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Supporting Information

Tuning the Temperature Dependence for Switching in Dithienylethene Photochromic Switches

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Table S1. The S_0 optimized structure of N-c[a] (in Angstroms)

Atom	X	Y	Z
S	1.842734	-2.244782	0.067178
C	0.639583	-0.871057	0.479244
C	1.434968	0.417969	0.213200
C	2.840368	0.198357	0.147812
C	3.219281	-1.114358	0.073572
C	-0.640155	-0.857488	-0.392035
C	-1.435136	0.426494	-0.099276
C	-0.722012	1.577631	0.061091
C	0.722921	1.576874	0.107253
C	-1.219404	2.985837	0.176742
C	-0.008755	3.835340	-0.305421
C	1.239316	2.984287	0.072331
S	-1.849959	-2.235624	-0.014479
C	-3.226168	-1.103424	-0.051360
C	-2.843673	0.209159	-0.092509
F	2.258217	3.177862	-0.814117
F	1.700277	3.396179	1.293963
F	-2.337004	3.246556	-0.556571

F	-1.500902	3.332853	1.472398
F	-0.071175	3.948174	-1.657529
F	0.016509	5.068370	0.235486
C	-0.353975	-0.900363	-1.915170
C	0.355319	-0.948205	2.000982
C	-4.597229	-1.618310	-0.018455
C	4.587798	-1.628953	-0.016768
H	3.543716	1.020013	0.081290
H	-3.547457	1.031852	-0.055651
H	-0.288914	-0.120155	2.312073
H	0.132175	-1.835460	-2.199974
H	-1.296970	-0.814864	-2.460678
H	1.299269	-0.877106	2.547033
H	-0.132433	-1.888565	2.265355
H	0.292524	-0.066888	-2.206563
C	-4.873561	-2.932476	0.402855
C	-6.181400	-3.409589	0.443196
C	-7.242092	-2.587125	0.060567
C	-6.983400	-1.281710	-0.366720
C	-5.678405	-0.802659	-0.409298

H	-4.060064	-3.580850	0.715818
H	-6.371410	-4.426066	0.776308
H	-8.261903	-2.960456	0.089739
H	-7.801311	-0.637192	-0.676642
H	-5.490612	0.204523	-0.767609
C	4.848586	-2.934970	-0.472227
C	6.153887	-3.411461	-0.565254
C	7.227482	-2.596516	-0.202824
C	6.984508	-1.299328	0.257405
C	5.682041	-0.821013	0.353039
H	4.024401	-3.576739	-0.770442
H	6.331881	-4.421441	-0.923780
H	8.245394	-2.969575	-0.273010
H	7.812926	-0.661041	0.551877
H	5.506940	0.178895	0.737161

[a]The S_0 energy is -2435.09936719 au.

Table S2. The S_0 optimized structure of N-o[a] (in Angstroms)

Atom	X	Y	Z
S	2.621464	-1.915272	1.538084
C	1.274387	-0.824065	1.384530

C	1.572923	0.191195	0.493214
C	2.899010	0.081891	-0.047611
C	3.598947	-1.010253	0.395137
C	-1.208498	-0.915188	-1.324865
C	-1.531863	0.132720	-0.481887
C	-0.655958	1.264369	-0.162840
C	0.660449	1.297565	0.172393
C	-1.240233	2.659106	-0.164019
C	-0.013148	3.598468	-0.222865
C	1.140118	2.724552	0.327303
S	-2.553092	-2.010106	-1.475809
C	-3.563604	-1.060600	-0.398560
C	-2.874074	0.045787	0.022482
F	2.298610	2.974931	-0.349962
F	1.371654	3.031036	1.635405
F	-2.090131	2.885680	-1.195936
F	-1.941776	2.897993	0.992622
F	0.237904	3.915773	-1.517113
F	-0.187614	4.734731	0.480510
C	0.050374	-1.166068	-2.099222

