Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Electrochromic electrically-conductive $Cu_3(HHTP)_2$ films with adaptations to diverse and low-concentration water

Yongsheng Liu,[§,a] Xiaoyu Zhang,[§,a] Ran Li,[a] Ziqiu Lu,[a] Xilu Wu,[a] Chengyi Hou,[a] Qinghong Zhang,[b] Yaogang Li,[b] Kerui Li*[,a] and Hongzhi Wang*[,a]

[a]State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Materials Science and Engineering, Donghua University, Shanghai 201620, People's Republic of China.
[b]Engineering Research Center of Advanced Glass Manufacturing Technology Ministry of Education, College of Materials Science and Engineering, Donghua University, Shanghai 201620, People's Republic of China.

[§] These authors equally contributed to this work.

***Corresponding Authors**
K. R. Li (likr@dhu.edu.cn); H. Z. Wang (wanghz@dhu.edu.cn)

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Section 1. Equations

Both the EIS and CV measurements can be used to extract the apparent ion diffusion coefficient D. Specifically, the apparent ion diffusion coefficients D_{CV} can be calculated as follows:[1]

$$I_p = 2.69 \times 10^5 \times n^{3/2} \times A \times D_x^{1/2} \times C_x \times v^{1/2} \quad \text{(S1)}$$

The formula for calculating the apparent ion diffusion coefficient D_{CV} involves several variables, including I_p (the peak current density), n (the number of electrons involved), A (the surface area), D_x (the ion-diffusion coefficient), C_x (the concentration of active ions in the electrolyte solution), and v (the scan rate).

D_{EIS} can be calculated from the Warburg region:

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \quad \text{(S2)}$$

$$Z' = R_s + R_{ct} + \sigma\omega^{-1/2} \quad \text{(S3)}$$

The formula for calculating the ion diffusion coefficient D involves several variables, including R (the molar gas constant, with a value of 8.314 J mol^{-1} K^{-1}), T (the absolute temperature), A (the electrode area), n (the electron transfer number), F (the Faraday constant, with a value of 96500 C mol^{-1}), C (the concentration of ions), σ (the Warburg factor), R_s (the internal resistance), R_{ct} (the charge-transfer resistance), and ω (the angular frequency).

Coloring efficiency (CE) determined by the ratio of the change in optical density (Δ OD) (the change between the bleached state and the colored state) to the injected electric quantity per unit electrode area (Q/A).[2] The calculation formula is as follows:

$$CE = log\,(Tb/Tc)/(Q/A) \quad \text{(S4)}$$

$$\Delta OD = log\,(Tb/Tc) \quad \text{(S5)}$$

Tb and Tc are the transmissivity values of the electrochromic material in the bleached and colored states at a specific wavelength, Q is the total number of input charges, and A is the electrode area.

Section 2. preparation and performance testing of electrodes

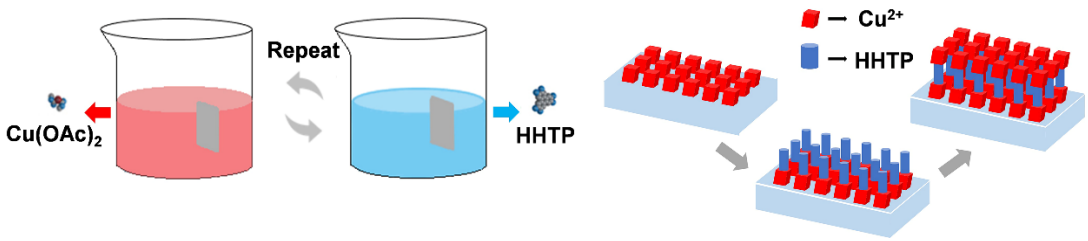

Figure S1. Illustration of preparation of the $Cu_3(HHTP)_2$ electrode.

