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#### Supporting information for

# Anion size control of the packing in the metallic versus semiconducting chiral radical cation salts (DM-EDT-TTF)<sub>2</sub>XF<sub>6</sub> (X = P, As, Sb)

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# Synthesis of the salts

 $[(S,S)-1]_2XF_6$ . 5 equiv. of  $[(n-Bu)_4N]XF_6$  (X = As, Sb) (33 mg for AsF<sub>6</sub> and 37 mg for SbF<sub>6</sub>) were dissolved in 6 mL CHCl<sub>3</sub> and the solution was poured into the cathodic compartment of the electrocrystallization cell. The anodic chamber was filled with 5 mg of [(S,S)-1] dissolved in 6 mL CHCl<sub>3</sub>. Single crystals of triclinic  $[(S,S)-1]_2SbF_6$ , as thin brown plates, grown in solution at 20 °C during two weeks by applying a constant current of 0.5  $\mu$ A on a platinum wire electrode. For the AsF<sub>6</sub><sup>-</sup> anion three crystalline phases were collected in the same conditions as above: triclinic  $[(S,S)-1]_2AsF_6$  (thin brown plates in solution), monoclinic  $[(S,S)-1]_4(AsF_6)_2$  (green plates on the electrode) and monoclinic  $[(S,S)-1]_2(AsF_6)_2$  (several black prisms in solution).

 $[(R,R)-1]_2XF_6$ . Same conditions and amounts as previously described were employed.

 $[(rac)-1]_2XF_6$ . 5 equiv. of  $[(n-Bu)_4N]XF_6$  (X = As, Sb) (33 mg for AsF<sub>6</sub> and 37 mg for SbF<sub>6</sub>) were dissolved in 6 mL CHCl<sub>3</sub> and the solution was poured into the cathodic compartment of the electrocrystallization cell. The anodic chamber was filled with 5 mg of (rac)-1, prepared from 2.5 mg [(S,S)-1] and 2.5 mg [(R,R)-1], dissolved in 6 mL CHCl<sub>3</sub>. Single crystals of the salt, as brown plates, grown in solution at 20 °C during 10 days by applying a constant current of 0.5  $\mu$ A on a platinum wire electrode.

### Crystallography

X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full-matrix least-square procedures on F<sup>2</sup>. The non-H atoms were refined with anisotropic displacement parameters. A summary of the crystallographic data and the structure refinement is given in Table S1. CCDC reference numbers: CCDC 1498583 [(*rac*)-1]<sub>2</sub>AsF<sub>6</sub>, CCDC 1498584 [(*S*,*S*)-1]<sub>2</sub>AsF<sub>6</sub>, CCDC 1498585 [(*rac*)-1]<sub>2</sub>SbF<sub>6</sub>, CCDC 1498586 [(*S*,*S*)-1]<sub>2</sub>SbF<sub>6</sub>, CCDC 1498587 [(*S*,*S*)-1]<sub>2</sub>(AsF<sub>6</sub>)<sub>2</sub> and CCDC 1498588 [(*R*,*R*)-1]<sub>2</sub>(AsF<sub>6</sub>)<sub>2</sub>. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

The observed chirality of the structures of enantiopure salts is genuine in spite of the pseudocentrosymmetric character. Indeed, enantiopure non-racemizable (stereogenic  $C_{sp}^{3}$  carbon atoms) precursors have been used in the electrocrystallization.

In the structures  $[(rac)-1]_2$ AsF<sub>6</sub> and  $[(rac)-1]_2$ SbF<sub>6</sub> the ethylene bridge carbon atoms C7 and C8 have been split over two positions A and B with site occupational factors (s.o.f.) of 0.5/0/5 for  $[(rac)-1]_2$ AsF<sub>6</sub> and 0.67/0/33 for  $[(rac)-1]_2$ SbF<sub>6</sub>.

