SUPPORTING INFORMATION

Chiral diethyl-EDT-TTF and tetraethyl-BEDT-TTF: synthesis, structural characterization, radical cation salt and charge transfer complexes

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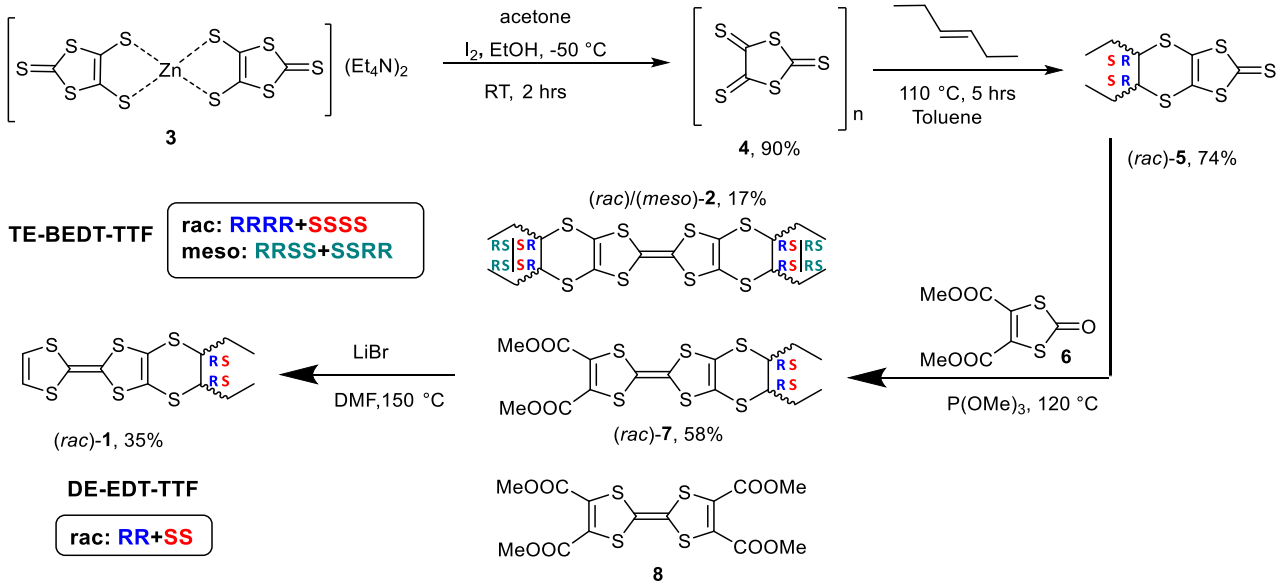
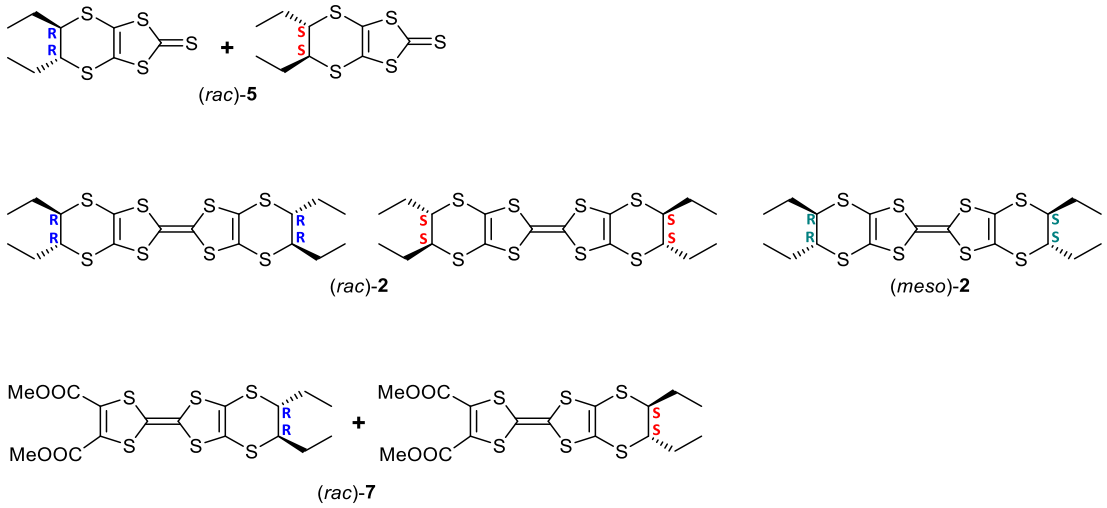
Materials and instrumentation

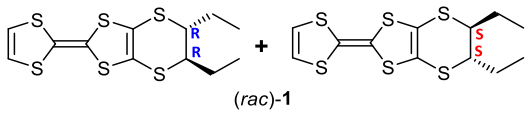
Reactions were carried out under nitrogen; dry solvents were obtained from distillation machines. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 300 spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: s, singlet; d, doublet; dq, doublet of quadruplets; m, massif. MALDI-TOF MS spectra were recorded on a Bruker Biflex-IIITM apparatus, equipped with a 337 nm N_2 laser. Elemental analysis was performed using a Flash 2000 Fisher Scientific Thermo Electron analyzer.

Synthesis



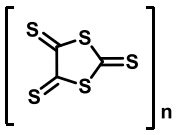
Details of the absolute configurations of the stereogenic centres





(*rac*)-**1**

1,3-dithiolane-2,4,5-trithione (4).



Synthesized following the published method.[1]

Bis(tetraethylammonium) bis(1,3-dithiole-2-thione-4,5-dithiolato)-zincate **3** (15 g, 21 mmol) was dissolved in acetone (150 mL) and cooled down to -50 °C. I_2 (10.7 g, 42 mmol) dissolved in ethanol (50 mL) was added dropwise to the solution and an orange precipitate starts to form. Then the solution was left under stirring for two hours at room temperature. The solid orange precipitate was filtered then washed with acetone, water, ethanol, diethyl ether and dried to afford **4** as an orange microcrystalline solid (7.1 g, 90 %).

[1] N. Svenstrup and J. Becher, *Synthesis*, 1995, **1995**, 215–235.

Electrochemistry:

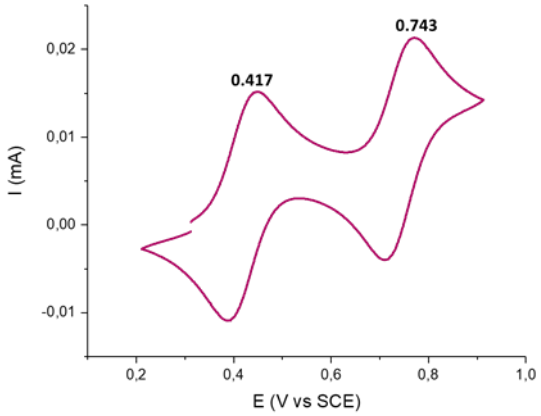
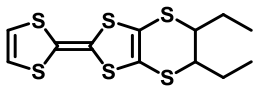


Fig. S1 Cyclic voltagram of compound **1**.

Cyclic voltammetry measurements show the classical reversible two single electron oxidation processes into radical cation and dication species at $\Delta E_{1/2}$= +0.42 and 0.74 V *vs* SCE, respectively.

