Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting information for

[4]Helicene based anions in electrocrystallization with tetrachalcogenafulvalene donors

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SUMMARY

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X-Ray structure determinations

Details about data collection and solution refinement are given in Table S1. Data collections were performed on a Rigaku Oxford Diffraction SuperNova diffractometer equipped with an Atlas CCD detector and micro-focus Cu-K_α radiation (λ = 1.54184 Å). The structures were solved by intrinsic phasing and refined on F^2 by full matrix least-squares techniques with SHELX programs (SHELXT 2018/2 and SHELXL 2018/3)[1,2] using the ShelXle and the Olex2 graphical user interfaces.[3,4] All non-H atoms were refined anisotropically and absorption was corrected by multiscan empirical absorption using spherical harmonics with CrysAlisPro program for **2**, **TMTTF-(2)$_2$, (TMTTF)$_2$([4]heliceneSO$_3$)$_2$**, **(TMTSF)$_5$([4]heliceneSO$_3$)$_5$,** and **(BEDT-TTF)$_2$([4]heliceneSO$_3$)**. The H atoms were placed at calculated positions and refined using a riding model. Crystallographic data for the five structures have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC 2142732 for **2**, 2142733 for **TMTTF-(2)$_2$**, 2142734 for **(TMTTF)$_2$([4]heliceneSO$_3$)$_2$**, 2142735 for **(TMTSF)$_5$([4]heliceneSO$_3$)$_5$,** 2142736 for **(BEDT-TTF)$_2$([4]heliceneSO$_3$)**. 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).

	2	**TMTTF-(2)$_2$**	**(TMTTF)$_2$ ([4]heliceneSO$_3$)$_2$**	**(TMTSF)$_5$ ([4]heliceneSO$_3$)$_5$**	**(BEDT-TTF)$_2$ ([4]heliceneSO$_3$)**
Formula sum	$C_{19}H_{12}O_2$	$C_{48}H_{34}O_4S_4$	$C_{56}H_{46}O_6S_{10}$	$C_{145}H_{123.40}Cl_{1.20}N_{2.50}O_{15.89}S_{5.60}Se_{20}$	$C_{38}H_{27.62}Cl_{2.01}O_{4.31}S_{18}$
Formula weight	272.29	802.99	1135.53	3956.37	1201.70
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	*P*bcn	$P2_1/n$	*P*-1	*P*-1
a/Å	15.8603(15)	14.0945(2)	12.5199(9)	11.9706(5)	12.7324(14)
b/Å	3.7729(4)	12.8991(2)	21.0758(15)	17.1872(7)	12.7345(13)
c/Å	22.243(2)	20.6753(3)	19.3165(10)	35.0341(7)	16.3097(11)
α/°	90	90	90	85.381(2)	81.224(7)
β/°	102.306(10)	90	102.089(6)	82.114(3)	78.147(7)
γ/°	90	90	90	76.022(4)	64.043(10)
V/Å^3	1300.4(2)	3758.61(11)	4984.0(6)	6920.0(4)	2321.1(4)
Z	4	4	4	2	2
D_c/g cm^{-3}	1.391	1.419	1.513	1.899	1.719
T/K	149.4(4)	150.00(10)	150.01(10)	150.01(10)	150.00(10)
μ/mm^{-1}	0.71	2.71	4.54	7.62	9.20
Reflections collected	4016	28205	18505	26058	16438
Independent reflection	2057[R_{int} = 0.0476]	3607[R_{int} = 0.0402]	6502[R_{int} = 0.0626]	21322[R_{int} = 0.0444]	7236[R_{int} = 0.0384]
final $R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0976/0.2849	0.0424/0.1186	0.0952/0.2419	0.0641/0.1688	0.0861/0.2312
$R_1{}^a$,$wR_2{}^b$ (all data)	0.1104/ 0.2961	0.0452/0.1217	0.1446/0.2851	0.0775/0.1812	0.1070/0.2488
goodness-of-fit on F^2	1.104	1.056	1.066	1.063	1.056
$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	-0.34/0.39	-0.26/0.43	-0.57/1.2	-1.3/1.2	-0.79/1.69
Completeness (%)	99.8	99.97	98.6	98.6	98.6
CCDC number	2142732	2142733	2142734	2142735	2142736

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_0^2)+(aP)^2+bP]$ where $P= [max(F_0^2, 0) + 2F_c^2]/3$.

