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Photoconductivity in Metal-Organic Framework Thin Films

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Abstract: Photoconductivity is a characteristic property of semiconductors, enabling various applications such as photoresponsive transistors and light-sensing. Here, we present a photo-conducting crystalline metal-organic framework, MOF, thin film with an on-off photocurrent ratio of two orders of magnitude. These oriented, surface-mounted MOF thin films, SURMOFs, contain porphyrin in the framework backbone and $C_{\rm 60}$ guests, loaded in the pores using a layer-by-layer process. By comparison with results obtained for reference MOF structures and based on density-functional theory calculations, we conclude that donor-acceptor interactions between the porphyrin of the host MOF and the C60 guests give rise to a rapid charge separation. Subsequently, holes and electrons are transported through separate channels formed by porphyrin and by C_{60} , respectively. The ability to tune the properties and energy levels of the active molecules, porphyrin and fullerene, combined with the controlled organization of donor-acceptor pairs in this regular framework offers a huge potential to increase the photoconduction onoff ratio in future work.

Metal-organic frameworks, MOFs, are crystalline, nanoporous hybrid materials composed of metal nodes connected by organic linker molecules.^[11] In recent years, in addition to applications in gas loading and separation,^[2] the electrical and electronic properties of MOFs have started to attract substantial attention.^[3] In this context, taking advantage of the enormous MOF chemical space, with the number of characterized members of this material's class approaching 100.000,^[4] various MOF applications have been investigated, ranging from electrocatalysis^[5] over field effect transistor^[6] to energy-storage^[7]. It was found that the conductivity of the MOF material can be significantly increased by loading with molecules like ferrocene,^[3c] TCNQ,^[3b] or C₆₀ fullerene.^[8] C₆₀ fullerenes are attractive charge acceptors, since the delocalized n-systems give rise to a large electron affinity and strong stability.^[9] In addition, they show efficient charge

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separation upon illumination.^[10] An interesting band structure of C₆₀ embedded in the regular MOF pores was theoretically predicted.^[11] On the other hand, MOFs with porphyrin linker molecules allow semi-conductor light-harvesting applications in photovoltaic^[12] devices and for photocatalysis.^[13] These applications take advantage of the fact that porphyrins are excellent electron donors with delocalized n-systems.[14] In the visible region, porphyrins exhibit sharp and intensive absorption bands, ideal for application in light harvesting.^[15] To this end, porphyrins are often integrated as active components in various opto-electronic devices.^[12, 16] Furthermore, the porphyrin properties can be tailored by various methods of organic chemistry, e.g. by adding electron rich or electron poor groups, allowing to tune photon absorption and other photophysical properties of the material. Combining porphyrin with fullerene results in electron donor-acceptor pairs.^[17] The light-induced electron transfer in such dyads was investigated in solution;[17] and it was demonstrated that materials of such molecules are suitable for applications like organic solar cells.^[18]

Recently, remarkable photoconductance in MOFs incorporating percolated titania nanoparticles has been reported.^[19] Irradiation with UV light of 266 nm wavelength (4.66 eV) resulted in a pronounced increase of electron mobility as detected by terahertz spectroscopy. Direct measurements of the photoinduced changes in the electrical conductivity, however, were not presented, likely due to problems in providing good electrical contacts to MOF powders under light irradiation. Photoconductivity in MOFs with functional organic moieties has not yet been reported, although the virtually unlimited possibilities to tune the properties of such materials are extremely attractive.

