magnetochemistry

Supplementary Materials: Chiral Radical Cation Salts of Me-EDT-TTF and DM-EDT-TTF with Octahedral, Linear and Tetrahedral Monoanions †

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† Dedicated to the memory of Professor Peter Day.

Single crystal X-ray crystallography

Table S1. Crystal Data and Structure Refinement for [(*rac*)-**1**]$_2$AsF$_6$, [(*S*)-**1**]$_2$AsF$_6$ and [(*R*)-**1**]$_2$AsF$_6$.

	[(*rac*)-1]$_2$AsF$_6$	**[(*S*)-1]$_2$AsF$_6$**	**[(*R*)-1]$_2$AsF$_6$**
formula	$C_{18}H_{16}AsF_6S_{12}$	$C_{18}H_{16}AsF_6S_{12}$	$C_{18}H_{16}AsF_6S_{12}$
M [g mol^{-1}]	805.95	805.95	805.95
T [K]	150.01(10)	293(2)	149.9(5)
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P1$	$P1$
a [Å]	6.6856(4)	6.6936(2)	6.690(5)
b [Å]	13.4236(7)	8.4895(3)	8.486(5)
c [Å]	8.4692(4)	13.4079(5)	13.366(5)
α [°]	92.809(4))	92.746(3)	92.550(5)
β [°]	90.048(4	90.233(3)	90.285(5)
γ [°]	113.180(4)	113.000(3)	112.966(5)
V [Å^3]	697.70(7)	700.32(4)	697.8(7)
Z	1	1	1
ϱ_{calcd}[g/cm^3]	1.918	1.911	1.918
μ [mm^{-1}]	10.541	10.502	10.540
Flack parameter	-	0.14(4)	0.490(13)
goodness-of-fit on F^2	1.044	1.102	1.093
final[a] R1/wR2 [I > 2σ(I)]	0.0322/ 0.0838	0.0436/ 0.1197	0.0947/ 0.2447
R1/wR2 (all data)	0.0336/ 1.044	0.0443/ 0.1226	0.0953/ 0.2451
CCDC number	2085699	2085700	2085701

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

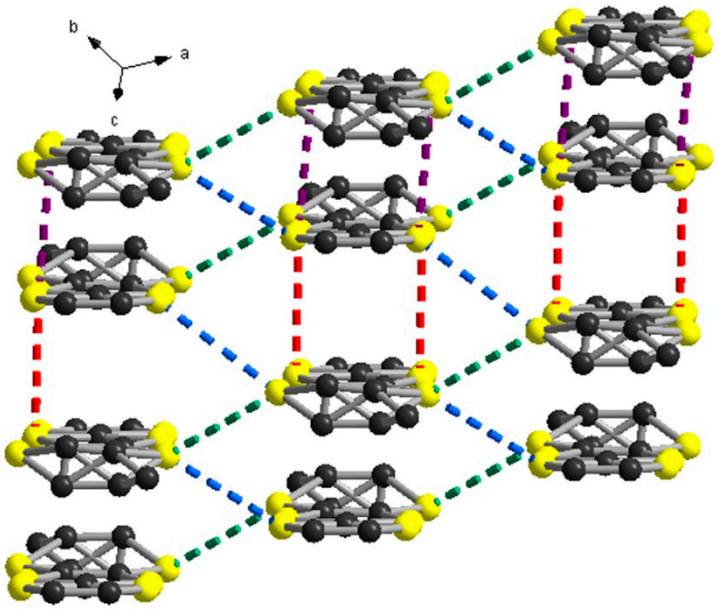

Figure S1. Layer of donors in the packing of [(*rac*)-**1**]$_2$AsF$_6$ with an emphasis on the S···S short contacts: red dotted lines (3.58 Å), purple dotted lines (3.61 Å), blue dotted lines (3.59-3.66 Å) and green dotted lines (3.65 Å).

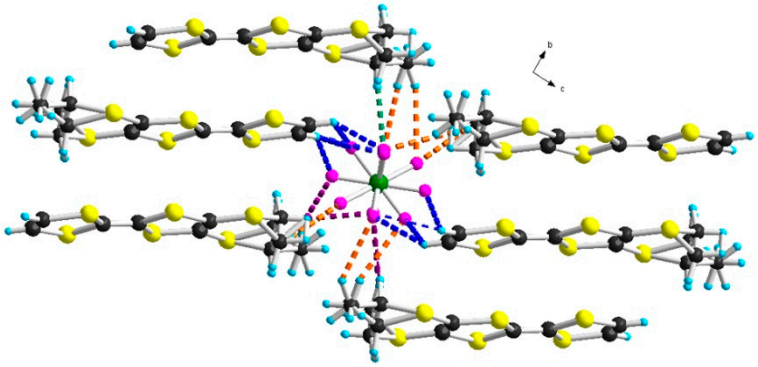

Figure S2. C–H···F short contacts in the packing of [(*rac*)-**1**]$_2$AsF$_6$ (see Table S2).

