Electrochemical and Mechanistic Study of Superoxide Scavenging by Pyrogallol 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$^-$ ↔ 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)
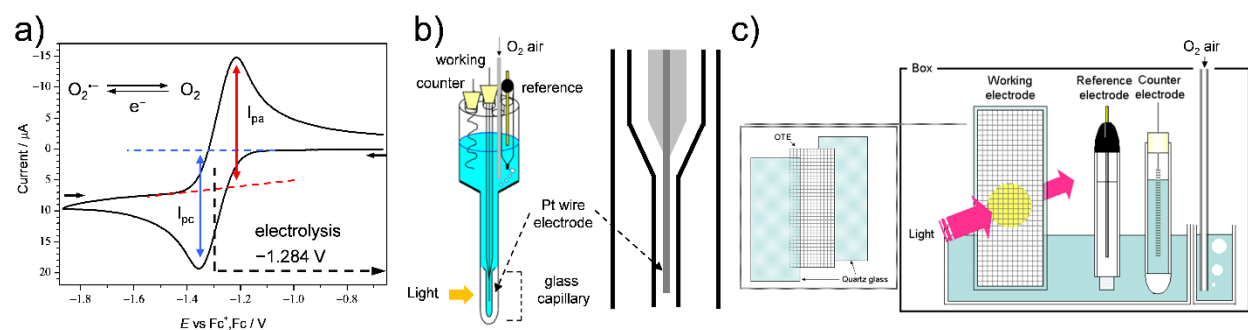
Figure S1. In situ electrolytic ESR/UV-vis spectral system. (a) Cyclic voltammograms of $O_2/O_2^{\bullet-}$ for potential determination. (b) In situ ESR system, composed of an electrochemical ESR cell with a glass small tip, air tube for O_2 bubbling, and three electrode system using a 0.5-mm-diameter straight Pt wire sealed in a glass capillary as working electrode. (c) An optically transparent thin layer electrochemical (OTTLE) cell using a Pt mesh working electrode for in situ electrolytic UV-vis spectrometry.

Table S2. ΔG° values (kJ mol^{-1}) for the PCET reaction between $O_2^{\bullet-}$ and the compounds (CatH$_2$, PyH$_3$, and MoCatH$_2$) in acetonitrile, calculated using (U)B3LYP/PCM/6-311+G(3df,2p) methods.

	PT1	PT2	PT3	PT4	ET1	ET2	ET3	PCET	2PCET
CatH$_2$	19.3	-365.4	378.5	-78.9	408.0	23.2	-434.2	-55.7	-36.3
PyH$_3$	17.8	-360.2	358.9	-67.9	406.4	28.3	-398.5	-39.5	-21.7
MoCatH$_2$	46.0	-336.5	380.6	-92.5	396.1	13.4	-459.6	-79.0	-32.9

Table S3. ΔG° values (kJ mol^{-1}) for the PCET reaction between $O_2^{\bullet-}$ and the compounds (CatH$_2$, PyH$_3$, and MoCatH$_2$) in dimethyl sulfoxide, calculated using (U)B3LYP/PCM/6-311+G(3df,2p) methods.

|	PT1	PT2	PT3	PT4	ET1	ET2	ET3	PCET	2PCET
CatH$_2$	19.8	-358.5	385.8	-78.3	400.9	22.5	-441.5	-55.7	-35.9
PyH$_3$	18.2	-353.3	353.1	-67.2	399.3	27.6	-392.6	-39.5	-21.2
MoCatH$_2$	46.0	-329.9	374.4	-92.0	389.0	13.0	-453.5	-79.0	-32.9

Table S4. ΔG° values (kJ mol^{-1}) for the PCET reaction between $O_2^{\bullet-}$ and the compounds (CatH$_2$, PyH$_3$, and MoCatH$_2$) in water, calculated using (U)B3LYP/PCM/6-311+G(3df,2p) methods.

