

Supporting Information

In Situ Switching Layer-by-Layer Assembly: One-Pot Rapid Layer Assembly via Alternation of Reductive and Oxidative Electropolymerizations

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1. Materials

TBAPF₆ (tetrabutylammonium hexafluorophosphate), indium tin oxide (ITO) (8-12 Ω/□), dichlorobenzene and acetonitrile were purchased from Aldrich Chemical Co. DvRu complex and CsF were synthesized as described in our previous papers.^{S1}

2. General techniques

Electronic absorption spectra were measured using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer. AFM images were obtained with a commercial AFM unit (SPA400-SPI4000, Seiko Instruments Inc., Chiba, Japan). AFM images were taken in dynamic force mode (DFM, i.e., tapping mode) at optimal force. Fluorescence measurements are carried out with RF-5301PC. The switching photocurrent-time (I-t) characteristics were measured using a two-point probe method in air using an Advantest picoammeter (R8340A) and dc voltage source (R6144). A 500W Ushio xenon lamp and an Acton Research monochromator with order sorting filters were used to obtain the monochromator light (0.5 mW/cm² at 360 nm and 1.0 mW/cm² at 450 nm).

3. Electrochemical experiments

For electrochemical experiments, the supporting electrolyte TBAPF₆ (tetrabutylammonium hexafluorophosphate) was dried for 24 h at 80 °C under vacuum before use. Cyclic voltammetry (CV) experiments were performed using a typical one-compartment, three-electrode electrochemical cell driven by a CHI Model

630B electrochemical analyzer. In all cases, Ag/0.01M AgNO₃ ($E_{1/2} = 0.26$ V vs Fc/Fc⁺) was used as reference. Indium tin oxide (ITO) (8-12 Ω/□, Aldrich) (deposition area: ~ 1.0 cm²) was used as working electrode; the counter electrode was a gold foil (area: ~ 2.0 cm²). After electrochemical processes, the resulting films were rinsed with CH₂Cl₂ to remove any unreacted precursors.

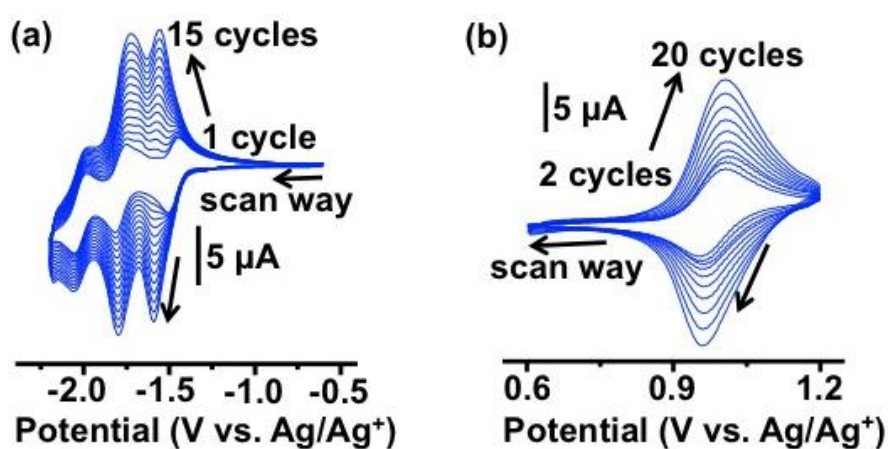


Figure S1. Reductive electropolymerization of DvRu at cathodic scan and its CV of poly[Csf] film at anodic scan.

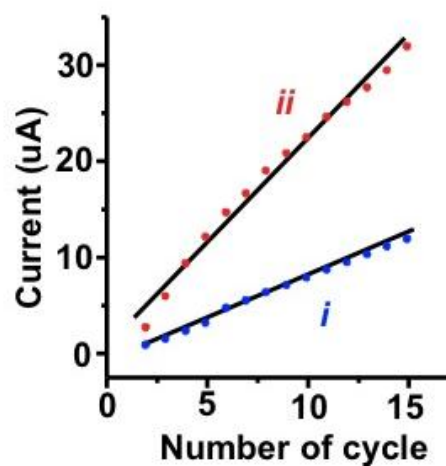


Figure S2. Layer number dependence of the oxidation currents of (i) poly[DvRu] film at 1.6 V and (ii) poly[CsF] film at 0.7 V.

