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Supporting Information

Unraveling the Structural Origins of Stimulated Emission Redshift in Cyanine Dye 1122C: A Combined AIMD and Machine Learning Study

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1. Exploration of reaction pathway in the ground state

The 1122C molecule possesses multiple conformational isomers (conformers) due to the presence of two ethyl side chains. In this study, we systematically explored the thermodynamically stable conformers in the electronic ground state using the single-component artificial force induced reaction (SC-AFIR) method¹, as implemented in the GRRM17 program¹⁻³. For this exploration, an artificial force parameter of $\gamma = 200 \text{ kJ mol}^{-1}$ was applied to specific atoms of 1122C (Fig. S1a), and a constrained exhaustive search (FirstOnly condition) was performed, in which newly obtained structures were not further explored. To reduce computational cost, SC-AFIR calculations were carried out using the density functional based tight binding (DFTB) method, specifically the DFTBA method,⁴ which employs analytical matrix elements implemented in the Gaussian16 program.⁵ The initial structure for the SC-AFIR search was a pre-optimized S_0 -MIN(*trans*) conformer with C_2 symmetry (see Fig. 3c). The stable conformers obtained from the SC-AFIR search were subsequently re-optimized using density functional theory (DFT) at the ω B97XD/6-31G(d) level. This procedure yielded the minimum-energy (MIN) structures corresponding to conformers in the ground state of the 1122C molecule, as shown in Fig. S1b. To further characterize the relationships between these structures, we employed the double-sphere AFIR (DS-AFIR) method¹ in the GRRM17 program, to compute intrinsic reaction coordinates (IRCs) connecting each of the S_0 -MIN structures. In this study, DS-AFIR calculations were performed for structures in which the ethyl chains were oriented in the same direction relative to the quinoline rings. Since the 1122C is a cationic molecule with an even number of electrons, its ground state was treated as a closed-shell singlet. All calculations were performed in the gas phase, and the counterion (iodine, I⁻) was excluded from consideration.

As a result of the structural search, nine stable conformers of 1122C were identified (Fig. S1b). These conformers were categorized into three groups: three *trans* conformers, four *cis* conformers with one twisted quinoline ring (single-twisted *cis*), and two *cis* conformers with both

quinoline rings twisted (double-twisted *cis*). Within each group, conformers exhibited slight variations in the orientation of the ethyl side chains. Among them, *trans*1, *trans*3, and *cis*5 possessed C_2 symmetry, whereas the remaining conformers were asymmetric. The *trans* conformers were found to be more thermodynamically stable than the *cis* conformers. The IRCs are summarized in Table S1 (a prime symbol indicates structures with inversion symmetry). The *trans* conformers were connected to the single-twisted *cis* conformers *via* IRCs with an energy barrier of approximately 0.4 eV. IRCs 5 and 6 connected the single-twisted *cis* conformers to the double-twisted *cis* conformers, with a higher energy barrier of approximately 0.6 eV. Notably, no direct IRCs were found between the *trans* conformers and the double-twisted *cis* conformers. Given the symmetry and energetic equivalence among the four identified reaction pathways, we focus in this study on the most stable *trans*1 conformer and the *cis*2 conformer, which is directly connected to *trans*1 *via* an IRC.

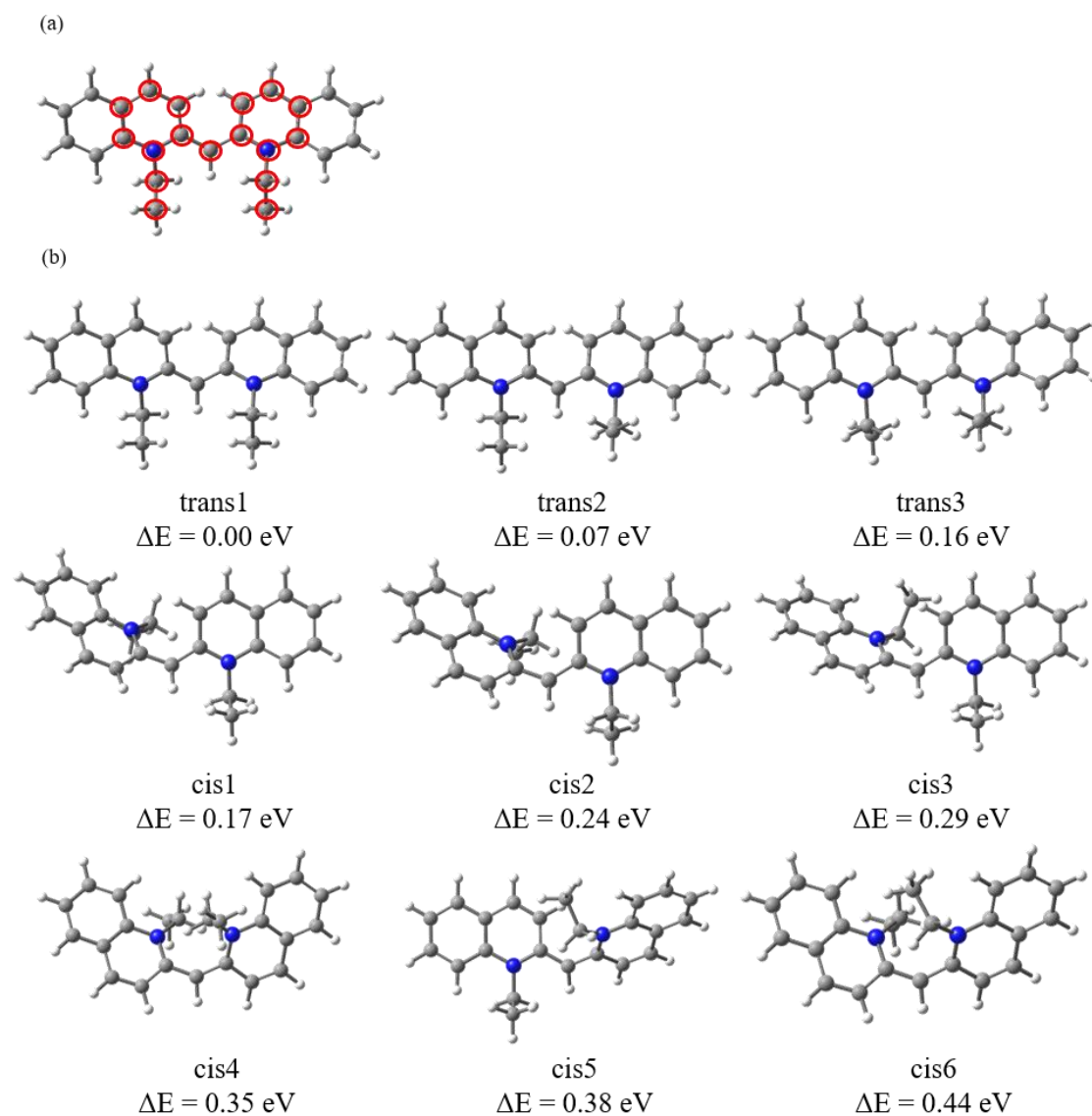


Figure S1. (a) Target atoms designated for the SC-AFIR search (circled in red). (b) Minimum energy conformers in the ground state obtained from SC-AFIR calculations at the ω B97XD/6-31G(d) level. Relative energies (ΔE) with respect to the most stable conformer are also shown.

