Order-disorder Phase Transition between High- and Low-Z’ crystal structures:
Crystallographic and non-linear optics study on transition

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Crystal structures with a multiple number of molecules in the asymmetric unit (Z’), i.e., high-Z’, are not only a scientific curiosity but also attract many scientists as an informative subset of crystal structures to understand crystallization and polymorphism. However, a systematic and quantitative answer responding to the intrinsic question ‘what is the reason behind the occurrence of a high -Z’ crystal structure?’ is difficult to obtain due to the small number of reports; thus, this question still remains unanswered. In fact, over 90% of crystal structures in Cambridge Crystallographic Data Centre correspond to this, while the crystal structure of organic compounds with Z’ ≥ 8 has been reported in only 310 cases out of more than 1,000,000 reports of crystal structures in the database in 2021. Herekin, we report a crystal structure of Boc-L-methionyl glycine methyl ester (MGP) with Z’ = 8. The phase transition behavior is revealed by single-crystal X-ray structure analysis and the temperature dependent second harmonic generation (SHG) technique. This is the first example to demonstrate that the SHG technique is applicable to detect a phase transition without a change of symmetry operations. The disorder of the methionine moiety of the high-temperature (HT) phase reflected the conformation of the low-temperature (LT) phase as shown in Figure 1. In this presentation, the detail of crystal structures, phase transition behaviour, and the theoretical calculation of the lattice energy will be described.

Figure 1. Order-disorder phase transition of MGP crystal at −113 °C.