Supporting information

Label-free visualization of heterogeneities and defects in metal-organic frameworks using nonlinear optics

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1. Experimental:

Synthesis of metal organic frameworks (MOFs): Microcrystals of CD-MOF (1) was synthesized according to the literature (Nanoscale, 2017, 9, 7454-7463). Microcrystals of MOF-177 (2) was synthesized according to the literature (J. Mater. Chem., 2007, 17, 3197–3204). Microcrystals of [(Co(SCN)_3(TPT)_4]n (3) was synthesized according to the literature (TPT: 2,4,6-tris(4-pyridyl)-1,3,5-triazine, Nat. Chem., 2010, 2, 780–783). Space groups for the MOFs are 1: R32, 2: P3̅1c, 3: Fm̅3m.

Introduction of C_{60} into MOFs: As-synthesized crystals of 1, 2 and 3 were immersed into a saturated toluene solution of fullerene C_{60} (10 mL) at room temperature. The suspension was heated to 60°C in an oven. After 1 day, the supernatant was removed by decantation, another 10 mL of saturated fullerene solution was added to the residue, and the resulting suspension was again allowed to stand at 60 °C. After 1 week with six solution-replacement cycles, the inclusion complex was obtained (Nat. Chem., 2010, 2, 780–783). MOFs accommodating C_{60} fullerene are denoted as 1\(\rightleftharpoons\)C_{60}, 2\(\rightleftharpoons\)C_{60} and 3\(\rightleftharpoons\)C_{60}.

Characterization: X-ray diffraction (XRD) measurements were carried out with SmartLab, Rigaku. The microcrystals of 1, 2 and 3 were observed by a desktop scanning electron microscope (SEM, Phenom Pro, Phenom-World).

Confocal Microscopy: Nonlinear optics (NLO) and Raman measurements were carried out using an inverted optical microscope (Ti-U, Nikon) equipped with a piezoelectric stage (P517.3CL, Physik Instrument).

For NLO experiments, two laser wavelengths were used at 820 nm (Mai Tai HP, Spectra-Physics, 120 fs, 80 MHz) and 1164 nm (Inspire HF 100, Spectra-Physics). The four-wave mixing (FWM) in this study is so-called degenerate-four-wave-mixing (DFWM) meaning two of the three in-going wavelengths are the same. Radiation is generated at:

\[ \omega = \omega_1 + \omega_1 - \omega_2 \]  

Raman spectra were recorded using a 785 nm solid-state laser (Excelsior 785, Spectra-Physics). For both measurements, the excitation beams were focused 2 μm above the glass-MOF interface using an objective lens (60x PlanApo, air, NA 0.95, Nikon). The backscattered NLO and Raman signals were corrected by the same objective, and spectra were recorded using a charge-coupled device (CCD) camera (DU920P, Andor) with a spectrograph (iHR320, Horiba). In order to block excitation light, a 750 short-pass (ET750sp, Chroma) and 800 nm long-pass filter (HQ800LP, Chroma) were used for FWM and
Raman, respectively. NLO and Raman signals from out of focus were removed by a pinhole (diameter 100 μm).
Maps were obtained by using AIST software (AIST-NT) for piezo-controlled movement together with Labspec software (Horiba) to collect spectra at every point. For all MOFs, maps were obtained with a pixel size of 200 x 200 nm². Accumulation time at every point was 1 second for NLO maps and 4 seconds for Raman maps. All maps are x,y-slices obtained by focusing the two laser beams 2 μm above the glass-MOF interface. Integration time at every point was 1 s and 4 s for NLO and Raman mapping, respectively.

Fig. S1 Schematic of experimental setup. MOFs were put on top of a coverslip which is placed on top of a piezo-controlled stage. The pump beams are focused by an objective below the sample. The generated signal is collected via the same objective. Maps were obtained roughly 2 μm above the coverslip by moving the sample over the objective.

Data analysis was performed using a self-written Python routine. The raw data spectra were smoothed using Savitzky-Golay-filter. The regions of interest were cut out from the spectra. Afterwards a linear background correction was applied. The maximum intensity of peaks was used for mapping.
2. MOF structures

Fig. S2 Structure of 1. The space group is \( R32 \).\(^1,2\)

Fig. S3 Structure of 2. The space group is \( P\bar{3}1c \).\(^1,3\)
Fig. S4 Structure of 3. The space group is $Fm\overline{3}m$.\textsuperscript{1,4}

3. SEM

Fig. S5 SEM images from 1 (a), 2 (b) and 3 (c).
4. XRD

Fig. S6 XRD data obtained from 1 (red) and simulation\textsuperscript{2,5} (black).

Fig. S7 XRD data obtained from 2 (red) and simulation\textsuperscript{3,5} (black).
Fig. S8 shows XRD obtained from 3 (red), 3$\supseteq$C$_{60}$ (blue) and simulation$^{4,5}$ (black).

Fig. S8 shows XRD obtained from 3 and 3$\supseteq$C$_{60}$. The semi-amorphous state can be seen in red and is characterized by a relatively strong peak at 13° and weak low-angle peaks. After accommodation of C$_{60}$ into the MOF, the data shown in blue is obtained. Compared to the before-mentioned data, it shows stronger low-angle peaks typical for a crystalline structure.

References