Supplementary data for

Electrochemical and Mechanistic Study of Structure–Activity Relationship of α-, β-, γ-, and δ-Tocopherol on Superoxide Elimination in *N*,*N*-Dimethylformamide through Proton-Coupled Electron Transfer

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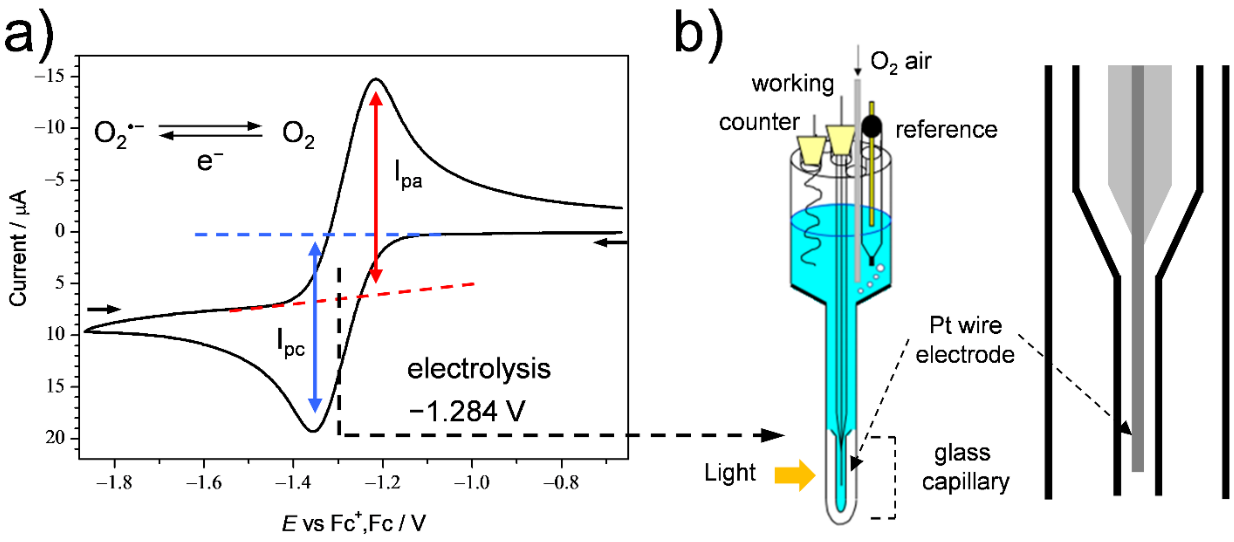

Figure S1. *In situ* electrolytic ESR spectral system. (a) Cyclic voltammograms of $O_2/O_2^{\bullet-}$ for potential determination. (b) *In* situ ESR system, composed of an electrochemical ESR cell with a glass small tip, air tube for O_2 bubbling, and three electrode system using a 0.5-mm-diameter straight Pt wire sealed in a glass capillary as working electrode.

Table S1. Free energy changes (ΔG°/kJ mol^{-1}, 298.15 K) of ET between (a) TO^- and $HO_2^\bullet$ (along intermolecular ET–PT), and between (b) TOH and $HO_2^\bullet$ (along PCET), in DMF.

	α-TO^-/α-TOH	β-TO^-/β-TOH	γ-TO^-/γ-TOH	δ-TO^-/δ-TOH
TO^- and $HO_2^\bullet$	−50.3	−40.1	−38.6	−28.4
TOH and $HO_2^\bullet$	100.7	103.3	111.4	117.1

[1] ΔG°s were calculated using DFT at the (U)B3LYP/PCM/6-311+G(d,p) level. [2] Electron transfer (ET), proton transfer (PT), proton-coupled electron transfer (PCET).

