Supporting information for

Chiral EDT-TTF precursors with one stereogenic centre: substituent size modulation of the conducting properties in the (R-EDT-TTF)$_2$PF$_6$ (R = Me or Et) series

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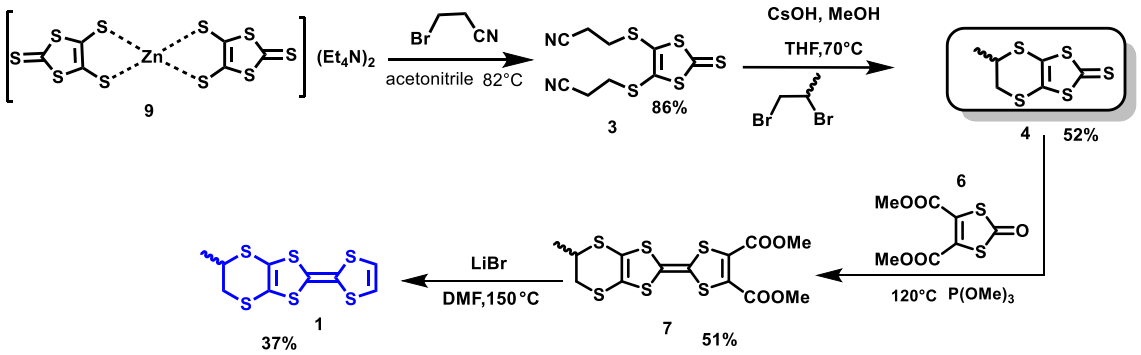
Experimental section

General comments. 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 1H and 75 MHz for 13C. 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 Bruker Biflex-IIITM apparatus, equipped with a 337nm N_2 laser. Elemental analysis were recorded using Flash 2000 Fisher Scientific Thermo Electron analyzer.

Synthesis of (*rac*)-1

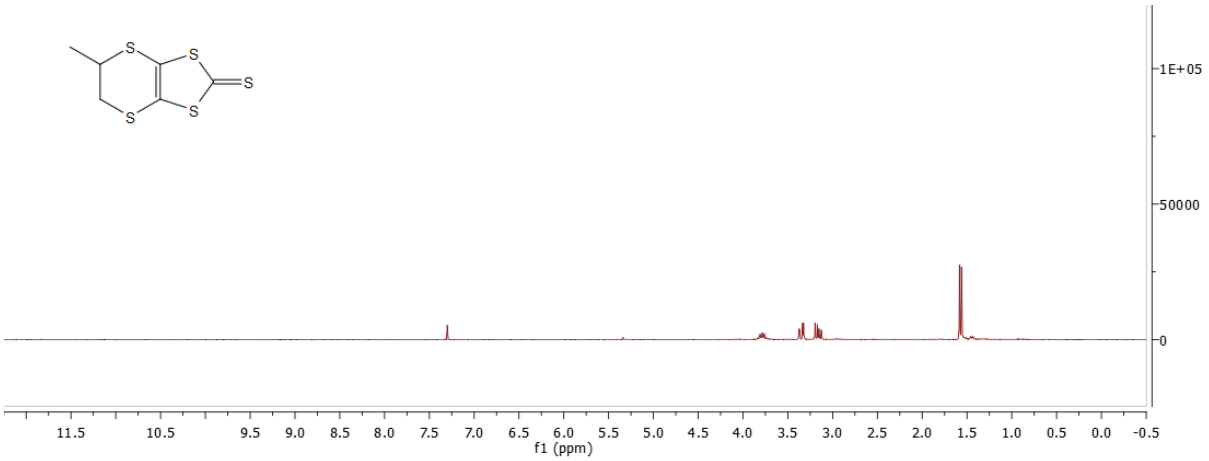


4,5-bis((2-isocyanoethyl)thio)-1,3-dithiole-2-thione (3): A mixture of compound **9** (20 g, 27.8 mmol) and bromopropionitrile (7.45 g, 55.7 mmol) was dissolved in acetonitrile (400 mL). The resulting bright red solution was heated under reflux for 1 night. After cooling to room temperature, the solvent was removed under vacuum and then the solid residue was dissolved in DCM, followed by filtration. The filtrate was washed with water and the combined organic phase was concentrated and the residue purified by recrystallization (toluene/petroleum ether) to give compound **3** as a yellow solid (14.6 g, 85%).^{1}H NMR (300 MHz, $CDCl_3$) δ ppm: 3.17 (t, J = 8.0 Hz, 4H, -CH_2CN), 2.83 (t, J = 8.0 Hz, 4H, -SCH_2-); ^{13}C NMR (76 MHz, $CDCl_3$) δ ppm: 211.9 (-C=S), 137.8 (-C=C-), 117.4 (-CN), 31.8 (CH_2-CH_2), 29.5 (CH_2-CH_2). MS (EI, m/z) = 304.1 (M+).

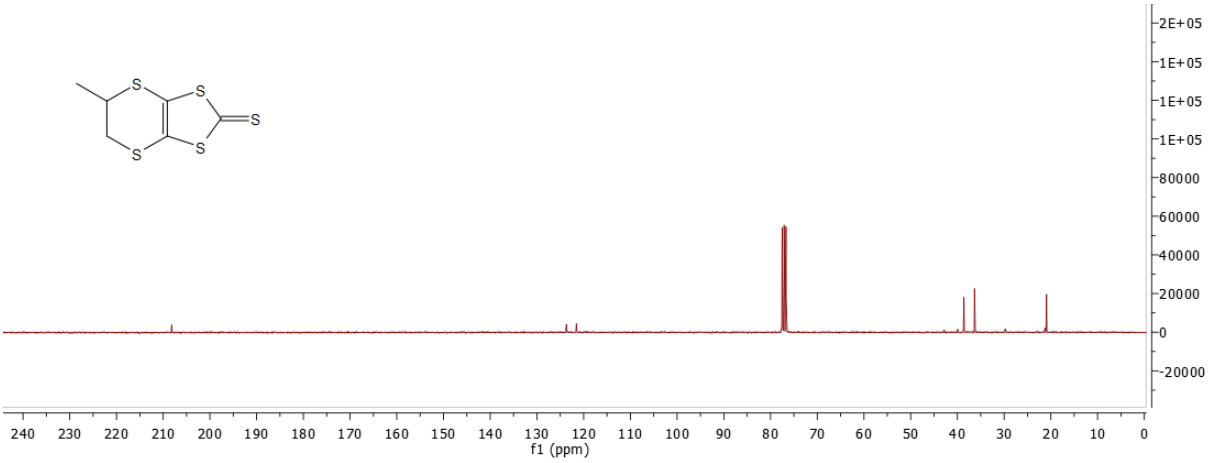
Reference: N. Svenstrup and J. Becher, *Synthesis*, 1995, 215–235.

