Supporting information for

Design, synthesis and evaluation of redox, second order nonlinear optical properties and theoretical DFT studies of novel bithiophene azo dyes functionalized with thiadiazole acceptor groups

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Here we show the results of the calculations for the 8 isomers in detail (Tables S1 – S4) and of the 12 possible transition states (Tables S5 – S6). The notation is based on the suggestion of Kinnibrugh et al [16] is explained in the main text and the corresponding structures for compound **4a** are shown as an example in Table S1. The transition state names indicate the molecule and the beginning and final configurations between which the transition state is located. For example, '**4a**_ccc_cct' signifies that the structure is **4a** and the transition takes place between the isomeric forms ccc and cct.

In Table S2 and S3 the HOMO and LUMO energies as well as the spectroscopic data of the isomers in Vacuum (Table 1) and DMF (Table S3) are shown. The data for the HOMO and LUMO energies were obtained from DFT calculations (B3LYP/6-311+G(2d,2p)). The spectroscopic data are the results of TDDFT calculations using B3LYP /6-31G* and 6 states (nstates=6). Table S4 served to evaluate the quality of the calculations. The resulting total energies (in hartree) obtained using different sets of large basis functions for the same functional (B3LYP) are compared, and the values are normalized by the reduction in energy compared to that obtained when the smallest

basis set used. The reduction in energy is greatest between the basis sets 6-31+G(d,p) and 6-311+G(2d,2p), the basis set that was used in most calculations.

In Table S5 and S6, the transition state energies as well as the energy differences between initial and final configurations are shown in for the molecules in the vacuum as well as in the solvent DMF. The transition states are calculated by employing the *Synchronous Transit-Guided Quasi-Newton* (STQN) algorithm [19].

Table S1. The different isomeric structures and the corresponding nomenclatures as well as the calculated values for the HOMO-LUMO gap ΔE, the spectroscopic energy gap ΔE_{spectr} with the corresponding absorption wavelength and the oscillator strength are given for DMF as solvent. Note that the values only vary marginally between the isomers.

[a] $\Delta E = E_{LUMO} - E_{HOMO}$. [b] Oscillator strength of the transition.

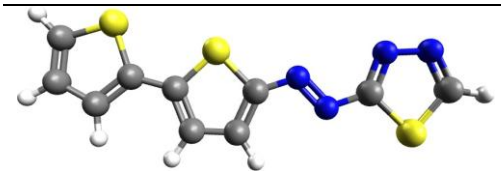
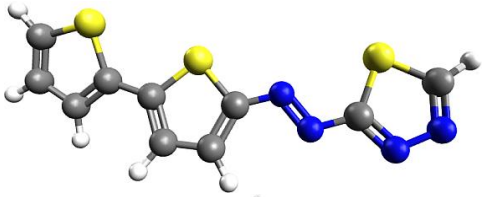
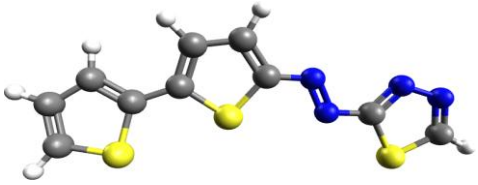
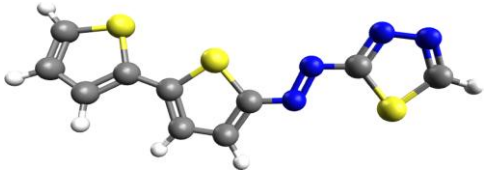
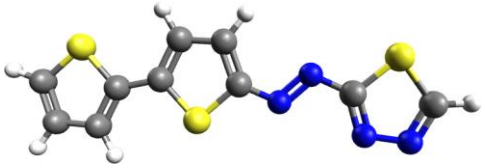
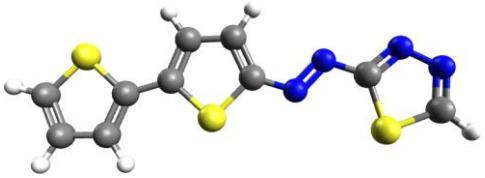
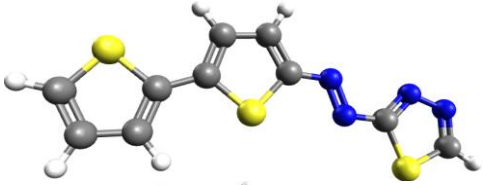
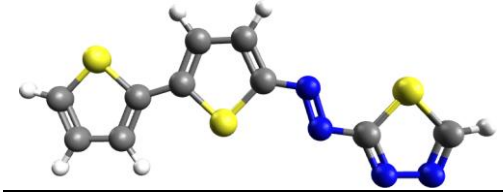
	Isomer	ΔE^{a} (eV)	E_{spectr} (eV)	λ_{max} (nm)	f-value[b]
	ccc	2.614763	2.4498	506.11	1.2046
	cct	2.604966	2.4433	507.45	1.1672
	ctc	2.623742	2.4564	504.75	1.1398
	ctt	2.618572	2.4563	504.75	1.1525
	tcc	2.611497	2.4366	508.83	1.1862
	tct	2.602245	2.4466	506.76	1.1521
	ttc	2.632450	2.4606	503.88	1.1615
	ttt	2.626464	2.459	504.21	1.1699

