Supporting Information

Chiral and SHG-Active Metal-Organic Frameworks Formed in Solution and on Surfaces: Uniformity, Morphology Control, Oriented Growth, and Post-assembly Functionalization

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Experimental section

Characterization and Reagents
1,3,5,7-Tetrakis(4-((E)-2-(pyridin-4-yl)vinyl)phenyl)adamantane (Ad-DB), 1,3,5-tris(4-pyridyl-trans-ethenyl)benzene (TPEB), and TPEB-based monolayers were prepared according to literature procedures (Scheme 1). Reagents, metal salts (NiBr$_2$, NiCl$_2$$\times$6H$_2$O, Ni(NO$_3$)$_2$$\times$6H$_2$O, and Ni(OAc)$_2$$\times$4H$_2$O), and solvents were purchased from Sigma-Aldrich and used without further purifying. Glass pressure tubes (Ace Glass, Inc.) were cleaned by immersion in a piranha solution (7:3 v/v, H$_2$SO$_4$/30% H$_2$O$_2$) for 10 min and washed with deionized (DI) water and then dried for 2 h at 120 °C. **Caution: piranha is an extremely dangerous oxidizing agent and should be handled with care using appropriate personal protection.**

NMR spectroscopy
A Bruker NMR spectrometer (300 MHz) was used for the $^1$H and $^{13}$C{$^1$H} NMR measurements.

Optical Microscopy
Optical microscopy images were taken using a Nikon E600 Pol microscope and a Nikon DS F1 camera.

FT-IR, Micro-Raman and UV/Vis spectroscopy
A Nicolet 460 single-beam infrared Fourier transform spectrophotometer (FT-IR) was used for obtaining IR spectra with KBr pallets. Raman experiments were conducted with a Renishaw Micro Raman Imaging Microscope with a 632.8 nm He-Ne laser. The laser power was 25 mW with a 10× objective used for focusing. The acquisition time was 10 s. The UV/Vis spectra were obtained using Varian Cary 100 spectrophotometers (in double-beam transmission mode).

Scanning electron microscopy (SEM)
SEM measurements were performed using HRSEM ULTRA-55 ZEISS and HRSEM SUPRA-55 VP ZEISS instruments at an EHT voltage of 1.5 kV. SEM samples were prepared by placing a drop of the crystals dispersed in ethanol on a silicon substrate, and allowing the solvent to evaporate.

Powder X-ray diffraction (PXRD)
Samples of surface-grown MOFs (sMOFs) on ITO were analyzed in the reflection geometry using an TTRAX III (Rigaku, Japan) diffractometer equipped with a rotating Cu anode operating at 50
kV and 200 mA and with a scintillation detector aligned at the diffracted beam after a bent Graphite monochromater. Next, 2θ/θ scans were performed under specular conditions in the Bragg-Brentano mode with variable slits and scanned from 1 to 35 degrees of 2θ with step sizes of 0.02 degrees and a scan speed of 0.5 degree/min. Samples of MOFs (obtained in solution) were scanned in reflection geometry using an Ultima III (Rigaku, Japan) diffractometer equipped with a sealed Cu anode X-ray tube operating at 40 kV and 40 mA. A bent graphite monochromator and a scintillation detector were aligned in the diffracted beam. Then θ/2θ scans were performed under specular conditions in the Bragg-Brentano mode with variable slits. The 2θ scanning range was from 2 to 60 degrees using a step size of 0.025 degrees and a scan speed of 0.5 degree/min.

Characterization of surface-grown MOFs (sMOFs) by electron diffraction
Scanning electron diffraction data were obtained in a double aberration-corrected Themis Z microscope (Thermo Fisher Scientific Electron Microscopy Solutions, Hillsboro, USA) equipped with a high-brightness FEG at an acceleration voltage of 200 kV. For the diffraction recording, an electron probe with a convergence angle of 0.2 mrad was adjusted in scanning transmission electron microscopy (STEM) microprobe mode and further defocused by typically 5-10 μm to reduce the probe size and electron flux. A primary beam current of less than 10 pA was used. The electron microscope pixel array detector (EMPAD) enabled a rapid data collection of the entire unsaturated diffraction pattern with a pixel dwell time of 1 ms for each pattern. Typically, diffraction patterns were acquired over a raster of 128 pixels × 128 pixels.

