Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Structural and electronic properties of 3,3'-Azothiophene photo-switching systems.

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PDB file for *anti(trans)-trans* conformer of 3,3'-azothiophene

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HEADER
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HETATM   12  C     2     2       5.201   3.452   4.067
HETATM   13  H     2     2       5.895   2.312   0.956
HETATM   14  H     2     2       1.002   1.568   3.379
HETATM   15  H     2     2       7.005   4.468   4.824
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PDB file for *anti(trans)-cis* conformer of 3,3'-azothiophene

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HETATM    5  S     2     2       7.834   3.074   0.597
HETATM    6  N     2     2       4.144   1.709   0.894
HETATM    7  N     2     2       3.866   1.170  -0.210
HETATM    8  C     2     2       2.580   0.626  -0.296
HETATM    9  C     2     2       2.187   0.012  -1.465
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PDB file for *syn(cis)-cis* conformer of 3,3'-azothiophene

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HETATM    4  S     2     2       0.824  -0.827   3.642
HETATM    5  C     2     2       0.790  -1.324   1.974
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HETATM    9  C     2     2       0.639   2.174  -0.245
HETATM   10  S     2     2      -0.326   2.259  -1.673
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HETATM   17  H     2     2       1.639  -0.649   0.117
HETATM   18  H     2     2       0.228  -2.201   1.689
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PDB file for *syn(cis)-trans* conformer of 3,3'-azothiophene

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HETATM   10  C     2     2       4.350   5.629  -1.177
HETATM   11  S     2     2       5.758   4.833  -1.816
HETATM   12  C     2     2       5.389   3.388  -0.955
HETATM   13  H     2     2       6.040   2.529  -1.007
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HETATM   16  H     2     2       2.718   5.118   0.132
HETATM   17  H     2     2       2.212   2.734  -1.979
HETATM   18  H     2     2      -0.240   3.388  -2.645
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PDB file for *anti(trans)-trans* conformer of 3,3'-azothiophene-methoxycarbonyl

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HEADER
HETATM    1  C     2     2       5.245   3.581   3.783
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HETATM    4  S     2     2       7.373   3.454   2.346
HETATM    5  C     2     2       6.569   3.910   3.801
HETATM    6  N     2     2       3.524   2.502   2.428
HETATM    7  N     2     2       3.374   1.378   1.907
HETATM    8  C     2     2       2.032   0.966   1.753
HETATM    9  C     2     2       1.653   0.299   0.552
HETATM   10  C     2     2       0.329  -0.030   0.534
HETATM   11  S     2     2      -0.475   0.426   1.990
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HETATM   26  O     2     2       1.983   1.545   4.786
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PDB file for *anti(trans)-cis* conformer of 3,3'-azothiophene-methoxycarbonyl

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HETATM    5  C     2     2       1.465  -1.547   0.961
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HETATM    8  C     2     2       5.070   2.578   0.531
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HETATM   11  C     2     2       6.039   4.637   0.989
HETATM   12  C     2     2       5.000   3.798   1.267
HETATM   13  C     2     2       2.159  -0.367  -2.698
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HETATM   18  H     2     2       1.013  -2.145   1.738
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HETATM   20  O     2     2       1.641  -1.136  -3.489
HETATM   21  C     2     2       2.884   1.008  -4.478
HETATM   22  H     2     2       3.433   1.942  -4.562
HETATM   23  H     2     2       3.421   0.201  -4.977
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HETATM   25  O     2     2       7.592   1.748  -1.979
HETATM   26  O     2     2       6.493   0.176  -0.793
HETATM   27  C     2     2       8.272   0.713  -2.724
HETATM   28  H     2     2       8.915   1.239  -3.425
HETATM   29  H     2     2       8.864   0.092  -2.052
HETATM   30  H     2     2       7.548   0.097  -3.258
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PDB file for *syn(cis)-cis* conformer of 3,3'-azothiophene-methoxycarbonyl

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HEADER
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HETATM    2  C     2     2       1.625   2.071  -0.541
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HETATM    4  S     2     2      -0.652   1.861  -1.745
HETATM    5  C     2     2       0.778   1.432  -2.604
HETATM    6  N     2     2       2.719   2.424   0.307
HETATM    7  N     2     2       2.991   1.866   1.384
HETATM    8  C     2     2       2.307   0.717   1.864
HETATM    9  C     2     2       1.961  -0.431   1.086
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HETATM   12  C     2     2       2.093   0.527   3.223
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HETATM   16  H     2     2       2.911   1.418  -2.218
HETATM   17  H     2     2       2.097  -0.506   0.018
HETATM   18  H     2     2       1.146  -2.424   1.526
HETATM   19  O     2     2       2.195   0.863   5.520
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HETATM   21  C     2     2       2.418   1.678   6.691
HETATM   22  O     2     2       0.334   3.272   1.791
HETATM   23  O     2     2      -1.685   2.899   0.854
HETATM   24  C     2     2      -0.307   3.856   2.948
HETATM   25  H     2     2       2.213   1.027   7.537
HETATM   26  H     2     2       3.451   2.025   6.718
HETATM   27  H     2     2       1.740   2.532   6.692
HETATM   28  H     2     2       0.505   4.099   3.627
HETATM   29  H     2     2      -0.855   4.753   2.660
HETATM   30  H     2     2      -0.987   3.137   3.405
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PDB file for *syn(cis)-trans* conformer of 3,3'-azothiophene-methoxycarbonyl