Table S1. Initial and final structures of IRCs and transition-state energies for 1122C conformers, calculated using DS-AFIR method. A structural name with a prime (') symbol denotes a mirror image isomer.

IRC	Initial	Final	TS / eV
1	trans1	cis2	0.41
2	trans2	cis1	0.44
3	trans3	cis3	0.44
4	trans2'	cis5	0.46
5	cis1	cis6	0.61
6	cis3	cis4	0.63

Table S2. Cartesian coordinates (in Å) of each structure optimized at the ω B97XD/6-31G(d) level.S₀-MIN (*trans*1): $E = -999.299465749945$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	0.200606691	1.239051979	-0.171682764
C	0.778569534	1.331772424	-1.480372881
H	1.060216991	0.412374571	-1.976915833
C	1.042546981	2.529265897	-2.052036321
H	1.496967496	2.577278479	-3.0373646
C	0.790755521	3.744094787	-1.3489934
C	1.10143067	4.999622194	-1.904567905
H	1.514625922	5.035794967	-2.908217758
C	0.890801312	6.156480952	-1.189580194
H	1.130092585	7.122430705	-1.619920618
C	0.373183153	6.071274234	0.110093794
H	0.218375363	6.976234817	0.68838447
C	0.059435151	4.852837667	0.681160748
H	-0.317263776	4.842319302	1.695059111
C	0.25099838	3.66396564	-0.047025185
N	-0.083476075	2.409651566	0.479124945
C	-0.796434119	2.356901456	1.767279239
H	-1.431775558	1.470132335	1.74374565
H	-1.472993968	3.211201408	1.804647163
C	0.139439364	2.34023053	2.971923215
H	-0.447786082	2.307938435	3.893881273
H	0.801679057	1.469208197	2.957049087
H	0.770910936	3.232598818	2.998792343
C	-0.00004734	-0.000006638	0.473677006
H	-0.000361107	0.000080856	1.551737154
C	-0.200402758	-1.239113746	-0.171680834
C	-0.777638748	-1.33193082	-1.480681152
H	-1.058977137	-0.412580737	-1.977477687
C	-1.04123559	-2.52948695	-2.052384104
H	-1.495160002	-2.577607365	-3.03793523
C	-0.789870133	-3.744244968	-1.349076282
C	-1.100265892	-4.999839248	-1.904647272

H	-1.512863743	-5.036108717	-2.908543417
C	-0.890036304	-6.156655883	-1.189472979
H	-1.129088624	-7.122641111	-1.619852758
C	-0.373117344	-6.071265549	0.110467405
H	-0.218686388	-6.976170331	0.688956045
C	-0.059710059	-4.852794268	0.681646441
H	0.316429451	-4.842175437	1.695747682
C	-0.250874029	-3.664013407	-0.046799114
N	0.083339494	-2.409644819	0.479398667
C	0.795572783	-2.356777487	1.767945106
H	1.430906429	-1.469991691	1.744723149
H	1.472123404	-3.211055883	1.805822865
C	-0.140955236	-2.339897766	2.972077027
H	0.44571343	-2.30757263	3.894384493
H	-0.803232157	-1.468913771	2.956738273
H	-0.772467928	-3.232252997	2.998681938

S₀-MIN (*trans*2): $E = -999.296869782124$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	-0.001621101	1.235218081	-0.070109362
C	0.569470061	1.345408371	-1.378427446
H	0.846248107	0.433506479	-1.890430658
C	0.840815247	2.551194396	-1.931546335
H	1.293952095	2.611546839	-2.916796751
C	0.59931205	3.754964965	-1.209121138
C	0.910482238	5.018261742	-1.748291251
H	1.314865424	5.068196673	-2.754897047
C	0.710598341	6.164012938	-1.013737183
H	0.94966266	7.135761101	-1.430947434
C	0.203727838	6.060722466	0.289525793
H	0.057133335	6.957488109	0.882506082
C	-0.109454457	4.835449946	0.844856115
H	-0.47847607	4.811235462	1.861253487
C	0.071021973	3.656742526	0.096568375
N	-0.264087195	2.395998301	0.605414842

C	-0.955622684	2.326803376	1.905270328
H	-1.585960579	1.436625312	1.881843882
H	-1.634542016	3.178047611	1.96354324
C	0.001345621	2.299554217	3.093039902
H	-0.57021003	2.257693951	4.0243795
H	0.664387722	1.429497167	3.058657939
H	0.632953549	3.191820784	3.118518308
C	-0.20673664	-0.012709506	0.568696078
H	-0.106932994	-0.013039475	1.641342229
C	-0.442176835	-1.237820256	-0.078060487
C	-0.947538123	-1.297997818	-1.423512023
H	-1.226203734	-0.368761984	-1.902275585
C	-1.148337239	-2.47595622	-2.053358344
H	-1.55984676	-2.496589466	-3.05826048
C	-0.838047245	-3.709726659	-1.40773295
C	-0.972471761	-4.94452257	-2.06810397
H	-1.326712221	-4.948067385	-3.094747837
C	-0.655258844	-6.122470675	-1.430323054
H	-0.755586288	-7.072733094	-1.942527929
C	-0.186751993	-6.075980384	-0.111223974
H	0.088863278	-6.995078756	0.395397719
C	-0.057044365	-4.877957718	0.565979774
H	0.337680015	-4.902117742	1.572602742
C	-0.396076501	-3.667923053	-0.067919496
N	-0.286570014	-2.430130655	0.583531058
C	0.062294344	-2.423959191	2.014385234
H	-0.343664581	-3.331577744	2.45741197
H	-0.487049842	-1.612046472	2.492194884
C	1.562809853	-2.306048121	2.253029222
H	1.76963533	-2.301636651	3.32685897
H	2.097112389	-3.148008194	1.803474096
H	1.958608645	-1.382891026	1.819984965

