CONDENSATION OF EXCITED MOLECULES UNDER PHOTO-EXCITATION

External fields, such as magnetic fields and pressure, frequently influence the order parameters of the physical system and thus cause phase transitions. In FeRh, for example, an external magnetic field forcibly aligns the Fe local spins, and eventually induces a transition from the antiferromagnetic ground state to the ferromagnetic state at around room temperature. Since photo-irradiation selectively excites molecular units in solid systems, we can expect a new type phase transition whose order parameter is the *density of the excited molecules.* In Fig. 1, we show schematic pictures of a molecular system under photo-excitation: open and filled circles represent the molecular units in the ground and excited states, respectively. Under weak photo-excitation, the process of creating the excited molecules balances the thermal and/or quantum relaxation processes acting upon them. What happens if we further increase the excitation power? In this case, the interaction between the excited molecules will stabilize either the excited molecular pairs or the dense regions of excited molecules (hatched region in Fig. 1). In other words, the lifetime of the dense region becomes much longer than that of the isolated excited molecules. Consequently, such regions tend to grow by the subsequent photo-excitations, and eventually the excited molecules condense.

To experimentally confirm the above-mentioned scenario, we have performed *in situ* synchrotron radiation X-ray (SRX) powder structural analysis of $[Fe(ptz)_6](BF_4)_2$ under photo-excitation at beamline **BL02B2** [1]. $[Fe(ptz)_6](BF_4)_2$ (ptz = propyltetrazole), consists of $Fe(ptz)_6$ molecular units, in which a divalent Fe^{2+} ion is surrounded by six N of ptz ligands. The $Fe(ptz)_6$ unit takes two well-defined states; one is the low-spin (LS) ground state, and the other one is the high-spin (HS) exited state. The Fe-N bond distance (2.2 Å) is larger in the HS state than that (2.0 Å) in the LS state.

Figure 2 shows the powder patterns for $[Fe(ptz)_6](BF_4)_2$ at 91 K under various photo-excitation conditions. A cw laser (532 nm) beam, which selectively excites the LS molecules into the HS state, was weakly focused onto the powdered

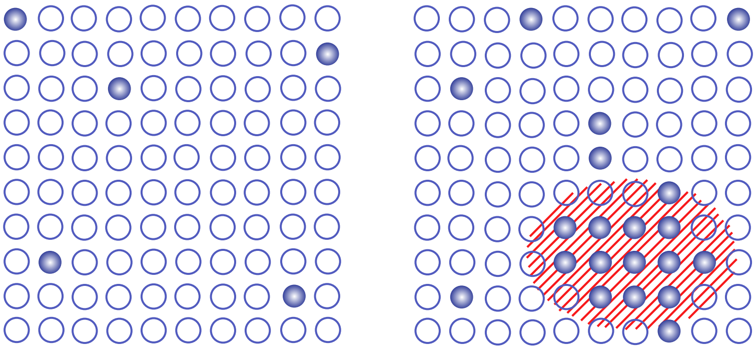
(a) Weak Excitation (b) Strong Excitation

*Fig. 1. Schematic pictures of a molecular system under **(a)** weak and **(b)** strong excitation. Open and filled circles represent the molecular units in the ground and excited states, respectively. Hatching in **(b)** indicates the dense region of the excited molecules.*

samples in a capillary; the laser spot size (*ca.* 2 mm) was larger than the collimator size (1 mm × 0.5 mm) for the SRX beam. The powder patterns showed negligible change in the weak excitation region ($P < 49$ mW; P is the excitation power), and were analyzed with the rhombohedral (R3; Z = 3) model [2]. At P = 55 mW and 70 mW, however, the Bragg reflection at 19.2° showed a shoulder structure in the lower-angle side. As a result, we adopted a two-phase model with the rhombohedral structures to determine the Rietveld analysis of these patterns.

