

Metal–Organic Framework Thin Films Composed of Free-Standing Acicular Nanorods Exhibiting Reversible Electrochromism

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S1. ¹H NMR and DRIFTS spectra

The ¹H NMR spectrum of the sample obtained from the **NU-901** thin films is shown in Figure S1. Signals from benzoic acid, TBAPy linkers and DMF can be found in the spectrum. From ratios of the integrated areas for the peaks of TBAPy linkers to those of benzoic acid, there are on average 1.3 benzates per linker and, therefore 2.7 benzoates (Bz) per Zr₆ node.^[S1] The number of Bz per node varies between 2 and 4, which conceivably may be affected by the washing process for the film after its growth. Figure S2 shows the DRIFTS spectrum of the sample obtained from the **NU-901** thin films. A broad peak for –OH stretching can be observed around 3650 cm⁻¹.^[S1] Both the NMR spectrum and the DRIFTS spectrum point to a formula for **NU-901** of Zr₆(μ₃-OH)₈(OH)_{8-2x}(Bz)_x(TBAPy)₂, with x having a value between 2 and 4.

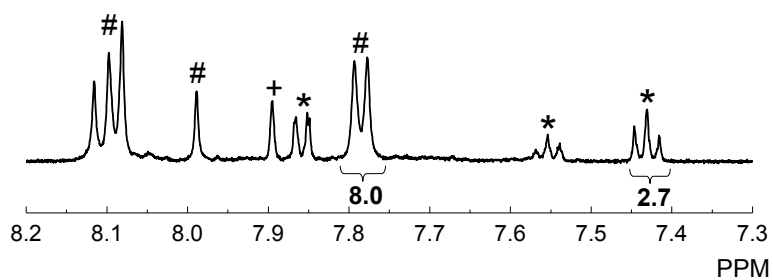


Figure S1. ^1H NMR spectrum of the sample from the as-prepared **NU-901** thin films, corresponding peaks of TBAPy linker (#), benzoic acid (*), and DMF (+).

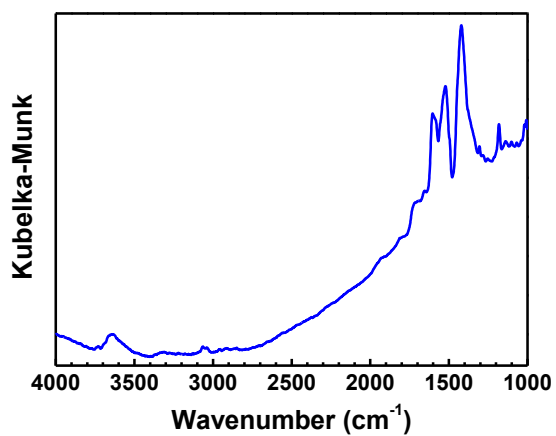


Figure S2. DRIFTS spectrum of the sample from the as-prepared **NU-901** thin films.

S2. Morphologies of the obtained thin films when the bare FTO substrates were directly used for thin film growth

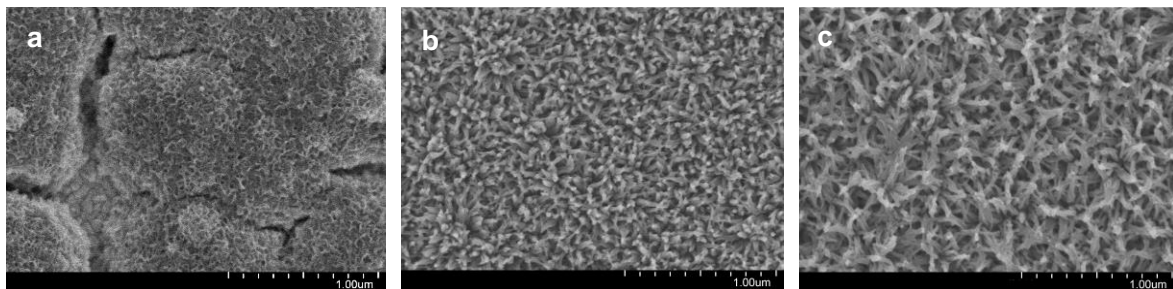


Figure S3. SEM images of the obtained films when the untreated (bare) FTO substrates were directly used for thin film growth: after a) 1.5 h, b) 3 h, and c) 4.5 h of film growth.

