Supporting Information

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π-Dimer formation via long-distance multicenter bonding of cation-radicals of tetrathiafulvalene analogues

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A) X-ray Structural Analysis

Single crystals of cation-radical salts of tetrathiafulvalene analogues with weakly-coordinating anions were crystallized by slow evaporation of solutions of these salts in dichloromethane/hexane (10:1) mixtures. Intensity data for X-ray crystallographic analysis were collected at 150 K with a Bruker AXS D8 Quest CMOS diffractometer using Cu $K\alpha$ or Mo $K\alpha$ radiation. The structures were solved by direct methods and refined by full matrix least-squares treatment. Crystallographic, data collection and structure refinement details, as well as geometric characteristics of the halogen bonds in these crystals are presented in Table S1 and in individual sections for each structure (after the table). Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 2011364-2011371, 2031395 and 2031396 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic, data collection and structure refinement details

	(ET)Me$_{12}$CAR	(TTF)Br$_6$CAR	(TMTSF)Br$_6$CAR	(ET)BArF	(ET)Br$_6$CAR·CH$_2$Cl$_2$
Chemical formula	C$_{13}$H$_{36}$B$_{11}$·C$_{10}$H$_8$S$_8$	CH$_6$B$_{11}$Br$_6$·C$_6$H$_4$S$_4$	CH$_6$B$_{11}$Br$_6$·C$_{10}$H$_{12}$Se$_4$	C$_{32}$H$_{12}$BF$_{24}$·C$_{10}$H$_8$S$_8$	CH$_6$B$_{11}$Br$_6$·C$_{10}$H$_8$S$_8$·CH$_2$Cl$_2$
M_r	695.97	820.76	1064.46	1247.87	1086.00
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/m$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
Temperature (K)	150	150	150	150	150
a, b, c (Å)	14.9617 (7), 15.7799 (7), 17.0816 (8)	8.1423 (6), 13.7726 (10), 10.2776 (7)	8.8819 (5), 21.3136 (10), 15.0603 (8)	10.1692 (3), 22.6293 (6), 20.9402 (6)	11.0183 (9), 11.7862 (8), 26.111 (2)
α, β, γ (°)	111.6576 (14), 101.2680 (14), 94.4328 (15)	92.209 (3)	92.345 (2)	91.6312 (13)	92.046 (3)
V (Å^3)	3626.2 (3)	1151.68 (14)	2848.6 (3)	4816.8 (2)	3388.7 (4)
Z	4	2	4	4	4
Radiation type	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	4.67	10.82	13.57	4.61	7.77
Crystal size (mm)	$0.33 \times 0.28 \times 0.11$	$0.31 \times 0.24 \times 0.11$	$0.32 \times 0.29 \times 0.13$	$0.15 \times 0.14 \times 0.01$	$0.16 \times 0.14 \times 0.11$
T_{min}, T_{max}	0.356, 0.754	0.419, 0.747	0.377, 0.747	0.472, 0.754	0.558, 0.747
No. of measured, ind and obs [$I > 2\sigma(I)$] reflections	61897, 26183, 23382	24760, 4530, 3233	90334, 10935, 8422	30941, 9829, 8435	36861, 12654, 8374
R_{int}	0.054	0.061	0.063	0.051	0.046
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.640	0.770	0.772	0.640	0.771
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.148, 1.06	0.037, 0.082, 1.01	0.033, 0.085, 1.07	0.041, 0.115, 1.08	0.039, 0.079, 1.02
No. of reflections	26183	4530	10935	9829	12654
No. of param.	784	136	294	819	358
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.21, -0.63	1.33, -1.32	1.42, -1.59	0.46, -0.46	1.55, -1.49

Table S1 (cont). Crystallographic, data collection and structure refinement details

	(TMTTF)Br$_6$CAR	(TMTSF)Me$_{12}$CAR$\cdot\frac{1}{3}$CH$_2$Cl$_2$	(TMTSF)BArF	(TMTSF)BArF$\cdot$½CH$_2$Cl$_2$	(TMTTF)Me$_{12}$CAR
Chemical formula	CH$_6$B$_{11}$Br$_6\cdot$ C$_{10}$H$_{12}$S$_4$	3(C$_{13}$H$_{36}$B$_{11}$)$\cdot$ 3(C$_{10}$H$_{12}$Se$_4$)$\cdot$CH$_2$Cl$_2$	C$_{32}$H$_{12}$BF$_{24}\cdot$ C$_{10}$H$_{12}$Se$_4$	2(C$_{32}$H$_{12}$BF$_{24}$)$\cdot$ 2(C$_{10}$H$_{12}$Se$_4$)$\cdot$CH$_2$Cl$_2$	C$_{13}$H$_{36}$B$_{11}\cdot$C$_{10}$H$_{12}$S$_4$
M_r	876.86	2363.01	1311.26	2707.45	571.76
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
Temperature (K)	150	150	150	150	150
a, b, c (Å)	9.0536 (4), 20.5662 (9), 15.0317 (7)	9.1263 (13), 74.893 (11), 15.658 (2)	10.4486 (3), 14.0122 (4), 15.7753 (4)	13.8745 (9), 14.2009 (8), 26.1484 (15)	9.0883 (16), 9.2043 (15), 10.2496 (17)
α, β, γ (°)	96.2939 (17)	104.505 (10)	89.036(1), 83.401 (1), 81.206 (1)	93.003 (2), 99.251 (2), 106.843 (2)	83.788 (7), 76.145 (7), 85.976 (7)
V (Å^3)	2782.0 (2)	10361 (3)	2267.35 (11)	4840.1 (5)	826.7 (2)
Z	4	4	2	2	1
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	8.96	5.65	3.37	3.21	0.30
Crystal size (mm)	$0.22 \times 0.20 \times 0.15$	$0.21 \times 0.06 \times 0.05$	$0.32 \times 0.11 \times 0.07$	$0.48 \times 0.41 \times 0.02$	$0.45 \times 0.21 \times 0.09$
T_{min}, T_{max}	0.513, 0.747	0.240, 0.390	0.598, 0.747	0.118, 0.209	0.687, 0.747
No. of measured, ind and obs [$I > 2\sigma(I)$] reflections	124275, 10617, 8362	81535, 21428, 18574	114138, 17310, 12660	86594, 24005, 14691	68434, 6312, 5219
R_{int}	0.055	0.035	0.045	0.073	0.042
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.770	0.637	0.771	0.669	0.771
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.024, 0.051, 1.02	0.051, 0.124, 1.12	0.032, 0.083, 1.02	0.062, 0.187, 1.08	0.038, 0.118, 1.03
No. of reflections	10617	21428	17310	24005	6312
No. of param.	312	1359	676	1591	180
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.30, -0.91	1.09, -1.08	0.88, -0.81	2.73, -2.15	0.35, -0.35

(ET)Me$_{12}$CAR:

The crystal under investigation was found to be non-merohedrally twinned. The orientation matrices for the two components were identified using the program Cell_Now, with the two components

being related by a 180 degree rotation around the reciprocal axis (-0.5 0 1). The two components were integrated using Saint and corrected for absorption using twinabs, resulting in the following statistics:

27547 data (11295 unique) involve domain 1 only, mean I/sigma 29.3

27464 data (11287 unique) involve domain 2 only, mean I/sigma 29.3

7018 data (3604 unique) involve 2 domains, mean I/sigma 51.0

The exact twin matrix identified by the integration program was found to be:

-0.69868 -0.31707 -0.84943

-0.00036 -1.00000 0.00005

-0.60240 0.63462 0.69868

The structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.5117(7).

