Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information: First principles prediction of wavelength-dependent isomerization quantum yields of a second generation molecular nanomotor

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1 Ground-state equilibrium structures

Table S1: Dihedral angles (°) of all initial conformers optimized by PBE0/def2-SVP.

Conformer	Nature	α	β	γ	δ	δ'
I1	*anti*-(M)	166.69	-34.50	95.42	37.78	-39.34
I2	*anti*-(M)	166.55	-34.49	95.38	37.59	-39.25
I3	*syn*-(P)	211.56	33.56	24.94	-16.44	-0.36
I4	*syn*-(P)	212.11	25.01	39.31	-2.86	17.43
I5	*syn*-(M)	171.01	-55.72	119.45	-28.37	17.36
I6	*syn*-(M)	169.40	-53.75	118.40	-24.16	12.16
I7	*anti*-(P)	187.30	42.12	6.21	-52.73	47.97

Table S2: CC2/def2-TZVP (PBE0/def2-SVP) relative energy (kcal/mol) and population at 300 K.

Conformer	Nature	E_{rel}	Population
I1	*anti*-(M)	$5.857 \cdot 10^{-3}$ (0.000)	$4.969 \cdot 10^{-1}$ ($4.982 \cdot 10^{-1}$)
I2	*anti*-(M)	0.000 ($1.684 \cdot 10^{-3}$)	$5.018 \cdot 10^{-1}$ ($4.968 \cdot 10^{-1}$)
I3	*syn*-(P)	4.174 (3.643)	$4.571 \cdot 10^{-4}$ ($1.106 \cdot 10^{-3}$)
I4	*syn*-(P)	4.763 (4.652)	$1.702 \cdot 10^{-4}$ ($2.035 \cdot 10^{-4}$)
I5	*syn*-(M)	4.356 (3.342)	$3.366 \cdot 10^{-4}$ ($1.831 \cdot 10^{-3}$)
I6	*syn*-(M)	4.288 (3.352)	$3.776 \cdot 10^{-4}$ ($1.800 \cdot 10^{-3}$)
I7	*anti*-(P)	8.167 (8.798)	$5.636 \cdot 10^{-7}$ ($1.940 \cdot 10^{-7}$)

1.1 Cartesian coordinates of the optimized structures using PBE0/def2-SVP obtained from the conformational search performed with CREST.

Conformer I1 (*anti-M*)

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C   -3.37154290088264     2.47684121383522     0.71174386145829
C   -1.97851102147958     2.32195729681424     0.57862321127428
C   -1.40941065796724     1.13249210698119     0.13332323268955
C   -2.25693384609338     0.10097996920650    -0.38827455399627
C   -3.67391405186982     0.25715600477170    -0.23556721136948
C   -4.19983507893285     1.44113759313710     0.34858493452860
C   -4.54019463119545    -0.75405158218571    -0.72652832248013
C   -4.04504744784673    -1.85016588149017    -1.39300116966836
C   -2.65581020225272    -1.96589068239015    -1.61324707718829
C   -1.78666631482505    -1.01805692418782    -1.12112206385170
H   -3.78508383902391     3.41199202647936     1.09825373583372
H   -5.28393438725942     1.53357413585964     0.45622377831936
H   -5.61755970450097    -0.63237080256143    -0.58449151398089
H   -4.72419489882086    -2.61708772769679    -1.77320523896916
H   -2.26497974226139    -2.81282917206138    -2.18229317802330
H   -0.71979748971537    -1.11257191881961    -1.31770946379091
C   -0.91711185315827     3.34676764256025     0.84174414836358
C    0.31389294316378     2.77227722611871     0.11004790576788
H   -0.71538848958516     3.43758828592961     1.92428465975505
H   -1.19979233299236     4.34894956037269     0.48107061408457
C    0.06453818473696     1.26825358980290     0.17915367154773
H    1.22083075527406     3.06413863229381     0.64686036496951
C    0.41845474730467     3.26635513884769    -1.33229834779867
H    0.55742546480358     4.35858889513575    -1.36346896639880
H   -0.49310114791203     3.02068385544227    -1.89951262211298
H    1.27288193063695     2.79856467482651    -1.84380909492198
C    1.01217036013510     0.29496930735945     0.33705208474472
C    2.47131026854366     0.45136191364293     0.10040499894701
C    3.12169557445621    -0.64844741133898    -0.49865396732416
O    2.47368096451662    -1.82747549545025    -0.71693351928013
C    1.44256827956871    -2.12814551940688     0.11997921454280
C    0.68722195797047    -1.10014376653270     0.70011524177989
C   -0.30053095244299    -1.46374142051317     1.62692738905434
C    1.17476728140649    -3.47234177458797     0.37153337738067
C    0.15968073078676    -3.80550272496433     1.26172710167117
H    1.78428116366479    -4.23153268209983    -0.12202832789558
C   -0.56519271016298    -2.79936178228903     1.90566597836873
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H	-0.87049048864789	-0.67610115829567	2.12357426323452
H	-1.34393814731029	-3.05948942751293	2.62568010772337
H	-0.05203220125046	-4.85655373380344	1.47176604104116
C	3.27603080464995	1.56779442342402	0.38461658006439
C	4.45775842162907	-0.59719785909716	-0.89266967397272
C	4.61669018696638	1.62170860532236	0.01796198605563
H	2.85514798234475	2.41303607605255	0.92499458079575
C	5.20628542297169	0.54637444702101	-0.64665952530076
H	4.88874147322749	-1.47889269820503	-1.37049879170504
H	6.25527447450986	0.58741005027865	-0.94872925807828
H	5.20435280232180	2.51087517567435	0.25673103851132

Conformer I2 (*anti-M*)

C	-3.37211086998563	2.47946916315069	0.72727599435457
C	-1.97797148561648	2.32909178661383	0.60058395661144
C	-1.40376154177446	1.14616519132156	0.14475379211954
C	-2.24593796674375	0.11908205054034	-0.39403245192305
C	-3.66411287763307	0.27046843329319	-0.24789233687826
C	-4.19606336429872	1.44637803827316	0.34709702991326
C	-4.52526089918920	-0.73676716384469	-0.75578950972176
C	-4.02370854906814	-1.82411007564574	-1.43181738133118
C	-2.63293715142652	-1.93427641904856	-1.64513097717789
C	-1.76880201714348	-0.99023606576475	-1.13709639744753
H	-3.78989906495757	3.40913827554283	1.12237449059473
H	-5.28096900380462	1.53525760562849	0.44949055082056
H	-5.60373086795324	-0.61894338302263	-0.61894209852617
H	-4.69891380841749	-2.58802900916412	-1.82489430557384
H	-2.23684197582436	-2.77376333686098	-2.22154704924914
H	-0.70061385858816	-1.07996009813892	-1.32869916195281
C	-0.92024689655941	3.35292873655296	0.88176334104255
C	0.31661539415595	2.78933374635815	0.15120085465381
H	-0.72529291495113	3.43243646303278	1.96643172368496
H	-1.20306441714896	4.35842587553656	0.53049117601501
C	0.06952637970059	1.28411151826167	0.20031909581734
H	1.21936486502947	3.07574018104506	0.69798450780156
C	0.42977147145492	3.30135855283581	-1.28422342575969
H	-0.47781228841737	3.06134902075734	-1.86015030114753
H	1.28806218825483	2.84107354422714	-1.79608833373684
H	0.56722928404971	4.39410996516219	-1.30108618301898
C	1.01761568550007	0.31006077316898	0.35166338033860
C	2.47750520472528	0.46960067998035	0.12246103972122
C	3.13156051692468	-0.62479928349737	-0.48264774348852
O	2.48566213646114	-1.80250552050971	-0.71430182291290
C	1.45048873097369	-2.11109886859269	0.11468181324286
C	0.69160669492388	-1.08865130474177	0.69989597059910
C	-0.30061654277076	-1.46098609607291	1.61848538106649
C	1.18222739356840	-3.45760115363253	0.35306697580695
C	0.16283909268082	-3.79918006964023	1.23509475692321
H	1.79469827747766	-4.21213927301705	-0.14397589077369
C	-0.56596299510163	-2.79912832892829	1.88410715000396
H	-0.87335440714689	-0.67798149669241	2.11928742361138
H	-1.34826985878239	-3.06601328338869	2.59777019745424
H	-0.04931596609446	-4.85216744175771	1.43477255229123
C	3.27987972899169	1.58477628330878	0.41825387813696
C	4.46943636902551	-0.56935530920622	-0.86986918822127
C	4.62215783287755	1.64272974161864	0.05823582040621
H	2.85551448478765	2.42569175236261	0.96258059389683
C	5.21588214351091	0.57285646400504	-0.61151353593032
H	4.90338997439026	-1.44690990529419	-1.35261429646736
H	6.26626726517066	0.61703064221077	-0.90826932571206
H	5.20786996406256	2.53064072727324	0.30630798032222

Conformer I3 (*syn-P*)

C	-3.46585942185626	2.42328537062139	-0.64879759405787
C	-2.07678277972564	2.21507643641824	-0.69397035203001
C	-1.47496214791742	1.10521650030229	-0.10381379552155
C	-2.26994775776491	0.21501236296422	0.69453059320096
C	-3.68674014251290	0.43007759399819	0.73139925736722
C	-4.25857390126763	1.52678959191931	0.03221107817211
C	-4.49872052601393	-0.44175805993997	1.50272771109828
C	-3.94470559685020	-1.46443080394353	2.23664398720829
C	-2.54489986372228	-1.64490115103895	2.24131559734217
C	-1.73053857390250	-0.82850744017679	1.48748198903076
H	-3.90779954728894	3.29076312419463	-1.14584025840923
H	-5.34214467629842	1.66579347381313	0.07418611757440
H	-5.57936906125866	-0.27495549343539	1.51334291700782
H	-4.58210719909183	-2.12516585924853	2.82923324161230
H	-2.10191998593406	-2.43586935727661	2.85142589957588
H	-0.65052652104157	-0.97393907436477	1.50940413373442
C	-1.03398362329049	3.08623881441931	-1.31376846360018
C	0.27855833122744	2.65263542795288	-0.61494253667827
H	-1.24175420850199	4.16191541443721	-1.20222945210637
H	-0.95488841716899	2.88268094159830	-2.39788177399518
C	-0.01959049245157	1.18569098906499	-0.26413925056392
H	0.34884824132239	3.25772390565711	0.31061616538780
C	1.48300834224367	2.94029329342084	-1.49983103733793
H	1.45215356437954	3.98913877293651	-1.83504158247345
H	1.46617646154547	2.29923120979877	-2.39526575536618
H	2.44466573535872	2.78434622357990	-0.99572171509779
C	0.91101994239405	0.15877386414052	-0.24368293365702
C	2.28096865710639	0.36721192450317	0.25399201531025
C	3.25817766885382	-0.63370867984077	0.10568872827839
O	2.98654823043472	-1.81831562442527	-0.48534035962088
C	1.71775778435879	-2.11980182645855	-0.85919249448486
C	0.65186819059084	-1.20248995883036	-0.75583477630728
C	-0.57049653505549	-1.62478144108320	-1.31928408621517
C	1.55655475155642	-3.39667478930526	-1.40271277921450
C	0.32288337968882	-3.79081543959148	-1.89591623356683
H	2.42914373448900	-4.05160844713702	-1.43427538886210
C	-0.74191775081184	-2.88677077350186	-1.86767241220873
H	-1.40705412131328	-0.92964584996720	-1.34273717289403
H	-1.71252217401639	-3.16312092020093	-2.28500324062768
H	0.19654907616471	-4.78955463044681	-2.31984661610550
C	2.65190337641510	1.47861264009400	1.03879710261970
C	4.55884815023937	-0.48340555539800	0.59293673221417
C	3.93548939874734	1.63804092082329	1.53962545106684
H	1.89387221460973	2.22514972557672	1.27562573297491
C	4.90537764447074	0.66095497773226	1.29539258591405
H	5.26983138171166	-1.29306870197933	0.41896746379554
H	5.92120500900730	0.77822754559486	1.67959411046812
H	4.17867907204112	2.51878969882852	2.13784726384814

