Supplementary Information

Electronic tuning effects via cyano substitution of a fused tetrathiafulvalene−benzothiadiazole dyad for ambipolar transport properties

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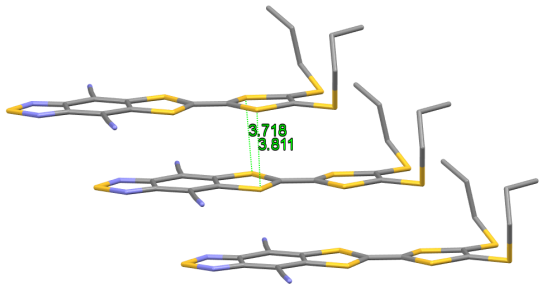


Fig. S1. View of the crystal packing arrangement of **1**. Hydrogen atoms have been omitted for clarity. A stack along the *a* axis is emphasized. Close S···S contacts are 3.718 Å (S2···S3) and 3.811 Å (S1···S4).

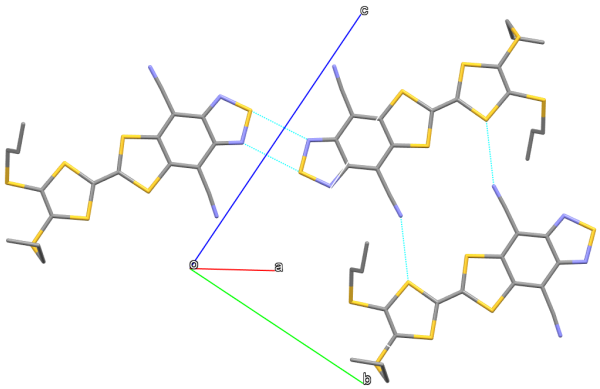


Fig. S2. View of the crystal packing arrangement of **1**. Hydrogen atoms have been omitted for clarity. Three molecules belonging to adjacent stacks are shown. Close N···S contacts are 3.221 Å (N4···S7) and 3.292 Å (N1···S2).

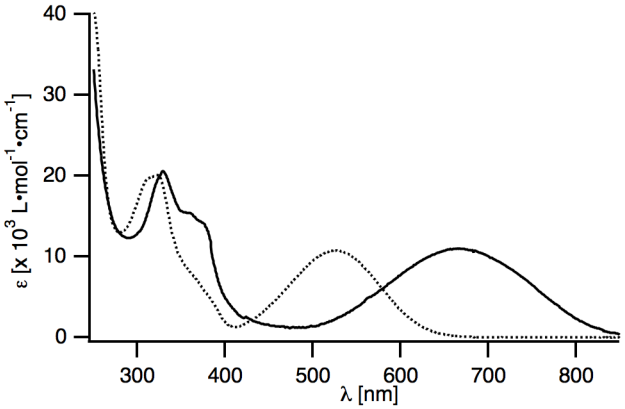


Fig. S3. UV-Vis spectra of **1** (black line) and the reference compound **2** (dotted line) in CH_2Cl_2 .

Table S1. Bond angles of the TTF moiety of dyad **1** optimized at the M06/cc-pVTZ and PBE0/cc-pVTZ level.

Atoms	**Angle [deg] M06**	**Angle [deg] PBE0**
S2-C9-C10	116.7	116.4
C9-C10-S4	116.7	116.4
C10-S4-C8	95.11	95.3
S4-C8-S2	113.0	112.9
C8-S2-C9	95.1	95.3
C7-C8-S4	123.3	123.5
C8-C7-S1	122.6	122.6
C7-S1-C3	95.6	95.9
S1-C3-C4	116.2	116.0
C3-C4-S3	116.2	116.0
C4-S3-C7	95.6	95.9
S3-C7-S1	114.9	114.8

Table S2. Selected backbone bond distances of dyad **1** optimized at the M06/cc-pVTZ and PBE0/cc-pVTZ level.

