Electronic Supporting Information

Fine Tuning the Performance of Multiorbital Radical Conductors by Substituent Effects

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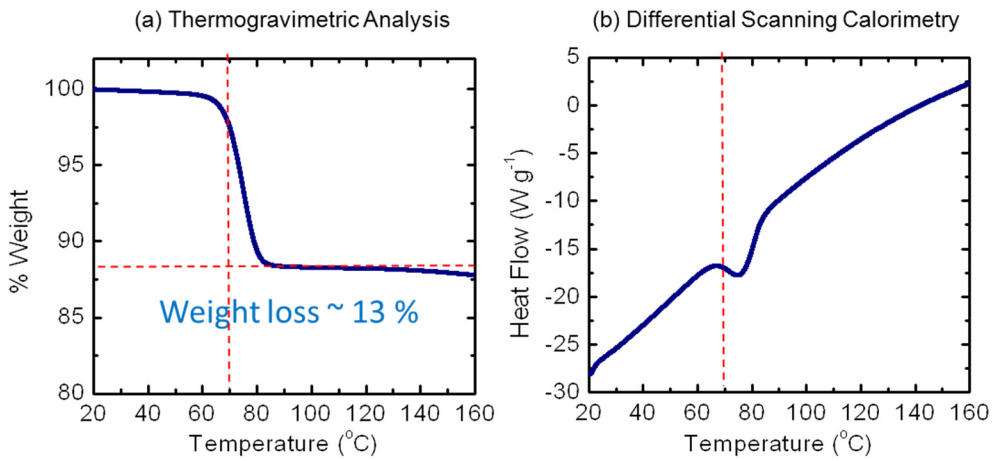


Figure S1. (a) TGA and (b) DSC Measurements on **2a**·MeCN. The loss of 1.0 mol MeCN from **2a**·MeCN requires a 12.4 % weight loss, in good agreement with the value of 13% obtained experimentally. The temperature of phase transition by DSC matches that obtained by TGA.

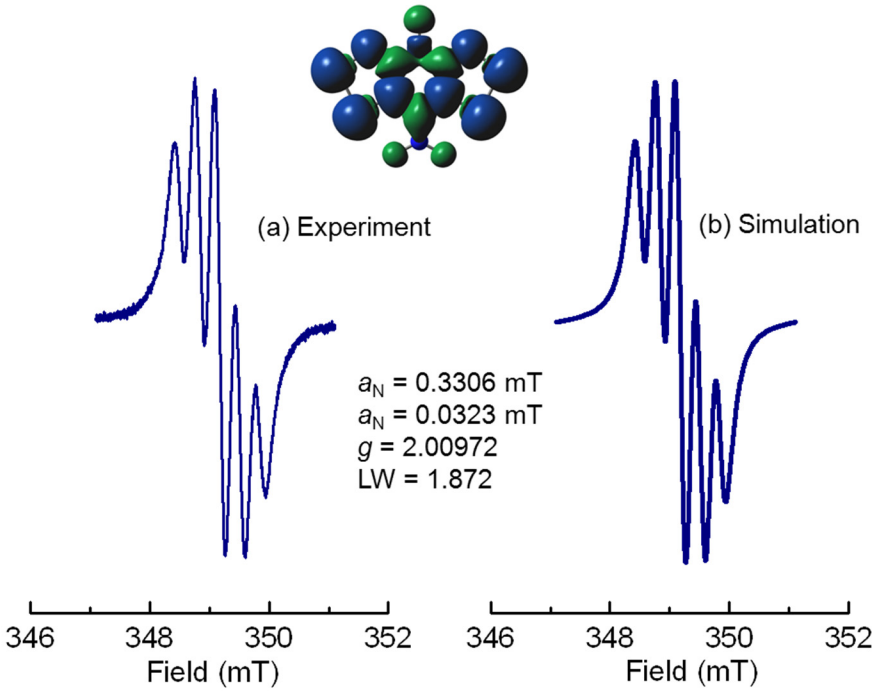


Figure S2. (a) Experimental and (b) simulated (with Winsim) EPR spectrum of **2a** in toluene (at ν=9.821796 GHz). The UB3LYP/6-311G(d,p) spin density distribution is also shown.

Table S1. Gaussian Archive Files for **2a** (PCM - Acetonitrile).

Radical


```
1|1|UNPC-OAKLEY-PC|FOpt|UB3LYP|6-311G(d,p)|C6N3O3S4(2)|RICHARD OAKLEY|
22-Apr-2014|0||# opt ub3lyp/6-311g(d,p) scrf=(solvent=acetonitrile,pcm
) geom=connectivity||ub3lyp/6-311g(d,p) full optimization run on NO2BB
O radical with PCM||0,2|C,-0.0001224193,0.938521604,-0.0000106043|C,1.2
650819803,-1.1736326852,0.0000279024|C,-1.2648482808,-1.1738943188,-0.
0000005504|C,1.2304017482,0.254479783,0.0000337945|C,-1.2304832456,0.2
542540518,-0.0000441108|N,2.4082380514,-1.8200678883,-0.0000004575|N,-
2.4078658994,-1.8205302423,0.0000170595|S,3.7602064884,-0.8953877782,-
0.0001480478|S,-3.7600060438,-0.8961456806,0.0000975597|S,2.797696582,
1.0392352919,0.0001433025|S,-2.7979385703,1.0386438281,-0.0001874208|O
,1.0880410024,2.9520746301,-0.000075209|O,-1.0887727893,2.9518028104,-
0.0000104448|N,-0.000288064,2.3600549275,-0.0000294439|C,0.0002061063,
-1.9797644811,0.0000469729|O,0.0003213134,-3.1910342124,0.0000155678||
Version=EM64W-G09RevD.01|State=2-A|HF=-2211.417761|S2=0.795332|S2-1=0.
|S2A=0.751071|RMSD=8.036e-009|RMSF=8.389e-006|Dipole=-0.0016493,0.6372
022,0.0000105|Quadrupole=18.7792845,-21.9219212,3.1426366,0.0059038,-0
.0003856,0.0002128|PG=C01 [X(C6N3O3S4)]||@
```