Atomic Force Microscopy (AFM)
The AFM measurements were made on a Bruker MMAFM system, with Nanoscope V control electronics. The PF-QNM mode was used, which allows obtaining topographical as well as nanomechanical maps. An AC160 probe (Olympus) was used with a calibrated spring constant and a tip radius of 35 N/m and 20 nm, respectively. Images were processed and analyzed using Gwyddion open source software (http://gwyddion.net/).

Fluorescent Microscopy
Confocal imaging was conducted by using an upright Leica TCS SP8, equipped with internal Hybrid (HyD) detectors and an Acusto Optical Tunable Filter (Leica Microsystems CMS GmbH, Germany). Dye excitation was performed using a laser (λ = 561 nm) at 8.0% power. The emission signal was collected using an internal HyD detector at a range of λ = 571–649 nm. Images were acquired using the galvometric scanner with a 20× air objective (HC PL APO 20X/0.75 CS2)
providing images with a field of view of 123.1 mm and a pixel size of 0.152 mm. Z-stacks were acquired using the galvo stage, with 0.684 μm intervals. The acquired images were visualized using ImageJ.

**Second-Harmonic Generation (SHG) Microscopy**

SHG imaging was performed on 2PM; a Zeiss LSM 510 META NLO equipped with a broadband Mai Tai-HP-femtosecond single box tunable Ti-sapphire oscillator, with automated broadband wavelength tuning $\lambda = 700$–$1020$ nm from Spectraphysics. Images were acquired using a laser wavelength of 940 nm and detection through a filter of $\lambda = 415$-$637$ nm. All SHG microscopy images were false colored.

**Single-Crystal SHG Microscopy Set-up**

For single-particle SHG measurements, 100fs pulses at $\lambda = 1000$ nm and at an 80 MHz repetition rate from a Ti:Sapphire laser (Coherent, Chameleon Ultra II), were passed through a half wave plate, coupled into an inverted microscope (Zeiss, Axiovert 200 inverted microscope) and focused using an objective (Zeiss, Plan-Apochromat 10×/0.45NA). The epi-detected signal was filtered using a dichroic mirror (Thorlabs, DMSP950R), a band pass filter (Semrock, FF01-500/24-25), and a color glass (Thorlabs, FGS900-KG3). A polarizer (analyzer) was placed right before a multimode fiber (Thorlabs, FG050LGA). The SHG signal was detected by a single-photon avalanche photodiode (ID Quantique, ID100) that was connected to a time-correlated single-photon counting (TCSPC) system (Picoquant HydraHarp 400). The laser trigger output was connected to the TSCPS for synchronization. Samples were drop cast on a #1 cover slip and left to dry. In all experiments the laser power was ~200 mW. For simplicity, single crystals were chosen, based on their orientation in the lab frame of reference such that their major axis was parallel to either the x or y coordinate in the lab. Mapping was done by scanning the sample position using a piezo stage (Mad City Labs, Nano-BioS100) and measuring the SHG intensity while the excitation and collection polarizations were kept fixed. Polarimetry was performed by measuring the SHG intensity from a single point on the microcrystal as a function of the half wave plate angle (changing the excitation polarization) for two analyzer positions (the x and y polarizations in the lab frame). In both the mapping and the polarimetry measurements the time-correlated single photon counting (TCSPC) was operated in histogram mode.
Single-crystal X-ray crystallography