Atoms	**d** [Å] **M06**	**d** [Å] **PBE0**
S7-N3	1.62	1.62
S7-N4	1.62	1.62
N3-N3	1.32	1.33
N4-C1	1.32	1.33
N3-C1	1.43	1.43
N3-C5	1.42	1.42
C1-C2	1.42	1.42
C5-C17	1.42	1.42
C2-C18	1.42	1.42
N1-C17	1.15	1.15

C18-N2	1.15	1.15
C5-C4	1.38	1.38
C2-C3	1.38	1.38
C4-C3	1.43	1.43
C4-S3	1.74	1.74
C3-S1	1.74	1.74
S3-C7	1.76	1.75
S1-C7	1.76	1.75
C7-C8	1.34	1.35
C8-S2	1.76	1.75
C8-S4	1.76	1.75
S2-C9	1.78	1.76
S4-C10	1.77	1.76
C9-C10	1.34	1.35
C9-S6	1.75	1.74
C10-S5	1.75	1.74

Table S3. TD-DFT input coordinates of dyad **1** optimized at the M06/cc-pVTZ and PBE0/cc-pVTZ level.

Element	M06			PBE0		
	X [Å]	Y [Å]	Z [Å]	X [Å]	Y[Å]	Z [Å]
S	13.942311	0.008305	1.825092	-13.957519	0.000248	1.825687
N	12.062876	-2.348697	1.267138	-12.074549	2.353401	1.303795
C	9.850002	-1.349575	0.667364	-9.860508	1.354705	0.687987
C	7.616724	-2.708777	0.033895	-7.619663	2.715334	0.077889
C	7.597038	-5.388336	0.007008	-7.579483	5.393544	0.087476
C	7.499693	-7.560458	-0.039756	-7.469155	7.568646	0.070486
C	5.479688	-1.352370	-0.556726	-5.482426	1.351111	-0.529204
S	2.669494	-2.807875	-1.468904	-2.668471	2.788707	-1.410884
C	0.869630	-0.012293	-1.555054	-0.891675	0.000133	-1.546104
C	-1.655259	-0.025088	-1.787236	1.640045	0.000022	-1.795449
S	-3.484476	2.743351	-1.977777	3.451125	-2.755553	-2.036187
C	-6.391950	1.223293	-1.343505	6.355105	-1.274381	-1.354938
S	-9.090945	3.112155	-1.051540	9.032461	-3.174183	-1.092123
C	-8.021371	5.474576	1.244677	8.149803	-5.311899	1.466940
C	-10.256683	7.101832	1.973727	10.295474	-7.166531	1.901734
C	-9.494707	9.129511	3.847217	9.686336	-9.010167	4.019895
C	-6.382312	-1.314194	-1.374731	6.355301	1.273764	-1.354864
S	-9.050010	-3.255553	-1.130698	9.033023	3.173045	-1.092209
C	-8.153567	-5.261713	1.547384	8.150873	5.311652	1.466305
C	-10.248009	-7.148989	2.019765	10.296932	7.166059	1.900079
C	-9.613948	-8.867840	4.221536	9.688743	9.010330	4.017971
S	-3.461665	-2.796820	-2.059291	3.451464	2.755423	-2.035656
S	2.642706	2.797895	-1.398492	-2.668736	-2.788312	-1.411594
C	5.466152	1.346642	-0.520852	-5.482541	-1.350684	-0.529558
C	7.588566	2.708079	0.109018	-7.619888	-2.714904	0.077160
C	7.540768	5.386931	0.154531	-7.579945	-5.393122	0.085909
N	7.419979	7.558361	0.165400	-7.469773	-7.568226	0.068210
C	9.835572	1.355185	0.706268	-9.860616	-1.354263	0.687653
N	12.037341	2.360433	1.336052	-12.074815	-2.352942	1.302925
H	-7.248453	4.485463	2.881153	7.788449	-4.187356	3.157169
H	-6.524375	6.619175	0.405338	6.418170	-6.306967	0.955423
H	-11.058952	7.964656	0.275082	10.668778	-8.201503	0.152020
H	-11.740265	5.905817	2.772846	12.023811	-6.124865	2.349304
H	-11.101236	10.297583	4.388724	11.241125	-10.331561	4.316240
H	-8.716320	8.295525	5.566142	9.353504	-8.021493	5.801290
H	-8.052973	10.372478	3.052212	7.996398	-10.114008	3.588078
H	-6.381774	-6.221713	1.107324	6.419319	6.306801	0.954697

