Supplementary Data

Divergent Functionalization of Aldehydes Photocatalyzed by Neutral Eosin Y with Sulfone Reagents

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Calculation of electrochemical potential of eosin Y-H species

Density functional theory (DFT) calculations were performed to study the electrochemical potential of eosin Y-H. The calculation method was adapted from Reference.[1] The redox potential $E_{1/2}^{o,calc}$ (vs SCE) was calculated according to the following equation:

$$E_{1/2}^{o,calc}(\text{vs SCE}) = -\frac{(G_{298}[reduced] - G_{298}[oxidized])}{n_e\mathcal{F}} - E_{1/2}^{o,SHE} - E_{1/2}^{o,SCE}$$

$E_{1/2}{}^{ox}$ (eosin Y-H) = -0.11 V vs SCE

Where n_e is the number of electrons transferred (n_e=1 in our calculation), $\mathcal{F}$ is the Faraday constant (23.061 kcal mol^{-1} V^{-1}). $E_{1/2}^{o,SHE}$ is the absolute value for the standard hydrogen electrode (SHE, value = 4.281 V), $E_{1/2}^{o,SCE}$ is the potential of the saturated calomel electrode (SCE) relative to SHE in acetonitrile (value = 0.141 V). $G_{298}[reduced]$ and $G_{298}[oxidized]$ (1 Hartrees = 630 kcal/mol) are the calculated Gibbs free energies with the solvation model.

Computational Details

The geometries optimization in this study was performed at the uB3LYP/Def2SVP level of theory. The free energies of the optimized geometries were calculated at the same level of theory, considering the solvent effect using the Solvation Model Density (SMD) solvation model. All calculations were performed using the Gaussian 16 Rev. A.03 software suite. [2]

Calculated Cartesian Coordinates

Structure 1. eosin Y-H

Sum of electronic and zero-point Energies= -11438.095727
Sum of electronic and thermal Energies= -11438.069559
Sum of electronic and thermal Enthalpies= -11438.068615
Sum of electronic and thermal Free Energies= -11438.158042

C	-0.17520	3.19224	-1.71564
C	0.06052	2.66549	-0.43202
C	0.37347	3.57132	0.61440
C	0.46124	4.94799	0.34035
C	0.22124	5.44770	-0.93731
C	-0.10251	4.56328	-1.97006
H	-0.41092	2.50428	-2.53116
H	0.71513	5.62171	1.16053
H	0.28638	6.52186	-1.12685
H	-0.29173	4.93779	-2.97945
C	0.63191	3.18143	2.03815

O	1.16511	3.91048	2.84724
O	0.19219	1.95776	2.36579
H	0.41178	1.81158	3.30617
C	0.00263	1.18358	-0.27356
C	1.20310	0.39772	-0.22981
C	2.50542	0.94540	-0.30257
C	1.10216	-1.01617	-0.11732
C	3.62440	0.12672	-0.25603
H	2.62801	2.02370	-0.39937
C	2.23370	-1.83263	-0.07033
C	3.52938	-1.27507	-0.13721
C	-1.25709	0.50103	-0.21031
C	-2.51367	1.15398	-0.23106
C	-1.26650	-0.91422	-0.09950
C	-3.70222	0.44144	-0.15808
H	-2.54496	2.24063	-0.30423
C	-2.46575	-1.62350	-0.02788
C	-3.71495	-0.96532	-0.05595
Br	2.05022	-3.71462	0.08327
O	4.59109	-2.09122	-0.08871
H	5.40785	-1.56455	-0.14561
Br	5.37519	0.89594	-0.35748
Br	-5.36399	1.37303	-0.19150
O	-4.88424	-1.61550	0.01194
H	-4.72145	-2.57312	0.08041
O	-0.11162	-1.62929	-0.05569
Br	-2.45023	-3.52395	0.11386