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

For directly measuring the photocurrent, as well as for device applications, e.g. in light sensors, the MOF material must be provided in the form of thin films. Thus, we have used surfacemounted MOF thin films, SURMOFs,^[20] grown on suitably functionalized substrates, providing interdigitated bottom contacts. This approach allows the measurement of electrical properties of empty and loaded MOFs in a straightforward and reproducible fashion. Here, several different MOF structures were investigated: While SURMOFs fabricated from phenyl-based linkers did not respond to light illumination, even after loading with fullerenes, SURMOFs fabricated from different porphyrinic linkers revealed superb photoconducting properties, likely a result of the interesting photophysical properties of these compounds.^[12] While the electrical resistivity of these porphyrinic MOF thin films is found to be rather high, the conductivity increased tremendously when embedding C60 molecules in the nanopores of these highly oriented SURMOFs, yielding C₆₀@Zn(TPP) (TPP 5,15-bis-(3,4,5-trimethoxyphenyl)-10.20bis-(4carboxyphenyl) porphyrinato zinc(II), see Figure 1). Remarkably, these MOF thin films showed pronounced photoconduction features: the electrical conductivity increased by 2 orders of magnitude when irradiated with visible light of 455 nm (2.72 eV). Detailed theoretical investigations using density functional theory (DFT) and time-dependent DFT calculations revealed the origin of the MOF photoconductivity. First, light is absorbed by the porphyrin moieties. Subsequently, the large electron affinity of the C₆₀ results in rapid charge separation.

For the sample preparation, Zn(TPP) and $C_{60}@Zn(TPP)$ SURMOF thin films as well as the phenyl-based Cu(BPDC) SURMOF films were synthesized directly on the functionalized electrode in a step-by-step fashion by alternately spin-coating the ethanolic metal acetate solution and the ethanolic linker molecule solution on the substrate, Figure 1 (BPDC = biphenyldicarboxylate). The C₆₀ molecules were loaded in the MOF pores during the synthesis by spin-coating the C₆₀ solution on the substrate after each linker step, see Figure 1.

The crystallinity of Zn(TPP) and Cu(BPDC) SURMOFs with and without embedded C₆₀ was monitored by X-ray diffraction (XRD), Figures 2a, S1 and S6. The experimental XRD data match well with the calculated diffractogram of the target structure. The absence of the (110), (001), (101) and (111) diffraction peaks reveals a high degree of orientation of the SURMOFs, i.e. the films are grown predominantly along the (100) orientation (see Figure S1). The XRD data recorded for $C_{60}@Zn(TPP)$ and Zn(TPP) also reveal that embedding C₆₀ did not affect the crystallinity of Zn(TPP), i.e. diffraction peak positions did not change and also the peak width was the same as before the loading. Importantly, however, the form factors showed substantial changes. The ratio of the (100) to (200) peak intensities increases from 3.33 for Zn(TPP) to 6.25 for C₆₀@Zn(TPP). This change in form factor is a consequence of the change in electron density, which increased substantially within the pores by the loading with C_{60} . Note that an exclusive decoration of the outer MOF surface can be excluded from this form factor change; such a change in relative diffraction peak intensities is only possible by affecting virtually every MOF pore.[21]

UV-vis absorption spectra of C_{60} @Zn(TPP) provide further evidence of the successful loading with C_{60} , Figure 2b. The absorption bands at 436 nm, 561 nm and 600 nm belong to the porphyrin chromophore, whereas the band at 330 nm originates from the C_{60} . From the relative intensity of the UV-vis absorption bands, the ratio of C_{60} to porphyrin in each unit cell could be determined and was found to amount to 0.92, indicating that almost every unit cell of the porphyrin MOF contains a C_{60} molecule. For details, see Figure S2. This value was verified by HPLC-mass spectrometry of the dissolved SURMOF sample, which showed an average loading of 0.90 C_{60} molecules per unit cell, Figure S3.



Figure 2. X-ray diffractograms (a) and UV-vis absorption spectra (b) of Zn(TPP) and C₆₀@Zn(TPP) SURMOFs. The UV-vis spectrum of C₆₀ solution in toluene is also shown. The inset shows a magnification from 300 nm to 370 nm.

The infrared spectra of Zn(TPP) and $C_{60}@Zn(TPP)$ are displayed in Figure S4. The bands at ~1590 cm⁻¹ and ~1410 cm⁻¹ of both MOFs are assigned to the carboxylate asymmetric and symmetric

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stretching modes. The band at 1425 cm⁻¹ observed for $C_{60}@Zn(TPP)$ appears after embedding of C_{60} .