Conformer I4 (*syn-P*)

C	-3.48751888285710	2.47117346936217	-0.28785647524142
C	-2.08986405774695	2.33187622605458	-0.36746826298238
C	-1.43759404536149	1.15564257875691	-0.00137885786017
C	-2.19418080911038	0.11752360573321	0.64972481742602
C	-3.61969481886654	0.25776361974977	0.70686831122825
C	-4.24201404641439	1.43210626741034	0.20304638621685
C	-4.39518086815120	-0.76231927807471	1.31590179225475
C	-3.79976661517301	-1.85890253787023	1.89449223905846
C	-2.39347975777659	-1.96235910167681	1.90549849981767
C	-1.61509894578749	-1.00125765433467	1.29753300490547
H	-3.96347006355898	3.39871757927126	-0.61672447153480
H	-5.33102305334366	1.51181217964557	0.25584623851022

H	-5.48251849388657	-0.64824513504647	1.33526142670616
H	-4.40951444008248	-2.63446306032566	2.36426674823746
H	-1.91350947218985	-2.80940596225975	2.40158461319504
H	-0.53084948451231	-1.09121297522088	1.33574804310606
C	-1.11605844993335	3.37201470562383	-0.81231303288480
C	0.27851615339787	2.77731650989280	-0.50232380522059
H	-1.29118615778589	4.33367183289538	-0.30342003666863
H	-1.21502264949117	3.57245051530997	-1.89413289013826
C	0.00691680232476	1.29521298632209	-0.21425789640233
H	0.66019046434692	3.28935472618022	0.40100196007139
C	1.23388556964532	3.01929818137939	-1.66992710493894
H	0.82623503329270	2.56529191003492	-2.58644853241468
H	2.23320968488228	2.59534273172579	-1.50813029825138
H	1.35132945608265	4.09963978333862	-1.85099484160063
C	0.95450375838724	0.28249257949341	-0.27162398094540
C	2.35470748740576	0.41950702071248	0.17636415015006
C	3.15344121442316	-0.74053052005806	0.29029863861650
O	2.70082661291311	-1.97907863718148	-0.02338298413023
C	1.51605069280720	-2.12395121516382	-0.66174970071421
C	0.62785781035867	-1.04760657219599	-0.82087380732373
C	-0.49920368048503	-1.28962012140527	-1.63110629070397
C	1.24637084971707	-3.39694864697676	-1.16872269811443
C	0.09001729399336	-3.61276829486445	-1.90355201019470
H	1.97318526510771	-4.19022445368730	-0.98481877590447
C	-0.77469292977364	-2.54338809052089	-2.15538517883831
H	-1.16985215945730	-0.45956040975197	-1.85395400861299
H	-1.66440208877779	-2.68768356795911	-2.77187237251865
H	-0.12535764681234	-4.60660475429212	-2.30236410765688
C	2.94252294667393	1.60515297141867	0.66975508262926
C	4.45856209050429	-0.70653395570970	0.78646203325646
C	4.23621114175945	1.65026564403707	1.16877578631364
H	2.35943379654177	2.52172518040459	0.68315355599344
C	5.01101523200468	0.48934380847440	1.21648572263125
H	5.01062482047823	-1.64713465700491	0.82894398110844
H	6.03315714450271	0.51435673323058	1.60061397620829
H	4.63923453338467	2.59803988692298	1.53222284015585

Conformer I5 (*syn-M*)

C	-3.18166535970166	2.20202270934506	1.25786279512848
C	-1.82574017736864	1.99570317396142	0.94947708087701
C	-1.42274714807777	0.97684525643106	0.09155449810081
C	-2.39639347013074	0.23369114673468	-0.64033703297373
C	-3.77886186856750	0.45621199914919	-0.33444686036029
C	-4.13791387369595	1.42296409831475	0.64140198443921
C	-4.76485146223071	-0.27557734838959	-1.04821654692878
C	-4.41173538836404	-1.15815638992641	-2.04160925784227
C	-3.04970218826838	-1.34183578122396	-2.37372502736555
C	-2.06690544112353	-0.66468621725794	-1.68892180693666
H	-3.47422001058457	2.98328472866972	1.96421617319224
H	-5.19793266748338	1.57050909692626	0.86475944815638
H	-5.81756640224861	-0.11254742551649	-0.80149928555533
H	-5.18246557625899	-1.70926992458580	-2.58578973108776
H	-2.77680671088208	-2.02471334823687	-3.18192673132167
H	-1.01511687524742	-0.80780163268108	-1.94657004094295
C	-0.62594023228622	2.80178822561625	1.36076208510519
C	0.37037017520167	2.50762267742671	0.20691426148219
H	-0.21424535285155	2.43811366602350	2.31884587870243
H	-0.84716076505492	3.87452859156835	1.47647737849151
C	0.04590772260603	1.02806929190912	-0.03522448714990
H	1.41230412393834	2.63231502314036	0.53667394136539
C	0.07684562254173	3.45813814599566	-0.95616526076335
H	0.25224815356923	4.50066539697997	-0.64769518544019
H	-0.97318922370504	3.37365956050726	-1.27673113543342
H	0.70644731667940	3.26613418254647	-1.83624570459303
C	0.98011815982908	0.01634767636416	0.01096524543002

C	2.39098287764002	0.28761665035897	-0.33886039285805
C	3.42029077298909	-0.52182693032924	0.16784319865700
O	3.15501604628277	-1.59941148574688	0.93755032892027
C	1.88492117728012	-2.07478321034156	1.00976912945965
C	0.76244648766986	-1.35157342348677	0.54643639490471
C	-0.48397878097030	-1.96554605854393	0.77933777948475
C	1.77325109683321	-3.32319877908856	1.62450115746803
C	0.52702561366826	-3.89996231154937	1.81138419150363
H	2.69323570454093	-3.81219820871371	1.94975358651733
C	-0.60739581630020	-3.20764479159392	1.38847021167896
H	-1.39327844584675	-1.45419413217364	0.48584982164483
H	-1.60282792575942	-3.63195147318447	1.53549142044407
H	0.44148658155064	-4.87839815326260	2.28948415533267
C	2.78156554512643	1.29593490005865	-1.23864537159980
C	4.76681146234427	-0.27241652336693	-0.10440816356765
C	4.11456168209012	1.55109154717753	-1.53205985712624
H	2.00576979352648	1.87330328832750	-1.73771287974130
C	5.11679716079310	0.77613352111084	-0.94302970307237
H	5.51421145360809	-0.93021717099436	0.34274464122674
H	6.16931438925020	0.96944202236561	-1.16274820414564
H	4.37286970374931	2.34589773018505	-2.23509536540761

Conformer I6 (*syn-M*)

C	-3.21393197899857	2.23449740974307	1.24362117657062
C	-1.85098694288844	2.02773129633752	0.96692738464853
C	-1.42692729366316	1.00426748552349	0.12484726969710
C	-2.38394919908006	0.24527213906092	-0.61396013594279
C	-3.77282946971715	0.46974550993689	-0.34182542982511
C	-4.15522441296110	1.44894695968128	0.61317577893458
C	-4.74169166567369	-0.27728756700320	-1.06265294683678
C	-4.36510165471195	-1.18195806348725	-2.02741616604545
C	-2.99567635852344	-1.37431609578197	-2.32077132847374
C	-2.02927958655521	-0.67992619463437	-1.62956269643685
H	-3.52296801557868	3.02107740131749	1.93699604503275
H	-5.22018079636387	1.59749956851995	0.81098790223162
H	-5.79992562070122	-0.11020438574330	-0.84366262112089
H	-5.12308691673327	-1.74551026137386	-2.57682351347219
H	-2.70307585902371	-2.07838873573722	-3.10353427718744
H	-0.97172243055333	-0.83108870890306	-1.85625850311915
C	-0.66269325850359	2.83849000159089	1.39998269657375
C	0.35518183974226	2.54307130533582	0.26632191163184
H	-0.26823973181876	2.48009113520560	2.36730847528112
H	-0.88893798016744	3.91099284595501	1.50831381242435
C	0.04375394409845	1.06113117564429	0.02162530074774
H	1.38998383996946	2.67380545661570	0.61586447771284
C	0.07372927507763	3.48902027667136	-0.90372972362190
H	0.26903505572990	4.53105898058342	-0.60548034639328
H	-0.97958679986687	3.42113493244730	-1.21764603062389
H	0.68918876048974	3.27961823254030	-1.79009859244239
C	0.97954213667285	0.04900880353113	0.06138236963562
C	2.39168765768084	0.31106346743264	-0.29437773947414
C	3.41112350700681	-0.56007137533061	0.12569812509779
O	3.14247067274997	-1.68640196707830	0.81923168161782
C	1.86027813558411	-2.10819313928844	0.95405040918597
C	0.74641845786698	-1.32199164895784	0.58406038281410
C	-0.50859638479575	-1.88387673771103	0.89611606595153
C	1.73243069684329	-3.37120298695999	1.53637393781562
C	0.47658146067837	-3.89746265120088	1.79135025588161
H	2.64902458690577	-3.90948876320244	1.78400725581779
C	-0.64974972596053	-3.13766496374987	1.47540728225271
H	-1.41015963846218	-1.31724787054664	0.69447817990497
H	-1.65196703810036	-3.51735158880455	1.68508203025920
H	0.37757247677457	-4.88663821019376	2.24422206402521
C	2.79731548435133	1.36973266201812	-1.12897993015048
C	4.75828365579204	-0.33052014478413	-0.16325113260765

C	4.12965158835441	1.60826686666562	-1.43682378144171
H	2.03385407084264	2.00458379127659	-1.57153129320718
C	5.12213358401766	0.76457354385164	-0.93225481887644
H	5.49313288468788	-1.04226190887352	0.21707852214716
H	6.17479325884955	0.94229718354363	-1.16428130985271
H	4.39328887683583	2.44466590821657	-2.08764920794177

Conformer I7 (*anti-P*)

