Supplementary Information for
Cathodic Electroorganic Reaction on Silicon Oxide Dielectric Electrode

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1. General.

1.1. Setup of H-type divided cell with Nafion® membrane for electrolysis.

Electrolysis was carried out in a home-made H-type divided cell (Fig. S1A-C) with working and counter electrode (WE and CE) chambers separated by Nafion® 117 proton exchange membrane (0.007-inch thickness, Sigma Aldrich). The working, counter, and reference electrodes were defective 200 nm n-Si/SiO$_2$, Pt wire (diameter of 0.5 mm), Ag/Ag$^+$ (10 mM AgNO$_3$ + 0.1 M TBAP in MeCN, BAS Inc.), respectively. Typical electrolysis solution in WE chamber composed of 5 mM of starting compound with 1 M acid dissolved in either MeCN or 25% v/v MeCN-H$_2$O. CE chamber was filled with acid-electrolyte solution. WE chamber was stirred 300 rpm and purged with N$_2$ gas (99.999%) throughout the reaction. The O-rings were all SuperViton® and the rings for Nafion® separator were Teflon-taped to shorten the inner diameter of ~1 mm to minimize crossover.
1.2. Chemical analysis of the product from the reaction of ANTH upon electrolysis.

Fig. S2. Representative Chemical analysis of the reaction of ANTH on defective 200 nm n⁺-Si/SiO₂. Representative LC of (A) before and (B) after the reaction mixture of ANTH. (C) MS of AQ (red) and ANTH (green). (D) ¹H-NMR of the product mixture obtained after the reaction of ANTH on defective 200 nm n⁺-Si/SiO₂ electrode. The original spectra of the above are all attached in section 4.
1.3. Examination of defective 200 nm $n^+$-$Si/SiO_2$ dielectric electrode after electrolysis by cyclic voltammetry, TEM, SEM, Raman, EELS, and XPS.

**Fig. S3.** Electrochemical measurements of defective 200 nm $n^+$-$Si/SiO_2$ in various states. (A) The typical $i$-$t$ curve during electrolysis. (B) Cyclic voltammograms of the defective 200 nm $n^+$-$Si/SiO_2$ electrode in large potential range with or without metal (Pd, Cr). (C) Cyclic voltammograms of the defective 200 nm $n^+$-$Si/SiO_2$ electrode comparison upon long period of electrolysis.

The scale of current densities in voltammograms, which were obtained before electrolysis, is as low as nA·cm$^{-2}$ scale. As electrolysis proceeds for a long period, however, the current gradually increases to the order of 100 μA·cm$^{-2}$ (Fig. S3A). Such high current could be suspected as generation of defects caused by a long period of cathodic bias. Physical damage of the dielectric layer might be large enough to allow direct electron transfer from the underlying conductor to reducible species in the solution. We checked and compared the dielectric layers before and after electrolysis.

Pd and Cr metals were electrodeposited on the electrodes that had experienced a long period of electrolysis and cyclic voltammetry was performed in 1 mM Ru$^{2+/3+}$ + 0.5 M H$_2$SO$_4$ aqueous solution (Fig. S3B). Any severe physical damage such as pinhole and crevice would have led to a short circuit between the electroplated metal film and underlying Si, at least enhanced electron tunneling. The result was clear that metal films on the SiO$_2$ layer did not modify the voltammogram appreciably, supporting that negligible physical defects appeared upon cathodic bias applied for a long time. In case of Pd deposited dielectric electrode, however, slight oxidative current is observed at approximately + 4.5 V that is far more positive than the redox potential of Ru$^{2+/3+}$, approximately -0.2 V. Probably electron tunneling upon a high overpotential is responsible for it.

The linear sweep voltammograms of the 5 mM ANTH + 1 mM BP + 1 M HCIO$_4$ in MeCN working solution was obtained before and after 12 h of electrolysis (Fig. S3C). It shows that the onset potential shifts in positive direction and the cathodic current increases. The voltammetric behavior, not completely, is recovered after under the condition free of potential bias. Although surface analysis techniques provided no evidence of appreciable chemical or physical defects, voltammetry implies that the cathodic damage caused by long electrolysis exists and appears to be semi-permanent. Upon negative bias, protons are expected to migrate across the thermal SiO$_2$ at a slow rate, lowering the resistance of the dielectric layer (1, 2). Protons should be expelled out of the layer when potential bias is reversed. Meanwhile, it is highly probable that chemical defects such as dangling bonds and atomic vacancies inside the SiO$_2$ layer are gradually accumulated under cathodic condition.
Fig. S4. Electron microscopy of the defective 200 nm $n^+$-Si/SiO$_2$ electrode upon electrolysis. HR-TEM of (A) before and (B) after electrolysis. FE-SEM of (C) before and (D) after electrolysis.