S₀-MIN (*trans*3) : $E = -999.293450997147$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
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C	0.23760704	1.230824766	0.02757533
C	0.740131557	1.282873442	-1.31755813
H	1.016855804	0.350710115	-1.790989955
C	0.950919876	2.457222773	-1.952675463
H	1.365507481	2.469986675	-2.956435689
C	0.649937039	3.694581134	-1.312789291
C	0.793336044	4.925901736	-1.979023573
H	1.147277391	4.922084871	-3.00572715
C	0.484538177	6.108224719	-1.346474765
H	0.591162703	7.055715139	-1.862533577
C	0.015783334	6.070514189	-0.026671926
H	-0.253903826	6.99370348	0.475653402
C	-0.121311989	4.877071392	0.656280337
H	-0.515903019	4.910103421	1.662533464
C	0.209049619	3.661060606	0.027902955
N	0.089749586	2.4264043	0.683797454
C	-0.274827208	2.432028849	2.112022102
H	0.128198429	3.342089378	2.551803753
H	0.266576314	1.624962502	2.605187325
C	-1.778425661	2.318778278	2.330189534
H	-2.00078703	2.3274517	3.400800977
H	-2.304676912	3.156034762	1.862697027
H	-2.167099717	1.390051882	1.903012823
C	0.006056019	0.00663354	0.689026897
H	0.015814459	0.020695604	1.764807827
C	-0.23740298	-1.234684621	0.064975299
C	-0.762018888	-1.32315171	-1.269856038
H	-1.044608146	-0.403983332	-1.764770714
C	-0.984773824	-2.514271864	-1.868592101
H	-1.415749371	-2.554133683	-2.86471487
C	-0.674958494	-3.734043577	-1.199727584
C	-0.830966496	-4.983113077	-1.829040316
H	-1.202044311	-5.007145733	-2.849398703
C	-0.512878249	-6.148003696	-1.169298145
H	-0.629191338	-7.109223523	-1.657117342
C	-0.02204275	-6.074570764	0.14092286

H	0.25491678	-6.983963883	0.664021998
C	0.12768449	-4.862899782	0.788239714
H	0.538780964	-4.868538869	1.788416665
C	-0.211700356	-3.664231596	0.131955478
N	-0.080030262	-2.412082588	0.751343233
C	0.307966275	-2.37883246	2.172926207
H	-0.089508198	-3.275118918	2.644801116
H	-0.223808518	-1.557150822	2.65223516
C	1.815125639	-2.262886081	2.363325353
H	2.055064552	-2.24261488	3.429977547
H	2.332118268	-3.113862834	1.910507298
H	2.198459702	-1.347200963	1.904372194

S₀-MIN (*cis1*) : $E = -999.293347236385$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	1.177937251	1.251743211	0.276982504
C	2.424181743	1.909015813	0.009081274
H	3.327930624	1.31677095	0.093666305
C	2.470015372	3.198547942	-0.395834828
H	3.42131642	3.67470455	-0.613987086
C	1.262192492	3.934100523	-0.599751597
C	1.262225786	5.237118889	-1.13161125
H	2.213362016	5.696955436	-1.382944242
C	0.079802639	5.912401174	-1.336786459
H	0.083572041	6.915228312	-1.749069504
C	-1.133137436	5.286485705	-1.017426171
H	-2.06995171	5.805190227	-1.192397323
C	-1.161411395	4.010716519	-0.487401238
H	-2.118722444	3.558071742	-0.262096818
C	0.039874583	3.316912501	-0.263831838
N	0.043861633	2.020285976	0.277102607
C	-1.133118066	1.611531359	1.079258484
H	-0.957378186	0.593142835	1.410103598
H	-2.021784262	1.587138467	0.443171123
C	-1.320223352	2.495178466	2.309172139

H	-2.163324249	2.112531041	2.891446628
H	-0.426182092	2.458260119	2.938298444
H	-1.524518637	3.538512607	2.062158122
C	1.208564929	-0.131087266	0.556770969
H	2.176261114	-0.48105459	0.890197575
C	0.248361255	-1.100662136	0.201508664
C	-0.776213897	-0.827834592	-0.765433269
H	-0.808010909	0.161993675	-1.202654415
C	-1.632695982	-1.789562851	-1.176421266
H	-2.386103242	-1.568645782	-1.92693898
C	-1.529963051	-3.120596557	-0.673387184
C	-2.388675368	-4.145767996	-1.111813737
H	-3.162363781	-3.902328762	-1.834033859
C	-2.248266087	-5.431008807	-0.639738823
H	-2.910777947	-6.219196685	-0.979362181
C	-1.22842937	-5.712719555	0.279108113
H	-1.099420521	-6.725415468	0.646715331
C	-0.370627834	-4.726284266	0.727110867
H	0.411898219	-5.001990196	1.421023361
C	-0.514879765	-3.404788489	0.26567167
N	0.312436278	-2.36780847	0.71599156
C	1.273802507	-2.65399412	1.795105511
H	0.798044643	-3.353344058	2.483537281
H	1.411902375	-1.727521044	2.354404274
C	2.603685027	-3.197977014	1.282874405
H	3.272342701	-3.389579532	2.12659316
H	2.467237084	-4.133815705	0.73396044
H	3.095370848	-2.489554099	0.609823662

S₀-MIN (*cis2*): $E = -999.290805679081$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	1.324749406	1.17165206	0.065062457
C	2.560816793	1.821906162	-0.251984459
H	3.461125573	1.218993466	-0.228140071
C	2.598917405	3.119757184	-0.634367092

H	3.542482483	3.591106725	-0.89281956
C	1.390403528	3.869008714	-0.761474501
C	1.375837563	5.183592081	-1.265677497
H	2.316993505	5.639868565	-1.557631847
C	0.191475119	5.873381921	-1.393380951
H	0.183443545	6.884653949	-1.784439618
C	-1.009766625	5.252071886	-1.022399014
H	-1.948798358	5.783553029	-1.136332939
C	-1.023685446	3.96602392	-0.518447658
H	-1.972308369	3.517964084	-0.251396717
C	0.180718888	3.255972814	-0.374834031
N	0.20012621	1.948265629	0.136777678
C	-0.934439464	1.534971877	0.997320388
H	-0.754766167	0.506190606	1.291650026
H	-1.85906732	1.540437069	0.414906239
C	-1.032119829	2.39171628	2.256042959
H	-1.845413905	2.008686283	2.878953928
H	-0.102982154	2.325639582	2.829513978
H	-1.232777405	3.44368687	2.044901955
C	1.358214192	-0.22042546	0.324166821
H	2.32084578	-0.556330526	0.682501554
C	0.392324261	-1.179781068	-0.022537706
C	-0.712603909	-0.848520496	-0.882854825
H	-0.747293613	0.151676446	-1.295123671
C	-1.642837348	-1.763906825	-1.227702729
H	-2.447220731	-1.499647909	-1.907988084
C	-1.584734193	-3.091785322	-0.707961529
C	-2.583664882	-4.04041017	-0.991989823
H	-3.408792662	-3.748612057	-1.635101192
C	-2.521300929	-5.309343924	-0.461784703
H	-3.293579713	-6.0383168	-0.680049636
C	-1.450570267	-5.642840719	0.377007922
H	-1.401274037	-6.631847705	0.820646193
C	-0.449106496	-4.734084344	0.663798423
H	0.337072002	-5.039430655	1.340806236
C	-0.489070677	-3.440417127	0.110862058