C	-3.42784428801745	2.37705128577345	-0.65806050646044
C	-2.04263233481691	2.29619506633492	-0.41879255035776
C	-1.44066038723893	1.12220515928110	0.01623708125778
C	-2.25713527314033	0.02827517178194	0.44179937853687
C	-3.66586454954477	0.10829405302719	0.18720356080370
C	-4.21600189832383	1.27974867758206	-0.39910865804248
C	-4.50241718682225	-0.96841539858884	0.58309588878993
C	-3.99155427179622	-2.05280235090903	1.25609250387922
C	-2.61744624514538	-2.09327354191473	1.58026241842645
C	-1.77396306468982	-1.08246008122282	1.18033334002137
H	-3.86775631614855	3.30311359150877	-1.03727107067092
H	-5.29245746265213	1.31329759575725	-0.58775411671539
H	-5.57172856990224	-0.90699008687463	0.36277142534804
H	-4.64893035503162	-2.86981866389279	1.56320067613571
H	-2.22000670728875	-2.93229109670409	2.15642222552941
H	-0.72037389755690	-1.11589797989156	1.45521217153700
C	-1.02305639664528	3.39037842900469	-0.49928797212536
C	0.12391084600250	2.83909470175870	0.37509798473575
H	-1.40740779132248	4.35769862068148	-0.13810587946206
H	-0.66377443523700	3.54581149981454	-1.53406339383632
C	0.03548096203446	1.33910861337477	0.06464400528117
H	-0.23863126190086	2.91380005487582	1.41881935799442
C	1.37967628328838	3.68369047598146	0.29102655020373
H	1.74109136903422	3.79667282383511	-0.74129320170370
H	2.19890981064770	3.29636663169190	0.90970524908596
H	1.13761345307283	4.69442226406261	0.65660995436190
C	0.98104949652743	0.40022451953251	-0.23069806022570
C	2.45749625728796	0.48062416479181	-0.06977590535655
C	3.05225262430850	-0.62351992042523	0.57352440791468
O	2.31614977633554	-1.73762653730259	0.86048956261512
C	1.32864841473837	-2.02496105496488	-0.04013659285163
C	0.63344041982626	-0.97703615448394	-0.65940657914731
C	-0.30191444881104	-1.30491587164775	-1.64815080913217
C	1.04733785785179	-3.35975575898827	-0.31789526182830
C	0.08187244942574	-3.66053546796071	-1.27425204710289
H	1.60652049735760	-4.13809593372343	0.20465583556886
C	-0.57741810453971	-2.63364734599501	-1.95385616196905
H	-0.82617811332480	-0.50004088256194	-2.16733949718252
H	-1.31634264812125	-2.87159857832091	-2.72199227630486
H	-0.14102591366928	-4.70449321517695	-1.50693878718951
C	3.32492919679199	1.47301518719708	-0.54457437922104
C	4.40770003402507	-0.65042222595021	0.89232519103534
C	4.68764741029958	1.44514932112178	-0.26164050429235
H	2.92322637020787	2.27235384005003	-1.16267552626259
C	5.22474647349148	0.40124784774089	0.49232399910378
H	4.80253623862478	-1.52166788655398	1.41816978271020
H	6.29088550396763	0.38202530106512	0.73015124376398
H	5.33434623264008	2.24052323172736	-0.63885199109952

2 Nature of the S_1 and S_2 transitions

anti-M

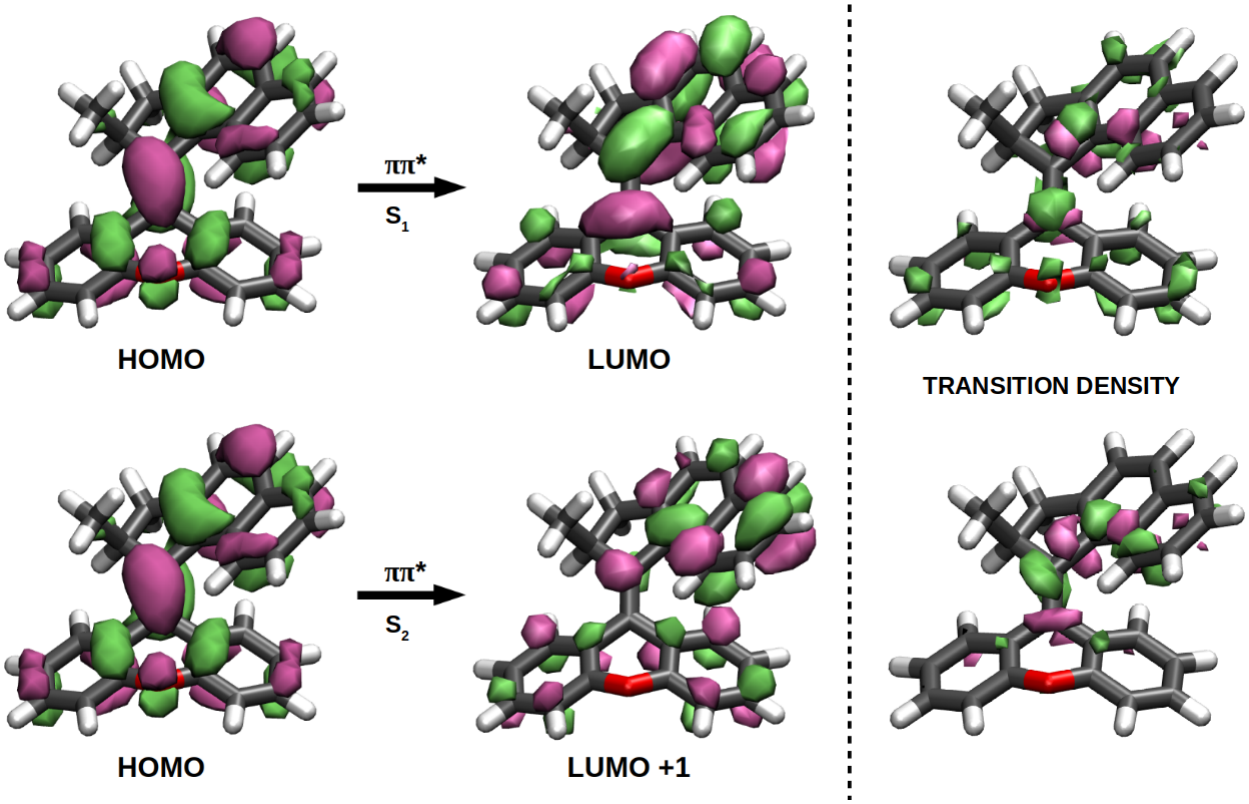

Figure S1: Schematic representation of the involved orbitals (electron density isovalue of 0.03 a.u.) in the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the anti-M conformer at the CC2/def2-TZVP level of theory. Transition density on the right side of each transition (electron density isovalue of 0.001 a.u.).

syn-P

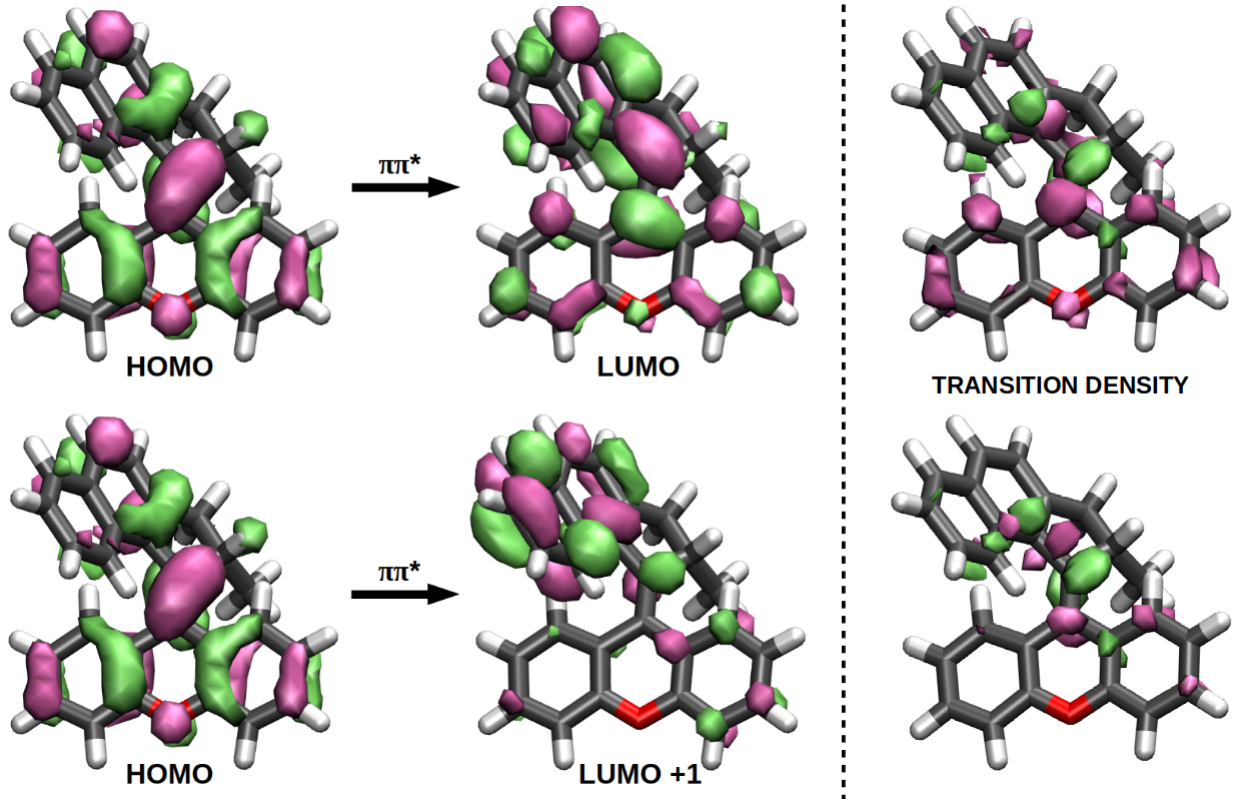

Figure S2: Schematic representation of the involved orbitals (electron density isovalue of 0.03 a.u.) in the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the syn-P conformer at the CC2/def2-TZVP level of theory. Transition density on the right side of each transition (electron density isovalue of 0.001 a.u.).

