Supporting Information for

Reviving BVDT-TTF and EVT-TTF salts

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SUMMARY

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

	(BVDT-TTF)(TaF_6)	**$(BVDT\text{-}TTF)_{2.5}(I_3)$**	**$(BVDT\text{-}TTF)_2(ReO_4)$**	**(EVT-TTF)(ClO_4)**
Formula sum	$C_{10}H_4S_8$, TaF_6	$C_{10}H_4S_8$, $I_{1.2}$	$C_{10}H_4S_8$, $(ClO_4)_{0.5}$	$C_{10}H_6S_8$, $(CH_2Cl_2)_{0.5}$, ClO_4
Formula weight	675.56	532.89	505.71	524.54
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Pnnm*	*Pnma*	*C*2/*m*	$P2_1/c$
a/Å	4.8259(3)	3.777(19)	33.133(3)	8.0005(4)
b/Å	17.8935(9)	12.18(14)	12.1739(14)	23.8718(10)
c/Å	10.1805(5)	33.1(9)	3.8263(6)	9.8100(5)
α/°	90	90	90	90
β/°	90	90	93.360(11)	100.649(5)
γ/°	90	90	90	90
V/Å^3	879.11(8)	1523(46)	1540.7(3)	1841.31(16)
Z	2	4	4	4
D_c/g cm^{-3}	2.552	2.324	2.180	1.892
T/K	200	200	200	297
μ/mm^{-1}	20.964	29.814	18.139	11.819
Reflections collected	883	1518	1714	6003
Independent reflection	826	1207	1035	2614
final $R_1{}^a$, $wR_2{}^b$ [$I > 2\sigma(I)$]	0.0393/0.1129	0.0795/0.2430	0.1192/0.3454	0.0570/0.1564
$R_1{}^a$,$wR_2{}^b$ (all data)	0.0408/0.1141	0.0943/0.2540	0.1249/0.3489	0.0646/0.1653
goodness-of-fit on F^2	1.099	1.131	1.097	1.055
$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	-1.305/2.169	-0.755/1.261	-0.971/1.102	-0.938/0.984
Completeness (%)	99.2	98.4	81.0	94.1
CCDC number	2296888-	2296889-	2296890-	2296891-

[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 $P= [max(F_0^2, 0) + 2F_c^2]/3$.

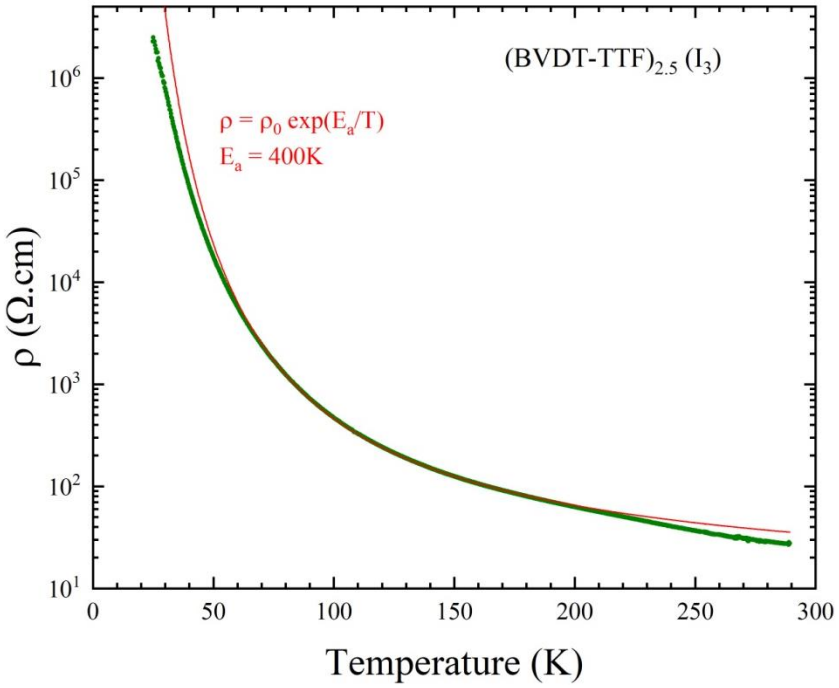

Fig. S1 Temperature dependent resistivity measurement on single crystal for **$(BVDT\text{-}TTF)_{2.5}(I_3)$**.

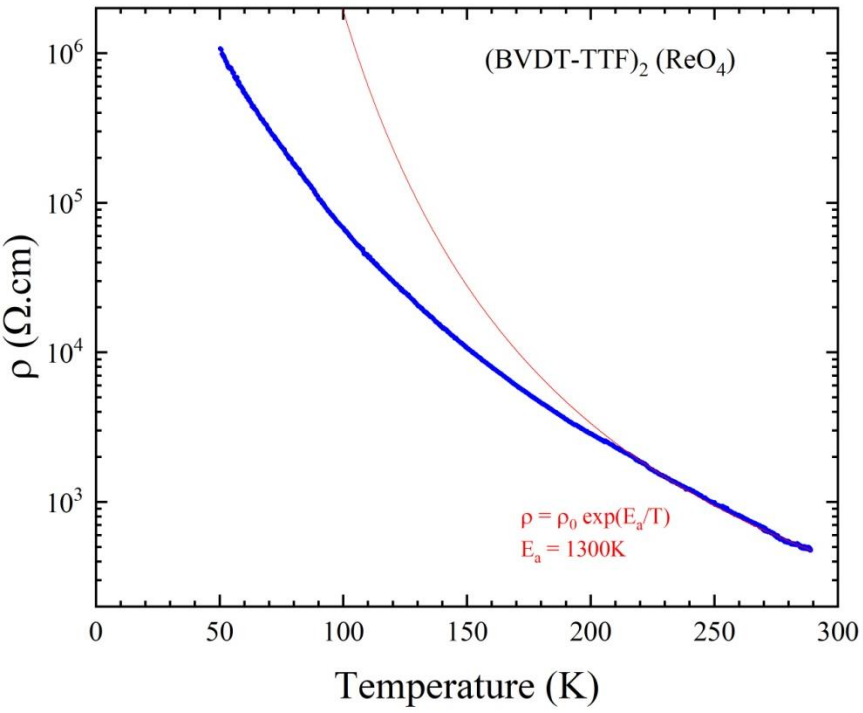

Fig. S2 Temperature dependent resistivity measurement on single crystal for **$(BVDT\text{-}TTF)_2(ReO_4)$** .