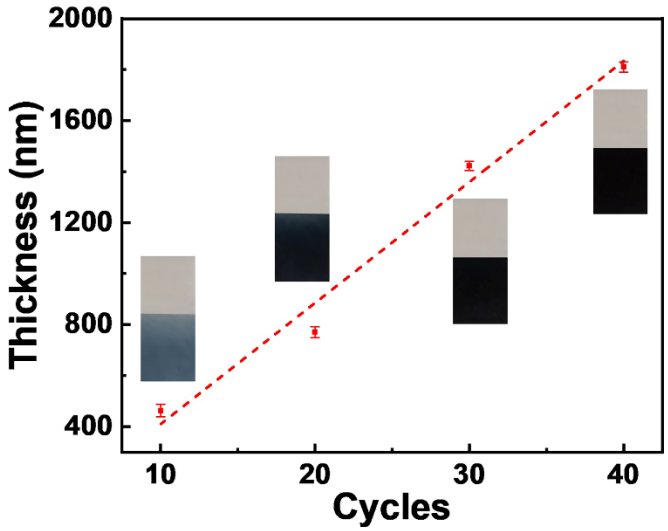

Figure S2. Relationship between film thickness and number of self-assemblies.

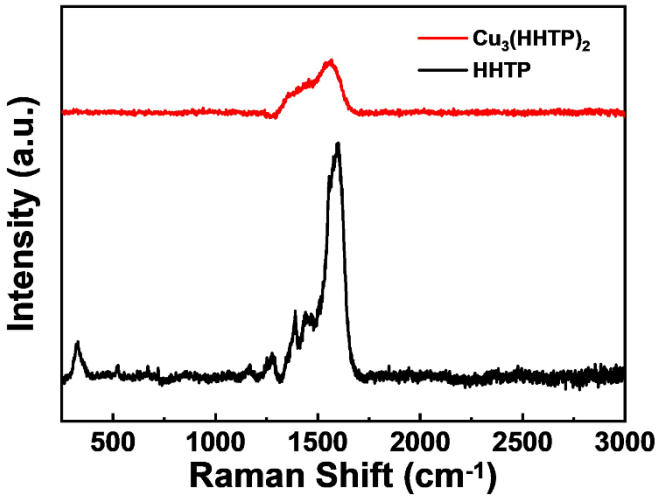

Figure S3. Raman spectra of $Cu_3(HHTP)_2$ and HHTP.

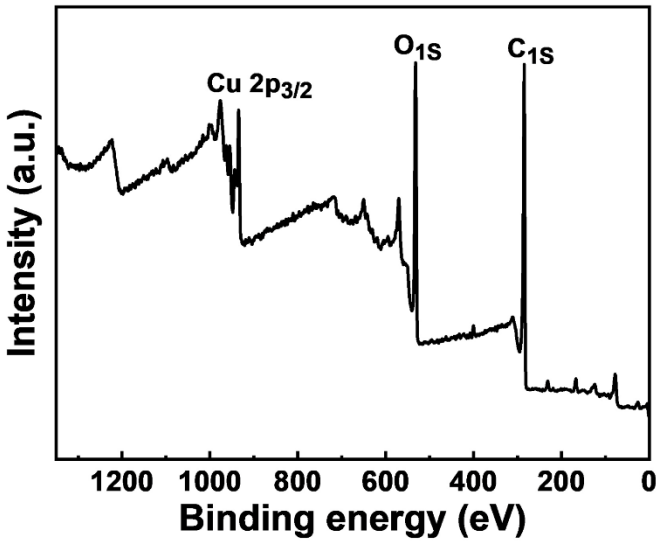

Figure S4. The full range XPS analysis of $Cu_3(HHTP)_2$.