C	0.036368	-1.043198	2.201725
C	-4.935893	-1.467378	-0.070087
C	4.960349	-1.431877	0.040945
H	3.294999	0.782284	-0.771651
H	-3.287151	0.777696	0.706155
H	-0.468412	-0.091083	2.389410
H	-0.160605	-1.672253	-3.046767
H	0.553378	-0.221028	-2.324098
H	0.274518	-1.497042	3.169164
H	-0.679505	-1.698640	1.690538
H	0.758658	-1.786620	-1.536774
C	-5.332146	-2.816026	-0.101819
C	-6.637549	-3.184512	0.217111
C	-7.573257	-2.215828	0.583634
C	-7.192493	-0.872410	0.620541
C	-5.891884	-0.499898	0.291016
H	-4.607435	-3.583590	-0.360585
H	-6.920716	-4.233210	0.187099
H	-8.590250	-2.503802	0.834803
H	-7.914899	-0.108327	0.894827

H	-5.615886	0.550396	0.291572
C	5.353912	-2.780247	0.104372
C	6.648912	-3.163190	-0.238999
C	7.576543	-2.209863	-0.662028
C	7.198367	-0.866989	-0.730909
C	5.908442	-0.479657	-0.377117
H	4.634669	-3.536552	0.407739
H	6.930120	-4.211388	-0.183562
H	8.585404	-2.509172	-0.932051
H	7.914928	-0.114485	-1.049089
H	5.635408	0.571127	-0.402345

[a]The S_0 energy is -2435.11921934 au.

Table S3. The S_0 optimized structure of M-c[a] (in Angstroms)

Atom	X	Y	Z
S	1.517053	-2.312263	-0.023302
C	0.469330	-0.818736	0.400644
C	1.415738	0.373002	0.199272
C	2.791160	-0.007046	0.170887
C	3.015688	-1.350411	0.062318
C	-0.796225	-0.661207	-0.490049

C	-1.407784	0.718780	-0.186978
C	-0.596108	1.772975	0.035901
C	0.848254	1.604981	0.102314
C	-0.928039	3.224528	0.202855
C	0.374988	3.942414	-0.252382
C	1.516287	2.947300	0.112935
C	-1.913708	-1.644544	-0.229095
C	-3.150022	-1.128760	-0.130251
S	-3.163735	0.678063	-0.199570
F	2.562816	3.052323	-0.755652
F	2.002652	3.272002	1.351363
F	-2.006781	3.630321	-0.517472
F	-1.164736	3.551316	1.510962
F	0.336671	4.089608	-1.601911
F	0.534614	5.152187	0.316293
C	-0.462677	-0.697799	-2.014953
C	0.119893	-0.914861	1.906529
C	-4.428321	-1.845873	0.003531
C	4.317660	-2.020201	-0.007634
H	3.587392	0.727780	0.152683

H	-0.413191	-0.017553	2.235479
H	-0.129526	-1.694296	-2.314251
H	-1.359909	-0.444607	-2.586275
H	1.036722	-1.007998	2.493881
H	-0.510813	-1.785778	2.105205
H	0.324580	0.019451	-2.263878
C	-4.470178	-3.108094	0.622811
C	-5.669569	-3.806151	0.732678
C	-6.853695	-3.254486	0.237018
C	-6.827392	-1.997590	-0.368102
C	-5.627097	-1.297705	-0.482493
H	-3.559664	-3.530609	1.037458
H	-5.682159	-4.778454	1.217632
H	-7.790080	-3.797595	0.329284
H	-7.742791	-1.558374	-0.754796
H	-5.618517	-0.326608	-0.969939
C	4.444862	-3.315297	-0.542919
C	5.688662	-3.937536	-0.618094
C	6.831471	-3.282204	-0.157011
C	6.719999	-1.998253	0.383711

C	5.478958	-1.374656	0.461540
H	3.565992	-3.831200	-0.919163
H	5.764604	-4.935714	-1.040223
H	7.801123	-3.768917	-0.213061
H	7.602355	-1.484579	0.755199
H	5.402054	-0.388621	0.908815
H	-1.731191	-2.714371	-0.270216

[a]The S_0 energy is -2435.08768761 au.