All crystals were coated in Paratone oil (Hampton Research) and mounted on MiTeGen loops. They were flash frozen in the liquid nitrogen stream of the Oxford Cryostream. Diffraction data of MOF-NiBr₂ (CCDC numbers: 1965786 and 1965784) and MOF-Ni(OAc)₂ (CCDC numbers 1965788 and 1965787) were measured at a low temperature of 100(2) K using Cu Kα \( \lambda = 1.54184 \) Å on a Rigaku XtaLab³³⁰ diffractometer equipped with a Dectris Pilatus 3R 200K-A detector or \( \lambda = 0.70 \) Å at the ESRF ID29 beamline with a Dectris Pilatus 6M detector. For ligand Ad-DB, the diffraction data were collected at 100K on a Bruker KappaApexII CCD system using MoKα \( \lambda = 0.71073 \) Å. Data were processed and reduced using the Bruker Apex3 Suite of programs. The Rigaku data were processed and reduced with 'CrysAlisPro 1.171.39.46 (Rigaku OD, 2018)'. The synchrotron data were collected with MXcube and EDNA (MxCuBE: a synchrotron beamline control environment customized for macromolecular crystallography experiments)⁵⁵ and processed with XDS. All structures were solved with SHELXT-2013 or SHELXT-2016/4 and refined with SHELXT-2016/4.⁶⁶ All non-hydrogen atoms were refined anisotropically and hydrogens were placed in calculated positions and refined in riding mode. The SQUEEZE protocol of Platon⁷⁷ was run on all structures. The crystal data and structural refinement are summarized in Table S1.

Preparation of the metallo-organic frameworks (MOFs).

![Chemical structure](image)

1,3,5,7-Tetrakis(4-((E)-2-(pyridin-4-yl)vinyl)phenyl)adamantine (Ad-DB, 18.0 mg, 0.021 mmol) is dissolved in 6.0 mL DMF. NiBr₂ (8.2 mg, 0.056 mmol) is dissolved in 4.0 mL DMF. To a 21 mL glass pressure tube, a solution (2.0 mL) of Ad-DB, 1.5 mL DMF, and 0.5 mL CHCl₃ is added and sonicated for 1 min. Then, a solution of NiBr₂ (1.0 mL) is added and the reaction mixture is sonicated for 1 min. The sonication is used to facilitate dissolving the materials; however, it is not
essential. The sealed tube is transferred to an oven and kept at 105 °C for 48 h. The thermostat of the oven was lowered 10 °C every hour, until reaching 25 °C. The MOFs are separated by centrifugation (4000 rpm, 5 min). After the solvent is discarded, the MOFs are washed with DMF, CHCl₃, and EtOH, and dried under vacuum (~10⁻² mbar) for 12 h, affording a light green powder (92% yield based on the ligand). Identical procedures for the formation of MOFs with NiCl₂, Ni(NO₃)₂, and Ni(OAc)₂ were used. The yields based on the ligand are: MOF-NiCl₂ (90%), MOF-Ni(NO₃)₂ (88%), MOF-Ni(OAc)₂ (85%).

Concentration effects
The procedure for preparing MOF-NiBr₂ under different concentrations is similar to that described above. The ligand-to-metal salt ratio was kept constant (mole ratio 1:2). The ligand (Ad-DB) concentration ranged from 0.47-5.64 μmol/mL (Figure S1).

Preparation of the Surface-Bound MOFs (sMOFs)
Ad-DB (18.0 mg, 0.021 mmol) is dissolved in DMF (6.0 mL). NiBr₂ (8.2 mg, 0.038 mmol) is dissolved in DMF (4.0 mL). The silicon or quartz substrates, functionalized with a TPEB-based monolayer (Scheme 1) or ITO/glass,³³ are placed inside a glass pressure tube with the monolayer or the metal-oxide layer facing the bottom. The solution of Ad-DB (2.0 mL), 1.5 mL DMF, and 0.5 mL CHCl₃ is added to the pressure tube and sonicated for 1 min. A solution of NiBr₂ (DMF, 1.0 mL) is added and the reaction mixture is sonicated for 1 min. The sealed pressure tube is transferred to an oven and kept at 105 °C for 48 h. Next, the thermostat of the oven is lowered 10 °C degrees every hour until reaching 25 °C. Finally, the substrate is washed with DMF, CHCl₃, and dried in the air. Identical procedures for the preparation of MOFs with Ni(NO₃)₂ and Ni(OAc)₂ are used.

Detachment of Surface-Bound MOFs (sMOFs)
A silicon substrate (1 cm × 1 cm) with surface-bound MOF-NiBr₂ is placed into a vial with ethanol (1.0 mL) and sonicated for 20 min. The mixture is transferred to a centrifuge tube (4 mL) and the detached MOFs are separated from the reaction mixture by centrifugation (4000 rpm, 5 min). The ethanol is decanted, and the MOFs are washed with DMF, CHCl₃, and EtOH.

