Anisotropic band-edge absorption of millimeter-size Zn(3-ptz)_2 single crystal metal-organic frameworks

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Abstract

Metal-organic frameworks (MOF) have emerged as promising tailor-design materials for developing next-generation solid-state devices with applications in linear and non-linear coherent optics. However, the implementation of functional devices is challenged by the notoriously difficult process of growing large MOF single-crystals of high optical quality. By controlling the solvothermal synthesis conditions, we succeed in producing large individual single crystals of the non-centrosymmetric MOF Zn(3-ptz)_2 (MIRO-101) with deformed octahedron habit, and unprecedented surface areas of up to 37 mm². We measure the polarized UV-visible absorption spectrum of individual Zn(3-ptz)_2 single crystals across different lateral incidence planes. Millimeter size single

crystals have band gap $E_g = 3.32$ eV and exhibit anisotropic absorption in the band edge region near 350 nm, whereas polycrystalline samples are fully transparent in the same frequency range. Using solid-state density functional theory (DFT), the observed size dependence of the optical anisotropy is correlated with the preferred orientation adopted by freely rotating pyridyl groups under conditions of slow crystal self-assembly. Our work thus paves the way for the development of optical polarization switches based on metal-organic frameworks.

Introduction

The crystal symmetry, electronic structure and chemical stability are key factors that determine the properties of materials for optical devices such as polarizers,¹ mirrors,² or detectors.³ Precise fabrication of optical materials is also key in the development of advanced technology such as entangle-photon sources^{4,5} and solid-state spin platforms for quantum technology.^{6,7} Organic polymers are promising optical materials because they are inexpensive,^{8,9} lightweight^{10,11} and moldable.^{10,12} However, their optical properties often degrade due to low mechanical resistance, inhomogeneity and temperature-sensitivity, limiting their application in precision optical devices such polarimetry and interferometry.¹³ In contrast, crystalline materials have better performance for these applications. For example, crystal birefringence is essential to amplify and modulate the polarization state of light in waveplates and Pockels cells.^{14,15} In many cases, birefringent crystals also exhibits non-linear responses due to their non-centrosymmetric lattice symmetry, allowing applications such as optical frequency conversion and optical parametric amplifiers.^{16,17}

Metal-organic frameworks (MOFs) are crystalline materials made of organic ligands and inorganic metal centers, which have attracted great interest in materials science due to their ability to be tailor-designed for specific applications.^{18,19} The molecular-level design of MOFs has enabled important advances in gas storage^{20,21} chemical sensing,^{22,23} and energy storage.^{24,25} MOFs also have great potential for nonlinear optical applications. Uniaxial

crystals and non-centrosymmetric coordination networks can be constructed from tetrahedral coordination geometries using d^{10} metal ions without inversion symmetry.¹⁷ The electronic structure of d^{10} metal ions such as Zn^{2+} and Cd^{2+} increases the chemical stability and optical transparency of MOF crystals, due to their inherent resistance to oxidation and the absence of $d-d$ band absorptions in the visible range.^{26,27} The presence of donor-acceptor (pull-push) type ligands in non-centrosymmetric Cd^{2+} or Zn^{2+} -based MOFs structures improve the non-linear response because molecules with large difference between ground and excited states and transition dipole moments increases the second-order non-linear optical susceptibility $\chi^{(2)}$.^{17,28}

The Cambridge Structural Database (CSD) contains almost 20,000 non-centrosymmetric and uniaxial MOFs reported to date.²⁹ However, no detailed optical studies are available on the characterization of applications-ready optical devices, such as Mueller matrix polarimetry.³⁰ Studies have been limited to the measurement of MOF band gaps and second harmonic generation (SHG) signals for polycrystalline MOF samples in powder form.^{17,28} The lack of precise optical characterization may be due to the notorious difficulty of growing large single-crystals MOFs.^{31,32} From the vast MOF literature, only a few reports of single-crystals MOFs grown beyond one millimeter can be found.³³⁻³⁶ Although efforts to understand the dynamics of self-assembly process in MOFs under solvothermal conditions are underway,^{37,38} a general understanding of this process is still elusive, limiting the available strategies for the growth of single-crystals for optical devices.

