Electronic Supplementary Information

for

Optical absorption in donor-acceptor polymers - alternating vs. random

Andreas Karolewski,[a] Anne Neubig,[b] Mukundan Thelakkat,[b*] Stephan Kümmel[a#]

[a] *Theoretical Physics IV, University of Bayreuth, 95440 Bayreuth, Germany.*
Fax: +49 (921) 55 3223; Tel: +49 (921) 55 3220.
[b] *Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany.*
Fax: +49 (921) 55 3109; Tel: +49 (921) 55 3108.

[*] Corresponding author for experimental part: mukundan.thelakkat@uni-bayreuth.de
[#] Corresponding author for theoretical part: stephan.kuemmel@uni-bayreuth.de

Table of Contents

Materials and Methods

All reactions were carried out in dry glassware and under inert atmosphere of purified argon using Schlenk techniques. All reagents and solvents were purchased from Aldrich, ABCR, Acros or TCI. They were used without further purification unless otherwise noted. 4,7-Dibromo-benzo[c][2,1,3]thiadiazole[1] and 4,7-Bis(3-hexylthiophen-2yl)benzo[c][2,1,3]thiadiazole[2] were synthesized according to modified literature procedures. Solvents used for precipitation were distilled under normal atmosphere.

^{1}H-NMR (300 MHz) spectra were recorded on a Bruker AC 300 spectrometer at room temperature. Chemical shifts for ^{1}H-NMR spectra are referenced relative to residual protons in the deuterated solvents ($CDCl_3$ δ=7.26 ppm; CD_2Cl_2 δ=5.33 ppm). Abbreviations used for splitting patterns are s (singlet), d (doublet), t (triplet), m (multiplet) and b (broad).

Mass spectroscopic data (MS) were obtained from a FINNIGAN MAT 8500 instrument.

UV/vis spectra of solutions in $CHCl_3$ with a concentration of 0.02 $mgmL^{-1}$ were recorded on a Hitachi 3000 spectrophotometer.

Oligomeric gel permeation chromatography was carried out in THF as eluent at a flow rate of 0.5 $mLmin^{-1}$ at room temperature using a column setup comprising a guard column (Varian, 5 x 0.8 cm, particle size 3 μm) and two analytical columns (Varian, 30 x 0.8 cm, particle size 3 μm). Oligomers were monitored with UV (Waters model 486) at 254 nm and RI (Waters model 410) detectors. Polystyrene standards and *o*-Dichlorobenzene as an internal standard were used for calibration. Preparative gel permeation chromatography was carried out in THF as eluent and a flow rate of $5mLmin^{-1}$ at room temperature using a column setup comprising a guard column (SDV, 50 x 7.5 mm, particle size 10 μm) and four analytical columns (PLgel 10^4 Å, 300 x 25 cm; PLgel 10^3 Å, 300 x 25 cm; PLgel 100 Å, 600 x 25 cm; PLgel 100 Å, 300 x 25 cm; particle size 10 μm each).

Matrix-assisted laser desorption ionization with time of flight detection (MALDI-ToF) mass spectrometry measurements were performed on a Bruker Reflex III using *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) as matrix material. The solutions of the analyte (1mg/200mL) and the matrix (1mg/100mL) in chloroform were mixed in the ratio 1:50 (v:v) and spotted onto the MALDI target plate prior to the measurement.

Gel Permeation Chromatography (GPC)

