Chemo- and Enantioselective Sulfoxidation of Bis(ethylenedithio)-Tetrathiafulvalene (BEDT-TTF) into Chiral BEDT-TTF-Sulfoxide

Marcos Chas,[a] Margareth Lemarié,[b] Mihaela Gulea,[b] and Narcis Avarvari*,[a]

SUPPORTING INFORMATION

Experimental section

General comments. Dry CH_2Cl_2 and CH_3CN were obtained by distillation over P_2O_5 and THF was distilled over sodium and benzophenone. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 500 spectrometer operating at 500.04 MHz for ^1H, 125.75 MHz for ^{13}C. Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used: m, multiplet. EI MS spectra were recorded on Thermo Electron Corporation TRACE-DSQ apparatus, with direct introduction probe at 70 eV. Elemental analyses were performed by the "Service d'Analyse du CNRS" at Gif/Yvette, France.

Synthesis of BEDT-TTF S-Oxide 2a-c: To a BEDT-TTF (1.00 g, 2.60 mmol) solution in THF (700 ml), (+), (-) or (rac)-(8,8-Dichlorocamphorylsulfonyl)-oxaziridine **1** (0.70 g, 2.37 mmol) in THF (10 ml) was added. The resulting solution was stirred at room temperature for 12 hours. The solvent was then evaporated under reduced pressure and the solid residue chromatographed through silica gel with CH_2Cl_2, and then CH_2Cl_2/AcOEt 20:1 as eluents to obtain the product as a yellow solid. Further purification may be achieved by recrystallization from hot toluene, affording 797 mg (84% yield) of the pure product. Single crystals suitable for X-ray diffraction were obtained by evaporation of a dilute solution of the product in CH_2Cl_2 or toluene. ^1H NMR ($CDCl_3$) δ 3.20-3.44 (m, 8H, $S(CH_2)_2S$); ^{13}C NMR ($CDCl_3$) δ 28.7 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 30.7 (CH_2); IR (KBr, cm^{-1}) 1034 (SO); MS (EI) *m/z* 400 (M^+), 384 (BEDT-TTF^+); Anal. Calc. for $C_{10}H_8O_1S_8$: C 29.98, H 2.01, O 3.99. Found: C 29.72, H 2.03, O 4.50%.

Synthesis of the CT complex (BEDT-TTF-bis(sulfoxide)][$TCNQF_4$] 3: To a solution of **2** (10 mg, 0.025 mmol) in CH_2Cl_2 (15 ml), a solution of $TCNQF_4$ (6.9 mg, 0.025 mmol) in 5 ml of CH_2Cl_2 was added The resulting mixture was left standing at room temperature in an open flask and after solvent evaporation, black single crystals were obtained. IR (KBr, cm^{-1}) 2192 (CN), 2165 (CN), 1583 (C=C TCNQF4), 1038 (SO); MS (EI) *m/z* 416 (BEDT-TTF-$(SO)_2^+$), 384 (BEDT-TTF^+); Anal. Calc. for $C_{22}H_8F_4N_4O_2S_8$: C 38.14, H 1.16, N 8.09 Found: C 38.82, H 1.25, N 7.76%.

Chiral HPLC analyses: The measurements have been performed with a Daicel Chiralpak column, AD-H 5 µm, 4.6x250 mm, 1 mL/min, 90% MeCN, 10% *iso*-propanol, 20 °C. Retention times 13.5-15 min. (enantiomer *S*) and 25.2-27.5 min (enantiomer *R*).

