

## Electronic Supporting Information

### Deliquescence caused by organic vapors

*Kazuyuki Ishii\*, Kei Yokomori, Kei Murata, Seiji Nakamura and Kyoko Enomoto*

*Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo  
153-8505, Japan*

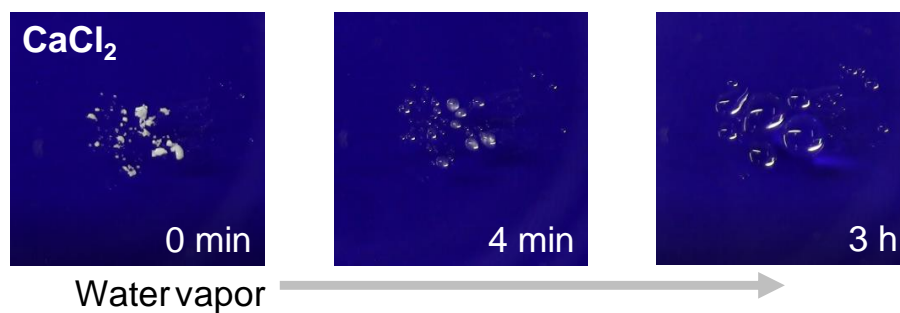
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## Materials and Methods

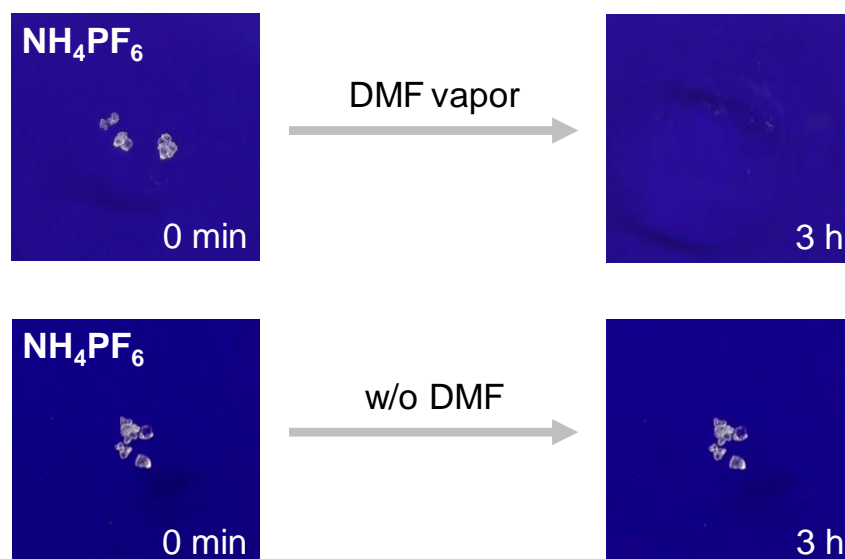
**Materials.** Tetrabutylammonium hexafluorophosphate (for electrochemical analysis,  $\geq 99.0\%$ ) and tetrabutylammonium benzoic acid (for electrochemical analysis,  $\geq 99.0\%$ ) were purchased from Merck KGaA. Ammonium hexafluorophosphate (Wako 1st Grade,  $>95.0\%$ ) ammonium tetrafluoroborate (Wako 1st Grade,  $98.0\%$ ), chloroform (Infinity Pure,  $>99.7\%$ ), *N,N*-dimethylformamide (DMF; Infinity Pure,  $>99.7\%$ ), and toluene (Infinity Pure,  $>99.8\%$ ) were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. Sodium chloride (special grade,  $>99.5\%$ ) was purchased from Kanto Chemical Co., Inc. Tetraphenylphosphonium bromide ( $>98.0\%$ ) was purchased from Tokyo Chemical Industry Co., Ltd. All chemicals were used as received without further purification.

