Different electronic states in the isomorphous chiral vs racemic organic conducting salts, β''-(BEDT-TTF)$_2$(*S*- and *rac*-PROXYL-CONHCH$_2$SO$_3$)

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Supplementary information

Table S1. Crystallographic data of (PPh$_4$)*rac*-, *R*- and *S*-**1**

Compound	(PPh$_4$)*R*-**1**	(PPh$_4$)*S*-**1**	(PPh$_4$)*rac*-**1**[*]
Name	(PPh$_4$)*S*-PROXYL-CONHCH$_2$SO$_3$	(PPh$_4$)*R*-PROXYL-CONHCH$_2$SO$_3$	(PPh$_4$)*rac*-PROXYL-CONHCH$_2$SO$_3$
Formula	$C_{34}H_{38}N_2O_5PS$	$C_{34}H_{38}N_2O_5PS$	$C_{34}H_{38}N_2O_5PS$
Fw	617.72	617.72	617.72
T (K)	106	106	294
Space Group	$P1$	$P1$	$P\bar{1}$
a (Å)	11.6227(2)	11.62009(14)	11.691(4)
b (Å)	11.83230(18)	11.83293(15)	12.042(3)
c (Å)	12.1976(2)	12.19880(15)	12.306(3)
α (°)	83.7248(13)	83.7027(10)	83.20(2)
β (°)	84.4992(14)	84.5080(10)	84.25(3)
γ (°)	68.9233(15)	68.9172(11)	68.48(2)
V (Å^3)	1552.96(5)	1552.75(4)	1597.4(8)
Z	2	2	2
d_{calc} (g·cm^{-1})	1.321	1.321	1.284
μ (cm^{-1})	2.006	2.006	1.950
F(000)	654	654	654
2θ range (°)	4-55	4-55	6-55
Total ref.	42137	47016	7690
Unique ref.	13469	13511	7333
R_{int}	0.0561	0.0479	0.0118
Parameters	775	775	388
R_1 ($I > 2\sigma(I)$)	0.0392	0.0347	0.0433
wR_2 (all data)	0.0976	0.0901	0.1386
S	1.065	1.069	1.044
$\Delta\rho_{max}$ (e Å^{-3})	0.35	0.30	0.30
$\Delta\rho_{min}$ (e Å^{-3})	-0.40	-0.37	-0.41
Flack parameters	0.02(4)	-0.01(3)	-
CCDC reference	2022036	2022034	685677

[*] Unit cell transformation was performed from reported cells[8] and re-refine the data.

Table S2. Crystallographic data of *rac*- and *S*-**2**

Compound	β´´-(BEDT-TTF)$_2$*S*-**1** (*S*-**2**)			β´´-(BEDT-TTF)$_2$*rac*-**1** (*rac*-**2**)		
Name	β´´-(BEDT-TTF)$_2$*S*-PROXYL-CONHCH$_2$SO$_3$			β´´-(BEDT-TTF)$_2$*Rac*-PROXYL-CONHCH$_2$SO$_3$		
Formula	$C_{30}H_{34}N_2O_5S_{17}$			$C_{30}H_{34}N_2O_5S_{17}$		
Fw	1047.63			1047.63		
T (K)	290	106	29	295*	106	28
Space Group	$P1$	$P1$	$P1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.26369(19)	9.1764(3)	9.14212(13)	9.326(3)	9.28307(18)	9.23250(8)
b (Å)	12.4438(2)	12.2807(3)	12.22911(18)	12.436(4)	12.2324(2)	12.13977(12)
c (Å)	19.5405(3)	19.4508(5)	19.4069(3)	19.528(6)	19.4799(4)	19.4474(2)
α (°)	83.5517(14)	84.035(2)	84.1246(13)	83.44(3)	83.644(6)	83.9780(10)
β (°)	82.9266(16)	83.606(2)	83.7827(13)	82.94(3)	83.390(6)	83.3850(10)
⍰ (°)	70.2178(17)	70.196(2)	70.2319(13)	69.78(3)	69.658(5)	69.6680(10)
V (Å^3)	2097.45(7)	2044.35(10)	2024.80(5)	2102.9(13)	2054.34(10)	2025.33(4)
Z	2	2	2	2	2	2
d_{calc} (g·cm^{-1})	1.659	1.702	1.718	1.654	1.693	1.718
μ (cm^{-1})	9.161	9.399	9.490	9.138	9.354	9.488
F(000)	1080	1080	1080	1080	1080	1080
2θ range (°)	4-55	4-55	4-55	5-55	4-55	4-55
Total ref.	56662	51519	104470	10383	20214	107410
Unique ref.	18190	17612	17596	9638	9348	9276
R_{int}	0.0613	0.0528	0.0831	0.0774	0.0163	0.0275
Parameters	973	973	980	493	505	512
R_1 ($I > 2\sigma(I)$)	0.0434	0.0486	0.0413	0.0665	0.0320	0.0353
wR_2 (all data)	0.1204	0.1405	0.1088	0.2341	0.0718	0.0771
S	1.050	1.037	1.058	0.935	1.070	1.342
$\Delta\rho_{\text{max}}$ (e Å^{-3})	0.61	1.13	0.96	0.64	0.66	0.61
$\Delta\rho_{\text{min}}$ (e Å^{-3})	-0.53	-0.63	-0.64	-0.59	-0.63	-0.62
Flack parameter	0.13(6)	0.11(6)	-0.01(3)	-	-	-
CCDC reference	2022041	2022039	2022037	685678	2022046	2022042