	PT1	PT2	PT3	PT4	ET1	ET2	ET3	PCET	2PCET
CatH$_2$	20.3	-349.5	378.1	-77.5	391.6	21.7	-434.0	-55.8	-35.4
PyH$_3$	18.8	-344.3	345.5	-66.2	390.0	26.8	-384.9	-39.4	-20.5
MoCatH$_2$	46.0	-321.4	366.4	-91.5	379.9	12.4	-445.5	-79.0	-33.0

Table S5. ΔG° values (kJ mol^{-1}) for the PCET reaction between $O_2^{\bullet-}$ and the compounds (CatH$_2$, PyH$_3$, and MoCatH$_2$) in vacuum, calculated using (U)B3LYP/PCM/6-311+G(3df,2p) methods.

	PT1	PT2	PT3	PT4	ET1	ET2	ET3	PCET	2PCET
CatH$_2$	-60.4	-1385.1	1279.3	-159.8	1444.0	119.3	-1319.8	-40.4	-100.9
PyH$_3$	-66.9	-1374.7	1212.8	-170.9	1437.1	129.3	-1254.4	-41.6	-108.5
MoCatH$_2$	-6.0	-1323.8	1241.7	-180.3	1417.8	100.0	-1322.1	-80.3	-86.4
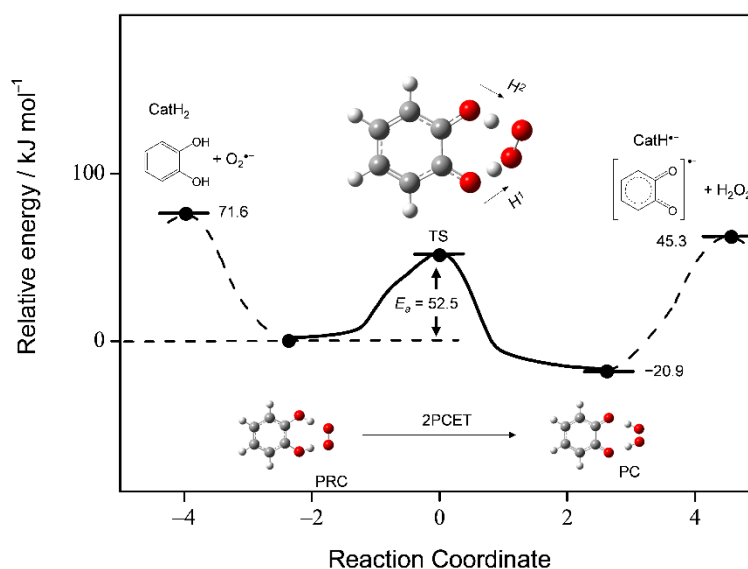
Figure S2. Energy profile (kJ mol^{-1}) along the IRC of the 2PCET between CatH$_2$ and O$_2^{\bullet-}$ in DMF with structures of FRs (CatH$_2$, O$_2^{\bullet-}$), PRC (CatH$_2$−O$_2^{\bullet-}$), TS, PC (Cat$^{\bullet-}$−H$_2$O$_2$), and FPs (Cat$^{\bullet-}$, H$_2$O$_2$), calculated using DFT-(U)B3LYP/PCM/6-311+G(3df,2p) method.
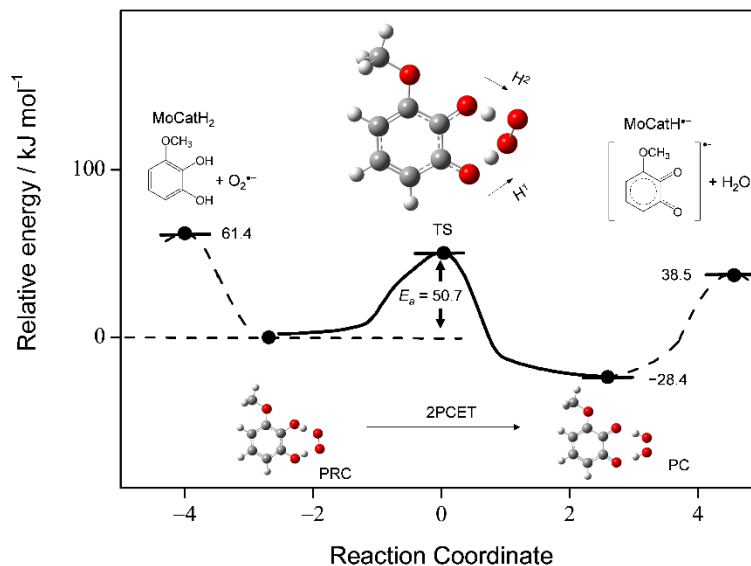
Figure S3. Energy profile (kJ mol^{-1}) along the IRC of the 2PCET between MoCatH$_2$ and O$_2^{\bullet-}$ in DMF with structures of FRs (MoCatH$_2$, O$_2^{\bullet-}$), PRC (MoCatH$_2$−O$_2^{\bullet-}$), TS, PC (MoCat$^{\bullet-}$−H$_2$O$_2$), and FPs (MoCat$^{\bullet-}$, H$_2$O$_2$), calculated using DFT-(U)B3LYP/PCM/6-311+G(3df,2p) method.