The Rint value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2012)).

The carbon atoms of the two carborane anions were refined as disordered over each two symmetry equivalent positions, disordered with boron atoms. The positions and the ADPs of the boron and carbon atoms were constrained to be each identical. Subject to these conditions the occupancy ratios refined to 0.61(3) to 0.39(3), and to 0.59(3) to 0.41(3). Partial other locations of the C atoms (disordered with other boron atoms) cannot be positively excluded.

(ET)BArF:

The ethylene groups of the sulfur compound are disordered by inversion at carbon. The major and Minor moieties were restrained to have similar geometries. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.813(9) to 0.813(9) (C4/C5) and 0.584(7) to 0.416(7) (C9/C10).

Three of the CF3 groups are rotationally disordered. They were restrained to have similar geometries as another well-defined CF3 moiety. F18 and F18B were constrained to share a common ADP. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.694(10) to 0.306(10) (C26), 0.354(10) to 0.646(10) (C33), and 0.878(4) to 0.122(4) (C34).

$(TMTSF)Me_{12}CAR \cdot \frac{1}{3} CH_2Cl_2$:

The position of the C atoms in the carborane anions were located from difference density maps and occupancy refinements. No indication of C/B disorder was observed for all three anions.

One of the carborane anions is disordered by rotation in space. The two disordered moieties were restrained to have similar geometries as the other two not disordered anions. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.521(4) to 0.479(4).

The methylene chloride solvate molecule is disordered over two orientations. The two disordered moieties were restrained to have similar geometries. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.526(6) to 0.474(6).

(TMTSF)BArF:

One CF3 group was refined as rotationally disordered. The two disordered moieties were restrained to have similar geometries as another not disordered CF3 group. U^{ij} components of ADPs for disordered

atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.709(4) to 0.291(4).

(TMTSF)BArF· ½CH₂Cl₂:

8 of the 12 trifluoromethyl groups were refined as rotationally disordered. All disordered moieties were restrained to have similar geometries as another not disordered CF_3 group. Major and minor C atoms of each group were constrained to have identical ADPs. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the major moiety occupancies refined to 0.732(7) (C35), 0.509(13) (C36B), 0.558(11) (C43), 0.587(10) (C51), 0.660(12) (C59), 0.692(9) (C76), 0.572(7) (C83), and 0.578(9) (C84).

A methylene chloride molecule was refined as disordered. The two moieties were restrained to have similar geometries and C-Cl distances were restrained to 1.72(2) Angstrom. U^{ij} components of ADPs for disordered atoms closer to each other than 2.0 Å were restrained to be similar. Subject to these conditions the occupancy ratio refined to 0.598(6) to 0.402(6).

Table S2. Average bond lengths (in Å) of the cores of the cation-radicals of TTF analogues in the salts with WCA.[a]
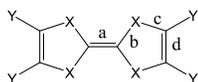
Salt	a	b	c	d
(TTF) Br₆CAR	1.391	1.721	1.723	1.340
(TMTSF)Br₆CAR	1.382	1.860	1.885	1.342
(TMTSF)BArF	1.383	1.858	1.880	1.346
(TMTSF)BArF ·½CH₂Cl₂[a]	1.376	1.858	1.874	1.350
	1.381	1.859	1.868	1.363
(TMTSF)Me₁₂CAR[b]	1.374	1.858	1.885	1.325
	1.374	1.861	1.891	1.329
	1.377	1.861	1.894	1.339
(TMTTF)Me₁₂CAR	1.394	1.714	1.734	1.347
(TMTTF)Br₆CAR	1.390	1.716	1.738	1.348
(ET)Br₆CAR	1.394	1.718	1.741	1.354
(ET)BArF	1.383	1.722	1.738	1.360
(ET)Me₁₂CAR [a]	1.394	1.719	1.339	1.361
	1.393	1.722	1.740	1.357

a) Values for two crystallographically independent moieties. b) Values for three crystallographically independent moieties

Table S3. Examples of the solid-state D_2^{2+} dimers (and the corresponding interatomic S…S or Se…Se distances) in the CCDC database.[a]

TTF		TMTTF		ET		TMTSF	
REFCODE	S...S, Å	REFCODE	S...S, Å	REFCODE	S...S, Å	REFCODE	Se...Se, Å
SUJMOC	3.29	ALATEN	3.42	GOXZIF	3.38	XOSFAP	3.54
AMEPEO	3.36	DERLER10	3.38	MOTYOM	3.46	CAQJAF	3.75
CEBWUC	3.29	GEGJUX	3.42	MOTYUS	3.44	CAVNES	3.54
CEBXAJ	3.35	GIMDIP	3.33	BAVBOR	3.51	CEBXIR	3.63
CERDOT	3.28	HOJQED	3.32	BAVBUX	3.50	QABBEA	3.60
COYXEV	3.41	MESFLV03	3.49	BEJHOQ	3.41	VOGHOO	3.63
DEBRUY	3.28	NEDRET	3.43	CERDUZ	3.44		
DEBSAF	3.52	QUFSER	3.47	CERFAH	3.44		
DEBSEJ	3.32	SIZYAB	3.44	DASVID	3.32		
DEJHUW	3.37	WIWMIY	3.41	DASVOJ	3.36		
DOSSUC	3.34	ZIFDEZ	3.43	DASWAW	3.36		
HENRIC	3.45			EMOZAH	3.41		
IRISIM	3.51			IXOPUI	3.38		
KAJBOM	3.51			MAJYUR	3.54		
KODROK	3.35			MEXVIW	3.51		
LAYTAH	3.26			MISDUP	3.44		
LAYTEL	3.35			MISFAX	3.44		
MEXFOK	3.39			MUVLOF	3.43		
MUFZEU	3.36			PAVZUN	3.40		
NIBVEA	3.45			PAVZAK	3.40		
NIBVIE	3.43			PIJPOO	3.32		
NIBVOK	3.25			RIHFAP	3.49		
OHAXAX	3.36			SINROY	3.40		
PARRUX	3.36			SISVUL	3.55		
PORQAQ	3.33			XASCIE	3.37		
QIKWEM	3.35			XUBJIP	3.38		
QUSTOP	3.43			ZASCED	3.45		
RIFQAY02	3.32			ZIFDAV	3.50		
ROFXER	3.40			ZIWNIC	3.44		
SATDEW	3.40						
SICFOB	3.42						
TOBRUZ	3.33						
TTFIOD	3.35						
VENQOW	3.32						
WACLUI	3.41						
YEDVUY	3.37						
ZZZBWA	3.40						

