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The coupling of (photo)chemical processes to optical cavity vacuum fields is an emerging method for modulating molecular and material properties. Recent reports have shown that strong coupling of the vibrational modes of solvents to cavity vacuum fields can influence the chemical reaction kinetics of dissolved solutes. This suggests that vibrational strong coupling might also effect other important solution-based processes, such as crystallization from solution. Here we test this hither-to unexplored notion, investigating pseudopolymorphism in the crystallization from water of ZIF metal-organic frameworks inside optical microcavities. We find that ZIF-8 crystals are selectively obtained from solution inside optical microcavities, where the OH stretching vibration of water is strongly coupled to cavity vacuum fields, whereas mixtures of ZIF-8 and ZIF-L are obtained otherwise. This work suggests that cavity vacuum fields might become a tool for materials synthesis, biasing molecular self-assembly and driving macroscopic material outcomes.

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Selective Crystallization via Vibrational Strong Coupling

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Abstract

The coupling of (photo)chemical processes to optical cavity vacuum fields is an emerging method for modulating molecular and material properties. Recent reports have shown that strong coupling of the vibrational modes of solvents to cavity vacuum fields can influence the chemical reaction kinetics of dissolved solutes. This suggests that vibrational strong coupling might also effect other important solution-based processes, such as crystallization from solution. Here we test this hitherto unexplored notion, investigating pseudopolymorphism in the crystallization from water of ZIF metal-organic frameworks inside optical microcavities. We find that ZIF-8 crystals are selectively obtained from solution inside optical microcavities, where the OH stretching vibration of water is strongly coupled to cavity vacuum fields, whereas mixtures of ZIF-8 and ZIF-L are obtained otherwise. This work suggests that cavity vacuum fields might become a tool for materials synthesis, biasing molecular self-assembly and driving macroscopic material outcomes.

Main Text

Over the last decade it has been realized that many chemical phenomena that can be modulated by intense optical fields in free space, can also be influenced by vacuum optical fields in confined cavities. The modulation of chemical reactivity by the strong coupling of molecular absorptions to cavity vacuum fields is a prominent example, thought to occur by the re-shaping of the reaction potential energy surface as occurs in ‘bond-softening’ using intense laser fields.

When, for example, the vibrational modes of molecules couple strongly to the optical modes of a Fabry–Pérot (FP) cavity, new vibro-polaritonic states, denoted by P+ and P−, are formed and are separated at resonance by the vacuum Rabi splitting energy \((\hbar \Omega_R)^{6-7}\) (Fig. 1a,b). The extent of Rabi splitting is proportional to the number of molecules \(N\) in the cavity field as \(\sqrt{N}\), and proportional to the number of photons \(n\) in the cavity mode as \(\sqrt{n + 1}\). In the vacuum limit \((n = 0)\), the interaction remains finite, occurring between the molecule and the zero-point energy of the cavity mode. Vibrational strong coupling (VSC) has been shown to effectively influence the kinetics of chemical reactions in a growing number of systems, attributed to a reordering of the energy landscape of the system that is the subject of much current experimental and theoretical investigation. VSC of solvent molecules can also alter the
kinetics of organic reactions\textsuperscript{10,13,14}, most relevant here being the modification of enzyme kinetics by VSC of the OH stretch of water in the vacuum field regime\textsuperscript{10}.

The latter results suggest that the nature of solvation can be changed under VSC, i.e. VSC could potentially be used to control many other solution-based processes including crystallization from solution and solubility-based purification (phase changes have also been shown to be modified by electronic strong coupling)\textsuperscript{15}. Indeed, while impressive studies have demonstrated control of crystal nucleation and growth using high intensity beams, so-called ‘laser trapping crystallization’\textsuperscript{16}, crystallization under VSC of solvent molecules relies on the mechanism different from laser trapping.

One of the key issues in crystallization is polymorphism: the same dissolved molecular components can assemble and precipitate in multiple crystalline phases. For example, the anti-inflammatory drug indomethacin gives three different crystal structures depending on the crystallization conditions\textsuperscript{17}. The medical efficacy of indomethacin depends on the crystal structure because the crystal structure significantly influences its solubility in the human body. Another example is the synthesis of metal–organic frameworks (MOFs)\textsuperscript{18–20}. MOFs are porous crystalline materials that are of enormous interest for applications including gas adsorption\textsuperscript{21–23}, chemical sensing\textsuperscript{24,25}, and catalysis\textsuperscript{26,27}. However, it is sometimes found that the same combination of metal ions and organic ligands in solution yields MOFs with various crystal structures\textsuperscript{28–30}, causing heterogeneity in their porous properties that may compromise performance. In general, the selectivity of crystalline phases relies on the energy landscape connecting free dissolved components and crystals. Classical nucleation models input thermodynamic quantities such as the crystal surface and bulk free energies as a function of size to predict behaviour. Since VSC of (solvent) molecules has been shown to modify the energy levels of ground states and activated complexes\textsuperscript{6}, it might also be a new tool for selective crystallization.

