

Supporting Information

Theoretical survey on photochemical deracemization mechanism of chiral allene 3-(3,3-dimethyl-1-buten-1-ylidene)-2-piperidinone

Kun Yuan*, Peng Wang*, Hui-Xue Li, Yan-Zhi Liu, Ling-Ling Lv*

College of Chemical Engineering and Technology, Tianshui Normal University, Tianshui 741001, China

Key Laboratory for New Molecule Materials Design and Function of Gansu Universities, Tianshui 741001, China

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* corresponding author, e-mail: yuankun@tsnu.edu.cn

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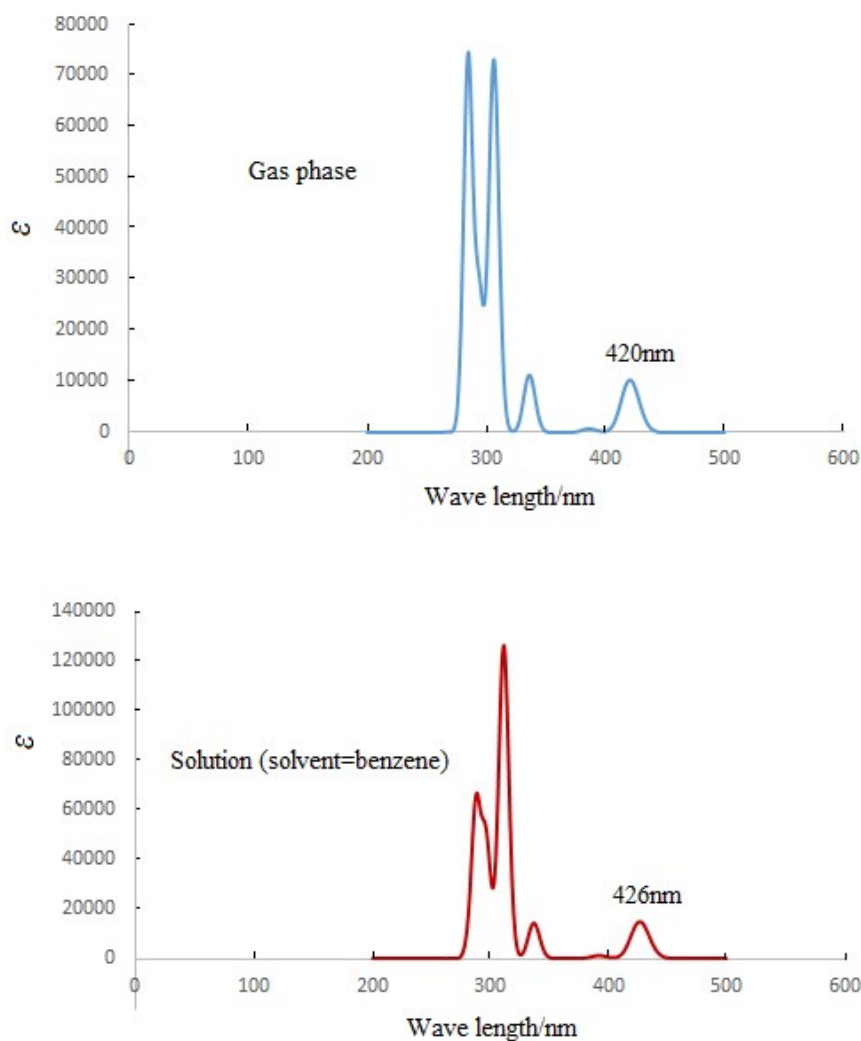


Fig. S1. UV-vis spectra of the photo-sensitizer **2** at the theoretical level of B97D3/6-311G(d, p) in gas phase and in solution (solvent=benzene)

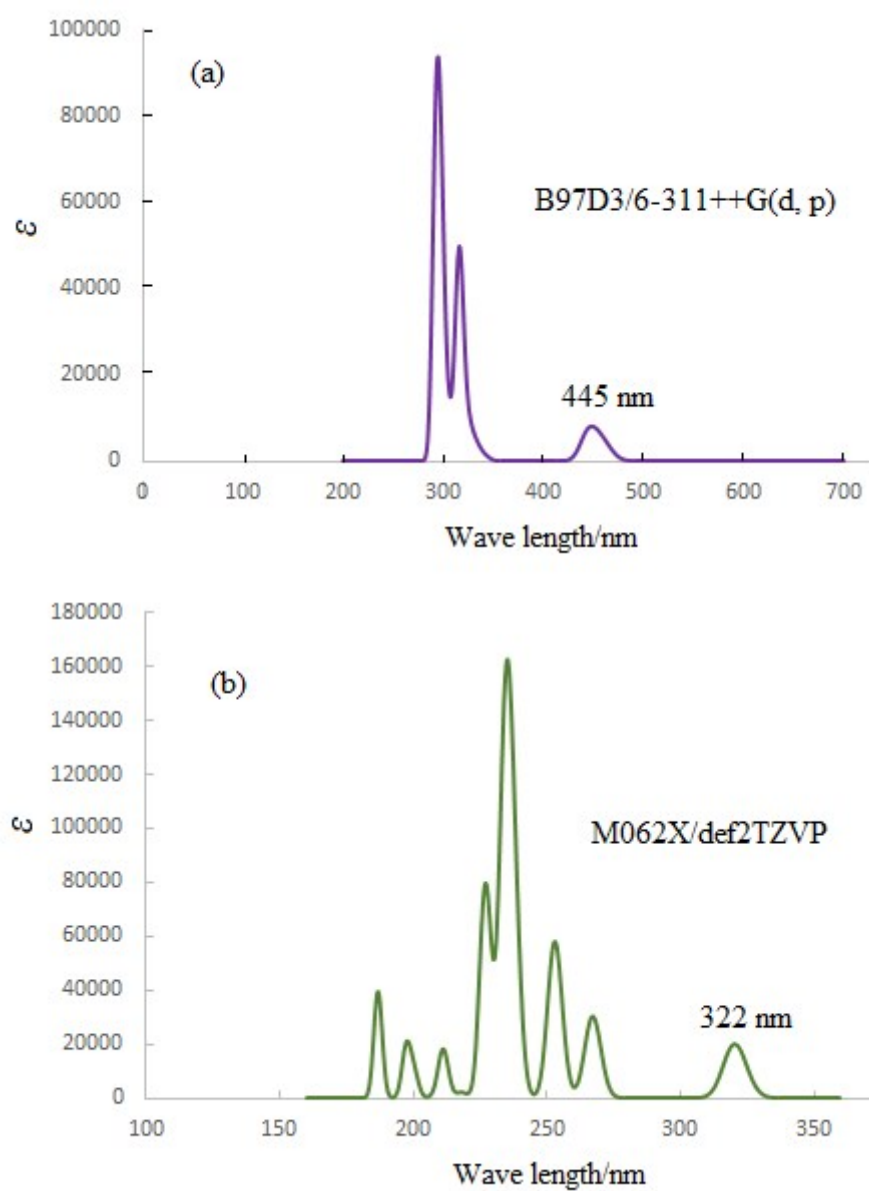


Fig. S2. UV-vis spectra of the photo-sensitizer **2** at the theoretical level of B97D3/6-311++G(d,p) (a) and M062X/def2TZVP (b) in gas phase

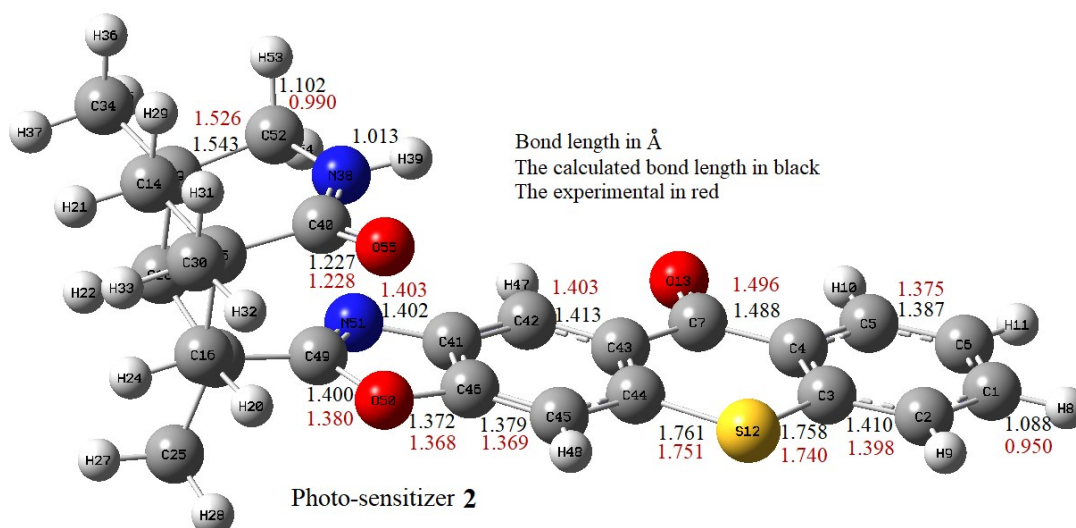


Fig. S3. Geometric configuration of the photo-sensitizer **2** at the theoretical level of B97D3/6-311G(d, p) (the corresponding experimental data are in red)

