

Solvent-Induced Galvanoluminescence of Metal–Organic Framework Electroluminescent Diodes

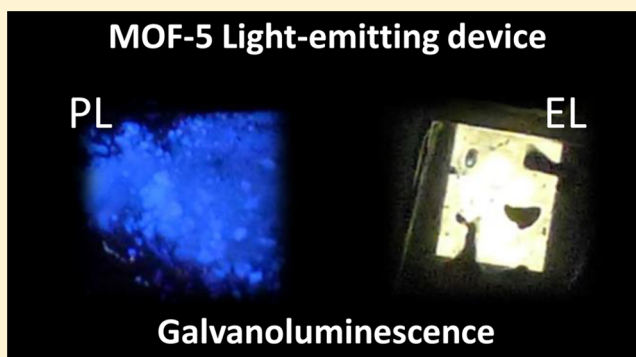
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ABSTRACT: Alternating current (AC) electroluminescent diodes were fabricated from MOF-5, a metal organic framework consisting of tetrahedral $[\text{Zn}_4\text{O}]^{6+}$ units linked by 1,4-benzenedicarboxylate ligands. An additional insulating layer was incorporated to prevent formation of electrical shorts. The electroluminescence spectrum was dramatically red-shifted with respect to the photoluminescence spectrum. By deliberately varying trapped solvent molecules, we demonstrate that the light emission does not originate from MOF-5 but is due to galvanoluminescence, emission of weak optical radiation in the visible region that occurs during anodic oxidation of the Al top electrode in contact with electrolytes.



INTRODUCTION

Metal organic frameworks (MOFs) are compounds consisting of metal ions or clusters that are joined by organic linkers into one-, two-, or three-dimensional coordination networks.¹ MOFs are insoluble, crystalline, and porous compounds. The porosity can be controlled by the size of the linker.² Hence, MOFs are being investigated to store gases, as a membrane for gas separation, and as catalyst for chemical reactions.³ In contrast, application of MOFs in electro-optical devices has hardly been reported.^{4,5} The electrical conductivity of MOFs is typically very small. Most MOFs are insulators. However, electrically conducting MOFs have been reported.^{4,6–9} Photoluminescent properties of MOFs are well-documented.¹⁰ Depending on their chemical composition, MOFs can exhibit strong photoluminescence with relatively high quantum efficiencies.⁹ Because of versatility in their chemical structures, there is a large library of luminescent MOFs.

A major bottleneck in realization of MOF-based electronic devices is fabrication of smooth, pinhole-free MOF thin films.¹¹ Conventional techniques such as spin-coating cannot be used as MOFs are insoluble compounds, and deposition by thermal evaporation or sputtering jeopardizes the structural integrity of the MOF. Inhomogeneous films can be made by doctor blade or screen printing a paste of the insoluble MOF in high boiling point solvents. However, the presence of pinholes in the film inevitably leads to electrical shorts on evaporation of the top electrode.

Despite the experimental hurdles, there are only a few reports on light-emitting diodes.^{12–15} It has been claimed that MOF based electroluminescent alternating current (AC) diodes can be fabricated. A light-emitting MOF-5¹⁶ AC-diode

was demonstrated in 2007.⁷ The emission mechanism and the nature of processes involved are still not understood. For instance, it has been mentioned that the presence of a solvent is highly beneficial for the luminescence efficiency. The emission intensity is considerably reduced, or even disappears, upon complete drying of the sample.⁶

Here, we reveal the origin of the emission in MOF-5 electroluminescent diodes. We circumvent the low-yield problem by fabricating AC electroluminescent diodes. To this end, an MOF-5 film is stacked together with a pinhole-free, insulating top layer that prevents the formation of electrical shorts. When sandwiched between two electrodes, a capacitor is formed. Application of an AC bias leads to a time-varying electric field. Charges in the film are accelerated, and impact ionization of luminescent centers can lead to light emission, as well documented for commercially available AC electroluminescent diodes, wherein typically ZnS particles are used as luminescent centers.^{17–20} AC electroluminescence was detected from the MOF-5 diodes, with a spectrum that was substantially red-shifted with respect to the photoluminescence spectrum. We demonstrate that the light emission is extrinsic, and thus not from MOF-5, and is due to galvanoluminescence, which is emission of weak optical radiation in the visible region that occurs during anodic oxidation of the Al electrode in contact with electrolytes.