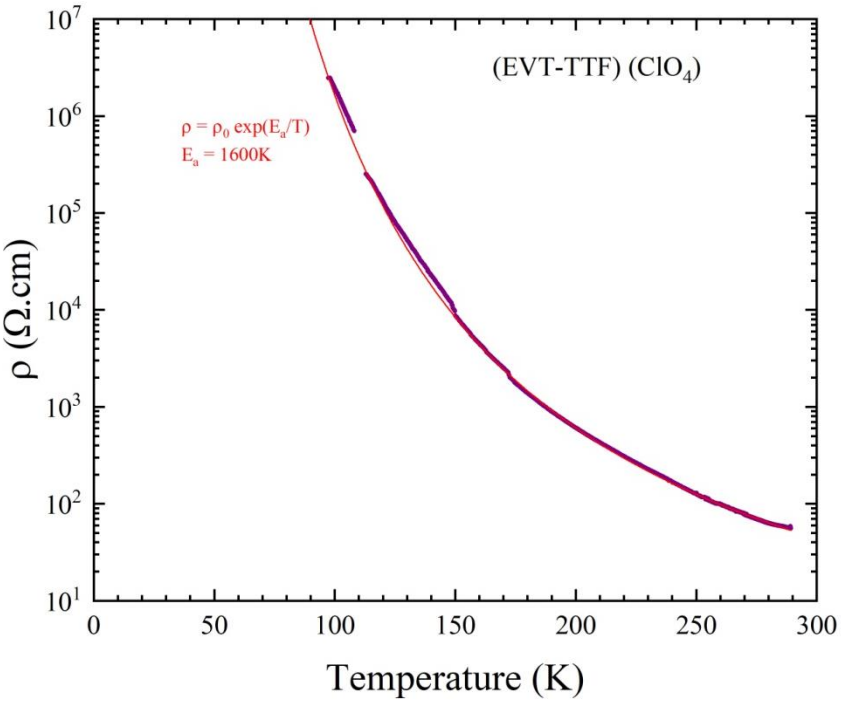

Fig. S3 Temperature dependent resistivity measurement on single crystal for **(EVT-TTF)(ClO_4)**.

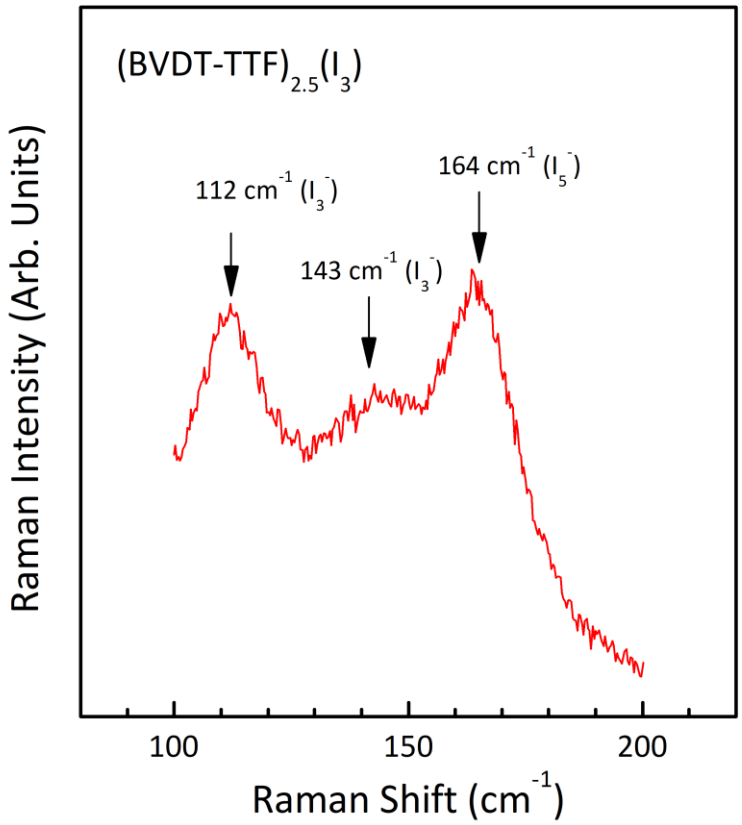

Fig. S4 Raman spectrum of $(BVDT\text{-}TTF)_{2.5}(I_3)$ measured at room temperature with the 632.8 nm excitation line, in the frequency range of the polyiodide stretching vibrations.

The Raman spectrum of $(BVDT\text{-}TTF)_{2.5}(I_3)$ in the frequency range of the stretching polyiodide modes reveals three distinct modes:

- the symmetric stretching of the centrosymmetric triiodide anion at 112 cm^{-1},

- the asymmetric stretching mode of the asymmetric triiodide ion at 143 cm^{-1},

- the band at 164 cm^{-1}, which is most likely related to the symmetric stretching of the L-shaped pentaiodide present in the structure.[1,2]

Table S2 Stoichiometry and conductivity of BVDT-TTF, EVT-TTF and BEDT-TTF salts.

