# Laser-Assisted Design of MOF-Derivative Platforms from Nano- to Centimeter Scales for Photonic and Catalytic Applications

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**ABSTRACT:** Laser conversion of metal—organic frameworks (MOFs) has recently emerged as a fast and low-energy consumptive approach to create scalable MOF derivatives for catalysis, energy, and optics. However, due to the virtually unlimited MOF structures and tunable laser parameters, the results of their interaction are unpredictable and poorly controlled. Here, we experimentally base a general approach to create nano- to centimeter-scale MOF derivatives with the desired nonlinear optical and catalytic properties. Five three- and two-dimensional MOFs, differing in chemical composition, topology, and thermal resistance, have been selected as precursors. Tuning the laser parameters (i.e., pulse duration from fs to ns and repetition rate from kHz to MHz), we switch between ultrafast nonthermal destruction and thermal decomposition of MOFs. We have established that regardless of the chemical composition and MOF topology, the tuning of the laser parameters allows obtaining a series of structurally different derivatives, and the transition from femtosecond to nanosecond laser regimes ensures the scaling of the derivatives from nano- to centimeter scales. Herein, the thermal resistance of

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MOFs affects the structure and chemical composition of the resulting derivatives. Finally, we outline the "laser parameters versus MOF structure" space, in which one can create the desired and scalable platforms with nonlinear optical properties from photoluminescence to light control and enhanced catalytic activity.

**KEYWORDS:** metal-organic framework, laser ablation, MOF derivatives, nanoparticles, surface, nonlinear optics, catalysis

## 1. INTRODUCTION

Metal-organic frameworks (MOFs) have recently emerged as a new paradigm in crystal engineering.<sup>1-3</sup> Combining organic and inorganic building blocks, packed into well-defined structures supported by strong and weak bonds, MOFs exhibit unprecedented porosity<sup>4</sup> along with a structural order and chemical diversity.<sup>5</sup> On the one hand, metal-organic nature and complex hierarchy provide MOF with gas storage and separation properties, energy storage, catalysis, drug delivery, sensing, and even photonic applications.<sup>6-11</sup> On the other hand, these specific properties allow MOF utilization as precursors for obtaining new forms of artificial nanostructures and derivatives,<sup>12–16</sup> which are inaccessible to be obtained by classical bottom-top fabrication techniques.<sup>17-19</sup> In turn, the resulting derivatives exhibit exceptional catalytic, capacitive, and optical properties, being nonspecific for their precursor analogues.

From a manufacturing point of view, the most common approach to fabricate MOF derivatives is thermal decomposition by holding the MOF powders at an elevated temperature (up to 1000  $^{\circ}$ C) for several hours in an oven.<sup>20–23</sup> However, recent studies have shown an alternative,

fast, and low-energy consumptive approach. Since MOFs are able to absorb laser energy efficiently and then transfer it into heat, intense laser irradiation stimulates fast decomposition of MOFs and their building block rearrangement under ambient conditions. Such laser-assisted conversion<sup>24</sup> (referring in the literature also as laser metallurgy,<sup>25</sup> manufacturing,<sup>26</sup> annealing,<sup>27</sup> scribing, or even ablation<sup>28</sup>) makes it possible to fabricate the MOF derivatives scalably in real time for optical, electronic, and catalytic applications.<sup>25–32</sup> However, due to a huge variety of MOF structures (more than 100.000 registered compounds in CCDC) and tunability of the laser parameters (wavelength, pulse fluence, and duration), the result of the interaction of intense laser light and MOF is yet unpredictable and poorly controllable.