|                                   | [( <i>rac</i> )-1] <sub>2</sub> AsF <sub>6</sub> | $[(S,S)-1]_2$ AsF <sub>6</sub> | [( <i>rac</i> )-1] <sub>2</sub> SbF <sub>6</sub> | $[(S,S)-1]_2$ SbF <sub>6</sub> | $[(S,S)-1]_2(AsF_6)_2$         | $[(R,R)-1]_2(AsF_6)_2$         |
|-----------------------------------|--|--------------------------------|--|--------------------------------|--------------------------------|--------------------------------|
| formula                           | $C_{20}H_{20}As_1F_6S_{12}$                      | $C_{20}H_{20}As_1F_6S_{12}$    | $C_{20}H_{20}Sb_1F_6S_{12}$                      | $C_{20}H_{20}Sb_1F_6S_{12}$    | $C_{20}H_{20}As_2F_{12}S_{12}$ | $C_{20}H_{20}As_2F_{12}S_{12}$ |
| M [gmol <sup>-1</sup> ]           | 834.00   | 834.00                         | 880.83   | 880.83                         | 1022.92                        | 1022.92                        |
| <i>T</i> [K]                      | 293(2)   | 293(2)                         | 293(2)   | 293(2)                         | 293(2)                         | 293(2)                         |
| crystal system                    | Triclinic  | Triclinic                      | Triclinic  | Triclinic                      | Monoclinic                     | Monoclinic                     |
| space group                       | <i>P</i> -1                                      | <i>P</i> 1                     | P-1  | <i>P</i> 1                     | $P2_1$                         | $P2_1$                         |
| <i>a</i> [Å]                      | 6.6588(7)  | 6.6849(5)                      | 6.6221(4)  | 6.6529(7)                      | 8.0663(7)                      | 8.0746(5)                      |
| <i>b</i> [Å]                      | 8.4075(15)                                       | 8.3964(8)                      | 8.4850(4)  | 8.4663(3)                      | 16.177(2)                      | 16.1837(7)                     |
| <i>c</i> [Å]                      | 15.219(5)  | 15.203(3)                      | 15.3114(9)                                       | 15.2766(11)                    | 14.023(2)                      | 14.0446(6)                     |
| α [°]                             | 83.79(3)   | 86.780(12)                     | 87.078(5)  | 87.151(6)                      | 90.00                          | 90.00                          |
| β[°]                              | 77.405(17)                                       | 77.306(9)                      | 77.556(5)  | 77.495(7)                      | 100.231(7)                     | 100.159(4)                     |
| γ [°]                             | 67.799(13)                                       | 68.018(6)                      | 68.221(4)  | 68.478(7)                      | 90.00                          | 90.00                          |
| V [Å <sup>3</sup> ]               | 769.6(3)   | 771.65(18)                     | 779.75(8)  | 781.06(10)                     | 1800.7                         | 1806.53(16)                    |
| Ζ                                 | 1  | 1                              | 1  | 1                              | 2                              | 2                              |
| $ ho_{calcd}  [ m gcm^{-3}]$      | 1.800  | 1.795                          | 1.876  | 1.873                          | 1.887                          | 1.881                          |
| $\mu [\mathrm{mm}^{-1}]$          | 1.969  | 1.964                          | 1.738  | 1.736                          | 2.631                          | 2.622                          |
| Flack parameter                   |  | 0.068(16)                      |  | 0.24(7)                        | 0.002(13)                      | 0.025(15)                      |
| goodness-of-fit on F <sup>2</sup> | 1.027  | 1.006                          | 1.013  | 1.062                          | 1.016                          | 1.008                          |
| final R1/wR2 [I > $2\sigma(I)$ ]  | 0.0453/0.1006                                    | 0.0413/0.0690                  | 0.0374/0.0771                                    | 0.0531/0.1354                  | 0.0443/0.0690                  | 0.0500/0.0773                  |
| R1/wR2 (all data)                 | 0.0837/0.1148                                    | 0.0971/0.0811                  | 0.0879/0.0882                                    | 0.0907/0.1523                  | 0.0996/0.0824                  | 0.1282/0.0952                  |

Table S1. Crystallographic data, details of data collection and structure refinement parameters for the radical cation salts of 1