Table S4. The S_0 optimized structure of M-o[a] (in Angstroms)

Atom	X	Y	Z
S	2.535758	-1.974042	1.547703
C	1.261524	-0.796091	1.416022
C	1.592569	0.174373	0.486394
C	2.885983	-0.040757	-0.101009
C	3.526316	-1.167658	0.343834
C	-1.376944	-0.823271	-1.140152
C	-1.527702	0.311891	-0.357900
C	-0.583595	1.389841	-0.110737
C	0.749370	1.333194	0.166064
C	-1.061559	2.825880	-0.141430

C	0.229558	3.668566	-0.271502
C	1.341539	2.722829	0.243501
C	-2.560920	-1.614016	-1.161585
C	-3.609359	-1.108129	-0.426615
S	-3.143199	0.394027	0.329984
F	2.475359	2.864767	-0.504344
F	1.671005	3.048396	1.526004
F	-1.920996	3.084742	-1.157600
F	-1.707946	3.149184	1.023825
F	0.444148	3.948710	-1.580417
F	0.169667	4.824323	0.418992
C	-0.153595	-1.178002	-1.940577
C	0.044355	-0.913294	2.283418
C	-4.949695	-1.676947	-0.241800
C	4.839462	-1.692178	-0.052658
H	3.299366	0.610449	-0.860183
H	-0.381761	0.074789	2.479688
H	0.526952	-1.825754	-1.374806
H	-0.437435	-1.711235	-2.854032
H	0.285678	-1.375104	3.246264

H	-0.736937	-1.518316	1.806532
H	0.412979	-0.287981	-2.227190
C	-5.146535	-3.067376	-0.335267
C	-6.415196	-3.619261	-0.177795
C	-7.513219	-2.798063	0.088558
C	-7.330427	-1.417851	0.192341
C	-6.064264	-0.861626	0.025317
H	-4.294194	-3.717019	-0.511297
H	-6.544661	-4.695663	-0.252048
H	-8.501713	-3.230358	0.216097
H	-8.178078	-0.768915	0.394803
H	-5.940537	0.216561	0.080719
C	5.138218	-3.064020	0.022857
C	6.387822	-3.544943	-0.362979
C	7.363195	-2.668273	-0.840923
C	7.079270	-1.303050	-0.921882
C	5.835402	-0.817965	-0.526057
H	4.379576	-3.761138	0.369029
H	6.595775	-4.609551	-0.297619
H	8.336425	-3.044139	-1.144028

H	7.834233	-0.609613	-1.282627
H	5.636598	0.249051	-0.561671
H	-2.643777	-2.519733	-1.753371

[a]The S_0 energy is -2435.11891698 au.

Table S5. The S_0 optimized structure of I-c[a] (in Angstroms)

Atom	X	Y	Z
C	1.639033	-1.746536	0.187407
C	0.636292	-0.656209	0.486062
C	1.409399	0.657919	0.282681
S	3.148953	0.413381	0.267687
C	2.927630	-1.373528	0.120445
C	-0.633138	-0.640738	-0.423806
C	-1.407757	0.664406	-0.179365
C	-0.732235	1.806994	0.043457
C	0.729321	1.811369	0.134212
C	-1.228505	3.214812	0.164908
C	-0.016823	4.062690	-0.317671
C	1.234111	3.224458	0.084389
C	-1.638543	-1.738751	-0.161472
C	-2.928522	-1.367031	-0.110310
S	-3.149218	0.422431	-0.240074

F	2.257082	3.410626	-0.793863
F	1.675679	3.652028	1.306123
F	-2.346034	3.469919	-0.565083
F	-1.500589	3.555598	1.462453
F	-0.067410	4.151952	-1.671706
F	-0.002025	5.303130	0.204513
C	-0.242577	-0.691909	-1.933441
C	0.247503	-0.755659	1.993414
C	-4.118527	-2.224354	0.013229
C	4.116499	-2.226942	-0.037577
H	-0.436635	0.048065	2.279869
H	0.244412	-1.643542	-2.168602
H	-1.139622	-0.600811	-2.551985
H	1.145753	-0.687482	2.613228
H	-0.241714	-1.713277	2.197940
H	0.444434	0.118807	-2.192484
C	-4.031760	-3.469285	0.662345
C	-5.145697	-4.298143	0.762051
C	-6.372363	-3.897204	0.226447
C	-6.474662	-2.658992	-0.408327