Table S2. C–H···F hydrogen bonding distances (Å) and angles in [(*rac*)-**1**]$_2$AsF$_6$.

[(*rac*)-1]$_2$AsF$_6$				
type	**C—H—F**	**d (H—F) Å**	**d(C—F) Å**	**<(C—H—F) °**
CH $_{vinyl}$	**C2— H2—F7**	2.5832(27)	3.3915(48)	145.60°
	C1—H1—F6B	2.4605(129)	2.9989(141)	116.95°
CH$_2$	**C8B—H8D—F7**	2.4600(29)	3.4165(105)	168.77°
CH$_3$	**C9— H9C—F5A**	2.4460(53)	3.3998(79)	172.17°
	C9— H9E—F5A	2.6560(51)	3.3998(79)	134.62°
	C9— H9D—F5	2.6352(81)	3.1301(93)	112.42°
CH	**C7B— H7B—F7**	2.4301(30)	3.3458(131)	155.14°

Table S3. C–H···F hydrogen bonding distances (Å) and angles in [(*S*)-**1**]$_2$AsF$_6$.

[(*S*)-1]$_2$AsF$_6$				
type	**C—H—F**	**d (H—F) Å**	**d(C—F) Å**	<(C—H—F) °
CH $_{vinyl}$	**C1A— H1A—F1**	2.4476(92)	3.240(13)	143.22°
	C2B—H2B—F4B	2.4035(83)	3.172(13)	139.92°
	C2B—F5—H2B	2.6102(55)	3.4119(11)	144.74°
CH$_2$	**C8A— H8A—F4B**	2.4970(76)	3.0937(96)	119.67°
CH$_3$	**C9A— H9A—F4A**	2.4246(155)	3.0948(209)	126.58°
	C9B— H9B—F1	2.5534(70)	3.4288(111)	151.61°
CH	**C7A—H7A—F5**	2.5367(64)	3.4622(97)	157.60°

Table S4. Crystal Data and Structure Refinement for [(*S*)-**1**]AsF$_6$·C$_4$H$_8$O and [(*R*)-**1**]AsF$_6$·C$_4$H$_8$O.

	[(*S*)-1]AsF$_6$·C$_4$H$_8$O	**[(*R*)-1]AsF$_6$·C$_4$H$_8$O**
Formula	C$_{13}$H$_{16}$AsF$_6$OS$_6$	C$_{13}$H$_{16}$AsF$_6$OS$_6$
M [g mol^{-1}]	569.54	569.54
T [K]	200.01(10)	150.00(10)
Crystal system	triclinic	triclinic
Space group	*P*1	*P*1
a [Å]	8.0199(2)	7.9786(2)
b [Å]	9.0833(3)	9.0196(3)
c [Å]	15.2242(4)	15.2555(5)
α [°]	103.145(2)	103.368(3)
β [°]	101.063(2)	100.887(2)
γ [°]	100.814(2)	100.873(2)
V [Å^3]	1028.41(5)	1017.40(6)
Z	2	2
ϱ_{calcd}[g/cm^3]	1.839	1.859
μ [mm^{-1}]	8.475	8.567
Flack parameter	0.06(5)	0.05(5)
goodness-of-fit on F^2	1.067	1.034
final[a] R1/*w*R2 [I > 2σ(I)]	0.0427/ 0.1126	0.0418/ 0.1050
R1/*w*R2 (all data)	0.0444/ 0.1144	0.0440/ 0.1069
CCDC number	2085702	2085703