N	0.511166132	-2.490194861	0.366753865
C	1.696361455	-2.911914979	1.132908856
H	2.564965571	-2.395477066	0.72472837
H	1.872752645	-3.964204277	0.918544757
C	1.543096133	-2.659904497	2.627852436
H	2.444304172	-2.984737913	3.154963688
H	1.390216092	-1.596124809	2.831808105
H	0.689766044	-3.212517693	3.031856961

S₀-MIN (*cis3*) : $E = -999.288757812168$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	1.17289266	1.361177881	0.120361178
C	2.347578522	1.987334216	-0.40799
H	3.23735705	1.375111924	-0.494691739
C	2.333270574	3.26516034	-0.850343487
H	3.224132327	3.709743832	-1.283868078
C	1.139013811	4.040311444	-0.770176967
C	1.087738063	5.368488406	-1.233069162
H	1.976077997	5.793451847	-1.69071895
C	-0.059948814	6.116418691	-1.099019079
H	-0.095685866	7.139767852	-1.455538792
C	-1.182580721	5.542017628	-0.48835913
H	-2.090142025	6.125106848	-0.371726308
C	-1.162739875	4.238294667	-0.030069267
H	-2.057265118	3.839484591	0.427557509
C	-0.000559912	3.45855132	-0.173189335
N	0.054082077	2.131636164	0.286924108
C	-1.024920959	1.706209493	1.20980651
H	-1.124119677	2.519403262	1.933653324
H	-0.638868509	0.846375532	1.755086173
C	-2.385937443	1.390140628	0.565094333
H	-2.432535785	1.727075571	-0.474039171
H	-2.598339811	0.321019034	0.578989152
H	-3.188357427	1.893512198	1.111514393
C	1.277808166	-0.002040327	0.490851118

H	2.286135552	-0.29241072	0.75825425
C	0.349201594	-1.035329987	0.268764609
C	-0.689948994	-0.90668977	-0.710475473
H	-0.771712302	0.037702625	-1.233406079
C	-1.489543189	-1.947847398	-1.031477479
H	-2.249888665	-1.839478979	-1.799616249
C	-1.318072831	-3.218774371	-0.403854632
C	-2.121079431	-4.324238986	-0.739353049
H	-2.90185268	-4.192948898	-1.482762562
C	-1.92031504	-5.54783792	-0.140880179
H	-2.541185211	-6.397711303	-0.401190194
C	-0.895097986	-5.685340716	0.803886435
H	-0.720162735	-6.648040239	1.272853711
C	-0.088889977	-4.617548786	1.150969587
H	0.700614153	-4.781957835	1.871819067
C	-0.294285152	-3.358520226	0.558202386
N	0.482315095	-2.243189666	0.899198344
C	1.471353239	-2.374989743	1.981898872
H	1.034029279	-3.009269388	2.754385662
H	1.586702844	-1.385306805	2.427342118
C	2.812410167	-2.925579623	1.506482728
H	3.500228465	-3.000012473	2.353263199
H	2.702803948	-3.919973711	1.065110993
H	3.268290551	-2.278458125	0.751461603

S₀-MIN (*cis4*) : $E = -999.286507216266$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	0.729146917	1.168949834	1.635272016
C	1.714909903	1.883389304	2.396935575
H	1.950178764	1.504131673	3.384377482
C	2.371253123	2.948212699	1.885829283
H	3.130395639	3.459687388	2.470026576
C	2.106726095	3.388825882	0.552845225
C	2.831837608	4.438799063	-0.039776262
H	3.613306769	4.922280212	0.538868394

C	2.558971183	4.843521433	-1.327433574
H	3.120290582	5.65256926	-1.781266004
C	1.548100374	4.194655854	-2.048466206
H	1.330608006	4.500560961	-3.066532335
C	0.817858257	3.162916165	-1.489156824
H	0.04747734	2.691896044	-2.085310799
C	1.086180441	2.742371372	-0.174925736
N	0.364908612	1.694078655	0.422852694
C	-0.944046523	1.346260764	-0.169757434
H	-1.315114863	0.45893995	0.327315512
H	-0.803910333	1.079755019	-1.21952195
C	-1.959800889	2.470280614	0.011239426
H	-2.916877404	2.160462245	-0.417738249
H	-2.110799415	2.671754025	1.075520957
H	-1.650965426	3.397809617	-0.475693384
C	0.186786047	0.00779769	2.226086021
H	0.286615545	0.012253099	3.306249634
C	-0.453896276	-1.157566693	1.754264404
C	-1.283165966	-1.865325412	2.688940447
H	-1.333901496	-1.478403394	3.699863157
C	-2.021340718	-2.933532122	2.314737832
H	-2.660245067	-3.440123574	3.031931528
C	-2.005554416	-3.383964363	0.959013454
C	-2.826710103	-4.43719634	0.516476513
H	-3.488568891	-4.916235893	1.231826805
C	-2.794643668	-4.850486024	-0.796755986
H	-3.429423136	-5.662046875	-1.134416857
C	-1.933906956	-4.206999973	-1.695627191
H	-1.90737376	-4.519551173	-2.734352704
C	-1.11378192	-3.172285311	-1.286616994
H	-0.466315957	-2.704887546	-2.016806395
C	-1.136173493	-2.743546294	0.051865507
N	-0.317272589	-1.692510801	0.499890803
C	0.861359618	-1.35085835	-0.324551457
H	1.319806608	-0.464120351	0.094797636
H	0.531434976	-1.085872892	-1.331448817

C	1.889037171	-2.478628628	-0.330857602
H	2.751909776	-2.173362959	-0.929411524
H	2.23259221	-2.679134063	0.687884662
H	1.492097701	-3.405519792	-0.750571258

S₀-MIN (*cis5*) : $E = -999.285653761100$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	-0.506909444	1.136932562	0.08384741
C	0.589193455	0.948701055	-0.82846194
H	0.655891346	-0.003640778	-1.33851482
C	1.459524992	1.940995787	-1.107175355
H	2.252364755	1.788351662	-1.833845229
C	1.354509534	3.206062625	-0.451662661
C	2.296409377	4.228074784	-0.66360827
H	3.109833165	4.048083606	-1.360476187
C	2.195972337	5.429007415	0.003265463
H	2.925625302	6.214199527	-0.159681629
C	1.144505049	5.616964485	0.908083567
H	1.067135037	6.548609923	1.458918305
C	0.196781094	4.633657881	1.125868075
H	-0.576561813	4.824229789	1.857614304
C	0.274540229	3.411499461	0.433627288
N	-0.673734786	2.392098537	0.613595889
C	-1.852066484	2.669629229	1.451124317
H	-2.711701014	2.16752525	1.007375608
H	-2.076940075	3.731128563	1.367716072
C	-1.647029687	2.250026082	2.901425235
H	-2.543112736	2.476653882	3.485577753
H	-1.45403418	1.175666649	2.973296044
H	-0.801526528	2.782992129	3.346326574
C	-1.431928385	0.111041796	0.311139488
H	-2.429487839	0.37435247	0.636455882
C	-1.332540611	-1.257869304	-0.066663395
C	-2.499970936	-1.863013116	-0.628054816
H	-3.374263969	-1.233927323	-0.745341581