C	-5.359776	-1.828544	-0.512628
H	-3.089981	-3.774729	1.108802
H	-5.059409	-5.254474	1.270744
H	-7.242527	-4.542118	0.311207
H	-7.424295	-2.336140	-0.825877
H	-5.450383	-0.873667	-1.023108
C	4.020649	-3.461003	-0.705799
C	5.133639	-4.286839	-0.836420
C	6.368144	-3.893336	-0.313432
C	6.479226	-2.665651	0.340019
C	5.365303	-1.838458	0.475625
H	3.072174	-3.760162	-1.142223
H	5.040251	-5.234814	-1.359279
H	7.237436	-4.535807	-0.422204
H	7.434909	-2.348697	0.748170
H	5.462502	-0.892368	1.000988
H	-1.337464	-2.782103	-0.163134
H	1.338884	-2.790136	0.175545

[a]The S_0 energy is -2435.07553591 au.

Table S6. The S_0 optimized structure of I-o[a] (in Angstroms)

Atom	X	Y	Z
C	-2.553439	-1.657508	-1.151694
C	-1.413800	-0.805463	-1.160352
C	-1.588933	0.305286	-0.344583
S	-3.180760	0.286599	0.404691
C	-3.594611	-1.224577	-0.361296
C	1.406277	-0.800184	1.170598
C	1.572574	0.289906	0.327317
C	0.674831	1.403365	0.078701
C	-0.679789	1.415215	-0.111305
C	1.232434	2.807899	0.006868
C	0.006410	3.733709	0.193547
C	-1.200969	2.835030	-0.171997
C	2.550297	-1.646972	1.175178
C	3.584723	-1.229031	0.367814
S	3.154239	0.256904	-0.439275
F	-2.234540	3.048885	0.695848
F	-1.657997	3.148258	-1.415909
F	2.178396	3.057738	0.946163
F	1.809797	3.045310	-1.214138

F	-0.076331	4.099609	1.495590
F	0.071835	4.842789	-0.569389
C	0.206164	-1.056318	2.040104
C	-0.211603	-1.078953	-2.022075
C	4.885218	-1.872841	0.148954
C	-4.894665	-1.868070	-0.137410
H	0.280361	-0.154255	-2.335150
H	-0.545466	-1.663851	1.520919
H	0.499917	-1.592871	2.948289
H	-0.506044	-1.630335	-2.921172
H	0.537621	-1.680075	-1.492177
H	-0.283496	-0.124868	2.336987
C	5.019921	-3.265220	0.304265
C	6.251247	-3.887204	0.115201
C	7.372594	-3.136345	-0.245015
C	7.250958	-1.755467	-0.411157
C	6.022779	-1.128831	-0.212975
H	4.147476	-3.861987	0.553502
H	6.332668	-4.963836	0.238434
H	8.331627	-3.623596	-0.397054

H	8.117374	-1.160692	-0.687170
H	5.948088	-0.049892	-0.318421
C	-5.021923	-3.264630	-0.257393
C	-6.251690	-3.887457	-0.060917
C	-7.379175	-3.132927	0.271372
C	-7.265146	-1.747608	0.401949
C	-6.038446	-1.120420	0.196431
H	-4.144878	-3.863439	-0.484751
H	-6.327171	-4.967336	-0.156496
H	-8.337023	-3.620673	0.429221
H	-8.136365	-1.149952	0.655783
H	-5.969695	-0.038761	0.274151
H	2.619225	-2.526784	1.806538
H	-2.613759	-2.552450	-1.762369

[a]The S_0 energy is -2435.11916751 au.

Table S7. The calculated results[a] of three lowest singlet vertical excited states of N-c and N-o[b]

Excited state	N-c			N-o		
	λ_{max} (nm)	**Oscillator strength**	**Character**	**λmax (nm)**	**Oscillator strength**	**Character**
S_1	**602**	**0.428**	**HOMO -> LUMO**	**352**	**0.064**	**HOMO -> LUMO**
S_2	**411**	**0.003**	**HOMO-1 -> LUMO**	**333**	**0.010**	**HOMO-1 -> LUMO**
S_3	**365**	**0.139**	**HOMO -> LUMO+1**	**296**	**0.450**	**HOMO ->LUMO+2**

[a]TDDFT(B3LYP)/6-31G*

[b]The S_0 energies of N-c and N-o are -2435.09936719 au and -2435.11921934 au, respectively.