In order to further characterize the as-synthesized MOF films, atomic force microscopy (AFM) was carried out to investigate the morphology and film thickness. The images in Figure S5c and S5d indicate that the Zn(TPP) and $C_{60}@Zn(TPP)$ are homogenous films with thicknesses of approximately 50 nm. Such MOF films are sufficiently thin, allowing the entire illumination of the sample, as also seen by the UV-vis spectrum (see Figure.2b) with a maximum absorbance of 0.6 absorption units.

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, S7a. Cu(BPDC) with empty pores (thickness is 270 nm, see S5a) shows a very low conductivity of approximately 2×10^{-13} S m⁻¹ (applied voltage was 2 V). The conductivity of the MOF thin film increased by approximately 4 orders of magnitude upon loading with C₆₀, see S7b. However, the conductivity is still only slightly affected by light irradiation, e.g. the current increases by less than 10 % when irradiated with light of 455 nm wavelength.

A rather different photoresponse 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 reproduced in Figures S1 and S6. Zn(TPP) SURMOFs, without C₆₀ embedment, shows a conductivity of approximately 1.5×10^{-11} S m⁻¹ (see S7c), which is low but clearly higher than that of empty Cu(BPDC). In pronounced contrast to the MOF thin films built with the phenyl-based linkers, the irradiation with light result 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 1.5×10^{-9} S m⁻¹. Irradiation with light substantially increases the current, see Figure 3. The observed change in photoconductivity strongly depends on 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. Photoconduction in C₆₀@Zn(TPP). a) The DC current at a voltage of 2 V is measured while the sample is irradiated with light of 640 nm, 530 nm, 455 nm, 400 nm and 365 nm wavelength. The current without light irradiation is 0.11 nA. The photoconduction action spectrum is shown in Figure S11. b) The current-voltage-curve of the sample in the dark (black spheres) and under irradiation with 455 nm (blue spheres). The log-plot of the data is present in Figure S8. c) The photocurrent at different intensities of the 455 nm light irradiation.

The current-voltage curve, Figure 3b, shows that, upon illumination, the conductivity of C60@Zn(TPP) increases over the entire voltage range between -5 V and +5 V. In the dark, the current increases with voltage more than linearly, roughly exponentially. This is an indication that more conducting paths become available with increasing voltage. Upon irradiation with light, a different scenario is observed. For light of 455 nm, the photocurrent is proportional to the voltage, revealing almost ideal ohmic conduction behavior with a conductivity of 1.3×10^{-7} S m⁻¹. A linear correlation between photocurrent and the intensity of incident light is observed (Figure 3c and Figure S9), demonstrating that two-photon processes appear to be absent. Repeated and long-time irradiation of the sample show the high stability of the photoconduction phenomenon in the C₆₀@Zn(TPP) SURMOF, Figure S10. Noteworthy, the light irradiation increases the conduction of this sample by approximately four orders of magnitude.

In order to elucidate the mechanism of charge transport in $C_{60}@Zn(TPP)$, a state-of-the-art quantum-chemical analysis has been carried out. To this end, we calculated the electronic coupling elements between the MOF linkers using a previously developed fully *ab initio* Quantum Patch method^[22] based on molecular orbitals, estimated from density functional theory (DFT). For these calculations, the $C_{60}@Zn(TPP)$ structure, optimized using periodic approach, as described in the Supporting Information, was used. Typical for MOFs, as a result of the charge localization and large distance between the molecular units in the MOF, the electronic coupling elements in the crystalline framework are generally small.^[23] We find that the

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electronic coupling of the Zn(TPP) HOMO orbitals (6.20 meV) is one order of magnitude larger than of other intermolecular pairs in the MOF (Table S2). This suggests that hole transport is provided within stacks of porphyrin linkers, which are localized along the z axis, Figure S13.

The electronic coupling of the porphyrin LUMO orbitals (0.27 meV) is approximately three times lower than for the LUMO orbitals in the $Zn(TPP)-C_{60}$ molecular pair (1meV), see Table S2, indicating higher propensity for direct electron transfer (ET) between porphyrin and C_{60} .