Table S2: HOMO and LUMO energies as well as the spectroscopic data for the isomeric structures of the different molecules in vacuum.

Structure	E(HO)/eV	E(LU)/eV	ΔE=E(LU)-E(HO) / eV	E-spectroc / eV	wavelength /nm	Oscillator strength
4a_ccc	-6,078527	-3,308114	2,770413	2,7148	456,69	1,022
4a_cct	-6,189278	-3,384307	2,804972	2,7255	454,9	0,9409
4a_ctc	-6,136216	-3,324713	2,811503	2,7395	452,58	0,9435
4a_ctt	-6,177577	-3,386484	2,791094	2,7241	455,14	0,9297
4a_tcc	-6,089684	-3,322264	2,767420	2,7011	459,02	1,005
4a_tct	-6,154448	-3,402538	2,751909	2,6844	461,87	0,9604
4a_ttc	-6,125331	-3,343761	2,781570	2,7212	455,62	0,9794
4a_ttt	-6,166693	-3,402811	2,763882	2,7067	458,06	0,974
4b_ccc	-6,154448	-3,441451	2,712997	2,652	467,51	1,1585
4b_cct	-6,254314	-3,513834	2,740480	2,6597	466,15	1,0701
4b_ctc	-6,203156	-3,456962	2,746195	2,6709	464,2	1,0673
4b_ctt	-6,219755	-3,518732	2,701023	2,6437	468,98	1,0689
4b_tcc	-6,164516	-3,453696	2,710820	2,6397	469,69	1,1407
4b_tct	-6,224109	-3,530977	2,693132	2,6232	472,65	1,0885
4b_ttc	-6,199619	-3,471384	2,728235	2,6607	465,99	1,1053
4b_ttt	-6,236082	-3,529889	2,706194	2,6455	468,66	1,1152
4c_ccc	-6,318261	-3,621320	2,696942	2,6607	465,99	1,0868
4c_cct	-6,418400	-3,707581	2,710820	2,6539	467,19	0,9869
4c_ctc	-6,355541	-3,627578	2,727963	2,6799	462,65	1,0106
4c_ctt	-6,394998	-3,708941	2,686057	2,6507	467,74	1,0186
4c_tcc	-6,327241	-3,634109	2,693132	2,6463	468,52	1,0691
4c_tct	-6,393910	-3,723363	2,670546	2,6218	472,9	1,0024
4c_ttc	-6,358535	-3,640096	2,718439	2,6747	463,54	1,0441
4c_ttt	-6,411053	-3,720914	2,690139	2,6517	467,56	1,0352
5a_ccc	-5,950633	-3,253691	2,696942	2,5655	483,27	1,4008
5a_cct	-5,993355	-3,324169	2,669186	2,5389	488,34	1,3213
5a_ctc	-5,956347	-3,274100	2,682247	2,5523	485,77	1,2893
5a_ctt	-5,951993	-3,332877	2,619117	2,5114	493,68	1,3607
5a_tcc	-5,923421	-3,271651	2,651770	2,5312	489,82	1,4102
5a_tct	-5,969681	-3,341040	2,628641	2,5078	494,4	1,3343
5a_ttc	-5,948184	-3,290699	2,657485	2,5372	488,67	1,327
5a_ttt	-5,968592	-3,344034	2,624559	2,5136	493,25	1,3782
5b_ccc	-5,991994	-3,308931	2,683064	2,5543	485,4	1,401
5b_cct	-6,034989	-3,379681	2,655308	2,5279	490,47	1,3232
5b_ctc	-5,998253	-3,328251	2,670002	2,5421	487,72	1,2895
5b_ctt	-5,994715	-3,387300	2,607416	2,5022	495,49	1,3644
5b_tcc	-5,965599	-3,326346	2,639253	2,5211	491,78	1,4116
5b_tct	-6,008593	-3,397368	2,611225	2,4947	496,99	1,3392
5b_ttc	-5,991178	-3,344578	2,646600	2,5279	490,45	1,3259
5b_ttt	-6,011587	-3,398729	2,612858	2,5046	495,03	1,3822
5c_ccc	-6,220028	-3,617510	2,602517	2,4688	502,21	1,4713
5c_cct	-6,272274	-3,705131	2,567142	2,431	510,01	1,3139
5c_ctc	-6,231456	-3,628939	2,602517	2,4711	501,74	1,3967
5c_ctt	-6,241797	-3,704859	2,536937	2,421	512,12	1,4132
5c_tcc	-6,197986	-3,630572	2,567414	2,4418	507,77	1,4757
5c_tct	-6,246423	-3,719554	2,526869	2,4008	516,43	1,3316
5c_ttc	-6,230096	-3,644722	2,585374	2,4603	503,94	1,4308
5c_ttt	-6,258940	-3,714111	2,544829	2,4254	511,19	1,4245