C	-2.496101622	-3.143844592	-1.066237638
H	-3.381101144	-3.573172868	-1.52637011
C	-1.320774868	-3.939275855	-0.945419681
C	-1.280291557	-5.271895964	-1.399217429
H	-2.161485783	-5.682567339	-1.882920416
C	-0.152710075	-6.04015196	-1.223242587
H	-0.124952949	-7.06643288	-1.571953657
C	0.960895313	-5.483204876	-0.579045143
H	1.852060403	-6.083577767	-0.428629658
C	0.952354051	-4.176805865	-0.130043134
H	1.838800986	-3.792604264	0.354399888
C	-0.189115298	-3.375097803	-0.316135537
N	-0.232760334	-2.044918238	0.133071953
C	0.830068393	-1.628151059	1.080519345
H	0.881253549	-2.426345947	1.825751617
H	0.450502042	-0.744618562	1.590621871
C	2.220292169	-1.366329563	0.472971667
H	2.985497122	-1.923684509	1.020222702
H	2.273022332	-1.675511144	-0.574399229
H	2.484070088	-0.309843574	0.522199786

S₀-MIN (*cis6*) : $E = -999.283490238029$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	0.844579184	1.024930189	1.654212767
C	1.930214779	1.679181194	2.327054921
H	2.255755217	1.254560966	3.269490766
C	2.565874508	2.738801643	1.780176979
H	3.405286886	3.202206867	2.290000067
C	2.164386442	3.242376382	0.505110732
C	2.847959705	4.300621172	-0.12075432
H	3.708078869	4.732762407	0.381978099
C	2.435707796	4.780025807	-1.344216174
H	2.965411225	5.595718197	-1.823420432
C	1.321250168	4.201045618	-1.963972144
H	0.988138835	4.569842046	-2.928483568

C	0.630408672	3.160442647	-1.371255327
H	-0.22736039	2.752242669	-1.888499691
C	1.044022056	2.658814186	-0.124149873
N	0.3722484	1.594623333	0.502793926
C	-1.001301079	1.29550099	0.042780162
H	-1.298117175	0.332046281	0.43815802
H	-0.997749662	1.184187665	-1.041005844
C	-1.979280936	2.368949296	0.505960719
H	-2.98457658	2.1205621	0.154385333
H	-1.999364458	2.416598223	1.59851501
H	-1.715578761	3.356910728	0.119955555
C	0.286426295	-0.110999661	2.278303281
H	0.388422187	-0.094573159	3.358964155
C	-0.381959706	-1.25879983	1.806151412
C	-1.333869557	-1.871272751	2.687444748
H	-1.476140157	-1.409078609	3.657142306
C	-2.078039747	-2.930879167	2.301579551
H	-2.823101152	-3.354497671	2.968407071
C	-1.906068596	-3.498265528	1.002572326
C	-2.67479179	-4.593281374	0.568198447
H	-3.437637087	-4.988116868	1.232630841
C	-2.457297208	-5.161108448	-0.667439387
H	-3.050793613	-6.006217453	-0.997831369
C	-1.451966429	-4.639104934	-1.490613638
H	-1.265763882	-5.083847045	-2.462632572
C	-0.685629216	-3.559288955	-1.092021118
H	0.075002001	-3.192794463	-1.767506929
C	-0.908082429	-2.960895793	0.16121527
N	-0.145495997	-1.862231314	0.597428377
C	1.097301324	-1.578295694	-0.153661399
H	1.568569964	-2.551549762	-0.31247439
H	1.750136147	-1.025282517	0.520583543
C	0.932152814	-0.843124911	-1.49298075
H	1.154441994	0.220699214	-1.407094006
H	1.62656238	-1.258969402	-2.228321636
H	-0.078372242	-0.951174511	-1.894943817

2. Assignment of excited states

Tables S3 and S4 present the vertical excitation states of the *trans*- and *cis*-S₀-MIN structures, respectively, while Fig. S2 illustrates the main molecular orbitals involved in the excitations. The S₁ state was found to lie more than 1.0 eV below the S₂ and S₃ states and exhibited a significantly large oscillator strength (*f*) of 1.0976. Therefore, the excitation of the 1122C molecule by incident light is attributed to the S₁ ($\pi\pi^*$) state.

Table S3. Vertical excitation energies, electronic configurations, configuration interaction (CI) coefficients, and oscillator strengths (*f*) for the S₀-MIN(*trans*) structure.

State	Excitation	CI coeff.	Excitation		<i>f</i>
			energy (eV)	(nm)	
S ₁	87a -> 88a	0.0692	3.06	406	1.0976
S ₂	87a -> 89a	0.654	4.12	301	0.0027
	84a -> 88a	0.169			
	85a -> 90a	-0.127			
S ₃	86a -> 88a	0.515	4.42	280	0.0022
	87a -> 90a	-0.408			
	85a -> 89a	-0.182			
	84a -> 89a	-0.105			

Table S4. Vertical excitation energies, electronic configurations, configuration interaction (CI) coefficients, and oscillator strengths (f) for the S_0 -MIN(*cis*) structure.

State	Excitation	CI coeff.	Excitation		
			energy (eV)	(nm)	f
S_1	87a -> 88a	0.691	2.98	416	0.8846
S_2	87a -> 89a	0.654	4.03	307	0.0177
	84a -> 88a	0.148			
S_3	85a -> 88a	0.598	4.36	284	0.0411
	87a -> 90a	-0.234			
	85a -> 89a	0.189			
	86a -> 88a	-0.153			

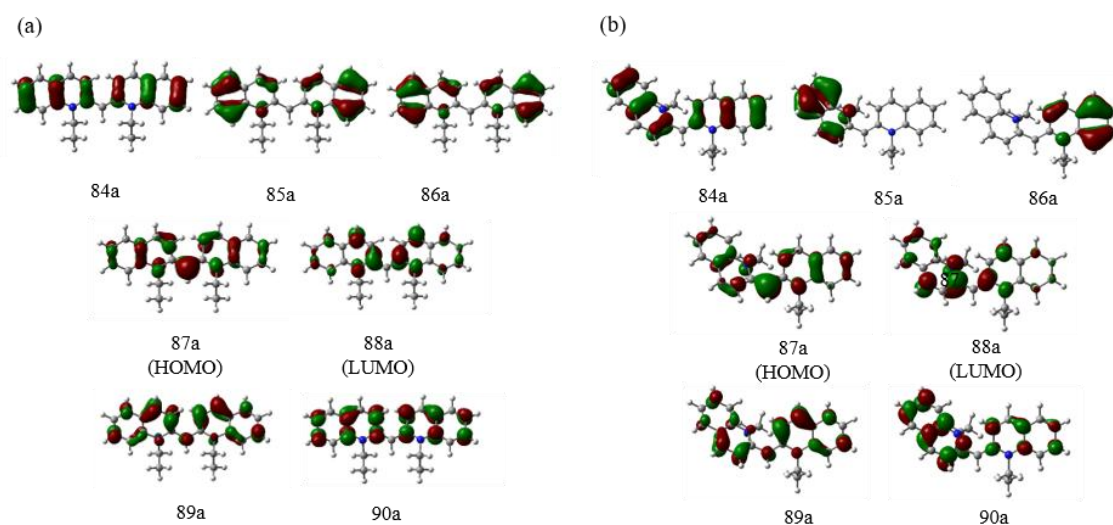


Figure S2. Representative molecular orbitals involved in the S_1 excited state of the *trans* (a) and *cis* (b) conformers.