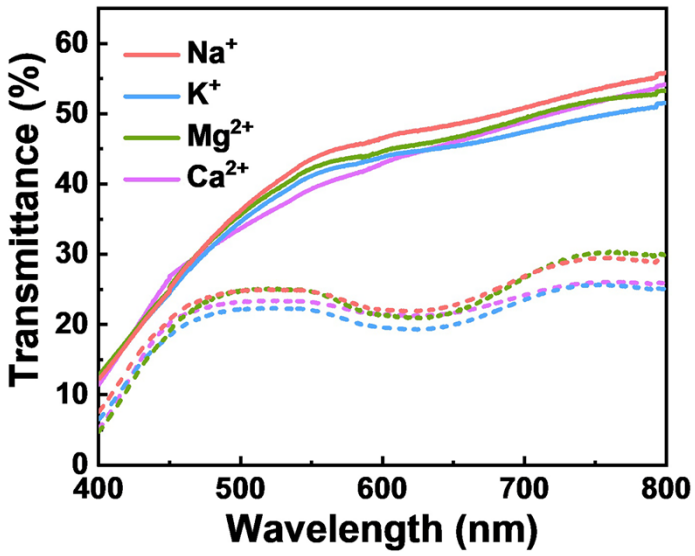

Figure S5 UV-Vis transmittance spectra of $Cu_3(HHTP)_2$ films in different ionic electrolytes (i.e. Na^+, K^+, Mg^{2+} and Ca^{2+}) at -0.6 V and 0.2 V.

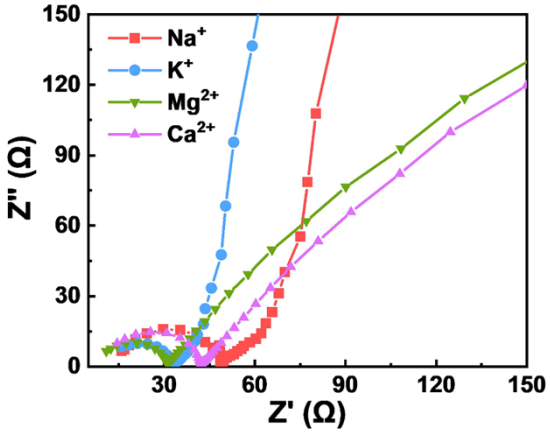

Figure S6 EIS spectra of $Cu_3(HHTP)_2$ films in different ionic electrolytes (i.e. Na^+, K^+, Mg^{2+} and Ca^{2+}) at -0.6 V and 0.2 V.

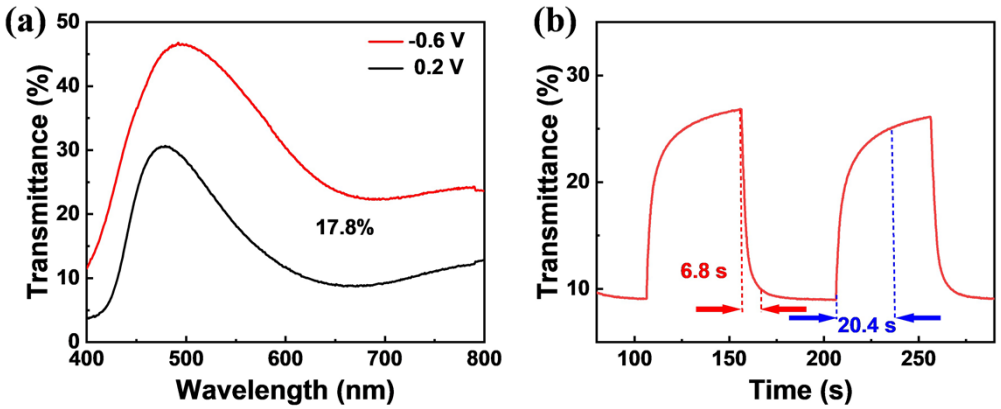

Figure S7. The UV-Vis transmission spectra and switching times of $Cu_3(HHTP)_2$ in 100 mM LiCl.