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RESULTS AND DISCUSSION

MOF-5, an abbreviation for $\text{Zn}_4\text{O}(\text{bdc})_3$, consists of tetrahedral $[\text{Zn}_4\text{O}]^{6+}$ units bridged by 1,4-benzenedicarboxylate (bdc) ligands and was synthesized following a reported literature procedure.^{21,22} Under a protective N_2 atmosphere, 100 mL of a 0.03 M solution of terephthalic acid in *N,N*-diethylformamide (DEF) was dropwise added to an equal volume of a 0.01 M solution of basic zinc acetate solution in DEF. The zinc acetate solution was stirred and heated to 100 °C before addition of terephthalic acid. The separation of the precipitated MOF-5 was carried out immediately after completion of the addition using a Schlenk frit. The collected powder was dried in vacuum and was stored in sealed vials.

The schematic crystal structure of MOF-5 is given in Figure 1a. The scanning electron microscopy (SEM) micrograph

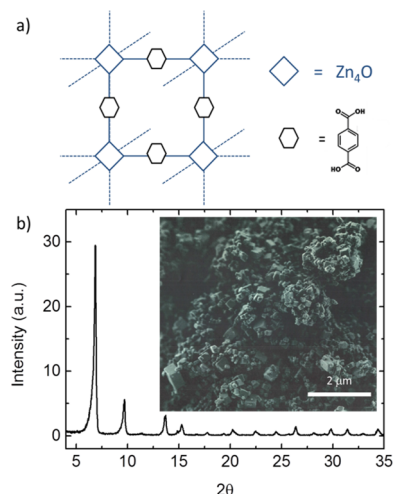


Figure 1. (a) Schematic crystal structure of the metal–organic framework MOF-5 mapped on two dimensions. MOF-5, an abbreviation for $\text{Zn}_4\text{O}(\text{bdc})_3$, consists of tetrahedral $[\text{Zn}_4\text{O}]^{6+}$ units bridged by 1,4-benzenedicarboxylate (bdc) ligands (b) Bragg–Brentano XRD diffractogram of MOF-5 powder. The inset shows an SEM micrograph.

presented in the inset of Figure 1b shows that the MOF powder consists of cubic particles of typically a few hundred cubic nanometers. The particles are highly crystalline as confirmed by the X-ray diffraction (XRD) diffractogram presented in Figure 1. The cubic crystals were confirmed to be MOF-5 by the coincidence of the XRD pattern with the reported literature diffraction patterns. MOF-5 crystallizes in a cubic unit cell with lattice constant of 2.577 nm, comparable to the values reported in the literature.²¹

To fabricate an AC diode, first a dielectric layer with a high dielectric constant and preferably transparency to optical wavelength is required. The dielectric constant should be constant over the operational frequency range of the AC-diode. Among polymers, the random copolymer of vinylidene fluoride with trifluoroethylene (P(VDF-TrFE)) has a relatively high dielectric constant of 15 at room temperature that is almost frequency independent up to 10 kHz. The high dielectric constant allows for the confinement of the electric field over the light-emitting layer.²³ P(VDF-TrFE) is transparent to optical frequencies which in combination with high dielectric constant renders it a suitable dielectric material for MOF electro-luminescent AC-diode. Typically, 2–5 μm of an insulating film of P(VDF-TrFE) was spin coated from a solution in

methylethylketon (MEK) on top of the indium tin oxide (ITO) electrodes. Subsequently, a paste was made from the MOF-5 powder in dimethylformamide (DMF) or terpineol. Thick films were screen printed on the P(VDF-TrFE) coated ITO substrates and subsequently were dried at 100 °C on a hot plate. The MOF-5 film thickness was typically between 5 and 15 μm. The AC diode was finished by evaporating an Al top electrode through a shadow mask or by placing an Al foil as the counter electrode.