Chiral HPLC separation for compound (*rac*)-DE-EDT-TTF (*rac*)-1



Analytical separation for compound (*rac*)-**1**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IG	Heptane / ethanol / dichloromethane (90/5/5)	5.54 (+)	0.88	6.34 (-)	1.15	1.31	3.40

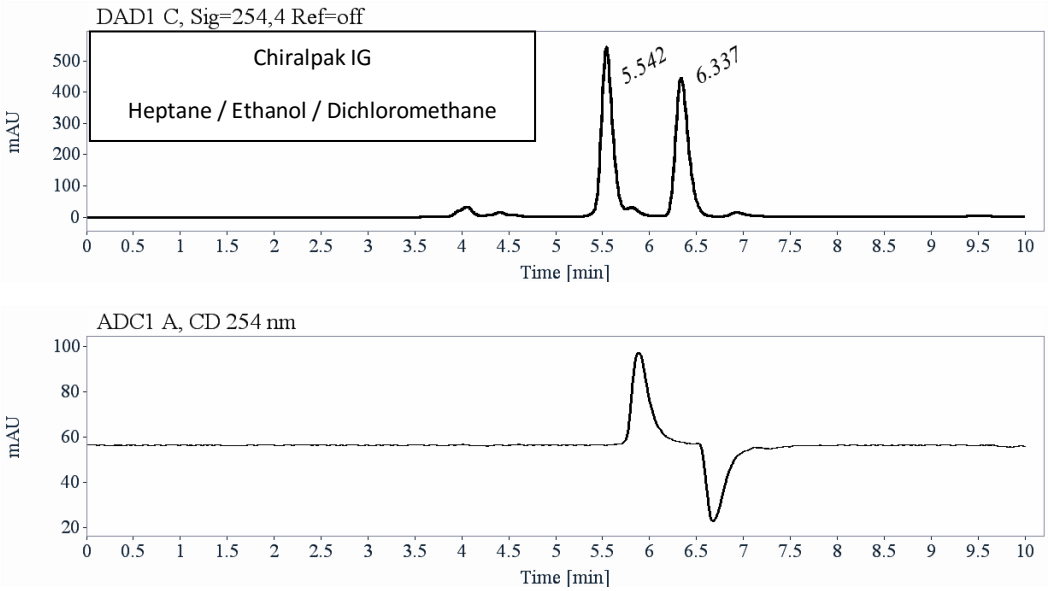


Fig. S2 Analytical chiral HPLC separation for compound (*rac*)-**1**.

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
5.54	4589	51.79	0.88		
6.34	4272	48.21	1.15	1.31	3.40
Sum	8861	100.00			

Semi-preparative separation for compound (*rac*)-**1**

• Sample preparation: About 300 mg of compound (*rac*)-DE-EDT-TTF are dissolved in 10 mL of a mixture of dichloromethane and hexane (50/50).

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), heptane / ethanol / dichloromethane (90/5/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 85 times 120 µL, every 3.5 minutes.

• First fraction: 125 mg of the first eluted ((+, CD 254nm)-enantiomer) with ee > 99 %

• Second fraction: 120 mg of the second eluted ((-, CD 254 nm)-enantiomer) with ee > 97 %

• Chromatograms of the collected fractions:

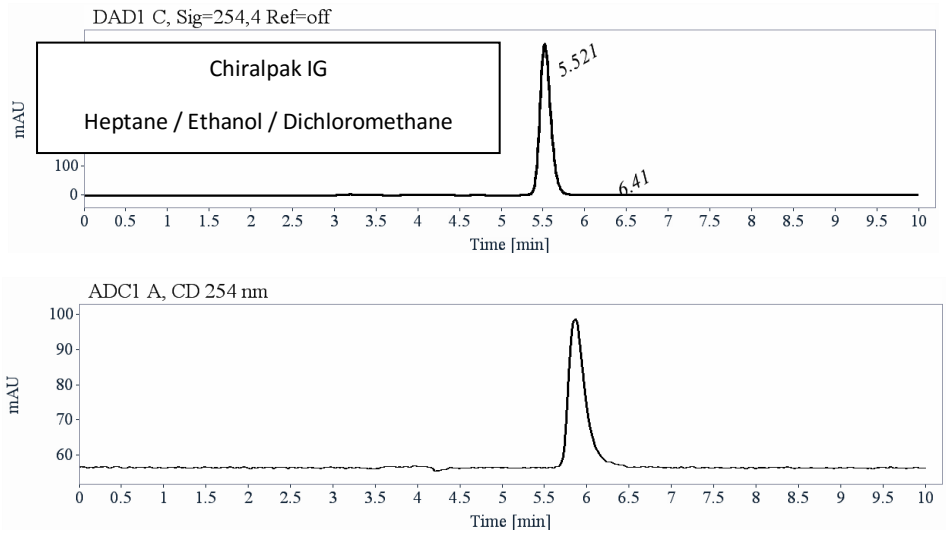


Fig. S3 Semi-preparative chiral HPLC separation for compound (*R*)-**1**.

RT [min]	Area	Area%
5.52	4780	99.70
6.41	14	0.30
Sum	4794	100.00

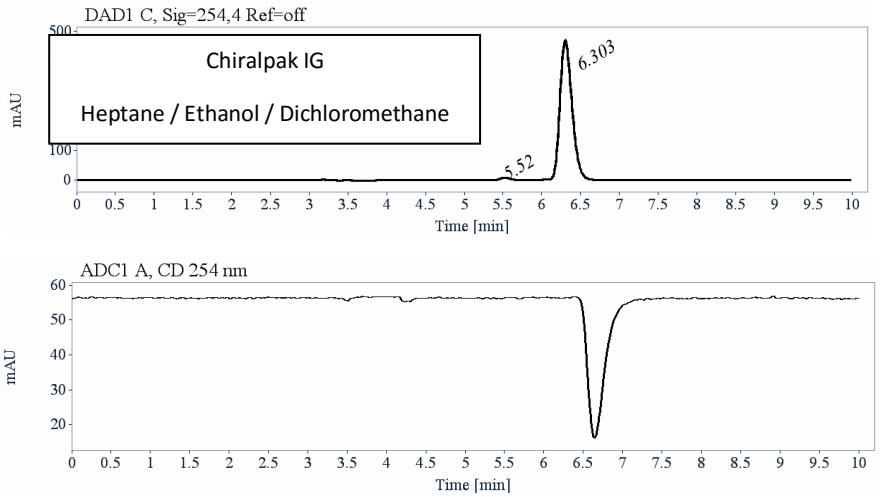


Fig. S4 Semi-preparative chiral HPLC separation for compound (*S*)-**1**.

RT [min]	Area	Area%
5.52	73	1.41
6.30	5135	98.59
Sum	5208	100.00

Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp (589 nm), a halogen lamp (578 nm and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

λ (nm)	(*R*)-**1** first eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.37)	(*S*)-**1** second eluted on Chiralpak IG $[\alpha]_{\lambda}^{25}$ (CH_2Cl_2, c =0.33)
589	+ 191	- 188
578	+ 198	- 196
546	+ 223	- 221

Electronic Circular Dichroism (ECD) and UV-Visible spectroscopy

(*R*)-**1**, first eluted on Chiralpak IG: green solid line, concentration = 1.11 mmol.L^{-1} in acetonitrile.

(*S*)-**1**, second eluted on Chiralpak IG: red dotted line, concentration = 1.10 mmol.L^{-1} in acetonitrile.

Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 1 nm, and 3 accumulations per sample.

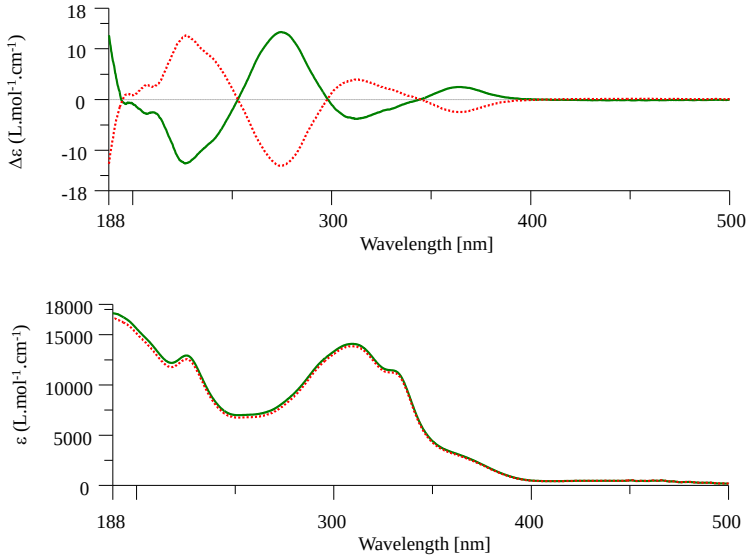
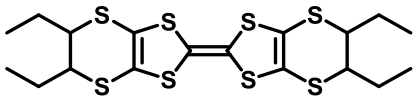


Fig. S5 CD (top) and UV-Vis (bottom) spectra of (*R*)-**1** (green line) and (*S*)-**1** (red dotted line).