H	-7.849611	-4.050929	3.189126	7.789621	4.187750	3.156981
H	-12.014086	-6.139423	2.385253	12.025237	6.124231	2.347417
H	-10.559862	-8.264263	0.307834	10.669907	8.200529	0.150002
H	-11.113732	-10.235054	4.568647	11.243801	10.331601	4.313463
H	-7.875133	-9.918598	3.863966	7.998809	10.114291	3.586433
H	-9.339105	-7.782752	5.954566	9.356369	8.022183	5.799746

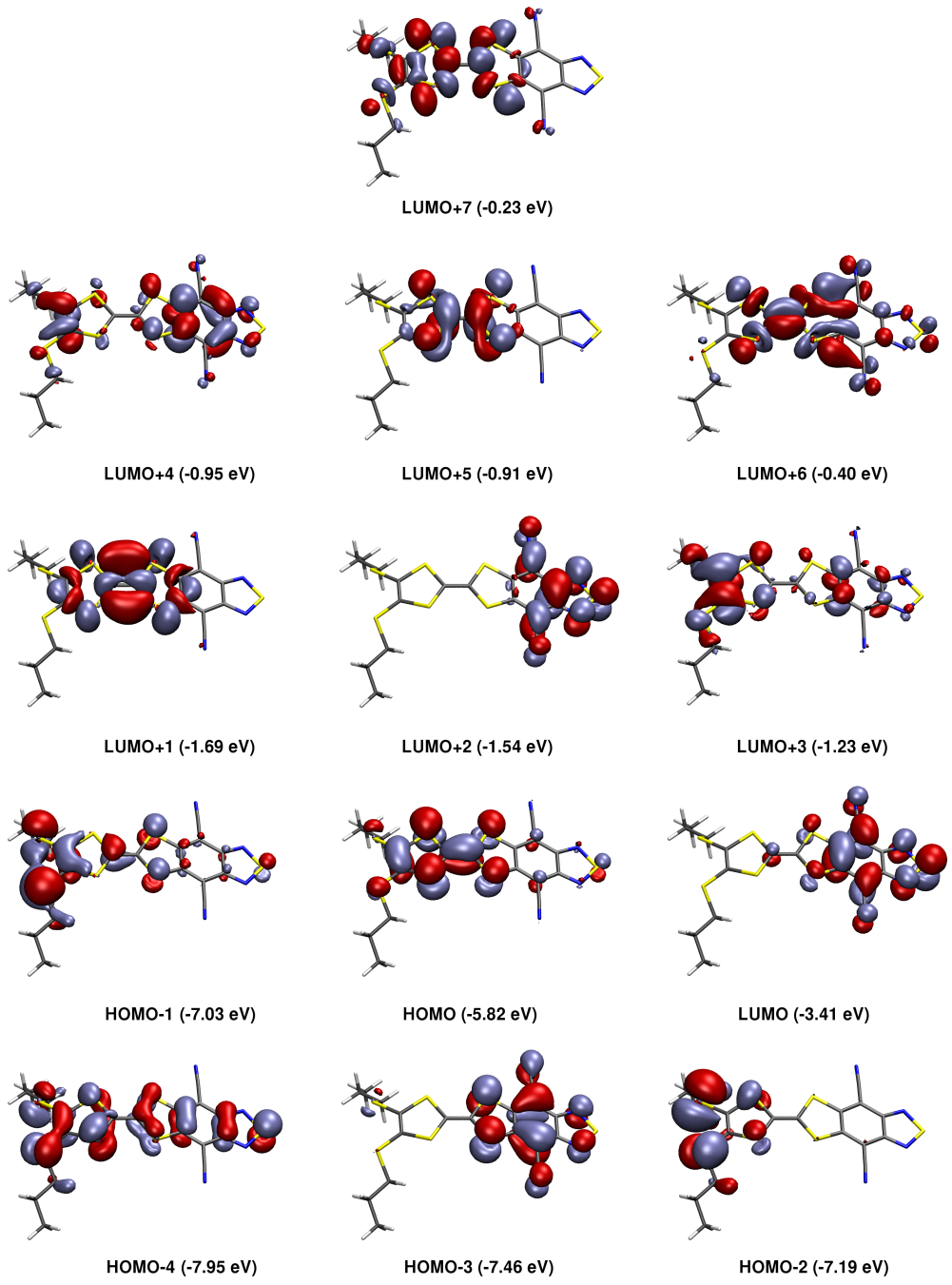


Fig. S4. Frontier molecular orbitals of dyad **1**.