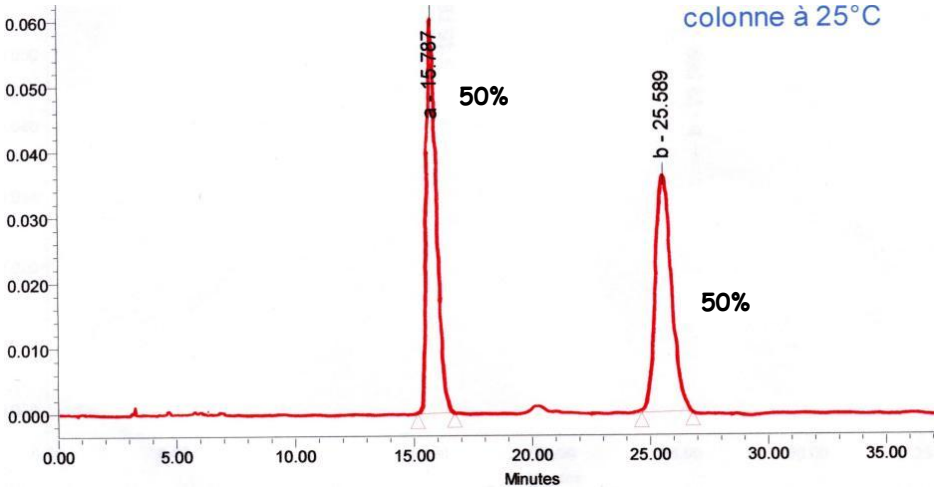


Fig. S1 Chiral HPLC chromatogram for **2c** (racemic).

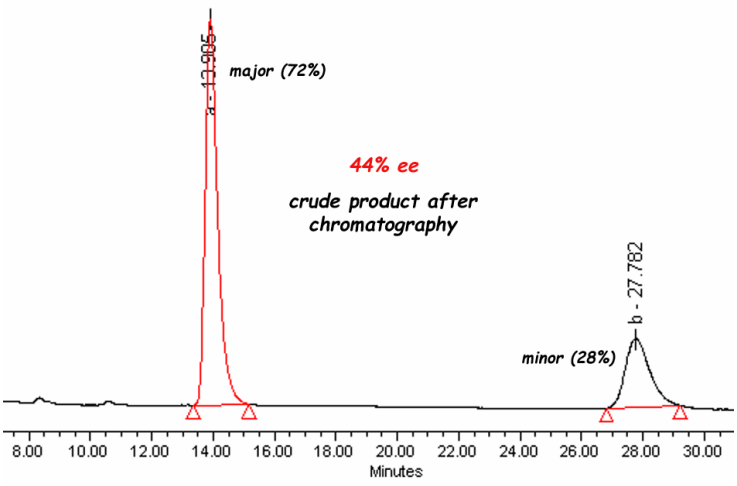


Fig. S2 Chiral HPLC chromatogram for **2a** (enantio-enriched). Solid after chromatography purification.

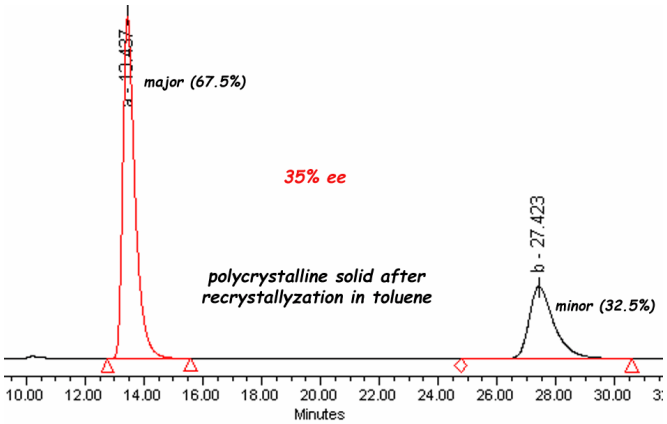


Fig. S3 Chiral HPLC chromatogram for **2a** (enantio-enriched). Solid after recrystallization in toluene.

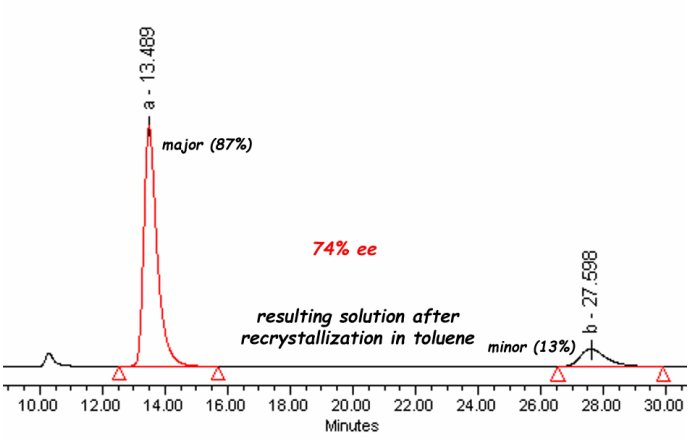


Fig. S4 Chiral HPLC chromatogram for **2a** (enantio-enriched). Mother liquors after recrystallization in toluene.

