Electrochromic 2,5-Dihydroxyterephthalic Acid Linker in Metal–Organic Frameworks

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Metal–organic frameworks (MOFs) are diverse in color owing to a large variety of molecular structures. Herein, electrochromism of M-MOF-74 (M = Mg, Mn, Co or Zn) is reported, which is a honeycomb nano-framework in which hexagonally packed 1D arrays of metal cations are coordinated with 2,5-dihydroxyterephthalic (dhtp) acid linker. Raman spectroscopy upon electrochemical doping combined with density functional theory calculations reveals redox reactions of the linker while the metal cations stay divalent as probed by X-ray photoemission spectroscopy (XPS). Excellent adhesion of the MOFs to glass allows the synthesis of quality thin films to be implemented into electrochromic devices that exhibit promising color contrast and durability.

1. Introduction

The electrochromic effect, that is material’s color change upon faradaic charge transfer, is known to occur in various inorganic (transition metal oxides), organic (molecules) and conducting polymers, and organic–inorganic hybrid materials (coordination polymers and metal complexes). Metal oxides are the most studied and they exhibit relatively high durability, but their synthesis requires expensive vacuum deposition systems. Organic or hybrid materials have the advantage of inexpensive production, but suffer from low stability and durability. In metal oxides and metal complexes, reversible electrical switching of the metal’s oxidation state accompanies color modulations.

Coordination polymers, known as metal–organic frameworks (MOFs), are naturally colorful owing to a variety of metal–ligand combinations available. Their open nanometric pores ensure effective doping as every active site can be accessed by electrolyte molecules with minimal structural deformation. This is principally advantageous as electrochromic materials. However, more extensive and detailed electrochemical studies of MOFs will be required to determine the applicability of MOFs as electrochromic materials. To date, several electrochromic MOFs were tailored based on known electrochromic molecules such as naphthalene diimide as linkers that function as chromophores in the framework.

Generally, the fact that many MOFs change their color reversibly upon solvent exchange or sorption of various molecules suggests their potential as electrochromic materials, specifically those having open-metal sites that can capture ions or molecules. Electrochromic effects reported on MOFs with non-electrochromic linkers support the importance of the role of metal ions. 2D coordination nanosheets (CONASH) with iron or cobalt were synthesized to exhibit electrochromic effects that were attributed to the redox reaction of iron or cobalt as in bis(terpyridine)iron or bis(terpyridine)cobalt complex wires. MOF-74, also known as CPO-27, M2(dhtp), or M2(dobdc), where M is divalent Mg, Mn, Fe, Co, Ni, or Zn, and dhtp (or dobdc) is tetravalent 2,5-dihydroxyterephthalic acid, (2,5-dioxido-1,4-benzenedicarboxylate), is a family of MOFs that was extensively studied for gas sorption as the densely packed open metal sites are expected to interact effectively with gaseous molecules. Among them, Zn-MOF-74 was reported to be electrochromic, but no mechanism for this effect was suggested. Co-MOF-74 is reportedly redox-active as an anode material for lithium-ion batteries. Stoichiometric oxidation of Mn-MOF-74 was demonstrated by chlorination of manganese cations with a mild oxidation agent, iodobenzene dichloride (PhICl2), as well as by fluorination and doping with tetracyanoquinodimethane (TCNQ). In the present work, we synthesize high-quality thin films of M-MOF-74 (M = Mg, Mn, Co, or Zn) directly on fluorine-doped tin oxide (FTO)-coated glass plates. We demonstrate that the color of all these films changes from ochre to brown upon cathodic electrochemical doping. The electrochromism observed universally for this family of MOFs with the least to the most redox-active transition metals suggests that the linker is redox-active. Among them, Mn-MOF-74 with the redox-active Mn⁴⁺ is the best-suited material for a deeper study in which the origin of the redox reaction can be identified. In situ Raman
spectroelectrochemistry on Mn-MOF-74 reveals a redox reaction of the dhtp linker as the cause of the electrochromism, which is in line with the divalent Mn state unchanged upon solid-state doping as probed by X-ray photoemission spectroscopy (XPS). The strong C=O stretching mode of the dhtp emerging upon doping is reproduced by density functional theory calculations on a model doped dhtp system. Finally, the scalable synthesis method utilizing excellent adhesion of the MOFs on FTO-coated glass plates allows fabrication of cathodic electrochromic devices with high durability and color contrast as demonstrated with Mn-MOF-74.