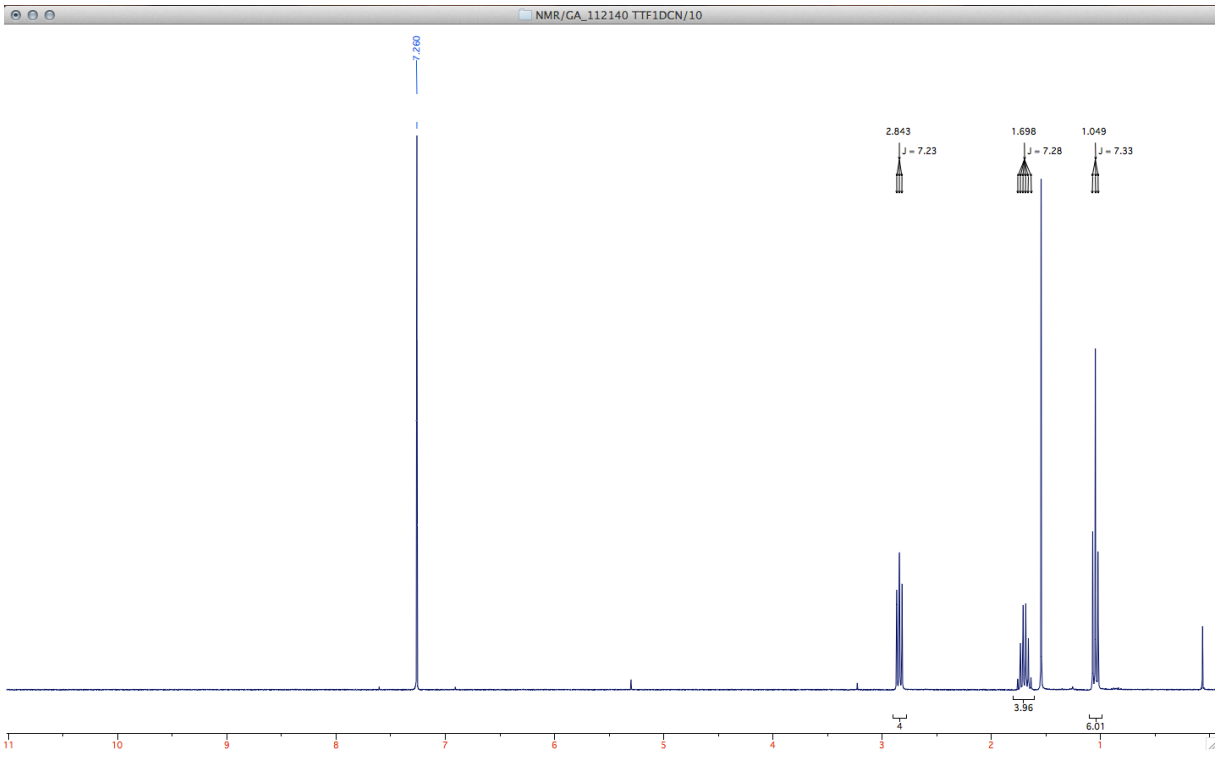
Table S4. Wavelength, oscillator strength, major orbital contributions, total electric dipole moments and nature of the transitions for the first ten excited states of dyad **1**.