X-Ray Structure Determinations. X-ray diffraction measurements were performed on a Bruker Kappa CCD diffractometer for, operating with a Mo-Kα (λ = 0.71073 Å) X-ray tube with a graphite monochromator. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full-matrix least-square procedures on F^2.[1] All non-H atoms were refined anisotropically, and hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined.

X-ray structure of 2.

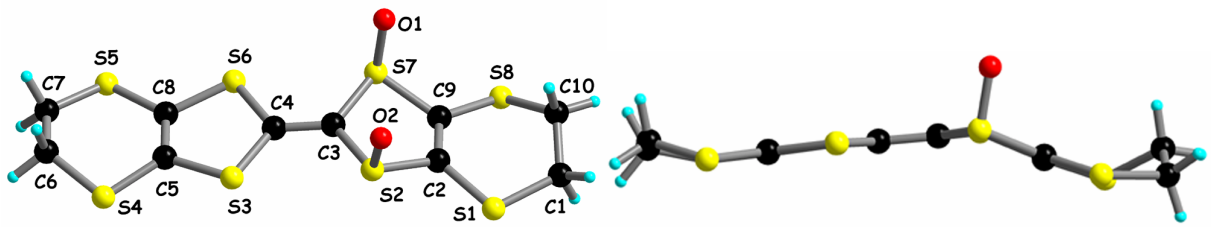


Fig. S5 Molecular structure of **2** along with the numbering scheme (left). The site occupational factors (s.o.f.) have been refined to 0.8 for O1 and 0.2 for O2. Side view of the molecule (right).

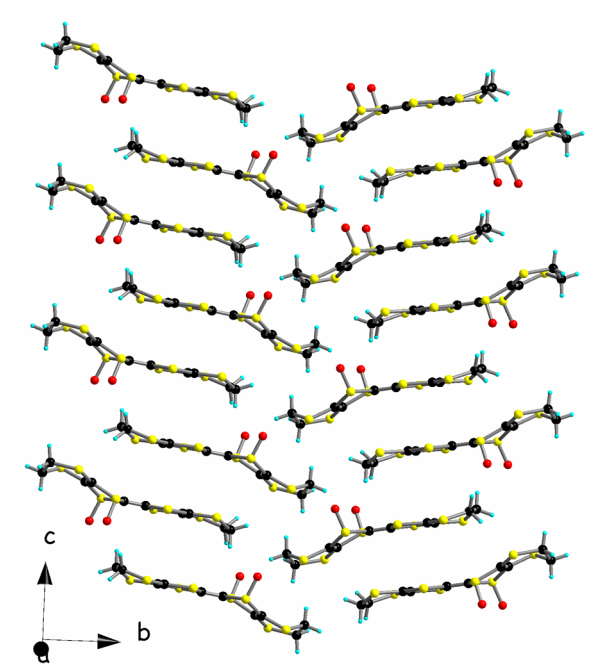


Fig. S6 Packing diagram of **2** along the *a* axis.

Bond Lengths (Å)

S1 C2 1.736(4)	S1 C1 1.807(5)	S2 O2 1.445(15)	S2 C3 1.755(4)
S2 C2 1.763(4)	S3 C4 1.733(4)	S3 C5 1.745(4)	S4 C6 1.716(6)
S4 C5 1.737(4)	S5 C7 1.703(6)	S5 C8 1.736(4)	S6 C4 1.739(4)

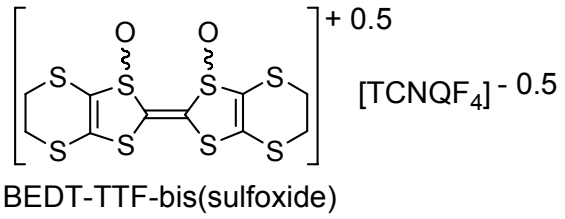
[1] G. M. Sheldrick, *Programs for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1996.