**Measurements.** The solid  $\rightarrow$  liquid changes in response to organic vapors were monitored by a video camera. The typical setup for a typical organic vapor exposure experiment is shown in Fig. 1A in the main text. Specifically,  $\sim 0.5$  mg of the solid chemical powder was added onto a thin glass plate, which was placed onto a blue cobalt glass specimen in a 9-cm petri dish. The blue color of the cobalt glass was helpful for monitoring the solid  $\rightarrow$  liquid changes. Next, 1.0 mL of organic solvent was split between two smaller petri dish reservoirs in the 9-cm petri dish in order to increase the surface area of organic solvent. A top glass cover was added and sealed by applying grease, thereby creating a closed system. The changes to the physical state of the powder were selectively monitored within this closed system. Organic deliquescent behaviors were monitored by recording video of the corresponding solid chemical on the blue cobalt glass under organic vapor exposure for up to 3 hours. Then, the system was opened up, and the weights of samples on the thin glass plate were measured using a microbalance (Sartorius ME5). In the water vapor-induced deliquescence experiments, the experimental setup was identical to that in the organic vapor-induced deliquescence experiments, except 4.0 mL of Milli-Q water were split between the two smaller petri dish reservoirs in the 9-cm petri dish.

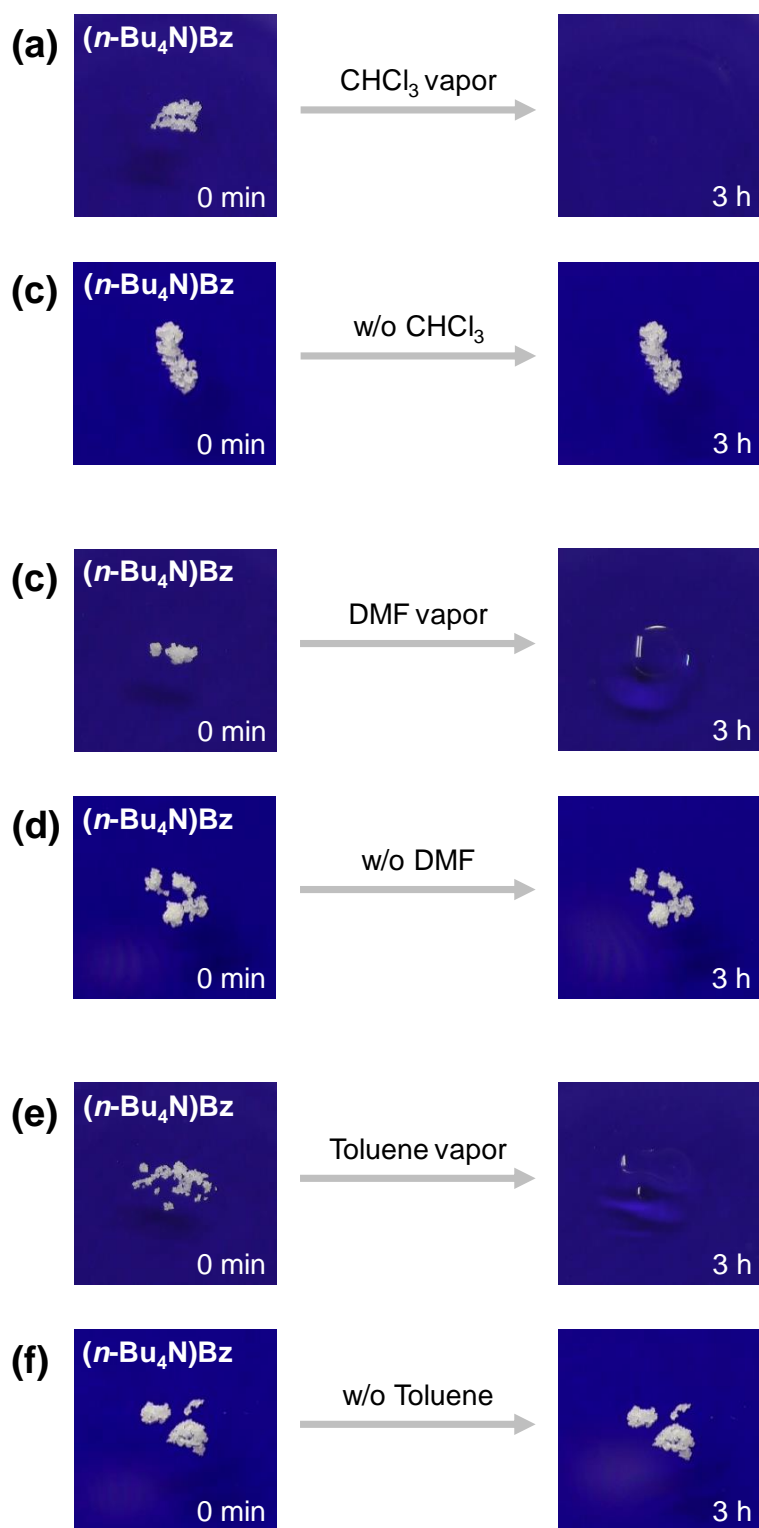
When  $(n\text{-Bu}_4\text{N})\text{PF}_6$  was exposed to DMF, the weight on the thin glass plate and the DMF vapor concentration were simultaneously monitored over time to directly confirm the organic deliquescent behavior. As shown in Movie S6, a closed system was constructed by sealing glass plates with grease inside of an analytical balance (A&D Company, Ltd., HR-202i). Approximately 5 mg of  $(n\text{-Bu}_4\text{N})\text{PF}_6$  was placed on a thin glass plate, and five small petri dish reservoirs were added, each containing 1.0 mL of DMF. The system was sealed by adding a top glass cover and applying grease. Then, a volatile organic compound (VOC) monitor (Honeywell, MiniRAE 3000) was connected to the closed system to monitor the DMF vapor concentration therein. The weight and DMF vapor concentration were monitored over time using a video camera, while the solid  $\rightarrow$  liquid changes were simultaneously monitored by a second video camera. Powder X-ray diffraction was measured by a Rigaku RINT2500 diffractometer.



