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Mechanically Stabilized Tetrathiafulvalene Radical Dimers

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SUPPORTING INFORMATION

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1. Interaction of Counterions with Oxidized TTF Dimers: In the generation of oxidized radical cation dimers of tetrathiafulvalene, it has been predicted,[S1] computationally, that the repulsive Coulombic force between the two TTF monocations is tempered by interaction with both solvent and counterions, thus endowing the radical dimer with the stability required to exist in solution. As such, we examined the solid-state structures of the oxidized [3]catenanes to investigate the possibility of short contacts between the TTF dimers and counterions in the structure (Figure S1). It should be noted that for each TTF dimer, there exist an additional four counterions associated with the tetracationic cyclophane.

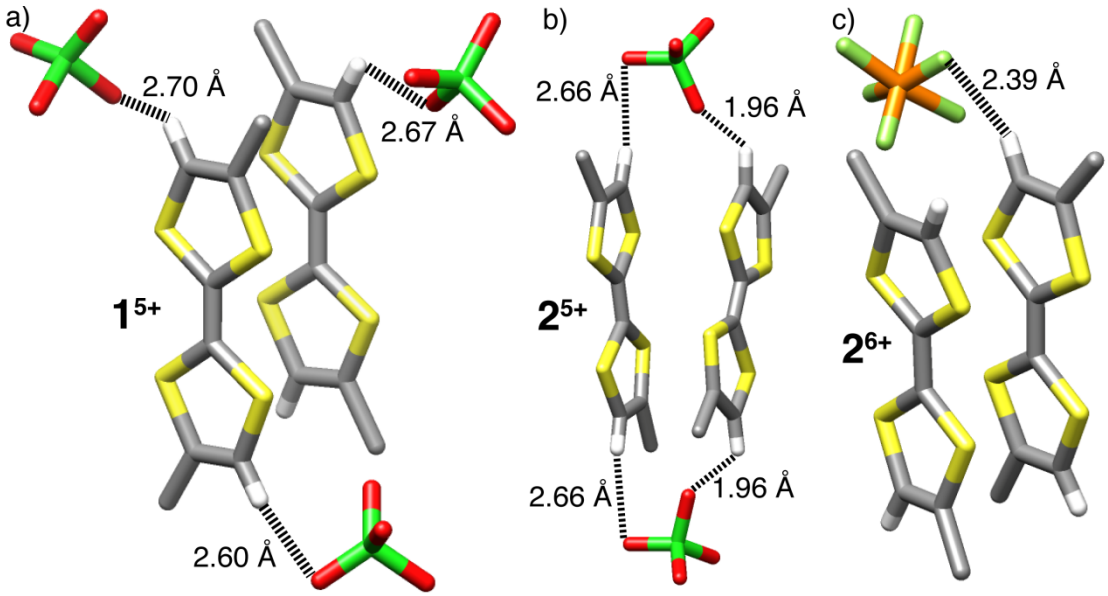


Figure S1. Tubular representations of short contacts between counterions and the oxidized TTF dimers within the solid-state structures of the oxidized [3]catenanes. ClO_4^- anions show contacts with the mixed-valence TTF dimer units found in **a)** $\mathbf{1}^{5+}$ and **b)** $\mathbf{2}^{5+}$, whilst **c)** a PF_6^- anion interacts with the radical cation dimer found in $\mathbf{2}^{6+}$.

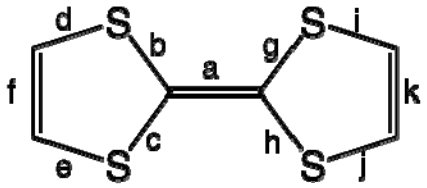
In each case, CH···O and CH···F contacts between the TTF dimers and the ClO_4^- and PF_6^- counterions are observed, but the structure of $\mathbf{2}^{6+}$, which holds the most positive charge, has the least interactions.