*Unit cell transformation was performed from reported cells[8] and re-refine the data.

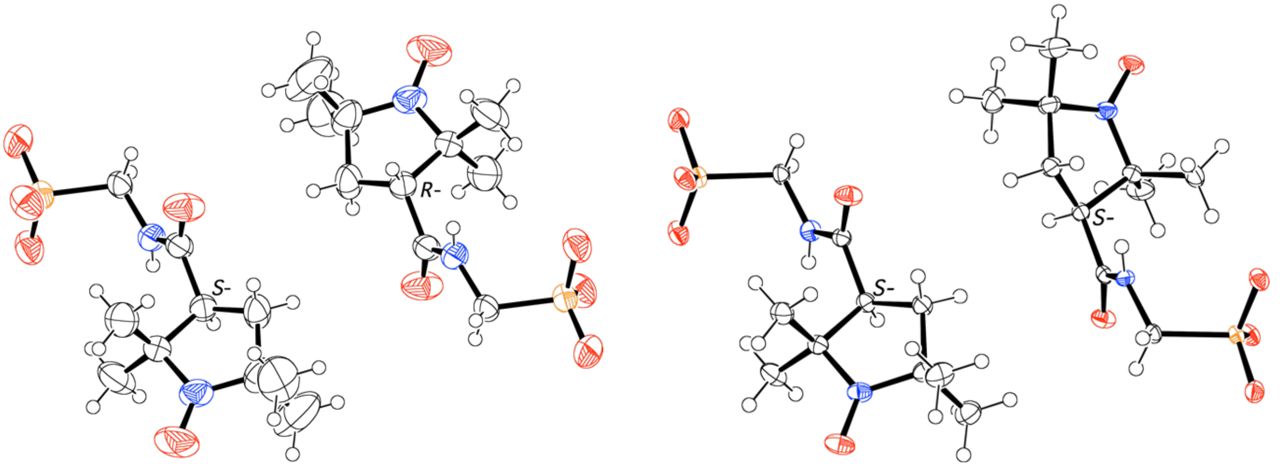


Fig. S1 Molecular structures of *rac*-**1** (left) and *S*-**1** (right) in their tetraphenylphosphonium salts at 294 and 105 K, respectively.