**Fig. S1 Control experiment for water vapor-induced deliquescence.** Water-induced deliquescent behavior of CaCl<sub>2</sub> exposed to water vapor. This phenomenon was monitored by capturing a video of the solid CaCl<sub>2</sub> on the blue cobalt glass under water vapor exposure (Movie S1).



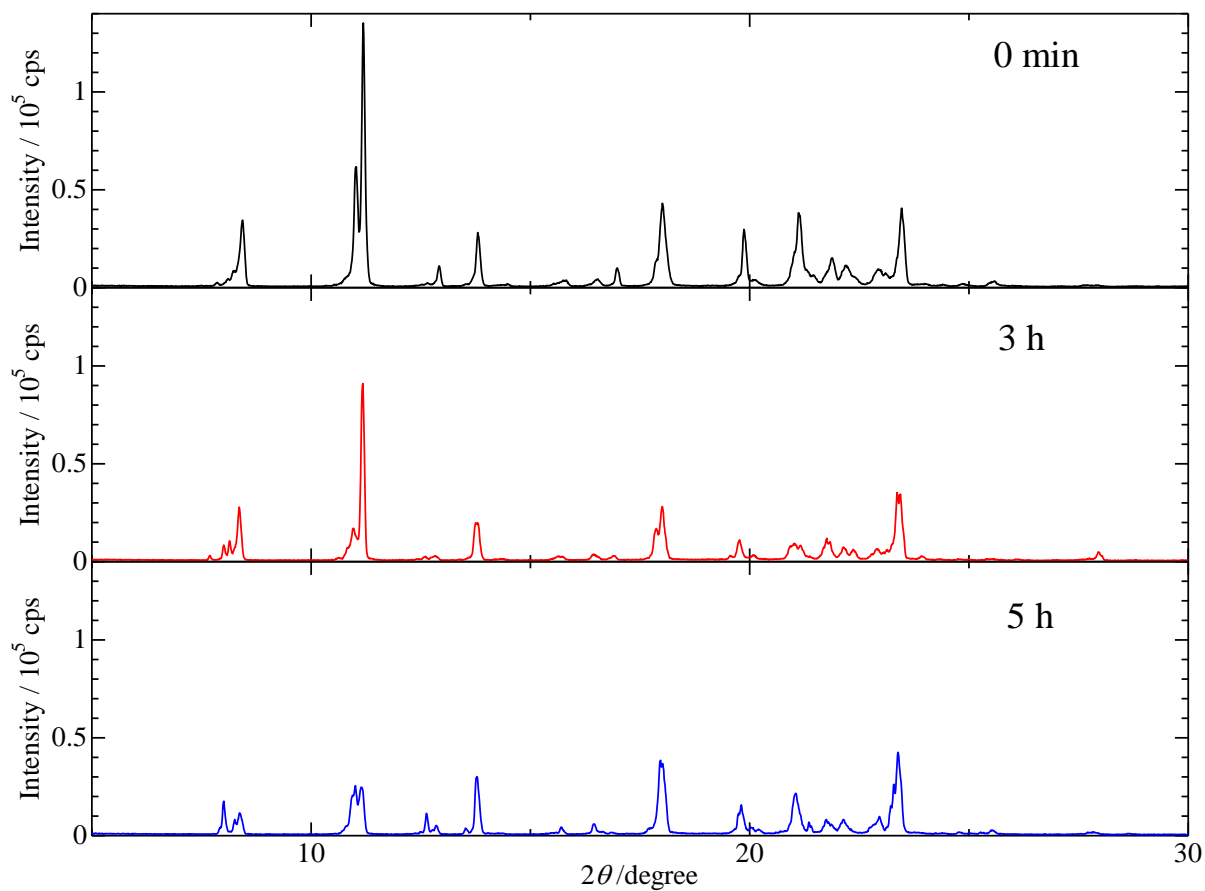
**Fig. S2 Control experiments for organic deliquescence.** Organic deliquescent behaviors of NH<sub>4</sub>PF<sub>6</sub> exposed to DMF vapor (top) or without DMF (bottom).



**Fig. S3 Control experiments for organic deliquescence II.** Organic deliquescent behaviors of  $(n\text{-Bu}_4\text{N})\text{Bz}$  exposed to  $\text{CHCl}_3$  (a), DMF (c), or toluene (e) vapors and without  $\text{CHCl}_3$  (b), without DMF (d), or without toluene (f).

**Table S1.** Summary of the weight changes after organic deliquescence and the solubility.

Molecular Salt	Solvent	Initial weight/mg	Weight/mg (after 3h)	Solubility to 1.0 g of solvent /g (at 20 °C)
<i>(n</i> -Bu <sub>4</sub> N)PF <sub>6</sub>	CHCl <sub>3</sub>	0.67	1.21	0.64
	DMF	0.65	2.13	1.27
NH <sub>4</sub> PF <sub>6</sub>	DMF	0.55	3.64	1.07
NH <sub>4</sub> BF <sub>4</sub>	DMF	0.57	3.36	0.29
(Ph <sub>4</sub> P)Br	CHCl <sub>3</sub>	0.57	0.88	0.29
	DMF	0.67	3.11	0.25
<i>(n</i> -Bu <sub>4</sub> N)Bz	CHCl <sub>3</sub>	0.60	0.66	2.06
	DMF	0.54	1.50	1.64
	toluene	0.52	0.56	2.42



**Fig. S4 Time dependence of powder X-ray diffraction during organic deliquescence of  $(n\text{-Bu}_4\text{N})\text{PF}_6$  exposed to DMF.** The organic deliquescence was initiated at 3 h, but it was not completed at 5 h. The powder of  $(n\text{-Bu}_4\text{N})\text{PF}_6$  was grinded in order to remove the anisotropic effects of crystals. Also, it was carefully checked that the peak intensities and angles were almost independent of sample setting processes.