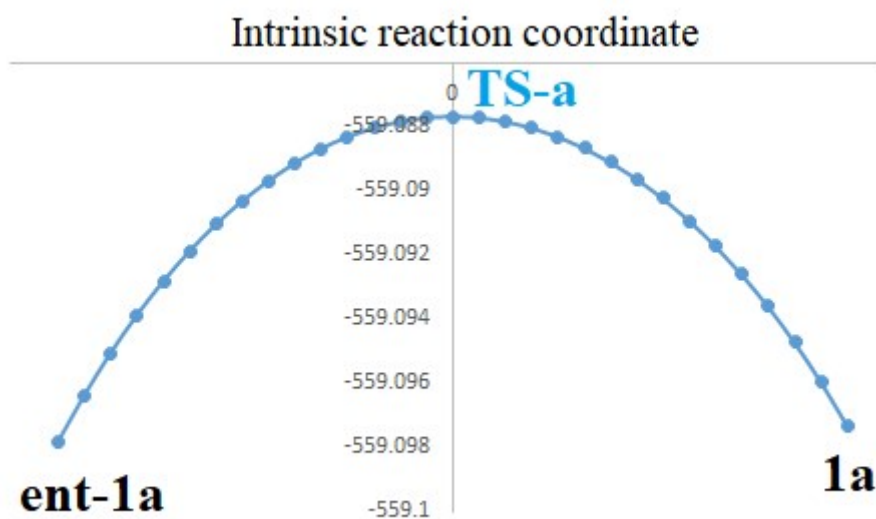


Fig. S4. The corresponding intrinsic reaction coordinate (IRC) of the one-step path

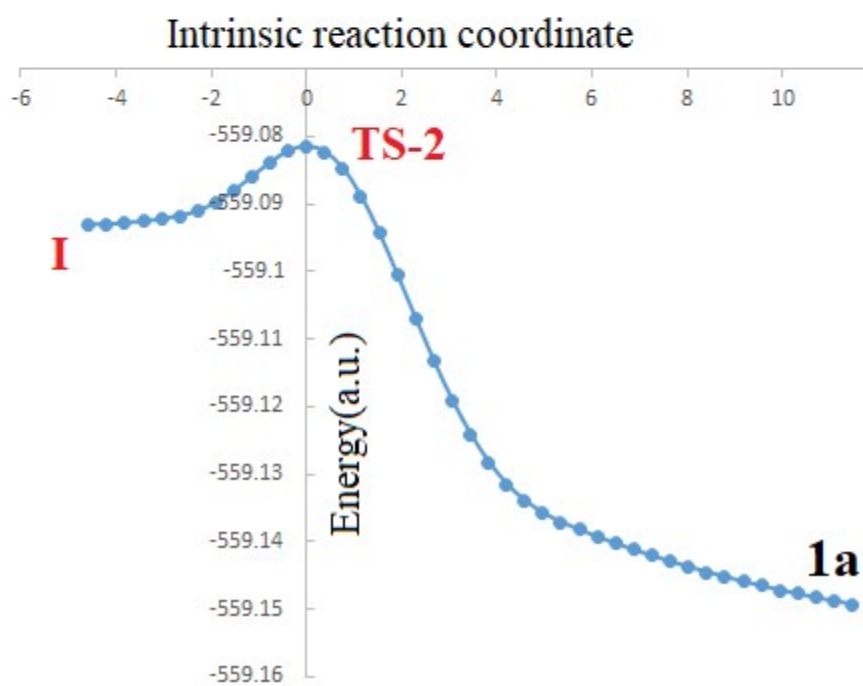
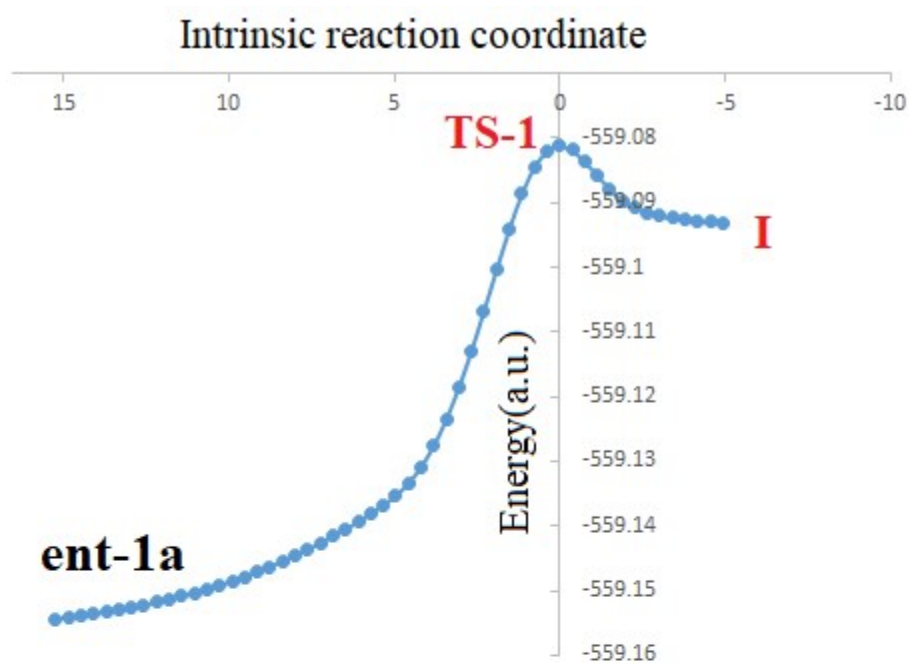


Fig. S5. The corresponding intrinsic reaction coordinate (IRC) of the two-steps path

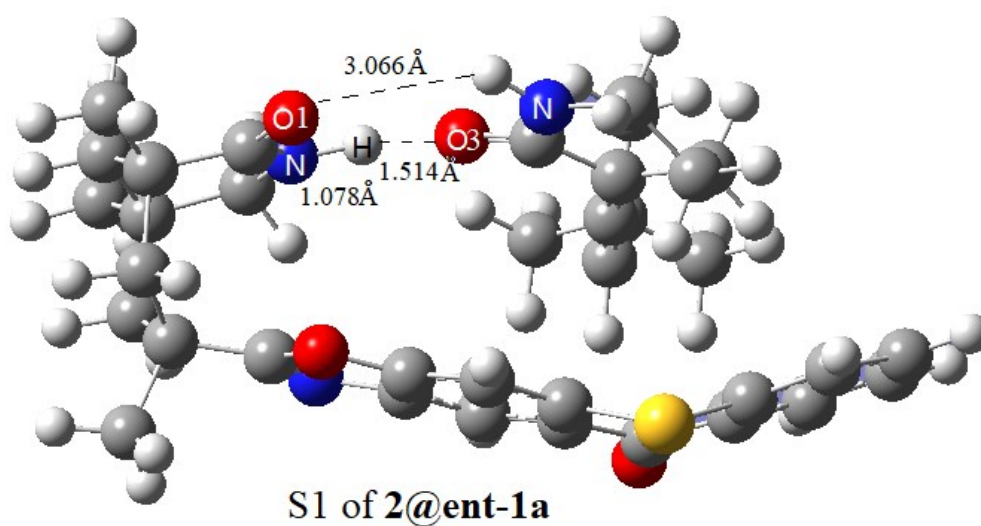
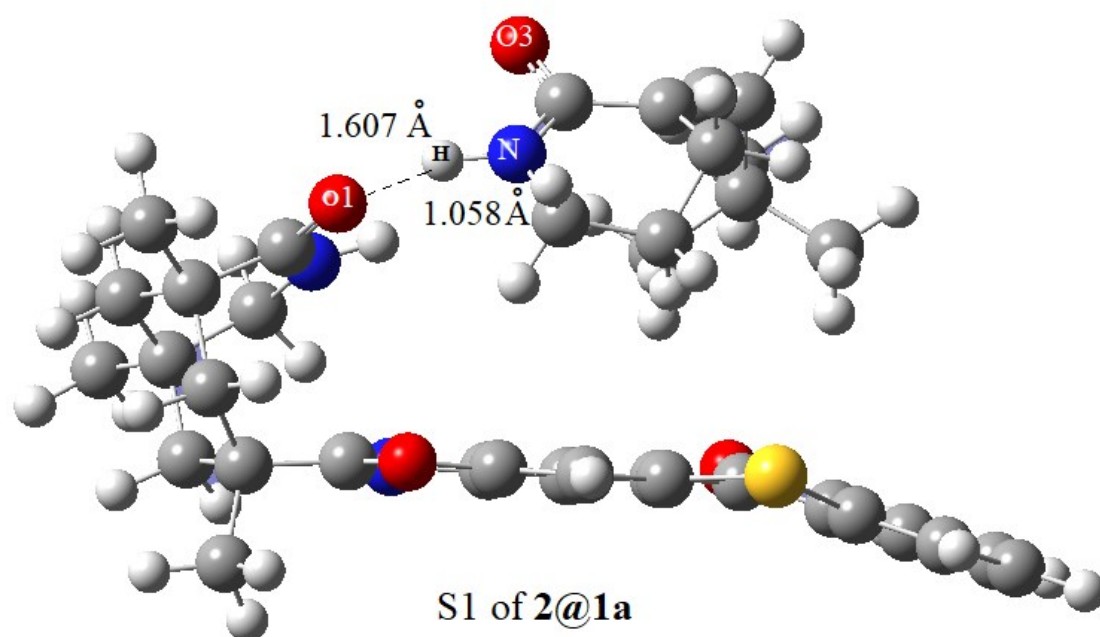