2. Analysis of Bond Lengths Distances and Angles of the TTF Units in the Solid-State:

Table S1. Bond Distances (Å) of the TTF Moieties Found in the Solid-State Structures of the Inclusion Complexes and [3]Catenanes Described in This Paper. Atom Labeling[a] is Detailed in the Schematic Diagram Below.

	a	b	c	d	e	f	g	h	i	j	k
$(TTF)_2 \subset MS^{4+}$	1.37(3)	1.75(2)	1.58(2)	1.72(2)	1.72(2)	1.36(3)	1.72(2)	1.75(2)	1.75(2)	1.72(2)	1.35(3)
$(TTF)_2 \subset MS^{4+}$	1.36(3)	1.68(2)	1.78(2)	1.76(3)	1.67(2)	1.37(3)	1.75(2)	1.76(2)	1.78(2)	1.72(2)	1.34(3)
$\mathbf{1}^{4+}$	1.325(8)	1.768(7)	1.763(6)	1.761(7)	1.750(8)	1.326(11)	1.753(6)	1.785(7)	1.751(7)	1.755(6)	1.352(9)
$\mathbf{1}^{4+}$	1.340(8)	1.754(6)	1.757(6)	1.722(8)	1.753(7)	1.347(10)	1.765(6)	1.752(5)	1.751(6)	1.762(6)	1.353(7)
$\mathbf{1}^{5+}$	1.340(8)	1.756(6)	1.726(6)	1.713(7)	1.748(7)	1.357(8)	1.759(6)	1.740(6)	1.726(7)	1.715(7)	1.352(8)
$\mathbf{1}^{5+}$	1.343(9)	1.736(7)	1.748(6)	1.770(8)	1.644(9)	1.355(10)	1.715(6)	1.760(6)	1.748(7)	1.699(7)	1.332(8)
$\mathbf{2}^{4+}$	1.449(15)	1.960(11)	1.497(10)	1.834(14)	1.678(12)	1.416(12)	1.705(8)	1.872(8)	1.736(11)	1.581(9)	1.511(13)
$\mathbf{2}^{5+}$[b]	1.29(3)	1.691(11)	1.794(15)	1.601(15)	1.691(15)	1.480(17)	1.691(11)	1.794(15)	1.601(15)	1.691(15)	1.480(17)
$\mathbf{2}^{5+}$[b]	1.27(3)	1.689(13)	1.810(16)	1.587(16)	1.689(10)	1.475(17)	1.689(13)	1.810(16)	1.587(16)	1.689(10)	1.475(17)
$\mathbf{2}^{6+}$	1.392(10)	1.720(7)	1.725(7)	1.730(8)	1.702(8)	1.327(10)	1.715(7)	1.724(7)	1.707(8)	1.748(7)	1.320(10)
$\mathbf{2}^{6+}$	1.404(9)	1.708(6)	1.721(7)	1.734(8)	1.736(7)	1.311(11)	1.695(7)	1.727(6)	1.712(7)	1.731(7)	1.327(10)

[a]The labeling scheme for the TTF units is based on the following diagram.

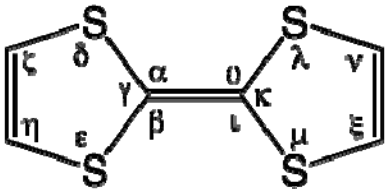


[b]Each half of the TTF units in this case is related by a centre of symmetry.

Table S2. Bond Angles (°) of the TTF Moieties Found in the Solid-State Structures of the Inclusion Complexes and [3]Catenanes Described in This Paper. Atom Labeling[a] is Detailed in the Schematic Diagram Below.