These considerations inspired us to investigate the influence of VSC of solvent molecules on MOF crystallization. Zeolitic imidazolate frameworks (ZIFs) are a subfamily of MOFs\textsuperscript{31}. They consist of tetrahedral metal nodes interconnected by imidazolate derivatives. Self-assembly of Zn(II) and 2-methylimidazole (Hmeim) gives dimorphic structures, i.e., [Zn(meim)\textsubscript{2}]\textsubscript{n} (ZIF-8, Fig. 1c) and [Zn(meim)\textsubscript{2}(Hmeim)]\textsubscript{n} (ZIF-L, Fig. 1d)\textsuperscript{32–34}. In principle, the ZIF-L and ZIF-8 forms constitute a pseudopolymorphism due to the difference in their chemical composition. The extent of this pseudopolymorphism is highly sensitive to experimental conditions and is therefore an excellent testing
ground for the notion that cavity vacuum fields may influence crystallization processes. Herein we show that ZIF crystallization inside optical cavities, and specifically under conditions of VSC of the solvent (water) to cavity vacuum fields, does indeed influence ZIF pseudopolymorphism. We find that ZIF-8 is selectively obtained inside the optical cavities (Fig. 1a), whereas mixtures of ZIF-8 and ZIF-L are obtained otherwise. This result suggests new avenues for addressing the challenges of crystal polymorphism and to our knowledge is the first example of cavity vacuum field interactions leading to macroscopic materials synthesis outcomes.

Results and Discussion

Prior to performing experiments in a FP cavity, crystallization of ZIF in open solution under ambient conditions was conducted as a control. In brief, an aqueous solution of Zn(NO$_3$)$_2$ and 2-methylimidazole was left to stand at room temperature for 2 h. A white powder was collected, centrifuged, and washed with ethanol to remove unreacted components. The powder was examined by scanning electron microscopy (SEM). A mixture of cuboctahedral crystals (ZIF-8) and flake-like crystals (ZIF-L) was obtained under these conditions (Fig. 2a). These morphologies are in very good agreement with previous reports on this well studied MOF system, in which ZIF-8 exhibits cuboctahedron or cubic structures and ZIF-L exhibits flake or crosshair-star structures (Fig. 2b)$.^{32-34}$ X-ray diffraction (XRD) further confirmed that the crystals were a mixture of ZIF-8 and ZIF-L (Fig. S1). The ratio of ZIF-8 to ZIF-L was estimated to be 74:26 by physical counting of several hundred crystals with different morphologies.

Next, optical cavities were constructed, within which the same crystallization could be undertaken under conditions of strong coupling of the solvent (water) OH stretching vibration to cavity vacuum fields. A Fabry-Pérot (FP) cavity consisting of two parallel mirrors separated by a ca. 10 µm Mylar film spacer was prepared. The mirrors were fabricated by sputtering 10 nm Au on 2 mm ZnSe windows, followed by spin-coating of a ca. 100 nm polydimethylsiloxane (PDMS) film to isolate the metal from solutions (Fig. S2). A transmission spectrum of the empty (air-filled) FP cavity is shown in Fig. 2d, showing the progression of optical cavity modes. The energy of these transmission peaks when the cavity is filled with water, but in the absence of the OH stretch absorption at 3360 cm$^{-1}$ (i.e. a flat background refractive index of 1.33) was simulated using the Transfer Matrix Method (in-house code).
Example mode energies and their angular dispersion are shown with dashed white lines in Fig. 3b. These simulations suggest that adjusting the mirror separation to 8.75 microns brings the 8th mode of the cavity into resonance with the OH stretching mode at 3360 cm$^{-1}$ at normal incidence, with a free spectral range (FSR, the peak-to-peak separation of cavity modes) of 420 cm$^{-1}$. This mirror separation was accurately achieved in experimental contexts by monitoring transmission spectra of the water-filled FP cavity and adjusting the FSR of cavity modes far from any solvent absorptions.

We note here that the resonance energies of all the simulated and experimental transmission spectra were in excellent agreement over a very broad energy range irrespective of conditions (air or water-filled), however the observed widths of the cavity modes were always much broader than predicted by simulation (compare Fig 3a and b). We attribute the broadening not to a degradation of the Q-factor of the FP cavity locally, but to the fact that the waist of the FTIR spectrometer probe beam is large (millimetre diameter) and probed a range of cavity separations as the FP mirrors are not able to be held perfectly flat against each other in the liquid cell holder. Simulations of this situation suggested a normal distribution of probed mirror separations over the range 8.75 ± 0.2 microns.

