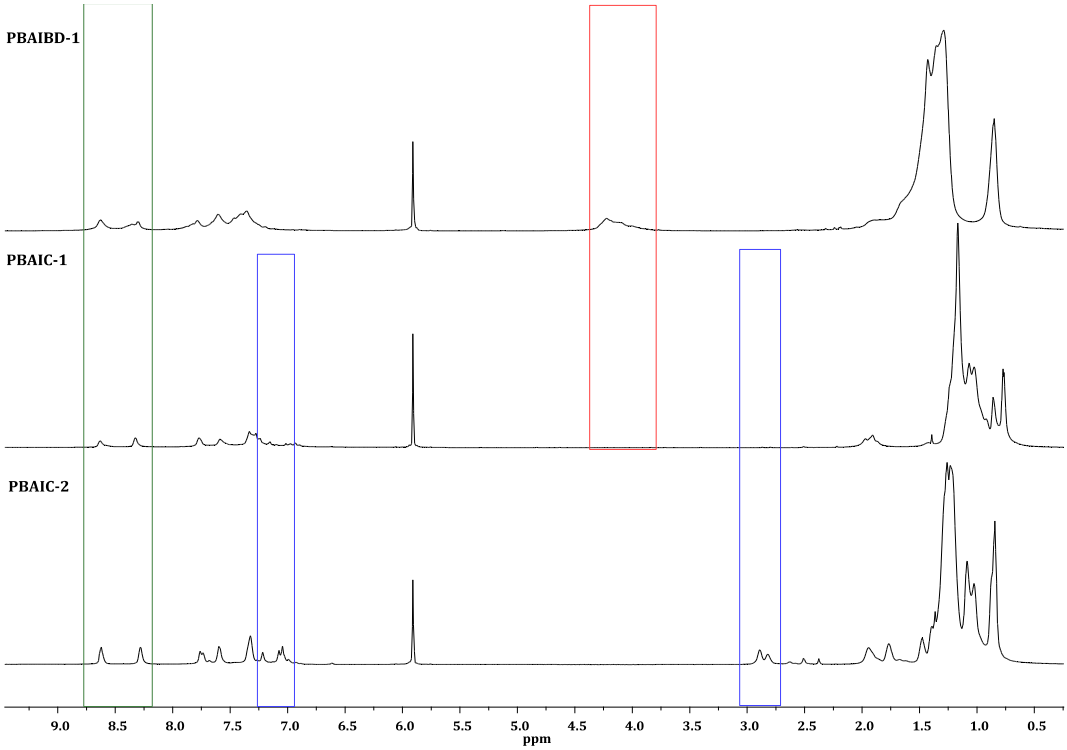


Figure SI1. ^{1}H NMR spectra of **PBAIBD-1** (top), **PBAIC-1** (middle), and **PBAIC-2** (bottom) recorded in $C_2D_2Cl_4$ (δ = 5.91ppm); phenyl protons of the BAI unit are highlighted in green, protons of the additional thiophene spacer units in blue, and ether methylene protons in red.

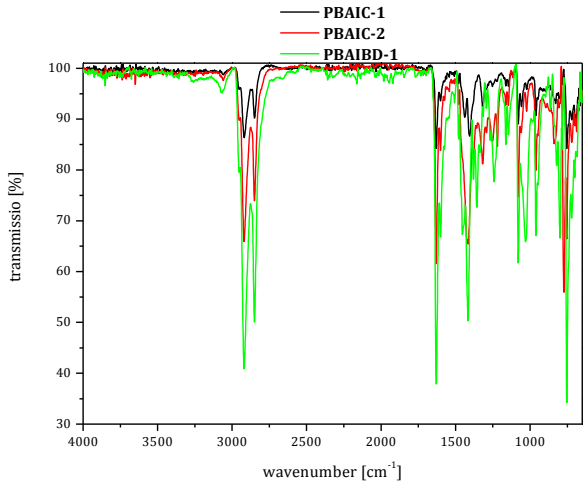


Figure SI2. IR spectra of BAI-containing polymers: **PBAIC-1** (black), **PBAIC-2** (red) and **PBAIBD-1** (green).