S6 C8 1.746(4)	S7 O1 1.492(4)	S7 C3 1.765(4)	S7 C9 1.776(4)
S8 C9 1.750(4)	S8 C10 1.804(5)	C1 C10 1.494(7)	C2 C9 1.342(6)
C3 C4 1.353(5)	C5 C8 1.340(6)	C6 C7 1.373(8)	

Bond Angles (°)

C2 S1 C1 104.7(2)	O2 S2 C3 109.1(6)	O2 S2 C2 105.8(6)	C3 S2 C2 91.86(19)
C4 S3 C5 95.9(2)	C6 S4 C5 102.7(3)	C7 S5 C8 104.0(3)	C4 S6 C8 95.68(19)
O1 S7 C3 109.3(2)	O1 S7 C9 108.2(2)	C3 S7 C9 90.97(19)	C9 S8 C10 98.1(2)
C10 C1 S1 117.4(3)	C9 C2 S1 128.5(3)	C9 C2 S2 117.4(3)	S1 C2 S2 114.1(2)
C4 C3 S2 122.6(3)	C4 C3 S7 122.2(3)	S2 C3 S7 115.2(2)	C3 C4 S3 122.2(3)
C3 C4 S6 123.3(3)	S3 C4 S6 114.5(2)	C8 C5 S4 126.5(3)	C8 C5 S3 116.9(3)
S4 C5 S3 116.6(3)	C7 C6 S4 126.1(5)	C6 C7 S5 127.0(5)	C5 C8 S5 127.5(3)
C5 C8 S6 116.9(3)	S5 C8 S6 115.6(3)	C2 C9 S8 125.4(3)	C2 C9 S7 117.4(3)
S8 C9 S7 116.9(2)	C1 C10 S8 115.8(4)		

X-ray structure of 3.



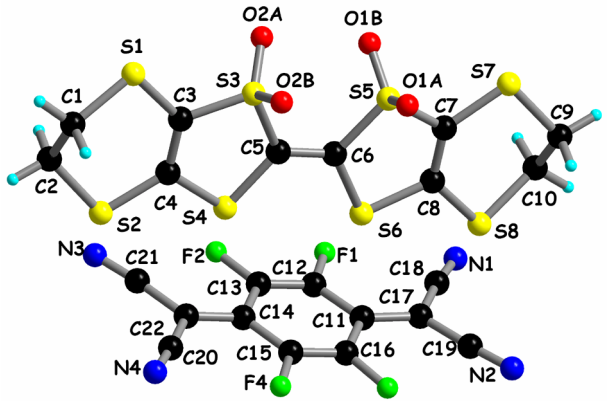


Fig. S7 Molecular structure of **3** along with the numbering scheme.

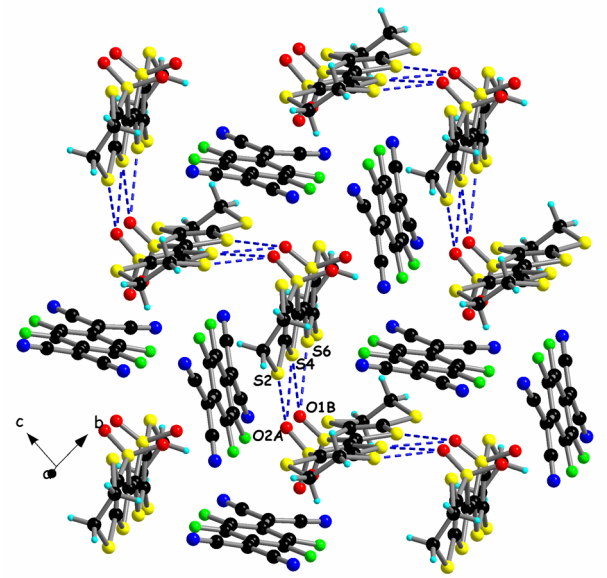


Fig. S8 Packing diagram of **3** along the *a* axis. Intermolecular S···O distances (Å): O2A···S4 2.97, O2A···S2 3.04, O1B···S4 3.08, O1B···S6 3.26. Short O···C contacts of 2.72-2.90 Å are also observed between adjacent BEDT-TTF-SO and $TCNQF_4$ molecules.