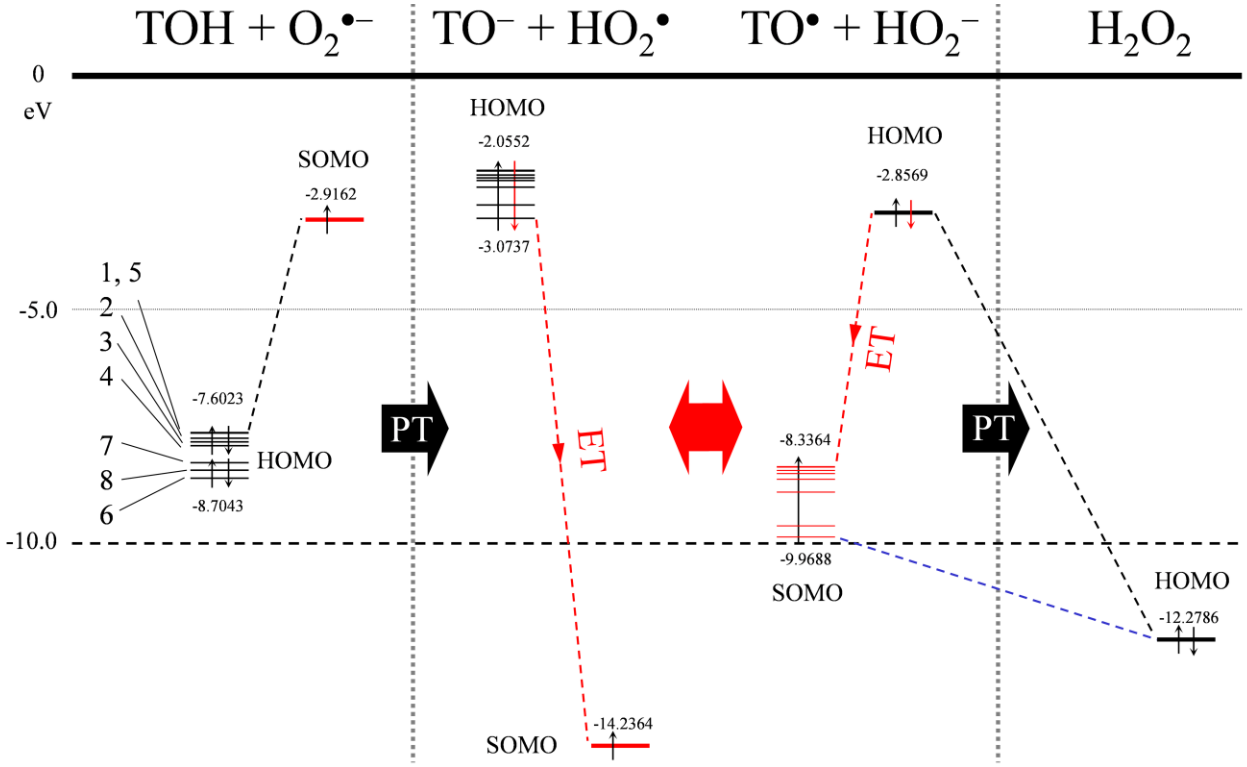

Figure S2. Change in highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO—LUMO) energies (E_h/a.u.) along the $O_2^{\bullet-}$ elimination reaction (the first proton transfer (PT), electron transfer (ET), and the second PT) by (a–d) α-, β-, γ-, and δ-TOH, (e) 2,2,5,7,8-pentamethyl-6-chromanol, (f) homogentisic acid γ-lactone, (g) 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran, and (h) trans-*para*-coumaric acid, calculated with the HF/6-311+G(d,p) method.