a) CSD version 5.41 (November, 2019). Structures included in this table show at least one intradimer S…S or Se…Se contact shorter than the van der Waals separation minus 0.1 Å.
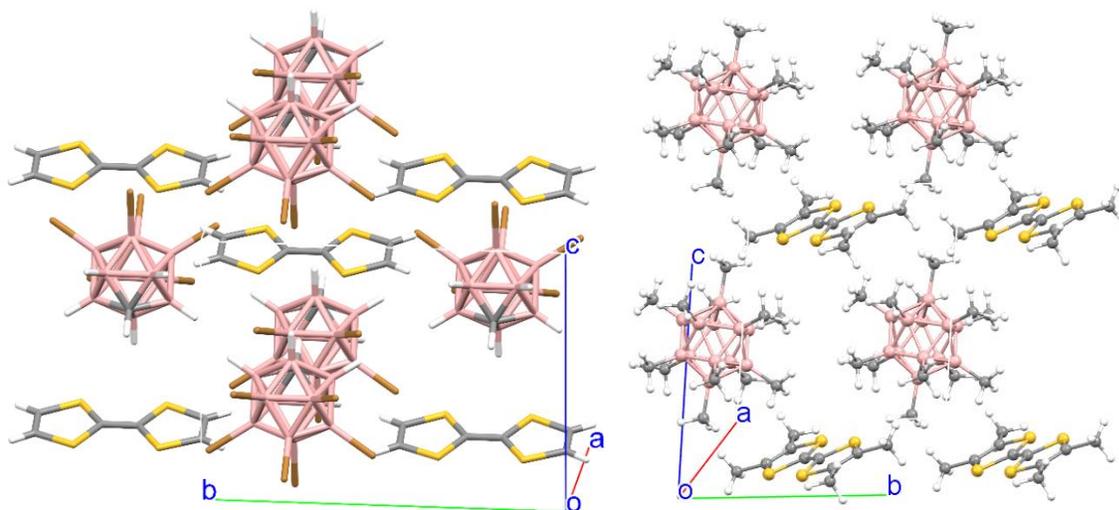
Figure S1. X-ray structure of (TTF)Br$_6$CAR (left) and (TMTTF)Br$_{12}$CAR salt showing separate cation radicals.
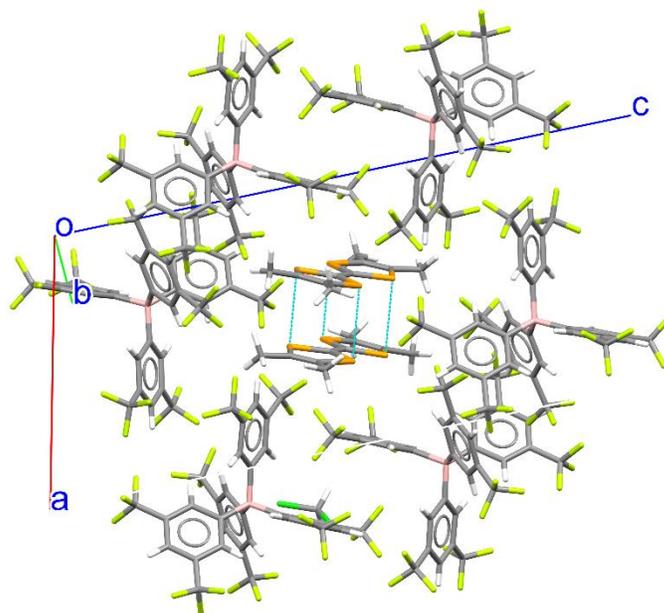
Figure S2. X-ray structure of (TMTSF)BArF·½CH$_2$Cl$_2$ salt showing (TMTSF)$_2^{2+}$ dimers.
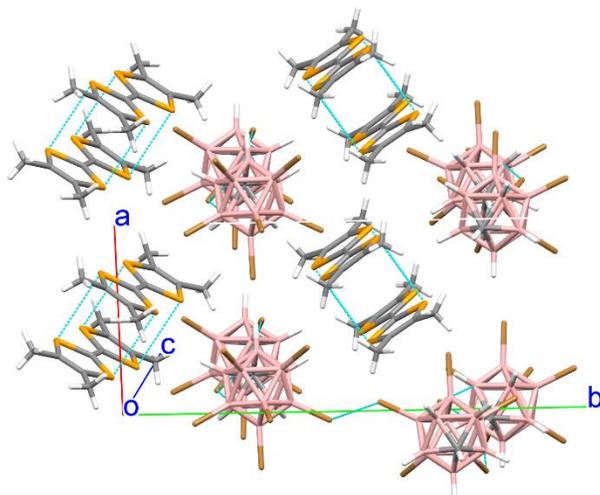
Figure S3. X-ray structure of (TMTSF)Br$_6$CAR showing (TMTTF)$_2^{2+}$ dimers.
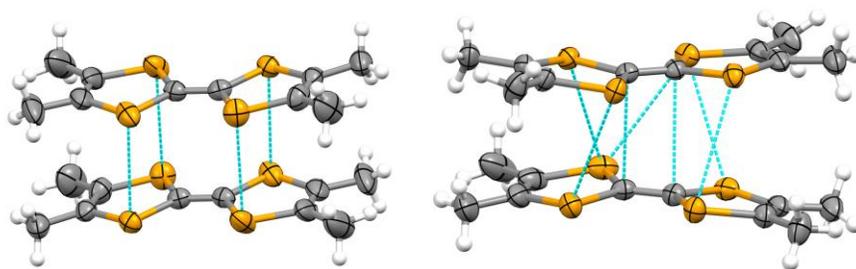
Figure S4. Two types of dimers in the (TMTSF)Me$_{12}$CAR crystals in which monomers are shifted (parallel to the main axis) or rotated relative to each other.
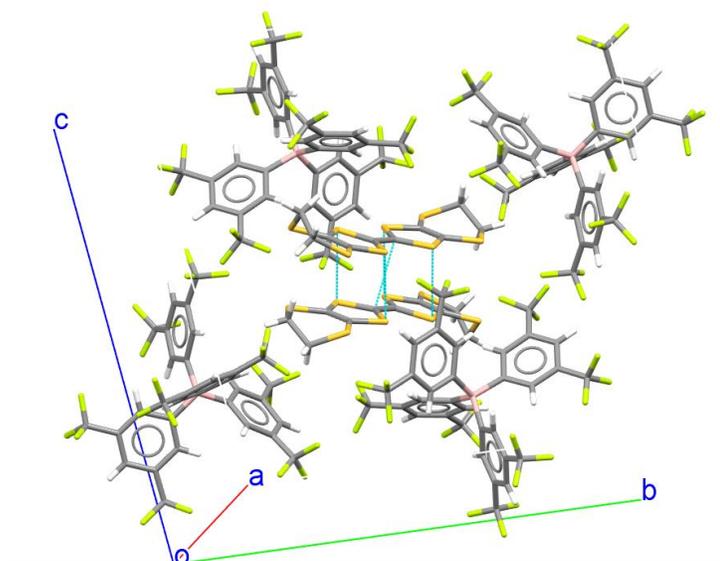
Figure S5. X-ray structure of (ET)BArF salt showing (ET)$_2^{2+}$ dimer.
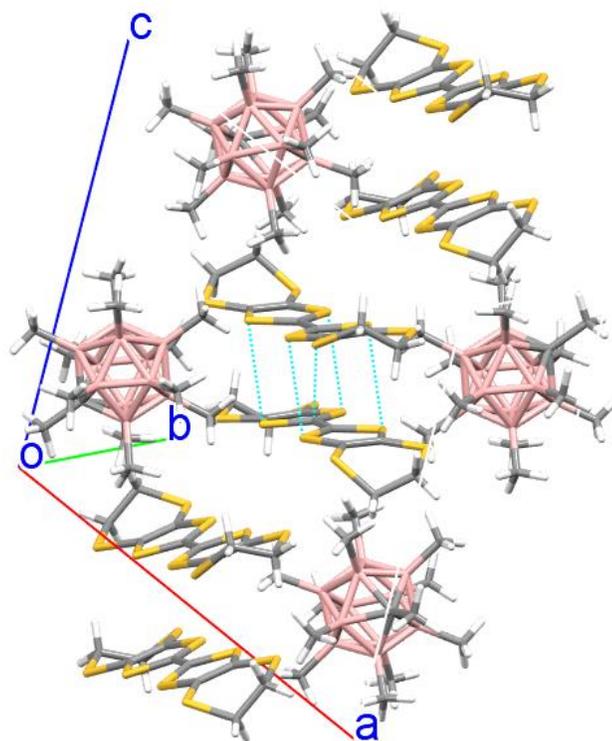
Figure S6. X-ray structure of (ET)Me$_{12}$CAR salt showing two types of dyads, one π-dimer with lateral shift along the main axis and multiple contacts which are shorter than the van der Waals separation and another pair with shift perpendicular to the main axis and all contacts longer than the van der Waals separations.
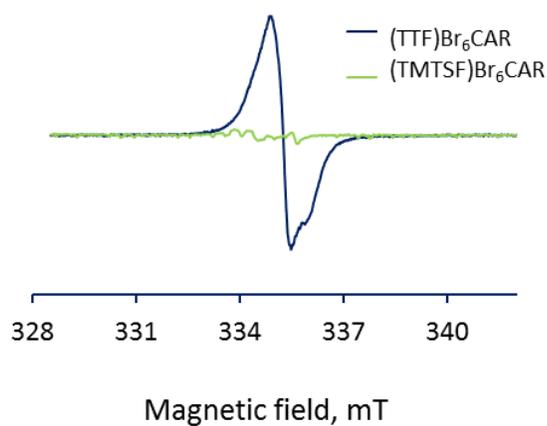
Figure S7. Solid-state EPR spectra of (TMTSF)Br$_6$CAR and (TTF)Br$_6$CAR.

