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## Photochromic Free MOF-Based Near-Infrared Optical Switch

Nikita K. Kulachenkov,\* Dapeng Sun, Yuri A. Mezenov, Andrei N. Yankin, Sergey Rzhevskiy, Vyacheslav Dyachuk, Alexandre Nominé, Ghouti Medjahdi, Evgeny A. Pidko, and Valentin A. Milichko\*

**Abstract:** We demonstrate herein an all-optical switch based on stimuli-responsive and photochromic-free metal–organic framework (HKUST-1). Ultrafast near-infrared laser pulses stimulate a reversible 0.4 eV blue shift of the absorption band with up to  $200 \text{ s}^{-1}$  rate due to dehydration and concomitant shrinking of the structure-forming  $[Cu_2C_4O_8]$  cages of HKUST-1. Such light-induced switching enables the remote modulation of intensities of photoluminescence of single crystals of HKUST-1 as well visible radiation passing through the crystal by 2 order of magnitude. This opens up the possibility of utilyzing stimuli-responsive MOFs for all-optical data processing devices.

Over the last two decades, unique properties of metalorganic frameworks (MOFs) have been attracting an increasing attention of industrial and researchers.<sup>[1]</sup> Next to high porosity, defined structures and chemical versatility, these materials may feature stimuli-responsive structure, which, in turn, allows for reversible/irreversible structural transformation such as crystal-to-amorphous or crystal-to-crystal ones.<sup>[2]</sup> The reversible transformations induced by external stimuli such as mechanical constrains,<sup>[3]</sup> guest uptake,<sup>[4]</sup> temperature,<sup>[5]</sup> UV-VIS light exposure<sup>[6]</sup> and others are utilized for controllable gas adsorption, separation<sup>[7]</sup> and catalysis.<sup>[8]</sup> The defined structural flexibility expands the utility of MOFs as "smart" materials for remotely controlled sensors or communication devices<sup>[9]</sup> such as memory devices<sup>[10]</sup> and optical switchers. Herein, such applications put additional requirements onto the MOF structural response, which has to be fast, highly-repeatable and take place under industrially-relevant near-infrared (NIR) laser irradiation (photoswitching). Conventionally, the introduction of photochromic ligands such as azobenzenes and spiropyrans or photochromic guests<sup>[11]</sup> into

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the MOF structure is used to enable the photoswithcing behavior.<sup>[12,13]</sup> The resulting composites show structural transformations induced by continuous UV or visible radiation with rates of  $\approx 0.1 \text{ s}^{-1}$ .

Here, we report on reversible structural transformation of photochromic-free HKUST-1 with a high endurance and rates induced by near-infrared ultrafast laser pulses. The optical measurements have revealed the dehydration of HKUST-1 upon irradiation that gives rise to a blue shift of the absorption band from 2.1 to 2.5 eV corresponding to initial hydrated (stable) and excited dehydrated (metastable) states at ambient conditions. Confocal Raman spectroscopy, X-Ray diffraction (XRD) analysis with temperature control, and density functional theory (DFT) have confirmed reversible shrinking of [Cu<sub>2</sub>C<sub>4</sub>O<sub>8</sub>] cages of irradiated HKUST-1 due to the dehydration. We have utilized this structural effect to demonstrate MOF-based optical switch operating at the rate of tens and hundreds of  $s^{-1}$  (depending on the atmosphere) and allowing one to turn off/on the light passing through the single crystal of MOF and modulate the intensity of initial photoluminescence (PL).

