Supporting information

1. Decomposition of the work-function shift into its three components for the benzoic acid derivatives.

Calculated work function (Φ) for the non-polar ZnO surface on which BA with different terminal groups are attached with different binding modes. ΔΦ corresponds to the difference with respect to the work function Φ obtained for the bare non-polar ZnO surface (4.47 eV): $\Delta\Phi = \Phi - \Phi_{ZnO}$. ΔV_{BA} is the potential shift associated to the molecular backbone. V_{ZnO} is the potential modification linked to the surface restructuration and BD is the bond-dipole potential. All values are in eV.

These values are related to Figure 5 of the paper.

BA-X		Modentate		Bidentate				Chelate
		BM1.1	BM1.2	BM2.1	BM2.2	BM2.3	BM2.4	BM3
-OCH_3	Φ	4.44	4.17	3.98	3.89	3.86	4.04	4.23
	ΔΦ	-0.03	-0.30	-0.49	-0.58	-0.61	-0.43	-0.24
	ΔV_{BA}	-1.78	-1.96	-1.91	-1.90	-2.07	-2.09	-1.84
	ΔV_{ZnO}	-0.20	-0.16	-0.39	-0.27	-0.31	-0.34	-0.30
	BD	+1.95	+1.82	+1.81	+1.59	+1.77	+2.00	+1.90
-H	Φ	4.63	4.42	4.34	4.18	4.18	4.31	4.31
	ΔΦ	+0.16	-0.05	-0.13	-0.29	-0.29	-0.16	-0.16
	ΔV_{BA}	-1.16	-1.27	-1.30	-1.27	-1.38	-1.39	-1.21
	ΔV_{ZnO}	-0.17	-0.25	-0.32	-0.28	-0.33	-0.30	-0.38
	BD	+1.49	+1.47	+1.49	+1.22	+1.42	+1.53	+1.41
-CN	Φ	5.80	5.83	5.55	5.43	5.49	5.70	5.68
	ΔΦ	+1.33	+1.36	+1.08	+0.96	+1.02	+1.23	+1.21
	ΔV_{BA}	-0.25	-0.20	-0.35	-0.24	-0.25	-0.29	-0.18
	ΔV_{ZnO}	-0.18	-0.25	-0.33	-0.28	-0.35	-0.31	-0.35
	BD	+1.76	+1.81	+1.76	+1.48	+1.62	+1.83	+1.74

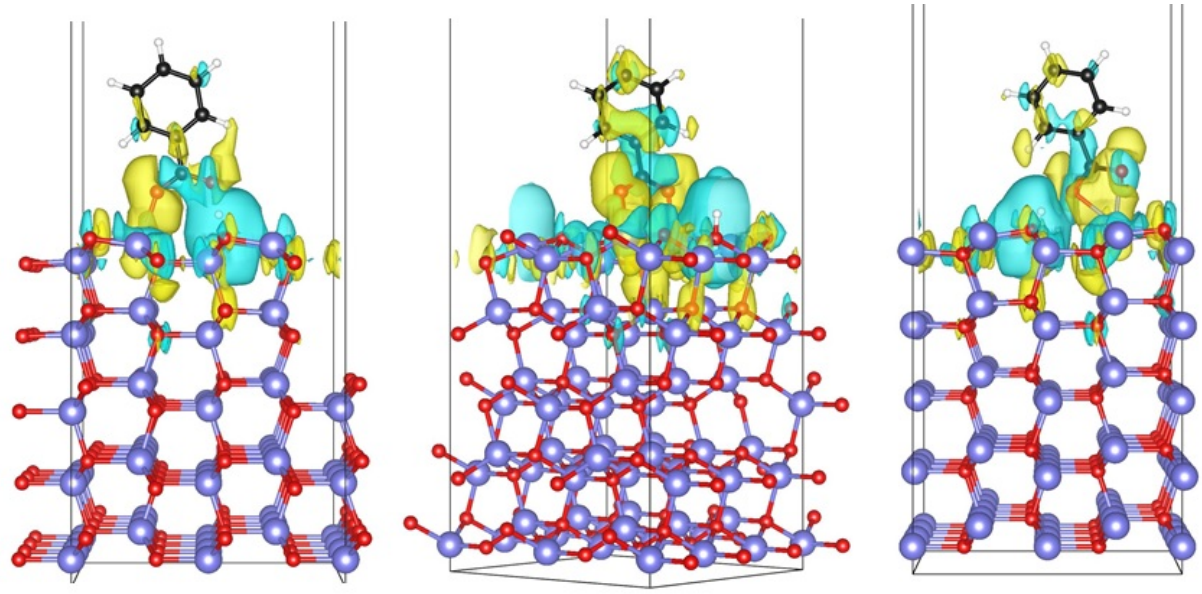
2. Three-dimensional mapping of electronic charge density difference (Δρ) for representative SAM/ZnO interfaces.

$\Delta\rho = \rho_{BA/ZnO} - [\rho_{BA} + \rho_{ZnO} + \rho_{H}]$ for BA/ZnO interface.

$\Delta\rho = \rho_{4TBP/ZnO} - [\rho_{4TBP} + \rho_{ZnO}]$ for 4TBP/ZnO interface.

