水溶性官能基を有するフェニレンジアミン類の酸化還元特性

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Redox Properties of Phenylendiamines Having Water-soluble Functional Groups (¹Graduate School of Engineering and Science, Shibaura Institute of Technology, ² College of Engineering, Shibaura Institute of Technology) OKaori Miyakoshi, ¹ Toshiki Tajima^{1, 2}

Quinones have been widely studied as organic redox active materials, but they have a serious problem of the limited solubility in water. On the other hand, quinonediimines, in which two carbonyl groups of quinones are replaced by imines, can introduce a functional group on the nitrogen of imines and have a reversible two-electron redox activity as well. The objective of this study was to introduce water-soluble functional groups into phenylenediamines and to evaluate phenylendiamine/quinonediimine redox properties in water.

2,3,5,6-Tetramethyl-1,4-phenylenediamine (**1**) and 1,3-propanesultone (**2**) were reacted in ethanol under argon atmosphere to introduce water-soluble functional groups. Electrochemical measurements of the products in water showed that the reversibility was not lost even after 300 potential sweeps. It was suggested that the steric hindrance of the water-soluble functional groups suppressed the nucleophilic attack of water.

Keywords: Organic Redox Active Materials, Quinone, Phenylendiamine

キノン類は有機活物質として広く研究されているが、水への低い溶解性が課題である¹⁾。一方、キノン類の2つのカルボニル基をイミンに置き換えたキノンジイミン類は、イミンの窒素上に官能基を導入可能であり、キノン類と同様に2電子の可逆的な酸化還元活性を有する。本研究では、フェニレンジアミン類に水溶性官能基を導入し、水中でのフェニレンジアミン/キノンジイミン類の酸化還元特性の評価を目的とした。

2,3,5,6-Tetramethyl-1,4-phenylenediamine ($\mathbf{1}$)と 1,3-propanesultone ($\mathbf{2}$)をエタノール溶媒中、アルゴン雰囲気下で反応させ、水溶性官能基を導入した。生成物の電気化学測定を水系で行ったところ、 $\mathbf{300}$ 回電位掃引を行っても可逆性が失われなかった。また、水溶性官能基の立体障害によって水の求核攻撃が抑制されたことが示唆された。

$$H_2N$$
 NH_2 + O
 O
 O
 $EtOH$
 HO_3S
 HN
 NH
 SO_3H

1) C. Friebe, A. Lex-Balducci, U. S. Schubert, ChemSusChem, 2019, 12, 4093-4115.