Supporting Information for "Characterization of ZnO as Substrate for DSSC"

Candela Mansilla Wettstein and Cristián G. Sánchez

S1 Mulliken Charges of the adsorption sites

In this section were tabulate the Mulliken charges of the adsorption site and of an internal Zn coordinated with four oxygens. In the following tables the Mulliken charges are shown for each dye anchored on a 3 nm ZnO nanoparticle presented in the manuscript and for the D149 indoline and Catechol dyes anchored on a 2 nm ZnO nanoparticle.

In table 1 and 5 it can be seen that the Zn-O (D149 indoline) bond, Zn-O (Coumarin 343) bond and one Zn-O (nanoparticle) bond on the adsorption site have a more covalent character than the others two oxygens coordinated to the Zn in that site. While in tables 2, 3 and 4 the Zn-O (alizarin) bond, Zn-O (1,2-naphtalenediol) bond and Zn-O (catechol) bond, in the adsorption site, present a more covalent character than the others oxygens coordinated to the Zn in the site.

In the case of a 2 nm nanoparticle, it was observed that Zn-O (D149 indoline) bond has a more ionic character that we observed in the bigger nanoparticle. Moreover the Zn-O (catechol) bond, on the 2 nm nanoparticle, present a less ionic character than the others Zn-O (nanoparticle) bonds in the adsorption site, as was observed in the 3 nm nanoparticle. The fact that the Zn-O bond, for D149 indoline and Coumarin 343, is more ionic may be due to both dyes have a carboxylate group in their anchor group.

We observed that the Zn-O(dye) bonds in the adsorption site are more covalent than inside of the nanoparticle. The only exception was found for dye D149 indoline, where the opposite effect was observed.

Table 1: Mulliken charges in the adsorption site (AS) for ZnO-D149 indoline and inside the 3 nm ZnO Nanoparticle (NP).

Atoms of the AS	Mulliken charges	Atoms inside the NP	Mulliken charges
Zn(D149)	0.5295591	Zn	0.5243845
O(D149)	-0.5433712	O	-0.5283494
O(NP)	-0.5828404	O	-0.5256801
O(NP)	-0.5956869	O	-0.5212445
O(NP)	-0.5235624	O	-0.5302572

Table 2: Mulliken charges in the adsorption site (AS) for ZnO-Alizarin and inside the 3nm ZnO Nanoparticle (NP).

Atoms of the AS	Mulliken charges	Atoms inside the NP	Mulliken charges
Zn(Alz)	0.5302219	Zn	0.5243940
O(Alz)	-0.4383912	O	-0.5283732
O(NP)	-0.5641117	O	-0.5257125
O(NP)	-0.6048059	O	-0.5212517
O(NP)	-0.5172424	O	-0.5303063

Table 3: Mulliken charges in the adsorption site (AS) for ZnO-1,2-Naphtalenediol and inside the 3nm ZnO Nanoparticle (NP).

Atoms of the AS	Mulliken charges	Atoms inside the NP	Mulliken charges
Zn(NAP)	0.5264072	Zn	0.5243626
O(NAP)	-0.4211864	O	-0.5283208
O(NP)	-0.4775057	O	-0.5256519
O(NP)	-0.5908957	O	-0.5212326
O(NP)	-0.6015182	O	-0.5302501

Table 4: Mulliken charges in the adsorption site (AS) for ZnO-Catechol and inside the 3nm ZnO Nanoparticle (NP).

Atoms of the AS	Mulliken charges	Atoms inside the NP	Mulliken charges
Zn(Cat)	0.5510381	Zn	0.5242820
O(Cat)	-0.5233796	O	-0.5283878
O(NP)	-0.5551405	O	-0.5255093
O(NP)	-0.6066901	O	-0.5212221
O(NP)	-0.5775354	O	-0.5302738

Table 5: Mulliken charges in the adsorption site (AS) for ZnO-Coumarin343 and inside the 3nm ZnO Nanoparticle (NP).

Atoms of the AS	Mulliken charges	Atoms inside the NP	Mulliken charges
Zn(Cou)	0.5499334	Zn	0.5244455
O(Cou)	-0.5051136	O	-0.5283918
O(NP)	-0.5835218	O	-0.5257139
O(NP)	-0.4838905	O	-0.5212502
O(NP)	-0.5785036	O	-0.5302773

Table 6: Mulliken charges in the adsorption site (AS) for ZnO-D149 and inside the 2nm ZnO Nanoparticle (NP).

Atoms of the AS	Mulliken charges	Atoms inside the NP	Mulliken charges
Zn(D149)	0.5593777	Zn	0.5530891
O(D149)	-0.5886073	O	-0.5626287
O(NP)	-0.5887542	O	-0.5560932
O(NP)	-0.5581946	O	-0.5720930
O(NP)	-0.4895439	O	-0.5511575

Table 7: Mulliken charges in the adsorption site (AS) for ZnO-Catechol and inside the 2nm ZnO Nanoparticle (NP).