Table S6. Optimized geometry of complexes (PRC, TS, and PC) formed along the 2PCET between PyH$_3$ and O$_2^{\bullet-}$ calculated using DFT-(U)B3LYP/PCM/6-311+G(3df,2p) in DMF.

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Center    Atomic            Coordinates (Angstroms)
Number    Number            X            Y            Z
-PRC-----------------------------------------------------------------
    1         6          1.181897    -1.84196    -0.06596
    2         6          0.06826     -1.03843     0.202336
    3         6          0.221736     0.356216    0.22686
    4         6          1.486161     0.908188   -0.01953
    5         6          2.592423     0.110095   -0.27751
    6         6          2.426881    -1.27204    -0.29633
    7         1          1.047691    -2.91533    -0.08233
    8         1          3.554319     0.569762   -0.45842
    9         1          3.277846    -1.90975    -0.49659
   10         8          1.616241     2.268443    0.016273
   11         1          0.733112     2.622022    0.203096
   12         8         -0.76731      1.237787    0.548122
   13         1         -1.66049      1.069864    0.077844
   14         8         -1.11312     -1.64656     0.472696
   15         1         -1.92325     -1.09988     0.236284
   16         8         -3.30296     -0.42191    -0.26998
   17         8         -3.04453      0.853596   -0.5295
-TS------------------------------------------------------------------
    1         6          1.481072     0.891171    0.059877
    2         6          0.201635     0.388281   -0.25156
    3         6         -0.02594     -1.03381    -0.30444
    4         6          1.092044    -1.87109    -0.03328
    5         6          2.330801    -1.34326     0.259256
    6         6          2.542867     0.045301    0.310444
    7         1          0.936235    -2.94151    -0.06901
    8         1          3.163025    -2.00692     0.456686
    9         1          3.516047     0.456834    0.539721
   10         8         -1.19241     -1.50821    -0.5994
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11	1	-2.23727	-0.9208	0.281739
12	8	-0.73629	1.294887	-0.54229
13	1	-1.73773	1.015622	-0.32236
14	8	-2.94759	-0.39799	0.81965
15	1	0.79236	2.643126	-0.10118
16	8	1.653703	2.246055	0.095463
17	8	-3.04835	0.777028	0.098148

-PC---

1	6	-1.6067	0.918052	-0.0358
2	6	-0.25561	0.405283	-0.01653
3	6	-0.06345	-1.05977	0.029501
4	6	-1.24505	-1.86692	0.065874
5	6	-2.49639	-1.30811	0.049218
6	6	-2.69765	0.096077	-0.00316
7	1	-1.114	-2.94054	0.103607
8	1	-3.36738	-1.95084	0.075757
9	1	-3.696	0.511511	-0.01592
10	8	1.099258	-1.56706	0.037436
11	1	2.574259	-0.86554	-0.27943
12	8	0.696442	1.246655	-0.0428
13	1	2.349146	1.007136	0.296185
14	8	3.42224	-0.37527	-0.45585
15	1	-0.80768	2.60238	-0.09488
16	8	-1.72331	2.270097	-0.08428
17	8	3.286694	0.741594	0.467989