

MERIT Collaborating Work Report

Application of Triptycenenomohydroquinonedibenzoquinone to a Monolayer Film

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Abstract

Triptycenenomohydroquinonebenzoquinone, in which three benzene rings in triptycene are replaced by two benzoquinone and one hydroquinone, has a unique unsymmetric structure composed of different oxidation states. In this work, we investigated the alignment of the molecule in a monolayer film on the surface of the electrode for the biosensing application. We conducted electrochemical measurements of the electrode that possessed the molecules on the surface and revealed the formation of the film in good alignment.

Authors

Yuta Takemasa is engaging in the research field of physical organic chemistry. In this study, Y. Takemasa is responsible for the synthesis of target molecules.

Shogo Himori is engaging in the development of electrochemical sensors. In this study, S. Himori is responsible for the electrochemical measurement.

1. Introduction

1,4-Benzoquinones (BQs) represent a class of compounds that plays important roles in biological processes. BQs undergo two successive reduction steps to form hydroquinones (HQs) via semiquinones (SQs). Recently, intensive efforts have been devoted to the introduction of multiple BQ moieties into a 3D molecular structure. Triptycenetribenzoquinone, (BQ)₃, is an example of such a 3D multi-BQ molecule in which the three benzene rings of triptycene are replaced by benzoquinone rings.¹ (BQ)₃ can accept 6 electrons to form (HQ)₃.^{2,3} Recently, we developed the synthesis of triptycenenomohydroquinonedibenzoquinone, (HQ)₁(BQ)₂ (Figure 1), in which one HQ unit and two BQ units coexist in triptycene framework.⁴ (HQ)₁(BQ)₂ has a unique polar structure composed of the units having different oxidation states. (HQ)₁(BQ)₂ molecules aligned in the same direction and formed a layer in the crystal. Therefore, the negative polarity is canceled between the layers. In this work, we investigated the anisotropic molecular alignment of (HQ)₁(BQ)₂ utilizing a modification method on the interface of electrode⁵ for application to the biosensing materials.

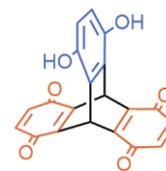


Figure 1. (HQ)₁(BQ)₂

2. Concept for this work

The $(\text{HQ})_1(\text{BQ})_2$ molecule is aligned on the surface which has strong interaction with BQ moiety having δ^- . It causes HQ moiety to be selectively exposed to the surface of a monolayer. We expect that such a layer will have a dielectric effect on the electrode and work as a proton transfer membrane.

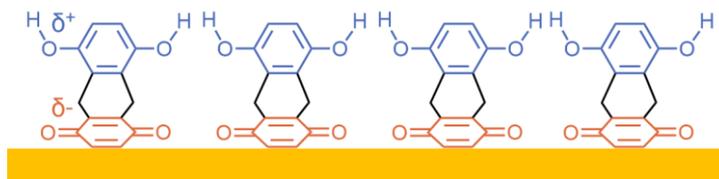


Figure 2. Schematic illustration of our concept

3. Results and Discussion

3.1. Synthesis

Based on the method developed by the author (Takemasa), $(\text{HQ})_1(\text{BQ})_2$ was synthesized by comproportionation of $(\text{HQ})_3$ and $(\text{BQ})_3$ in dimethylsulfoxide (DMSO) and isolated by the recrystallization from dioxane and hexane after via slow evaporation.

3.2. Consideration of membrane formation

We tried the spin coat method and immersion method for the formation of the membrane of $(\text{HQ})_1(\text{BQ})_2$ on the Au electrode surface. We conducted cyclic voltammetry (CV) on the electrode modified with each method (Reference: Ag/AgCl, Counter: Pt, Reference Solution: $1 \times \text{PBS}$).

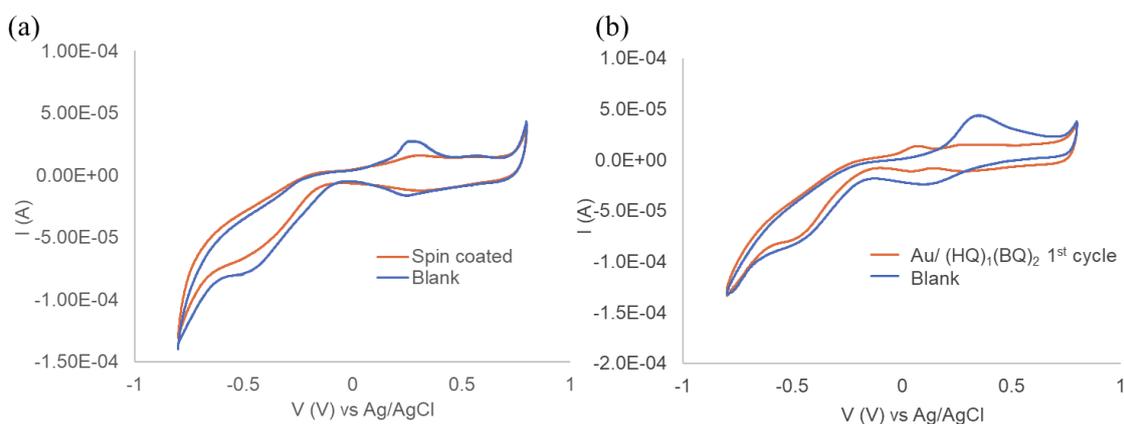


Figure 3. Cyclic voltammogram of the Au electrode modified with (a) spin coat method and (b)immersion method