S3. Thin-film XRD patterns of the NU-901 thin films after electrochemical switches

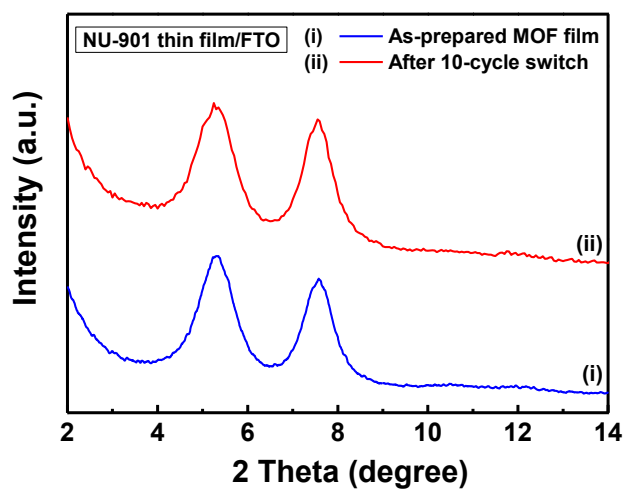


Figure S4. Thin-film XRD patterns of the **NU-901** thin films on FTO substrates (i) before the electrochemical switch, and (ii) after 10-cycle switch from 0 to 1.6 V.

S4. Raman spectra

Raman spectra of the **NU-901** thin film at various applied potentials *vs.* Ag/AgCl/KCl (sat'd) were measured with a 594 nm laser, and the spectra are shown in Figure S4. No significant Raman signals could be observed at 0 V and 1.2 V, because the film's absorbance is not in resonance with the excitation source energy. When 1.4 and 1.6 V were applied, strong resonance Raman signals could be observed, indicating the color change of the MOF thin film from yellow to blue. The strong peaks at 1603 and 1378 cm^{-1} are associated with the ring stretches of the polyaromatic structure,^[S2] these two peaks agree with the typical Raman spectra of pyrene-based species.^[S2] The SERS spectrum of the H₄TBAPy ligand is also shown in Figure S4 for comparison. The spectra of the **NU-901** thin film obtained at 1.4 and 1.6 V agree well with the SERS spectrum of the linker except the peak at 1264 cm^{-1} shifts to 1290 cm^{-1} ; this shift may be attributed to the oxidation of the pyrene, which occurred on the thin film at 1.4 and 1.6 V.

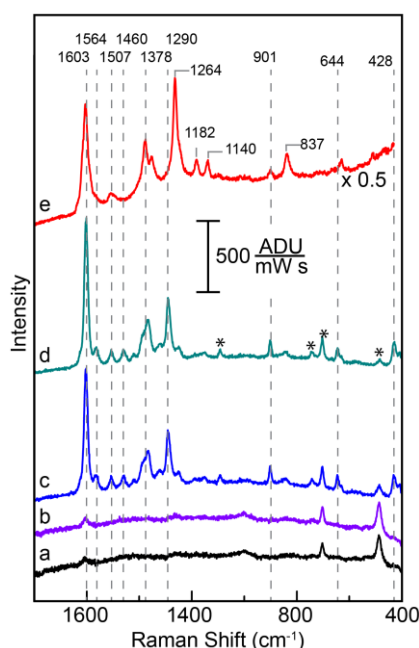


Figure S5. Raman spectra of the **NU-901** thin film at a) 0 V, b) 1.2 V, c) 1.4 V, and d) 1.6 V *vs.* Ag/AgCl/KCl (sat'd). All spectra were taken using a 20x objective with 594 nm excitation. e) SERS spectrum of the H₄TBAPy ligand (scaled by 0.5). Peaks labeled in d) with asterisks and corresponding peaks are attributed to solvent and room light peaks.