Table S1 : Crystallographic data, details of data collection and structure refinement parameters.

2			**TMTTF-(2)$_2$**		
C1	C2	1.366(7)	S001	C009	1.8162(17)
C1	C6	1.411(7)	S001	C00C	1.7684(17)
C2	C3	1.403(7)	S002	C009	1.8101(16)
C3	C4	1.375(8)	S002	C00B	1.7633(16)
C4	C5	1.412(8)	O003	C007	1.3652(19)
C5	C6	1.425(6)	O003	C009	1.4487(19)
C5	C7	1.426(8)	O004	C007	1.206(2)
C6	C10	1.461(7)	C005	C006	1.405(2)
C7	C8	1.340(8)	C005	C00D	1.451(3)
C8	C9	1.425(7)	C005	C00H	1.429(2)
C10	C14	1.443(7)	C006	C008	1.380(2)
C10	C9	1.408(7)	C007	C008	1.475(2)
C11	C12	1.354(8)	C008	C00F	1.410(2)
C11	C9	1.434(8)	C009	C009	1.559(3)
C12	C13	1.425(7)	C00A	C00D	1.451(3)
C13	C14	1.433(7)	C00A	C00G	1.410(3)
C13	C15	1.408(7)	C00A	C00L	1.428(3)
C14	C18	1.415(6)	C00B	C00C	1.326(3)
C15	C16	1.363(7)	C00B	C00I	1.501(2)
C16	C17	1.417(6)	C00C	C00P	1.498(2)
C17	C18	1.371(6)	C00D	C00J	1.415(3)
C17	C19	1.484(6)	C00E	C00F	1.374(3)
C19	O20	1.286(5)	C00E	C00H	1.406(3)
C19	O21	1.250(6)	C00G	C00N	1.384(3)
			C00H	C00K	1.421(3)
			C00J	C00M	1.425(3)
			C00J	C00S	1.423(3)
			C00K	C00M	1.361(3)
			C00L	C00Q	1.404(3)
			C00L	C00R	1.426(3)
			C00N	C00O	1.394(3)
			C00O	C00Q	1.372(3)
			C00R	C00S	1.363(4)

Table S2. Selected bond distances (Å) for compounds **2** and **TMTTF-(2)$_2$.**

$(TMTTF)_2([4]heliceneSO_3)_2$								
O1	S1	1.448(7)	C5	C7	1.412(19)	C26	C27	1.473(14)
S1	O2	1.443(7)	C7	C8	1.272(17)	C27	C28	1.375(16)
S1	O3	1.452(8)	C18	C17	1.360(18)	C27	C29	1.424(16)
S1	C15	1.788(11)	C2	C1	1.356(17)	C28	C32	1.446(13)
S2	O4	1.452(8)	S4	C39	1.751(9)	C29	C30	1.336(15)
S2	O5	1.449(7)	S4	C41	1.704(9)	C30	C31	1.459(13)
S2	O6	1.441(8)	S5	C42	1.681(9)	C31	C32	1.417(13)
S2	C33	1.773(9)	S5	C43	1.739(9)	C31	C33	1.430(13)
S3	C38	1.736(9)	S6	C42	1.714(8)	C32	C36	1.429(14)
S3	C41	1.721(9)	S6	C44	1.719(9)	C33	C34	1.379(13)
C6	C10	1.465(13)	S7	C48	1.739(10)	C34	C35	1.404(12)
C6	C5	1.423(15)	S7	C51	1.717(9)	C35	C36	1.362(14)
C6	C1	1.372(16)	S8	C49	1.730(9)	C37	C38	1.500(12)
C12	C13	1.414(13)	S8	C51	1.727(9)	C38	C39	1.343(13)
C12	C11	1.362(13)	S9	C52	1.723(10)	C39	C40	1.494(13)
C10	C14	1.437(13)	S9	C53	1.750(9)	C41	C42	1.426(11)
C10	C9	1.405(13)	S10	C52	1.721(9)	C43	C44	1.347(13)
C13	C15	1.438(13)	S10	C54	1.752(10)	C43	C46	1.510(12)
C13	C14	1.444(13)	C19	C20	1.388(17)	C44	C45	1.509(12)
C15	C16	1.381(15)	C19	C24	1.41(2)	C47	C48	1.513(13)
C16	C17	1.397(18)	C20	C21	1.40(2)	C48	C49	1.342(14)
C11	C9	1.401(13)	C21	C22	1.34(2)	C49	C50	1.510(12)
C14	C18	1.401(15)	C22	C23	1.28(2)	C51	C52	1.393(12)
C9	C8	1.433(13)	C23	C24	1.53(2)	C53	C54	1.340(14)
C3	C4	1.41(2)	C23	C25	1.42(2)	C54	C55	1.504(13)
C3	C2	1.34(2)	C24	C28	1.451(14)			
C4	C5	1.404(18)	C25	C26	1.40(2)			