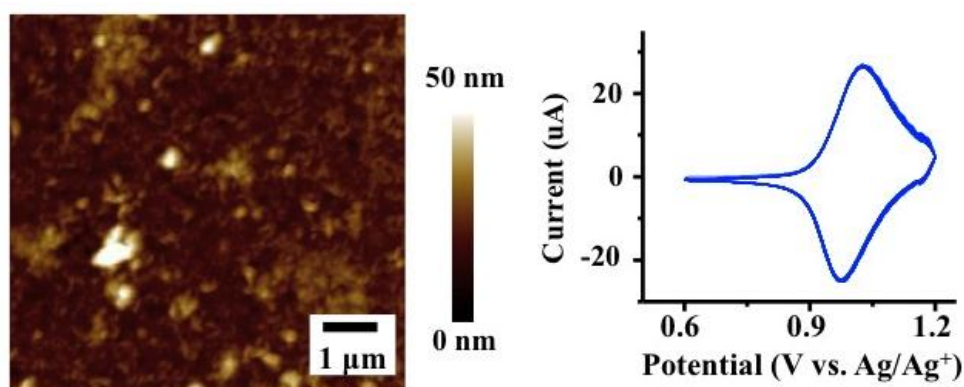


Figure S3. AFM image of poly[DvRu] film prepared at 100 mV/s and its CV in monomer free electrolyte on Pt electrode at 200 mV/s for 100 cycles.

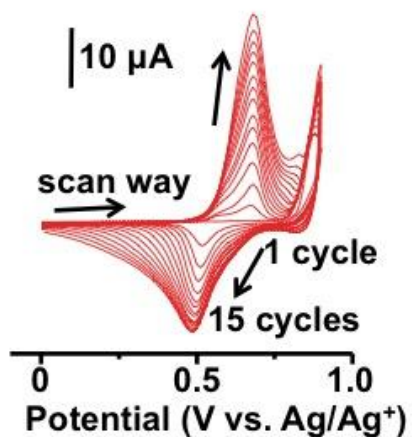


Figure S4. Oxidative electropolymerization of CsF at anodic scan.

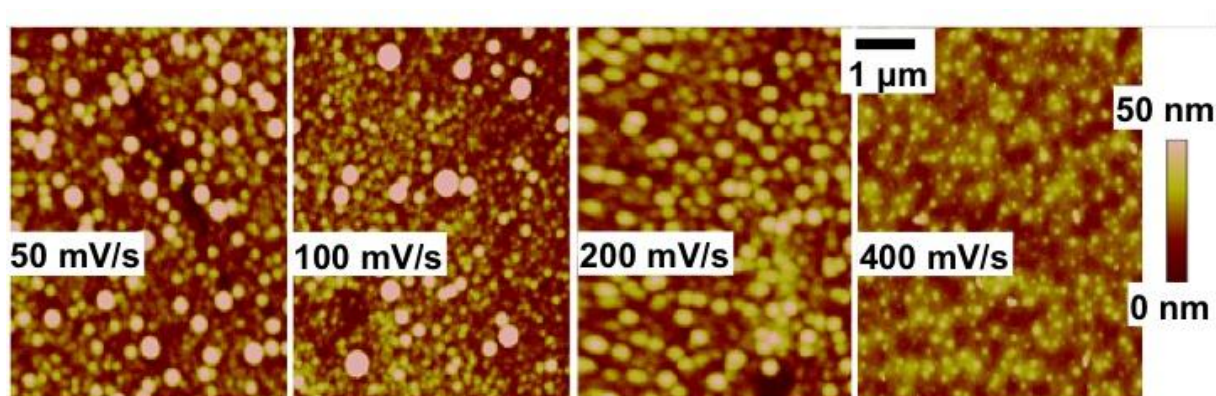


Figure S5. AFM images of poly[CsF] films prepared by using different scan rates.

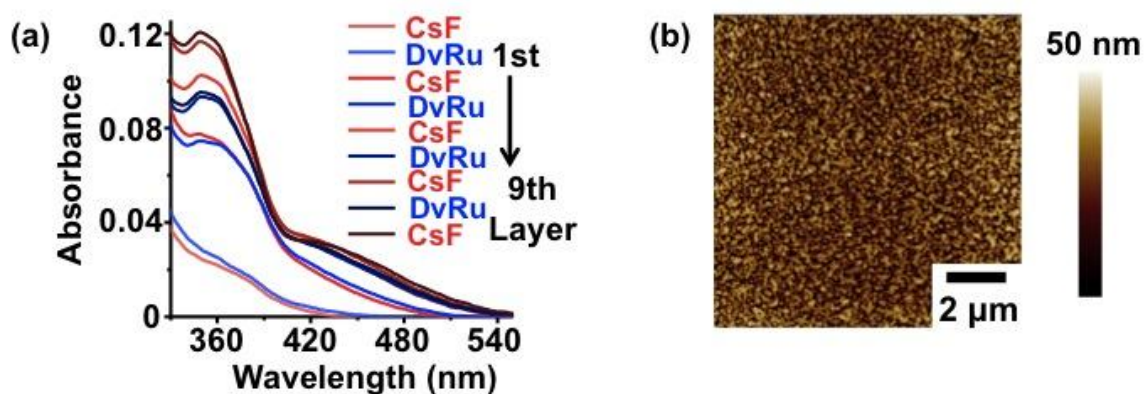


Figure S6. (a) UV-vis spectra of poly[CsF]/poly[DvRu] multilayer and (b) AFM image of multilayer.

