Supporting Information

Selective Crystallization via Vibrational Strong Coupling

Kenji Hirai,*^{1, 2, 3} Hiroto Ishikawa,^{1,3} Thibault Chervy,⁴ James A. Hutchison,⁵ Hiroshi Uji-i*^{1, 3,6}

¹Division of Photonics and Optical Science, Research Institute for Electronic Science (RIES), Hokkaido University, North 20 West 10, Kita ward, Sapporo, Hokkaido, Japan
²Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan.
³Division of Information Science and Technology, Graduate School of Information Science and Technology, Hokkaido University, North 14 West 9, Kita ward, Sapporo, Hokkaido, Japan
⁴Institute of Quantum Electroncis, ETH Zürich, CH-8093 Zürich, Switzerland
⁵School of Chemistry, The University of Melbourne, Masson Rd, Parkville VIC 3052, Australia.
⁶Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, 3001 Heverlee, Leuven, Belgium.

1. Experimental details

Preparation of the reference samples of ZIF-8.^{S1} Zn(NO₃)₂·6H₂O (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} $Zn(NO_3)_2 \cdot 6H_2O$ (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. Structural Differences of ZIF-8 and ZIF-L



Figure S1. Crystal structures of (a) ZIF-8,^{S1} (b) ZIF-L viewed from the *a* axis and (c) ZIF-L viewed from the *c* axis.^{S2} 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, $\alpha = \beta = \gamma = 90^{\circ}$.

3. X-ray Diffraction Measurements



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

4. Microcavity Design



Figure S3. (a) Schematic illustration of the microcavity; (b) photograph of the microcavity cell holder, designed for FTIR spectroscopy of liquids (Specac company).

5. Broadened cavity modes compared to theoretical model



Figure S4. The experimental transmission spectrum of an air-filled mirror cavity used in this work (red curve) is significantly broadened compared to the Transfer Matrix Model (TMM) simulation of the same cavity (blue curve). A similar broadening of the transmission modes can be obtained in simulation assuming a Gaussian distribution of widths are probed with mirror separations \pm 200 nm from the average value (here 20 microns, black curve). Such variations in cavity thickness are reasonable given the \ge 1 mm diameter spot examined in FTIR measurements.

6. Optical Cavity Spectral Dispersion with Angle



Figure S5. 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.

7. Crystal Size of ZIF obtained in various synthetic conditions

	ZIF-8	ZIF-L
Free solution	$2.42\pm0.54~\mu m$	$1.66\pm0.35~\mu m$
Cell without mirrors	$0.97\pm0.14~\mu m$	$0.60\pm0.15~\mu m$
On a single mirror	$2.04\pm0.29~\mu m$	$1.37\pm0.68~\mu m$
Under VSC	$262\pm48~\text{nm}$	-

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

8. SEM images of ZIF-8 and ZIF-L



Figure S6. 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.^{\$1,\$2}

9. SEM Images of ZIF Crystals under Different Conditions



Figure S7. 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.

10. Fitting of the Raman signals



Figure S8. 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).

11. Cavity with 100 µm Separation



Figure S9. IR transmittance spectra of a mirror cavity with 100 microns mirror separation: (a) filled with water, (b) filled with air.

12. Cavity length dependence of ZIF polymorph selectivity.



Figure S10. Ratio of ZIF-8 to ZIF-L crystals obtained in mirror(no-mirror) cavities plotted against the mirror(wall) separation. The red and black dots indicate crystallization in a FP cavity and in a cell without mirrors, respectively.

13. Detuning the cavity modes for OH and OD stretching vibration



Figure S11. IR transmittance spectra of the mixed H_2O/D_2O (volume ratio: 1:1) solution (black), OFF-resonance in a FP cavity (red) and ON-resonance in a FP cavity (blue). The *n* in the k_n labels indicates the order of the cavity modes various peaks are associated with.



Figure S12. SEM images of the crystals obtained in a mixture of H₂O and D₂O: (a) ON-resonance and (b) OFF-resonance in the FP cavities.



Figure S13. Raman spectra of the crystals obtained in the mixture of H_2O and D_2O : (a) OFF-resonance and (b) ON-resonance in the FP cavities. The red arrow indicates the position of the characteristic peak of ZIF-L, however the ratio of ZIF-8 to ZIF-L cannot be estimated reliably in this case owing to the possible exchange of protons and deuterium ions in solution, which can influence the peak intensity.

14. Crystallization in D₂O



Figure S14. IR transmittance spectra of D₂O solution (black) and ON-resonance in a FP cavity (red).



Figure S15. SEM image of the crystals obtained in D_2O : (a) free solution, (b) ON-resonance in a FP cavity.



Figure S16. Raman spectra of the crystals obtained in D_2O : (a) free solution, (b) ON-resonance in a FP cavity. The red arrow indicates the position of the characteristic peak of ZIF-L, however the ratio of ZIF-8 to ZIF-L cannot be estimated reliably in this case owing to the possible exchange of protons and deuterium ions in solution, which can influence the peak intensity.

15. Effect of the Q-factor on selective crystallization of ZIF-8



Figure S17. IR spectra of the solution in a FP cavity. The thickness of the Au layer was varied: 10 nm (black) and 6 nm (red). The Q-factors were estimated to be 32 and 24 for 10 and 6 nm thick Au layer cavities, respectively.



Figure S18. 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 S19. 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.

16. Raman Spectra of Crystals Prepared with Various Starting Material Ratios.

 $Zn(NO_3)_2 \cdot 6H_2O$ 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.

complag	Zn(NO ₃) ₂ ·6H ₂ O	2-methylimidazole	MilliQ water	Molar ratio
samples				Zn : Hmeim
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

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



Figure S20. Raman spectra of crystals obtained under various conditions as indicated in Table S2: 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	$24\pm5^*$	
	in FP cavity	0	
solution-B	outside FP cavity	$26\pm4^{*}$	
	in FP cavity	0	
solution-C	outside FP cavity	$68 \pm 5^*$	
	in FP cavity	$24\pm7^*$	

*estimated from the relative intensity of the peaks around 3165 cm^{-1} and ~3140 cm^{-1}

17. Diagram of a Squeezed Morse Potential under VSC

coupled to optical cavities as observed in this work.



Figure S21. 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

18. SEM images of the crystals obtained in alcohol solutions



Figure S22. 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 S23. 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 S24. 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.

17. Kinetics of ZIF crystallization.



Figure S25. (a–c) Temporal shift of the high order cavity modes far from the OH stretch energy: crystallization in (a) H_2O in a no-mirror cavity, (b) ethanol in a no-mirror cavity and (c) H_2O in a mirror cavity under VSC of OH stretching vibration. Each color indicates the cavity optical mode 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).

References

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