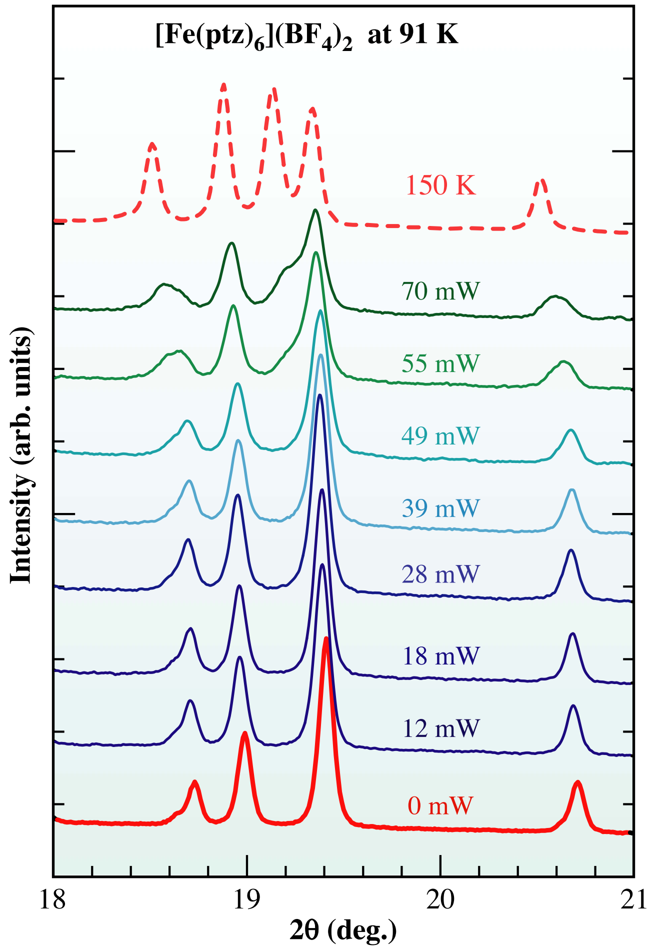

Fig. 2. In situ synchrotron-radiation X-ray powder diffraction patterns under various excitation powers for $[Fe(ptz)_6](BF_4)_2$ at 91 K. X-ray wavelength is 1.0010 Å. The thick solid curve is the powder pattern without photo-excitation. The broken curve is the powder pattern at 150 K in the high-temperature phase.

In Fig. 3 we summarized the P-dependence of physical quantities for $[Fe(ptz)_6](BF_4)_2$ at 91 K. The lattice constants (Fig. 3(a)) gradually change with P in the weak excitation region ($P < 49$ mW). At P = 55 mW, however, the secondary phase (square symbols) suddenly appears. The lattice constant a (10.82 - 10.83 Å) for this secondary phase is much smaller than the high-temperature value (10.89 Å), indicating that the present observation cannot be ascribed to the conventional heating effects. These structural changes are maintained only under photo-excitation, and soon disappear if we stop it. Figure 3(b) shows the P-dependence of the Fe-N bond distance $d_{\text{Fe-N}}$ determined by the Rietveld structural analysis. The longer $d_{\text{Fe-N}}$ (2.1 Å) suggests that the secondary phase should be ascribed to the condensed phase of the photo-excited HS molecules. Figure 3(c) shows the mass fraction of the secondary phase.

Now, let us investigate the interrelation between P and the order parameter, that is, density n_{HS} of the HS molecules, which can be estimated by varying the LS absorption band [3]. In Fig. 4, we plotted n_{HS} against P for $[Fe(ptz)_6](BF_4)_2$ at 77 K; solid and open circles represent the data obtained in P-increasing and decreasing runs, respectively. We used the 514.5 nm (2.41 eV) line of a cw Ar^+ laser as the excitation and probe light sources (pump & probe technique). In the weak-excitation region ($P < 60$ mW/cm^2), n_{HS} remains small (< 0.1). With a further increase in P, however, n_{HS} steeply increases and reaches *ca.* 0.5. Such an abrupt change of n_{HS} against P can be regarded as the phase transition into the condensed state of the HS molecules. We further observed a clear optical hysteresis, indicating that this phase transition is of the first order.