Table S3: HOMO and LUMO energies as well as the spectroscopic data for the isomeric structures of the different molecules in DMF.

Structure	E(HO)/eV	E(LU)/eV	ΔE=E(LU)-E(HO) / eV	E-spectroc / eV	wavelength/nm	Oscillator strength
4a_ccc	-6,047506	-3,432743	2,614763	2,4498	506,11	1,2046
4a_cct	-6,067643	-3,462676	2,604966	2,4433	507,45	1,1672
4a_ctc	-6,082609	-3,458866	2,623742	2,4564	504,75	1,1398
4a_ctt	-6,100569	-3,481996	2,618572	2,4563	504,75	1,1525
4a_tcc	-6,052948	-3,441451	2,611497	2,4366	508,83	1,1862
4a_tct	-6,072541	-3,470295	2,602245	2,4466	506,76	1,1521
4a_ttc	-6,091861	-3,459411	2,632450	2,4606	503,88	1,1615
4a_ttt	-6,109004	-3,482541	2,626464	2,459	504,21	1,1699
4b_ccc	-6,063017	-3,544855	2,518161	2,3571	526	1,348
4b_cct	-6,079344	-3,573972	2,505372	2,3487	527,89	1,3002
4b_ctc	-6,098664	-3,563631	2,535033	2,3682	523,53	1,2618
4b_ctt	-6,111997	-3,587849	2,524148	2,3649	524,26	1,2972
4b_tcc	-6,067643	-3,553563	2,514080	2,3443	528,87	1,3287
4b_tct	-6,091045	-3,529617	2,561428	2,3871	519,39	1,2789
4b_ttc	-6,107099	-3,567985	2,539114	2,3686	523,44	1,2852
4b_ttt	-6,119889	-3,590026	2,529862	2,3659	524,04	1,3124
4c_ccc	-6,300030	-3,664858	2,635171	2,6334	470,81	1,1391
4c_cct	-6,367787	-3,754112	2,613674	2,6127	474,54	1,0668
4c_ctc	-6,321255	-3,678192	2,643063	2,6314	471,17	1,0459
4c_ctt	-6,375678	-3,759010	2,616667	2,6151	474,11	1,0549
4c_tcc	-6,307377	-3,673294	2,634083	2,6206	473,11	1,1211
4c_tct	-6,169142	-3,646627	2,522515	2,3744	522,16	1,2124
4c_ttc	-6,335405	-3,685539	2,649866	2,6353	470,48	1,0723
4c_ttt	-6,389828	-3,765269	2,624559	2,6183	473,53	1,0721
5a_ccc	-5,968592	-3,443084	2,525509	2,3097	536,79	1,558
5a_cct	-5,969409	-3,476010	2,493399	2,2839	542,85	1,4976
5a_ctc	-5,993355	-3,465669	2,527686	2,3097	536,8	1,4489
5a_ctt	-5,996620	-3,490704	2,505916	2,2959	540,02	1,5289
5a_tcc	-5,968048	-3,451791	2,516257	2,2962	539,96	1,5475
5a_tct	-5,970497	-3,458322	2,512175	2,2913	541,1	1,4853
5a_ttc	-6,002335	-3,469207	2,533128	2,3119	536,29	1,4788
5a_ttt	-6,006416	-3,493425	2,512991	2,2985	539,41	1,5444
5b_ccc	-5,968592	-3,448798	2,519794	2,305	537,89	1,5577
5b_cct	-5,977572	-3,480364	2,497209	2,2856	542,45	1,4929
5b_ctc	-5,994171	-3,471112	2,523060	2,3059	537,68	1,4484
5b_ctt	-5,996620	-3,496146	2,500474	2,2918	540,99	1,5309
5b_tcc	-5,968592	-3,457506	2,511086	2,2919	540,96	1,5474
5b_tct	-5,969409	-3,462948	2,506460	2,2868	542,16	1,4904
5b_ttc	-6,002607	-3,476554	2,526053	2,3062	537,6	1,4778
5b_ttt	-6,006961	-3,498595	2,508365	2,2951	540,22	1,5479
5c_ccc	-6,039615	-3,625674	2,413941	2,1886	566,49	1,5973
5c_cct	-6,058119	-3,682818	2,375301	2,1504	576,56	1,4259
5c_ctc	-6,075534	-3,638735	2,436799	2,2047	562,37	1,5107
5c_ctt	-6,083697	-3,690709	2,392988	2,1686	571,73	1,5358
5c_tcc	-6,044513	-3,633021	2,411492	2,182	568,2	1,5856
5c_tct	-6,051588	-3,664314	2,387274	2,1571	574,77	1,4326
5c_ttc	-6,083153	-3,643905	2,439248	2,2052	562,24	1,5324
5c_ttt	-6,094038	-3,693703	2,400335	2,1731	570,55	1,545