Table S3. Selected bond distances (Å) for compound **$(TMTTF)_2([4]heliceneSO_3)_2$.**

$(TMTSF)_5([4]heliceneSO_3)_5$

C1C	C2C	1.378(11)	S1E	O2E	1.410(11)	Se4B	C20B	1.876(8)	C13E	C15E	1.392(7)
C1C	C6C	1.407(11)	S1E	O3E	1.472(11)	Se4B	C23B	1.860(7)	C13D	C17D	1.413(11)
C2C	C3C	1.376(12)	S1E	C15E	1.759(11)	Se4E	C32E	1.880(7)	C13B	C14B	1.396(10)
C3C	C4C	1.378(13)	Se1E	C35E	1.889(7)	Se4E	C34E	1.861(7)	C13B	C15B	1.437(10)
C4C	C5C	1.411(12)	Se1E	C36E	1.895(8)	C5A	C6A	1.416(10)	C15A	C16A	1.384(10)
C5C	C6C	1.420(10)	C26C	C25C	1.510(11)	C5A	C7A	1.426(11)	C14E	C18E	1.420(9)
C5C	C7C	1.424(13)	C26C	C27C	1.348(11)	C6A	C10A	1.462(11)	C14E	C28E	1.411(10)
C6C	C10C	1.466(10)	C26C	Se2C	1.887(7)	C5E	C6E	1.388(14)	C14D	C15D	1.374(11)
C7C	C8C	1.360(13)	C24C	C23C	1.353(10)	C5E	C7E	1.444(16)	C14B	C18B	1.437(9)
C8C	C9C	1.429(11)	C24C	Se2C	1.863(7)	C5E	C4E	1.397(10)	C16A	C17A	1.396(11)
C9C	C11C	1.424(11)	C23C	Se3C	1.859(6)	C5E	C24E	1.405(10)	C15D	C16D	1.400(11)
C9C	C10C	1.397(11)	C23C	Se4C	1.889(6)	C5D	C9D	1.466(11)	C15B	C16B	1.375(10)
C14C	C13C	1.446(10)	C22C	C21C	1.503(10)	C5D	C19D	1.413(12)	C17A	C18A	1.351(10)
C14C	C10C	1.450(10)	C21C	C20C	1.327(10)	C5B	C6B	1.421(10)	C16D	C17D	1.378(10)
C14C	C18C	1.409(10)	C21C	Se3C	1.878(7)	C5B	C7B	1.428(11)	C16B	C17B	1.398(12)
C13C	C12C	1.422(10)	C20C	Se4C	1.892(6)	C7A	C8A	1.353(11)	C18B	C17B	1.364(11)
C13C	C15C	1.432(10)	N1H	C1H	1.144(15)	C6E	C10E	1.445(13)	C19B	C20B	1.500(11)
C12C	C11C	1.347(11)	C1H	C2H	1.456(16)	C6E	C1E	1.409(9)	C20A	C21A	1.325(11)
C16C	C15C	1.381(11)	C1G	N1G	1.149(15)	C6E	C21E	1.422(10)	C20A	C19A	1.510(12)
C16C	C17C	1.407(11)	C1G	C2G	1.431(15)	C6D	C7D	1.339(13)	C21A	C22A	1.497(12)
C15C	S1C	1.781(8)	C28C	C27C	1.504(10)	C6B	C10B	1.470(10)	C20D	C21D	1.354(11)
C17C	C18C	1.370(10)	C2A	C3A	1.394(13)	C8A	C9A	1.413(10)	C20D	C18D	1.504(10)
S1A	O1A	1.457(5)	Se2A	C24A	1.864(8)	C7E	C8E	1.374(17)	C20B	C21B	1.343(12)
S1A	O2A	1.449(5)	Se2A	C26A	1.890(7)	C7D	C8D	1.439(10)	C21D	C22D	1.506(10)
S1A	O3A	1.454(5)	C2B	C3B	1.394(12)	C7B	C8B	1.359(11)	C21B	C22B	1.502(11)
S1A	C15A	1.797(7)	Se2B	C24B	1.871(7)	C9A	C10A	1.417(10)	C23A	C24A	1.361(11)
Se1A	C24A	1.868(7)	Se2B	C27B	1.879(7)	C9A	C11A	1.426(11)	C23D	C24D	1.390(10)
Se1A	C27A	1.874(8)	Se2E	C35E	1.853(8)	C8E	C9E	1.421(15)	C23B	C24B	1.374(11)
C19C	C20C	1.529(9)	Se2E	C38E	1.883(8)	C8D	C9D	1.411(11)	C25A	C26A	1.495(11)
C1A	C2A	1.376(11)	C2D	C3D	1.349(15)	C8D	C10D	1.427(11)	C26A	C27A	1.340(11)
C1A	C6A	1.420(11)	Se2D	C24D	1.854(7)	C8B	C9B	1.427(10)	C25D	C26D	1.493(11)
S1B	O1B	1.453(6)	Se2D	C26D	1.879(7)	C10A	C14A	1.426(10)	C25B	C26B	1.513(10)
S1B	O2B	1.453(6)	C2I	C1I	1.45(3)	C9E	C10E	1.462(14)	C27A	C28A	1.497(11)
S1B	O3B	1.451(6)	C1I	N1I	1.17(3)	C9E	C11E	1.432(15)	C26D	C27D	1.345(11)
S1B	C15B	1.786(7)	Se3A	C20A	1.893(8)	C9D	C13D	1.452(9)	C26B	C27B	1.341(11)
Se1B	C24B	1.852(7)	Se3A	C23A	1.872(7)	C9B	C10B	1.409(9)	C27D	C28D	1.518(10)
Se1B	C26B	1.871(8)	C3A	C4A	1.365(12)	C9B	C11B	1.430(10)	C28B	C27B	1.504(11)
C1B	C2B	1.364(11)	C3D	C4D	1.424(12)	C11A	C12A	1.344(11)	C30E	C31E	1.512(11)
C1B	C6B	1.418(10)	Se3D	C20D	1.873(7)	C10E	C14E	1.380(13)	C31E	C32E	1.357(11)
C1D	C2D	1.397(12)	Se3D	C23D	1.856(7)	C10D	C11D	1.357(10)	C32E	C33E	1.522(12)