We examined the dielectric layers in the middle of electrolysis by HR-TEM and FE-SEM (Fig. S4). Collecting several number of images at random spots, we found no observable physical defects such as pinholes or cracks.
Fig. 5. The analyses of defective 200 nm n⁺-Si/SiO₂ by Raman, EELS, and XPS. (A) Raman spectra of n⁺-Si/SiO₂ in ambient before and after electrolysis. (B) Electrochemical Raman spectra of n⁺-Si/SiO₂ at -1.67 V. EELS of n⁺-Si/SiO₂ before electrolysis in (C) horizontal and (D) vertical line profile. EELS of n⁺-Si/SiO₂ after electrolysis in (E) horizontal and (F) vertical line profiles. XPS of n⁺-Si/SiO₂ (G) before (black) and (H) after (red) electrolysis.
With regard to chemical defects, we investigated the SiO$_2$ film before and after electrolysis in various ways of surface analysis (Fig. S5), i.e., Raman spectroscopy, electron energy loss spectroscopy (EELS), and X-ray photoelectron spectroscopy (XPS).

The Raman spectra were obtained for both dry sample in ambient and electrochemically biased at -1.67 V in solution of 0.5 M H$_2$SO$_4$ aqueous solution (Fig. S5A-B), normalized to silicon peak (527 cm$^{-1}$). The Raman-active defects are 495 and 606 cm$^{-1}$ related to the defects in network according to the previous report (3, 4). The peak heights were all low and no distinguishable change was observed before and after electrolysis (Fig. S5A). In addition, we did not find distinct change upon in situ Raman spectra due to electrolysis of -1.67 V in strongly acidic aqueous solution either (Fig. S5B).

The EELS at the interface of n$^+$-Si/SiO$_2$ for both vertical and horizontal line profiles were conducted in order to characterize bond defects of O-Si-O networks (Fig. S5C-F). However, both the vertical and horizontal line profile exhibits indistinguishable chemical transition at the interface upon electrolysis.

The XPS before and after electrolysis of n$^+$-Si/SiO$_2$ allows the nature of chemical bonds at the surface. There was no significant change upon electrolysis (Fig. S5G-H).

In short, all of these gave no significant difference. This might be because such surface analysis techniques were not sensitive enough to detect the chemical defects caused by prolonged cathodic bias, or the SiO$_2$ films were reversibly healed when free of bias between electrolysis and post-analysis. Since most of the physical damages are hardly restored reversibly, faradaic current through the SiO$_2$ films is deemed to come from chemical defects rather than pinholes or crevices.

In summary of this section, both the proton permeation and chemical defects are supposedly responsible for the quasi-reversible change in film properties.
1.4. The electroorganic reaction of ANTH and its derivatives on n+Si/SiO₂: extended and miscellaneous.

Table S1. The extended version of Table 1 with faraday efficiency.

| Entry | Concentration of 1α (mM) | Concentration of Acid (M) | Consumed (μmol) | Consumed (%) | Generated (μmol) | Selectivity (%) | F.E. Cons. (%) | F.E. Gen. (%) |
|-------|--------------------------|--------------------------|-----------------|--------------|-----------------|----------------|----------------|--------------|
| 1     | 5                        | 1.00                     | 16.55(±2.25)    | 36.4(±4.4)   | 4.56(±1.51)     | 25(±8)         | 3.6(±1.7)      | 0.3(±1.9)    |
| 2     | 5                        | 0.10                     | 5.12(±2.61)     | 9.7(±5.0)    | 2.41(±0.59)     | 47(±26)        | 6.0(±2.3)      | 2.8(±0.8)    |
| 3     | 5                        | 0.01                     | 1.60(±0.82)     | 3.2(±1.6)    | 0.89(±0.55)     | 56(±45)        | 36.8(±15.7)    | 20.6(±9.9)   |
| 4     | 2                        | 1.00                     | 3.15(±0.91)     | 14.5(±4.2)   | 2.56(±0.50)     | 81(±28)        | 0.9(±0.1)      | 0.7(±0.1)    |
| 5     | 0.7                      | 1.00                     | 2.06(±0.16)     | 28.8(±4.3)   | 2.13(±0.80)     | 103(±39)       | 1.7(±0.0)      | 1.8(±3.5)    |

The reaction was carried out for 10 mL volume of the solution. *Quantification done by LC-MS. r.t., room temperature.

Selectivity, similar to the yield of the reaction, is the percentage of the generated amount of product over the consumed amount of reactant. Faraday efficiency is defined as the efficiency with which charge (electron) is transferred in a system facilitating an electrochemical reaction. Therefore, it is the percentage of consumed or generated amount over total charge. The faraday efficiency was calculated for both consumption and generation based on the proposed reaction mechanism in Fig. 3.