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

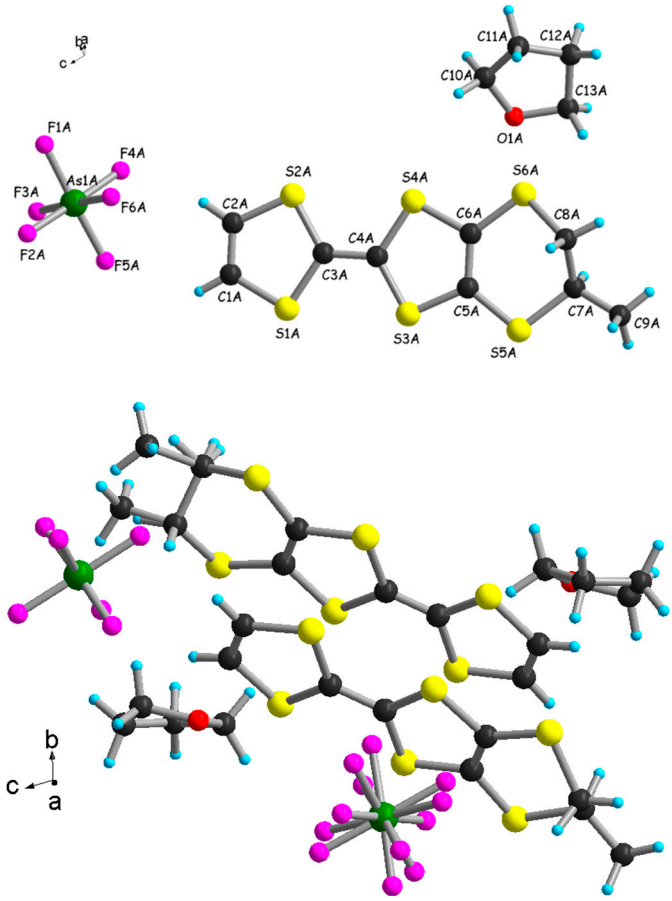

Figure S3. View of the ordered donor molecule and anion in the crystal structure of [(*R*)-**1**]$AsF_6 \cdot C_4H_8O$ (top); Molecular structure of [(*R*)-**1**]$AsF_6 \cdot C_4H_8O$. C9B atom is disordered over two positions A (s.o.f. 0.72) and B (s.o.f. 0.28). F1B-F6B atoms are disordered over two positions A (s.o.f. 0.51) and B (s.o.f. 0.49) (bottom).

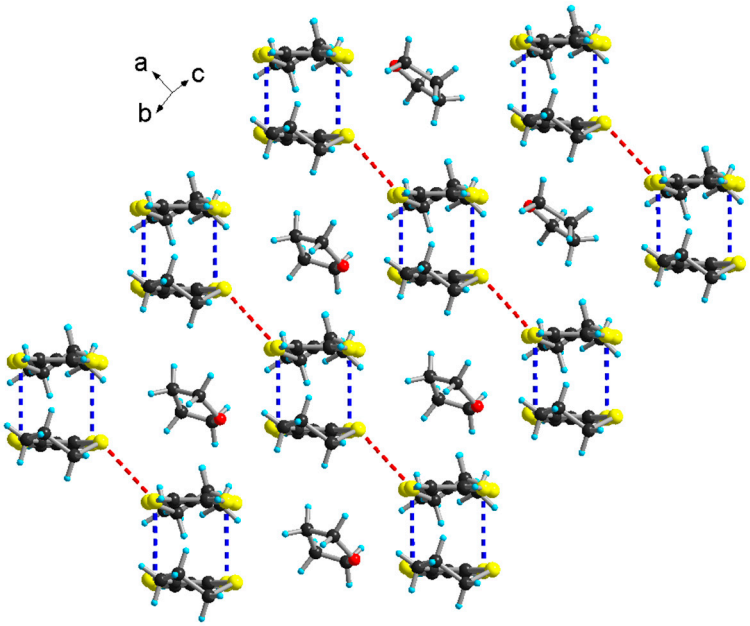

Figure S4. Packing of the donors in the structure of [(*S*)-**1**]$AsF_6 \cdot C_4H_8O$ with emphasis on the S···S short contacts: blue dotted lines for (3.33 – 3.37 Å), red dotted lines for (3.59 – 3.66 Å). THF molecules are also shown.