Table S4: Total energies (in hartree) for the all isomeric forms of structures **4a**, **4b** and **5a**. In the columns labeled 'normalized', the reductions in the energies compared to those obtained using the smallest basis set are indicated.

Structure	6-31G*	6-31+G(d,p)	6311+G(2d,2p)	6311+G(3df,2pd)	6-31+G(d,p) normalized	6-311+G(2d,2p) normalized	6-311+G(3df,2pd) normalized
4a_ccc	-1798,138910	-1798,174478	-1798,403243	-1798,444137	-0,035568	-0,264333	-0,305227
4a_ctc	-1798,145486	-1798,180685	-1798,409146	-1798,449779	-0,035198	-0,263659	-0,304292
4a_tcc	-1798,140395	-1798,175960	-1798,404412	-1798,445278	-0,035565	-0,264017	-0,304883
4a_cct	-1798,146511	-1798,181687	-1798,41037	-1798,451237	-0,035176	-0,263859	-0,304726
4a_ctt	-1798,151957	-1798,186669	-1798,415182	-1798,455839	-0,034712	-0,263224	-0,303881
4a_tct	-1798,147833	-1798,182811	-1798,411253	-1798,452062	-0,034978	-0,263420	-0,304229
4a_ttc	-1798,146866	-1798,182019	-1798,410216	-1798,450847	-0,035153	-0,263350	-0,303981
4a_ttt	-1798,153435	-1798,188108	-1798,416339	-1798,456991	-0,034673	-0,262905	-0,303556
4b_ccc	-4369,237340	-4369,294651	-4371,934495	-4371,985219	-0,057311	-2,697155	-2,747879
4b_ctc	-4369,243891	-4369,300764	-4371,941856	-4371,990847	-0,056874	-2,697965	-2,746956
4b_tcc	-4369,238804	-4369,296095	-4371,937135	-4371,986341	-0,057291	-2,698331	-2,747537
4b_cct	-4369,245689	-4369,302493	-4371,943795	-4371,992964	-0,056804	-2,698106	-2,747275
4b_ctt	-4369,251070	-4369,307396	-4371,943795	-4371,997557	-0,056326	-2,692725	-2,746488
4b_tct	-4369,251070	-4369,303686	-4371,944654	-4371,996635	-0,052616	-2,693584	-2,745565
4b_ttc	-4369,245267	-4369,302137	-4371,942935	-4371,991899	-0,056870	-2,697667	-2,746632
4b_ttt	-4369,252563	-4369,308920	-4371,949758	-4371,998732	-0,056357	-2,697196	-2,746169
5a_ccc	-2029,202983	-2029,251719	-2029,52985	-2029,579355	-0,048735	-0,326866	-0,376371
5a_ctc	-2029,209402	-2029,257694	-2029,535584	-2029,584860	-0,048291	-0,326182	-0,375458
5a_tcc	-2029,204348	-2029,252996	-2029,530856	-2029,580354	-0,048648	-0,326507	-0,376005
5a_cct	-2029,210939	-2029,259194	-2029,285936	-2029,586717	-0,048256	-0,074997	-0,375778
5a_ctt	-2029,216159	-2029,263965	-2029,541969	-2029,591246	-0,047806	-0,325810	-0,375087
5a_tct	-2029,212159	-2029,260347	-2029,538127	-2029,588353	-0,048188	-0,325968	-0,376194
5a_ttc	-2029,210783	-2029,259032	-2029,536658	-2029,585909	-0,048249	-0,325875	-0,375126
5a_ttt	-2029,217712	-2029,265567	-2029,543213	-2029,592469	-0,047856	-0,325502	-0,374757