Table S2. Electroorganic reactions of 1α to 2α on different oxides on n⁺-Si electrode. The solution components are 1α (5 mM), 1 mM biphenyl (BP, internal standard), and 1 M HClO₄ in MeCN at room temperature in N₂ atmosphere.

| Entry | Oxide          | Accumulated Charge (C) | Consumed (%) |
|-------|----------------|-------------------------|--------------|
| 1     | Defective Thermal | 48.4                    | 36.4*        |
| 2     | TEOS CVD        | 52.3                    | 9.2*         |
| 3     | PECVD           | 1121                    | 5.5*         |

The reaction was carried out for 10 mL volume of the solution. *Quantification done by LC-MS. r.t., room temperature.

The 200 nm thick n⁺-Si/SiO₂ electrode can be fabricated as well by tetraethylorthosilicate (TEOS) chemical vapor deposition (CVD) and plasma-enhanced chemical vapor deposition (PECVD) on n⁺-Si. The preparation method of defective thermal SiO₂ is described in the manuscript. The wafers were all cleaned by standard SPM and SC-1,2 cleaning consecutively then stripping native oxide by diluted HF. The target 200 nm-thick TEOS CVD oxide was prepared inside the CVD chamber (P-5000 II, AMIK) with both 150 sccm of TEOS/He and O₂ under 9 Torr pressure with 350 W RF power. The target 200 nm-thick PECVD oxide was prepared at the CVD chamber (PlasmaPro System 100, Oxford Instrument) with 5% SiH₄/N₂ at 350 C.
The electrolysis of 1a was conducted on these various oxides for comparison (Table S2). The 200 nm thick n⁺-Si/SiO₂ electrode can be fabricated as well by tetraethylorthosilicate (TEOS) chemical vapor deposition (CVD) and plasma-enhanced chemical vapor deposition (PECVD) on n⁺-Si with the same thickness. By and large, the oxides as made exhibit the electrochemical behavior similar to what the defective 200 nm n⁺-Si/SiO₂ in this study does: current increasingly flows upon a constant negative bias. The limiting current of PECVD is in mA cm⁻² scale that is too high to be considered as an insulator (See the accumulated charge in Table S2). PECVD gives oxide films that have more physical defects such as pinhole or cracks through which direct electron transfer occurs between n⁺-Si and the electrolyte solution. Although TEOS CVD oxide allows low current, far less 1a is consumed probably because of much less intrinsic chemical defects than the defective 200 nm n⁺-Si/SiO₂ electrode.

![Image](Image)

**Fig. S6.** The plot of log (Consumed %) against $E^\circ$ (V) of ANTH and its derivatives based on Table 2.

As mentioned in the main-text, 1b is converted to 2b upon cathodic reduction on 200 nm thick n⁺-Si/SiO₂ electrode, similar to the reaction of 1a to 2a. This observation might complicate to the fact that the 2-substituted methyl (benzyllic peripheral ring of acene) may be more labile than the 9,10- site (central ring of acene). To resolve this matter, we oxidized 1b using chemical oxidant of KMnO₄ to check which site is truly reactive. As a result, 2b was produced and no other side products were observed (section 4). We are still unclear why 9,10- site is more reactive than 2- site of 1b but we could infer it. In general, the unpaired electron in radical species of PAHs is more stable at the central ring than the peripheral ring, so the central ring is oxidized rather than 2- site. In addition, the reaction may proceed to produce a thermodynamically stable product, as 2b is stable than the oxidized product at 2- site.

The amounts of the PAHs electrolyzed in this study linearly correlate with the reduction potentials ($E$) rather than BDE except for 1d as shown in Fig. S6. The PAH, which is reduced more easily, is consumed more. As described in the manuscript, 1d is considered to be in a different family of reactions to ANTH derivatives so it is not correlated. The reason for such relationship needs further research. Nonetheless, we can infer it. First of all, the manifest dependence on reduction potentials ($E$) indicates that the electrochemical electron transfer process is involved in the entire reaction as a crucial step, which can determine the apparent reaction rate.

