Chemistry–A European Journal

Supporting Information

Light-Responsive Oligothiophenes Incorporating Photochromic Torsional Switches

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Supporting Information

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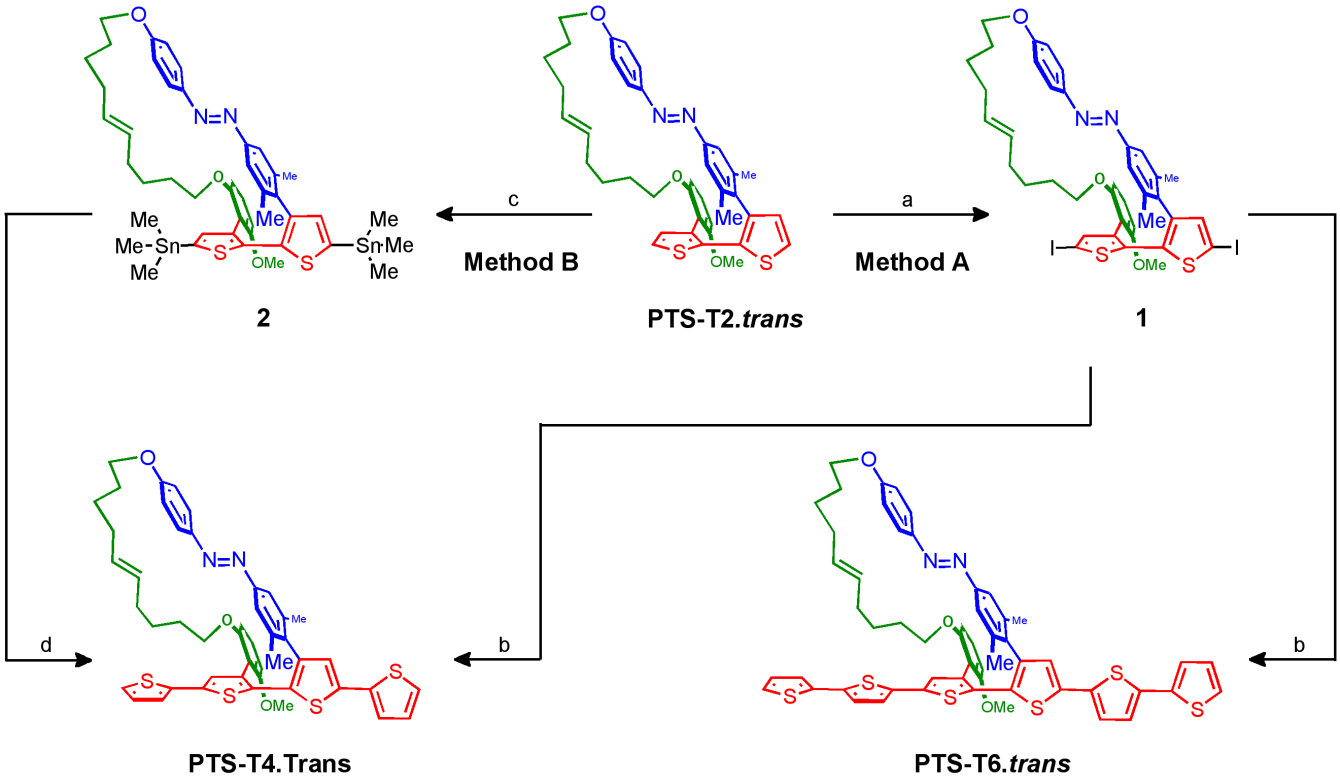
Section 1: General Experimental Details

Manipulations of air or water sensitive compounds were performed using standard high vacuum techniques. DCM, acetone, petroleum ether, heptanes, EtOAc and toluene solvents were purchased from Reactolab SA and distilled under reduced pressure before their use. All other reagents were used as commercially supplied. THF (99.99%), and diisopropylamine were purchased from Fischer Scientific. K_2CO_3 (99+%, anhydrous), n-butyllithium (1.6 M in hexane) and DMF (99.8%, extra dry, acroseal) were purchased from Acros organics. Iodine, 2-bromothiophene, and 2-([2,2'-Bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane were purchased from TCI. Dioxane (>99.5%), $Pd(PPh_3)_4$, trimethyltin chloride, and Grubbs catalyst 2nd generation were purchased from Sigma-Aldrich. Analytical thin layer chromatography (TLC) was carried out on Merck aluminium backed silica gel 60 GF254 plates. Column chromatography was carried out on silica gel 60 GF254 (particle size 40 – 63 µm, Merck) using positive air pressure. NMR spectra were recorded at ambient probe temperature using the following Fourier transform instruments: Bruker Avance III 400 MHz (9.0 T) equipped with BBFO probe, and Bruker Avance III 600 MHz (14.1 T) equipped with TCI CryoProbe. Chemical shifts (δ_H and δ_C) are reported in parts per million (ppm) relative to the residual solvent peak. Coupling constants (*J*) are reported in Hertz. ^{1}H and ^{13}C resonances were assigned with the aid of additional information from 1D & 2D NMR spectra (H,H-COSY, DEPT 135, HSQC and HMBC). Accurate mass determinations using ESI (HR ESI-MS) were performed on a Xevo G2-S QTOF mass spectrometer. UV-Vis spectra were recorded on a JASCO V-670 spectrophotometer and the absorption wavelengths (λ) are reported in nm (extinction coefficient ε in $M^{-1}cm^{-1}$). Photoisomerizations were carried using a Camag UV lamp TL 900/U.

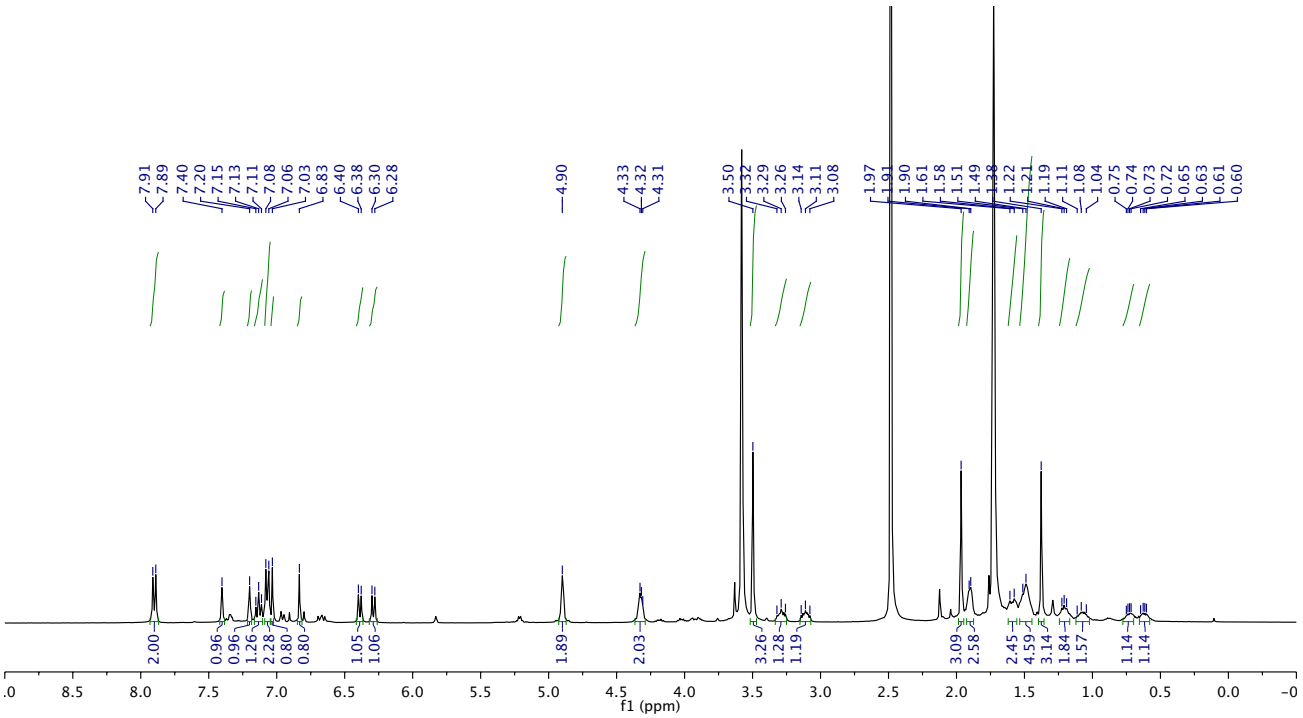
Section 2: Characterization



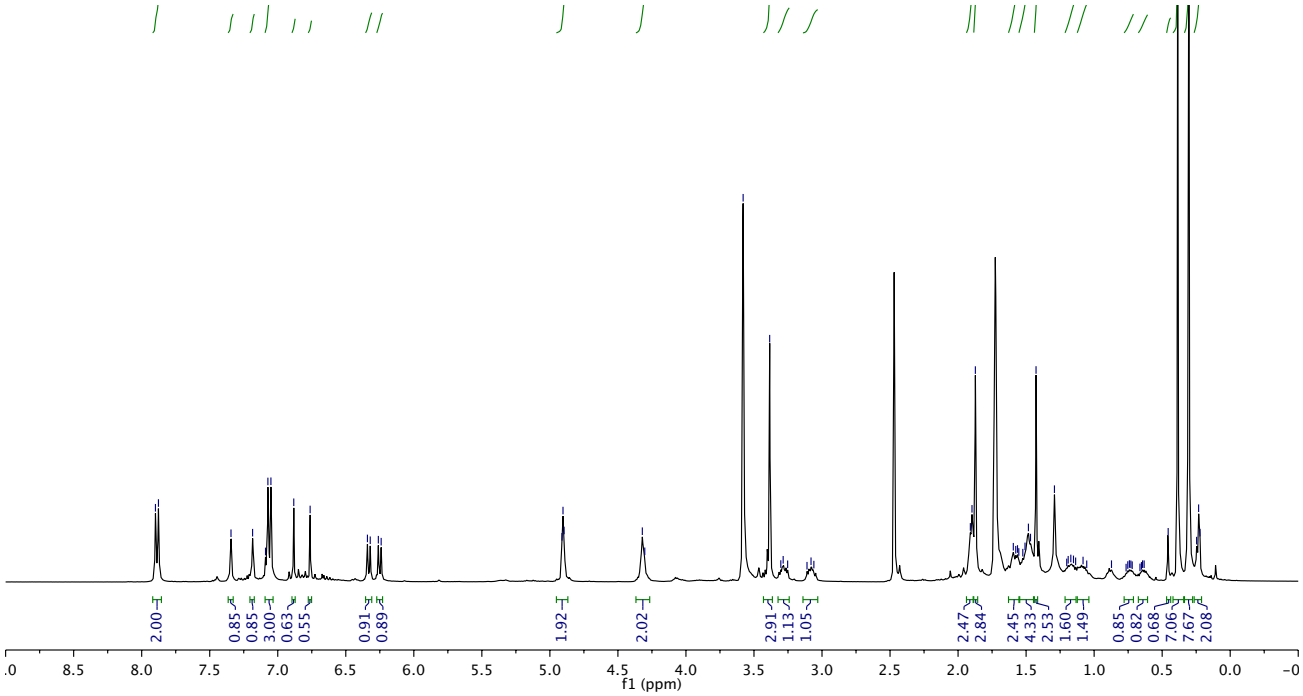
Scheme S1: Synthetic scheme for the preparation of the photochromic torsional switches **PTS-T4** and **PTS-T6**. (a) i) Diisopropylamine, n-Butyllithium, THF, ii) iodine; (b) 2-bromothiophene o 2-([2,2'-Bithiophen]-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, $Pd(PPh_3)_4$, K_2CO_3, DMF; (c) i) Diisopropylamine, n-Butyllithium, THF, ii) trimethyltin chloride; (d) 2-bromothiophene, $Pd(PPh_3)_4$, DMF.