Dye Loading Experiment
(I) Detached crystals of sMOF-NiBr₂ (10 mg) were added to a solution of sodium resorufin (0.72 mg, 0.0031 mmol, and 2.0 mL ethanol) for 24 h. The dye solution was discarded. The purple
crystals were washed twice with ethanol (2 × 2.0 mL), and drop-casted on glass slides for further characterization. (II) sMOF-NiBr₂ on ITO-coated glass slides were immersed into a solution of sodium resorufin (0.72 mg, 0.0031 mmol in 2.0 mL ethanol) for 30 min. The slides were washed by immersion into ethanol (2 × 4.0 mL), and the functionalized sMOF-NiBr₂ were characterized by confocal fluorescent microscopy. The dye-loaded sMOF-NiBr₂ were detached from the ITO surface by sonication in ethanol (0.5 mL), and drop-casted on glass slides.

Figure S1. (A) SEM image of MOF-NiCl₂. (B) Histogram showing the length distribution based on the SEM data.
Figure S2. Concentration effect of Ad-DB and NiBr$_2$ on the dimensions of MOF-NiBr$_2$. The experiments shown were carried out with a constant molar ratio: Ad-DB:NiBr$_2$ = 1:2, DMF/CHCl$_3$ = 9/1, v/v, 105 °C, scale bar: 10 μm. (A) (C) SEM images of MOF-NiBr$_2$. Concentration of Ad-DB: (A) 0.47 μmol/mL, (B) 1.41 μmol/mL, (C) 2.82 μmol/mL. (D) Relation between the length distribution and the concentration of Ad-DB (0.47 μmol/mL – 5.64 μmol/mL). The blue dots labelled A–C correspond to the SEM images (A–C).

Figure S3. Optical images of MOF-Ni(OAc)$_2$, unpolarized light (left), and polarized light (right). Scale bar: 50 μm.
Figure S4. Cross-Nicols polarized images of MOF-NiBr$_2$ formed in solution. The sample was rotated counter clockwise from horizontal (A and B), 45° (C and D), and 90° (E and F). Scale bar: 25 μm.

Figure S5. Cross-Nicols polarized images of MOF-NiBr$_2$ formed in solution from the hexagonal side, the sample was rotated counter clockwise from horizontal (A and B), 60° (C and D), and 120° (E and F). Scale bar: 25 μm.
**Figure S6.** Cross-Nicols polarized images of MOF-Ni(OAc)$_2$ formed in solution; the sample was rotated counter clockwise from horizontal (A and B), 45° (C and D), and 90° (E and F). Scale bar: 25 μm.

**Figure S7.** FT-IR spectra of Ad-DB and of MOFs prepared from nickel salts with different counter-anions.
**Figure S8.** FT-IR spectra of MOF-Ni(NO$_3$)$_2$ (red) and Ni(NO$_3$)$_2$×6H$_2$O (purple). The adsorption bands at $\nu=1384$ cm$^{-1}$ and $\nu=1627$ cm$^{-1}$ are assigned to NO$_3^-$.$^8$

**Figure S9.** Crystal structure of ligand Ad-DB, space group: $P-4$, unit cell parameter: $a = b = 13.6468$ Å $c = 7.0913$ Å, $\alpha = \beta = \gamma = 90^\circ$. A. The view down axis $c$; B. The conformation of ligand; Channels are presented in C-D (yellow). C. The view of channels down axis $c$. D. The view from axis $a$. Hydrogen atoms have been omitted for clarity. Crystals of Ad-DB suitable for single-crystal X-ray analysis were obtained from solution by slow evaporation of the solvents at room temperature (18.0 mg, 0.021 mmol of Ad-DB in 1.5 mL CH$_2$Cl and 0.5 mL CH$_3$OH).
Figure S10. Network topology of the crystallographic structure of two crystals of MOF-NiBr$_2$ showing the helical channels and the connections between the ligand (gray) and the nickel centers (green).$^{9,10}$ (A) Perspective view from axis c (CCDC: 1965786). (B) View from axis b (CCDC: 1965786). (C) Top view and side view of helical channels with opposite chirality: right-handed helix (CCDC: 1965786) and left-handed helix (CCDC: 1965784).
Figure S11. AFM images of MOF-NiBr$_2$ grown on a silicon substrate functionalized with a monolayer of TPEB,$^3$ and of crystals formed in parallel in solution. (A) AFM image of a surface-bound crystal and the height profiles along the scans shown in the image. (B) AFM image of the same crystal formed in solution and the height profiles along the profiles shown in the image. (C) 3D view of a non-oriented crystal grown in solution. Surface-grown crystals were prepared with a ligand concentration of 4.8 $\mu$mol/mL.