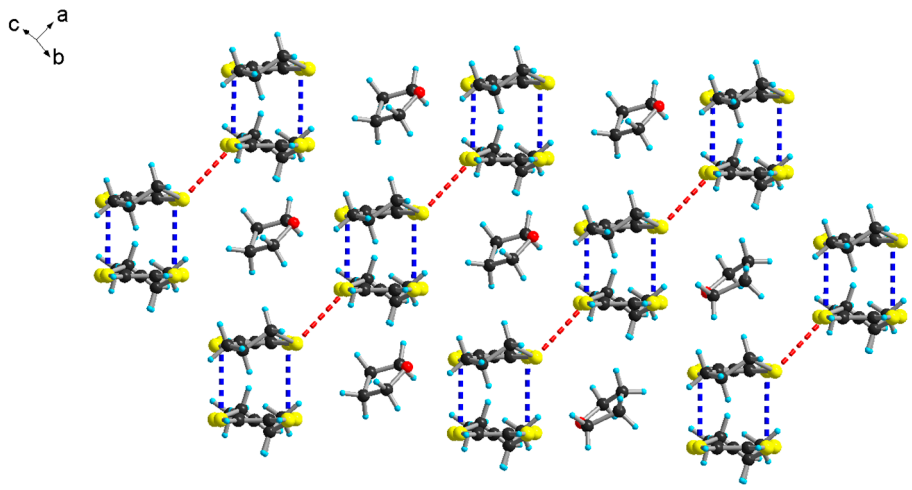

Figure S5. Packing of the donors in the structure of [(*R*)-**1**]$AsF_6 \cdot C_4H_8O$ with emphasis on the S···S short contacts: blue dotted lines for (3.31 – 3.37 Å), red dotted lines for (3.58 – 3.63 Å). THF molecules are also shown.

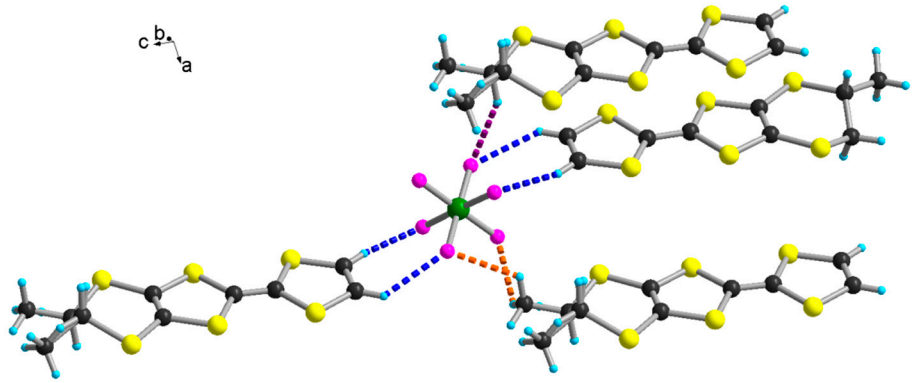

Figure S6. View of the structure of [(*R*)-**1**]$AsF_6 \cdot C_4H_8O$ with an emphasis on the C–H···F short contacts: blue dotted lines for CH_{vinyl} (2.41 – 2.62 Å), orange dotted lines for Me (2.59 – 2.62 Å), violet dotted line for CH (2.65 Å).

Table S5. C–H···F hydrogen bonding distances (Å) and angles in [(*S*)-**1**]$AsF_6 \cdot C_4H_8O$.

[(*S*)-1]$AsF_6 \cdot C_4H_8O$				
type	***C—H—F***	***d (H—F) Å***	***d(C—F) Å***	*<(C—H—F) °*
CH vinyl	***C1A—H1A—F3A***	*2.6243(82)*	*3.3354(126)*	*133.660(671)*
	C2A—H2A—F4A	*2.4045(81)*	*3.3141(118)*	*165.769(706)*
	C1B—H1B—F2A	*2.4132(85)*	*3.3357(130)*	*171.626(715)*
	C2B—H2B—F1A	*2.6367(76)*	*3.2539(12)*	*124.394(656)*
CH	***C7B—H7BA—F3A***	*2.6544(105)*	*3.5174(190)*	*147.960(926)*
CH_2 (THF)	***C12A—H12A—F5A***	*2.6644(100)*	*3.5232(208)*	*147.387(1095)*
CH_3	***C9BA—H9BA—F1A***	*2.5907(100)*	*3.0595(256)*	*110.453(1273)*
	C9BA—H9BB—F6A	*2.6216(126)*	*3.2682(256)*	*124.925(1271)*

Table S6. C–H···F hydrogen bonding distances (Å) and angles in [(*R*)-**1**]$AsF_6 \cdot C_4H_8O$.

[(*R*)-1]$AsF_6 \cdot C_4H_8O$				
type	***C—H—F***	***d (H—F) Å***	***d(C—F) Å***	*<(C—H—F) °*

CH *vinyl*	***C1A—H1A—F5A***	*2.5610(84)*	*3.2645(130)*	*132.794(671)*
	C2A—H2A—F4A	*2.4001(80)*	*3.3070(129)*	*164.947(779)*
	C1B—H1B—F2A	*2.3966(79)*	*3.3183(117)*	*171.163(687)*
	C2B—H2B—F1A	*2.6133(83)*	*3.2453(126)*	*125.717(670)*
CH	***C7B—H7BB—F5A***	*2.6496(110)*	*3.5030(194)*	*146.915(931)*
CH₃	***C9BA—H9BA—F1A***	*2.5842(114)*	*3.0055(254)*	*106.945(1187)*
	C9BA—H9BC—F6A	*2.6127(109)*	*3.2496(243)*	*123.904(1234)*

Table S7. Crystal Data and Structure Refinement for [(*rac*)-**1**]I_3, [(*S*)-**1**]I_3 and [(*R*)-**1**]I_3.