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HETATM    2  C     2     2       4.150   3.583  -0.018
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HETATM    4  C     2     2       4.137   5.847  -0.515
HETATM    5  S     2     2       5.466   5.278  -1.453
HETATM    6  N     2     2       3.831   2.426   0.751
HETATM    7  N     2     2       2.668   1.992   0.850
HETATM    8  C     2     2       1.610   2.447   0.010
HETATM    9  C     2     2       0.351   2.780   0.480
HETATM   10  S     2     2      -0.753   3.048  -0.839
HETATM   11  C     2     2       0.469   2.676  -1.996
HETATM   12  C     2     2       1.669   2.379  -1.415
HETATM   13  C     2     2       6.147   2.611  -1.366
HETATM   14  C     2     2      -0.150   2.965   1.847
HETATM   15  H     2     2       3.877   6.895  -0.537
HETATM   16  H     2     2       2.693   5.009   0.859
HETATM   17  H     2     2       2.553   2.096  -1.969
HETATM   18  H     2     2       0.232   2.697  -3.049
HETATM   19  O     2     2       0.827   2.923   2.763
HETATM   20  O     2     2      -1.325   3.143   2.115
HETATM   21  C     2     2       0.423   3.058   4.145
HETATM   22  H     2     2       1.343   2.988   4.719
HETATM   23  H     2     2      -0.056   4.024   4.304
HETATM   24  H     2     2      -0.262   2.255   4.418
HETATM   25  O     2     2       5.766   1.380  -1.001
HETATM   26  O     2     2       7.137   2.846  -2.036
HETATM   27  C     2     2       6.625   0.291  -1.408
HETATM   28  H     2     2       6.156  -0.606  -1.011
HETATM   29  H     2     2       6.684   0.243  -2.495
HETATM   30  H     2     2       7.623   0.420  -0.987
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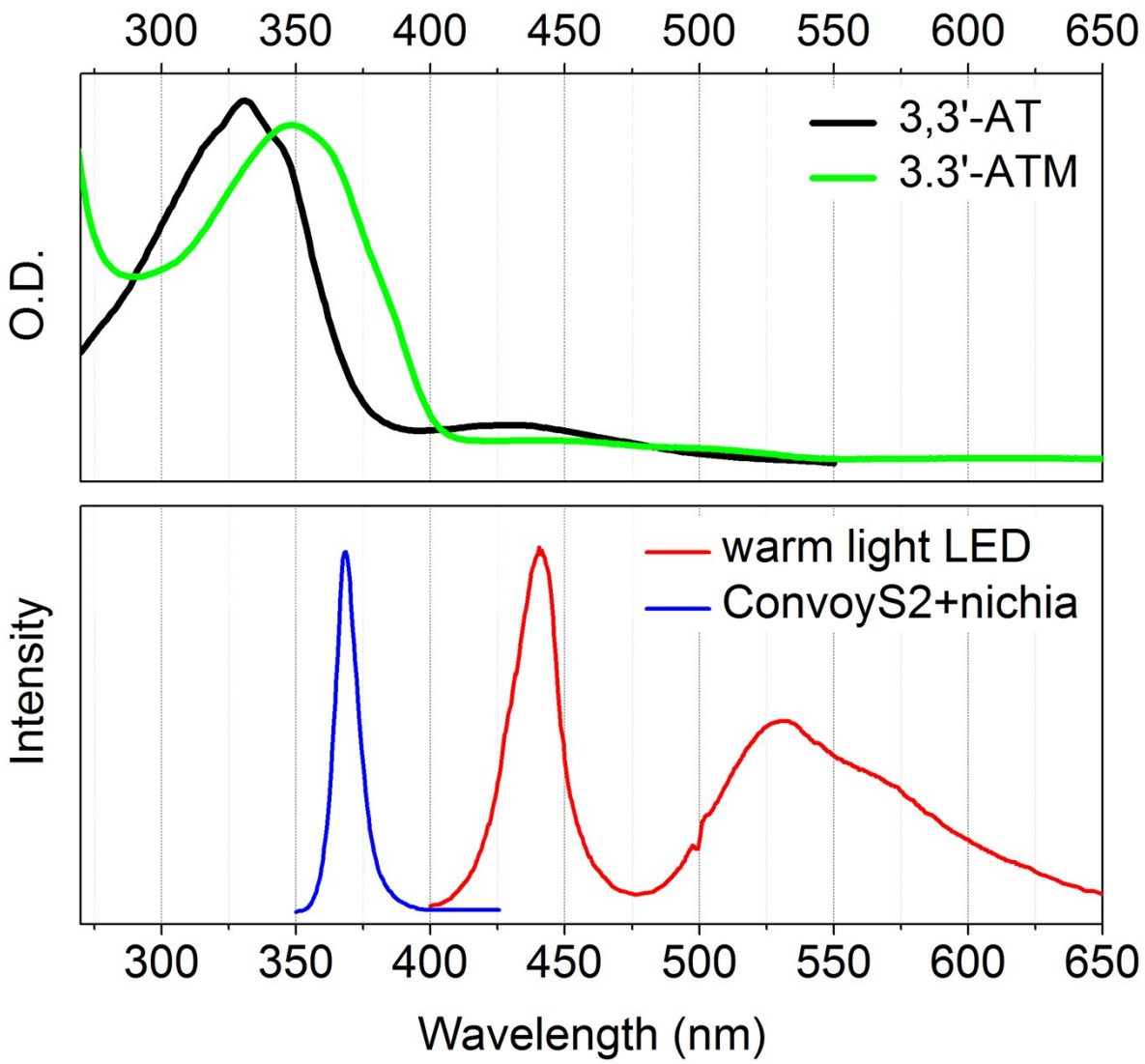

