

**s7.m3.o5** Cooperative electron transfer at thermo- and photo-induced neutral-ionic phase transformations. E. Collet<sup>1</sup>, M. H. Lemée-Cailleau<sup>2</sup>, M. Buron<sup>2</sup>, H. Cailleau<sup>2</sup>, T. Luty<sup>3</sup>, S. Koshihara<sup>4</sup>, S. Techert<sup>5</sup>, M. Wulf<sup>6</sup> and F. Moussa<sup>1</sup>, <sup>1</sup>LLB CEA-Saclay France, <sup>2</sup>GMCM Univ. Rennes I France, <sup>3</sup>IPTC Technical Univ. Wroclaw Poland, <sup>4</sup>DMS TIT Tokyo and KAST Kawasaki Japan, <sup>5</sup>ESRF Grenoble France.

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New types of multistability take place in some molecular materials, where structural changes are strongly coupled with the change of the electronic state, so that new concepts emerge from charge-transfer (CT) processes. This situation is carried to extreme in mixed-stack CT complexes which present the neutral-ionic (N-I) phase transition<sup>1</sup>. This is associated with a change of charge on ionic species, in relation with the chain multistability, between a regular neutral state .. D<sup>0</sup> A<sup>0</sup> D<sup>0</sup> A<sup>0</sup> D<sup>0</sup>.. and two degenerate dimerized ionic states of opposite polarization ...(D<sup>+</sup>A<sup>-</sup>)(D<sup>+</sup>A<sup>-</sup>)... and ...(A<sup>-</sup>D<sup>+</sup>)(A<sup>-</sup>D<sup>+</sup>)... This unusual phase transition may be induced by temperature, pressure and also light. It proceeds via a cascade of cooperative phenomena : the formation of lattice-relaxed CT strings, their three-dimensional condensation and their three dimensional ordering. These non-conventional ferroelectric compounds present intriguing features such as :

- a singular gas-liquid-solid like pressure-temperature phase diagram, i.e. between respectively Npara, Ipara and Iferro phases, which can be discussed in terms of condensation and ferroelectric ordering of non-linear CT excitations<sup>2</sup>.

- ultra-fast photo-induced phase transformations, i.e. when light triggers an out-of-equilibrium change of the macroscopic state, opening the way to induce by light a ferroelectric phase within a 100 ps time scale<sup>3</sup>. These photo-induced cooperative phenomena are highly non-linear (converted fraction vs. number of photons) and very efficient (one photon can transform a few hundreds of DA pairs).

These different features can be illustrated by means of different structural studies : neutron diffraction under pressure, high-resolution X-ray diffraction and ultra-fast time-resolved crystallography.

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