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

Bond lengths (Å) $[(rac)-1]_2AsF_6$  $[(rac)-1]_2SbF_6$ C3-C41.368(5)C3-C41.369(4)S1-C31.743(4)S1-C31.736(3)S2-C31.739(4)S2-C31.742(3)S3-C41.744(4)S3-C41.739(3)S4-C41.734(4)S4-C41.740(3)

**Table S2**. Selected bond distances for  $[(rac)-1]_2AsF_6$  and  $[(rac)-1]_2SbF_6$ 



**Figure S1.** Solid state structure of  $[(rac)-1]_2$ PF<sub>6</sub>, with an emphasis on the C–H···F short contacts: red dotted lines for CH<sub>vinyl</sub> (3.38 Å), blue dotted lines for CH<sub>3</sub> (3.43 and 3.52 Å) and green dotted lines for CH<sub>Me</sub> (3.57 Å).



**Figure S2.** Solid state structure of  $[(rac)-1]_2$ AsF<sub>6</sub>, with an emphasis on the C–H···F short contacts: red dotted lines for CH<sub>vinyl</sub> (3.37 and 3.38 Å), blue dotted lines for CH<sub>3</sub> (3.51 and 3.82 Å) and green dotted lines for CH<sub>Me</sub> (3.25 Å).

|                     | $[(rac)-1]_2 PF_6$ |                 |                 |        |
|---------------------|--------------------|-----------------|-----------------|--------|
| type                | C–H···F            | $d(H \cdots F)$ | $d(C \cdots F)$ | <(CHF) |
| CH <sub>vinyl</sub> | C2–H2…F2           | 2.49            | 3.38            | 160.0° |
| -                   | C1–H1…F3           | 2.66            | 3.38            | 134.3° |
| CH <sub>3</sub>     | C9–H9B…F1          | 2.71            | 3.52            | 142.4° |
|                     | C9–H9C…F1          | 2.64            | 3.43            | 140.2° |
| CH <sub>Me</sub>    | C7–H7…F2           | 2.71            | 3.57            | 146.9° |

**Table S3.** C–H···F hydrogen bonding distances (Å) and angles in  $[(rac)-1]_2XF_6$ 

|                     |               | $[(rac)-1]_2A$   | sF <sub>6</sub> |        |
|---------------------|---------------|------------------|-----------------|--------|
| type                | C–H···F       | $d(H \cdots F)$  | $d(C \cdots F)$ | <(CHF) |
| CH <sub>vinyl</sub> | C2–H2···F2    | 2.48             | 3.37            | 160.7° |
| -                   | C1-H1F3       | 2.64             | 3.38            | 137.1° |
| CH <sub>3</sub>     | C10-H10DF1    | 2.86             | 3.82            | 176.6° |
|                     | C9–H9C…F1     | 2.95             | 3.51            | 118.4° |
| CH <sub>Me</sub>    | C7A–H7A····F2 | 2.49             | 3.25            | 133.7° |
|                     |               | $[(rac)-1]_2$ St | $bF_6$          |        |
| type                | C−H···F       | $d(H \cdots F)$  | $d(C \cdots F)$ | <(CHF) |
| CH <sub>vinyl</sub> | C2–H2…F3      | 2.58             | 3.35            | 139.6° |
|                     | C1-H1F2       | 2.46             | 3.35            | 162.2° |
| CH <sub>3</sub>     | C10-H10A…F1   | 2.67             | 3.31            | 124.0° |
|                     | C10-H10C…F1   | 2.76             | 3.49            | 133.2° |
| CHMe                | C8A–H8A…F2    | 2.59             | 3.35            | 134 9° |



**Figure S3.** Solid state structure of  $[(S,S)-1]_2$ AsF<sub>6</sub>, with an emphasis on the C–H···F short contacts: red dotted lines for CH<sub>vinyl</sub> (3.32, 3.32, 3.43 and 3.45 Å), blue dotted lines for CH<sub>3</sub> (3.38, 3.40, 3.60 and 3.61 Å) and green dotted lines for CH<sub>Me</sub> (3.32, 3.48 and 3.58 Å).