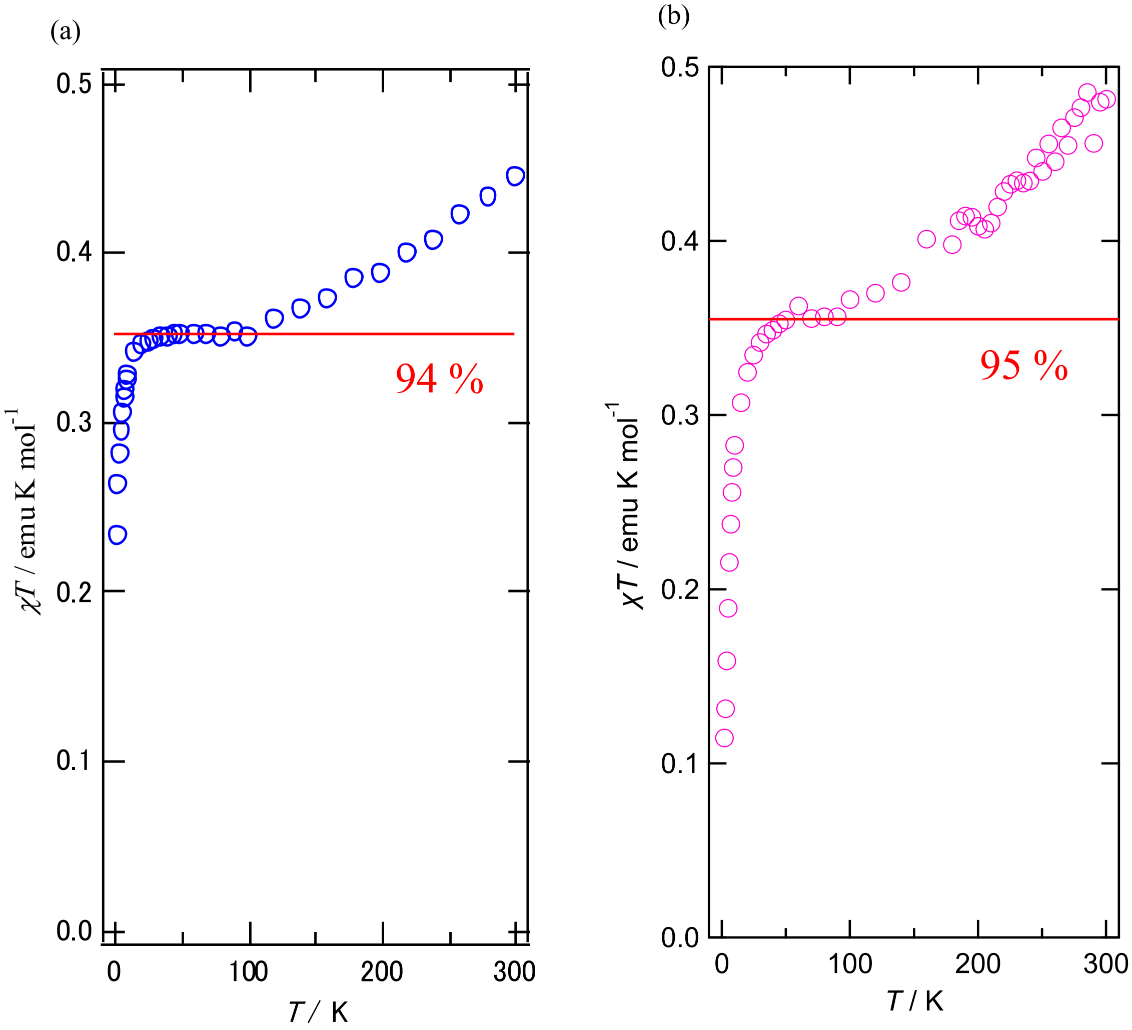
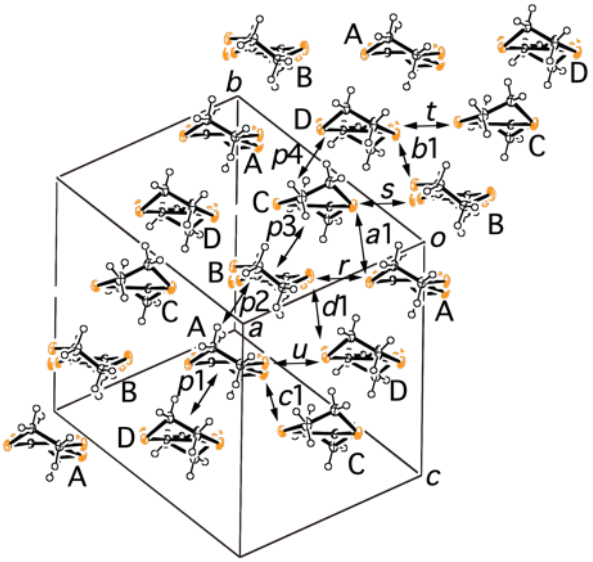


Fig. S2 Temperature-dependent magnetic susceptibility of *rac*-**2** (left)[7] and *S*-**2** (right). The red horizontal lines indicate the spin concentrations of $s = 1/2$ attributed to organic free radicals of the anions. The *S*-**2** data can be fitted by the combination of a Curie-Weiss and a Singlet-Triplet models with $C = 0.355$ emu K mol^{-1} (0.355 / 0.375 = 0.95), ⍰ = -0.37 K and $J_{\text{Singlet-Triplet}} = -3.8$ K.