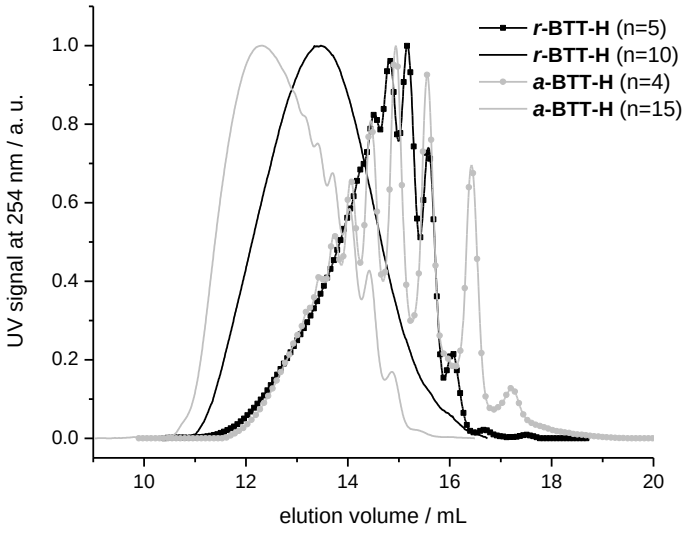


Figure S1: GPC traces of the systems ***r*-BTT-H (n=5), *r*-BTT-H (n=10), *a*-BTT-H (n=4)** and ***a*-BTT-H (n=15)**. All curves are normalized to the maximum.

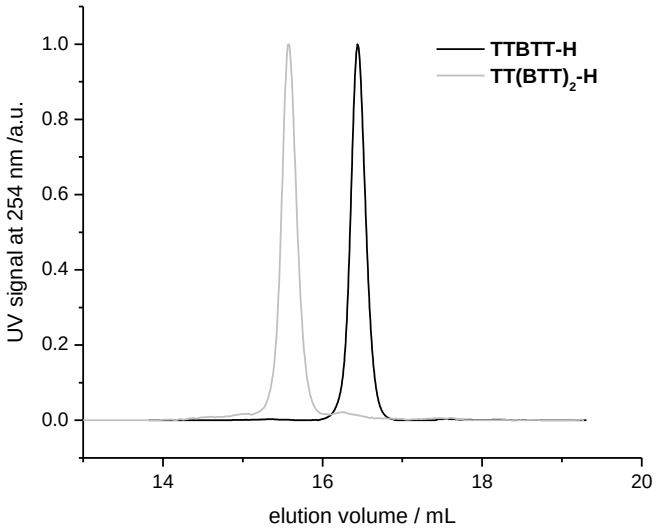


Figure S2: GPC traces of the fractionated **TTBTT-H** and **TT(BTT)$_2$-H** oligomers. All curves are normalized to the maximum. The **TTBTT-H** fraction has a very low polydispersity index (PDI) of 1.01 analogous to monodisperse compounds and did not show any shoulders on either side. Similarly the **TT(BTT)$_2$-H** fraction has a polydispersity index of 1.04. It is clearly shown that we separated the two well-defined low molecular weight systems from each other.

Matrix-Assisted Laser Desorption Ionization – Time of Flight (MALDI-ToF) Mass Spectrometry