(*rac*)-4

^{1}H NMR

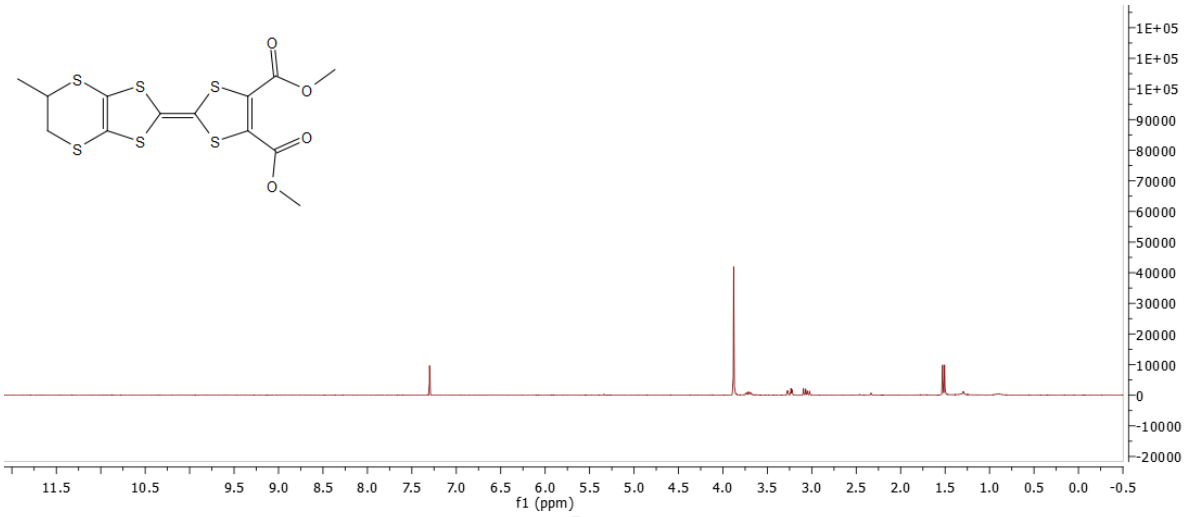


^{13}C NMR

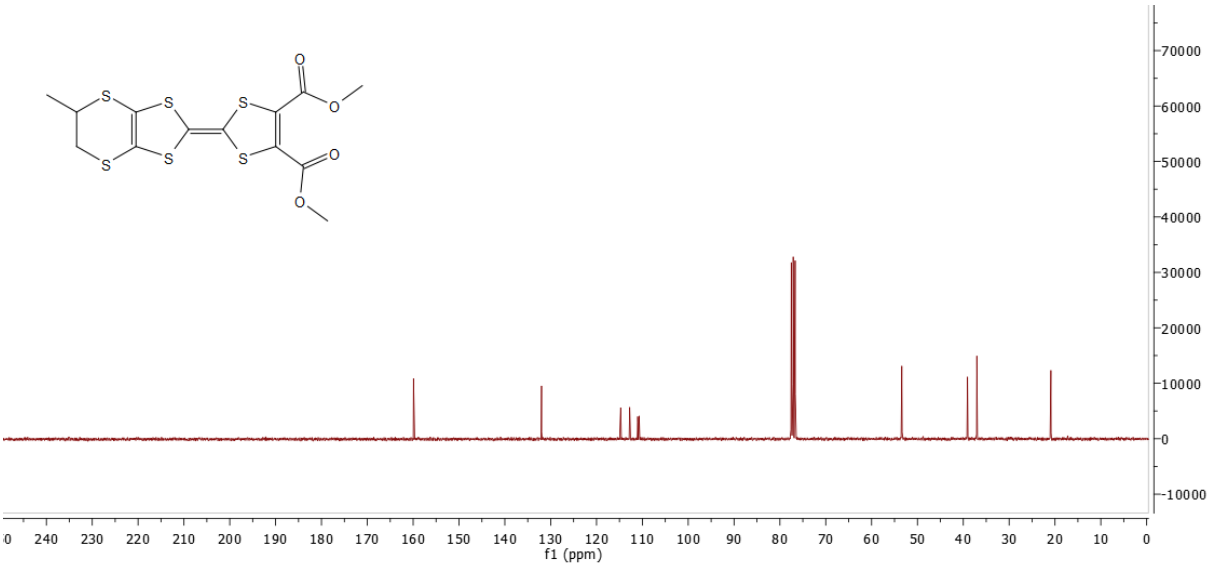


(*rac*)-7

^{1}H NMR

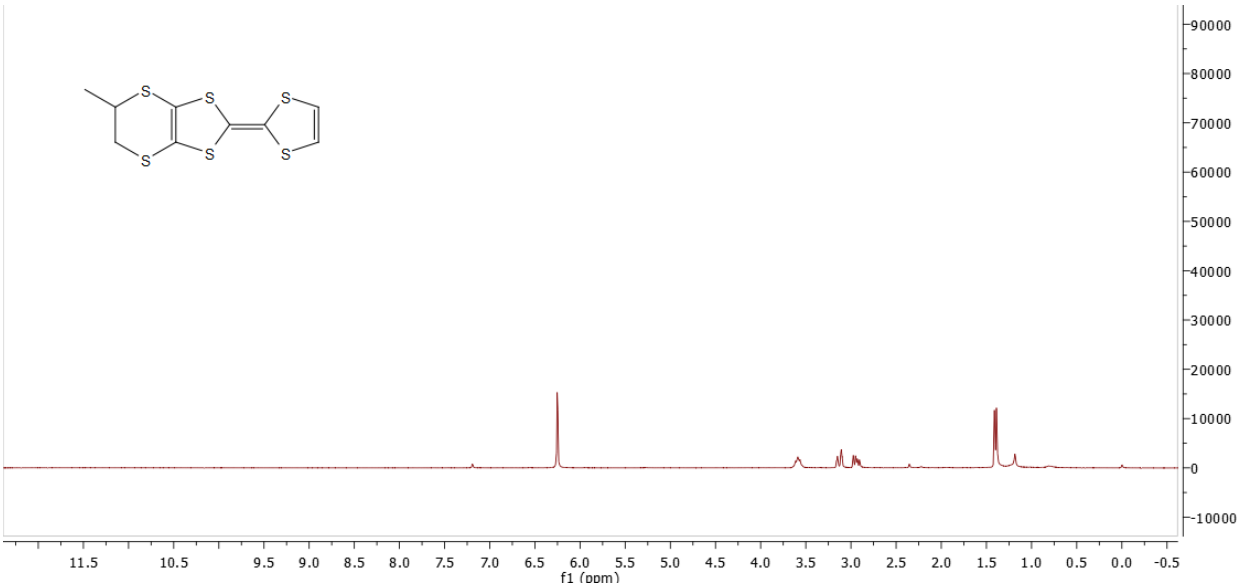


^{13}C NMR

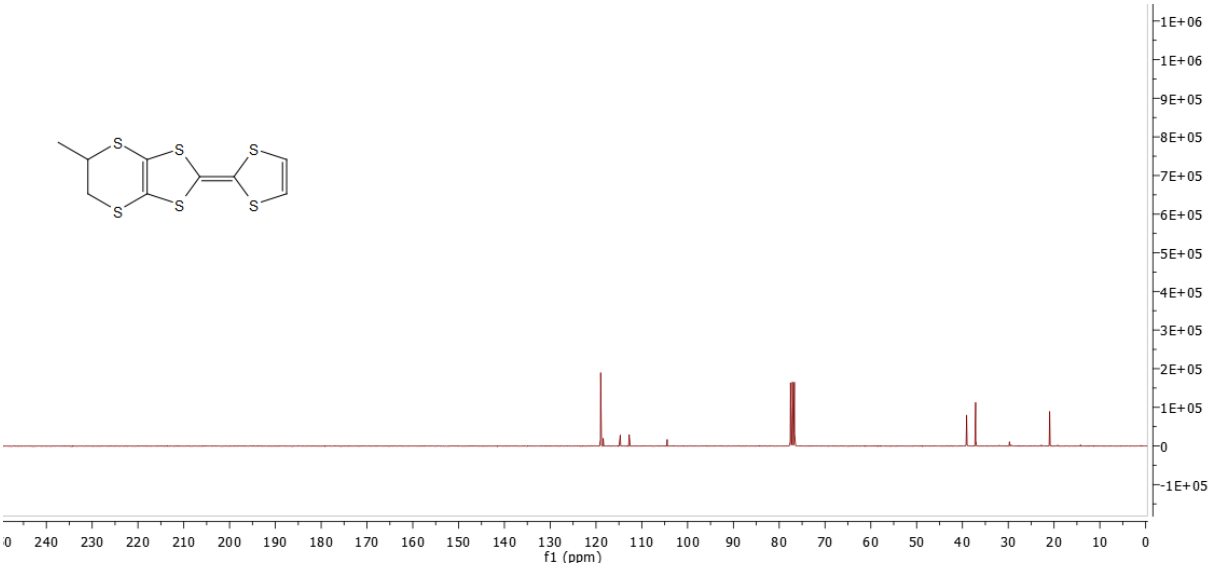


(*rac*)-1

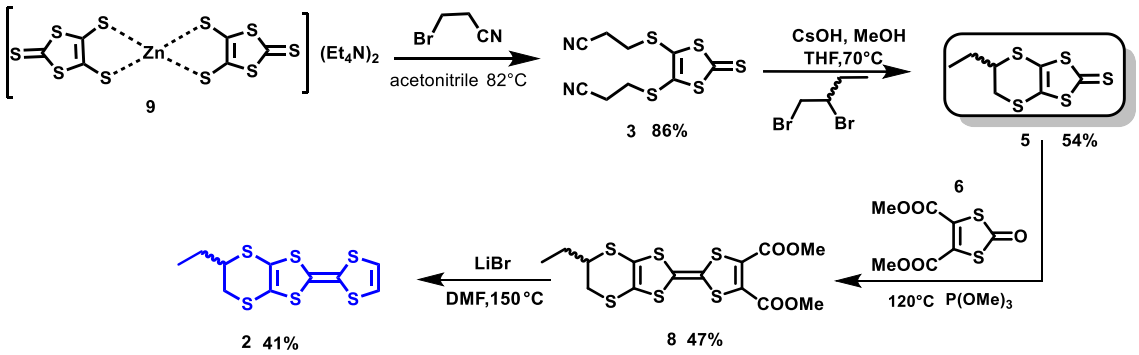
^{1}H NMR



^{13}C NMR

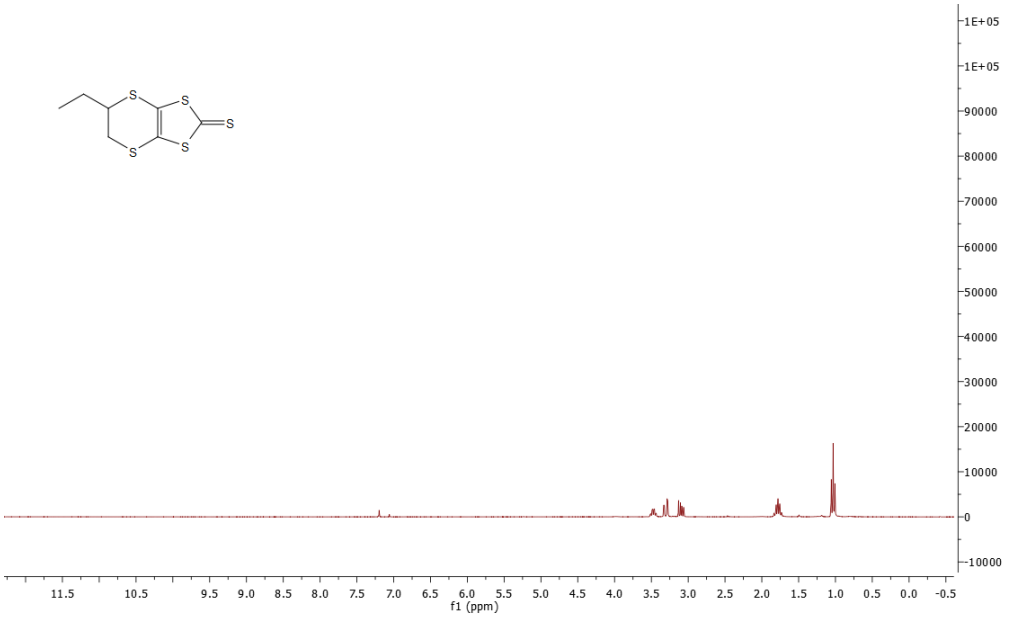


Synthesis of (*rac*)-2

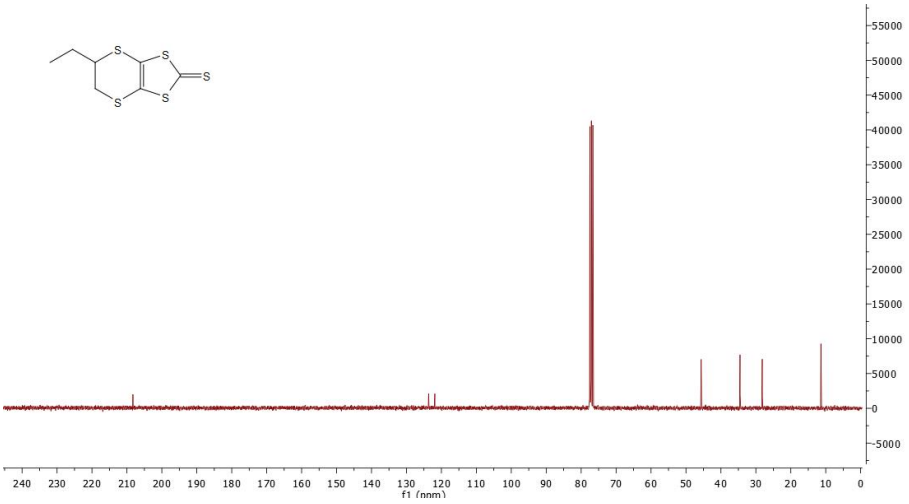


(*rac*)-5

^{1}H NMR

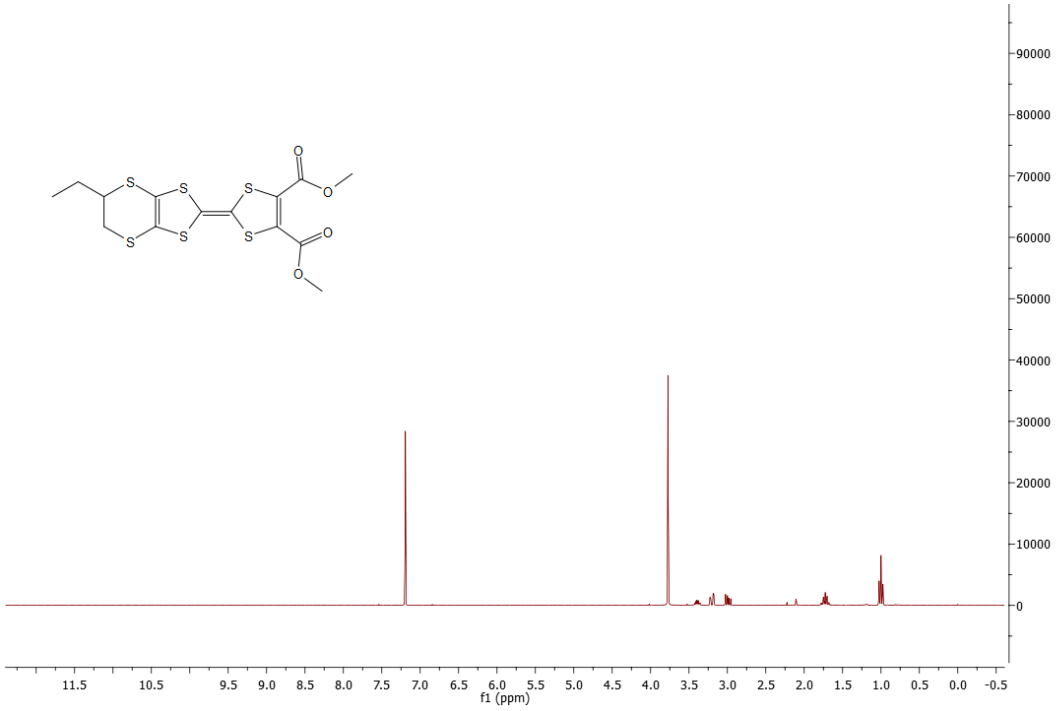


^{13}C NMR

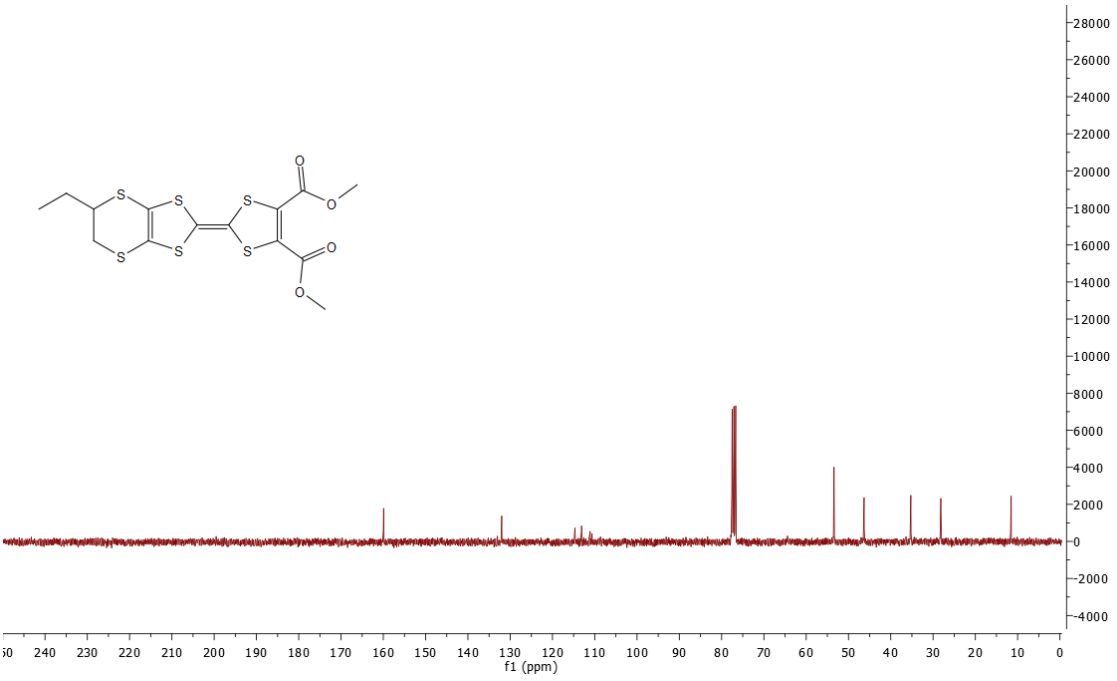


(*rac*)-8

^{1}H NMR

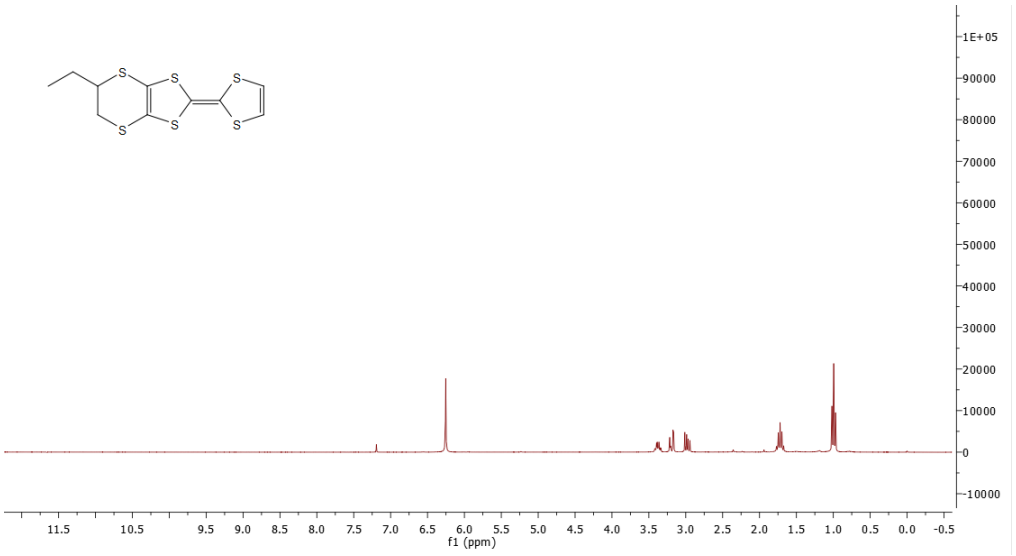


^{13}C NMR

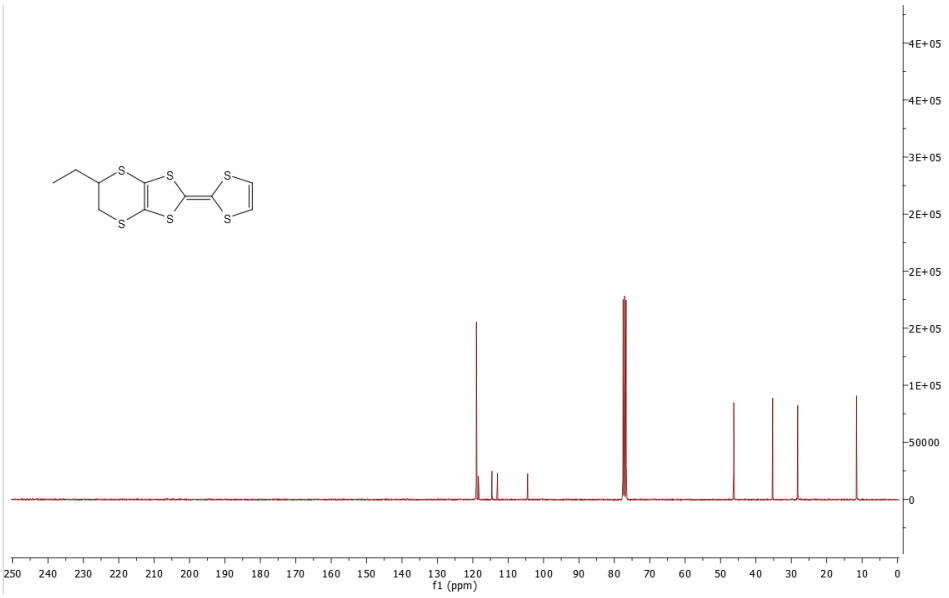


(*rac*)-2

^{1}H NMR



^{13}C NMR



Cyclic voltammetry

Cyclic voltammetry measurements were carried out with a Biologic SP-150 potentiostat in a glove box containing dry, oxygen-free (<1 ppm) argon at 293 K, by using a three-electrode cell equipped with a platinum millielectrode of 0.126 cm^2 area, an Ag/Ag+ pseudo-reference electrode and a platinum wire counter electrode. The potential values were then re-adjusted with respect to the saturated calomel electrode (SCE). The electrolytic media involved a 0.1 mol/L solution of (*n*-Bu_4N)PF_6 in acetonitrile. All experiments were performed at room temperature at 0.1 V/s.

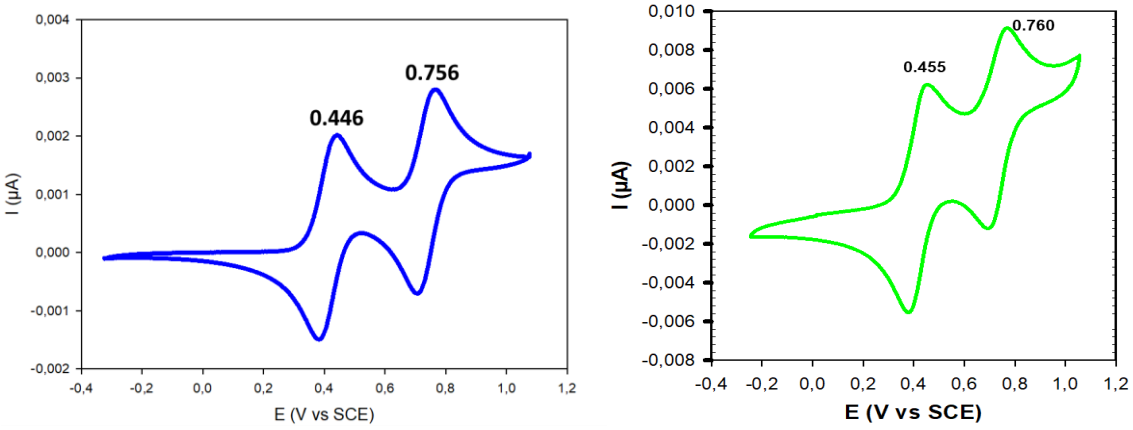
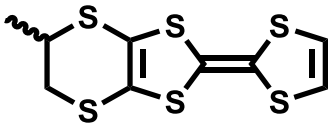


Fig. S1 Cyclic voltammograms of **1** (left) and **2** (right).

Chiral HPLC

Analytical chiral HPLC 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
Lux-Cellulose-3	Heptane / Ethanol (50/50)	18.15 (+)	5.15	20.90 (-)	6.09	1.18	4.73

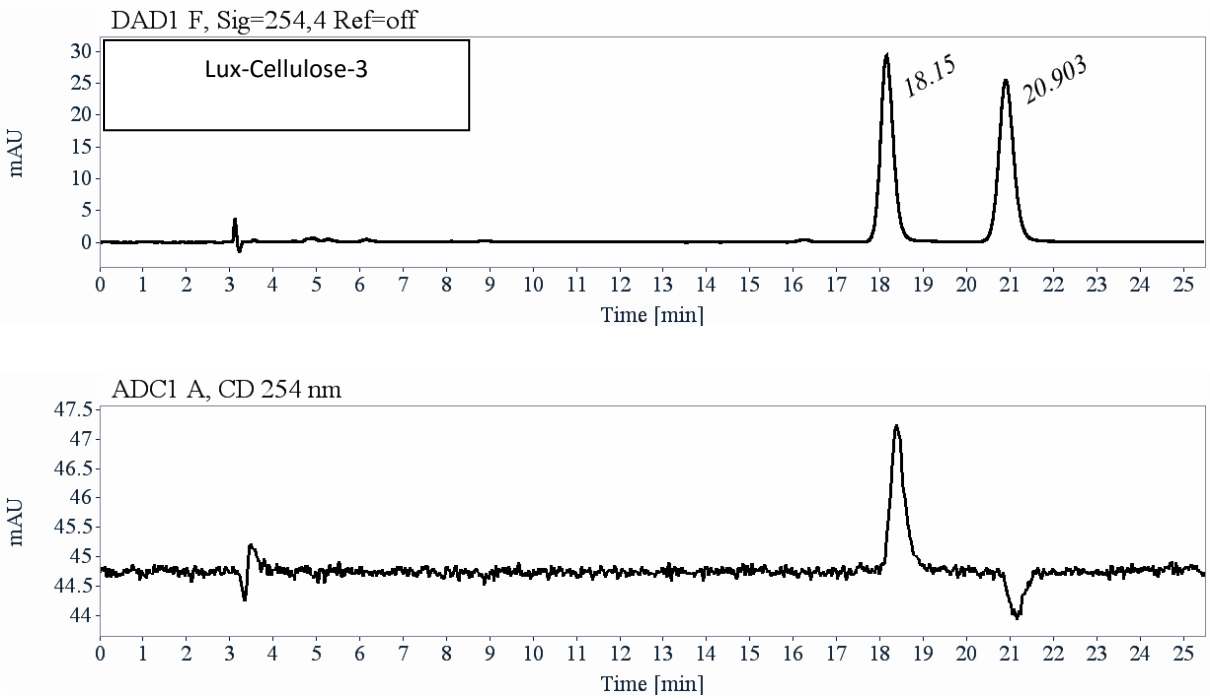


Fig. S2 Analytical chiral HPLC separation for compound (*rac*)-**1**.

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
18.15	618	49.87	5.15		
20.90	621	50.13	6.09	1.18	4.73
Sum	1239	100.00			

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

• Sample preparation: About 325 mg of compound (*rac*)-**1** are dissolved in 110 mL of ethanol.

• Chromatographic conditions: Chiralcel OJ-H (250 x 10 mm), hexane / ethanol (50/50) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 220 times 500 µL, every 5.6minutes.

• First fraction: 145 mg of the first eluted ((+, CD 254nm)-enantiomer) with ee > 99%

• Second fraction: 145 mg of the second eluted ((-, CD 254 nm)-enantiomer) with ee > 98%

• Chromatograms of the collected fractions:

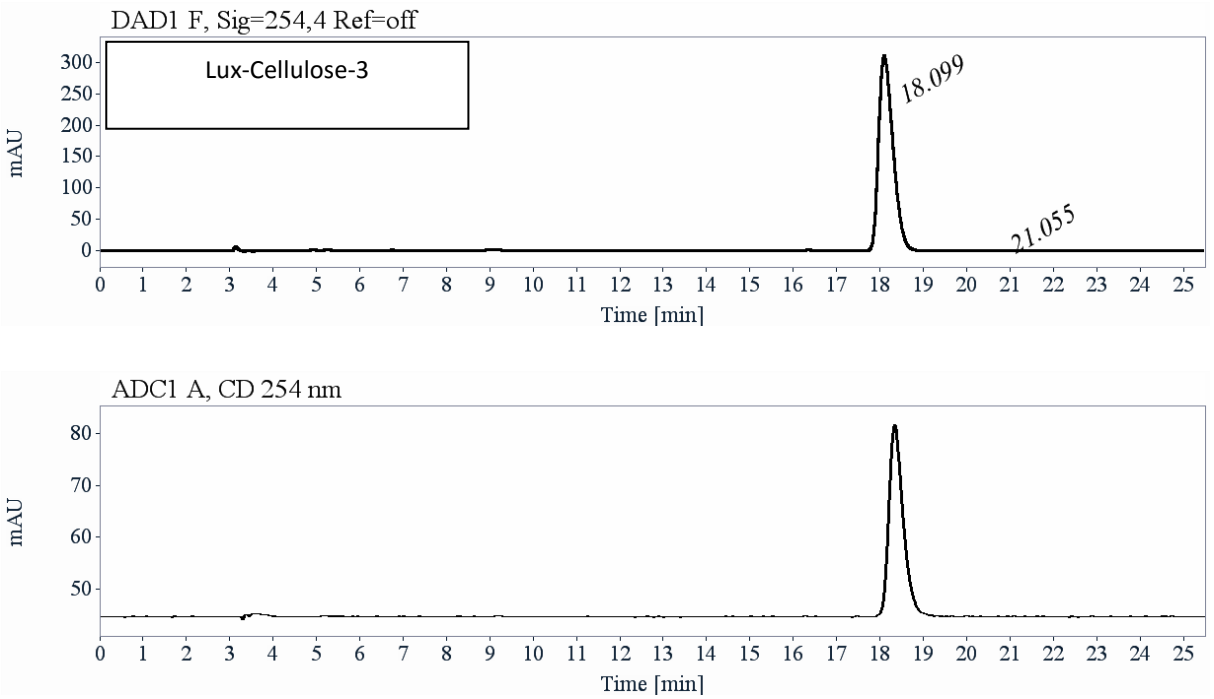


Fig. S3 Chiral HPLC separation for compound (*R*)-**1**.

RT [min]	Area	Area%
18.10	7206	99.73
21.06	19	0.27
Sum	7225	100.00

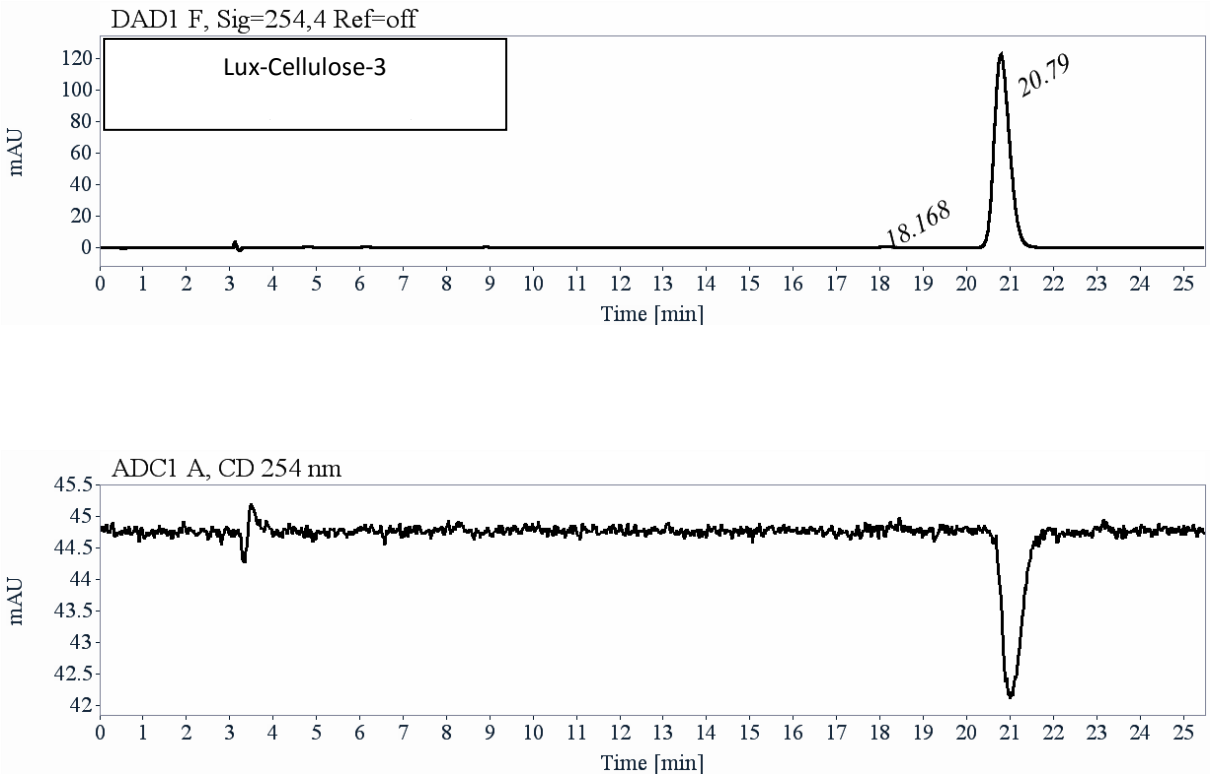


Fig. S4 Chiral HPLC separation for compound (*S*)-**1**.