Additionally, due to the donor-acceptor interactions in Zn(TPP)-C₆₀ and the strong electronegative character of C₆₀ with the low energy levels (Figure 4), there is a high rate for light-induced electron transfer to C₆₀, which permits carriers to move towards the respective electrode through the C₆₀ channels. Here, the electronic coupling element of the LUMO orbitals is 0.33 meV, but is prone to increase significantly when the fullerene intermolecular distance decreases. As a result, the photo-induced charge carriers in C₆₀@Zn(TPP) flow in separated domains: holes within porphyrin linkers and electrons within fullerene channels. A similar phenomenon was reported for hexa-zirconium(IV) MOF loaded with C₆₀.^[8] The same tendency was predicted theoretically^[24] and proven experimentally^[25] for porphyrinfullerene organic films.



Figure 4: a) Visualized HOMO and LUMO orbitals of the Zn(TPP) linker (left) and C₆₀ (right) with the corresponding orbital energies. While the energies of the Zn(TPP)-C₆₀ complex are shown in black, the energies of the isolated Zn(TPP) and C₆₀ are red. The labeling of orbitals, i.e. HOMO-7 and LUMO+3, corresponds to orbitals in the Zn(TPP)-C₆₀ complex. b) and c) Electron density difference upon the singlet-singlet excitation of isolated porphyrin (b) and porphyrin in Zn(TPP)-C₆₀ complex (c). The electron accepting and donating regions are labelled in red and blue, respectively. The electron transition from TPP to C₆₀ is clearly visible. Electronic properties were calculated using B3LYP functional with def2-SV(P) basis set and Grimme D3 dispersion correction using Turbomole^[26] 7.1 (see SI).

Combination of Zn(TPP)-SURMOF with C_{60} results in more efficient photoactivated ET and exciton separation. This is depicted in Figure 4b-c, which shows the electron density difference after the porphyrin photoexcitation. The donor-acceptor

interface in C60@Zn(TPP), Figure S13, enables intermolecular charge separation (Figure 4c), where the recombination of the generated electron-hole pair and the rate of electron back-transfer decrease. This increases the number of mobile charge carriers after the photoexcitation in C_{60} @Zn(TPP). Therefore, the photoconductance of C₆₀@Zn(TPP) results from the combination and mutual orientation of both, electron-donor porphyrin and electron-acceptor C₆₀: The Soret band of the electron-donor porphyrin is optically excited by blue (455 nm) light and the electron-acceptor C₆₀ significantly improves the photoactivated electron transfer from porphyrin due to the effective long-range charge separation and the reduction of the charge recombination, as known for C₆₀.^[27] The structure of C₆₀@Zn(TPP) with high density of donor-acceptor interfaces, together with the spatially continuous network of interpenetrating donor and acceptor domains, provides a mechanism not only for exciton formation upon photoexcitation, but also an efficient charge separation and transport of the generated charge carriers through the MOF material, resulting in enhanced photoconduction properties of C₆₀@Zn(TPP).

Among the advantages of using combinations of functional molecules in the regular order of a MOF is that both active components, porphyrin and fullerene, can be modified without modifying the crystal structure. This is demonstrated by constructing a different SURMOF, C₆₀-COOH@Zn(DAP) containing fullerene guests (C60-COOH), built from a different porphyrin linker (DAP = [10,20-bis(4-carboxyphenyl)-5,15diazaporphyrinato]zinc(II), see S14). For this different MOF thin film, the photoconductance properties are similar (S18). The current increase upon blue light irradiation also amounts to about 2 orders of magnitude, however, the absolute current values in C_{60} -COOH@Zn(DAP) are smaller than in C_{60} @Zn(TPP). Remarkably, as a result of the different electronic structures and absorption spectra of the DAP porphyrin, the photoconduction response to light of different wavelengths is slightly different. For example, while the ratio of the photocurrent during irradiation with 455 nm compared to irradiation with 400 nm is 2.2 for C_{60} @Zn(TPP), it is 2.6 in C_{60} -COOH@Zn(DAP).