When an aqueous solution of Zn(NO$_3$)$_2$ and 2-methylimidazole was placed in a FP cavity with mirrors adjusted to a separation of 8.75 µm, the transmission spectrum shows a clear band gap at the energy of the OH stretching mode of water (Fig. 2d, red curve, note that the solutes are present in only millimolar concentrations and the mode structure is determined by the solvent refractive index). The eighth-order cavity mode is split into two new vibro-polaritonic states, denoted by P+ and P− around the the OH stretching vibration (3360 cm$^{-1}$, Fig. 2d, black line), with the intensity of P− relatively reduced due to the asymmetric shape of the OH absorption. The energy gap (Rabi splitting) between P+ and P− is 758 cm$^{-1}$ (Fig. 3a), a value larger than both the width of the OH stretching band (FWHM = 480 cm$^{-1}$) and the cavity mode (FWHM = 82 cm$^{-1}$), confirming that the system is well inside the strong coupling regime (a Rabi splitting of 728 cm$^{-1}$ is predicted in the simulations).

Angle-dependent transmission spectra (0-15°) reveal a relatively flat dispersion of the upper and lower polariton peaks around the anti-crossing at the OH stretch absorption peak position (Fig. 3a and S3). Again, simulated dispersion curves facilitate interpretation of the coupling behavior (Fig. 3b). At normal incidence (in-plane momentum, $k_x = 0$) the 8th cavity mode is resonant with the OH stretch and disperses to higher energy as incidence angle is increased, but at 15° incidence ($k_x = 5.3$ µm$^{-1}$) the
7th cavity mode has already moved into resonance with the OH stretch with similarly strong interaction. The overall observed result of this strong coupling of successive cavity modes is a relatively flat polariton dispersion. Other consequences of the cavity FSR being similar to the width of the OH stretch band are discussed further on.

Two hours after the aqueous solution of Zn(NO$_3$)$_2$ and 2-methylimidazole was placed in the FP cavity, the cavity was opened and the crystal solution collected, centrifuged and washed with ethanol as before. SEM images showed the formation of cuboctahedral crystals of 262 ± 48 nm in size (Fig. 2c and Table S1), however in contrast with the experiment in free solution, no formation of star/flake-like crystals was observed suggesting selective formation of ZIF-8. As the yields of crystals formed are drastically reduced in the ~4.5 microliter volume of the cavity, crystal counting to determine ZIF-L/ZIF-8 ratios is less reliable. However, ZIF-8 and ZIF-L can also be distinguished by Raman spectroscopy$^{32-34}$. The spectra in Fig. 4(a) and (b) show the Raman signatures of pure samples of ZIF-8 and ZIF-L, respectively (see Figs. S4 and S5), where the band at 3165 cm$^{-1}$ assigned to the N–H stretch is clearly present for only ZIF-L$^{36}$. The Raman spectrum of the product of crystallization in free solution clearly shows that a mixture of ZIF-8 and ZIF-L is present (Fig. 4c). However microscopic Raman spectroscopy of the washed crystals extracted from the FP cavity (Fig. 4d) shows no sign of the 3160 cm$^{-1}$ band, in very good agreement with the morphological result (Fig. 2c) and confirming that ZIF-8 was selectively formed in the FP cavity.

To confirm that this selectivity is an optical effect rather than a consequence of physical confinement, the same aqueous Zn(NO$_3$)$_2$/2-methylimidazole solution was placed in a ca. 9 µm width cavity but where the ZnSe/Au/PDMS mirrors were replaced with PDMS-coated ZnSe. In the absence of Au layers, the cavity cell does not support confined vacuum fields but merely provides a microscopic confined space with equivalent PDMS surfaces in contact with solution as before. Two hours after the aqueous solution had been placed in that confined space, a mixture of ZIF-8 and ZIF-L was obtained morphologically very similar to that obtained in free solution (compare SEM image in Fig. S6a with Fig. 2a). This result also indicates that PDMS did not contribute to selective crystallization of ZIF-8. The size of the crystals formed in the cell without mirrors was approximately 0.97 ± 0.14 µm, which was smaller than the crystals obtained in free solution (2.42 ± 0.54 µm), most likely because of the confinement effect$^{37}$ (Table S1). Microscopic Raman spectroscopy confirms the similarity with the relative intensity
of the characteristic peak (~3165 cm\(^{-1}\)) against the strongest peak (~3140 cm\(^{-1}\)) very similar for the no-mirror cavity and the free solution crystallization (compare Fig. 4f and 4c). Given that 26 ± 3% of the crystals formed in the ZIF-L phase in free solution crystallization (as determined by counting), \(ca.\) 20 ± 6% of the crystals were estimated to be in the ZIF-L phase for the no-mirror sample based on the Raman intensity ratios obtained by peak fitting (see Table 1 and Fig. S7). As another control the same aqueous Zn(NO\(_3\))\(_2\)/2-methylimidazole solution was placed on a single mirror consisting of PDMS-coated, Au-sputtered ZnSe and left for 2 h. The resultant crystals morphology (Fig. S6b) and Raman spectrum (Fig. 4e) both indicated once again that a mixture of ZIF-8 and ZIF-L were obtained with very similar morphology and ratio to the free solution experiment (equivalent 22 ± 4% ZIF-L crystals, Table 1, Table S1). Once again, the selectivity for ZIF-8 is only observed inside the FP cavity.