Cation


```
1|1|UNPC-OAKLEY-PC|FOpt|RB3LYP|6-311G(d,p)|C6N3O3S4(1+)|RICHARD OAKLEY
|21-Apr-2014|0||# opt b3lyp/6-311g(d,p) scrf=(solvent=acetonitrile,pcm
) geom=connectivity||b3lyp/6-311g(d,p) full optimization run on NO2BBO
 cation with PCM||1,1|C,-0.0126046194,-1.5331577358,0.0661739736|C,-1.
2622974608,0.5992258218,-0.026433354|C,1.2496346295,0.5918459987,-0.02
56143483|C,-1.2349767402,-0.837277232,0.0358387429|C,1.2137888893,-0.8
444262794,0.0366406985|N,-2.4197665459,1.2128399586,-0.0534007008|N,2.
4107486202,1.1985719036,-0.051719613|S,-3.7408085854,0.2992741103,-0.0
140905697|S,3.7263449852,0.2771348511,-0.0114746895|S,-2.7724898964,-1
.5953767856,0.068553021|S,2.7467755313,-1.6115231388,0.0703830757|O,-1
.1078876998,-3.5323306091,0.1527088612|O,1.0718746698,-3.5379193619,0.
1534232017|N,-0.0165442077,-2.9551058327,0.1279406744|C,-0.0039417854,
1.4102733879,-0.0613244584|O,-0.0003700444,2.6150541132,-0.1131211153|
|Version=EM64W-G09RevD.01|State=1-A|HF=-2211.2394728|RMSD=5.011e-009|R
MSF=4.821e-005|Dipole=-0.002684,-0.3992757,0.0170825|Quadrupole=35.342
5106,-26.9999415,-8.3425691,-0.185422,0.0174672,0.8079855|PG=C01 [X(C6
N3O3S4)]||@
```


Closed Shell Singlet Anion


```
 1|1|UNPC-OAKLEY-PC|FOpt|RB3LYP|6-311G(d,p)|C6N3O3S4(1-)|RICHARD OAKLEY
|22-Apr-2014|0||# opt b3lyp/6-311g(d,p) scrf=(solvent=acetonitrile,pcm
) geom=connectivity||b3lyp/6-311g(d,p) full optimization run on NO2BBO
 anion with PCM||-1,1|C,-0.0122045335,-1.5157382384,0.0628500443|C,-1.
2833187548,0.5764657858,-0.0225087451|C,1.2700661982,0.5697111087,-0.0
218299894|C,-1.2472727458,-0.8374529099,0.0351324438|C,1.2264522823,-0
.8439762576,0.035732996|N,-2.4079945712,1.2646910998,-0.0506527195|N,2
.3983928088,1.2519760238,-0.0493215691|S,-3.7954702874,0.3315340734,-0
.0127970641|S,3.7808735643,0.3114548997,-0.0106916195|S,-2.8475829922,
-1.6423287936,0.0677404539|S,2.8224958049,-1.6573785367,0.0691782629|O
,-1.1048231948,-3.5338724378,0.1448286103|O,1.0696183928,-3.5396597798
,0.1454300135|N,-0.0159641777,-2.9330319002,0.1205641157|C,-0.00449807
33,1.3699437003,-0.0547727944|O,-0.0012899803,2.5847653323,-0.10439903
93||Version=EM64W-G09RevD.01|State=1-A|HF=-2211.5512286|RMSD=9.290e-00
9|RMSF=1.765e-005|Dipole=-0.0030768,-0.9287994,0.0379806|Quadrupole=2.
1579546,-16.8498135,14.6918589,-0.0517619,0.0001229,1.2872465|PG=C01 [
X(C6N3O3S4)]||@
```

Table S1. Gaussian Archive File for **2a** (PCM - Acetonitrile), continued.

