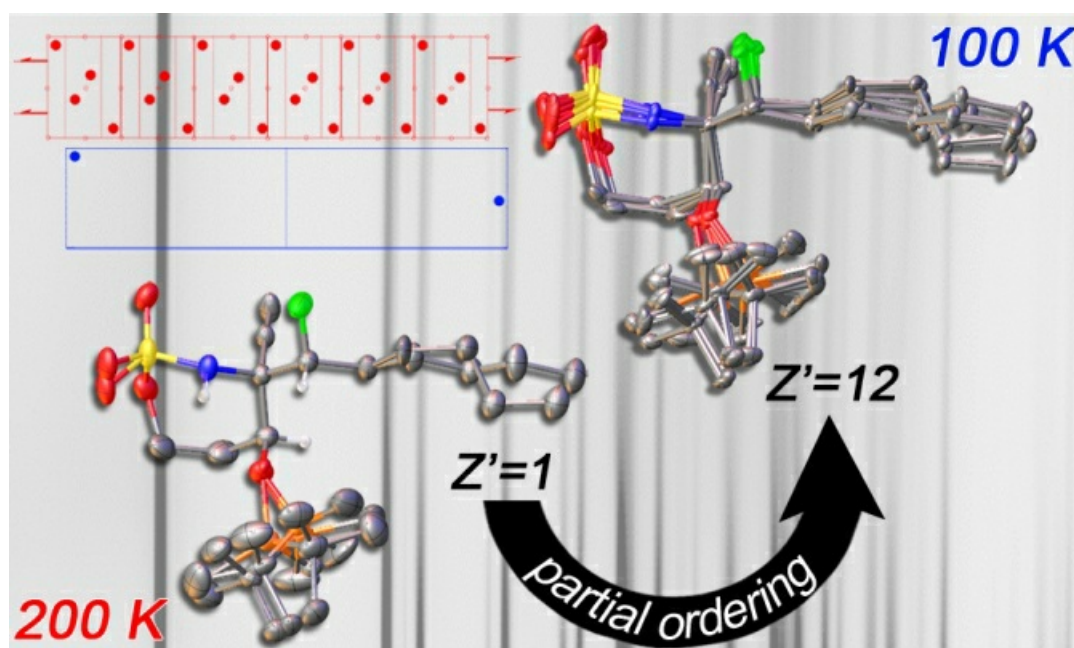


*Enantiotropic phase transition in a molecular solid involving  $Z'=12$* Ilia Guzei<sup>1</sup>, Anastasiya Vinokur<sup>1</sup>, Andrey Yakovenko<sup>2</sup>, Lu Liu<sup>1</sup>, Jennifer Schomaker<sup>1</sup><sup>1</sup>University Of Wisconsin-Madison, Madison, United States, <sup>2</sup>Argonne National Laboratory, Argonne, United States  
E-mail: iguzei@chem.wisc.edu

A structural study of the complex aminated stereotriads, [(tert-butyl dimethylsilyl)oxy]-4-ethynyl-4-(1-fluorohexyl)-1,2,3-oxathiazocane-2,2-dione (1) and its reduced analogue, [(tert-butyl dimethylsilyl)oxy]-4-ethenyl-4-(1-fluorohexyl)-1,2,3-oxathiazocane-2,2-dione (2), revealed a k12-type second-order phase transition in 1 and phase stability over the same temperature range in 2. The observed phase transition in 1 has been linked to the partial ordering of the extensive positional disorder of the high temperature phase (Space group P21/c,  $a=16.0697(14)$  Å,  $b=10.0140(7)$  Å,  $c=14.2762(9)$  Å,  $\beta=97.805(8)^\circ$ ,  $V=2276.1(3)$  Å<sup>3</sup>) upon cooling as revealed by single crystal X-ray diffraction. The ordering breaks the translational symmetry and introduces differences in the molecular volumes of the packed species and results in a low temperature crystal structure with  $Z'=12$  (Space group Pc,  $a=15.7977(14)$  Å,  $b=59.820(5)$  Å,  $c=14.1775(8)$  Å,  $\beta=97.574(9)^\circ$ ,  $V=13281.1(18)$  Å<sup>3</sup>). The in situ powder X-ray diffraction studies suggest that the transition occurs between 237 K and 180 K upon cooling, but the complete amorphization in the range of 244 K to 274 K complicated the assignment of the transition temperature upon heating. The observed loss of crystallinity has been linked to the phase transition and suggests that the loss of long range order is due to the crystallites undergoing the transformation independent of one another. Furthermore, the observed ongoing changes in the cell parameters at 100 K suggest existence of a second low temperature phase with potentially even higher  $Z'$  value.



**Keywords:** [Phase transition](#), [High  \$Z'\$](#) , [Disorder](#)