Supplementary material

Details on ESI mass spectrometry:
The sample was analysed by direct infusion to the electrospray ion source by a flow rate of 5 µL/min. Mass spectra were acquired in positive ion mode on a quadrupole-Time of Flight mass spectrometer (model "Synapt" from Waters, Milford, MA, USA) using the following ion source settings (gentle declustering conditions), spray (capillary) voltage 3600 V, cone voltage 26 V, extraction cone voltage 2.0 V, ion source temperature 70°C.

Details on theoretical calculations:
Calculations were performed using Time Dependent Density Functional Theory (TDDFT) with B3LYP with a localised basis-set code and with LDA exchange-correlation functional with a real-space time-propagation code (see *Castro, A.; Appel, H.; Oliveira, M.; Rozzi, C. A.; Andrade, X.; Lorenzen, F.; Marques, M. A. L.; Gross, E. K. U.; Rubio, A. Phys. Stat. Sol. B* ***2006****, 243 2465.*). In the case of TTF conformers we include additionally calculations with CAM-B3LYP exchange-correlation and with complete active space SCF method (CASSCF) using the ORCA[1] code.

For each of the radical cations we present also the optical absorption spectrum (labeled with a) and the corresponding Kohn-Sham orbitals (labeled with b) that contribute more in each electronic transitions.

In Figure 1a we have the results of the optical absorption for $TTF^{\bullet+}$. Here we see that similar results are obtained using the LDA method compared to more accurate exchange-correlation functionals (see *M.A.L. Marques, A. Castro, A. Rubio. Journal of Chemical Physics 115, 3006 - 3114 (2001)*) and CASSCF methods; this behaviour appears also in the other cationic conformers (see Fig. 2a and Fig. 3a).

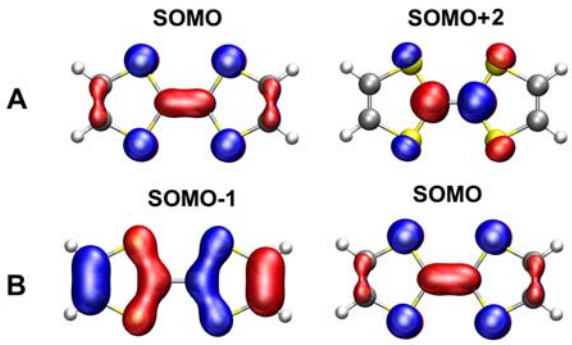


Figure1b. Main Kohn-Sham orbitals corresponding to the labeled transitions (A and B) in Figure 1a for $TTF^{\bullet+}$ obtained using DFT/B3LYP level.

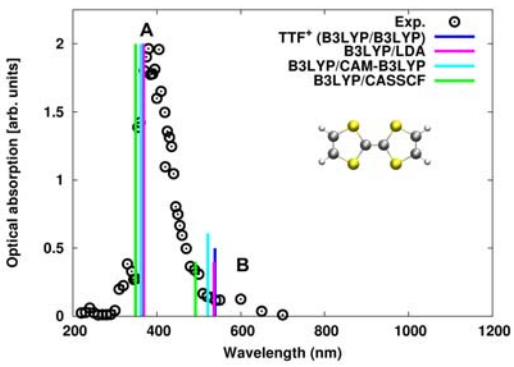


Figure 1a. Optical absorption spectrum of $TTF^{\bullet+}$ obtained using TDDFT with B3LYP functional (in blue), LDA with Perdew-Zunger (in magenta), CAM-B3LYP (in aquamarine) and CASSCF (in green) methods compared with the experimental results. The main transition peaks are labeled with A and B (inserted the structure).

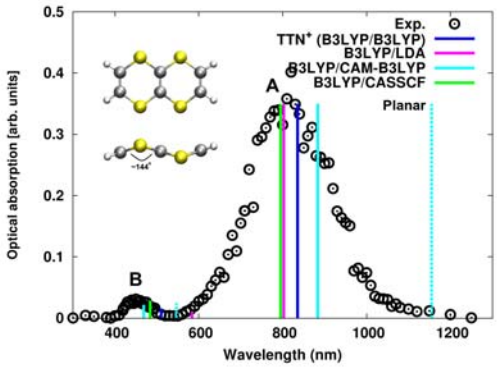


Figure 2a. Optical absorption spectrum of $TTN^{\bullet+}$ obtained using TDDFT with B3LYP functional (in blue), LDA with Perdew-Zunger (in magenta), CAM-B3LYP (in aquamarine) and CASSCF (in green) methods compared with the experimental results. The main transition peaks are labeled with A and B. The aquamarine dotted line represents the optical absorption of the planar structure.