The density of vacuum field modes for a \(ca.\) 9 \(\mu\)m mirror separation cavity makes it difficult to tune the cavity modes to be non-resonant with the OH stretching vibration (the cavity FSR and the width of the OH stretch band are both in the order of 500 cm\(^{-1}\), see Fig. 3). Making cavities with significantly reduced mirror separation (<5 \(\mu\)m) would be desirable to test a genuinely non-resonant FP cavity control, however this is technically difficult to fabricate and the resulting much smaller solution volume and crystal numbers would be more difficult again to characterize accurately. Furthermore, the additional physical confinement might start to influence the morphology of larger crystals. Nevertheless, we attribute the optical cavity-induced selectivity of crystallization of ZIF-8 to the interaction of the cavity fields with the OH stretch of the solvent as there are no other strong cavity field-water interactions detected over a 1-25 micron broad spectral range (some weak interactions are evident with the OH bending mode at 1640 cm\(^{-1}\)). We were however able to verify that FP cavities with larger mirror separation (e.g. 17 \(\mu\)m), with equivalent Rabi splitting at the OH stretch, exhibited the same selectivity for ZIF-8. To clarify the volume effect of the solution on the selectivity of the crystals, the mirror distance was varied. Under VSC of OH stretching vibration, pure ZIF-8 was obtained regardless of the mirror distance (Fig. S8). The distance of the ZnSe windows without Au sputtering was also varied. The ratio of ZIF-8 to ZIF-L was not changed by changing the distance of the ZnSe windows (Fig. S8). Additionally, the effect of the coupling strength on selective crystallization was investigated by reducing the mirror reflectivity. The splitting energy was reduced by decreasing the thickness of the Au layer from 10 to 6 nm (Fig. S9). The crystals formed in the cell with a 6 nm thick Au layer did not show the
characteristic peak of ZIF-L in the Raman spectrum (Figs. S10 and S11). This suggests that crystals of ZIF-8 can be selectively obtained if the cavity and vibrational mode are in the strong coupling regime.

The detuning experiment was performed with a mixture of H$_2$O and D$_2$O. Equal amounts of the solvents (H$_2$O and D$_2$O) reduce the peak intensities of the OH and OD stretching vibrations. It is then possible to detune the cavity modes for the OH and OD stretching vibrations (Fig. S12). The crystals obtained in free solution, the cavity with OFF-resonance and the cavity with ON-resonance were characterized by SEM and Raman spectroscopy (Figs. S13 and S14). A mixture of ZIF-8 and ZIF-L was obtained in free solution and for OFF-resonance, but ZIF-8 selectively formed under VSC of OH stretching vibration. The coupling strength was weaker than that in pure H$_2$O, but ZIF-8 was still obtained under VSC of OH stretching vibration. These results suggest that selective crystallization of ZIF-8 originates from VSC of OH stretching vibration.

In all the above experiments, a Zn:Hmeim ratio of 1:4.1.6 was employed to give significant yields of both ZIF-8 (74%) and ZIF-L (26%) crystals in free solution (and giving 100% ZIF-8 in the FP cavity). However it is well known for ZIF crystallization that the ratio of ZIF-L obtained increases with increasing relative amount of 2-methylimidazole over Zn(NO$_3$)$_2$. For example, a 1:28 Zn:Hmeim ratio affords majority (68%) ZIF-L crystals in free solution. We checked a range of ratios of starting materials and found in all cases a cavity-induced modification of the crystal phase in favour of ZIF-8, but not always lead to complete suppression (Tables S1-2, Fig. S15). For the 1:28 Zn:Hmeim ratio experiment, the 68 ± 5% ZIF-L crystal majority in free solution, becomes a 24 ± 7% minority inside the FP cavity.

The relative stability of crystal polymorphs can be estimated from their solubility ($s$) ratio as:

$$\Delta G_{B\to A} = -RT \ln \left( \frac{s_B}{s_A} \right)$$

Where $\Delta G_{B\to A}$ is the Gibbs free energy for transformation of crystal phase B to phase A.$^{38}$ Assuming the change in the observed ZIF-L/ZIF-8 crystal ratio outside and inside the FP cavity is proportional to the change in solubility ratio in each environment, we can make a rudimentary estimate for the cavity-induced relative stabilization of the ZIF-8 form. For the 1:28 Zn:Hmeim ratio starting material experiment, this yields an estimated 395 cm$^{-1}$ stabilization energy. We note cautiously that this energy is of the same order as half the Rabi splitting (380 cm$^{-1}$) which is the expected stabilization of the first vibrational state of the water OH stretch in the cavity due to VSC (Fig. 1b).
The mechanism of cavity-induced stabilization of the ZIF-8 phase over ZIF-L, and whether the absolute energies of just one or both phases are affected, is a matter for speculation at this stage. Theoretical and experimental studies of the effects of VSC are yet to marry into a single satisfactory picture, with recent theoretical work even suggesting that the Morse potential picture of the coupled bond (Fig. 1b) is perturbed beyond recognition under VSC. One common thread is that several experimental works have measured reductions in chemical reactivity as a result of VSC, in concert with some theory that has predicted a strengthening/shortening of the coupled bond (a squeezed the Morse potential, see Fig. S16). If any of these energy and bond strength changes are occurring for the water OH stretch in the cavity due to VSC herein, the critical parameters for crystal nucleation and growth, the crystal surface and bulk free energies, are both likely to be affected as water can enter inside the pores of the both phases. Whether the size-dependence of the crystal surface and bulk free energies is changed inside the optical cavity, and thus if the ‘burst nucleation’ of the La Mer model and Ostwald ripening still operate, is also an open and fertile question.