B) **UV-Vis measurements and their treatments**

The spectral characteristics of monomers and dimers and thermodynamic characteristics of dimerization were determined via UV-Vis measurements similarly to those in our earlier work.[1,2] UV-Vis measurements were carried out on a CARY 5000 spectrophotometer in a Dewar equipped with a quartz lens and the temperature was adjusted with an ethanol-liquid nitrogen bath (± 0.5 K). The solutions of the cation-radical salts for the UV-vis measurements were prepared in a Schlenk tube and transferred under an argon atmosphere into the quartz (1-mm path length) spectroscopic cell equipped with a Teflon valve fitted with Viton O-rings.

Spectral characteristics of the cation-radical monomers were established using solutions with low concentrations (~0.1 mM) of the cation-radical salts at room temperature. Under such conditions, the intensity of bands of monomers (at wavelengths λ_M) was directly proportional to the initial concentration of the cation-radicals (according to Beer–Lambert law). This indicated that concentrations of dimers in such solutions are negligible and allowed to determine extinction coefficients of the cation-radical monomers at the maxima of their absorption bands, ε_M (as well as at the maxima of absorption bands of the corresponding dimers, $\varepsilon_M{}^D$).

At higher concentrations (≥ 1 mM) and/or lower temperatures, new absorption bands appeared with maxima at λ_D. These band intensities increased substantially with the lowering of the temperature, and their growth was accompanied by the decrease of absorption intensity at λ_M (Figure 2). The temperature-dependent spectral changes observed in the solutions in acetonitrile and propanenitrile were reversible, and the existence of clear isosbestic points indicated a quantitative interchange between two absorbing species.[*] The extinction coefficients ε_D for the dimers were determined from the temperature-modulated spectral changes (Figure 2), in which the decrease of absorbance at λ_M (ΔA_M) upon lowering the temperature was linearly related to the absorbance increase at λ_D (ΔA_D). Absorption intensities at these wavelength can be expressed as

$$A_D = (c_M \, \varepsilon_M{}^D + c_D \, \varepsilon_D) \, l \qquad\qquad (S1)$$

$$A_M = (c_M \, \varepsilon_M + c_D \, \varepsilon_D{}^M) \, l \qquad\qquad (S2)$$

where c_M is concentration of monomer, c_D is concentration of dimer, $\varepsilon_M{}^D$ and ε_D are extinction coefficients of monomer and dimers at λ_D and ε_M and $\varepsilon_D{}^M$ are extinction coefficients of monomer and dimers at λ_M. Taking into account material balance

$$c_M + 2c_D = c_0 \qquad\qquad (S3)$$

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[*] Small deviations from the isosbestic points were apparently related to absorption bands narrowing at low temperatures.

where c_0 is concentration of the salt in the solution, ε_D can be expressed from the changes of the absorption bands intensity at λ_M and λ_D as:[†]

$$\varepsilon_L = -(2\varepsilon_M - \varepsilon_D^M) \times \Delta A_L / \Delta A_M \tag{S4}$$

Based on the values of ε_M^λ and ε_D^λ at a certain wavelength λ, concentration of the dimer can be calculated from the absorption intensity at this wavelength, A_λ as:

$$c_D = (A_\lambda - c_0\varepsilon_M^\lambda)/(\varepsilon_D^\lambda - 2\varepsilon_M^\lambda) \tag{S5}$$

The concentrations of the dimers c_D were calculated at different temperatures and concentration of salts c_0 from the absorption intensity at different wavelengths. While this equation is valid at any wavelength, most accurate evaluations of c_D could be done using wavelength with the largest difference of the extinction coefficients of the cation-radical monomers and dimers (typically, at the absorption band maxima of the monomer and the dimer). Specifically, values of c_D for TTF$^{+\bullet}$ were established from the intensities of absorption of solutions at 437 nm and 730 nm, for TMTTF$^{+\bullet}$ at 652 nm and 759 nm, for TMTSF$^{+\bullet}$ at 659 nm, and for ET$^{+\bullet}$ at 484 nm and 850 nm. The values of c_D led to the equilibrium constant as:

$$K = c_D /(c_0 - 2c_D)^2 \tag{S6}$$

The thermodynamic parameters for dimerization (Table 1) were calculated by the least-squares procedure from van't Hoff plots (linear dependence of ln K on 1/T), which are illustrated in Figure S5. The values of $\Delta H^\ominus$ (from the slopes of the linear dependences) and $\Delta S^\ominus$ (from the intersect of the linear dependences) were calculated as an average of several values (3-5) calculated at different values of c_0 and λ. Values of $\Delta G^\ominus(298)$ and their errors were calculated from values of K (obtained from the linear regression) measured for several series.

References.

[1] J.-M. Lü, S.V. Rosokha, J.K. Kochi, *J. Am. Chem. Soc.* **2003**, *125*, 12161.