As a model MOF we have utilized the commercial compound of the dehydrated HKUST-1 (Basolite C 300 by Sigma Aldrich). This is highly porous open-framework metal coordination polymer [Cu3(BTC)2(H2O)3]n (BTC, benzene-1,3,5-tricarboxylate) with face-centered-cubic structure containing an intersecting three-dimensional system of large square-shaped pores  $(9 \times 9 \text{ Å})$ .<sup>[14a]</sup> Cu<sup>2+</sup> ions of HKUST-1 also form cages, where each copper atom is coordinated by four oxygen atoms, coming from the BTC ligand and by one water molecule (Figure 1, inset). Removal of the H<sub>2</sub>O from the Cu<sup>2+</sup> sites upon the dehydration of HKUST-1 under vacuum or at elevated temperature results in shrinking of [Cu<sub>2</sub>C<sub>4</sub>O<sub>8</sub>] structure-forming cages.<sup>[15]</sup> Simultaneously, HKUST-1 crystals change color from cyan (hydrated) to navy blue (dehydrated). Besides, HKUST-1 can demonstrate other types of reversible structural transformation, namely, the cluster rotation, which takes place at elevated pressure and is responsible for its auexetic behavior.<sup>[16]</sup> Very recently, this stimuli-responsive compound has been utilized as a redox-based data storage material<sup>[17]</sup> and a host<sup>[18]</sup> for photoswitching guests. However, its initial photophysical and structure-related properties, which are significant for optical communication devices, remain unexplored.

For an all-optical switching, single crystals of the hydrated HKUST-1 have been placed on glass substrate. The measurements of optical transmission spectrum has been carried out in air using the self-made confocal microscope setup (Figure S1). The excitation of the single crystal has been

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**Figure 1.** The normalized transmission spectrum of the hydrated HKUST-1 single crystal in air before (initial state, a) and during NIR laser irradiation (excited state, b). Optical images correspond to initial (a) and excited (b) states, and the mapping of excited crystal demonstrating that the whole crystal can be switched ( $\Delta$ HWHM corresponds to the absorption band shift in nm). Scale bar: 10 µm.

implemented via  $10 \times /0.26$  NA objective by white light. The transmission signal has been collected with a  $50 \times /0.65$  NA objective and then analyzed by confocal spectrometer HORIBA Labram. The switching of the structure between initial stable and excited metastable states at ambient conditions has been performed by two coherent sources: Yb<sup>3+</sup> laser with 1050 nm central wavelength (150 fs pulse duration, 80 MHz repetition rate), and supercontinuum laser source yielding a beam with 800 nm central wavelength (6 ps pulse duration, 60 MHz repetition rate). For these two wavelengths, the hydrated HKUST-1 has different transmittance as one can see in Figure S2. Moreover, the diameter of the laser beam for that wavelengths was 4.9 and 3.8 µm, respectively, compared to average 10 µm size of the single crystals. The specific transmission spectra with/without NIR laser irradiation are represented in Figure 1. The hydrated HKUST-1 in air has light cyan color and is transparent in the wide spectral range up to 2.1 eV (initial stable state). Under the pulsed laser irradiation the color changes to blue navy and the absorption band shifts to 2.5 eV (exited metastable state). The metastability is characterized by the relaxation to the initial state with light cyan color as soon as the NIR laser turns off. Such a substantial band shift of 0.4 eV (19% compared to the initial position) can be attributed to the appearance of the high-energy shoulder in the d-d band of Cu<sup>2+</sup> species due to a loss of degeneracy of d levels produced by water removal.<sup>[15]</sup>

We have also analyzed the all-optical switching for the dehydrated HKUST-1 soaked in advance in dimethylformamide (DMF), 1,4-dioxane and deionized  $H_2O$  (for details, see SI). Based on the previous results,<sup>[14b,c]</sup> such solvents specifically adsorb to HKUST-1 (Figure S3). Similar to the case of hydrated HKUST-1 in air (Figure 1), DMF and 1,4-dioxane molecules also induce the blue shift of the absorption band ( $\approx 0.4 \text{ eV}$ ), while we detect 0.01 eV shift for HKUST-1 dispersed in water (Figure S4).