Table S5: Transition state energies and the energy differences between the initial and final configurations both in vacuum and in DMF for structures **4a**, **4b** and **4c**.

Structure	VACUUM E(TS)-E(educt) kcal/mol	DMF E(TS)-E(educt) kcal/mol	VACUUM E(prod)-E(educt) kcal/mol	DMF E(prod)-E(educt) kcal/mol
4a_ccc_cct	4,123430961	4,390800422	-4,769483882	-4,333100877
4a_ccc_ctc	12,61755065	13,345776	-4,12649321	-4,183408367
4a_ccc_tcc	3,463673222	4,427597608	-0,931789599	-0,618197752
4a_ctt_cct	16,14402507	17,34226169	3,417595163	3,878105927
4a_ctt_ctc	8,518322748	8,605584289	4,060585834	4,027798437
4a_tct_tcc	8,838446975	8,711269523	4,667162101	4,2969061
4a_tct_cct	4,275903341	5,049296866	0,829467818	0,582002975
4a_ttc_tcc	16,92126523	17,51785154	4,06028463	4,167093107
4a_ttc_ctc	4,829599339	5,593893969	0,865581019	0,601882492
4a_ttt_ctt	4,852208525	5,59329156	0,927051898	0,596504731
4a_ttt_tct	16,41606321	17,33811385	3,515179243	3,892607683
4a_ttt_ttc	8,56017139	8,566069984	4,122056714	4,022420676
4b_ccc_cct	4,222050432	4,478036862	-5,238848811	-4,855653555
4b_ccc_ctc	13,22228831	14,17904026	-4,110686233	-4,165825537
4b_ccc_tcc	3,605233203	4,679894278	-0,918862893	-0,588729882
4b_ctt_cct	16,65085235	18,15449809	3,37658111	3,836966371
4b_ctt_ctc	9,049120907	9,185271752	4,504743688	4,526794389
4b_tct_tcc	9,425300602	9,332880929	5,150758958	4,851568465
4b_tct_cct	4,427585058	5,325809147	0,83077304	0,584644792
4b_ttc_tcc	17,51242358	18,33632538	4,055634781	4,175790396
4b_ttc_ctc	4,975740144	5,852189635	0,86381144	0,598694741
4b_ttt_ctt	4,996353847	5,84748331	0,936991657	0,562732142
4b_ttt_tct	16,93443667	18,12174206	3,482799727	3,815053722
4b_ttt_ttc	9,099961767	9,125476323	4,577923904	4,490831791
4c_ccc_cct	3,950652358	4,544126215	-4,803206269	-4,537135754
4c_ccc_ctc	13,73392231	14,88790065	-4,211721618	-4,258747218
4c_ccc_tcc	3,675740227	4,841766758	-0,889420124	-0,557781089
4c_ctt_cct	17,31430612	19,0165525	3,42152965	3,851706581
4c_ctt_ctc	8,491082539	8,968008964	4,013014302	4,130095117
4c_tct_tcc	8,78986515	9,042255947	4,722439457	4,525369941
4c_tct_cct	4,499353377	5,50919267	0,808653311	0,546015276
4c_ttc_tcc	18,01448805	18,99383664	4,068222631	4,18487674
4c_ttc_ctc	5,035786575	1,425313664	0,745921137	0,483910611
4c_ttt_ctt	5,099271762	6,079756137	0,926135734	0,548839071
4c_ttt_tct	17,59117608	18,96065391	4,193228898	3,854530376
4c_ttt_ttc	8,535240417	16,03384687	4,193228898	4,195023577

