Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Stabilization and Isolation of Radical Cation and Dication of a Tetrathiafulvalene Derivative Functionalized with Amino Groups†

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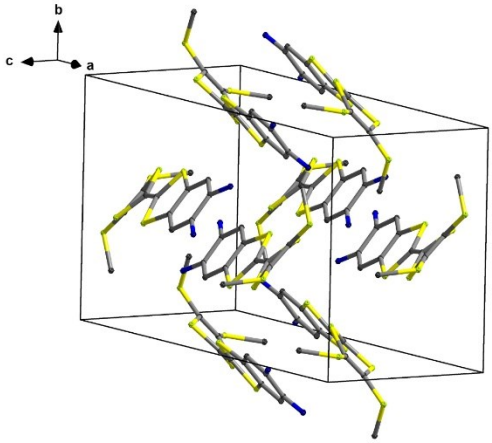


Fig. S1 The extended structure of **1**. Hydrogen atoms have been omitted for clarity (C grey, N blue, and S yellow).

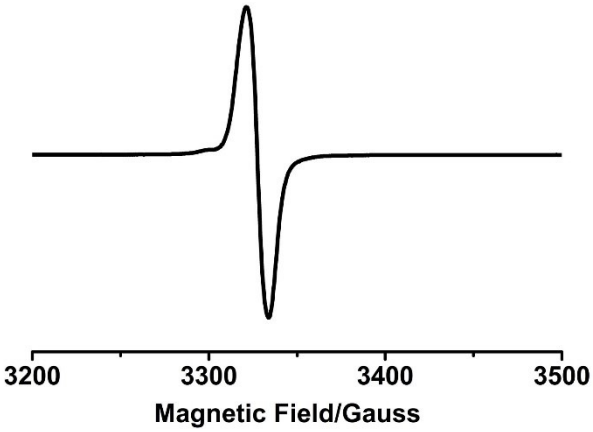


Fig. S2 EPR spectra of $1^{\bullet+}$ in solid state at 77 K.

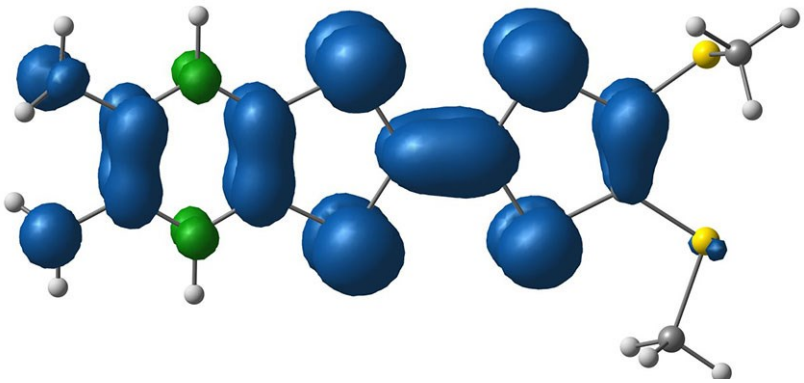


Fig. S3 Spin density distribution of $1^{\bullet+}$.