Bond Lengths (Å)

S1 C3 1.761(5)	S1 C1 1.780(7)	S2 C4 1.745(5)	S2 C2 1.785(5)
S3 O2A 1.406(7)	S3 O2B 1.455(8)	S3 C3 1.728(5)	S3 C5 1.746(4)
S4 C4 1.734(4)	S4 C5 1.740(4)	S5 O1B 1.357(6)	S5 O1A 1.479(5)
S5 C7 1.739(4)	S5 C6 1.750(4)	S6 C6 1.754(4)	S6 C8 1.768(5)
S7 C7 1.741(4)	S7 C9 1.780(5)	S8 C8 1.745(4)	S8 C10 1.801(6)
C1 C2 1.504(9)	C3 C4 1.358(6)	C5 C6 1.346(5)	C7 C8 1.339(6)
C9 C10 1.469(8)	F1 C12 1.329(5)	F2 C13 1.322(5)	F3 C16 1.334(5)
F4 C15 1.332(5)	N1 C18 1.136(6)	N2 C19 1.137(6)	N3 C21 1.141(6)
N4 C22 1.123(6)	C11 C17 1.388(6)	C11 C12 1.423(6)	C11 C16 1.432(6)
C12 C13 1.339(6)	C13 C14 1.440(6)	C14 C20 1.384(6)	C14 C15 1.421(6)
C15 C16 1.343(5)	C17 C19 1.425(7)	C17 C18 1.433(7)	C20 C22 1.404(7)
C20 C21 1.431(7)			

Powder X-ray diffraction.

Powder X-ray diffraction measurements were carried out on a D8 Brucker diffractometer using CuK$\alpha_{1,2}$ radiation, equipped with the linear Vantec super speed detector. 45 minutes diffractograms were collected in the range 4-30° (2θ).

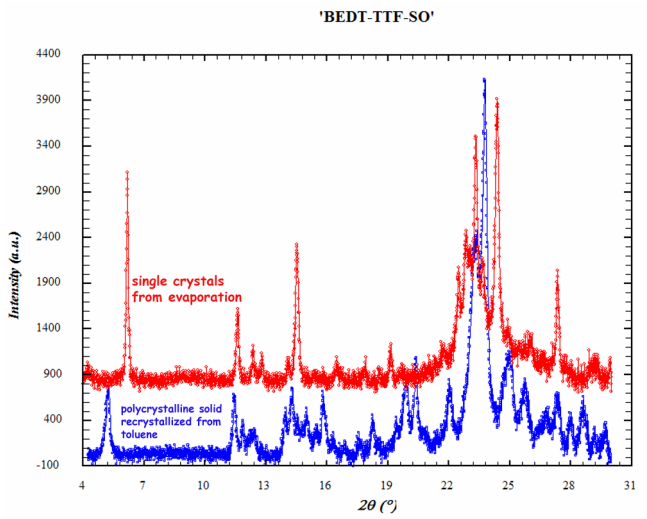


Fig. S9 Combined powder X-ray diffractogram of **2**, emphasizing the differences between the single crystals obtained by evaporation and the polycrystalline solid resulted from recrystallization in toluene.

Theoretical Calculations

The optimized geometries have been obtained with the Gaussian03[2] package at the DFT level of theory. The B3LYP functional[3] with the 6-31+G* basis set has been used. Vibrations frequency calculations performed on the optimized structures at the same level of theory yielded only positive values.

Theoretical calculations on BEDT-TTF-sulfoxide 2.

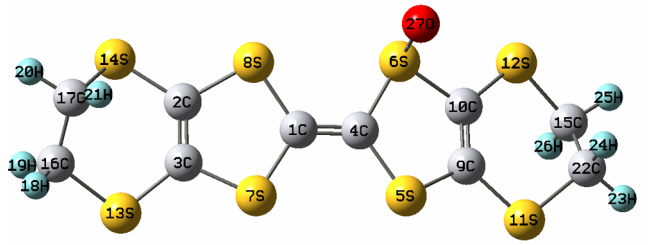


Fig. S10 Optimized geometry for **2**.