Triplet Anion


```
1|1|UNPC-OAKLEY-PC|FOpt|UB3LYP|6-311G(d,p)|C6N3O3S4(1-,3)|RICHARD OAKL
EY|22-Apr-2014|0||# opt ub3lyp/6-311g(d,p) scrf=(solvent=acetonitrile,
pcm) geom=connectivity||ub3lyp/6-311g(d,p) full optimization run on NO
2BBO triplet anion with PCM||-1,3|C,-0.0001133743,0.954378738,0.000000
3333|C,1.2524498317,-1.1709494807,0.0001178763|C,-1.2522257834,-1.1712
138279,0.0000054763|C,1.2269639059,0.2402848866,0.0001670252|C,-1.2270
367439,0.2400240753,-0.0001163121|N,2.4149941132,-1.8482386896,-0.0000
834116|N,-2.4146290793,-1.8487458495,0.0000719915|S,3.7742267223,-0.89
01097224,-0.0005745451|S,-3.7740706774,-0.8909113885,0.0001813073|S,2.
7914512231,1.0500037442,0.0006052705|S,-2.7916935199,1.0494120938,-0.0
004975999|O,1.0932139711,2.963583467,-0.000199008|O,-1.0939085633,2.96
33225936,0.0000821225|N,-0.0002738007,2.3450274126,-0.0000562112|C,0.0
001950498,-1.9574890642,0.0001338584|O,0.0003246851,-3.1897693484,0.00
00376966||Version=EM64W-G09RevD.01|State=3-A|HF=-2211.5706369|S2=2.022
554|S2-1=0.|S2A=2.000266|RMSD=8.157e-009|RMSF=1.297e-005|Dipole=-0.000
0953,1.3952769,-0.0000148|Quadrupole=7.5214872,-22.7180931,15.1966059,
0.0031401,-0.0000595,0.0006144|PG=C01 [X(C6N3O3S4)]||@
```


Broken Symmetry Singlet Anion


```
1|1|UNPC-OAKLEY-PC|FOpt|UB3LYP|6-311G(d,p)|C6N3O3S4(1-)|RICHARD OAKLEY
|23-Apr-2014|0||# opt ub3lyp/6-311g(d,p) guess=mix SCF=tight vshift=20
0 scrf=(solvent=acetonitrile,pcm) geom=connectivity||ub3lyp/6-311g(d,p
) full optimization run on NO2BBO BSS anion with PCM||-1,1|C,-0.00
01103386,0.9521099903,-0.0000278811|C,1.2554848945,-1.1669863392,-0.00
00642058|C,-1.2552611014,-1.1672484602,-0.0000056964|C,1.2284257181,0.
2387225195,-0.0001107322|C,-1.2284950861,0.2384699875,0.0000468522|N,2
.4173439943,-1.849778852,0.000069701|N,-2.4169699686,-1.8502959871,-0.
0000244002|S,3.7752097448,-0.8910365086,0.0003442713|S,-3.7750448156,-
0.8918483562,-0.0000819605|S,2.7953623952,1.0530492957,-0.0003640474|S
,-2.7955792098,1.0525139419,0.0002581139|O,1.0933953365,2.96039574,0.0
000454971|O,-1.0941296074,2.9601001466,-0.0001362366|N,-0.0002841629,2
.3410214548,-0.0000133181|C,0.0001955248,-1.9558927568,-0.0000869396|O
,0.0003246423,-3.184686176,0.0000268525||Version=EM64W-G09RevD.01|Stat
e=1-A|HF=-2211.5684995|S2=1.006863|S2-1=0.|S2A=0.157073|RMSD=8.279e-00
9|RMSF=2.753e-005|Dipole=0.0001081,1.2097439,-0.000003|Quadrupole=7.19
94677,-22.2767473,15.0772796,0.0026491,0.0000141,0.0005256|PG=C01 [X(C
6N3O3S4)]||@
```


Summary of Derived Parameters (for Table 1, main text)

State	Energy, H	Energy, eV	$<S^2>$			Energy, eV	Rel. to *U*′, eV
Radical	-2211.41776100	-60176.21554523	0.7953		*IP*	4.85150800	
Cation	-2211.23947277	-60171.36403723			*EA*	3.63186830	
CSS Anion	-2211.55122865	-60179.84741353			*EA′*	4.15999866	
BSS Anion	-2211.56849952	-60180.31738154	1.0069		*EA″*	4.04547203	
TS Anion	-2211.57063693	-60180.37554388	2.0226		*U*	1.21963969	0.52813035
					U′	0.69150934	0.00000000
OSS Anion		-60180.26101726			*U″*	0.80603597	0.11452662

Table S2. Gaussian Archive Files for **2b** (PCM - Acetonitrile).

Radical


```
1|1|UNPC-OAKLEY-PC|FOpt|UB3LYP|6-311G(d,p)|C6H1N2O1S4(2)|RICHARD OAKLE
Y|31-Jul-2013|0||# ub3lyp/6-311g(d,p) Opt SCRF=(PCM, solvent=acetonitr
ile)||ub3lyp/6-311g(d,p) full optimization run on HBBO radical with PC
M||0,2|C,-1.2643087809,0.6839744978,0.0000152873|C,-1.2052740295,-0.74
95542698,0.0000399864|C,-0.000000455,-1.4480789307,0.0000190121|C,1.20
52752546,-0.749549441,-0.0000086898|C,1.26431297,0.6839751289,-0.00003
53559|C,0.0000029967,1.4933776626,-0.0000756858|S,2.7882417409,-1.5424
280596,-0.0000087552|S,3.7660658787,0.3892443167,-0.0000358205|N,2.409
8105834,1.318535277,-0.0000464236|N,-2.4098038139,1.3185330984,0.00004
71654|S,-3.7660609253,0.3892477854,0.0001119011|S,-2.7882435305,-1.542
4258208,0.000106884|O,0.0000018084,2.7070618296,0.0000095383|H,0.00000
13025,-2.5295380744,0.0000419562||Version=EM64W-G09RevD.01|State=2-A|H
F=-2006.8564114|S2=0.819503|S2-1=0.|S2A=0.752008|RMSD=4.557e-009|RMSF=
6.114e-005|Dipole=-0.0000963,-2.4872239,-0.0000146|Quadrupole=10.43821
24,-8.4323559,-2.0058565,-0.0000833,-0.0002478,-0.0001372|PG=C01 [X(C6
H1N2O1S4)]||@
```