Donor	Anion	Stoichiometry	Single crystal conductivity ($S \cdot cm^{-1}$, 290K)
BVDT-TTF	TaF_6^-	1 : 1	$4.4 \cdot 10^{-2}$
BVDT-TTF	I_3^-	2.5 : 1	$1.4 \cdot 10^{-1}$
BVDT-TTF	ReO_4^-	2 : 1	$3.1 \cdot 10^{-3}$
EVT-TTF	ClO_4^-	1 : 1	$1.8 \cdot 10^{-2}$
BEDT-TTF[3]	TaF_6^-	1 : 1	$5 \cdot 10^{-4}$
β-BEDT-TTF[4]	I_3^-	2 : 1	20
BEDT-TTF[5]	ReO_4^-	2 : 1	$5 \cdot 10^{-3}$
BEDT-TTF[6]	ClO_4^-	2 : 1	26.31

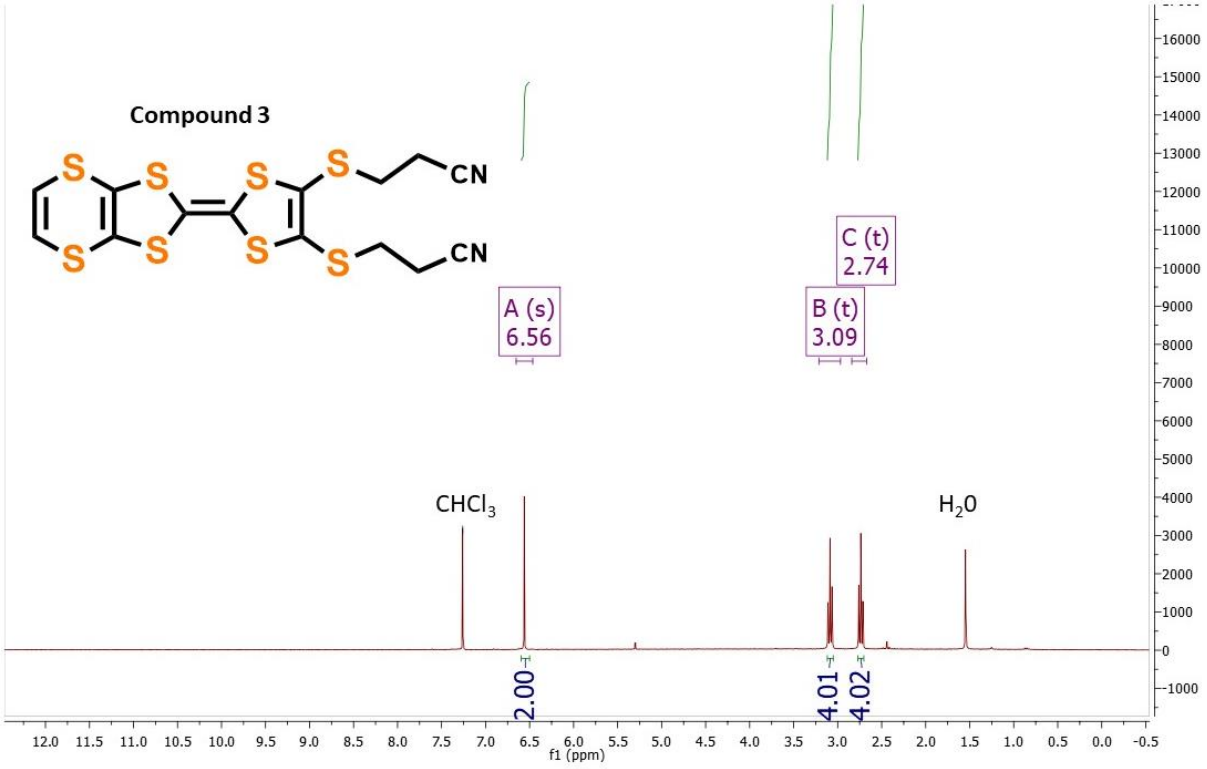

Fig. S5 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **3**.

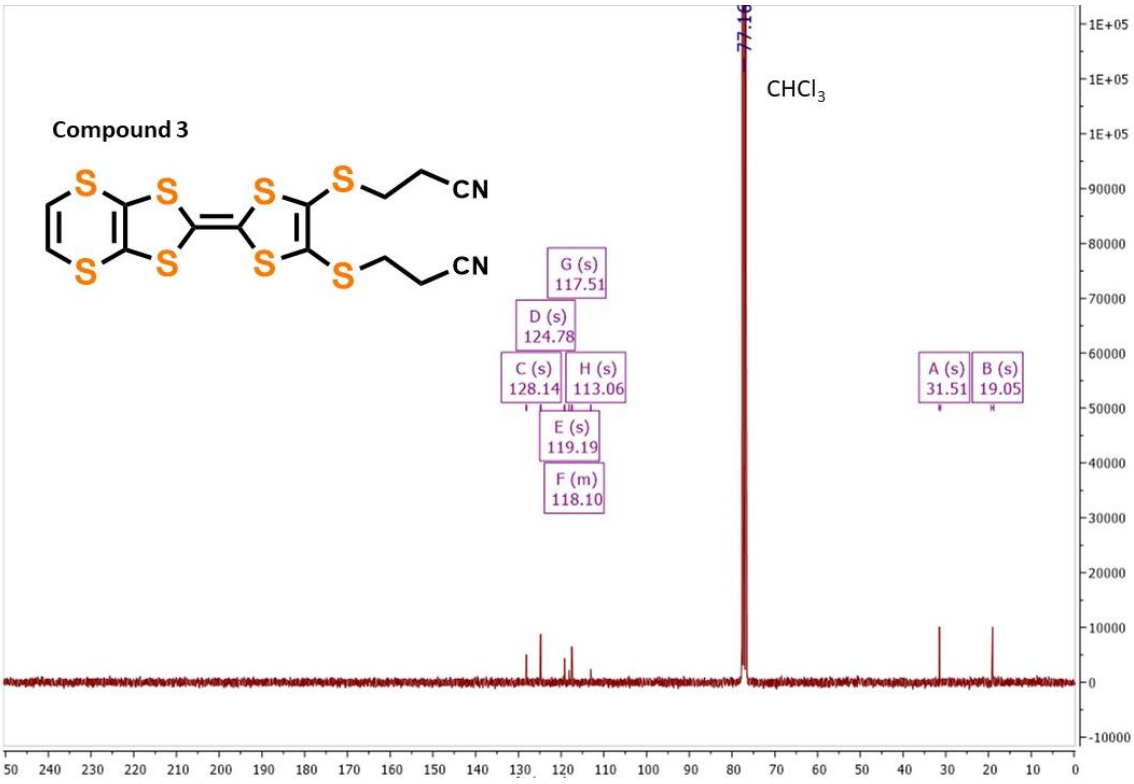

Fig. S6 ^{13}C NMR (76 MHz, $CDCl_3$) of compound **3**.

