First principles modeling of eosin-loaded ZnO films: a step forward the understanding of a dye-sensitized solar cell performances

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SUPPLEMENTARY INFORMATION

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[69] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Scalmani, G.; Kudin, K. N.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.;Honda, Y.; Kitao, O.; Nakai, H.; Li, X.; Hratchian, H. P.; Peralta, J. E.; Izmaylov, A. F.; Brothers, E.; Staroverov, V.;Kobayashi, R.; Normand, J.; Burant, J. C.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo,C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.;Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A.D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Chen, W.; Wong, M. W.; Pople, J. A. *Gaussian DVP, Revision F.01*; Gaussian, Inc.: Wallingford, CT, 2008.

Table S1: Selected structural parameters (in Å and degrees) of isolated and adsorbed EY. Labeling of EY corresponds to that of figure 2, while all Zn surface atoms are labeled using the corresponding number of their closest EY atom. A prime denotes an oxygen atom belonging to the same ZnO dimer pattern as the corresponding Zn atom.

	Isolated	Adsorbed
Bond lengths (Å)		
$C_{(13)}O_{(14)}/C_{(13)}O_{(15)}$	1.254/1.251	1.254/1.267
$CO_{(6)}/CO_{(3)}$	1.241/1.241	1.269/1.265
$CBr_{(7)}/CBr_{(2)}$	1.969/1.969	1.959/1.954
$O_{(14)}Zn_{(14)}/O_{(14)}Zn_{(15)}$		2.067/2.016
$O_{(6)}Zn_{(6)}/O_{(3)}Zn_{(3)}$		2.115/2.124
$Br_{(7)}Zn_{(7)}/Br_{(2)}Zn_{(2)}$		3.036/2.868
Valence angles (degrees)		
$O_{(14)}C_{(13)}O_{(15)}$	129.7	126.5
$O_{(14)}C_{(13)}C_{(12)}$	114.3	116.8
$C_{(13)}O_{(14)}Zn_{(14)}/C_{(13)}O_{(15)}Zn_{(15)}$		136.5/122.6
$O_{(6)}Zn_{(6)}O'_{(6)}/O_{(3)}Zn_{(3)}O'_{(3)}$		93.7/124.4
$Br_{(7)}Zn_{(7)}O'_{(7)}/Br_{(2)}Zn_{(2)}O'_{(2)}$		94.8/92.1
Dihedral angles (degrees)		
$C_{(a)}C_{(b)}C_{(9)}C_{(c)}$	-3.5	10.2
$C_{(13)}C_{(12)}C_{(11)}C_{(9)}$	-0.0	0.9
$O_{(14)}C_{(13)}C_{(12)}C_{(11)}$	-0.0	-4.8
$Zn_{(14)}O_{(14)}O_{(15)}Zn_{(15)}$		-21.9

Table S2. Main displacements (Å) of selected outermost substrate atoms along different directions, both for the bare surface relaxation and upon EY adsorption. All values reported for the bare surface are computed with respect to the optimized bulk ZnO positions, while those for the combined EY/surface system correspond to additional relaxations computed with respect to the fully-relaxed surface positions. All Zn surface atoms are labeled using the corresponding number of their closest EY atom (see figure 2).

	Clean surface		EY/Surface	
Atoms	[0001]	[10-10]	[0001]	[10-10]
$Zn_{(14)}$	-0.14	-0.45	-0.14	+0.30
$Zn_{(15)}$	-0.14	-0.45	+0.36	+0.30
$Zn_{(7)}$	-0.14	-0.45	+0.04	+0.15
$Zn_{(6)}$	-0.14	-0.45	-0.21	+0.31
$Zn_{(2)}$	-0.14	-0.45	+0.13	+0.18
$Zn_{(3)}$	-0.14	-0.45	-0.15	+0.44

Figure S1. Γ-point computed HOMO (top left), LUMO (top right) and LUMO+2 (bottom) crystalline orbitals of computed for symmetrically adsorbed EY on ZnO. The HOMO-1 orbital (energetically degenerate to the HOMO) and LUMO+1 orbital (energetically degenerate to the LUMO) simply correspond to the HOMO and LUMO but are localized on the other EY molecule.