**Table S4**. Selected bond distances for  $[(S,S)-1]_2AsF_6$  and  $[(S,S)-1]_2SbF_6$ 

| Bond lengths (Å)               |                   |                                |                   |  |
|--------------------------------|-------------------|--------------------------------|-------------------|--|
| $[(S,S)-1]_2$ AsF <sub>6</sub> |                   | $[(S,S)-1]_2$ SbF <sub>6</sub> |                   |  |
| donor A                        | donor <b>B</b>    | donor A                        | donor <b>B</b>    |  |
| C3A-C4A 1.353(16)              | C3B-C4B 1.367(15) | C3A-C4A 1.380(20)              | C3B-C4B 1.430(20) |  |
| S1A-C3A 1.741(13)              | S1B-C3B 1.746(12) | S1A-C3A 1.741(17)              | S1B-C3B 1.747(16) |  |
| S2A-C3A 1.714(15)              | S2B-C3B 1.768(13) | S2A-C3A 1.680(20)              | S2B-C3B 1.791(16) |  |
| S3A-C4A 1.761(13)              | S3B-C4B 1.717(14) | S3A-C4A 1.746(13)              | S3B-C4B 1.700(20) |  |
| S4A-C4A 1.748(12)              | S4B-C4B 1.746(12) | S4A-C4A 1.774(13)              | S4B-C4B 1.701(18) |  |

