

# Conduction and Photoconduction in Fullerene- and Porphyrin-Containing Metal-Organic Framework Thin Films

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Photoconductivity is a characteristic property of semi-conductors, enabling various applications such as photoresponsive transistors and light-sensing. Some crystalline metal-organic framework, MOF, composed of functional organic components show interesting photoconduction properties. Here, we compare the light-responsive conductivity of four different MOF thin films with similar structure, but different compositions, possessing C<sub>60</sub> fullerene and porphyrin or phenyl moieties. The results show that the embedment of fullerene, as well-known n-conducting component, increases the conductivity but shows little photo-response. While the total conductivity values are small, the conduction in the porphyrin sample shows noticeable photo-response, in particular when exciting the Soret band with blue light. Taking advantage of donor-acceptor interactions, the combination of C<sub>60</sub> and porphyrin in close proximity of the MOF structure, results in thin films with strong photo-response and conductivities increased by 2 orders of magnitude upon blue light irradiation.

## Introduction

Metal-organic frameworks, MOFs, are nanoporous crystalline materials composed of metal nodes connected by multi-topic organic linker molecules.<sup>1-2</sup> In recent years, the electrical and electronic properties of MOFs have attracted substantial attention.<sup>3-5</sup> Taking advantage of the huge chemical diversity of MOFs, with more than 70.000 published structures,<sup>6</sup> various MOF applications have been explored, like in electrocatalysis<sup>7</sup>, as field effect transistor<sup>8</sup> and in energy-storage<sup>9</sup>. The conductivity of the MOF material can be tremendously increased by loading with molecules like ferrocene,<sup>5</sup> TCNQ,<sup>4</sup> or C<sub>60</sub> fullerene, being attractive charge acceptors.<sup>10-11</sup> MOFs with porphyrin moieties allow semi-conductor light-harvesting applications in photovoltaic<sup>12</sup> devices and for photocatalysis.<sup>13</sup> These applications take advantage of the electron-donor properties of porphyrins.<sup>14</sup> Combining porphyrin with fullerene results in electron donor-acceptor pairs.<sup>15-16</sup> The light-induced electron transfer in such dyads was investigated in solution,<sup>15</sup> and it was demonstrated that materials of such molecules are suitable for applications like organic solar cells.<sup>17-18</sup> The immobilization of the porphyrin and fullerene in the crystalline MOF scaffold allows crystalline donor-acceptor networks.<sup>19</sup>

For directly measuring the photocurrent, but also for device applications like in photo-sensors, the MOF material must be provided in the form of thin films. Therefore,

we use surface-mounted MOF thin films, SURMOFs,<sup>20</sup> grown on suitably functionalized substrates. By using interdigitated bottom electrodes, electrical properties of empty and loaded SURMOFs can be measured in a straightforward and reproducible fashion.

Here, the conduction and photoresponse of four different SURMOFs with similar structures, referred to as SURMOF-2-structure, are investigated: SURMOFs fabricated from phenyl-based linkers, referred to as Cu(BPDC), showed no response to light illumination, even after incorporation of fullerenes, resulting in C<sub>60</sub>@Cu(BPDC). On the other hand, SURMOFs containing porphyrin moieties, referred to as Zn(TPP) (TPP = 5,15-bis-(3,4,5-trimethoxyphenyl)-10,20-bis-(4-carboxyphenyl) porphyrinato zinc(II)), show strong photoconduction properties. The conductivity significantly increased when embedding C<sub>60</sub> molecules in the nanopores of these highly oriented SURMOFs, yielding C<sub>60</sub>@Zn(TPP). Remarkably, these MOF thin films presented pronounced photoconduction features and the electrical conductivity increased by 2 orders of magnitude when irradiated with blue light.

## Experimental

The SURMOF films were synthesized in a layer-by-layer fashion.<sup>20-21</sup> All four SURMOF samples were prepared in the same way, using the spin-coating method.<sup>22</sup> In detail, the SURMOFs were Cu(BPDC), based on biphenyl-4,4'-dicarboxylate containing no fullerene or porphyrin moieties, C<sub>60</sub>@Cu(BPDC) containing fullerene, Zn(TPP) where TPP stands for 5,15-bis-(3,4,5-trimethoxyphenyl)-10,20-bis-(4-carboxyphenyl) porphyrinato zinc(II) containing porphyrin and C<sub>60</sub>@Zn(TPP) containing fullerene and porphyrin. Briefly, the metal node solution (Zn or Cu acetate) and the linker solution (BPDC = biphenyl-4,4'-dicarboxylic acid or 5,15-bis-(3,4,5-trimethoxyphenyl)-10,20-bis-(4-carboxyphenyl)porphyrinato zinc(II) = TPP) were alternately dropped on the rotating substrate with spin speed of 1500 rpm. In between, the substrates were rinsed with ethanol. In detail, Cu(BPDC) was prepared from Cu-acetate and BPDC. C<sub>60</sub>@Cu(BPDC) were prepared similar to Cu(BPDC) but with an addition C<sub>60</sub> step. This means the following spin procedure was employed: Cu acetate, ethanol, BPDC, ethanol, C<sub>60</sub> solution and ethanol. All time steps were 20s. Zn(TPP) was prepared from Zn-acetate and TPP and C<sub>60</sub>@Zn(TPP) were prepared similar to Zn(TPP) but with an additional C<sub>60</sub> step. The samples were prepared on glass substrates on which interdigitated gold electrodes (IDE) had been deposited. The IDE substrates with a total electrode gap length of 3.38 m and a gap width of 5 μm were obtained from DropSens. Prior to SURMOF synthesis, substrate functionalization was carried out by UV-ozone treatment for 30 min. The samples were characterized by X-ray diffraction, infrared and UV-vis spectroscopy as well as chromatography, verifying the composition and targeted structure, see ref.<sup>19</sup>