	α	β	γ	δ	ε	ζ	η	θ	ι	κ	λ	μ	ν	ξ
$(TTF)_2 \subset MS^{4+}$	122.2(16)	122.2(14)	115.1(10)	95.1(10)	94.0(10)	116.4(15)	118.9(15)	121.9(15)	121.3(14)	116.7(11)	93.2(10)	94.7(10)	118.5(7)	116.6(17)
$(TTF)_2 \subset MS^{4+}$	124.5(15)	119.4(14)	116.2(11)	94.5(12)	94.4(11)	116.0(19)	116.0(19)	122.5(15)	122.7(15)	114.7(11)	94.6(10)	95.6(9)	116.7(17)	118.4(16)
$\mathbf{1}^{4+}$	121.9(5)	123.8(5)	114.3(3)	93.7(4)	95.4(4)	119.4(6)	116.4(6)	124.5(5)	121.9(5)	113.5(3)	94.9(3)	94.8(3)	118.0(5)	116.6(5)
$\mathbf{1}^{4+}$	121.8(5)	123.1(4)	115.0(4)	95.5(3)	93.6(3)	117.0(5)	118.3(6)	121.7(4)	124.1(5)	114.1(3)	94.2(3)	95.1(3)	118.2(5)	115.9(5)
$\mathbf{1}^{5+}$	122.3(4)	123.0(4)	114.7(4)	95.2(3)	95.9(3)	118.5(6)	115.6(5)	122.4(5)	123.2(4)	114.4(4)	95.7(3)	94.8(3)	115.7(5)	119.3(5)
$\mathbf{1}^{5+}$	122.2(5)	122.1(5)	115.7(4)	94.2(4)	94.2(3)	113.4(6)	122.5(6)	123.1(3)	122.3(5)	114.7(4)	95.5(3)	94.7(3)	115.8(5)	119.3(5)
$\mathbf{2}^{4+}$	102.8(6)	141.4(7)	115.7(6)	90.7(4)	101.0(5)	110.9(9)	120.6(10)	142.1(7)	106.8(5)	110.8(5)	95.3(6)	102.2(4)	120.6(9)	110.1(7)
$\mathbf{2}^{5+[b]}$	116.4(13)	129.4(16)	114.1(7)	94.9(16)	98.7(7)	114.5(12)	117.6(11)	116.4(13)	129.4(16)	114.1(7)	94.9(16)	98.7(7)	114.5(12)	117.6(11)
$\mathbf{2}^{5+[b]}$	113.3(14)	132.3(18)	114.4(9)	95.8(7)	96.3(8)	111.1(13)	122.4(12)	113.3(14)	132.3(18)	114.4(9)	95.8(7)	96.3(8)	111.1(13)	122.4(12)
$\mathbf{2}^{6+}$	122.5(8)	122.3(5)	115.1(4)	95.3(3)	94.7(3)	115.9(6)	118.9(6)	123.5(5)	120.5(5)	115.9(4)	94.3(3)	94.7(3)	119.7(6)	115.3(6)
$\mathbf{2}^{6+}$	120.7(5)	123.7(5)	115.6(4)	95.2(3)	94.5(3)	116.9(6)	117.7(6)	121.8(5)	121.6(5)	116.5(4)	94.5(3)	94.2(3)	118.5(6)	116.3(5)

[a] The labeling scheme for the TTF units is based on the following diagram.



[b]Each half of the TTF units in this case is related by a centre of symmetry.

Single crystals of **1**·2PF_6·3ClO_4·$(MeCN)_4$, were grown by vapor diffusion of Et_2O into a solution of the [3]catenane and one equivalent of [$Fe(ClO_4)_3$] in MeCN at 0 ºC. X-Ray diffraction data were collected on a Bruker Kappa diffractometer, equipped with a CuKα sealed-tube source and an APEX II CCD detector.

Crystal data for ***[1·2PF$_6$·3ClO$_4$·4CH$_3$CN]***: Crystal color: black. Crystal shape: rod. Crystal size: 0.72 x 0.10 x 0.09 mm. Formula: $C_{116}H_{128}N_4O_{20}S_8$·$(PF_6)_2$·$(ClO_4)_3$·-$(CH_3CN)_4$, M_r = 2907.21, monoclinic, space group $P2_1/n$, a = 18.8354(4), b = 26.6616(5), c = 30.5877(6) Å, β = 92.929(1) °, V = 15340.5(5) Å^3, ρ_{calc} = 1.259 g cm^{-3}, Z = 4, T = 100(2) K, $\mu(Cu_{K\alpha})$ = 2.466 mm^{-1}, reflections collected = 91095, unique reflections, (R_{int}) = 21832 (0.0507), R_1 = 0.0909 [F>4σ(F)], wR_2 = 0.2856 for all data.