Figure S1. Upper panel: UV-VIS spectra of 3,3′-AT (black line) and 3,3′-ATM (green line) at room temperature under thermal equilibrium. Lower panel: output spectra of warm light LED and Convoy S2+ nichia LED used for photo-switching of azothiophene molecular systems.

Table S1. Contributions of Canonical Molecular Orbitals (CMO) into the most intense UV-VIS optical transitions for *anti(trans)*-cis conformer of 3,3' Azothiophene.

N	λ (nm)	Strength	CMO involved
1	448.4	0	H-1->L (99%)
2	360.8	0.7039	H->L (98%)
3	320	0.115	H-2->L (95%)
4	315.2	0.0606	H-3->L (97%)
7	243.2	0.1299	H->L+1 (83%)
8	232.7	0.0869	H->L+2 (90%)
13	213.3	0.1268	H-2->L+1 (97%)
14	210.3	0.1562	H-3->L+1 (85%)

Table S2. Contributions of CMO into the most intense UV-VIS optical transitions for *anti(trans)*-trans conformer of 3,3' Azothiophene.

N	λ (nm)	Strength	CMO involved
1	469.9	0	H-1->L (99%)
2	380.3	0.5852	H->L (99%)
3	334.9	0	H-2->L (98%)
4	322.9	0.239	H-3->L (98%)
5	266.6	0	H-4->L (93%)
6	245	0	H-1->L+1 (99%)
8	228.6	0.1497	H->L+2 (93%)
13	212.1	0.348	H-2->L+1 (92%)

Table S3. Contributions of CMO into the most intense UV-VIS optical transitions for *syn(cis)*-trans conformer of 3,3' Azothiophene.

N	λ (nm)	Strength	CMO involved
1	471.4	0.0854	H->L (88%), H-3->L (11%)
2	326.2	0.0032	H-1->L (98%)
3	315.4	0.0036	H-2->L (95%)
4	308.2	0.3579	H-3->L (87%), H->L (10%)
5	280.1	0.0457	H-4->L (96%)
6	276	0.0805	H->L+1 (95%)
11	222.9	0.1608	H-1->L+1 (61%), H-2->L+1 (17%), H->L+4 (10%)
12	222.9	0.0621	H-2->L+1 (64%), H-1->L+1 (17%), H-1->L+2 (11%)
13	219.4	0.0248	H-3->L+1 (90%)

Table S4. Contributions of CMO into the most intense UV-VIS optical transitions for *syn(cis)*-cis conformer of 3,3' Azothiophene.

N	λ (nm)	Strength	CMO involved
1	472.7	0.0694	H->L (89%)
2	336.7	0.0221	H-1->L (88%)
3	315.2	0.0855	H-2->L (79%)
4	298.8	0.131	H-3->L (81%), H-2->L (11%)
5	289.4	0.0338	H-4->L (80%), H->L+1 (15%)
6	272.4	0.1385	H-4->L (14%), H->L+1 (75%)
7	252.3	0.0375	H->L+2 (92%)
9	230.8	0.1384	H-1->L+1 (77%), H->L+3 (11%)
12	223.2	0.0567	H-2->L+1 (71%)

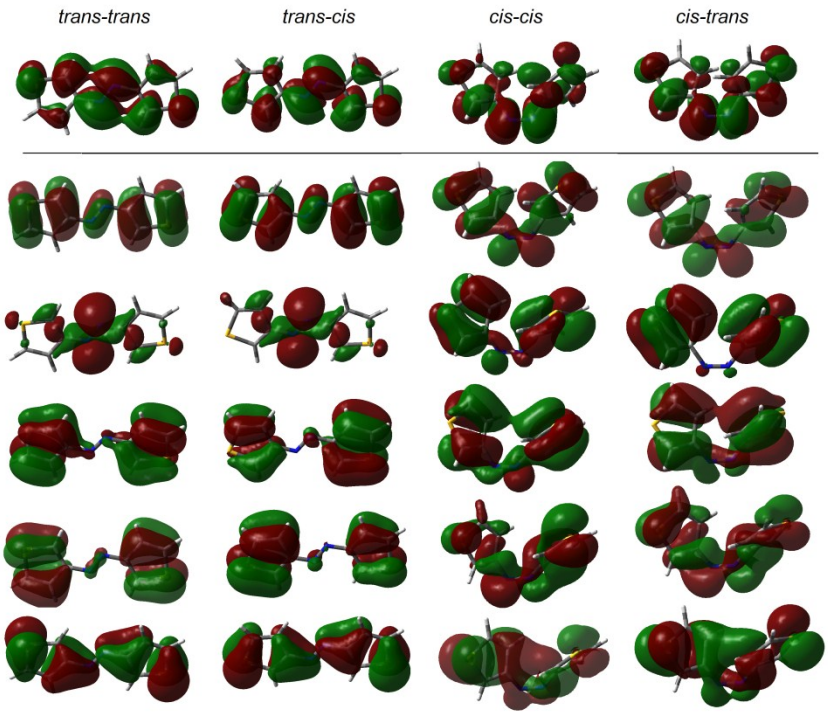

Figure S2. CMO for the conformers of 3,3' Azothiophene: HOMO at the top, LUMO and the lower states are presented below in descending order

