## Electronic Supplementary Information (ESI) for:

Bio-inspired Protonic Memristor Devices Based on Metal Complexes with Proton-Coupled Electron Transfer

Yusuke Hiruma, Kai Yoshikawa and Masa-aki Haga*

Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University 1-12-27 Kasuga, Bunkyo-ku, Tokyo, Japan.

E-mail: mhaga@kc.chuo-u.ac.jp

## List of Electronic Supporting Information (ESI)

1. Proton electron transfer equilibria in the Ru complex RuNH-OH
2. AFM images for the ITO surface with RCA treatment and the ITO modified by 5 layered RuNH-OH LbL film
3. Summary of contact angle measurements
4. $I-V$ plots for various combination of two-terminal devices.

Scheme S1. Proton electron transfer equilibria in the Ru complex RuNH-OH. (Reprinted with permission from ref. 36. Copyright 2018 American Chemical Society)

2. AFM images for the ITO surface with RCA treatment and the ITO modified by 5 layered RuNHOH LbL film



Figure S1. AFM image for the ITO surface after RCA treatment $(5 \times 5 \mu \mathrm{~m})$


Figure S2. AFM image for the ITO surface modified by 5 layered RuNH LbL complexes ( $5 \times 5 \mu \mathrm{~m}$ and $1 \times 1 \mu \mathrm{~m}$ scale)

## 3. Summary of contact angle measurements

Table.S1. Summary of contact angle measurements for bare ITO and the modified ITO electrodes of ITO|(RuLbL film) and ITO|(RuLbL film)/P4VP at room temperature and their photographs

| ITO | Bare <br> (RCA treatment) | $I \mathrm{ITO} \mid(\mathrm{RuCH}-\mathrm{OH})_{3}$ | $\mathrm{ITO} \mid(\mathrm{RuNH}-\mathrm{OH})_{3}$ | $\mathrm{ITO} \mid(\mathrm{RuCH}-\mathrm{OH})_{3} / \mathrm{P} 4 \mathrm{VP}$ | ITO\|(RuNH-OH)$/ \mathrm{P4VP}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| C. A. <br> [deg.] | $40.7 \pm 1.2$ | $78.4 \pm 2.9$ | $75.5 \pm 2.0$ | $65.2 \pm 0.7$ | $66.1 \pm 0.6$ |
|  |  | - |  |  |  |

4. I-V plots for various combination of two-terminal devices.


Figure S3. I- $V$ plots of ITO $\left|(\mathbf{R u N H}-\mathbf{O H})_{3} /(\mathbf{R u C H}-\mathbf{O H})_{3}\right| I T O$ without P4VP polymer layer


Figure S4. I-V plots of $\mathrm{ITO}\left|(\mathbf{R u C H}-\mathbf{O H})_{3} /(\mathbf{R u N H}-\mathbf{O H})_{3}\right| \mathrm{PEDOT}$ without P4VP polymer layer


Figure S5. $I-V$ plots of $\mathrm{ITO} \mid(\text { RuNMe- } \mathbf{O H})_{3} / \mathrm{P} 4 \mathrm{VP} /(\mathbf{R u C M e}-\mathbf{O H})_{3} \mid \mathrm{ITO}$


Figure S6. I-V plots of ITO $\left|(\mathbf{R u C H}-\mathbf{O H})_{3} / \mathrm{P} 4 \mathrm{VP}\right| \mathrm{ITO}$


Figure S7. I- $V$ plots of ITO $\left|(\mathbf{R u N H}-\mathbf{O H})_{3} / \mathrm{P} 4 \mathrm{VP}\right| \mathrm{ITO}$


Figure S8. Semi-log $I-V$ plots of ITO| $(\mathbf{R u N H}-\mathbf{O H})_{3} / \mathrm{P} 4 \mathrm{VP} /(\mathbf{R u C H}-\mathbf{O H})_{3} \mid \mathrm{ITO}$ for the average of 10 different devices as shown in Fig. 8 in the manuscript.

