

Nanoscale morphology and electronic coupling at the interface between indium tin oxide and organic molecular materials

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Supplementary Information

The force-field for In_2O_3 and ITO systems was defined in term of pairwise contributions to Coulomb and repulsion/dispersion energies. These latter, constituting van der Waals interactions, were described in terms of a Buckingham potential. Coulombic terms were described as interaction between point charges, assigned to atoms on the basis of the formal ionic charge (In:3+; Sn:4+; O:2-). In addition, polarization of oxygen atoms was taken into account by considering a pair of opposite point charges (core and shell), for each atomic center, attached to each other through an harmonic potential. The set of parameter used is taken from Ref. 52 and adapted to the current GROMACS implementation. The full set of parameters used is shown in Table S1.

Table S1. Potential parameters used in molecular mechanics calculations of In_2O_3 and ITO systems.

Buckingham terms	Pair	A (eV)	1/B (\AA^{-1})	C (eV \AA^{-6})
	$\text{In}^{3+} \text{O}^{2-}$	2719.77	0.2917	0.0
	$\text{Sn}^{4+} \text{O}^{2-}$	2180.89	0.3076	0.0
	$\text{O}^{2-} \text{O}^{2-}$	25.41	0.6937	32.32
Bonded terms	Pair	K (eV \AA^{-2})		
	$\text{O}^{2-} \text{O}^{2-}$	20.53		

The optimized unit cell side lengths are 10.116 \AA , 10.129 \AA and 10.148 \AA for In_2O_3 and ITO at 5 and 10 wt% tin doping, respectively. Therefore, this set of parameters provided structural data for In_2O_3 and ITO bulk crystals in excellent agreement with DFT and experimental values (Ref. 52). Moreover, short MD equilibrations at room temperature in an NPT ensemble (in which all cell parameters were allowed to relax) and annealing at 500 K (in the same ensemble) suggested a remarkable structural stability of the simulated systems.

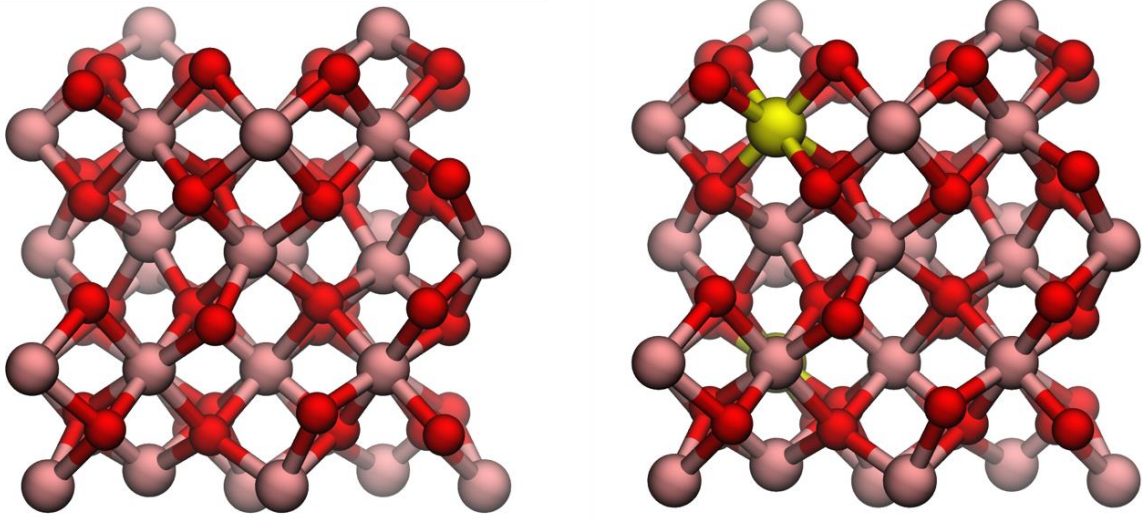


Fig. S1 DFT optimized models of In₂O₃ bulk structure (left) and ITO bulk 5 wt% (right).