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Here, we report on the laser-assisted rational design of MOF derivatives with the desired structure, composition, scale, and corresponding nonlinear optical and catalytic properties. The concept is based on the precise control of the thermal effect of laser radiation on the MOF structure, allowing one to operate in either ultrafast nonthermal destruction or thermal decomposition regimes (i.e., conversion of initial MOFs into derivatives of varied structures and functionalities). Using four commercially available 3D MOFs (HKUST-1, ZIF-8, ZIF-67, and UiO-66) and a 2D MOF  $(\{[Zn(tr_2btd)(bpdc)] \cdot DMF\}_n)$ where  $tr_2btd = 4,7-di(1H-1,2,4-triazol-1-yl)-2,1,3-benzothia$ diazole and bpdc = 4,4'-biphenyldicarboxylate)<sup>33</sup> with different structures, chemical compositions, and thermal resistance (Table S1), we have discovered the general rules for the laser conversion of MOFs into the desired nano- and centimeter-scale derivatives via tuning the laser parameters (pulse duration from fs to ns and repetition rate from kHz to MHz) and the MOF structures (Figure 1). We reveal that the



Figure 1. Scheme of fs to ns laser conversion of MOF to produce different derivatives.

tuning of the laser parameters (from nanoseconds to femtoseconds) allows extending a series of MOF derivatives from carbon aggregates, carbon aggregates with metal and/or metal oxide nanocrystals, to MOF nanocrystals, amorphous metal—organic nanoparticles with intact ligands, and metal—organic nanoparticles containing metal and/or metal oxide nanocrystals. Finally, the resulting MOF derivatives exhibit distinctive optical properties for targeted applications from the photoluminescence of nanometer-scale derivatives to modulated photoluminescence from adsorbed dyes and the catalytic activity of the 4 cm<sup>2</sup> surface of MOF derivatives.

#### 2. MATERIALS AND METHODS

**2.1. Laser Conversion.** In general, laser conversion (including ablation) is a well-known process for transforming different materials into a variety of structures for applications ranging from catalysis to photonics. Herein, the time of laser exposure to the material is one of the key criteria affecting the yield. Depending on this time, it is customary to divide the laser conversion (also ablation) into two opposite processes that differ fundamentally in the mechanisms of material modification. The first, so-called "cold" laser ablation, is typical for the action of ultrashort laser pulses, with photon energy exceeding the chemical binding energy of the material. In this case,

the ablation of the material causes its ionization, followed by the breaking of the chemical bonds in a time shorter than the electronphonon relaxation. However, when the energy of such ultrashort laser pulses is insufficient for ionization, an increase in the laser intensity can lead to a multiphoton absorption process. When the intensity exceeds app. TW/cm<sup>2</sup>, the ablation process causes a huge amount of valence electrons to be detached via Zener tunneling.<sup>34</sup> Then, due to the relative inert reaction of the material, ionization occurs, followed by hydrodynamic expansion. Here, some authors advocate for the phenomenon of Coulomb explosion.<sup>35</sup> In contrast, when the duration of the laser pulse, interacting with the material, is comparable to the electron-phonon relaxation time (ps to ns),<sup>36</sup> an opposite ablation process is observed. In this case, electrons and phonons are out of thermodynamic equilibrium. Thermalization of electrons due to electron-electron interaction in fractions of picoseconds leads to a new Fermi distribution, while electron-phonon interaction in picoseconds leads to an increase in the temperature of the material. The latter leads to material modification caused by the so-called "hot" laser ablation.

Apart from the laser conversion (ablation) of inorganic materials,<sup>37,38</sup> the use of organics for producing different photonic and medical structures is also widespread.<sup>39</sup> However, the laser conversion,<sup>24</sup> metallurgy,<sup>25</sup> manufacturing,<sup>26</sup> annealing,<sup>27</sup> scribing, or even ablation<sup>28</sup> of hierarchical metal–organic materials like MOFs was started less than 4 years ago.<sup>25,32</sup> Nevertheless, these results are highly promising for photonics, electronics, and catalysis. Indeed, the laser conversion of MOFs makes it possible to obtain complex and even unique forms of nanomaterials such as metal oxides,<sup>24,26</sup> carbides<sup>40</sup> and sulfides,<sup>41</sup> multicomponent alloys,<sup>28,31,42–44</sup> carbon,<sup>29</sup> and metal–carbon and organometallic nanostructures,<sup>30,32,45</sup> as well as to initiate the structural defects<sup>46</sup> and laser writing.<sup>25,27,47</sup> Most of these works have been carried out in the nanosecond laser regime, paying special attention to the effect of the initial structure and composition of the MOF precursors<sup>24–32,40–45,48</sup> and the laser power<sup>24,25,27,30,40,43</sup> on the decomposition yield.