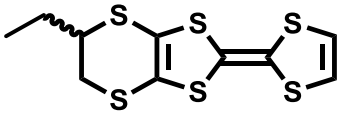
RT [min]	Area	Area%
18.17	23	0.76
20.79	3041	99.24
Sum	3064	100.00

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 Lux-Cellulose-3 $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c = 0.42)	(*S*)-**1** second eluted on Lux-Cellulose-3 $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c = 0.42)
589	+ 70	- 70
578	+ 73	- 72
546	+ 84	- 83

Analytical chiral HPLC separation for compound (*rac*)-**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
Lux-Cellulose-3	Heptane / Ethanol (50/50)	15.89 (+)	4.39	18.37 (-)	5.23	1.19	4.42

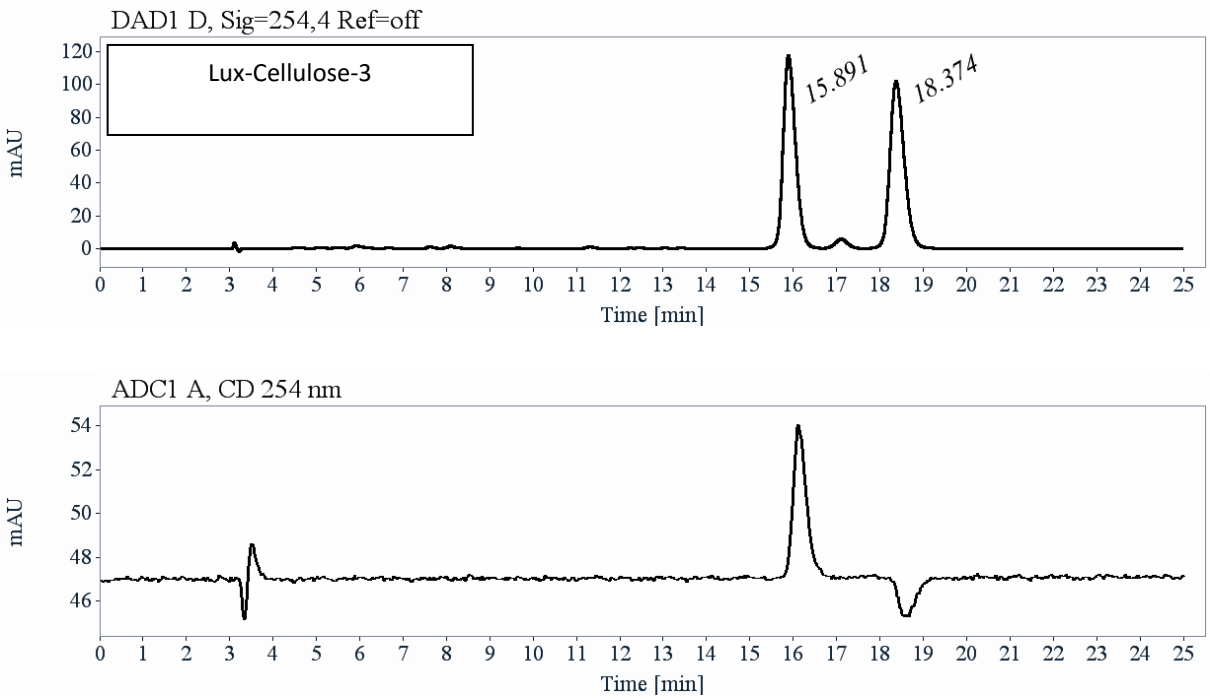


Fig. S5 Analytical chiral HPLC separation for compound (*rac*)-**2**.

RT [min]	Area	Area%	Capacity Factor	Enantioselectivity	Resolution (USP)
15.89	2332	49.90	4.39		
18.37	2341	50.10	5.23	1.19	4.42
Sum	4673	100.00			

Semi-preparative separation for compound (*rac*)-**2**:

• Sample preparation: About 183 mg of compound (*rac*)-**2** are dissolved in 450 mL of ethanol.

• Chromatographic conditions: Chiralcel OJ-H (250 x 10 mm), hexane / ethanol (50/50) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

• Injections (stacked): 140 times 3200 µL, every 6.8 minutes.

• First fraction: 80.2 mg of the first eluted ((+, CD 254nm)-enantiomer) with ee > 99%

• Second fraction: 81.2 mg of the second eluted ((-, CD 254 nm)-enantiomer) with ee > 99%

• Chromatograms of the collected fractions:

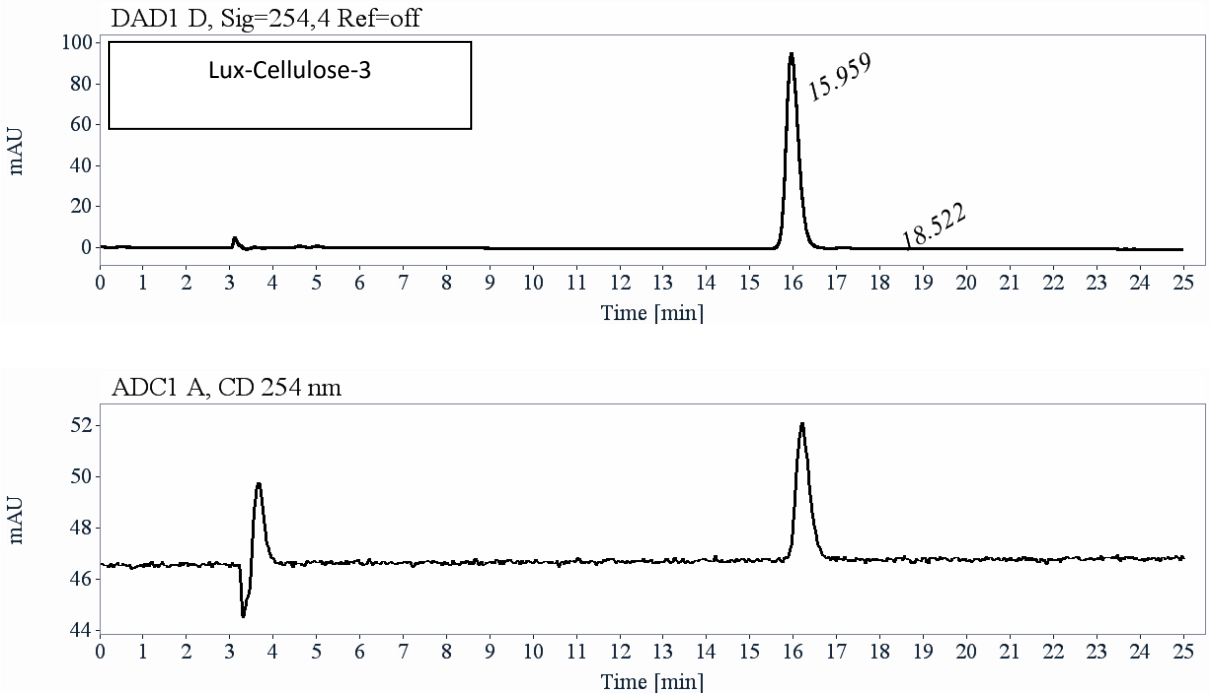


Fig. S6 Chiral HPLC separation for compound (*R*)-**2**.

RT [min]	Area	Area%
15.96	1899	99.67
18.52	6	0.33
Sum	1905	100.00

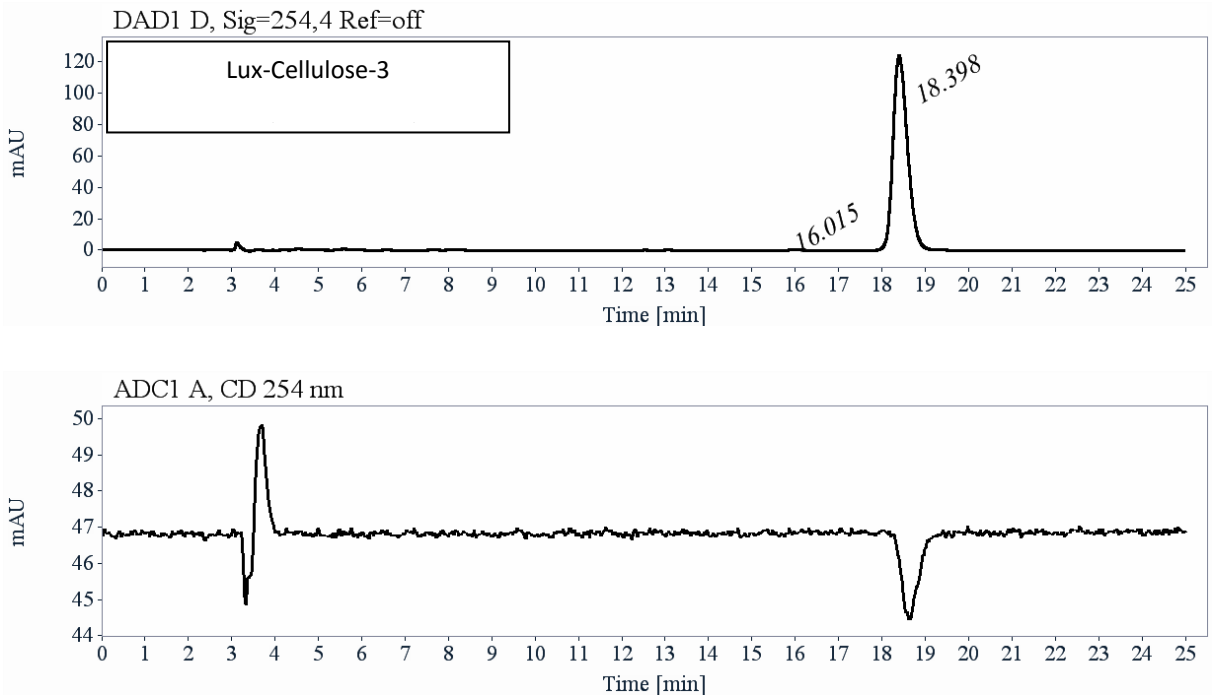


Fig. S7 Chiral HPLC separation for compound (*S*)-**2**.

RT [min]	Area	Area%
16.02	10	0.33
18.40	2900	99.67
Sum	2910	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), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

λ (nm)	(*R*)-**2** first eluted on Lux-Cellulose-3 $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c = 0.204)	(*S*)-**2** second eluted on Lux-Cellulose-3 $[\alpha]_\lambda^{25}$ (CH_2Cl_2, c = 0.076)
589	+ 88	- 88
578	+ 92	- 91

Electronic Circular Dichroism (ECD) and UV-Visible spectroscopy

ECD and UV-Vis 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.

Compound 1

(*R*)-**1**, first eluted on Lux-Cellulose-3: green solid line, concentration = 0.998 mmol.L^{-1} in acetonitrile.

(*S*)-**1**, second eluted on Lux-Cellulose-3: red dotted line, concentration = 0.994 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.

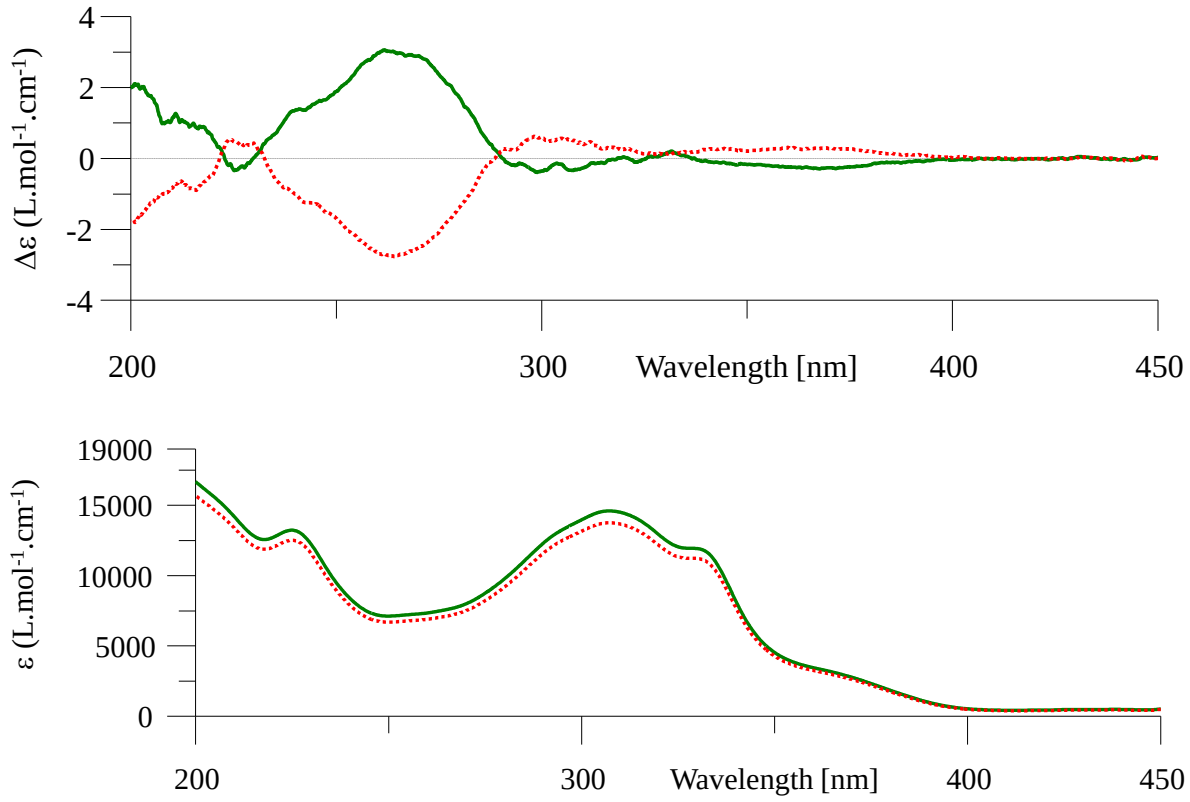


Fig. S8 CD (top) and UV-Vis (bottom) spectra of (*R*)-**1** (green line) and (*S*)-**1** (red dotted line).

Compound 2

(*R*)-**2**, first eluted on Lux-Cellulose-3: green solid line, concentration = 1.07 mmol.L^{-1} in acetonitrile.

(*S*)-**2**, second eluted on Lux-Cellulose-3: red dotted line, concentration = 1.07 mmol.L^{-1} in acetonitrile.

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

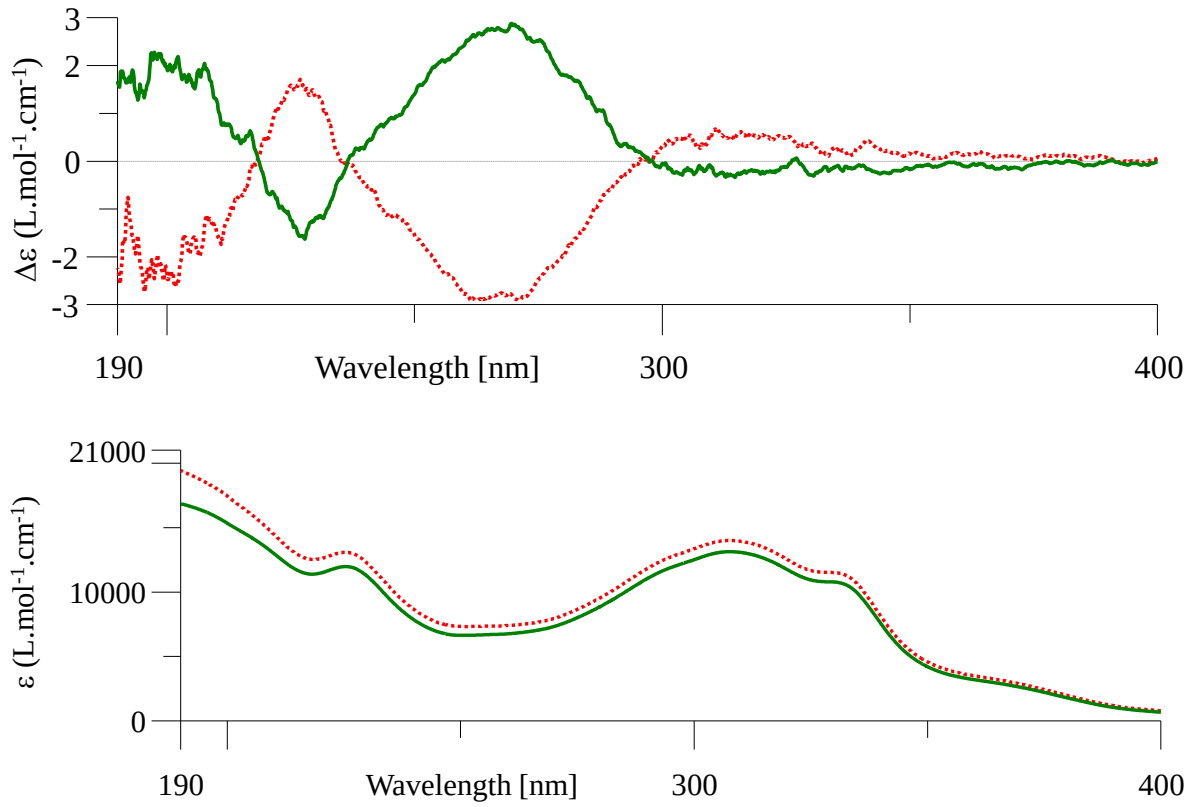


Fig. S9 CD (top) and UV-Vis (bottom) spectra of (*R*)-**2** (green line) and (*S*)-**2** (red dotted line).

X-Ray structure determinations

Details about data collection and solution refinement are given in Tables S1, S2 and S3. Single crystals of the compounds were mounted on glass fibre loops using a viscous hydrocarbon oil to coat the crystal and then transferred directly to cold nitrogen stream for data collection. Data collection were mostly performed at 150 K on an Agilent Supernova with CuKα (λ = 1.54184 Å). The structures were solved by direct methods with the SIR92 program and refined against all F_2 values with the SHELXL-97 program[1] using the WinGX graphical user interface.[2]

All non-H atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined.

Crystallographic data for the nine structures have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC 1937687 ((*rac*)-**2**), 1938735 ((*R*)-**2**), 1937689 ((*S*)-**2**), 1938736 ([(*rac*)-**1**]$_2$PF$_6$), 1937685 ([(*R*)-**1**]$_2$PF$_6$), 1937688 ([(*S*)-**1**]$_2$PF$_6$), 1938737 ([(*rac*)-**2**]PF$_6$), 1937686 ([(*R*)-**2**]$_2$PF$_6$), 1937690 ([(*S*)-**2**]$_2$PF$_6$). These data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

[1] G. M. Sheldrick, *Programs for the Refinement of Crystal Structures,* ed. **1996**

[2] L. Farrugia, *Journal of applied crystallography* **1999**, *32*, 837.