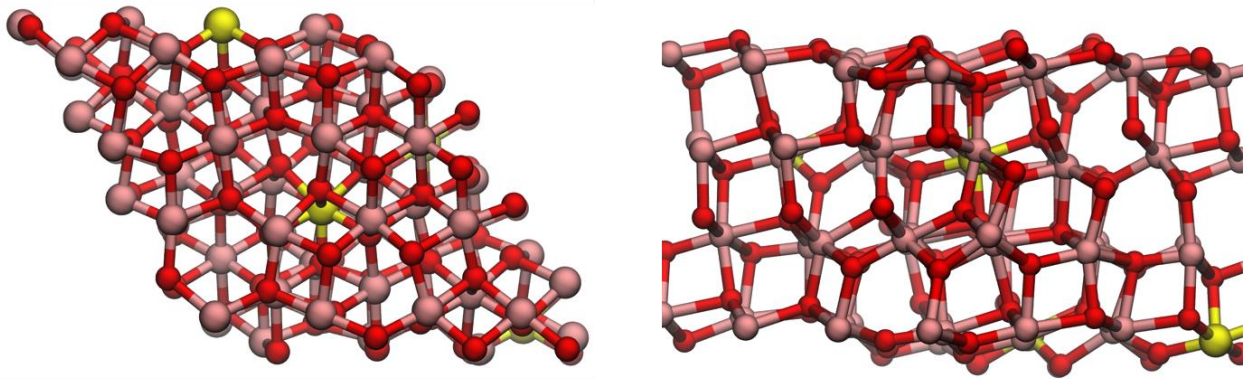


Fig. S2 DFT optimized model of the (111) ITO slab. Top (left) and side (right) view.

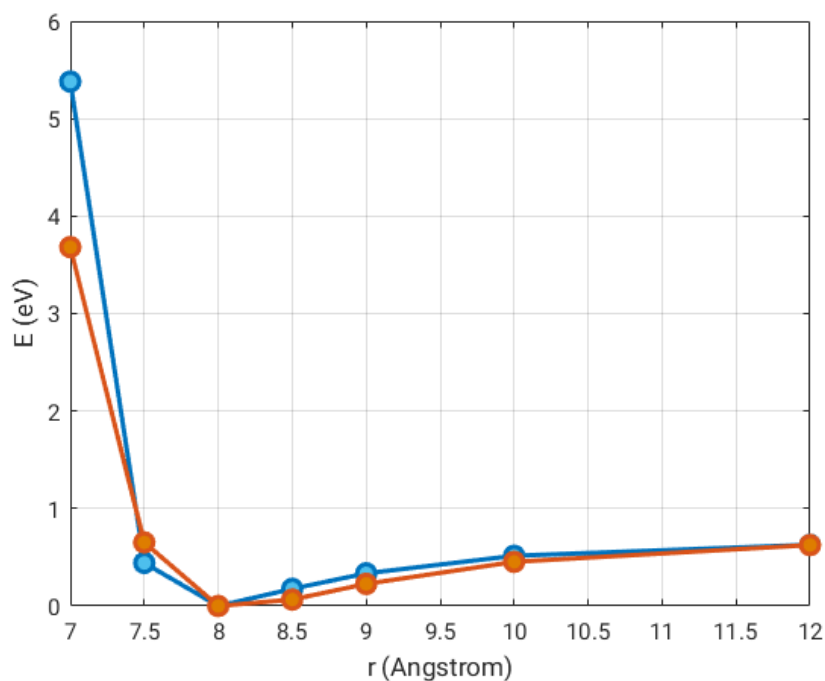


Fig. S3 Comparison between the interaction energy, as a function of the distance, for a DPBIC molecule adsorbed onto an ITO surface, computed at the DFT (red) and FF (blue) levels.

Table S2. Calibration DFT calculations on the In_2O_3 cubic bulk structure. US: UltraSoft pseudopotentials. MT: Martin-Troulliers pseudopotentials. Energy cut-off (r_{cut} : wavefunction cut-off, d_{cut} : electron density cut-off) in Ry; cell parameter a in Å.

Functional	Pseudo	r_{cut}	d_{cut}	k-point sampling	a
LDA	US	30	120	3 3 3	10.111
PBE	US	30	120	3 3 3	10.321
		50	200	3 3 3	10.404
		70	280	3 3 3	10.284
MT ($\text{In}_{d^{10}}$)		50	200	3 3 3	9.864
		70	280	3 3 3	10.284
		80	320	3 3 3	10.334
MT (In_{d^0})		70	280	3 3 3	10.011
		80	320	3 3 3	10.047