COMBINATORIAL APPROACH OF REDOX-ACTIVE Ru/Os COMPLEX UNITS TOWARDS LAYERED MOLECULAR DEVICES

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The layer-by-layer growth by the use of coordination bond is one of the promising synthetic strategies for the construction of well-defined nanostructure on the surface. Redox-active rod-shaped metal complexes bridged by bis tridentate ligands are stereochemically defined, and therefore these complexes are one of potential candidates for molecular devices such as molecular wires or sensors. A series of Ru/Os complexes containing free-standing phosphonate ligand (LP) and metal bridging bis-tridentate ligand (BL) have been synthesized as a building module (Fig. 1). AFM measurement for the self-assembled monolayer of dinuclear Ru/Os complexes, [M(XP)(BL)M(XP)](M = Ru or Os) on an flat ITO electrode revealed clear molecular domain images with constant molecular height, depending on the length of BL (Fig. 2). Electrochemistry of self-assembled monolayer [M(XP)(BL)M(XP)] on an ITO electrode showed a one-step two-electron process at +0.93 V for M = Ru and +0.66 V for M = Os, respectively. The surface coveragea are in the range of 5.3 x 10^{-11} ~ 5.7 x 10^{-11} M. Layer-by-layer growth was achieved by the successive immersion of [M(XP)(BL)M(XP)] solution in CH_3CN/MeOH with Zr(IV) or Cu(II) aqueous solution. The current increases with increasing the number of layers until 6 layers. Above 6 layers, the current gradually reach the saturation. Electron mediation through the bridging ligands and hopping between layers are responsible for this saturation. Multilayer process was also monitored by quartz crystal microbalance method using the ITO coated quartz crystals. In order to check the pinhole or defect in the films, the blocking for the oxidation of $K_4[Fe(CN)_6]$ was measured. Above two layers films not only the complete blocking but also the catalytic wave were observed, as shown in Fig. 3. Photochemical response and molecular rectifying effect will be also discussed for the multilayer Ru/Os films.

[Ref] M. Haga, T. Takasugi, A. Tomie, M. Ishizuya, M. Ishizuya, T. Yamada, M. D. Hossain, and M. Inoue, *Dalton Trans*., 2069(2003)

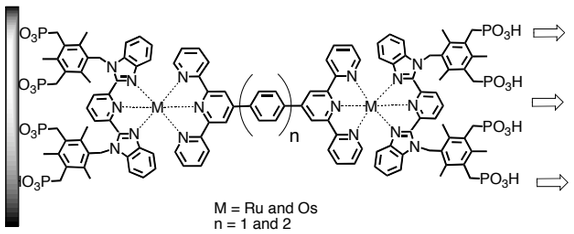

Fig. 1. Structure of [M(XP)(BL)M(XP)]

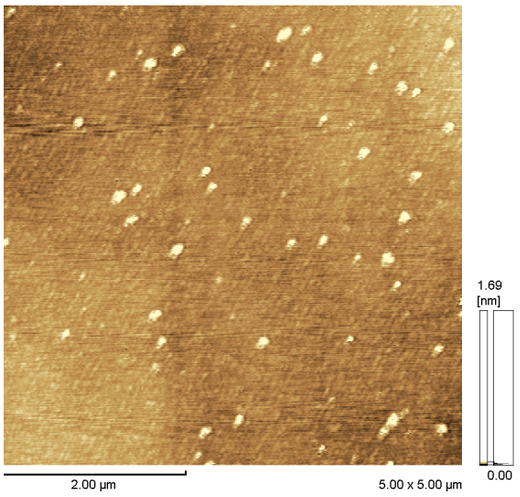

Fig. 2. AFM image of monolayered [Ru(XP)(BL)Ru(XP)] on flat ITO electrode

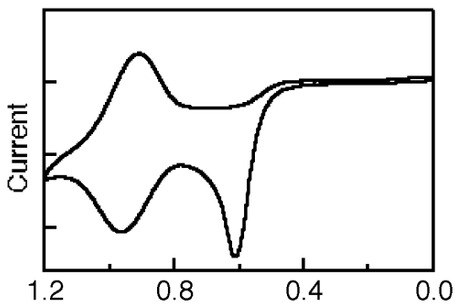

Fig.3. Cyclic voltammogram of two layered [Ru(XP)(BL)Ru(XP)] films on ITO electrode (n = 1 in BL) in $K_4[Fe(CN)_6]$ solution