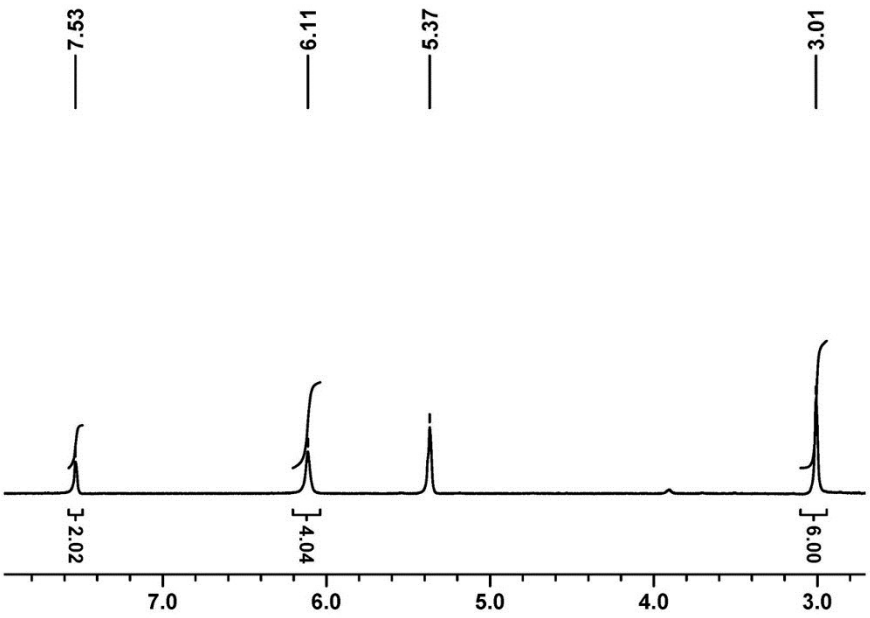


Fig. S4 ^{1}H NMR spectra of $\mathbf{1}^{2+}$ in CD_2Cl_2. Peaks around 5.37 ppm are ascribed to CD_2Cl_2.

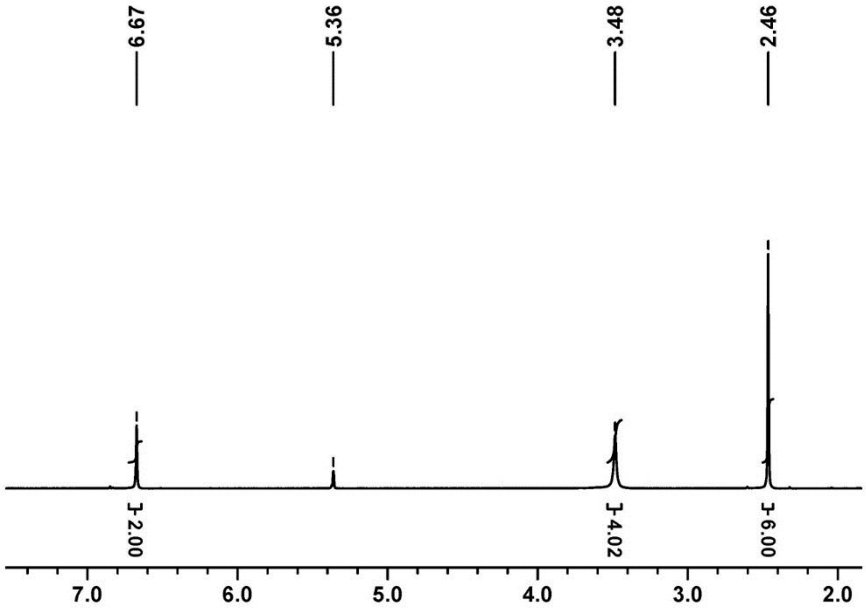


Fig. S5 ^{1}H NMR spectra of **1** in CD_2Cl_2. Peaks around 5.36 ppm are ascribed to CD_2Cl_2.

Table S1. Selected Bond Lengths (Å) and Bond Angles (°) for 1, $1^{\bullet+}$, and 1^{2+}.

1		**$1^{\bullet+}$**		**1^{2+}**	
C7–C8	1.338(4)	C6–C8	1.405(13)	C33–C36	1.415(6)
C7–S1	1.747(3)	C6–S1	1.715(11)	C33–S1	1.704(4)
C7–S2	1.747(3)	C6–S2	1.714(10)	C33–S2	1.697(4)
S1–C5	1.751(3)	S1–C15	1.723(14)	S1–C35	1.728(5)
S2–C4	1.750(2)	S2–C10	1.752(18)	S2–C34	1.727(5)
C8–S3	1.754(3)	C8–S3	1.688(9)	C36–S3	1.697(4)
C8–S4	1.751(3)	C8–S4	1.722(10)	C36–S4	1.702(4)
S3–C9	1.765(3)	S3–C2	1.706(9)	S3–C41	1.710(4)
S4–C10	1.754(3)	S4–C3	1.727(10)	S4–C42	1.719(5)
C1–N1	1.395(3)	C12–N1	1.423(14)	C38–N1	1.344(6)
C2–N2	1.409(3)	C11–N2	1.382(14)	C39–N2	1.350(6)
S5–C11	1.792(5)	S5–C27	1.770(3)	S5–C43	1.822(10)
S6–C12	1.794(5)	S6–C28	1.740(2)	S6–C44	1.793(5)
S1–C7–S2	115.71(14)	S1–C6–S2	115.9(6)	S1–C33–S2	114.3(3)
S3–C8–S4	113.29(14)	S3–C8–S4	117.3(6)	S3–C36–S4	115.5(3)
S1–C7–C8	122.6(2)	S1–C6–C8	121.7(7)	S1–C33–C36	123.1(3)
S3–C8–C7	123.6(2)	S4–C8–C6	120.1(7)	S3–C36–C33	122.0(3)
C9–S5–C11	102.64(18)	C10–S5–C27	103.1(12)	C34–S5–C43	99.8(4)
C10–S6–C12	101.44(16)	C15–S6–C28	101.1(8)	C35–S6–C44	102.8(2)
N1–C1–C2	118.1(2)	N1–C12–C11	122.2(13)	N1–C38–C39	119.1(5)
N2–C2–C1	118.2(2)	N2–C11–C12	121.6(11)	N2–C39–C38	118.2(4)