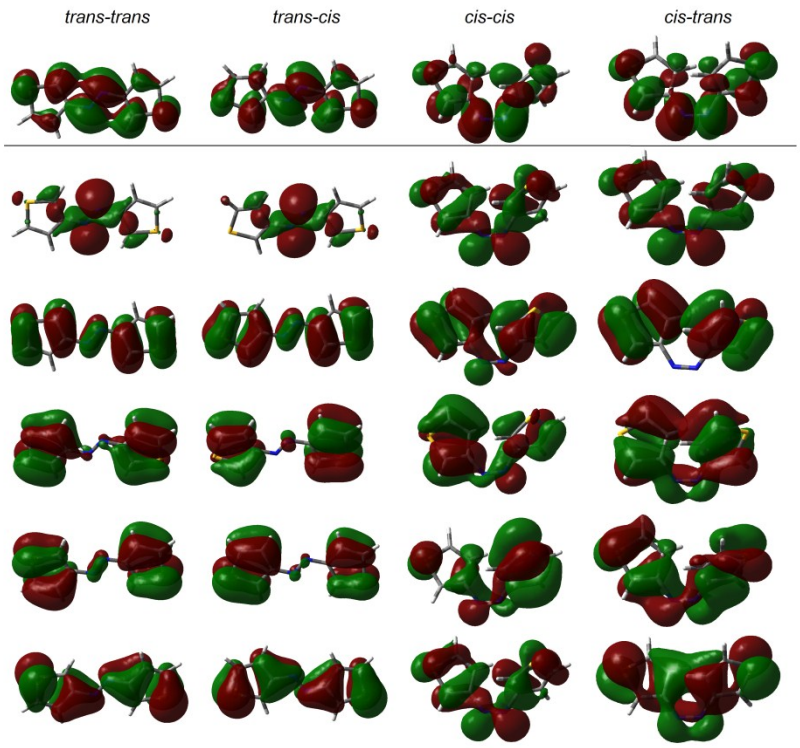

Figure S3. Natural Transition Orbitals (NTO) for the conformers of 3,3' Azothiophene: ELECTRON (receiving) states are shown at the top, HOLE states are presented below in descending order according to the energy gap of the corresponding electron-hole pairs.

Table S5. Contributions of CMO into the most intense UV-VIS optical transitions for *anti(trans)*-cis conformer of 3,3'-Azothiophene-Methoxycarbonyl.

N	λ (nm)	Strength	MO involved
1	510.3	0.0517	H->L (73%), H-1->L (17%)
2	371.9	0.2586	H-1->L (79%), H->L (18%)
3	343.9	0.2447	H-2->L (87%)
4	341.1	0.1421	H-3->L (94%)
10	259.7	0.2072	H-1->L+1 (68%), H->L+1 (15%)
11	248.9	0.0606	H-2->L+1 (56%), H-7->L (15%), H-3->L+1 (12%)
15	238.5	0.1555	H-1->L+2 (70%), H->L+2 (11%)
19	221.2	0.0885	H-3->L+2 (64%), H-2->L+2 (16%)

Table S6. Contributions of CMO into the most intense UV-VIS optical transitions for *anti(trans)*-trans conformer of 3,3'-Azothiophene-Methoxycarbonyl.

N	λ (nm)	Strength	CMO involved
1	468.2	0	H->L (93%)
2	372.1	0.3311	H-1->L (98%)
3	342	0	H-2->L (97%)
4	330.1	0.1904	H-3->L (98%)
5	297.8	0.0793	H->L+1 (93%)
11	253.7	0.1479	H-2->L+1 (87%)
13	241.8	0.3153	H-1->L+2 (85%)

Table S7. Contributions of CMO into the most intense UV-VIS optical transitions for *syn(cis)*-trans conformer of 3,3'-Azothiophene-Methoxycarbonyl.

N	λ (nm)	Strength	MO involved
1	477.9	0.0905	H->L (90%)
2	350.1	0.0038	H-1->L (93%)
3	336.9	0.0389	H-2->L (97%)
4	314.8	0.3128	H-4->L (85%)
6	295.5	0.054	H->L+2 (89%)
10	253.3	0.245	H-1->L+1 (95%)
12	245.1	0.1168	H-1->L+2 (78%), H-2->L+1 (12%)
13	241.2	0.0507	H-2->L+2 (93%)
18	227.3	0.0936	H-4->L+2 (85%)

Table S8. Contributions of CMO into the most intense UV-VIS optical transitions for *syn(cis)*-cis conformer of 3,3'-Azothiophene-Methoxycarbonyl.