Fig. S6. Geometric configuration of the S1 states of the two complexes at the theoretical level of B97D3/6-311G(d,p)

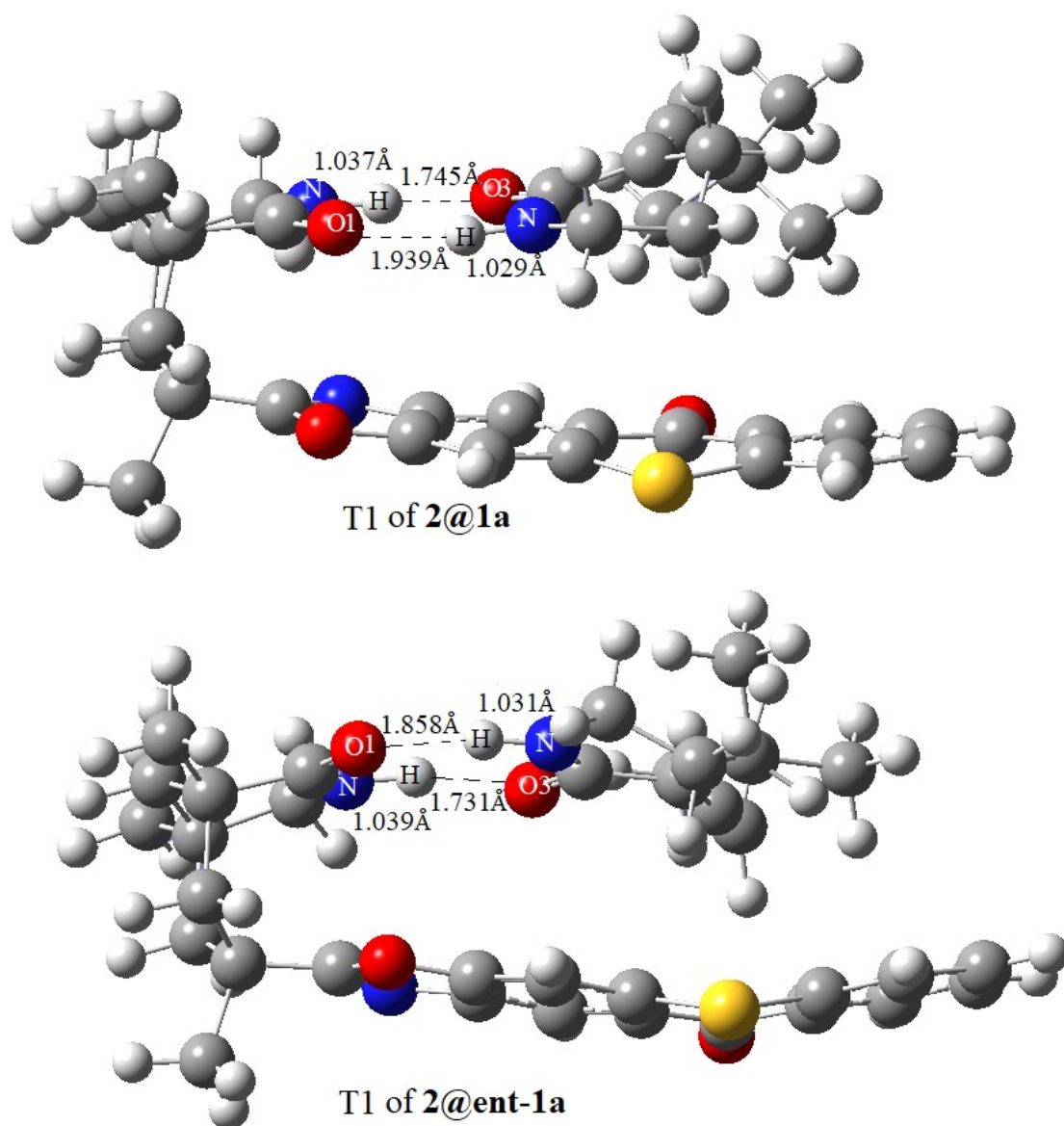


Fig. S7. Geometric configuration of the T1 states of the two complexes at the theoretical level of B97D3/6-311G(d,p)