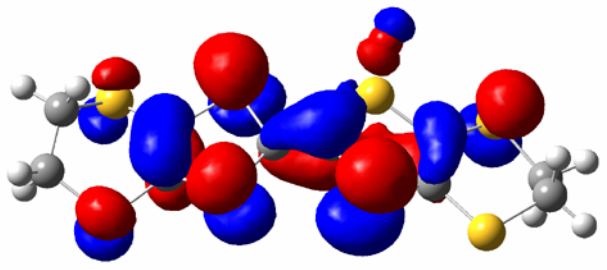


Fig. S11 HOMO of **2**. E = -5.556 eV.

Orientation for 2.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.728450	0.037542	0.352336
2	6	0	3.174535	-0.633183	-0.270481
3	6	0	3.202157	0.715051	-0.181831
4	6	0	-0.625221	0.061674	0.433090
5	16	0	-1.572909	1.525959	0.701510
6	16	0	-1.577646	-1.484928	0.297784
7	16	0	1.724115	1.507348	0.412875
8	16	0	1.688891	-1.452527	0.257696

[2] J. A. Pople et al., *Gaussian03*, Revision B.03; Gaussian, Inc.: Wallingford CT, 2004.
[3] (*a*) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785; (*b*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

9	6	0	-3.073135	0.787557	0.094917
10	6	0	-3.083640	-0.545789	-0.122894
11	16	0	-4.395103	1.942598	-0.124715
12	16	0	-4.409493	-1.582108	-0.682973
13	16	0	4.546248	1.789144	-0.566436
14	16	0	4.586658	-1.613822	-0.661526
15	6	0	-5.662599	-0.332419	-1.165799
16	6	0	6.054494	0.746991	-0.225442
17	6	0	5.786280	-0.638175	0.344137
18	1	0	6.668473	1.320344	0.478233
19	1	0	6.586028	0.670386	-1.176812
20	1	0	6.719490	-1.211782	0.343787
21	1	0	5.408394	-0.592346	1.369163
22	6	0	-5.824805	0.793906	-0.145275
23	1	0	-6.675106	1.427895	-0.419016
24	1	0	-5.994662	0.399202	0.859817
25	1	0	-6.593512	-0.905416	-1.240669
26	1	0	-5.425970	0.071643	-2.153531
27	8	0	-1.775551	-2.155682	1.639378

Mode	1	2	3	4	5
Symmetry	A	A	A	A	A
Frequencies	18.9212	26.8293	34.7346	40.4526	51.4588

Theoretical calculations on BEDT-TTF.

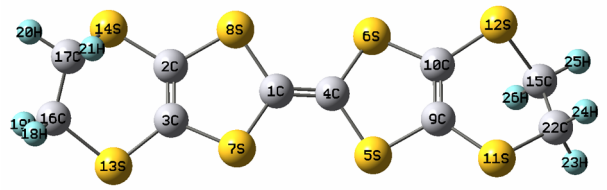


Fig. S12 Optimized geometry for **BEDT-TTF**.

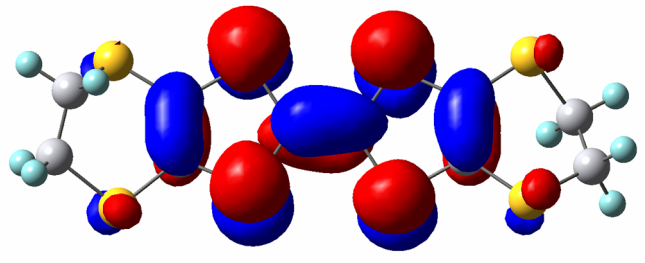


Fig. S13 HOMO of **BEDT-TTF**. E = -4.827 eV.

Orientation for BEDT-TTF.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.671035	0.035051	0.074811
2	6	0	-3.185787	0.703433	-0.156796
3	6	0	-3.187127	-0.647700	-0.152909
4	6	0	0.671174	0.035024	-0.077642
5	16	0	1.643471	-1.457173	-0.212689
6	16	0	1.648445	1.522227	-0.208715
7	16	0	-1.643174	-1.457242	0.209883
8	16	0	-1.648181	1.522239	0.206265
9	6	0	3.186856	-0.647677	0.152715
10	6	0	3.185509	0.703423	0.156792
11	16	0	4.561228	-1.715237	0.443971
12	16	0	4.649073	1.675936	0.305339
13	16	0	-4.561736	-1.715494	-0.441933
14	16	0	-4.649441	1.676213	-0.303458
15	6	0	5.697045	0.619748	-0.784133
16	6	0	-6.022882	-0.732518	0.169557
17	6	0	-5.696284	0.619627	0.786761
18	1	0	-6.528845	-1.361312	0.911060
19	1	0	-6.680879	-0.606348	-0.693533
20	1	0	-6.627222	1.174048	0.948319