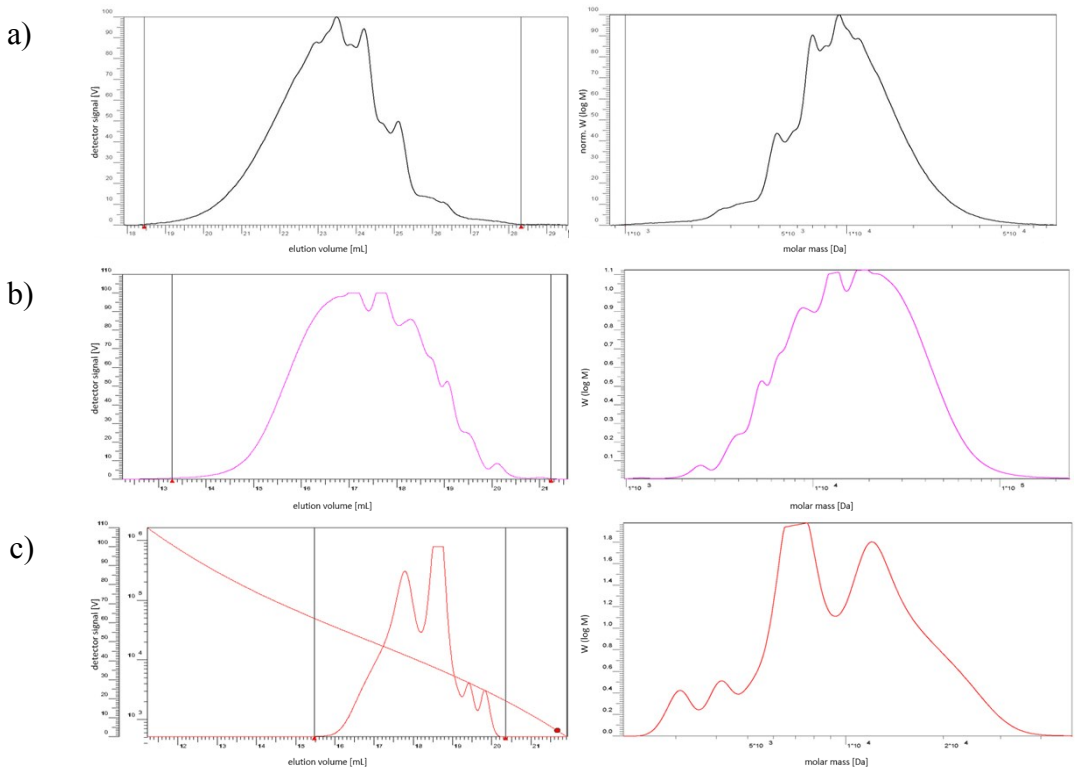


Figure SI3. GPC results of BAI-containing polymers: GPC elugrams (left) and molecular weight distributions (right) of a) PBAIC-1 (high temperature GPC with 1,2,4-trichlorobenzene as eluent at 160 °C), b) PBAIC-2 (GPC at room temperature with THF as eluent) and c) PBAID-1 (GPC at room temperature with THF as eluent).

Table SI1. Molecular weight data of the **BAI** copolymers.

Compound	$\bar{M}_n$(g·mol^{-1})	$\bar{M}_W$ (g·mol^{-1})	PD
PBAIC-1	8300	11500	1.39
PBAIC-2	11300	21900	1.94
PBAIBD-1	8400	11200	1.33

[a] mean and weight average molecular weights ($\bar{M}_n$, $\bar{M}_W$) and polydispersity (PD) values of the copolymers under investigation.

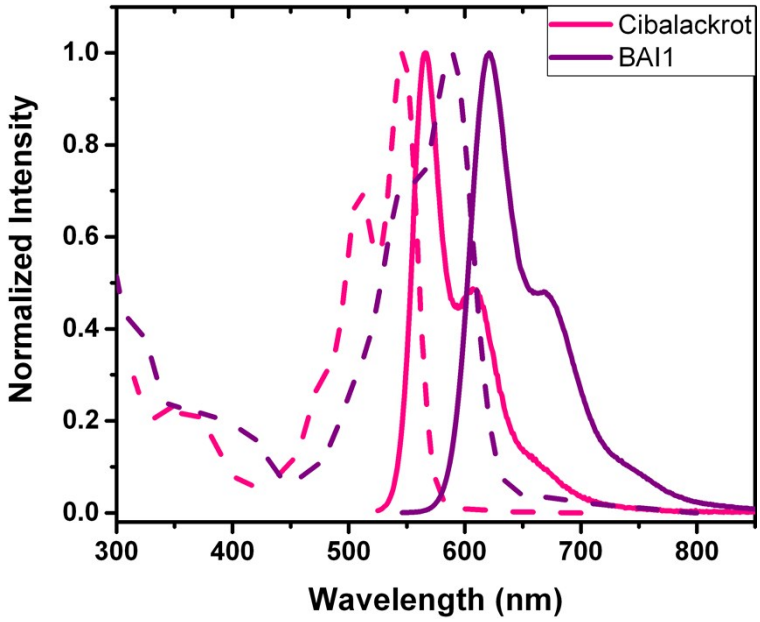


Figure SI4. Comparison of the normalized absorption (dashed lines) and emission (solid lines) spectra of **Cibalackrot** and **BAI1** in 2-meTHF.

Table SI2. Comparison of photophysical properties (absorption and emission maxima, Stokes shifts and fluorescence quantum yields) of **Cibalackrot** and **BAI1** in 2-meTHF.

