

Supporting Information

Electrochromic, Surface-Anchored Metal-Organic Frameworks for Stabilized Silver Nanowires Flexible Transparent Electrodes

*Antoine Mazel**, *Ambreen Khan*, *Stéphane Diring*, *Fabrice Odobel*, *Daniel Bellet*, *Aline Rougier**

All the SurMOFs synthesis, optical and electrochemical characterizations were performed at room temperature in air. Ethanol, DMF, isopropanol (analytical grade) and zinc acetate were purchased from Aldrich and used without further purification. LiTFSI(0.3 M)-EMITFSI was purchased from Solvionics. ITO/glass substrates with a resistance of 30 Ω /sq were purchased from Solems. Corning® glass (1.1 mm) was purchased from Delta Technologies, Limited, Loveland, CO, USA, which was used as substrates. AgNWs dispersed in isopropanol (23.6 g/L of concentration) obtained from Protavic® 28202, have an average length of 10 μ m and a diameter of 70 nm.

Deposition of AgNWs: AgNWs solution is first diluted up to a concentration of 0.23 g/L in isopropanol solvent and spray deposited on cleaned corning glass or PET substrate using an airbrush which moves in two directions. The spray deposition was performed at a temperature of

110 °C in order to facilitate the evaporation of isopropanol solvent. The resistance of the AgNW networks was controlled by measuring *in situ* resistance thanks to the monitor prepared by applying silver paste (L-200N, CDS electronics) to make two parallel contacts on a cleaned glass which is connected to the multimeter. The AgNW networks having an areal mass density (*amd*) of 70 mg/m² was used in this study. The average *amd* was calculated from ten SEM images using 'Ridge detection' plugin of imageJ.

Preparation of {Zn₂(PDICl₄)₂} SurMOFs: All the SurMOFs were fabricated by spray technique in a layer-by layer fashion on activated substrate. The substrates were subjected to UV/O₂ activation treatment for 15 min to remove impurities and generate a surface with hydroxyl groups. 1 mM zinc acetate ethanolic solution and 20 μM of PDICl₄ solutions (5% DMF + 95 % Ethanol) were sequentially deposited onto the substrates for 15 s and 25 s, respectively, in a layer-by-layer fashion. After waiting for 35 s to allow for further coordination, the samples were rinsed with ethanol after each cycle to remove unreacted or by-products from the surface. The thickness of the samples was controlled by the number of deposition cycles.

Characterizations and measurements: X-ray diffraction measurements were carried out using a PANalytical X'pert PRO MPD with Bragg-Brentano θ - 2θ geometry equipped with a secondary monochromator ($\lambda_{\text{K}\alpha\text{Cu}} = 1.5418 \text{ \AA}$) and an X'Celerator detector over an angular range of $2\theta = 3$ - 20° .

Electrochemical measurements were carried out in a three-electrode cell configuration using a BioLogic SP50 potentiostat/galvanostat apparatus and SurMOF on ITO/glass as the working electrode. The counter-electrode and reference electrode consisted of a platinum foil and Saturated

Calomel Electrode, SCE ($E(\text{SCE}) = 0.234 \text{ V/ENH}$). The operating voltage was controlled between $[-0.8 \text{ V}, 0.5 \text{ V}]$, at $20 \text{ mV}\cdot\text{s}^{-1}$ in a lithium-based electrolyte, namely 0.3 M lithium bis-trifluoromethanesulfonimide in 1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl)-imide (LiTFSI-EMITFSI).

Regarding the optical properties of the films, absorbance of the SurMOF was measured *in situ* using a Varian Cary 5000 UV-Vis-NIR spectrophotometer coupled with a BioLogic SP50 potentiostat/galvanostat apparatus in the same three-electrode cell configuration as electrochemical measurements. A home-made quartz cell was used to record the optical properties during electrochemical cycling.