Figure S12. (A) Stiffness mapping of MOF-NiBr$_2$. (B) Histogram of stiffness data taken from (A) with 7.3 ± 2 GPa.
**Figure S13.** Concentration effects on the dimensions of the sMOFs. SEM images of sMOF-NiBr$_2$ grown on a silicon substrate modified with a monolayer of TPEB$_{53}$ at two ligand concentrations: (A and B) 0.47 $\mu$mol/mL; (C and D) 1.41 $\mu$mol/mL. (B and D are higher magnifications of A and C, respectively.)

**Figure 14.** Secondary growth on sMOF-NiBr$_2$. (A) Schematic representation, (B) SEM images, and (C,D) AFM images of the secondary crystals. (E) Height profiles along the two scan profiles shown in (D).

$H_1 = 46.3$ nm  
$H_2 = 34.3$ nm  
$\Delta H_1 = 6.8$ nm  
$\Delta H_2 = 14.2$ nm
Figure S15. SEM images of FIB-etched (A and B) oriented sMOF-NiBr$_2$ grown on silicon modified with a monolayer of TPEB$^{53}$ (Scheme 1) and (C, D) MOF-NiBr$_2$ formed parallel in solution.

Figure S16. Optical images of sMOF-NiBr$_2$ grown on silicon modified with a monolayer of TPEB$^{53}$ (A) Crossed-Nicols polarized and (B) unpolarized light.
**Figure S17.** SEM images of MOF-NiBr₂ detached by sonication from a silicon substrate (1 cm × 1 cm) functionalized with a TPEB-based monolayer (Scheme 1).\textsuperscript{S3}

**Figure S18.** (A) Confocal z-axis scanning fluorescent micrographs of sMOF-NiBr₂. These MOFs were functionalized with sodium resorufin after detachment from the ITO surface. Scale bar: 5 µm. Excited at \( \lambda = 561 \) nm, collected at \( \lambda = 571–649 \) nm. (B) Optical image of sMOF-NiBr₂ grown on ITO after loading with sodium resorufin. (C) Confocal z-axis scanning fluorescent micrographs of sMOF-NiBr₂ grown on ITO. These MOFs were functionalized with sodium resorufin before detachment from the surface. Scale bar: 5 µm. Excited at \( \lambda = 561 \) nm, collected at the range \( \lambda = 571–649 \) nm. (D) Polarized-dependent emission (left) and optical images (right) of sMOF-NiBr₂ functionalized with sodium resorufin before detachment from the surface. Scale bar: 5 µm. Fluorescent images (left), excited at \( \lambda = 561 \) nm, collected at \( \lambda = 571–649 \) nm. \( \theta \) is defined as the polarization direction of the laser beam related to the c-axis of the crystal.
Figure S19. (A) Optical image of the measured crystal close to the parallel lab X axis. Inset: SEM images of the same batch of crystals with an arch surface, scale bar: 10 μm. Raster scans and polarization-dependent measurements of a single crystal of MOF-NiBr$_2$ with different excitation and collection polarizations ($\lambda_{ex} = 1000$ nm). (B) Lab X axis direction. (C) Lab Y axis direction. (D) Polar plot of the SHG intensity at the location indicated in (B). (E) Polar plot of the SHG intensity at the location indicated in (C). (F) Simulated SHG based on a 622 symmetry.