The conduction of the sample in a pure argon atmosphere was measured with a Keithley 2635B Sourcemeater. The light irradiation was performed with LEDs from PrizMatix, with emission maxima at 365 nm, 400 nm, 455 nm, 530 nm, and 640 nm, and power densities of approximately 140 mW cm<sup>-2</sup>, 115 mW cm<sup>-2</sup>, 127 mW cm<sup>-2</sup>, 86 mW cm<sup>-2</sup>, and 250 mW cm<sup>-2</sup>, respectively.

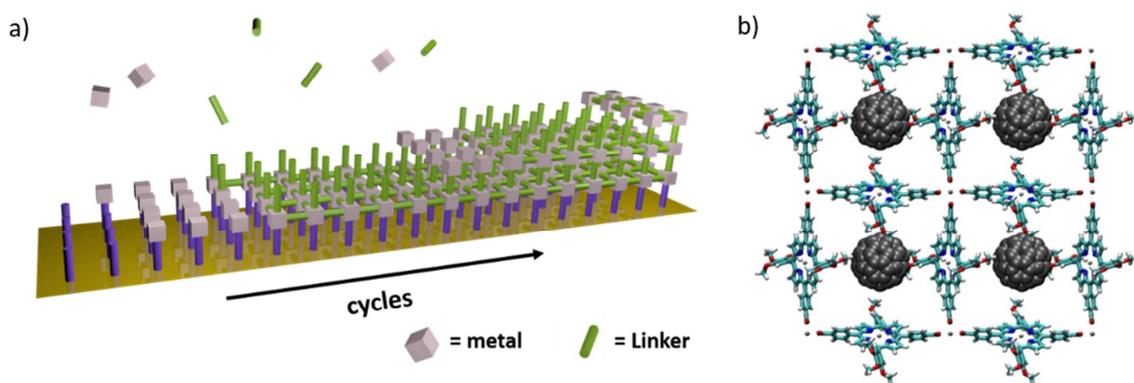


Figure 1. a) Sketch of the layer-by-layer SURMOF synthesis. The metal nodes are sketched as grey cubes, the linkers as green sticks. b) The structure of  $C_{60}@Zn(TPP)$ . O atoms are pictured red, Zn dark grey, N blue, H white. For clarity, C of the MOF scaffold is shown in cyan, C of fullerene is grey.

## Results and Discussion

The electrical conductivities of the SURMOF samples deposited on substrates with interdigitated gold electrodes were determined by 2-probe DC conduction measurements. Cu(BPDC)-SURMOF-2, a phenyl-based MOF structure, showed no significant increase upon irradiation with various wavelengths of the visible spectra, Figure 2a. Cu(BPDC) with a thickness of 270 nm displayed a conductivity of approximately  $2 \times 10^{-13} \text{ S m}^{-1}$ . The conductivity of the MOF thin film increased by approximately four orders of magnitude upon loading with  $C_{60}$ , see Figure 2b. The conductivity is only slightly affected by light irradiation, in detail the current increases by less than 10 % when irradiated with light of 455 nm wavelength.