Compound	λ^{abs} (nm)	λ^{em} (nm)	Δ_{SS} (cm^{-1})	ϕ_F
Cibalackrot	510 (sh), 547	566, 610 (sh)	614	0.733
BAI1	550 (sh), 588	621, 669 (sh)	904	0.389

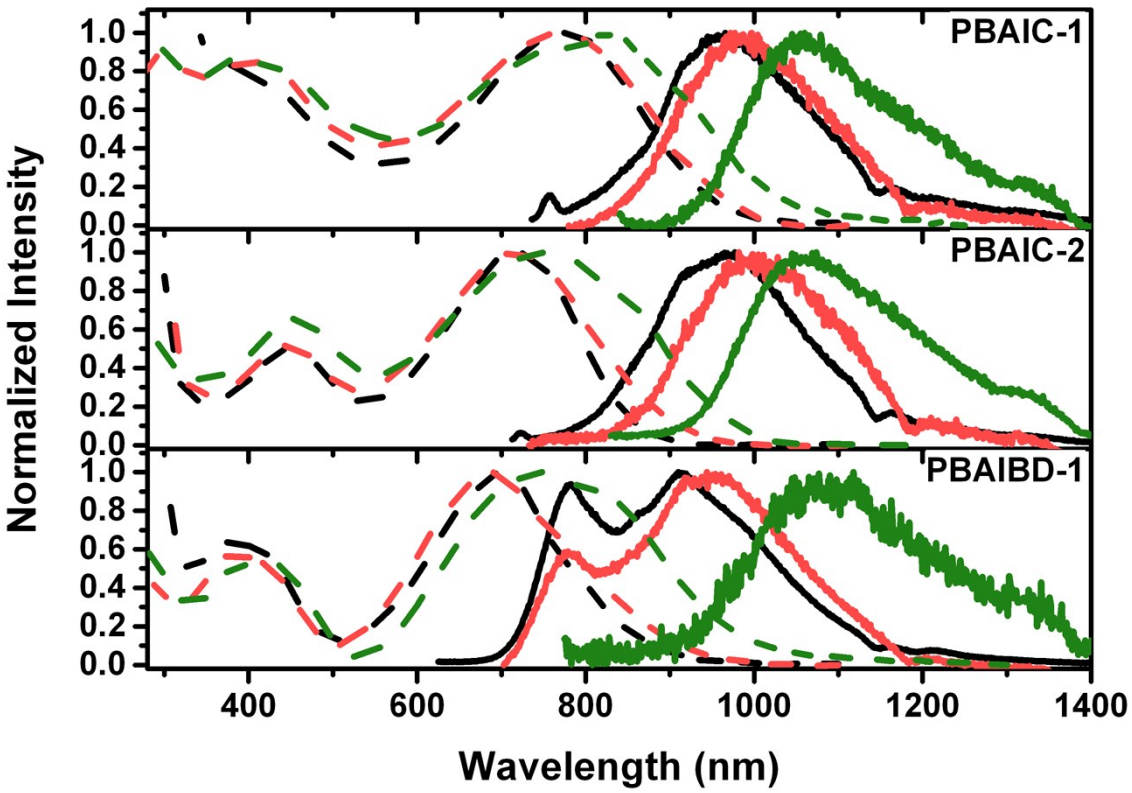


Figure SI5. Comparison of normalized absorption (dashed lines) and emission spectra (solid lines) of BAI polymers in toluene (black lines), 2-MeTHF (orange lines) and in thin films (green lines).

Table SI3. Comparison of photophysical properties (absorption and emission maxima, and Stokes shift) of BAI polymers in solution.

Polymers	Solvent	λ^{abs} (nm)	λ^{em} (nm)	Δ_{SS} (cm^{-1})
PBAIC-1	Toluene	405 (sh), 777	966	2518
	2-meTHF	404, 775	997	2873
PBAIC-2	Toluene	449, 719	977	3673
	2-meTHF	447, 716	982	3783
PBAIBD-1	Toluene	379,700	910	3297
	2-meTHF	378, 688	944	3942