Chiral HPLC separation for the mixture (*rac*)-TE-BEDT-TTF (*rac*)-2 and (*meso*)-TE-BEDT-TTF (*meso*)-2



Analytical separation for the mixture (*rac*)-**2** and (*meso*)-**2**

The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

2 contains two enantiomers (*S*,*S*,*S*,*S*)/(*R*,*R*,*R*,*R*) and the *meso* compound (*S*,*S*,*R*,*R*).

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IG	Heptane / ethanol / dichloromethane (85/5/10)	4.7 (+) and meso	0.60	6.12 (-)	1.08	1.80	4.82

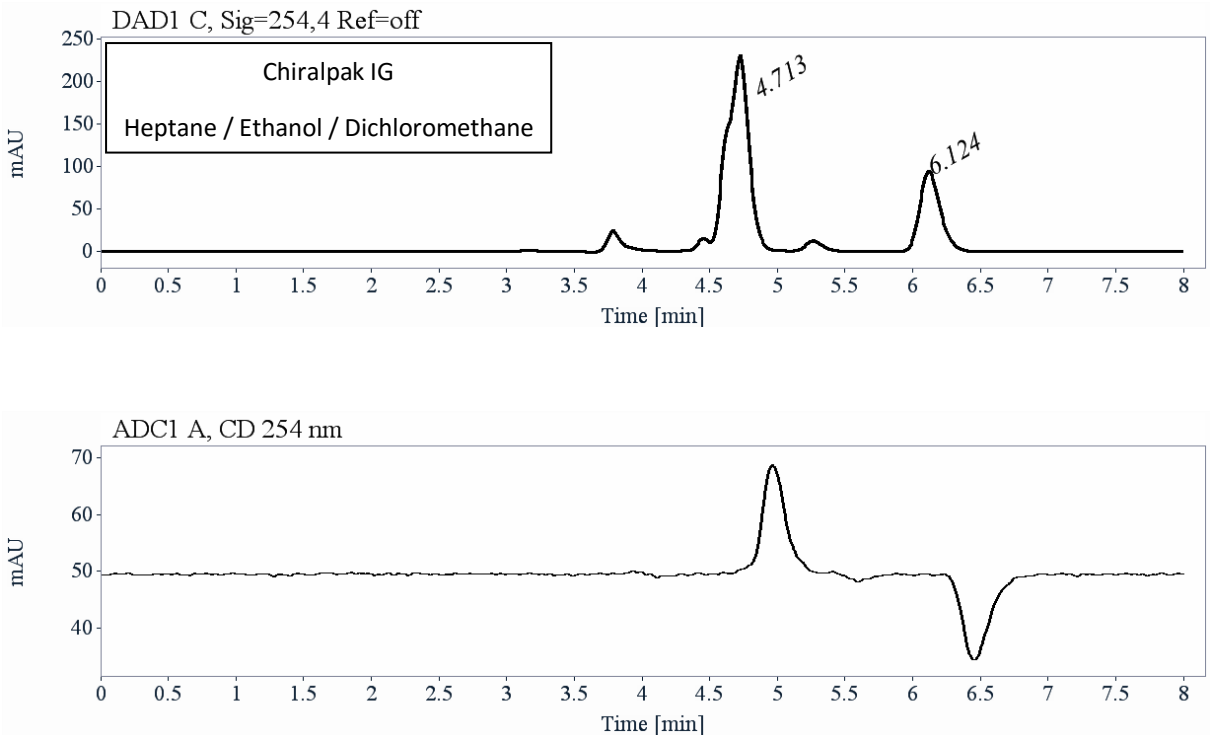


Fig. S6 Analytical chiral HPLC separation for the mixture (*rac*)-**2** and (*meso*)-**2**.

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
4.71	2688	72.73	0.60		
6.12	1008	27.27	1.08	1.80	4.82
Sum	3696	100.00			

Analytical chiral HPLC separation for the *meso* form and the (+, CD 254 nm)-enantiomer of **2**

• The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

Column	Mobile Phase	t1	k1	t2	k2	α	Rs
Chiralpak IG	Heptane / ethanol (95/5)	8.37 (+)	1.84	10.15 (meso)	2.44	1.33	3.38

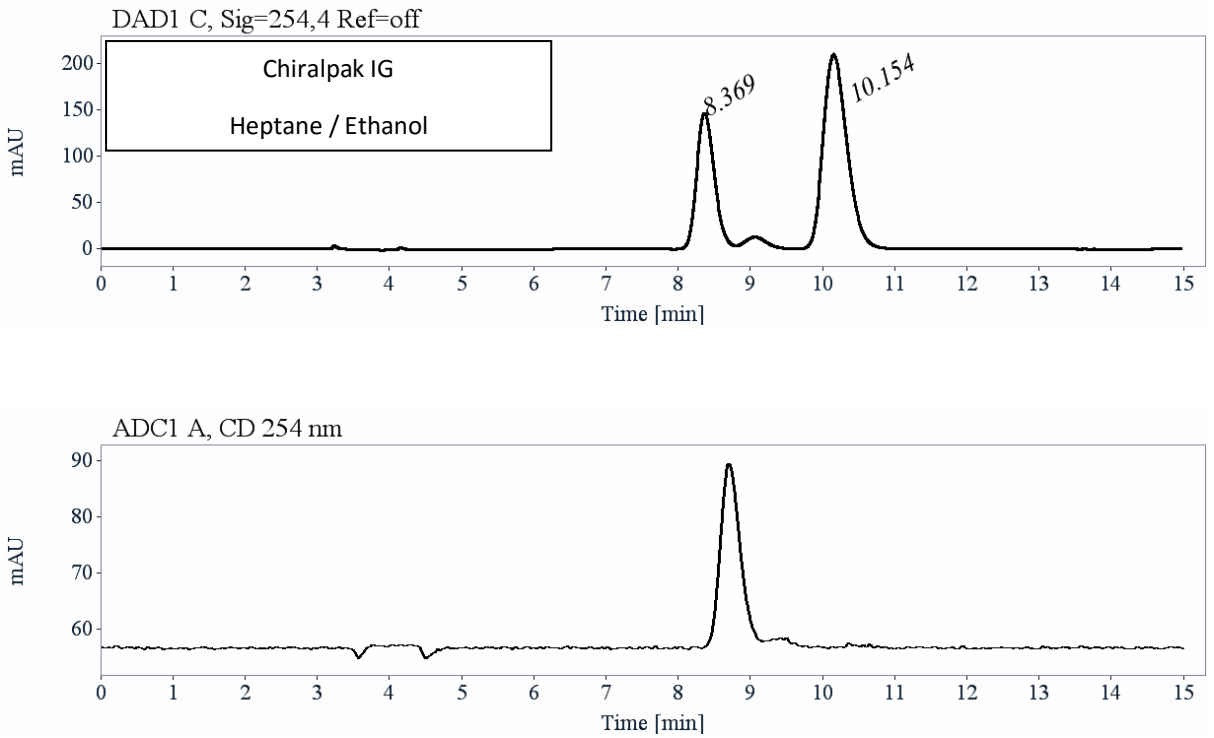


Fig. S7 Analytical chiral HPLC separation for the mixture (*meso*)-**2** and (*R*)-**2**.

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
8.37	2525	34.26	1.84		
10.15	4845	65.74	2.44	1.33	3.38
Sum	7370	100.00			

Semi-preparative separation for compound **2**

*Semi-preparative separation for the mixture of [the meso form and the (+, CD 254 nm)-enantiomer] and the (-, CD 254 nm)-enantiomer of **2***

• Sample preparation: About 145 mg of compound **2** are dissolved in 18 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), heptane / ethanol / dichloromethane (85/5/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 225 times 80 µL, every 3.3 minutes.