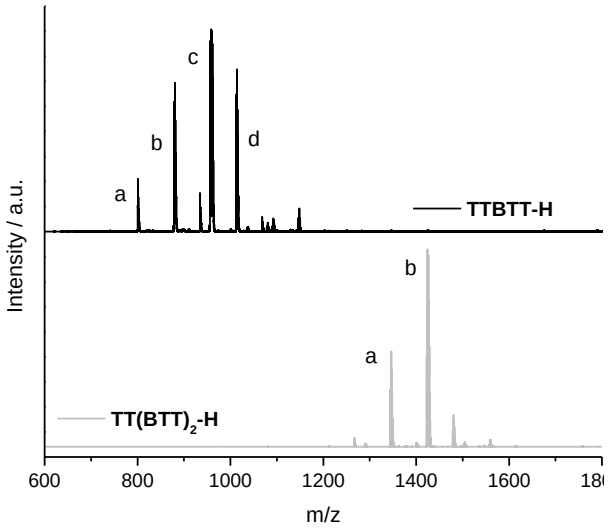


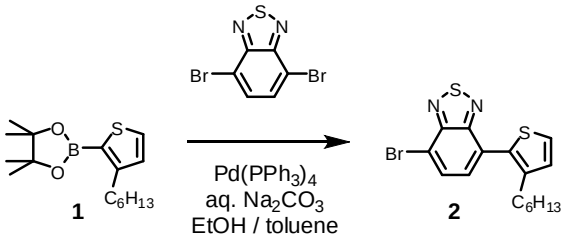
Figure S3: MALDI-ToF spectra of the **TTBTT-H** fraction (top) and **TT(BTT)$_2$-H** fraction (bottom). Each oligomer produces several peaks. This can be explained by the Suzuki-Miyaura polycondensation method which is used. The peaks correlate to the respective oligomer but with different end-groups which we all identified. For instance the four main peaks of the **TTBTT-H** can be clearly assigned as the **TTBTT-H** oligomer a) with H/H end-groups, b) with H/Br end-groups, c) Br/Br end-groups and d) with H/Br end-groups and one **B** unit. The two main peaks of the MALDI-ToF spectra of **TT(BTT)$_2$-H** can be correlated to the **TT(BTT)$_2$-H** oligomer a) with H/Br end-groups and b) with Br/Br end-groups. The corresponding mass-to-charge ratios are listed in Table S1. It is important to note that we clearly separated the two systems from each other in the sense that the species observed in the **TTBTT-H** spectrum are different from the species observed in the **TT(BTT)$_2$-H** spectrum.

Table S1: *Mass-to-charge ratio (m/z) calculated and determined with MALDI-ToF mass spectrometry of the oligomers* ***TTBTT-H*** *and* ***TT(BTT)$_2$-H*** *with the respective end-groups.*

Sample		m/z (MALDI)	m/z (calc)	End-groups
TTBTT-H	a	800.974	800.336	H-/H-
	b	878.646	878.247	Br-/H-
	c	956.456	956.157	Br-/Br-
	d	1012.484	1012.240	H-/Br-
TT(BTT)$_2$-H	a	1344.509	1344.404	Br-/H-
	b	1422.391	1422.314	Br-/Br-

Monomer Synthesis

Synthesis of 4-Bromo-7-(3-hexylthiophen-2-yl) benzo [c] 2,1,3-thiadiazole (2)

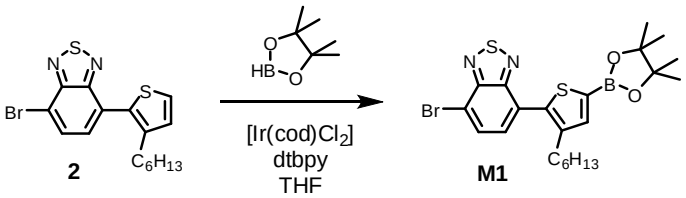


To a 500mL three-necked round bottom flask were added 3-Hexylthiophene-2-boronic acid pinacol ester **1** (10g, 34mmol), 4,7-Dibromo-2,1,3-benzothiadiazole (15g, 50mmol), 140mL of toluene, 100mL of EtOH and Na_2CO_3 (7.2g, 68mmol) diluted in 100mL water. The reaction mixture was degassed for 40 minutes and heated to reflux under stirring. $Pd(PPh_3)_4$ (393mg, 0.34mmol) was added and the mixture was refluxed for 16h. After evaporating the solvent under reduced pressure, H_2O (200mL) and methylene chloride (200mL) were added. The aqueous layer was extracted with methylene chloride (80mL) three times. The combined organic phases were washed with water (60mL) three times, dried with Na_2SO_4 and filtrated. After the solvent was removed by rotary evaporation **2** was obtained by distillation under vacuum as yellow oil. Yield: 7.3g (56%).

^{1}H-NMR (300MHz, $CDCl_3$): δ ppm 7.90 (d, *J* 7.5Hz, 1H-*BT-5H*); 7.47 (d, *J* 7.55Hz, 1H-*BT-6H*); 7.43 (d, *J* 5.0Hz, 1H-*Th-5H*); 7.08 (d, *J* 5.0Hz, 1H-*Th-4H*); 2.58 (t, *J* 7.6Hz, 2H-*α-H)*; 1.67-1.49 (m, 2H-*β-H)*; 1.28-1.08 (m, 6H, *-CH_2-)*; 0.81 (t, *J* 6.9Hz, 3H,*-CH_3*).

MS (EI) m/z: 382 (43) [M^+] (calcd. 382.0).