	[(*rac*)-1]I_3	**[(*S*)-1]I_3**	**[(*R*)-1]I_3**
formula	$C_9H_8I_3S_6$	$C_{18}H_{16}I_6S_{12}$	$C_{18}H_{16}I_6S_{12}$
M [g mo^{-1}]	689.21	1378.43	1378.43
T [K]	187(50)	286(13)	150.01(10)
crystal system	Triclinic	Triclinic	Triclinic
space group	*P*–1	*P* 1	*P* 1
a [Å]	8.9803(16)	9.0826(6)	9.023(2)
b [Å]	9.0821(16)	9.0886(7)	9.045(2)
c [Å]	12.634(2)	12.7544(9)	12.728(3)
α [°]	84.646(15)	71.788(7)	71.75(3)
β [°]	73.354(16)	85.360(6)	85.05(3)
γ [°]	60.631(19)	60.966(8)	60.57(3)
V [Å^3]	859.0(3)	871.25(13)	856.3(4)
Z	2	1	1
ϱ_{calcd}[g/cm^3]	2.665	2.627	2.673
μ [mm^{-1}]	49.531	48.834	49.684
Flack parameter	-	0.054(13)	0.061(17)
goodness-of-fit on F^2	1.103	1.062	1.039
final[a] R1/*w*R2 [I > 2σ(I)]	0.1084/ 0.2952	0.0545/0.1481	0.0577/ 0.1606
R1/*w*R2 (all data)	0.1587/ 0.3612	0.0617/0.1580	0.0693/ 0.1705
CCDC number	2085704	2085705	2085706

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

Table S8. Selected C=C and C–S internal bond lengths for [(*S*)-**1**]I_3.

	Bond lengths (Å)	
A	**C3A—C4A**	1.41(3)
	S1A—C3A	1.697(19)
	S2A—C3A	1.71(2)
	S3A—C4A	1.723(19)
	S4A—C4A	1.721(19)
B	**C4B—C3B**	1.38(3)
	S1B—C3B	1.74(2)
	S2B—C3B	1.72(2)
	S3B—C4B	1.713(19)
	S4B—C4B	1.72(2)

Table S9. Crystal Data and Structure Refinement for [(*rac*)-**2**]I_3, [(*S,S*)-**2**]I_3 and [(*R,R*)-**2**]I_3.

	[(*rac*)-2]I_3	**[(*S,S*)-2]I_3**	**[(*R,R*)-2]I_3**
formula	$C_{10}H_{10}S_6I_3$	$C_{20}H_{20}I_6S_{12}$	$C_{10}H_{10}S_6I_3$
M [g mo^{-1}]	703.24	1406.48	703.24
T [K]	293(2)	293(2)	293(2)
crystal system	Triclinic	Triclinic	Triclinic
space group	P–1	P1	P1
a [Å]	7.6086(2)	7.6146(9)	7.6112(7)
b [Å]	11.2297(5)	11.2273(11)	11.1976(6)
c [Å]	11.6074(4)	11.6249(11)	11.6449(9)
α [°]	72.975(3)	73.037(9)	73.117(5)
β [°]	89.161(3)	89.070(10)	88.944(7)
γ [°]	88.603(2)	88.536(8)	88.405(4)
V [Å^3]	947.99(6)	950.24(18)	949.26(12)
Z	2	1	2
ϱ_{calcd}[g/cm^3]	2.464	2.458	2.460
μ [mm^{-1}]	5.591	5.578	5.584
Flack parameter	-	0.41(10)	0.08(4)
goodness-of-fit on F^2	1.060	1.029	1.031
final[a] R1/*w*R2 [I > 2σ(I)]	0.0307 / 0.0598	0.0494 / 0.1046	0.0274 / 0.0472
R1/*w*R2 (all data)	0.0608 / 0.0702	0.1294 / 0.1242	0.0651 / 0.0557
CCDC number	2085707	2085708	2085709

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

Table S10. Selected C=C and C–S internal bond lengths for (**2**)I_3.