Table S2. **Selected Experimental and Calculated Structural Parameters for 1, $1^{\bullet+}$, and 1^{2+}.**

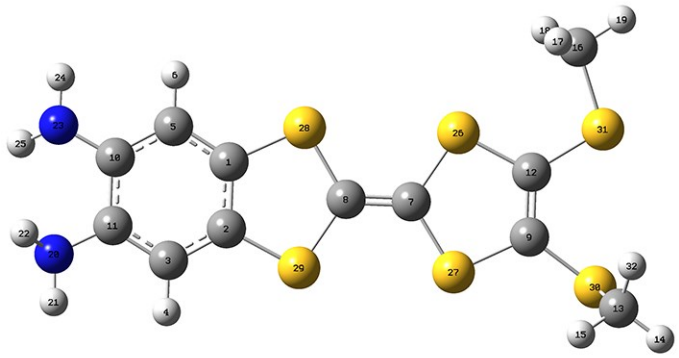
	1	**$1^{\bullet+}$**	**1^{2+}**
Central C=C bond for TTF core (Å)	1.338(4) (exp.) 1.352 (cal.)	1.405(13) (exp.) 1.388 (cal.)	1.415(6) (exp.) 1.410 (cal.)
Average N−C bonds (Å)	1.402 (exp.) 1.410 (cal.)	1.403 (exp.) 1.386 (cal.)	1.347 (exp.) 1.361 (cal.)
Average S−C bonds for TTF core (Å)	1.752 (exp.) 1.781 (cal.)	1.718 (exp.) 1.755 (cal.)	1.710 (exp.) 1.737 (cal.)
Average ∠C−S−C for TTF core (°)	94.77 (exp.) 94.55 (cal.)	95.38 (exp.) 96.37 (cal.)	97.15 (exp.) 97.28 (cal.)

Table S3. Selected Experimental and Calculated Optical Transitions for 1, $1^{\bullet+}$, and 1^{2+}.

	Orbital Excitation	Major Contribs	Osc. Strength	λ / nm (exp.)	λ / nm (cal.)
1	HOMO-1→LUMO	50%	0.2833	315, 335	319
	HOMO→LUMO+2	39%			
$1^{\bullet+}$	HOMO (β)→LUMO (β)	99%	0.3423	1025	1029
	HOMO (α)→LUMO+2 (α)	25%	0.2054	445, 401	389
	HOMO-4 (β)→LUMO (β)	61%			
1^{2+}	HOMO→LUMO	106%	0.8455	885	876
	HOMO-3→LUMO	99%	0.0115	453	448

Table S4. Mulliken Spin Densities for the Optimized Geometry of $1^{\bullet+}$.

1	C	-0.115972	0.053198
2	C	-0.116223	0.053546
3	C	-0.206850	-0.035365
4	H	0.169792	0.001014
5	C	-0.206675	-0.035217
6	H	0.168628	0.001012
7	C	-0.341350	0.110559
8	C	-0.294808	0.067033
9	C	-0.323247	0.061265
10	C	0.317900	0.051600
11	C	0.318314	0.051691
12	C	-0.247656	0.007636
13	C	-0.597216	0.005551
14	H	0.216464	0.000143
15	H	0.202122	-0.000377
16	C	-0.647260	-0.000327
17	H	0.215312	0.000440
18	H	0.217156	0.000328
19	H	0.229877	-0.000104
20	N	-0.802338	0.034100
21	H	0.351352	-0.001211
22	H	0.354759	0.000930
23	N	-0.802336	0.033925
24	H	0.350908	-0.001200
25	H	0.354858	0.000931
26	S	0.381850	0.099399
27	S	0.412128	0.154832
28	S	0.362810	0.134690
29	S	0.369095	0.134281
30	S	0.206947	-0.003733
31	S	0.291856	0.019684
32	H	0.209803	-0.000253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