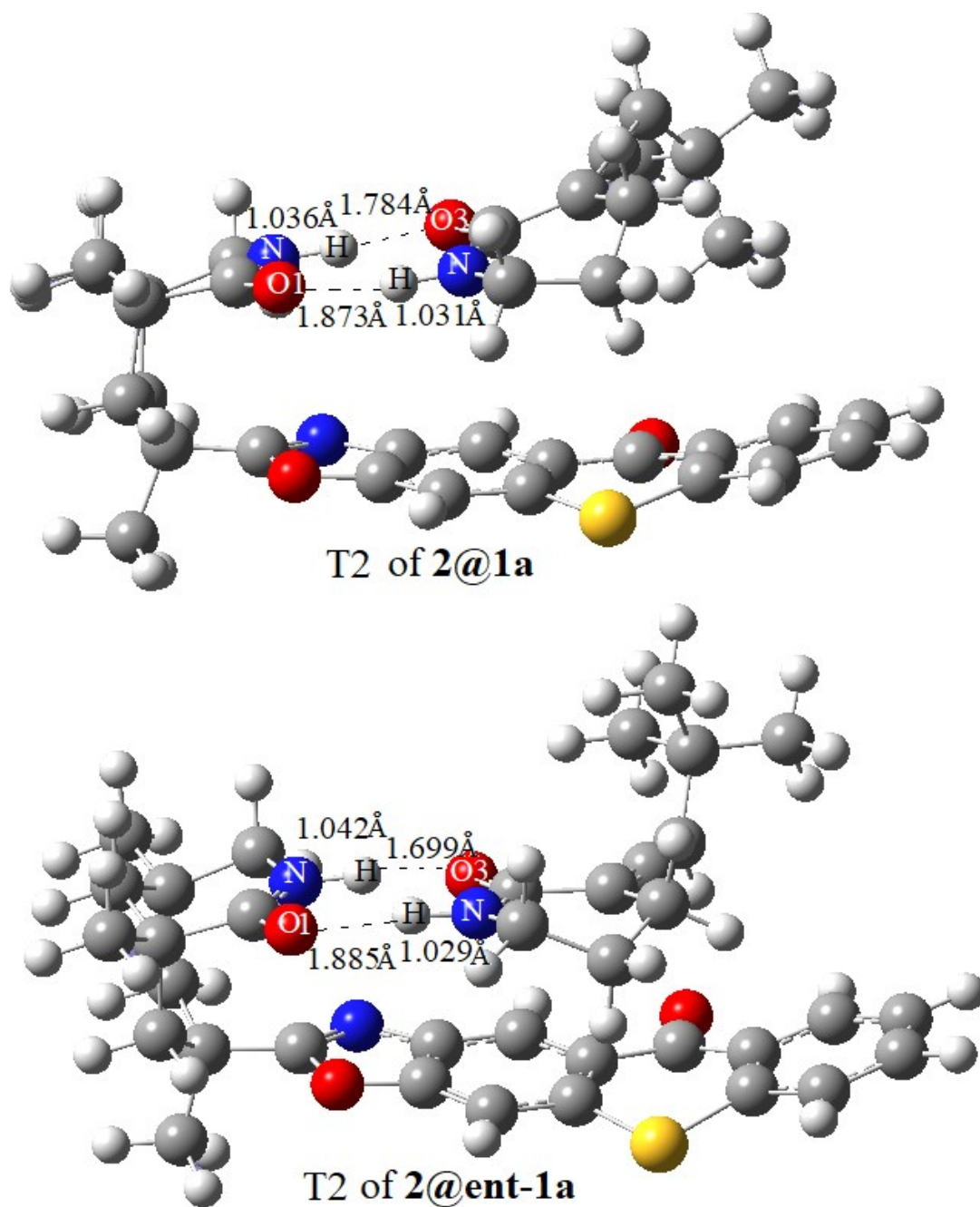


Fig. S8. Geometric configuration of the T2 states of the two complexes at the theoretical level of B97D3/6-311G(d,p)

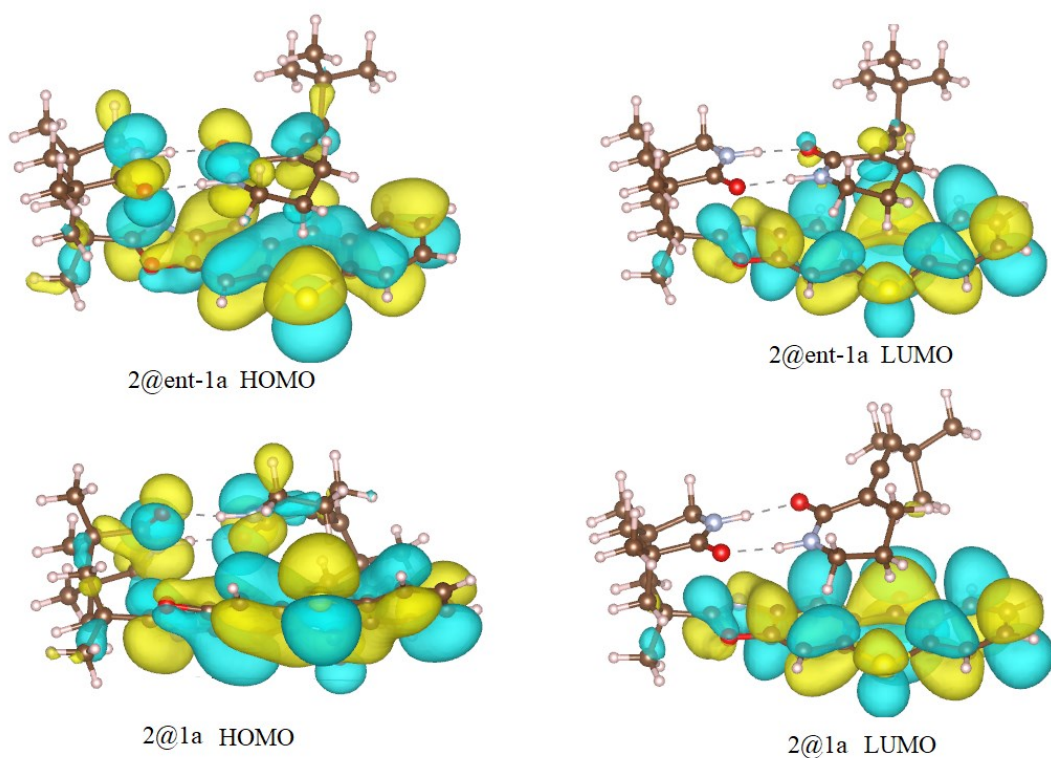


Fig. S9 The frontier molecular orbital of **2@ent-1a** and **2@1a** complexes

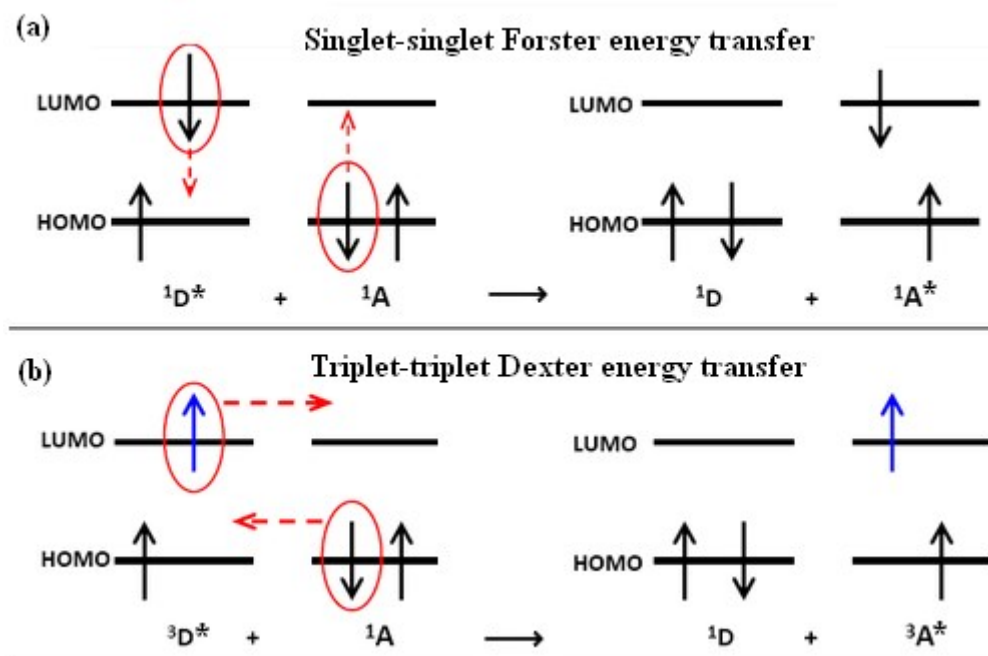


Fig. S10 Förster mechanism (a) and Dexter mechanism (b) of energy transfer (The arrows present the two simultaneous electronic transitions)

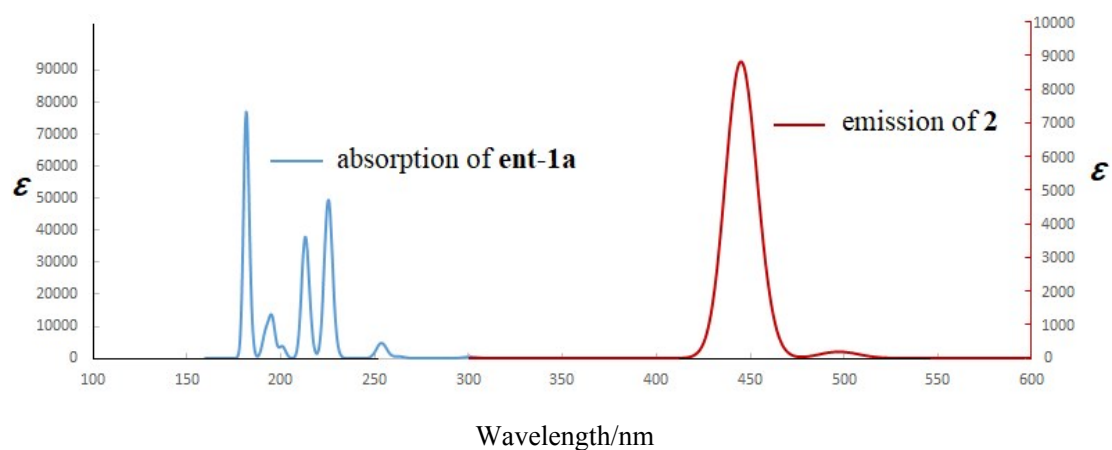


Fig. S11 The emission spectrum of **2**^{*}(S1) and absorption spectrum of **ent-1a**(S0)