[2] S.V. Rosokha, J.K. Kochi *J. Am. Chem. Soc.,* **2007**, *129*, 828.

[†] Note that the residual absorption of dimer ε_D^M at the monomer band maximum λ_M were calculated by step-by-step approximations and apparent changes in concentrations due to the volume changes with temperature were taken into account to ensure accuracy.
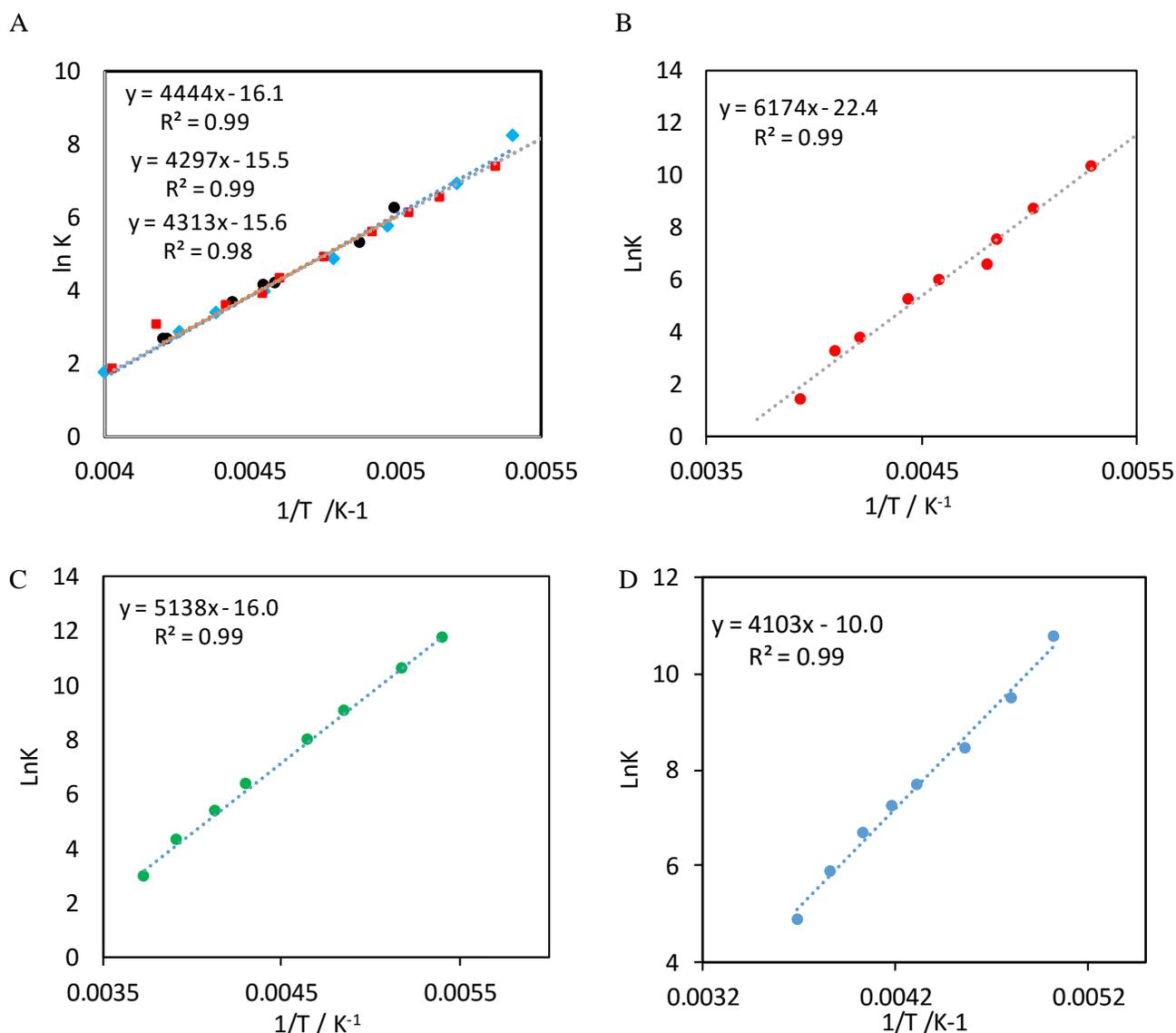
Figure S8. Van't Hoff graphs for dimerization of cation-radicals measured in propanenitrile for: (A) 2.0 mM (TTF)BArF (◆), 2.1 mM (TTF)Br$_6$CAR (●), and (TTF)Me$_{12}$CAR 2.0 mM (■); B)   1.4 mM (TMTTF)BArF (●); C) 1.1 mM (ET)BArF (●) and D) 1.3 mM (TMTSF)BArF (●).
Results of the regression analysis of the series:[a]

	Intercept	Standard Error	X variable(Slope)	Standard Error
(TTF)BArF	-16.14	0.81	4444	171
(TTF)Br$_6$CAR	-15.46	0.82	4297	179
(TTF)Me$_{12}$CAR	-15.56	0.87	4313	180
(TMTTF)BArF	-22.41	1.26	6174	274
(ET)BArF	-15.98	0.42	5138	92
(TMTSF)BArF	-10.04	0.70	4103	163

a)   Note that errors in Table 2 were evaluated from the variations of values in 3-5 independently measured series with the same cation radicals (taken with the same or different counter-ions).

Table S4. Experimental and calculated spectral characteristics of monomers and dimers the $D^{+\bullet}$ monomers and D_2^{2+} dimers resulting from the TD DFT UM06L/def2TZVPP computations (CH_3CN).[a]

$D^{+\bullet}$		λ_M, nm ($\log\varepsilon$)	λ_D, nm ($\log\varepsilon$)
$TTF^{+\bullet}$	Exp	581 (3.5) 436 (4.2)	733 (4.3) 520(4.0), 396(4.4)
	Calc	523 (3.5), 390 (4.2)	700(4.1), 482(3.7), 349(4.4)
$TMTTF^{+\bullet}$	Exp	654 (3.8), 462 (4.1)	779(4.0), 573(4.0), 412(4.3)
	Calc	602 (3.8), 403(4.2)	805 (4.0), 537 (4.0), 367(4.4)
$TMTSF^{+\bullet}$	Exp	782(3.8), 451 (3.9)	830(4.2), 649(4.3), 391(4.2)
	Calc	690(3.8), 402(4.1)	890(4.0), 588(4.1), 355(3.7)
$ET^{+\bullet}$	Exp	954 (4.0), 452 (4.0)	854(4.4), 440 (4.2)
	Calc	1042 (4.0), 436 (4.0)	1123 (4.0), 900 (4.3)
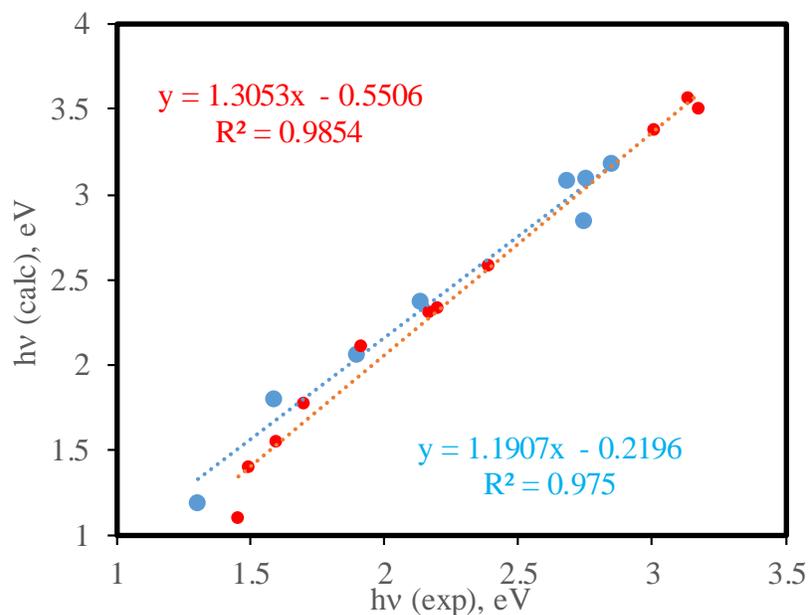
Figure S9. Correlation between experimental and calculated energies of electronic transitions in monomers (blue) and dimers (red) of cation-radicals of tetrathiafulvalene analogues.

