

Supporting Information:

Pillared metal-organic frameworks act as chromatic polarizers

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Experimental details

Materials

Preparation of protonated dabco-H⁺ salt: 22.4 g (0.2 mol) 1,4-diazabicyclo[2.2.2]octane (dabco) was dissolved in an aqueous solution of nitric acid (1 M, 200 mL) using magnetic stirring. The solution was allowed to evaporate at 80 °C overnight.

Synthesis of **1**: Cobalt(II) nitrate hexahydrate (436 mg, 1.5 mmol) and terephthalic acid (249 mg, 1.5 mmol) were dissolved in N,N-dimethylformamide (DMF; 30 mL) together with 168 mg of dabco-H⁺ salt. To promote heterogeneous nucleation, a clean glass slide was added to the reaction vessel. The solution was sealed in a 45 mL Teflon-lined autoclave and placed in an oven at 110 °C for 48 h. The autoclave was allowed to cool down to room temperature, and the product was filtered and washed with 30 mL DMF. The solid product was then dried at room temperature under vacuum for 12 h.

Synthesis of **2**: Cobalt(II) nitrate hexahydrate (218.5 mg, 0.75 mmol) and 2-aminoterephthalic acid (135.8 mg, 0.75 mmol) were dissolved in DMF (30 mL) together with 84 mg of dabco-H⁺ salt. To promote heterogeneous nucleation, a clean glass slide was added to the reaction vessel. The solution was sealed in a 45 mL Teflon-lined autoclave and placed in an oven at 125 °C for 48 h. The autoclave was allowed to cool down to room temperature, and the product was filtered and washed with 30 mL DMF. The solid product was then dried at room temperature under vacuum for 12 h.

Synthesis of **3**: Cobalt(II) nitrate hexahydrate (218.5 mg, 0.75 mmol) and 2-nitroterephthalic acid (158.3 mg, 0.75 mmol) were dissolved in DMF (30 mL) together with 84 mg of protonated dabco-H⁺ salt. To promote heterogeneous nucleation, a clean glass slide was added to the reaction vessel. The solution was sealed in a 45 mL Teflon-lined autoclave and placed in an oven at 125 °C for 48 h. The autoclave was allowed to cool down to room temperature, and the product was filtered and washed with 30 mL DMF. The solid product was then dried at room temperature under vacuum for 12 h.

Synthesis of **4**: Cobalt(II) nitrate hexahydrate (109.2 mg, 0.375 mmol), zinc(II) nitrate hexahydrate (111.5 mg, 0.375 mmol), dabco (67.3 mg, 0.6 mmol), and terephthalic acid (124.5 mg, 0.75 mmol) were dissolved in DMF (30 mL). To promote heterogeneous nucleation, a clean glass slide was added to the reaction vessel. The solution was sealed in a 45 mL Teflon-lined autoclave and placed in an oven at 110 °C for 48 h. The autoclave was allowed to cool down to room temperature, and the product was filtered and washed with 30 mL DMF. The solid product was then dried at room temperature under vacuum for 12 h.

Measurements

The powder XRD patterns were measured with a Bruker-AXS D5005 diffractometer, equipped with a Co-K α source ($\lambda=1.789$ nm). The measurements were conducted with a step size of 0.02° with a 2 θ range of 5°-50°, and variable divergence slit. Polarized light microscopy images were taken using a Nikon Eclipse E600 POL microscope fitted with Nikon DS-Ri1 camera. A JEOL JSM-6010LA scanning electron microscope

was used to perform energy dispersive X-ray spectroscopy using the backscatter electron detector and 20 kV acceleration voltage. Samples were deposited on conductive adhesive carbon tape and sputtered with a layer of gold to avoid charging effects.

Ultraviolet-Visible (UV-Vis) Spectroscopy: A Perkin-Elmer Lambda-900 spectrophotometer equipped with an integration sphere was used. For diffuse reflectance measurements, spectra were referenced to a blank reading of BaSO₄. An acquisition time of 200 nm/min was used. Sample preparation included grinding and dilution with BaSO₄. Single-crystal measurements were performed by mounting a large single crystal in a demountable quartz cuvette (Hellma 26 μ L) using Fluorolube oil as a medium. The separation between front and back sides of the cuvette was maintained constant by placing a 100 μ m spacer in between. A mask with a 200 μ m diameter pinhole was placed on the front side of the cuvette, centered on the crystal to reduce the incident light area. Spectra were acquired with the polarizer set at 0° and 90° with respect to the long edge of the crystal. Blank measurements (i.e., the same cuvette, mask, and medium without the crystal) were subtracted from all single crystal measurements for both polarization angles. Acquisition times of 15 nm/min or 30 nm/min were used depending on the quality of the spectra. The data reported in Figs. 3, S2 and S3 correspond to the average of five acquisitions, with the shaded area representing the confidence interval of one standard deviation.

Supporting Figures

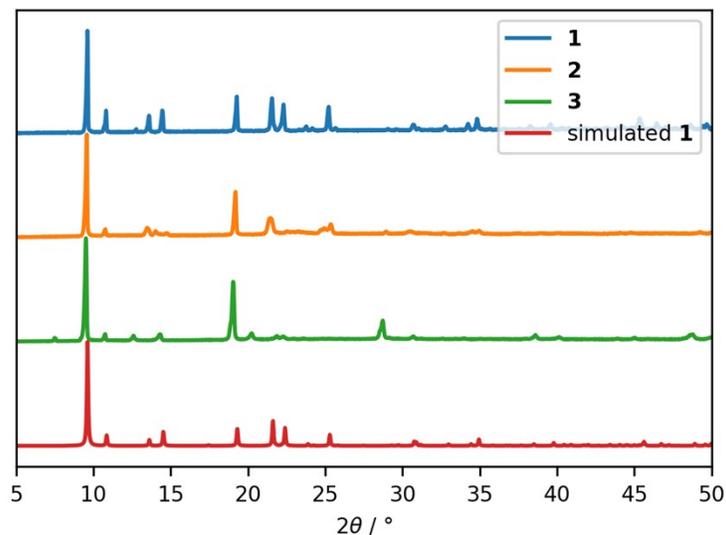


Fig. S1. Powder XRD patterns of **1**, **2**, and **3**, compared to the simulated pattern from the reported structure of **1** with CCDC Refcode: TORXEE.