Structure 2. eosin Y^+-H

Sum of electronic and zero-point Energies= -11437.939649

Sum of electronic and thermal Energies= -11437.913967

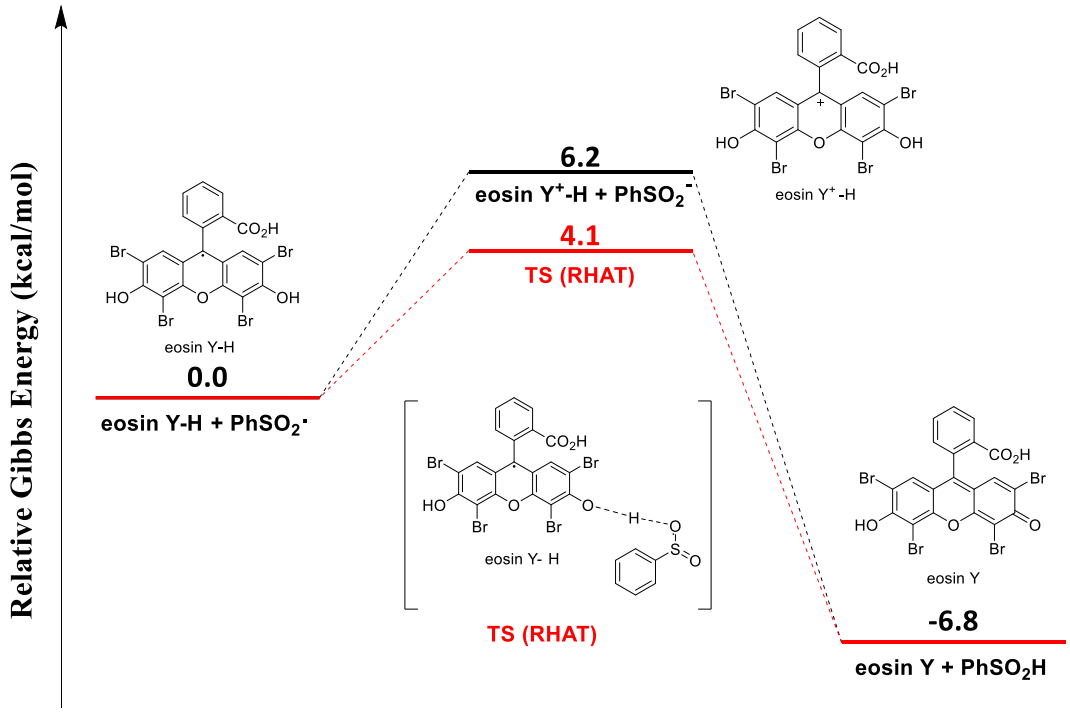
Sum of electronic and thermal Enthalpies= -11437.913023

Sum of electronic and thermal Free Energies= -11438.000243

C	-0.01505	3.07454	-1.78299
C	0.02978	2.63590	-0.44946
C	0.11569	3.59078	0.59151
C	0.15837	4.95562	0.26379
C	0.11367	5.38145	-1.06193
C	0.02571	4.43712	-2.08746
H	-0.07928	2.33946	-2.58827
H	0.22462	5.67807	1.07906
H	0.14615	6.44829	-1.29428
H	-0.01106	4.75590	-3.13190
C	0.15685	3.25762	2.05036

O	0.29167	4.07816	2.92857
O	0.01988	1.94584	2.30316
H	0.06012	1.81490	3.27066
C	0.00260	1.15690	-0.24067
C	1.21161	0.41940	-0.19118
C	2.49474	1.03111	-0.24424
C	1.14999	-1.00030	-0.08790
C	3.62785	0.25926	-0.19709
H	2.56292	2.11606	-0.32239
C	2.30484	-1.78676	-0.04105
C	3.56669	-1.16788	-0.09504
C	-1.22687	0.45647	-0.19253
C	-2.49634	1.10081	-0.23553
C	-1.19903	-0.96327	-0.08810
C	-3.65671	0.36973	-0.17935
H	-2.53341	2.18728	-0.31242
C	-2.37987	-1.70844	-0.03768
C	-3.62662	-1.05887	-0.07942
Br	2.18979	-3.66668	0.08996
O	4.64592	-1.92780	-0.05099
H	5.45691	-1.38540	-0.09609
Br	5.35351	1.06112	-0.26600
Br	-5.34231	1.23309	-0.22858
O	-4.77745	-1.70301	-0.03066
H	-4.63816	-2.66748	0.03637
O	-0.03630	-1.62995	-0.04092
Br	-2.32916	-3.60010	0.08467

DFT calculation on SET and RHAT pathways for eosin Y regeneration



Supplementary Figure 17. Density functional theory (DFT) calculations on eosin Y regeneration.