Modification of (HQ)₁(BQ)₂ by the spin coat method was not observed. We concluded an immersion method could be effective. However, judging from the fact that the redox peak was shifted during CV measurement (Figure 4) and the peak intensity itself was weak, the interaction between (HQ)₁(BQ)₂ molecule and Au surface was not strong enough for our purpose.

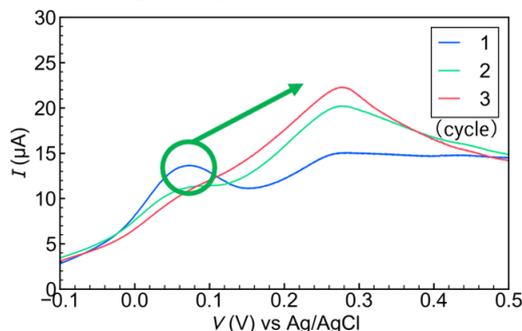


Figure 4. Cyclic voltammogram of the Au electrode modified with the immersion method

The weak interaction is because normal aromatic hydrocarbons interact with the Au surface on π-surface of the substance while triptycene's structure cannot be absorbed via such interaction on the flat surface of the electrode due to the rigid 3D structure. We determined to find the optimal electrode interacting with (HQ)₁(BQ)₂ molecule.

3.3. Optimization of electrode

We conducted the immersion method on indium tin oxide (ITO) or glassy carbon electrodes. As for ITO, BQ or HQ moieties in the organic layer have expected to form hydrogen bonding with the hydroxy group on the ITO, and as for the glassy carbon, C-H bonds in the organic film have CH-π interaction with the carbon surface.

While a unique peak change was not observed on the ITO surface corresponding to the absorption of (HQ)₁(BQ)₂ molecule, the glassy carbon electrode showed a unique peak in the cyclic voltammogram (Figure 5).

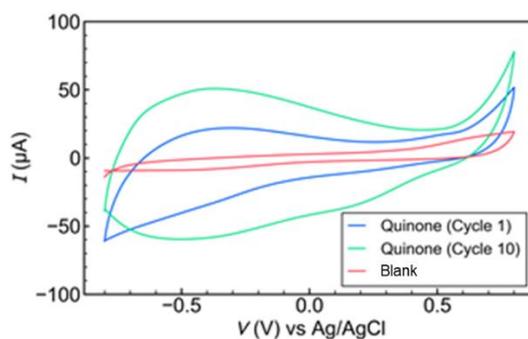


Figure 5. Cyclic voltammogram of modified glassy carbon electrode

Peak intensity was increased during the potential cycles of measurement (Figure 5, blue line vs. green line). This result suggested the molecular orientation was aligned by the applied potential to the layer and increased dielectric character (Figure 6).

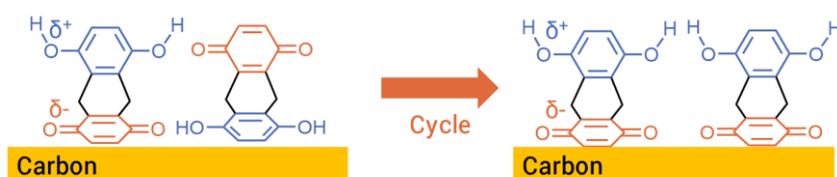


Figure 6. A plausible mechanism of oriented molecules

Although the aligned structure was suggested, the observed redox peak was broad compared to typical organic molecules. We assumed that this is due to the rough surface of the electrode.

Therefore, we conducted the same CV measurement on a single-layer graphene electrode, which has a flat surface (Figure 7).