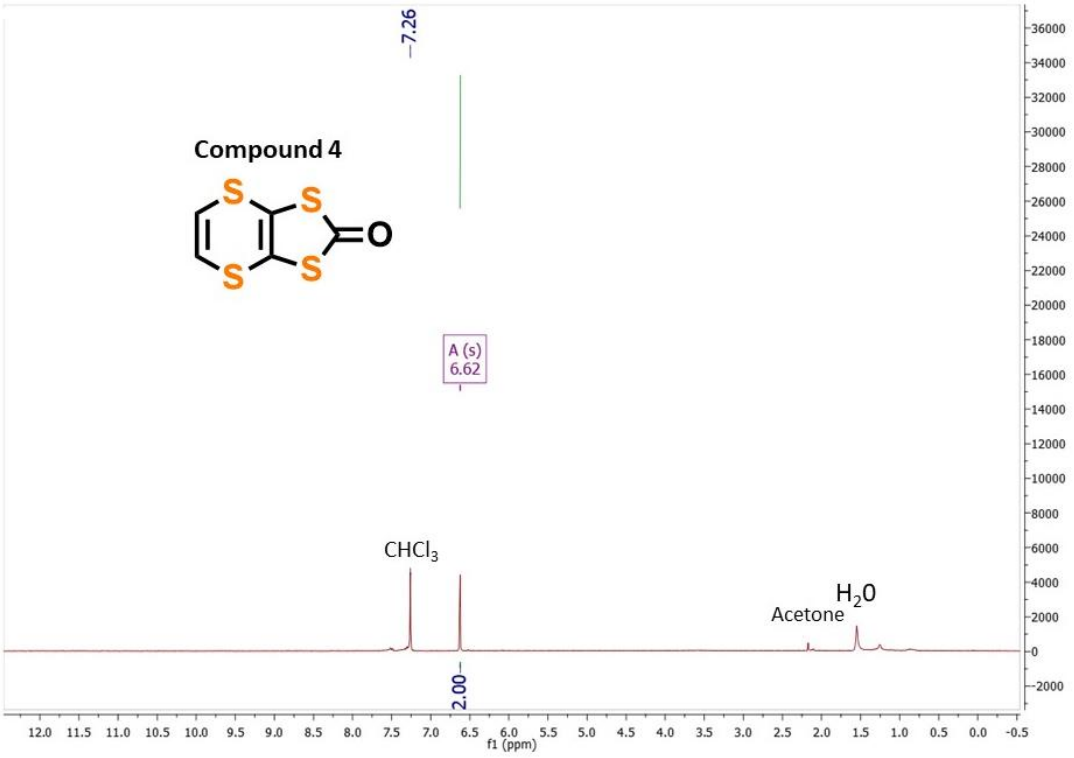

Fig. S7 ^{1}H NMR (300 MHz, $CDCl_3$) of compound **4**.