The non-linear dependence of absorption band shift on the laser fluence is also observed (Figure 2). The shift of 25 meV per mJ cm<sup>-2</sup> can be achieved at lower fluence up  $20 \text{ mJ cm}^{-2}$ , while the shift of 0.6 meV per mJ cm $^{-2}$  is detected under the higher values. Further increase of fluence  $(>130 \text{ mJ cm}^{-2}, 80 \text{ MHz}$  repetition rate) leads to burning of the crystal that we have detected optically. Moreover, the reversibility of the absorption band shift is detected by no less than 10 circles that confirms the resistance of HKUST-1 to NIR irradiations in terms of its optical response (inset, Figure 2 and Figure S5). To confirm the resistance of the crystal structure to heating, which can be induced by NIR radiation, we have carried out powder XRD analysis at different temperatures. X'Pert PRO MPD equipped with the Anton Paar HTK 1200N has been used to confirm that the structure of the dehydrated HKUST-1 has high crystallinity with corresponding Fm3m space group<sup>[19]</sup> similar to the hydrated HKUST-1 (Figure S6). XRD analysis at different temperatures from 30 to 300°C has declared the stability of the structure up to 250 °C. These are in a good agreement with previous results<sup>[19]</sup> on the effect of heating of the hydrated and dehydrated HKUST-1.

We then investigated experimentally the rate of structural response of the hydrated HKUST-1 in air (Figure 3a) and water (Figure 3b) on laser pulses using transmission spectroscopy with time resolution. At a constant value of fluence of pumping NIR single pulse (1050 nm, 150 fs, 28 kJ cm<sup>-2</sup>) we have probed the intensities of transmitted light with different wavelengths (500, 530, 560, and 590 nm, 6 ps, 60 MHz,  $0.3 \text{ mJ cm}^{-2}$ ) on time by collecting signal on photodetector coupled to oscilloscope. Figure 3a demonstrates that the switching from the initial to excited state occurs for 22 to  $40 \text{ s}^{-1}$  depending on the probing wavelength (Figure S7), while the relaxation to the initial state is slower (0.31 to



*Figure 2.* The fluence dependance and repeatability (inset) of absorption band shift for the hydrated HKUST-1 in air irradiated by NIR femtocecond (150 fs, 1050 nm) and picosecond (6 ps, 800 nm) laser pulses (pumping fluence is 80 mJ cm<sup>-2</sup>, inset).

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**Figure 3.** Rates of switching of the hydrated HKUST-1 in air (a) and water (b) induced by single-shot NIR pulse: 1–2 the drop of normalized transmittance of HKUST-1 at a wavelength of 500 nm (a) and 530 nm (b) for 22 s<sup>-1</sup> and 200 s<sup>-1</sup>, respectively, upon irradiation; 2–3 relaxation to the initial state for 0.5 s<sup>-1</sup> (a) and 200 s<sup>-1</sup> (b).

 $0.52 \text{ s}^{-1}$ ). In contrast, the switching from the initial to excited states and the relaxation for HKUST-1 dispersed in water occurs for  $200 \text{ s}^{-1}$  (Figure 3b) that can be explained by a higher number of coordinated and guest water molecules. In turn, such fast process explains inability to detect 0.4 eV blue shift of the absorption band (Figure S4) utilizing conventional spectrometer (Figure S1). In addition, the correlation between increases of the switching rate (Figure S7a) and the absorption coefficient (Figure 1) at wavelength from 500 to 600 nm have been observed. This indicates that the more photons are absorbed by HKUST-1, the more likely the switching process is. It should be noted, that such absorption band shift can be also achieved under continues visible laser irradiation (Figure S8). However, such radiation is inconvenient for the optical switchers, where the rate of the structural response to incoming optical pulses is important.

Concerning the well-developed photochromic compounds, the photochromic ligands themselves usually demonstrate THz rate of their structural transformation.<sup>[20]</sup> However, to the best of our knowledge, the MOFs containing such ligands are characterized by slower structural transformation due to steric hindrance effect.<sup>[21]</sup> Therefore, HKUST-1 can be considered as a representative of the photochromic-free MOF family with rapid structural reaction to light avoiding the problems on steric hindrance and degradation under UV radiation.