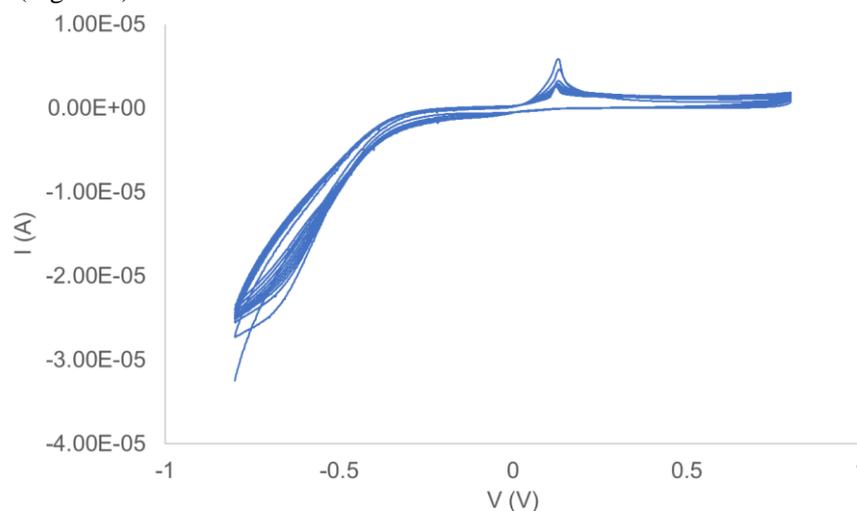


Figure 7. Cyclic voltammogram of single-layer graphene electrode

As a result, the unique peak was not observed corresponding to the absorption of the molecule. We assumed that this is because graphene was exfoliated during the immersion process. We concluded that glassy carbon electrode is the best condition to absorb $(\text{HQ})_1(\text{BQ})_2$ molecule, and a control experiment was conducted.

3.4. Control experiment.

We conducted the same CV measurement using $(\text{BQ})_3$ or $(\text{HQ})_3$ as a different oxidation state in the same triptycene structure and BQ and HQ, which have the same oxidation state but do not have triptycene structure.

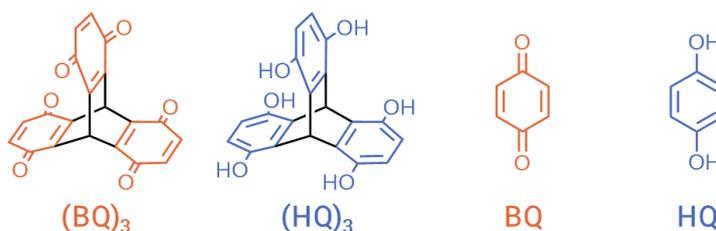


Figure 8. Molecules used in the control experiment

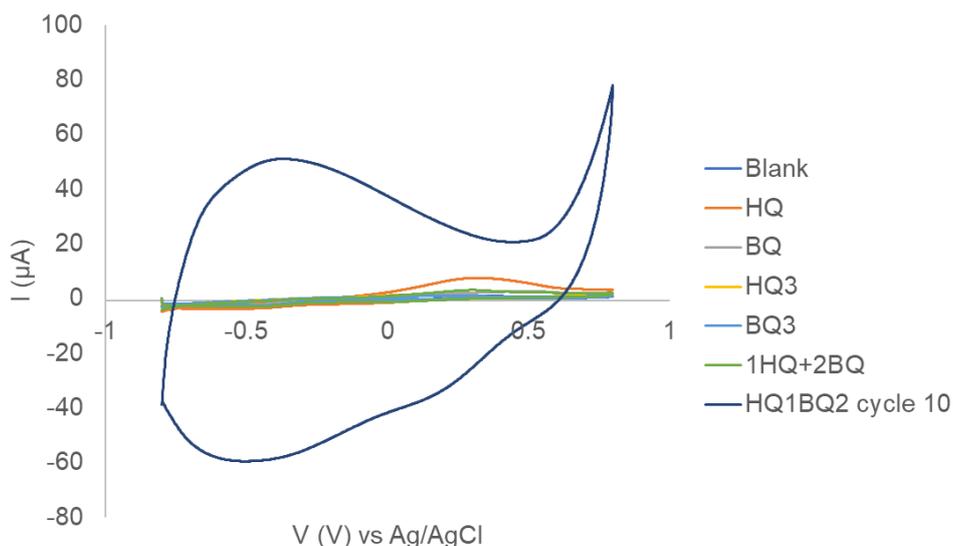


Figure 9. Cyclic voltammograms of control experiments

In both cases of $(\text{BQ})_3$ and $(\text{HQ})_3$ having triptycene-like structures, the unique redox peak in $(\text{HQ})_1(\text{BQ})_2$ was not observed. The results suggest the necessity of the unsymmetric structure of triptycene with the coexistence of BQ and HQ.

To confirm the influence of the triptycene structure, we tried the same measurement on hydroquinone (HQ) (Figure 9, orange), benzoquinone (BQ) (Figure 9, gray), and the mixture of HQ and BQ (Figure 9, green). The unique peak was not also observed.

As a result, the $(\text{HQ})_1(\text{BQ})_2$ structure, where HQ and BQ moieties coexist in a triptycene framework, is necessary to realize the specific redox behavior.

Conclusion and Perspective

In this work, we investigated the redox behavior of the electrode modified by $(\text{HQ})_1(\text{BQ})_2$ having redox units in the triptycene structure by CV measurements. When the molecules were modified on the glassy carbon electrode, the unique redox peak appeared corresponding to absorption. We also observed the controlled alignment on the surface by applying an electric field during CV measurement. We assumed that this is due to the rigid and unsymmetric structure. The results of this cooperative investigation demonstrated the behavior of the non-planar aromatic compound on the surface of electrodes and under an electric field.

We will try to confirm reproducibility and optimize the immersion condition. We will also focus on the detailed surface structure.

Acknowledgements

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