Secondly, BDFE may be related. According to the reaction mechanism, we believe that the homolytic bond dissociation free energy (BDFE, $\Delta G_{BDFE}$) is an important parameter to be considered. Note that this term differs from the BDE which is the enthalpy of PAHs. As the free
energies are state functions, the thermochemical cycle can be written as follows to describe the 
BDFE for the reactant of $\phi - \text{H}$, the C-H bond of 9 site in case of ANTH,
\[
\begin{align*}
\phi - \text{H} + e^- &\rightleftharpoons \phi - \text{H}^- & E^o &\quad [S1] \\
\phi - \text{H}^- &\rightleftharpoons \phi \cdot + \text{H}^- & \Delta G_{\phi - \text{H}^-/\phi} &\quad [S2] \\
\text{H} \cdot + e^- &\rightleftharpoons \text{H}^- & E^o_{\text{H}/\text{H}^-} &\quad [S3]
\end{align*}
\]
\[
\begin{align*}
\phi - \text{H} &\rightleftharpoons \phi \cdot + \text{H} & \Delta G_{\text{BDFE}} &\quad [S4] \\
\Delta G_{\text{BDFE}} &= -FE^o + \Delta G_{\phi - \text{H}^-/\phi} + FE^o_{\text{H}/\text{H}^-} & [S5]
\end{align*}
\]
where $E^o$ is the reduction potential of $\phi - \text{H}$ and $E^o_{\text{H}/\text{H}^-}$ is the standard reduction potential of $\text{H} \cdot$. A few values of $E^o_{\text{H}/\text{H}^-}$ were reported in the literature as a function of solvents (5).

The BDFE including the terms such as solvation energy and entropy can be considered as arbitrary constant $C$,
\[
\Delta G_{\text{BDFE}} = -FE^o + \Delta G_{\phi - \text{H}^-/\phi} + C &\quad [S6]
\]
As shown in Fig. S6, the amounts of the PAHs electrolyzed in this study linearly correlate with $E^o$ as long as the reactions are in the same class. Therefore, $E^o$ is the dominant factor to determine $\Delta G_{\text{BDFE}}$ although we have no information about the values of $\Delta G_{\phi - \text{H}^-/\phi}$.

Since the consumed amount in the fixed period of electrolysis was reproducible, we can assume that it is linearly proportional to the average reaction rate constant. This tells that the logarithmic consumed amount should correlate with $\Delta G_{\text{BDFE}}$.

**Table S3.** Electroorganic reaction of 1a to 2a on defective 200 nm n+-Si/SiO$_2$ electrode at room temperature in O$_2$ atmosphere.

| Acid-Electrolyte | H$_2$O in MeCN (v/v %) | Consumed (μmol) | Consumed (%) | Generated (μmol) | Selectivity (%) |
|------------------|------------------------|-----------------|--------------|-----------------|----------------|
| HClO$_4$         | 4                      | 11.57(±4.99)$^a$| 22.7(±9.8)$^a$| 2.24(±1.39)$^a$| 19(±15)$^a$   |
| TFA-NaBF$_4$     | 0                      | 4.55(±1.52)$^a$ | 8.9(±3.0)$^a$ | 1.40(±0.49)$^a$| 31(±15)$^a$   |

The reaction was carried out for 10 mL volume of the solution. $^a$Quantification done by LC-MS. Selectivity calculated as the percentage of the generated amount of the product over the consumed amount of the reactant. r.t., room temperature.

The electrolysis of 1a to 2a on thermal oxide cathode was investigated in O$_2$ atmosphere (Table S3). The extent of reaction was less than that of N$_2$ atmosphere. The role of O$_2$ is not certain but it is clear that H$_2$O is the better O source than O$_2$ in such EOS system.
1.5. Capturing the intermediates of the electroorganic reaction of ANTH on n$^+$-Si/SiO$_2$ using TEMPO.

**Fig. S7.** The summary of intermediate capture experiments. (A) Schematic illustration of the proposed mechanism of the intermediate capture strategy using TEMPO. (B) Schematic illustration of the experimental setup for intermediate capture using TEMPO in an undivided cell and (C) CE separated by double junction of Vycor tips. (D) Photo of the undivided cell and double junction of Vycor tips in a solution-filled vial. (E) LC and (F) MS of the proposed intermediate captured by TEMPO. The large version is attached in section 4.

Such setup must not involve Nafion® membrane. Because TEMPO is unstable in an acidic media (<pH 3), the acidity from Nafion® may induce disproportionation of TEMPO. Therefore, the electrolysis using TEMPO was performed in the undivided cell where the CE was separated by double junction of Vycor tips.
1.6. Quantification method by UV-VIS measurement.