2. Results and Discussion

Cyclic voltammetry of the M-MOF-74 (M = Mg, Mn, Co or Zn) thin films prepared on FTO-coated glass is performed in 0.2 M LiClO$_4$ acetonitrile (MeCN) electrolyte solution in the homemade electrochemical cell, as shown in Figure 1. It is shown that the color of M-MOF-74 thin films on the FTO-coated glass turns dark upon electrochemical doping with positive biasing as excess ClO$_4^-$ anions neutralize the charge of the M-MOF-74 working electrode. The same color change has also been observed with other electrolyte solutions such as KCl in water and 1 M of 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM – BF$_4$) in MeCN (see Section 5, Supporting Information). The corresponding cyclic voltammogram at a scan rate of 0.1 V s$^{-1}$ in the bias range between −0.2 and 1.0 eV exhibits reproducibly broad redox peaks coinciding with the color change.

Figure 2 shows that the peak current versus square root of the scan rate follows a linear function, demonstrating that the redox process is purely diffusion-controlled. From the fit to Randles–Sevcik equation, we get a diffusion coefficient of
The specific capacity estimated from the 0.01 V s\(^{-1}\) data reaches 29 C g\(^{-1}\) or 8.0 mAh g\(^{-1}\) corresponding to 0.095 e per M2(dhtp) (see Figure S2, Supporting Information). Spectroelectrochemistry is a powerful tool for elucidating the nature of electrochromism.\(^{(40)}\) The optical absorption spectra of the Mn-MOF-74 film upon electrochemical doping are plotted in Figure 2c. The color change can be associated with the optical absorption peak at 490 nm emerging upon positive biasing. The contrast ratio, defined as the absorption intensity integrated over the visible range (380–780 nm) at each measured potential normalized by that at zero potential.

\[ \text{Contrast ratio} = \frac{\text{Absorption intensity at each potential}}{\text{Absorption intensity at zero potential}} \]

Further information on the charge state of the framework is gained from Raman spectroelectrochemistry. Figure 3a shows...
the Raman spectra of the Mn-MOF-74 film measured at a laser wavelength of 514.5 nm upon positive biasing in 0.2 M LiClO4 MeCN electrolyte solution. The spectra at potentials up to 0.4 V exhibit multiple spectral features including three prominent peaks at Raman frequencies of 560, 1284, 1403 cm⁻¹, indicated by the dashed black lines, associated with the C=H bending of the benzene ring, C=O stretching, and O–C–O symmetric stretching modes of the dhtp⁺⁻ ligand, respectively, where δ₀(tentatively 4) denotes the valency of the dhtp in non-doped Mn-MOF-74. Upon biasing at higher voltages, all three peaks diminish and multiple new peaks emerge at frequencies highlighted by the dashed red lines. The most prominent peak located at 1625 cm⁻¹ was previously observed upon oxidation of the Mn-MOF-74 by fluorination as well as by doping with TCNQ, and can be associated with the ring C=O stretching mode of the divalent dhtp⁻⁻ ligand, meaning that the framework’s linker is stoichiometrically doped. This is also in agreement with the previously reported IR stretching mode of carbonyl group observed in chlorinated Mn-MOF-74.

Here, further insight into the charge state of the doped dhtp can be given by density functional theory calculations. Despite the use of the local density approximation, an agreement between experiment and theory is satisfactory for judging the stoichiometric valency. As calculations of phonon modes of M-MOF-74, whose unit cell contains 164 atoms, are not feasible, we model a compact system with a dhtp sandwiched by two tetra-fluoroborate (BF₄⁻) anions (see the optimized structure in Figure S10, Supporting Information). The charge state of the dhtp estimated by the Bader analysis is +1.46. This corresponds to δ = 2.5 or dhtp¹.₅⁺ for the dhtp unit without four hydrogens as in the Mn-MOF-74. Figure 3b shows the Raman lines of this [dhtp]¹.₅⁺[2BF₄]¹.₅⁻. The most prominent mode located at 1653 cm⁻¹ is in line with the emerging ring C = O peak of the dhtp linker upon electrochemical doping. This supports the divalent dhtp, i.e., δ = 2, as claimed previously in the doped Mn-MOF-74 materials.