We have recently reported a method to grow large single-crystals of MOF $\text{Zn}(\text{3-ptz})_2$,³⁸ which has a non-centrosymmetric unit cell, tetrahedral d^{10} coordination geometry and tetrazole push-pull ligands [**3-ptz** = 5-(3-Pyridyl)-1H-tetrazolate]. In this work, we study the polarized absorption of large individual $\text{Zn}(\text{3-ptz})_2$ single-crystals along different crystal planes, and discuss the size dependence on the anisotropic absorption spectrum. Finally, we carry out solid-state density functional theory (DFT) calculations to rationalize the relationship between the crystallographic structure and optical response of our large single-crystals sam-

Figure 1: **Optical setup for single-crystal absorption measurements.** (a) Top view, relative to the plane of the sample holder, which defines the xy plane in the laboratory frame. The MOF crystal attenuates polarized light incident along the z direction on one of the lateral planes, at normal incidence. (b) Front view of the sample in the direction of the incident light. The field polarization angle is set to $\phi = 165^\circ$. In a reference crystal orientation, the crystallographic b -axis coincides with the lab-frame y direction. The sample can be rotated in the yz plane. (c) Relation between the fractional crystal coordinate system (a, b, c) and the xyz lab-frame in the reference configuration.

ples.

Methods

All reactants were purchased from Sigma-Aldrich and utilized without any further purification, except 3-cyanopyridine, which was sublimated at 60°C . The Zn(3-ptz)_2 crystals were synthesized based on the methodology previously reported.³⁸ Large single-crystals were obtained from a mixture of $\text{Zn}(\text{CH}_3\text{COO})_2$ (3.26 mmol), 3-cyanopyridine (6.52 mmol), sodium azide (9.78 mmol) and acetic acid (3.26 mmol) dissolved in 14 mL of distilled water in a glass bottle of 50 mL and adjusting the pH value to 2.7 using HNO_3 (70%). The glass bottle was introduced to a tube furnace at 113°C for 40 hrs (Nabertherm, model 50-250/11) using a horizontal operation and filling the furnace with alumina bulk fiber. All crystals were filtered immediately after finishing the reaction time and washed using ethanol absolute. The planes of crystal faces were characterized by indexing in a SMART CCD diffractometer using the orientation matrix. The representation of the planes were done using the software WinXMorph.^{39,40}

Single-crystals were measured by transmittance in a PerkinElmer Lambda 750S spec-

Figure 2: **Reconstructed crystal habit of MIRO-101.** (a) Top crystal view, displaying the three distinguishable incidence lateral planes along which absorption is measured: $G1$, $G2$, and $G3$; (b) Bottom crystal view.

trophotometer in a quartz cell, holding the $(\bar{1}01)$ plane on the bottom of the quartz cell. We label the crystallographic planes of a moderate size single crystal ($\bar{1}01$ area of 6.4 mm^2). The absorption spectra for the obtained crystal was recorded by orienting the beam through the planes (101) , $(0\bar{1}\bar{1})$ and $(01\bar{1})$ of that crystal sample. The lab-frame coordinates $[x, y, z]^T$ are related to the fractional crystal coordinates $[a, b, c]^T$ by the transformation $[a, b, c]^T = M[x, y, z]^T$, where

$$M = \begin{pmatrix} 8.1146 & 0 & -8.13469 \\ 0 & 10.119 & 0 \\ 6.04545 & 0 & 10.9189 \end{pmatrix}.$$

The propagation vector $\mathbf{k}$ was set to be on the lab-frame z direction, with polarization in the xy at an angle $\phi = 165^\circ$ from the y direction, as illustrated in Fig. 1. The simulated absorption spectra were calculated using DFT with PBE-GGA functionals and Grimme dispersion (D3) function correction, as implemented in CASTEP.^{41–45} Static structural disorder is present in the crystal structure of $\text{Zn}(3\text{-ptz})_2$ (CSD: 184958)⁴⁶ with space group $I-42d$, due to the superposition of a nitrogen and carbon atom in the pyridine ring of the 3-ptz ligand. This is corrected by eliminating the superposed atoms and duplicated hydrogen atoms, and

fixing the position of the nitrogen and carbon thought the pyridyl group in the unit cell to form two possible symmetric cell that we label as Cell A and B, both in space group 82. Both crystal structures (A and B) are valid representations of $\text{Zn}(\text{3-ptz})_2$ and both were used in calculations. By comparing single-point energy calculations, we determinate an optimal k-point mesh of $2 \times 2 \times 2$ and a cutoff of 1100 eV for optimization and absorption calculations. We carry out a two-step optimization procedure for each unit cell: First, only atomic coordinates are minimized. Second, both cell parameters and atomic coordinates were allowed to be optimized. The optimized coordinates and cell parameters were employed for the estimation of the absorption spectra [See details in the Supplementary Material (SM)]. The direction of the electric field vector used in the calculations was estimated by transforming the lab-frame polarization direction to the body-fixed fractional crystal coordinates using the matrix M above. These field directions were used to simulate the MOF absorption spectra. The simulated polycrystalline spectrum was obtained from calculations without a definite direction of the electric field (isotropic dielectric tensor average).

