Supporting Information

Spatial Factors for Triplet Fusion Reaction of Singlet Oxygen Photosensitization

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SI-1. Brief introduction to the DtC model

Diverse groups have developed methods for computation of reaction rates.¹⁻⁷ Each of these formulations have different ranges of applicability and accuracy. In the present work, we should deal with internal conversion in PS-O₂ complexes, which are weakly-coupled floppy structures for singlet oxygen photosensitization. A model tailored to deal exactly with this kind of system is the Divide-to-Conquer (DtC) model, which we have introduced in ref.³.



Figure S1 – (a) Marcus parabolas in the inverted region. (b) Extension to parabolic sheets along direction **D**. Figure reproduced from ref. 3 .

The DtC model is an extension of the semiclassical Marcus theory, from parabolic potential curves to parabolic sheets (Figure S1). Although the semiclassical Marcus expression was originally derived for charge transfer problems, it is much more general, being the classical limit at high temperature of the Fermi's Golden rule,⁸ and therefore also valid for energy transfer problems.

The potential energy profiles illustrated in Figure S1 correspond to the inverted region of the Marcus theory. Although this is generally the case for photosensitization problems, the reaction may also take place in the regular region. The DtC model is able to address both of them.

The extension of the semiclassical Marcus theory into parabolic sheets is done along an additional dimension **D**, corresponding to the intermolecular coordinate between PS and O_2 . This dimension should be taken into account due to the fact that, first, the complex does not form rigid structures and, second, **D** does not contribute to the crossing between the initial and final states, but impacts the diabatic coupling strength. This crossing occurs along the intramolecular coordinates **R** of PS. Under the hypothesis that the interaction energy between the monomers mainly depends on **D**, we showed in ref. ³ that the quantities needed to calculate the internal conversion rate as a function of **D**—the activation energy, the reorganization energy, and the diabatic coupling (see eq. (2) in the paper)—can all be obtained by a minimum set of routine quantum chemical calculations.

In brief, for an internal conversion problem of the type ${}^{1}(TT) \rightarrow {}^{1}(SS)$, the main steps to apply the Divide-to-Conquer model are:

1. For the isolated PS, the minimum of the triplet state \mathbf{R}_0 , the intersystem crossing point \mathbf{R}_{isc} (between the singlet and the triplet state of PS), and the potential energy profile between these two geometries are computed.

- 2. An initial relative orientation between PS and O_2 is chosen, and the potential energy profile for the PS- O_2 complex along **D** at fixed **R**₀ and **r**₀ is calculated. (**r**₀ is the ground state equilibrium geometry of O_2 .)
- 3. Based on the previous information, DtC is used to determine \mathbf{R}_x , the crossing point for the complex and the activation energy ΔE^{\ddagger} .
- 4. With the energies of the isolated PS, the reorganization energy λ is computed.
- 5. The diabatic coupling V_{ij} along **D** for fixed \mathbf{R}_0 and \mathbf{r}_0 is determined (see below).
- 6. The reaction rate along **D** is obtained with Eqn. (2) of the main text.

Steps 1 to 6 may be repeated starting from all relative orientations of interest.

Diabatic couplings are computed by integration of nonadiabatic coupling vectors in the following way:⁹

- 1. Nonadiabatic couplings vectors are computed along **D** for fixed \mathbf{R}_0 and \mathbf{r}_0 .
- 2. They are projected on a 1-D path along **D** and numerically integrated to obtain the adiabatic-to-diabatic rotation angle.
- 3. With the rotation angle, $V_{ii}(D)$ is determined.

The reader interested in more technical details on the model, including its limits of validity is invited to check ref. 3 .

SI-2. Computational details

Geometry optimizations and excited states of 6n-2tThy and O_2 were calculated with the complete active space perturbation theory to the second order (CASPT2) in its multi-state (MS) version. The active space is shown in Table S1. For 6n-2tThy the active space is composed of 10 electrons in 7 orbitals (10, 7). For O_2 , the space is (6, 6). For both molecules, the ANO-RCC-VTZP basis set was used. Standard IPEA (0.25 a.u.)¹⁰ was globally adopted in the CASPT2 calculations and no level shift was employed. All these calculations were done with Molcas 8.¹¹ Cartesian coordinates for the optimized structures are given in Table S3 and Table S4.