2.1. ^{1}H-NMR spectra of PTS-T4.*trans*, PTS-T6.*trans* and related precursors

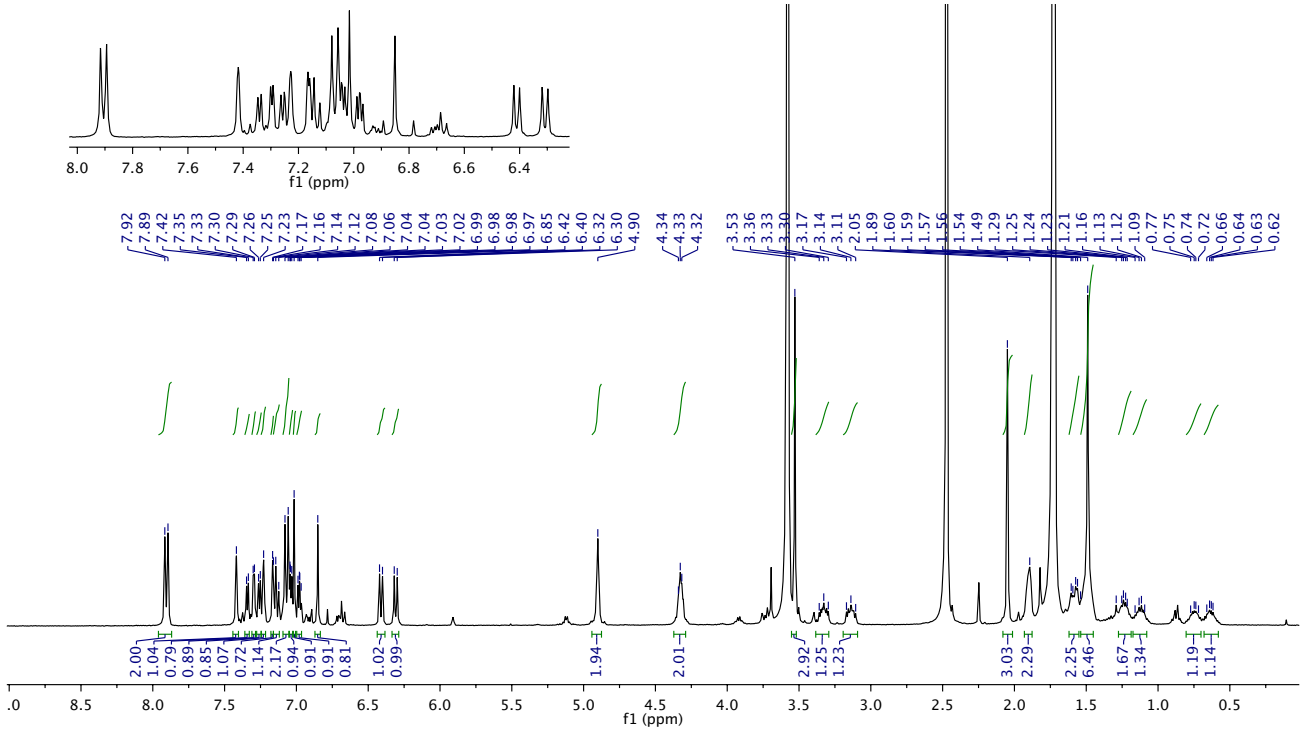
Compound 1:



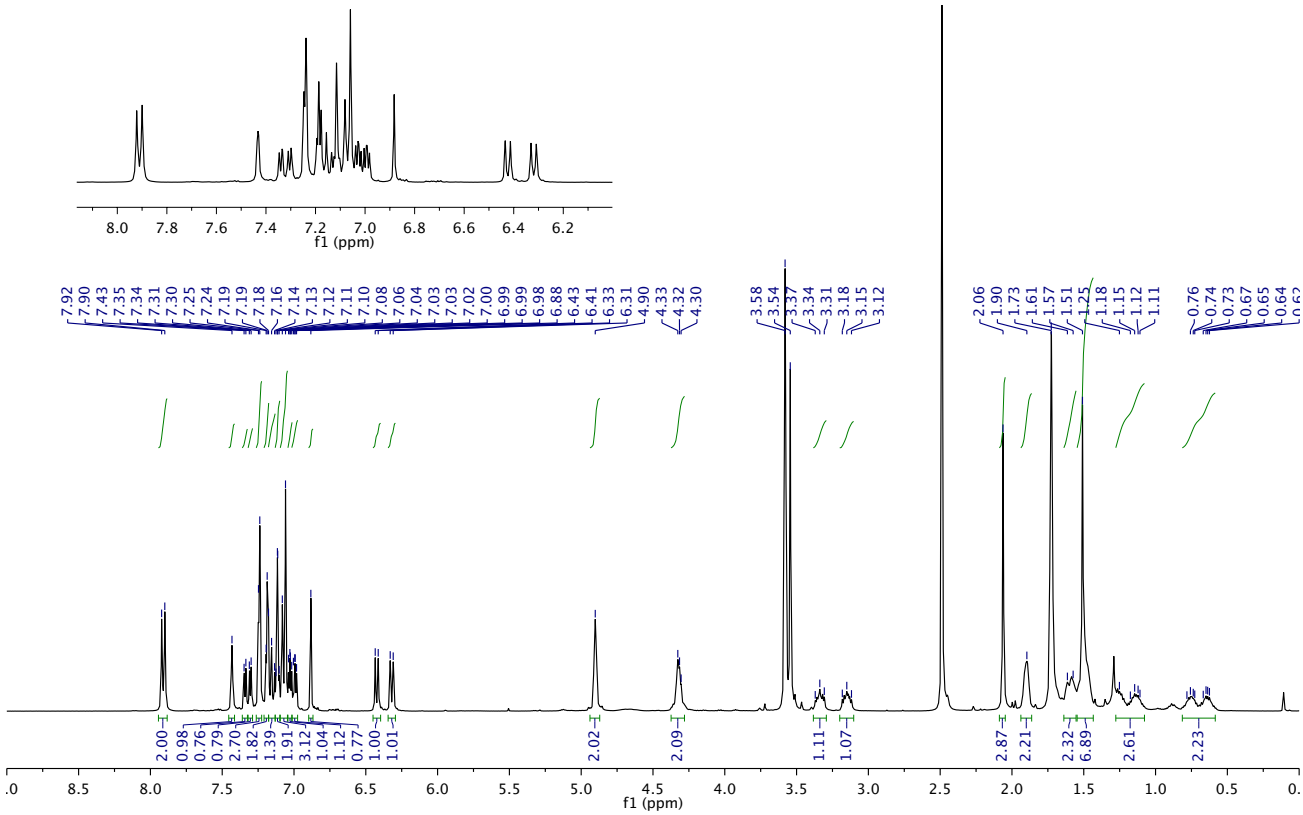
Compound 2:



PTS-T4.*trans*

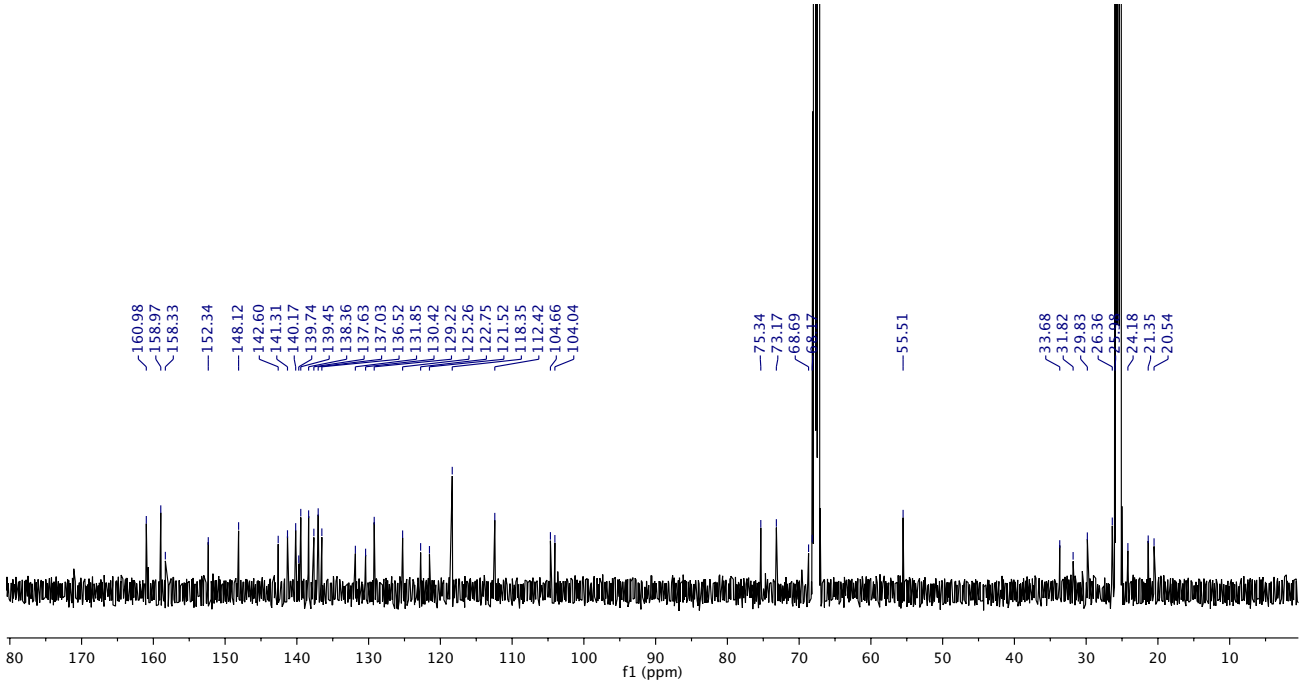


PTS-T6.*trans*

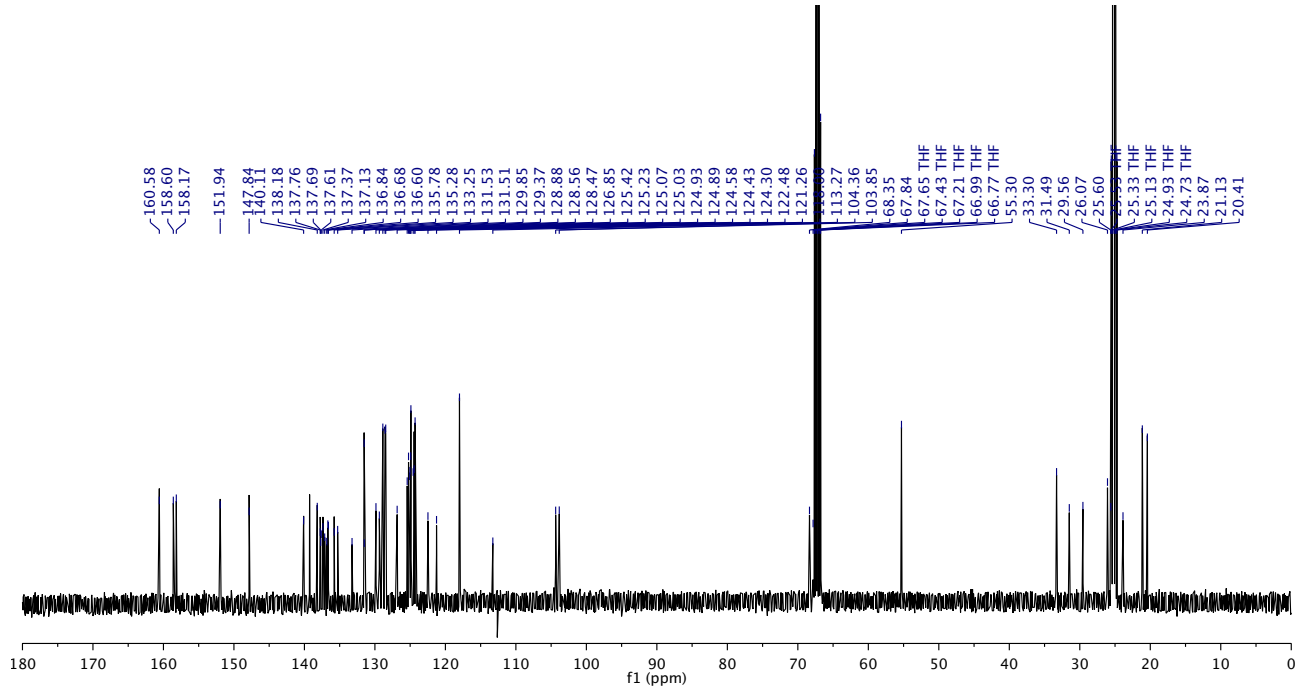


2.2. ^{13}C-NMR spectra of PTS-T4.*trans*, PTS-T6.*trans* and related precursors

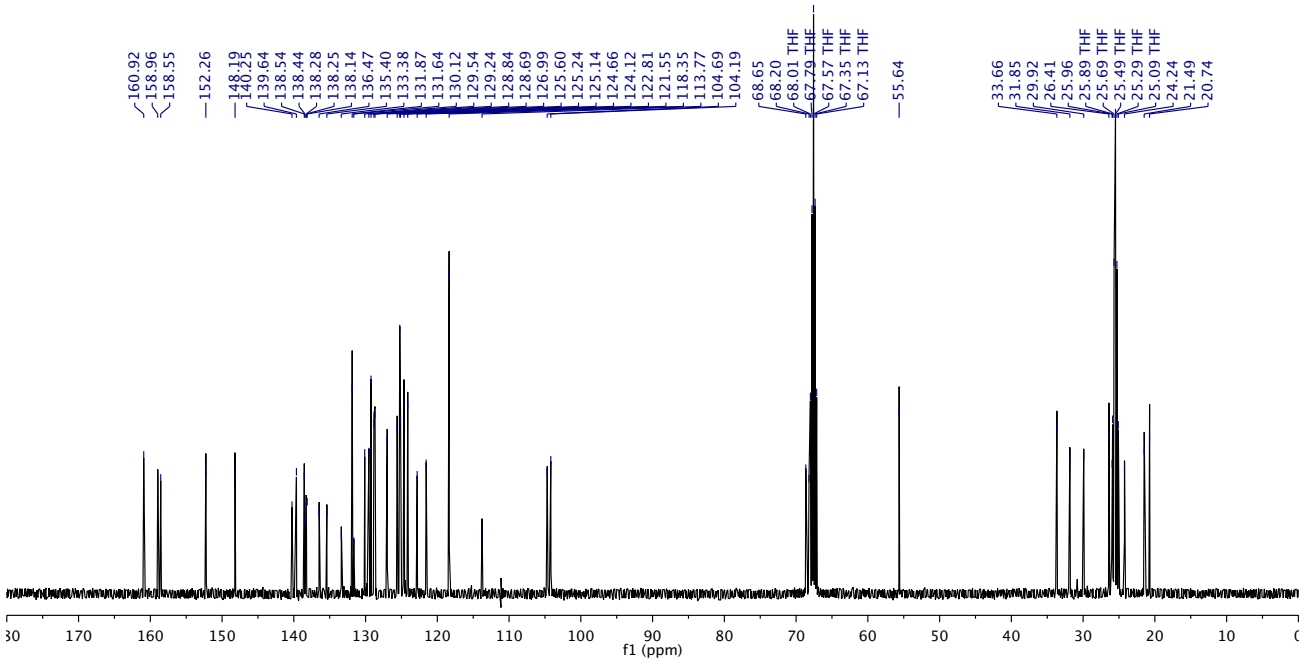
Compound 1:



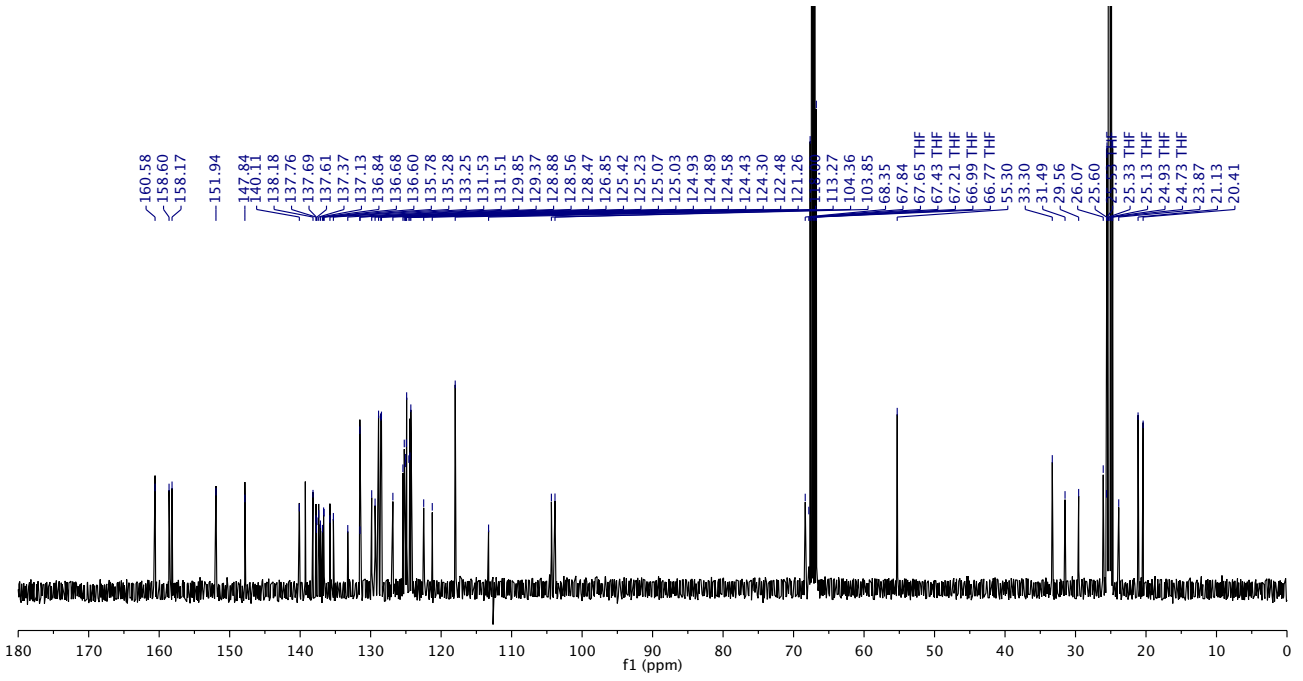
Compound 2:



PTS-T4.*trans*



PTS-T6.*trans*



2.3. ^{1}H-NMR Spectra: *trans*-to-*cis* isomerization and PSS of PTS-T4.*trans*

^{1}H-NMR spectroscopy shows that **PTS-T4** has ~6% of **PTS-T4.*cis***. When **PTS-T4.*trans*** is exposed to 350nm light, ~49% of **PTS-T4.*trans*** is converted to **PTS-T4.*cis***. This process can be inverted by irradiating **PTS-T4.*cis*** with 254nm light to recover the initial state consisting ~74% of **PTS-T4.*trans*** and ~26% of **PTS-T4.*cis*.**

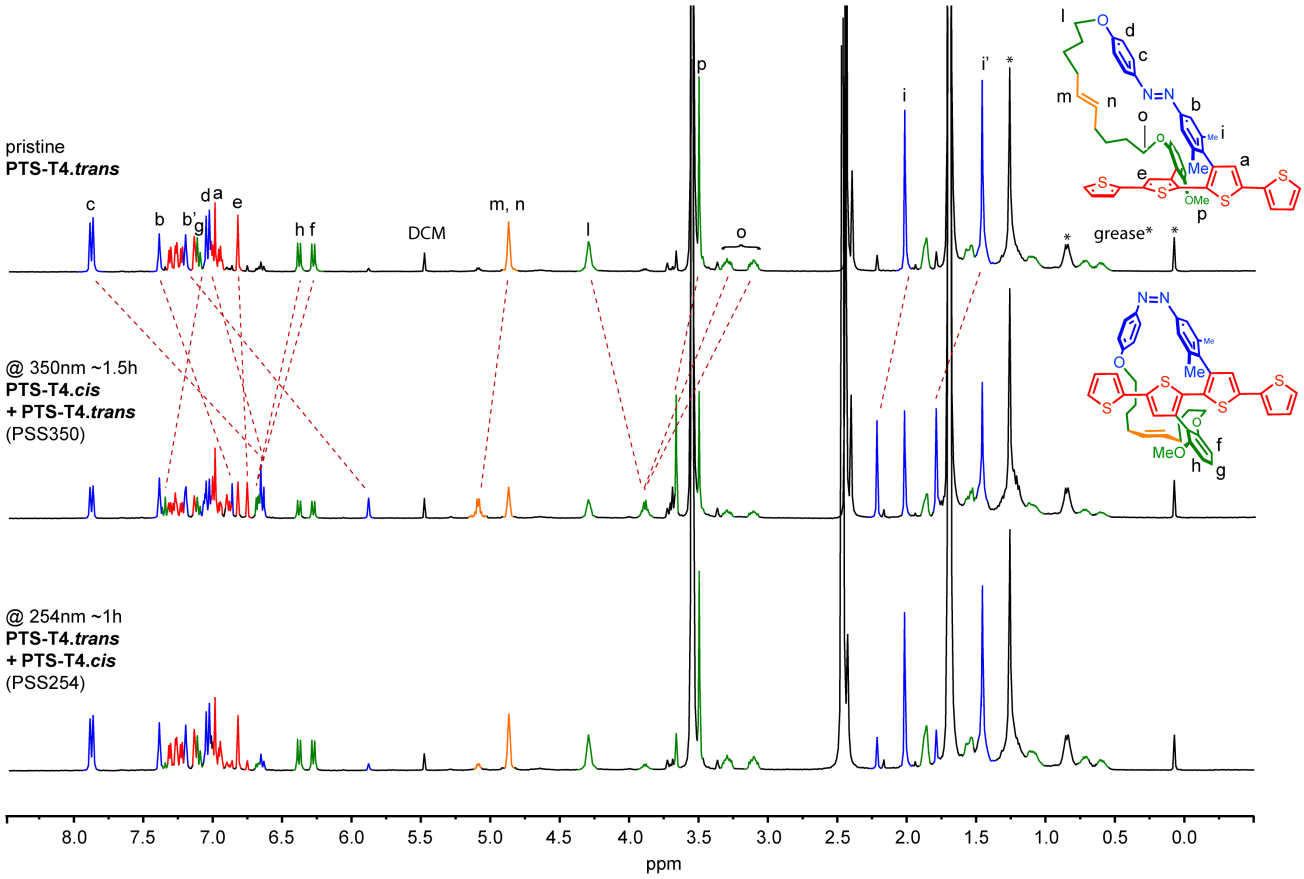


Figure S1: ^{1}H-NMR spectrum of compound **PTS-T4** in tetrahydrofuran-d8. Before (top), after (middle) 1.5 h of irradiation at 350 nm, and after (bottom) 1 h of irradiation at 254 nm.

2.4. ^{1}H-NMR Spectra: *trans*-to-*cis* isomerization and PSS of PTS-T6.*trans*

^{1}H-NMR spectroscopy shows that when **PTS-T6.*trans*** is exposed to 350nm light, ~57% of **PTS-T6.*trans*** is converted to **PTS-T6.*cis***. This process can be inverted by irradiating **PTS-T6.*cis*** with 254nm light to recover the initial state obtain reach the consisting of ~71% of **PTS-T6.*trans*** and ~29% of **PTS-T6.*cis***.

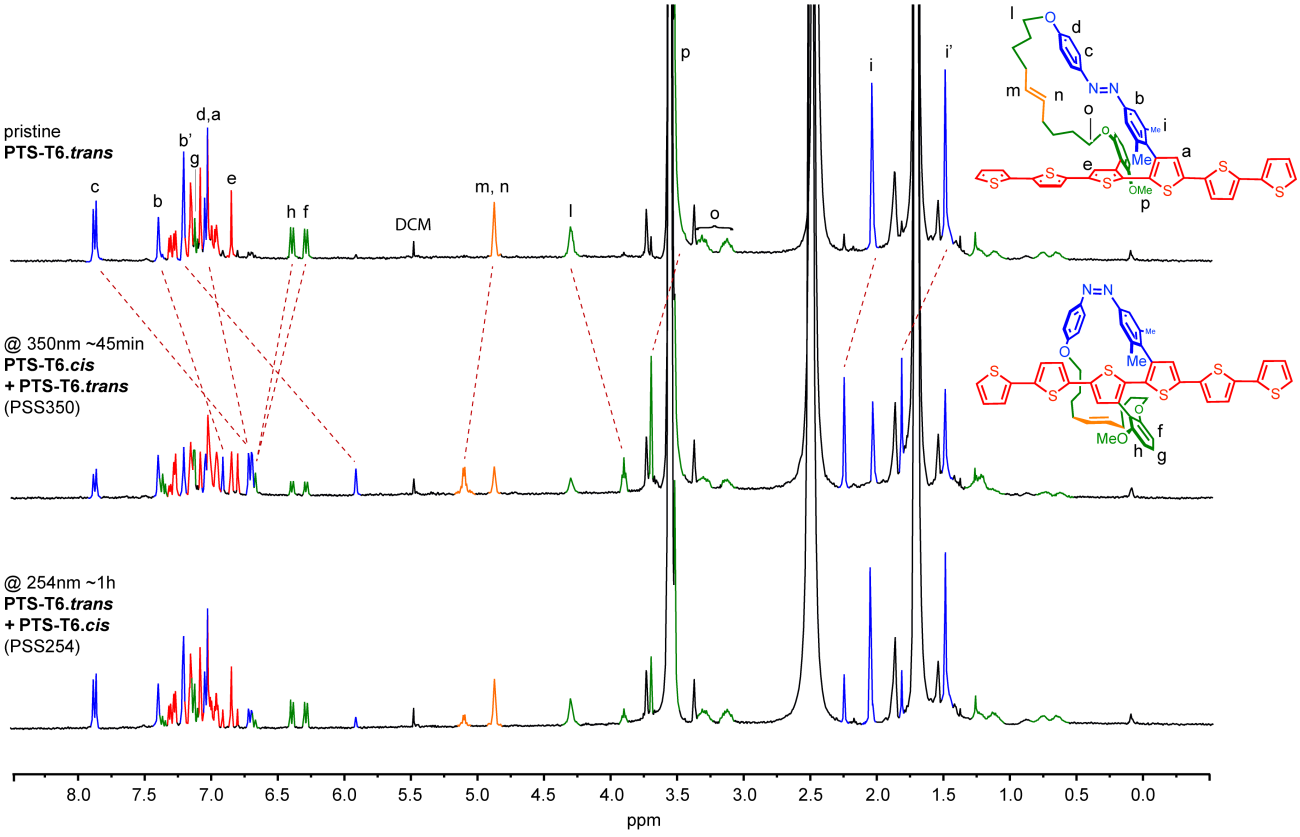


Figure S2: ^{1}H-NMR spectrum of compound **PTS-T6** in tetrahydrofuran-d8. Before (top), after (middle) 45 min of irradiation at 350 nm, and after (bottom) 1 h of irradiation at 254 nm.

