Synthesis of quinones having crown ether moiety and electrochemical capturing of carbon dioxide.

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Introduction. One of the technologies for CO_2 capture, utilization, and storage (CCUS) is an electrolytic reaction that enable reversibly capture and release CO_2 at normal temperature and pressure. Quinones are known to form reversible adducts with CO_2 through electrolytic reactions[1]. We aim at efficient formation of CO_2 adducts in cooperation with alkaline earth metals that make bonds with the oxygen atoms of CO_2 with quinone molecules. In this study, a quinone (Q-15-C-5) having crown ether moiety capable of trapping an alkaline earth metal ion was synthesized and its reactivity with CO_2 was evaluated from electrochemical measurements.

Synthesis. Q-15-C-5 was synthesized as shown in Figure 1. Aza-15-crown 5-ether and dimethoxyphenyl carboxylic acid were linked by an amide bond[2], and the desired compound was obtained by concurrent demethylation and oxidation with cerium diammonium nitrate[3]. The resulting product was purified by silica gel column chromatography and identified by NMR measurements (^{1}H NMR, ^{13}C NMR, HMQC).

Electrochemistry. Cyclic voltammetry measurements of Q-15-C-5 were performed under N_2 and CO_2, using DMF as solvent and Et_4NClO_4 as supporting electrolyte (Figure 2). Two reduction peaks were observed, suggesting the formation of a semiquinone radical at around -1.1 V and a dianion at around -1.8 V. Two oxidation peaks were also observed, suggesting a reversible change from anion to neutral quinone. On the other hand, only one reduction peak was observed under CO_2, and the current value was increased compared to that under N_2. These results indicate that the second reduction peak is shifted to positive and overlaps with the first reduction peak. This suggests that the second reduction take places at higher potential because of the formation of an adduct between the semiquinone radical and CO_2. The oxidation peak also shifted to positive, which suggests that more positive potential is required to oxidize an adduct than to oxidize anion.

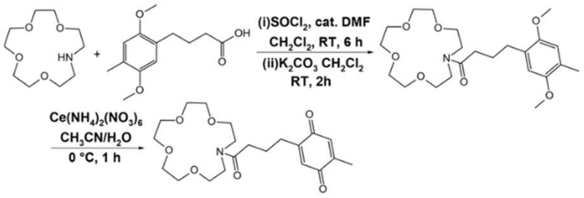

Figure1. Synthetic scheme of Q-15-C-5

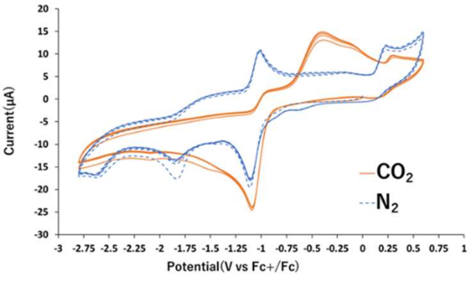

Figure2. Voltammograms of Q-15-C-5

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