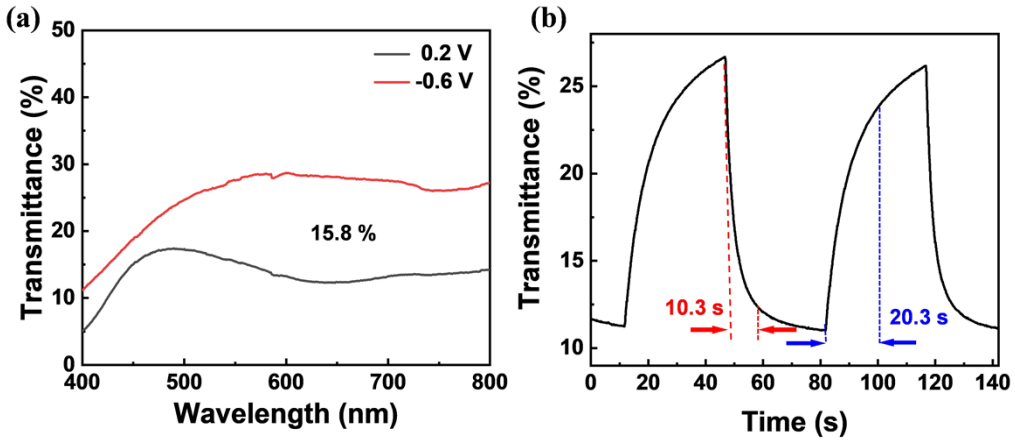

Figure S8. The UV-Vis transmission spectra and switching times of $Cu_3(HHTP)_2$ in 100 mM $LiClO_4$/PC.

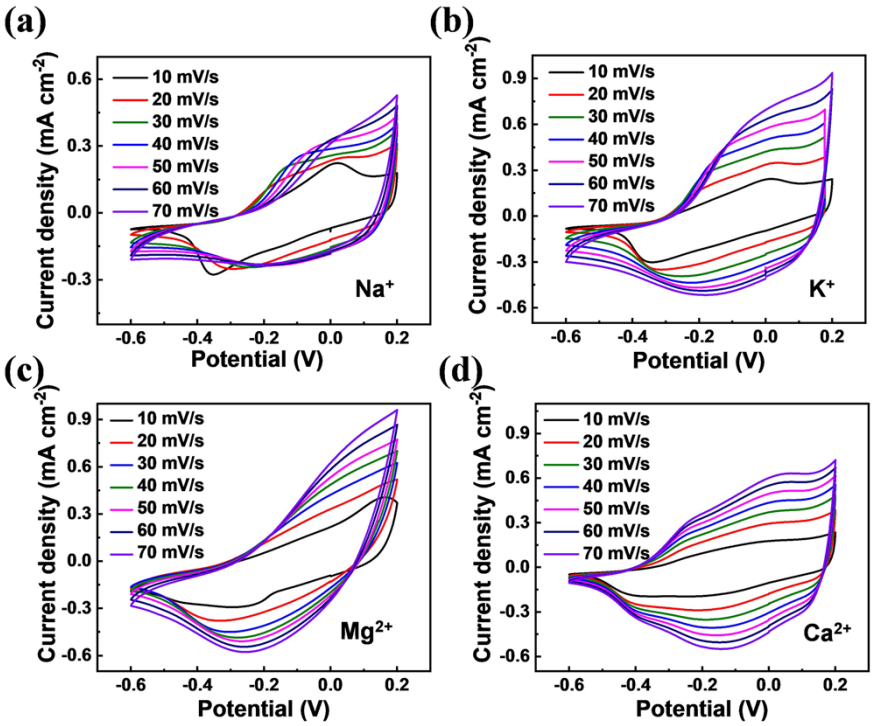

Figure S9 Cyclic voltametric curves of $Cu_3(HHTP)_2$ films in 100 mM (a) NaCl, (b) KCl, (c) $MgCl_2$, (d) $CaCl_2$ solution at sweep rates from 10 to 70 mV s^{-1}.