The quantification of the electroorganic reaction described in the manuscript could be done by UV-VIS measurement. The absorption of ANTH at $\lambda_{357\text{nm}}$ and AQ at $\lambda_{272\text{nm}}$ did not overlap, thereby appropriate to be calculated using Beer’s law:

$$A = \varepsilon d C \quad \text{[S7]}$$

where $A$: absorbance, $\varepsilon$: molar extinction coefficient, $d$: cell length, and $C$: concentration. In addition, $\lambda_{251\text{nm}}$ could be used for quantification of crossed amount from WE to CE. The linear calibration curve was obtained from standard ANTH and AQ solution in MeCN. The slope and the intercept are summarized in Fig. S8C. The cell length for UV-VIS measurement was 1 cm, so the absorbance and the concentration relation is written as the following.

$$A = \varepsilon C + b \quad \text{[S8]}$$

The percentage consumption of ANTH could be calculated as follows.

$$\text{Consumption (\%)} = 100 \cdot \frac{C_f - C_i}{C_i} = 100 \cdot \frac{A_f - A_i}{A_i - b} \quad \text{[S9]}$$

where the subscript $i$ is initial and $f$ is final. This calculation is valid at $\lambda_{357\text{nm}}$.

The percentage generation of AQ could be calculated as shown below.

$$\text{Generation (\%)} = 100 \cdot \frac{C_f - C_i}{C_{I\text{ANTH}}} = 100 \cdot \frac{\varepsilon_{AQ,272\text{nm}} A_f - A_i}{C_{I\text{ANTH}}} \quad \text{[S10]}$$

where $C_{I\text{ANTH}}$ is the initial concentration of ANTH in the working chamber. This calculation is valid at $\lambda_{272\text{nm}}$.

Note that the volume of the solution in H-type divided cell changes due to the evaporation by continuous N$_2$ purging. The volume should be checked through the meniscus then adjusted by adding or evaporating the solvent. In addition, we calculated for the derivative compounds of ANTH in the same way (methods not shown).
1.7. Quantification method by LC-MS.

In order to perform chromatography, the electrolyte and strong acids must be removed by work-up. The internal standard was dissolved together in the working solution. We chose biphenyl (BP) that undergoes neither chemical reaction nor crossover during the experiment.

In LC-MS/MS, the signal was detected by selected ion monitoring (SIM) mode for specific m/z. Relative area in LC chromatogram allows quantifications. AQ was quantified based on SIM mode of m/z of 209.1. ANTH was measured by UV (350 nm) since its m/z of 178.1 did not match [M+H] but [M]. BP was detected by UV (254 nm) since it was not ionized by atmospheric-pressure chemical ionization (APCI), inappropriate for SIM mode. The calibration curve of each chemical gave quantitative information about the chemical components. Note that at least three times of measurement for each sample were performed and averaged for quantitative analysis. Moreover, calibration curves were obtained for a day-by-day experiment to ensure deviation upon column usage.
2. Control Experiments.

2.1. The possible anticipated side-reactions of ANTH and investigation by electrolysis on conventional electrodes and n*-Si (oxide removed).

We suspected two probable mechanisms of ANTH reaction at conductor electrode other than the defective 200 nm n*-Si/SiO₂. Reactive oxygen species generated at the cathode could attack ANTH to produce AQ in the presence of oxygen. Since the electrolysis is conducted at defective 200 nm n*-Si/SiO₂ dielectric electrode continuously supplying N₂ to purge out oxygen from the solution, we could rule out such mechanism. Even in the absence of oxygen, we can imagine radical anion as a result of electrochemical reduction of ANTH. If no AQ is produced by electrolysis at conductor electrode in N₂ atmosphere, the second mechanism should not be responsible for AQ production at defective 200 nm n*-Si/SiO₂ dielectric electrode.

When the cathodic bias of -1.17 V was applied to the solution of ANTH in 1 M HClO₄-MeCN in air for electrolysis of 12 h, ANTH was significantly consumed and AQ was generated (Fig. S9B). The potential bias applied is much less than that of ANTH, Eₐ₁/₂ = -2.02 V, but negative enough to generate oxygen species (6, 7) which could provoke an unwanted radical reaction which is similar.
to ozonation (8). Changing to N₂ atmosphere to purge dissolved oxygen in the solution, we could exclude oxygen effect as shown in Fig. S9C. No observable change occurred, confirming that direct ANTH electroreduction could be avoided by applying the lower voltage than its reduction potential. In addition, electrolyses of ANTH in 1 M HClO₄-MeCN with various conventional working electrodes (conductors) in N₂ atmosphere for 12 h were investigated (Fig. S9D). The applied voltages are -1.67 V and -2.17 V, which are lower and higher than the 1st reduction potential of ANTH (Eccoli/2 = -2.02 V), respectively. In all cases, ANTH was not consumed, indicating that electrochemical conversion of ANTH to AQ uniquely occurs at defective 200 nm n⁺-Si/SiO₂ dielectric electrode without dissolved oxygen. Note that the ANTH was not electrochemically consumed at -2.17 V applied, probably due to vigorous hydrogen evolution in highly acidic solution. The electrolysis in N₂ atmosphere with n⁺-Si, the substrate of thermal oxide, as working electrode was performed with -1.67 V for approximately 3 days, the same voltage and time as described for the electrolysis with n⁺-Si/SiO₂ in the manuscript. The i-t curves (Fig. S9E) were obtained for comparison. The native oxide was fully etched by dipping in HF for 1 h prior to the electrolysis. ANTH does not react in such electrochemical condition (Fig. S9F).
2.2. Crossover and stability of ANTH.