• First fraction: 88 mg of the first eluted (+, CD 254 nm)-enantiomer and the *meso* compound)

• Second fraction: 32 mg of the second eluted ((-, CD 254 nm)-enantiomer) with ee > 99.5%

• Chromatograms of the second fraction:

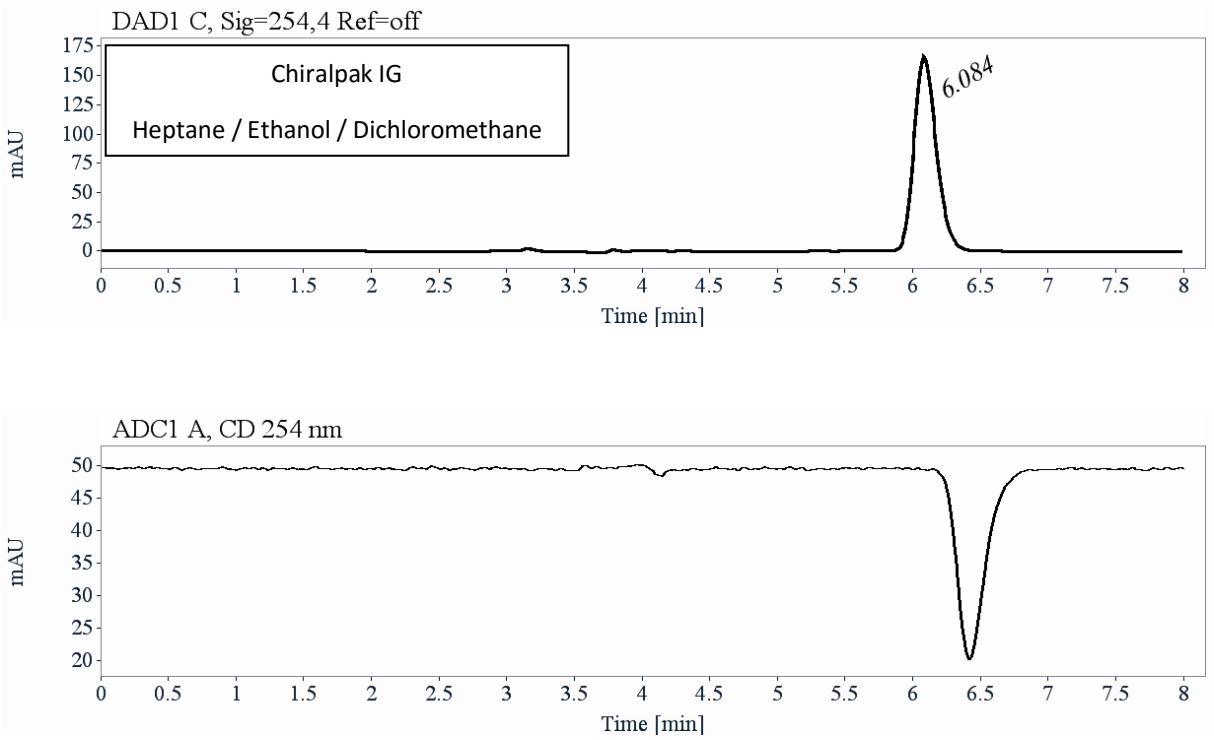


Fig. S8 Semi-preparative chiral HPLC separation for compound (*S*)-**2**.

RT [min]	Area	Area%
6.08	1899	100.00
Sum	1899	100.00

*Semi-preparative separation for the meso form and the (+, CD 254 nm)-enantiomer of **2***

• Sample preparation: About 88 mg of [the (+, CD 254 nm)-enantiomer and *meso* form] of compound **2** are dissolved in 12 mL of dichloromethane.

• Chromatographic conditions: Chiralpak IG (250 x 10 mm), heptane / ethanol (95/5) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 240 times 50 µL, every 4 minutes.

• First fraction: 26 mg of the first eluted (+, CD 254 nm)-enantiomer) with ee > 99.5%

• Second fraction: 54 mg of the *meso* form

• Chromatograms of the collected fractions:

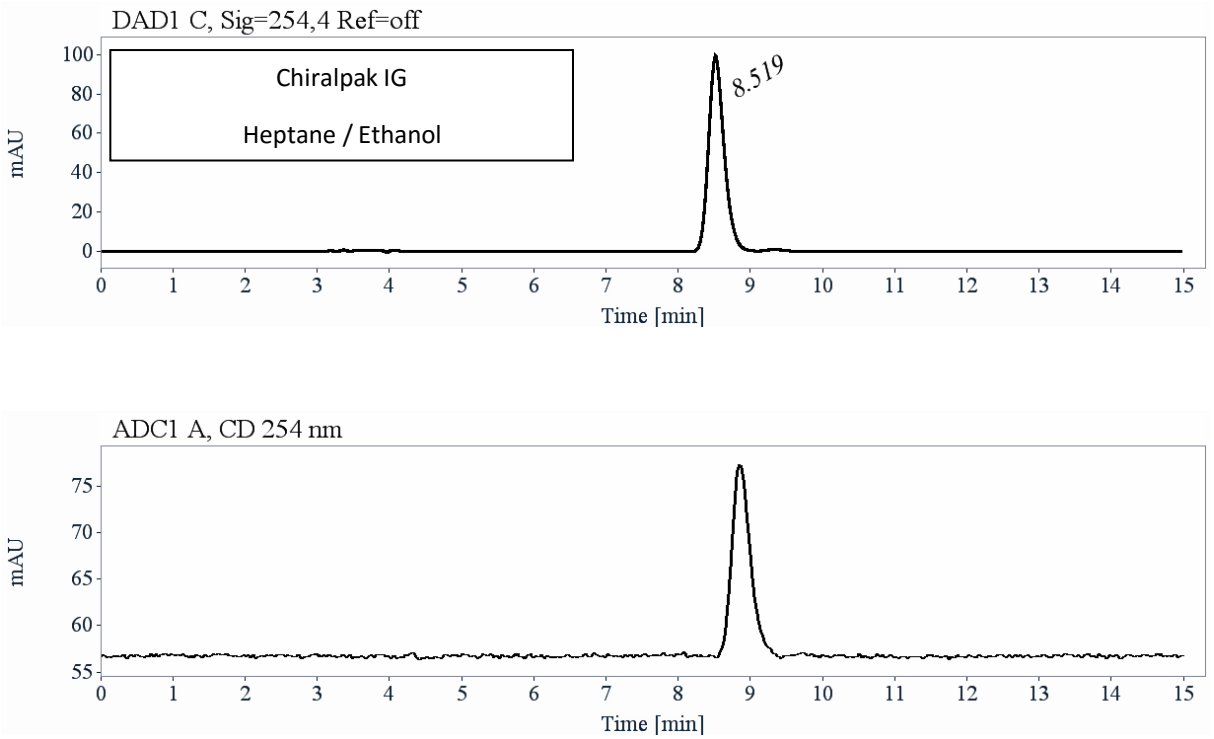


Fig. S9 Semi-preparative chiral HPLC separation for compound (*R*)-**2**.