We then implemented Raman spectroscopy and DFT to describe the mechanism of switching. In situ Raman scattering measurements under excitation by a 632.8 nm He-Ne continuous laser radiation in reflection mode through  $100 \times / 0.9$  NA objective have confirmed that the coordination sphere of the copper cluster is changing under NIR laser pulses.

Indeed, Raman lines due to  $\nu$ (Cu–Cu),  $\nu$ (Cu–O<sub>w</sub>), and  $\nu$ (Cu– O) stretching modes at  $\approx 180$ ,  $\approx 280$ , and 495 cm<sup>-1</sup>, respectively<sup>[22]</sup> change significantly under NIR irradiation (Figure S5a).  $O_w$  indicates the oxygen from the guest molecule of water, which absorbed on the copper ions. The  $\nu$ (Cu–Cu) and  $\nu$ (Cu–O) stretching modes (O indicates the oxygen atoms of carboxylate bridges) shift to  $\approx 224$  and 508 cm<sup>-1</sup>, respectively, while  $\nu(Cu-O_w)$  decreases in intensity and shifts to 325 cm<sup>-1</sup>. In case of Cu-O mode, it also demonstrates an additional doubly generated mode of Cu-O near the main peak at 450 cm<sup>-1</sup>. These effects are attributed to the desorption of water molecules from [Cu<sub>2</sub>C<sub>4</sub>O<sub>8</sub>] cages.<sup>[15]</sup> The peaks corresponding to organic moieties (e.g. C-H in the range of 750- $820\ \text{cm}^{-1}$  and  $\approx 939\ \text{cm}^{-1},\ \text{C=C}$  at  $\approx 1000\ \text{cm}^{-1}$  from the aromatic ring) remain unchanged under the NIR radiation<sup>[22]</sup> confirming the high photostability of the organic BTC ligand.

The structural and electronic properties of the hydrated/ dehydrated HKUST-1 were calculated by spin polarized density functional theory using the Vienna Ab initio Simulation Package (VASP).<sup>[23]</sup> The antiferromagnetic state of HKUST-1 presented the most stable structure (Figure S9), and the optimized lattice constant of the dehydrated HKUST-1 was 26.46 Å. The hydrated HKUST-1 was modelled by adding additional two water molecules at one of the  $[Cu_2C_4O_8]$  cages. The lattice constant of the hydrated HKUST-1 was slightly increased by 0.05 Å, and the Cu-Cu distance in the cage was enlarged from 2.45 to 2.54 Å due to water adsorption (Figure S9). The adsorption energy per water molecule in HKUST-1 was -0.33 eV, which thermodynamically implies flexible hydration/dehydration processes. The density of states (DOS) of both hydrated and dehydrated HKUST-1 were calculated using HSE06 functional.<sup>[24]</sup> From Figure 4, the calculated band gap of HKUST-1 was increased by 0.34 eV after dehydration. This is in a good agreement with experimentally detected 0.4 eV blue shift of the absorption band (Figure 1). The density of states projected on each element (pDOS) and the band-decomposed partial charge densities were also calculated. Important that for the



**Figure 4.** Electronic properties of the hydrated (upper-row) and the dehydrated (lower-row) HKUST-1. a,d) The projected density of states (pDOS). b,e) Isosurfaces of the band-decomposed partial charge density of the valence band maximum, and c,f) the conduction band minimum.

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hydrated HKUST-1 the valance band maximum (VBM) is mainly composed by O 2p orbitals localized in the wateradsorbed [Cu<sub>2</sub>C<sub>4</sub>O<sub>8</sub>] cage. The conduction band minimum (CBM) is mainly composed by Cu 3d orbitals. While for the dehydrated HKUST-1 the VBM is mainly composed by the O 2p and the  $\pi$ -orbitals delocalized among the aromatic hydrocarbon chains, and the composition of CBM is similar as that of the dehydrated system.