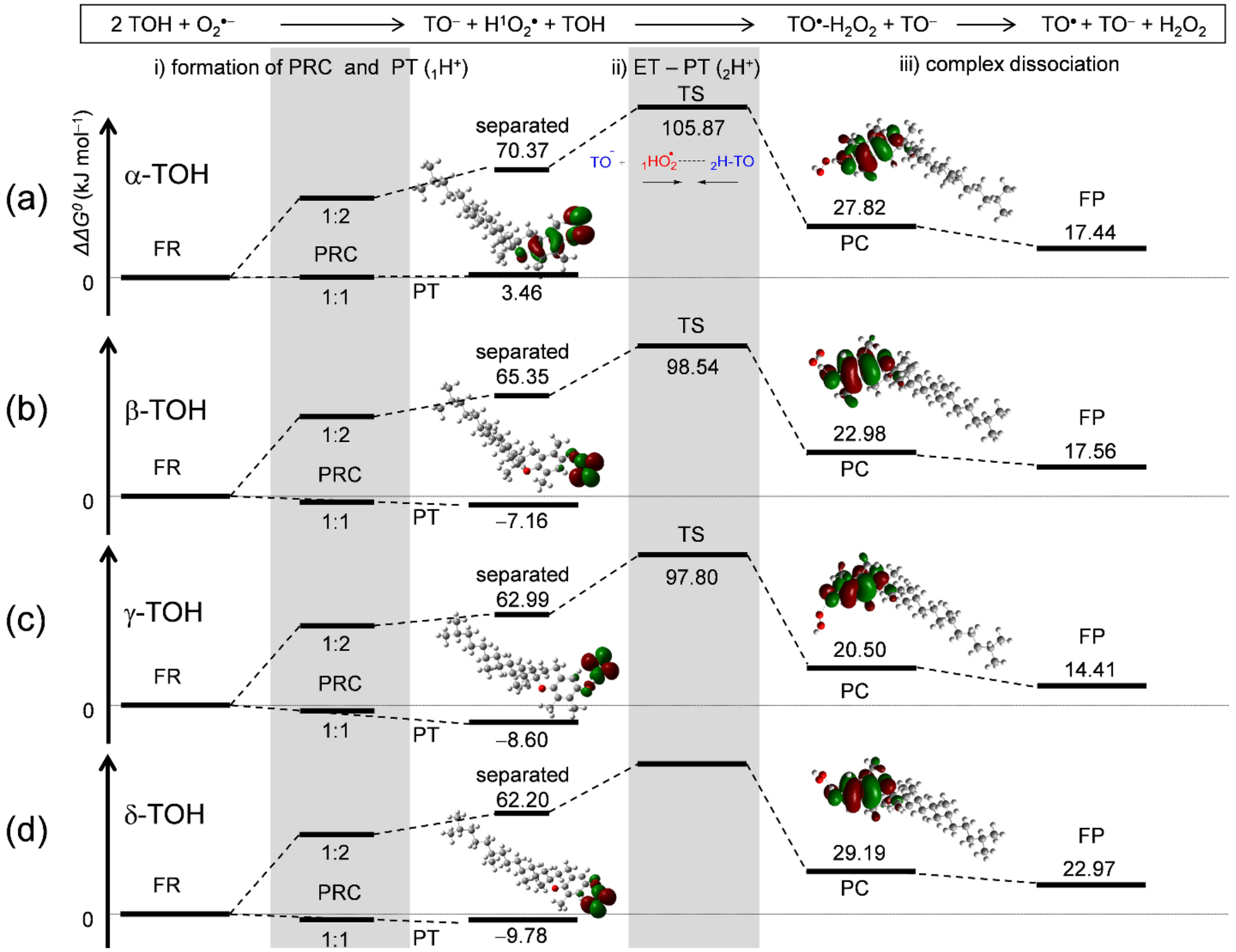

Figure S3. Energy profiles along PCET involving two PTs and one ET between two molecule of TOH (α-, β-, γ-, and δ-TOH) and $O_2^{\bullet-}$ in DMF, calculated using DFT-(U)B3LYP/PCM/6-311+G(d,p) method. Activation energies (kJ mol^{-1}) of transition states (TS) were obtained for the 1:1 ET-PT pathway between TOH (α-, β-, and γ-TOH) and $HO_2^{\bullet}$.