Table S6: Transition state energies and the energy differences between the initial and final configurations in vacuum and in DMF for structures **5a**, **5b** and **5c**.

Structure	VACUUM E(TS)-E(educt) kcal/mol	DMF E(TS)-E(educt) kcal/mol	VACUUM E(prod)-E(educt) kcal/mol	DMF E(prod)-E(educt) kcal/mol
5a_ccc_cct	4,825037342	5,025570712	-4,992061678	-4,552384247
5a_ccc_ctc	12,50085889	13,18606843	-4,027955315	-4,174347122
5a_ccc_tcc	3,491892347	4,395870703	-0,856588801	-0,615116678
5a_ctt_cct	15,65201958	16,2070961	3,275834379	3,861169432
5a_ctt_ctc	9,398920081	9,42582771	4,239940743	4,239206556
5a_tct_tcc	9,80137362	9,596391203	4,901204506	4,558960552
5a_tct_cct	4,224478896	5,024020763	0,765731628	0,621692982
5a_ttc_tcc	16,59384306	17,2565752	4,037769571	4,168442253
5a_ttc_ctc	4,783640507	5,559757425	0,866403057	0,609211808
5a_ttt_ctt	4,784387244	5,519741113	0,974353602	0,602039369
5a_ttt_tct	15,96350927	16,92425846	3,484456353	3,841515818
5a_ttt_ttc	9,481487847	9,397916065	4,347891288	4,232034117
5b_ccc_cct	4,837838546	5,049579245	-5,054028291	-4,59309082
5b_ccc_ctc	12,63111741	13,20084629	-4,037298938	-4,1714041
5b_ccc_tcc	3,522822315	4,402647811	-0,855409082	-0,614288364
5b_ctt_cct	15,89886946	15,70300477	3,277811035	3,853620486
5b_ctt_ctc	9,472602305	9,500175095	4,294540388	4,275307206
5b_tct_tcc	9,881274468	9,665599281	4,968335525	4,604342075
5b_tct_cct	4,930145267	5,025721315	0,769716316	0,625539618
5b_ttc_tcc	16,72557624	17,26646476	4,038842613	4,162160878
5b_ttc_ctc	4,80801927	5,568875146	0,856952756	0,605045142
5b_ttt_ctt	5,180866887	5,5252381	0,969910832	0,600822
5b_ttt_tct	16,0816945	16,92058752	3,47800555	3,828902868
5b_ttt_ttc	9,552779258	9,454737096	4,407498463	4,271084064
5c_ccc_cct	4,638001711	5,017827239	-4,854906818	-4,475420145
5c_ccc_ctc	13,66310781	14,16802746	-4,061006266	-4,171335074
5c_ccc_tcc	3,781940019	4,707586295	-0,848952004	-0,589840575
5c_ctt_cct	16,8787075	17,97704453	3,3948542	3,861370235
5c_ctt_ctc	9,190222805	9,577088996	4,188754752	4,165455306
5c_tct_tcc	9,600702197	6,314087196	4,840166608	4,483948006
5c_tct_cct	4,523819992	5,329473805	0,834211794	0,598368435
5c_ttc_tcc	17,78315022	12,31846683	4,049416156	4,156017555
5c_ttc_ctc	5,0750185	5,854806352	0,837361894	0,574523055
5c_ttt_ctt	5,107830998	5,862167044	0,943091054	0,580158095
5c_ttt_tct	8,249033106	17,95752897	3,50373346	3,843159895
5c_ttt_ttc	9,255803875	9,333357836	4,294483912	4,171090346

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