Electronic supplementary information for

"Effects of Fe Cations in Ruthenium-Complex Multilayers Fabricated by the Layer-by-Layer Method"

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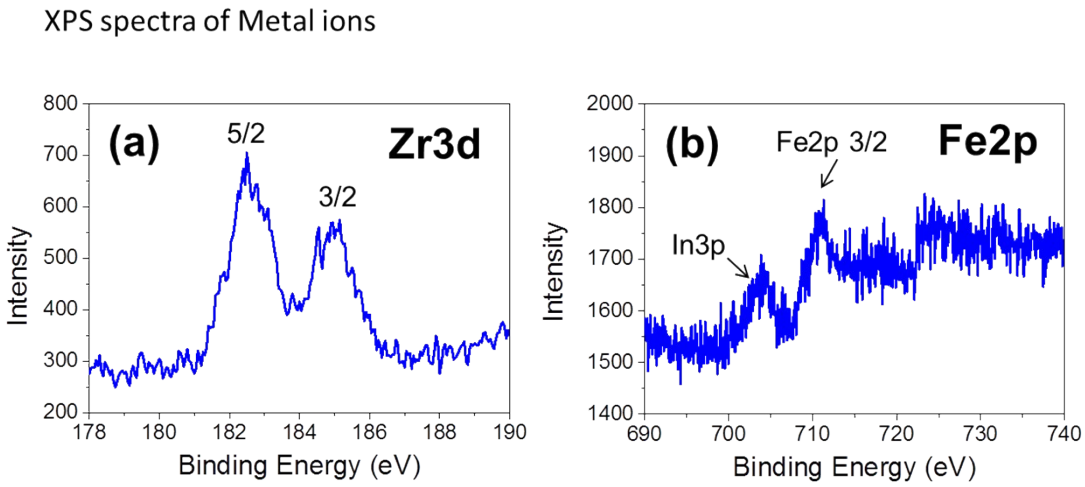

Figure S1 XPS spectra of third layers of films containing (a) Zr and (b) Fe cations.

Table S1 XPS peak positions of metal cation species in third layers of Ru-complex films.

Cation	Binding Energy (eV)	Assigned Species
Zr (3d)	182.6	Zr(IV)
Fe (2p)	710.9	Fe (III)

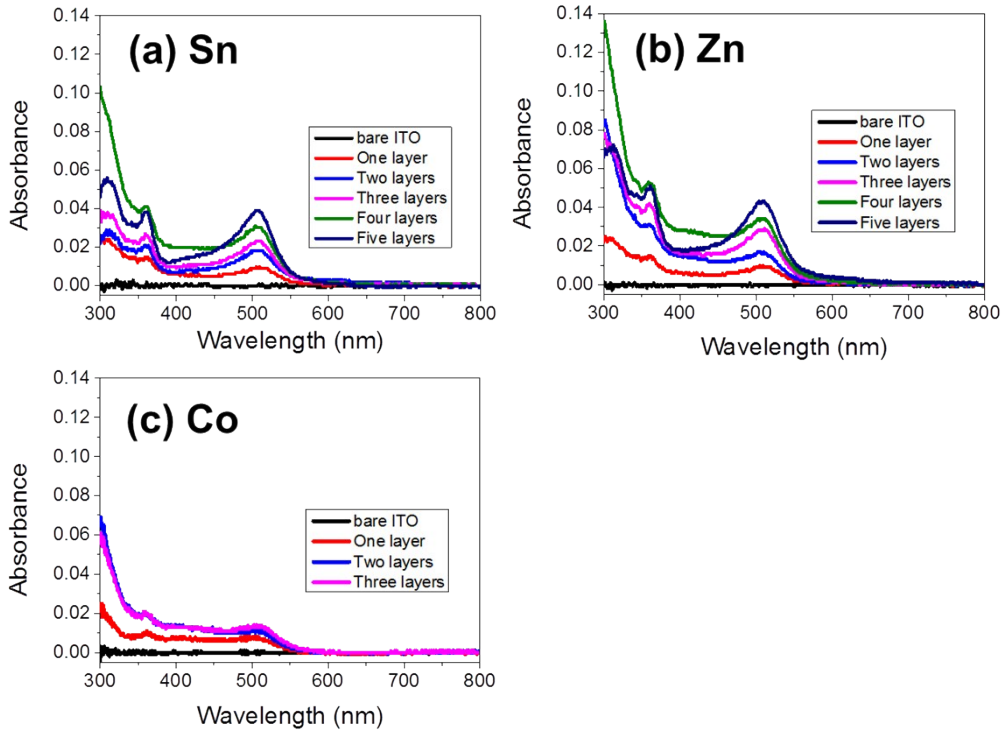

Figure S2 UV-vis spectra of Ru-complex multilayer films containing (a) Sn, (b) Zn, and (c) Co cations.