[1] http://www.thch.uni-bonn.de/tc/orca/

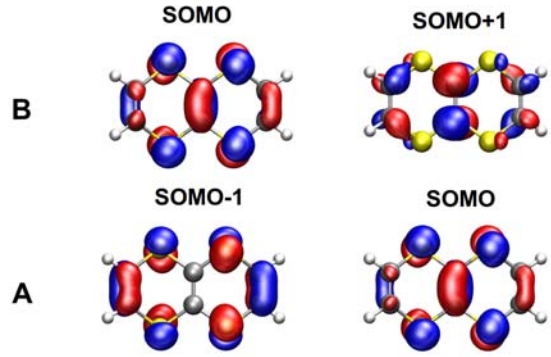


Figure 2b. Main Kohn-Sham orbitals corresponding to the labeled transitions (A and B) in Figure 2a for $TTN^{\bullet+}$ obtained using DFT/B3LYP level.

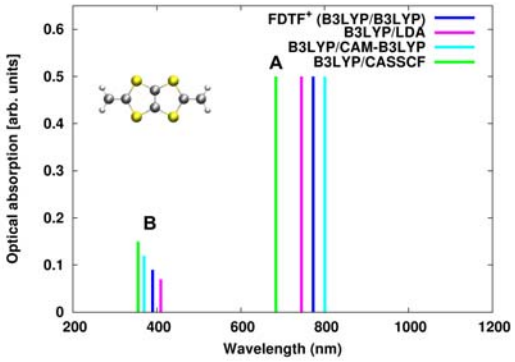


Figure 3a. Optical absorption spectrum of $FDTF^{\bullet+}$ obtained using TDDFT with B3LYP functional (in blue). LDA with Perdew-Zunger (in magenta), CAM-B3LYP (in aquamarine) and CASSCF (in green) methods. The main transition peaks are labeled with A and B. Inserted appears the structure.

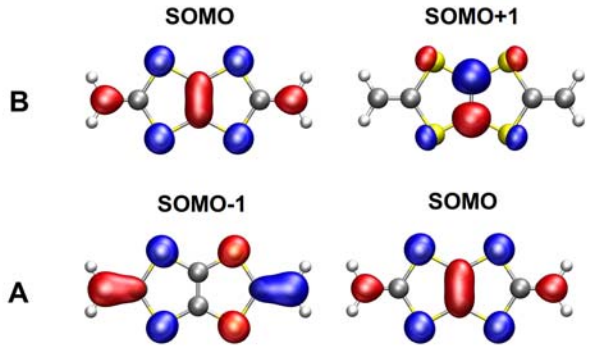


Figure 3b. Main Kohn-Sham orbitals corresponding to the labeled transitions (A and B) in Figure 3a for $FDTF^{\bullet+}$ obtained using DFT/B3LYP level.

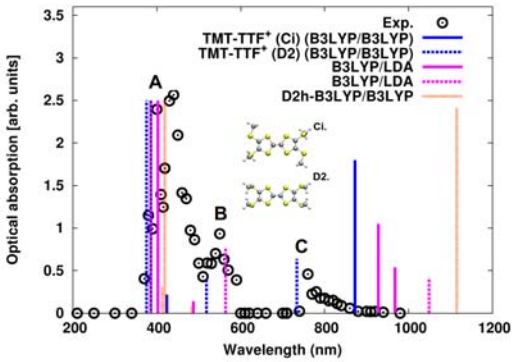


Figure 4a. Optical absorption spectrum of the two lowest energy $TMT\text{-}TTF^{\bullet+}$ conformers obtained by using TDDFT with B3LYP exchange-correlation functional and LDA with Perdew-Zunger (in magenta) compared with the experimental results. The lowest energy conformer (*Ci*) absorption is depicted with a continuous blue line and the second one (*D2*) with a blue dotted line. The main transitions are labeled A, B and C.