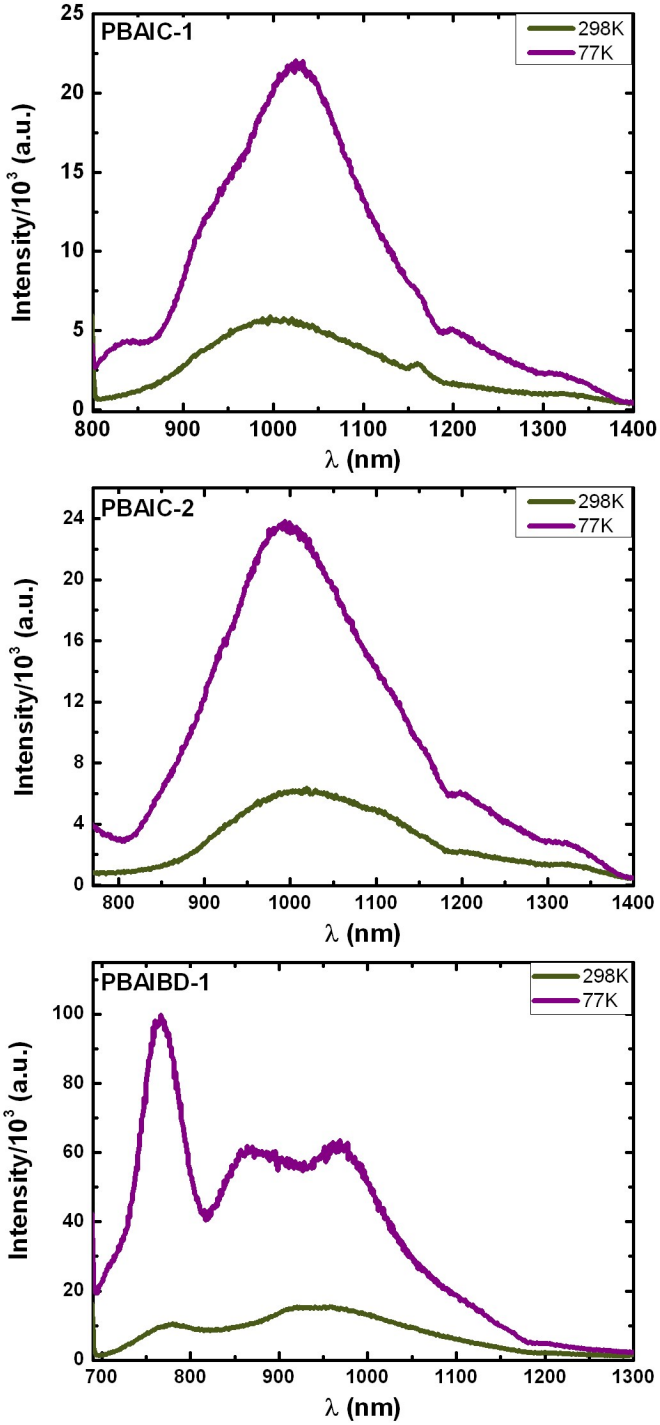


Figure SI6: Comparison of emission spectra of BAI polymers in 2-MeTHF at 298 and 77K.

Table SI4. Comparison of emission area and correlation to their respective fluorescence quantum yields of BAI polymers in 2-MeTHF at 298 and 77K.

Polymer	$Area^{298K}$	$Area^{77K}$	$Area^{77K}/Area^{298K}$	ϕ_F ^{298K}	ϕ_F ^{77K}
PBAIC-1	$1.58x10^6$	$5.16x10^6$	3.26	0.015	0.049
PBAIC-2	$1.82x10^6$	$6.16x10^6$	3.38	0.013	0.044
PBAIBD-1	$4.61x10^6$	$2.19x10^7$	4.75	0.018	0.086

