Reactivities of Hydroxycinnamic Acid Derivatives Involving Caffeic Acid toward Electrogenerated Superoxide in *N,N*-Dimethylformamide through Proton-coupled Electron Transfer

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Table S1. CV parameters

Working Electrode	Planar Radius 1.0 mm diameter			
Geometry Spherical (Hemispherical)[1]		Diffusion Semi-infinite 1D		Temperature 298.3 K
Charge Transfer Reaction				
$O_2 + e^- \leftrightarrow O_2^{\bullet-}$	Redox Potential (V vs Fc^+/Fc)		Coefficient	Kinetics (cm s^{-1})
	$E = -1.284$		$\alpha = 0.005$	$k_s = 0.00927$
Species				
	Diffusion Coefficient (cm^2 s^{-1})		Initial Concentration (mol L^{-1})	
O_2	$4.76 \pm 0.24 \times 10^{-5}$		0.0048	
$O_2^{\bullet-}$	$2.15 \pm 0.24 \times 10^{-5}$		0	

[1]Operating conditions were spherical diffusion (to mimic edge diffusion to the disk)
[2]Digielch 4.5 ElchSoft inc. (Digital CV Simulation Software)
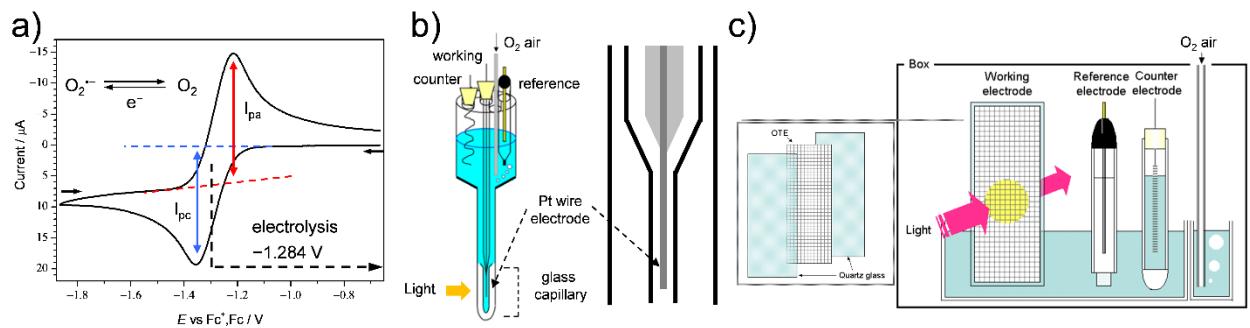
Figure S1. In situ electrolytic ESR and UV-vis spectral system. (a) Cyclic voltammograms of $O_2/O_2^{\bullet-}$ for potential determination. (b) In situ ESR system, composed of an electrochemical ESR cell with a glass small tip, air tube for O_2 bubbling, and three electrode system using a 0.5-mm-diameter straight Pt wire sealed in a glass capillary as working electrode (5.0 mm). (c) An optically transparent thin layer electrochemical (OTTLE) cell using a Pt mesh working electrode (10.0 mm $\times$ 20.0 mm) for in situ electrolytic UV-vis spectrometry.

Table S2. Optimized geometry of caffeic acid calculated using DFT-(U)B3LYP/PCM/6-311+G(3df,2p) in DMF.