In Figure 2b we show the results for the $TTN^{\bullet+}$ conformer. In the inset the minimum energy structure is shown. In the same figure we included also the optical absorption for another minimum in which the molecule is found planar (0.22 eV higher in energy than the folded one). CAM-B3LYP results for the planar structure are displayed with a dotted-magenta line. Our results show a red-shift of 271 nm from the planar to folded structure in the main peak (A).

In the case of $TMT\text{-}TTF^{\bullet+}$ we considered two structures having a very small difference in energy but with a notable different absorption spectrum (see Fig. 4a). The structure with *Ci* symmetry (the more stable) has a spectrum (continuous blue line) which presents a good agreement with the peaks labelled with A (position and intensity) and C (position). The other structure has *D2* symmetry and has an absorption spectrum that fits better with the intensities and positions of the peaks. Results with LDA (in magenta) show a good agreement for the A and B peaks but produce an underestimation in the low energy absorption peaks. This underestimation can be ascribed to the nature of this transition which is more charge-transfer like. An additional symmetry was included in the figure with a dotted orange line, this structure with *D2H* symmetry is 159 meV more energetic than the absolute minimum (*Ci),* its related spectrum fits in good agreement the main peak (A) but poorly reproduces the intensity and position of the other peaks. These results confirm the fact that the A peak is an electronic transition associated with the TTF ring.

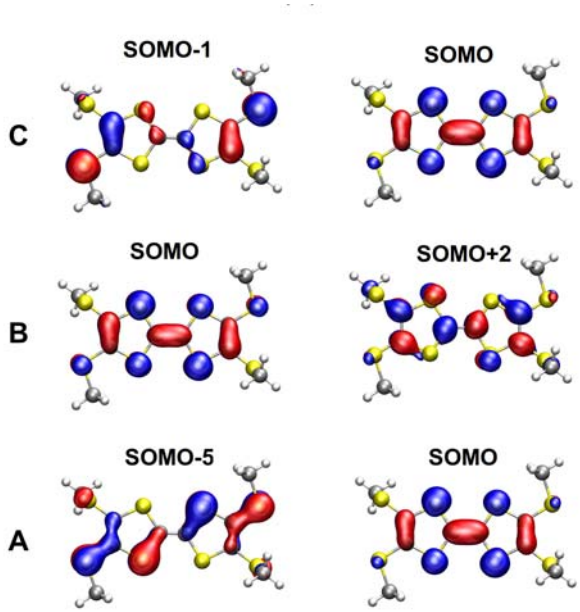


Figure 4b. Main Kohn-Sham orbitals corresponding to the labeled transitions (A, B and C) in Figure 4a for the lowest energy conformer of TMT-TTF$^{\bullet+}$ (blue continuous curve) with *Ci* symmetry obtained using DFT/B3LYP level.

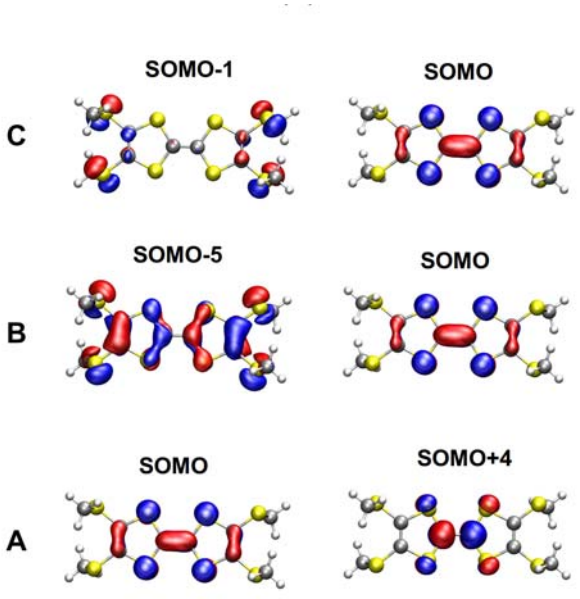


Figure 4c. Main Kohn-Sham orbitals corresponding to the labeled transitions (A, B and C) in Figure 4a for the second-lowest energy conformer of TMT-TTF$^{\bullet+}$ (blue dotted curve) with *D2* symmetry obtained using DFT/B3LYP level.