S5. Current recorded during the electrochromic switching

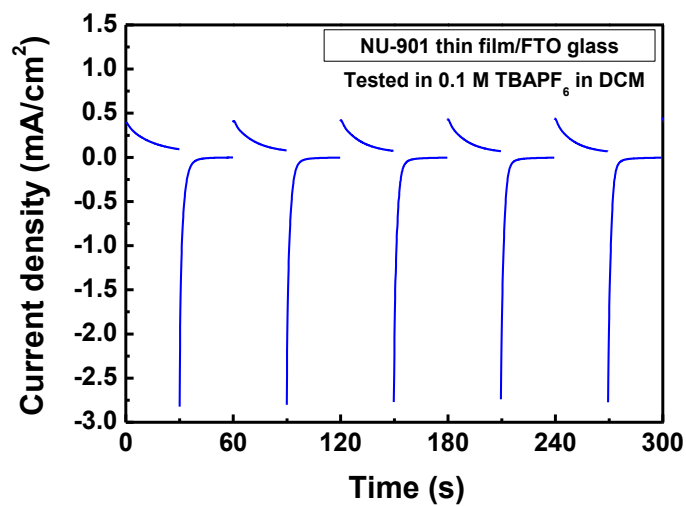


Figure S6. Current recorded during the first five cycles of switching of the **NU-901** thin film between 0 and 1.6 V *vs.* Ag/AgCl/KCl (sat'd).

S6. Removal of benzotes from the NU-901 thin films

0.5 mL of 8 M hydrochloric acid aqueous solution was mixed with 13 mL of DMF; 0.05 mL of the obtained solution was then mixed with 49.95 mL of DMF to form the diluted acidic solution. The obtained **NU-901** thin film was then soaked in the diluted acidic solution in a 100 °C oven for 48 h. The obtained film was washed with acetone and dried in air. The obtained MOF (activated-**NU-901**) film was examined by NMR. As shown in Figure S5a, all the peaks from benzoic acid disappear, indicating that all the benzotes in the MOF film have been removed. Thin-film XRD pattern and SEM image of the activated-**NU-901** film suggest that both crystal structure and morphology of the MOF film are maintained, as shown in Figure S5b and Figure S5c. The kinetic curve for electrochromic switching of the activated-**NU-901** film/FTO is shown in Figure S5d. The limiting transmittance change ($\Delta T\%$), bleaching time, and coloration time were found to be 64.8%, 6 s and 10 s, respectively; these electrochromic parameters are nearly the same as those of the **NU-901**-coated electrode before the removal of benzoates.