syn-M

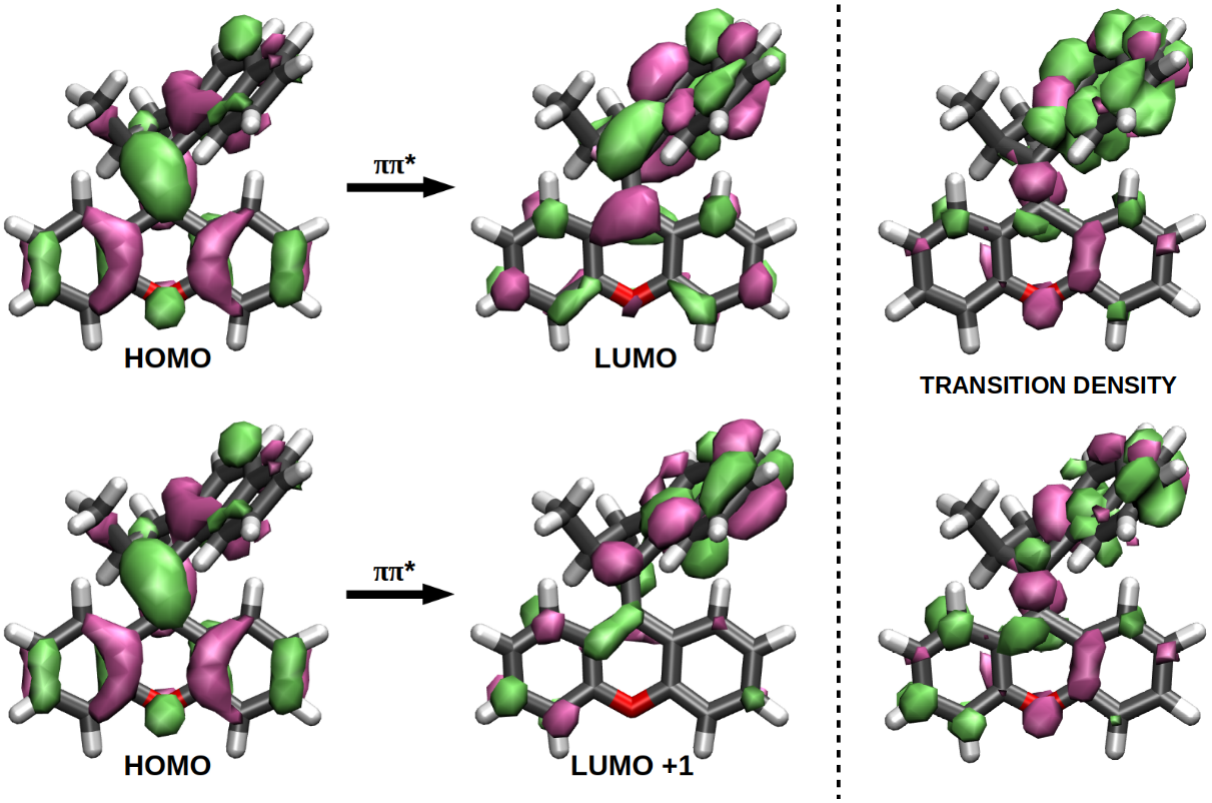

Figure S3: Schematic representation of the involved orbitals (electron density isovalue of 0.03 a.u.) in the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the syn-M conformer at the CC2/def2-TZVP level of theory. Transition density on the right side of each transition (electron density isovalue of 0.001 a.u.).

anti-P

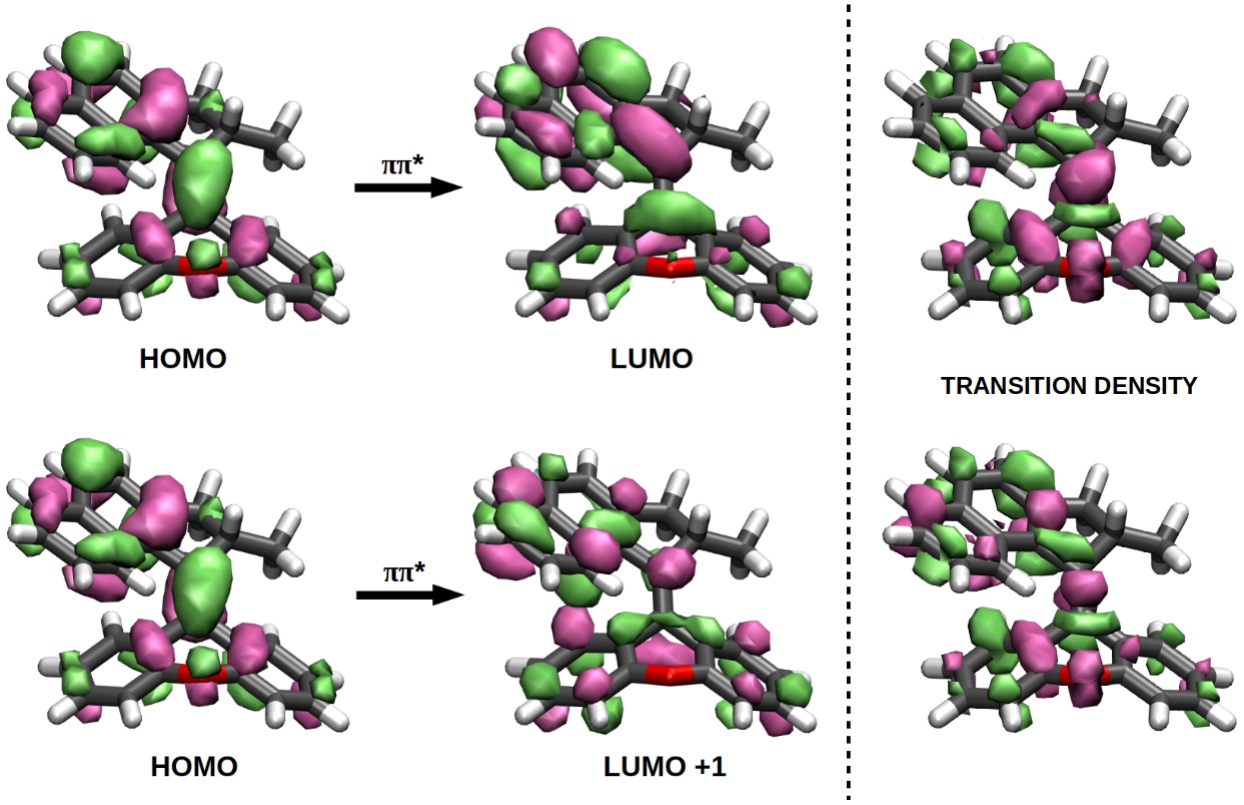

Figure S4: Schematic representation of the involved orbitals (electron density isovalue of 0.03 a.u.) in the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ transitions of the anti-P conformer at the CC2/def2-TZVP level of theory. Transition density on the right side of each transition (electron density isovalue of 0.001 a.u.).

A comparison between CC2 and TDPBE0 ground and excited state potential energies along the torsional coordinate α shows generally good agreement between the two methods (Figure S5). However, we note convergence problems of CC2 for several structures in the region around 45 degrees, which led to deviations between CC2 and TDPBE0 for some structures. In the S_1/S_0 intersection region, we note larger instabilities of CC2 compared to TDPBE0.

Table S3: TD-PBE0 excitation energies in eV, oscillator strengths in au (in parentheses), and dominant orbital contribution for the five lowest excited states of ground state equilibrium geometries of all four conformers optimized with PBE0/def2-SVP. H and L denote highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively.

	S_1	S_2	S_3	S_4	S_5
anti-M	3.271	3.881	4.085	4.150	4.290
	(0.4664)	(0.01527)	(0.02311)	(0.01093)	(0.01911)
	H → L (95%)	H → L+1 (57%)	H-1 → L (44%)	H → L+2 (31%)	H-2 → L (72%)
		H-1 → L (30%)	H → L+2 (19%)	H-3 → L (22%)	H → L+1 (13%)
anti-P	3.533	4.004	4.189	4.269	4.444
	(0.3781)	(0.01104)	(0.01555)	(0.01422)	(0.02519)
	H → L (97%)	H → L+1 (46%)	H-1 → L (42%)	H → L+1 (32%)	H-2 → L (62%)
		H-1 → L (39%)	H-2 → L (20%)	H → L+2 (22%)	H-3 → L (13%)
syn-M	3.062	3.757	3.981	4.011	4.082
	(0.4662)	(0.09900)	(0.006067)	(0.008237)	(0.002753)
	H → L (97%)	H → L+1 (71%)	H → L+2 (50%)	H-1 → L (51%)	H → L+3 (85%)
		H-1 → L (18%)	H-3 → L (16%)	H → L+2 (22%)	H-3 → L (4%)
syn-P	2.712	3.511	3.695	3.799	3.818
	(0.5105)	(0.03660)	(0.005866)	(0.007452)	(0.009836)
	H → L (94%)	H → L+1 (73%)	H → L+2 (94%)	H-1 → L (49%)	H → L+3 (63%)
		H-1 → L (16%)	H → L+3 (2%)	H-2 → L (34%)	H-3 → L (23%)

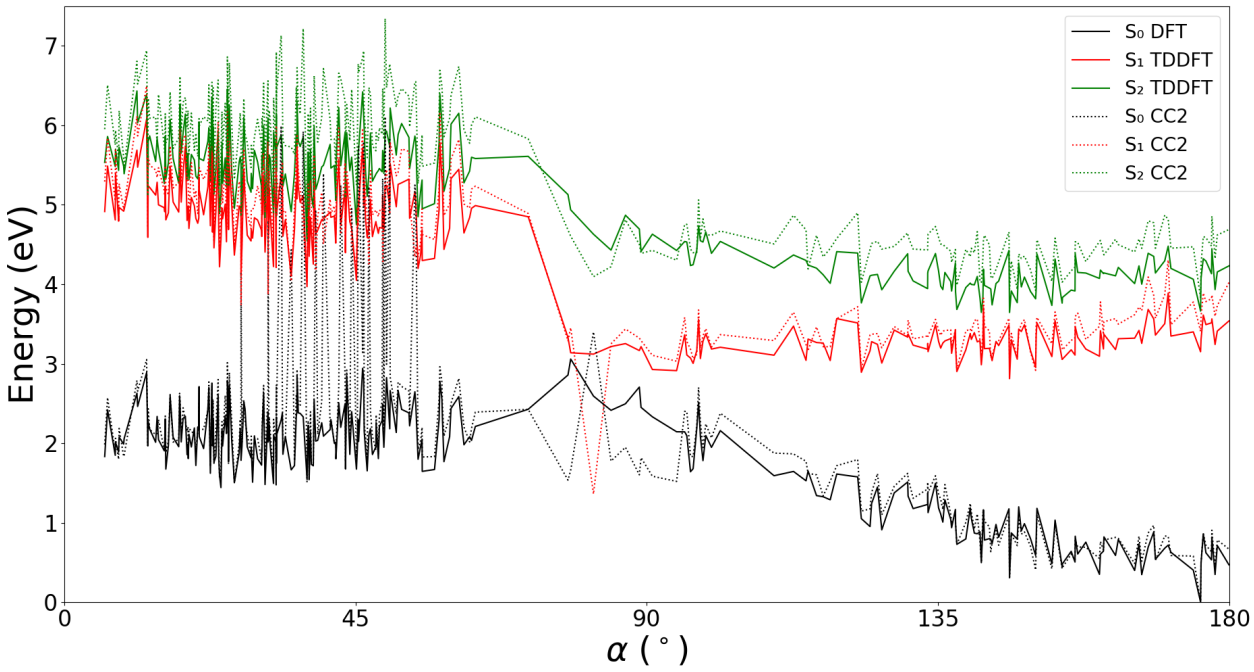

Figure S5: TDPBE0/def2-SVP and CC2/def2-SVP potential energies as a function of α. Structures were taken from one trajectory of **anti-M**. CC2 values were computed every 10 MD steps.