RT [min]	Area	Area%
8.52	1505	100.00
Sum	1505	100.00

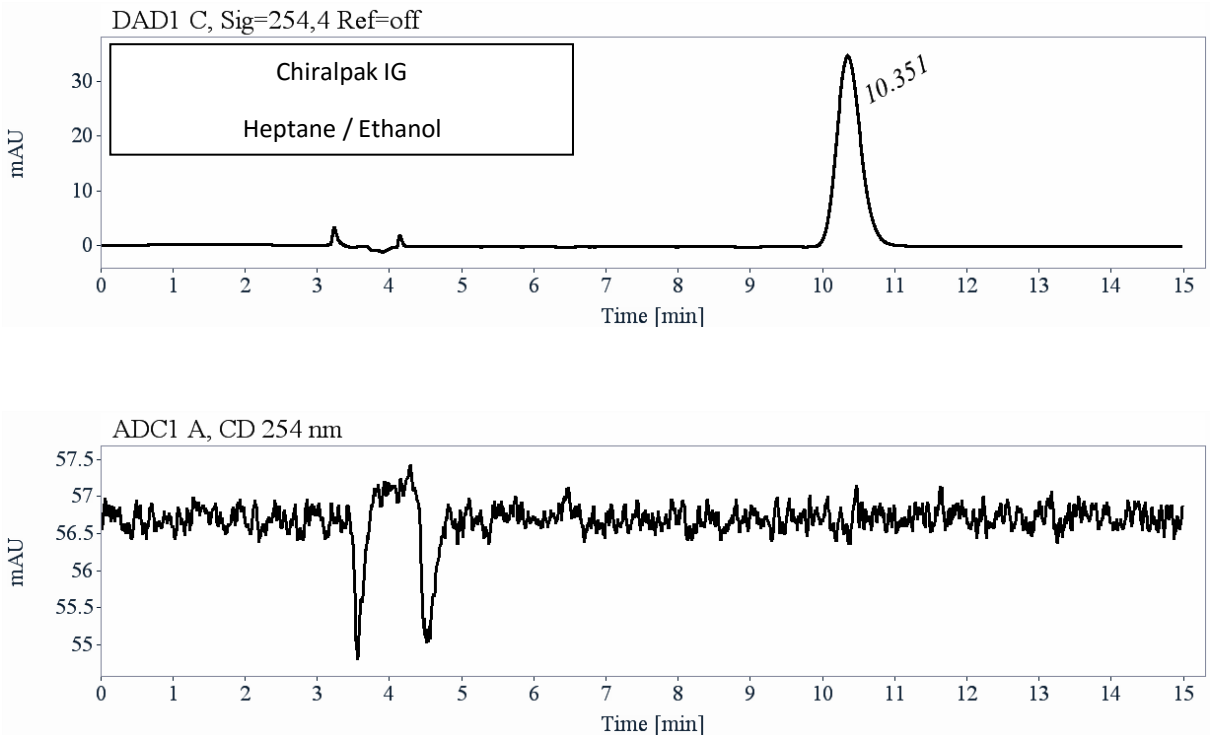


Fig. S10 Semi-preparative chiral HPLC separation for compound (*meso*)-**2**.

RT [min]	Area	Area%
10.35	820	100.00
Sum	820	100.00

Optical rotations

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp (589 nm), a halogen lamp (578 nm and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

λ (nm)	(*R*)-**2** first eluted on Chiralpak IG $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c =0.14)	(*S*)-**2** second eluted on Chiralpak IG $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c =0.14)
589	+ 202	- 202
578	+ 210	- 210
546	+ 240	- 240

Electronic Circular Dichroism

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted.

The baseline was always measured for the same solvent and in the same cell as the samples.

The spectra are presented without smoothing and further data processing.

(*R*)-**2**, first eluted on Chiralpak IG: green solid line, concentration =0.646 mmol.L^{-1} in Dichloromethane.

(*S*)-**2**, second eluted on Chiralpak IG: red dotted line, concentration = 0.644 mmol.L^{-1} in Dichloromethane.

Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 1 nm, and 3 accumulations per sample.

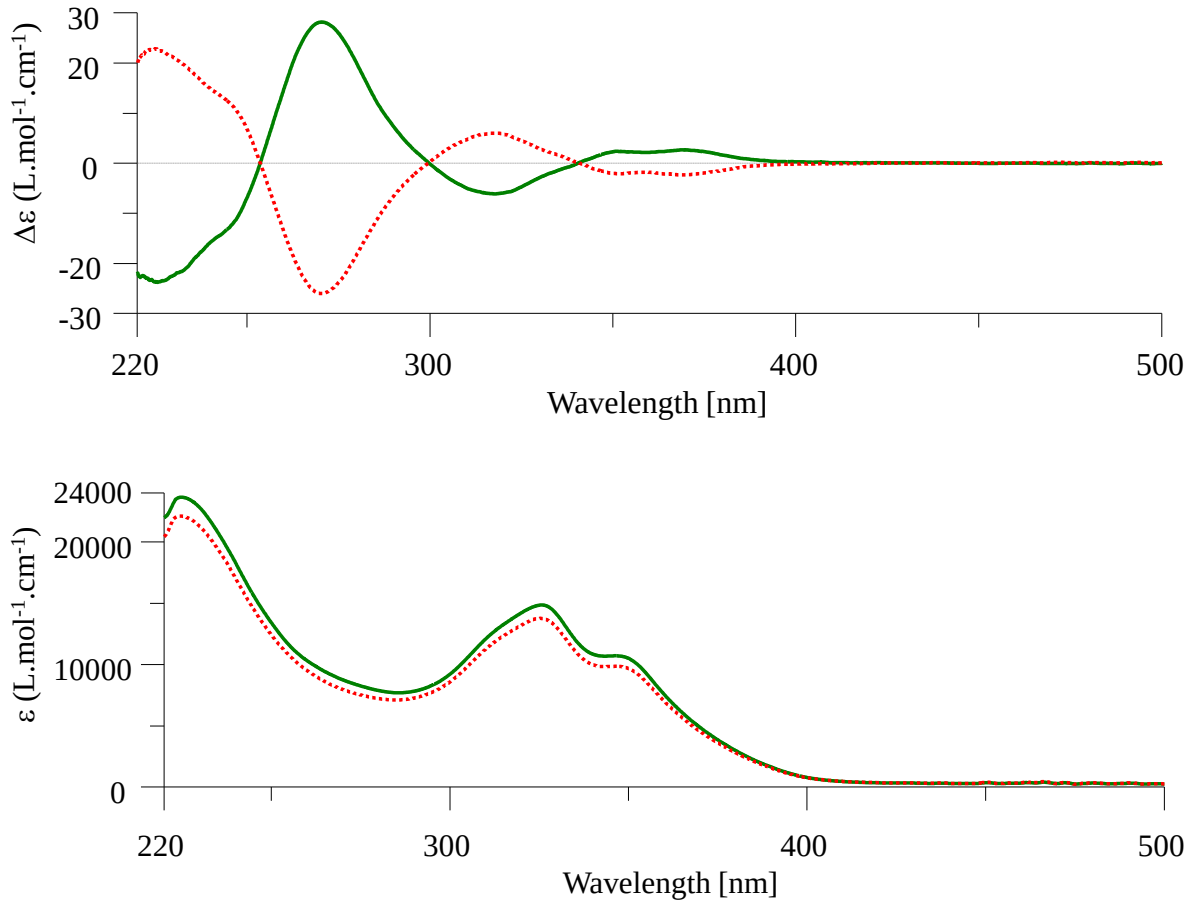


Fig. S11 CD (top) and UV-Vis (bottom) spectra of (*R*)-**2** (green line) and (*S*)-**2** (red dotted line).

X-ray structure determinations

Table S1 Crystallographic data, details of data collection and structure refinement parameters for **1** and its derivatives.