Bond	**Bond lengths (Å)**		
	[(*rac*)-2]I_3	**[(*S,S*)-2]I_3**	**[(*R,R*)-2]I_3**
C3—C4	1.390(4)	1.43(4), 1.38(4)	1.37(3), 1.42(2)
S1—C3	1.720(3)	1.86(3), 1.87(3)	1.72(2), 1.710(18)
S2—C3	1.728(3)	1.57(3), 1.59(3)	1.733(19), 1.738(19)
S3—C4	1.715(3)	1.78(3), 1.83(4)	1.731(18), 1.691(19)
S4—C4	1.724(3)	1.63(3), 1.64(4)	1.74(2), 1.712(18)

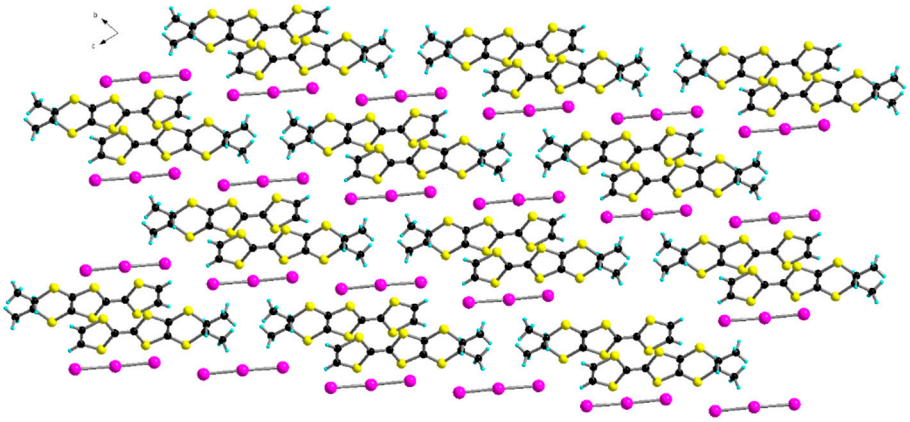

Figure S7. View in the *bc* plane of the packing within [(*rac*)-**2**]I_3.

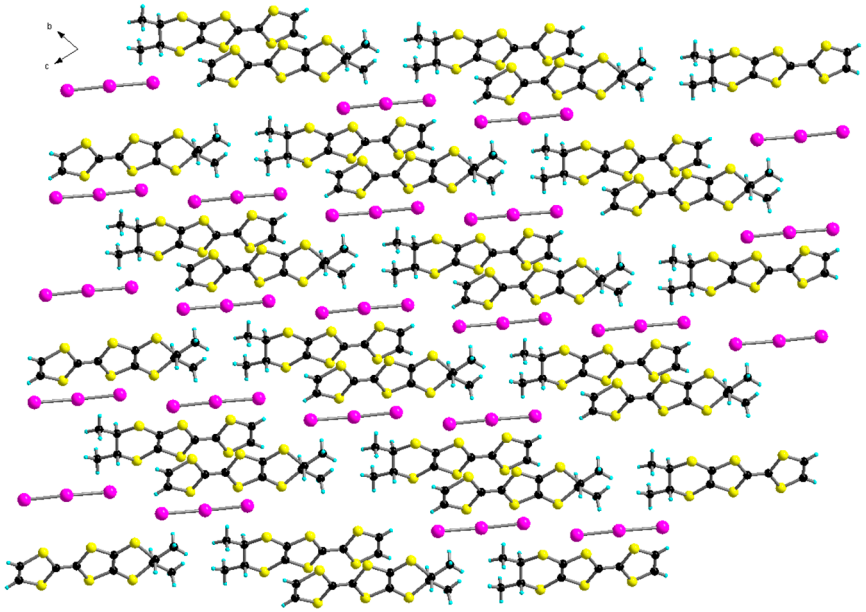

Figure S8. View in the *bc* plane of the packing within [(*R*,*R*)-**2**]I_3.