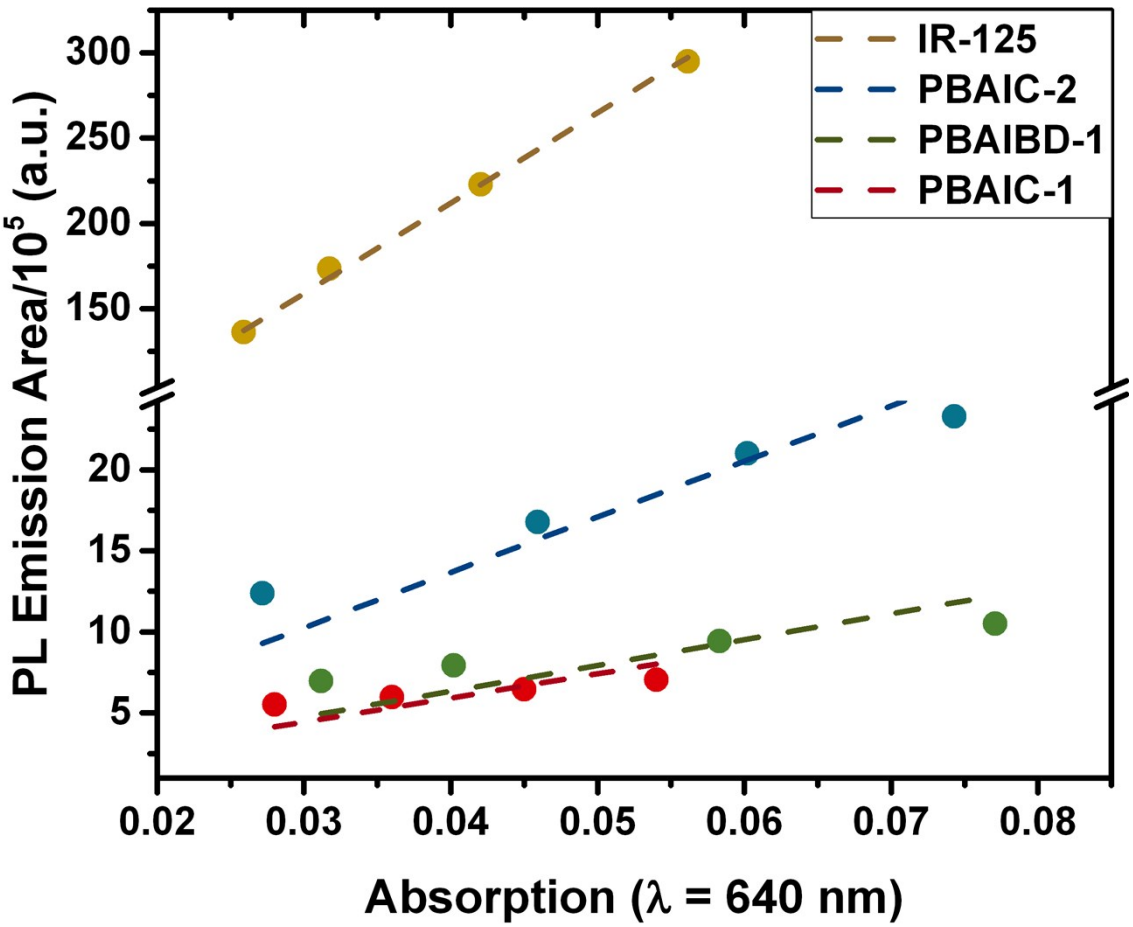


Figure SI7. Correlation of the absorption at the excitation wavelength (640nm) of IR-125 (2-[7-[1,3-dihydro-1,1-dimethyl-3-(4-sulfobutyl)-2H-benz[e]indol-2-ylidene]-1,3,5-heptatrienyl]-1,1-dimethyl-3-(4- sulfobutyl)-1H-benz[e]indolium hydroxide, inner salt, sodium salt) in ethanol, and BAI-polymers, in 2-MeTHF.

Table SI5. Energy levels of BAI copolymers estimated by spectroscopy for the polymers in solution.

Polymer	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
PBAIC-1	–5.03	–3.55	1.48
PBAIC-2	–5.07	–3.78	1.29
PBAIBD-1	–5.53	–3.98	1.54

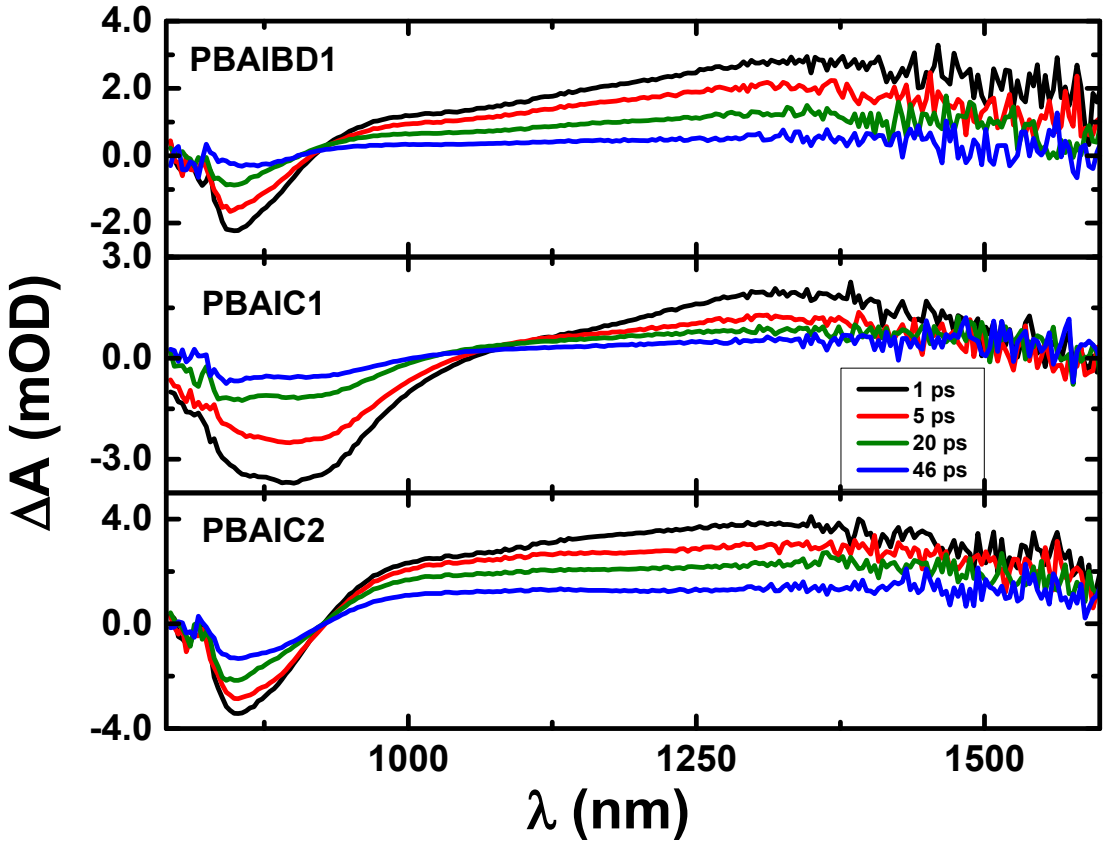


Figure SI8. Room temperature time resolved transient absorption spectra (fs-TA) for the investigated polymers in thin films obtained with excitation at 770 nm and collected in NIR range (800-1600 nm).