Cation


```
1|1|UNPC-OAKLEY-PC|FOpt|RB3LYP|6-311G(d,p)|C6H1N2O1S4(1+)|RICHARD OAKL
EY|31-Jul-2013|0||# b3lyp/6-311g(d,p) Opt SCRF=(PCM, solvent=acetonitr
ile)||b3lyp/6-311g(d,p) full optimization run on HBBO cation with PCM|
|1,1|C,1.2526634194,0.6925698782,0.0000804567|C,1.1971882193,-0.756773
4731,-0.0000147042|C,-0.0000161848,-1.4671570053,0.0000268997|C,-1.197
2266795,-0.7567845332,0.000020139|C,-1.2526781575,0.6925646806,0.00011
91085|C,-0.000009613,1.5116369873,0.0003935711|S,-2.7476993739,-1.5175
106025,0.0001615701|S,-3.7364374974,0.3702704142,-0.0003677086|N,-2.41
20448886,1.2888433782,0.0000736727|N,2.4120347728,1.2888351905,-0.0000
199322|S,3.7364135454,0.3702530186,-0.0005405867|S,2.747666597,-1.5175
217739,0.0000639283|O,-0.0000154457,2.7202246274,0.0001552989|H,0.0000
032863,-2.5470617869,0.0000572867||Version=EM64W-G09RevD.01|State=1-A|
HF=-2006.6870066|RMSD=3.728e-009|RMSF=1.114e-004|Dipole=-0.0000048,-3.
0768688,-0.0002559|Quadrupole=27.6560461,-14.4926948,-13.1633513,-0.00
00034,-0.0009361,-0.0017574|PG=C01 [X(C6H1N2O1S4)]||@
```


Closed Shell Singlet Anion


```
1|1|UNPC-OAKLEY-PC|FOpt|RB3LYP|6-311G(d,p)|C6H1N2O1S4(1-)|RICHARD OAKL
EY|31-Jul-2013|0||# b3lyp/6-311g(d,p) Opt SCRF=(PCM, solvent=acetonitr
ile)||b3lyp/6-311g(d,p) full optimization run on HBBO anion with PCM||
-1,1|C,1.2797737004,0.6761157753,-0.000038474|C,1.2129125237,-0.740205
1077,-0.0000204667|C,0.0000002369,-1.4251147717,-0.0000373732|C,-1.212
9122772,-0.7402063397,-0.0000048756|C,-1.2797749479,0.6761147314,0.000
0055497|C,-0.0000010987,1.4771316482,-0.0001576788|S,-2.827897087,-1.5
676377172,0.0000468156|S,-3.7977590517,0.4050432633,0.0001994987|N,-2.
4089732358,1.3519227436,0.0001013913|N,2.4089712747,1.3519252322,-0.00
00455174|S,3.7977581826,0.4050461687,-0.0000598352|S,2.8278970695,-1.5
676351625,0.0001146486|O,-0.0000015566,2.694557337,0.0001921251|H,0.00
00012671,-2.508881801,-0.0000258082||Version=EM64W-G09RevD.01|State=1-
A|HF=-2006.9804626|RMSD=5.398e-009|RMSF=9.107e-005|Dipole=-0.0000052,-
1.9974619,-0.0002107|Quadrupole=-7.0408857,-2.2582355,9.2991213,-0.000
0124,0.0001565,-0.000977|PG=C01 [X(C6H1N2O1S4)]||@
```

Table S2. Gaussian Archive File for **2b** (PCM - Acetonitrile), continued.

Triplet Anion


```
1|1|UNPC-OAKLEY-PC|FOpt|UB3LYP|6-311G(d,p)|C6H1N2O1S4(1-,3)|RICHARD OA
KLEY|31-Jul-2013|0||# opt ub3lyp/6-311g(d,p) SCRF=(PCM, solvent=aceton
itrile)||ub3lyp/6-311g(d,p) full optimization run on triplet HBBO anio
n with PCM||-1,3|C,1.2384373849,0.6983563112,0.0000276572|C,1.19464560
33,-0.7334709128,0.0000596008|C,0.0000001679,-1.4508816,0.0000519863|C
,-1.194645424,-0.7334711767,0.0000005612|C,-1.2384375233,0.6983560368,
-0.0000341595|C,-0.0000001557,1.4849022172,-0.0000010436|S,-2.76845196
11,-1.551374052,-0.0000322562|S,-3.7728134355,0.3757987954,-0.00011771
58|N,-2.4202849235,1.3411829777,-0.0000936162|N,2.4202846431,1.3411835
142,0.0000295711|S,3.7728133665,0.3757996344,0.0000709287|S,2.76845232
11,-1.5513734394,0.0001052923|O,-0.0000002938,2.7378969809,-0.00008268
81|H,0.0000002871,-2.5321880569,0.0000749419||Version=EM64W-G09RevD.01
|State=3-A|HF=-2006.9955949|S2=2.026528|S2-1=0.|S2A=2.000376|RMSD=8.98
3e-009|RMSF=6.602e-005|Dipole=0.0000004,-3.6152397,0.0001031|Quadrupol
e=-1.1537646,-7.0363457,8.1901103,0.0000007,-0.0002441,0.0004812|PG=C0
1 [X(C6H1N2O1S4)]||@
```