2.2. MOF Selection. In our work, we have considered the "cold," "hot," and intermediate laser conversion regimes for four representative 3D MOFs based on Cu, Zn, Co, and Zr and organic ligands like benzene-1,3,5-tricarboxylic acid, 2-methylimidazole, and 1,4-benzodicarboxylic acid (i.e., HKUST-1, ZIF-8, ZIF-67, and UiO-66), as well as for a 2D MOF based on Zn, tr<sub>2</sub>btd, and bpdc ligands.<sup>33</sup> The selected MOFs differ in their structure and thermal resistance (Table S1 and SI, Part VI). Since the thermal decomposition of MOFs is generally the result of the breaking of bonds between metal ions and organic ligands, their thermal resistance is related to the strength and number of these bonds. Moreover, the decomposition can also take the form of MOF amorphization and/or melting.<sup>49</sup> For the selected MOF like HKUST-1, the average thermal decomposition temperature is quite low and usually ranges from 250 to 300 °C.<sup>50</sup> Regarding ZIFs, due to their similarity to crystalline zeolites, a good thermal resistance up to 300-400 °C can be observed.<sup>51</sup> In contrast, UiO-66 demonstrates excellent thermal resistance: the decomposition temperature ranges from 425 to 600 °C depending on the environmental conditions (see details in the SI, Part VI).<sup>52</sup> The selected 2D MOF shows an average value of the thermal resistance  $(320 \ ^{\circ}C)^{33}$  close to the ZIF series.

Then, the selected MOFs were subjected to laser conversion (see the Methods in the SI). For this, the single MOF crystals with average thicknesses of 100  $\mu$ m (for HKUST-1), 40  $\mu$ m (for ZIF-67 and UiO-66), and 5  $\mu$ m (for ZIF-8) were placed on a glass or indium tin oxide (ITO) substrate. The laser radiation (100 ns laser pulses with a center wavelength of 1070 nm, and 200 fs laser pulses with a center wavelength of 1030 nm) was focused on the single MOF crystal using an objective (Mitutoyo 50× or 10×). The repetition rate of the laser pulses for fs radiation was set at 1 kHz and 1 MHz, while for ns radiation, a 10 kHz repetition rate was chosen. The laser fluence was varied from several  $\mu$ J cm<sup>-2</sup> to J cm<sup>-2</sup> regardless of the laser pulse duration (see the SI, Part I). During the laser conversion of MOFs, the products (i.e., MOF derivatives: HKUST-1 DER, ZIF-8 DER, ZIF-67 DER, UiO-66 DER, and 2D MOF DER) were deposited on



**Figure 2.** Electron microscopy of MOF derivatives. A series of MOF structures: HKUST-1 (A1), ZIF-67 (A2), ZIF-8 (A3), and UiO-66 (A4) arranged in order of increasing thermal resistance. (B1–B4) Corresponding SEM micrographs of the initial MOF crystals, respectively. (C) TEM micrographs of the results of femtosecond (1 kH) laser conversion of MOFs: (C1, C2) HKUST-1 DER (fs, 1 kHz), (C3, C4) ZIF-67 DER (fs, 1 kHz), (C5, C6) ZIF-8 DER (fs, 1 kHz), and (C7, C8) UiO-66 DER (fs, 1 kHz). (D) TEM micrographs of the results of femtosecond (1 MH) laser conversion of MOFs: (D1, D2) HKUST-1 DER (fs, 1 MHz), (D3, D4) ZIF-67 DER (fs, 1 MHz), (D5, D6) ZIF-8 DER (fs, 1 MHz), and (D7, D8) UiO-66 DER (fs, 1 MHz). (E) SEM micrographs of the results of nanosecond (10 kH) laser conversion of MOFs: (E1) HKUST-1 DER (ns, 10 kHz), (E2) ZIF-67 DER (ns, 10 kHz), (E3) ZIF-8 DER (ns, 10 kHz), and (E4) UiO-66 DER (ns, 10 kHz).