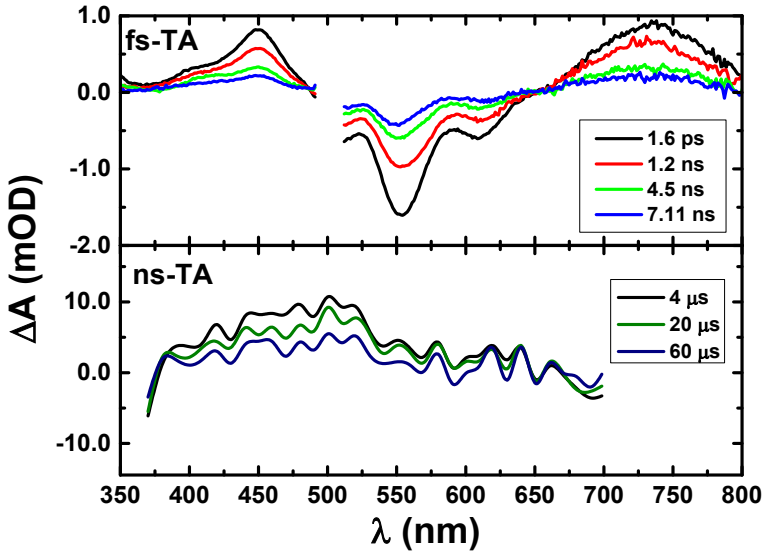


Figure SI9. Room temperature time resolved transient absorption spectra (fs- and ns-TA) for **BAI1** in 2-MeTHF solution collected with excitation at 500 nm, fs-TA, and 355 nm, ns-TA (τ_T= **54 μs**).

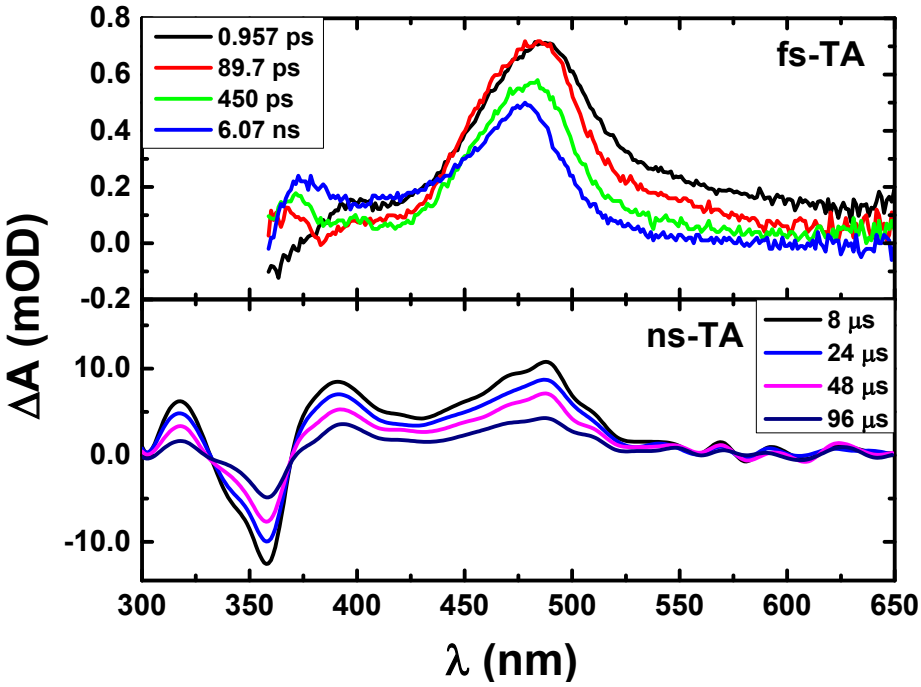


Figure SI10. Room_temperature time resolved transient absorption spectra (fs- and ns-TA) for **BDT** in 2-MeTHF solution collected with excitation at 330 nm, fs-TA, and 355 nm, ns-TA.