Computational details

Density functional theory (DFT) calculations were performed to shed light on the mechanism of eosin Y regeneration (Supplementary Figure 17). Reverse hydrogen atom transfer (RHAT, red line) is the favored pathway, which features a barrier 2.1 kcal/mol lower than an alternative single electron transfer (SET, black line). The geometries optimization in this study was performed at the uB3LYP density functional with a standard def2-SVP basis set. The nature of the stationary points (minima with no imaginary frequency or transition states with one imaginary frequency) were confirmed. The free energies of the optimized geometries were calculated at the same level of theory, considering the solvent effect of acetone using an SMD continuum solvation model. Unless specified otherwise, the Gibbs free energy was used throughout. For transition state, intrinsic reaction coordinate (IRC) calculations were performed to verify whether it connected with correct reactants and products or intermediates. All calculations were performed using the Gaussian 16 Rev. A.03 software suite.[2]

Calculated Cartesian Coordinates

$PhSO_2$·

Sum of electronic and zero-point Energies= -779.715038
Sum of electronic and thermal Energies= -779.707423

Sum of electronic and thermal Enthalpies= -779.706479
Sum of electronic and thermal Free Energies= -779.748770

C	2.16539	1.21528	0.03415
C	0.77114	1.22604	-0.05578
C	0.10036	0.00001	-0.08355
C	0.77119	-1.22602	-0.05617
C	2.16543	-1.21525	0.03372
C	2.85902	0.00003	0.07770
H	2.71022	2.16177	0.07080
H	0.21597	2.16501	-0.08934
H	0.21608	-2.16502	-0.08994
H	2.71032	-2.16172	0.06999
H	3.94986	0.00004	0.14462
S	-1.70522	-0.00011	-0.25892
O	-2.21959	-1.29615	0.27148
O	-2.21968	1.29628	0.27054

Eosin Y-H
Sum of electronic and zero-point Energies= -11438.097330
Sum of electronic and thermal Energies= -11438.071167
Sum of electronic and thermal Enthalpies= -11438.070223
Sum of electronic and thermal Free Energies= -11438.159590

C	-0.17520	3.19224	-1.71564
C	0.06052	2.66549	-0.43202
C	0.37347	3.57132	0.61440
C	0.46124	4.94799	0.34035
C	0.22124	5.44770	-0.93731
C	-0.10251	4.56328	-1.97006
H	-0.41092	2.50428	-2.53116
H	0.71513	5.62171	1.16053
H	0.28638	6.52186	-1.12685
H	-0.29173	4.93779	-2.97945
C	0.63191	3.18143	2.03815
O	1.16511	3.91048	2.84724
O	0.19219	1.95776	2.36579
H	0.41178	1.81158	3.30617
C	0.00263	1.18358	-0.27356
C	1.20310	0.39772	-0.22981
C	2.50542	0.94540	-0.30257
C	1.10216	-1.01617	-0.11732
C	3.62440	0.12672	-0.25603
H	2.62801	2.02370	-0.39937

C	2.23370	-1.83263	-0.07033
C	3.52938	-1.27507	-0.13721
C	-1.25709	0.50103	-0.21031
C	-2.51367	1.15398	-0.23106
C	-1.26650	-0.91422	-0.09950
C	-3.70222	0.44144	-0.15808
H	-2.54496	2.24063	-0.30423
C	-2.46575	-1.62350	-0.02788
C	-3.71495	-0.96532	-0.05595
Br	2.05022	-3.71462	0.08327
O	4.59109	-2.09122	-0.08871
H	5.40785	-1.56455	-0.14561
Br	5.37519	0.89594	-0.35748
Br	-5.36399	1.37303	-0.19150
O	-4.88424	-1.61550	0.01194
H	-4.72145	-2.57312	0.08041
O	-0.11162	-1.62929	-0.05569
Br	-2.45023	-3.52395	0.11386

$PhSO_2^-$

Sum of electronic and zero-point Energies= -779.865145
Sum of electronic and thermal Energies= -779.857451
Sum of electronic and thermal Enthalpies= -779.856507
Sum of electronic and thermal Free Energies= -779.898401