Table S2 Thicknesses of Ru-complex multilayers with various metal ions using XPS data.

Molecular layer thickness (nm)	1	2	3	4	5
Sn cations	-	5.1	7.8	9.1	11.0
Zn cations	-	4.1	6.4	7.2	9.6

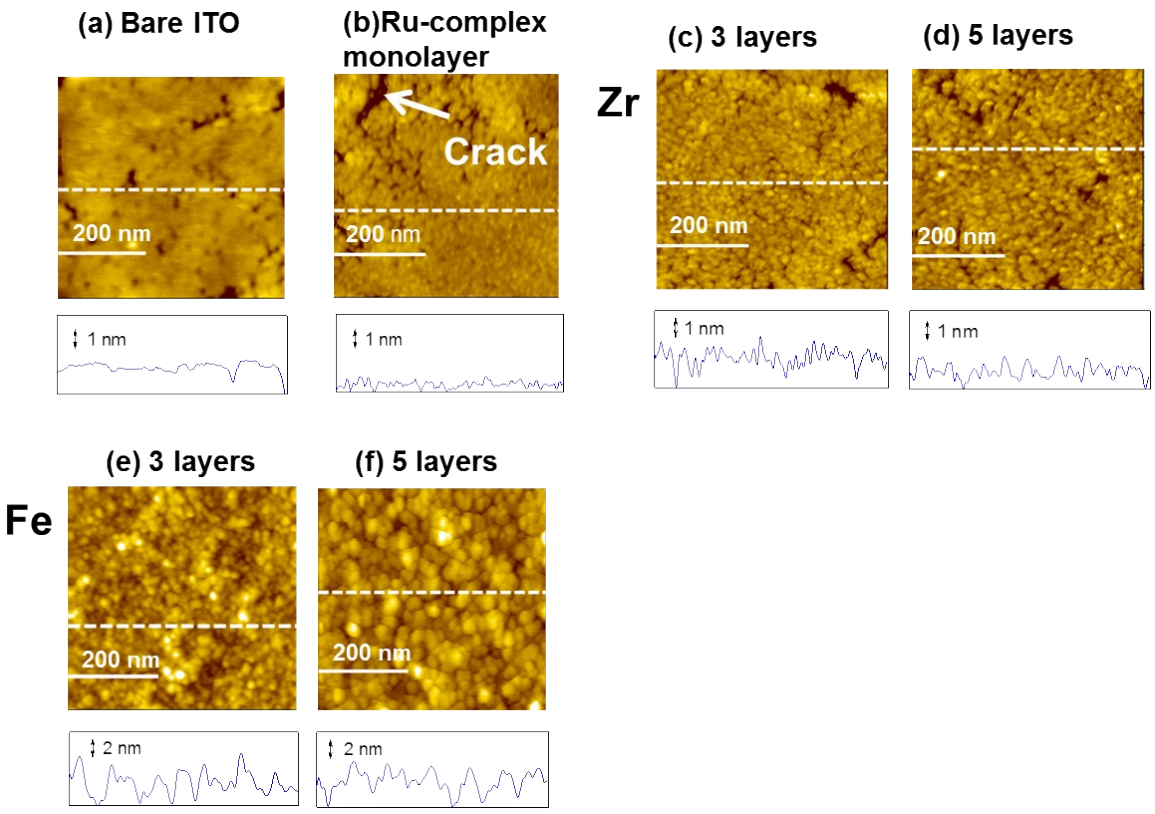

Figure S3 AFM images of Ru-complex multilayers containing metal cations on ITO surfaces. (a) Bare ITO surface before immobilizing Ru complex, (b) Ru-complex monolayer, (c) third layer with Zr cations, (d) fifth layer containing Zr cations, (e) third layer with Fe cations, and (f) fifth layer containing Fe cations. Height profiles are shown beneath AFM images.

Estimation of least thicknesses of multilayers.

The AFM height profiles of the multilayers (Fig. S3) indicate the maximum variances of the film thicknesses, which were estimated to be approximately 3 nm for multilayers containing Fe cations with increased roughness. The average film thickness estimated by XPS corresponds to the half-height of the vertical axis of the height

profiles of the AFM images. The roughness effect was determined based on the height variance to avoid overestimating β. We previously[17] evaluated β using this method, in which the electron current pathway is determined by the shortest through-bond path.[12] The least thicknesses of the multilayers (Table S3) were estimated using the lowest positions, corresponding to 0 in the height profiles. These estimates provided upper bounds on β.