Synthesis of 4-Bromo-7-(5-boronic acid pinacolyl-3-hexylthiophen-2-yl) benzo-2,1,3-thiadiazole (M1)



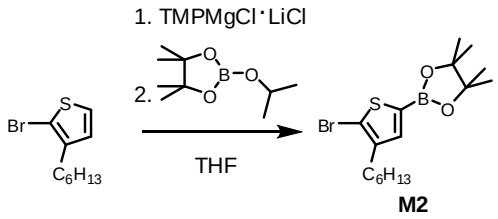
To a 250mL schlenk round bottom flask were added 4-Bromo-7-(3-hexylthiophen-2-yl) benzo [c] 2,1,3-thiadiazole **2** (3.3g, 8.65mmol) in 25mL THF. $Ir(COD)Cl_2$ (57mg, 0.086mmol) and 4,4´-Di-tert-butyl bipyridine (23mg, 0.086mmol) were added and the mixture was degassed with argon for 20min, which was followed by addition of 4,4´-5,5´-Tetramethyl-[1,3,2]dioxaborolane (2.437g, 9.08mmol) and an additional amount of THF (25mL). After degassing for further 10min the mixture was stirred and heated under reflux for 46h. After having been allowed to cool to room temperature the reaction mixture was quenched with 200mL ice water. THF was removed by rotary evaporation. The residue was extracted with ethyl acetate (120mL) for three times. The combined organic layers

were washed with brine (50mL) for three times, dried with Na_2SO_4 and filtrated. After the solvent was removed the product **M1** was recrystallized from petrolether. Yield: 2.0g (46%).

^{1}H-NMR (300MHz, $CDCl_3$): δ ppm 7.90 (d, *J* 7.8Hz, 1H-*BT-5H*); 7.60 (s, 1H-*Th-4*); 7.46 (d, *J* 7.33Hz, 1H-*BT-6H*); 2.56 (t, *J* 7.8Hz, 2H-*α-H)*; 1.66-1.48 (m, 2H-*β-H)*; 1.36 (s, 12H, -CH_3); 1.27-1.08 (m, 6H, -CH_2-*)*; 0.80 (t, *J* 6.7Hz, 3H,-CH_3).

MS (EI) m/z: 506 (70) [M^+] (calcd. 506.1).

Synthesis of 5-Bromo-4-hexylthiophene-2-boronic acid pinacol ester (M2)



M2

To a solution of 2-Bromo-3-hexylthiophene (10g, 40.45mmol) in 160mL THF was added 2,2,6,6-Tetramethylpiperidinylmagnesium chloride lithium chloride solution (1M in THF/toluene) (14.71g, 60.68mmol) in one portion. The reaction mixture was stirred at room temperature for 24h after which 2-Isopropoxy-4,4´,5,5´-tetramethyl-1,3,2-dioxaborolane (15.05g, 80.9mmol) was added. The reaction mixture was allowed to stir at room temperature for further 4h and was then quenched with 50mL water. The organic solvents were removed under reduced pressure after which water was added and extracted with diethyl ether. The combined organic layers were washed with saturated NaCl-solution, dried with Na_2SO_4 and filtrated. After evaporation of the solvent the crude product was distilled under vacuum to afford **M2** as yellowish oil. Yield: 10.72g (71%).

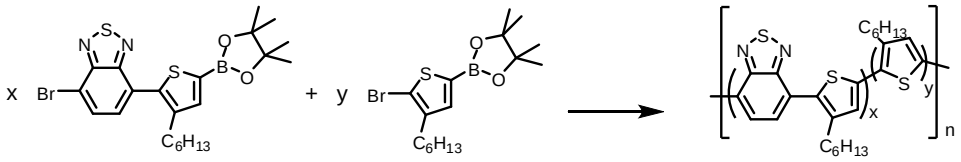
^{1}H-NMR (300MHz, $CDCl_3$): δ ppm 7.31 (s, 1H-*3H*); 2.54 (t, *J* 7.7Hz, 2H-*α-H)*; 1.70-1.47 (m, 2H-*β-H)*; 1.42-1.18 (m, 18H, -CH_2-, -CH_3*)*; 0.88 (t, *J* 6.6Hz, 3H,-CH_3).

MS (EI) m/z: 374 (26) [M^+] (calcd. 374.1).

Polymer Synthesis

All polymers were synthesized via palladium catalyzed Suzuki coupling polycondensation. Monomers **M1** and **M2** were used to obtain the copolymers ***r*-BTT-H**. Using monomers **M3** and **M4** the alternating copolymers ***a*-BTT-H** were obtained. A variation of the reaction conditions led to different molecular weights for ***r*-BTT-H** (n=5; 10) and ***a*-BTT-H** (n=4; 15).