Broken Symmetry Singlet Anion


```
1|1|UNPC-RTO2008|FOpt|UB3LYP|6-311G(d,p)|C6H1N2O1S4(1-)|USER|01-Aug-20
13|0||# opt ub3lyp/6-311g(d,p) guess=mix scf=tight vshift=200 SCRF=(PC
M, solvent=acetonitrile)||ub3lyp/6-311g(d,p) full optimization run on
BSS HBBO anion with PCM||-1,1|C,1.2451654751,0.6888398432,0.0000157234
|C,1.1972053057,-0.7307554656,0.0000537173|C,0.0000001604,-1.446276134
6,0.0000412714|C,-1.1972051343,-0.7307557172,-0.0000078144|C,-1.245165
6088,0.6888395775,-0.0000473393|C,-0.0000001497,1.4812311653,-0.000043
2803|S,-2.7810646828,-1.5539853321,-0.0000050864|S,-3.7766241913,0.383
6230238,-0.0001062804|N,-2.4223327257,1.3475377365,-0.0000858386|N,2.4
223324577,1.347538255,0.0000258791|S,3.7766241209,0.3836238341,0.00011
55656|S,2.7810650288,-1.5539847452,0.0000956034|O,-0.0000002812,2.7229
90303,-0.0000648351|H,0.000000275,-2.5277491136,0.0000717743||Version=
IA32W-G09RevA.02|State=1-A|HF=-2006.9912887|S2=0.955675|S2-1=0.|S2A=0.
094032|RMSD=9.078e-009|RMSF=3.510e-005|Dipole=0.0000004,-3.1698561,0.0
000848|Quadrupole=-2.0877701,-6.1435635,8.2313336,0.0000007,-0.0001313
,0.0003745|PG=C01 [X(C6H1N2O1S4)]||@
```


Summary of Derived Parameters (for Table 1, main text)

State	Energy, H	Energy, eV	$<S^2>$
Radical	-2006.85641137	-54609.77392364	0.8195
Cation	-2006.68700664	-54605.16414989	
CSS Anion	-2006.98046262	-54613.14955663	
BSS Anion	-2006.99128868	-54613.44415104	0.9557
TS Anion	-2006.99559492	-54613.56133073	2.0265
OSS Anion		-54613.34246692	

	Energy, eV	Rel. to *U'*, eV
IP	4.60977375	
EA	3.37563299	
EA'	3.78740709	
EA"	3.56854329	
U	1.23414076	0.41177409
U'	0.82236666	0.00000000
U"	1.04123047	0.21886380

Table S3. Gaussian Archive Files for **2c** (PCM - Acetonitrile).

Radical


```
1|1|UNPC-YOUR-9431D622DB|FOpt|UB3LYP|6-311G(d,p)|C6F1N2O1S4(2)|USER|04
 -Mar-2014|0||# opt ub3lyp/6-311g(d,p) SCRF=(PCM, solvent=acetonitrile)
 ||ub3lyp/6-311g(d,p) full optimization run on FBBO radical in acetonit
 rile||0,2|C,-1.2654855231,0.8648563027,0.0000372983|C,-1.2157528565,-0
 .5682921516,0.0000847039|C,0.0000003972,-1.2350811121,0.000111583|C,1.
 2157531293,-0.5682938355,0.0000996418|C,1.2654852828,0.8648559246,0.00
 00528985|C,-0.0000002463,1.6752046369,0.0000050326|N,2.4147736518,1.48
 85413192,0.0000445136|N,-2.4147744691,1.4885426227,0.0000150354|S,2.77
 64958176,-1.3859595942,0.0001406525|S,-2.7764947621,-1.3859594279,0.00
 0107021|S,3.7643566049,0.5519417657,0.0000886428|S,-3.764356996,0.5519
 413258,0.0000431587|O,0.0000001661,2.8875358886,0.0000084913|F,-0.0000
 009991,-2.585494665,0.0001583265||Version=IA32W-G09RevA.02|State=2-A|H
 F=-2106.1153378|S2=0.820399|S2-1=0.|S2A=0.75201|RMSD=4.956e-009|RMSF=6
 .567e-005|Dipole=0.0000177,-1.7231177,0.0000303|Quadrupole=13.8879426,
 -13.2464354,-0.6415072,0.0000289,0.0000857,0.0002757|PG=C01 [X(C6F1N2O
 1S4)]||@
```