Results and Discussion

Size-dependent optical anisotropy

We study the absorption of the $\text{Zn}(\text{3-ptz})_2$ (MIRO-101) single crystals along different lateral crystal planes. For a moderate size sample with a surface area of a few square millimeters, we indexed the crystal habit planes by single-crystal X-ray diffraction (SXRD). The plane indices are shown in Fig. 2. Typical large-size crystal samples have opposing parallel triangular and hexagonal faces, corresponding to the planes $(10\bar{1})$ and $(\bar{1}01)$, respectively. Crystals also exhibit three visually distinguishable lateral faces, which we denote for the sample in Fig. 2 as face groups $G1 = \{(101), (221)\}$, $G2 = \{(0\bar{2}\bar{1}), (0\bar{1}\bar{1})\}$ and $G3 = \{(02\bar{1}), (01\bar{1})\}$. For different crystal samples, the indexing of the lateral planes is ambiguous. However, the parallel triangular (top view) and hexagonal faces (bottom view), as well as three distinguishable

Figure 3: **Anisotropic band-edge absorption of MIRO 101.** Single crystal absorbance, for polarized light incident on the lateral plane groups $G1$, $G2$ and $G3$. The average difference in absorbance at 350 nm, along the different incidence planes defines the absorption anisotropy factor ΔA . The inset shows the measured single crystal band gap $E_g = 3.32$ eV.

lateral faces, are can always be defined.

For the sample characterized in Fig. 2, we plot in Fig. 3 its absorption spectra across the lateral planes $G1$, $G2$ and $G3$. In the region below 310 nm, the three three lateral planes have the same absorption, but an orientation-dependent lower energy band is measured in the range 336 – 365 nm. This low-energy band gives the single crystal band gap of $E_g = 3.32$ eV for MIRO 101 (see Fig. 3 inset), which should be compared with the higher band gap value (3.9 eV²⁷) obtained for polycrystalline samples. This anisotropic optical response near the band edge is expected, given the large birefringence of the MIRO 101 crystal lattice.⁴⁷

Given the observed difference between the optical band gap of polycrystalline samples²⁷ and the results in Fig. 3, we carry out a systematic study of the size dependence of the band edge absorption spectrum for MIRO 101. By controlling the synthesis conditions as described in the Methods section and the Supplementary Material, we prepare individual single crystals with top view surface areas in the range 2 – 37 mm², as measured by optical

Figure 4: **Size-dependence of the band-edge absorption.** (a) Absorbance along the incidence plane $G1$ for single crystal MIRO 101 samples of different top surface areas. The powder absorption is shown for comparison. (b) Average relative absorption ΔA across lateral planes at 350 nm, for crystal samples with different top surface areas.

imaging. For each sample, the absorbance across the three distinguishable lateral planes was measured using the setup in Fig. 1. The average band-edge anisotropy across the different lateral planes ΔA , was measured as described in Fig. 3. For each sample, we label as $G1$ the lateral face with the highest absorbance in the band edge region.

The crystal size dependence of the absorption spectra of MIRO 101 is shown in Fig. 4. We control the size of the crystal samples by controlling the reaction temperature, dilution and concentration of acid modulators.^{27,38,48} We measure the absorbance for crystal samples varying in size from micron-size powder grains, to individual single crystals with top surface areas of 37 mm². Figure 4a shows that crystals with surface areas in the few mm² develop a low energy shoulder that is not present in polycrystalline samples. The extracted band gap converges to 5.3 eV for the largest samples measured in the millimeter regime (see Fig. 3). While in Fig. 4a we show the absorbance across the $G1$ plane only, in Fig. 4b we show average absorbance difference ΔA across the three lateral incidence planes. ΔA increases with the crystal size until reaching a plateau at $\Delta A = 0.16$. Note that since ΔA is obtained from normalized absorption spectra, it is independent of the optical path.

This crystal size dependence on the band-gap and anisotropy absorbance of MIRO 101 can

be explained in terms of two alternative orientations that tetrazole ligands adopt in the unit cell during growth, a type of polymorphism that is sensitive to the synthesis conditions.^{49,50} Under its first reported synthesis conditions,⁴⁶ Zn(3-ptz)_2 (MIRO 101) was obtained in powder form. The x-ray diffraction pattern shows that the asymmetric unit of MIRO 101 exhibits static disorder in which the nitrogen atom of pyridyl group is located in the same crystallographic position of the carbon atom at position 3 in the pyridine, producing two types of pyridil orientations in the unit cell that coexist in a polycrystalline sample. We denote these two observed unit cells as *A* and *B*. We show in Fig. 5a, that unit cell *A* has the nitrogen atoms of pyridyl group oriented toward the center of the unit cell (red dot). In contrast, the nitrogen atoms of the pyridil groups in unit cell *B* are oriented outward. Since the two unit cells have the same type and number of atoms, we use periodic DFT to compute the formation energy E_f of the two structures. From the minimized total energy of each unit cell, we obtain that the formation energy of cell *A* is 0.87 eV (20 kcal/mol) lower than the formation energy of cell *B* (see DFT methods in the Supplementary Material).