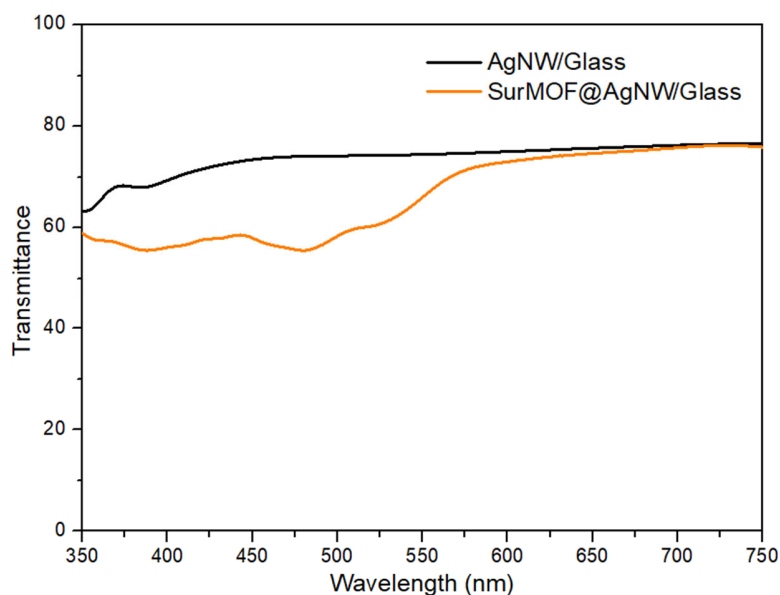


Figure S1. Transmittance spectra of AgNW/Glass and SurMOF@AgNW/Glass.

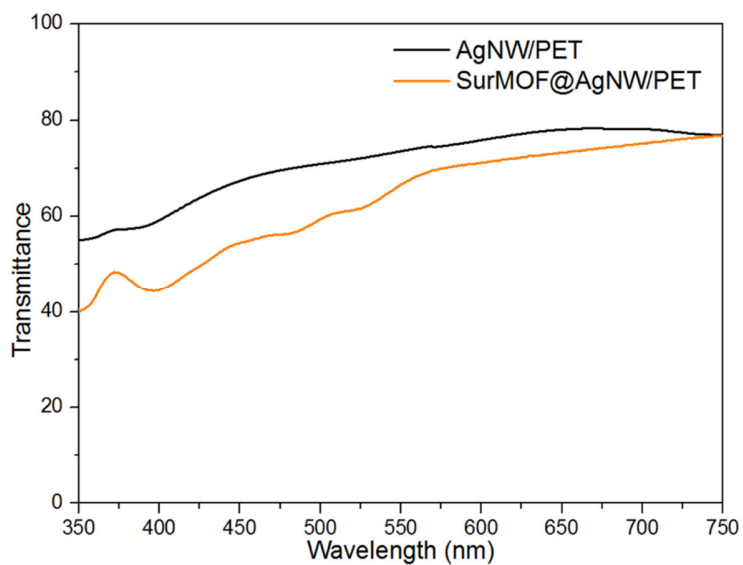


Figure S2. Transmittance spectra of AgNW/PET and SurMOF@AgNW/PET.

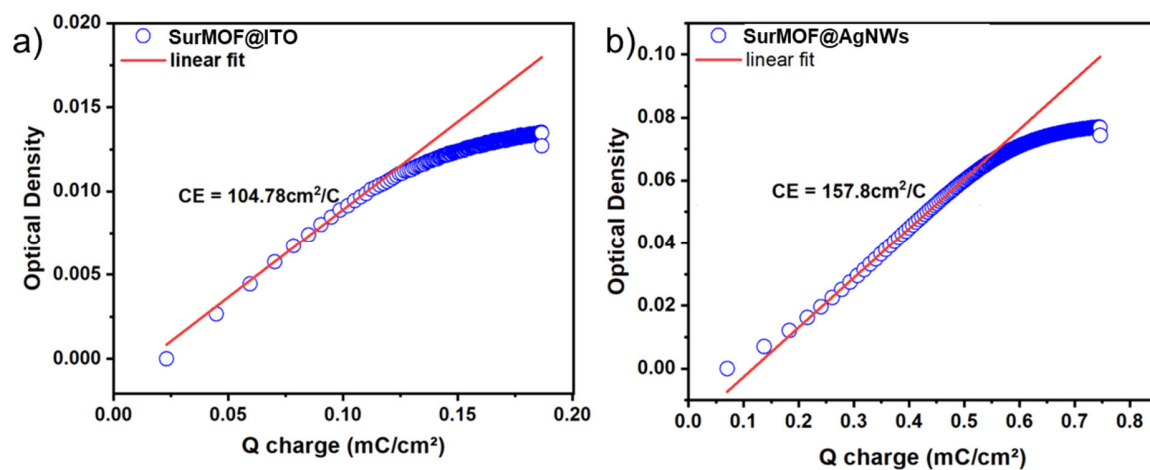


Figure S3. Color efficiency of a) SurMOF@ITO and b) SurMOF@AgNWs