Quantum-mechanical computations.

Table S5. Energies (in Hartree, unless noted otherwise) of the $D^{+\bullet}$ monomers and D_2^{2+} dimers resulting from the UM06L/def2TZVPP computations.

		TTF	TMTTF	TMTSF	ET
		In acetonitrile			
$D^{+\bullet}$	E	-1823.69255	-1981.00771	-9994.09552	-3571.36553
	ZPE	0.08341	0.19413	0.18922	0.16027
	G	-1823.64689	-1980.86104	-9993.95882	-3571.25603
D_2^{2+} (singlet)	E	-3647.40374	-3962.04039	-19988.21966	-7142.7626
	ZPE	0.16881	0.39267	0.38091	0.32264
	G	-3647.28466	-3961.71134	-19987.91089	-7142.51056
	BSSE	0.00192	0.00239	0.00325	0.00365
D_2^{2+} (triplet)[a]	E	-3647.39116	-3962.02966	-19988.20954	-7142.75166
D_2^{2+} (triplet)[b]	E	-3647.37934	-3962.01958	-19988.20321	-7142.74846
		In propanenitrile			
$D^{+\bullet}$	E	-1823.69211	-1981.00733	-9994.09516	-3571.36515
	ZPE	0.18934	0.19376	0.18934	0.16025
	G	-1823.60866	-1980.86303	-9993.95645	-3571.25582
D_2^{2+} (singlet)	E	-3647.40238	-3962.03921	-19988.21858	-7142.76146
	ZPE	0.16876	0.39092	0.38122	0.32269
	G	-3647.28333	-3961.70845	-19987.90784	-7142.50919
ΔE_{FOR}, (kcal/mol)		-9.0	-11.8	-14.1	-15.9

a) Optimized triplet state; b) Energy of triplet in the geometry of the optimized singlet.

Table S6. Characteristics of the critical points along S…S (or Se…Se) and C…C bond paths. [a]

	Bond path	ρ	$\nabla^2\rho$	H(r)
TTF	S…S	1.08E-02	2.81E-02	1.22E-03
	C…C	5.70E-03	1.62E-02	8.17E-04
TMTTF	S…S	1.09E-02	2.83E-02	1.18E-03
	C…C	6.38E-03	1.74E-02	8.61E-04
TMTSF	Se…Se	9.93E-03	2.08E-02	7.04E-04
	C…C	5.78E-03	1.58E-02	7.41E-04
ET	S…S	7.94E-03	2.40E-02	1.25E-03
	C…C	8.40E-03	2.36E-02	8.78E-04

a) ρ is the electron density, $\nabla^2\rho$ is Laplacian of electron density, H(r) is the total energy density (in a.u.).

Table S7. Atomic coordinates (in Å) and ESP charges (in a.u.) which were used in calculations of electrostatic interaction between monomers in π-dimers.

(TTF)$_2^{2+}$

Atom	Coordinates			Charge
S	1.77443	1.543355	1.451333	0.176315
S	1.662055	-1.70186	-1.45135	0.179324
C	1.863157	3.065277	0.670903	-0.1335
C	1.732177	0.616628	0	-0.02923
C	1.6829	-0.77431	0	-0.03569
C	1.656102	-3.22585	-0.67104	-0.13264
S	1.77443	1.543355	-1.45133	0.176315
S	1.662055	-1.70186	1.451349	0.179324
C	1.863157	3.065277	-0.6709	-0.1335
C	1.656102	-3.22585	0.671039	-0.13264
H	1.654313	-4.10762	-1.29162	0.221056
H	1.654313	-4.10762	1.291616	0.221056
H	1.91212	3.945945	1.291257	0.221582
H	1.91212	3.945945	-1.29126	0.221582
S	-1.77455	-1.5433	-1.45133	0.1714
C	-1.73227	-0.61658	0	-0.01583
C	-1.86346	-3.06521	-0.6709	-0.13152
S	-1.66203	1.701894	-1.45135	0.176791
C	-1.68295	0.774357	0	-0.03288
C	-1.65588	3.225882	-0.67104	-0.13474
S	-1.66203	1.701894	1.45135	0.176791
C	-1.65588	3.225882	0.67104	-0.13474
S	-1.77455	-1.5433	1.451332	0.1714
C	-1.86346	-3.06521	0.670903	-0.13152
H	-1.6539	4.10766	1.291609	0.222814
H	-1.6539	4.10766	-1.29161	0.222814
H	-1.91255	-3.94588	1.291241	0.219929
H	-1.91255	-3.94588	-1.29124	0.219929

(TMTTF)$_2^{2+}$

Atom	Coordinates			Charge
S	1.114266	-1.92088	1.363453	0.066902
S	-2.25196	-1.41297	-1.3401	0.084711
C	3.813585	-2.42572	1.318492	-0.41408
H	4.717437	-2.20834	0.757299	0.15116
H	3.853328	-3.46942	1.627515	0.165997
H	3.823635	-1.82378	2.224483	0.161039
C	2.601042	-2.15897	0.499572	0.123673