Table S1. Crystal Data and Structure Refinement for (*rac*)-**2**, (*R*)-**2** and (*S*)-**2**.

Compound	(*rac*)-**2**	(*R*)-**2**	(*S*)-**2**
empirical formula	$C_{10}H_{10}S_6$	$C_{10}H_{10}S_6$	$C_{10}H_{10}S_6$
fw	322.54	322.54	322.54
T (K)	150.01(10)	153.26(10)	150.00(10)
wavelength (Å)	1.54184 Å	1.54184 Å	1.54184 Å
cryst syst	Orthorhombic	Orthorhombic	Orthorhombic
space group	*P*bca	$P2_12_12_1$	$P2_12_12_1$
a (Å)	11.3175(5)	8.2254(2)	8.2240(2)
b (Å)	14.3860(7)	12.4077(2)	12.4006(3)
c (Å)	16.3317(9)	13.2789(3)	13.2720(3)
α(deg)	90.00	90.00	90.00
β(deg)	90.00	90.00	90.00
γ(deg)	90.00	90.00	90.00
V (Å^3)	2658.8(2)	1355.22(5)	1353.50(6)
Z	8	4	4
D_c (g cm^{-3})	1.612	1.581	1.581
abs coeff (mm^{-1})	9.245	9.069	9.080
cryst size (mm^3)	0.3× 0.2 × 0.1	0.6 × 0.3 × 0.2	0.3 × 0.2 × 0.2
Flack parameter	-	-0.05(2)	-0.008(16)
GOF on F^2	1.100	1.092	1.021
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0568, wR_2 = 0.1634	R_1 = 0.0230, wR_2 = 0.0596	R1 = 0.0223, wR2 = 0.0553
R indices (all data)	R_1 = 0.0657, wR_2 = 0.1740	R_1 = 0.0243, wR_2 = 0.0628	R1 = 0.0238, wR2 = 0.0562

[a] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w(F_o^2) = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

Table S2. Crystal Data and Structure Refinement for [(*R*)-**1**]$_2$PF$_6$, [(*S*)-**1**]$_2$PF$_6$ and [(*rac*)-**1**]$_2$PF$_6$.

Compound	[(*R*)-**1**]$_2$PF$_6$	[(*S*)-**1**]$_2$PF$_6$	[(*rac*)-**1**]$_2$PF$_6$
empirical formula	C18 H16 F6 P S12	C18 H16 F6 P S12	C18 H16 F6 P S12
fw	762.00	762.00	762.00
T (K)	150(10)	292.88(10)	150(2)
wavelength (Å)	1.54184	1.54184	1.54184
cryst syst	triclinic	triclinic	triclinic
space group	P1	P1	P-1
a (Å)	6.6874(3)	6.7396(3)	6.7028(4)
b (Å)	8.4353(3)	8.5079(3)	8.3786(6)
c (Å)	13.3471(7)	13.4369(6)	13.3275(15)
α(deg)	86.724(4)	93.626(3)	93.076(7)
β(deg)	89.892(4)	90.268(4)	90.018(8)
γ(deg)	66.719(4)	113.096(4)	113.210(6)
V (Å^3)	690.30(5)	706.93(5)	686.72(10)
Z	1	1	1
D_c (g cm^{-3})	1.833	1.790	1.843
abs coeff (mm^{-1})	9.871	9.638	9.922
cryst size (mm^3)	0.25× 0.25 × 0.1	0.25× 0.25 × 0.1	0.25× 0.25 × 0.1
Flack parameter	0.03(3)	0.17(5)	-
GOF on F^2	1.027	1.099	1.077
final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0335, wR_2 = 0.0917	R1 = 0.0519, wR2 = 0.1332	R_1 = 0.0507, wR_2 = 0.1368
R indices (all data)	R_1 = 0.0341, wR_2 = 0.0933	R1 = 0.0538, wR2 = 0.1360	R_1 = 0.0589, wR_2 = 0.1418

Table S3. Crystal Data and Structure Refinement for [(*R*)-**2**]$_2$PF$_6$, [(*S*)-**2**]$_2$PF$_6$ and [(*rac*)-**2**]PF$_6$•(C_4H_8O).

	[(*R*)-**2**]$_2$PF$_6$	[(*S*)-**2**]$_2$PF$_6$	[(*rac*)-**2**]PF$_6$•(C_4H_8O)
formula	C20 H20 F6 P S12	C20 H20 F6 P S12	C14 H18 F6 P S6 O
M [gmol^{-1}]	736.13(7)	736.13(7)	539.61
T [K]	150.01(10)	150.01(10)	294.54(10) K
wavelength (Å)	1.54184 Å	1.54184	1.54184 Å
crystal system	triclinic	triclinic	triclinic
space group	P1	P1	P-1
a [Å]	6.6481(3) Å	6.6574(8)	8.1196(4)
b [Å]	8.7844(5) Å	8.7901(11)	10.5643(5)
c [Å]	13.9788(5)	13.9791(11)	13.0740(7)
α [°]	103.905(4)°	104.001(9)	98.689(4)
β [°]	93.412(4)°	93.385(8)	99.065(4)
γ [°]	109.901(5)°	110.082(12)	101.231(4)
V [Å^3]	736.13(7)	736.36(14)	1066.95(9)
Z	1	1	2
D_c (g cm^{-3})	1.782	1.782	1.680
abs coeff (mm^{-1})	9.281	9.278	7.172
cryst size	0.5× 0.2 × 0.1	0.3× 0.2 × 0.1	0.3× 0.2 × 0.1
Flack parameter	0.01(3)	0.00(6)	-
goodness-of-fit on F^2	1.050	1.163	1.067
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0468, wR_2 = 0.1161	R1 = 0.0565, wR2 = 0.1619	R_1 = 0.0619, wR_2 = 0.1732
R indices (all data)	R_1 = 0.0511, wR_2 = 0.1218	R1 = 0.0676, wR2 = 0.1977	R_1 = 0.0735, wR_2 = 0.1924

Compound (*R*)-**2**

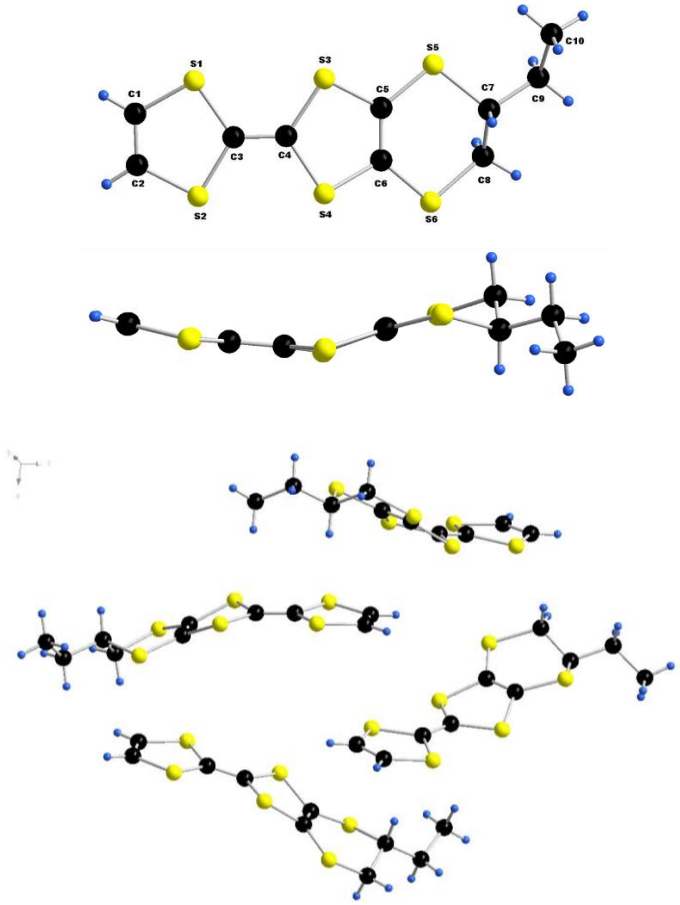


Fig. S10 Molecular structure of (*R*)-**2** together with the atom numbering scheme (top), a side view (middle) and a packing diagram (bottom).

Table S4. Selected lengths (Å) and angles (º) for (*R*)-**2**

Bond lengths [Å]			
S(1)-C(1)	1.747(3)	C(7)-C(8)	1.517(4)
S(1)-C(3)	1.759(3)	C(7)-C(9)	1.531(4)
S(3)-C(4)	1.756(2)	C(7)-H(7)	0.9800
S(3)-C(5)	1.765(2)	C(2)-C(1)	1.314(5)
S(5)-C(5)	1.743(3)	C(2)-H(2)	0.9300
S(5)-C(7)	1.825(2)	C(9)-C(10)	1.519(4)
S(4)-C(4)	1.756(2)	C(9)-H(9A)	0.9700
S(4)-C(6)	1.763(3)	C(9)-H(9B)	0.9700
S(2)-C(2)	1.745(3)	C(8)-H(8A)	0.9700
S(2)-C(3)	1.758(2)	C(8)-H(8B)	0.9700
S(6)-C(6)	1.743(2)	C(10)-H(10A)	0.9600
S(6)-C(8)	1.817(3)	C(10)-H(10B)	0.9600
C(4)-C(3)	1.336(3)	C(10)-H(10C)	0.9600
C(6)-C(5)	1.337(3)	C(1)-H(1)	0.9300

Angles [°]			
C(5)-C(6)-S(4)	116.80(19)	C(1)-C(2)-H(2)	120.9
S(6)-C(6)-S(4)	113.62(14)	S(2)-C(2)-H(2)	120.9
C(8)-C(7)-C(9)	111.0(2)	C(10)-C(9)-C(7)	114.6(2)
C(8)-C(7)-S(5)	111.10(18)	C(10)-C(9)-H(9A)	108.6
C(9)-C(7)-S(5)	106.40(17)	C(7)-C(9)-H(9A)	108.6
C(8)-C(7)-H(7)	109.4	C(7)-C(8)-H(8B)	108.4
C(9)-C(7)-H(7)	109.4	S(6)-C(8)-H(8B)	108.4
S(5)-C(7)-H(7)	109.4	H(8A)-C(8)-H(8B)	107.5
C(6)-C(5)-S(5)	127.53(19)	C(9)-C(10)-H(10 A)	109.5
C(6)-C(5)-S(3)	117.0(2)	C(9)-C(10)-H(10 B)	109.5
S(5)-C(5)-S(3)	115.34(13)	H(10A)-C(10)-H(10B)	109.5
C(1)-C(2)-S(2)	118.3(2)	C(9)-C(10)-H(10 C)	109.5
C(10)-C(9)-H(9B)	108.6	H(10A)-C(10)-H(10C)	109.5
C(7)-C(9)-H(9B)	108.6	H(10B)-C(10)-H(10C)	109.5
H(9A)-C(9)-H(9B)	107.6	C(2)-C(1)-S(1)	118.0(2)
C(7)-C(8)-S(6)	115.52(18)	C(2)-C(1)-H(1)	121.0
C(7)-C(8)-H(8A)	108.4	S(1)-C(1)-H(1)	121.0
S(6)-C(8)-H(8A)	108.4		

Compound (*S*)-**2**

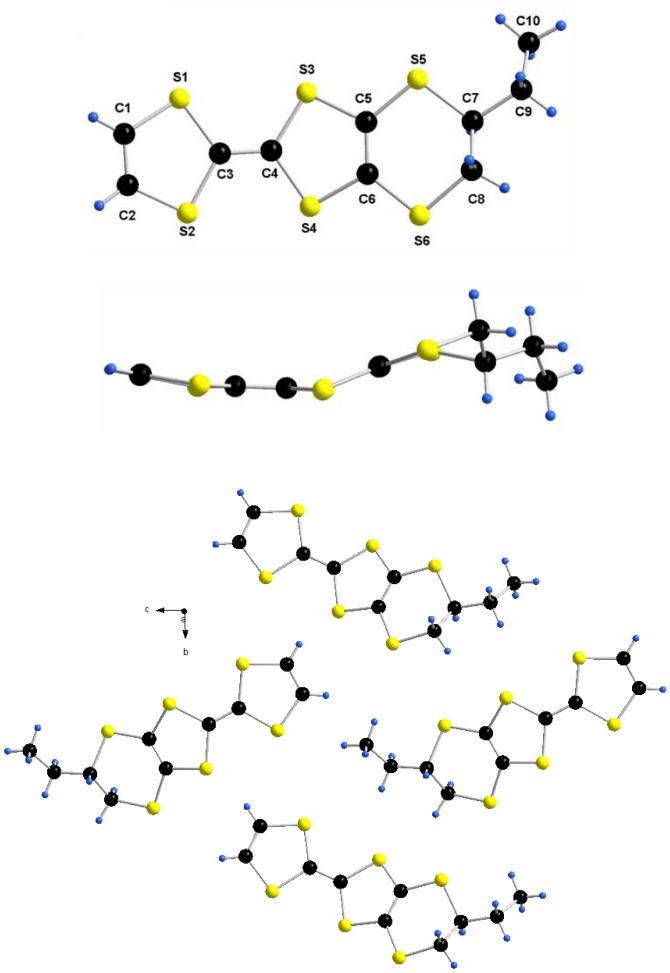


Fig. S11 Molecular structure of (*S*)-**2** together with the atom numbering scheme (top), a side view (middle) and a packing diagram (bottom).

Table S5. Selected lengths (Å) and angles (º) for (*S*)-**2**

Bond lengths [Å]

S(3)-C(5)	1.765(2)	S(4)-C(6)	1.762(3)
S(1)-C(1)	1.748(3)	S(6)-C(6)	1.743(3)
S(1)-C(3)	1.759(3)	S(6)-C(8)	1.815(3)
S(2)-C(2)	1.741(3)	C(4)-C(3)	1.337(4)
S(2)-C(3)	1.755(3)	C(6)-C(5)	1.336(4)
S(5)-C(5)	1.742(3)	C(8)-C(7)	1.515(4)
S(5)-C(7)	1.827(2)	C(2)-C(1)	1.322(5)
S(4)-C(4)	1.756(3)	C(7)-C(9)	1.526(4)

Angles [°]

C(4)-S(3)-C(5)	93.92(13)	C(5)-C(6)-S(4)	116.9(2)
C(1)-S(1)-C(3)	94.18(14)	S(6)-C(6)-S(4)	113.64(15)
C(2)-S(2)-C(3)	94.62(14)	C(6)-C(5)-S(5)	127.7(2)
C(5)-S(5)-C(7)	100.49(12)	C(6)-C(5)-S(3)	116.9(2)
C(4)-S(4)-C(6)	93.91(12)	S(5)-C(5)-S(3)	115.20(14)
C(6)-S(6)-C(8)	102.20(13)	C(7)-C(8)-S(6)	115.85(19)
C(3)-C(4)-S(3)	124.84(19)	C(1)-C(2)-S(2)	117.8(2)
C(3)-C(4)-S(4)	121.82(19)	C(8)-C(7)-C(9)	111.2(2)
S(3)-C(4)-S(4)	113.34(15)	C(8)-C(7)-S(5)	110.9(2)
C(4)-C(3)-S(2)	122.2(2)	C(9)-C(7)-S(5)	106.51(18)
C(4)-C(3)-S(1)	123.2(2)	C(10)-C(9)-C(7)	114.6(2)
S(2)-C(3)-S(1)	114.59(15)	C(2)-C(1)-S(1)	118.0(2)
C(5)-C(6)-S(6)	129.4(2)		

Compound (*rac*)-**2**

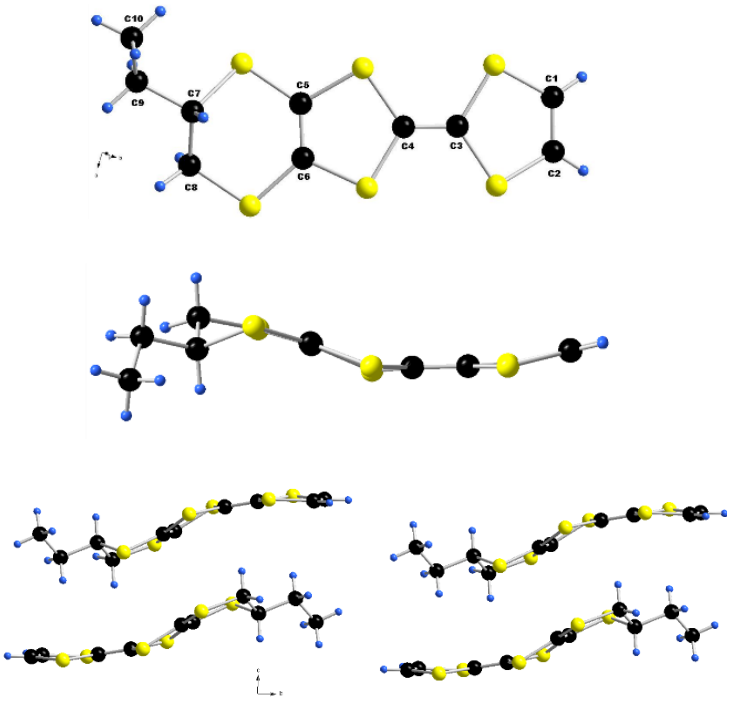


Fig. S12 Molecular structure of (*rac*)-**2** together with the atom numbering scheme (top), a side view (middle) and a packing diagram (bottom).