Section 3: Quantum chemical calculations

3.1. Conformational screening and DFT calculations

A conformational screening for each PTS-Tn species was performed by using the algorithm CREST (Conformer Rotamer Ensemble Search Tool), as recently introduced by Grimme et al.[2] The conformational search is based on meta-dynamics simulations (MTD) coupled with DFT-based semiempirical approaches, called GFNn-xTB (here we used the GFN2-xTB).[3] For **PTS-T4.*trans*** we found 294 conformers and for **PTS-T4.*cis*** 1011, all lying within 6 kcal/mol. For **PTS-T6.*trans*** we found 928 conformers and for **PTS-T6.*cis*** 573. The low-energy (< 0.05 kcal/mol) structures were re-optimized at the DFT level, by using the range-separated functional with diffusion corrections (wB97X-D) and a triple-split Pope basis set with diffusion and polarization functions (6-311+G*). TDDFT calculations were performed at the same level of theory and more than 50 excited states were considered for each species. DFT and TDDFT calculations were carried out with the program Gaussian16/C.01.[4] The lowest energy structures, as optimized at the DFT level for **PTS-T4.*trans/cis*** and **PTS-T6.*trans/cis***, are reported in Figure S3.

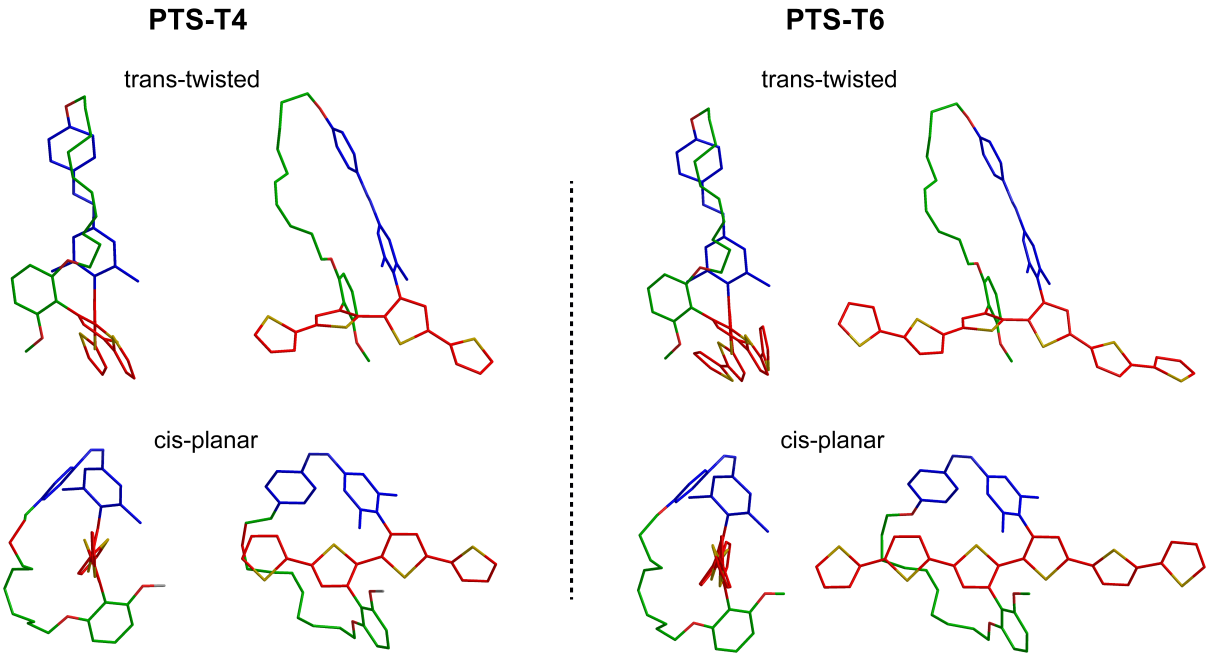


Figure S3: DFT(ωB97X-D/6-311+G*) optimized structures for **PTS-T4** (left, trans - top, and cis - bottom) and **PTS-T6** (right, trans - top, and cis – bottom).

[2] 'Extended tight-binding quantum chemistry methods' Bannwarth, C.; Caldeweyher, E.; Ehlert, S.; Hansen, A.; Pracht, P.; Seibert, J.; Spicher, S.; Grimme, S. *WIREs Comput Mol Sci.* 2020, **11,** e01493

[3] 'GFN2-xTB An Accurate and Broadly Parametrized Self-ConsistentTight-Binding Quantum Chemical Method with MultipoleElectrostatics and Density-Dependent Dispersion Contributions' Bannwarth, C.; Ehlert, S.; Grimme, S. *J. Chem. Theory Comput.* 2019, **15**, 1652−1671

[4] 'Gaussian 16, Revision C.01' Frisch, M. J. *et al.* Gaussian, Inc., Wallingford CT, 2016.

3.2 Frontier molecular orbitals for PTS-T4 and PTS-T6

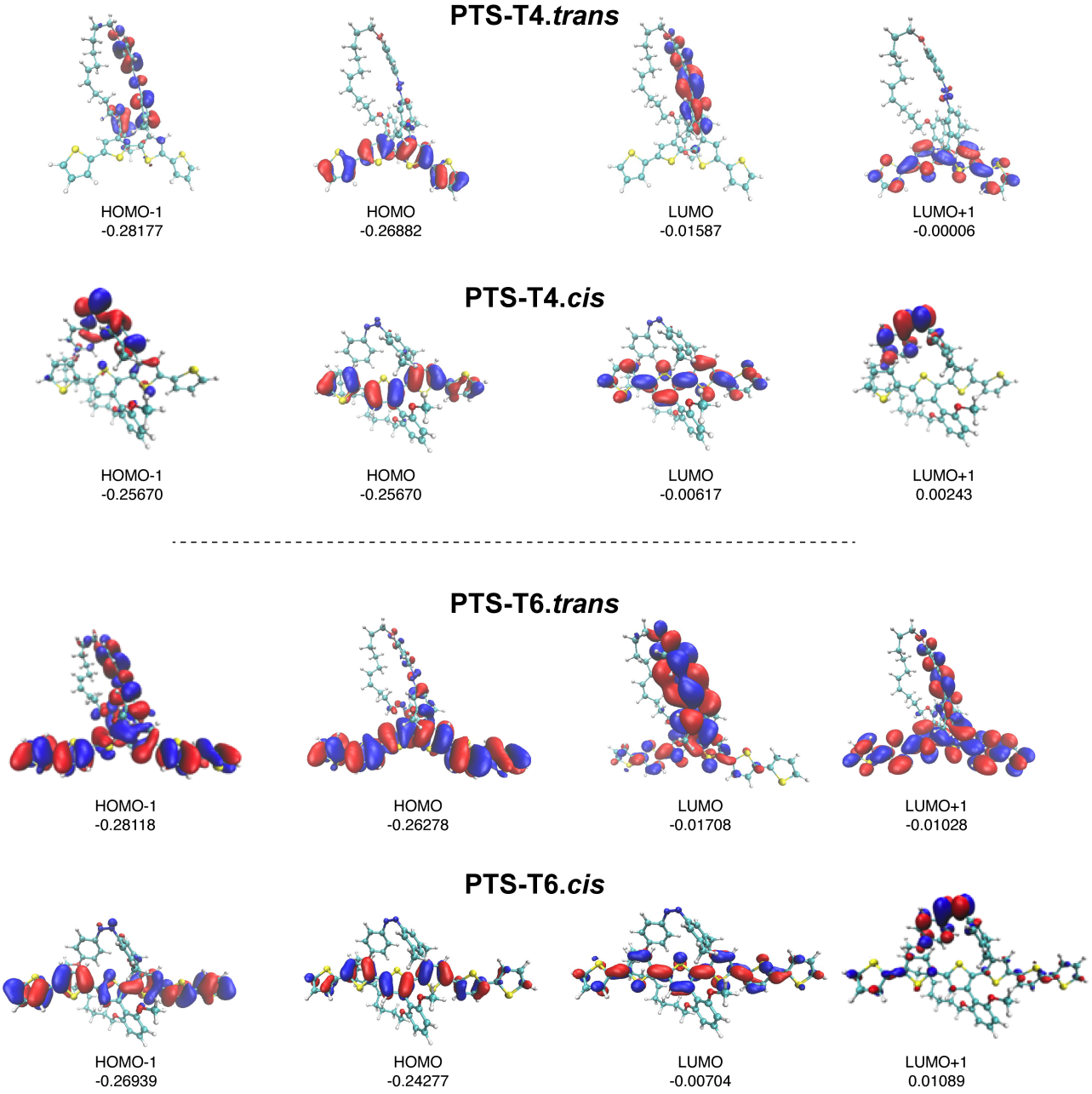


Figure S4: Relevant DFT (ωB97X-D/6-311+G*) frontier molecular orbitals involved in the S_0->S_{thio} and S_0-S_{azo} transitions (see main text). Molecular orbital energies are reported in atomic units (a.u.).

PTS-T4.*trans* optimized structure (wB97X-D/6-311+G*)

Total SCF energy = -3745.14369561 Hartree

C	0.462366	-1.062814	3.844102
C	1.809603	-0.707989	3.815870
C	2.257293	0.120767	2.798204
C	1.387381	0.616820	1.797346
C	0.036474	0.248260	1.861839
C	-0.409990	-0.599358	2.887917
C	1.998998	1.514945	0.782827
C	2.889142	1.112621	-0.180143
S	3.487742	2.472243	-1.087117
C	2.577036	3.593782	-0.131640
C	1.850959	2.932387	0.814118
C	3.451965	-0.210195	-0.441007
C	2.838927	-1.404142	-0.725340
C	3.779098	-2.460508	-0.909355
C	5.081887	-2.079842	-0.769247
S	5.181519	-0.396824	-0.375311
C	1.375941	-1.613227	-0.858757
C	0.720033	-2.440482	0.074255
C	-0.651876	-2.606246	-0.015568
C	-1.369729	-1.982292	-1.030866
C	-0.708392	-1.231872	-1.991200
C	0.666276	-1.026076	-1.915325
C	1.475915	-3.124384	1.182843
N	-2.784438	-2.021079	-1.145001
N	-3.370424	-2.468564	-0.144768
C	-4.782642	-2.463484	-0.225616
C	-5.462465	-2.681421	0.971649
C	-6.840731	-2.590198	1.022786
C	-7.565943	-2.285875	-0.130461
C	-6.892260	-2.138720	-1.347157
C	-5.510210	-2.219006	-1.389269
C	1.342188	-0.174578	-2.958205
O	-8.905903	-2.169260	0.036925
C	-9.705560	-1.436759	-0.887383
C	-9.783631	0.057765	-0.591921
C	-8.458465	0.831914	-0.662815
C	-7.693825	0.882107	0.670827
C	-6.179046	1.034522	0.517555
C	-5.751386	2.268975	-0.234982
C	-4.521413	2.777900	-0.284747
C	-3.291590	2.247659	0.393741