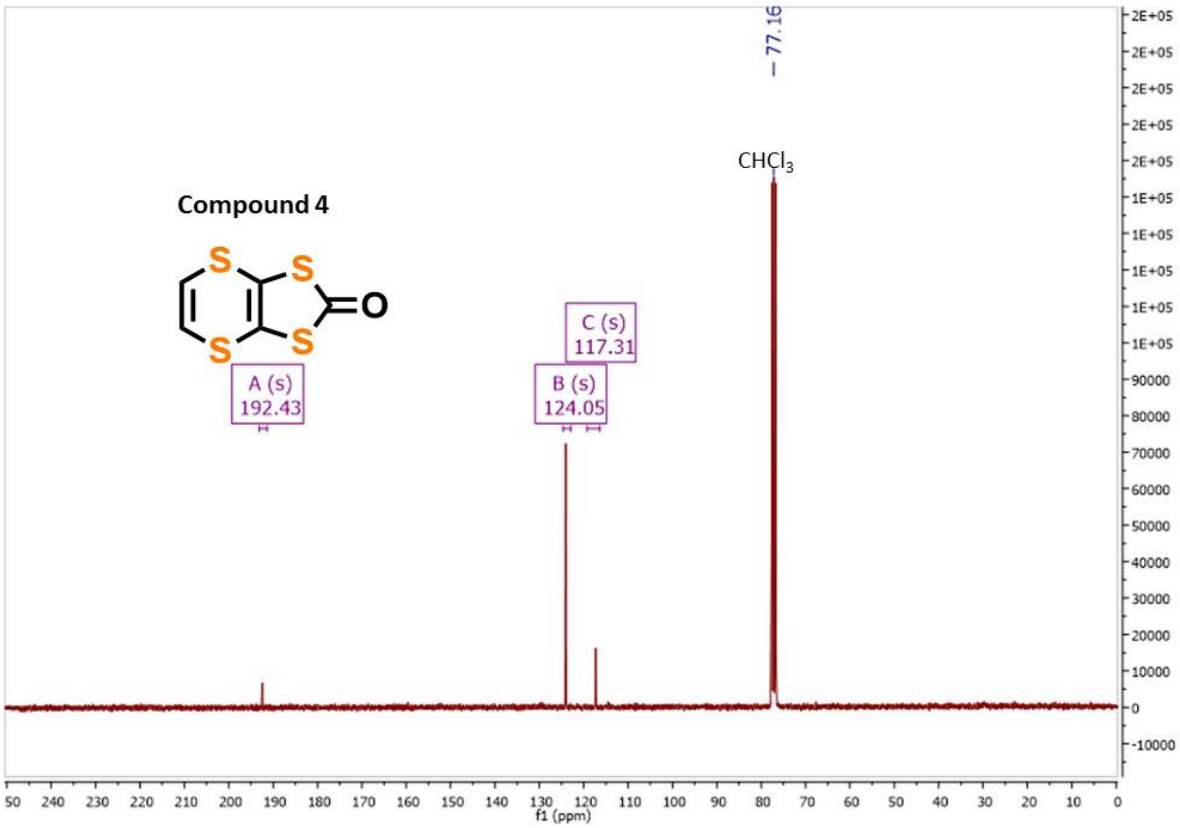

Fig. S8 ^{13}C NMR (76 MHz, $CDCl_3$) of compound **4**.

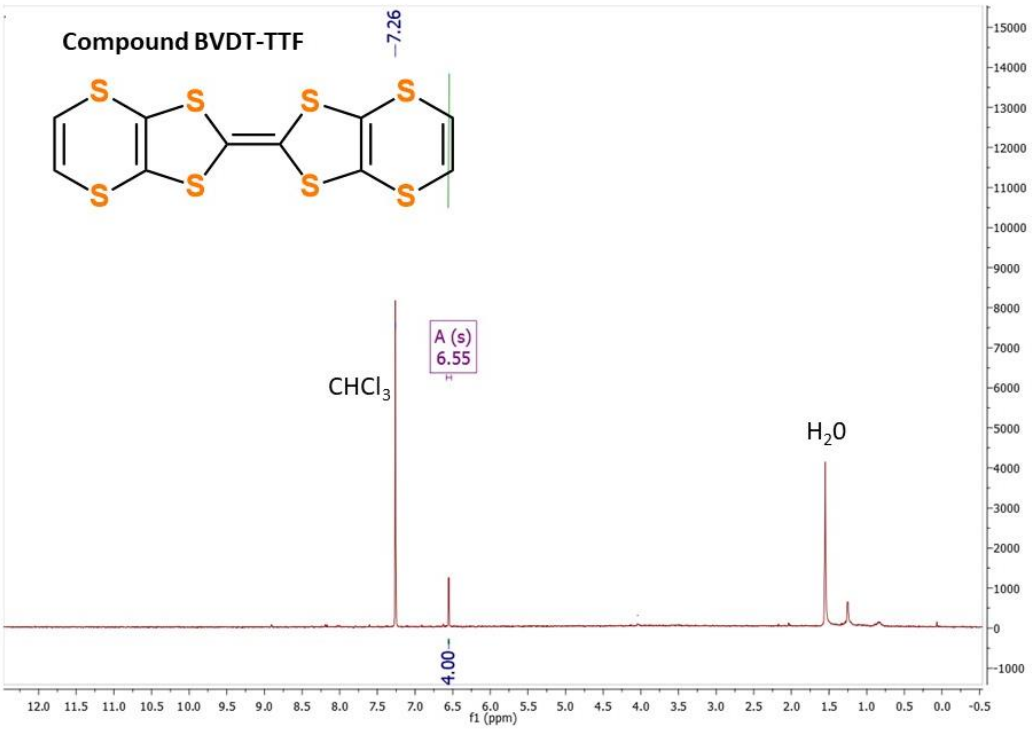

Fig. S9 ^{1}H NMR (300 MHz, $CDCl_3$) of **BVDT-TTF**.

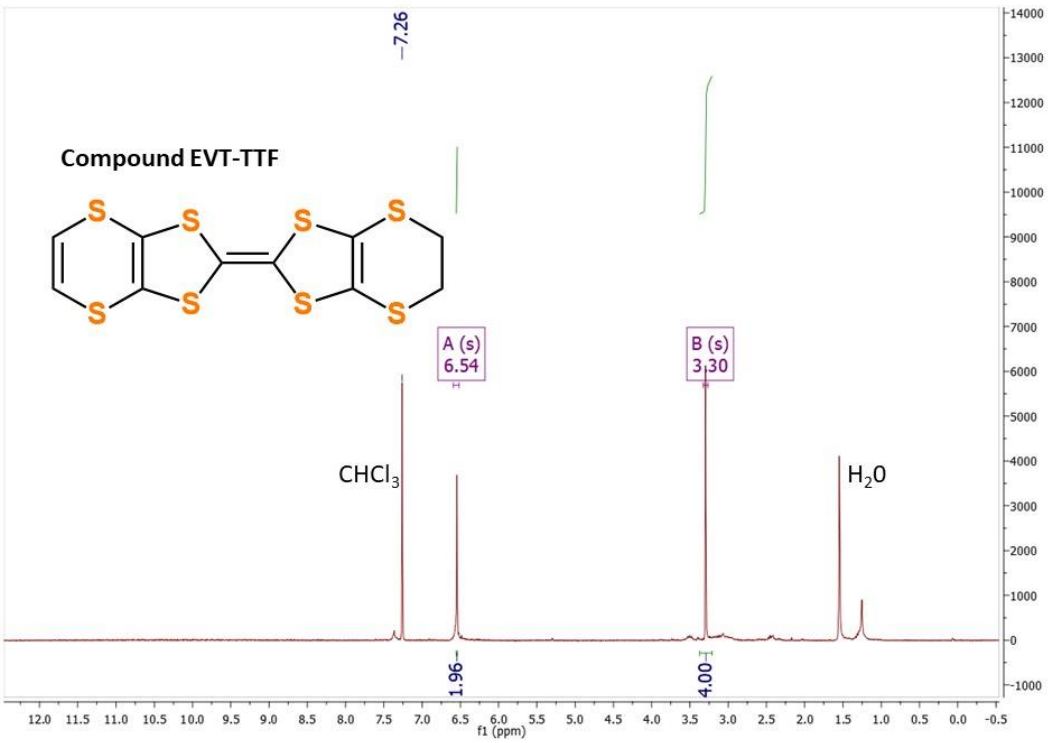

Fig. S10 ^{1}H NMR (300 MHz, $CDCl_3$) of **EVT-TTF**.