Table S6. Selected lengths (Å) and angles (º) for (*rac*)-**2**

Angles [°]

C(8)-C(7)-C(9)	111.0(2)	C(7)-C(9)-H(9B)	108.6
C(8)-C(7)-S(5)	111.10(18)	H(9A)-C(9)-H(9B)	107.6
C(9)-C(7)-S(5)	106.40(17)	C(7)-C(8)-S(6)	115.52(18)
C(8)-C(7)-H(7)	109.4	C(7)-C(8)-H(8A)	108.4
C(9)-C(7)-H(7)	109.4	S(6)-C(8)-H(8A)	108.4
S(5)-C(7)-H(7)	109.4	C(7)-C(8)-H(8B)	108.4
C(6)-C(5)-S(5)	127.53(19)	S(6)-C(8)-H(8B)	108.4
C(6)-C(5)-S(3)	117.0(2)	H(8A)-C(8)-H(8B)	107.5
S(5)-C(5)-S(3)	115.34(13)	C(9)-C(10)-H(10 A)	109.5
C(1)-C(2)-S(2)	118.3(2)	C(9)-C(10)-H(10 B)	109.5
C(1)-C(2)-H(2)	120.9	H(10A)-C(10)-H(10B)	109.5
S(2)-C(2)-H(2)	120.9	C(9)-C(10)-H(10 C)	109.5
C(10)-C(9)-C(7)	114.6(2)	H(10A)-C(10)-H(10C)	109.5
C(10)-C(9)-H(9A)	108.6	H(10B)-C(10)-H(10C)	109.5
C(7)-C(9)-H(9A)	108.6	C(2)-C(1)-S(1)	118.0(2)
C(10)-C(9)-H(9B)	108.6	C(2)-C(1)-H(1)	121.0
		S(1)-C(1)-H(1)	121.0

Bond lengths [Å]

S(5)-C(7)	1.861(5)	S(5)-C(5)	1.744(4)
S(2)-C(2)	1.735(4)	S(6)-C(6)	1.742(4)
S(2)-C(3)	1.750(4)	S(6)-C(8)	1.782(5)
S(3)-C(4)	1.752(4)	C(8)-C(7)	1.496(7)
S(3)-C(5)	1.766(4)	C(5)-C(6)	1.338(6)
S(1)-C(1)	1.741(4)	C(4)-C(3)	1.342(5)
S(1)-C(3)	1.756(4)	C(1)-C(2)	1.326(6)
S(4)-C(4)	1.758(4)	C(7)-C(9)	1.553(6)
S(4)-C(6)	1.758(4)	C(9)-C(10)	1.489(7)

Salt [(*rac*)-**1**]$_2$PF$_6$

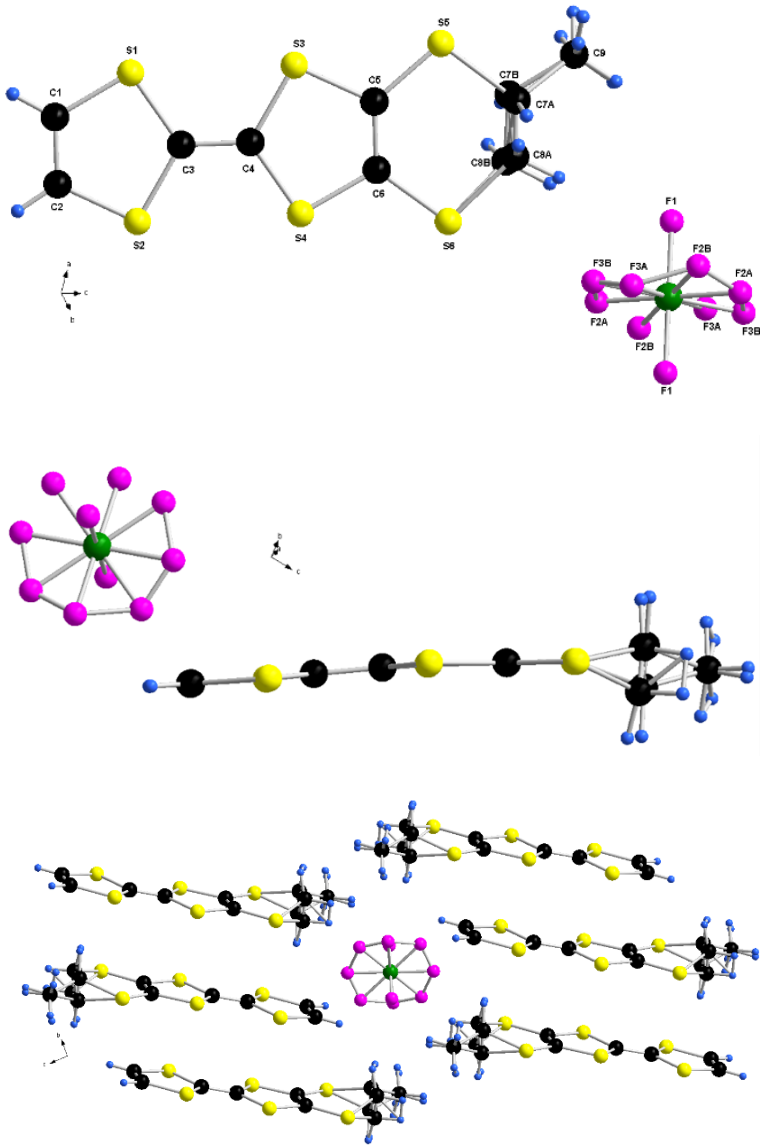


Fig. S13 Molecular structure of [(*rac*)-**1**]$_2$PF$_6$ together with the atom numbering scheme (top), a side view (middle) and a packing diagram (bottom).

Table S7. Selected lengths (Å) and angles (º) for [(*rac*)-**1**]$_2$PF$_6$

Bond lengths [Å]

C(1)-C(2)	1.329(9)	C(5)-S(3)	1.748(5)	C(8Aa)-H(8B)	0.9900	F(2A)-P(1)	1.589(11)
C(1)-S(1)	1.728(5)	C(6)-S(4)	1.742(5)	C(8Bb)-S(6)	1.847(11)	F(2B)-F(3A)	1.367(13)
C(1)-H(1)	0.9500	C(6)-S(6)	1.753(5)	C(8Bb)-H(8C)	0.9900	F(2B)-P(1)	1.569(8)
C(2)-S(2)	1.741(6)	C(7Aa)-C(9)	1.562(12)	C(8Bb)-H(8D)	0.9900	F(3A)-F(3B)	1.166(14)
C(2)-H(2)	0.9500	C(7Aa)-C(8A)	1.565(16)	C(9)-H(9A)	0.9800	F(3A)-P(1)	1.564(12)
C(3)-C(4)	1.372(7)	C(7Aa)-S(5)	1.866(11)	C(9)-H(9B)	0.9800	F(3B)-F(2A)#1	1.257(15)
C(3)-S(1)	1.736(5)	C(7Aa)-H(7A)	1.0000	C(9)-H(9C)	0.9800	F(3B)-P(1)	1.587(6)
C(3)-S(2)	1.740(5)	C(7Bb)-C(8B)	1.421(17)	C(9)-H(9D)	0.9800	P(1)-F(3A)#1	1.564(12)
C(4)-S(4)	1.726(5)	C(7Bb)-C(9)	1.531(12)	C(9)-H(9E)	0.9800	P(1)-F(2B)#1	1.569(8)
C(4)-S(3)	1.746(5)	C(7Bb)-S(5)	1.838(10)	C(9)-H(9F)	0.9800	P(1)-F(1)#1	1.584(4)
C(5)-C(6)	1.349(7)	C(7Bb)-H(7B)	1.0000	F(1)-P(1)	1.584(4)	P(1)-F(3B)#1	1.587(6)
C(5)-S(5)	1.742(5)	C(8Aa)-S(6)	1.777(11)	F(2A)-F(2B)	1.157(15)	P(1)-F(2A)#1	1.589(12)
		C(8Aa)-H(8A)	0.9900	F(2A)-F(3B)#1	1.257(15)		

Angles [°]

C(2)-C(1)-S(1)	117.7(4)	C(7Aa)-C(8Aa)-S(6)	111.2(8)	F(3A)-F(2B)-P(1)	64.0(7)	F(2B)#1-P(1)-F(3B)#1	91.0(5)
C(2)-C(1)-H(1)	121.1	C(7Aa)-C(8Aa)-H(8A)	109.4	F(3B)-F(3A)-F(2 B)	125.2(11)	F(2B)-P(1)-F(3B) #1	89.0(5)
S(1)-C(1)-H(1)	121.1	S(6)-C(8Aa)-H(8 A)	109.4	F(3B)-F(3A)-P(1)	69.3(8)	F(1)#1-P(1)-F(3 B)#1	87.4(3)
C(1)-C(2)-S(2)	117.5(4)	C(7Aa)-C(8Aa)-H(8B)	109.4	F(2B)-F(3A)-P(1)	64.3(6)	F(1)-P(1)-F(3B) #1	92.6(3)
C(1)-C(2)-H(2)	121.2	S(6)-C(8Aa)-H(8 B)	109.4	F(3A)-F(3B)-F(2 A)#1	131.7(10)	F(3B)-P(1)-F(3B)#1	180.00(18)
S(2)-C(2)-H(2)	121.2	H(8Aa)-C(8Aa)-H(8B)	108.0	F(3A)-F(3B)-P(1)	67.2(6)	F(3A)#1-P(1)-F(2A)#1	90.9(7)
C(4)-C(3)-S(1)	123.0(4)	C(7Bb)-C(8Bb)-S(6)	119.0(8)	F(2A)#1-F(3B)-P(1)	66.7(7)	F(3A)-P(1)-F(2A)#1	89.1(7)
C(4)-C(3)-S(2)	121.7(4)	C(7Bb)-C(8Bb)-H(8C)	107.6	F(3A)#1-P(1)-F(3A)	180.0(3)	F(2B)#1-P(1)-F(2A)#1	43.0(6)
S(1)-C(3)-S(2)	115.3(3)	S(6)-C(8Bb)-H(8 C)	107.6	F(3A)#1-P(1)-F(2B)#1	51.7(6)	F(2B)-P(1)-F(2A)#1	137.0(6)
C(3)-C(4)-S(4)	122.8(4)	C(7Bb)-C(8Bb)-H(8D)	107.6	F(3A)-P(1)-F(2B)#1	128.3(6)	F(1)#1-P(1)-F(2 A)#1	93.4(5)
C(3)-C(4)-S(3)	121.8(4)	S(6)-C(8Bb)-H(8 D)	107.6	F(3A)#1-P(1)-F(2B)	128.3(6)	F(1)-P(1)-F(2A) #1	86.6(5)
S(4)-C(4)-S(3)	115.4(3)	H(8Cb)-C(8Bb)-H(8D)	107.0	F(3A)-P(1)-F(2B)	51.7(6)	F(3B)-P(1)-F(2A)#1	46.6(6)
C(6)-C(5)-S(5)	128.9(4)	C(7Aa)-C(9)-H(9 A)	109.5	F(2B)#1-P(1)-F(2B)	180.0(7)	F(3B)#1-P(1)-F(2A)#1	133.4(6)
C(6)-C(5)-S(3)	116.5(4)	C(7Aa)-C(9)-H(9 B)	109.5	F(3A)#1-P(1)-F(1)#1	99.7(5)	F(3A)#1-P(1)-F(2A)	89.1(7)
S(5)-C(5)-S(3)	114.6(3)	H(9Aa)-C(9)-H(9 B)	109.5	F(3A)-P(1)-F(1) #1	80.3(5)	F(3A)-P(1)-F(2A)	90.9(7)
C(5)-C(6)-S(4)	117.5(4)	C(7Aa)-C(9)-H(9 C)	109.5	F(2B)#1-P(1)-F(1)#1	84.0(4)	F(2B)#1-P(1)-F(2A)	137.0(6)
C(5)-C(6)-S(6)	127.9(4)	H(9Aa)-C(9)-H(9 C)	109.5	F(2B)-P(1)-F(1) #1	96.0(4)	F(2B)-P(1)-F(2A)	43.0(6)
S(4)-C(6)-S(6)	114.6(3)	H(9Ba)-C(9)-H(9 C)	109.5	F(3A)#1-P(1)-F(1)	80.3(5)	F(1)#1-P(1)-F(2 A)	86.6(5)
C(9)-C(7Aa)-C(8 A)	108.4(8)	C(7Bb)-C(9)-H(9 D)	109.5	F(3A)-P(1)-F(1)	99.7(5)	F(1)-P(1)-F(2A)	93.4(5)
C(9)-C(7Aa)-S(5)	103.2(7)	C(7Bb)-C(9)-H(9 E)	109.5	F(2B)#1-P(1)-F(1)	96.0(4)	F(3B)-P(1)-F(2A)	133.4(6)
C(8Aa)-C(7Aa)-S(5)	109.4(8)	H(9Db)-C(9)-H(9 E)	109.5	F(2B)-P(1)-F(1)	84.0(4)	F(3B)#1-P(1)-F(2A)	46.6(6)
C(9)-C(7Aa)-H(7 A)	111.8	C(7Bb)-C(9)-H(9 F)	109.5	F(1)#1-P(1)-F(1)	180.0(3)	F(2A)#1-P(1)-F(2A)	180.0
C(8Aa)-C(7Aa)-H(7A)	111.8	H(9Db)-C(9)-H(9 F)	109.5	F(3A)#1-P(1)-F(3B)	136.6(5)	C(4)-S(4)-C(6)	95.3(2)
S(5)-C(7Aa)-H(7 A)	111.8	H(9Eb)-C(9)-H(9 F)	109.5	F(3A)-P(1)-F(3B)	43.4(5)	C(4)-S(3)-C(5)	95.1(2)
C(8Bb)-C(7Bb)-C(9)	107.0(9)	F(2B)-F(2A)-F(3 B)#1	132.7(12)	F(2B)#1-P(1)-F(3B)	89.0(5)	C(3)-S(2)-C(2)	94.5(3)
C(8Bb)-C(7Bb)-S(5)	109.3(8)	F(2B)-F(2A)-P(1)	67.6(7)	F(2B)-P(1)-F(3B)	91.0(5)	C(1)-S(1)-C(3)	94.9(3)
C(9)-C(7Bb)-S(5)	105.8(7)	F(3B)#1-F(2A)-P(1)	66.6(6)	F(1)#1-P(1)-F(3 B)	92.6(3)	C(6)-S(6)-C(8A)	99.9(4)
C(8Bb)-C(7Bb)-H(7B)	111.5	F(2A)-F(2B)-F(3 A)	125.6(11)	F(1)-P(1)-F(3B)	87.4(3)	C(6)-S(6)-C(8B)	99.3(4)
C(9)-C(7Bb)-H(7 B)	111.5	F(2A)-F(2B)-P(1)	69.4(7)	F(3A)#1-P(1)-F(3B)#1	43.4(5)	C(5)-S(5)-C(7B)	102.0(4)
S(5)-C(7Bb)-H(7 B)	111.5			F(3A)-P(1)-F(3B)#1	136.6(5)	C(5)-S(5)-C(7A)	101.9(4)

Salt [(*R*)-**1**]$_2$PF$_6$

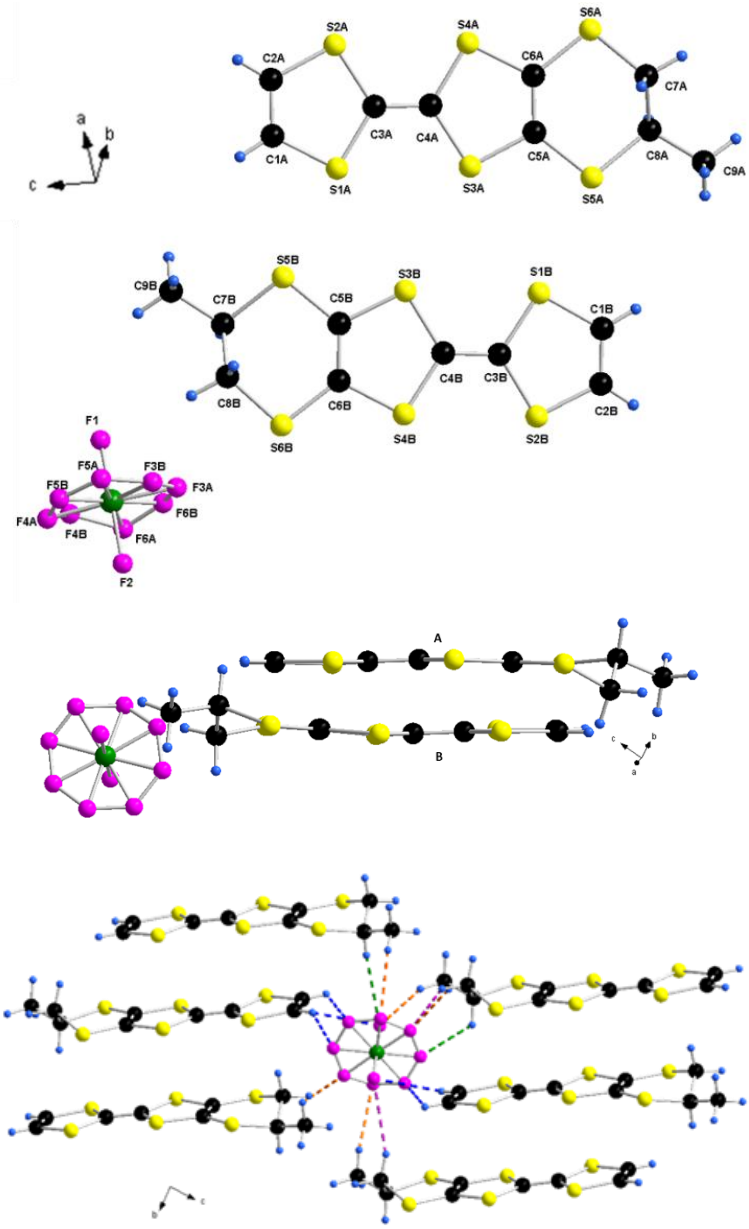


Fig. S14 Molecular structure of [(*R*)-**1**]$_2$PF$_6$ together with the atom numbering scheme (top), a side view (middle) and a packing diagram with a focus on the C–H···F short contacts: blue for CH_{vinyl} (2.52-2.57 Å), violet for CH_2 (2.46-2.63 Å), orange for Me (2.46-2.93 Å) and green for CH_{Me} (2.61 Å) (bottom).

Table S8. Selected lengths (Å) and angles (º) for [(*R*)-**1**]$_2$PF$_6$

Bond lengths [Å]

C(2A)-C(1A)	1.340(10)	C(8A)-H(8A1)	0.9700	C(7B)-C(8B)	1.478(7)	F(2)-P(1)	1.605(4)
C(2A)-S(2A)	1.742(7)	C(8A)-H(8A2)	0.9700	C(7B)-C(9B)	1.519(9)	F(3A)-F(6B)	1.199(15)
C(2A)-H(2A)	0.9300	C(1B)-C(2B)	1.312(10)	C(7B)-S(5B)	1.833(5)	F(3A)-F(3B)	1.215(19)
C(1A)-S(1A)	1.741(7)	C(1B)-S(1B)	1.735(7)	C(7B)-H(7B)	0.9800	F(3A)-P(1)	1.582(6)
C(1A)-H(1A)	0.9300	C(1B)-H(1B)	0.9300	C(8B)-S(6B)	1.797(5)	F(3B)-F(5A)	1.265(19)
C(3A)-C(4A)	1.359(8)	C(2B)-S(2B)	1.732(6)	C(8B)-H(8B1)	0.9700	F(3B)-P(1)	1.606(11)
C(3A)-S(1A)	1.734(5)	C(2B)-H(2B)	0.9300	C(8B)-H(8B2)	0.9700	F(4A)-F(4B)	1.163(17)
C(3A)-S(2A)	1.744(6)	C(3B)-C(4B)	1.377(7)	C(7A)-C(9A)	1.529(8)	F(4A)-F(5B)	1.223(16)
C(4A)-S(4A)	1.736(5)	C(3B)-S(2B)	1.737(6)	C(7A)-S(5A)	1.826(5)	F(4A)-P(1)	1.594(6)
C(4A)-S(3A)	1.744(6)	C(3B)-S(1B)	1.740(5)	C(7A)-H(7A)	0.9800	F(4B)-F(6A)	1.332(18)
C(6A)-C(5A)	1.356(7)	C(4B)-S(3B)	1.733(6)	C(9B)-H(9B1)	0.9600	F(4B)-P(1)	1.548(11)
C(6A)-S(6A)	1.746(5)	C(4B)-S(4B)	1.742(5)	C(9B)-H(9B2)	0.9600	F(5A)-F(5B)	1.227(17)
C(6A)-S(4A)	1.744(6)	C(5B)-C(6B)	1.349(8)	C(9B)-H(9B3)	0.9600	F(5A)-P(1)	1.562(7)
C(5A)-S(3A)	1.749(6)	C(5B)-S(5B)	1.741(6)	C(9A)-H(9A1)	0.9600	F(5B)-P(1)	1.566(10)
C(5A)-S(5A)	1.746(6)	C(5B)-S(3B)	1.757(5)	C(9A)-H(9A2)	0.9600	F(6A)-F(6B)	1.191(15)
C(8A)-C(7A)	1.537(6)	C(6B)-S(6B)	1.741(6)	C(9A)-H(9A3)	0.9600	F(6A)-P(1)	1.585(7)
C(8A)-S(6A)	1.794(5)	C(6B)-S(4B)	1.747(6)	F(1)-P(1)	1.581(4)	F(6B)-P(1)	1.579(11)

Angles [°]