Observing the oxidation state of manganese upon electrochemical doping is challenging, but the electrochemically doped state of the Mn-MOF-74 can also be sustained to some extent by fast-drying the MOF film immediately after positive biasing in 0.2 M LiClO₄ MeCN electrolyte solution. Figure 4a shows the Raman spectrum of the Mn-MOF-74 film that was biased at 0.4 V, then taken out and dried in air. As compared with the spectrum of the non-doped Mn-MOF-74 film, the peak emerging at a frequency of 1611 cm⁻¹ indicated by the dashed red line is consistent with the C=O stretching mode of the dhtp⁺⁺ observed upon electrochemical doping in Figure 3, meaning that the dried films are still dominantly doped with ClO₄⁻ anion.

These doped solid films allow XPS analysis of the oxidation state of the manganese ion in the framework. Figure 4b shows the Mn 3s spectra for the doped and non-doped Mn-MOF-74 films. Binding energies were referenced to the lowest binding energy C 1s peak assigned to 285.0 eV. The difference in binding energy between the resolved two 3s peaks, 7S and 5S, located at binding energies of ≈ 84 and 90 eV, respectively, originate from the exchange coupling between the 3s core hole and the 3d electrons in the photoemission final state. This exchange splitting energy is known to decrease proportionally as the valence number of manganese increases. Despite the difference in doping level, the exchange splitting energy for both samples is ≈ 6 eV, indicating that the oxidation state of manganese stays divalent, i.e., Mn²⁺.

Figure 4c shows the Mn 2p spectra of the doped and non-doped Mn-MOF-74 exhibiting the Mn 2p₃/₂ major peak located at 641.7 eV and the shake-up satellite at 646.3 eV, both typical for Mn²⁺. These XPS results are in line with the previously reported effective magnetic moment corresponding to a half-filled Mn²⁺ state unchanged upon chlorination of Mn-MOF-74. For further details, see Section 6, Supporting Information.

Here, the combined Raman and XPS analysis has revealed that the redox reaction of the dhtp linker is responsible for the color change of the framework upon positive electrochemical doping.

Finally, toward optoelectronic applications, a Mn-MOF-74 film synthesized onto an FTO-coated glass is encapsulated in an electrochromic device together with 0.2 M LiClO₄ MeCN electrolyte solution, see Figure 5. The color of the MOF device changes reversibly upon alternating positive and negative biasing, see the pictures of the device being biased at −3 and 5 V in Figure 5 as well as a video in the SI. The corresponding chronocamperogram in Figure 5 exhibits its performance sustained over 100 cycles. The device reaches a charge of ≈ 9 mC upon biasing at 5 V for 10 s and −8 mC at −3 V for 10 s, which are...
Figure 4. a) Raman, b) Mn 3s photoemission, and c) Mn 2p photoemission spectra of Mn-MOF-74 and doped Mn-MOF-74 (the Mn-MOF-74 film that was biased at 0.4 V, then taken out and dried in air). The overlapping photoemission spectral features were resolved into individual peaks using the damped nonlinear least squares method after subtraction of Shirley’s background using Gaussian–Lorentzian line shape.

Figure 5. a) A diagram of the electrochromic device. Layer 1 on which an MOF film is deposited on, and layers 2 and 3 are glued together encapsulating an electrolyte. b) Mn-MOF-74-based electrochromic device encapsulating 0.2 M LiClO₄ MeCN electrolyte solution biased at −3 V. The scale bar is 10 mm. c) Mn-MOF-74-based electrochromic device encapsulating 0.2 M LiClO₄ MeCN electrolyte solution biased at +5 V. The scale bar is 10 mm. d) The inset shows the chronoamperogram upon bias switching between −3 and 5 V at 95–100 cycles. The corresponding maximum charge accumulated in the device upon biasing at −3 and 5 V for 10 s. e) Cyclic voltammogram of the Mn-MOF-74-based electrochromic device at a scan rate of 0.1 V s⁻¹ in the bias range between −3 and 5 V.
reduced to 52% and 53%, respectively, after 100 cycles, yet the electrochromic effect is sustainable for further cycling.

3. Conclusion

Electrochemical doping is a powerful technique to alter the physical properties of solid states. We have demonstrated that the M-MOF-74 (M = Mg, Mn, Co, or Zn) thin films synthesized directly on the transparent electrode exhibit electrochromism that originates from the redox reaction of 2,5-dihydroxyterephthalic acid like while the metal oxidation state stays divalent. The electrochromic device fabricated based on the Mn-MOF-74 thin film has shown its promising performance and stability. Provided that all densely packed redox-active sites are principally accessible throughout the nano-framework of a large volume, electrochromic MOFs of a large variety could serve as viable alternatives to some of the common electrochromic materials.