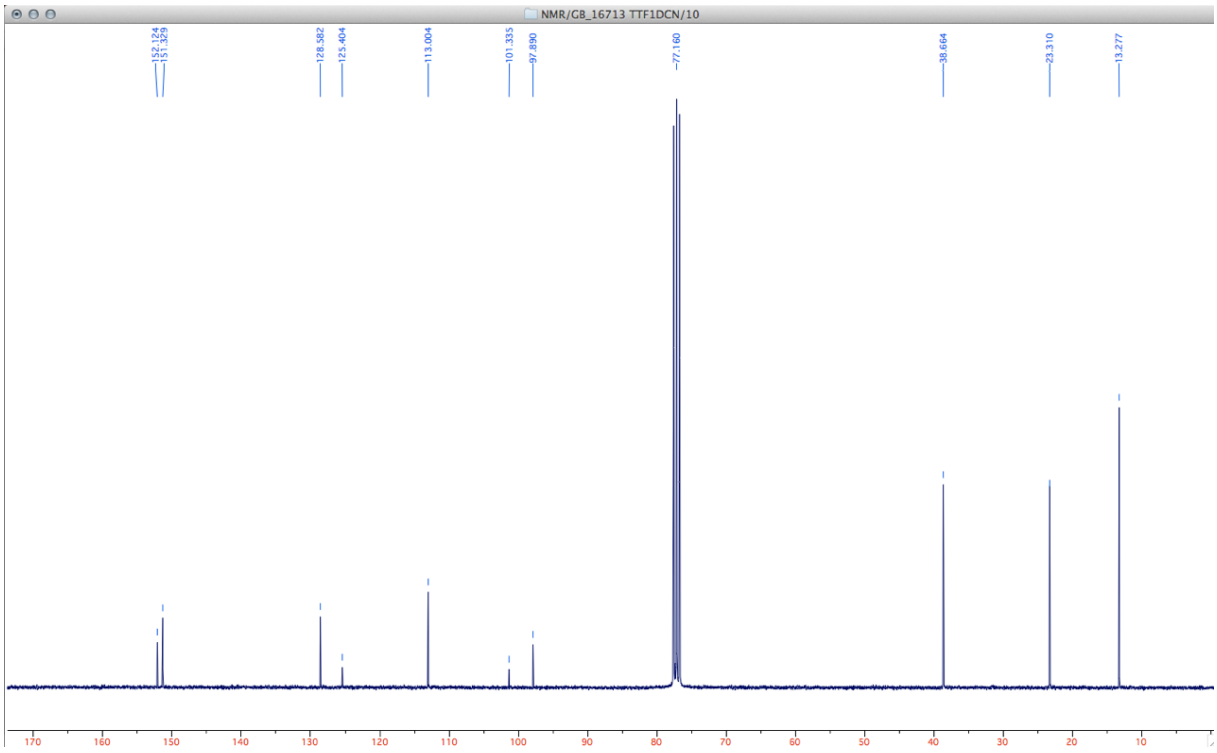
State	Wavelength [nm]		Oscillator strength f_{calc}		Major contributions [%]			μ [Debye]		Character
	M06	PBE0	M06	PBE0		M06	PBE0	M06	PBE0	
S_0								5.32	5.48	
S_1	653.19	668.7	0.2426	0.2458	HOMO → LUMO	100	100	10.54	10.90	π → π* CT
S_2	436.10	422.58	0.0004	0.0001	HOMO → LUMO+1	100	100	5.33	5.49	π → σ*
S_3	397.89	400.11	0.1017	0.0897	HOMO-1 → LUMO	100	100	6.65	6.67	π → π* CT
S_4	380.01	387.11	0.0354	0.0064	HOMO-3 → LUMO HOMO-2 → LUMO	29 71	2 98	5.76	5.56	π → π* π → π* CT
S_5	367.02	365.71	0.0474	0.0786	HOMO-3 → LUMO HOMO-2 → LUMO	70 30	98 2	5.89	6.43	π → π* π → π* CT
S_6	345.28	345.26	0.0335	0.0296	HOMO → LUMO+3 HOMO → LUMO+6 HOMO-4 → LUMO HOMO → LUMO+2	97 4 - -	- - 3 97	5.70	5.82	π → π* π → σ* π → π* π → π* CT
S_7	339.88	343.99	0.0244	0.0270	HOMO-4 → LUMO HOMO → LUMO+2 HOMO → LUMO+3	4 96 -	- - 100	5.59	5.79	π → π* CT π → π* CT π → π*
S_8	317.39	317.06	0.3016	0.2640	HOMO-4 → LUMO HOMO → LUMO+2 HOMO → LUMO+4 HOMO → LUMO+5	76 3 8 13	92 3 - 5	8.47	8.20	π → π* CT π → π* CT π → π* CT π → π*
S_9	316.98	315.14	0.0700	0.0331	HOMO-4 → LUMO HOMO → LUMO+2 HOMO → LUMO+4 HOMO → LUMO+6	8 3 86 3	- - 100 -	6.05	5.82	π → π* CT π → π* CT π → π* CT π → σ*
S_{10}	307.44	297.75	0.0559	0.1968	HOMO-4 → LUMO HOMO-4 → LUMO+1 HOMO-4 → LUMO+2 HOMO-1 → LUMO+1 HOMO → LUMO+5 HOMO → LUMO+7	11 - 2 29 36 23	3 2 - 23 57 15	5.89	7.41	π → π* CT π → σ* π → π* CT π → π* CT π → π* π → σ*