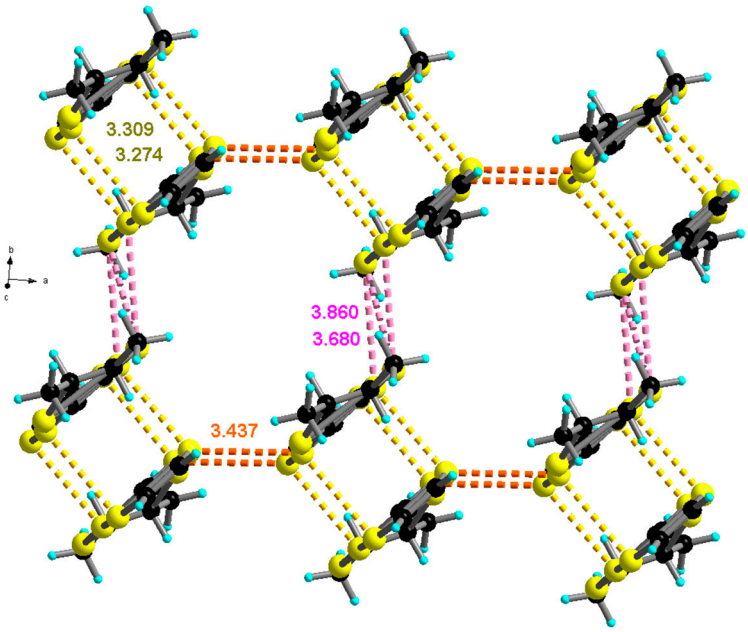

Figure S9. Packing of the donors and highlight of the S···S short contacts for [(*rac*)-**2**]I_3. The anions are not shown.

Table S11. Crystal Data and Structure Refinement for (*meso*)-**2**, [(*meso*)-**2**]ClO_4, [(*meso*)-**2**]PF_6 and [(*meso*)-**2**]ReO_4.

	(*meso*)-2	**[(*meso*)-2]ClO_4**	**[(*meso*)-2]PF_6**	**[(*meso*)-2]ReO_4**
formula	$C_{10}H_{10}S_6$	$C_{10}H_{10}ClO_4S_6$	$C_{10}H_{10}F_6PS_6$	$C_{10}H_{10}O_4ReS_6$
M [g mo^{-1}]	322.54	421.99	467.51	572.74
T [K]	150.00(10)	153.26(10) K	150.00(10)	150.00(10)
crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
space group	$P2_1/c$	P–1	$P2_1/n$	P–1
a [Å]	8.4110(3)	6.4793(6)	6.5671(2)	6.5583(3)

b [Å]	16.6502(6)	10.7956(8)	11.1233(4)	10.5579(5)
c [Å]	9.5635(3)	10.8754(16)	22.4614(8)	11.4661(9)
α [°]	90	92.826(9)	90	96.326(5)
β [°]	93.903(3)	94.844(1)	97.469(3)	96.382(5)
γ [°]	90	91.178(6)	90	92.742(4)
V [Å^3]	1336.21(8)	756.84(14)	1626.84(10)	782.76(8)
Z	4	2	4	2
ϱ_{calcd}[g/cm^3]	1.603	1.852	1.909	2.430
μ [mm^{-1}]	9.198	10.090	9.243	22.776
goodness-of-fit on F^2	1.028	1.121	1.414	1.150
final[a] R1/*w*R2 [I > 2σ(I)]	0.0427/ 0.1122	0.1434/ 0.4072	0.0683/ 0.1122	0.0594/ 0.1591
R1/*w*R2 (all data)	0.0514/ 0.1200	0.1612/ 0.4150	0.1039/ 0.2979	0.0669/ 0.1670
CCDC number	2085710	2085711	2085712	2085713

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

Table S12. Selected C=C and C–S internal bond lengths for (*meso*)-**2**, [(*meso*)-**2**]ClO_4, [(*meso*)-**2**]PF_6 and [(*meso*)-**2**]ReO_4.

	Bond lengths (Å)			
bond	**(*meso*)-2**	**[(*meso*)-2]ClO_4**	**[(*meso*)-2]PF_6**	**[(*meso*)-2]ReO_4**
C3—C4	1.339(5)	1.40(2)	1.387(6)	1.407(18)
S1—C3	1.750(3)	1.716(18)	1.721(5)	1.731(13)
S2—C3	1.763(3)	1.715(17)	1.715(4)	1.703(14)
S3—C4	1.758(3)	1.697(17)	1.720(4)	1.701(13)
S4—C4	1.759(3)	1.749(17)	1.717(4)	1.729(12)

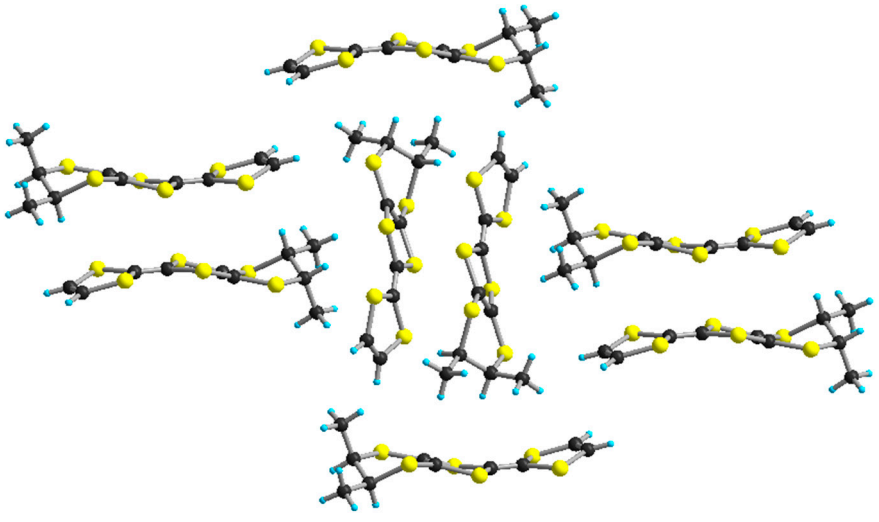

Figure S10. Packing diagram for (*meso*)-**2**.