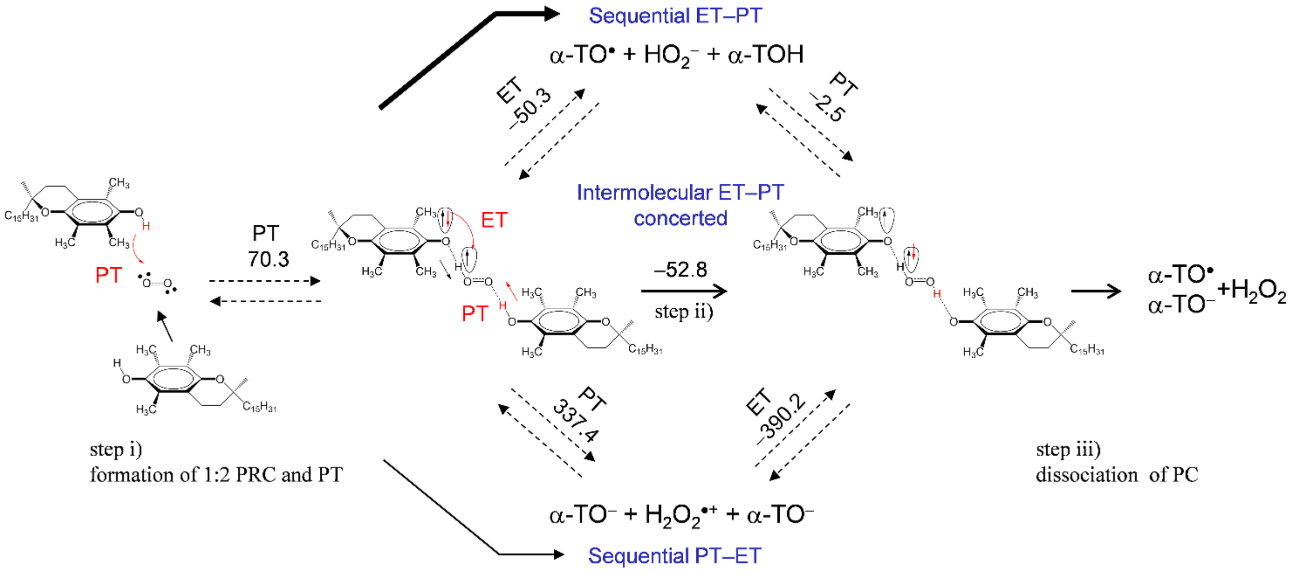

Figure S4. Plausible mechanism and the Δ*G*°s (kJ mol^{-1}, 298.15 K) for the PCET pathways between $O_2^{\bullet-}$ and α-TOH involving two PTs and one ET in DMF. The Δ*G*°s were calculated using DFT-(U)B3LYP/PCM/6-311+G(d,p) method.

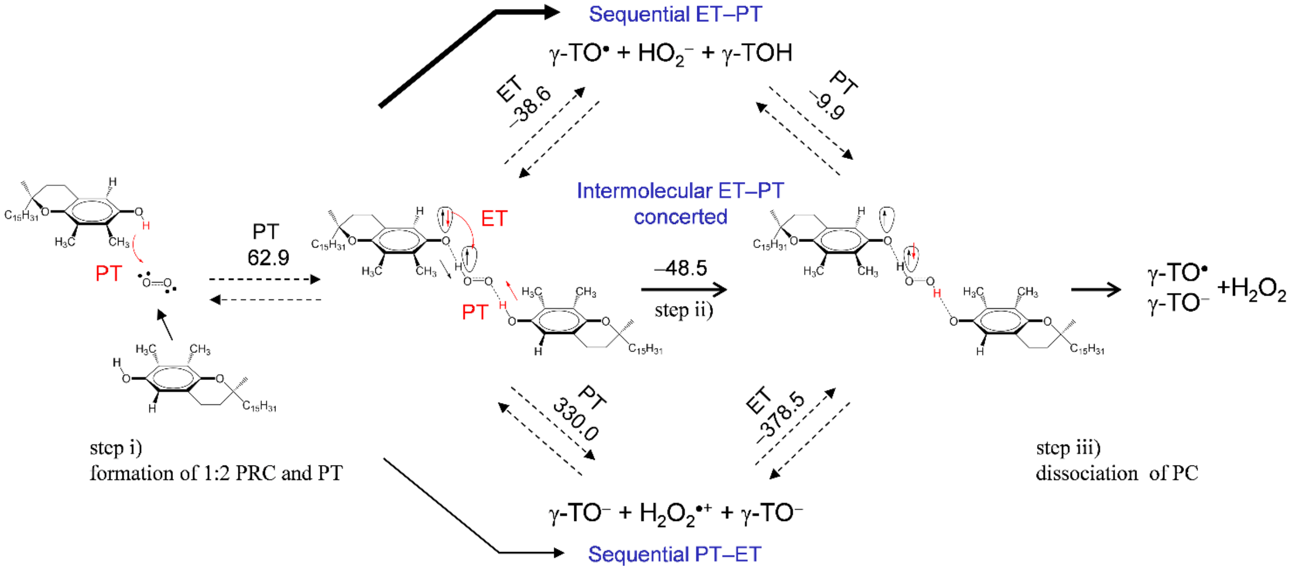

Figure S5 Plausible mechanism and the Δ*G*°s (kJ mol^{-1}, 298.15 K) for the PCET pathways between $O_2^{\bullet-}$ and γ-TOH involving two PTs and one ET in DMF. The Δ*G*°s were calculated using DFT-(U)B3LYP/PCM/6-311+G(d,p) method.