In Fig. 5b, we correlate the pyridyl group orientation in unit cell *A* with the presence of the absorption band in the region 345 – 365 nm, which coincides with the observed band edge absorption of large single crystal samples (see Fig. 3).

Solid-state DFT analysis show that both cells present differences in the absorption intensity around 320 nm and only the unit cell *A* exhibits the absorption band at 350 nm, suggesting that pyridyl groups tend to arrange in an orientation type unit cell *A* for larger single-crystals. The calculated band gap of MIRO 101 assuming unit cell *A* is $E_g = 3.15$ eV, which should be compared with the 3.32 eV single-crystal band gap from Fig. 3. The simulated absorption spectrum of MIRO 101 assuming the more energetic cell *B* conformation only exhibits the high energy band at 310 – 320 nm, which is common to both types of unit cell configurations.

We also analyze the molecular orbital structure at the edge of the valence and conduction band shows for unit cells *A* and *B*. Assuming the edge of the lower optical transitions is

Figure 5: **Microscopic origin of the band-edge anisotropy in MIRO 101.** (a) Geometry of two experimentally observed unit cells for MIRO 101, differing in the orientations that the pyridyl groups take relative to the center of unit cell volume (red dot), upon crystallization. In Cell A, the nitrogen atoms of the center pyridil groups point inward, and in Cell B they point outward. Other atoms are omitted for clarity. (b) DFT absorption spectra for MIRO 101 with unit cells A (black) or B (red). Cell B leads to absorption at the measured band edge.

related to the molecular orbital in the edge of the Fermi level, we see in Figure 6 that cell A has an *inter*-pyridyl group transition, which favors a large isotropic behavior. Meanwhile, in cell B this type of transition is an *intra*-pyridyl group, which is less sensitive to the relative orientation of the pyridyl-tetrazole ligand.

The orientation of pull-push molecules, such as pyridyl-tetrazole, during the self-assembly of molecular crystals in solution plays a critical role in the formation lower energy bands of excitonic states, primarily due to the relative orientation of permanent and transition dipole moments.^{51,52} Under synthesis conditions that favor high nucleation rates and fast crystal growth leading to polycrystalline samples, the dynamics of crystal packing and dissolution of pyridyl-tetrazole ligands during MIRO 101 self-assembly is under thermodynamic control. Although the optically anisotropic unit cell A is energetically more stable than cell B, both crystal structures can be explored fast crystallization-dissolution equilibria. On the other hand, the conditions of slow nucleation and slow crystal growth that lead to large MIRO 101 single crystals, the MOF growth process is this under kinetic control. Since the energy barrier for dissolution of unit cell B is lower than cell A by about 0.8 eV, only the latter prevails in the steady state.

Figure 6: **Molecular orbitals at the edge of the valence and conduction bands.** Panels (a) and (d) show the geometry of the pyridyl groups in unit cells A and B, respectively. (b) and (e) show the corresponding isosurfaces of the valence band edge. (c) and (f) show the corresponding isosurfaces of the conduction band edge. Isovalue is set to 0.03.

Conclusion

We study the anisotropic absorption of individual large single-crystals of the metal-organic framework $\text{Zn}(\text{3-ptz})_2$ (MIRO-101) as a function of crystal size, for polycrystalline samples in the micrometer regime, to single crystals with surface areas of up to 37 mm^2 . Using accurate solid-state DFT calculations, we correlate the relative orientation that the pyridyl-tetrazole ligands adopt in the unit cell under conditions of slow crystal self-assembly, with the anisotropic absorbance of millimeter-size MIRO 101 single-crystals across its lateral planes, upon polarized UV-vis excitation. From the anisotropic band edge absorption spectra, the estimated band gap for MIRO 101 is found to vary monotonically from 3.9 eV, for micron-size polycrystalline samples, to 3.3 eV, for millimeter-size single crystals. Our precise characterization of the anisotropic optical response of a large non-centrosymmetric MOFs is a significant step forward in the development of birefringent MOF crystals for efficient polarization modulation and frequency conversion devices.

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Supporting Information Available

- The Supplementary Material contains technical details of the DFT calculations.

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Graphical TOC Entry

Figure 7