Supplementary Material

for

Electrochromic Thin Films of Zn-based MOF-74 Nanocrystals Facilely Grown on Flexible Conducting Substrates at Room Temperature

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Materials characterization methods

Powder X-ray diffraction (PXRD) patterns were collected using the Rigaku MiniFlex diffractometer (600 W) equipped with a Cu Kα source (1.541 Å). The diffraction data were collected at 2θ angle from 5° to 30°, using a 0.01° step size at 1°/min step speed.

Thermogravimetric analysis was performed using the TA Instrument Q50, from 50-600 °C at a heating rate of 20 °C min⁻¹ under constant nitrogen flow.

Atomic force microscopy (AFM) images were collected using the Neaspec neaSNOM operating under the tapping mode. Height topography, amplitude and phase maps were collected using the NuNano Scout350 probe, which has a nominal tip radius of 5 nm, a spring constant of 42 N/m and resonant frequency of 350 kHz.

Field emission scanning electron microscopy (FESEM) images were obtained using the Carl Zeiss Merlin equipped with a high-resolution field emission gun. Micrographs were attained under high vacuum with an accelerating voltage of 10 kV and in secondary electron imaging mode. SEM samples were used as obtained from each processing step of the room temperature fabrication of DHTP@Zn-MOF-74 thin film.

The cyclic voltammetry (CV) measurements were performed using the IviumStat.h impedance spectrometer equipped with a three-electrode electrochemical setup depicted in Fig. S1. The scan rates were varied from 50, 100, 200, 400, 800 to 1000 mV/s, all of which collected using a potential step of 10 mV.
Figure S1. A three-electrode electrochemical test system for cyclic voltammetry. Ag/AgCl as the reference electrode, platinum as the counter electrode, and the transparent film of DHTP@Zn-MOF-74 as the test electrode. The clear electrolyte is 0.1 M tributylmethylammonium methyl sulfate conduction salt (MTBS) solution in DMF.
Figure S2. Zinc coating (grain size ~50 nm) deposited on the surface of ITO (on PET substrate) using the cyclic voltammetry (CV) technique. Five cycles were applied between -0.85 V to -1.055 V in a three-electrode electrochemical cell.
Figure S3. FESEM images showing the microstructures of Zn deposited on the ITO coated PET substrate. Note that the regions located in the vicinity of the liquid interface exhibit a non-regular flake-like microstructures due to the edge effect. The Zn coating found away from the interface was found to be more uniform.
Figure S4. FESEM micrographs showing the nanoscale columnar-like morphologies of the DHTP@Zn-MOF-74 electrochromic film grown on the ITO-coated PET substrate (post-deposited with a layer of polycrystalline Zn, see Fig. S3).
Figure S5. AFM height profiles across the (a) Zn to ITO interface, and (b) DHTP@Zn-MOF-74 to Zn interface.
Figure S6. PXRD patterns of the as-synthesized nanocrystals (thoroughly washed to remove entrapped guests) and DHTP@Zn-MOF-74 sample compared to the simulated pattern.
Figure S7. Thermogravimetric analysis curves for comparing the weight loss of the thoroughly washed Zn-MOF-74 versus DHTP@Zn-MOF-74 composite (a guest@MOF system) to determine the formula of the DHTP@Zn-MOF-74 compound as $[\text{Zn}_2(\text{DHTP})(\text{DMF})_2]_{12} \cdot \text{DHTP}$.
Figure S8. Evolution of the CV curves of a DHTP@Zn-MOF-74 thin film sample subject to a total of 500 cycles at 50 mV/s. (a) – (f) shows the first 300 cycles. Note that panel (a) is identical to data shown in Figure 4 in the main manuscript.
Figure S8 [continue]. Evolution of the CV curves of a DHTP@Zn-MOF-74 thin film sample subject to a total of 500 cycles at 50 mV/s. Panels (g)-(j) show cycles 301 – 500.