4. Experimental Section

Sample Preparation: M-MOF-74 crystals were synthesized at room temperature (M = Mg, Mn, Co, and Zn) by mixing two precursor components, 20 μmol of M(II) acetate tetrahydrate in 4 mL of methanol, and 10 μmol of 2,5-dihydroxyterephthalic acid (dhtp), also called 2,5-dihydroxy-1,4-benzenedicarboxylic acid (dobdc), in 4 mL of N,N-dimethylformamide (DMF) or methanol. Crystals that slowly precipitated and fell on the bottom of the glass vial overnight were extracted by decantation and rinsed with toluene or MeCN.

M-MOF-74 (M = Mg, Mn, Co, and Zn) thin films were synthesized on FTO-coated glass plates (10 mm × 20 mm × 2 mm) as follows. An FTO-coated glass was placed in a 5 mL glass vial in which 1.5 mL of the DMF or methanol solution of dhtp and 1.5 mL of the methanol solution of metal acetate were poured one after the other and mixed by shaking. Once a thin film was formed on the glass after a day, the glass plate was taken out and rinsed with and stored in toluene or MeCN. The solvents were exchanged by decantation several times before measurements.

It is noteworthy that the adhesion of M-MOF-74 (M = Mg, Mn, Co, and Zn) on the FTO-coated glass is in the order of Mg, Mn, Co, and Zn, making the M-MOF-74 (M = Mg and Mn) perfect candidate as electrochromic device elements. According to the literature, the standard enthalpies of metal(II) monooxides, MgO, MnO, CoO, and ZnO are −602, −385, −238, and −348 kJ mol⁻¹, respectively. Although not perfectly in line with the order of good adhesion, considering there are other oxides especially of Mn and Co that tend to have larger negative enthalpies, the metal-dependent adhesion of M-MOF-74 on glass could be attributed to the enthalpy of formation of metal oxides. For a more detailed study on the film deposition, see Section 1, Supporting Information.

Electrochemistry: Electrochemical measurements were performed with an M-MOF-74 thin film on an FTO-coated glass plate as a working electrode, silver wire as a reference electrode, and platinum as a counterelectrode in MeCN. The solvents were exchanged by decantation several times before measurements.

Solid-State Doping: A Mn-MOF-74 film on an FTO-coated glass plate was biased at 0.4 V in 0.2 M Li⁺[ClO₄⁻] in MeCN or at 1 V in 1 M [BMIM]⁺[BF₄]⁻ ionic liquid in MeCN.

XPS and Raman spectroscopy analysis: A diagram of the electrochromic device fabricated is depicted in Figure 5. 1 M [BMIM]⁺[BF₄]⁻ ionic liquid in MeCN or 0.2 M Li⁺[ClO₄⁻] in MeCN was sealed in between a Mn-MOF-74 film on an FTO-coated glass plate as a working electrode and another FTO-coated glass plate as a counter electrode by using a film of thermoplastic resin (DuPont, Surlyn) as a sealant, or a film of PET as a spacer glued by a UV curable resin.

XPS: A Mn-MOF-74 film, LiClO₄-doped Mn-MOF-74 film, and [BMIM]⁺[BF₄]⁻-doped Mn-MOF-74 film on FTO-coated glass plates were measured by means of XPS. The XPS data were recorded at room temperature with a modified ESCA3 MkII (VG Scientific, UK) electron spectrometer equipped with a hemispherical electron analyzer operated at a pass energy of 20 eV and an Al Kα radiation source. The energy resolution, given as the full width at half maximum (FWHM) of Au 4f/2, was 1.2 eV. The binding energy scale was calibrated using Au 4f/2 (84.0 eV) and Cu2p1/2 (932.6 eV) photoemission lines. The electron detection angle was 45° with respect to the macroscopic sample surface. The pressure of residual gases in the analyzer chamber during spectra acquisition was 5 × 10⁻¹⁰ mbar.

Density Functional Theory: Structure optimizations were carried out using Quantum ESPRESSO, an open-source plane-wave periodic density functional theory code, with local density approximations (LDA) to exchange-correlation energy within norm-conserving pseudopotentials. Phonon calculations were performed based on the density functional perturbation theory.

Electronic charges on individual atoms in doped dhtps were calculated based on the Bader partitioning scheme by using CPAW code which is based on the projector-augmented wave (PAW) method and the atomic simulation environment (ASE). A grid spacing of h = 0.25 Å was used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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