3 TDDFT-SH trajectories

3.1 Evolution of the dihedral angles along the TDDFT-SH trajectories

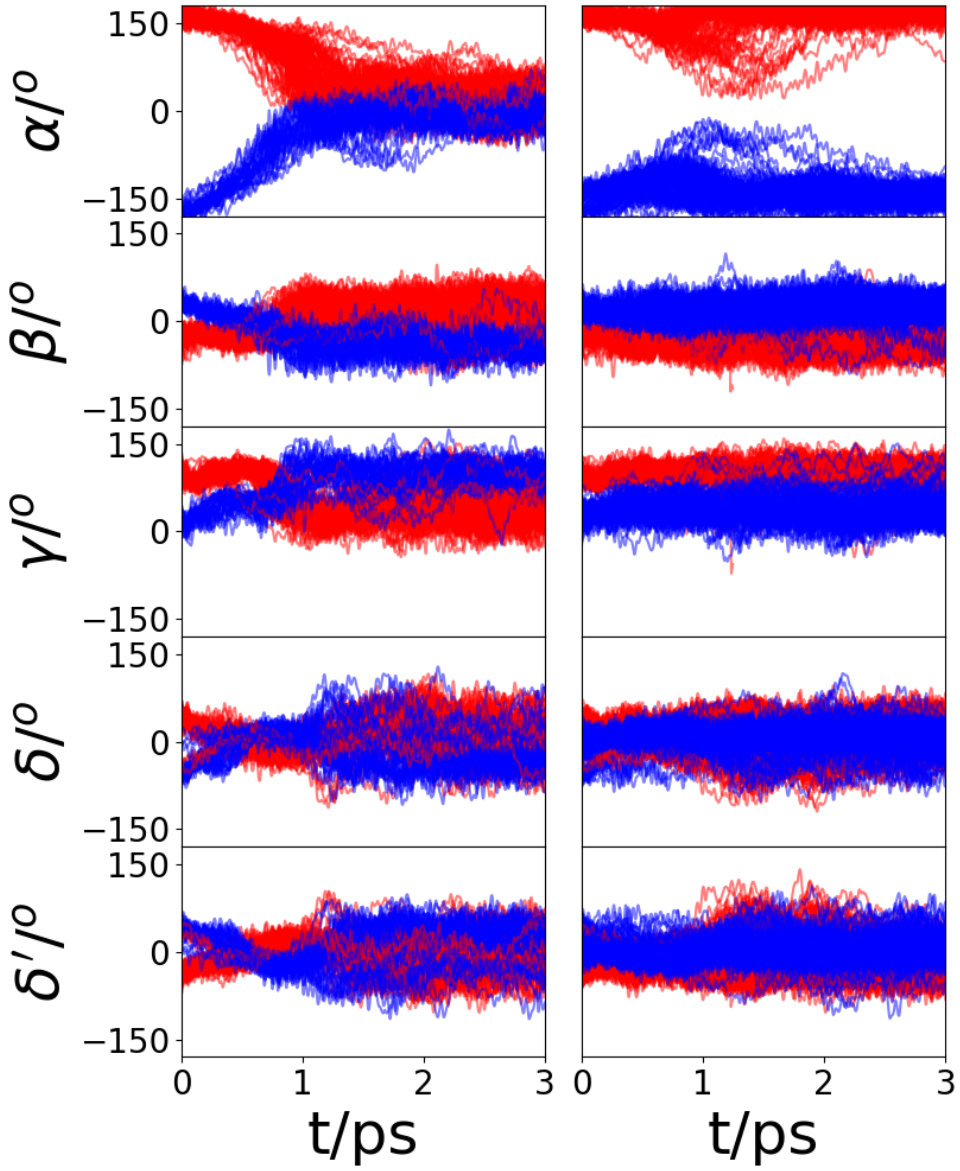

Figure S6: Evolution of the dihedral angles along the trajectories. Panels on the left represent trajectories that isomerize whereas panels on the right account for trajectories without isomerization. Red lines are associated to trajectories with initial M-conformers while blue lines represent trajectories with initial P-conformers.

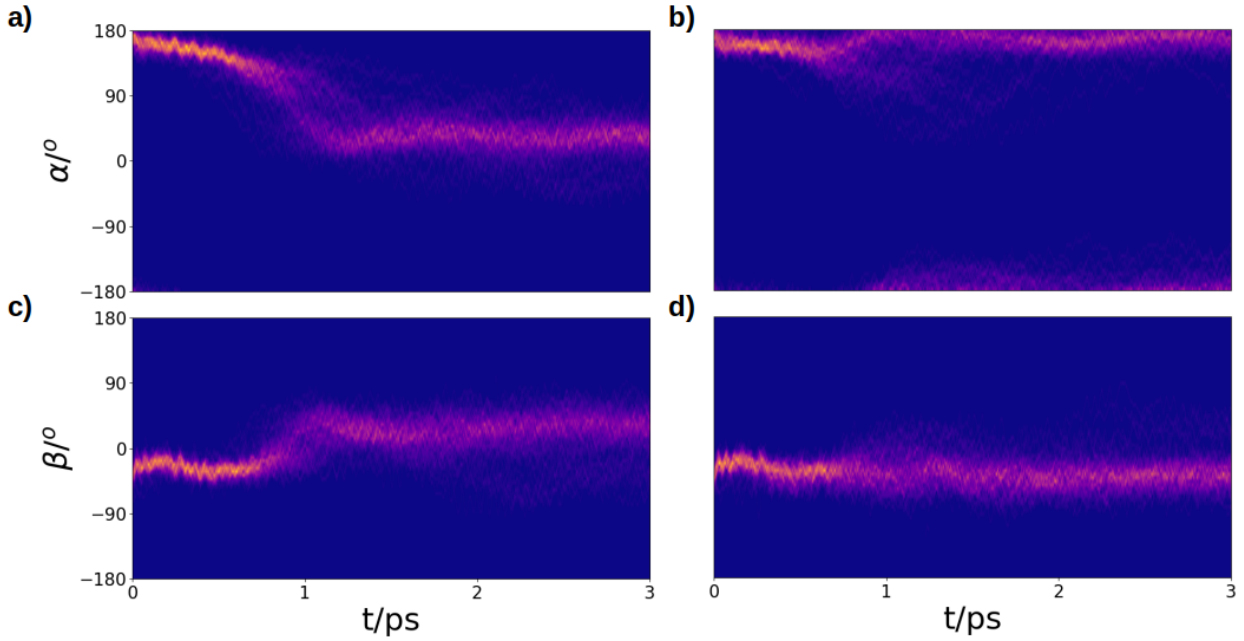

Figure S7: Density plot for the evolution of dihedral angles α (a, b) and β (c, d) along the trajectories with initial M-conformers. Panels on the left (a, c) represent trajectories that isomerize, whereas panels on the right (b, d) account for trajectories without isomerization.

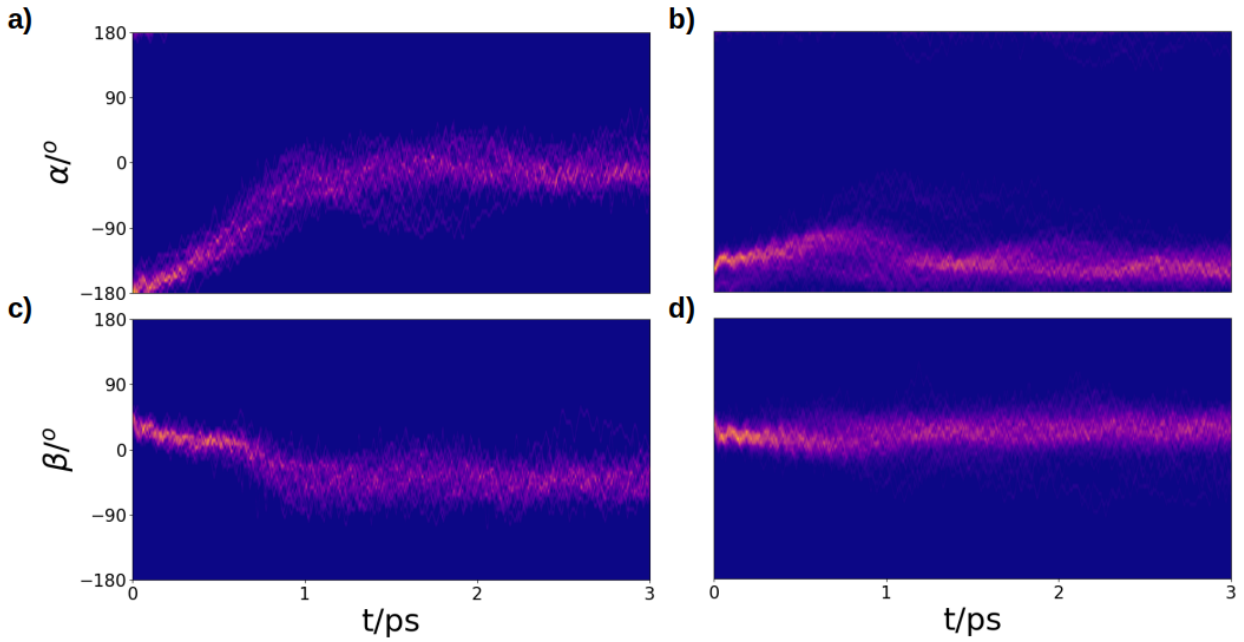

Figure S8: Density plot for the evolution of dihedral angles α (a,b) and β (c, d) along the trajectories with initial P-conformers. Panels on the left (a, c) represent trajectories that isomerize, whereas panels on the right (b, d) account for trajectories without isomerization.