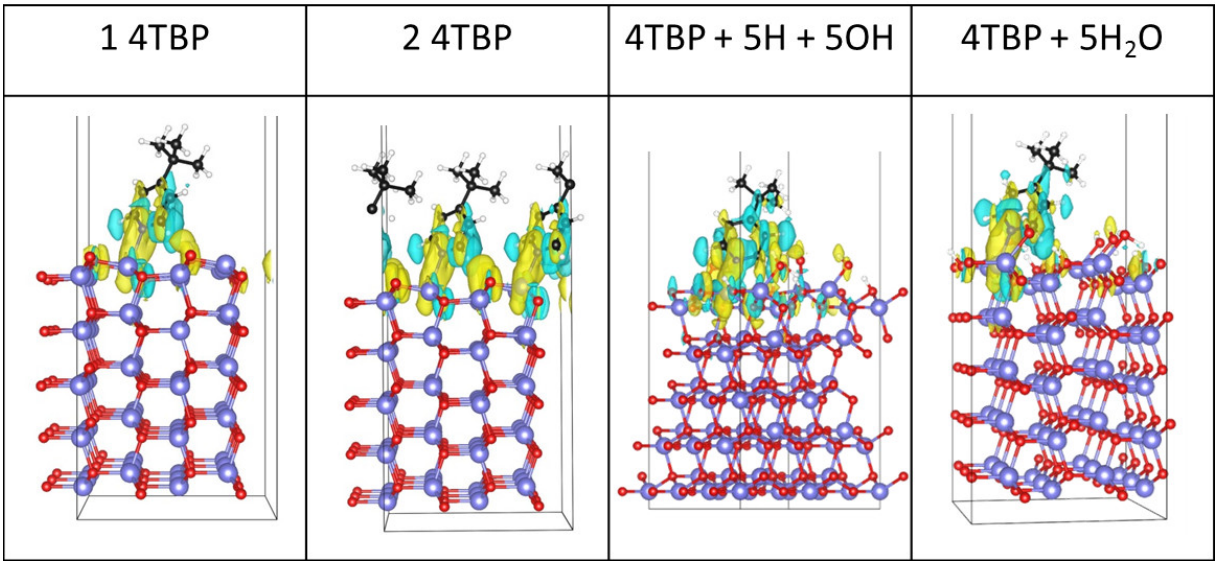
The charge density data files have been generated from the SIESTA output using the program DENCHAR available in the SIESTA package. All pictures have been generated with the VESTA software.

a) Benzoic acid on ZnO(10-10)



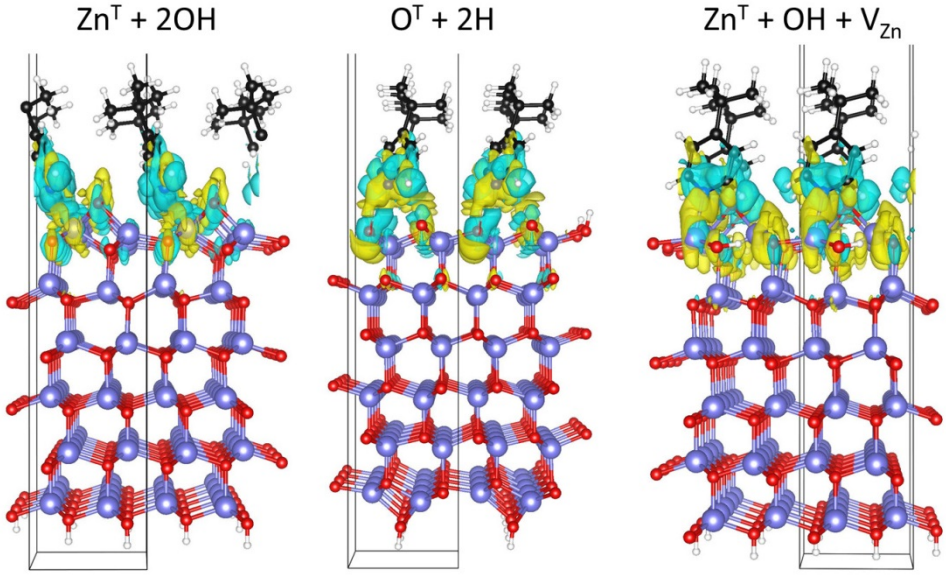
Charge density difference (isovalue 0.005 e/A^3) for BA-H adsorbed on ZnO(10-10). The three modes of anchoring are illustrated: (left) monodentate [BM1.2] ; (middle) bidentate [BM2.3] ; (right) chelate [BM3]

b) 4TBP (with and without co-adsorbant) on ZnO(10-10)



Charge density difference (isovalue 0.005 e/A^3) for 4TBP on ZnO(10-10) in the different cases discussed in the paper (see text for the notation).

c) 4TBP on polar ZnO



Charge density difference (isovalue 0.005 e/A^3) for 4TBP on polar ZnO using the models described in the text: Zn-terminated, O-terminated and Zn-terminated + vacancy. The unit cell is duplicated for sake of clarity.