N	λ (nm)	Strength	CMO involved
1	483.9	0.0489	H->L (91%)
2	349.1	0.0148	H-1->L (85%)
3	333	0.0162	H-2->L (95%)
4	317.7	0.0663	H->L+1 (63%), H-3->L (17%), H-4->L (10%)
5	311.2	0.0793	H-4->L (53%), H-3->L (36%)
6	299.2	0.1631	H->L+2 (37%), H->L+1 (11%), H-3->L (17%), H-4->L (11%)
11	259.7	0.1859	H-2->L+1 (80%), H-1->L+1 (10%)
13	244.8	0.0712	H-1->L+2 (46%), H-4->L+1 (40%)
14	240.9	0.1182	H-4->L+1 (39%), H-1->L+2 (21%), H-7->L (19%)

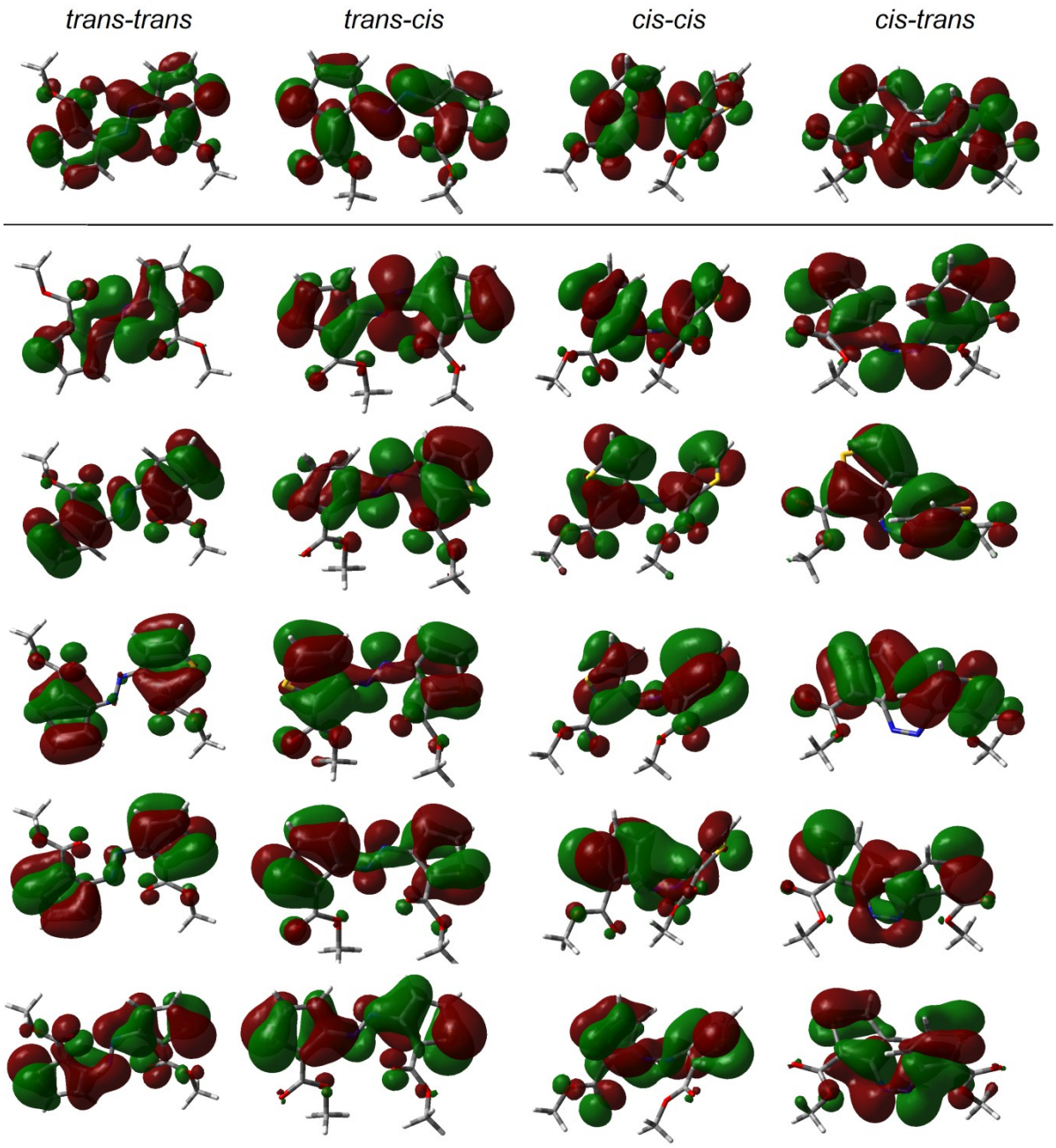

Figure S4. CMO for the conformers of 3,3'-Azothiophene-Methoxycarbonyl: HOMO at the top, LUMO and lower states are presented below in descending order