Synthesis of *r*-BTT-H



M1 **M2** ***r*BTT-H**

***r*-BTT-H** (n=5)

To a Schlenk tube monomer **M1** (190mg, 0.375mmol) and **M2** (140mg, 0.375mmol) were dissolved in THF (8mL). An aqueous solution of Na_2CO_3 (1M, 2mL) and two drops of Aliquat 336 were added to the solution and degassed with argon for 1h. Afterwards $Pd(PPh_3)_4$ (8.7mg, 0.0075mmol) was added and the solution was degassed again for 10min. The mixture was stirred under microwave conditions under reflux for 1 day. After cooling to room temperature the solvent was evaporated and the polymer was dissolved in chloroform and precipitated in methanol. Than it was dissolved in methylene chloride, extracted with water and again precipitated into methanol. The crude polymer was collected by filtration, dried and loaded into an extraction thimble to be washed with methanol, ethanol, acetone and methylene chloride. The methylene chloride fraction was freeze dried from benzene to afford a dark solid. Yield: 19%.

^{1}H-NMR (300MHz, CD_2Cl_2): δ ppm 8.29-7.10 (b, 3.2H-*Ar-H*); 3.00-2.56 (m, 2H-*α-H)*; 1.90-1.62 (m, 2H-*β-H)*; 1.42-1.13 (m, 6H, -*CH_2)*; 0.97-0.76 (m, 3H,-*CH_3*).

UV-vis ($CHCl_3$, nm): 497nm (2.49eV).

Oligomeric GPC: M_w : 3636 gmol^{-1}; M_p: 1888 g,mol^{-1}; M_w/M_n: 1.46.

***r*-BTT-H** (n=10)

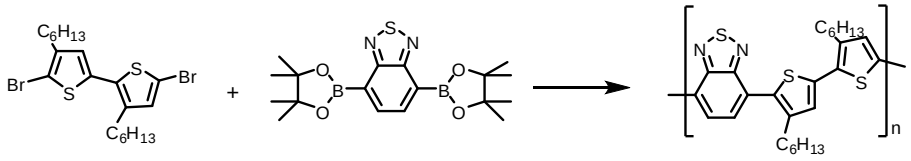
In a 20mL high pressure microwave reactor tube, equipped with a sealed septum monomer **M1** (150mg, 0.296mmol) and **M2** (110mg, 0.296mmol) were dissolved in toluene (4mL). Two drops of Aliquat 336, an aqueous solution of Na_2CO_3 (1M, 1mL) and $Pd(PPh_3)_4$ (13.7mg, 0.0118mmol) were added to the solution. Then the tube was sealed and degassed with argon for 35min. The reaction mixture was heated 7 days at 120°C (oil bath temperature). The end-capping procedure was performed in 2 separate steps. After cooling to room temperature, a degassed solution of phenylboronic acid pinacol ester (60.34mg, 0.296mmol) in 1mL toluene was added first, followed by heating for 5.5h at 120°C. After cooling to room temperature, degassed bromobenzene (92.29mg, 0.591mmol) was added, followed by heating for 15.5h at 120°C. After cooling to room temperature the polymer was dissolved in methylene chloride, extracted with water and precipitated into methanol. The crude polymer was collected by filtration, dried and loaded into an extraction thimble to be washed with methanol, ethanol, acetone, *n*-hexane and methylene chloride. The methylene chloride fraction was freeze dried from benzene to afford a dark solid. Yield: 15%.

^{1}H-NMR (300MHz, CD_2Cl_2): δ ppm 8.22-6.94 (b, 2.5H-*Ar-H*); 3.07-2.37 (m, 2H-*α-H)*; 1.89-1.59 (m, 2H-*β-H)*; 1.49-1.10 (m, 6H, -*CH_2)*; 0.97-0.75 (m, 3H,-*CH_3*).

UV-vis ($CHCl_3$, nm): 507nm.

Oligomeric GPC: M_w : 7132 gmol^{-1}; M_p: 5507 g,mol^{-1}; M_w/M_n: 1.59.