Cation


```
 1|1|UNPC-YOUR-9431D622DB|FOpt|RB3LYP|6-311G(d,p)|C6F1N2O1S4(1+)|USER|0
 4-Mar-2014|0||# opt b3lyp/6-311g(d,p) SCRF=(PCM, solvent=acetonitrile)
 ||b3lyp/6-311g(d,p) full optimization run on FBBO cation in acetonitri
 le||1,1|C,1.2546472379,0.8733772892,0.0000294705|C,1.2082036915,-0.574
 0877968,-0.0000066791|C,0.0000000585,-1.255441755,-0.000047258|C,-1.20
 82036124,-0.5740879215,-0.0000397081|C,-1.25464732,0.873377183,-0.0000
 031608|C,-0.0000000727,1.6932829564,-0.0000264649|N,-2.4179661996,1.45
 93488694,0.0000462204|N,2.4179660464,1.4593491224,0.0000857403|S,-2.73
 92118873,-1.3600703908,-0.0000598627|S,2.73921205,-1.3600701388,0.0000
 448391|S,-3.7366192251,0.5350823986,0.0000969397|S,3.7366191515,0.5350
 827353,0.0000714478|O,-0.0000001264,2.9003906005,0.0001104195|F,0.0000
 001181,-2.5952271519,-0.0000649436||Version=IA32W-G09RevA.02|State=1-A
 |HF=-2105.9395332|RMSD=5.883e-009|RMSF=1.077e-004|Dipole=0.0000004,-1.
 9952511,-0.000079|Quadrupole=31.0501259,-19.3300125,-11.7201134,0.0000
 013,-0.0000346,-0.0003928|PG=C01 [X(C6F1N2O1S4)]||@
```


Closed Shell Singlet Anion


```
 1|1|UNPC-YOUR-9431D622DB|FOpt|RB3LYP|6-311G(d,p)|C6F1N2O1S4(1-)|USER|0
 4-Mar-2014|0||# opt b3lyp/6-311g(d,p) SCRF=(PCM, solvent=acetonitrile)
 ||b3lyp/6-311g(d,p) full optimization run on FBBO Anion in acetonitril
 e||-1,1|C,-1.2805591931,0.856871368,-0.0000462206|C,-1.2231843036,-0.5
 607101755,0.0000141584|C,-0.0000000349,-1.2109178769,0.000034144|C,1.2
 2318429,-0.5607102706,0.0000281687|C,1.2805592341,0.8568712824,-0.0000
 308032|C,0.0000000383,1.6592856456,-0.0001733494|N,2.4130014712,1.5208
 600125,-0.0000084096|N,-2.4130014057,1.5208601783,-0.0000394563|S,2.81
 26034351,-1.4135165949,0.0001130547|S,-2.8126035028,-1.4135164256,0.00
 00842851|S,3.7943525703,0.5646543154,0.0000962755|S,-3.79435255,0.5646
 545788,0.0000462117|O,0.0000000982,2.8751431284,0.0000474417|F,-0.0000
 00112,-2.5730971659,0.0001034994||Version=IA32W-G09RevA.02|State=1-A|H
 F=-2106.2454965|RMSD=7.369e-009|RMSF=4.702e-005|Dipole=-0.0000002,-1.5
 283135,-0.0000978|Quadrupole=-3.576416,-7.0279189,10.6043349,-0.000001
 6,-0.0000819,-0.000153|PG=C01 [X(C6F1N2O1S4)]||@
```

Table S3. Gaussian Archive File for **2c** (PCM - Acetonitrile), continued.

Triplet Anion


```
1|1|UNPC-YOUR-9431D622DB|FOpt|UB3LYP|6-311G(d,p)|C6F1N2O1S4(1-,3)|USER
|05-Mar-2014|0||# opt ub3lyp/6-311g(d,p) SCRF=(PCM, solvent=acetonitri
le)||ub3lyp/6-311g(d,p) full optimization run on FBBO TSAnion in Aceto
nitrile||-1,3|C,1.238276355,0.8808854609,0.000113182|C,1.205934196,-0.
5548880589,0.0000769501|C,0.0000000351,-1.234042885,0.0000519232|C,-1.
2059342738,-0.5548882641,0.0000623592|C,-1.2382766405,0.8808852489,0.0
000982934|C,-0.0000002372,1.6669688398,0.0001101598|N,-2.4242754374,1.
5088616802,0.0001174926|N,2.4242749945,1.5088621601,0.0001465812|S,-2.
7569248146,-1.3947174436,0.0000433058|S,2.7569249451,-1.3947169288,0.0
000760203|S,-3.7696555697,0.538727531,0.0000912658|S,3.769655343,0.538
7281566,0.0001374684|O,-0.0000003384,2.921394398,0.0001909992|F,0.0000
001651,-2.5983488949,0.0000259991||Version=IA32W-G09RevA.02|State=3-A|
HF=-2106.2559093|S2=2.027659|S2-1=0.|S2A=2.000404|RMSD=9.323e-009|RMSF
=9.121e-005|Dipole=0.,-3.2242313,-0.0001069|Quadrupole=3.0047748,-12.8
994076,9.8946328,0.0000009,-0.0000398,-0.0007309|PG=C01 [X(C6F1N2O1S4)
]||@
```