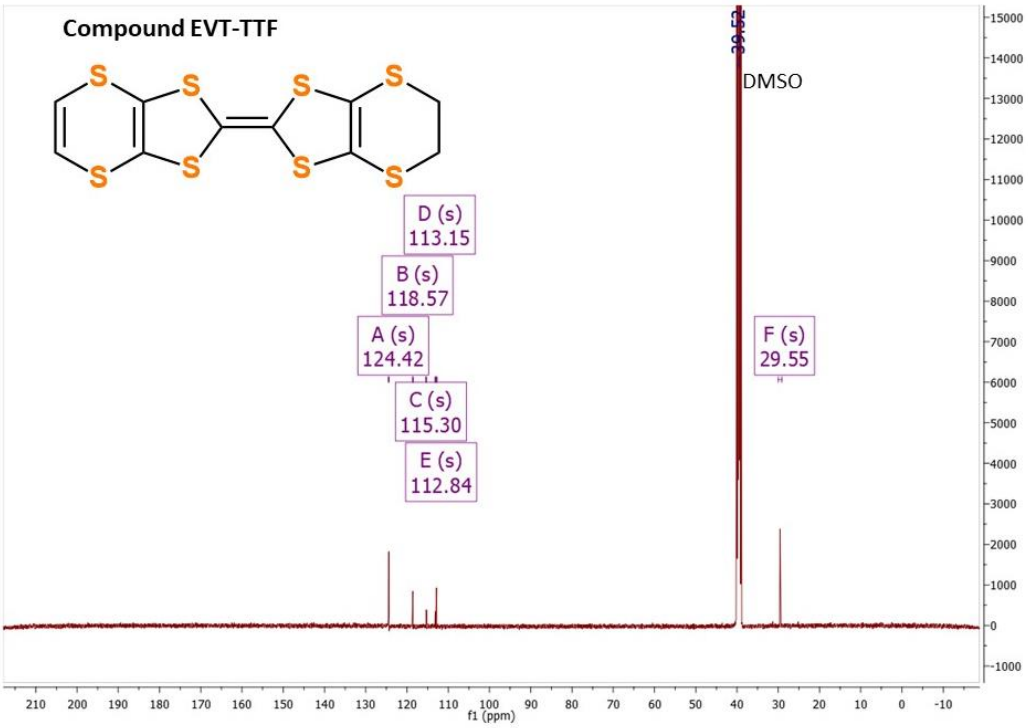

Fig. S11 ^{13}C NMR (126 MHz, DMSO-d_6) of **EVT-TTF**.

Mass spectrum:

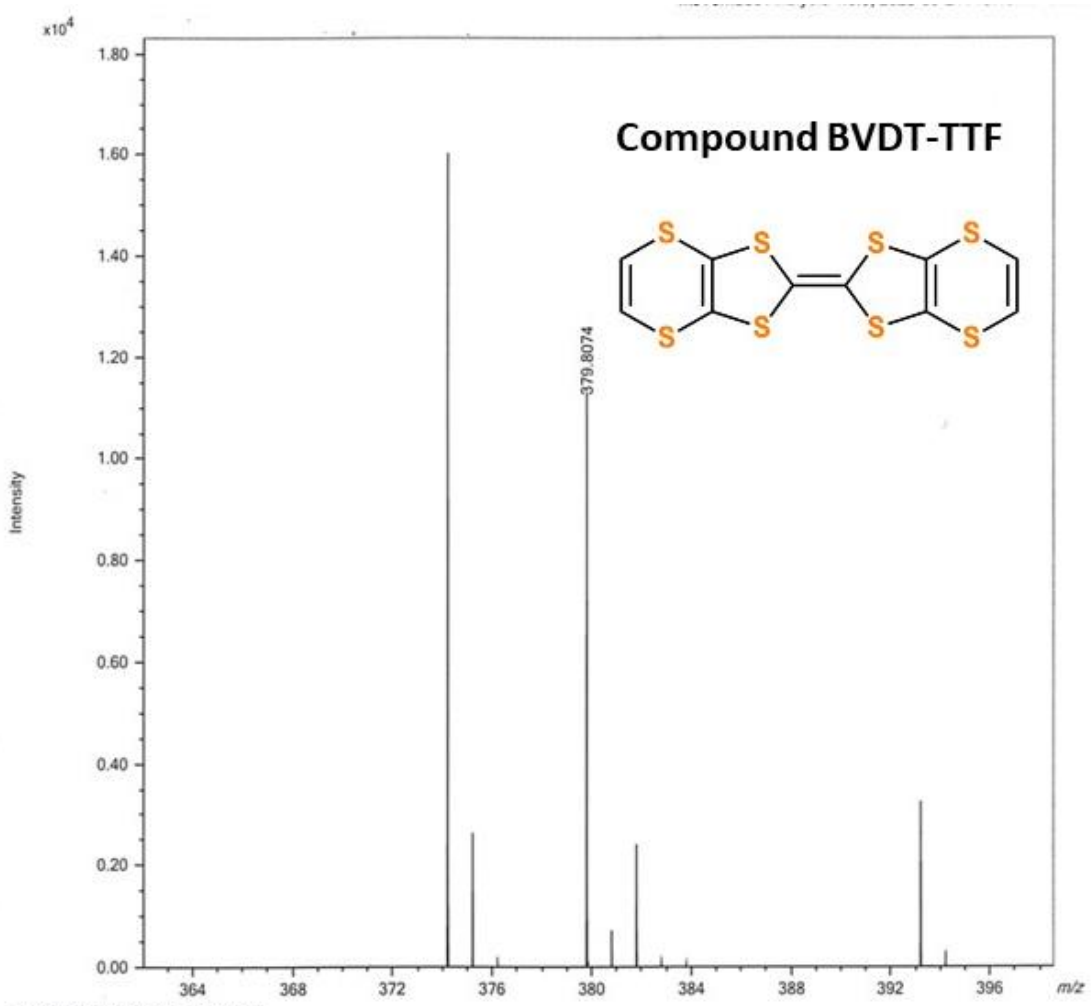

Fig. S12 MS (MALDI-TOF) of **BVDT-TTF**.