![Graph A](image)

**Fig. S10.** The summary of control experiments regarding the homogenous change of the solution. (A) Crossover check of ANTH in H-type divided cell with Naftion® membrane for 64 h. Stability check of ANTH in 1 M HClO₄-MeCN solution by observing (B) the peak of ANTH (λ_max=357 nm) and (C) the peak of AQ (λ_max=272 nm) upon time from UV-VIS measurement.

Since it is well-known that organics penetrates Naftion®, the extent of crossover must be examined (Fig. S10A). According to the UV-VIS spectra, the crossed amount of ANTH from WE to CE was estimated to be 0.6%. This is a negligible amount for the calculation of ANTH consumption. Note that the crossover was minimized in our system by shortening the inner diameter of the O-rings for Naftion®, described in Fig. S1. If the O-rings were larger, the cross-section of Naftion® should be large and thereby cannot neglect the crossover.

It is well-known that ANTH and its derivatives undergo photooxidation to AQ (9). We must check the extent of photooxidation. First of all, ANTH is stable in dark (brown vial). UV-VIS measurements tell that ANTH oxidation is negligible at least 5 days in stray-light. Because the electrolysis in H-type divided cell is inconvenient for dark experiment, the electrolysis period was limited to 3-5 days in this study. Note that periodic on/off of the UV-VIS spectrometer can cause the baseline variation, consequently contributing to the noise of absorbance at 357 nm (Fig. S10B). The photooxidation readily occurs when the lamps are irradiated to the solution. In addition, photooxidation of the ANTH derivatives (Table 2) should be AQ irrespective of their functional group at 9, 10- substituent (9). Therefore, the cathodic electroorganic reaction is not the result of photooxidation.
3. Structural and Electrochemical Analyses.

3.1. Structural and electrochemical information of the starting compounds.

**Anthracene (1a):** Purchased from Sigma Aldrich (≥99.0% GC) and used as received. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.42 (s, 2H), 7.98 (dd, $J$ = 6.6, 3.0 Hz, 4H), 7.45 (dd, $J$ = 6.6, 3.0 Hz, 4H). LC-MS (APCI): calcd. for C$_{14}$H$_{11}$ [M+H]$^+$ 179; found 178.1 as C$_{14}$H$_{10}$ [M]. Sometimes observed [2M] calcd. as C$_{28}$H$_{20}$ 356; found 356.4.

Cyclic voltammogram of 1a was measured from N$_2$-purged 5 mM 1a + 0.1 M TBAP in MeCN on glassy carbon electrode with scan rate of 100 mV/s.

![Cyclic voltammogram of Anthracene (1a)](image)

**2-Methylanthracene (1b):** Purchased from Sigma Aldrich (97%) and used as received. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.37 (s, 1H), 8.30 (s, 1H), 7.96 (dd, $J$ = 4.8, 4.5 Hz, 2H), 7.90 (d, $J$ = 8.7 Hz, 1H), 7.74 (s, 1H), 7.43 (m, 2H), 7.28 (d, $J$ = 8.4 Hz, 1H), 2.54 (s, 3H). LC-MS (APCI): calcd. for C$_{15}$H$_{13}$ [M+H]$^+$ 193; found 192.1 as C$_{15}$H$_{12}$ [M].

Cyclic voltammogram of 1b was measured from N$_2$-purged 5 mM 1b + 0.1 M TBAP in MeCN on glassy carbon electrode with scan rate of 100 mV/s.

![Cyclic voltammogram of 2-Methylanthracene (1b)](image)

**9-Methylanthracene (1c):** Purchased from Sigma Aldrich (98%) and used as received. $^1$H-NMR
(300 MHz, CDCl$_3$): $\delta$ 8.33 (s, 1H), 8.28 (ddd, $J$ = 8.1, 2.4, 0.9 Hz, 2H), 7.99 (dd, $J$ = 8.1, 0.6 Hz, 2H), 7.47 (m, 4H), 3.09 (d, $J$ = 0.6 Hz, 3H). LC-MS (APCI): calcd. for C$_{15}$H$_{13}$ [M+H]$^+$ 193; found 192.1 as C$_{15}$H$_{12}$ [M].