3. Spectroelectrochemistry Experiments Performed on the [3]Catenane 1^{4+}

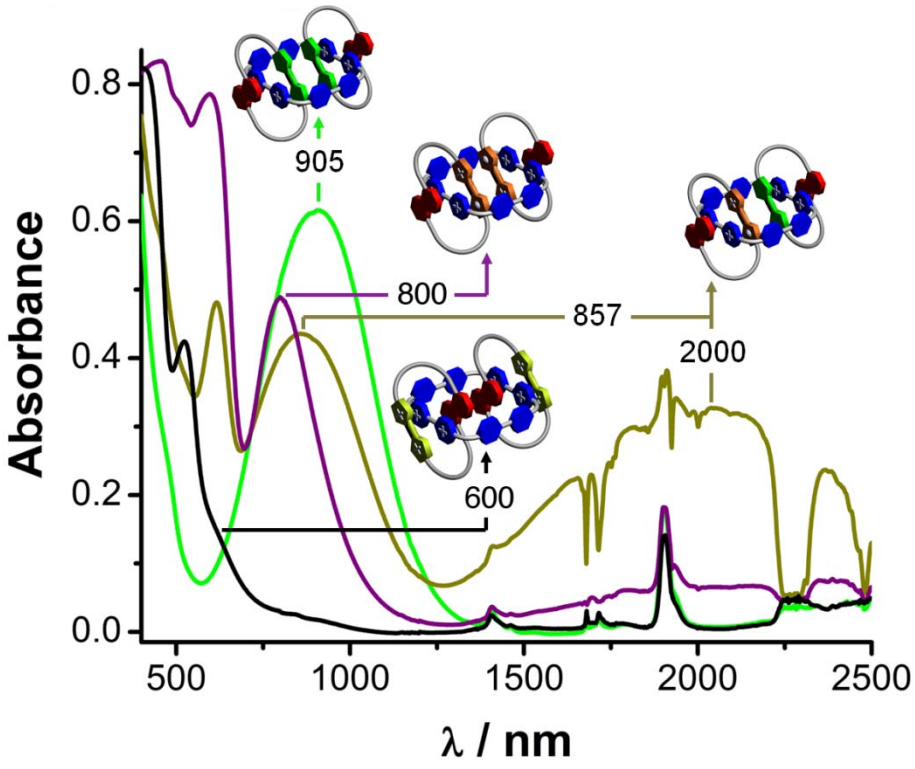


Figure S2. The SEC overlays of the resultant spectra of the [3]catenane $\mathbf{1}^{4+}$ after applying a potential of 0 V (green trace), +500 mV (yellow trace), +800 mV (purple trace), and +1200 mV (black trace). All spectra were recorded in argon purged MeCN at 1 mM concentrations in a 2 mm cell path length.

Reference 11 in the Main Text:

Spruell, J. M.; Coskun, A.; Friedman, D. C.; Forgan, R. S.; Sarjeant, A. A.; Trabolsi, A.; Fahrenbach, A. C.; Barin, G.; Paxton, W. F.; Dey, S. K.; Olson, M. A.; Benitez, D.; Tkatchouk, E.; Colvin, M. T.; Carmielli, R.; Caldwell, S. T.; Rosair, G. M.; Hewage, S. G.; Duclairoir, F.; Seymour, J. L.; Slawin, A. M. Z.; Goddard, W. A.; Wasielewski, M. R.; Cooke, G.; Stoddart, J. F. *Nature Chem.* **2010**, *2*, 870–879.

References

S1) Garcia-Yoldi, I.; Miller, J. S.; Novoa, J. J.; *J. Phys. Chem. A* **2009**, *113*, 484–492.