

Electrochemical Doping of Protonated *Meso*-tetrakis(sulfothienyl)porphyrin J-aggregates

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Molecular assembly is one of the key technology to construct nano-structure. Especially for the construction of molecule-based electronic materials, self-assembly of π -radical is considered to be useful as a bottom-up approach. In purpose of developing nano-scale electronic material, we have been examining conductivity of porphyrin J-aggregates, which forms various nano-structures by self-organization. In this study, we synthesized and investigated *meso*-tetrakis(sulfothienyl)porphyrin (TSThP, Fig. 1). When the TSThP was protonated, it formed a metallic film of J-aggregates on the substrate. Although the as-grown TSThP J-aggregate film had insulating character, electrochemically doped TSThP J-aggregate is a good candidate for the self-organized organic conducting nano-wire, which was not reported to date. With this in mind, we investigated electrochemical doping of TSThP J-aggregate.

The TSThP was synthesized by a sulfuric acid sulfonation of *meso*-tetrakis(thienyl)porphyrin (TThP) prepared by typical Adler's method. In this reaction, obtained TSThP was a mixture of several isomers of which sulfonic groups were located at 4- or 5- position at the thienyl groups.

The J-aggregate films were prepared by casting HCl acidic aqueous solutions of the TSThP onto a FTO electrode. By the use of this electrode as a working electrode, the TSThP J-aggregates were electro-reduced or oxidized in 0.1 M LiClO₄/PhCN at the voltage of -2.4 V and 2.4 V, respectively. Their absorption spectral changes during the electrolysis were measured in situ. The absorption spectral changes during reduction are shown in Fig. 2. After the reduction small peaks at 530 nm and 610 nm were observed with another broad peak at longer than 1000 nm, which were attributed to the absorption of radical anions. At the same time, Soret band (490 nm) and Q band (702 nm) decreased and blue-shifted because of the formation of radical anions which shortened the coherent length of exciton in the J-aggregates. After returning voltage to 0 V the absorption of radical anion disappeared and a large part of absorption of J-aggregate recovered. The reversible change indicates that the J-aggregate forms radical anion with keeping its structure under the electrolysis condition. The redox process of the J-aggregate was also investigated in the oxidation (Fig. 3), however it was not reversible. This indicates a radical cation is not so stable compared with its radical anion.

In conclusion, TSThP formed J-aggregate with π -radical. This is an important result for making electronic materials with self-assembled organic molecules. In the presentation, we will also report the results for *meso*-tetrakis(sulfophenyl)porphyrin (TSPP).

Acknowledgments

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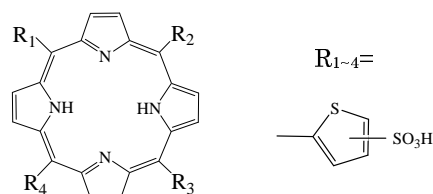


Fig. 1. Structure of *meso*-tetrakis(sulfothienyl)porphyrin (TSThP).

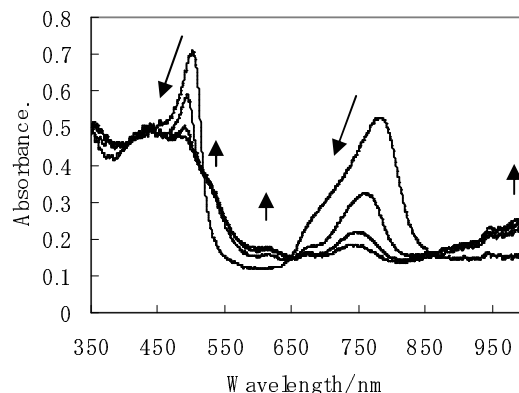


Fig.2. Time course of absorption spectral changes of protonated TSThP J-aggregate during electro-reduction.

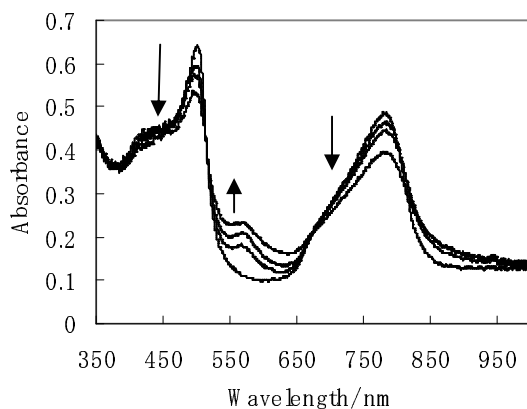


Fig.3. Time course of absorption spectral changes of protonated TSThP J-aggregate during electro-oxidation.