Coordinates of the optimized molecular structures:

TTF$^{\bullet+}$

```
scf done: -1823.668481
S 1.644163 1.466878 -0.000005
S 1.644185 -1.466475-0.000003
S -1.643864 1.466853 -0.000005
S -1.643841 -1.466500 -0.000003
C 3.190953 0.671562 0.000002
C 0.697950 0.000194 -0.000004
C -0.697629 0.000184 -0.000003
C 3.190963 -0.671135 0.000003
C -3.190643 0.671513 0.000003
C -3.190631 -0.671185 0.000003
H 4.072395 1.298718 0.000006
H 4.072415 -1.298277 0.000007
H -4.072094 1.298656 0.000006
H -4.072074 -1.298340 0.000007
```

TTN$^{\bullet+}$

```
scf done: -1823.632213
S -1.324805 1.676242 0.950249
S -1.309687 -1.694483 0.982210
S 1.389804 1.678867 -0.053991
S 1.405213 -1.691772 -0.021233
C 0.037066 0.677165 0.457726
C 0.043198 -0.692738 0.470897
C 2.783338 0.670814 0.317828
C 2.789309 -0.664037 0.330776
C -2.709087 0.648688 0.598294
C -2.703119 -0.686187 0.610915
H -3.610643 1.209592 0.378029
H -3.599575 -1.259237 0.401372
H 3.679752 1.243945 0.527305
H 3.690878 -1.224848 0.551242
```

FDTF$^{\bullet+}$

```
scf done: -1823.638077
S 1.531713 1.498599 -0.000001
S 1.531650 -1.498742 -0.000002
S -1.531666 1.498659 0.000000
S -1.531725 -1.498679 -0.000001
C 2.497792 -0.000107 -0.000001
C 0.000008 0.692522 -0.000001
C -0.000023 -0.692599 -0.000001
C -2.497805 0.000014 -0.000001
C 3.835377 -0.000112 -0.000001
C -3.835390 0.000033 -0.000001
H 4.398774 0.924898 -0.000001
H 4.398770 -0.925125 -0.000001
H -4.398774 0.925051 0.000000
H -4.398797 -0.924972 -0.000001
```

TMT-TTF$^{\bullet+}$ (Ci)

scf done: -3573.825195

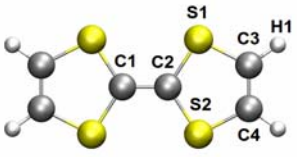
C 4.170434 -3.263175 -0.030442
C -4.914822 -2.120249 1.732301
S 4.734000 -1.527771 0.101494
S 1.673748 -1.431125 0.062163
S -1.613336 -1.497073 -0.000929
S -4.624695 -1.799029 -0.058081
C 3.235242 -0.616240 0.043288
C -3.207472 -0.749164 -0.000092
C 0.692919 0.023505 0.010106
C -0.692919 -0.023505 -0.010106
C 3.207472 0.749164 0.000092
C -3.235242 0.616240 -0.043288
S 4.624695 1.799029 0.058081
S 1.613336 1.497073 0.000929
S -1.673748 1.431125 -0.062163
S -4.734000 1.527771 -0.101494
C 4.914822 2.120249 -1.732301
C -4.170434 3.263175 0.030442
H 5.091312 -3.846407 -0.013734
H 3.653825 -3.446550 -0.972243
H 3.559132 -3.552636 0.824318
H -5.795751 -2.762038 1.765985
H -5.121763 -1.190934 2.259562
H -4.069489 -2.644889 2.174328
H 4.069489 2.644889 -2.174328
H 5.121763 1.190934 -2.259562
H 5.795751 2.762038 -1.765985
H -3.559132 3.552636 -0.824318
H -3.653825 3.446550 0.972243
H -5.091312 3.846407 0.013734

TMT-TTF$^{\bullet+}$ (D2)