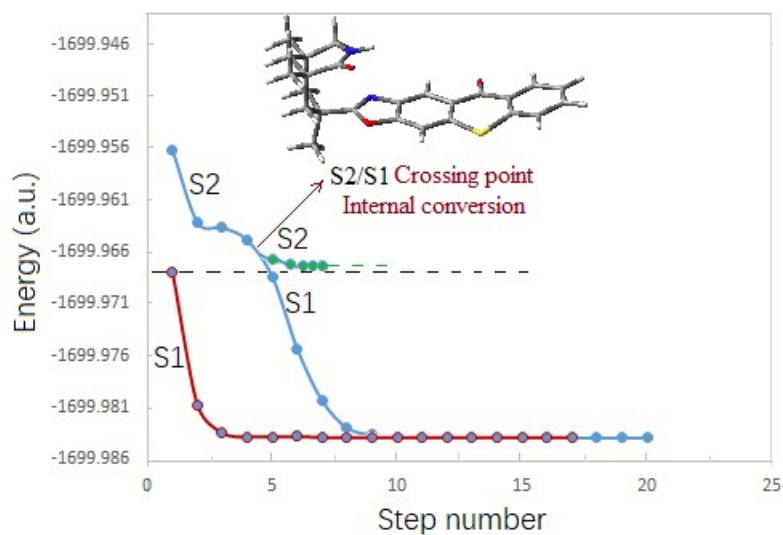


Fig. S12 The potential surface crossing between S1 and S2 states of photo-sensitizer **2**

Table S1 Computed total absolute energies, values of imaginary frequencies and their numbers of the target or optimized structures

Species/State	Absolute energy/a.u.	Imaginary frequency/cm ⁻¹	Number of imaginary frequencies	Feature
1a/S0	-559.1553670		0	stable
1a/T1	-559.0852320		0	stable
ent-1a/S0	-559.1557530		0	stable
ent-1a/T1	-559.085232		0	stable
TS-a	-559.0876682	-386.17	1	transition
TS1	-559.0811725	-525.62	1	transition
I	-559.0931410		0	stable
TS2	-559.0814697	-523.19	1	transition
2/S0	-1700.069340		0	stable
2/S1	-1699.983889		0	stable
2/T1	-1699.978313		0	stable
2@1a	-2259.267171		0	stable
2@ent-1a	-2259.272612	□	0	stable

Table S2 Cartesian coordinates of T1 state of **1a**

C	3.07153500	-1.49184100	0.39162800
C	1.66000000	-1.49892400	-0.20930900
C	0.99229100	-0.14213800	-0.06734200
C	1.80500200	1.09777300	0.00421200
C	3.88136300	-0.33776200	-0.19687300
H	3.00955500	-1.36839700	1.48105700
H	1.72305700	-1.75506100	-1.28132300
H	3.69809000	1.78866900	-0.01182800
H	4.86619000	-0.27209700	0.28240100
H	3.57992600	-2.44292900	0.18784900
H	1.03899000	-2.27391500	0.25799300
H	4.05106800	-0.51626600	-1.27396000
N	3.17656200	0.92202000	0.02287100
O	1.30479300	2.22382400	0.06586600
C	-0.37781700	-0.01156100	-0.03618100
C	-1.53624400	-0.70016100	-0.06707700
H	-1.51906300	-1.79859100	-0.14928100

C	-2.91805500	-0.07881100	0.00668000
C	-2.82467800	1.45278400	0.11878500
C	-3.69708100	-0.46983700	-1.27204100
C	-3.64662400	-0.65725100	1.24336700
H	-3.82940900	1.89164500	0.17118200
H	-2.26645300	1.74623600	1.01530200
H	-2.30085700	1.87720400	-0.74545100
H	-3.71481600	-1.75167700	1.18748200
H	-3.11577500	-0.39211100	2.16550100
H	-4.66666300	-0.25489700	1.30323300
H	-4.71771000	-0.06667700	-1.23065900
H	-3.20295000	-0.06883500	-2.16503900
H	-3.76561400	-1.56066300	-1.37657400

Table S3 Cartesian coordinates of S1 state of photo-sensitizer **2**

C	7.47519400	-0.28884400	1.05466400
C	6.43667800	-1.15415900	0.66421700
C	5.23692900	-0.64009800	0.17911500
C	4.99509000	0.75920500	0.09439500
C	6.06549600	1.60754500	0.50269100
C	7.27396000	1.09636100	0.96016200
C	3.74669600	1.36992700	-0.33338200
H	8.41543800	-0.69660300	1.41842100
H	6.57176900	-2.23333900	0.72549500
H	5.88584400	2.67659600	0.43129600
H	8.07026100	1.78060200	1.25224200
S	4.05815000	-1.83112600	-0.44857900
O	3.61841200	2.62720900	-0.43436900
C	-5.22302900	0.43259100	0.88579200
C	-4.39504100	-0.85192200	1.06905800
C	-4.00515800	-1.44329800	-0.31913400
C	-3.36103900	-0.46666500	-1.33650200
C	-4.08155000	0.90167500	-1.30176500
C	-4.43512700	1.48251200	0.09021800
H	-3.36824200	-2.32337800	-0.19123100
H	-6.13121400	0.15186100	0.33964900
H	-5.03291900	0.78485200	-1.83873500
H	-3.48060500	1.62638200	-1.85896800
H	-4.95744900	-1.79605200	-0.73539300
C	-3.51955000	-1.08067400	-2.75219600
H	-3.07893200	-0.41161000	-3.49859700

H	-4.57997900	-1.22808000	-2.99448500
H	-3.00430800	-2.04443800	-2.81349800
H	-5.53872800	0.82795000	1.86093000
C	-5.16281100	-1.90032000	1.89533400
H	-5.38906000	-1.53406300	2.90255700
H	-4.61248800	-2.84314400	1.97773600
H	-6.10894600	-2.10746100	1.38794200
C	-5.28309800	2.75028700	-0.11083800
H	-4.70790400	3.52325900	-0.63393400
H	-5.62075700	3.16162600	0.84871100
H	-6.16808400	2.52338600	-0.71587800
N	-2.61569500	0.76694700	1.69349100
H	-1.70422700	0.93804800	2.10790000
C	-3.11546000	-0.43062800	1.78696300
C	0.14273900	0.43902400	-0.85171500
C	1.30991900	1.19089500	-0.69755200
C	2.53742100	0.51592100	-0.51710200
C	2.54217700	-0.91232000	-0.50271500
C	1.36624100	-1.67570000	-0.61974200
C	0.19128600	-0.95672100	-0.80246100
H	1.33776500	2.27580600	-0.73146200
H	1.39006500	-2.76112900	-0.58745700
C	-1.87862300	-0.28482400	-1.09322800
O	-1.12573900	-1.43326400	-0.95118400
N	-1.20644600	0.82539100	-1.04627100
C	-3.19790500	1.88728100	0.91532400
H	-3.46130800	2.65243900	1.65362500
H	-2.39841800	2.24100900	0.26150000
O	-2.55162300	-1.33334500	2.50064600

Table S4 Cartesian coordinates of T1 state of photo-sensitizer **2**

C	7.52458200	-0.65077700	0.56997000
C	6.37959900	-1.39342900	0.26803700
C	5.14838200	-0.74413800	0.09326600
C	5.00979100	0.67180700	0.21489100
C	6.19506000	1.39223500	0.51108000
C	7.41468500	0.74582500	0.69498300
C	3.76037200	1.39416000	0.03784300
H	8.47894100	-1.15096100	0.70865900
H	6.43764000	-2.47468300	0.15519100
H	6.10975300	2.47105600	0.59838800