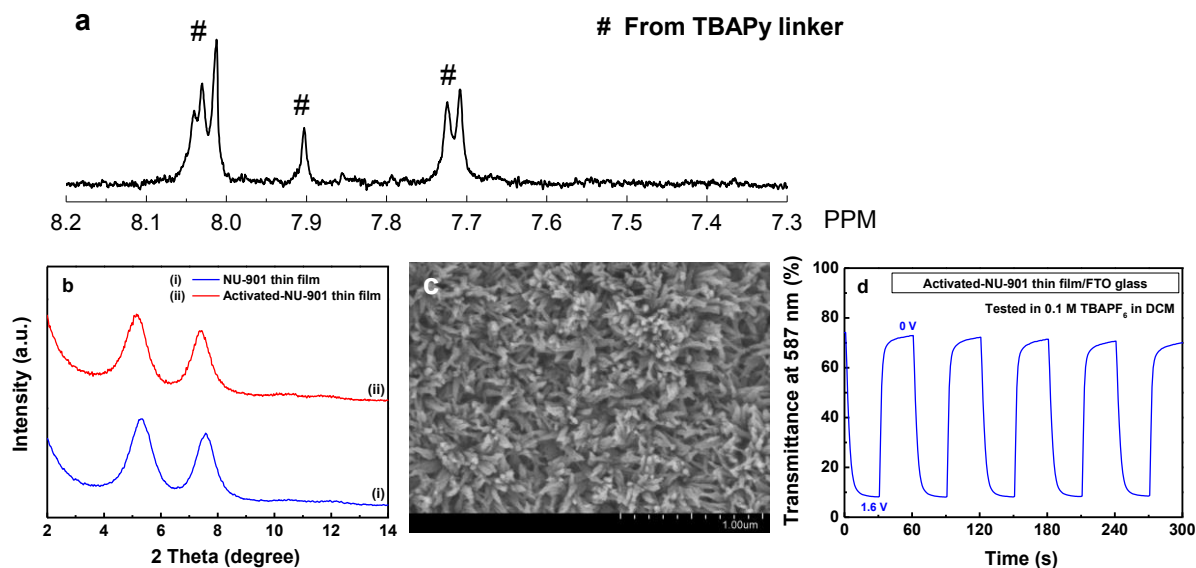


Figure S7. a) ^1H NMR spectrum of the sample from the activated-**NU-901** thin films. b) Thin-film XRD patterns of the **NU-901** film and activated-**NU-901** film. c) SEM image of the activated-**NU-901** film. d) Optical transmittance kinetic curve of the activated-**NU-901** film/FTO measured by switching the potential from 0 to 1.6 V vs. Ag/AgCl/KCl (sat'd).