The calculations for the PS-O₂ complex, including the excited state energies and nonadiabatic coupling vectors, were done at the complete active space self-consistent field level with 12 electrons in 9 orbitals (CASSCF(12, 9)) and 6-31G^{**} basis set, using the COLUMBUS software.¹² In this active space, a (6, 5) subspace described the PS, and a (6, 4) subspace described the oxygen molecule. The active space is shown in Table S2.

For quantitative assessment of reaction rates, solvent effects must be accounted for. This work, however, aims at delivering a fundamental insight on how the rates profoundly depend on the relative incidence direction, orientation, and distance between PS and O_2 . This goal was achieved by a simple analysis of the electronic properties of these monomers. Thus, to include solvent effects would increase the complexity of the analysis, without providing any direct advantage. For this reason, all calculations in this work were done in the gas phase.



Table S1. Molecular orbitals in the (10,7) active space of 6n-2tThy and (6,6) active space of O₂ used for optimization and single-point calculation with CASPT2.



Table S2.Molecular orbitals in the (12,9) active space of 6n-2tThy-O2 complex used for energy and nonadi-
abatic coupling calculations with CASSCF.

SI-3. Geometries and results for all directions

The results for perp-56-o are given in the main text.















SI-4. Cartesian coordinates

\mathbf{S}_0			
С	-3.10291522	-0.44586745	0.36912952
С	-1.02060302	0.63619153	-0.39678897
С	-1.79992364	1.89842237	-0.43550016
Ν	-3.05766668	1.95113842	-0.12878225
0	0.16567790	0.55785890	-0.68489080
С	-1.08479716	3.14054917	-0.84964906
Н	-0.24784050	3.33370442	-0.17115290
н	-0 66028369	3 01071502	-1 85008272
и п	-1 77398864	3 98542290	-0.84222419
п	-1.77590004	1 70014100	-0.84222419
S	-3.93938382	-1.78014108	0.90502091
Ν	-3.66931879	0.79985722	0.24447745
Η	-4.64677861	0.89116274	0.48841670
N	-1.77073908	-0.46173700	0.00545755
Η	-1.29575404	-1.35768217	0.06412992
T ₁			
С	-3.14065956	-0.44866186	0.34175350
С	-1.00672930	0.74682795	0.29402651
С	-1.75023778	1.87930507	-0.13485974
Ν	-3.19784853	1.94942313	-0.09946238
0	0.22326187	0.64549088	0.35485659
С	-1.09168508	3.10234707	-0.63713185
Η	-0.00682667	2.98669458	-0.63064080
Н	-1.43591438	3.32802375	-1.65490791
Η	-1.37473168	3.96208957	-0.01470804
S	-4.05898001	-1.84853838	0.40520213
Ν	-3.72337009	0.73650704	0.00719837
Η	-4.73157723	0.68854161	-0.12034321
Ν	-1.81356819	-0.37709839	0.64996400
Н	-1.32461338	-1.24723999	0.82269584

Table S3.6n-2tThy optimized structures using CASPT2(10,7)/ano-rcc-vdzp (xyz, Angstrom).

S ₀ /T ₁ ISC crossing point					
С	-3.03196309	-0.30143035	0.08938081		
С	-0.92284445	0.80704064	0.67773961		
С	-1.68751597	2.01701804	0.38763073		
С	-1.29064806	2.87160049	-0.77318076		
Ν	-3.06956095	1.95290156	0.79309070		
Ν	-3.58562656	0.97279705	0.00144471		
Ν	-1.79594686	-0.31880205	0.68608083		
0	0.28382766	0.66860355	0.79589287		
S	-3.85214808	-1.63349139	-0.41622938		
Н	-0.26059887	2.65025185	-1.06679725		
Н	-1.95057189	2.73309548	-1.63678206		
Н	-1.34180092	3.92651653	-0.47732092		
Н	-4.57824879	0.98582516	-0.22429913		
Н	-1.34987719	-1.22818213	0.74697435		

Table S4.O2 optimized structure using CASPT2(6,6)/ano-rcc-vdzp calculation (xyz, Angstrom).

T_1			
0	-2.31826714	1.71428600	0.00000000
0	-1.09982886	1.71428600	0.0000000

SI-5. Additional references

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