Figure S20. SHG images and spectra of MOF-NiBr$_2$. (A) SHG spectra of MOF-NiBr$_2$ using different wavelengths. Inset: SHG image obtained by exciting at $\lambda = 940$ nm. Scale bar: 20 μm. (B) Z-scanning of SHG images of MOF-NiBr$_2$. Scale bar: 10 μm.
Figure S21. SEM images of ZnO crystals used for Hyper-Rayleigh Scattering measurement. Scale bar: 5 μm.

**Calculation of Second Harmonics**

The polarization of light interacting with MOF-NiBr$_2$ was calculated and plotted in MATLAB. In order to calculate the induced second harmonic generation polarization, the second order nonlinear susceptibility tensor of the MOF crystal is multiplied by the polarization vectors of the incoming field.

\[
(1) \quad \vec{P}(2\omega) = 2\tilde{d}_{eff}\vec{E}(\omega)^2
\]

Since the MOF has a symmetry of 622, the $\tilde{d}_{eff}$ matrix has only 2 components that are connected to each other, such as $d_{44} = -d_{25}^{S11}$ (note that both components would vanish if the Kleinmann symmetry is valid, i.e., for far-detuned excitation); these components were assigned arbitrary units and marked as 1 and -1, respectively. Because the crystal in the microscope is not perfectly aligned with the laboratory axes, rotation matrices have been introduced. We used the Euler rotation convention of Z-Y'-Z'', where the first angle of rotation around the Z axis determines the angle of the crystal within the plane. The second rotation angle around the Y axis determines the out-of-plane angle between the surface and the crystal. The third angle defines rotation along the crystal main axis, which, due to the symmetry of the crystal (622), does not affect the second-harmonic polarization. The incident light in the lab axis was rotated to the crystal frame:

\[
\text{Rot} \times \begin{bmatrix} E_x(\omega) \\ E_y(\omega) \\ E_z(\omega) \end{bmatrix} = \vec{E}'(\omega) \rightarrow \vec{E}'(\omega)^2 = \begin{bmatrix} E_x'(\omega)^2 \\ E_y'(\omega)^2 \\ E_z'(\omega)^2 \\ 2E_y'(\omega)E_z'(\omega) \\ 2E_x'(\omega)E_z'(\omega) \\ 2E_x'(\omega)E_y'(\omega) \end{bmatrix}
\]
Equation (1) was then used to obtain the second-harmonic polarization, first in the frame of the crystal:

\[ \vec{P}'(2\omega) = 2\tilde{d}_{\text{eff}}\vec{E}'(\omega)^2 \]

And then rotated back to the lab axis:

\[ \overrightarrow{\text{Rot}^{-1}} \times \vec{P}'(2\omega) = \vec{P}(2\omega) \]

In MATLAB, the light amplitude was arbitrarily defined to be 1. 360 angles between 0 and 279 degrees; it was used for the various angles of polarization. The calculations mentioned above were done for all the polarization angles of incident light and for all rotation angles for the first Z rotation and the second Y' rotation. The result was plotted in MATLAB’s app designer on polar plots, with the intensity on the X axis, and on the Y axis separately, and with the ability to choose different rotation angles for the crystal orientation.

**Calculation of the Effective Hyperpolarizability for ZnO and MOF in a Hyper-Rayleigh Scattering Configuration**

For measured HRS with a constant wavelength and intensity:

\[ (2) \text{Signal}(2\omega) = <\beta^2> \cdot P(\omega)^2 \cdot N \]

where \(<\beta^2>\) is the rotational average for the second-harmonic intensity, \(P(\omega)^2\) is the incident excitation field, and \(N\) is the number density of the particles in the solution. \(^{512}\) Since a similar \(P(\omega)\) was used for measuring both the MOF and the ZnO (Fig. S21), it is possible to obtain \(<\beta^2>_{\text{MOF}}\) from the ratio of the measured signals by:

\[ <\beta^2>_{\text{MOF}}=\frac{\text{Signal}_{\text{MOF}}(2\omega)}{\text{Signal}_{\text{ZnO}}(2\omega)} \cdot \frac{N_{\text{ZnO}}}{N_{\text{MOF}}} \]

