Quantification of the redox entropy of the second solvation shell by the guest binding to ruthenium complexes attached with aza-crown ether unit

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Recently, the control of second solvation shell attracts much attention because it plays an important role in catalytic reactions. In this study, we used thermocell as a novel probe to investigate the solvation behavior of the second solvation shell. The thermocell is an emerging class of a thermoelectric conversion device that harvests electricity from the temperature dependence of the redox potential of redox species. The Seebeck coefficient (S_e) is defined as the generated voltage per unit temperature difference, and is proportional to the entropy change of the redox reaction (ΔS_r). In this study, we synthesized a ruthenium complex modified with aza-crown ethers, [Ru(bpy)$_2$(4ba15)](PF$_6$)$_2$ (**1**) (Fig. 1). The redox entropy of the complex with and without including guest K$^+$ ions were evaluated.

1 was synthesized by stepwise reactions of Ru(1,5-cyclooctadiene)Cl$_2$, bpy, and 4,4'-bis(aza-15-crown-5-ether)-2,2'-bipyridine. The compound was identified with ^{1}H NMR, MASS and elemental analysis. The encapsulation of K$^+$ was confirmed by ^{1}H NMR titration. One ruthenium complex binds up to two K$^+$ with 0.2 M KPF$_6$. The S_e of the ruthenium complex in acetonitrile was measured by monitoring the open circuit voltage (OCV) under elevating temperature. The evaluated S_e in TBAPF$_6$ was 0.85 mV K^{-1} (Fig. 2) which is similar to that of [Ru (bpy)$_3$] complex. The S_e with the presence of K$^+$ ion of [Ru$^{II/III}$(bpy)$_2$(4ba15)](PF$_6$)$_2$ increased to ca. 0.90 mV K^{-1}. The improvement of ΔS_r could be derived from the strong solvation of K$^+$ cation in aza-crown ether of **1**.

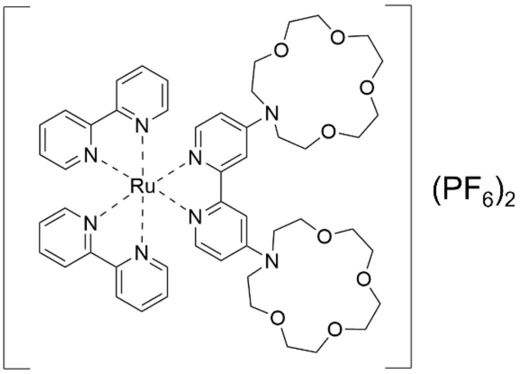

Figure 1. Structure of [Ru(bpy)$_2$(4ba15)](PF$_6$)$_2$.

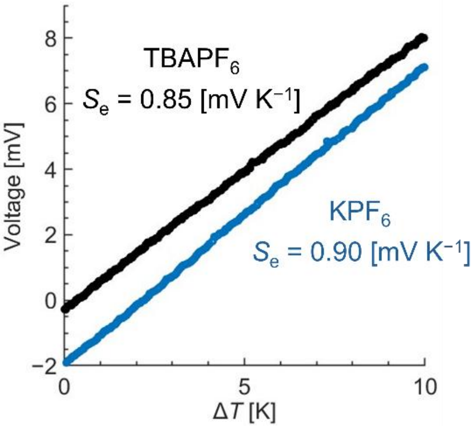

Figure 2. Temperature dependence of the OCV of Ru complex.