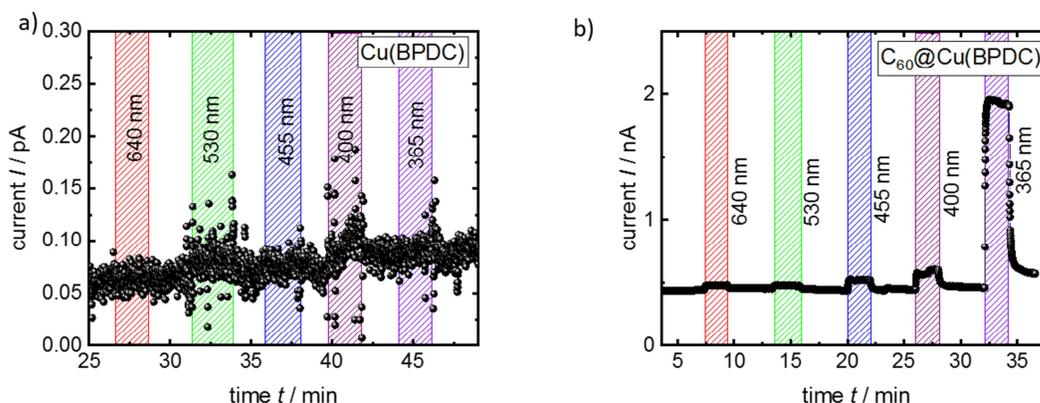


Figure 2. Conduction in a) Cu(BDPC) and b)  $C_{60}@Cu(BDPC)$ . The DC currents at a voltage of 2 V were measured while the samples were irradiated with light of 640 nm, 530 nm, 455 nm, 400 nm and 365 nm wavelength.

A rather different photo-response was observed for the porphyrinic SURMOFs; although the lattice constants and pore sizes of Zn(TPP)-SURMOF-2 and Cu(BPDC)-SURMOF-2 are very similar, see the XRD data ref.<sup>19</sup>. Zn(TPP) SURMOFs, without  $C_{60}$  embedment, shows a conductivity of approximately  $1.5 \times 10^{-11} \text{ S m}^{-1}$ , Figure 3a, which is

low but clearly higher than that of empty Cu(BPDC). In pronounced contrast to the MO thin films built with the phenyl-based linkers, the irradiation with light results in a substantial increase of the conductivity of the porphyrinic SURMOF.

Embedding fullerene in the porphyrin SURMOFs increases the electrical conductivity. When applying 2 V to the  $C_{60}@Zn(TPP)$  sample, the current in the dark is approximately 0.11 nA, corresponding to a conductivity of  $1.5 \times 10^{-9} \text{ S m}^{-1}$ . Irradiation with light substantially increases the current, see Figure 3b. The observed change in photoconductivity strongly depends on the photon wavelength. The largest increase is obtained at 455 nm, i.e. by exciting the porphyrin Soret band. There, a value of approximately 9 nA is reached, corresponding to a conductivity increase upon illumination by 2 orders of magnitude.

This observation, and the comparison with the previous reference experiments, indicate that the observed photoconductivity in  $C_{60}@Zn(TPP)$  SURMOFs must be related to a cooperative effect of the porphyrin moieties and the  $C_{60}$  guests.

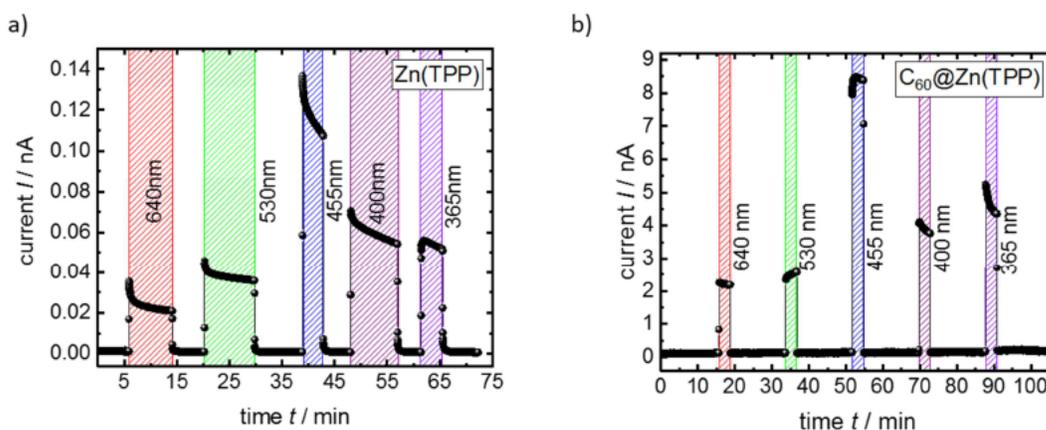


Figure 3. Conduction in a) Zn(TPP) and b)  $C_{60}@Zn(TPP)$ . The DC currents at a voltage of 2 V were measured while the samples were irradiated with light of 640 nm, 530 nm, 455 nm, 400 nm and 365 nm wavelength. The current without light irradiation is 0.001 nA (a) and 0.11 nA (b).

### Conclusion

Thin films of crystalline MOFs with porphyrinic linkers and  $C_{60}$  embedded in the pores were prepared. It was found that the  $C_{60}$  incorporation increases the conductivity by 2 to 3 orders of magnitude. For MOFs containing porphyrin, pronounced photoconduction behavior under irradiation with blue light, exciting the porphyrin Soret band, was found. For  $C_{60}@Zn(TPP)$ , the photoconduction is caused by both, the photosensitive porphyrin acting as the electron donor and the  $C_{60}$  acting as the electron acceptor. Due to the efficient exciton separation and transport of the generated electron-hole pairs within the spatially continuous network of donor and acceptor domains, hole and electron transport is provided through the close-packed Zn(TPP) MOF linkers and  $C_{60}$  channels, respectively.

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