C1D	C19D	1.388(11)	C3B	C4B	1.346(12)	C10B	C14B	1.457(10)	C34E	C35E	1.363(11)
S1D	O1D	1.461(5)	Se3B	C21B	1.879(8)	C12A	C13A	1.439(10)	C36E	C37E	1.530(11)
S1D	O2D	1.460(5)	Se3B	C23B	1.862(7)	C11E	C12E	1.329(16)	C36E	C38E	1.317(12)
S1D	O3D	1.451(5)	Se3E	C31E	1.865(8)	C11D	C12D	1.432(10)	C38E	C39E	1.517(12)
S1D	C14D	1.776(8)	Se3E	C34E	1.863(7)	C11B	C12B	1.348(10)	C15E	C16E	1.403(9)
Se1D	C24D	1.859(7)	Se4A	C21A	1.874(8)	C13A	C14A	1.436(10)	C15E	S1F	1.748(17)
Se1D	C27D	1.884(7)	Se4A	C23A	1.863(7)	C13A	C15A	1.429(9)	C16E	C17E	1.54(3)
S1C	O1C	1.458(5)	C4A	C5A	1.416(11)	C12E	C13E	1.444(14)	C16E	C27E	1.34(3)
S1C	O2C	1.449(6)	C4D	C5D	1.420(10)	C12D	C13D	1.419(10)	C4E	C3E	1.397(9)
S1C	O3C	1.465(6)	C4D	C6D	1.417(13)	C12D	C14D	1.432(9)	C3E	C2E	1.417(17)
Se1C	C24C	1.865(7)	Se4D	C21D	1.876(7)	C12B	C13B	1.426(9)	C2E	C1E	1.329(17)
Se1C	C27C	1.863(7)	Se4D	C23D	1.851(7)	C14A	C18A	1.416(9)	C17E	C18E	1.329(17)
S1E	O1E	1.433(9)	C4B	C5B	1.417(11)	C13E	C14E	1.440(12)	C24E	C23E	1.403(7)
C23E	C22E	1.406(9)	O2F	S1F	1.430(14)	S1G	Cl2G	2.046(15)	S1H	Cl1H	2.051(14)
C22E	C21E	1.333(17)	S1F	O3F	1.461(15)	S1G	Cl3G	1.794(14)	S1H	Cl4H	1.724(16)
C27E	C28E	1.326(18)	S1G	O1G	1.365(14)	S1H	O2H	1.340(15)	Cl1H	O5G	1.80(5)
O1F	S1F	1.442(14)									