Further clues might be gained by observing the solvent dependence of ZIF pseudopolymorphism. Leaving bulk alcohol solutions of Zn(NO$_3$)$_2$·6H$_2$O and 2-methylimidazole to stand for 2 h leads to the exclusive formation of ZIF-8 for methanol, ethanol, and isopropanol (Figs. S17-19). Since alcoholic solvents give similar selectivity for ZIF-8 as does water under VSC in optical cavities, some parallels may be drawn. The polarity of alcoholic OH groups is weaker than that of water, thus we speculate that VSC may decrease the polarity of the OH groups in water, bringing their solvation properties closer to those in alcohols. Our experimental works have suggested that changes in bond polarity may occur under VSC, a picture that is consistent with the squeezed Morse potential picture of VSC where the average displacement of a polar bond is reduced in excited states (Fig. S16). This speculation can be verified by monitoring the kinetics of crystallization. Crystallization slightly changes the refractive index of the solution owing to the changes in the concentrations of the components or formation of crystalline particles. The speed of crystallization was observed by the temporal shift of the resonant peaks. The change of the refractive index of crystallization in ethanol was faster than that in water (Fig. S20). In previous work, a weak polar solvent accelerated crystallization of ZIF structures. Interestingly, the change of the refractive index of crystallization under VSC was also
faster than that without VSC. This suggests that solvation of water under VSC is changed and more resembled that of ethanol.

There are further possibilities, such as cooperative VSC between the water OH stretch and the near-isoenergetic N-H vibration in 2-methylimidazole. Recent literature\textsuperscript{13} suggests that such cooperative coupling can accelerate bond cleavage, and cleavage of the N-H bond of 2-methylimidazole is required to form ZIF-8\textsuperscript{32-34} (Fig. S4), accounting for the observed preferential formation of ZIF-8. However, ZIF-8 was selectively obtained under VSC of OD stretching vibration (Figs. S21–23). Because cooperative coupling of O–H stretching and N–H vibration does not occur in D\textsubscript{2}O, selective crystallization of ZIF-8 is attributed to VSC of OH stretching vibration rather than cooperative coupling of O–H stretching and N–H vibration.

This array of possible mechanisms testifies to the rich opportunities afforded by coupling chemical processes such as crystallization to cavity vacuum fields, and the broad array of work that is still to be done to deepen understanding in this area. The ability to selectively control (pseudo)polymorphism using cavity vacuum fields demonstrated here has enormous potential in the domain of crystallography with particular application for biomedical materials. This may also be the first example of VSC applied to self-assembly of macroscopic structures, and opening up a new cross-disciplinary domain between quantum photonics and materials synthesis.

**Methods**

**Cavity Setup.** A cavity cell was made by TTC Inc., Japan. Mylar film of thickness 1 \( \mu \)m was purchased from Micron Wings, Australia. ZnSe windows were purchased from Specac Ltd., UK. The ZnSe windows were sputter-coated with an Au layer of thickness 10 nm. The Au layer was spin-coated with Sylgard and then the assembly was dried in an oven.

**Crystallization.** Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and 2-methylimidazole were purchased from the FUJIFILM Wako Pure Chemical Corporation. Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (7.44 mg, 2.5 \( \times \) 10\textsuperscript{−2} mmol) and 2-methylimidazole (86.2 mg, 1.05 mmol) were dissolved in MilliQ water (2 mL). A portion of the solution was placed in or outside the cavity at room temperature. After crystallization, the white powder was collected, centrifuged and washed with ethanol to remove the unreacted components. The collected powder was
analyzed by Raman spectroscopy and SEM. The crystallization experiments were repeated five times to determine the average ratio of ZIF-8 to ZIF-L.

**Instrumentation.** IR spectra were recorded with a JASCO FT-IR 6800 instrument. Au sputtering was performed with an ACS-4000-C3-HS instrument (ULVAC, Inc., Japan) or MSP-1S vacuum device (Japan). SEM was performed with a Phenom Pro desktop instrument. XRD patterns were recorded with a Rigaku SmartLab system. Microscopic Raman spectroscopy was performed with a Renishaw inVia™ instrument.

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**Author Contributions**

K. H. and H. U. conceived the project. K. H. and J. A. H. designed the experiments. H. I. and K. H. performed the experiments, J.A.H. performed the simulations. All authors discussed the results and commented on the manuscript.

**Competing interests**

The authors declare no competing interests.
**Figure 1. Vibrational strong coupling in optical cavities** (a) Schematic illustration of Fabry-Perot (FP) optical cavity consisting of two parallel mirrors. The cavity mode is strongly coupled with OH stretching vibration of water included in FP cavity. (b) Schematic energy level diagram of vibro-polaritonic states, separated by the Rabi splitting energy ($\hbar \Omega_R$) formed by the strong coupling of a molecular vibrational transition ($v_0 - v_1$) and a resonant optical cavity mode. Crystal structures of (c) ZIF-8 and (d) ZIF-L. Tetrahedral green object, blue sphere, and gray sphere indicate Zn, nitrogen and carbon, respectively. Hydrogen atoms are omitted for the clarity.
Figure 2. Crystallization outside and inside optical cavities (a-b) SEM image of ZIF crystals formed in free solution (no optical cavity), the larger, cuboctahedral-shaped crystals are the ZIF-8 phase and the smaller, crosshair-star shaped crystals are the ZIF-L phase, the latter are magnified in (b); (c) SEM image of crystals formed inside the Fabry-Perot cavity, the ZIF-8 phase is present but no crosshair-star shaped crystals due to ZIF-L are observed; (d) IR transmission spectra of an aqueous solution of the ZIF crystal starting materials, the broad and strong absorption at 3360 cm$^{-1}$ is the OH stretch of water (black), the same solution in an optical cavity with strong coupling of a cavity mode to the OH stretch of water producing the upper and lower polaritons (P$^+$ and P$^-$) as indicated (red), and of the empty (air-filled) optical cavity (blue).
Figure 3. Dispersion of optical cavity transmission with angle (in-plane momentum, $k_x$). (a) Experimental dispersion showing a band gap at the water O-H stretch energy, 3360 cm$^{-1}$ (red dashed line). A Rabi splitting of 758 cm$^{-1}$ between the upper and (weak intensity) lower polariton bands at normal incidence ($k_x = 0$) is indicated (white dashed line). The color scale represents % transmission. (b) Theoretical dispersion of the same cavity simulated using Transfer Matrix Method. At normal incidence ($k_x = 0$) the 8th cavity mode is resonant with the OH stretch, at 15° incidence ($k_x = 5.3$ µm$^{-1}$) the 7th cavity mode has already moved into resonance, resulting in weakly dispersive polariton bands (cavity mode energies calculated assuming a flat 1.33 refractive index in the region of the water OH stretch).
Figure 4. Raman spectroscopy of ZIF crystals. Raman spectra of crystals obtained under various conditions: (a) reference sample of ZIF-8, (b) reference sample of ZIF-L, (c) ZIF crystals formed in free aqueous solution (no optical cavity), (d) ZIF crystals formed in an optical cavity where the water OH stretch is strongly coupled to vacuum fields, (e) ZIF crystals formed on single mirror, and (f) ZIF crystals formed in cavity cell without Au mirrors sputtered on the ZnSe windows (i.e. a confined space but not an optical cavity). The red shaded area indicates the energy of the N-H stretching vibration, N-H bonding is only present in the ZIF-L phase.
Table 1. Relative intensity of the ZIF-L N-H vibrational peak from Raman spectroscopy and the estimated percentage of crystals formed in the ZIF-L phase under various conditions.

| samples                                      | ratio of ZIF-L (%)^[a]\|
|----------------------------------------------|--------------------------|
| Pure ZIF-8                                   | 0                        |
| Pure ZIF-L                                   | 100                      |
| ZIF crystals formed in free solution         | 26 ± 3                   |
| ZIF crystals formed inside optical cavity    | 0                        |
| ZIF crystals formed on a single mirror       | 22 ± 4                   |
| ZIF crystals formed in cavity without mirrors| 20 ± 6                   |

^[a] Relative intensity at ~3165 cm\(^{-1}\) against the strongest peak at 3140 cm\(^{-1}\). The signals were fitted as shown in Fig. S7.
Supporting Information

1. Experimental details

**Preparation of the reference samples of ZIF-8.**\(^{S1}\) Zn(NO\(_3\))\(_2\)·6H\(_2\)O (66.1 mg, 2.23 × 10\(^{-1}\) mmol) and 2-methylimidazole (16.6 mg, 2.03 × 10\(^{-1}\) mmol) were dissolved in N,N-dimethylformamide (DMF, 5 mL). The resulting solution was kept in a Teflon-lined hydrothermal synthesis autoclave reactor at 140 °C for 24 h. The obtained white powder was collected by centrifugation and washed with ethanol three times.

**Preparation of the reference samples of ZIF-L.**\(^{S2}\) Zn(NO\(_3\))\(_2\)·6H\(_2\)O (59 mg, 19.9 × 10\(^{-2}\) mmol) and 2-methylimidazole (130 mg, 1.59 mmol) were dissolved in MilliQ water (8 mL). The resulting solution was stirred for 4 h. The obtained white powder was collected by centrifugation and washed with ethanol three times.
2. X-ray Diffraction Measurements

Figure S1. (a) XRD pattern of crystals formed outside cavity; simulated XRD patterns for (b) pure ZIF-8\textsuperscript{S1} and (c) pure ZIF-L\textsuperscript{S2} The simulated patterns were produced from the cif files by Mercury.
3. Microcavity Design

Figure S2. (a) Schematic illustration of the microcavity; (b) photograph of the microcavity cell holder, designed for FTIR spectroscopy of liquids (Specac company).
4. Optical Cavity Spectral Dispersion with Angle

Figure S3. IR transmission spectra of an aqueous solution in an optical cavity as incident angle was varied from 0° to 15° (from bottom to top); 0° is defined as normal incidence, perpendicular to the cavity. The large band gap corresponds to the absorption of the OH stretch of water at 3360 cm⁻¹, the eighth order cavity mode is resonant with this band at normal incidence with the upper polariton visible at 3753 cm⁻¹, and the weak-intensity lower polariton visible at 2995 cm⁻¹, giving a Rabi splitting of 758 cm⁻¹. At 15° incidence, the 7th mode of the cavity has moved into resonance at 3360 cm⁻¹, creating another avoided crossing and resulting in a relatively flat polariton dispersion.
5. Structural Differences of ZIF-8 and ZIF-L

Figure S4. Crystal structures of (a) ZIF-8, (b) ZIF-L viewed from the $a$ axis and (c) ZIF-L viewed from the $c$ axis. Green, blue and gray indicate Zn, N and C. The hydrogen atoms are omitted for clarity. The unit cells of ZIF-8 and ZIF-L are shown by black squares with the $a$, $b$ and $c$ axes labeled. The brown circle in (c) indicates uncoordinated 2-methylimidazole molecules. The crystal data are as follows. ZIF-8: space group $I-43m$, $a = b = c = 16.9910(12)$ Å, $\alpha = \beta = \gamma = 90^\circ$. ZIF-L: space group $Cmca$, $a = 24.11910(46)$ Å, $b = 17.06045(33)$ Å, $c = 19.73984(37)$ Å, $\alpha = \beta = \gamma = 90^\circ$. 
Figure S5. SEM images of pure (a) ZIF-8 and (b) ZIF-L. The pure ZIF-8 and ZIF-L as reference samples were synthesized according to previous reports. $^{51,52}$
7. SEM Images of ZIF Crystals under Different Conditions

Figure S6 SEM images of ZIF crystals formed (a) in a cell without mirrors and (b) on a single mirror. Both ZIF-8 and ZIF-L were observed in each case with relative size and morphology similar to those formed in free solution.
8. Crystal Size of ZIF obtained in various synthetic conditions

Table S1. Crystal size of ZIF obtained under various synthetic conditions

| Condition                     | ZIF-8       | ZIF-L       |
|-------------------------------|-------------|-------------|
| Free solution                 | 2.42 ± 0.54 µm | 1.66 ± 0.35 µm |
| Cell without mirrors          | 0.97 ± 0.14 µm | 0.60 ± 0.15 µm |
| On a single mirror            | 2.04 ± 0.29 µm | 1.37 ± 0.68 µm |
| Under VSC                     | 262 ± 48 nm  | -           |
9. Fitting of the Raman signals

Figure S7. Fitting of the Raman spectra: (a) pure ZIF-8, (b) pure ZIF-L and (c) a mixture of ZIF-8 and ZIF-L (obtained by crystallization in free solution).
10. Effect of the solution volume on the ratio of ZIF-8 to ZIF-L

**Figure S8.** Ratio of ZIF-8 to ZIF-L plotted against the mirror separation. The red and black dots indicate crystallization in a FP cavity and a cell without mirrors, respectively.
11. Effect of the Q-factor on selective crystallization of ZIF-8

**Figure S9.** IR spectra of the solution in a FP cavity. The thickness of the Au layer was varied: 10 nm (black) and 6 nm (red).

**Figure S10.** SEM images of the crystals formed in a FP cavity. The thickness of Au layer was varied: (a) 10 nm and (b) 6 nm.
Figure S11. Raman signals of the crystals formed in a FP cavity. The thickness of the Au layer was varied: (a) 10 nm and (b) 6 nm.
12. Detuning the cavity modes for OH and OD stretching vibration

![Graph showing IR transmittance spectra](image)

**Figure S12.** IR transmittance spectra of the mixed solution (black), OFF-resonance in a FP cavity (red), and ON-resonance in a FP cavity (blue). $n$ in $k_n$ indicates the order of the cavity modes.

![SEM images](image)

**Figure S13.** SEM images of the crystals obtained in a mixture of H$_2$O and D$_2$O: (a) OFF-resonance and (b) ON-resonance in the FP cavities.
Figure S14. Raman spectra of the crystals obtained in a mixture of H$_2$O and D$_2$O: (a) OFF-resonance and (b) ON-resonance in the FP cavities. The red arrow indicates the characteristic peak of ZIF-L.
13. **Raman Spectra of Crystals Prepared with Various Starting Material Ratios.**
Zn(NO$_3$)$_2$$\cdot$6H$_2$O and 2-methylimidazole were dissolved in MilliQ water (2 mL) in various proportions. ‘Original condition’ indicates the ratio used for the majority of experiments. A portion of the solutions was placed in or outside an optical cavity at room temperature and the crystalline products examined by Raman spectroscopy after 2 hours.

**Table S2.** Range of solutions tested with different ratios of starting materials

| samples          | Zn(NO$_3$)$_2$$\cdot$6H$_2$O | 2-methylimidazole | MilliQ water | Molar ratio  |
|------------------|-------------------------------|-------------------|--------------|--------------|
| original condition | 7.44 mg                       | 86.2 mg           | 2 mL         | 1:41.6       |
| solution-A       | 7.44 mg                       | 80.5 mg           | 2 mL         | 1:39.2       |
| solution-B       | 7.44 mg                       | 69.0 mg           | 2 mL         | 1:33.6       |
| solution-C       | 7.44 mg                       | 57.5 mg           | 2 mL         | 1:28         |

**Figure S15.** Raman spectra of crystals obtained under various conditions as indicated in Table S1: ZIF crystals formed from (a) solution-A outside optical cavity, (b) solution-A inside optical cavity, (c) solution-B outside
optical cavity, (d) solution-B inside optical cavity, (e) solution-C outside optical cavity, and (f) solution-C inside optical cavity.

**Table S3.** Relative intensity of the ZIF-L N-H vibrational peak from Raman spectroscopy and the estimated percentage of crystals formed in the ZIF-L phase for various starting material ratios, inside and outside the Fabry-Perot (FP) cavity.

| samples     | ratio of ZIF-L (%) |
|-------------|-------------------|
| **original condition** |                     |
| outside FP cavity | 26 ± 3            |
| in FP cavity     | 0                 |
| solution-A      |                   |
| outside FP cavity | 24 ± 5*          |
| in FP cavity     | 0                 |
| solution-B      |                   |
| outside FP cavity | 26 ± 4*          |
| in FP cavity     | 0                 |
| solution-C      |                   |
| outside FP cavity | 68 ± 5*          |
| in FP cavity     | 24 ± 7*           |

*estimated from the relative intensity of the peaks around 3165 cm$^{-1}$ and ~3140 cm$^{-1}$
Figure S16. Schematic energy level diagram of vibro-polaritonic states. Theories and experiment suggest that the typical Morse potential of a vibration may be ‘squeezed’ (red-brown curve) compared to normal (green dot line) due to strong coupling. This points to bond strengthening (evidenced by reduction in bond cleavage rates in experiments), and points to reduced polarity for polar bonds (atomic displacement is reduced) which may play a role in the changing solvation properties of water strongly coupled to optical cavities as observed in this work.
15. SEM images of the crystals obtained in alcohol solutions

Figure S17. SEM images of ZIF crystals formed in (a) methanol, (b) ethanol, and (c) isopropanol. Morphologies are characteristic of the ZIF-8 phase, no ZIF-L phase is observed.

Figure S18. XRD patterns of the crystals formed in (a) methanol, (b) ethanol and (c) 1-propanol. Simulated XRD patterns of (d) ZIF-8 (CCDC 602542) and (e) ZIF-L (CCDC 1509273).
Figure S19. Raman spectra of the crystals formed in (a) methanol, (b) ethanol and (c) 1-propanol. The characteristic signal of ZIF-L at about 3160 cm$^{-1}$ was not observed, indicating pure ZIF-8 was obtained.
Kinetics of crystallization

Figure S20. (a–c) Temporal shift of the higher order cavity modes: crystallization in (a) H₂O without a cavity, (b) ethanol without a cavity and (c) H₂O under VSC of OH stretching vibration. Each color indicates the cavity peak at a certain reaction time: red (0 min), orange (4 min), yellow (8 min), green (12 min), blue (16 min) and purple (20 min). (d) Relative changes of the refractive index in H₂O without a cavity (open red circles), ethanol without a cavity (open blue circles) and H₂O under VSC of OH stretching vibration (solid red circles).
16. Crystallization in D$_2$O

![IR transmittance spectra of D$_2$O solution (black) and ON-resonance in a FP cavity (red).](image)

**Figure S21.** IR transmittance spectra of D$_2$O solution (black) and ON-resonance in a FP cavity (red).

![SEM image of the crystals obtained in D$_2$O: (a) free solution and (b) ON-resonance in a FP cavity.](image)

**Figure S22.** SEM image of the crystals obtained in D$_2$O: (a) free solution and (b) ON-resonance in a FP cavity.
Figure S23. Raman spectra of the crystals obtained in D$_2$O: (a) free solution and (b) ON-resonance in a FP cavity.
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