C(1A)-C(2A)-S(2A)	117.3(5)	S(5B)-C(5B)-S(3B)	114.4(3)	F(3A)-F(3B)-P(1)	66.6(6)	F(6B)-P(1)-F(3A)	44.6(6)
C(1A)-C(2A)-H(2A)	121.4	C(5B)-C(6B)-S(6B)	128.2(4)	F(5A)-F(3B)-P(1)	64.6(7)	F(1)-P(1)-F(3A)	89.9(3)
S(2A)-C(2A)-H(2A)	121.4	C(5B)-C(6B)-S(4B)	117.1(4)	F(4B)-F(4A)-F(5B)	129.3(9)	F(6A)-P(1)-F(3A)	87.7(5)
C(2A)-C(1A)-S(1A)	117.2(5)	S(6B)-C(6B)-S(4B)	114.7(3)	F(4B)-F(4A)-P(1)	66.2(6)	F(4B)-P(1)-F(4A)	43.4(7)
C(2A)-C(1A)-H(1A)	121.4	C(8B)-C(7B)-C(9B)	111.0(4)	F(5B)-F(4A)-P(1)	66.0(6)	F(5A)-P(1)-F(4A)	91.7(5)
S(1A)-C(1A)-H(1A)	121.4	C(8B)-C(7B)-S(5B)	112.1(3)	F(4A)-F(4B)-F(6A)	126.9(11)	F(5B)-P(1)-F(4A)	45.5(6)
C(4A)-C(3A)-S(1A)	122.9(4)	C(9B)-C(7B)-S(5B)	106.0(4)	F(4A)-F(4B)-P(1)	70.4(7)	F(6B)-P(1)-F(4A)	132.9(7)
C(4A)-C(3A)-S(2A)	122.0(4)	C(8B)-C(7B)-H(7B)	109.2	F(6A)-F(4B)-P(1)	66.3(6)	F(1)-P(1)-F(4A)	93.0(3)
S(1A)-C(3A)-S(2A)	115.1(3)	C(9B)-C(7B)-H(7B)	109.2	F(5B)-F(5A)-F(3B)	133.6(10)	F(6A)-P(1)-F(4A)	89.3(5)
C(3A)-C(4A)-S(4A)	122.8(4)	S(5B)-C(7B)-H(7B)	109.2	F(5B)-F(5A)-P(1)	67.1(6)	F(3A)-P(1)-F(4A)	176.1(5)
C(3A)-C(4A)-S(3A)	122.0(4)	C(7B)-C(8B)-S(6B)	117.0(3)	F(3B)-F(5A)-P(1)	68.3(7)	F(4B)-P(1)-F(3B)	175.5(10)
S(4A)-C(4A)-S(3A)	115.2(3)	C(7B)-C(8B)-H(8B1)	108.1	F(5A)-F(5B)-F(4A)	135.1(9)	F(5A)-P(1)-F(3B)	47.1(7)
C(5A)-C(6A)-S(6A)	127.1(5)	S(6B)-C(8B)-H(8B1)	108.1	F(5A)-F(5B)-P(1)	66.7(6)	F(5B)-P(1)-F(3B)	92.4(10)
C(5A)-C(6A)-S(4A)	117.5(4)	C(7B)-C(8B)-H(8B2)	108.1	F(4A)-F(5B)-P(1)	68.4(6)	F(6B)-P(1)-F(3B)	89.3(10)
S(6A)-C(6A)-S(4A)	115.4(3)	S(6B)-C(8B)-H(8B2)	108.1	F(6B)-F(6A)-F(4B)	123.3(9)	F(1)-P(1)-F(3B)	95.7(6)
C(6A)-C(5A)-S(3A)	116.4(4)	H(8B1)-C(8B)-H(8B2)	107.3	F(6B)-F(6A)-P(1)	67.7(6)	F(6A)-P(1)-F(3B)	130.9(9)
C(6A)-C(5A)-S(5A)	129.4(4)	C(9A)-C(7A)-C(8A)	110.8(4)	F(4B)-F(6A)-P(1)	63.4(6)	F(3A)-P(1)-F(3B)	44.8(7)
S(3A)-C(5A)-S(5A)	114.2(3)	C(9A)-C(7A)-S(5A)	106.4(4)	F(6A)-F(6B)-F(3A)	133.3(10)	F(4A)-P(1)-F(3B)	137.4(9)
C(7A)-C(8A)-S(6A)	113.8(3)	C(8A)-C(7A)-S(5A)	111.2(3)	F(6A)-F(6B)-P(1)	68.1(7)	F(4B)-P(1)-F(2)	100.2(6)
C(7A)-C(8A)-H(8A1)	108.8	C(9A)-C(7A)-H(7A)	109.5	F(3A)-F(6B)-P(1)	67.8(6)	F(5A)-P(1)-F(2)	91.0(4)
S(6A)-C(8A)-H(8A1)	108.8	C(8A)-C(7A)-H(7A)	109.5	F(4B)-P(1)-F(5A)	132.1(9)	F(5B)-P(1)-F(2)	87.4(4)
C(7A)-C(8A)-H(8A2)	108.8	S(5A)-C(7A)-H(7A)	109.5	F(4B)-P(1)-F(5B)	87.6(9)	F(6B)-P(1)-F(2)	94.0(5)
S(6A)-C(8A)-H(8A2)	108.8	C(7B)-C(9B)-H(9B1)	109.5	F(5A)-P(1)-F(5B)	46.2(7)	F(1)-P(1)-F(2)	179.9(4)
H(8A1)-C(8A)-H(8A2)	107.7	C(7B)-C(9B)-H(9B2)	109.5	F(4B)-P(1)-F(6B)	90.5(9)	F(6A)-P(1)-F(2)	84.5(3)
C(2B)-C(1B)-S(1B)	118.3(5)	H(9B1)-C(9B)-H(9B2)	109.5	F(5A)-P(1)-F(6B)	135.3(7)	F(3A)-P(1)-F(2)	90.2(3)
C(2B)-C(1B)-H(1B)	120.8	C(7B)-C(9B)-H(9B3)	109.5	F(5B)-P(1)-F(6B)	177.9(10)	F(4A)-P(1)-F(2)	87.0(3)
S(1B)-C(1B)-H(1B)	120.8	H(9B1)-C(9B)-H(9B3)	109.5	F(4B)-P(1)-F(1)	79.8(6)	F(3B)-P(1)-F(2)	84.3(6)
C(1B)-C(2B)-S(2B)	117.6(5)	H(9B2)-C(9B)-H(9B3)	109.5	F(5A)-P(1)-F(1)	89.1(4)	C(3A)-S(2A)-C(2A)	95.1(3)
C(1B)-C(2B)-H(2B)	121.2	C(7A)-C(9A)-H(9A1)	109.5	F(5B)-P(1)-F(1)	92.6(5)	C(3A)-S(1A)-C(1A)	95.3(3)
S(2B)-C(2B)-H(2B)	121.2	C(7A)-C(9A)-H(9A2)	109.5	F(6B)-P(1)-F(1)	86.0(5)	C(4A)-S(4A)-C(6A)	95.4(3)
C(4B)-C(3B)-S(2B)	122.6(4)	H(9A1)-C(9A)-H(9A2)	109.5	F(4B)-P(1)-F(6A)	50.3(7)	C(4A)-S(3A)-C(5A)	95.5(3)
C(4B)-C(3B)-S(1B)	122.0(4)	C(7A)-C(9A)-H(9A3)	109.5	F(5A)-P(1)-F(6A)	175.3(5)	C(6A)-S(6A)-C(8A)	99.6(2)
S(2B)-C(3B)-S(1B)	115.4(3)	H(9A1)-C(9A)-H(9A3)	109.5	F(5B)-P(1)-F(6A)	134.5(8)	C(5A)-S(5A)-C(7A)	103.1(2)
C(3B)-C(4B)-S(3B)	122.9(4)	H(9A2)-C(9A)-H(9A3)	109.5	F(6B)-P(1)-F(6A)	44.2(5)	C(4B)-S(3B)-C(5B)	95.3(3)
C(3B)-C(4B)-S(4B)	121.8(4)	F(6B)-F(3A)-F(3B)	136.1(11)	F(1)-P(1)-F(6A)	95.5(3)	C(4B)-S(4B)-C(6B)	95.3(3)
S(3B)-C(4B)-S(4B)	115.3(3)	F(6B)-F(3A)-P(1)	67.6(7)	F(4B)-P(1)-F(3A)	134.7(9)	C(1B)-S(1B)-C(3B)	94.1(3)
C(6B)-C(5B)-S(5B)	128.9(4)	F(3B)-F(3A)-P(1)	68.6(7)	F(5A)-P(1)-F(3A)	91.1(5)	C(2B)-S(2B)-C(3B)	94.6(3)
C(6B)-C(5B)-S(3B)	116.7(4)	F(3A)-F(3B)-F(5A)	129.7(11)	F(5B)-P(1)-F(3A)	137.1(8)	C(5B)-S(5B)-C(7B)	101.7(2)

Salt [(*S*)-**1**]$_2$PF$_6$

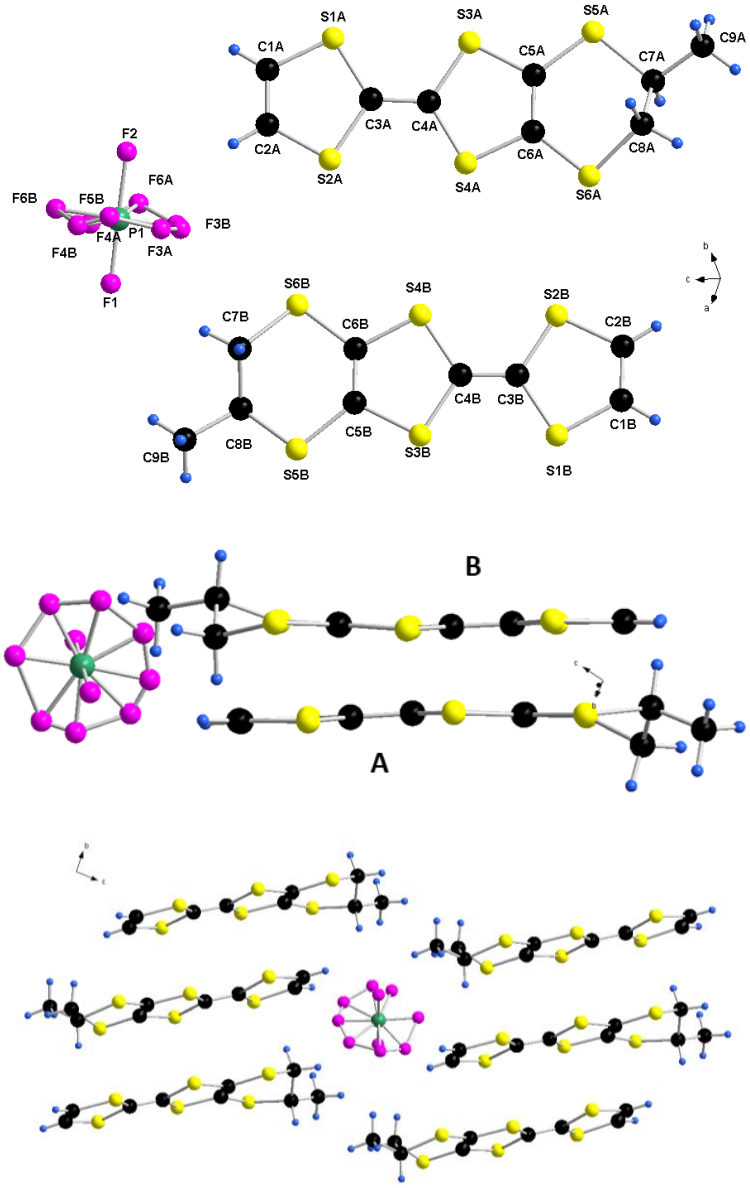


Fig. S15 Molecular structure of [(*S*)-**1**]$_2$PF$_6$ together with the atom numbering scheme (top), a side view (middle) and a packing diagram (bottom).

Table S9. Selected lengths (Å) and angles (º) for $[(S)\text{-}\mathbf{1}]_2PF_6$

Bond lengths [Å]

C(9A)-C(7A)	1.468(13)	C(7B)-H(7B2)	0.9700	F(6B)-F(4B)	1.73(3)	S(1A)-C(1A)	1.723(10)
C(9A)-H(9A1)	0.9600	C(8B)-C(9B)	1.563(10)	F(4B)-F(4A)	0.82(4)	S(1A)-C(3A)	1.726(8)
C(9A)-H(9A2)	0.9600	C(8B)-S(5B)	1.825(7)	F(5A)-F(6A)	1.37(3)	S(6A)-C(6A)	1.729(9)
C(9A)-H(9A3)	0.9600	C(8B)-H(8B)	0.9800	F(6A)-F(5B)	1.25(2)	S(6B)-C(6B)	1.754(8)
P(1)-F(4A)	1.51(3)	C(7A)-C(8A)	1.512(10)	S(4B)-C(6B)	1.731(8)	S(5A)-C(5A)	1.741(9)
P(1)-F(6B)	1.528(8)	C(7A)-S(5A)	1.848(7)	S(4B)-C(4B)	1.733(8)	S(2A)-C(2A)	1.700(11)
P(1)-F(5A)	1.534(10)	C(7A)-H(7A)	0.9800	S(3B)-C(4B)	1.749(8)	S(2A)-C(3A)	1.751(8)
P(1)-F(5B)	1.55(2)	C(8A)-S(6A)	1.794(7)	S(3B)-C(5B)	1.760(9)	C(4A)-C(3A)	1.374(10)
P(1)-F(3B)	1.55(3)	C(8A)-H(8A1)	0.9700	S(3A)-C(4A)	1.728(8)	C(3B)-C(4B)	1.350(11)
P(1)-F(1)	1.541(6)	C(8A)-H(8A2)	0.9700	S(3A)-C(5A)	1.736(8)	C(1B)-C(2B)	1.307(13)
P(1)-F(3A)	1.583(9)	C(9B)-H(9B1)	0.9600	S(2B)-C(3B)	1.738(9)	C(1B)-H(1B)	0.9300
P(1)-F(4B)	1.591(12)	C(9B)-H(9B2)	0.9600	S(2B)-C(2B)	1.742(11)	C(5B)-C(6B)	1.311(11)
P(1)-F(2)	1.617(7)	C(9B)-H(9B3)	0.9600	S(4A)-C(4A)	1.734(9)	C(2B)-H(2B)	0.9300
P(1)-F(6A)	1.67(3)	F(3A)-F(3B)	0.89(4)	S(4A)-C(6A)	1.755(9)	C(5A)-C(6A)	1.374(11)
C(7B)-C(8B)	1.495(9)	F(3A)-F(4A)	1.29(4)	S(1B)-C(3B)	1.736(9)	C(2A)-C(1A)	1.346(14)
C(7B)-S(6B)	1.791(8)	F(3B)-F(5A)	1.09(2)	S(1B)-C(1B)	1.746(10)	C(2A)-H(2A)	0.9300
C(7B)-H(7B1)	0.9700	F(6B)-F(5B)	1.38(2)	S(5B)-C(5B)	1.760(8)	C(1A)-H(1A)	0.9300

Angles [°]

C(1A)-C(2A)-S(2A)	117.3(5)	S(5B)-C(5B)-S(3B)	114.4(3)	F(3A)-F(3B)-P(1)	66.6(6)	F(6B)-P(1)-F(3A)	44.6(6)
C(1A)-C(2A)-H(2A)	121.4	C(5B)-C(6B)-S(6B)	128.2(4)	F(5A)-F(3B)-P(1)	64.6(7)	F(1)-P(1)-F(3A)	89.9(3)
S(2A)-C(2A)-H(2A)	121.4	C(5B)-C(6B)-S(4B)	117.1(4)	F(4B)-F(4A)-F(5B)	129.3(9)	F(6A)-P(1)-F(3A)	87.7(5)
C(2A)-C(1A)-S(1A)	117.2(5)	S(6B)-C(6B)-S(4B)	114.7(3)	F(4B)-F(4A)-P(1)	66.2(6)	F(4B)-P(1)-F(4A)	43.4(7)
C(2A)-C(1A)-H(1A)	121.4	C(8B)-C(7B)-C(9B)	111.0(4)	F(5B)-F(4A)-P(1)	66.0(6)	F(5A)-P(1)-F(4A)	91.7(5)
S(1A)-C(1A)-H(1A)	121.4	C(8B)-C(7B)-S(5B)	112.1(3)	F(4A)-F(4B)-F(6A)	126.9(11)	F(5B)-P(1)-F(4A)	45.5(6)
C(4A)-C(3A)-S(1A)	122.9(4)	C(9B)-C(7B)-S(5B)	106.0(4)	F(4A)-F(4B)-P(1)	70.4(7)	F(6B)-P(1)-F(4A)	132.9(7)
C(4A)-C(3A)-S(2A)	122.0(4)	C(8B)-C(7B)-H(7B)	109.2	F(6A)-F(4B)-P(1)	66.3(6)	F(1)-P(1)-F(4A)	93.0(3)
S(1A)-C(3A)-S(2A)	115.1(3)	C(9B)-C(7B)-H(7B)	109.2	F(5B)-F(5A)-F(3B)	133.6(10)	F(6A)-P(1)-F(4A)	89.3(5)
C(3A)-C(4A)-S(4A)	122.8(4)	S(5B)-C(7B)-H(7B)	109.2	F(5B)-F(5A)-P(1)	67.1(6)	F(3A)-P(1)-F(4A)	176.1(5)
C(3A)-C(4A)-S(3A)	122.0(4)	C(7B)-C(8B)-S(6B)	117.0(3)	F(3B)-F(5A)-P(1)	68.3(7)	F(4B)-P(1)-F(3B)	175.5(10)
S(4A)-C(4A)-S(3A)	115.2(3)	C(7B)-C(8B)-H(8B1)	108.1	F(5A)-F(5B)-F(4A)	135.1(9)	F(5A)-P(1)-F(3B)	47.1(7)
C(5A)-C(6A)-S(6A)	127.1(5)	S(6B)-C(8B)-H(8B1)	108.1	F(5A)-F(5B)-P(1)	66.7(6)	F(5B)-P(1)-F(3B)	92.4(10)
C(5A)-C(6A)-S(4A)	117.5(4)	C(7B)-C(8B)-H(8B2)	108.1	F(4A)-F(5B)-P(1)	68.4(6)	F(6B)-P(1)-F(3B)	89.3(10)
S(6A)-C(6A)-S(4A)	115.4(3)	S(6B)-C(8B)-H(8B2)	108.1	F(6B)-F(6A)-F(4B)	123.3(9)	F(1)-P(1)-F(3B)	95.7(6)
C(6A)-C(5A)-S(3A)	116.4(4)	H(8B1)-C(8B)-H(8B2)	107.3	F(6B)-F(6A)-P(1)	67.7(6)	F(6A)-P(1)-F(3B)	130.9(9)
C(6A)-C(5A)-S(5A)	129.4(4)	C(9A)-C(7A)-C(8A)	110.8(4)	F(4B)-F(6A)-P(1)	63.4(6)	F(3A)-P(1)-F(3B)	44.8(7)
S(3A)-C(5A)-S(5A)	114.2(3)	C(9A)-C(7A)-S(5A)	106.4(4)	F(6A)-F(6B)-F(3A)	133.3(10)	F(4A)-P(1)-F(3B)	137.4(9)
C(7A)-C(8A)-S(6A)	113.8(3)	C(8A)-C(7A)-S(5A)	111.2(3)	F(6A)-F(6B)-P(1)	68.1(7)	F(4B)-P(1)-F(2)	100.2(6)
C(7A)-C(8A)-H(8A1)	108.8	C(9A)-C(7A)-H(7A)	109.5	F(3A)-F(6B)-P(1)	67.8(6)	F(5A)-P(1)-F(2)	91.0(4)
S(6A)-C(8A)-H(8A1)	108.8	C(8A)-C(7A)-H(7A)	109.5	F(4B)-P(1)-F(5A)	132.1(9)	F(5B)-P(1)-F(2)	87.4(4)
C(7A)-C(8A)-H(8A2)	108.8	S(5A)-C(7A)-H(7A)	109.5	F(4B)-P(1)-F(5B)	87.6(9)	F(6B)-P(1)-F(2)	94.0(5)
S(6A)-C(8A)-H(8A2)	108.8	C(7B)-C(9B)-H(9B1)	109.5	F(5A)-P(1)-F(5B)	46.2(7)	F(1)-P(1)-F(2)	179.9(4)
H(8A1)-C(8A)-H(8A2)	107.7	C(7B)-C(9B)-H(9B2)	109.5	F(4B)-P(1)-F(6B)	90.5(9)	F(6A)-P(1)-F(2)	84.5(3)
C(2B)-C(1B)-S(1B)	118.3(5)	H(9B1)-C(9B)-H(9B2)	109.5	F(5A)-P(1)-F(6B)	135.3(7)	F(3A)-P(1)-F(2)	90.2(3)
C(2B)-C(1B)-H(1B)	120.8	C(7B)-C(9B)-H(9B3)	109.5	F(5B)-P(1)-F(6B)	177.9(10)	F(4A)-P(1)-F(2)	87.0(3)
S(1B)-C(1B)-H(1B)	120.8	H(9B1)-C(9B)-H(9B3)	109.5	F(4B)-P(1)-F(1)	79.8(6)	F(3B)-P(1)-F(2)	84.3(6)
C(1B)-C(2B)-S(2B)	117.6(5)	H(9B2)-C(9B)-H(9B3)	109.5	F(5A)-P(1)-F(1)	89.1(4)	C(3A)-S(2A)-C(2A)	95.1(3)
C(1B)-C(2B)-H(2B)	121.2	C(7A)-C(9A)-H(9A1)	109.5	F(5B)-P(1)-F(1)	92.6(5)	C(3A)-S(1A)-C(1A)	95.3(3)
S(2B)-C(2B)-H(2B)	121.2	C(7A)-C(9A)-H(9A2)	109.5	F(6B)-P(1)-F(1)	86.0(5)	C(4A)-S(4A)-C(6A)	95.4(3)
C(4B)-C(3B)-S(2B)	122.6(4)	H(9A1)-C(9A)-H(9A2)	109.5	F(4B)-P(1)-F(6A)	50.3(7)	C(4A)-S(3A)-C(5A)	95.5(3)
C(4B)-C(3B)-S(1B)	122.0(4)	C(7A)-C(9A)-H(9A3)	109.5	F(5A)-P(1)-F(6A)	175.3(5)	C(6A)-S(6A)-C(8A)	99.6(2)
S(2B)-C(3B)-S(1B)	115.4(3)	H(9A1)-C(9A)-H(9A3)	109.5	F(5B)-P(1)-F(6A)	134.5(8)	C(5A)-S(5A)-C(7A)	103.1(2)
C(3B)-C(4B)-S(3B)	122.9(4)	H(9A2)-C(9A)-H(9A3)	109.5	F(6B)-P(1)-F(6A)	44.2(5)	C(4B)-S(3B)-C(5B)	95.3(3)
C(3B)-C(4B)-S(4B)	121.8(4)	F(6B)-F(3A)-F(3B)	136.1(11)	F(1)-P(1)-F(6A)	95.5(3)	C(4B)-S(4B)-C(6B)	95.3(3)
S(3B)-C(4B)-S(4B)	115.3(3)	F(6B)-F(3A)-P(1)	67.6(7)	F(4B)-P(1)-F(3A)	134.7(9)	C(1B)-S(1B)-C(3B)	94.1(3)
C(6B)-C(5B)-S(5B)	128.9(4)	F(3B)-F(3A)-P(1)	68.6(7)	F(5A)-P(1)-F(3A)	91.1(5)	C(2B)-S(2B)-C(3B)	94.6(3)
C(6B)-C(5B)-S(3B)	116.7(4)	F(3A)-F(3B)-F(5A)	129.7(11)	F(5B)-P(1)-F(3A)	137.1(8)	C(5B)-S(5B)-C(7B)	101.7(2)