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Figure 3. Structural characterization of MOFs. (A) STEM micrograph and (B) STEM EDX map of HKUST-1 DER (fs, 1 kHz). (C, D) Raman spectra for HKUST-1 and ZIF-67 derivatives obtained by fs and ns laser conversion regimes.



Figure 4. Structural characterization of MOFs. (A) STEM micrograph and (B) STEM EDX map of ZIF-8 DER (fs, 1 MHz). (C, D) Raman spectra for ZIF-8 and UiO-66 derivatives obtained by fs and ns laser conversion regimes.

the same glass or ITO substrate (or carbon grid). Then, the resulting MOF derivatives were subjected to morphological, structural, elemental, and optical analysis using scanning and transmission

electron microscopy (SEM, TEM), fast Fourier transformation (FFT) in high-resolution TEM (HRTEM) mode, energy-dispersive X-ray spectroscopy (EDX), powder X-ray diffraction (PXRD) analysis,



Figure 5. Photoluminescence of MOF derivatives. (A) PL from the initial MOF crystals (UiO-66 and ZIF-8) and their derivatives, obtained by fs laser conversion, excited by 400 nm. Power dependence of PL from ZIF-8 DER (fs, 1 kH). (B) PL from the derivatives of MOFs, obtained by ns laser conversion (10 kHz), excited by 400 nm.

atomic force microscopy (AFM), Raman, optical, and photoluminescence (PL) confocal microspectroscopy, and catalytic analysis.

### 3. RESULTS AND DISCUSSION

3.1. HKUST-1. The results of the laser conversion of HKUST-1 single crystals are summarized in Figure 2A1-E1 (Figures S1 and S4). As one can see, fs laser light (fs, 1 kHz) allows conversion of the MOF into melted particles (HKUST-1 DER (fs, 1 kHz)), consisting mainly of metal oxide with the presence of a sufficient amount of carbon, as confirmed by TEM, FFT (Figure S8 and Table S3), EDX (Figure S4), and Raman analysis in Figure 3A-C. An increase in the repetition rate of fs laser pulses (fs, 1 MHz) did not significantly change the results of the conversion: the amorphous particles of metal oxide with the presence of carbon are usually detected (Figure S9 and Table S4). However, the ns laser regime (ns, 10 kHz) made it possible to obtain a larger amount of pure metal (metal oxide, to a lesser extent) particles coated with a thick carbon shell, as seen from the Raman analysis in Figure 3C:<sup>53</sup> intense peaks in the region of 100-250 cm<sup>-1</sup>, corresponding to the Cu-O bond, and pronounced D and G carbon peaks centered at 1320 and 1600 cm<sup>-1.54</sup> Statistical analysis of the obtained MOF derivatives also showed that increasing the pulse duration from 200 fs to 100 ns does not affect their size distribution (Figure S1):  $50 \pm 10$  nm size of the particles is observed for the (fs, 1 kHz) and (fs, 1 MHz) regimes (with the maximum size of 600 nm); and for the (ns, 10 kHz) regime, 40  $\pm$  20 nm particles are detected (with the maximum size of 300 nm).