Kohn-Sham energy

E_{KS} = -0.21400 a.u. = -5.82 eV

NMR spectra of dyad **1** in $CDCl_3$





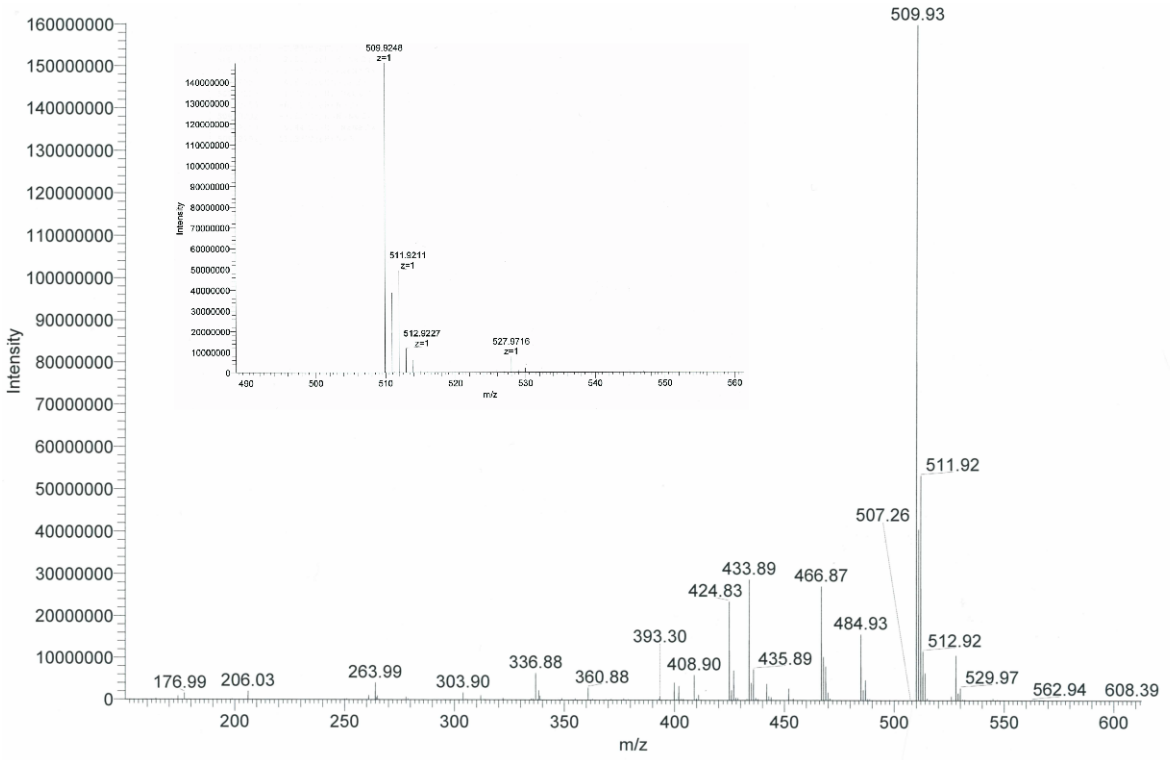


Fig. S5. ESI-MS spectrum of dyad **1**.