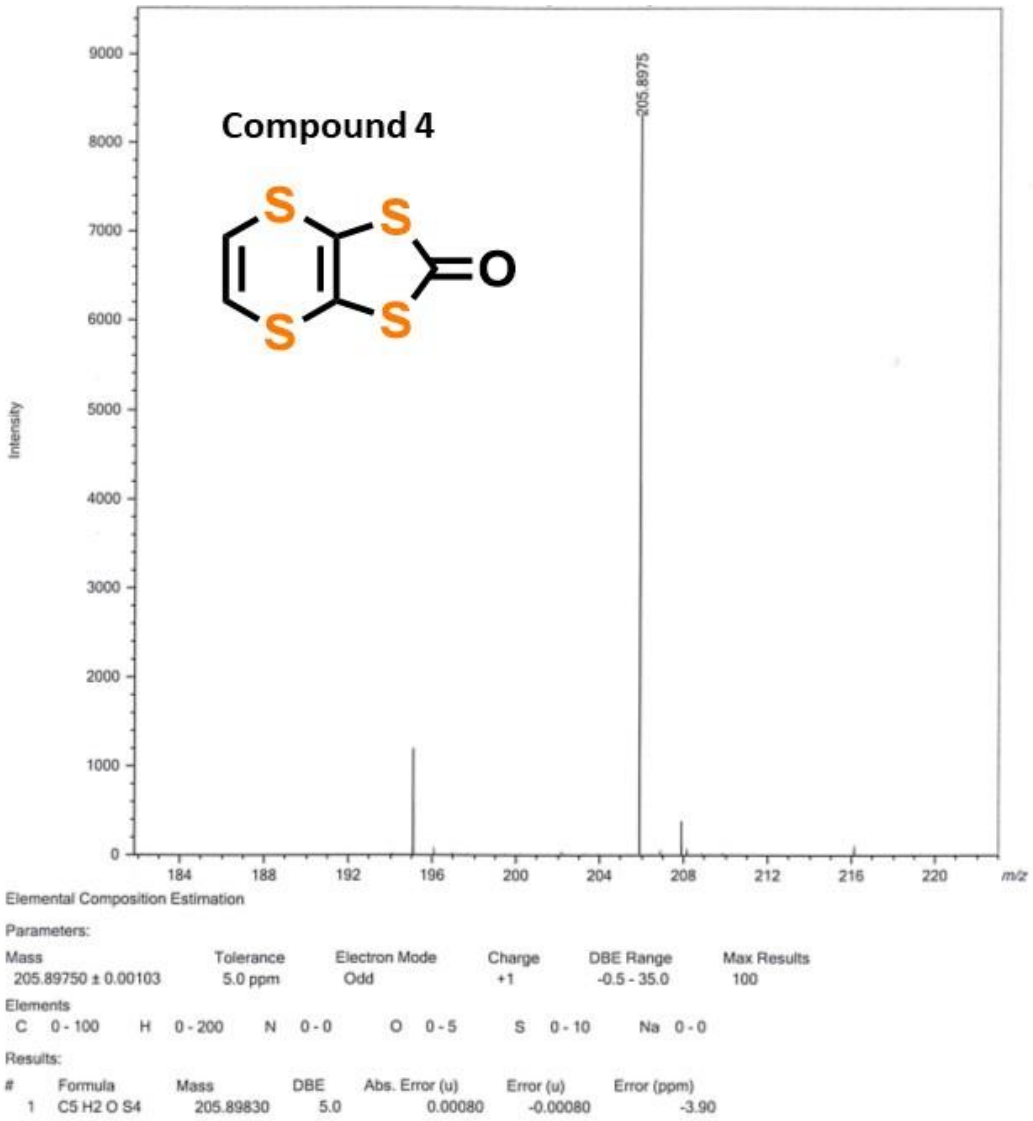

Fig. S13 MS (MALDI-TOF) of compound **4**.