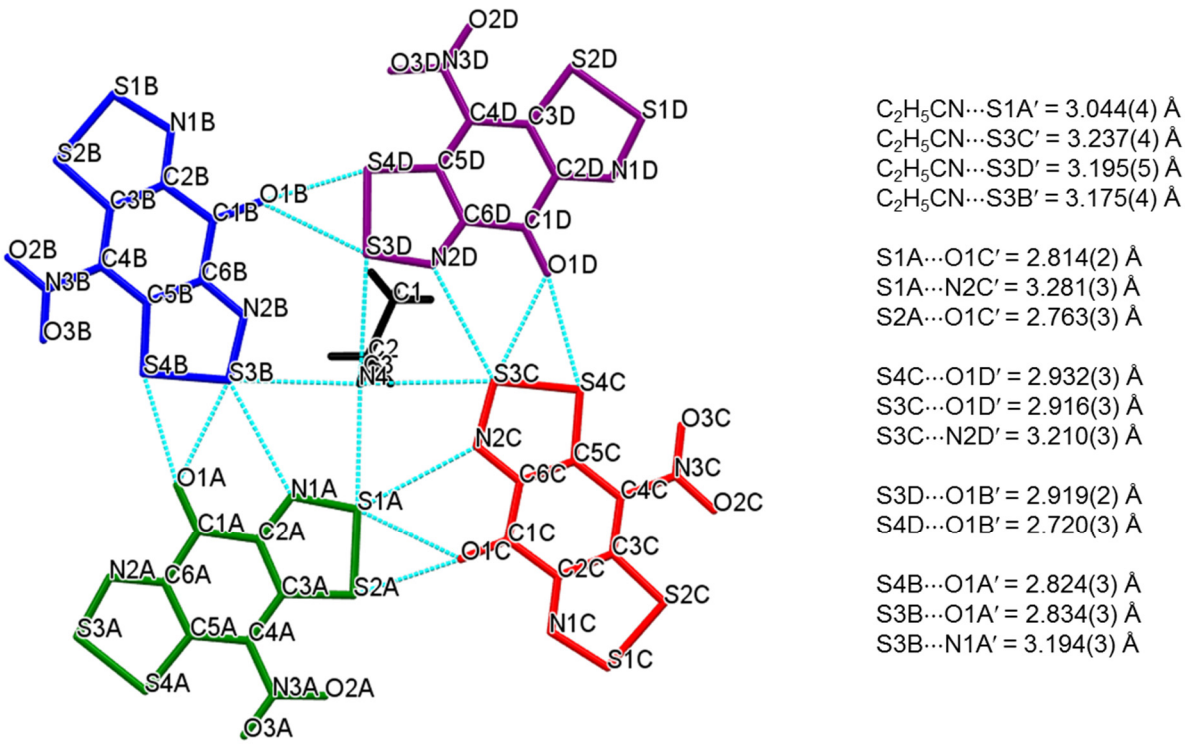

Broken Symmetry Singlet Anion


```
1|1|UNPC-YOUR-9431D622DB|FOpt|UB3LYP|6-311G(d,p)|C6F1N2O1S4(1-)|USER|0
6-Mar-2014|0||# opt ub3lyp/6-311g(d,p) guess=mix SCF=tight vshift=300
SCRF=(PCM, solvent=acetonitrile)||ub3lyp/6-311g(d,p) full optimization
 run on FBBO BSS Anion||-1,1|C,-1.2506136196,0.8642120473,0.0000731084
|C,-1.2105013164,-0.5575784269,0.0000956371|C,-0.0000002573,-1.2305001
269,0.0001026721|C,1.2105009345,-0.5575785772,0.0001102599|C,1.2506134
027,0.8642118042,0.0000882117|C,-0.0000000118,1.6578921433,0.000073491
6|N,2.4240986827,1.5125493235,0.0000815222|N,-2.4240987247,1.512549537
1,0.0000520629|S,2.7759147534,-1.4055734959,0.0001123795|S,-2.77591532
87,-1.4055729337,0.0000795142|S,3.7769970016,0.5445641066,0.000117271|
S,-3.7769971366,0.5445647733,0.0000708026|O,0.0000000636,2.896115488,-
0.0001671002|F,-0.0000002903,-2.5955166627,0.0001071671||Version=IA32W
-G09RevA.02|State=1-A|HF=-2106.2523759|S2=0.877237|S2-1=0.|S2A=0.08505
2|RMSD=9.378e-009|RMSF=1.350e-004|Dipole=-0.0000014,-2.5582463,0.00020
56|Quadrupole=1.0447216,-11.0000346,9.955313,-0.000002,-0.000053,0.001
3711|PG=C01 [X(C6F1N2O1S4)]||@
```


Summary of Derived Parameters (for Table 1, main text)

State	Energy, H	Energy, eV	$<S^2>$
Radical	-2106.11533776	-57310.76812499	0.8204
Cation	-2105.93953322	-57305.98420217	
CSS Anion	-2106.24549647	-57314.30995174	
BSS Anion	-2106.25237590	-57314.49715204	0.8772
TS Anion	-2106.25590934	-57314.59330260	2.0277
OSS Anion		-57314.42615691	

	Energy, eV	Rel. to *U'*, eV
IP	4.78392282	
EA	3.54182675	
EA'	3.82517761	
EA"	3.65803192	
U	1.24209607	0.28335085
U'	0.95874521	0.00000000
U"	1.12589090	0.16714569



$C_2H_5CN\cdots S1A' = 3.044(4)$ Å
$C_2H_5CN\cdots S3C' = 3.237(4)$ Å
$C_2H_5CN\cdots S3D' = 3.195(5)$ Å
$C_2H_5CN\cdots S3B' = 3.175(4)$ Å

S1A···O1C′ = 2.814(2) Å
S1A···N2C′ = 3.281(3) Å
S2A···O1C′ = 2.763(3) Å

S4C···O1D′ = 2.932(3) Å
S3C···O1D′ = 2.916(3) Å
S3C···N2D′ = 3.210(3) Å

S3D···O1B′ = 2.919(2) Å
S4D···O1B′ = 2.720(3) Å

S4B···O1A′ = 2.824(3) Å
S3B···O1A′ = 2.834(3) Å
S3B···N1A′ = 3.194(3) Å

Figure S3. Pinwheel intermolecular contacts in **2a**·¼ EtCN.