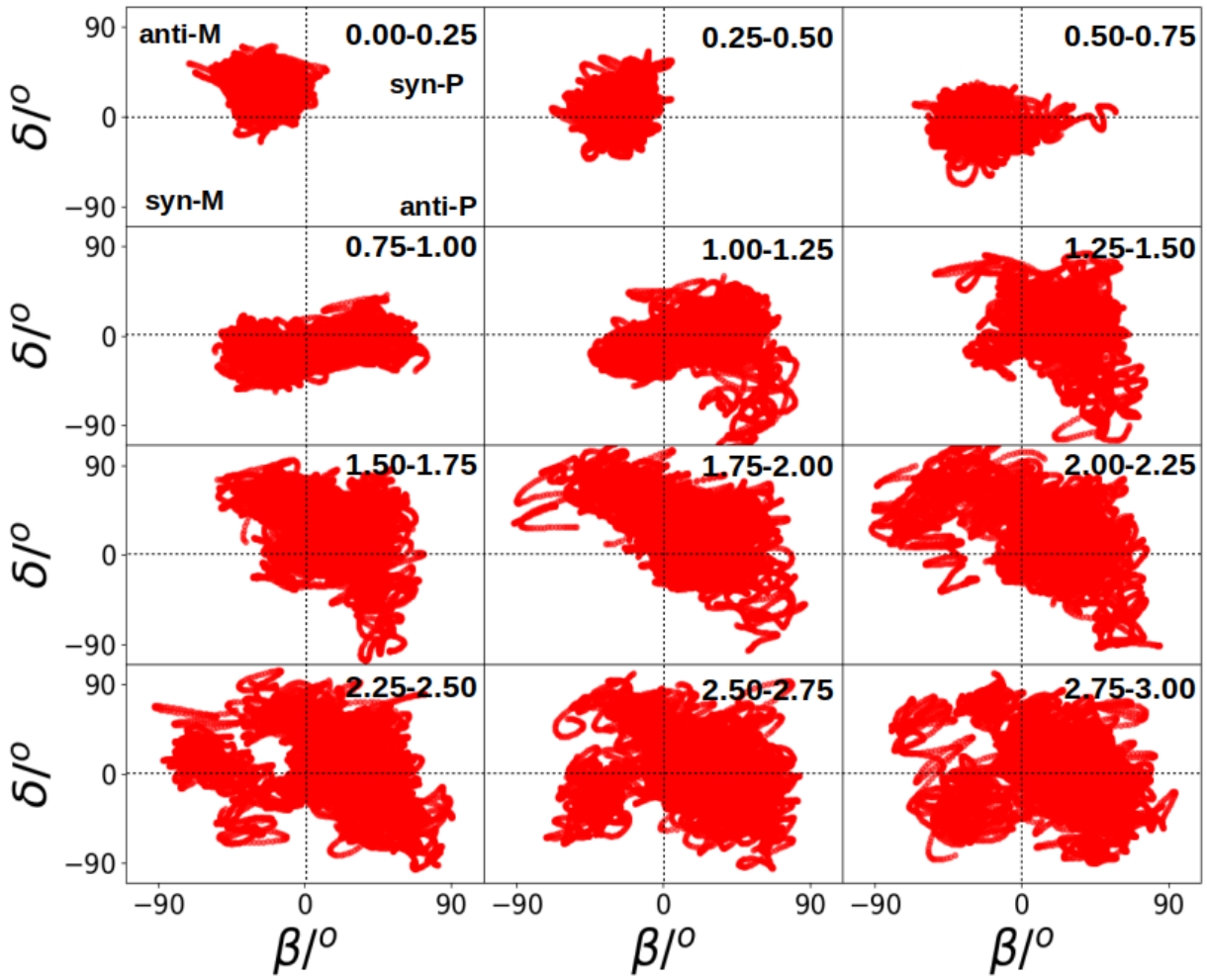

Figure S9: Correlation between dihedral angles δ and β for different times (in ps) in intervals of the TDDFT-SH simulations. All 114 trajectories displayed were started from initial anti-M conformers.

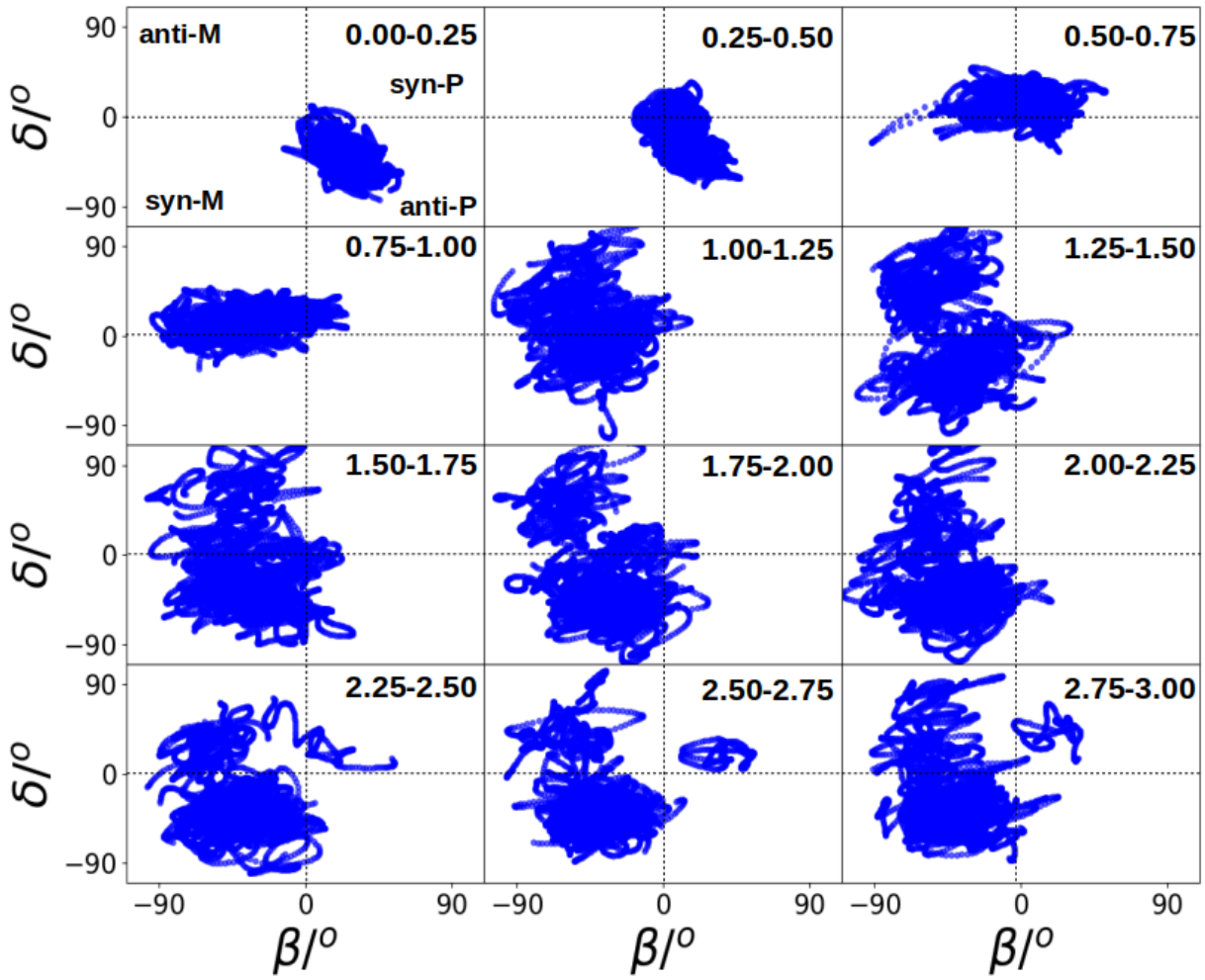

Figure S10: Correlation between dihedral angles δ and β for different times (in ps) in intervals of the TDDFT-SH simulations. All 30 trajectories displayed were started from initial anti-P conformers.

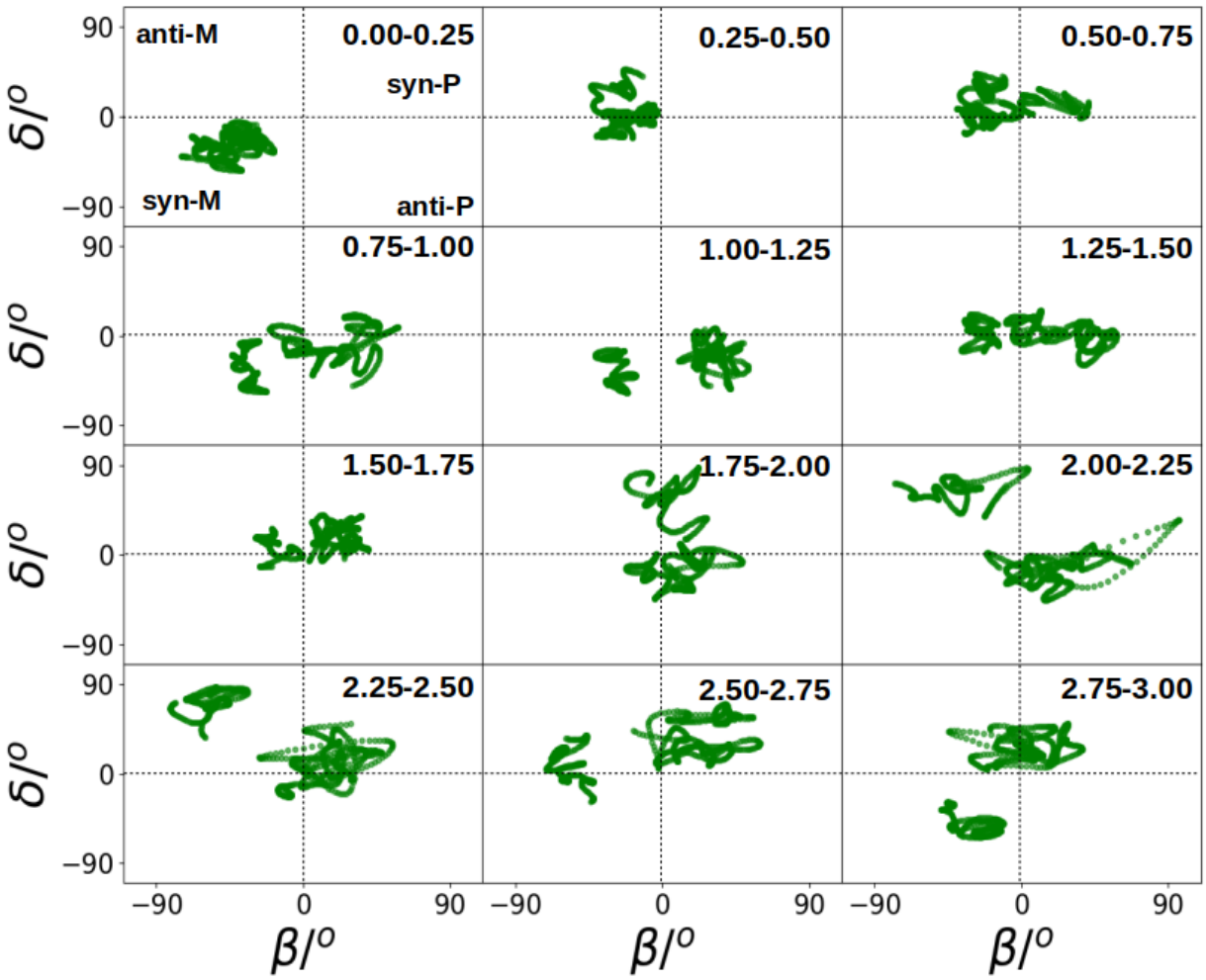

Figure S11: Correlation between dihedral angles δ and β for different times (in ps) in intervals of the TDDFT-SH simulations. All 3 trajectories displayed were started from initial syn-M conformers.