Table S4. Selected bond distances (Å) for compound **$(TMTSF)_5([4]heliceneSO_3)_5$.**

(BEDT-TTF)$_2$([4]heliceneSO$_3$)								
O19A	S22A	1.462(10)	C17	C18	1.378(12)	S10B	Cl2B	2.184(4)
O20A	S22A	1.472(10)	S1A	C2A'	1.71(3)	O1C	S10C	1.494(14)
O21A	S22A	1.482(9)	S1A	C2A	1.87(3)	S10C	Cl2C	2.132(4)
S22A	C15A	1.767(11)	S1A	C3A	1.743(6)	S10C	Cl3C	2.184(4)
C15A	C16A	1.390(12)	S2A	C1A	1.906(19)	C7A	C8A	1.507(18)
C15A	C13	1.351(12)	S2A	C1A'	1.70(3)	C7A'	C8A'	1.489(19)
C16A	C17	1.451(12)	S2A	C4A	1.739(6)	S1B	C2B	1.807(12)
S22B	O19B	1.465(13)	S3A	C3A	1.747(6)	S1B	C2B'	1.737(12)
S22B	O20B	1.464(13)	S3A	C5A	1.730(6)	S1B	C3B	1.743(6)
S22B	O21B	1.472(14)	S4A	C4A	1.746(6)	S2B	C1B	1.768(10)
S22B	C15B	1.799(15)	S4A	C5A	1.737(6)	S2B	C1B'	1.800(14)
C15B	C16B	1.438(16)	S5A	C6A	1.732(6)	S2B	C4B	1.734(6)
C15B	C13	1.491(14)	S5A	C9A	1.747(6)	S3B	C3B	1.744(6)
C16B	C17	1.363(14)	S6A	C6A	1.734(6)	S3B	C5B	1.723(6)
C1	C2	1.369(10)	S6A	C10A	1.757(6)	S4B	C4B	1.743(6)
C1	C6	1.411(10)	S7A	C9A	1.735(6)	S4B	C5B	1.722(6)
C2	C3	1.387(11)	S7A	C7A	1.790(14)	S5B	C6B	1.723(5)
C3	C4	1.374(13)	S7A	C7A'	1.804(12)	S5B	C9B	1.737(6)
C4	C5	1.404(12)	S8A	C8A	1.841(11)	S6B	C6B	1.722(6)
C5	C6	1.428(10)	S8A	C8A'	1.776(13)	S6B	C10B	1.733(6)
C5	C7	1.416(11)	S8A	C10A	1.740(6)	S7B	C9B	1.746(6)
C6	C10	1.437(10)	C1A	C2A'	1.59(3)	S7B	C7B	1.789(10)
C10	C9	1.394(11)	C1A'	C2A	1.40(3)	S8B	C10B	1.743(6)
C10	C14	1.452(11)	C3A	C4A	1.331(9)	S8B	C8B	1.769(9)
C8	C9	1.433(14)	C5A	C6A	1.355(8)	C1B	C2B	1.539(16)
C8	C7	1.340(14)	C9A	C10A	1.344(9)	C1B'	C2B'	1.522(18)
C9	C11	1.415(14)	O1A	S10A	1.577(12)	C3B	C4B	1.349(9)
C11	C12	1.343(18)	S10A	Cl2A	2.132(4)	C5B	C6B	1.370(8)
C12	C13	1.467(16)	S10A	Cl3A	2.053(5)	C9B	C10B	1.345(9)
C13	C14	1.430(10)	O1B	S10B	1.494(14)	C7B	C8B	1.446(15)
C14	C18	1.391(13)	S10B	Cl3B	2.053(5)			

Table S5. Selected bond distances (Å) for compound **(BEDT-TTF)$_2$([4]heliceneSO$_3$).**

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