H	8.29533500	1.33422400	0.94660500
S	3.78459600	-1.78318900	-0.28153900
O	3.75034400	2.66892600	0.14857200
C	-5.17132400	-0.01201900	1.00003500
C	-4.33684700	-1.22053000	0.54195500
C	-4.05060800	-1.09020800	-0.97746400
C	-3.38334600	0.23729400	-1.41617900
C	-4.09649100	1.43779700	-0.74851400
C	-4.40810500	1.29855200	0.76092400
H	-3.45074700	-1.94301700	-1.31141200
H	-6.12397200	0.00191900	0.44980600
H	-5.05893000	1.56009700	-1.26551000
H	-3.51429300	2.34846100	-0.92822200
H	-5.01834600	-1.15159200	-1.49527000
C	-3.49442700	0.37257300	-2.96118500
H	-3.03475900	1.30861900	-3.29739400
H	-4.55049500	0.37102900	-3.25722700
H	-2.99104800	-0.46340900	-3.46031100
H	-5.41837900	-0.11160900	2.06709000
C	-5.08554500	-2.53394800	0.80277500
H	-5.32368700	-2.63946500	1.86801900
H	-4.47166000	-3.39038100	0.51061300
H	-6.02460500	-2.55068200	0.23488200
C	-5.25527700	2.50904800	1.18664000
H	-4.69386300	3.44491700	1.06643100
H	-5.55986500	2.42520900	2.23747400
H	-6.16301800	2.57883400	0.57474400
N	-2.47612900	-0.03301800	1.64377100
H	-1.57098000	-0.09104900	2.09714600
C	-2.98649200	-1.25438900	1.28413400
C	0.11987100	0.83115900	-0.69087700
C	1.32700600	1.47774400	-0.37889800
C	2.50687900	0.70474200	-0.26626300
C	2.40791200	-0.72101500	-0.44409700
C	1.19879100	-1.38056200	-0.75782400
C	0.08411200	-0.56865900	-0.87344400
H	1.38572800	2.54958800	-0.22788800
H	1.14689600	-2.45970500	-0.86718500
C	-1.91367100	0.27350000	-1.10291900
O	-1.21608000	-0.91964800	-1.16386500
N	-1.16496700	1.32750000	-0.86166800
C	-3.14340500	1.27060500	1.64298500
H	-3.43055900	1.52543100	2.67555300
H	-2.42799500	2.02436900	1.29295800

O	-2.35951100	-2.29074900	1.47849800
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Table S5 Cartesian coordinates of S0 state of **1a**

C	0.91531200	-0.17824000	-0.52345500
C	1.71398200	-1.47305000	-0.57991400
C	1.60907000	1.10771900	-0.14630400
C	2.82091900	-1.46909300	0.47982500
H	1.04214600	-2.32943900	-0.45453200
H	2.17584300	-1.57003600	-1.57590000
C	-0.37507200	-0.12640000	-0.78255100
N	2.92243700	0.97101600	0.24918300
O	1.05650800	2.20377400	-0.14915300
C	3.72167300	-0.25280700	0.27245200
H	3.42241500	-2.38466400	0.41581000
H	2.37541000	-1.42661500	1.48312900
C	-1.66245000	-0.04343200	-0.97749900
H	3.37247000	1.85181700	0.46428500
H	4.45598100	-0.16999000	1.08401900
H	4.28564500	-0.36893200	-0.66966700
C	-2.72266700	-0.10272300	0.12116900
H	-2.03612100	0.13088200	-1.99103100
C	-2.08282000	-0.36908500	1.49295400
C	-3.73073700	-1.21993000	-0.22071700
C	-3.44139000	1.26558500	0.14005200
H	-1.55766900	-1.33240000	1.50136800
H	-2.85518800	-0.39132400	2.27193100
H	-1.35890500	0.41515800	1.74242600
H	-4.18961400	-1.05023900	-1.20353900
H	-4.53370600	-1.25190900	0.52765900
H	-3.23672400	-2.19929600	-0.23889700
H	-3.90957100	1.47820400	-0.82984300
H	-4.22798800	1.27164700	0.90651200
H	-2.72846000	2.06857300	0.35913600

Table S6 Cartesian coordinates of S0 state of **ent-1a**

C	-3.14540300	-1.37679300	-0.31818800
C	-1.70526800	-1.52035200	0.18881600
C	-0.90372400	-0.27968500	-0.17093400
C	-1.56748700	1.07075000	-0.06380400

C	-3.78528700	-0.13340600	0.29669800
H	-3.14314300	-1.28630600	-1.41288200
H	-1.72120300	-1.63825800	1.28474700
H	-3.34451100	1.95749900	0.22361900
H	-4.76600700	0.06144100	-0.15667800
H	-3.74225800	-2.25892800	-0.05412100
H	-1.22114900	-2.41171900	-0.22431700
H	-3.95017300	-0.30207300	1.37544200
N	-2.93745000	1.04030200	0.08736100
O	-0.95634600	2.13413900	-0.11945600
C	0.35068400	-0.31946100	-0.56864000
C	1.60877100	-0.29837400	-0.91442700
H	1.87438700	-0.37582000	-1.97295500
C	2.77469600	-0.09843300	0.05292200
C	2.27731100	-0.01475600	1.50489000
C	3.76250600	-1.27290900	-0.10604200
C	3.46675100	1.22813400	-0.33498900
H	3.12193500	0.15634100	2.18402300
H	1.56215600	0.80753800	1.62122300
H	1.77877700	-0.94546100	1.80343400
H	3.83093700	1.19536500	-1.37018800
H	2.76465100	2.06467700	-0.24428200
H	4.32646300	1.41464400	0.32255100
H	4.63528800	-1.12814100	0.54443100
H	3.28527800	-2.22327700	0.16341000
H	4.12018600	-1.35104600	-1.14115300

Table S7 Cartesian coordinates of T1 state of **ent-1a**

C	-3.07153700	-1.49181400	-0.39163500
C	-1.66008000	-1.49893200	0.20953800
C	-0.99225900	-0.14223000	0.06750900
C	-1.80486600	1.09775900	-0.00410200
C	-3.88137300	-0.33762600	0.19663200
H	-3.00936600	-1.36847400	-1.48106500
H	-1.72339000	-1.75490700	1.28158300
H	-3.69790900	1.78878200	0.01189300
H	-4.86611500	-0.27196200	-0.28282000
H	-3.58002600	-2.44284200	-0.18783800
H	-1.03906500	-2.27406500	-0.25751400
H	-4.05125600	-0.51599500	1.27371400
N	-3.17646800	0.92209000	-0.02319500

O	-1.30457600	2.22377200	-0.06562900
C	0.37782800	-0.01171200	0.03620600
C	1.53621500	-0.70034900	0.06686000
H	1.51917300	-1.79877800	0.14908500
C	2.91802500	-0.07882600	-0.00672300
C	2.82444200	1.45273300	-0.11909000
C	3.69676400	-0.46956800	1.27218100
C	3.64691400	-0.65733000	-1.24319300
H	3.82913200	1.89170900	-0.17134000
H	2.26635300	1.74596100	-1.01576300
H	2.30036000	1.87724400	0.74494400
H	3.71525600	-1.75173900	-1.18714400
H	3.11620700	-0.39238300	-2.16546100
H	4.66690900	-0.25484200	-1.30292100
H	4.71721600	-0.06590900	1.23119000
H	3.20215900	-0.06888000	2.16506200
H	3.76580800	-1.56036500	1.37668500

Table S8 Cartesian coordinates of **TS-a**

C	-3.02719578	-1.52025253	-0.39241888
C	-1.61769378	-1.54383253	0.21253912
C	-0.93261378	-0.19478753	0.07106912
C	-1.73275478	1.05567347	-0.00224088
C	-3.82543278	-0.35732853	0.19441112
H	-2.96071078	-1.39697253	-1.48163488
H	-1.68650278	-1.79725653	1.28474812
H	-3.61795078	1.76708347	0.01046812
H	-4.80771478	-0.27946653	-0.28821788
H	-3.54740678	-2.46537953	-0.19085788
H	-1.00395078	-2.32616353	-0.25197788
H	-4.00098478	-0.53464853	1.27067812
N	-3.10551278	0.89486547	-0.02105688
O	-1.21948678	2.17532747	-0.06450588
C	0.43778622	-0.07940753	0.04139612
C	1.60490622	-0.75749153	0.07082112
H	1.60066422	-1.85613653	0.15398712
C	2.98040622	-0.11896653	-0.00634388
C	2.86692722	1.41142347	-0.11745988
C	3.76757122	-0.50018953	1.26983312
C	3.71251422	-0.68693553	-1.24539688
H	3.86564622	1.86342847	-0.17322088

H	2.30174522	1.69832947	-1.01178688
H	2.34071222	1.82906847	0.74867612
H	3.79457022	-1.78050653	-1.19059188
H	3.17547522	-0.42805253	-2.16581188
H	4.72733622	-0.27202453	-1.30869088
H	4.78279522	-0.08366653	1.22710912
H	3.27018822	-0.10669853	2.16447012
H	3.85079222	-1.59012853	1.37343312