C	-2.240521	1.753693	-0.609906
C	-0.866302	1.579240	0.004168
O	-0.957909	0.577380	1.006381
O	3.546129	0.525460	2.682430
C	4.517277	-0.064373	3.514377
H	3.483747	-3.467175	-1.180935
H	1.247833	3.441658	1.556372
H	-1.183402	-3.198005	0.720080
H	-1.290048	-0.779494	-2.788761
H	2.340652	-0.544405	-3.200407
H	1.459929	0.857582	-2.613912
H	0.753321	-0.150006	-3.877483
H	2.198727	-2.453407	1.649262
H	2.028033	-3.993687	0.812383
H	0.790800	-3.469855	1.957967
H	-4.887516	-2.888176	1.867966
H	-4.982527	-2.072745	-2.324104
H	-7.428459	-1.938527	-2.265632
H	-7.378692	-2.720447	1.954917
H	-10.698190	-1.881413	-0.794797
H	-9.371763	-1.611081	-1.914314
H	-10.245276	0.202276	0.391656
H	-10.493117	0.464142	-1.323069
H	-8.667940	1.853118	-0.995420
H	-7.818494	0.399477	-1.439764
H	-7.885513	-0.032069	1.238267
H	-8.093404	1.702307	1.280091
H	-5.793442	0.147648	0.001556
H	-5.718304	1.018708	1.510745
H	-4.365878	3.671492	-0.889716
H	-3.534193	1.441435	1.088963
H	-2.848550	3.053730	0.994814
H	-2.134844	2.481976	-1.423502
H	-2.571369	0.816242	-1.066444
H	-0.547613	2.523423	0.453684
H	-0.131137	1.290528	-0.750298
H	2.483335	-1.079884	4.576211
H	-1.457490	-0.876569	2.888346
H	0.099800	-1.717084	4.630427
H	5.473348	0.342412	3.189782
H	4.530894	-1.153590	3.397078
H	4.355379	0.189672	4.567590
H	-6.523866	2.779875	-0.807555
C	6.284907	-2.888357	-0.898566

C	2.640574	5.023568	-0.392108
C	7.519996	-2.516785	-1.355536
C	8.464695	-3.579712	-1.339566
C	7.936089	-4.743789	-0.872007
S	6.282990	-4.559525	-0.427875
C	3.699960	5.766573	-0.836712
C	3.393137	7.147766	-0.979228
C	2.106351	7.436338	-0.641299
S	1.242517	6.027196	-0.159929
H	7.737552	-1.518231	-1.715133
H	9.490430	-3.481299	-1.671926
H	8.422003	-5.702147	-0.760610
H	4.104492	7.893991	-1.309732
H	4.675877	5.338899	-1.032379
H	1.613137	8.397436	-0.646984

PTS-T4.*cis* optimized structure (wB97X-D/6-311+G*)

Total SCF energy = -3745.13004061Hartree

S	-3.536431	0.503847	-0.573499
C	-2.165906	-0.440111	-0.057316
C	-2.444512	-1.789589	-0.152523
C	-3.761446	-2.038796	-0.628161
C	-4.475298	-0.910353	-0.910025
C	-0.967131	0.221385	0.451897
C	-0.883627	1.406464	1.144677
C	0.423692	1.674268	1.625606
C	1.341119	0.720049	1.293381
S	0.607249	-0.510655	0.318379
C	-2.000626	2.352617	1.358429
C	-3.002127	2.118417	2.303251
C	-4.056172	3.020310	2.454224
C	-4.091797	4.152408	1.651297
C	-3.108635	4.413066	0.706466
C	-2.060242	3.504073	0.565482
O	-2.874039	0.971664	3.009978
C	-3.924697	0.586835	3.866807
O	-1.057142	3.624835	-0.330624
C	-1.039698	4.709614	-1.240100
C	0.200183	4.559645	-2.101728
C	1.497175	4.642077	-1.299856
C	2.763524	4.605601	-2.168691

C	2.983812	3.295847	-2.883891
C	3.665538	2.256303	-2.401714
C	4.317479	2.192452	-1.050874
C	5.844015	2.366604	-1.067302
C	6.646286	1.303562	-1.823418
C	6.483006	-0.109123	-1.290632
O	5.237800	-0.610971	-1.759321
C	4.716285	-1.723692	-1.210328
C	5.402812	-2.607293	-0.376523
C	4.742621	-3.722679	0.122155
C	3.394234	-3.966295	-0.148527
C	2.726642	-3.073557	-1.002929
C	3.383239	-1.981593	-1.530144
N	2.935451	-5.203008	0.423424
N	1.766263	-5.509220	0.697982
C	0.649723	-4.635355	0.494060
C	0.006594	-4.582188	-0.735664
C	-1.023366	-3.674363	-0.949253
C	-1.467906	-2.875935	0.121001
C	-0.941786	-3.068322	1.407428
C	0.132240	-3.939339	1.576621
C	-1.586629	-3.524673	-2.340382
C	-1.474755	-2.306661	2.592279
H	-4.155601	-3.039060	-0.763578
H	0.648808	2.536908	2.241621
H	0.378628	-5.187605	-1.557182
H	0.589914	-4.057748	2.553930
H	-2.555403	-2.167499	2.519295
H	-1.253474	-2.835210	3.522066
H	-1.034006	-1.307456	2.661650
H	-1.691946	-2.473559	-2.618769
H	-2.578515	-3.976879	-2.427265
H	-0.940703	-4.010591	-3.074333
H	5.273985	-4.437458	0.741393
H	6.445971	-2.447946	-0.131443
H	2.862561	-1.288890	-2.181752
H	1.694673	-3.215994	-1.270499
H	6.487687	-0.111240	-0.193272
H	7.290821	-0.760892	-1.645311
H	6.391301	1.304637	-2.888300
H	7.709508	1.560946	-1.761806
H	2.533547	3.199283	-3.870431
H	3.625954	4.833877	-1.535178
H	2.713132	5.413679	-2.908424

H	1.527189	3.820201	-0.577752
H	1.497021	5.573526	-0.718643
H	0.144812	3.605480	-2.635789
H	0.178432	5.352071	-2.860208
H	-1.949537	4.693880	-1.853415
H	-1.012907	5.659074	-0.688015
H	-4.843132	2.851236	3.177535
H	-3.169095	5.303450	0.093915
H	-4.911796	4.854033	1.765803
H	-3.636032	-0.379640	4.276629
H	-4.055338	1.299791	4.688097
H	-4.866635	0.481473	3.318277
H	6.192328	2.391659	-0.026966
H	6.080840	3.346417	-1.497788
H	4.065875	1.236301	-0.584496
H	3.901412	2.960422	-0.395638
H	3.760642	1.364988	-3.018596
C	2.723292	0.606840	1.725759
C	-5.837587	-0.797565	-1.406661
C	3.535391	-0.493886	1.698118
C	4.832255	-0.246065	2.225597
C	4.989238	1.034726	2.657874
S	3.555701	1.963363	2.427687
C	-6.397391	0.206398	-2.149619
C	-7.765341	-0.024381	-2.462511
C	-8.228593	-1.199493	-1.955717
S	-7.009044	-2.036638	-1.074266
H	-9.216468	-1.626363	-2.049697
H	-8.373719	0.651510	-3.050171
H	-5.840376	1.074930	-2.480044
H	3.211471	-1.458988	1.328395
H	5.604987	-1.001411	2.292371
H	5.857862	1.487855	3.113310

PTS-T6.*trans* optimized structure (wB97X-D/6-311+G*)

Total SCF energy = -4848.74339008 Hartree

S	-2.470658	5.300486	0.010314
C	-0.758638	5.115426	-0.208309
C	-0.200778	6.290887	-0.623591
C	-1.147371	7.344478	-0.753822
C	-2.421696	6.971516	-0.441727

C	-0.112854	3.834989	0.033525
S	1.241564	3.323867	-0.917751
C	1.379178	1.828676	-0.037299
C	0.396135	1.723591	0.913710
C	-0.429755	2.884400	0.958224
C	0.293698	0.622185	1.906902
C	1.284010	0.598506	2.918469
C	1.290054	-0.362085	3.918531
C	0.290728	-1.333147	3.917663
C	-0.686167	-1.340004	2.950382
C	-0.702507	-0.363350	1.942119
O	2.209158	1.585781	2.831386
C	3.335431	1.532983	3.675092
O	-1.720826	-0.548836	1.071613
C	-2.122373	0.387948	0.082782
C	-3.397443	-0.123418	-0.556427
C	-4.568056	-0.230177	0.430636
C	-5.890376	-0.359310	-0.268490
C	-6.711950	-1.407657	-0.251845
C	-6.488771	-2.708555	0.476759
C	-7.735497	-3.588049	0.593112
C	-8.356800	-3.978660	-0.758647
C	-9.132204	-5.304672	-0.728321
C	-8.326372	-6.562196	-1.038883
O	-7.284507	-6.828545	-0.104020
C	-6.057257	-6.269741	-0.240699
C	-5.293796	-6.203908	0.926114
C	-4.047459	-5.606494	0.906875
C	-3.543815	-5.057873	-0.271470
C	-4.279815	-5.176898	-1.449334
C	-5.523906	-5.785372	-1.439340
C	2.522034	0.957870	-0.302322
C	2.577762	-0.377903	-0.610792
C	3.917407	-0.832937	-0.788652
C	4.863810	0.135597	-0.620476
S	4.119485	1.643345	-0.206851
C	1.408394	-1.276846	-0.773367
C	1.235022	-2.336555	0.138765
C	0.123723	-3.154671	0.022550
C	-0.797526	-2.946631	-0.999052
C	-0.581289	-1.950541	-1.939147
C	0.512825	-1.096064	-1.836330
C	6.309501	0.022703	-0.736372
C	7.208977	0.955757	-1.165553

C	8.553125	0.489721	-1.143595
C	8.680764	-0.792976	-0.695812
S	7.126063	-1.441327	-0.286081
C	2.218323	-2.579344	1.253315
N	-2.008666	-3.673924	-1.140852
N	-2.312260	-4.371306	-0.158208
C	0.692895	-0.003458	-2.857729
H	4.157398	-1.849835	-1.076264
H	-1.213046	3.017416	1.695009
H	-0.055015	-3.944587	0.742232
H	-1.301901	-1.828865	-2.742270
H	1.746538	0.170572	-3.085572
H	0.283422	0.946479	-2.500384
H	0.178073	-0.255220	-3.787241
H	2.512001	-1.647999	1.739707
H	3.130795	-3.057098	0.883267
H	1.784683	-3.231351	2.012572
H	-3.458845	-5.523734	1.814278
H	-3.877317	-4.770783	-2.369563
H	-6.075240	-5.854313	-2.368060
H	-5.713096	-6.601054	1.843555
H	-8.974643	-7.438164	-0.975284
H	-7.934159	-6.528195	-2.059390
H	-9.620353	-5.426541	0.245460
H	-9.938443	-5.282548	-1.471638
H	-9.035777	-3.184894	-1.084607
H	-7.575298	-4.024674	-1.524989
H	-7.462002	-4.490431	1.145659
H	-8.495350	-3.082660	1.202053
H	-5.709880	-3.280822	-0.040219
H	-6.094028	-2.517089	1.480003
H	-6.186043	0.507539	-0.860057
H	-4.391603	-1.065318	1.111513
H	-4.586692	0.677252	1.050043
H	-3.653669	0.578808	-1.359386
H	-3.218885	-1.093146	-1.030165
H	-2.314286	1.357852	0.549204
H	-1.331967	0.512589	-0.660681
H	2.051174	-0.369330	4.687269
H	-1.462234	-2.095835	2.928203
H	0.287672	-2.095653	4.689898
H	3.972419	2.362364	3.372993
H	3.883066	0.592873	3.546304
H	3.058149	1.655360	4.727790

H	-7.627578	-1.330121	-0.835952
H	6.915350	1.939541	-1.511763
H	9.397397	1.089403	-1.460011
H	-0.885219	8.349146	-1.061163
H	0.860903	6.404951	-0.806751
C	9.803083	-1.720990	-0.501975
C	9.585171	-2.812265	0.408255
C	10.762367	-3.648153	0.512110
C	11.790458	-3.133539	-0.320252
S	11.459876	-1.723603	-1.219252
H	8.634092	-2.922810	0.913693
H	10.598065	-4.474647	1.199392
H	12.696869	-3.733052	-0.270755
C	-3.726329	7.643341	-0.392009
C	-4.866207	6.763579	-0.453648
C	-6.088091	7.521634	-0.400409
C	-5.806013	8.918026	-0.305552
S	-4.116211	9.156069	-0.291663
H	-6.477064	9.770284	-0.247799
H	-7.118561	7.176949	-0.424477
H	-4.908458	5.683146	-0.531377

PTS-T6.*cis* optimized structure (wB97X-D/6-31+G*)