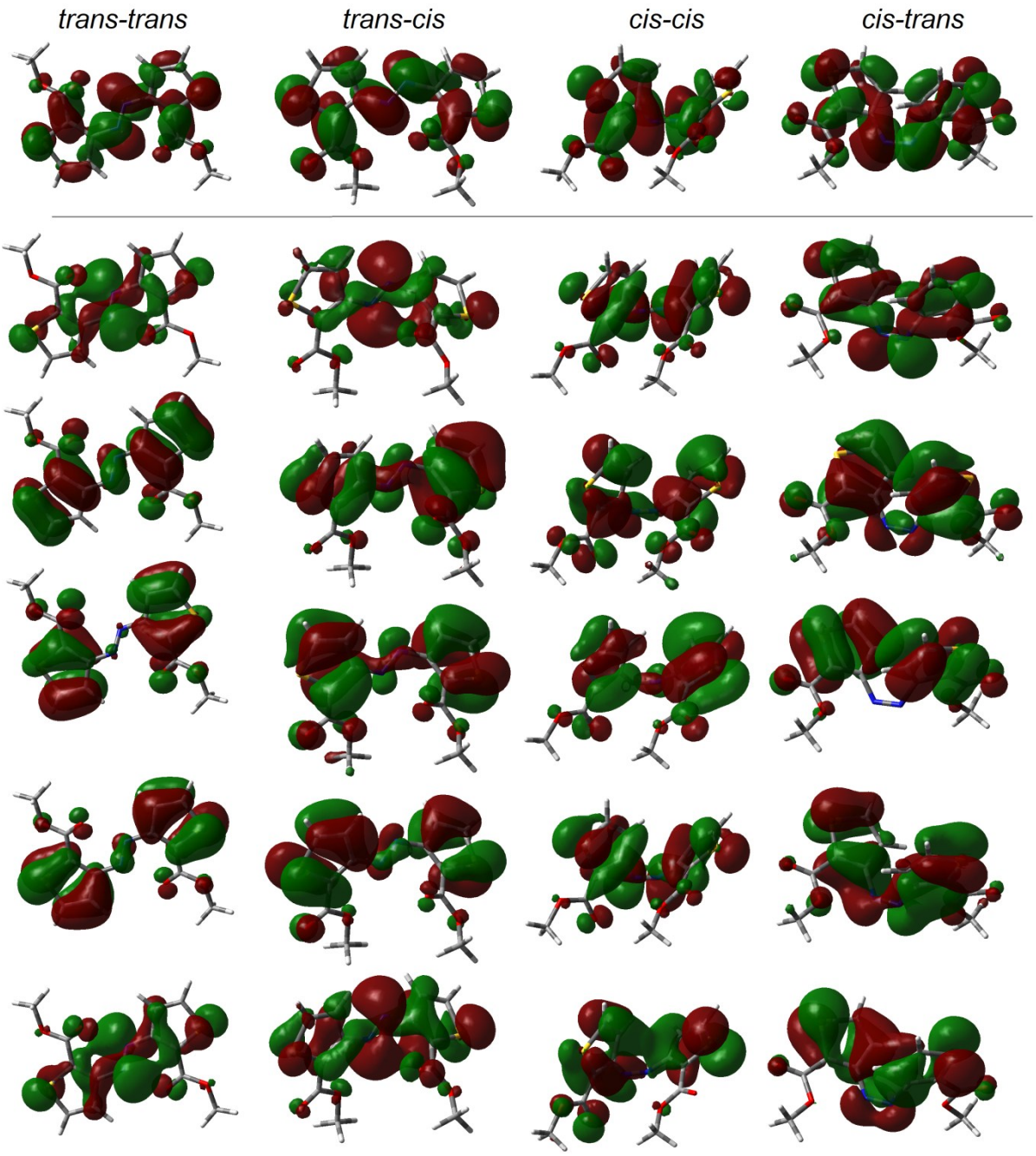

Figure S5. NTO for the conformers of 3,3'-Azothiophene-Methoxycarbonyl: ELECTRON (receiving) states are shown at the top, HOLE states are presented below in descending order according the energy gap of the corresponding electron-hole pairs.

