## Supporting Information

## Redox-Induced Unusual Partner Radical Formation and Its Dynamic Balance with Radical Dimer in Cucurbit[8]uril

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Figure S1. Absorption spectra in water solution $(0.1 \mathrm{M} \mathrm{NaCl})$ in the presence of increasing concentrations of CB[8] (0-1.3 equiv). The concentration of 1 was $10 \mu \mathrm{M}$. Insert: The Job-plot curve determined from UV difference absorption spectra. The total concentration of $\mathbf{1}$ and $\mathrm{CB}[8]$ is $25 \mu \mathrm{M}$.


Figure S2. Differential pulse voltammograms (DPV) of complex 1 and EV with and without the presence of $\mathrm{CB}[8]$ in $0.1 \mathrm{M}(\mathrm{pH}=7)$ phosphate buffer solution, a) compound 1 alone ( 0.4 mM ), b) $\mathbf{1 + C B}[8](1: 1)$, c) 1+ $C B[8]+E V(1: 1: 1)$, d) $\mathbf{1}(1: 1: 3)$, e) $1+C B[8]+H P(1: 1: 40)$, f) $E V$ alone ( 0.4 mM ), and g) $E V+C B[8]$ (1:1). The scan 5 rate is $25 \mathrm{mVs}^{-1}$.


Figure S3. DPV of complex 1-CB[8] ( 0.4 mM , black), $1: 1$ mixture of $1-\mathrm{CB}[8]$ and EV (red), 1:2 mixture of 1$C B[8]$ and $E V$ (blue), 1:2 mixture of 1-CB[8] and 4-hydroxyphenol (cyan) and 1:100 mixture of 1-CB[8] and 4hydroxyphenol (pink) .

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Figure S4. DPV of EV ( 0.4 mM , solid line) and in the presence of 100 equiv of 4-hydroxyphenol (dash line).


Figure S5. DPV of a) $1: 1$ mixture of $E V$ and $C B[8](0.4 \mathrm{mM})$ (solid line), b) 1:1:2 mixture of $\mathrm{EV}, \mathrm{CB}[8]$ and 4hydroxyphenol (dot line), and c) 1:1:100 mixture of EV,CB[8] and 4-hydroxyphenol (dash line).


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Figure S6. DPV of a) 4-hydroxyphenol ( 0.4 mM ), b) 1:1 mixture of 4-hydroxyphenol and EV, and c) 1:1:1 the mixture of 4-hydroxyphenol, EV, and CB[8].