Atomic Number	Coordinates (Angstromes)		
	X	Y	Z
6	1.898663	-1.577959	0.000123
6	0.542727	-1.295764	0.00001
6	0.088744	0.031052	-0.0001
6	1.040054	1.063844	-0.000093
6	2.395077	0.78814	0.000021
6	2.828816	-0.543695	0.000131
1	2.243247	-2.604414	0.000209
1	-0.159886	-2.116284	0.000009
1	0.721652	2.098051	-0.000177
6	-1.318978	0.393437	-0.000216
1	-1.526183	1.458504	-0.000292
6	-2.38264	-0.427095	-0.000261
1	-2.291756	-1.503662	-0.000187
6	-3.743318	0.112435	-0.000425
8	-4.670976	-0.874408	0.000231
1	-5.545729	-0.459084	0.00056
8	-4.061088	1.285335	-0.00002
8	4.178345	-0.72359	0.000243
1	4.406856	-1.659407	0.000315
8	3.293193	1.811888	0.000027
1	4.187937	1.448698	0.000112
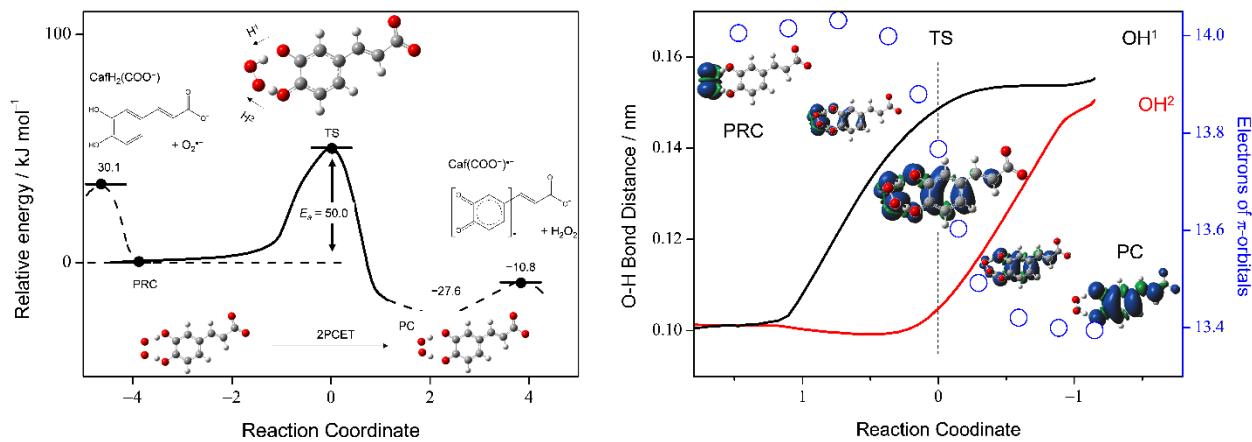
Figure S2. (a) Energy profile (kJ mol^{-1}) along the intrinsic reaction coordinate of the 2PCET between CafH$_2$(COO$^-$) and O$_2^{\bullet-}$ in DMF, along with the structures of free reactants, the prereactive HB complex, the transition state, product complex, and free products (Caf(COO)$^{\bullet 2-}$, H$_2$O$_2$). (b) Left and right vertical axes represent the O−H bond distances (OH^1: black line, OH^2: red line, nm) and the number of electrons (open circles) in the π-orbitals of CafH$_2$(COO$^-$), respectively. Calculations were performed using the DFT-(U)B3LYP/PCM/6-311+G(3df,2p) method.

Table S3. Optimized geometry of TS of 2PCET between CafH$_2$(COOH) and O$_2^{\bullet-}$ calculated using DFT-(U)B3LYP/PCM/6-311+G(3df,2p) in DMF.

Atomic Number	Coordinates (Angstromes)		
	X	Y	Z
6	0.274357	-0.864632	0.313259
6	1.642802	-0.50551	0.386349
6	1.950801	0.907061	0.24344
6	0.905385	1.829742	0.047014
6	-0.407881	1.430155	-0.009667
6	-0.748337	0.059445	0.122776
1	1.168809	2.87491	-0.051924
1	-1.180354	2.171478	-0.156469
8	3.184474	1.363683	0.340875
1	3.980153	0.678928	0.12878
8	2.567051	-1.3765	0.596313
1	3.724786	-1.313996	-0.399194
8	5.092051	-0.028218	-0.302494
8	4.563197	-1.136897	-0.953181
1	0.036967	-1.9161	0.421825
6	-2.115333	-0.418273	0.067674
1	-2.240639	-1.489417	0.188514
6	-3.236155	0.304522	-0.115408
1	-3.22453	1.376674	-0.247388
6	-4.547088	-0.340949	-0.145945
8	-5.542611	0.558012	-0.343542
1	-6.380234	0.072371	-0.354215
8	-4.780251	-1.527515	-0.016906

Table S4. Optimized geometry of TS of 2PCET between CafH$_2$(COO$^-$) and O$_2^{\bullet-}$ calculated using DFT-(U)B3LYP/PCM/6-311+G(3df,2p) in DMF.