Table S8. The calculated results[a] of three lowest singlet vertical excited states of M-c and M-o[b]

Excited state	M-c			M-o		
	λ_{max} (nm)	Oscillator strength	Character	λmax (nm)	Oscillator strength	Character
S_1	521	0.248	HOMO -> LUMO	379	0.312	HOMO -> LUMO
S_2	379	0.020	HOMO-1 -> LUMO	345	0.330	HOMO-1 -> LUMO
S_3	358	0.096	HOMO -> LUMO+1	302	0.368	HOMO ->LUMO+2

[a]TDDFT(B3LYP)/6-31G*

[b]The S_0 energies of M-c and M-o are -2435.08768761 au and -2435.11891698 au, respectively.

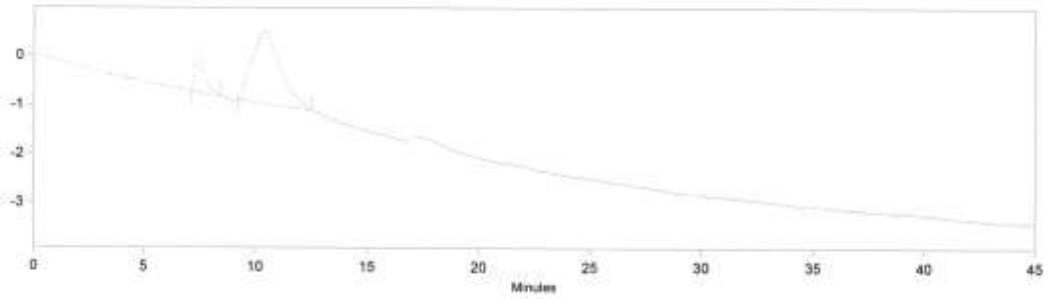
Table S9. The calculated results[a] of three lowest singlet vertical excited states of I-c and I-o[b]

Excited state	I-c			I-o		
	λ_{max} (nm)	Oscillator strength	Character	λmax (nm)	Oscillator strength	Character
S_1	455	0.051	HOMO -> LUMO	406	0.798	HOMO -> LUMO
S_2	348	0.002	HOMO -> LUMO+1	344	0.060	HOMO-1 -> LUMO
S_3	340	0.003	HOMO -1-> LUMO	302	0.126	HOMO-1 ->LUMO

[a]TDDFT(B3LYP)/6-31G*

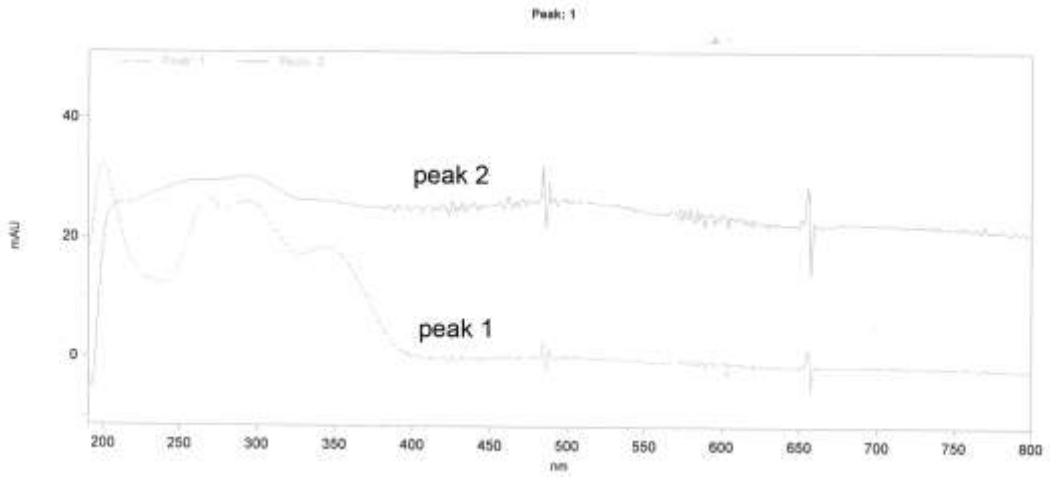
[b]The S_0 energies of M-c and M-o are -2435.07553591 au and -2435.11916751 au, respectively.