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C	2.17417	1.21752	0.05878
C	0.77782	1.20715	-0.04940
C	0.08890	-0.00636	-0.12330
C	0.79424	-1.21283	-0.08550
C	2.19044	-1.20747	0.02048
C	2.88268	0.00913	0.08983
H	2.71333	2.16794	0.12492
H	0.19844	2.13544	-0.05789
H	0.23186	-2.15095	-0.12006
H	2.74244	-2.15211	0.05588
H	3.97335	0.01505	0.17309
S	-1.78175	-0.01580	-0.35702
O	-2.17439	-1.26948	0.42854
O	-2.17574	1.29382	0.33033

Eosin Y^+-H

Sum of electronic and zero-point Energies= -11437.939381
Sum of electronic and thermal Energies= -11437.913746
Sum of electronic and thermal Enthalpies= -11437.912801

Sum of electronic and thermal Free Energies= -11438.000015

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C	-0.01505	3.07454	-1.78299
C	0.02978	2.63590	-0.44946
C	0.11569	3.59078	0.59151
C	0.15837	4.95562	0.26379
C	0.11367	5.38145	-1.06193
C	0.02571	4.43712	-2.08746
H	-0.07928	2.33946	-2.58827
H	0.22462	5.67807	1.07906
H	0.14615	6.44829	-1.29428
H	-0.01106	4.75590	-3.13190
C	0.15685	3.25762	2.05036
O	0.29167	4.07816	2.92857
O	0.01988	1.94584	2.30316
H	0.06012	1.81490	3.27066
C	0.00260	1.15690	-0.24067
C	1.21161	0.41940	-0.19118
C	2.49474	1.03111	-0.24424
C	1.14999	-1.00030	-0.08790
C	3.62785	0.25926	-0.19709
H	2.56292	2.11606	-0.32239
C	2.30484	-1.78676	-0.04105
C	3.56669	-1.16788	-0.09504
C	-1.22687	0.45647	-0.19253
C	-2.49634	1.10081	-0.23553
C	-1.19903	-0.96327	-0.08810
C	-3.65671	0.36973	-0.17935
H	-2.53341	2.18728	-0.31242
C	-2.37987	-1.70844	-0.03768
C	-3.62662	-1.05887	-0.07942
Br	2.18979	-3.66668	0.08996
O	4.64592	-1.92780	-0.05099
H	5.45691	-1.38540	-0.09609
Br	5.35351	1.06112	-0.26600
Br	-5.34231	1.23309	-0.22858
O	-4.77745	-1.70301	-0.03066
H	-4.63816	-2.66748	0.03637
O	-0.03630	-1.62995	-0.04092
Br	-2.32916	-3.60010	0.08467

TS (HAT)

Sum of electronic and zero-point Energies= -12217.824902

Sum of electronic and thermal Energies= -12217.790042

Sum of electronic and thermal Enthalpies= -12217.789098

Sum of electronic and thermal Free Energies= -12217.901894

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C	2.86194	3.16522	-1.63468
C	2.46652	2.68693	-0.37482
C	2.57160	3.54137	0.74945
C	3.06011	4.84678	0.57342
C	3.44894	5.31026	-0.68131
C	3.35008	4.46467	-1.78888
H	2.78152	2.50910	-2.50429
H	3.12884	5.49160	1.45106
H	3.82797	6.32854	-0.79460
H	3.65067	4.81297	-2.78009
C	2.19507	3.16380	2.14881
O	2.20261	3.93543	3.08123
O	1.85433	1.87330	2.28544
H	1.61886	1.71847	3.22090
C	1.94470	1.28622	-0.33110
C	2.84869	0.19245	-0.18289
C	4.24219	0.36006	0.01866
C	2.33363	-1.13006	-0.23256
C	5.05963	-0.73769	0.15433
H	4.65432	1.36772	0.06577
C	3.16790	-2.24682	-0.10172
C	4.54849	-2.06864	0.09433
C	0.58064	1.01974	-0.52626
C	-0.40258	2.04220	-0.70418
C	0.13423	-0.34230	-0.54737
C	-1.72071	1.72007	-0.86919
H	-0.08353	3.08401	-0.69859
C	-1.20470	-0.66934	-0.72388
C	-2.19156	0.34808	-0.88305
Br	2.45601	-3.99550	-0.18247
O	5.31792	-3.14170	0.21523
H	6.24888	-2.88173	0.34796
Br	6.93495	-0.52258	0.43158
Br	-3.01702	3.08881	-1.08720
O	-3.44200	0.10766	-1.06164
O	1.01857	-1.34905	-0.40727
Br	-1.73871	-2.48401	-0.80917
H	-3.95987	-0.66663	-0.38595
C	-6.54701	-0.69749	0.74723
C	-7.54118	-1.31003	-0.02075
C	-6.79058	0.51151	1.40518