Total SCF energy = -4848.07627157 Hartree

S	-7.137431	1.014479	-0.037924
C	-5.866892	-0.016053	0.553677
C	-6.387480	-1.052970	1.284020
C	-7.801714	-1.008290	1.393494
C	-8.362980	0.061409	0.746230
C	-4.476596	0.273028	0.248170
S	-3.286351	-0.987347	0.256865
C	-2.013096	0.112778	-0.197701
C	-2.507864	1.397693	-0.336593
C	-3.908038	1.470045	-0.091448
C	-0.657996	-0.379714	-0.433214
C	-0.273252	-1.610023	-0.923471
C	1.125047	-1.697387	-1.154952
C	1.811655	-0.559575	-0.834669
S	0.736849	0.637337	-0.187804
C	-1.670127	2.591968	-0.624494
C	-1.493971	3.557801	0.385498

C	-0.581476	4.589658	0.186147
C	0.207130	4.617247	-0.959606
C	-0.051544	3.734370	-2.002396
C	-1.003113	2.726324	-1.854162
C	-1.163743	-2.767915	-1.160712
C	-2.096419	-2.794399	-2.202912
C	-2.929473	-3.901861	-2.378978
C	-2.811745	-4.978103	-1.506475
C	-1.888854	-4.984986	-0.466615
C	-1.064463	-3.870467	-0.299786
C	3.221623	-0.278720	-1.029504
C	3.861683	0.933381	-1.037258
C	5.257751	0.825925	-1.263800
C	5.684258	-0.464816	-1.439944
S	4.348028	-1.571628	-1.326418
O	-2.130032	-1.683044	-2.976855
C	-3.183268	-1.545810	-3.904238
O	-0.141716	-3.734712	0.679231
C	0.035531	-4.755925	1.642243
C	1.126427	-4.287675	2.592887
C	2.478151	-4.088411	1.903579
C	3.621383	-3.728165	2.869234
C	3.491764	-2.362000	3.493051
C	4.167464	-1.261669	3.148780
C	5.188078	-1.143450	2.052873
C	6.623149	-0.855121	2.523099
C	6.857912	0.496626	3.207405
C	6.469298	1.703319	2.365122
O	5.062430	1.874898	2.476408
C	4.438096	2.774736	1.692323
C	5.074660	3.680327	0.838851
C	4.303611	4.563615	0.091298
C	2.905046	4.551746	0.133293
C	2.284009	3.638785	1.006885
C	3.041929	2.776435	1.775489
N	2.339165	5.594726	-0.677272
N	1.188945	5.642286	-1.150183
C	-2.217312	3.461175	1.707229
C	-1.261944	1.765789	-2.987614
H	-4.466314	2.397545	-0.161638
H	1.585786	-2.579410	-1.585651
H	-0.417159	5.331189	0.963744
H	0.512163	3.822486	-2.926605
H	-2.335322	1.587056	-3.107893

H	-0.868387	2.164310	-3.927034
H	-0.796013	0.789383	-2.811670
H	-2.106739	2.464095	2.146203
H	-3.291342	3.643628	1.598494
H	-1.826052	4.194453	2.417993
H	4.782035	5.296597	-0.550645
H	6.155431	3.719224	0.764676
H	2.563105	2.066871	2.442192
H	1.212248	3.590583	1.104950
H	6.740091	1.543924	1.311430
H	6.972611	2.612682	2.720385
H	6.317461	0.558090	4.159123
H	7.924575	0.584029	3.446827
H	2.757989	-2.276630	4.294618
H	4.569826	-3.808591	2.329019
H	3.660989	-4.483419	3.667122
H	2.386017	-3.304228	1.143344
H	2.743428	-5.016066	1.377116
H	0.798188	-3.354021	3.063927
H	1.221860	-5.036955	3.390397
H	-0.906866	-4.930496	2.180041
H	0.327654	-5.693620	1.146241
H	-3.663510	-3.931867	-3.174687
H	-1.822927	-5.836523	0.200071
H	-3.460956	-5.838214	-1.641524
H	-3.060520	-0.557744	-4.349238
H	-3.127819	-2.305219	-4.694311
H	-4.159308	-1.604268	-3.407299
H	7.281383	-0.912608	1.645482
H	6.942123	-1.651591	3.206799
H	4.868724	-0.346400	1.371180
H	5.211792	-2.058383	1.455504
H	3.957315	-0.339116	3.688952
H	-8.384960	-1.724868	1.960986
H	-5.770598	-1.809610	1.755942
H	3.348094	1.878555	-0.904303
H	5.919315	1.683548	-1.315058
C	7.036159	-0.950735	-1.660304
C	7.448010	-2.135540	-2.212822
C	8.864958	-2.271695	-2.258581
C	9.514888	-1.191360	-1.742430
S	8.408373	0.006023	-1.179047
C	-9.764924	0.438211	0.653381
C	-10.306101	1.686486	0.484930

C	-11.728981	1.678641	0.440982
C	-12.252176	0.427790	0.578555
S	-11.018366	-0.764481	0.746332
H	6.756651	-2.879365	-2.593113
H	9.373995	-3.136048	-2.668066
H	10.580209	-1.027154	-1.659238
H	-9.704051	2.585936	0.418560
H	-12.333323	2.570045	0.322210
H	-13.293521	0.137044	0.590020

Section 4: Steady-state Spectroscopy

4.1. Absorption Spectra and Cyclability

A dilute solutions of **PTS-T4.*trans*** and **PTS-T6.*trans*** (~1 x 10^{-4} M) in THF were placed ~3.5 cm from the light source and irradiated with repeated alternating cycles of 30 sec with 350 nm and 254 nm wavelengths (each 6 W).

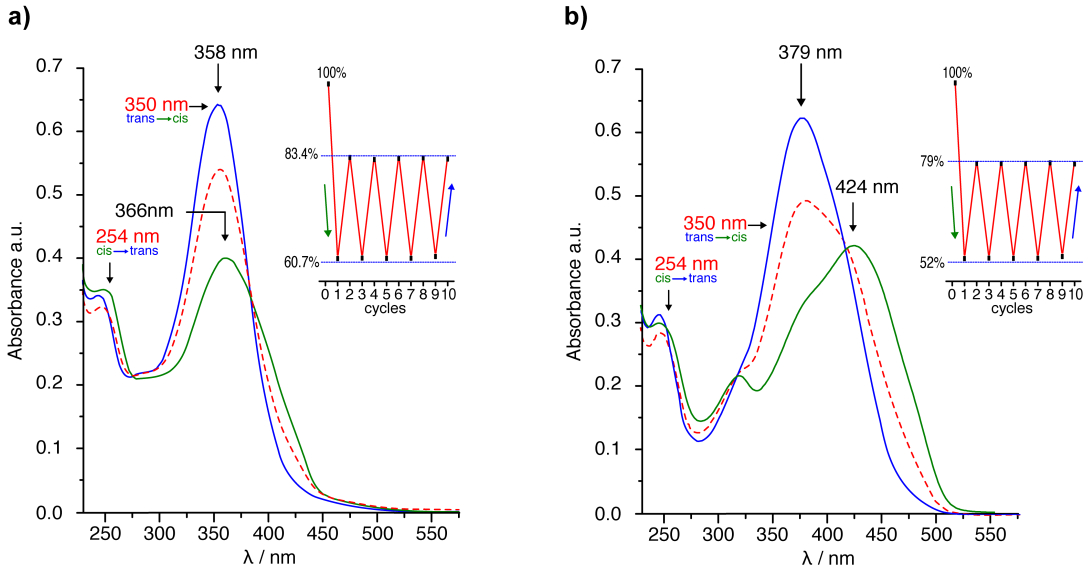


Figure S5: (a) Absorption spectrum of **PTS-T4.*trans*** (solid blue line***)***, **PTS-T4.*cis*** (solid green line), photostationary state from-*cis*-to-*trans* (red dashed line); inset shows measured absorbance at 358 nm of **PTS-T4** in THF solution alternating irradiation at 350 nm (green arrow) and at 254 nm (blue arrow) in repeated switching cycles. (b) Absorption spectrum of **PTS-T6.*trans*** (solid blue line***)***, **PTS-T6.*cis*** (solid green line), photostationary state from-*cis*-to-*trans* (red dashed line); inset shows measured absorbance at 379 nm of **PTS-T6** in THF solution alternating irradiation at 350 nm (green arrow) and at 254 nm (blue arrow) in repeated switching cycles.

4.2. Thermal relaxation

Dilute solutions of **PTS-T4.*trans*** and **PTS-T6.*trans*** (~1 x 10^{-4} M) in THF were irradiated with 350 nm wavelengths (~30 sec) to isomerize into the corresponding *cis* form. The solutions were then stored at 25°C in the dark, and absorption spectra measured every 3 h.

It was observed that compounds **PTS-T4.*cis*** and **PTS-T6.*cis*** have respectively a half-life ($\tau_{1/2}$) of ~17 h and ~8 h. These times are significantly shorter than that of **PTS-T2.*cis*** which exhibits a thermal relaxation with a $\tau_{1/2}$ = 120 h. Considering that the intrinsic properties of the azobenezene in **PTS-T2** should be comparable to those of **PTS-T4.*cis*** and **PTS-T6.*cis***, the fast thermal relaxation of **PTS-T4.*cis*** and **PTS-T6.*cis*** can be associated to a cross-talk between the molecular orbitals of the azobenzene with those of oligothiophenes. This interaction gradually increases from **PTS-T4.*cis*** to **PTS-T6.*cis*** and it leads to an electron directing-like behavior that reassembles push-pull functionalized azobenzenes. It is noteworthy that azobenzenes with not structural constrain such as hydroxyl-azobenzene and the alkoxy-azobenzene analogues have $\tau_{1/2}$ of ~12 h and ~16 h, respectively, that are longer half-life than **PTS-T6.*cis***.

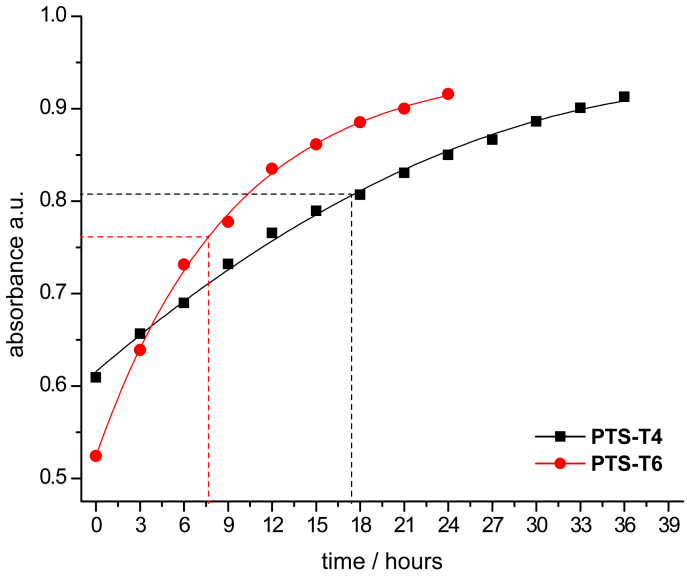


Figure S5: Measured absorbance at the corresponding λ_{max} of **PTS-T4** and **PTS-T6** in THF solution during the thermal relaxation. Dashed lines indicate the corresponding absorbance intensity at the observed half-life ($\tau_{1/2}$).

Section 5: Time Dependent Density Functional Theory (TDDFT) calculations

5.1. Computed absorption spectra

Excited states and electronic vertical transitions were evaluated at the TDDFT level of theory (wB96XD/6-311+G**), on top of the lowest-energy structures as derived from the CREST/GFN2-xTB conformational screening (see Section 3). Figure S6 reports the oscillator strengths and absorption spectra (as obtained from a convolution of Lorentzian functions peaked on each vertical transition, FWHM = 0.3 eV), for **PTS-T4** and **PTS-T6** in their trans-twisted and cis-planar conformations. TDDFT calculations, with the use of range-separated functionals, tend to overestimate the transitions energies.[5,6] Although in the current calculations we do not take into account the vibronic relaxations and spectral broadening effects,[7] the computed transition energies and band intensity ratio are consistent and in good agreement with the experimental findings. All calculations were performed in *vacuum*; small effects on the vertical transition energies are expected to occur with the inclusion of explicit or implicit solvent.

In **PTS-T4** the spectral shift between the calculated transition S_0->S_3 (**PTS-T4.*trans***) and S_0->S_2 (**PTS-T4.*cis***) is 42 nm. In **PTS-T6** the spectral shift between the calculated transition S_0->S_2 (**PTS-T6.*trans***) and S_0->S_2 (**PTS-T6.*cis***) is 37 nm.