The layout of the diode and the measurement setup are schematically depicted in Figure 2. An alternating triangular

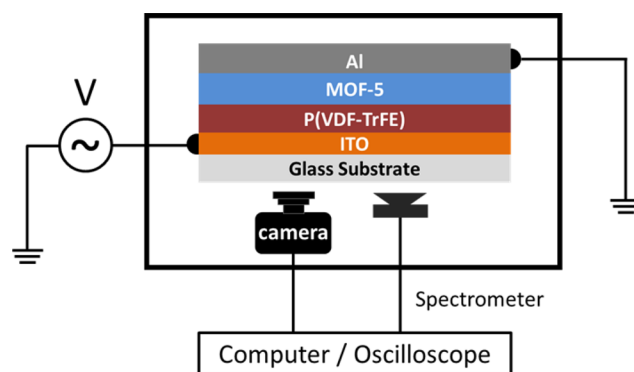


Figure 2. Schematic layout of the light-emitting AC-diode and the measurement setup. A variable voltage of 0–400 V_{pp} is applied. Current transients are measured using a series resistor and a computer-controlled digital oscilloscope. A photodiode and a spectrometer are used to detect the light and its electroluminescence spectra, respectively. A digital camera was mounted on top to visually record the light. The measurements were carried out in a sealed, dark steel box.

voltage of 0–400 V_{pp} (peak-to-peak value) at different frequencies was applied to the ITO electrode. Current response of the diode was recorded by measuring the voltage drop over a reference resistor. Simultaneously, intensity of the light emission was measured with a Si-photo diode. The spectrum was captured using a spectrometer. A digital camera was mounted on top to record visual light emitted from the electroluminescent (EL)-device. All measurements were carried out in a sealed steel box.

The photoluminescence spectrum of MOF-5 powder as measured upon excitation with UV light of 248 nm is presented by the blue line in Figure 3. The spectrometer was not calibrated which might explain the cut off below 400 nm. However, the shape of the spectrum is similar to those reported in the literature for MOF-5 showing peak positions between 400 and 420 nm. The variation in peak position might be due to differences in water content.^{24,25} An optical micrograph showing the bluish emission is presented as an inset in Figure 3.

The MOF-5 diodes showed weak electroluminescence when driven by an AC bias. The light was not visible to the naked eye. The photoluminescence spectrum and optical photographs could only be obtained using an integration time of a few minutes, leading to the conclusion that the quantum efficiency is well below 0.1%. The spectrum is presented by the red line in Figure 3. The shape of the spectrum does not depend on frequency that was varied between 10 Hz and 1 kHz. An optical micrograph of the light-emitting MOF-5 diode showing a yellowish light is presented in the inset.

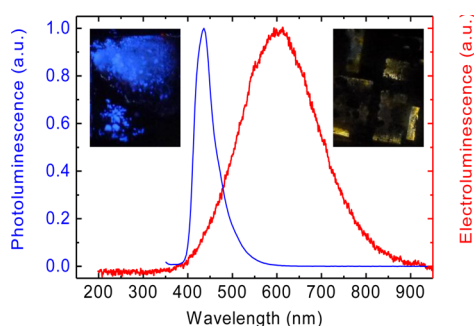


Figure 3. Photoluminescence spectrum of MOF-5 powder (blue line) and AC electroluminescence spectrum of MOF-5 diode (red line). The AC diode was driven at 100 Hz with 200 V_{pp} bias. The left inset shows an optical micrograph of the photoluminescence of the powder under 248 nm UV excitation. The right inset shows an optical micrograph of the light-emitting MOF-5 diode.