3. Details of *ab initio* molecular dynamics (AIMD) simulation

The AIMD simulations were performed according to the flowchart in Fig. S3 using the in-house program SPPR⁶. The initial samplings were conducted by the normal mode sampling, which samples the initial energy generated by the Boltzmann distribution at 300 K for initial coordinate displacements and velocities to their respective normal modes. These initial coordinates and velocities are based on harmonic approximation. To correlate for anharmonicity, we adjusted the norm of the velocity vector, corresponding to the amount of total kinetic energy, according to adjust the energy difference ΔE_{pot} between the harmonic potential energy E_{pot} and the real potential energy $E_{\text{pot}}^{\text{real}}$. In other words, if ΔE_{pot} was a shortage, we shortened the norm of the velocity vector, and if it was an excess, we lengthened the norm. This potential energy difference ΔE_{pot} is shown in Fig. S4.

The coordinate and velocity were developed by the velocity-Verlet algorithm:

$$\begin{aligned}\mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \mathbf{v}(t)\Delta t - \frac{1}{2} \frac{\mathbf{g}(t)}{\mathbf{M}} \Delta t^2 \\ \mathbf{v}(t + \Delta t) &= \mathbf{v}(t) - \frac{1}{2} \frac{\mathbf{g}(t) + \mathbf{g}(t + \Delta t)}{\mathbf{M}} \Delta t\end{aligned}$$

where $\mathbf{r}(t)$, $\mathbf{v}(t)$, and $\mathbf{g}(t)$ are vectors for molecular coordinates, velocities, and potential gradients at time t , respectively; Δt is the simulation timestep; $\mathbf{M}$ is the atomic mass matrix.

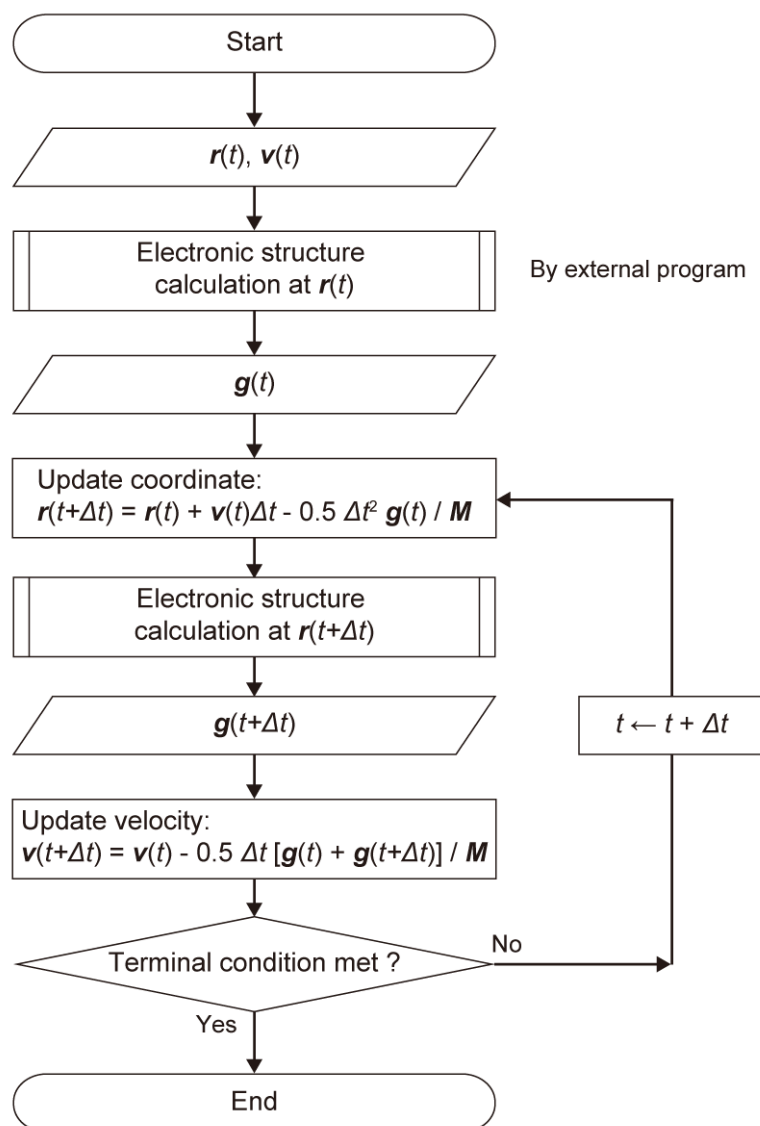


Figure S3. Flowchart of velocity-Verlet algorithm in the SPPR program.

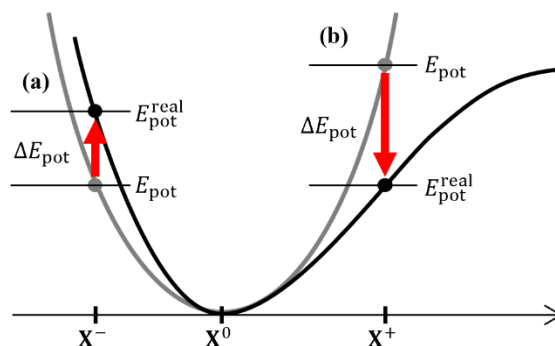


Figure S4. Schematic illustration of energy correction under the harmonic approximation.

4. AIMD for S₁ excited state

We performed AIMD simulations in the S₁ excited state and obtained 50 trajectories. A representative trajectory is shown in Fig. S5, where the time evolution of potential energy and internal coordinates is presented. This trajectory highlights changes in internal geometry that are likely critical for the reaction.

In the Franck–Condon (FC) region, the energy gap $\Delta E(S_1-S_0)$ relative to the S₀-MIN(*trans*) structure was approximately 3 eV (413 nm). As the dihedral angle of the quinoline ring, $\varphi(N1-C1-C2-C3)$, decreased from $\sim 180^\circ$ to $\sim 90^\circ$, the S₁ energy decreased while the S₀ energy increased. Consequently, $\Delta E(S_1-S_0)$ narrowed to ~ 2 eV (620 nm) within ~ 300 fs. The minimum energy gap observed during the trajectory was approximately 1.2 eV (1033 nm).