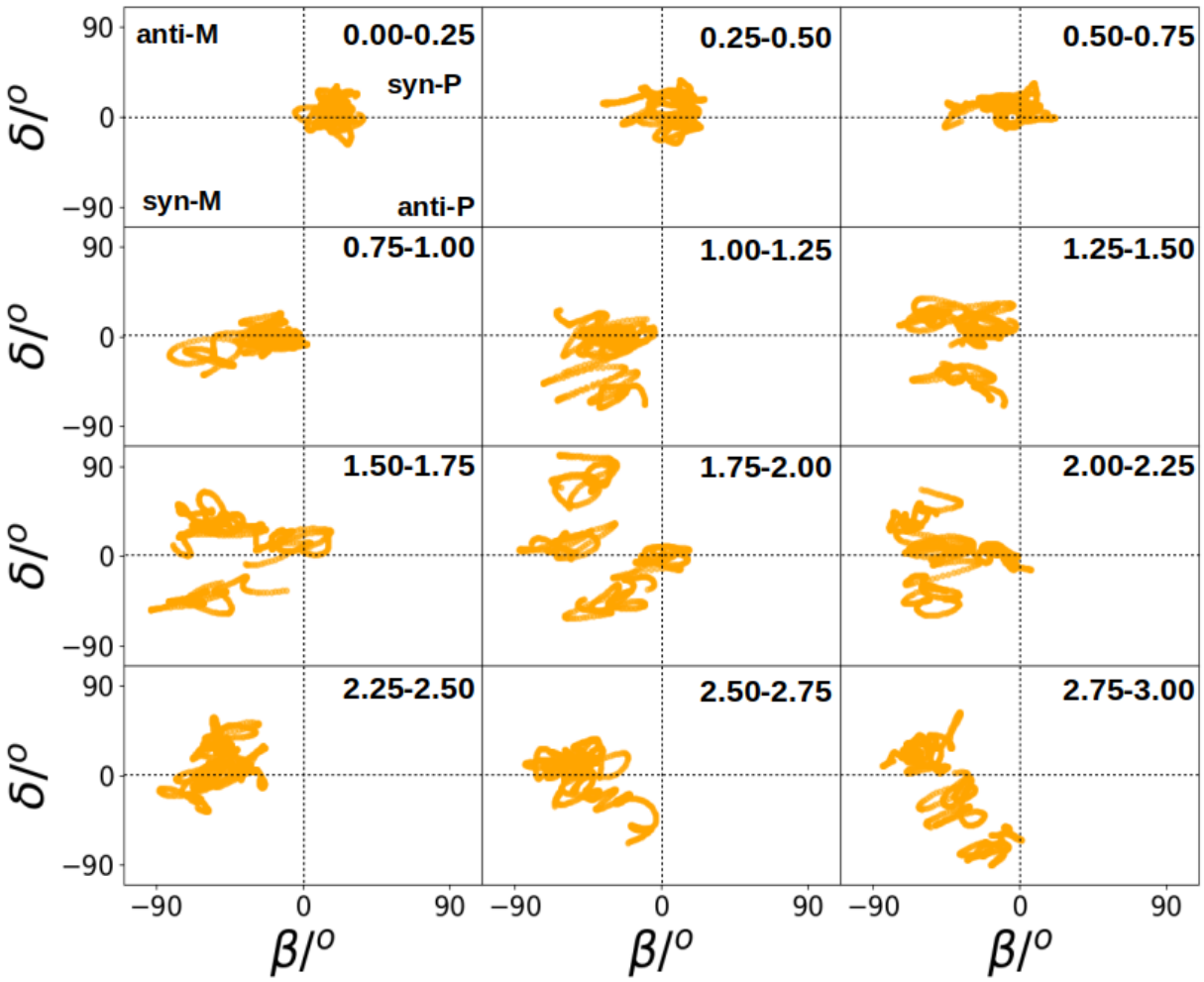

Figure S12: Correlation between dihedral angles δ and β for different times (in ps) in intervals of the TDDFT-SH simulations. All 4 trajectories displayed were started from initial syn-P conformers.

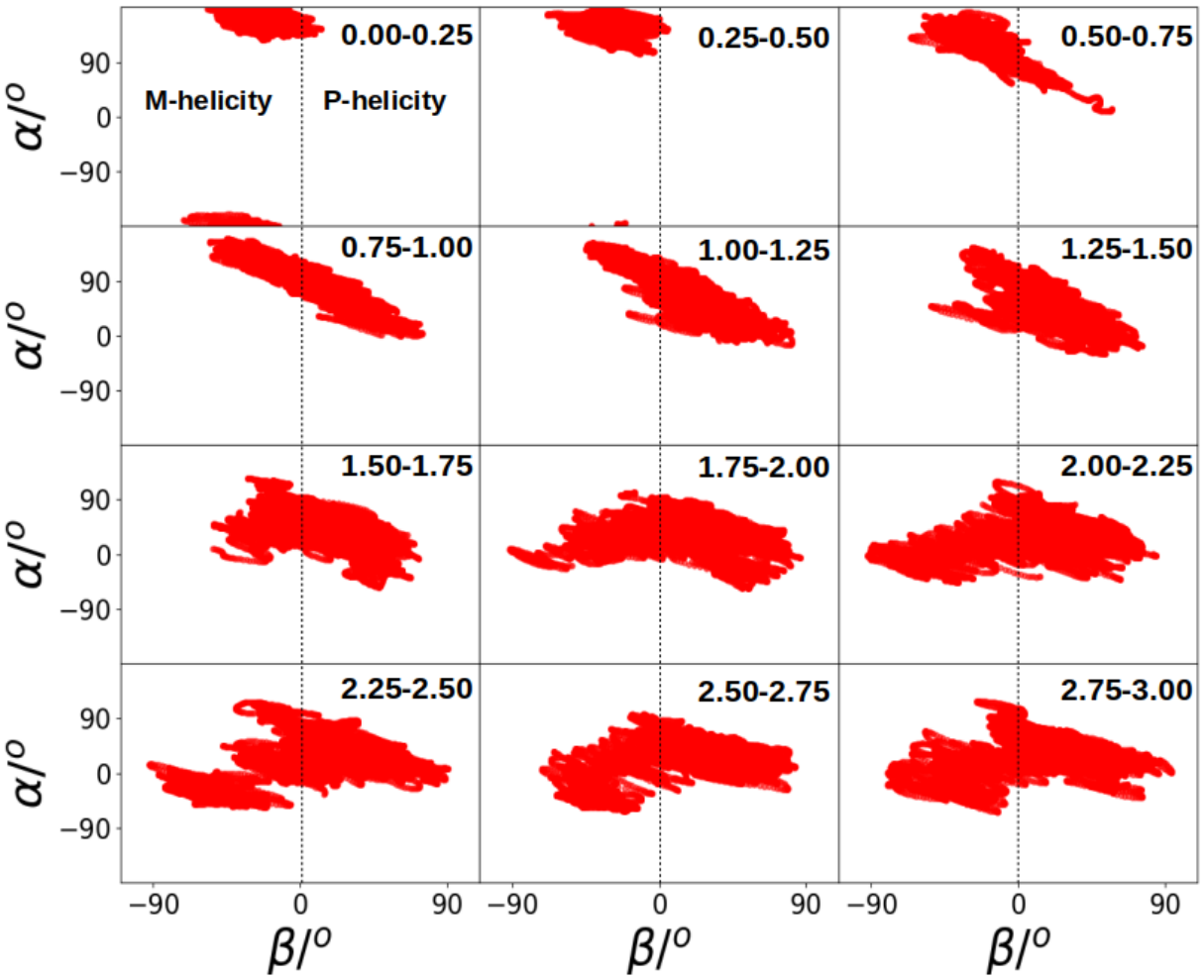

Figure S13: Correlation between dihedral angles α and β for different times (in ps) in intervals of the TDDFT-SH simulations. All 114 trajectories displayed were started from initial anti-M conformers.

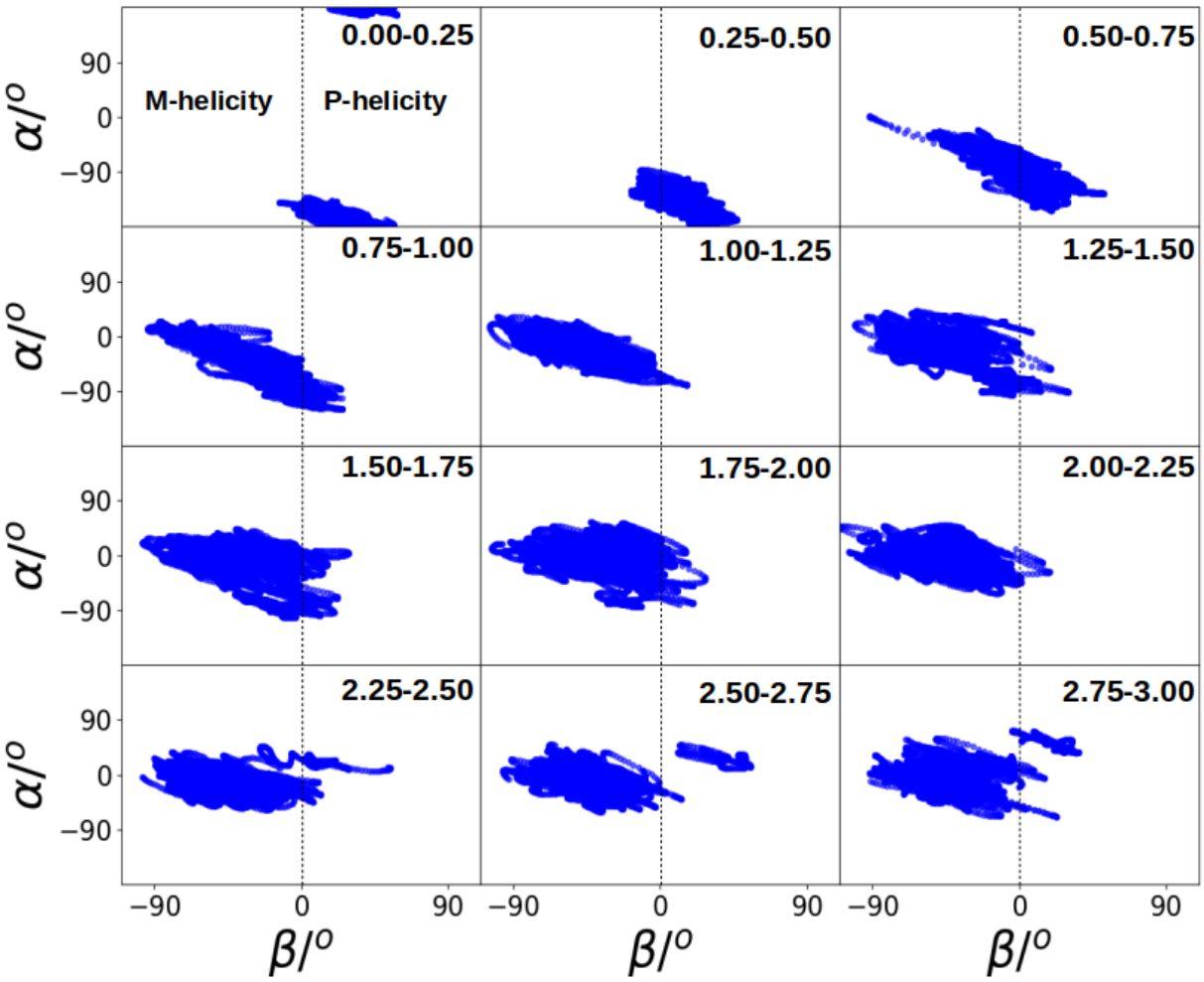

Figure S14: Correlation between dihedral angles α and β for different times (in ps) in intervals of the TDDFT-SH simulations. All 30 trajectories displayed were started from initial anti-P conformers.