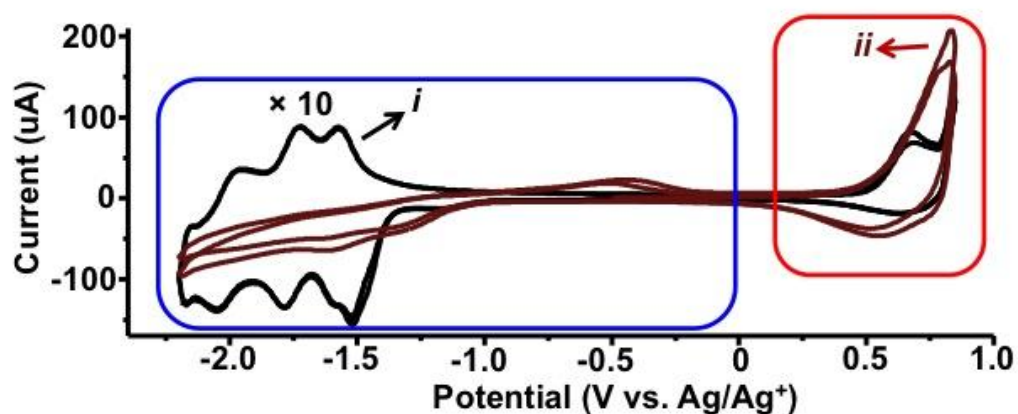


Figure S7. CV of multilayer films prepared by (i) CV mode on Pt (the intensity was magnified 10 times) and (ii) potential step switching mode on ITO

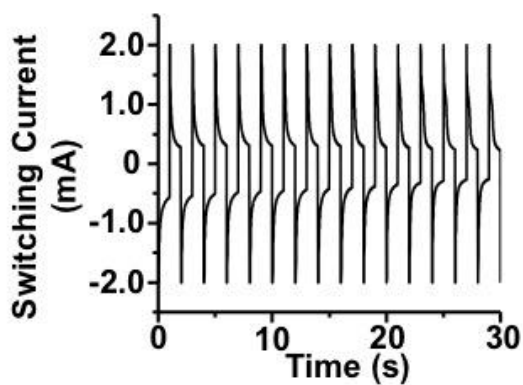


Figure S8. Switching current of ITO with applying step potentials at -2.2 and 0.85 V with an interval of 1s.

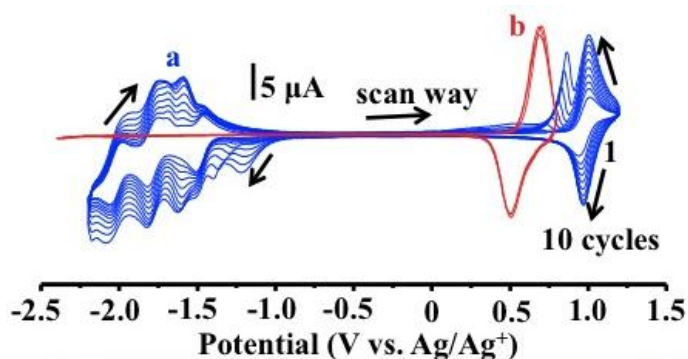


Figure S9. (A) Cyclic voltammogram of poly[DvRu] film on Pt electrode for 10 cycles. (B) Cyclic voltammogram of poly[CsF] film on Pt electrode in monomer free electrolyte.

The poly[DvRu] film shows sharp prewaves at 0.75 and -1.2 V, the magnitude of which spikes depends on electrode history and disappears when the potential sweeps between only negative (-0.6 ~ -2.2 V) or positive (0.9~1.2 V) potential (**Figure S1**) for multicycles. The prewaves are indicative of charges trapped in the film that are discharged as the film starts to be doped.

Reference

- S1.** a) H. J. Nie, J. Y. Shao, J. Wu, J. Yao, Y. W. Zhong, *Organometallics* **2012**, *31*, 6952–6959; b) M. Li, S. Tang, F. Shen, M. Liu, W. Xie, H. Xia, L. Liu, L. Tian, Z. Xie, P. Lu, M. Hanif, D. Lu, G. Cheng, Y. G. Ma, *Chem. Commun.* **2006**, 3393–3395.