|  | $[(S,S)-1]_2$ AsF <sub>6</sub>   |  |   |  |
|--|--|--|---|--|
| type   | C–H···F  | $d(H \cdots F)$  | $d(C \cdots F)$   | <(CHF)   |
| CH <sub>vinyl</sub>  | C2A-H2A···F1   | 2.72   | 3.45  | 135.5°   |
|  | C2B-H2B···F2   | 2.58   | 3.32  | 137.1°   |
|  | C1B-H1B····F5  | 2.53   | 3.43  | 162.2°   |
|  | C1A-H1A···F6   | 2.43   | 3.32  | 160.4°   |
| CH <sub>3</sub>  | C10A-H10C…F4   | 2.49   | 3.38  | 153.2°   |
|  | C10A-H10A…F5   | 2.69   | 3.60  | 157.5°   |
|  | C10B-H10DF3  | 2.69   | 3.40  | 131.3°   |
|  | C10A-H10A…F3   | 2.77   | 3.61  | 145.8°   |
| CH <sub>Me</sub>   | C8B-H8B···F1   | 2.66   | 3.58  | 157.0°   |
|  | C7A−H7A···F2   | 2.58   | 3.48  | 153.7°   |
|  | C8B–H8B…F6   | 2.56   | 3.32  | 134.6°   |
|  | $[(S,S)-1]_2$ SbF <sub>6</sub>   |  |   |  |
|  |  | $[(S,S)-1]_2$ St   | $F_6$   |  |
| type   | С–Н…F  | $\frac{[(S,S)-1]_2 \text{St}}{d(\text{H}\cdots\text{F})}$  | $d(C\cdots F)$  | <(CHF)   |
| type<br>CH <sub>vinyl</sub>  | C–H···F<br>C2A–H2A···F1  | $\frac{[(S,S)-1]_2St}{d(H\cdots F)}$ 2.72  | $ \frac{d(C\cdots F)}{3.42} $   | <(CHF)<br>133.3°   |
| type<br>CH <sub>vinyl</sub>  | C–H…F<br>C2A–H2A…F1<br>C2B–H2B…F2  | $[(S,S)-1]_2St d(H\cdots F) 2.72 2.51$   |   | <(CHF)<br>133.3°<br>144.7°   |
| type<br>CH <sub>vinyl</sub>  | C–H…F<br>C2A–H2A…F1<br>C2B–H2B…F2<br>C1B-H1B…F5  | [( <i>S</i> , <i>S</i> )- <b>1</b> ] <sub>2</sub> St<br>d(H…F)<br>2.72<br>2.51<br>2.37   |   | <(CHF)<br>133.3°<br>144.7°<br>154.5°   |
| type<br>CH <sub>vinyl</sub>  | C–H…F<br>C2A–H2A…F1<br>C2B–H2B…F2<br>C1B-H1B…F5<br>C1A-H1A…F6  | [( <i>S</i> , <i>S</i> )- <b>1</b> ] <sub>2</sub> St<br>d(H…F)<br>2.72<br>2.51<br>2.37<br>2.54   |   | <(CHF)<br>133.3°<br>144.7°<br>154.5°<br>167.7°   |
| type<br>CH <sub>vinyl</sub>  | C–H···F<br>C2A–H2A···F1<br>C2B–H2B···F2<br>C1B-H1B···F5<br>C1A-H1A···F6<br>C10A–H10C···F4  | [( <i>S</i> , <i>S</i> )- <b>1</b> ] <sub>2</sub> St<br>d(H…F)<br>2.72<br>2.51<br>2.37<br>2.54<br>2.39                                 | bF6           d(C···F)           3.42           3.31           3.23           3.45           3.19   | <(CHF)<br>133.3°<br>144.7°<br>154.5°<br>167.7°<br>141.7°   |
| type<br>CH <sub>vinyl</sub><br>CH <sub>3</sub>                     | C-H···F<br>C2A-H2A···F1<br>C2B-H2B···F2<br>C1B-H1B···F5<br>C1A-H1A···F6<br>C10A-H10C···F4<br>C10A-H10A···F5                                    | [( <i>S</i> , <i>S</i> )- <b>1</b> ] <sub>2</sub> St<br>d(H…F)<br>2.72<br>2.51<br>2.37<br>2.54<br>2.39<br>2.73                         | bF6           d(C···F)           3.42           3.31           3.23           3.45           3.19           3.62  | <(CHF)<br>133.3°<br>144.7°<br>154.5°<br>167.7°<br>141.7°<br>154.4°   |
| type<br>CH <sub>vinyl</sub><br>CH <sub>3</sub>                     | C-H···F<br>C2A-H2A···F1<br>C2B-H2B···F2<br>C1B-H1B···F5<br>C1A-H1A···F6<br>C10A-H10C···F4<br>C10A-H10A···F5<br>C10B-H10D···F3                  | [( <i>S</i> , <i>S</i> )- <b>1</b> ] <sub>2</sub> St<br>d(H…F)<br>2.72<br>2.51<br>2.37<br>2.54<br>2.39<br>2.73<br>2.77                 | $\begin{array}{c} F_6 \\ \hline d(C \cdots F) \\ 3.42 \\ 3.31 \\ 3.23 \\ 3.45 \\ \hline 3.19 \\ 3.62 \\ 3.44 \\ \end{array}$  | <(CHF)<br>133.3°<br>144.7°<br>154.5°<br>167.7°<br>141.7°<br>154.4°<br>128.2°                               |
| type<br>CH <sub>vinyl</sub><br>CH <sub>3</sub>                     | C-HF<br>C2A-H2AF1<br>C2B-H2BF2<br>C1B-H1BF5<br>C1A-H1AF6<br>C10A-H10CF4<br>C10A-H10AF5<br>C10B-H10DF3<br>C10A-H10AF3                           | [( <i>S</i> , <i>S</i> )- <b>1</b> ] <sub>2</sub> St<br>d(H…F)<br>2.72<br>2.51<br>2.37<br>2.54<br>2.39<br>2.73<br>2.77<br>2.84         | $\begin{array}{c c} & & & \\ \hline & d(C \cdots F) \\ \hline & 3.42 \\ \hline & 3.31 \\ \hline & 3.23 \\ \hline & 3.45 \\ \hline & 3.45 \\ \hline & 3.19 \\ \hline & 3.62 \\ \hline & 3.44 \\ \hline & 3.56 \\ \hline \end{array}$ | <(CHF)<br>133.3°<br>144.7°<br>154.5°<br>167.7°<br>141.7°<br>154.4°<br>128.2°<br>132.3°                     |
| type<br>CH <sub>vinyl</sub><br>CH <sub>3</sub>                     | C-HF<br>C2A-H2AF1<br>C2B-H2BF2<br>C1B-H1BF5<br>C1A-H1AF6<br>C10A-H10CF4<br>C10A-H10AF3<br>C10A-H10AF3<br>C10A-H10AF3                           | [( <i>S</i> , <i>S</i> )- <b>1</b> ] <sub>2</sub> St<br>d(H…F)<br>2.72<br>2.51<br>2.37<br>2.54<br>2.39<br>2.73<br>2.77<br>2.84<br>2.63 | $\begin{array}{c c} & & & \\ \hline & d(C \cdots F) \\ \hline & 3.42 \\ 3.31 \\ 3.23 \\ 3.45 \\ \hline & 3.19 \\ 3.62 \\ 3.44 \\ \hline & 3.56 \\ \hline & 3.55 \\ \hline \end{array}$  | <(CHF)<br>133.3°<br>144.7°<br>154.5°<br>167.7°<br>141.7°<br>154.4°<br>128.2°<br>132.3°<br>157.6°           |
| type<br>CH <sub>vinyl</sub><br>CH <sub>3</sub><br>CH <sub>Me</sub> | C-HF<br>C2A-H2AF1<br>C2B-H2BF2<br>C1B-H1BF5<br>C1A-H1AF6<br>C10A-H10AF3<br>C10A-H10AF3<br>C10A-H10AF3<br>C10A-H10AF3<br>C8B-H8BF1<br>C7A-H7AF2 | [(S,S)- <b>1</b> ] <sub>2</sub> St<br>d(H…F)<br>2.72<br>2.51<br>2.37<br>2.54<br>2.39<br>2.73<br>2.77<br>2.84<br>2.63<br>2.54           | $\begin{array}{c c} \mathbf{b} \mathbf{F}_6 \\ \hline \mathbf{d} (\mathbf{C} \cdots \mathbf{F}) \\ \hline 3.42 \\ 3.31 \\ 3.23 \\ 3.45 \\ \hline 3.19 \\ 3.62 \\ 3.44 \\ \hline 3.56 \\ \hline 3.55 \\ 3.43 \\ \end{array}$         | <(CHF)<br>133.3°<br>144.7°<br>154.5°<br>167.7°<br>141.7°<br>154.4°<br>128.2°<br>132.3°<br>157.6°<br>150.2° |