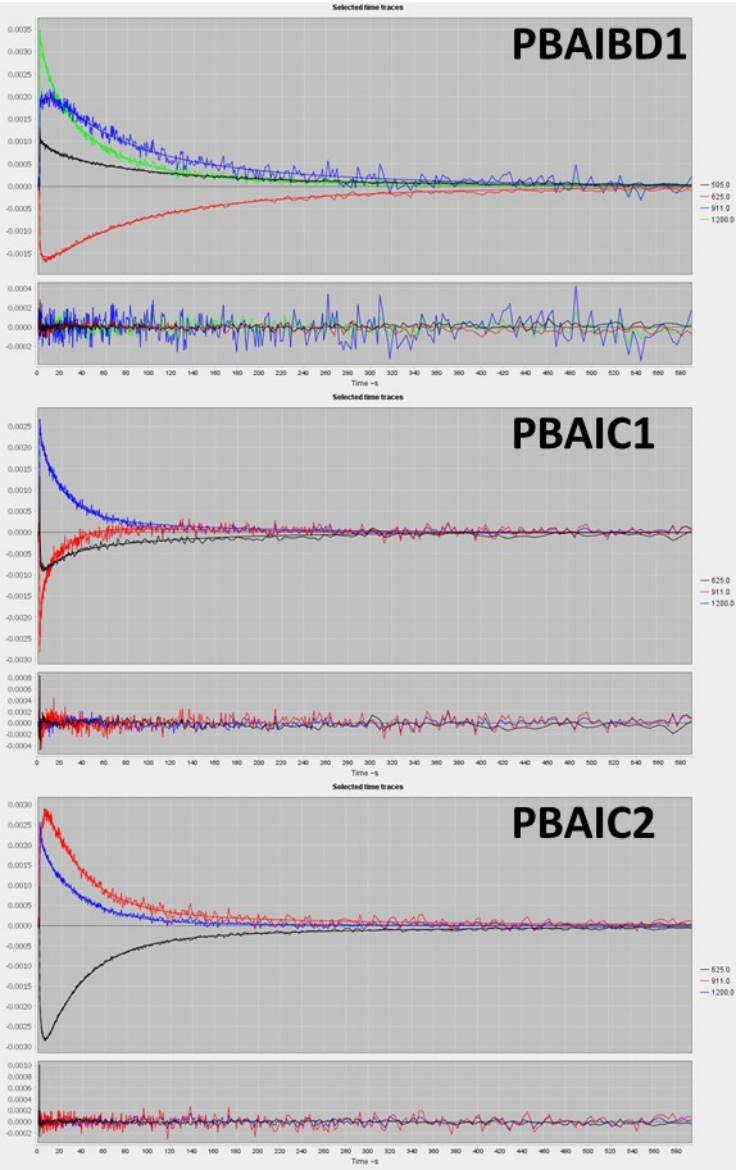


Figure SI11. Representative kinetics and fits of the time-resolved transient absorption data for the investigated polymers in 2-MeTHF solution. Also presented, for the judgment of the quality of the fits, are the weighted residuals distribution (W.R.).

Table SI6. Room temperature decay times obtained from fs-TA for the **BAI** copolymers in 2MeTHF solution and in thin films, at T=293 K.

compound		τ_1 **(ps)**	τ_2 **(ps)**	τ_3 **(ps)**
PBAIDB-1	2MeTHF	8.9	49.7	163.1
	Film	1.6	14.9	55.6
PBAIC-1	2MeTHF	0.71	19.4	114.7
	Film	3.0	20.9	167.3
PBAIC-2	2MeTHF	2.4	36.7	230.8
	Film	6.1	58.4	1948

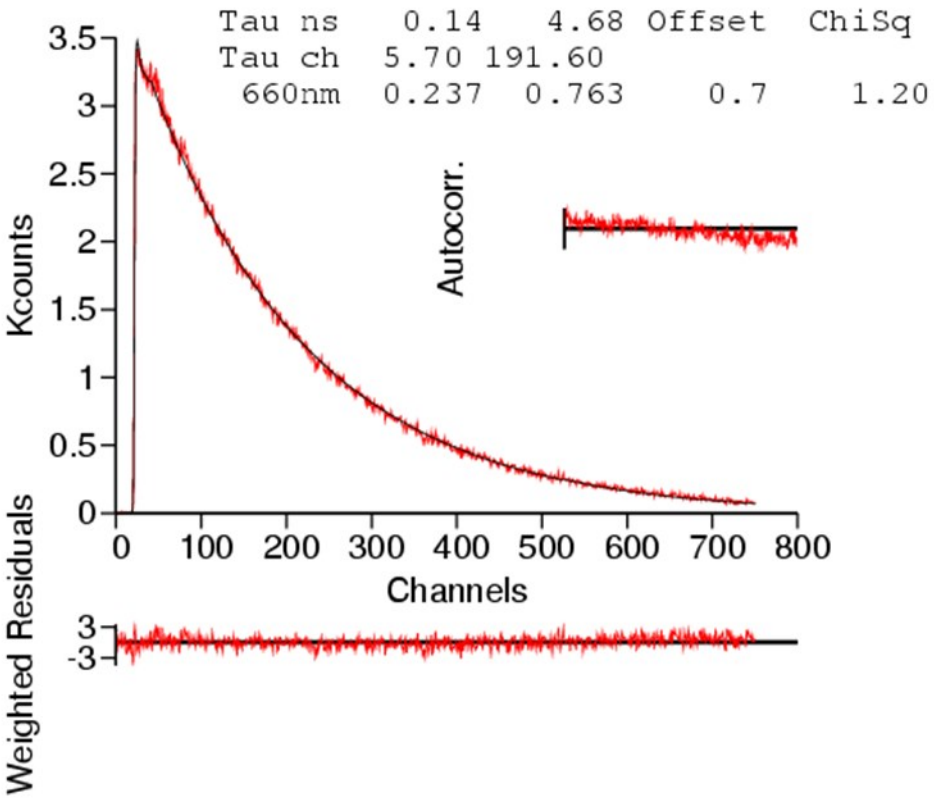


Figure SI12. Room-temperature fluorescence decay for **BAI1** in 2-MeTHF solution collected with excitation at 412 nm. For a better judgment of the quality of the fit, weighted residuals (W.R.), autocorrelation function (A.C.) and χ^2 values are also presented.