	[(*rac*)-**1**]	[(*S*)-**1**]	[(*R*)-**1**]	[(*rac*)-**1**]PF_6	[(*S*)-**1**]PF_6	[(*R*)-**1**]$TCNQF_4$
formula	C24 H28 S12	C12 H14 S6	C12 H14 S6	C12 H14 F6 P S6	C12 H14 F6 P S6	C24 H14 F4 N4 S6
M [$gmol^{-1}$]	701.18	350.59	350.59	495.56	495.56	626.75
T [K]	297(1)	298(2)	150.01(10)	293(2)	293(2)	149.9(5)
crystal system	orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
space group	$Pna2_1$	$P2_1$	$P2_1$	$P\bar{1}$	$P1$	$P1$
a [Å]	31.2707(11)	6.1770(3)	6.1216(3)	8.0122(5)	8.1638(4)	7.6595(1)
b [Å]	9.2527(4)	10.9534(6)	10.8073(5)	15.3709(9)	15.558(3)	14.5463(2)
c [Å]	10.9540(4)	11.7837(8)	11.7028(6)	16.0099(10)	16.203(3)	22.7605(3)
α [°]	90	90	90	68.821(5)	68.670(10)	95.079(1)
β [°]	90	96.154(5)	95.501(4)	88.312(5)	88.608(8)	99.545(1)
γ [°]	90	90	90	86.553(5)	87.047(8)	90.995(1)
V [$Å^3$]	3169.4(2)	792.68(8)	770.67(7)	1835.1(2)	1914.4(5)	2489.66(6)
Z	4	2	2	4	4	4
ρ_{calcd}[g/cm^3]	1.469	1.469	1.511	1.794	1.719	1.672
μ [mm^{-1}]	7.802	7.798	8.021	8.234	0.848	5.570
Flack parameter	0.03(4)	-0.03(4)	-0.05(4)	-	0.05(4)	0.043(12)
goodness-of-fit on F^2	1.027	1.020	0.909	1.039	1.016	1.039
final R1/*w*R2 [I > 2σ(I)]	0.0441/ 0.1032	0.0357/0.0942	0.0362/0.0946	0.1273/0.3201	0.0491/0.102	0.0460/ 0.1242
R1/*w*R2 (all data)	0.0568/ 0.1136	0.0392/0.0973	0.0394/0.0982	0.1408/0.3345	0.0884/0.1157	0.0477/ 0.1285
CCDC numbers	2179911	2179912	2179913		2179914	2179915

Table S2 Crystallographic data, details of data collection and structure refinement parameters for **2** and its derivatives.

	[(*rac*)-**2**]	[(*S*)-**2**]	[(*R*)-**2**]	[(*meso*)-**2**]	[(*meso*)-**2**]$TCNQF_4$
formula	C18 H24 S8	C18 H24 S8	C18 H24 S8	C18 H24 S8	C15 H12 F2 N2 S4
M [$gmol^{-1}$]	496.85	496.85	496.85	496.85	386.51
T [K]	293(2)	293(2)	149.8(7)	293(2)	293(2)
crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	$P4_12_12$	$P2_1$	$P2_1$	$P2_1/c$	$P\bar{1}$
a [Å]	13.7056(2)	8.2148(4)	8.0812(2)	6.1944(3)	7.0619(6)
b [Å]	13.7056(2)	10.2029(4)	10.1708(2)	11.0828(5)	10.1071(10)
c [Å]	23.9209(5)	13.8985(8)	13.7159(3)	16.5640(9)	12.5228(11)
α [°]	90	90	90	90	93.828(8)
β [°]	90	93.622(5)	92.804(2)	92.272(4)	101.369(7)
γ [°]	90	90	90°	90	108.957(8)
V [$Å^3$]	4493.38(16)	1162.57(10)	1125.99(4)	1136.25(10)	820.47(14)
Z	8	2	2	4	2
ρ_{calcd}[g/cm^3]	1.469	1.419	1.465	1.452	1.564
μ [mm^{-1}]	7.370	7.121	7.352	7.286	5.504
Flack parameter	0.00(4)	-0.03(4)	-0.024(17)	-	-
goodness-of-fit on F^2	1.153	1.070	1.050	1.065	1.035
final R1/*w*R2 [I > 2σ(I)]	0.0486 / 0.1004	0.0441/0.1121	0.0300/0.0743	0.0693/ 0.1612	0.0678/ 0.1636
R1/*w*R2 (all data)	0.0579 / 0.1045	0.0555/0.1166	0.0316/0.0762	0.0786/ 0.1696	0.0912/ 0.1856
CCDC numbers	2179916	2179917	2179918	2179919	2179920

Crystal structures of neutral DE-EDT-TTF donors

(*R*)-1

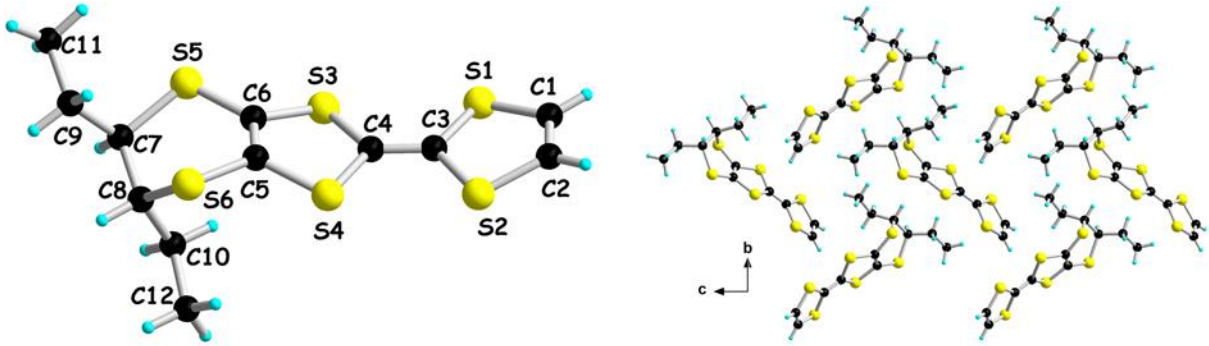


Fig. S12 Molecular structure of (*R*)-**1** together with the atom numbering scheme (left) and a packing diagram in the *bc* plane side view (right).

(*rac*)-1

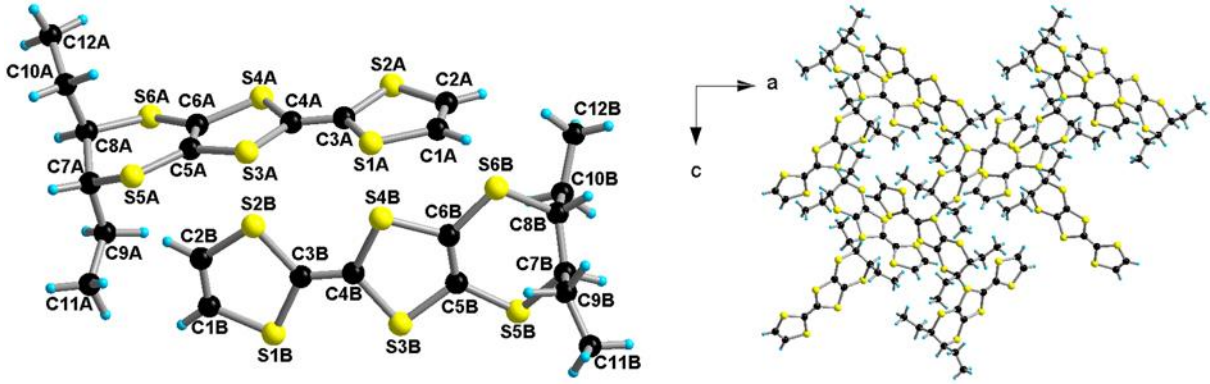


Fig. S13 Molecular structure of (*rac*)-**1** together with the atom numbering scheme; the two independent molecules shown have (*R*) configuration (left) and a packing diagram in the *ac* plane (right).

Table S3 Selected bond lengths for enantiopure and racemic **1**.