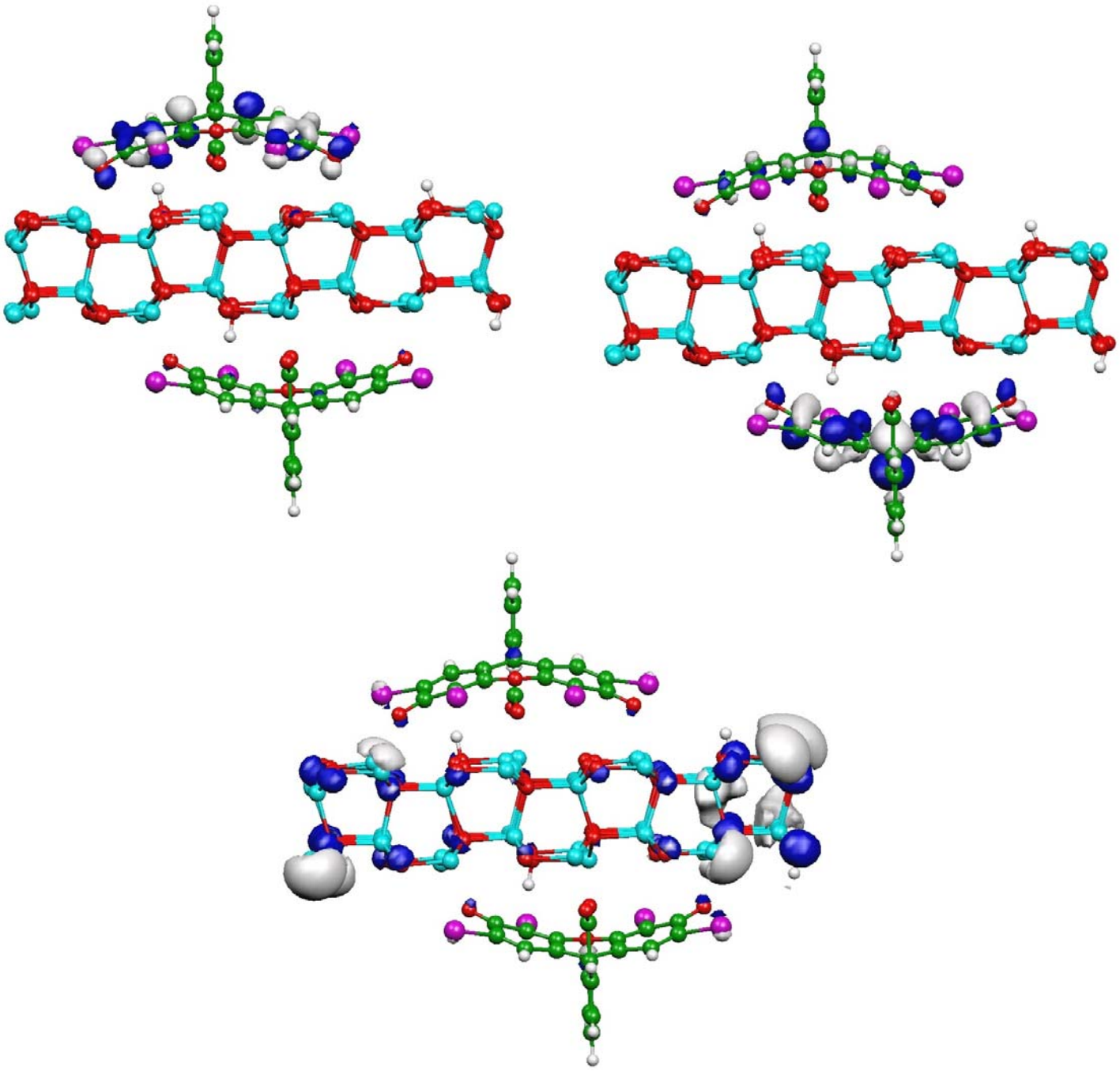

Figure 8. Γ-point computed spin densities of the reduced EY/ZnO system: monoreduced (top left); bireduced (top right) and trireduced specie (bottom). Isovalue: 0.0005 a.u.