scf done: -3573.823200

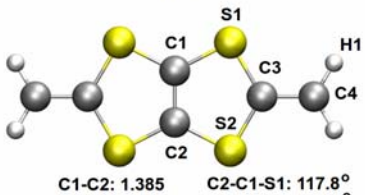
H 6.101782 -2.287906 1.746384
H 5.568048 -0.595232 1.898472
H 4.484118 -1.941589 2.400888
C 5.245897 -1.614208 1.695786
C 3.229275 0.680114 -0.007355
S 4.631128 -1.763118 -0.032219
S 1.650035 1.461551 0.002674
C 0.695857 0.000000 0.000000
S 1.650035 -1.461551 -0.002674
S 4.631128 1.763118 0.032219
C 3.229275 -0.680114 0.007355
C 5.245897 1.614208 -1.695786
H 5.568048 0.595232 -1.898472
H 4.484118 1.941589 -2.400888
H 6.101782 2.287906 -1.746384
H -6.101782 2.287906 1.746384
H -4.484118 1.941589 2.400888
H -5.568048 0.595232 1.898472
C -5.245897 1.614208 1.695786
C -3.229275 -0.680114 -0.007355
S -4.631128 1.763118 -0.032219
S -1.650035 -1.461551 0.002674
C -0.695857 0.000000 0.000000
S -1.650035 1.461551 -0.002674
S -4.631128 -1.763118 0.032219
C -3.229275 0.680114 0.007355
C -5.245897 -1.614208 -1.695786
H -4.484118 -1.941589 -2.400888
H -5.568048 -0.595232 -1.898472
H -6.101782 -2.287906 -1.746384

TTF+



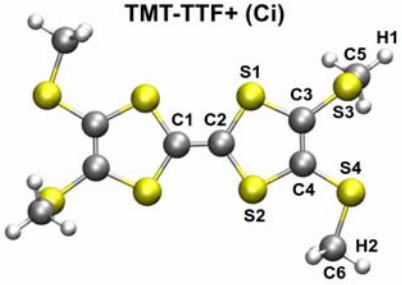
C1-C2: 1.396 C2-S1-C3: 95.6°
C2-S1: 1.745 S2-C2-S1: 114.3°
S1-C3: 1.739 S1-C3-C4: 117.2°
C3-H1: 1.082 H1-C3-C4: 125.4°
C3-C4: 1.343

FDTF+



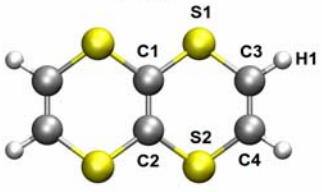
C1-C2: 1.385 C2-C1-S1: 117.8°
C1-S1: 1.731 C1-S1-C3: 95.05°
S1-C3: 1.783 S1-C3-S2: 114.4°
C3-C4: 1.338 S1-C3-C4: 122.8°
C4-H1: 1.083 C3-C4-H1: 121.3°

TMT-TTF+ (Ci)



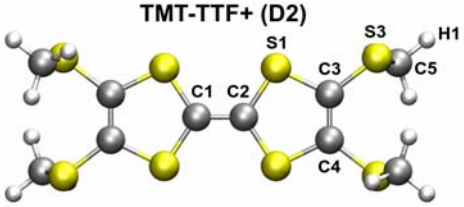
C1-C2: 1.387 C1-C2-S1: 123.9°
C2-S1: 1.737 C2-S1-C3: 96.9°
S1-C3: 1.761 S1-C3-C4: 116.3°
C3-C4: 1.366 C3-C4-S2: 116.4°
C4-S2: 1.761 C4-S2-C2: 96.4°
C2-S2: 1.755 S1-C3-S3: 118.3°
C3-S3: 1.765 C3-S3-C5: 101.4°
S3-C5: 1.842 S2-C4-S4: 121.1°
C4-S4: 1.755 C4-S4-C6: 103.1°
S4-C6: 1.829
C5-H1: 1.089
C6-H2: 1.090

TTN+



C1-C2: 1.370 C1-C2-S2: 124.7°
C1-S1: 1.759 C1-S1-C3: 102.8°
S1-C3: 1.760 S1-C3-H1: 113.1°
C3-C4: 1.335 S1-C3-C4: 125.3°
C3-H1: 1.084

TMT-TTF+ (D2)



C1-C2: 1.392 C1-C2-S1: 123.1°
C2-S1: 1.745 C2-S1-C3: 96.8°
S1-C3: 1.762 S1-C3-C4: 116.3°
C3-S3: 1.772 S1-C3-S3: 116.0°
S3-C4: 1.390 C3-S3-C5: 101.2°
S3-C5: 1.840
C5-H1: 1.088

TTF+: -1823.668481 Eh
FDTF+: -1823.638077 Eh
TTN+: -1823.632213 Eh
TMT-TTF+(Ci): -3573.825195 Eh
TMT-TTF+(D2): -3573.823200 Eh

Electronic Supplementary Material (ESI) for Chemical Communications