C	0.119183	-1.71288	-0.02081	-0.02288
C	-1.25512	-1.52423	0.054651	-0.06955
C	-3.74141	-1.19081	-0.49993	0.186745
C	-4.99973	-1.09627	-1.28965	-0.48845
H	-5.64292	-0.31284	-0.89421	0.16393
H	-5.55501	-2.03183	-1.23511	0.176337
H	-4.81394	-0.88467	-2.33793	0.187359
S	0.95252	-1.8037	-1.51947	0.051471
S	-2.09938	-1.37366	1.539478	0.098846
C	3.632379	-2.29781	-1.82029	-0.38723
H	4.590199	-2.35072	-1.31382	0.130656
H	3.504264	-3.21724	-2.3893	0.168617
H	3.66769	-1.48124	-2.54068	0.150935
C	2.523621	-2.11326	-0.84959	0.126216
C	-3.67091	-1.18709	0.857017	0.145293
C	-4.83782	-1.10761	1.775974	-0.48571
H	-5.61535	-0.47471	1.356152	0.155479
H	-5.26879	-2.09686	1.927533	0.183044
H	-4.56692	-0.71625	2.752105	0.188893
S	-0.95225	1.804294	-1.52185	0.042966
C	-0.11896	1.714813	-0.02311	-0.00603
C	-2.52343	2.114117	-0.85229	0.104336
C	-3.63221	2.297396	-1.82322	-0.32215
H	-4.59009	2.350238	-1.31685	0.112062
H	-3.66704	1.480176	-2.5429	0.133951
H	-3.50449	3.216405	-2.39299	0.153974
S	2.252089	1.413461	-1.34221	0.082914
C	1.255314	1.526001	0.052491	-0.05792
C	3.741353	1.190867	-0.5019	0.151478
C	4.999617	1.09483	-1.29149	-0.43826
H	5.642793	0.312185	-0.89447	0.151695
H	5.5549	2.030506	-1.23886	0.167083
H	4.813783	0.881108	-2.33932	0.175602
S	2.099475	1.375995	1.537404	0.08691
C	3.670819	1.18789	0.855049	0.161574
C	4.837626	1.107629	1.774034	-0.46657
H	5.613479	0.471871	1.355446	0.149256
H	5.271233	2.096075	1.923339	0.176552
H	4.565918	0.718958	2.751003	0.185045
S	-1.11406	1.923861	1.360963	0.05839
C	-2.60089	2.160777	0.496819	0.146617
C	-3.81361	2.427253	1.315539	-0.46616
H	-4.71724	2.208055	0.754717	0.165747
H	-3.82284	1.826167	2.22209	0.175045
H	-3.85461	3.471225	1.623439	0.176495

(TMTSF)$_2$$^{2+}$

Atom	Coordinates			Charge
Se	-2.59466	-1.32889	-1.53819	0.193844
Se	-2.59471	-1.24449	1.593765	0.188444
C	-1.59632	-1.47578	0.032918	-0.16884
C	-4.19311	-0.88712	0.694834	0.125145
C	-4.19366	-0.92654	-0.66044	0.094237
C	-5.41495	-0.63651	1.513527	-0.49695
H	-5.19451	-0.52113	2.570476	0.190028
H	-6.11928	-1.46131	1.410464	0.182612
H	-5.92425	0.265709	1.177763	0.161733
C	-5.4163	-0.73247	-1.49258	-0.45673
H	-5.18908	-0.59902	-2.54609	0.179352
H	-5.97615	0.138694	-1.15688	0.151719
H	-6.07769	-1.59413	-1.40486	0.175443
Se	0.762039	-1.85714	1.609638	0.123199
Se	0.751813	-1.94243	-1.53148	0.121275
C	-0.23707	-1.71661	0.037356	-0.07045
C	2.3801	-2.25267	-0.63105	0.065883
C	2.385314	-2.21262	0.715763	0.081091
C	3.546512	-2.51931	-1.51594	-0.32074
H	3.657135	-1.73897	-2.26989	0.137398
H	4.470813	-2.574	-0.94983	0.12124
H	3.427909	-3.45993	-2.05187	0.148624
C	3.558968	-2.42907	1.605403	-0.37832
H	3.476642	-3.37231	2.143839	0.160264
H	4.487079	-2.44644	1.04262	0.136098
H	3.636234	-1.64265	2.35651	0.154871
Se	2.594628	1.2442	-1.59377	0.181971
Se	2.594583	1.328672	1.538179	0.182954
Se	-0.75191	1.942096	1.53147	0.119442
Se	-0.76212	1.856906	-1.60965	0.120724
C	4.193034	0.886871	-0.69483	0.121248
C	4.193594	0.926329	0.660438	0.105231
C	1.596236	1.475504	-0.03293	-0.13979
C	0.236985	1.716325	-0.03737	-0.07935
C	-2.38018	2.252404	0.631042	0.079158
C	-2.38539	2.212414	-0.71578	0.071858
C	5.414883	0.636229	-1.51351	-0.52263
H	5.194457	0.520907	-2.57047	0.200178
H	6.119263	1.460973	-1.41039	0.18919
H	5.924099	-0.26605	-1.17778	0.167833
C	5.416239	0.732255	1.492569	-0.48203
H	6.077785	1.593769	1.404569	0.181178

H	5.189062	0.599139	2.546125	0.188287
H	5.975908	-0.13911	1.157072	0.157551
C	-3.54659	2.519047	1.515936	-0.35051
H	-3.65724	1.738686	2.269858	0.143669
H	-3.42796	3.459643	2.051903	0.156042
H	-4.47089	2.573791	0.949821	0.127899
C	-3.55902	2.429006	-1.60542	-0.35392
H	-3.47645	3.372167	-2.14397	0.154874
H	-3.6365	1.642532	-2.35645	0.148332
H	-4.48711	2.446717	-1.04262	0.130138

$(ET)_2{}^{2+}$

Atom	Coordinates			Charge
S	-0.73568	-1.70472	-1.48261	0.098512
S	2.383085	-1.44858	1.526473	0.086029
C	-2.29652	-1.93597	-0.75971	-0.00693
C	0.130743	-1.59817	0.002863	-0.01396
C	1.507213	-1.4972	0.041891	0.016559
C	3.955008	-1.31636	0.803017	0.023799
S	-0.82947	-1.72022	1.428871	0.088396
S	2.476911	-1.5101	-1.3792	0.066892
C	-2.34383	-1.94009	0.60402	0.06783
C	3.990861	-1.31809	-0.5634	0.043111
S	-3.60081	-2.11272	-1.88563	0.006336
S	-3.71271	-2.14716	1.648138	-0.03387
S	5.419055	-1.24018	-1.5478	-0.00406
S	5.265127	-1.22254	1.932695	-0.0473
C	6.555443	-2.0847	-0.41199	-0.26543
H	6.206099	-3.10226	-0.2615	0.143932
H	7.497407	-2.12334	-0.95323	0.205808
C	6.75123	-1.34339	0.883008	0.061305
H	7.134862	-0.34173	0.710453	0.073909
H	7.463263	-1.8702	1.515554	0.12434
C	-4.85588	-2.8425	-0.80543	-0.30096
H	-5.75864	-2.82334	-1.41181	0.229911
H	-4.59816	-3.87966	-0.61128	0.176802
C	-5.07797	-2.06041	0.464555	-0.12016
H	-5.92047	-2.46755	1.0194	0.201916
H	-5.29047	-1.01572	0.252003	0.069899
S	0.831459	1.765114	1.361133	0.099434
C	-0.13056	1.588786	-0.05945	-0.03325
C	2.344924	1.953072	0.526749	0.073299
S	-2.36445	1.487202	1.485748	0.05191
C	-1.50695	1.490748	-0.00408	0.010728