Table S9 Cartesian coordinates of **TS1**

C	-3.54340200	-0.93162600	-0.32828500
C	-2.25846100	-1.63035700	0.19157700
C	-1.16794400	-0.61426900	0.05363600
C	-1.37939000	0.75182100	-0.03065300
C	-3.73634300	0.49373600	0.22775200
H	-3.49500500	-0.86999900	-1.42325900
H	-2.39964300	-1.95821800	1.23500500
H	-2.63488400	2.33702100	0.16369800
H	-4.64001600	0.93989900	-0.20281300
H	-4.43215500	-1.52006600	-0.06766400
H	-2.07235700	-2.53613800	-0.40160700
H	-3.86708800	0.44811100	1.32177700
N	-2.58659200	1.36311200	-0.11049800
O	-0.19078100	1.32820000	-0.05705900
C	0.22889500	-0.50190700	-0.04305500
C	1.47934200	-0.88662400	-0.23435800
H	1.57975300	-1.89621700	-0.64368000
C	2.75869600	-0.08583000	0.00313800
C	2.96417700	0.90599900	-1.16568300
C	2.67852600	0.69072500	1.33486200
C	3.94534400	-1.06905200	0.05804200
H	3.89364000	1.47627000	-1.02501000
H	3.03103400	0.37005000	-2.12113700
H	2.12314000	1.60360000	-1.22145800
H	3.82217000	-1.78819200	0.87807500
H	4.03604700	-1.63055600	-0.88146400
H	4.88416500	-0.52384400	0.21888700
H	3.61063700	1.24741900	1.50371100
H	1.84440400	1.39796400	1.32046600
H	2.53191200	-0.00018300	2.17458900

Table S10 Cartesian coordinates of **I**

C	-3.58185300	0.87909400	0.34136500
C	-2.31153000	1.64460300	-0.13488800
C	-1.21321800	0.63510600	-0.11310100
C	-1.42078100	-0.69878300	0.01078300
C	-3.72335200	-0.54419700	-0.25022900
H	-3.54836500	0.78763100	1.43476500
H	-2.47257500	2.07477700	-1.13700200
H	-2.57878700	-2.35128500	-0.22175700
H	-4.63944900	-1.01139900	0.12727400
H	-4.48901500	1.44094500	0.08556500
H	-2.12867600	2.49188900	0.54192000
H	-3.79153200	-0.47979400	-1.34886000
N	-2.57437900	-1.40450700	0.14322200
O	-0.09934800	-1.13499100	0.05905300
C	0.21222400	0.33134200	-0.06212400
C	1.44384300	0.84550600	-0.08123300
H	1.48599900	1.93187000	-0.16327300
C	2.76211800	0.08425000	0.00337600
C	2.84947800	-0.69002800	1.33975900
C	2.88677000	-0.90807400	-1.17659400
C	3.92119500	1.09908800	-0.06766000
H	3.81045800	-1.21848000	1.41275000
H	2.76959000	-0.00136300	2.19027400
H	2.03973000	-1.42213100	1.41631900
H	3.89287900	1.66288200	-1.00953000
H	3.86730800	1.81586800	0.76245700
H	4.88784600	0.58286100	-0.00901900
H	3.84827700	-1.43835200	-1.12903000
H	2.07876700	-1.64562400	-1.14962000
H	2.83362000	-0.37627000	-2.13493400

Table S11 Cartesian coordinates of **TS2**

C	3.55532900	-0.91060500	0.35333600
C	2.25529500	-1.64122000	-0.08017300
C	1.17048500	-0.60969000	-0.09117400
C	1.37902200	0.75463000	0.02211600

C	3.72339100	0.48439100	-0.29157600
H	3.54513300	-0.77800200	1.44294900
H	2.39452000	-2.10129200	-1.07270700
H	2.66035100	2.35946100	0.01351600
H	4.64349200	0.95366400	0.07378500
H	4.43473500	-1.51581900	0.10039100
H	2.04870700	-2.46487900	0.61863700
H	3.80032800	0.38500900	-1.38685100
N	2.58859500	1.35313100	0.06796200
O	0.18764400	1.32380400	0.09266600
C	-0.22841500	-0.48262500	-0.14246800
C	-1.48188500	-0.84303400	-0.36430800
H	-1.58777700	-1.78897600	-0.90330300
C	-2.75747900	-0.08663600	0.00256900
C	-2.65843400	0.49310300	1.42994000
C	-2.98089400	1.06110900	-1.00995700
C	-3.94337800	-1.06987400	-0.06586100
H	-3.58799600	1.01834500	1.68957700
H	-2.49970400	-0.30985300	2.16068600
H	-1.82440600	1.19664600	1.50473900
H	-4.04735400	-1.49275300	-1.07412900
H	-3.80846200	-1.89782100	0.64204000
H	-4.87992000	-0.55506500	0.18395500
H	-3.90868900	1.60296300	-0.77639800
H	-2.14150400	1.76228100	-0.97760800
H	-3.06099900	0.66645400	-2.03100400

Table S12 Cartesian coordinates of T1 state of photo-sensitizer **2**

C	7.52458200	-0.65077700	0.56997000
C	6.37959900	-1.39342900	0.26803700
C	5.14838200	-0.74413800	0.09326600
C	5.00979100	0.67180700	0.21489100
C	6.19506000	1.39223500	0.51108000
C	7.41468500	0.74582500	0.69498300
C	3.76037200	1.39416000	0.03784300
H	8.47894100	-1.15096100	0.70865900
H	6.43764000	-2.47468300	0.15519100
H	6.10975300	2.47105600	0.59838800
H	8.29533500	1.33422400	0.94660500
S	3.78459600	-1.78318900	-0.28153900

O	3.75034400	2.66892600	0.14857200
C	-5.17132400	-0.01201900	1.00003500
C	-4.33684700	-1.22053000	0.54195500
C	-4.05060800	-1.09020800	-0.97746400
C	-3.38334600	0.23729400	-1.41617900
C	-4.09649100	1.43779700	-0.74851400
C	-4.40810500	1.29855200	0.76092400
H	-3.45074700	-1.94301700	-1.31141200
H	-6.12397200	0.00191900	0.44980600
H	-5.05893000	1.56009700	-1.26551000
H	-3.51429300	2.34846100	-0.92822200
H	-5.01834600	-1.15159200	-1.49527000
C	-3.49442700	0.37257300	-2.96118500
H	-3.03475900	1.30861900	-3.29739400
H	-4.55049500	0.37102900	-3.25722700
H	-2.99104800	-0.46340900	-3.46031100
H	-5.41837900	-0.11160900	2.06709000
C	-5.08554500	-2.53394800	0.80277500
H	-5.32368700	-2.63946500	1.86801900
H	-4.47166000	-3.39038100	0.51061300
H	-6.02460500	-2.55068200	0.23488200
C	-5.25527700	2.50904800	1.18664000
H	-4.69386300	3.44491700	1.06643100
H	-5.55986500	2.42520900	2.23747400
H	-6.16301800	2.57883400	0.57474400
N	-2.47612900	-0.03301800	1.64377100
H	-1.57098000	-0.09104900	2.09714600
C	-2.98649200	-1.25438900	1.28413400
C	0.11987100	0.83115900	-0.69087700
C	1.32700600	1.47774400	-0.37889800
C	2.50687900	0.70474200	-0.26626300
C	2.40791200	-0.72101500	-0.44409700
C	1.19879100	-1.38056200	-0.75782400
C	0.08411200	-0.56865900	-0.87344400
H	1.38572800	2.54958800	-0.22788800
H	1.14689600	-2.45970500	-0.86718500
C	-1.91367100	0.27350000	-1.10291900
O	-1.21608000	-0.91964800	-1.16386500
N	-1.16496700	1.32750000	-0.86166800
C	-3.14340500	1.27060500	1.64298500
H	-3.43055900	1.52543100	2.67555300
H	-2.42799500	2.02436900	1.29295800
O	-2.35951100	-2.29074900	1.47849800