21	1	0	-5.183495	0.515095	1.746759
22	6	0	6.022962	-0.732761	-0.167319
23	1	0	6.528678	-1.361512	-0.908972
24	1	0	6.680819	-0.607248	0.695962
25	1	0	6.628121	1.174254	-0.944524
26	1	0	5.185287	0.515602	-1.744724

Mode	1	2	3	4	5
Symmetry	A	A	A	A	A
Frequencies	6.4364	35.8582	47.2007	47.3264	50.2707

Theoretical calculations on the radical cation of BEDT-TTF-sulfoxide $2^{+\bullet}$.

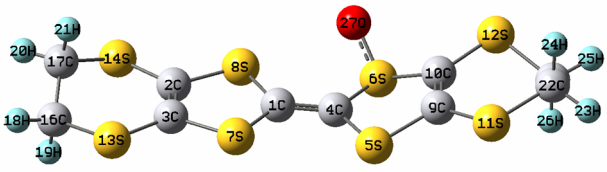


Fig. S14 Optimized geometry for $2^{+\bullet}$.

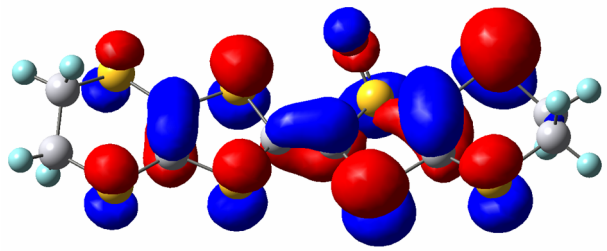


Fig. S15 SOMO of $2^{+\bullet}$.

Orientation for $2^{+\bullet}$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.718612	-0.110005	-0.233157
2	6	0	-3.215638	0.616461	-0.047377
3	6	0	-3.244698	-0.761166	-0.001024
4	6	0	0.645494	-0.158269	-0.389843
5	16	0	1.606616	-1.604792	-0.448994
6	16	0	1.625967	1.362960	-0.600014
7	16	0	-1.685458	-1.563970	-0.075969
8	16	0	-1.640943	1.382481	-0.130979
9	6	0	3.136979	-0.791899	0.013959
10	6	0	3.129153	0.563454	0.059758
11	16	0	4.457243	-1.910147	0.296868
12	16	0	4.483023	1.627802	0.374212
13	16	0	-4.621954	-1.838049	0.137003
14	16	0	-4.580985	1.720641	-0.000968
15	6	0	5.835145	0.530081	-0.222926
16	6	0	-6.039547	-0.675474	-0.031031
17	6	0	-5.859647	0.627610	0.736218
18	1	0	-6.880171	-1.242147	0.383224
19	1	0	-6.230966	-0.495756	-1.091453
20	1	0	-6.777484	1.221287	0.673535
21	1	0	-5.630711	0.456211	1.791104

22	6	0	5.907006	-0.786177	0.540341
23	1	0	6.756101	-1.379667	0.184513
24	1	0	6.026251	-0.613065	1.611656
25	1	0	6.753323	1.098622	-0.043674
26	1	0	5.726496	0.377203	-1.299896
27	8	0	1.063402	2.427351	0.302866

Mode	1	2	3	4	5
Symmetry	A	A	A	A	A
Frequencies	20.4720	31.2482	37.1278	43.3038	54.8976

Electrochemical studies. Cyclic voltammetry measurements were performed using a three-electrode cell equipped with a platinum millielectrode of 0.126 cm^2 area, an Ag/Ag^+ pseudo-reference and a platinum wire counter-electrode. The potential values were then re-adjusted with respect to the saturated calomel electrode (SCE). The electrolytic media involved a 0.1 $mol.L^{-1}$ solution of $(n\text{-}Bu_4N)PF_6$ in MeCN. All experiments have been performed at room temperature at 0.1 $V.s^{-1}$. Experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation.