Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Interactions of water confined in a metal–organic framework as studied by a combined approach of Raman, FTIR, and IR electroabsorption spectroscopies and multivariate curve resolution analysis

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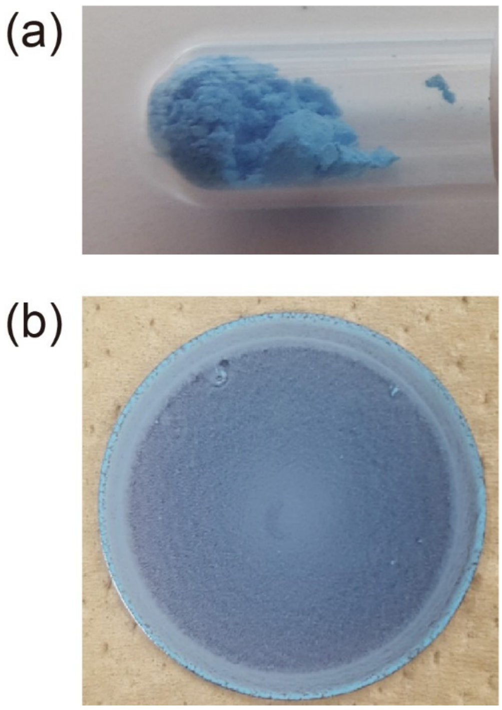

Fig. S1 Pictures of as-synthesized CPL-1 microcrystals (a) and a CPL-1 thin film formed on a Si substrate used for the IREA measurements (b).

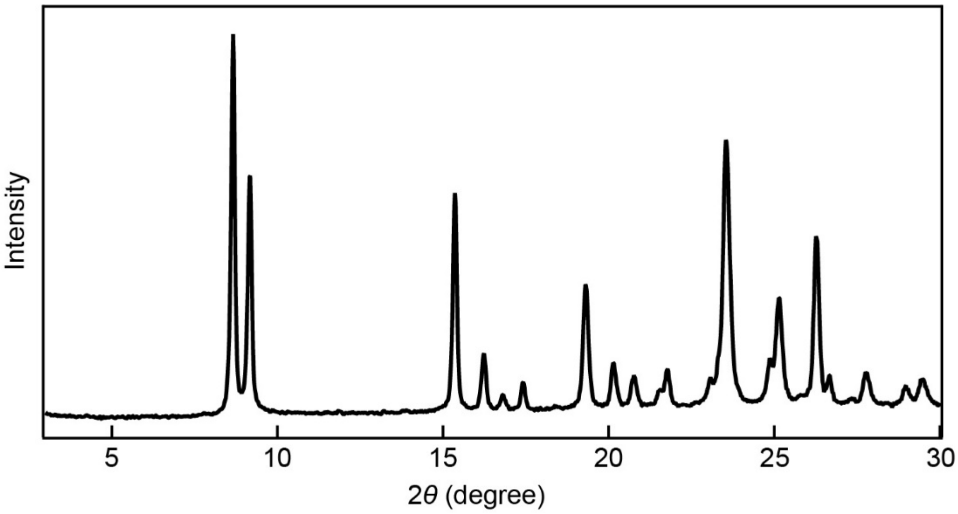

Fig. S2 X-ray powder diffraction pattern of the synthesized CPL-1.

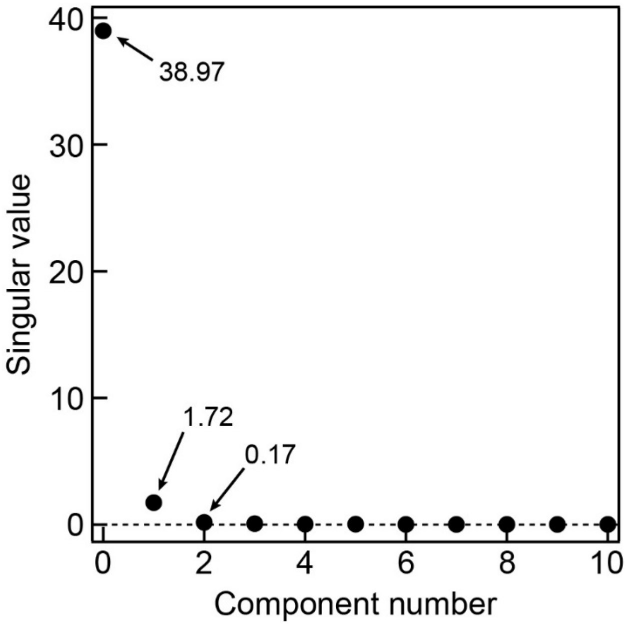

Fig. S3 Plot of singular values obtained from SVD of the data in the 1300–3800 cm^{-1} interval after t = 10 min (represented by a 2594 × 170 matrix).

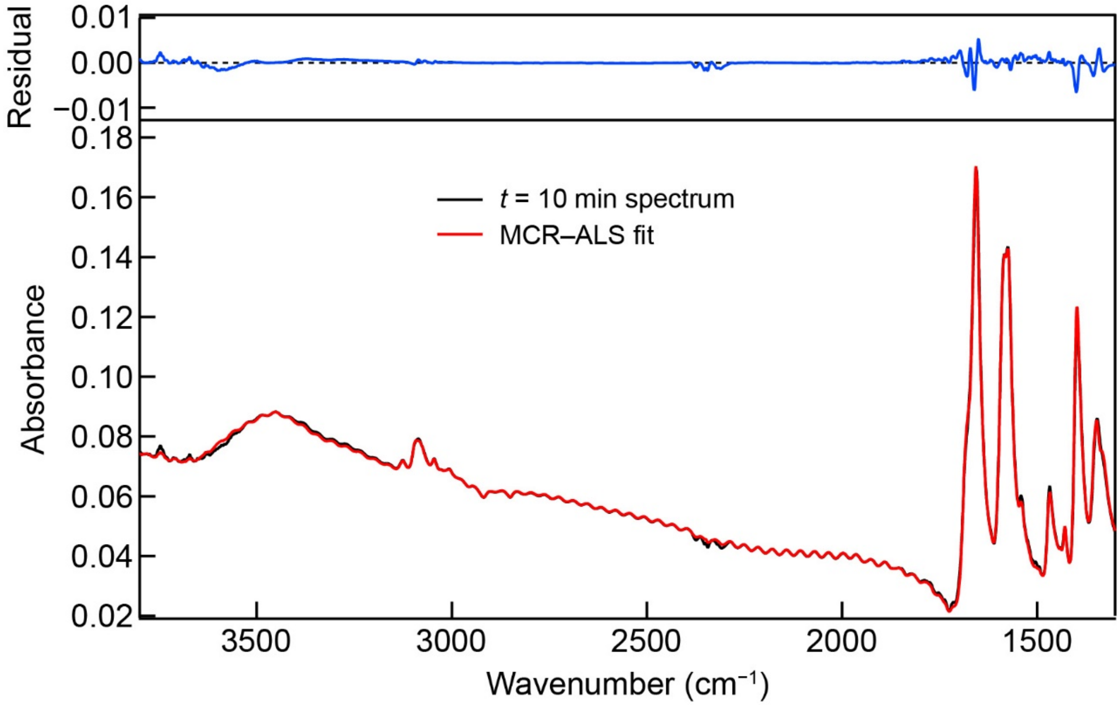

Fig. S4 Comparison of the original FTIR spectrum at t = 10 min (black line, bottom panel) and the fitted spectrum derived from the MCR–ALS analysis assuming two components (red line, bottom panel). The fitting residual (red minus black) is shown by a blue line in the top panel.

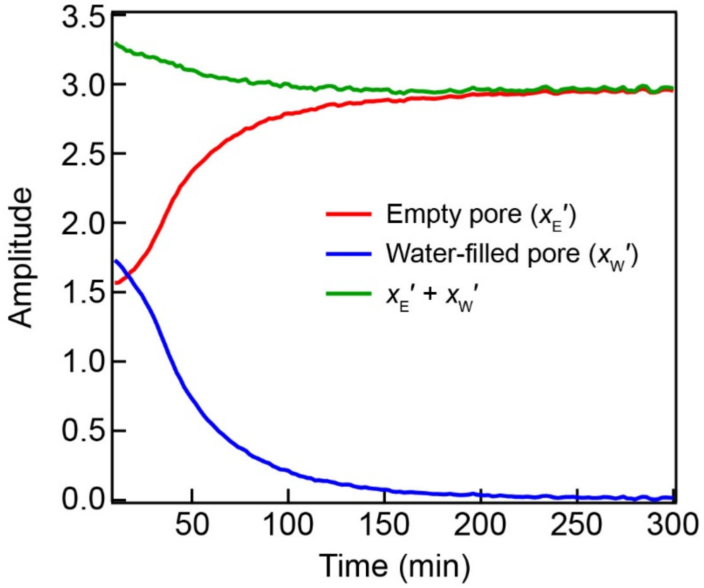

Fig. S5 Unscaled temporal profiles of the two components assumed in the MCR–ALS analysis, which are directly obtained from the matrix **H**. The red line represents the component attributable to the empty pore (x_E'), the blue line the water-filled pore (x_W'), and the green line the sum of the two temporal profiles (*i.e.*, $x_E' + x_W'$).

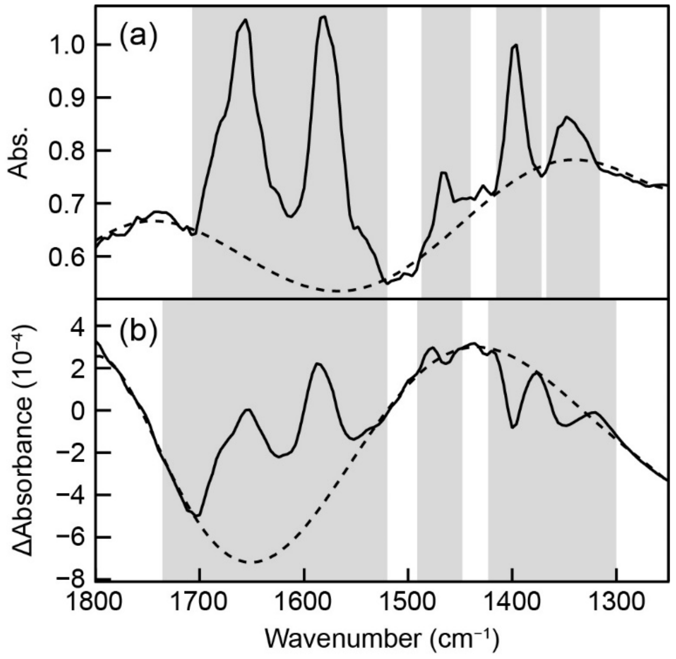

Fig. S6 Baseline fitting of the IR absorption (a) and Δ*A* spectrum (b) of a hydrated CPL-1 thin film using a six-order polynomial. The solid lines represent the raw data and the dashed lines the fitted baseline curves. The gray areas indicate the masked spectral regions that display IR bands and were excluded from the fitting.

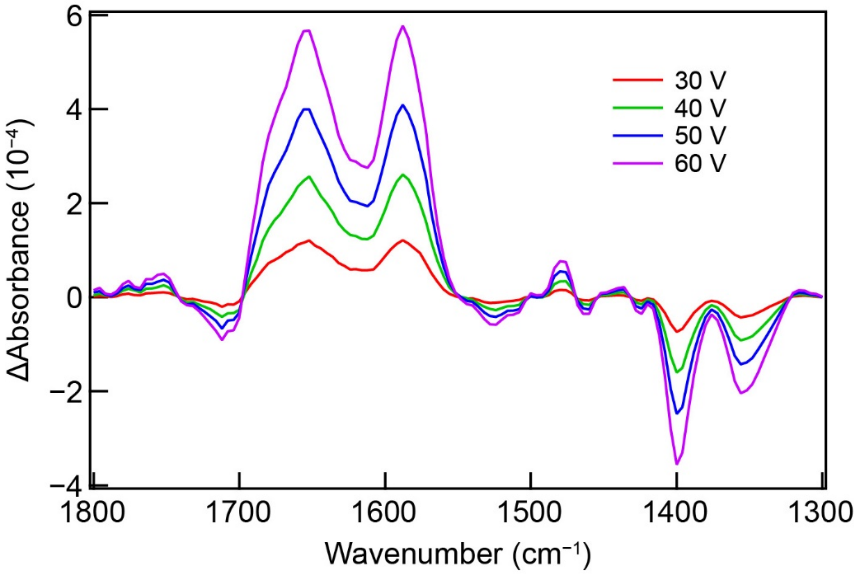

Fig. S7 Baseline-corrected Δ*A* spectra of a CPL-1 thin film obtained with *E* = 30 (red line), 40 (green line), 50 (blue line), and 60 (purple line) V.

Supplementary methods

The output at ~532 nm of a continuous-wave semiconductor laser (Coherent, Genesis CX532-2000SLM-CDRH) was used as the Raman excitation light. The laser beam was passed through an optical isolator and a spatial filter consisting of a 10× objective and a 25 µm pinhole, and subsequently expanded by a factor of 3.6. A portion (~10%) of the expanded beam was introduced into an inverted microscope (Olympus, IX73) and focused onto the sample mounted on the microscope stage by a 20×, NA 0.75 objective (Olympus, UPLSAPO20X). Back-scattered light was collected by the same objective and filtered with three volume Bragg gratings (OptiGrate, BragGrate™ notch filters). After passing through a 100 µm pinhole for achieving confocal detection, the scattered light was analyzed by an imaging spectrometer (SOL Instruments, MS3504i) and detected by a thermoelectrically-cooled charge-coupled device (CCD) detector (Andor Technology, DU401A-BV) with 1024 × 127 pixels operating at −65 °C.