**3.2.** ZIFs. Conversion of the ZIF series, an intermediate between the MOFs with high and low thermal resistance, showed the following. For ZIF-67 (Figures 2A2–E2 and S2),

the fs laser regime (fs, 1 kHz) makes it possible to obtain the fragments of the crystal itself with the presence of metal oxide and some amorphization (Raman results in Figure 3D, EDX in Figure S5, and FFT in Figure S10). Increasing the repetition rate of the femtosecond laser pulses (fs, 1 MHz) led to the appearance of completely amorphous particles (Figures S11 and 3D). The nanosecond laser conversion (ns, 10 kHz), as in the case of HKUST-1, leads to the formation of metal/metal oxide particles (as confirmed by Raman, Figure 3D) covered with a carbon shell. For ZIF-8 (Figures 2A3-E3 and S2), the fs laser regime (fs, 1 kHz) with an increased laser fluence (Table S2)<sup>55</sup> results in the creation of crystal fragments and some amorphous particles. Increasing the repetition rate of the fs laser pulses (fs, 1 MHz) leads to sufficient particle amorphization (Figure 4A-C and FFT in Figure S12). Again, the nanosecond laser conversion (nanoseconds, 10 kHz), as in the case of HKUST-1 and ZIF-67, leads to the formation of metal/metal oxide particles covered with a thick carbon shell (as confirmed by Raman, Figure 4C, and EDX, Figure S5). In contrast to HKUST-1 (Figure S1), the statistical analysis of the obtained ZIF-67 and ZIF-8 derivatives showed that increasing the pulse duration from 200 fs to 100 ns affects their size distribution (Figure S2):  $50 \pm 20$  nm size of the particles is detected for both MOFs at the (fs, 1 kHz) regime (with the maximum size of 1200 nm); the (fs, 1 MHz) regime provides  $50 \pm 10$  and  $25 \pm 20$  nm (and also  $120 \pm 10$  nm) sizes of the particles for ZIF-67 and ZIF-8, respectively (with the maximum size of 400 nm); and for the (ns, 10 kHz) laser regime,  $100 \pm 50$  and  $50 \pm 30$  nm sizes of the particles are detected for ZIF-67 and ZIF-8, respectively (with the maximum size of 1000 nm).

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**Figure 6.** (A) PL and scattering (in dark field geometry, DF) spectra from UiO-66 DER (fs, 1 kHz) and (fs, 1 MHz). Inset: TEM micrograph of the corresponding nanometer-scale UiO-66 DER (fs, 1 MHz). (B) Reflectance from the surface of the HKUST-1 initial crystal (black curve), pure Cu substrate (dashed curve), and 4 cm<sup>2</sup> MOF derivatives with corresponding optical images, obtained at different angles (perpendicular to the surface and to 60° relative to the surface normal): (C1) optical image of the fs laser conversion (fs, 1 kHz), (C2) optical image of the fs laser conversion (fs, 1 MHz), and (C3) optical image of the ns laser conversion (ns, 10 kHz) of HKUST-1. (D) Space of "laser parameters versus MOF structure" for the prediction of the structure of the MOF derivatives from nano- to centimeter scales.

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**Figure 7.** (A, B) SEM and (C, D) CLSM images of 4 cm<sup>2</sup> surfaces based on HKUST-1 after fs laser conversion with 100 kHz (A, C) and 1 MHz (B, D) repetition rates. Inset: Scale bars, 20  $\mu$ m (A), 100  $\mu$ m (B). (E, F) PL spectra for BSA-FITC (E) and BSA-Cy5 (F) conjugates covering HKUST-1 DER (fs, 100 kHz), HKUST-1 DER (fs, 1 MHz) surfaces, and a gold film as a reference. (G, H) Degradation of Rh800 in an aqueous solution with the presence of HKUST-1 DER (fs, 100 kHz), (fs, 500 kHz), and (fs, 1 MHz) surfaces.