To calculate \(<\beta^2>_{\text{ZnO}}\) we used the known \(\tilde{a}_{\text{eff}}\) matrix for ZnO (of 6 mm symmetry). \(^{513}\) The experiment was done with incident light polarized only in the Y direction; therefore, we can derive the excitation field.
Rot × \[
\begin{bmatrix}
0 \\
E_y(\omega) \\
0
\end{bmatrix}
\] = \vec{E}'(\omega) → \vec{E}'(\omega)^2 = 
\begin{bmatrix}
E'_x(\omega)^2 \\
E'_y(\omega)^2 \\
E'_z(\omega)^2 \\
2E'_y(\omega)E'_z(\omega) \\
2E'_z(\omega)E'_x(\omega) \\
2E'_x(\omega)E'_y(\omega)
\end{bmatrix}

where Rot is the rotation matrix for the Z-X'-Z'' convention.

\[
Rot = R_{x_3}R_{x_2}R_{x_1} = 
\begin{pmatrix}
\cos (\phi) & -\sin (\phi) & 0 \\
\sin (\phi) & \cos (\phi) & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & \cos (\psi) & -\sin (\psi) \\
0 & \sin (\psi) & \cos (\psi)
\end{pmatrix}
\begin{pmatrix}
\cos (\theta) & -\sin (\theta) & 0 \\
\sin (\theta) & \cos (\theta) & 0
\end{pmatrix}
\]

The final polarizability of the second-harmonic generated light for each crystal orientation is thus:

\[
P(2\omega) = Rot^{-1} × 2\vec{d}_{\text{eff}}\vec{E}'(\omega)^2
\]

To obtain \(< \beta^2 >_{ZnO} \), the intensity of the HRS signal at a detector placed along a given direction in the lab frame was summed by integration over all crystal angles:

\[
< \beta^2 >_{ZnO} = \int_{\theta=0}^{\pi} \int_{\phi=0}^{\pi} \int_{\psi=0}^{2\pi} |\vec{P}(2\omega)|^2 d\psi = 
\begin{pmatrix}
4 & \frac{105}{46} (20d^2_{31} - 4d_{31}d_{33} + 3d^2_{33}) \\
\frac{35}{4} & (24d^2_{31} + 12d_{31}d_{33} + 5d^2_{33}) \\
\frac{105}{4} & (20d^2_{31} - 4d_{31}d_{33} + 3d^2_{33})
\end{pmatrix}
\]

Since the detectors were placed both from transmission and from 90 degrees from the incident angle to the sample, there are two relevant \(< \beta^2 >_{ZnO} \) values to consider:

For the transmission measurement: \(< \beta^2_x > + < \beta^2_y > \)

For the 90 degrees measurement: \(< \beta^2_x > + < \beta^2_z > \)

These values are the same:

\[
< \beta^2_{\text{eff}} >_{ZnO} = \frac{8}{105} (46d^2_{31} + 16d_{31}d_{33} + 9d^2_{33})
\]

The values of \(d_{31}\) and \(d_{33}\) for ZnO are 5.9 \[\frac{pm}{V}\] and 18 \[\frac{pm}{V}\] respectively,\(^{13}\) therefore, \(< \beta^2_{\text{eff}} > \) is as shown in Table S3.
Table S1 Crystal data and structural refinement of MOF-NiBr₂, MOF-Ni(OAc)₂, and Ad-DB.

