Supporting Information

for

Trifluoromethyl-substituted tetrathiafulvalenes

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Optimized geometries of the model molecules TTF, TTF–CN, TTF–CF_3 and TTF–CO_2Me and results of the TD-DFT calculations

TTF

Optimized geometry

C	0	0.04201	0.05705	0.00807
C	0	0.04248	0.05622	1.34516
S	0	1.58895	-0.12695	2.17271
C	0	2.56465	-0.0755	0.67564
S	0	1.58789	-0.12511	-0.8208
C	0	3.91307	-0.01055	0.6752
S	0	4.89017	0.03206	2.17163
C	0	6.41134	0.36298	1.34309
C	0	6.41086	0.36381	0.006
S	0	4.88911	0.0339	-0.82187
H	0	-0.84376	0.14133	-0.61065
H	0	-0.84285	0.13974	1.96461
H	0	7.28494	0.53122	1.96197
H	0	7.28403	0.53281	-0.61329

TD-DFT calculations

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Excitation energies and oscillator strengths:

 Excited State   1:   Singlet-A      2.7062 eV  458.14 nm  f=0.0000
      52 -> 53         0.69382
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:   Singlet-A      3.4293 eV  361.54 nm  f=0.0179
      52 -> 54         0.65004
      52 -> 57        -0.23097

 Excited State   3:   Singlet-A      3.8998 eV  317.93 nm  f=0.0147
      51 -> 53         0.19439
      52 -> 56         0.32967
      52 -> 58         0.57776

 Excited State   4:   Singlet-A      3.9193 eV  316.34 nm  f=0.0000
      52 -> 55         0.68308

 Excited State   5:   Singlet-A      3.9232 eV  316.02 nm  f=0.0276
      52 -> 54         0.21966
      52 -> 57         0.65123
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TTF–CF_3

Optimized geometry

C	0	-1.75661	1.51707	0.05699
C	0	-2.06113	0.21559	-0.03132
C	0	-3.43852	-0.33843	0.16339
S	0	-0.08714	1.99161	-0.19127
S	0	-0.75097	-0.91681	-0.417
F	0	-3.78506	-1.15792	-0.85356
F	0	-4.35498	0.64756	0.23369
F	0	-3.53186	-1.06354	1.29804
C	0	0.52926	0.3122	-0.21917
S	0	2.45119	-1.67257	-0.14101
C	0	1.83954	0.00421	-0.11542
S	0	3.12258	1.23432	0.05327
C	0	4.39363	0.06659	0.41728
C	0	4.09336	-1.23322	0.32951
H	0	-2.48165	2.2981	0.25034
H	0	5.36979	0.46231	0.67196
H	0	4.79123	-2.04399	0.50282

TD-DFT calculations

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Excitation energies and oscillator strengths:

 Excited State   1:   Singlet-A      2.7637 eV  448.62 nm  f=0.0009
      68 -> 69         0.69257
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:   Singlet-A      3.2003 eV  387.41 nm  f=0.0203
      68 -> 70         0.67392
      68 -> 73         0.11717

 Excited State   3:   Singlet-A      3.8349 eV  323.30 nm  f=0.0014
      68 -> 70         0.10970
      68 -> 71         0.57886
      68 -> 72        -0.17355
      68 -> 73        -0.30536

 Excited State   4:   Singlet-A      3.9706 eV  312.25 nm  f=0.0337
      67 -> 69        -0.21361
      68 -> 71         0.14081
      68 -> 72         0.35061
      68 -> 73         0.16073
      68 -> 74         0.51165

 Excited State   5:   Singlet-A      4.1038 eV  302.12 nm  f=0.0270
      68 -> 71         0.28553
      68 -> 72        -0.12653
      68 -> 73         0.58092
      68 -> 74        -0.16251
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TTF–CN

Optimized geometry

C	0	0.07531	0.09509	-0.00462
C	0	0.071	0.13686	1.33152
S	0	1.60022	-0.12576	2.17057
C	0	2.5799	-0.1651	0.67923
S	0	1.60931	-0.21778	-0.81687
C	0	3.93025	-0.16196	0.6801
S	0	4.90341	-0.09722	2.1803
C	0	6.3897	0.31961	1.36616
C	0	6.41355	0.27887	0.01707
S	0	4.91225	-0.22395	-0.8091
C	0	7.56162	0.56263	-0.76731
N	0	8.49506	0.79023	-1.42555
H	0	-0.80022	0.21542	-0.63173
H	0	-0.80803	0.29565	1.94498
H	0	7.24951	0.56959	1.97668

TD-DFT calculations

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Excitation energies and oscillator strengths:

 Excited State   1:   Singlet-A      2.7043 eV  458.46 nm  f=0.0018
      58 -> 59         0.14392
      58 -> 60         0.67513
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:   Singlet-A      2.7392 eV  452.63 nm  f=0.0263
      58 -> 59         0.66354
      58 -> 60        -0.14505

 Excited State   3:   Singlet-A      3.7153 eV  333.71 nm  f=0.0000
      58 -> 61         0.59940
      58 -> 63         0.32388

 Excited State   4:   Singlet-A      3.9499 eV  313.89 nm  f=0.0444
      57 -> 60         0.23427
      58 -> 62        -0.41278
      58 -> 63        -0.10919
      58 -> 64         0.45433
      58 -> 65        -0.14349

 Excited State   5:   Singlet-A      4.0841 eV  303.58 nm  f=0.0212
      58 -> 61        -0.30085
      58 -> 63         0.57610
      58 -> 64         0.18685
```

TTF–CO_2Me

Optimized geometry

C	0	-0.30472	2.52951	1.5161
C	0	0.76005	2.00396	0.88184
C	0	2.13014	2.49984	1.12797
S	0	-1.88951	1.91514	1.13911
S	0	0.44961	0.72175	-0.30801
O	0	2.41381	3.37973	1.91607
O	0	3.02908	1.84974	0.35823
C	0	4.39595	2.2647	0.51895
C	0	-1.29601	0.61472	0.0607
S	0	-1.50985	-1.65913	-1.49358
C	0	-2.10008	-0.35446	-0.42536
S	0	-3.84831	-0.45319	-0.06844
C	0	-4.06052	-2.03785	-0.81299
C	0	-3.01569	-2.57581	-1.45047
H	0	-0.21764	3.33445	2.2367
H	0	4.72112	2.11133	1.55101
H	0	4.50595	3.3213	0.26187
H	0	4.97138	1.6398	-0.1639
H	0	-5.04098	-2.49279	-0.73527
H	0	-3.02815	-3.53028	-1.96355

TD-DFT calculations

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Excitation energies and oscillator strengths:

 Excited State   1:   Singlet-A      2.6315 eV  471.16 nm  f=0.0390
      67 -> 68         0.67844
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle
RhoCI density.

 Excited State   2:   Singlet-A      2.7502 eV  450.83 nm  f=0.0001
      67 -> 69         0.69394

 Excited State   3:   Singlet-A      3.6607 eV  338.69 nm  f=0.0027
      67 -> 70         0.59596
      67 -> 72        -0.33253

 Excited State   4:   Singlet-A      3.9442 eV  314.35 nm  f=0.0189
      66 -> 69        -0.14978
      67 -> 70         0.25124
      67 -> 71         0.25532
      67 -> 72         0.48644
      67 -> 73        -0.29687

 Excited State   5:   Singlet-A      4.0397 eV  306.91 nm  f=0.0216
      66 -> 69         0.14195
      67 -> 70         0.22206
      67 -> 71        -0.18993
      67 -> 72         0.32929
      67 -> 73         0.50892
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