3.3. UiO-66. In contrast, UiO-66 demonstrates a high resistivity of the organic part to femtosecond and nanosecond laser conversion, producing UiO-66 DER with a more complex structure and morphology (Figures 2A4-E4 and S3). Indeed, femtosecond laser conversion (fs, 1 kHz) produces crystal fragments with insufficient amorphization (as confirmed by Raman in Figure 4D, and powder X-ray diffraction in Figure S16), while an increasing the repetition rate of the femtosecond laser pulses (femtosecond, 1 MHz) stimulates the amorphization and forms inclusions of metal oxide particles (EDX in Figure S6, FFT results in Figures S13–S15 and Table S5). The nanosecond laser regime (ns, 10 kHz) still preserves the integrity of the ligand and MOF structure (see Raman spectrum in Figure 4D for UiO-66 DER (ns, 10 kHz) and powder X-ray diffraction in Figure S16), allowing observation mostly of the amorphous organic particles containing metal oxide (Figure S6) with some carbon contamination. Here, as in the case of HKUST-1, the statistical analysis of the obtained MOF derivatives also showed that increasing the pulse duration from 200 fs to 100 ns does not affect their size distribution (Figure S3):  $50 \pm 40$ ,  $50 \pm 20$ , and  $50 \pm 20$  nm

sizes of the particles are observed for the (fs, 1 kHz), (fs, 1 MHz), and (ns, 10 kHz) laser regimes, respectively (with the maximum size of 1200 nm).

**3.4. 2D MOF.** We also confirmed a similar dependence of morphology, size, and composition of the MOF derivatives for the selected 2D MOF. The (fs, 1 kHz) laser regime provides the shapeless and dendrite-like<sup>32</sup> amorphous particles of  $40 \pm 20$  nm size (Figure S1), consisting mainly of metal oxide with the presence of an organic ligand, as confirmed by TEM (Figure S7), EDX (Figure S4), and Raman analysis (Figure S18). An increase in the repetition rate of femtosecond laser pulses (fs, 1 MHz) also led to obtaining shapeless amorphous particles of  $60 \pm 40$  nm size (Figure S1), consisting mainly of metal oxide (Figures S4 and S18). Finally, the nanosecond laser regime (ns, 10 kHz) made it possible to obtain smaller particles (15 ± 10 nm) of the metal oxide and the presence of carbon (Figures S1, S4, and S18).

**3.5. Photoluminescence.** The results of the structural analysis are in good agreement with those of the PL for the MOF derivatives. Figure 5 shows that the femtosecond laser conversion of the MOFs with high thermal resistance slightly

changes the spectrum of PL (i.e., for UiO-66 DER in comparison with the initial MOF crystal). For less thermally stable frameworks, ZIF-8 DER demonstrates a blue-shifted PL spectrum; 2D MOF DER shows red-shifted PL (Figure S17), while ZIF-67 DER and HKUST-1 DER did not show any PL emission. However, the ns laser regime, regardless of the MOF structure and chemical composition, makes it possible to obtain the derivatives with the same PL spectra (pumped with 400 nm), similar to that of carbon and its allotropic forms.<sup>56</sup>

3.6. Laser Parameters versus MOF Structure. Taking into account the thermal resistance of the MOFs and the laser conversion parameters, the results of electronic and optical spectroscopy (Figures 2-5) for the derivatives can be represented as follows (Figure 6D). An increase in the thermal resistance of the MOFs subjected to the (fs, 1 kHz) laser regime makes it possible to obtain structures from amorphous carbon particles with a metal or metal oxide impurity to crystal fragments with a low degree of amorphization. The (nanosecond, 10 kHz) laser conversion regime of the MOFs with increased thermal resistance makes it possible to obtain the structures from pure carbon and metal or metal oxide particles to amorphous organometallic particles with metal oxide inclusions. With such a harsh laser conversion regime, the integrity of the ligand is almost never observed (a rare exception for UiO-66, Figure 4D). At the same time, the intermediate laser conversion regime (i.e., fs, 1 MHz) gives the results balancing between the "hot" and "cold" laser ablation, making it possible to obtain both metal and metal oxide particles with a carbon shell and metal oxide particles with an organic shell and even crystal fragments with significant amorphization. This analysis made it possible to outline the "laser parameters versus MOF structure" space for predicting the results of the laser-assisted design of MOF derivatives.