Synthesis of *a*-BTT-H



M3 **M4** ***a*-BTT-H**

***a*-BTT-H** (n=4)

To a Schlenk tube 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) **M4** (385mg, 0.94mmol) and **M3** (461.0mg, 0.94mmol) were dissolved in THF (8mL). An aqueous solution of Na_2CO_3 (1M, 4mL), two drops of Aliquat 336 and $Pd(PPh_3)_4$ (54.1mg, 0.00468mmol) were added to the solution and degassed with argon for 30min. The mixture was stirred under microwave conditions under reflux for 18h. After cooling to room temperature the solvent was evaporated and the polymer was dissolved in methylene chloride, extracted with water and precipitated into methanol. The crude polymer was collected by filtration, dried and loaded into an extraction thimble to be washed with methanol, ethanol, acetone and methylene chloride. The methylene chloride fraction was freeze dried from benzene to afford a dark solid. Yield: 41%.

^{1}H-NMR (300MHz, CD_2Cl_2): δ ppm 8.09-6.91 (b, 2.6H-*Ar-H*); 3.14-2.33 (m, 2H-*α-H)*; 1.89-1.57 (m, 2H-*β-H)*; 1.51-1.13 (m, 6H, -*CH_2)*; 1.04-0.77 (m, 3H,-*CH_3*).

UV-vis ($CHCl_3$, nm): 521nm.

Oligomeric GPC: M_w : 3200 gmol^{-1}; M_p: 2157 gmol^{-1}; M_w/M_n: 1.74.

***a*-BTT-H** (n=15)

In a 20mL high pressure microwave reactor tube, equipped with a sealed septum **M3** (261mg, 0.53mmol) and 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) **M4** (204.9mg, 0.53mmol) were dissolved in toluene (7mL). Two drops of Aliquat 336, an aqueous solution of Na_2CO_3 (1M, 1.75mL) and $Pd(PPh_3)_4$ (12.2mg, 0.011mmol) were added to the solution. The tube was sealed and the mixture was degassed with argon for 45min. The reaction was heated 2 days at 120°C (oil bath temperature). The end-capping procedure was performed in 2 separate steps. After cooling to room temperature, a degassed solution of phenylboronic acid pinacol ester (108.2mg, 0.53mmol) in 3mL toluene was added first, followed by heating for 5h at 120°C. After cooling to room temperature, degassed bromobenzene (166.4mg, 1.06mmol) was added, followed by heating for 12h at 120°C.

After cooling to room temperature the polymer was dissolved in methylene chloride, extracted with water and precipitated into methanol. The crude polymer was collected by filtration, dried and loaded into an extraction thimble to be washed with methanol, ethanol, acetone and methylene chloride. The methylene chloride fraction was freeze dried from benzene to afford a dark solid. Yield: 32%.

^{1}H-NMR (300MHz, CD_2Cl_2): δ ppm 8.55-6.85 (b, 5H-*Ar-H*); 2.99-2.49 (m, 4H-α-*H)*; 1.88-1.57 (m, 4H-β-*H)*; 1.50-1.13 (m, 6H, -CH_2*)*; 1.04-0.75 (m, 3H,-CH_3).

UV-vis ($CHCl_3$, nm): 525nm.

Oligomeric GPC: M_w : 11800 gmol^{-1}; M_p: 12310 gmol^{-1}; M_w/M_n: 1.64.

Natural Transition Orbital Pairs of r-BTT

Fig. S4 shows the dominant natural transition orbital pairs for the lowest excitation of *r*-BTT with n=10. Taking all these transitions into account confirms that the first excitation is of mixed valence-CT type.