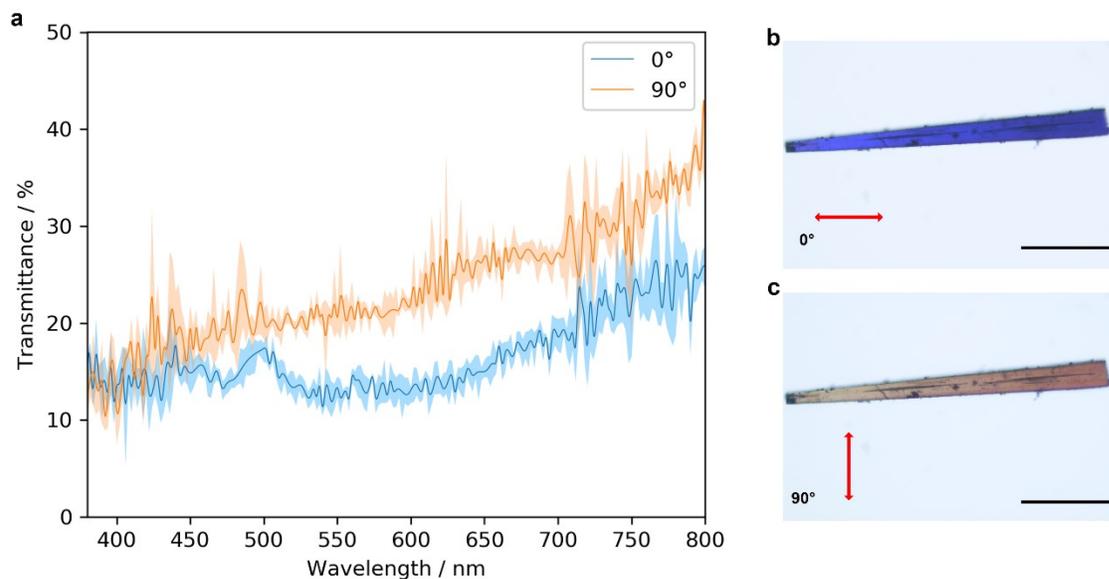


Fig. S2. (a) UV-visible spectra of **2** in single-crystal transmission mode with two relative polarization directions (0° shown in blue and 90° in orange). The shaded area corresponds to one standard deviation. (b and c) Optical microscope images of an isolated crystal of **2** whose long axis is parallel and perpendicular to the polarized light orientation (red arrows); scale bar represents $200\ \mu\text{m}$.

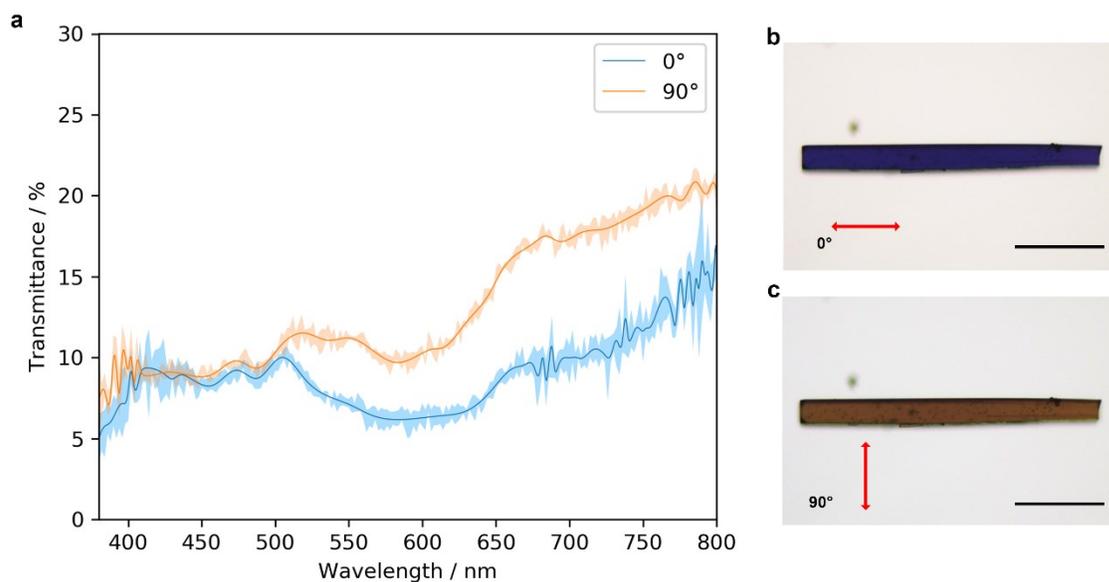


Fig. S3. (a) UV-visible spectra of **3** in single-crystal transmission mode with two relative polarization directions (0° shown in blue and 90° in orange). The shaded area corresponds to one standard deviation. (b and c) Optical microscope images of an isolated crystal of **3** whose long axis is parallel and perpendicular to the polarized light orientation (red arrows); scale bar represents $200\ \mu\text{m}$.