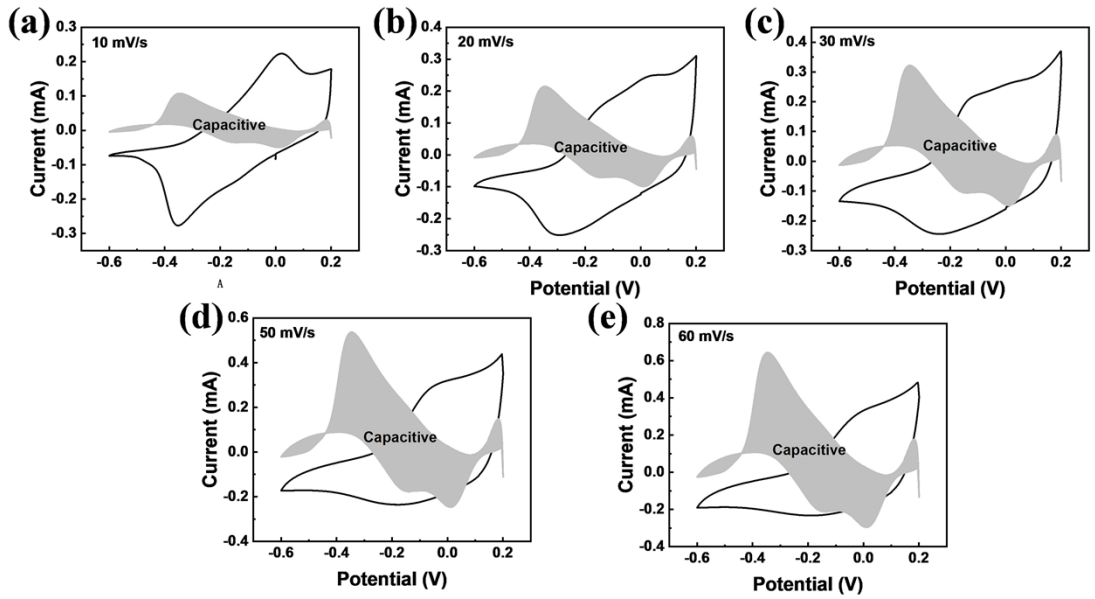

Figure S10. Correlation kinetic analysis of $Cu_3(HHTP)_2$. Detailed plots of the capacitive contribution of $Cu_3(HHTP)_2$ at different sweep speeds compared to the diffusion control of $Cu_3(HHTP)_2$.

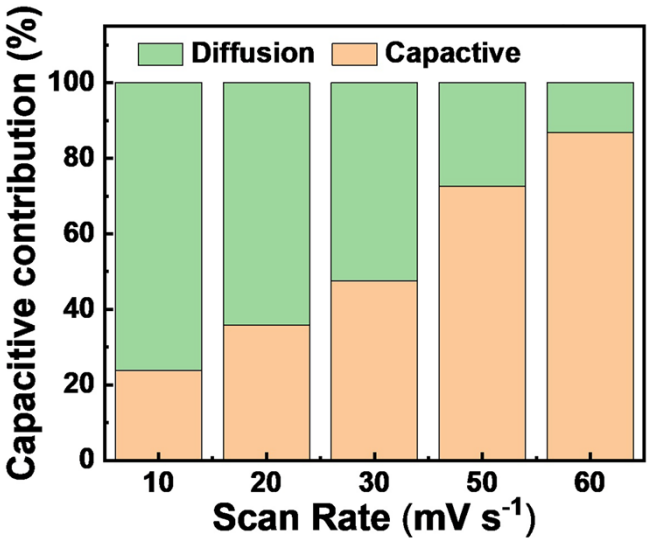

Figure S11 Correlation kinetic analysis of $Cu_3(HHTP)_2$. Capacitive contribution of $Cu_3(HHTP)_2$ compared to diffusion control of $Cu_3(HHTP)_2$.

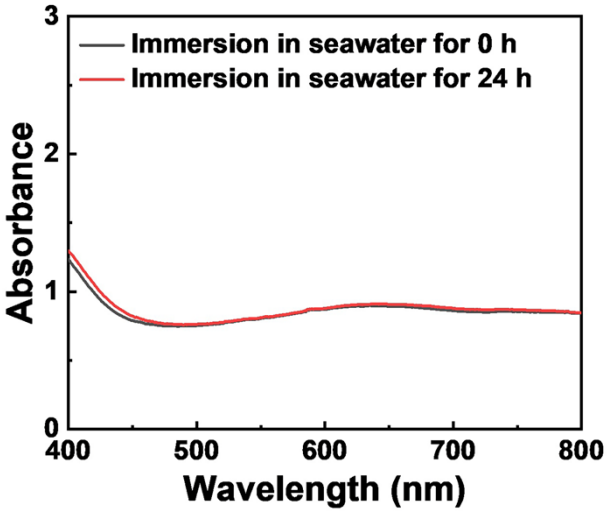

Figure S12. The UV-Vis absorption spectra of $Cu_3(HHTP)_2$ before and after 24h immersion in seawater.