C	-3.94103	1.350617	0.788602	0.117944
S	-2.49443	1.465648	-1.4186	0.125939
C	-4.00763	1.32729	-0.57718	-0.05243
S	0.73446	1.637947	-1.54728	0.078469
C	2.297022	1.892378	-0.83566	0.00677
S	-5.40222	1.228232	-1.60239	-0.02261
S	-5.2826	1.313112	1.888843	-0.01464
S	3.604902	2.01422	-1.96673	0.009411
S	3.710758	2.211314	1.560905	-0.06761
C	-6.79691	1.311917	-0.43406	0.060819
H	-7.5808	1.793096	-1.01569	0.124988
H	-7.12436	0.30138	-0.20548	0.082443
C	-6.5226	2.095589	0.821539	-0.32004
H	-7.41978	2.12651	1.434605	0.227168
H	-6.21371	3.116535	0.615938	0.160822
C	5.077627	2.062671	0.385467	-0.0285
H	5.922324	2.488099	0.923228	0.175164
H	5.284144	1.009754	0.210658	0.047717
C	4.860714	2.789722	-0.91813	-0.27358
H	5.763962	2.740361	-1.52197	0.207117
H	4.605056	3.835039	-0.77136	0.159892

Table S8. Energies for calculation of dispersion in dimers of tetrathiafulvalene analogues [a]

		TTF	TMTTF	TMTSF	ET
E(MP2), Hartrees	Dimers	-3642.432432	-3956.28908	-19975.4634	-7133.21
	Monomers	-1821.189057	-1978.10904	-9987.68983	-3566.56
ΔE(MP2), kcal/mol		-34.08486503	-44.5472165	-52.5172571	-56.6146
E(HF), Hartrees	Dimers	-3639.093277	-3951.50887	-19969.8391	-7127.07
	Monomers	-1819.574857	-1975.78646	-9984.9526	-3563.58
ΔE(HF), kcal/mol[b]		35.41495168	40.1996203	41.4911409	53.63989
E_{DIS}, kcal/mol[c]		69.5	84.7	94.0	110.3
E(B97D), Hartrees	Dimers	-3647.241131	-3961.69681	-19998.1228	-7142.54
	Monomers	-1823.610695	-1980.83461	-9999.04389	-3571.25
ΔE(B97D), kcal/mol		-12.3872265	-17.3089412	-22.0011415	-16.9808
E(B98), Hartrees	Dimers	-3646.970313	-3961.5093	-19988.6895	-7141.95
	Monomers	-1823.486399	-1980.75772	-9994.34856	-3570.98
ΔE(B98), kcal/mol		1.560059125	3.8470268	4.775024	10.21593
E_{DIS}, kcal/mol[d]		13.9	21.2	26.8	27.2

a) Energies obtained from single-point calculations using indicated method and def2tzvpp basis set using coordinates of the monomers and dimers optimized via UM06L/def2tzvpp calculations in CH_3CN. b) $\Delta E = E(Dimer) - 2E (Monomer)$. c) $E_{DIS} = \Delta E(HF) - \Delta E(MP2)$. D) $E_{DIS} = \Delta E(B98) - \Delta E(B97D)$.

Table S9. Calculations of the differences of interaction energies in the neutral and dicationic dimers. [a]

Energy	TTF	TMTTF	TMTSF	ET
E_D, Hartrees	-3647.40374	-3962.04039	-19988.21966	-7142.76260
E_M, Hartrees	-1823.69252	-1981.00682	-9994.09497	-3571.36426
E_{INT}, kcal/mol	-11.73	-16.78	-18.64	-21.38
E_D^N, Hartrees	-3647.68775	-3962.31444	-19988.50769	-7143.06073
E_M^N, Hartrees	-1823.84605	-1981.15327	-9994.24590	-3571.51693
E_{INT}^N, kcal/mol	2.72845157	-4.9601867	-9.97407485	-16.8570847
ΔE_{INT}, kcal/mol	14.46	11.82	8.67	4.52

a] $\Delta E_{INT} = E_{INT}^N - E_{INT}$, where $E_{INT} = E_D - 2E_M$ and $E_{INT}^N = E_D^N - 2E_M^N$ are interaction energies between cationic and neutral monomers in the dicationic and neutral dimers, respectively, E_D is an energy of optimized dicationic dimer, E_D^N is an energy of neutral dimer with the same geometry, E_M and E_M^N are energies of cationic and neutral monomers in the same geometry taken from the dicationic dimer.
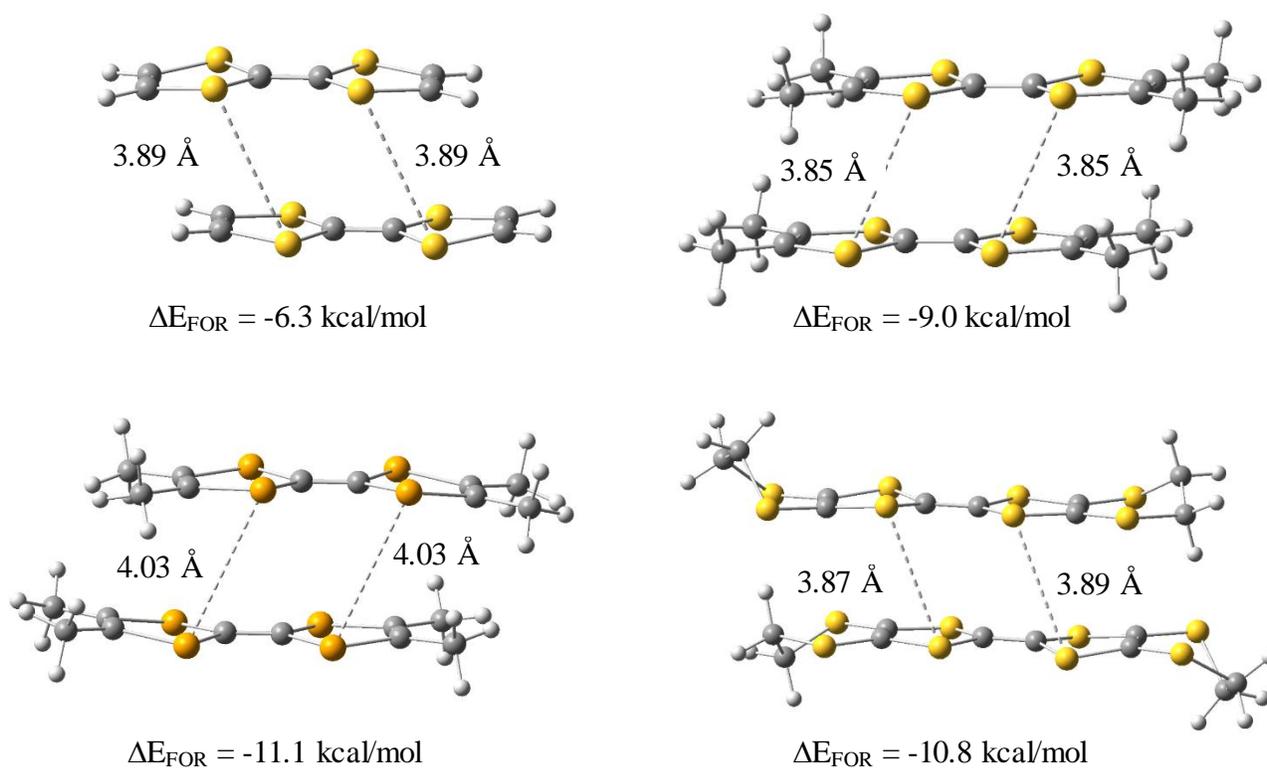
Figure S10. Structures and formation energies of the dimers formed by neutral TTF analogues.