**Table S5.** C–H···F Hydrogen bonding distances (Å) and angles in  $[(S,S)-1]_2XF_6$ 



**Figure S4.** Complex network of C–H···F interactions in the structure of  $[(S,S)-1]_2$ PF<sub>6</sub>: red dotted lines for CH<sub>vinyl</sub> (2.41-2.86 Å), blue dotted lines for CH<sub>3</sub> (2.44-2.72 Å).



**Figure S5.** C–H…F interactions in the structure of  $[(S,S)-1]_2$ PF<sub>6</sub> for P1 anion: red dotted lines for CH<sub>vinyl</sub> (2.41-2.78 Å), blue dotted lines for CH<sub>3</sub> (2.44-2.68 Å).



**Figure S6.** C–H…F interactions in the structure of  $[(S,S)-1]_2$ PF<sub>6</sub> for P2 anion: red dotted lines for CH<sub>vinyl</sub> (2.42-2.86 Å), blue dotted lines for CH<sub>3</sub> (2.62-2.72 Å).



**Figure S7.** C–H···F interactions in the structure of monoclinic  $[(S,S)-1]_2(AsF_6)_2$ : red dotted lines for CH<sub>vinyl</sub> (2.49-2.75 Å), blue dotted lines for CH<sub>3</sub> (2.70-2.71 Å) and green dotted lines for CH<sub>Me</sub> (2.48-2.77 Å).



**Figure S8.** Step-chain dimers of monoclinic  $[(S,S)-1]_2(AsF_6)_2$ ; short intra-dimer S···S contacts: 3.34-3.49 Å, short inter-dimer S···S contacts: 3.74-3.80 Å.