Table S3. Transfer integrals of *rac*- and *S*-**2**



	Racemic		*S*-	
$\times 10^{-3}$	106 K	28 K	106 K	29 K
*p*1	-2.66	-3.27	-2.66	-2.66
*p*2	7.82	8.23	7.32	7.81
*p*3	-5.61	-5.66	-4.62	-4.54
*p*4	= *p*2	= *p*2	6.93	7.06
r	-12.01	-13.14	-13.15	-14.03
s	10.57	11.27	11.00	11.74
t	-9.34	-9.61	-9.64	-9.90
u	= *s*	= *s*	10.70	10.83
*a*1	17.75	18.39	17.14	17.56
*b*1	10.76	10.97	9.82	9.98
*c*1	= *b*1	= *b*1	10.47	10.86
*d*1	= *a*1	= *a*1	16.66	17.08

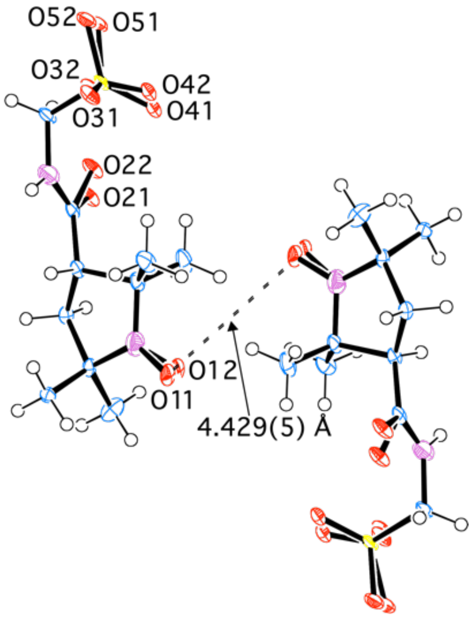
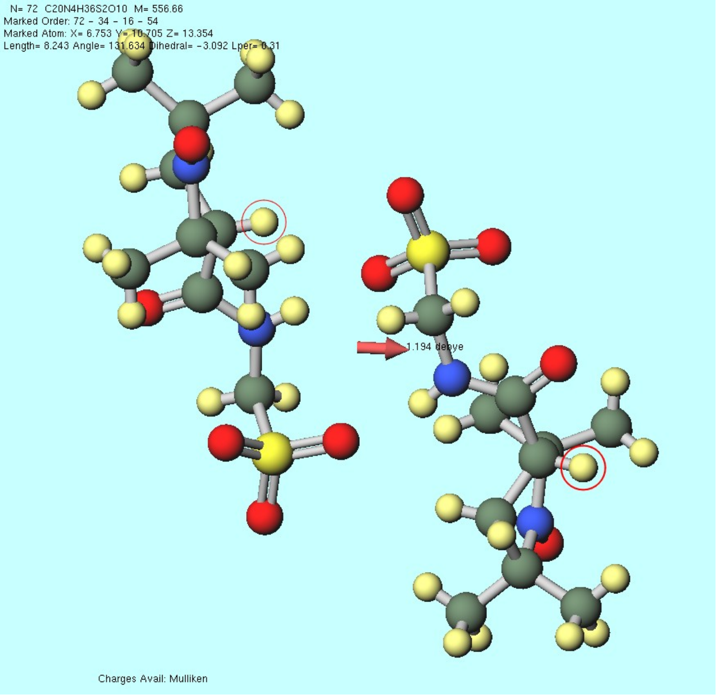


Fig. S3 Molecular structure of the *rac*-**1** anion dimer in *rac*-**2** at 28 K. Positional disorders are observed at only 28 K for the radical centre oxygen (O11 and O12), an oxygen of ketone (O21 and O22) and three oxygens of sulfo groups (O31-O51 and O32-052). The occupancies of the main atoms are 0.94(3), 0.948(10) and 0.904(17) for O11, O21 and O31-51, respectively. Those of the sub atoms are 0.06(3), 0.052(10) and 0.096(17) for O12, O22 and O32-52, respectively. The occupancy of O12 is so small therefore magnetic contribution is so small that here only the distance of O11···O11 is shown.



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N= 72  C20N4H36S2O10  M= 556.66
Marked Order: 72 - 34 - 16 - 54
Marked Atom: X= 6.753 Y= 10.705 Z= 13.354
Length= 8.243 Angle= 131.634 Dihedral= -3.092 Lper= 0.31
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Charges Avail: Mulliken
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Fig. S4 Result of MOPAC2016 calculation using PM3 Hamiltonian. We calculate the dipole moment for the two anion molecules, which practically has point symmetry apart from the chiral centre C-H bonds. The resultant dipole moment of 1.194 debye is calculated. Therefore, one anion has 0.6 debye of a net dipole moment in the crystal.