The electroluminescence spectrum is dramatically red-shifted with respect to the photoluminescence spectrum. MOF-5 is a porous compound that might trap solvent molecules. To investigate if the red-shifted electroluminescence could be related to trapped solvents, diodes were fabricated by deliberately drying the MOF-5 film for 2 h at 110 °C in vacuum. AC-diodes were finished by depositing a top Al electrode. No electroluminescence was observed for such diodes consisting of a vacuum-dried MOF-5 layer. We note that the drying condition as mentioned earlier might be mild. Furthermore, we note that electrical measurements on MOF device (prepared without any drying step) were performed under high vacuum of typically 10^{−6} mbar. Such high vacuums can remove any traces of solvent molecules. Again, there was no light emission from MOF-5 device. To unambiguously confirm that the solvent molecules play a crucial role, subsequently different solvents were sprayed onto the diodes composed of the vacuum-dried MOF-5 films. All wetted diodes showed again AC-electroluminescence. The spectra are presented in Figure 4.

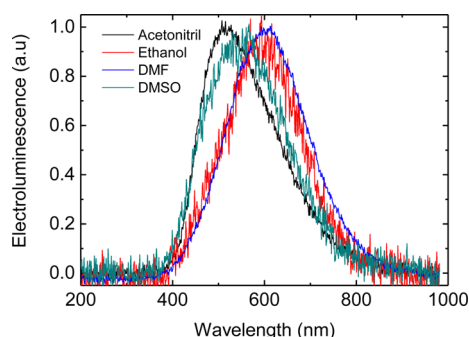


Figure 4. Electroluminescence spectra of wetted MOF-5 AC diodes. Spectra were recorded under excitation of AC bias 200 V_{pp} at 100 Hz. Solvents used are acetonitrile, ethanol, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).

For all solvents used, a similar red-shifted spectrum as in Figure 3 is obtained. Hence, the electroluminescence is observed only when the solvent molecules are present. Importantly, however, the electroluminescence is not related to the presence of MOF-5 as the photoluminescence spectrum of MOF-5 does not change upon drying or subsequent wetting.

To pinpoint the origin of the electroluminescence, we fabricated solvent-only diodes. MOF-5 was deliberately left out.

A pool of solvent was deposited on an Al-foil, and an ITO-coated glass was put upside down on top of it. A weak electroluminescence was obtained under AC bias. The spectrum is presented in Figure 5. For comparison, the

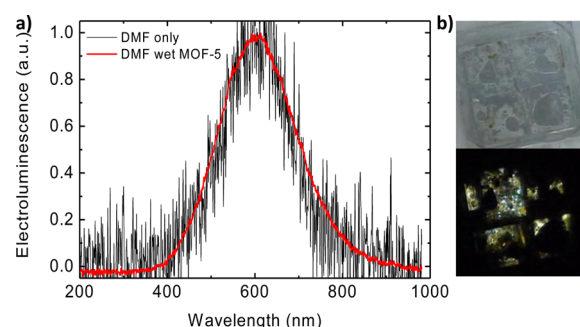


Figure 5. (a) Electroluminescence spectrum of a DMF solvent-only diode (black line). For comparison, the electroluminescence spectrum of an MOF-5 diode wetted with DMF is included as well. (b) Photographs of a fabricated DMF solvent-only diode (top) and an optical micrograph of light-emitting DMF solvent-only AC diode (bottom).

spectrum of an MOF-5 diode wetted in the same solvent, DMF, is included as well. The spectra are identical. The solvents used for the diode do not show any photoluminescence in the visible range. The emitted light therefore does not originate from the solvent. It is only obtained when using Al as an electrical contact. AC diodes with two identical ITO electrodes do not show any emission. Hence, the observed light emission can be ascribed to galvanoluminescence, a weak visible emission that is obtained during anodic oxidation of Al.^{26,27} Typically, a broad peak at around 600 nm is obtained.²⁸ Details of the spectra depend on the type of electrolyte.

CONCLUSIONS

In summary, AC electroluminescent diodes were fabricated using the MOF-5 as the active light-emitting compound. The MOF-5 diodes showed very weak electroluminescence when driven by an AC bias with quantum efficiency well below 0.1%. The electroluminescence, however, is not related to the presence of MOF-5, but is due to solvent-induced galvanoluminescence of Al electrode. As Al is a commonly used electrode in electro-optical devices, interpretation of the emission spectrum is not unambiguous, especially when using porous materials that can entrap solvents.

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Notes

The authors declare no competing financial interests.

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