### Single crystal conductivity measurements

Electrical resistivity was measured on platelet-shaped single crystals of  $[(rac)-1]_2XF_6$  and  $[(S,S)-1]_2XF_6$  (X = As, Sb) using a four point method except for  $[(rac)-1]_2SbF_6$  which was measured in two points due to the size and fragility of the single crystals. As the resistance of the contacts has an important impact on the measured resistance, the intrinsic value of the room temperature conductivity of this salt is certainly higher than 4 S·cm<sup>-1</sup> and its temperature dependence is not accurately known. Crystals of  $[(R,R)-1]_2XF_6(X = As, Sb)$  were too small and fragile to be contacted. Gold contacts were evaporated on both faces of the crystals and gold wires were glued with silver paste on those contacts. A low frequency (< 100 Hz) lock-in technique was used with a measuring current  $I_{ac} = 1 \ \mu A$ . Resistivity measurements were performed in the range 4 – 300 K in a home-made cryostat equipped with a 4K pulse tube using a cernox thermometer.



**Figure S9.** Temperature dependence of the electrical resistivity  $\rho$  for a single crystal of  $[(rac)-1]_2$ PF<sub>6</sub> (green circles), a single crystal of  $[(rac)-1]_2$ AsF<sub>6</sub> (red circles), and a single crystal of  $[(rac)-1]_2$ SbF<sub>6</sub> (blue circles). The  $[(rac)-1]_2$ SbF<sub>6</sub> crystal has been measured in two points contact.

# **Computational details**

The tight-binding band structure calculations (Whangbo, M.-H.; Hoffmann, R. *J. Am. Chem. Soc* **1978**, 100, 6093-6098) were of the extended Hückel type. A modified Wolfsberg-Helmholtz formula was used to calculate the non-diagonal  $H_{\mu\nu}$  values (Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686-3692). All valence electrons were taken into account in the calculations and the basis set consisted of Slater-type orbitals of double- $\zeta$  quality for C 2s and 2p, S 3s and 3p and of single- $\zeta$  quality for H. The ionization potentials, contraction coefficients and exponents were taken from previous work (Pénicaud, A.; Boubekeur, K.; Batail, P.; Canadell, E.; Auban-Senzier, P.; Jérome, D., J. Am. *Chem. Soc.* **1993**, *115*, 4101-4112).

### **Electronic structures**

# $[(S,S)-1]_2$ SbF<sub>6</sub>

| Interaction | S…S (<3.9 Å)               | $ \beta$ номо-номо $ $ (eV) |
|-------------|----------------------------|-----------------------------|
| Ι           | 3.686, 3.706, 3.708, 3.713 | 0.6435                      |
| II          | 3.647, 3.651, 3.850        | 0.5367                      |
| III         | 3.480, 3.517, 3.672, 3.727 | 0.0507                      |
| IV          | 3.556, 3.583, 3.799        | 0.0207                      |
| V           | 3.607, 3.816, 3.854        | 0.0628                      |
| VI          | 3.637, 3.794, 3.805        | 0.0627                      |

**Table S6.** S···S distances shorter than 3.9 Å and absolute values of the  $|\beta_{HOMO-HOMO}|$  interaction energies (eV) for the different donor···donor interactions in the  $[(S,S)-1]_2$ SbF<sub>6</sub> salt at room temperature.

 $[(S,S)-1]_2$ AsF<sub>6</sub>



**Figure S10.** Donor layer of  $[(S,S)-1]_2$ AsF<sub>6</sub> triclinic salt with the different intermolecular interactions.

**Table S7.** S...S distances shorter than 3.9 Å and absolute values of the  $|\beta_{HOMO-HOMO}|$  interaction energies (eV) for the different donor...donor interactions in the  $[(S,S)-1]_2$ AsF<sub>6</sub> salt at room temperature.

| Interaction | S…S (<3.9 Å)               | $ \beta$ номо-номо $ $ (eV) |
|-------------|----------------------------|-----------------------------|
| Ι           | 3.666, 3.677, 3.697, 3.706 | 0.6866                      |
| II          | 3.633, 3.643, 3.826        | 0.5797                      |
| III         | 3.472, 3.475, 3.720, 3.747 | 0.0439                      |
| IV          | 3.554, 3.576, 3.791        | 0.0233                      |
| V           | 3.669, 3.875, 3.889        | 0.0663                      |
| VI          | 3.680, 3.796, 3.847        | 0.0593                      |



**Figure S11.** Calculated band structure (left) and Fermi surface (right) for the donor layers of  $[(S,S)-1]_2AsF_6$  at room temperature. The dashed line (left) refers to the Fermi level and  $\Gamma = (0, 0)$ ,  $X = (a^*/2, 0)$ ,  $Y = (0, b^*/2)$ ,  $M = (a^*/2, b^*/2)$  and  $S = (-a^*/2, b^*/2)$ .