Cyclic voltammogram of 1c was measured from N$_2$-purged 5 mM 1c + 0.1 M TBAP in MeCN on glassy carbon electrode with scan rate of 100 mV/s.

9-Anthracenecarboxylic acid (1d): Purchased from Sigma Aldrich (99%) and used as received. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.59 (s, 1H), 8.32 (d, $J$ = 8.7 Hz, 2H), 8.05 (d, $J$ = 8.4 Hz, 2H), 7.60 (m, 2H), 7.52 (m, 2H). $^1$H from the carboxylic acid not found. LC-MS (APCI): calcd. for C$_{15}$H$_{11}$O$_2$ [M+H]$^+$ 223; found 223.1.

Cyclic voltammogram of 1d was measured from N$_2$-purged 5 mM 1d + 0.1 M TBAP in MeCN on glassy carbon electrode with scan rate of 100 mV/s.

Phenantherene (3a): Purchased from Sigma Aldrich (≥98.0%) and used as received. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.70 (dd, $J$ = 7.8, 0.9 Hz, 2H), 7.91 (dd, $J$ = 7.5, 1.8 Hz, 2H), 7.75 (s, 2H), 7.63 (m, 4H). LC-MS (APCI): calcd. C$_{14}$H$_{11}$ [M+H]$^+$; not found.

Cyclic voltammogram of 3a was measured from N$_2$-purged 5 mM 3a + 0.1 M TBAP in MeCN on glassy carbon electrode with scan rate of 100 mV/s.
Pyrene (4a): Purchased from Sigma Aldrich (98%) and used as received. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.18 (dd, $J = 7.5, 1.5$ Hz, 4H), 8.07 (d, $J = 1.8$ Hz, 4H), 8.01 (td, $J = 8.1, 0.9$ Hz, 2H). LC-MS (APCI): calcd. for C$_{16}$H$_{11}$ [M+H]$^+$ 203; found 203.2.

Cyclic voltammogram of 4a was measured from N$_2$-purged 5 mM 4a + 0.1 M TBAP in MeCN on glassy carbon electrode with scan rate of 100 mV/s.
3.2. Structural information of the internal standard.

Biphenyl (BP): Purchased from Sigma Aldrich (99.5%) and used as received. $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.62 (ddd, $J$ = 8.1, 2.4, 1.2 Hz, 4H), 7.46 (ddd, $J$ = 8.1, 7.2, 1.5 Hz, 4H), 7.36 (m, 4H). LC-MS (APCI): not ionized, calcd. C$_{12}$H$_{11}$ [M+H]$^+$ 155.2; not found.
3.3. Structural information of the products and standard compounds comparison.

**Anthraquinone (2a):** Purchased from Sigma Aldrich (97%) and used as received to compare the product mixture as standard. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.30 (dd, $J = 5.7$, $3.3$ Hz, 4H), 7.79 (dd, $J = 5.7$, $3.3$ Hz, 4H). LC-MS (APCI): calcd. for C$_{14}$H$_9$O$_2$ [M+H]$^+$ 209; found 209.1.

**2-Methylanthraquinone (2b):** Purchased from TCI (99%) and used as received. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.28 (m, 2H), 8.18 (d, $J = 8.1$ Hz, 1H), 7.76 (m, 2H), 7.57 (dd, $J = 7.8$, 0.9 Hz, 1H). LC-MS (APCI): calcd. for C$_{15}$H$_{11}$O$_2$ [M+H]$^+$ 223; found 223.1.

**9-Anthracenecarboxaldehyde (2c):** Purchased from Sigma Aldrich (97%) and used as received. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 11.49 (s, 1H), 8.95 (d, $J = 9.0$ Hz, 2H), 8.64 (s, 1H), 8.02 (d, $J = 8.4$ Hz, 2H), 7.66 (ddd, $J = 8.7$, 6.6, 1.2 Hz, 2H), 7.52 (m, 2H). LC-MS (APCI): calcd. for C$_{15}$H$_{11}$O [M+H]$^+$ 207; found 207.1.

**9,10-Anthracenediol:** Purchased from Ark Pharm. Inc. (98%) and used as received to compare the 2a. $^1$H-NMR (300 MHz, CDCl$_3$): $\delta$ 8.31 (dd, $J = 5.7$, $3.3$ Hz, 4H), 7.79 (dd, $J = 5.7$, $3.3$ Hz, 4H). LC-MS (APCI): calcd. for C$_{14}$H$_9$O$_2$ [M+H]$^+$ 211; found 209.1, matched to C$_{14}$H$_9$O$_2$.

As mentioned in the manuscript, 9,10-anthracenediol is found to be identical to anthraquinone (AQ, 2a) in both $^1$H-NMR and LC-MS spectra.
4. \(^1\)H-NMR and LC-MS spectra for reaction mixtures and standard compounds.