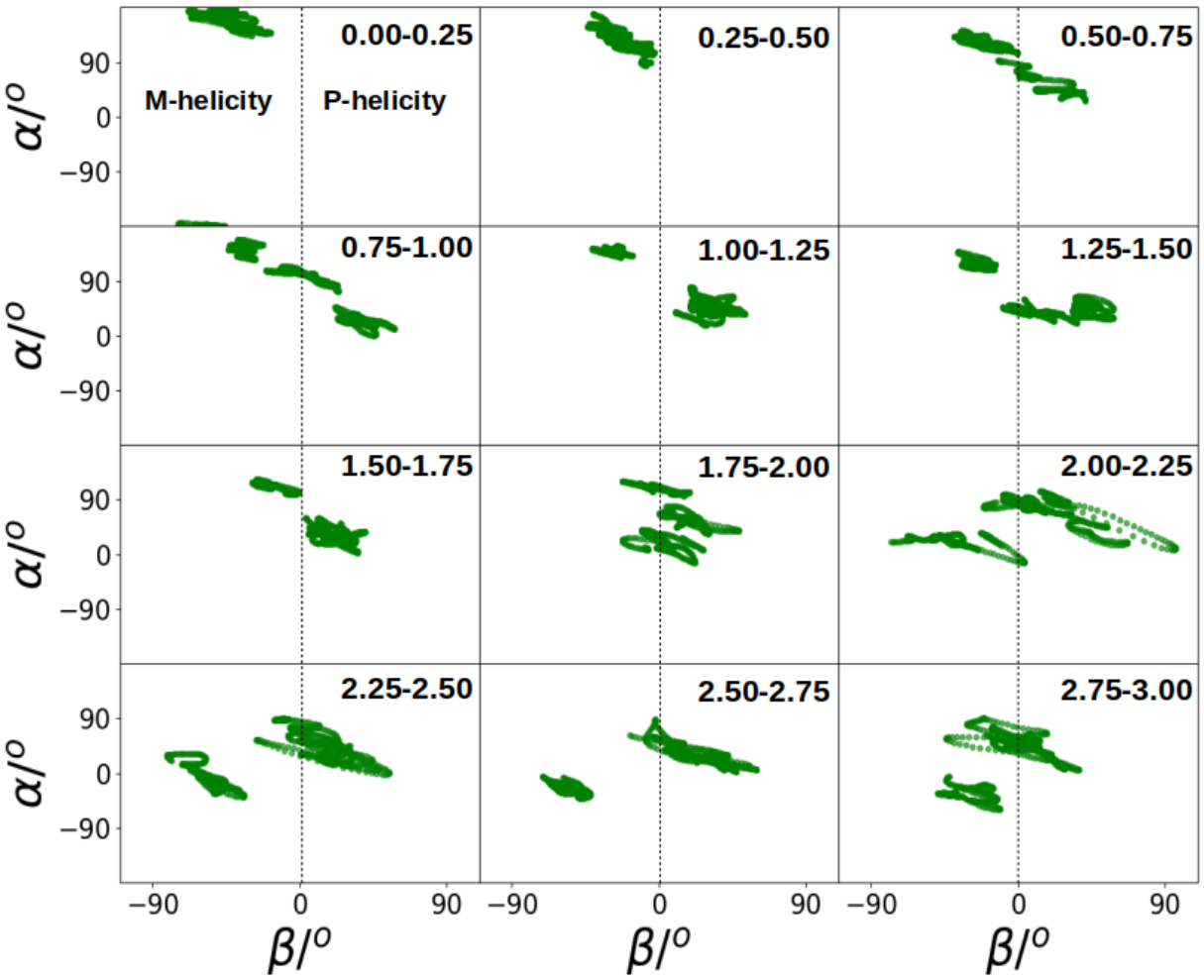

Figure S15: Correlation between dihedral angles α and β for different times (in ps) in intervals of the TDDFT-SH simulations. All 3 trajectories displayed were started from initial syn-M conformers.

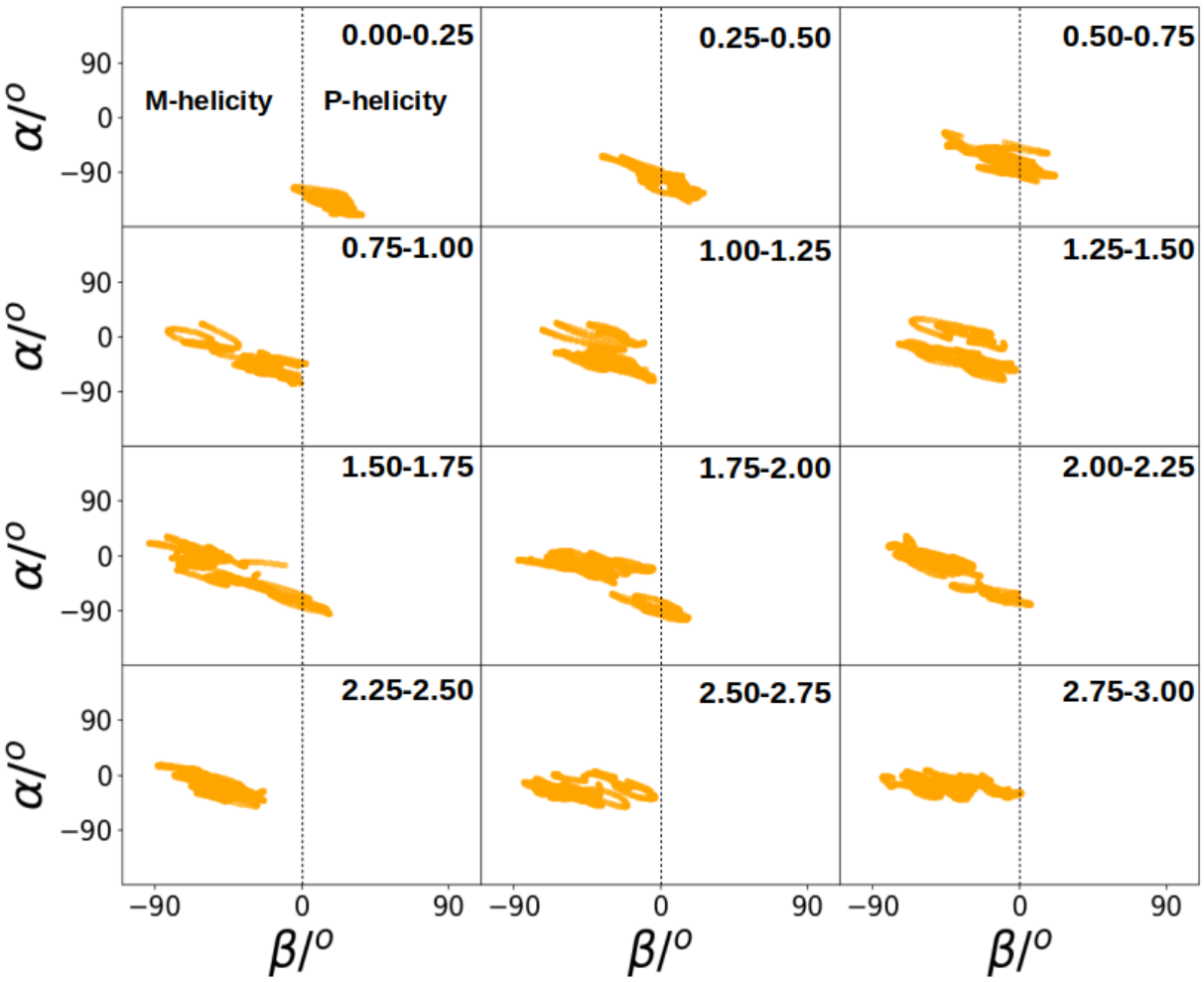

Figure S16: Correlation between dihedral angles α and β for different times (in ps) in intervals of the TDDFT-SH simulations. All 4 trajectories displayed were started from initial syn-P conformers.

3.2 Non-adiabatic couplings between S_0 and S_1

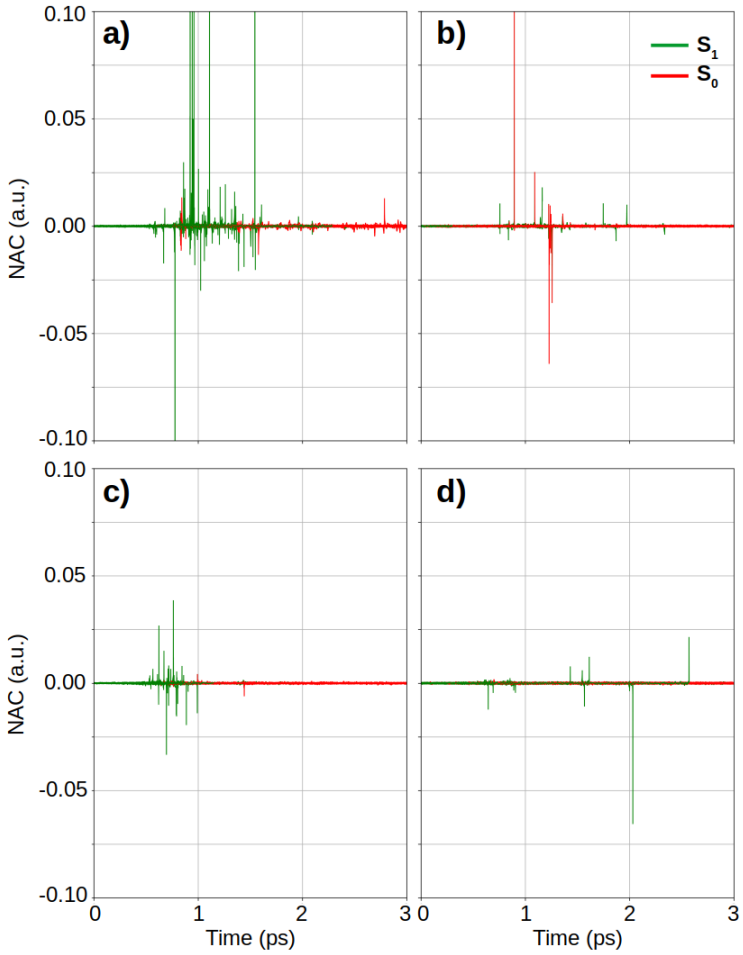

Figure S17: S_0 – S_1 non-adiabatic coupling (NAC) along the trajectories of each conformer. a) Reactive trajectories of M-helical initial structures, b) unreactive trajectories of M-helical initial structures, c) reactive trajectories of reactive P-helical initial structures, and d) unreactive trajectories of P-helical initial structures. Green: trajectory is in S_1; red: trajectory is in S_0.