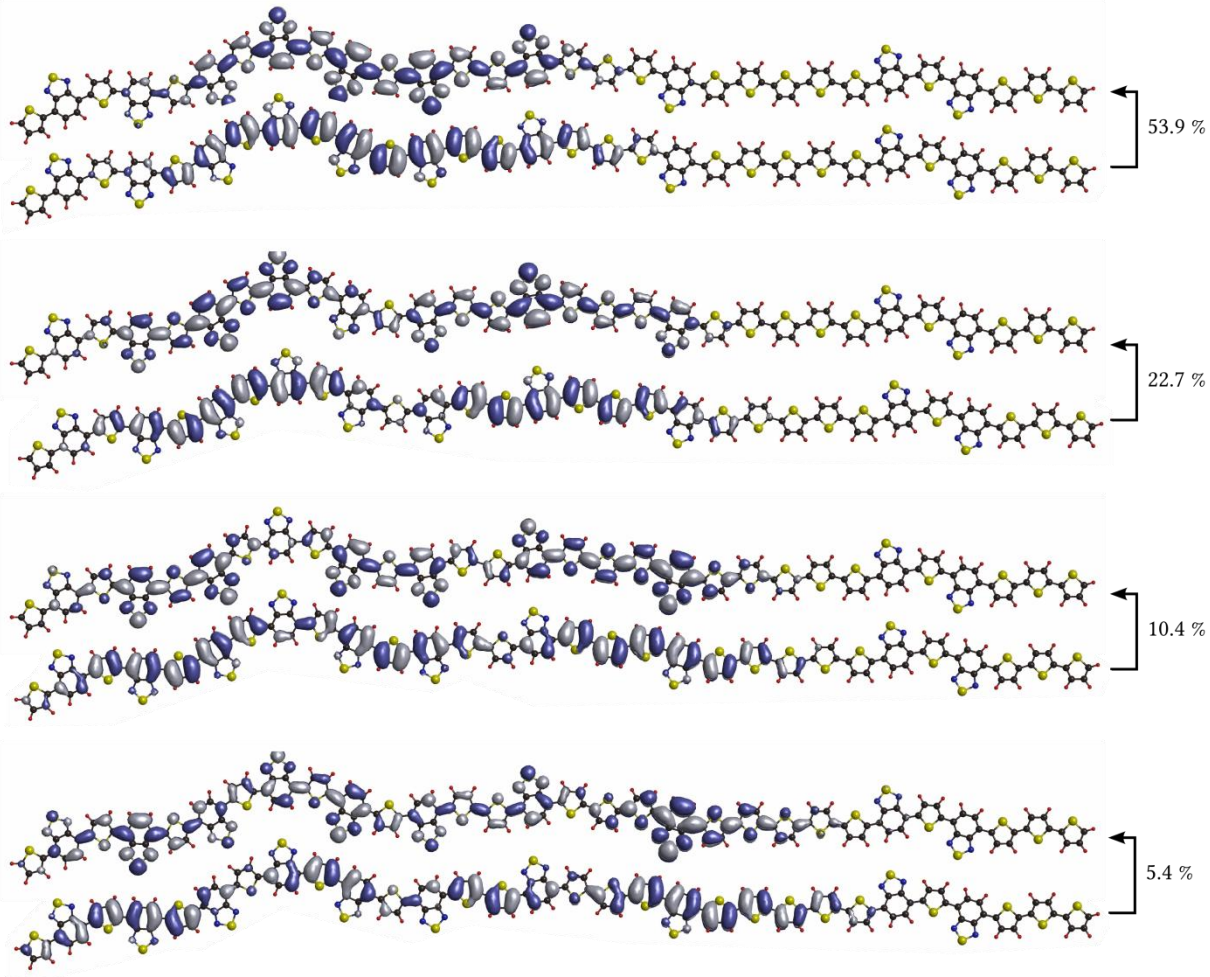


Figure S4: Most dominant natural transition orbital hole/electron pairs of the lowest excitation for *r*-BTT with n=10 from a BNL calculation with an optimized range separation parameter. The isosurface value is 0.01. The weight factors indicate the contribution to the lowest excitation for each pair.

Highest Occupied and Lowest Unoccupied Orbitals of r-BTT

Fig. S5 shows the four highest occupied orbitals and the four lowest unoccupied orbitals. Table S1 lists the corresponding orbital energies, obtained with the BNL functional and the optimized range separation parameter $\gamma = 0.121\ a_0^{-1}$.