Salt [(*rac*)-**2**]PF_6•(C_4H_8O)

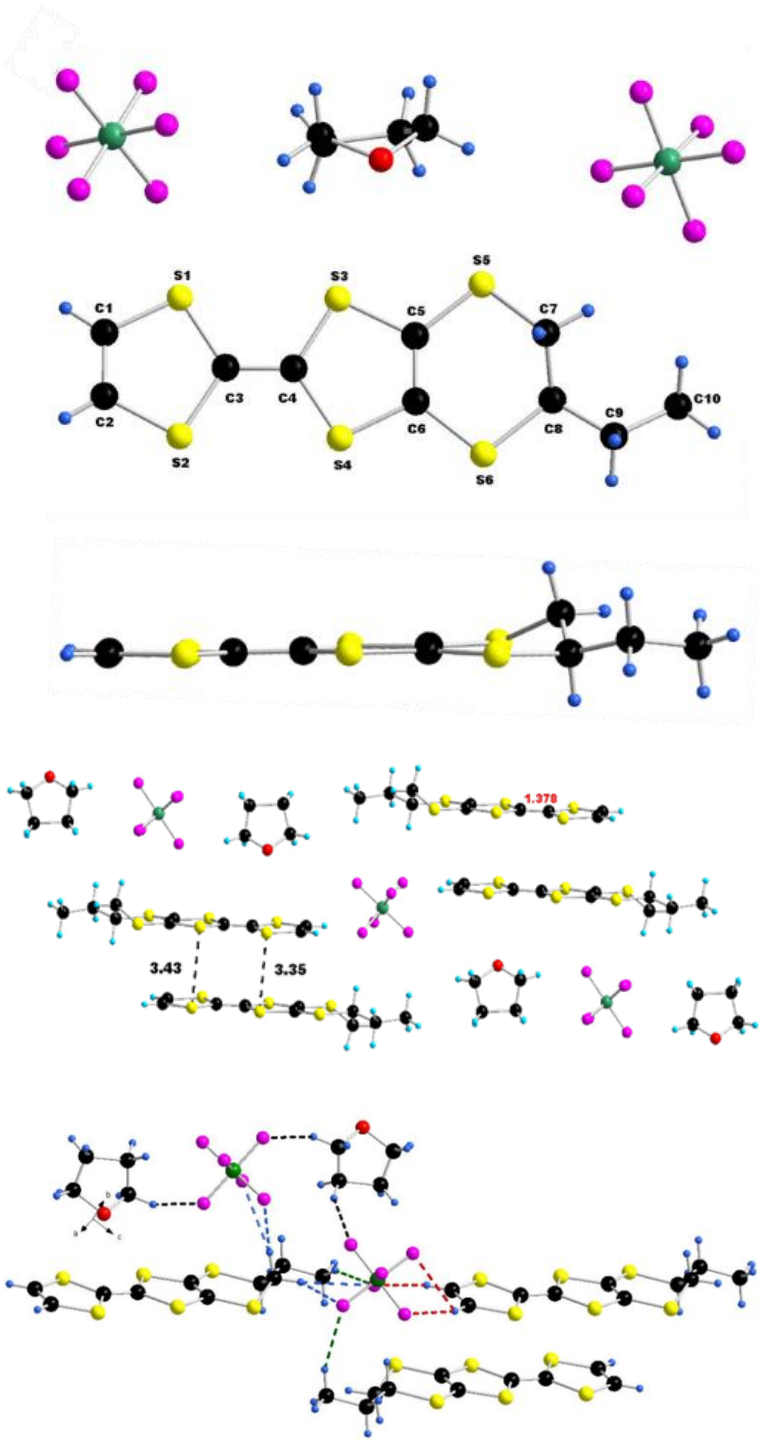


Fig. S16 Molecular structure of [(*rac*)-**2**]PF_6•(C_4H_8O) together with the atom numbering scheme (top), a side view of the donor (top middle), a packing diagram with intra-dimer short S···S distances highlighted (bottom middle) and focus of on the C–H···F short contacts: red dotted lines for CH_{vinyl} (2.37-2.56 and 2.83 Å), blue dotted lines for CH_2 (2.77-2.46 and 2.69 Å), green dotted lines for Me (2.75Å) and black dotted line for CH_2(THF) (2.50-2.73 Å).

Table S10. Selected lengths (Å) and angles (º) for [(*rac*)-**2**]PF_6•(C_4H_8O)

Bond lengths [Å]

S(4)-C(4)	1.717(4)	P(2)-F(4)#2	1.576(4)
S(4)-C(6)	1.737(4)	P(2)-F(4)	1.576(4)
S(3)-C(4)	1.716(4)	P(2)-F(5)#2	1.584(4)
S(3)-C(5)	1.737(4)	P(2)-F(5)	1.584(4)
S(2)-C(2)	1.717(5)	P(2)-F(6)	1.589(4)
S(2)-C(3)	1.720(4)	P(2)-F(6)#2	1.589(4)
S(1)-C(3)	1.722(4)	C(4)-C(3)	1.378(6)
S(1)-C(1)	1.727(5)	C(6)-C(5)	1.355(6)
S(5)-C(5)	1.736(4)	C(1)-C(2)	1.327(8)
S(5)-C(7)	1.827(6)	C(7)-C(8)	1.427(8)
S(6)-C(6)	1.737(4)	C(7)-C(9)	1.499(7)
S(6)-C(8)	1.796(7)	C(9)-C(10)	1.495(9)
P(1)-F(1)#1	1.579(4)	O(1)-C(11)	1.392(11)
P(1)-F(1)	1.579(4)	O(1)-C(12)	1.407(11)
P(1)-F(3)#1	1.586(4)	C(12)-C(14)	1.281(15)
P(1)-F(3)	1.586(4)	C(11)-C(13)	1.301(16)
P(1)-F(2)#1	1.586(3)	C(14)-C(13)	1.594(18)
P(1)-F(2)	1.586(3)		

Angles [°]

C(4)-S(4)-C(6)	95.92(19)	F(3)#1-P(1)-F(2)	90.2(2)
C(4)-S(3)-C(5)	95.8(2)	F(3)-P(1)-F(2)	89.8(2)
C(2)-S(2)-C(3)	95.7(2)	F(2)#1-P(1)-F(2)	180.000(1)
C(3)-S(1)-C(1)	95.1(2)	F(4)#2-P(2)-F(4)	180.00(7)
C(5)-S(5)-C(7)	102.5(2)	F(4)#2-P(2)-F(5)# 2	89.4(2)
C(6)-S(6)-C(8)	98.7(3)	F(4)-P(2)-F(5)#2	90.6(2)
F(1)#1-P(1)-F(1)	180.000(3)	F(4)#2-P(2)-F(5)	90.6(2)
F(1)#1-P(1)-F(3)# 1	88.7(3)	F(4)-P(2)-F(5)	89.4(2)
F(1)-P(1)-F(3)#1	91.3(3)	F(5)#2-P(2)-F(5)	180.000(2)
F(1)#1-P(1)-F(3)	91.3(3)	F(4)#2-P(2)-F(6)	89.7(2)
F(1)-P(1)-F(3)	88.7(3)	F(4)-P(2)-F(6)	90.3(2)
F(3)#1-P(1)-F(3)	180.000(3)	F(5)#2-P(2)-F(6)	89.6(3)
F(1)#1-P(1)-F(2)# 1	89.7(2)	F(5)-P(2)-F(6)	90.4(3)
F(1)-P(1)-F(2)#1	90.3(2)	F(4)#2-P(2)-F(6)# 2	90.3(2)
F(3)#1-P(1)-F(2)# 1	89.8(2)	F(4)-P(2)-F(6)#2	89.7(2)
F(3)-P(1)-F(2)#1	90.2(2)	F(5)#2-P(2)-F(6)# 2	90.4(3)
F(1)#1-P(1)-F(2)	90.3(2)	F(5)-P(2)-F(6)#2	89.6(3)
F(1)-P(1)-F(2)	89.7(2)	F(6)-P(2)-F(6)#2	180.000(1)

Salt [(*R*)-**2**]$_2$PF$_6$

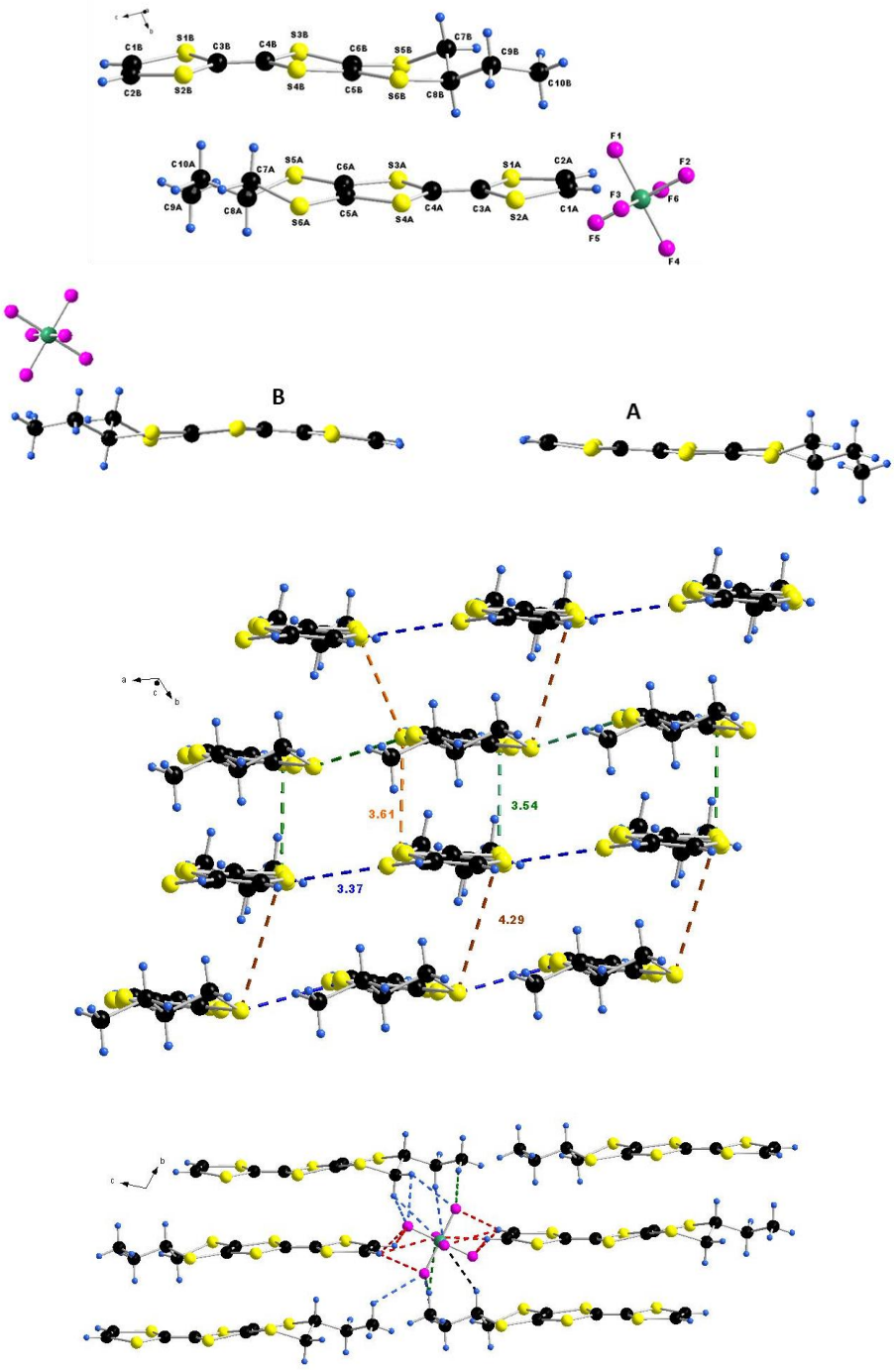


Fig. S17 Molecular structure of [(*R*)-**2**]$_2$PF$_6$ together with the atom numbering scheme (top), a side view of the donors (top middle), packing diagram highlighting short S···S contacts (bottom middle) and focus on the C–H···F short contacts: red dotted lines for CH_{vinyl} (2.62 - 2.73), blue dotted lines for CH_2 (2.58 - 2.84), green dotted lines for Me (2.65 -2.78 Å) and black dotted line for CH_{Me} (2.71 - 2.78 Å).

Table S11. Selected lengths (Å) and angles (º) for [(*R*)-**2**]$_2$PF$_6$

Bond lengths [Å]

P(1)-F(5)	1.574(4)	S(2A)-C(3A)	1.741(5)
P(1)-F(1)	1.582(4)	S(1A)-C(2A)	1.715(5)
P(1)-F(4)	1.582(4)	S(1A)-C(3A)	1.738(5)
P(1)-F(2)	1.585(4)	S(5A)-C(6A)	1.744(5)
P(1)-F(6)	1.598(3)	S(5A)-C(8A)	1.830(5)
P(1)-F(3)	1.603(3)	S(6B)-C(6B)	1.746(6)
C(9B)-C(10B)	1.522(8)	S(6B)-C(8B)	1.826(5)
C(9B)-C(8B)	1.558(7)	S(1B)-C(1B)	1.732(6)
C(7A)-C(8A)	1.500(7)	S(1B)-C(3B)	1.737(5)
C(7A)-S(6A)	1.813(6)	S(5B)-C(5B)	1.744(5)
C(10A)-C(9A)	1.544(7)	S(5B)-C(7B)	1.804(6)
S(3A)-C(4A)	1.735(5)	S(6A)-C(5A)	1.739(5)
S(3A)-C(6A)	1.755(5)	C(6A)-C(5A)	1.356(7)
S(4B)-C(4B)	1.745(5)	C(4B)-C(3B)	1.363(7)
S(4B)-C(6B)	1.759(5)	C(3A)-C(4A)	1.383(6)
S(4A)-C(4A)	1.730(5)	C(8A)-C(9A)	1.526(7)
S(4A)-C(5A)	1.754(5)	C(2B)-C(1B)	1.318(9)
S(3B)-C(5B)	1.740(6)	C(8B)-C(7B)	1.498(8)
S(3B)-C(4B)	1.744(5)	C(6B)-C(5B)	1.338(8)
S(2B)-C(2B)	1.736(6)	C(2A)-C(1A)	1.325(8)
S(2B)-C(3B)	1.742(5)		

Angles [°]

F(5)-P(1)-F(1)	89.2(3)	C(2B)-S(2B)-C(3B)	94.4(3)
F(5)-P(1)-F(4)	90.4(3)	C(1A)-S(2A)-C(3A)	94.6(2)
F(1)-P(1)-F(4)	179.1(3)	C(2A)-S(1A)-C(3A)	94.7(2)
F(5)-P(1)-F(2)	179.9(4)	C(6A)-S(5A)-C(8A)	102.4(2)
F(1)-P(1)-F(2)	90.7(3)	C(6B)-S(6B)-C(8B)	103.9(2)
F(4)-P(1)-F(2)	89.7(3)	C(1B)-S(1B)-C(3B)	94.3(2)
F(5)-P(1)-F(6)	90.15(18)	C(5B)-S(5B)-C(7B)	100.2(3)
F(1)-P(1)-F(6)	89.7(2)	C(5A)-S(6A)-C(7A)	100.7(2)
F(4)-P(1)-F(6)	89.5(2)	C(5A)-C(6A)-S(5A)	128.3(4)
F(2)-P(1)-F(6)	89.86(19)	C(5A)-C(6A)-S(3A)	116.6(4)
F(5)-P(1)-F(3)	90.03(18)	S(5A)-C(6A)-S(3A)	115.1(3)
F(1)-P(1)-F(3)	90.8(2)	C(3B)-C(4B)-S(3B)	122.2(4)
F(4)-P(1)-F(3)	90.0(2)	C(3B)-C(4B)-S(4B)	122.7(4)
F(2)-P(1)-F(3)	89.96(18)	S(3B)-C(4B)-S(4B)	115.0(3)
F(6)-P(1)-F(3)	179.5(2)	C(4B)-C(3B)-S(1B)	122.6(4)
C(10B)-C(9B)-C(8B)	112.1(4)	C(4B)-C(3B)-S(2B)	122.1(4)
C(8A)-C(7A)-S(6A)	115.5(4)	S(1B)-C(3B)-S(2B)	115.3(3)
C(4A)-S(3A)-C(6A)	95.3(2)	C(4A)-C(3A)-S(1A)	122.3(4)
C(4B)-S(4B)-C(6B)	94.9(2)	C(4A)-C(3A)-S(2A)	122.7(4)
C(4A)-S(4A)-C(5A)	95.2(2)	S(1A)-C(3A)-S(2A)	115.0(3)
C(5B)-S(3B)-C(4B)	94.8(2)	C(7A)-C(8A)-C(9A)	108.8(4)