The study results revealed no significant change in absorbance before and after immersion, suggesting that the discoloration of the film was not attributed to adsorption.

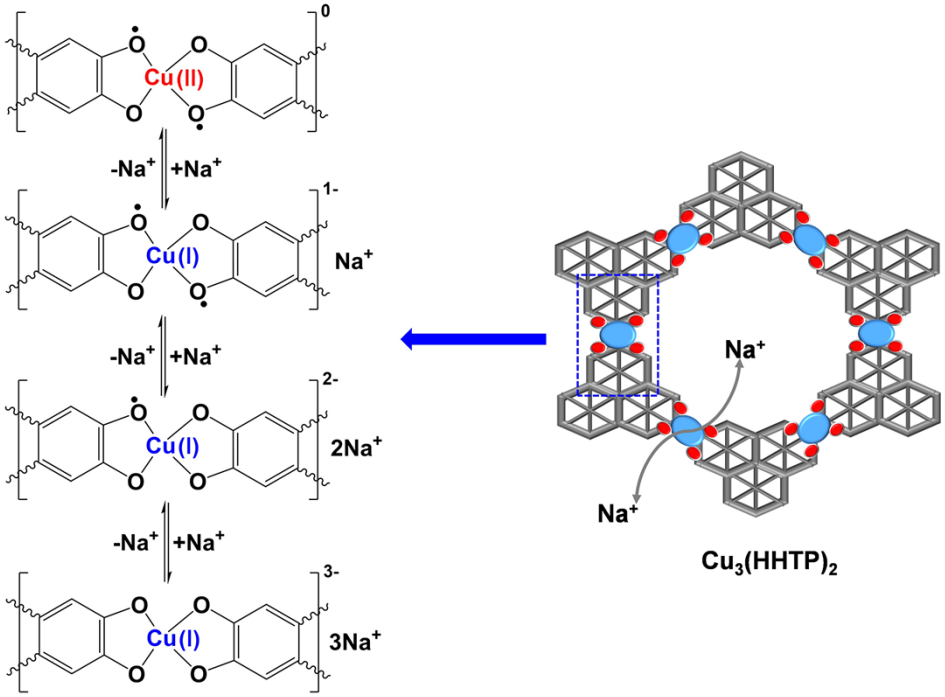

Figure S13. Schematic diagram of the insertion/extraction process of ions in $Cu_3(HHTP)_2$ materials, with Na^+ as an exemplary case.

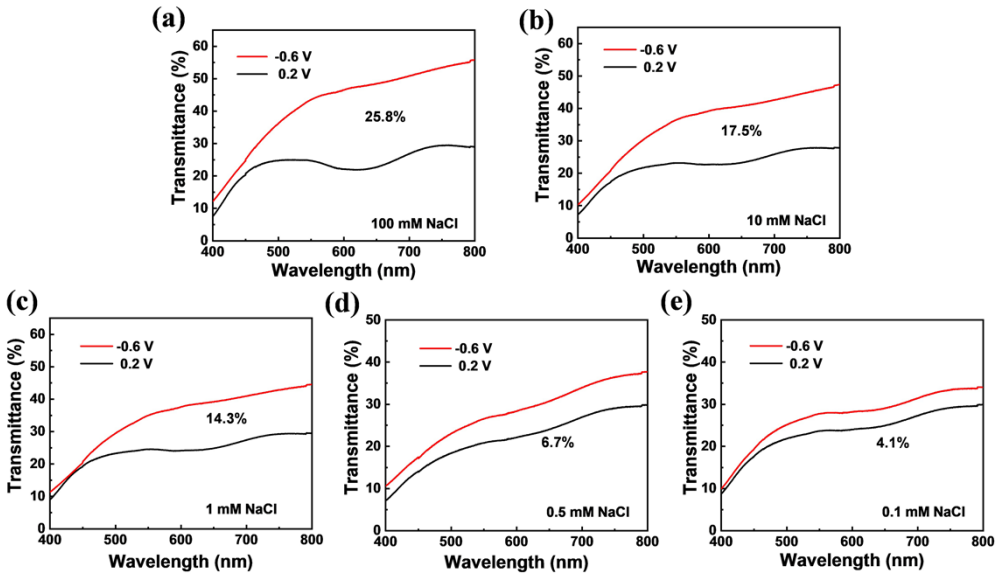

Figure S14 UV-Vis transmittance spectra of $Cu_3(HHTP)_2$ films in (a) 100 mM, (b) 10 mM, (c) 1 mM, (d) 0.5 mM, (e) 0.1 mM NaCl solution at -0.6 V and 0.2 V.