Table S13 Cartesian coordinates of S0 state of **2@1a**

C	2.46142000	-0.70105800	2.53843000
C	2.83796000	0.77282900	2.69259900
C	1.95269000	1.63470500	1.80240200
C	0.54716000	1.18888700	1.51186100
C	0.98119200	-0.89516600	2.84908200
H	2.66021000	-1.01713100	1.51025600
H	2.69987400	1.07679600	3.74268100
H	-0.85287600	-0.20180900	1.99718700
H	0.67088400	-1.92420000	2.62866700
H	3.06459000	-1.33394300	3.20099100
H	3.89121500	0.94263000	2.44337100
H	0.79482200	-0.71931300	3.92216800
N	0.15756600	-0.00047500	2.03947200
O	-0.22336000	1.88473300	0.82479000
C	2.35109300	2.79488600	1.32048200
C	2.73786000	3.94311600	0.83642300
C	6.33028200	-2.47728500	0.23097700
C	5.11855200	-3.12445800	0.44207300
C	3.94423200	-2.63892200	-0.16645500
C	3.99192600	-1.50332300	-1.00195900
C	5.23735100	-0.87050300	-1.20121100
C	6.39266900	-1.34029600	-0.59276700
C	2.80896800	-0.92429700	-1.69533900
H	7.22954900	-2.85502100	0.71320800
H	5.06806000	-4.00111000	1.08482300
H	5.24863100	-0.00209500	-1.85358900
H	7.34102600	-0.83278600	-0.75300900
S	2.46966500	-3.53927300	0.16693300
O	2.95992600	-0.05432100	-2.55557200
C	-5.69254100	1.09457300	0.61587800
C	-4.93489500	-0.08369000	1.24756800
C	-5.07689300	-1.31151500	0.31697500
C	-4.54239400	-1.08708400	-1.12225500
C	-5.04279100	0.26996000	-1.67713000
C	-5.04199300	1.48834800	-0.71702100
H	-4.58274100	-2.17698700	0.76849900
H	-6.74437100	0.81052500	0.46141900
H	-6.08778100	0.10796800	-1.97753800
H	-4.48353900	0.51664800	-2.58726200
H	-6.14795000	-1.54696200	0.23958900

C	-5.05818500	-2.23110100	-2.03782600
H	-4.70192200	-2.09182700	-3.06532500
H	-6.15471700	-2.23210100	-2.04446700
H	-4.71075400	-3.20538800	-1.67700700
H	-5.68717700	1.95654700	1.29834400
C	-5.50533500	-0.42594200	2.63151300
H	-5.45195400	0.44343900	3.29838700
H	-4.93469900	-1.23933800	3.08830500
H	-6.55730300	-0.72686700	2.54139700
C	-5.82907900	2.62106000	-1.39746600
H	-5.33348600	2.94402800	-2.32271100
H	-5.91286200	3.49130100	-0.73451700
H	-6.84328100	2.29027000	-1.65445700
N	-2.94810600	1.26379200	0.65539300
H	-1.93259700	1.45431400	0.74622200
C	-3.43429700	0.24760700	1.39131400
C	-0.92381700	-0.98327600	-1.46614200
C	0.36686400	-0.60764400	-1.80016500
C	1.44692800	-1.36791000	-1.29926200
C	1.19698900	-2.49569900	-0.46799300
C	-0.11238600	-2.88318400	-0.11866200
C	-1.13059300	-2.10451700	-0.63080400
H	0.58093300	0.24982400	-2.42895000
H	-0.30595400	-3.73565800	0.52582500
C	-3.04039500	-1.16689400	-1.15544900
O	-2.47765200	-2.23873600	-0.43847800
N	-2.17455400	-0.43498000	-1.78543400
C	-3.63185000	2.01632500	-0.39222600
H	-3.71080800	3.06543800	-0.06870400
H	-3.00157500	1.99016700	-1.28959000
O	-2.71008800	-0.42912400	2.14693400
H	2.56119700	4.84614100	1.42972200
C	3.36829400	4.16353400	-0.53662800
C	3.68605500	2.82447100	-1.21554100
C	2.35100100	4.95343800	-1.39127900
C	4.65853000	4.99103200	-0.36017000
H	4.12958900	2.99047900	-2.20477700
H	4.39364200	2.23893400	-0.61555100
H	2.78309000	2.22262200	-1.35076700
H	4.45067700	5.95050000	0.13197100
H	5.39094000	4.44603400	0.24845200
H	5.11164700	5.20175900	-1.33786500
H	2.76616500	5.15310600	-2.38830800
H	1.42364800	4.38028800	-1.50393800

H	2.10493300	5.91632700	-0.92444200
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Table S14 Cartesian coordinates of S0 state of **2@ent-1a**

C	2.35879800	-1.16710000	2.78924300
C	2.99931800	0.16776100	2.39670900
C	2.13863000	0.90106300	1.37946900
C	0.64684000	0.73412600	1.41545500
C	0.92069200	-0.95425700	3.25338300
H	2.36085100	-1.84299500	1.92931400
H	3.10407300	0.79781900	3.29488500
H	-0.87568100	-0.29520000	2.28652900
H	0.41324600	-1.91543300	3.40231100
H	2.93510900	-1.64911300	3.58936300
H	4.00427300	0.01629100	1.98794800
H	0.91128900	-0.42806200	4.22334300
N	0.15161000	-0.19573400	2.26861900
O	-0.09679300	1.41326100	0.68102800
C	2.63325900	1.71231200	0.46604900
C	3.05070200	2.55507700	-0.43624200
C	6.27937200	-2.03355600	0.32589600
C	5.11596000	-2.79318400	0.38581400
C	3.96267400	-2.36979600	-0.30184000
C	3.98152800	-1.18525900	-1.06623300
C	5.17746900	-0.44048400	-1.11533200
C	6.31196500	-0.84766800	-0.42630700
C	2.80926800	-0.66559500	-1.82348500
H	7.16160600	-2.36130000	0.87198200
H	5.08501200	-3.70740200	0.97506400
H	5.17370100	0.46530100	-1.71382600
H	7.22040500	-0.25137300	-0.46832100
S	2.54736900	-3.41233900	-0.17784300
O	2.95740300	0.23495000	-2.65392000
C	-5.63540600	1.08681700	0.73944200
C	-4.90655300	-0.15058400	1.28749800
C	-5.04411800	-1.30199400	0.25946500
C	-4.52684400	-0.97349300	-1.16679200
C	-5.03014100	0.42067500	-1.61180400
C	-4.97835100	1.56087900	-0.56408400
H	-4.54539500	-2.19791400	0.64186700
H	-6.69334600	0.83885900	0.56529600
H	-6.08623300	0.29337700	-1.88993300

H	-4.49401600	0.72539900	-2.51810300
H	-6.11495100	-1.53545200	0.17240300
C	-5.06225000	-2.04715600	-2.15402100
H	-4.71998500	-1.83543500	-3.17374200
H	-6.15884000	-2.04458000	-2.14429000
H	-4.71321100	-3.04592000	-1.86915200
H	-5.61182800	1.89670800	1.48289800
C	-5.51071900	-0.59407700	2.62704300
H	-5.45497700	0.21632500	3.36422800
H	-4.96466600	-1.45272200	3.02742400
H	-6.56579500	-0.86594500	2.49280600
C	-5.72913500	2.77001800	-1.14624400
H	-5.22915800	3.14624900	-2.04865300
H	-5.77745600	3.58847600	-0.41698800
H	-6.75621200	2.49552100	-1.41796800
N	-2.87505600	1.14829900	0.75440400
H	-1.84492800	1.25667300	0.80750900
C	-3.40586200	0.14573400	1.47940800
C	-0.92194400	-0.84928000	-1.62771400
C	0.35789400	-0.43394700	-1.96249100
C	1.45697000	-1.18889800	-1.50119700
C	1.23778500	-2.35870100	-0.72116700
C	-0.05602300	-2.78057500	-0.36180300
C	-1.09557700	-1.99750200	-0.82442200
H	0.54697700	0.46614600	-2.53667800
H	-0.22207900	-3.65027700	0.26664700
C	-3.02544800	-1.04905000	-1.24354900
O	-2.43592400	-2.14011000	-0.58296200
N	-2.18489900	-0.29624400	-1.88439600
C	-3.54589300	2.00849500	-0.21711700
H	-3.58441000	3.02925800	0.19419600
H	-2.92747100	2.03598500	-1.12192200
O	-2.71622900	-0.55484800	2.24488500
H	3.28468100	2.17756400	-1.43513100
C	3.16253600	4.06426400	-0.23791300
C	2.81833400	4.46270000	1.20579000
C	4.60095400	4.50219400	-0.58445400
C	2.16179000	4.72485100	-1.21324400
H	2.88092700	5.55184900	1.32459100
H	1.80252600	4.14078700	1.46293600
H	3.51266200	3.99798600	1.91706400
H	2.38501200	4.44910100	-2.25178800
H	1.13992000	4.40017500	-0.98560000
H	2.21322000	5.81898000	-1.12989100

H	4.70078300	5.59269000	-0.50047600
H	5.32397500	4.03579000	0.09645100
H	4.86240900	4.21410700	-1.61097400