| Compound          | MOF-NiBr₂ | MOF-NiBr₂ | MOF-Ni(OAc)₂ | MOF-Ni(OAc)₂ | Ad-DB |
|-------------------|-----------|-----------|--------------|--------------|-------|
| Measurement name  | V240      | V303      | V333         | V360         | V199  |
| CCDC              | 1965786   | 1965784   | 1965788      | 1992014      | 1965785|
| Crystal description| Prism barrel | Split prism | Oval prism | eyeball needle |  |
| Crystal size mm   | 0.025 x 0.003 x 0.003 | 0.032 x 0.032 x 0.047 x 0.200 x | 0.021 x 0.022 x 0.404 x 0.300 x 0.100 x |  |
| Diffractometer    | ESRF ID29 | Rigaku XtaLab³ | Rigaku XtaLab³ | Rigaku XtaLab³ | Bruker Kappa Apex II CCD |
| Empirical formula | C62 H52 Ni N4 O2 + [solvent] | C62 H52 Ni O2 + [solvent] | C62 H52 N4 Ni Cl2 + [solvent] | C62 H52 N4 Ni Cl2 + [solvent] | C62 H52 N4 Ni Cl2 + [solvent] |
| Formula weight (g/mol) | 943.78 | 1071.60 | 943.78 | 982.68 | 853.07 |
| Temperature (K)   | 100       | 100       | 100         | 100          | 100   |
| Wavelength (Å)    | 0.70      | 1.54184   | 1.54184     | 1.54184      | 0.71073|
| Crystal system    | hexagonal | hexagonal | hexagonal   | hexagonal     | tetragonal |
| Space group       | P622      | P622      | P622        | P622         | P-4   |
| a (Å)             | 25.930(3) | 25.8466(8)| 25.7380(18) | 25.9120(8)   | 13.6468(9)|
| b (Å)             | 25.930(3) | 25.8466(8)| 25.7380(18) | 25.9120(8)   | 13.6468(9)|
| c (Å)             | 17.800(4) | 18.0005(4)| 17.903(1)   | 17.7714(4)   | 7.0913(4)|
| a,β,γ °          | 90,90,90  | 90,90,90  | 90,90,90    | 90,90,90     | 90,90,90 |
| Volume (Å³)       | 10365(3)  | 10414.1(7)| 10270.9(15) | 10333.7(7)   | 1320.65(19)|
| Z                 | 6         | 6         | 6           | 6            | 1     |
| Density calculated (Mg/m³) | 0.907 | 1.025 | 0.916 | 0.947 | 1.073 |
| Absorption coefficient (mm⁻¹) | 0.304 | 1.997 | 0.682 | 1.367 | 0.062 |
| F(000)            | 2976      | 3300      | 2976        | 3084         | 452   |
| Theta range for data collection (°) | 0.893 to 23.157 | 4.899 to 47.989 | 4.816 to 48.105 | 61.824 to 25.350 | 2.327 to 14.868 |
| Reflection collected (Unique) | 45582(5081) | 13662     | 35416       | 21248        | 5303 (2300)|
| R int             | 0.058     | 0.0535    | 0.0551      | 0.0379       | 0.0336 |
| Completeness %    | 81.5      | 99.4      | 99.1        | 99.3         | 98.9   |
| Index range h,k,l | -29.29, -29.29, -29.29 | -24.17; -24.17; -24.24; -24.17 | -25.21; -25.21; -25.21 | -10, -10, -10 | -16, -16, -16 |
| Data/restraints/parameters | 5081 / 23 / 301 | 3256 / 6 / 3233 / 21 / 5326 / 215 / 2300 / 1 / | 307 / 313 / 327 / 159 |
| Goodness-of-fit on F² | 1.009 | 1.150 | 1.293 | 1.002 | 0.907 |
| Final R [I>2σ(I)] | R1=0.0872 | R1=0.0901 | R1=0.1031 | R1=0.0796 | R1=0.0572 |
| R (all data)      | R1=0.1036 | R1=0.0980 | R1=0.1031 | R1=0.1054 | R1=0.0832 |
| Absolute structure parameter | 0.059(13) | 0.027(16) | 0.06(6) | 0.06(5) | NA |
| Helicity | P | M | M | P |
Table S2. Concentration of materials used for the Hyper-Rayleigh Scattering measurements.

| Materials  | Concentration (1/L) |
|------------|---------------------|
| ZnO        | $6.18 \cdot 10^7$   |
| MOF-NiBr$_2$ | $7.78 \cdot 10^7$   |

The concentration is estimated from the number of crystals in solution of 5 µL.

Table S3. Hyper-Rayleigh Scattering coefficients of ZnO and MOF-NiBr$_2$

| Materials   | Signal | $\beta^2_{side}$ [pm$^2$/V$^2$] |
|-------------|--------|----------------------------------|
| ZnO         | 569    | 473.64                           |
| MOF-NiBr$_2$| 510    | 282.65                           |

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