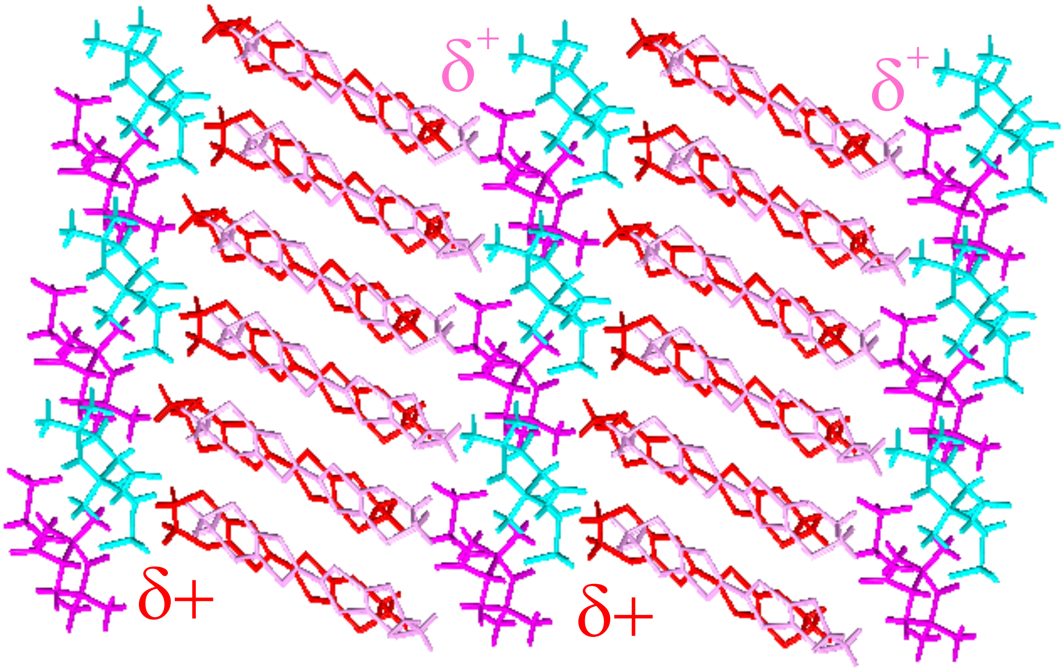

Fig. S5 Crystal structure of *S*-2. The red coloured BEDT-TTF molecules of B and C have larger positive charges than those of the pink coloured A and D molecule.

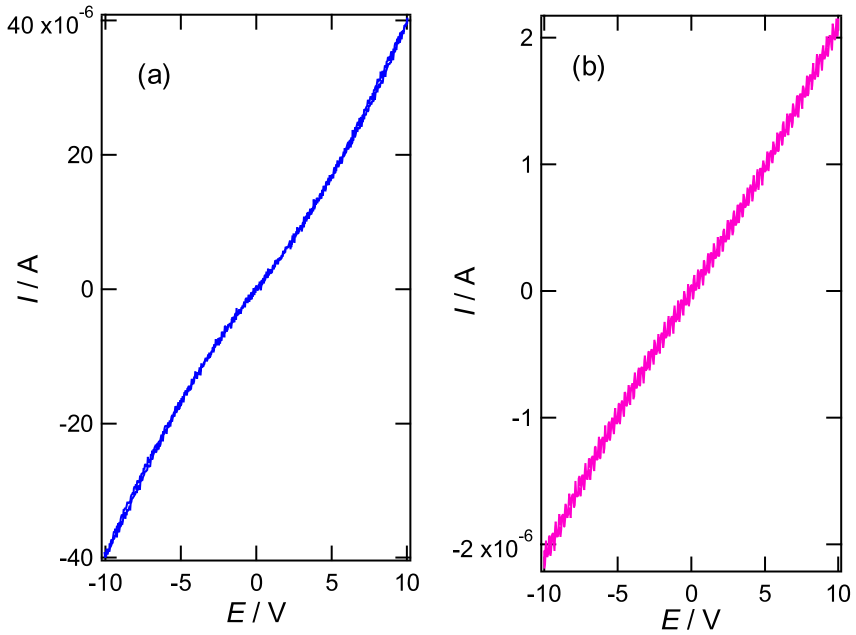

Figure S6. I-V curves of *rac*-**2** (a) and *S*-**2** (b) at 50 K at 1 Hz.