Supporting information

Cathodic synthesis of Cu-catecholate metal-organic framework

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Figure S1. FT-IR spectra of the Cu-CAT-1 powder (black) and cathodically deposited Cu-CAT-1 film (red) on ITO substrate.



Figure S2. XPS spectra of Cu-CAT-1 film: a) full survey scan; b) high resolution spectrum of Cu $2p_{3/2}$ scan.



Figure S3. CV curves recorded for the Ar-saturated DMF background and H_6 HHTP solutions with/without addition of NaOH (20 mM) on GC electrode at room temperature and at a scan rate of 100 mV/s.



Figure S4. CV curves of air-saturated (red) and oxygen-saturated (black) Cu-CAT-1 precursor solutions containing $Cu(NO_3)_2$ (5 mM) and H_6HHTP (3.33 mM) measured on a glass carbon electrode at scan rates of 100 mV/s and with (NBu₄)PF₆ (10 mM) as the supporting electrolyte.



Figure S5. Consecutive CV curves of air-saturated Cu-CAT-1 precursor solutions containing $Cu(NO_3)_2$ (5 mM) and H₆HHTP (3.33 mM) measured on a glass carbon electrode at scan rates of 100 mV/s and with (NBu₄)PF₆ (10 mM) as the supporting electrolyte.



Figure S6. Top-view and cross-sectional SEM images of Cu-CAT-1 films on ITO substrate deposited at -0.1 V for 10 min from the supporting-electrolyte-free and air-saturated precursor solutions with $Cu(NO_3)_2$ concentration of a, b) 1mM, c, d) 2mM, e, f) 3mM, g, h) 4mM, and i, j) 5mM. The molar ratio of $Cu(NO_3)_2/H_6HHTP$ is fixed to 3:2.



Figure S7. Cross-sectional SEM images of Cu-CAT-1 films on ITO substrate deposited at a) 0 V, b) -0.1 V, c) -0.2 V, d) -0.3 V, e) -0.4 V, and f) -0.5 V (versus Ag/AgCl) for 10 min. The air-saturated and supporting electrolyte-free precursor solution containing 1 mM Cu(NO₃)₂ and 0.66 mM H₆HHTP was used for the cathodic synthesis.



Figure S8. Top-view and cross-sectional SEM images of Cu-CAT-1 films on ITO substrate prepared by depositing at -0.1 V for a) 1, b) 10, c) 20, d) 30, e) 60, and f) 120 min from the air-saturated and supporting electrolyte-free precursor solution containing 1 mM Cu(NO₃)₂ and 0.66 mM H₆HHTP.