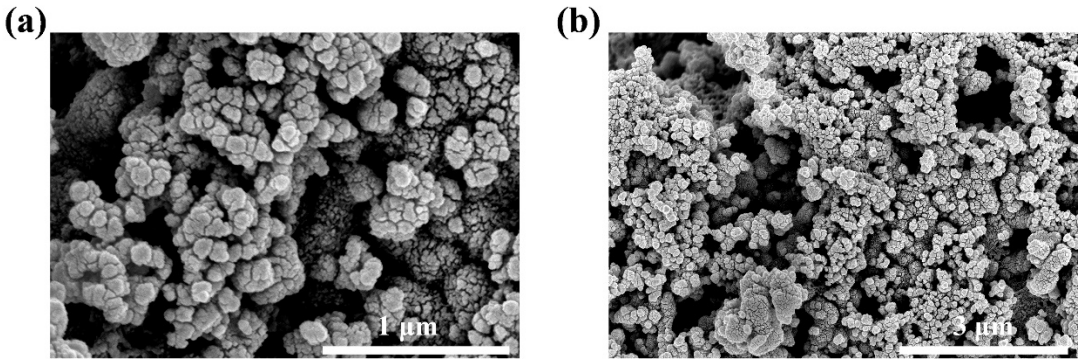

Figure S15. SEM images of the synthesized $Cu_3(HHTP)_2$ after 500 cycles.

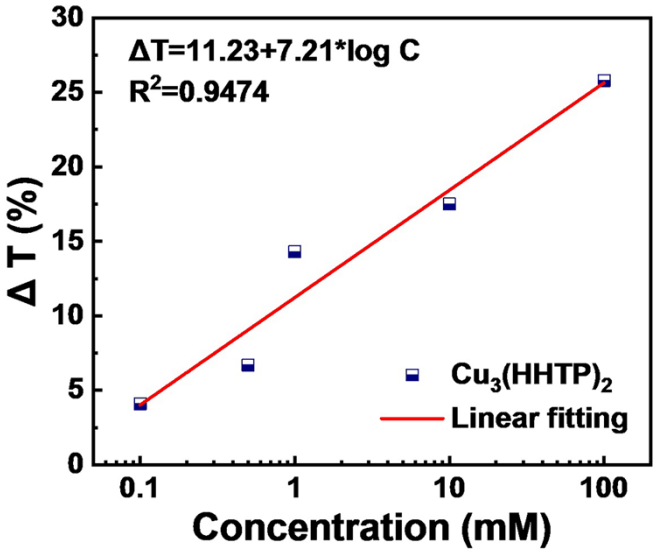

Figure S16. Linear fit plot of ion concentration and optical contrast variation.

In Figure S16, the standard curve was calibrated utilizing the logarithm of concentration on the horizontal axis and the corresponding change in optical contrast on the vertical axis. The resultant fit exhibited a linear response, aligning with the requirements for its application as an electrochromic sensor in the assessment of ion concentration. Specifically, the linear equation is as follows:

$$\Delta T = 11.23 + 7.21 * log\ C \quad \text{(S6)}$$

ΔT is the change in optical contrast and C is the concentration of the solution.