Bond lengths (Å)						
	(*rac*)-1		(*S*)-1		(*R*)-1	
A	**C3A—C4A**	1.334(8)	**C3—C4**	1.341(6)	**C3—C4**	1.339(7)
	S1A—C3A	1.758(6)	**S1—C3**	1.756(5)	**S1—C3**	1.751(6)
	S2A—C3A	1.752(6)	**S2—C3**	1.753(5)	**S2—C3**	1.763(6)
	S3A—C4A	1.749(6)	**S3—C4**	1.757(4)	**S3—C4**	1.762(5)
	S4A—C4A	1.751(6)	**S4—C4**	1.754(5)	**S4—C4**	1.761(5)
B	**C3B—C4B**	1.339(8)				
	S1B—C3B	1.744(7)				
	S2B—C3B	1.760(6)				
	S3B—C4B	1.752(6)				
	S4B—C4B	1.756(6)				

Crystal structures of neutral TE-BEDT-TTF donors

(*S*)-2

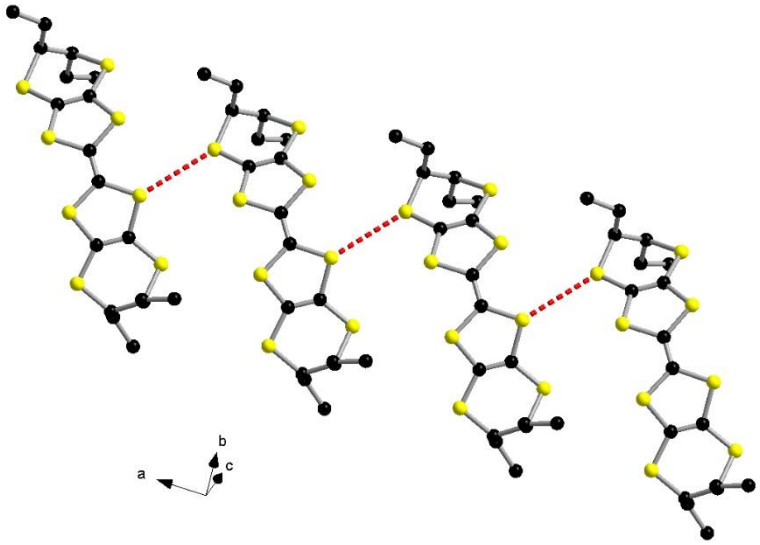


Fig. S14 Packing diagram of (*S*)-**2** showing the shortest S···S intermolecular distances (3.77 Å) highlighted as red dotted lines, along the *a* direction.

(*R*)-2

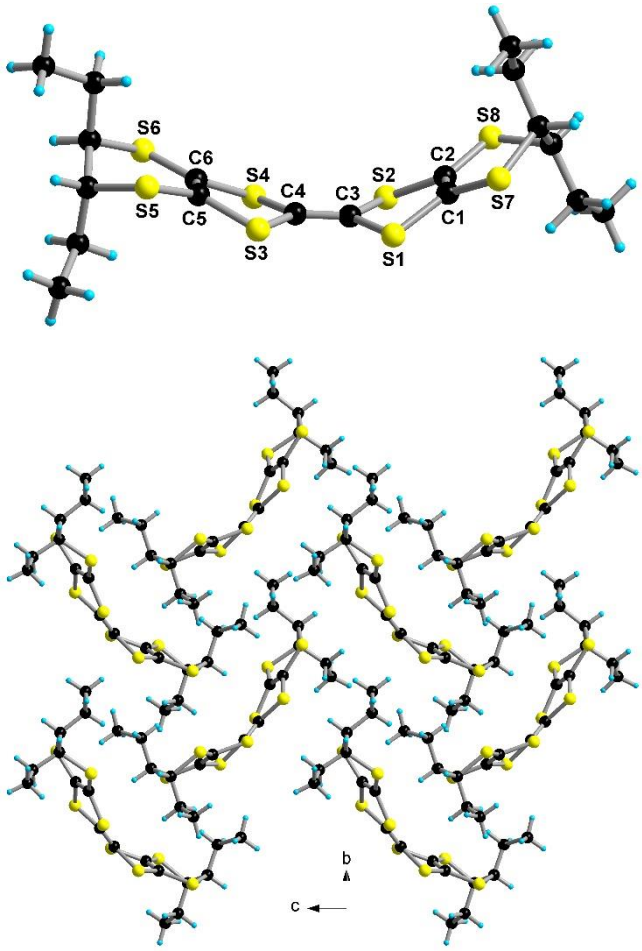


Fig. S15 Molecular structure of (*R*)-**2** together with the atom numbering scheme (top) and a packing diagram in the *bc* plane (right). The folding angles around the internal S···S hinges are 30.9° (S1···S2) and 23.6° (S3···S4).

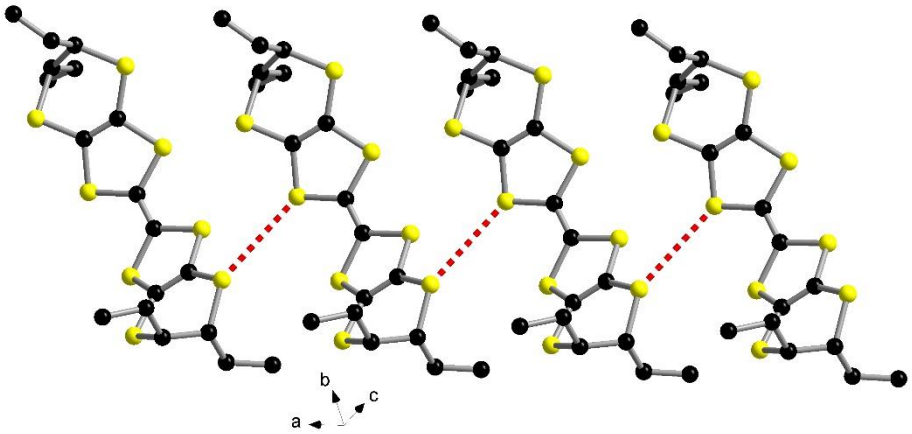


Fig. S16 Packing diagram of (*R*)-**2** showing the shortest S···S intermolecular distances (3.70 Å) highlighted as red dotted lines, along the *a* direction.

(*meso*)-2

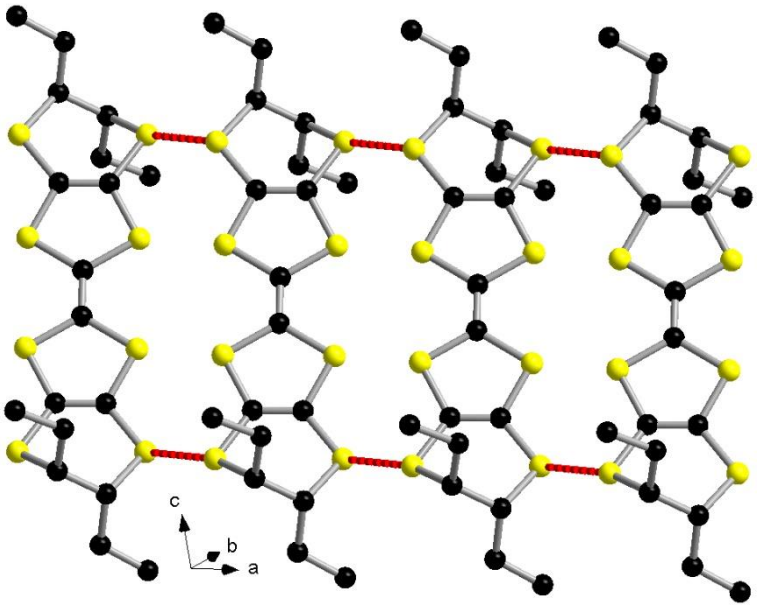


Fig. S17 Packing diagram of (*meso*)-**2** showing the shortest S···S intermolecular distances (3.84 Å) highlighted as red dotted lines, along the *a* direction.

Table S4 Selected bond lengths for racemic, enantiopure and meso **2**.