Product mixture of anthraquinone (AQ, 2a) after the electroorganic reaction of anthracene (ANTH, 1a) for days on defective 200 nm n^-Si/SiO\(_2\). Large peaks of 2a observed together with 1a. Chemical shifts under 6 ppm seem to be impurities. LC-MS also attached.
Product mixture of anthraquinone (AQ, 2a) after the reaction of anthracene (ANTH, 1a) for 12 h. Slight peaks of 2a observed. Chemical shifts under 6 ppm seem to be impurities.
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| Time (min) | 0.1% Formic Acid in DI water | 0.1% Formic Acid in MeCN |
|------------|-------------------------------|--------------------------|
| 0.0        | 50                            | 50                       |
| 10.0       | 0                             | 100                      |
| 12.0       | 0                             | 100                      |
| 12.1       | 50                            | 50                       |
| 15.0       | 50                            | 50                       |

Product mixture of 2-methylanthraquinone (2-Me-AQ) after the reaction of 2-methylanthracene (2-Me-ANTH, 1b) for days. LC-MS attached.
Product mixture of 9-anthracenecarboxaldehyde (9-CHO-ANTH, 2c) after the reaction of 9-methylanthracene (9-Me-ANTH, 1c) for days. LC-MS attached.
Product mixture of anthraquinone (AQ, 2a) after the reaction of 9-anthracenecarboxylic acid (9-COOH-ANTH, 1d) for days. LC-MS attached.
The almost no consumption with no identifiable products after the reaction of phenanthrene (Phen, 3a) for days. LC attached.
No identifiable products after the reaction of pyrene (Py, 4a) for days. LC-MS attached.
Product of 2-methylanthraquinone (2b) from 2-methylanthracene (1b) after oxidation using KMnO₄ oxidant (¹H-NMR and GC-MS).
Intermediate capture of ANTH (1a) reaction on n-\text{-Si/SiO}_2 with TEMPO. LC-MS attached.
Anthracene (1a)
| Time (min) | 0.1% Formic Acid in DI water | 0.1% Formic Acid in MeCN |
|-----------|-------------------------------|--------------------------|
| 0.0       | 95                            | 5                        |
| 5.0       | 0                             | 100                      |
| 12.0      | 0                             | 100                      |
| 12.1      | 95                            | 5                        |
| 15.0      | 95                            | 5                        |
2-Methylanthracene (1b)
9-Methylnanthracene (1c)
9-Anthracene carboxylic acid (1d)
Phenanthrene (3a)
| Time (min) | 0.1% Formic Acid in DI water | 0.1% Formic Acid in MeCN |
|-----------|-------------------------------|--------------------------|
| 0.0       | 50                            | 50                       |
| 10.0      | 0                             | 100                      |
| 12.0      | 0                             | 100                      |
| 12.1      | 50                            | 50                       |
| 15.0      | 50                            | 50                       |

Mass Peak: Positive Mode, Not Detected
Pyrene (4a)
| Time (min) | 0.1% Formic Acid in DI water | 0.1% Formic Acid in MeCN |
|-----------|------------------------------|-------------------------|
| 0.0       | 50                           | 50                      |
| 10.0      | 0                            | 100                     |
| 12.0      | 0                            | 100                     |
| 12.1      | 50                           | 50                      |
| 15.0      | 50                           | 50                      |

**Mass Peak: Positive Mode**
Biphenyl (internal standard)
Anthraquinone (2a)
| Time (min) | 0.1% Formic Acid in DI water | 0.1% Formic Acid in MeCN |
|-----------|----------------------------|-------------------------|
| 0.0       | 95                         | 5                       |
| 5.0       | 0                          | 100                     |
| 12.0      | 0                          | 100                     |
| 12.1      | 95                         | 5                       |
| 15.0      | 95                         | 5                       |

Mass Peak: Positive Mode
9,10-Anthracenediol

Note that both the $^1$H-NMR and LC-MS are identical to anthraquinone (AQ, 2a). It is readily oxidized to 2a.
| Time (min) | 0.1% Formic Acid in DI water | 0.1% Formic Acid in MeCN |
|-----------|------------------------------|--------------------------|
| 0.0       | 95                           | 5                        |
| 10.0      | 0                            | 100                      |
| 12.0      | 0                            | 100                      |
| 12.1      | 95                           | 5                        |
| 15.0      | 95                           | 5                        |
2-Methylantraquinone (2b)
9-Anthracenecarboxaldehyde (2c)
$^1$H-NMR of the blank CDCl$_3$ solvent was measured. The impure CHCl$_3$ and water peaks are observed.
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