S7. Repetitive CV curve and long-term electrochromic switching

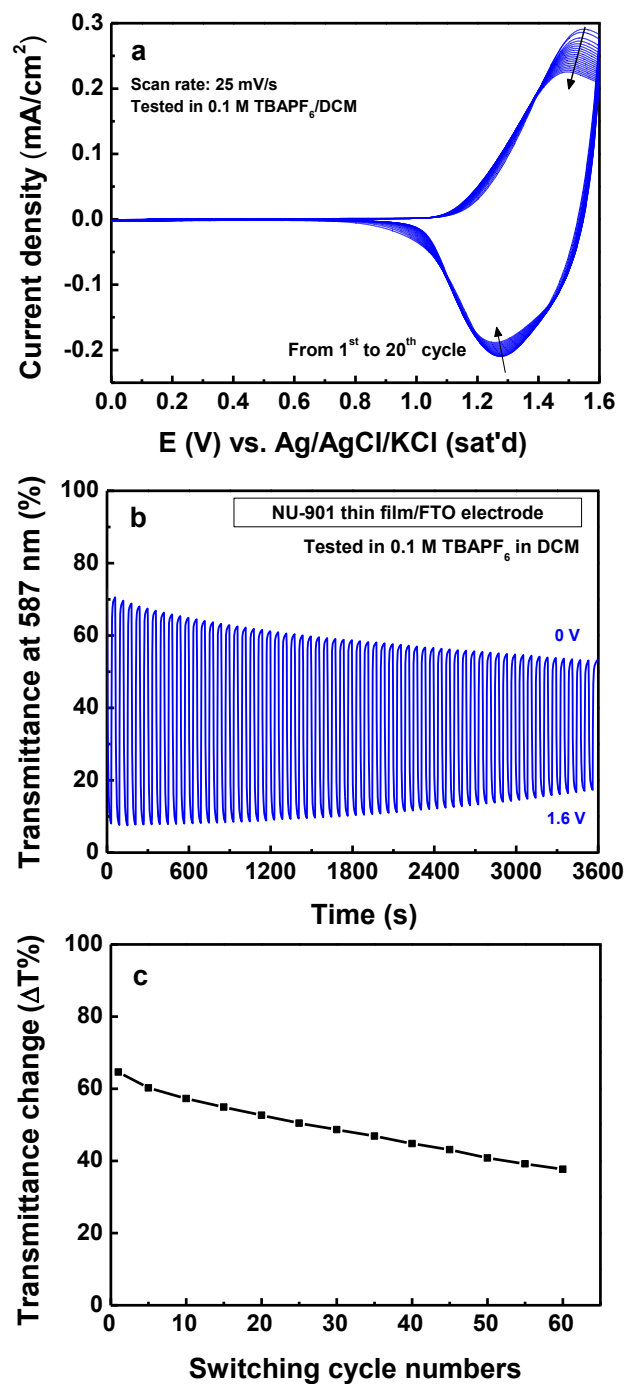


Figure S8. a) 20-cycle repetitive CV curve of the **NU-901** thin film/FTO electrode, and b) kinetic curve for 60-cycle electrochromic switching of the **NU-901** thin film/FTO electrode. Both experiments were conducted in 0.1 M TBAPF₆ in DCM. c) The plot of transmittance change vs. switching cycle number obtained from b.

S8. Electrochromic switching in wet electrolyte

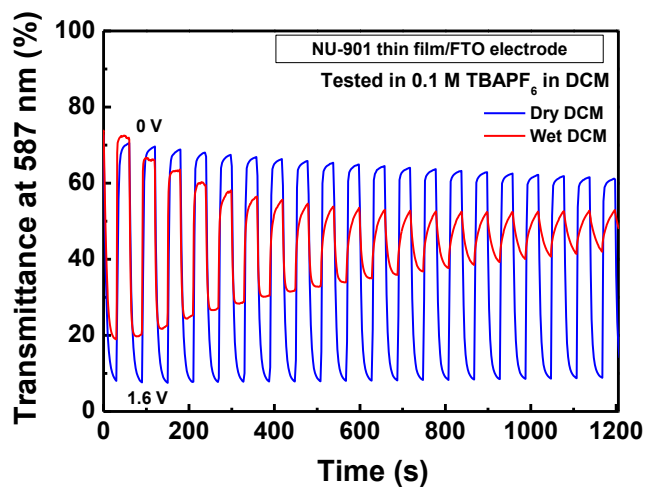


Figure S9. Optical transmittance kinetic curves of the **NU-901** thin film/FTO electrodes measured in 0.1 M TBAPF₆ in dry DCM and wet DCM.

S9. CV curve measured in the H₄TBAPy solution

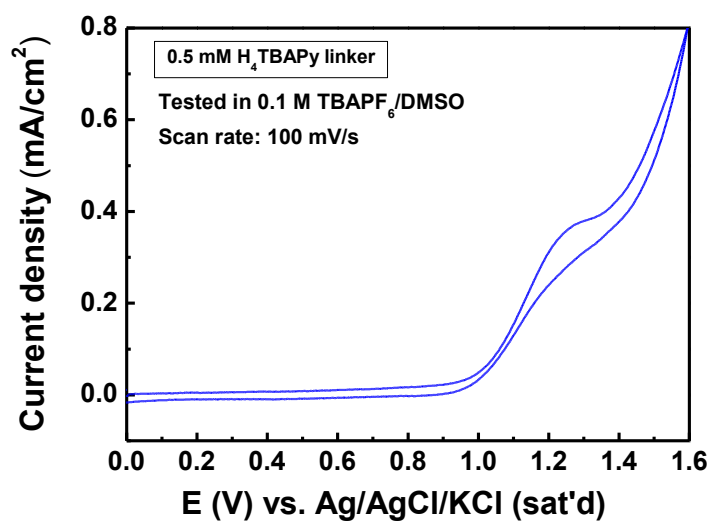


Figure S10. CV curve of the 0.5 mM H₄TBAPy ligand solution in DMSO.

Reference

- [S1] Mondloch, J. E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; Demarco, E. J.; Weston, M. H.; Sarjeant, A. A.; Nguyen, S. T.; Stair, P. C.; Snurr, R. Q.; Farha, O. K.; Hupp, J. T. *J. Am. Chem. Soc.* **2013**, *135*, 10294.
- [S2] Chua, Y. T.; Stair, P. C. *J. Catal.* **2003**, *213*, 39.