Bond lengths (Å)								
(*rac*)-2			(*R*)-2		(*S*)-2		(*meso*)-2	
A	C3A—C4A	1.358(10)	C3—C4	1.332(10)	C3—C4	1.338(5)	C3—C3	1.345(8)
	S1A—C3A	1.764(6)	S1—C3	1.755(8)	S1—C3	1.757(4)	S1—C3	1.760(4)
	S2A—C3A	1.757(6)	S2—C3	1.762(7)	S2—C3	1.758(4)	S2—C3	1.756(4)
B	C3B—C4B	1.358(10)	S3—C4	1.763(8)	S3—C4	1.755(4)		
	S1B—C3B	1.753(4)	S4—C4	1.762(8)	S4—C4	1.757(4)		
	S3B—C4B	1.752(4)						

Radical cation salts:

[(*S*)-1]PF_6

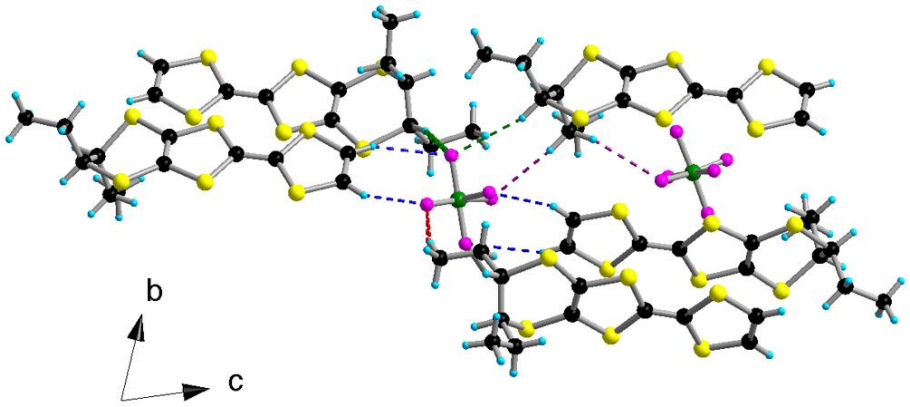


Fig. S18 Packing diagram of [(*S*)-**1**]PF_6 in the *bc* plane, with an emphasis on the C–H···F short contacts: blue dotted lines for CH vinyl (2.47-2.54-2.80-2.87 Å), red dotted lines for Me (2.44-2.87 Å), green dotted lines for H_{CH} (2.48−2.85 Å) and violet dotted lines for CH_2 (2.67-2.81 Å).

Table S5 Selected bond lengths for [(*S*)-**1**]PF_6.

Bond lengths (Å)					
A	C3A—C4A	1.394(12)	C	C3C—C4C	1.392(11)
	S1A—C3A	1.713(9)		S1C—C3C	1.739(9)
	S2A—C3A	1.729(8)		S2C—C3C	1.729(9)
	S3A—C4A	1.736(9)		S3C—C4C	1.715(9)
	S4A—C4A	1.712(10)		S4C—C4C	1.717(9)
B	C3B—C4B	1.411(12)	D	C3D—C4D	1.406(11)
	S1B—C3B	1.710(9)		S1D—C3D	1.711(8)
	S2B—C3B	1.727(9)		S2D—C3D	1.717(9)
	S3B—C4B	1.723(9)		S3D—C4D	1.719(8)
	S4B—C4B	1.711(9)		S4D—C4D	1.714(9)

Charge transfer complexes:

[(*R*)-**1**]$TCNQF_4$:

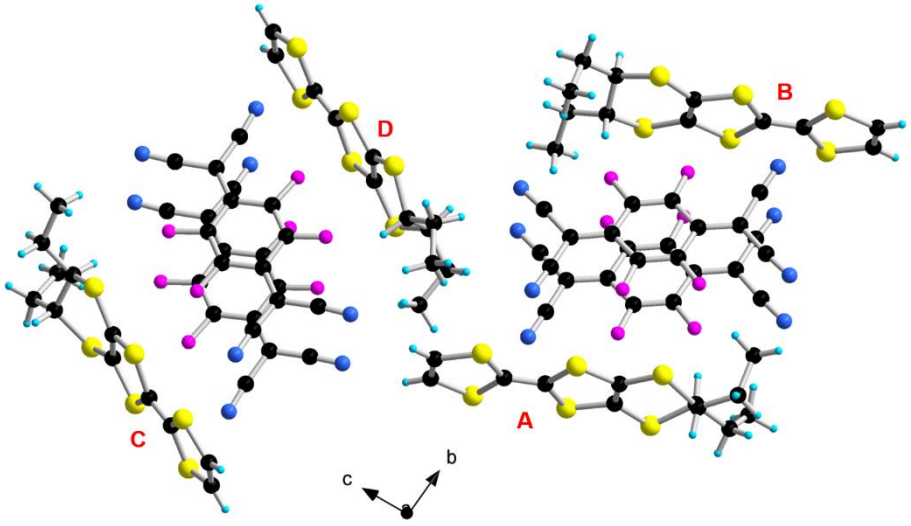


Fig. S19 Four independent donors and acceptors in the asymmetric unit of [(*R*)-**1**]$TCNQF_4$.

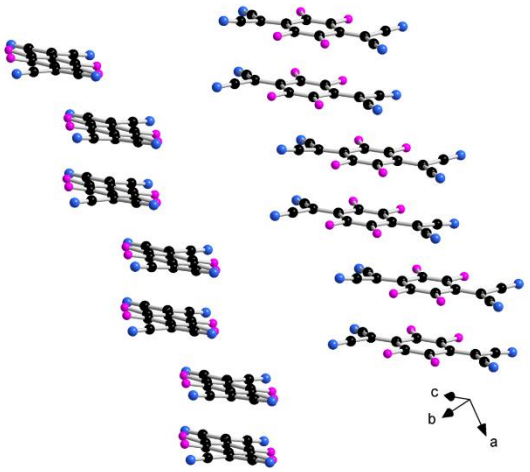


Fig. S20 Packing of $TCNQF_4$ in the structure of [(*R*)-**1**]$TCNQF_4$, showing the lateral and longitudinal shifts between the dimeric units.

Table S6 Selected C=C and C–S internal bond distances for [(*R*)-**1**]$TCNQF_4$.

[(*R*)-1]$TCNQF_4$					
A	C3A—C4A	1.404(7)	C	C3C—C4C	1.392(7)
	S1A—C3A	1.722(6)		S1C—C3C	1.716(5)
	S2A—C3A	1.705(6)		S2C—C3C	1.717(5)
	S3A—C4A	1.709(5)		S3C—C4C	1.721(5)

	S4A—C4A	1.709(5)		**S4C—C4C**	1.727(5)
B	**C3B—C4B**	1.394(7)	**D**	**C3D—C4D**	1.387(7)
	S1B—C3B	1.720(5)		**S1D—C3D**	1.726(5)
	S2B—C3B	1.716(6)		**S2D—C3D**	1.713(5)
	S3B—C4B	1.715(6)		**S3D—C4D**	1.719(5)
	S4B—C4B	1.720(6)		**S4D—C4D**	1.719(5)

[(*meso*)-**2**]TCNQF$_4$

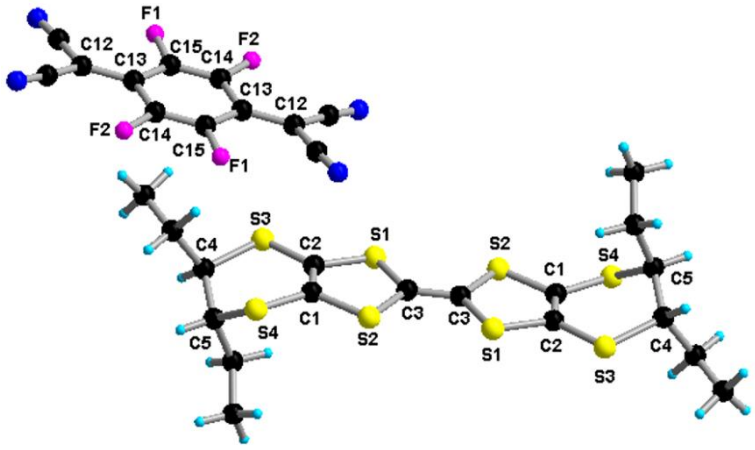


Fig. S21 Molecular structure of [(*meso*)-**2**]TCNQF$_4$ along with a partial atom numbering scheme.

Table S7 C=C and C–S internal bond distances for [(*meso*)-**2**]TCNQF$_4$.

Bond length(Å)	
C3—C3*	1.388(10)
S1—C3	1.729(5)
S2—C3	1.715(5)