In addition, we have found that the laser conversion of HKUST-1 above the threshold fluence of 10  $\mu$ J cm<sup>-2</sup> (for ns, 10 kHz) and 0.1 mJ cm<sup>-2</sup> (for fs, 1 MHz) was accompanied by the emission of white light (Figure 6D). We speculate here about the emission of a blackbody heated to several thousand K.<sup>25</sup> Nevertheless, the laser conversion products have also been formed, corresponding to the MOF derivatives in Figure 2E.

**3.7. Application, Part I.** Using the "laser parameters versus MOF structure" space, we have selectively chosen opposite MOFs (in terms of thermal resistance, Table S1) and applied separately two opposite laser conversion regimes (fs, 1 kHz and ns, 10 kHz) to obtain scalable derivatives. As one can see in Figure 6A, the laser conversion (fs, 1 kHz) of UiO-66 makes it possible to obtain nanometer-scale particles (up to 100 nm in diameter for UiO-66 DER), demonstrating the PL signal, partly inherent in their bulk counterparts. The size of UiO-66 DER obtained contributes to the PL enhancement for potential light control at the nanoscale.<sup>32</sup> On the other hand, the (ns, 10 kHz) laser conversion regime of such MOFs will make it possible to obtain scalable surfaces consisting of amorphous organics with metal oxide inclusions, which are potentially useful for data storage application.<sup>57</sup>

At the same time, the scalable laser conversion of HKUST-1 (regardless of the regime) has been performed in reflection geometry for a 0.5 mm thin film consisting of pressed HKUST-1 microcrystals on a fused silica substrate. This allows for obtaining a 4 cm<sup>2</sup> surface (Figure 6C) of different ratios of carbon and pure metal (Cu) inclusions, which demonstrates a similar optical reflection behavior as a bulk infrared Cu mirror (Figure 6B).<sup>58</sup> It should be noted that the optical properties of

the derivatives from such optically active and structurally adaptive MOFs, such as UiO-66 and HKUST-1, both fundamentally and technologically differ from the precursor analogues used for nonlinear optics.<sup>59–61</sup>

3.8. Application, Part II. The surfaces obtained from the laser conversion of HKUST-1 in Figure 6C also turned out to be promising for detection and control of the fluorescently labeled biomolecules. To demonstrate this, on the one hand, we used their metallic nature and created a series of 4 cm<sup>2</sup> surfaces by fs laser conversion of HKUST-1 with 100 kHz, 500 kHz, and 1 MHz repetition rates (the resulting roughness of which is approximately the same, Figure S20). The SEM micrographs of the developed surfaces are presented in Figure 7A,B. We assumed that the copper nature of such centimeterscale derivatives would be able to modulate the intensity of the PL signal from adsorbed fluorescent biomolecules in the region of 580 nm.<sup>62</sup> For this, we covered the surfaces with bovine serum albumin (BSA) conjugated with cyanine 5 (Cy5) and fluorescein isothiocyanate (FITC) dyes for bright fluorescence centered at 675 nm (BSA-Cy5) and 530 nm (BSA-FITC). In detail, 10 µL of BSA-Cy5 or BSA-FITC was added to the surface, followed by drying at 40 °C for 20 min. Then, the resulting surfaces were analyzed by confocal laser scanning microscopy (CLSM) with 633 nm (for BSA-Cy5) and 488 nm (for BSA-FITC) laser pumps (Figure 7C,D). As a reference, we have also used a gold film covered by BSA-Cy5 and BSA-FITC conjugates, prepared and analyzed under the same conditions. As one can see in Figure 7F, a detailed analysis of the Cy5 system showed PL emission in the region of 675 nm for the gold film and the surfaces, while statistically, we have found that the intensity of PL from the HKUST-1 DER (fs, 1 MHz) surface is 2 times higher than that from gold and HKUST-1 DER (fs, 100 kHz) surfaces. This can be explained by the formation of a larger number of metallic elements during the fs laser conversion at an enhanced repetition rate. In this case, we have also observed an increase in PL intensity in the region of Cu plasmon resonance for the surfaces. Regarding the FITC system (Figure 7E), we have observed a similar shape of the PL spectra on different surfaces; however, the HKUST-1 DER (fs, 100 kHz) surface provided a PL signal on average 5 times greater than gold and HKUST-1 DER (fs, 1 MHz) surfaces.