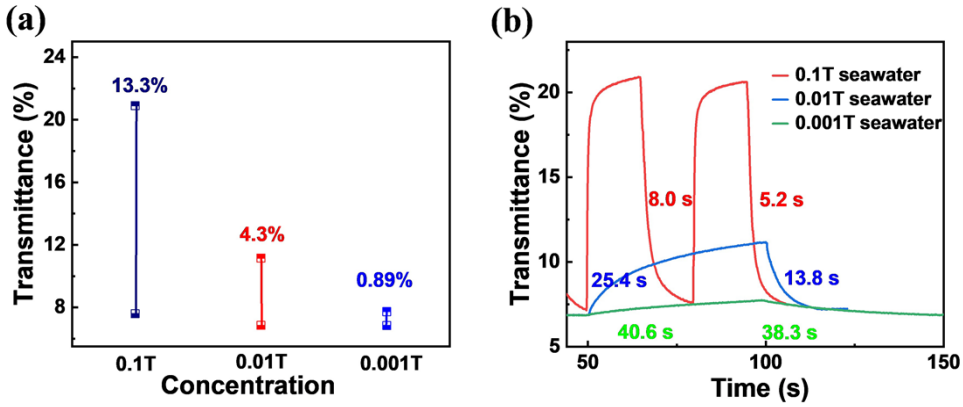

Figure S17. Optical contrast and switching times of $Cu_3(HHTP)_2$ films extracted from the transmittance spectra measured in seawater with different concentrations. (i.e. 0.1T, 0.01T, and 0.001T) at 650 nm. (Note: 1T is the seawater concentration)

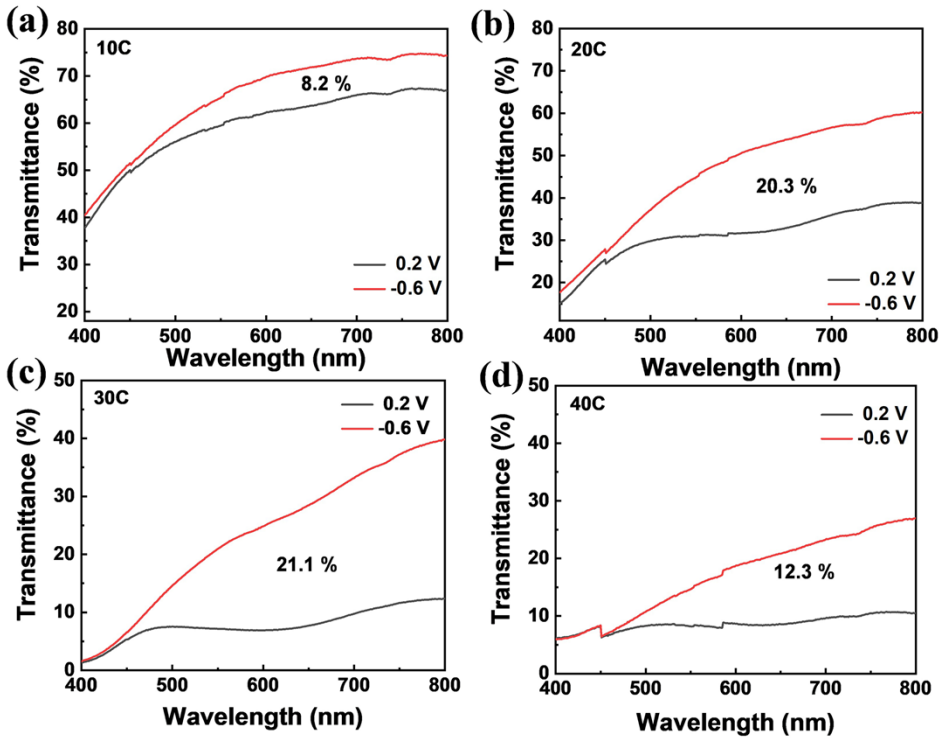

Figure S18. The UV-Vis absorption spectra of $Cu_3(HHTP)_2$ at (a) 10C; (b) 20C; (c) 30C and (d) 40C in seawater.

The optical contrast of the 30C film exhibited the highest performance in seawater at various cycle numbers, achieving a maximum value of 21.1%.

References

1. R. Li, K. Li, G. Wang, L. Li, Q. Zhang, J. Yan, Y. Chen, Q. Zhang, C. Hou and Y. Li, ACS Nano, 2018, **12**, 3759-3768.
2. H. Liang, R. Li, C. Li, C. Hou, Y. Li, Q. Zhang and H. Wang, *Mater. Horiz.*, 2019, **6**, 571-579.