In comparison to other thin film possessing photoactive porphyrin, e.g. films of porphyrin-functionalized gold nanoparticles or porphyrin-decorated on graphene sheets,^[28] the C₆₀@Zn(TPP)-SURMOF has a significantly larger on-off photocurrent ratio. The superior photoconduction properties of the SURMOF are presumably caused by the regular, crystalline order, allowing a high charge carrier mobility.^[12] Similarly large photocurrent ratios as in C₆₀@Zn(TPP) were achieved with ordered molecular assemblies of various porphyrin derivatives in the form of crystalline nanorods and nanowires, [18a, 29] however, the crystalline assembly of such materials in the form of thin films with controlled thickness has not yet been demonstrated. The crystalline assembly also allows for the precise structure determination, enabling a thorough theoretical analysis of the charge transport with a reliable identification of basic mechanisms. In addition, the oriented SURMOF structure results in efficient charge transfer in the direction of the closely packed C₆₀ and porphyrin molecules, which are forming charge transfer channels parallel to the surface, connecting the electrodes. These

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channels resemble ideal nanostructured donor-acceptor hole and electron transporting highways for photocurrent generation.

In conclusion, crystalline, oriented MOF thin films with porphyrinic linkers and C_{60} embedded in the pores were prepared. Photoconduction behavior under irradiation with blue light, exciting the porphyrin Soret band, was found to increase the electrical conductivity of the SURMOFs by 2 orders of magnitude. The photoconductance is a result of both, the photosensitive porphyrin acting as the electron donor and the C_{60} acting as the electron acceptor, in addition to the designed MOF structure, which enables effective electronic coupling within the donor and acceptor phases. 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.

Based on the virtually unlimited possibilities to tune the properties by appropriate molecular functionalizations of C_{60} as an electron acceptor and porphyrin as an electron donor as well as to tune the absorption properties and absorption wavelength, the MOF photoconductivity properties can be varied and adopted.

Experimental

The porphyrinic SURMOFs and hybrid materials were deposited on different substrates in a layer-by-layer process using a spin coater. The samples were characterized by XRD, IR, Raman, SEM, AFM and UV. Full details of substrates treatment, preparation and characterization techniques are available in the supporting information.

For measuring the electrical conductivity, the SURMOF samples were prepared on quartz substrates on which interdigitated gold electrodes had been deposited. The interdigitated gold electrode substrates with a total electrode gap length of 3.38 m and a gap width of 5 µm were obtained from DropSens. Prior SURMOF synthesis, substrate functionalization was carried out by UV-ozone treatment for 30 min to remove impurities as well as to increase the number of surface -OH functional groups. The conduction of the sample in a pure argon atmosphere was measured with a Keithley 2635B Sourcemeter. For the current-voltage curves, the current was measured in 3 cycles and the arithmetic average value with the standard deviation is shown. More details for the setup can be found in ref.^[23b, 30].

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⁻², 115 mW cm⁻², 127 mW cm⁻², 86 mW cm⁻², and 250 mW cm⁻², respectively.

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Keywords: photoconduction • metal-organic frameworks • porphyrin • C_{60} fullerene • density functional theory

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SUPPORTING INFORMATION

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Layout 1:

COMMUNICATION

A photo-conducting crystalline metalorganic framework, MOF, thin film with high on-off photocurrent ratio is presented. The donor-acceptor interactions between the porphyrin in the framework backbone of these oriented MOF thin films and C₆₀ guests in the pores give rise to a rapid charge separation. Subsequently, holes and electrons are transported through separate channels formed by porphyrin and by C₆₀, respectively.



Xiaojing Liu, Mariana Kozlowska, Timur Okkali, Danny Wagner, Tomohiro Higashino, Gerald Brenner-Weiß, Stefan Marschner, Zhihua Fu, Qiang Zhang, Hiroshi Imahori, Stefan Bräse, Wolfgang Wenzel, Christof Wöll and Lars Heinke

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