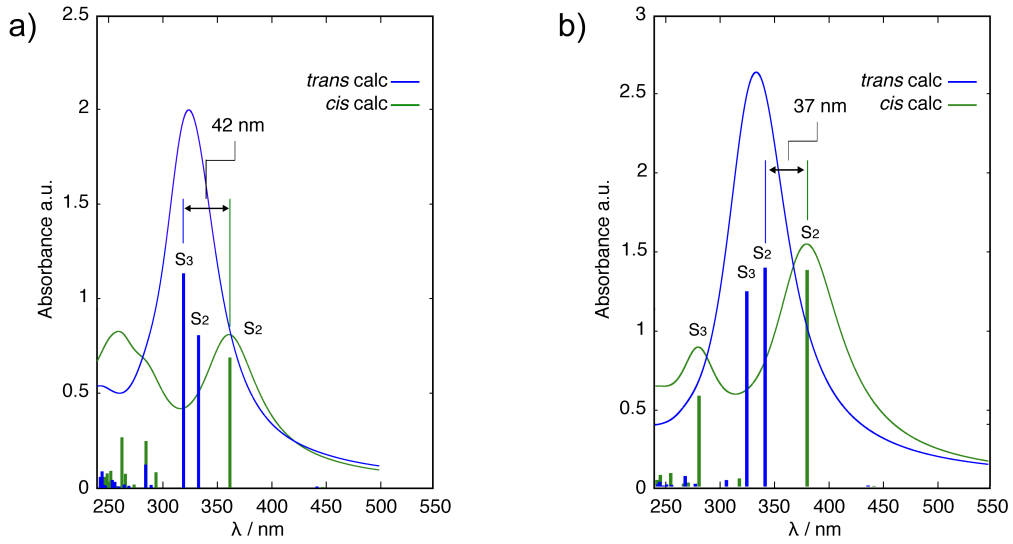


Figure S6. TDDFT (wB97X-D/6-311+G**) vertical transitions for **PTS-T4** and **PTS-T6**. Relevant excited states identified for the spectroscopic assignments (see manuscript) are reported. (a) Calculated absorption spectra of **PTS-T4.*trans*** (blue) and **PTS-T4.*cis*** (green). (b) Calculated absorption spectra of **PTS-T6.*trans*** (blue) and **PTS-T6.*cis*** (green).

[5] 'TD-DFT benchmarks: A review'A. D. Laurent; D. Jacquemin, I*nt. J. Quantum Chem.* 2013, **113**, 2019–2039

[6] 'Electronic Energy Gaps for π-Conjugated Oligomers and Polymers Calculated with Density Functional Theory' H. Sun, J. Autschbach, *J. Chem. Theory Comput.* 2014, **10**, 1035−1047

[7] 'Spectrum simulation and decomposition with nuclear ensemble: formal derivation and application to benzene, furan and 2-phenylfuran' R. Crespo-Otero and M. Barbatti, *Theor. Chem. Acc.*, 2012, **131**, 1237

5.2. Excited states assignments: MOs picture

As discussed in the manuscript, the conformational changes of the bithiophene unit, as induced by the *trans-cis* azobenzene isomerization, can be traced by monitoring the energy shift of the electronic transition that shows a large molecular orbital contribution localized on the thiophene segments. This transition has been called S_0->S_{thio}.

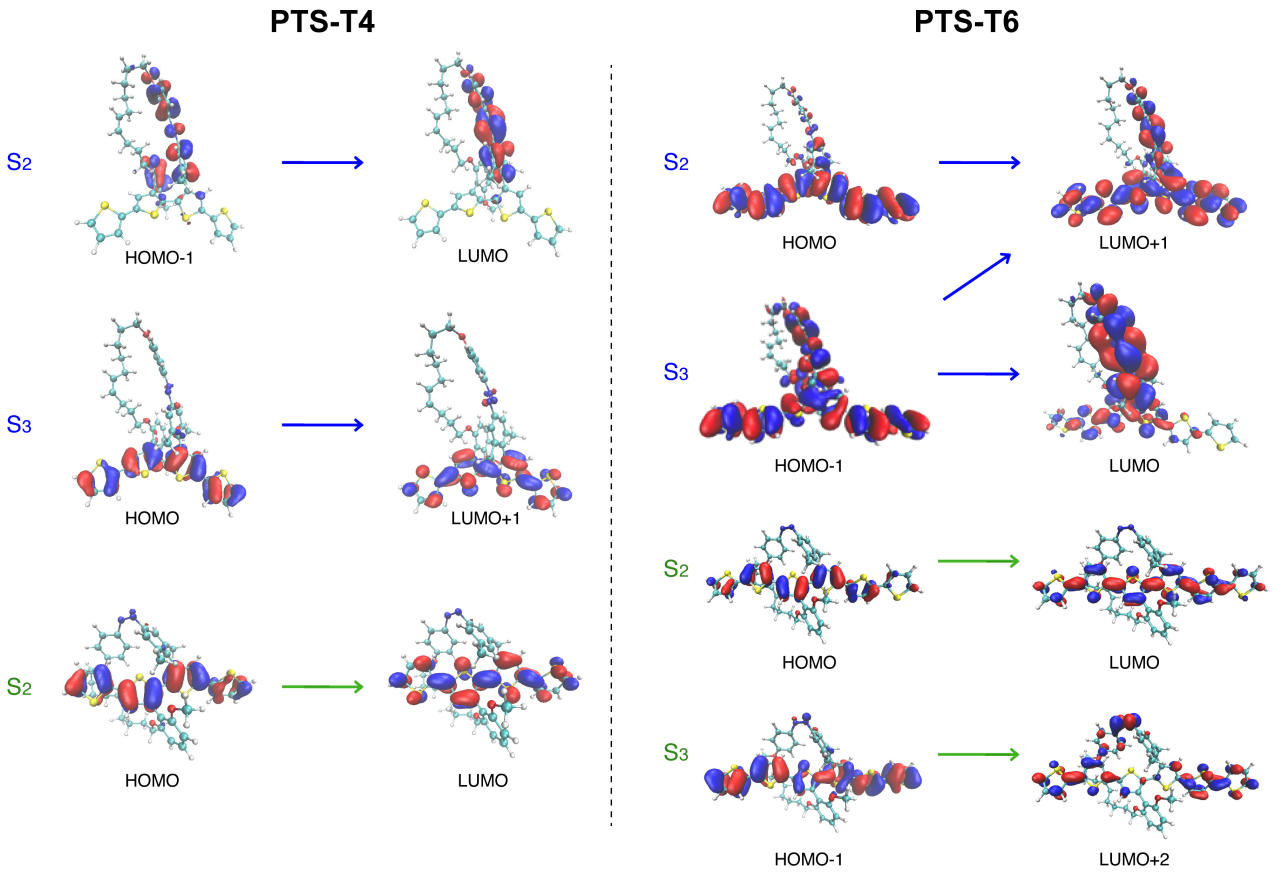


Figure S7: Association of molecular orbitals to S_0->S_{thio} transition.

In the tables below we report the assignments, based on a molecular orbitals (MOs) picture of each electronic transition discussed in the manuscript. Only the relevant MOs contributions for each electronic transition are shown.

PTS-T4	*energy*	*oscillator strength*	*MO contributions*
trans			
S_0 -> S_2 (S_0->S_{azo})	3.74 eV (330 nm)	f = 0.80	H-1 -> L
S_0 -> S_3 (S_0->S_{thio})	3.90 eV (317 nm)	f = 1.13	H -> L+1
cis			
S_0 -> S_2 (S_0->S_{thio})	3.45 eV (359 nm)	f=0.70	H -> L
S_0 -> S_2 (S_0->S_{azo})	4.24 eV (292 nm)	f=0.1	H -> L+1

PTS-T6	*energy*	*oscillator strength*	*MO contributions (main contribution)*
trans			
S_0 -> S_2 (S_0->S_{thio})	3.55 eV (348 nm)	f = 1.52	H -> L+1
S_0 -> S_3 (S_0->S_{azo})	3.72 eV (332 nm)	f = 1.36	H-1 -> L
cis			
S_0 -> S_2 (S_0->S_{thio})	3.21 eV (385 nm)	f=1.51	H -> L
S_0 -> S_2 (S_0->S_{azo})	3.80 eV (325 nm)	f=0.05	H -> L+1

Section 6: Field Effect Transistors

Bottom gate bottom contact transistor substrates were purchased from Fraunhofer Institute for Photonic Microsystems. The n-doped silicon wafer is used as bottom gate electrode, and a 230 nm SiO_2 is applied for dielectric layer. Au is used for source and drain electrodes, which is the most commonly used metal for source and drain electrodes in n-type OFETs because of its environmental stability, although its high work function may lead to a decrease of measured electron mobility. The thickness of Au is 30 nm, and 10 nm high work function ITO is used as the adhesion layer. The channel length (*L*) and width (*W*) are 2.5 μm and 10 mm, respectively. The substrates were successively cleaned by water, isopropanol, and acetone. After dried by argon, a 35 nm organic layer was spin coated on the substrates at 1000 rpm from a solution of **PTS-T6** in anhydrous THF with a concentration of 4 mg mL^{-1}. The current-voltage (*I-V*) characteristics of the transistors were measured in a nitrogen glovebox using a custom-built probe station and a Keithley 2612A dual-channel source measure unit. The electron mobility of the transistors was extracted from saturation regime according to the equation:

$$\mu = 2\left(\frac{\partial\sqrt{I_D}}{\partial V_{GS}}\right)^2 \frac{L}{WC_i}$$

Where *L* and *W* are the channel length and width, respectively. I_D is the current between source and drain electrode, and V_{GS} is the gate voltage. C_i (1.4×10^{-8} F cm^{-2}) is the capacity of the dielectric layer.

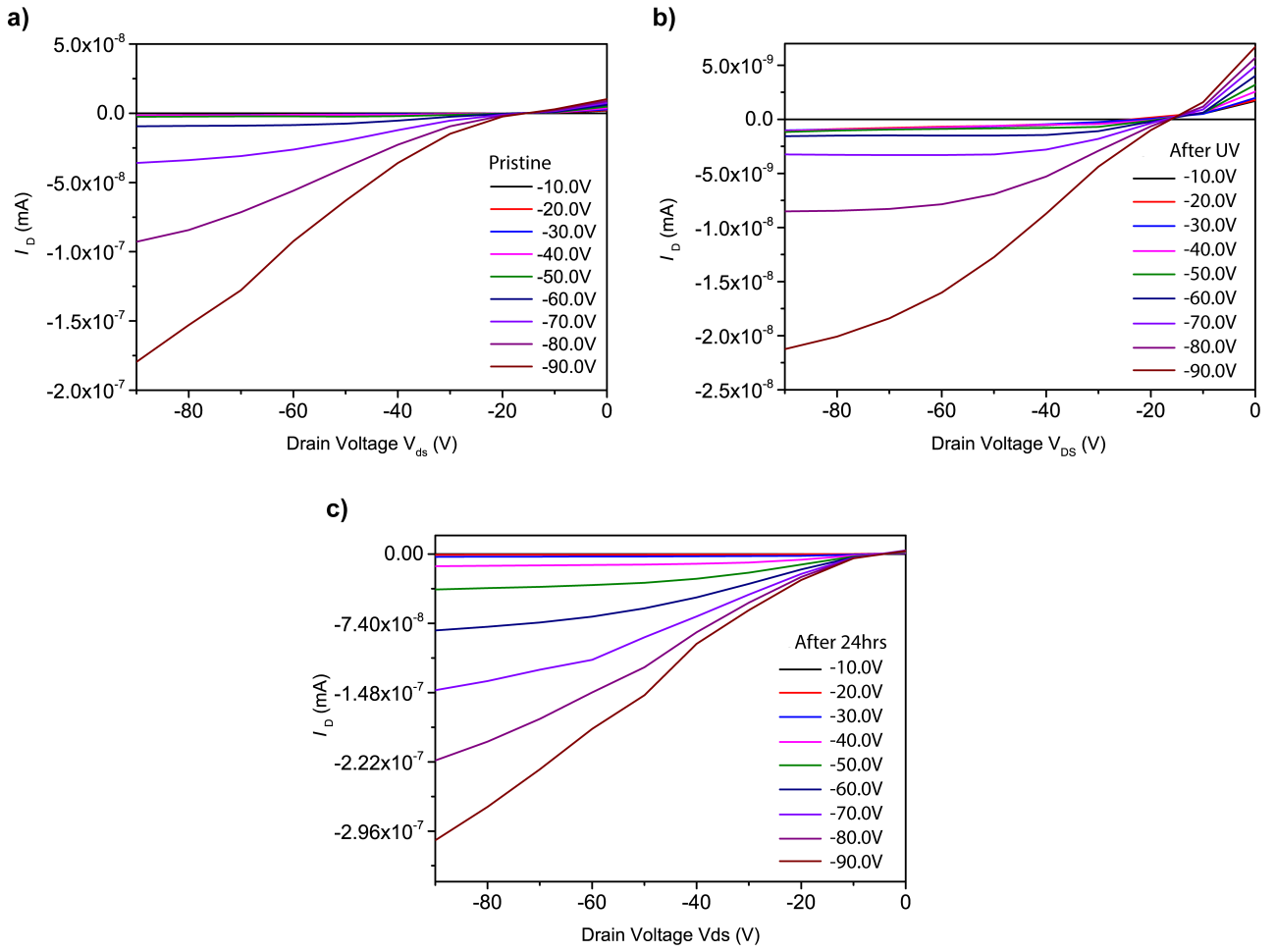


Figure S8: Output curve of: pristine **PTS-T6.*trans*** (a); **PTS-T6** after irradiation at 350nm (b); **PTS-T6** after irradiation at 350nm and 24 h of thermal relaxation.