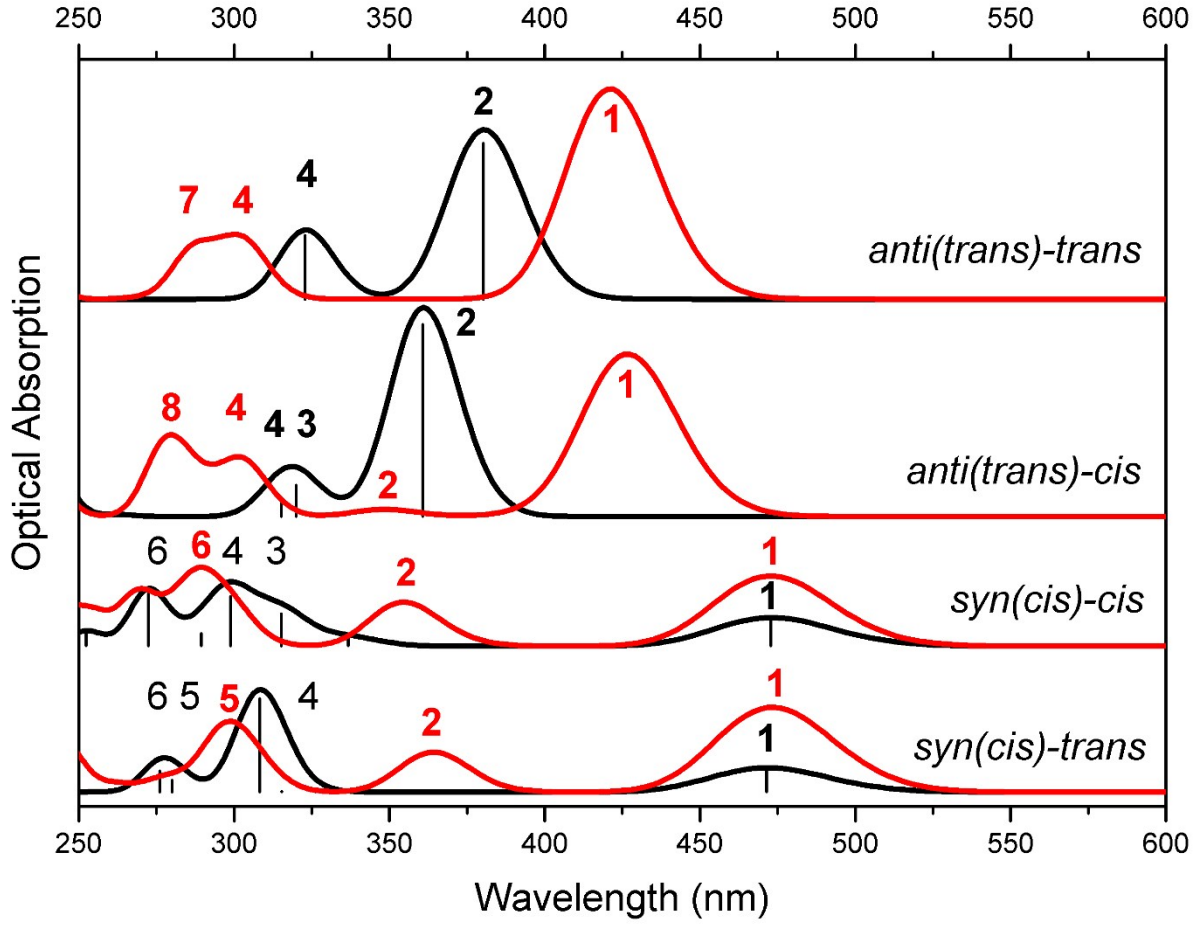

Figure S6. Calculated UV-VIS spectra for the four lowest energy conformers of 3,3′-AT (black lines) and 3,3′-AT-NH_2 (red lines).