Continuing the story of the metallic carbon nature of the surfaces based on HKUST-1, we have also tested their catalytic activity<sup>63</sup> using the decomposition of dyes (Figure 7G,H). For this, 2 mL of rhodamine 800 (Rh800) aqueous solution (62.5 mg  $L^{-1}$ , 0.126 mmol) and the surfaces (100 kHz, 500 kHz, and 1 MHz) were charged in a beaker. Then, 0.1 mL of  $H_2O_2$  (30 wt %) aqueous solution was added and kept at room temperature for 24 h. The content of Rh800 in the solution was determined by a Shimadzu UV-3600 ultraviolet spectrometer in 0, 1, 2, 4, 8, and 24 h. An aqueous solution of Rh800 (62.5 mg  $L^{-1}$ ) with 0.1 mL of H<sub>2</sub>O<sub>2</sub> (30 wt %) served as a reaction control. As one can see (Figure 7G,H), a 2-fold increase in the reaction rate is observed for the HKUST-1 DER surface (fs, 100 kHz), while a more metalized (via fs, 1 MHz) surface and the control show similar results. Thus, photocatalytic degradation of Rh800 showed that the HKUST-1 DER (fs, 100 kHz) surface provided the most significant photocatalytic activity compared to HKUST-1 (fs, 500 kHz, 1 MHz) with the same surface roughness (Figure S20) and control experiments.

We report on statistical analysis of different processes of interaction of laser light with metal-organic frameworks and establish the general concept for the controlled laser-assisted design of nano- to centimeter-scale MOF derivatives with the desired nonlinear optical and catalytic properties. Five representative 3D and 2D MOFs, differing in chemical composition, topology, and thermal resistance, have been selected as precursors. Tuning the laser parameters (duration of the laser pulses from fs to ns and their repetition rate from 1 kHz to 1 MHz), we discovered two distinct regimes of lightmatter interaction: ultrafast nonthermal destruction and thermal decomposition through laser metallurgy. We have discovered that regardless of the chemical composition and MOF topology, the tuning of the laser parameters (from ns to fs) allows extending a series of MOF derivatives from carbon aggregates, carbon aggregates with metal and/or metal oxide nanocrystals, to MOF nanocrystals, amorphous metal-organic nanoparticles with intact ligands, and metal-organic nanoparticles containing metal and/or metal oxide nanocrystals (Figure 1). In addition, regardless of the composition and MOF topology, the transition from femtosecond to nanosecond laser pulses ensures the scaling of specific MOF derivatives from nano- to centimeter scales. Herein, the thermal resistance of MOF precursors directly affects the structure and chemical composition of the resulting derivatives. The statistical analysis of the MOF derivatives by electronic and optical spectroscopy made it possible to outline the "laser parameters versus MOF structure" space (Figure 6D), in which one can create the materials with the desired structure and functionality. The resulting scalable MOF derivatives with controlled structures have shown exceptional optical properties from the photoluminescence of single-nanometer-scale MOF derivatives to modulated photoluminescence from adsorbed dyes and the enhanced catalytic activity of the 4 cm<sup>2</sup> surface of MOF derivatives.

# ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.3c10193.

Methods description; SEM; EDX; statistical analysis of size distribution; TEM; FFT; PXRD; AFM; and optical spectra (PDF)

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# Notes

The authors declare no competing financial interest.

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