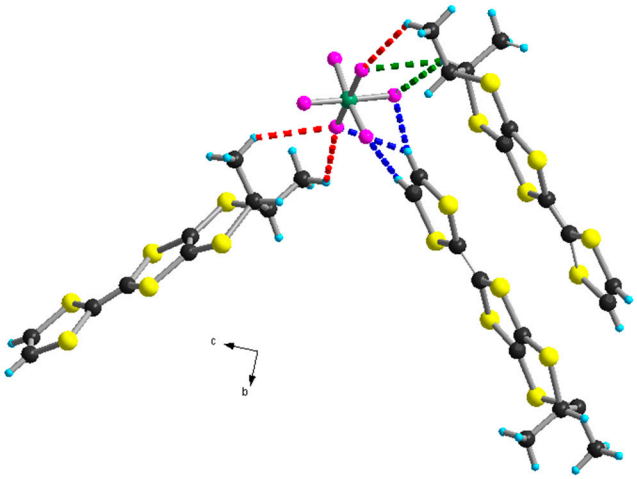

Figure S11. Solid state structure of [(*meso*)-**2**]PF_6 with an emphasis on the C–H···F short contacts: blue dotted lines for CH vinyl (2.32 – 2.36Å), red dotted lines for Me (2.53 – 2.65 – 2.72 Å) and green dotted lines for H_{CH} (2.45 – 2.65 Å).

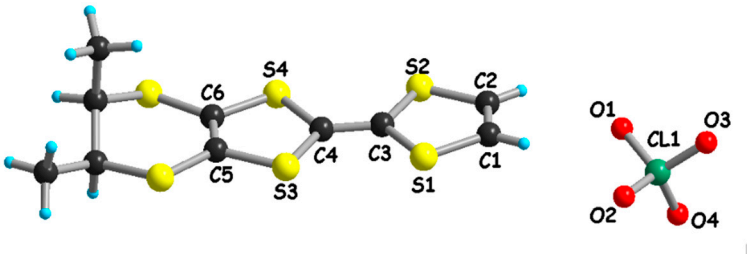

Figure S12. Molecular structure of [(*meso*)-**2**]ClO_4.

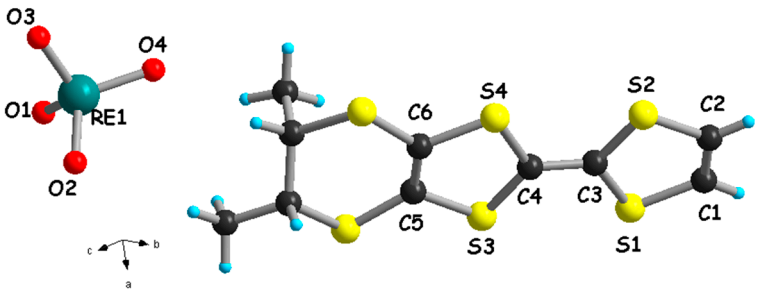

Figure S13. Molecular structure of [(*meso*)-**2**]ReO_4.

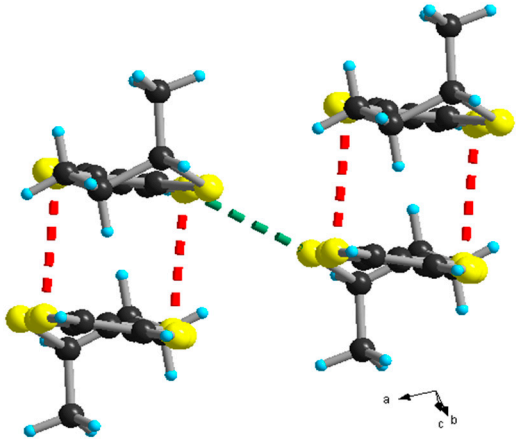

Figure S14. Packing diagram for [(*meso*)-**2**]ReO_4 with an emphasis on short S···S interactions. Red dotted lines (3.29 Å) and green dotted lines (3.37 Å).