 $[(rac)-1]_2 PF_6$ 

The electronic structure of this salt has been thoroughly discussed in ref. 20. We give here only the values for the interaction energies for comparison purpose with the  $AsF_6$  and  $SbF_6$  salts.

**Table S8.** S...S distances shorter than 3.9 Å and absolute values of the  $|\beta_{HOMO-HOMO}|$  interaction energies (eV) for the different donor...donor interactions in the  $[(rac)-1]_2PF_6$  salt at room temperature.

| Interaction | S…S (<3.9 Å)          | <b>β</b> номо-номо  ( <b>eV</b> ) |
|-------------|-----------------------|-----------------------------------|
| Ι           | 3.662 (×2) 3.670 (×2) | 0.7198                            |
| II          | 3.628 (×2)            | 0.6097                            |
| III         | 3.467 (×2) 3.782 (×2) | 0.0400                            |
| IV          | 3.571 (×2) 3.798      | 0.0285                            |
| V           | 3.709, 3.781, 3.896   | 0.0692                            |

 $[(rac)-1]_2$ AsF<sub>6</sub>



Figure S12. Donor layer of  $[(rac)-1]_2$ AsF<sub>6</sub> triclinic salt with the different intermolecular interactions.

**Table S9.** S...S distances shorter than 3.9 Å and absolute values of the  $|\beta_{HOMO-HOMO}|$  interaction energies (eV) for the different donor...donor interactions in the  $[(rac)-1]_2$ AsF<sub>6</sub> salt at room temperature.

| Interaction | S…S (<3.9 Å)           | βномо-номо  (eV) |
|-------------|------------------------|------------------|
| Ι           | 3.686 (x2), 3.678 (x2) | 0.6923           |
| II          | 3.630 (x2), 3.895      | 0.5921           |
| III         | 3.474 (x2), 3.736 (x2) | 0.0454           |
| IV          | 3.569 (x2), 3.799      | 0.0254           |
| V           | 3.675, 3.795, 3.856    | 0.0691           |



**Figure S13.** Calculated band structure (left) and Fermi surface (right) for the donor layers of  $[(rac)-1]_2AsF_6$  at room temperature. The dashed line (left) refers to the Fermi level and  $\Gamma = (0, 0)$ ,  $X = (a^*/2, 0)$ ,  $Y = (0, b^*/2)$ ,  $M = (a^*/2, b^*/2)$  and  $S = (-a^*/2, b^*/2)$ .

 $[(rac)-1]_2$ SbF<sub>6</sub>

| Interaction | S…S (<3.9 Å)           | <b>β</b> номо-номо  (eV) |
|-------------|------------------------|--------------------------|
| Ι           | 3.699 (x2), 3.712 (x2) | 0.6562                   |
| II          | 3.639 (x2)             | 0.5741                   |
| III         | 3.505 (x2), 3.700 (x2) | 0.0524                   |
| IV          | 3.581 (x2), 3.804      | 0.0249                   |
| V           | 3.632, 3.774, 3.809    | 0.0708                   |

| Table S10. S···S distances shorter than 3.9 Å | and absolute values of the $ \beta_{HOMO-HOMO} $ interaction energies (eV) for |
|---|--|
| the different donor donor interactions in the | $[(rac)-1]_2$ SbF <sub>6</sub> salt at room temperature.                       |



**Figure S14.** Calculated band structure (left) and Fermi surface (right) for the donor layers of  $[(rac)-1]_2$ SbF<sub>6</sub> at room temperature. The dashed line (left) refers to the Fermi level and  $\Gamma = (0, 0)$ ,  $X = (a^*/2, 0)$ ,  $Y = (0, b^*/2)$ ,  $M = (a^*/2, b^*/2)$  and  $S = (-a^*/2, b^*/2)$ .