Structurally, one of the quinoline rings twisted immediately after excitation, reaching the S₁-MIN^{TW} region around 300 fs. This timescale matched the evolution of $\Delta E(S_1-S_0)$, supporting the idea that the redshift observed in transient absorption spectra is primarily caused by ring twisting. After reaching the S₁-MIN^{TW} region, the molecule oscillated around $\varphi \approx 90^\circ$ up to 1 ps. Due to the flatness of the S₁ potential energy surface in this region (Figs. 3a, b), the molecule appeared to remain in a quasi-stable state. Beyond 600 fs, changes in the dihedral angle φ_3 (defined as $\varphi(C4-N1-C1-C2)$; see Fig. 2), which reflects the ring distortion characteristic of the minimum energy conical intersection (MECI) structure, became more pronounced. This suggests that after passing through the S₁-MIN^{TW} region, the molecule gradually evolved toward the MECI region.

Although the discussion above is based on a single representative trajectory, all 50 trajectories exhibited similar trends. This consistency suggests a two-step reaction mechanism in the excited state: (i) twisting of one quinoline ring from the FC region to S₁-MIN^{TW}, and (ii) subsequent structural evolution involving φ_3 as the system proceeds from S₁-MIN^{TW} toward the MECI region. However, φ_3 may not be the only internal coordinate involved in step (ii), and further analysis is required to identify other contributing factors.

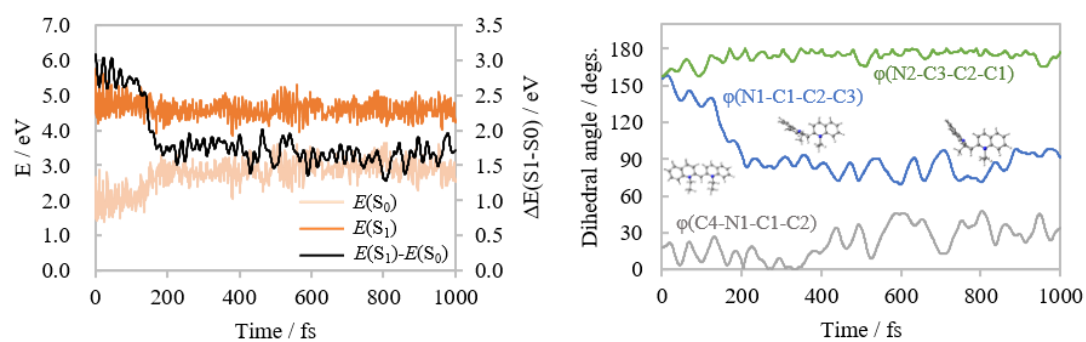


Figure S5. Temporal evolution of potential energy (left), and internal coordinates (right) along a representative trajectory.

5. Details of machine learning analysis

Machine learning was conducted using the Random Forest (RF) and the extreme gradient boosting (XGB) methods to investigate the relationship between the stimulated emission wavelength and internal coordinates. Both methods are supervised machine learning methods based on the decision tree concept. The former builds multiple independent trees and aggregates their outputs, whereas the latter sequentially improves prediction by correcting the residuals from previous trees.

To comprehensively capture all internal motions of the molecule, we employed redundant internal coordinates as input features. A total of 264 redundant coordinates were extracted from the S_0 -MIN (*trans*) structure using Gaussian. Because the original dataset was heavily biased toward the 650–850 nm range, random under sampling was performed to balance the data distribution. Specifically, the dataset was divided into four regions: 650–750 nm, 750–850 nm, 850–950 nm, and above 950 nm. In each region, the number of data points was randomly reduced to 1000, 1000, 1000, and 260, respectively.

To tune hyperparameters and evaluate the generalization performance of the prediction models, we split the dataset by using the nested cross-validation procedure. The inner cross-validation for the hyperparameter tuning divided the initial dataset into five subsets, and the outer cross-validation for performance evaluation further split the subsets into five subsets. The averaged R^2 scores for XGB and RF were 0.95 and 0.78, respectively, indicating that XGB learned the regression task more appropriately than RF. The XGB hyperparameters in the best model were chosen as $n_estimators = 100$, $max_depth = 10$, $learning_rate = 0.1$.

The results of the machine learning analysis are presented in Fig. 6. Among all features, "ring distortion" was identified as the most influential. As the distortion deviates from the equilibrium geometry—approximately 9.6° , corresponding to a nearly planar structure—the stimulated emission wavelength shifts toward longer wavelengths. The maximum observed distortion reached approximately 70° . In addition, analysis of potential energy revealed that the stimulated emission wavelength increases with rising S_0 energy, while the S_1 energy remains

relatively constant. This trend suggests that the flat PES of the S_1 state allows such variations in emission wavelength to occur. The correlation plots for those three internal coordinates, shown in Fig. S6, indicate that the SE wavelength becomes redshifted when all three coordinates are increased simultaneously.

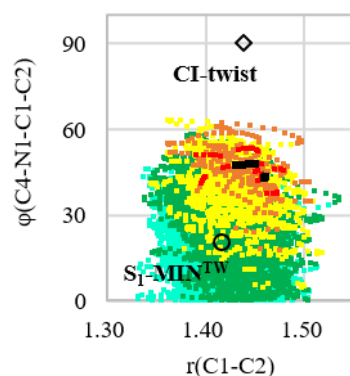


Figure S6. Correlation plots between "ring distortion" and "C=C stretch," Marker color indicates the SE wavelength, categorized as follows: violet (350–450 nm), blue (450–550 nm), cyan (550–650 nm), emerald green (650–750 nm), green (750–850 nm), yellow (850–950 nm), orange (950–1050 nm), red (1050–1150 nm), and black (> 1150 nm).

6. Significant structures in the S₁ state of the 1122C

Table S5. Cartesian coordinates (in Å) of each structure optimized at the ω B97XD/6-31G(d) level.