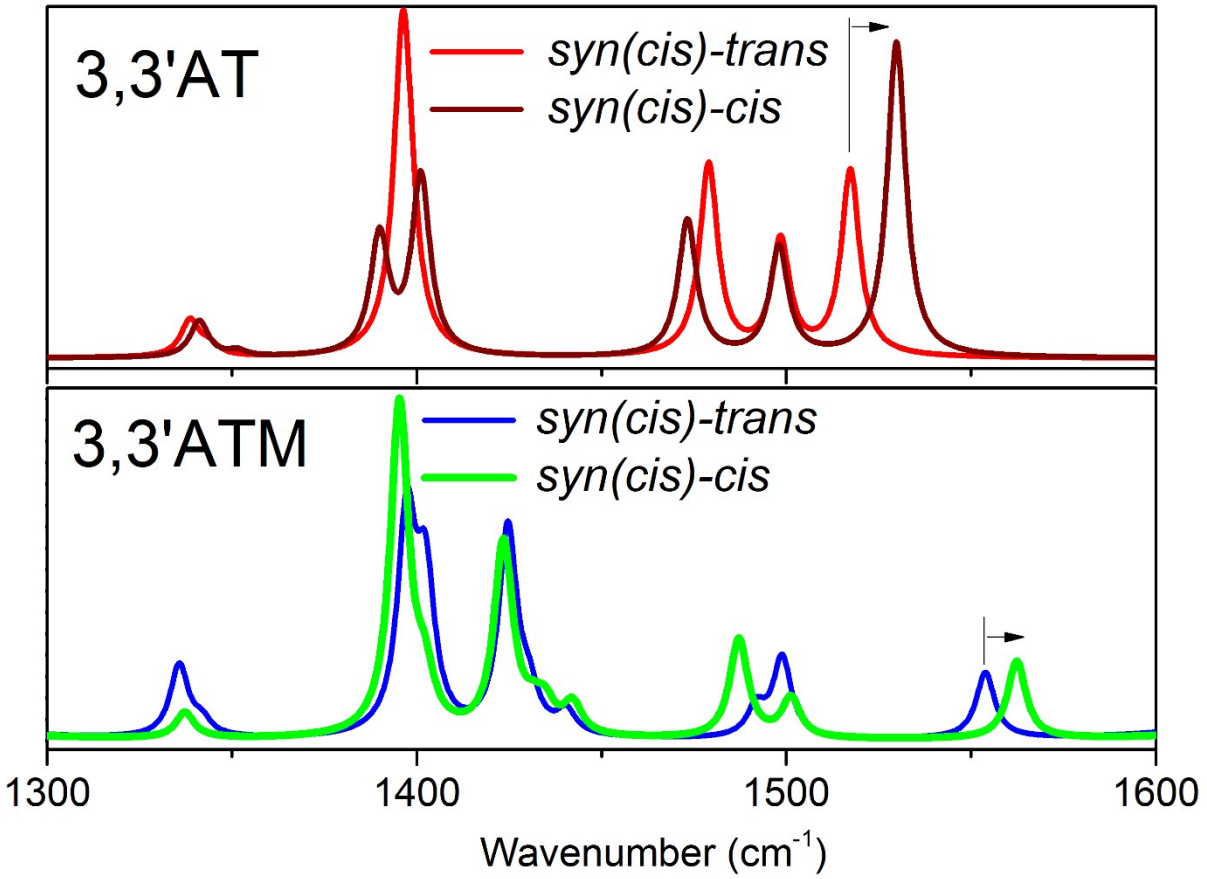

Figure S7. Comparison of DFT calculated infrared spectra of *syn(cis)-trans* and of *syn(cis)-cis* for 3,3′-AT and 3,3′-ATM as indicated. Frequency and intensity of mode 42 of *syn(cis)-cis* 3,3′-AT are higher and stronger comparing to the frequency and intensity of the same mode 42 of *syn(cis)-trans* 3,3′-AT. At the same time, in Figure 3b in the main text the photo-induced difference FTIR spectrum indicated no strong positive spectral signature at and about 1529 cm^{-1}. This lends additional support, beside the probabilities (see values in brackets in Figure 1 of the main text) according to the energies of *syn(cis)-trans* and of *syn(cis)-cis* conformers, that the *syn(cis)-trans conformer of* 3,3′-AT is a dominant conformer of the photoproduct state for 3,3′-AT.

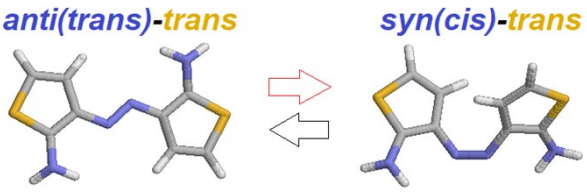

Figure S8. NH_2 substituted 3,3′-azothiophene (3,3′-AT-NH_2), as the NH_2 side groups are of electron donating character.

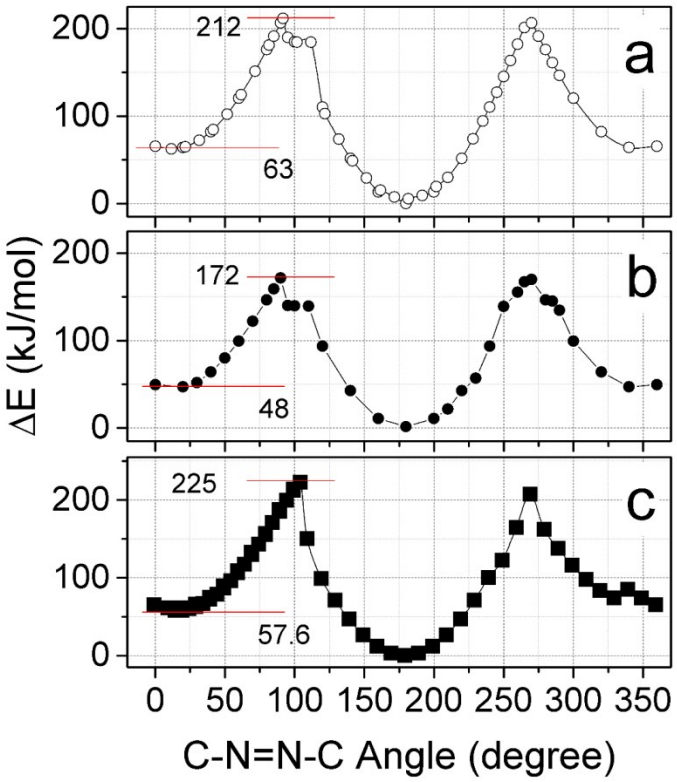

Figure S9. Thermodynamic properties. a-c: Potential energies for optimized conformers of 3,3′-AT, 3,3′-ATM and 3,3′-AT-NH_2, respectively, sampled for a series of fixed $C_3NN'C'_3$ dihedral angles along the path from *syn* to *anti* geometry of the -N=N- moiety.

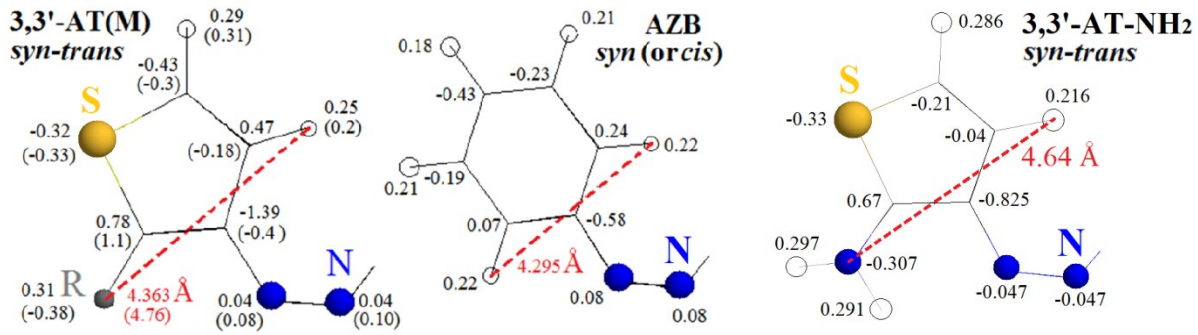

Figure S10. Mulliken atomic partial charges and geometric properties for the structural moieties of *syn(cis)-trans* 3,3′-AT, 3,3′-ATM, *cis*(*syn*) azobenzene and *syn(cis)-trans* 3,3′-AT-NH_2. R is either hydrogen or the side group of 3,3′-AT, 3,3′-ATM, respectively. Properties of 3,3′-ATM are provided in brackets.