Salt [(*S*)-**2**]$_2$PF$_6$

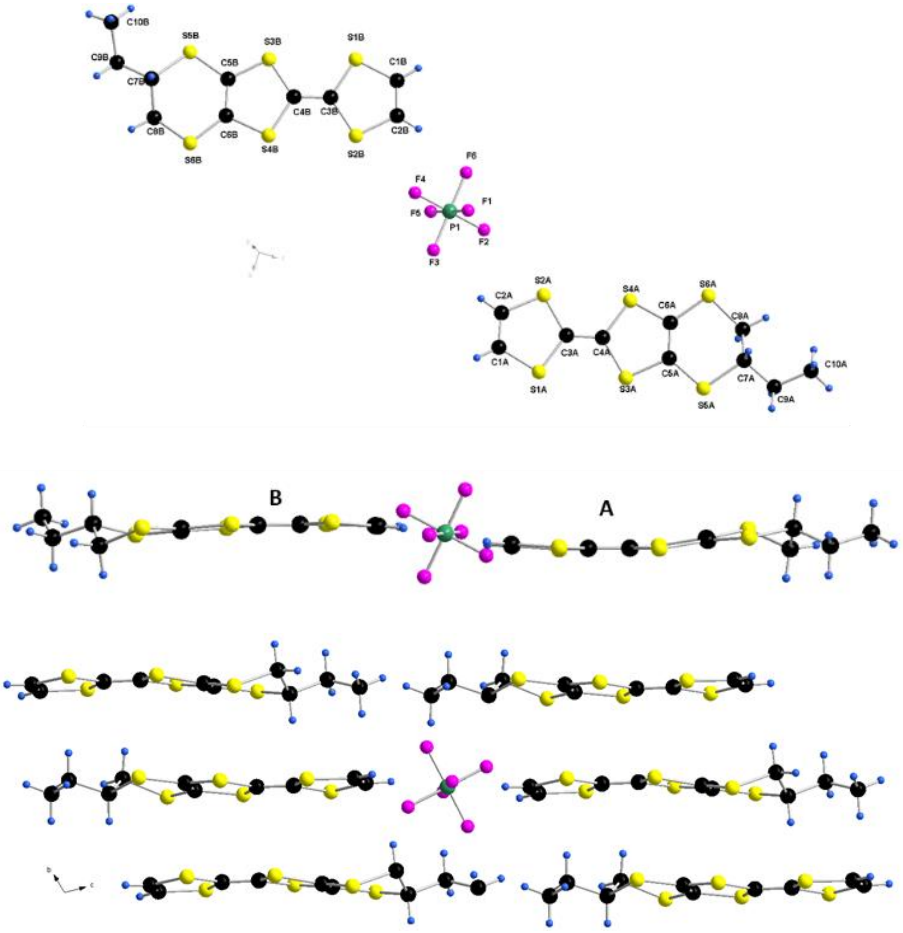


Fig. S18 Molecular structure of [(*S*)-**2**]$_2$PF$_6$ together with the atom numbering scheme (top), a side view of the donors (middle) and a packing diagram (bottom).

Table S12. Selected lengths (Å) and angles (º) for $[(S)\text{-}\mathbf{2}]_2PF_6$

Bond lengths [Å]

C(1A)-C(2A)	1.34(2)	C(3B)-C(4B)	1.369(16)
C(1A)-S(1A)	1.746(14)	C(3B)-S(1B)	1.732(14)
C(2A)-S(2A)	1.735(16)	C(3B)-S(2B)	1.751(13)
C(3A)-C(4A)	1.347(18)	C(4B)-S(4B)	1.763(12)
C(3A)-S(1A)	1.747(13)	C(6B)-C(5B)	1.42(2)
C(3A)-S(2A)	1.750(12)	C(6B)-S(6B)	1.711(14)
C(4A)-S(4A)	1.744(15)	C(6B)-S(4B)	1.764(13)
C(4A)-S(3A)	1.761(13)	C(5B)-S(3B)	1.693(14)
C(5A)-C(6A)	1.34(2)	C(5B)-S(5B)	1.763(13)
C(5A)-S(5A)	1.726(14)	C(7B)-C(8B)	1.502(19)
C(5A)-S(3A)	1.777(15)	C(7B)-C(9B)	1.524(17)
C(6A)-S(6A)	1.735(15)	C(7B)-S(5B)	1.855(14)
C(6A)-S(4A)	1.753(13)	C(9B)-C(10B)	1.54(2)
C(7A)-C(8A)	1.51(2)	C(8B)-S(6B)	1.810(12)
C(7A)-C(9A)	1.535(19)	F(1)-P(1)	1.578(10)
C(7A)-S(5A)	1.833(14)	F(2)-P(1)	1.573(9)
C(8A)-S(6A)	1.820(13)	F(3)-P(1)	1.596(8)
C(9A)-C(10A)	1.51(2)	F(4)-P(1)	1.589(9)
C(2B)-C(1B)	1.34(2)	F(5)-P(1)	1.588(10)
C(2B)-S(2B)	1.745(14)	F(6)-P(1)	1.601(8)
C(1B)-S(1B)	1.731(13)		

Angles [°]

C(2A)-C(1A)-S(1A)	116.7(11)	S(3B)-C(5B)-S(5B)	117.3(7)
C(1A)-C(2A)-S(2A)	118.6(11)	C(8B)-C(7B)-C(9B)	110.2(11)
C(4A)-C(3A)-S(1A)	122.8(10)	C(8B)-C(7B)-S(5B)	112.1(8)
C(4A)-C(3A)-S(2A)	122.1(10)	C(9B)-C(7B)-S(5B)	108.0(10)
S(1A)-C(3A)-S(2A)	115.2(7)	C(7B)-C(9B)-C(10B)	115.0(11)
C(3A)-C(4A)-S(4A)	122.8(10)	C(7B)-C(8B)-S(6B)	116.3(9)
C(3A)-C(4A)-S(3A)	122.6(11)	F(2)-P(1)-F(1)	90.5(7)
S(4A)-C(4A)-S(3A)	114.6(8)	F(2)-P(1)-F(5)	90.3(7)
C(6A)-C(5A)-S(5A)	130.7(11)	F(1)-P(1)-F(5)	178.9(7)
C(6A)-C(5A)-S(3A)	115.4(11)	F(2)-P(1)-F(4)	179.9(9)
S(5A)-C(5A)-S(3A)	113.9(8)	F(1)-P(1)-F(4)	89.6(7)
C(5A)-C(6A)-S(6A)	126.0(11)	F(5)-P(1)-F(4)	89.6(7)
C(5A)-C(6A)-S(4A)	118.7(11)	F(2)-P(1)-F(3)	89.5(5)
S(6A)-C(6A)-S(4A)	115.3(7)	F(1)-P(1)-F(3)	89.9(5)
C(8A)-C(7A)-C(9A)	111.0(11)	F(5)-P(1)-F(3)	90.7(5)
C(8A)-C(7A)-S(5A)	114.0(9)	F(4)-P(1)-F(3)	90.3(5)
C(9A)-C(7A)-S(5A)	104.0(10)	F(2)-P(1)-F(6)	90.0(5)
C(7A)-C(8A)-S(6A)	114.3(9)	F(1)-P(1)-F(6)	90.2(5)
C(10A)-C(9A)-C(7A)	112.2(12)	F(5)-P(1)-F(6)	89.2(5)
C(1B)-C(2B)-S(2B)	117.6(10)	F(4)-P(1)-F(6)	90.1(5)
C(2B)-C(1B)-S(1B)	117.2(10)	F(3)-P(1)-F(6)	179.5(5)
C(4B)-C(3B)-S(1B)	122.0(10)	C(1A)-S(1A)-C(3A)	95.0(7)
C(4B)-C(3B)-S(2B)	123.1(10)	C(2A)-S(2A)-C(3A)	94.4(7)
S(1B)-C(3B)-S(2B)	114.9(7)	C(4A)-S(3A)-C(5A)	95.5(7)
C(3B)-C(4B)-S(3B)	123.1(10)	C(4A)-S(4A)-C(6A)	95.2(6)
C(3B)-C(4B)-S(4B)	121.5(9)	C(5A)-S(5A)-C(7A)	103.8(7)
S(3B)-C(4B)-S(4B)	115.4(7)	C(6A)-S(6A)-C(8A)	100.2(6)
C(5B)-C(6B)-S(6B)	131.6(10)	C(2B)-S(2B)-C(3B)	94.5(6)
C(5B)-C(6B)-S(4B)	113.3(9)	C(1B)-S(1B)-C(3B)	95.6(6)
S(6B)-C(6B)-S(4B)	115.1(9)	C(4B)-S(4B)-C(6B)	95.9(6)
C(6B)-C(5B)-S(3B)	119.1(9)	C(5B)-S(3B)-C(4B)	96.4(6)
C(6B)-C(5B)-S(5B)	123.6(10)	C(5B)-S(5B)-C(7B)	104.6(6)
		C(6B)-S(6B)-C(8B)	100.8(7)

Conductivity measurements

Electrical resistivity was measured on needle-shaped single crystals 0.3-0.5 mm long. Gold wires were glued with silver paste directly on both ends of the crystals. Only one crystal of [(*rac*)-**1**]$_2$PF$_6$ could be measured in four contacts using an AC current of 10µA and low-frequency (< 100 Hz) lock-in detection. Different techniques were used to measure resistivity in two points, either applying a DC current (1 - 0.1 µA) and measuring the voltage with a Keithley 2401 microvoltmeter (data in Figures 2-S19) or, for higher resistance values, applying a constant voltage of 0.1 - 0.2 V (data in Figures S21-S22) or 10 V (data in Figure S20) and measuring the current using a Keithley 6487 Picoammeter/Voltage Source. We have checked for each crystal that both techniques give the same resistance value at room temperature. Low temperature was provided by a homemade cryostat equipped with a 4 K pulse-tube.

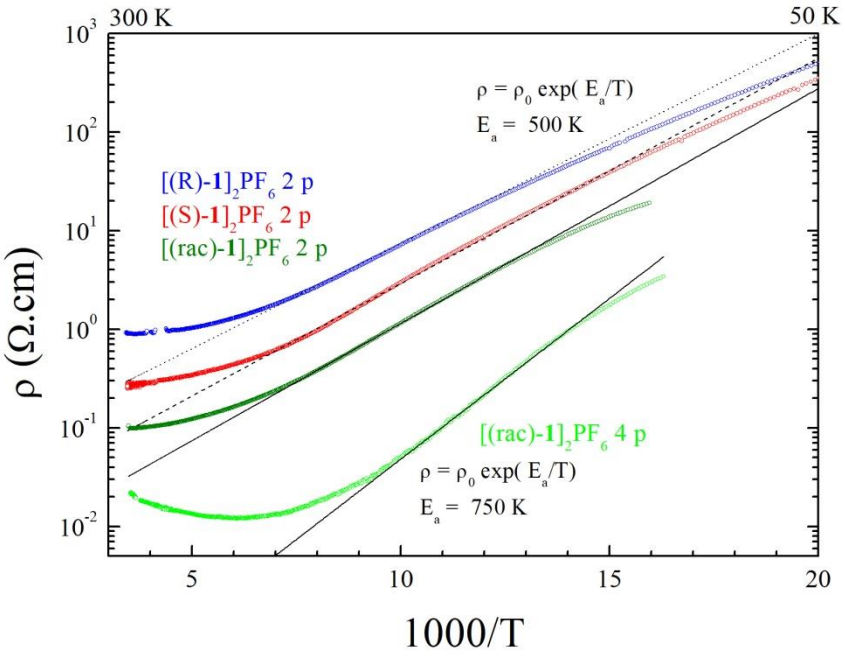


Fig. S19 Temperature dependence of the electrical resistivity plotted as log ρ *versus* 1000/T for two single crystals of [(*rac*)-**1**]$_2$PF$_6$ (green data points) measured in 4 points and 2 points, for a single crystal of [(*S*)-**1**]$_2$PF$_6$ (red data points) measured in 2 points and a single crystal of [(*R*)-**1**]$_2$PF$_6$ (blue data points) measured in 2 points. The black lines are the linear fit giving the activation energy from the law $\rho = \rho_0 \exp(E_a/T)$ below 150 K.

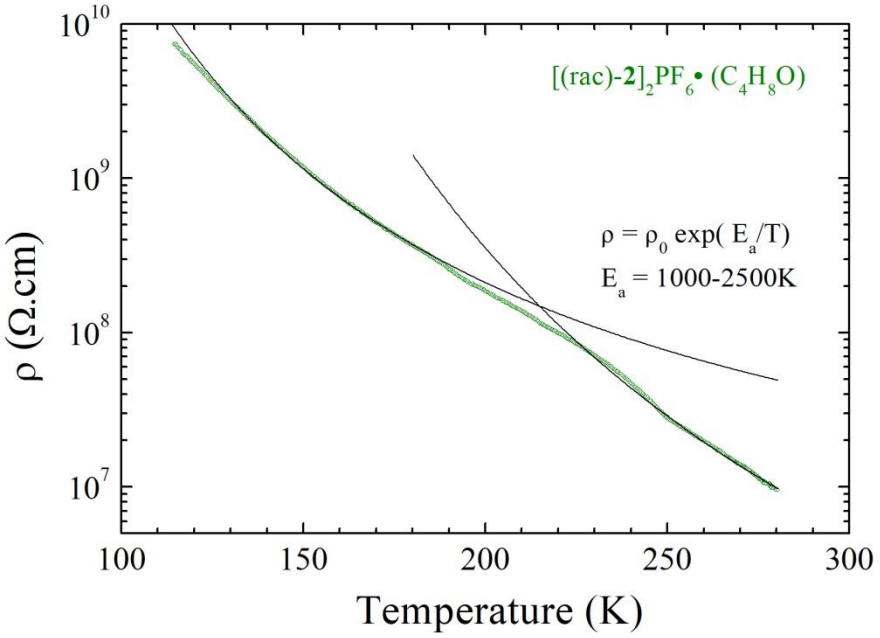


Fig. S20 Temperature dependence of the electrical resistivity ρ for a single crystal of [(*rac*)-**2**]PF_6•(C_4H_8O).

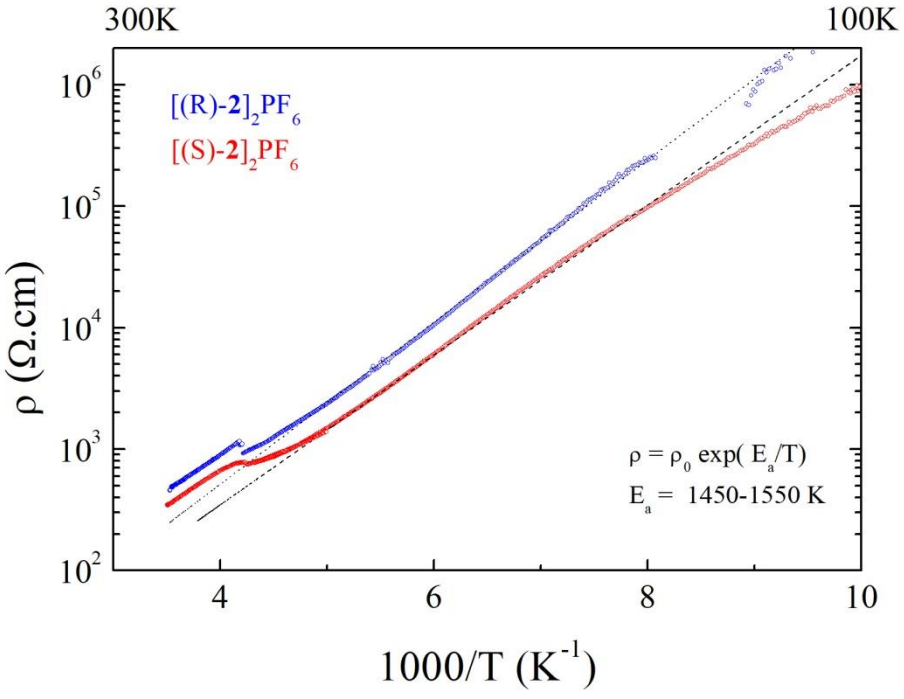


Fig. S21 Temperature dependence of the electrical resistivity plotted as log ρ *versus* 1000/T for a single crystal of [(*S*)-**2**]$_2PF_6$ (red data points) and a single crystal of [(*R*)-**2**]$_2PF_6$ (blue data points). The black lines are the linear fit to the data giving the activation energy.

Band structure calculations

The tight-binding band structure calculations were of the extended Hückel type.[1] A modified Wolfsberg-Helmholtz formula was used to calculate the non-diagonal $H_{\mu\nu}$ values.[2] All valence electrons were taken into account in the calculations and the basis set consisted of Slater-type orbitals of double-ζ quality for C 2s and 2p, S 3s and 3p and of single-ζ quality for H. The ionization potentials, contraction coefficients and exponents were taken from previous work.[3]

Electronic structure for the [(*S*)-**2**]$_2$PF$_6$ salt

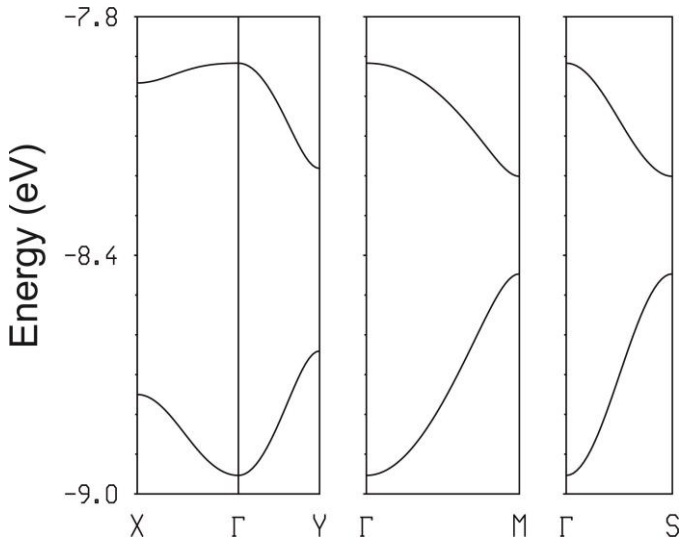


Fig. S22 Calculated band structure for the donor layers of [(*S*)-**2**]$_2$PF$_6$ where Γ = (0, 0), X = (*a**/2, 0), Y = (0, *b**/2), M = (*a**/2, *b**/2) and S = (-*a**/2, *b**/2).

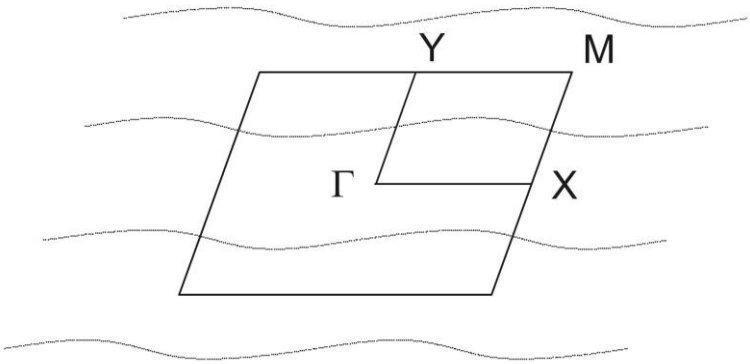


Fig. S23 Calculated Fermi surface for the hypothetical metallic state of [(*R*)-**2**]$_2$PF$_6$ where Γ = (0, 0), X = (*a**/2, 0), Y = (0, *b**/2), M = (*a**/2, *b**/2) and S = (-*a**/2, *b**/2).

References

1 M.-H. Whangbo and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 6093-6098.

2 J. H. Ammeter, H.-B. Bürgi, J. Thibeault and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686-3692.

3 A. Pénicaud, K. Boubekeur, P. Batail, E. Canadell, P. Auban-Senzier, D. Jérome, *J. Am. Chem. Soc.*, 1993, **115**, 4101-4112.