Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics
This journal is © The Owner Societies 2012

Electronic Supplementary Informations.

Domenico Di Sante,[*a,b] **Alessandro Stroppa,**[a] **and Silvia Picozzi**[a]

1 Wannier Functions Analysis

Here we focus on the effect of different xc functionals, by limiting to PBE and HSE, on the electronic component of the ferroelectric polarization. We calculate the displacement of Wannier centers along a path from the centric phase to the structure with intermolecular hydrogen atoms in their ferroelectric positions, while keeping all the other atoms in their centrosymmetric positions. We focus our study to four Wannier functions (plotted in real-space in Fig. 1) which show the character of σ-bonded combinations of sp^2 hybrid orbitals (a, b and c panels), and p_z orbital (d panel) with the z-axis taken orthogonal to the Croconic ring plane.

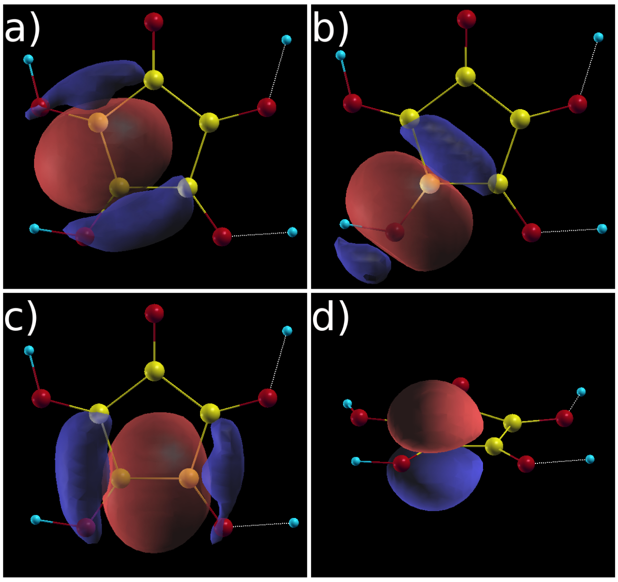

Fig. 1 MLWFs having the character of σ-bonded combinations of sp^2 orbitals (a, b and c panels) and p_z orbital (d panel).

We find that sp^2-like Wannier function are centered in proximity of the middle of $C_1 = C_2$, $C_1 - O_1$ and $C_1 - C_5$ bonds, while p_z-like Wannier function is centered very close to C_1 carbon atom. When hydrogen atoms H_1 and H_2 move toward their ferroelectric positions, Wannier centers move, giving rise to the electronic contribution to the polarization coming from the four valence electrons of C_1 carbon atom. In Tab. 1 we report the sum of displacements for the z-component of Wannier centers as calculated within PBE and HSE (at the PBE fixed geometries in order to exclude structural contributions), and the relative value of the electronic polarization. The sum over the Wannier centers displacements is defined as $\Delta = \sum_i (\mathbf{r}_\mathbf{i}^\mathbf{FE} - \mathbf{r}_\mathbf{i}^\mathbf{PE})$, where the i-index runs over the four Wannier functions, **PE** label refers to the paraelectric structure and the **FE** label refers to the non-centrosymmetric structure with hydrogen atoms sited in their ferroelectric positions. The electronic polarization is given by $P_z = -2e\Delta_z/V$, where V is the volume of the unit cell.

Table 1 z-component of Wannier centers displacements and relative contributions to the electronic polarization in PBE and HSE approximations.

	$\Delta_z(\mathring{A})$	$P_z(\mu C/cm^2)$
PBE	0.023	-0.150
HSE	0.022	-0.143

The table suggests that, as far as the electronic contribution to the polarization is concerned, the introduction of exact exchange does not increase the polarization, but rather decreases it (in absolute value). The study of Wannier function centers reinforces the correlation between inter-molecular hydrogen distortion and double(π)-bond switching of carboxylic bonds. When hydrogen atoms H_1 and H_2 move inside the hydrogen bonds toward their non-centrosymmetric positions, the center of the Wannier function plotted in Fig. 1a moves along the $C_1 = C_2$ bond, as a consequence of the pile-up of out-of-plane charge density, the fingerprint of a double(π)-bond switching (see Fig. 5 in the main text)[1].

References

1 A. Stroppa, D. Di Sante, S. Horiuchi, Y. Tokura, D. Vanderbilt and S. Picozzi, *Phys. Rev. B*, 2011, **84**, 014101.

---

[a] *Consiglio Nazionale delle Ricerche – Superconducting and Innovative Devices (CNR-SPIN), 67100 L'Aquila, via Vetoio, Italy.*
E-mail: domenico.disante@aquila.infn.it
[b] *Physics Department, University of L'Aquila, 67100 L'Aquila, via Vetoio, Italy.*