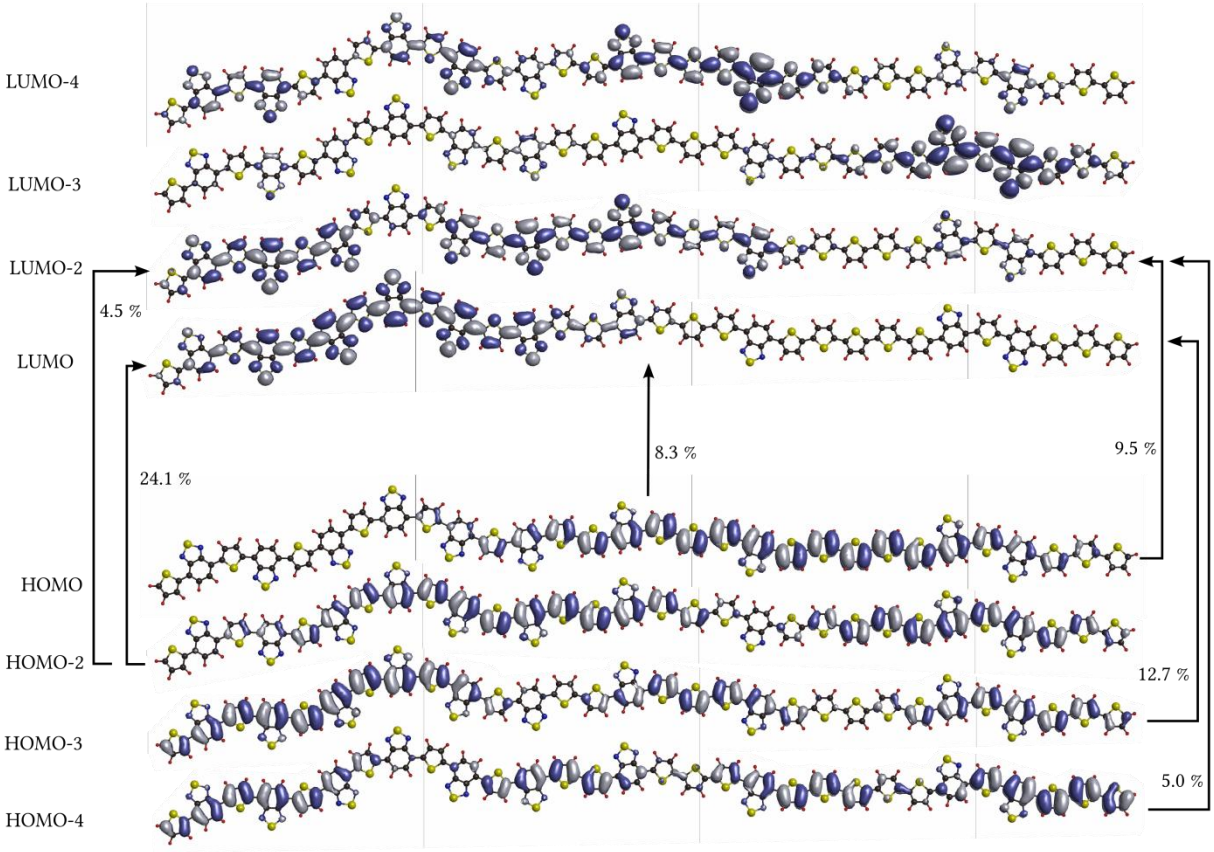


Figure S5: The four lowest unoccupied and highest occupied molecular orbitals for r-BTT with n=10 from a BNL calculation with an optimized range separation parameter. The isosurface value is 0.01. The weight factors indicate the most dominant contributions to the lowest excitation.

orbital	eigenvalue [eV]
LUMO+3	-1.820
LUMO+2	-1.917
LUMO+1	-1.948
LUMO	-2.091
HOMO	-5.414
HOMO-1	-5.512
HOMO-2	-5.616
HOMO-3	-5.727

Table S1: Frontier orbital energies of *r*-BTT (n=10).

References

1. DaSilveira Neto, B. A.; Lopes, A. S. A.; Ebeling, G.; Goncalves, R. S.; Costa, V. E. U.; Quina, F. H.; Dupont, J. *Tetrahedron* **2005,** 61, (46), 10975-10982.

2. Kim, J.-J.; Choi, H.; Lee, J.-W.; Kang, M.-S.; Song, K.; Kang, S. O.; Ko, J. *Journal of Materials Chemistry* **2008,** 18, (43), 5223-5229.