Table S4. High Pressure Powder Crystallographic Data for **2a**·MeCN.

Pressure	2.0 GPa	4.4 GPa	6.1 GPa
Formula[a]	$C_6N_3O_3S_4$	$C_6N_3O_3S_4$	$C_6N_3O_3S_4$
fw	290.32	290.32	290.32
a, Å	3.3487(12)	3.2557(8)	3.2128(6)
b, Å	30.019(15)	29.515(8)	29.387(7)
c, Å	10.792(4)	10.6182(29)	10.5438(21)
β, deg	88.20(7)	87.58(6)	87.03(4)
V, Å^3	1084.3(6)	1019.4(4)	994.15(27)
ρ(calcd), g cm^{-3}	1.778	1.892	1.940
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	4
temp, K	296(2)	296(2)	296(2)
λ, Å	0.509176	0.509176	0.509176
Solution method	powder data	powder data	powder data
R, Rw (on F^2)	0.0097, 0.0149	0.0101, 0.0145	0.0103, 0.0147

[a] The solvent molecule was not included in the solution (in DASH) or Rietveld refinement (in GSAS). The formula and mass correspond to the radical itself.

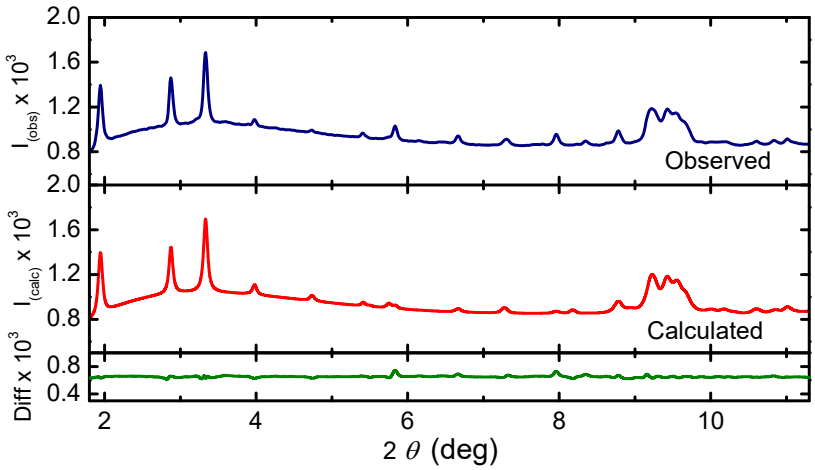


Figure S4. Powder diffraction pattern for **2a**·MeCN at 2.0 GPa.

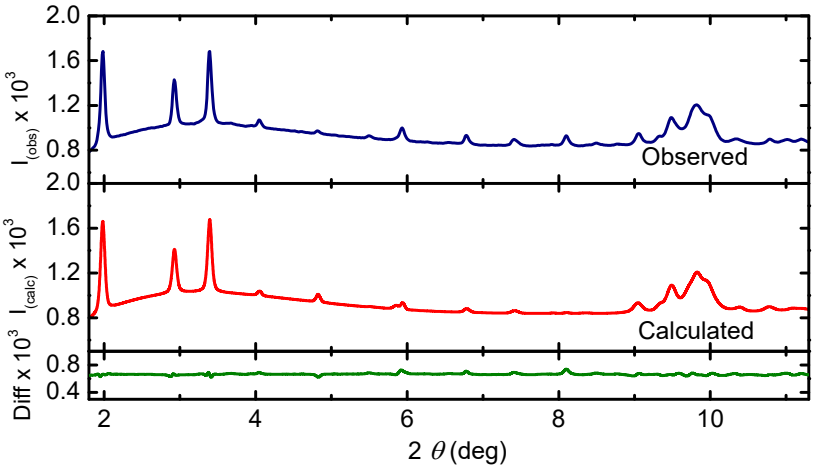


Figure S5. Powder diffraction pattern for **2a**·MeCN at 4.4 GPa.

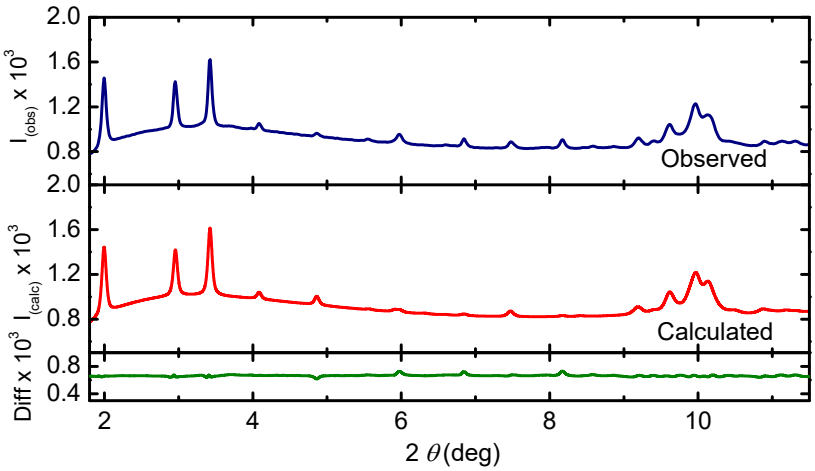


Figure S6. Powder diffraction pattern for **2a**·MeCN at 6.1 GPa.