Atomic Number	Coordinates (Angstromes)		
	X	Y	Z
6	0.219529	-0.885646	-0.233816
6	1.594562	-0.542242	-0.322853
6	1.913491	0.868481	-0.260668
6	0.879591	1.805147	-0.125507
6	-0.442824	1.421605	-0.055742
6	-0.797602	0.050802	-0.104782
1	1.150525	2.852842	-0.087194
1	-1.209236	2.177879	0.038479
8	3.170598	1.300811	-0.398626
1	3.842588	0.746369	0.185778
8	2.498818	-1.447604	-0.480379
1	3.924325	-1.296567	-0.087486
8	4.759237	0.002639	1.010698
8	4.881544	-1.156042	0.256954
1	-0.024108	-1.940594	-0.28226
6	-2.182336	-0.413109	-0.028656
1	-2.317433	-1.488649	-0.086399
6	-3.292056	0.325369	0.101697
1	-3.242776	1.405969	0.16609
6	-4.685144	-0.255953	0.163057
8	-5.620297	0.587377	0.259659
8	-4.818833	-1.506113	0.113908

Table S5. Optimized geometry of TS of 2PCET between Et-CafH$_2$ and O$_2^{\bullet-}$ calculated using DFT-(U)B3LYP/PCM/6-311+G(3df,2p) in DMF.

Atomic Number	Coordinates (Angstromes)		
	X	Y	Z
6	-1.281829	-0.920982	-0.33298
6	-2.639734	-0.517598	-0.372276
6	-2.896598	0.905566	-0.241908
6	-1.816897	1.795165	-0.0885
6	-0.515776	1.352914	-0.063419
6	-0.224238	-0.029626	-0.185715
1	-2.042854	2.849807	0.002702
1	0.284428	2.070281	0.050548
8	-4.118185	1.402657	-0.312334
1	-4.924358	0.748979	-0.066652
8	-3.598073	-1.360499	-0.542412
1	-4.723476	-1.246661	0.485844
8	-6.051719	0.081272	0.414692
8	-5.53748	-1.03539	1.063657
1	-1.082475	-1.981271	-0.432564
6	1.129535	-0.55229	-0.163107
1	1.215769	-1.62845	-0.273149
6	2.276552	0.13504	-0.02187
1	2.302071	1.208892	0.095396
6	3.573785	-0.550337	-0.018802
8	4.58334	0.329532	0.134767
8	3.755091	-1.747939	-0.136039
6	5.926988	-0.204876	0.156051

1	6.105753	-0.732793	-0.780612
1	6.001388	-0.926154	0.969715
6	6.88319	0.951792	0.341001
1	7.906672	0.576621	0.359669
1	6.797451	1.667161	-0.476809
1	6.693789	1.471791	1.279962

Table S6. Optimized geometry of TS for 2PCET between CatH$_2$ and O$_2^{\bullet-}$ calculated using DFT-(U)B3LYP/PCM/6-311+G(3df,2p) in DMF.

Atomic Number	Coordinates (Angstromes)		
	X	Y	Z
6	-1.553795	-1.34724	0.076302
6	-2.710996	-0.614002	0.265952
6	-2.67657	0.788113	0.169724
6	-1.493555	1.433803	-0.115158
6	-0.275619	0.72727	-0.32767
6	-0.336528	-0.719257	-0.220186
8	0.731212	-1.480887	-0.451624
8	0.821349	1.333601	-0.623829
8	2.995831	-0.625946	0.093175
1	1.663769	-1.033561	-0.289809
8	2.782871	0.555459	0.798315
1	1.991046	0.950064	0.294508
1	-1.563213	-2.427746	0.145416
1	-1.455871	2.513397	-0.193926
1	-3.582881	1.360454	0.32072
1	-3.64092	-1.119998	0.488749