Sample ID: mixedPSS Data Name: C:\CLASS-VP\Data\20091023\20091023_02
User: System Method Name: C:\CLASS-VP\Methods\Algemeen\Chiralpak AD\AD 85_15 20 min.met
Vial # : 13 Inj. Vol : 1 ul
Sample Amt: 1
Acquired: 10/23/2009 2:46:52 PM Printed: 10/23/2009 3:37:43 PM

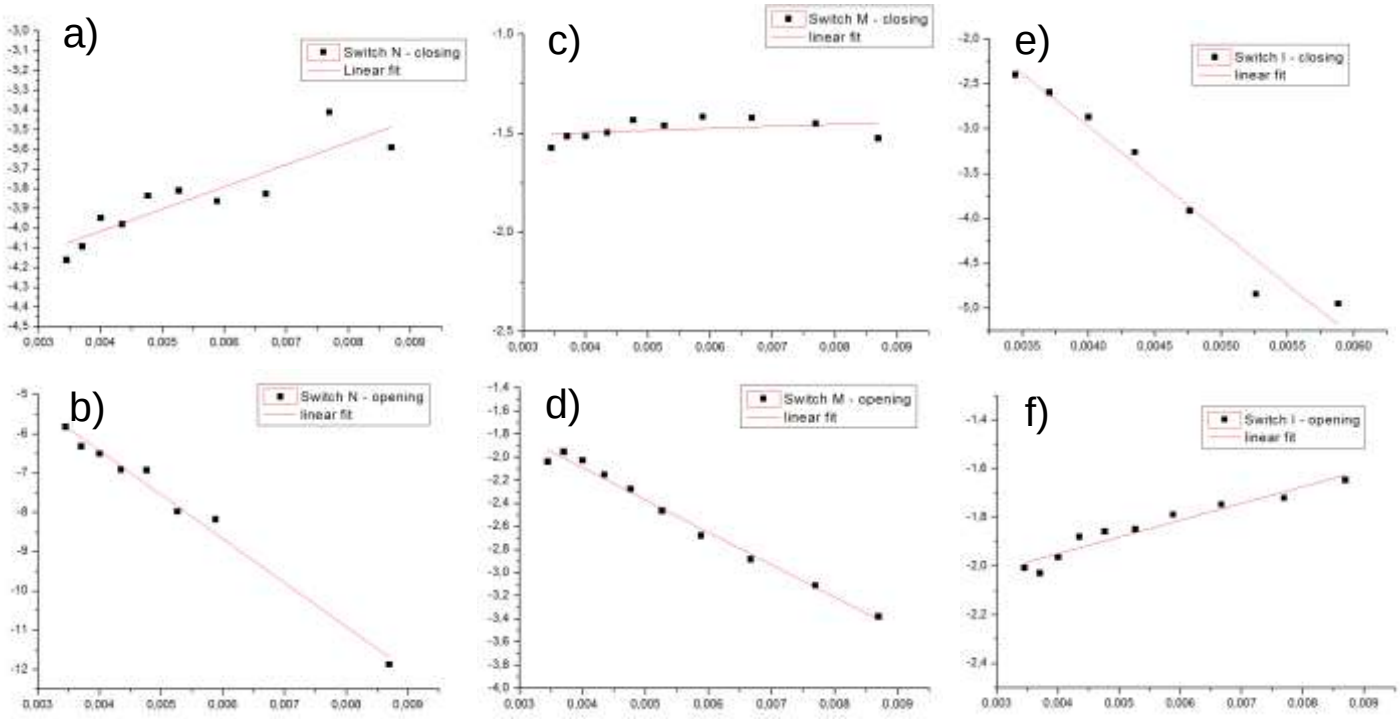


1: 500 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	7.467	26920	17.19
2	2	10.389	129675	82.81
Totals			156595	100.00



Supporting Figure 1. Determination of the photostationary state (PSS) of the switch **M**.



Supporting Figure 2. Temperature dependence of the rate constants for a) ring closing of switch N, b) ring opening of switch N, c) ring closing of switch M, d) ring opening of switch M, e) ring closing of switch I, f) ring opening of switch I, also with the corresponding linear fits (red curves) from which the activations energies were determined.

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