C	-8.79762	-0.70405	-0.12910
H	-7.32737	-2.26117	-0.51421
C	-8.04829	1.11389	1.29326
H	-5.99954	0.96367	2.00820
C	-9.05035	0.50759	0.52563
H	-9.58316	-1.18017	-0.72272
H	-8.24910	2.05686	1.80966
H	-10.03267	0.98001	0.43924
O	-4.33637	-1.03405	2.17975
O	-5.11507	-2.92691	0.63179
S	-4.87671	-1.45765	0.84026

$PhSO_2H$

Sum of electronic and zero-point Energies= -780.311851

Sum of electronic and thermal Energies= -780.304312

Sum of electronic and thermal Enthalpies= -780.303368

Sum of electronic and thermal Free Energies= -780.345025

——

C	-2.18685	1.21526	-0.03283
C	-0.79181	1.22316	0.04602
C	-0.11461	-0.00001	0.08600
C	-0.79185	-1.22316	0.04616
C	-2.18689	-1.21523	-0.03269
C	-2.88063	0.00002	-0.07051
H	-2.73293	2.16114	-0.06818
H	-0.23506	2.16196	0.06816
H	-0.23514	-2.16199	0.06837
H	-2.73299	-2.16111	-0.06792
H	-3.97196	0.00003	-0.13271
O	2.18528	-1.27852	-0.31195
O	2.18530	1.27859	-0.31159
S	1.67458	-0.00003	0.20576
H	1.86595	-0.00023	1.57547

Eosin Y

Sum of electronic and zero-point Energies= -11437.512694

Sum of electronic and thermal Energies= -11437.487032

Sum of electronic and thermal Enthalpies= -11437.486087

Sum of electronic and thermal Free Energies= -11437.574106

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C	-0.15096	3.08714	-1.75740
C	-0.04019	2.62192	-0.43605
C	0.10157	3.56726	0.60990

C	0.12350	4.93792	0.29800
C	0.01133	5.38390	-1.01659
C	-0.12630	4.45262	-2.04887
H	-0.25701	2.36265	-2.56806
H	0.22964	5.64897	1.11890
H	0.03030	6.45423	-1.23482
H	-0.21584	4.78493	-3.08613
C	0.22920	3.23103	2.06440
O	0.38395	4.05919	2.93489
O	0.15490	1.91913	2.33209
H	0.25172	1.80599	3.29745
C	-0.06080	1.13688	-0.24820
C	1.18478	0.40925	-0.20673
C	2.45044	1.03093	-0.27103
C	1.13868	-1.00082	-0.09900
C	3.60401	0.27263	-0.22456
H	2.51070	2.11551	-0.35888
C	2.31022	-1.76817	-0.05328
C	3.56811	-1.14185	-0.11422
C	-1.25485	0.43521	-0.19928
C	-2.54773	1.07161	-0.23793
C	-1.23025	-1.00885	-0.08849
C	-3.69045	0.34215	-0.17865
H	-2.58636	2.15814	-0.31493
C	-2.38376	-1.75020	-0.03106
C	-3.71791	-1.14018	-0.07135
Br	2.21711	-3.65307	0.08894
O	4.66459	-1.89690	-0.06861
H	5.45925	-1.33493	-0.12012
Br	5.31790	1.11472	-0.30888
Br	-5.38453	1.20148	-0.22917
O	-4.75967	-1.78304	-0.02097
O	-0.03819	-1.65531	-0.04116
Br	-2.31559	-3.63919	0.10738

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