Section 7: X-Ray Crystal Structures and Packing

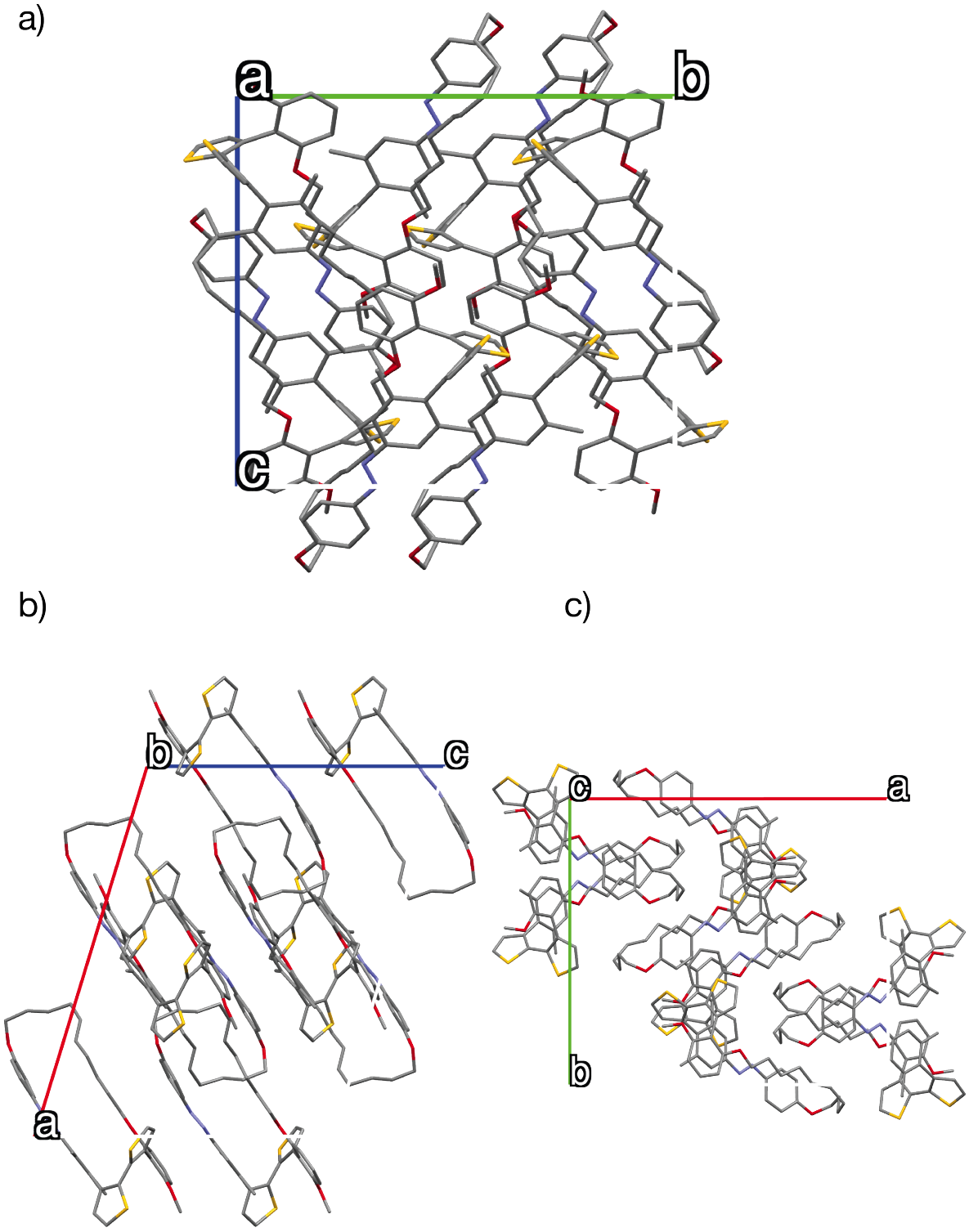


Figure S8: Unit cell structure of **PTS-T2** viewed along *a* (a), *b* (b) and *c* (c) axis.

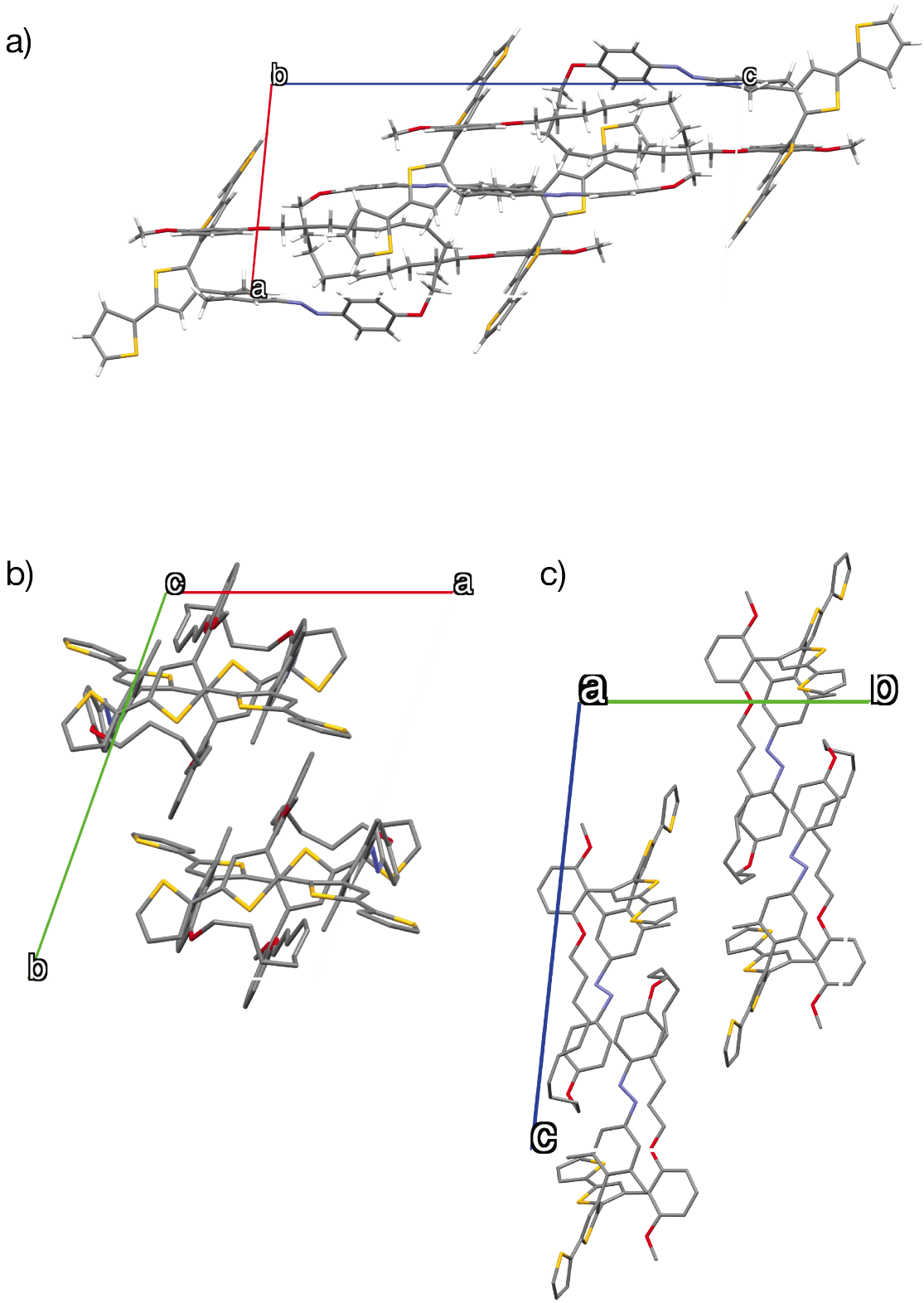


Figure S9: Unit cell structure of **PTS**-**T4** viewed along *b* (a), *c* (b) and *a* (c) axis.

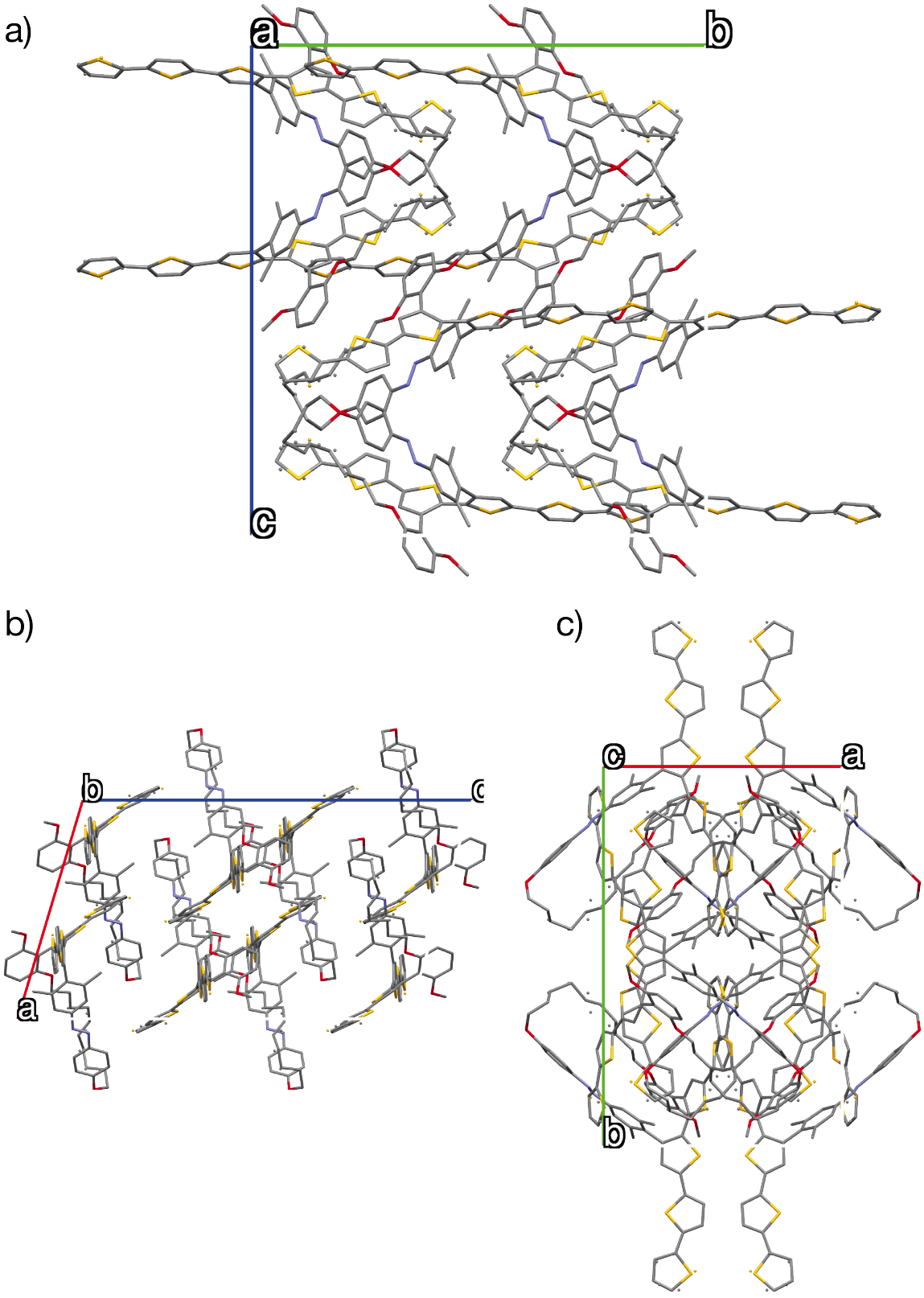


Figure S10: Unit cell structure of **PTS-T6** viewed along *a* (a), *b* (b) and *c* (c) axis.