Thus, our *in situ* SRX powder structural analysis, in addition to results of the pump & probe experiment of $[Fe(ptz)_6](BF_4)_2$, suggests that condensation of excited molecules is realized under strong-excitation. Present *in situ* SRX powder structural analysis is a powerful tool for determining the atomic coordinates in the photo-excited steady state, and for exploring the physics of excited states.

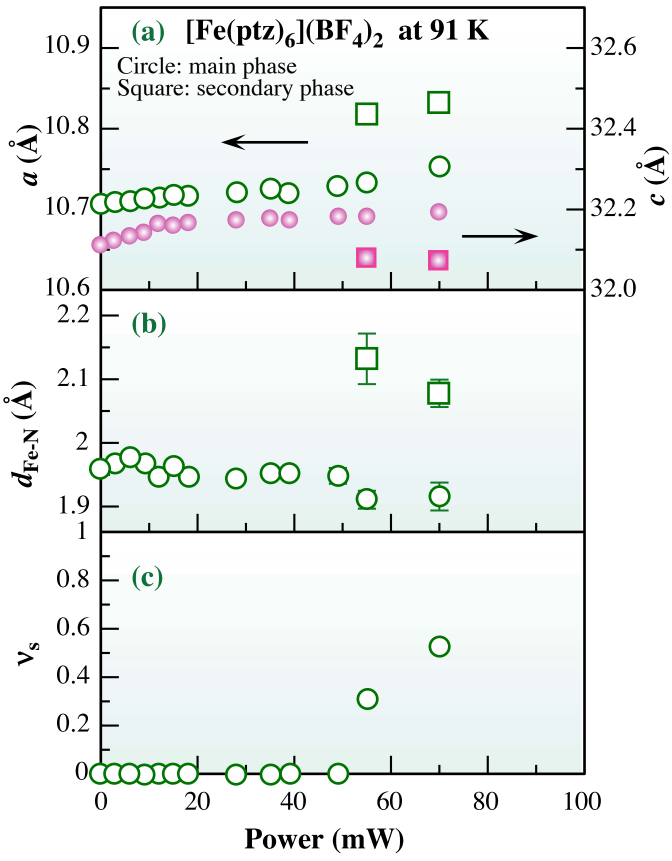

*Fig. 3. Excitation power dependence of **(a)** lattice constants, a and c, **(b)** Fe-N bond distance $d_{Fe\text{-}N}$ and **(c)** mass fraction ν_s of the secondary phase for $[Fe(ptz)_6](BF_4)_2$ at 91 K. Square symbols represent values for the photo-induced secondary phase.*

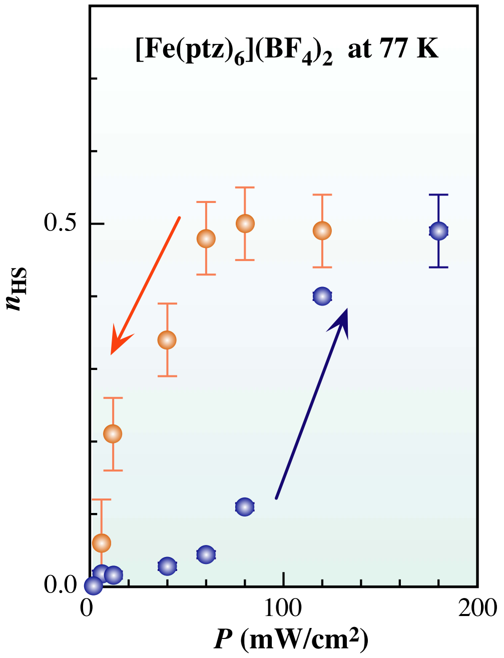

Fig. 4. Density n_{HS} of the HS molecules against excitation power density P for $[Fe(ptz)_6](BF_4)_2$ at 77 K.

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