S₁-MIN^{TW}: $E = -999.206544428427$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	1.108242008	1.195634779	0.081754129
C	2.128410805	1.554491157	-0.79863268
H	2.920199441	0.836413715	-0.984935024
C	2.128501375	2.768965101	-1.430243239
H	2.924603326	3.048120555	-2.109802985
C	1.060730007	3.698156308	-1.167155978
C	1.019253253	4.958028595	-1.7799059
H	1.81197879	5.218085467	-2.475381224
C	0.005927589	5.861911355	-1.508635567
H	-0.005006365	6.832791135	-1.991760953
C	-0.991847606	5.513418943	-0.602605659
H	-1.788519883	6.21218428	-0.370511081
C	-0.979802485	4.270893948	0.019999776
H	-1.768931082	4.044889946	0.725692666
C	0.032609655	3.345555755	-0.257104261
N	0.042604478	2.066009262	0.338929403
C	-0.818622255	1.804751372	1.490342691
H	-0.895751674	0.721831653	1.612686249
H	-1.830887889	2.140929667	1.257062643
C	-0.306623562	2.443432595	2.779056925
H	-0.980766578	2.216772799	3.610311206
H	0.691249357	2.067299496	3.027225772
H	-0.238887284	3.529949266	2.678370325
C	1.070322297	-0.150276228	0.660723722
H	1.562807627	-0.324723037	1.612285069
C	0.404399246	-1.220838436	0.014316404
C	-0.325187766	-0.961072726	-1.178079263
H	-0.298696252	0.043291241	-1.576081578
C	-1.034676038	-1.95081925	-1.789526395
H	-1.5855221	-1.746838224	-2.702337676

C	-1.077596197	-3.249595438	-1.231980326
C	-1.838142693	-4.283273054	-1.826783453
H	-2.384139079	-4.064563753	-2.738913918
C	-1.88718776	-5.529242249	-1.259241881
H	-2.47160239	-6.320686544	-1.714234229
C	-1.177166017	-5.774354953	-0.066229323
H	-1.230279655	-6.754664727	0.395156433
C	-0.419674495	-4.796747422	0.535415741
H	0.085996318	-5.033220144	1.461305291
C	-0.343082659	-3.508989389	-0.042772274
N	0.419243888	-2.495231968	0.518452336
C	1.258277291	-2.802754441	1.698833195
H	2.14901693	-2.179127549	1.641679489
H	1.616054484	-3.824845846	1.587209346
C	0.509351443	-2.603827894	3.010690685
H	1.165138097	-2.857265109	3.847508482
H	0.187317125	-1.565135896	3.131676578
H	-0.377682766	-3.241158938	3.064050617

S₁-MIN^{C2}: $E = -999.193342618144$ hartree, $\langle S^2 \rangle = 0.00$

Atom	x	y	z
C	0.329085	1.164785	1.138605
C	1.624981	1.315763	0.598047
H	2.409795	0.659888	0.955536
C	1.883883	2.25456	-0.352714
H	2.886238	2.38262	-0.748223
C	0.82461	3.068851	-0.857888
C	1.034166	3.994944	-1.896656
H	2.030911	4.084913	-2.318171
C	0	4.771538	-2.371824
H	0.170022	5.483496	-3.171811
C	-1.275481	4.633871	-1.810559
H	-2.096328	5.239894	-2.179455
C	-1.512744	3.734728	-0.786966
H	-2.513386	3.663448	-0.381065

C	-0.466469	2.936611	-0.294845
N	-0.666346	2.022093	0.74707
C	-1.905974	2.104655	1.539011
H	-1.966133	1.203753	2.147355
H	-2.761454	2.079929	0.859795
C	-1.930332	3.330716	2.446757
H	-2.861821	3.3434	3.019492
H	-1.09342	3.300085	3.150385
H	-1.865252	4.261485	1.878034
C	0	0	1.974179
H	0	0	3.060578
C	-0.329085	-1.164785	1.138605
C	-1.624981	-1.315763	0.598047
H	-2.409795	-0.659888	0.955536
C	-1.883883	-2.25456	-0.352714
H	-2.886238	-2.38262	-0.748223
C	-0.82461	-3.068851	-0.857888
C	-1.034166	-3.994944	-1.896656
H	-2.030911	-4.084913	-2.318171
C	0	-4.771538	-2.371824
H	-0.170022	-5.483496	-3.171811
C	1.275481	-4.633871	-1.810559
H	2.096328	-5.239894	-2.179455
C	1.512744	-3.734728	-0.786966
H	2.513386	-3.663448	-0.381065
C	0.466469	-2.936611	-0.294845
N	0.666346	-2.022093	0.74707
C	1.905974	-2.104655	1.539011
H	1.966133	-1.203753	2.147355
H	2.761454	-2.079929	0.859795
C	1.930332	-3.330716	2.446757
H	2.861821	-3.3434	3.019492
H	1.09342	-3.300085	3.150385
H	1.865252	-4.261485	1.878034

Table S6. Cartesian coordinates (in Å) of MECI near S₁-MIN^{TW} optimized using the MRSF-TDDFT approach at the BHHLYP/6-31G(d) level.

MECI: $E = -998.940568179448$ hartree, $\langle S^2 \rangle = 0.00$

Atom	X	y	z
C	1.319441617	1.150746147	0.575972495
C	2.258231604	1.564829718	-0.292882354
H	3.053126587	0.89338302	-0.607144615
C	2.124527875	2.845652096	-0.905199674
H	2.883806553	3.224798548	-1.573810069
C	0.808606668	3.440651092	-0.877067279
C	0.413652054	4.45739608	-1.752965874
H	1.147499993	4.879075596	-2.431322244
C	-0.89092195	4.927161244	-1.765071405
H	-1.168770434	5.722925312	-2.446497981
C	-1.84136322	4.375869729	-0.916666836
H	-2.863379144	4.734874777	-0.930078776
C	-1.470116368	3.364354626	-0.0372971
H	-2.19442289	2.931723099	0.643965753
C	-0.159108715	2.920829298	0.009995559
N	0.234494768	1.975212534	1.01873232
C	0.446552481	2.582074846	2.347713302
H	0.634174442	1.763316767	3.052989076
H	-0.506935529	3.025057022	2.646512101
C	1.557468825	3.612227557	2.454434247
H	1.628569372	3.968735581	3.48634041
H	2.525713215	3.19058953	2.173659195
H	1.361833038	4.474331281	1.813186652
C	1.04267575	-0.220724528	1.044100473
H	1.17368866	-0.438426364	2.098188507
C	0.403002352	-1.214434828	0.223481838
C	-0.05003871	-0.841058138	-1.051343873
H	0.137835404	0.172130796	-1.374973458
C	-0.726184115	-1.738734891	-1.828976429
H	-1.084606467	-1.450161428	-2.810317313
C	-0.969968521	-3.035647669	-1.357634633

C	-1.676766864	-3.982133642	-2.137950692
H	-2.021283638	-3.684957721	-3.12089945
C	-1.9171238	-5.23329968	-1.657418367
H	-2.459123033	-5.957952775	-2.251768963
C	-1.458891619	-5.585023219	-0.36897203
H	-1.662566689	-6.577421259	0.014798354
C	-0.764835603	-4.703095002	0.412275692
H	-0.451015123	-5.018751179	1.394270108
C	-0.496879273	-3.399965025	-0.065310048
N	0.19756505	-2.476568633	0.679596954
C	0.733106187	-2.883249074	2.004810589
H	1.649792166	-2.325328858	2.170213546
H	1.040376631	-3.921277384	1.917085758
C	-0.262246351	-2.67949888	3.130713373
H	0.193536006	-3.003031174	4.06933532
H	-0.544976969	-1.629329888	3.234613512
H	-1.174068973	-3.260182791	2.977612925

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