

## *Supporting Information for*

# **Evidence for Point Transformations in Photo Active Molecular Crystals by the Photo-induced Creation of Diffuse Diffraction Patterns**

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The initiation of the molecular switching process of  $\alpha$ -styrylpyrylium TFMS is based on a local event, namely the dimerization of two monomer molecules into one dimer molecule (figure S1A). The structural analysis of the dynamics shows that this local reaction is ultrafast (see also ref<sup>16</sup>). This is one aspect of the photoreaction. The other aspect concerns the transformation properties of the whole crystalline bulk, as sketched in fig. S1B. Under the present optical excitation conditions, two transformation mechanisms (**M1** and **M2**) are possible. Here, the black and gray squares present monomer and dimer unit cells, respectively; on the left side of the figure the structures of one pair of monomer molecules and one dimer molecule are shown. According to mechanism **M1** (left side of Figure S1B), the switching process propagates throughout the crystal without influence of surrounding molecules. The dimerization probability of a pair of monomer molecule is absolute equal in the whole crystal for a homogeneous illumination setup. For homogeneous transformation of light-sensitive materials, the intensity of the transmitted light should not drop below  $I = I_0/e$ . In this way, a uniform solid state reaction is ensured, which is the most considerate illumination scheme to avoid stress in the sample. Mechanism **M2** (right side of Figure S1B) is based on a photoinduced generation of dimer seeds, which continue to grow cooperatively upon light irradiation. The growth can be one-, two- or three-dimensional. The ultrafast switching of  $\alpha$ -styrylpyrylium TFMS has been used to generate local disorder in the periodic lattice. The two mechanisms in figure 1 can be distinguished studying the transformation from the seed to the bulk with the present time-resolved X-ray diffraction techniques.

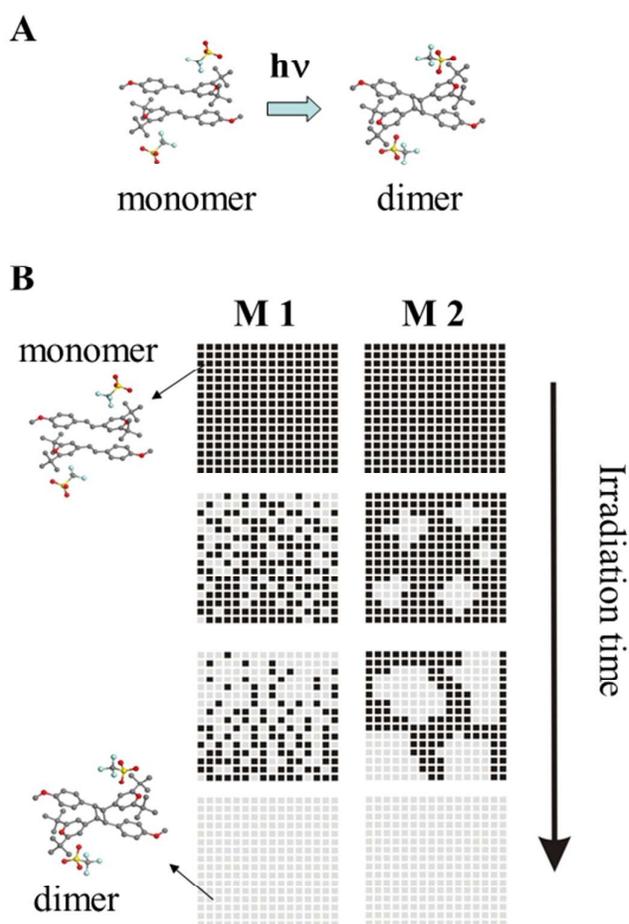


Figure S1;Hallmann et al.

Figure S1: Photodimerization of  $\alpha$ -styrylpyrylium TFMS. A) Photodimerization from the monomer to the dimer system as the first step of the switching mechanism. B) Transformation mechanism of the whole bulk. The black square presents a monomer unit cell and the grey square a dimer unit cell. Two different transformation mechanisms (**1** and **2**) within the bulk are shown. Mechanism **1** (left side) presents a transformation without cooperativity. Mechanism **2** (right side) presents a mechanism with photoformation of the dimer seeds under occurrence of cooperativity. Both mechanism leads to a completely transformed crystal consisting of dimer molecules of  $\alpha$ -styrylpyrylium TFMS.