As the first demonstration of the potential application of photochromic-free MOF for NIR optical switching we have realized an all-optical remote control of HKUST-1 optical properties. At first, we have modulated the transmittance of the hydrated HKUST-1 single crystal in air within the visible range by NIR laser pulses to decrease its transmittance by 2 order of magnitude. This allowed us to turn off and on the light (530 nm wavelength) passing through this crystal by increasing/decreasing the fluence of NIR laser (Figure 5a, inset). The rate of switching was  $27 \text{ s}^{-1}$ , while the relaxation



**Figure 5.** a) Photoluminescence spectra of the hydrated HKUST-1 in air excited by 530 and 450 nm (6 ps, 60 MHz repetition rate,  $45 \text{ mJ} \text{ cm}^{-2}$ ) with corresponding modulation of the intensity (b) by an increase of the fluence of additional pumping radiation (150 fs, 80 MHz repetition rate). Inset (a) – Modulation of transmittance of HKUST-1 single crystal allowing one to turn on (1) and off (2) the intensity of the radiation (530 nm) passing through the crystal by additional NIR fs laser pulses; inset (b) – optical scheme of PL modulation of HKUST-1.

process was slower ( $0.52 \text{ s}^{-1}$ ). It should be noted, that the maximal change in transmittance (2 order of magnitude) is achieved at a wavelength of 530 nm (Figure S10), while the transmittance at UV and NIR ranges remain the same. Herein, the higher rates of switching (up to  $40 \text{ s}^{-1}$ ) correspond to 550-600 nm (Figure S7a) that makes the wavelength of 550 nm to be optimal to observe efficient and fast  $(34 \text{ s}^{-1})$ switching. At second, we have achieved the modulation of initial PL intensity recently demonstrated for photochromic MOFs.<sup>[21]</sup> Indeed, the dehydration of HKUST-1 results in significant changes of electronic transitions (Figure 4). Therefore, it is expected to observe the changes of photoemission properties. For this, we have excited PL by different wavelengths as 450 and 530 nm (6 ps, 60 MHz repetition rate,  $45 \text{ mJ cm}^{-2}$ ). As one can see in Figure 5 a, the intensity of PL excited by 530 nm is five time higher due to increased absorption at this wavelength (Figure 1). Herein, the increase of intensity of additional NIR radiation (150 fs, 1050 nm) results in decreasing of PL intensity (Figure 5b) by 30%. Intriguingly, the same PL excited by 450 nm can be increased by this additional NIR radiation up to 20%. To the best of our knowledge, such optical modulation have been demonstrated for the first time in photochromic-free metal-organic frameworks.

In summary we demonstrate a highly reversible absorption band shift from 2.1 eV to 2.5 eV of HKUST-1 with tens to hundreds of s<sup>-1</sup> rates due to dehydration of single crystals induced by near-infrared (800 and 1050 nm) ultrafast (fs and ps) laser pulses. The process associated with reversible shrinking of  $[Cu_2C_4O_8]$  cages of HKUST-1 was confirmed by in situ Raman spectroscopy, XRD analyzes and DFT calculation. This effect can be applied for communication devices as MOF-based optical switch operating at kHz rate which allows one to turn off/on the visible light passing through the single crystal and modulate the intensity of initial photoluminescence by NIR laser pulses.

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## **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** all-optical switch · HKUST-1 · metalorganic frameworks · photoswitching

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**Communications** 



## **Communications**



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Photochromic Free MOF-Based Near-Infrared Optical Switch



Ultrafast near-infrared laser pulses stimulate reversible blue shift of the absorption band of photochromic-free MOFs with rates up to hundreds of  $s^{-1}$ . This optical switching can be applied for MOF-based communication devices allowing the remote modulation of the intensities of initial photoluminescence and the visible light passing through the MOFs.

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