Table S3 R_{ms} values and least thicknesses of Ru-complex multilayers with various metal ions.

Molecular layers	R_{ms} (nm)	Least thickness (nm)
Bare ITO	0.21	-
Ru-complex monolayer	0.44	2.70
Zr cations		
Two layers	0.47	5.10
Three layers	0.58	7.23
Four layers	0.37	8.65
Five layers	0.42	10.7
Fe cations		
Two layers	0.94	3.93
Three layers	1.56	6.92
Four layers	1.34	8.27
Five layers	1.26	11.24

Table S4 Estimated β values taken into account the surface roughness with various potentials

Molecular layer	Potential (V)	β values ($Å^{-1}$)		
		Lower bounds	Medians	Upper bounds
Zr cations	+ 0.1	0.061	0.066	0.071
	- 0.1	0.058	0.063	0.067
	+ 0.2	0.059	0.064	0.069
	- 0.2	0.059	0.064	0.069
	+ 0.3	0.056	0.061	0.065
	- 0.3	0.059	0.064	0.069
	+ 0.5	0.051	0.056	0.060
	- 0.5	0.056	0.060	0.064
Fe cations	+ 0.1	0.011	0.013	0.016
	- 0.1	0.008	0.009	0.011
	+ 0.2	0.010	0.012	0.015
	- 0.2	0.009	0.010	0.012
	+ 0.3	0.009	0.011	0.013
	- 0.3	0.009	0.011	0.013
	+ 0.5	0.008	0.010	0.011
	- 0.5	0.010	0.011	0.013

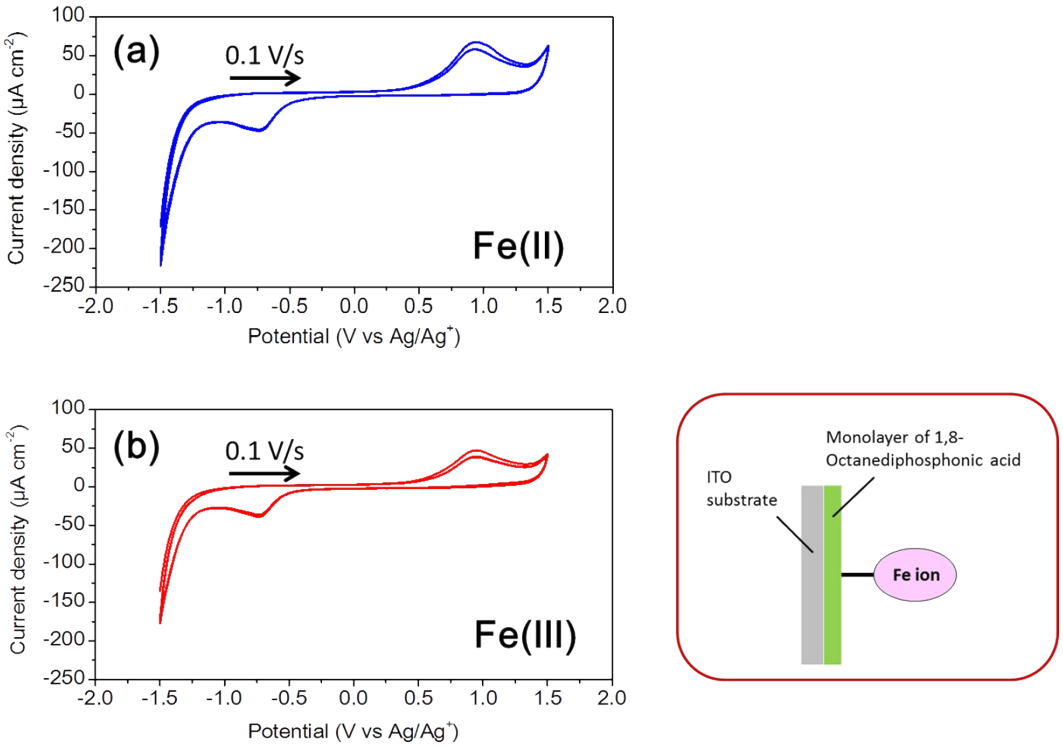

Figure S4 CVs of (a) octane phosphonic acid monolayer with no cations and monolayers with (b) and (b) Fe(III) cations. In the both CV data, Fe (II/III) oxidation peaks at around +1.0V are observable.