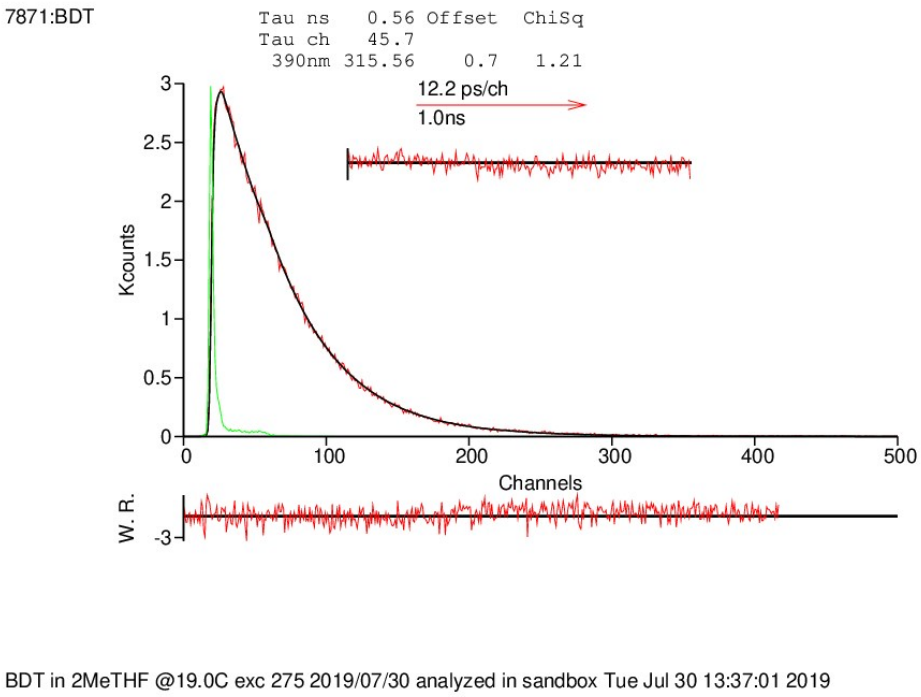


Figure SI13. Room-temperature fluorescence decay for **BDT** in 2-MeTHF solution collected with excitation at 275 nm. For a better judgment of the quality of the fit, weighted residuals (W.R.), autocorrelation function (A.C.) and χ^2 values are also presented. The green line in the decay corresponds to the instrumental response function.

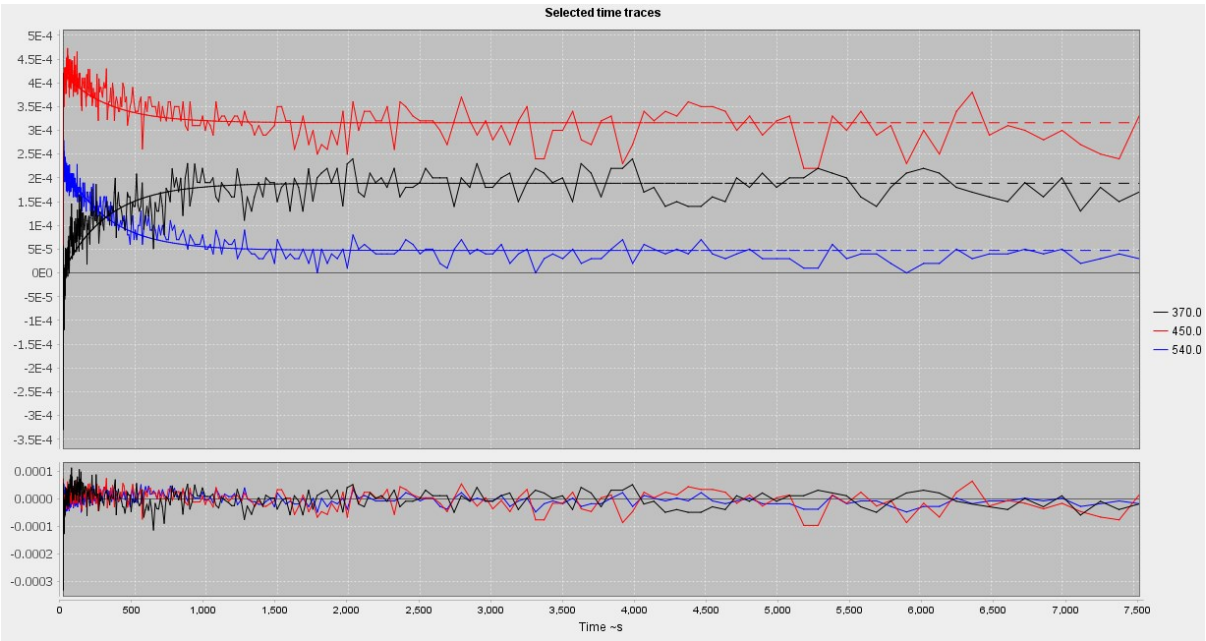


Figure SI14. Representative kinetics and fits of the time-resolved transient absorption data for BDT in 2-MeTHF solution. Also presented, for the judgment of the quality of the fits, are the weighted residuals distribution (W.R.).