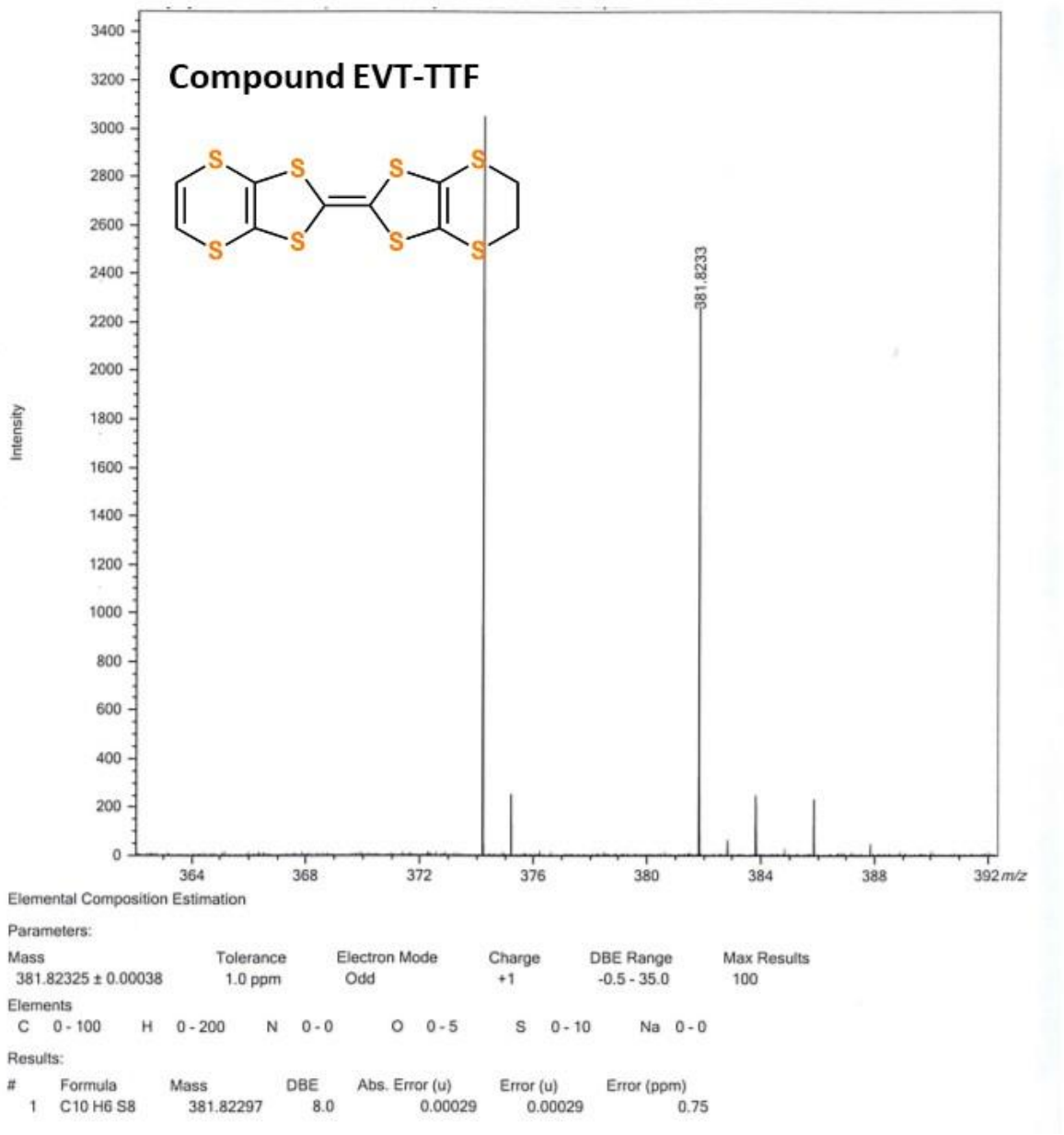

Fig. S14 MS (MALDI-TOF) of **EVT-TTF**.

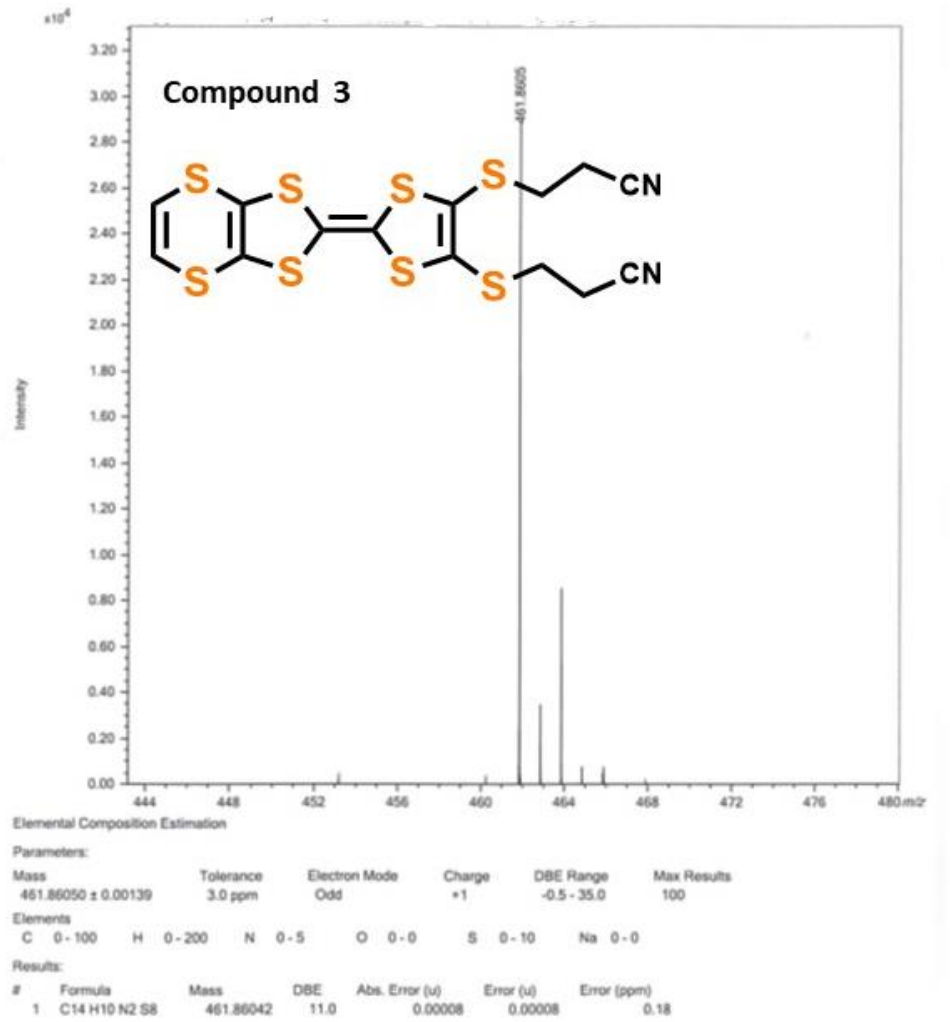

Fig. S15 MS (MALDI-TOF) of compound **3**.

References

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