Atoms of the AS	Mulliken charges	Atoms inside the NP	Mulliken charges
Zn(Cat)	0.5227699	Zn	0.5530119
O(Cat)	-0.5360789	O	-0.5626321
O(NP)	-0.5757799	O	-0.5560431
O(NP)	-0.5403295	O	-0.5724120
O(NP)	-0.5107422	O	-0.5510645

S2 Different conformations of D149 indoline and orientations respect to ZnO nanoparticle

We explored different conformations of the D149 indoline dye and orientations on the 3 nm ZnO nanoparticle. In figure S2 are shows the 3 conformations analyzed. The spectrum for each conformation was calculated (see figure S3 a, S4 a and S5 a). The ZnO+D149 indoline spectra (solid line) show the same bands present in the free dye spectrum (dashed line). It is worth noting that the intensity ratio between the first and second peak in the spectrum varies according to the conformation. In figure S3 b, S4 b the charge transfer between the dye and nanoparticle are shown, when a sinusoidal perturbation tuned to the low energy peak of the spectra (indicated with an arrow), is applied in the maximal polarization direction, for 100 fs. It can be observed that the D149 indoline injects holes in the nanoparticle, for the 3 conformations. These results evidence that the photoinjection process and the charge transfer, is the same regardless of the conformations and orientation on the ZnO nanoparticle.

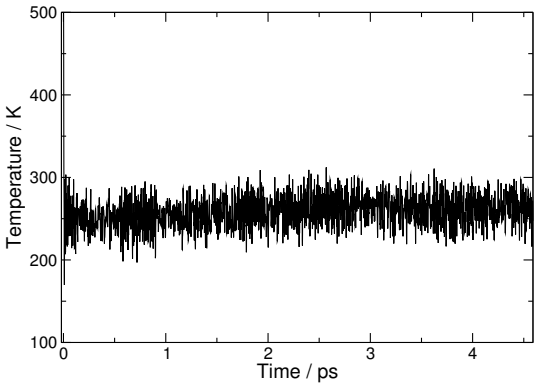


Figure S1: Temperature vs. time of the molecular dynamics with DFTB.

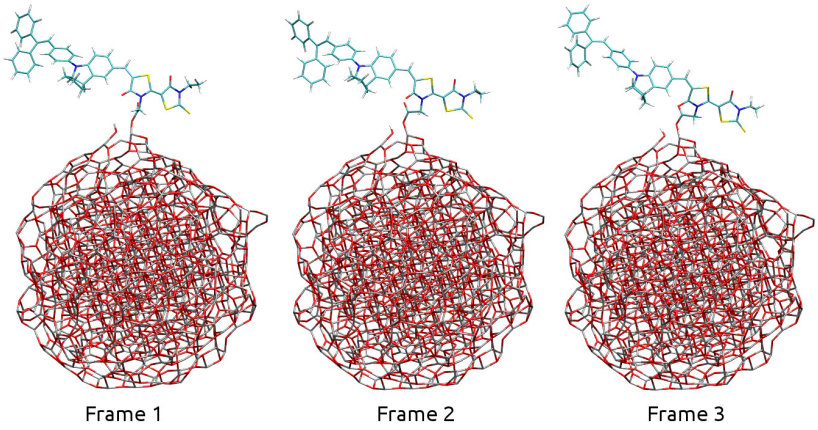
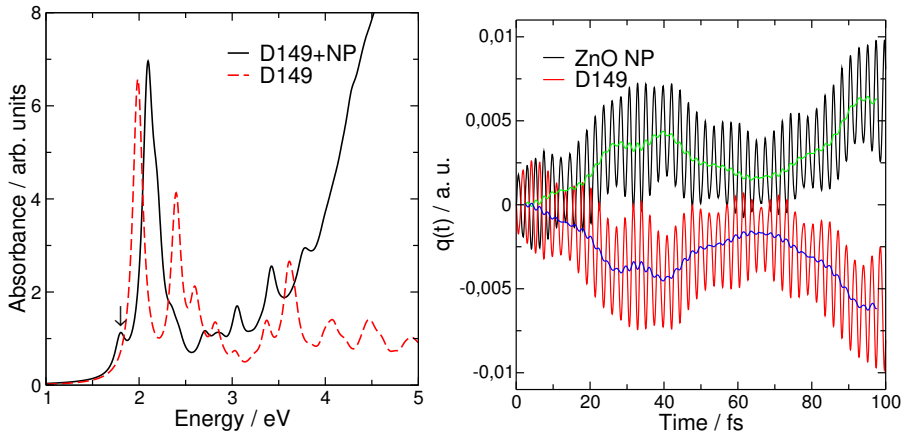
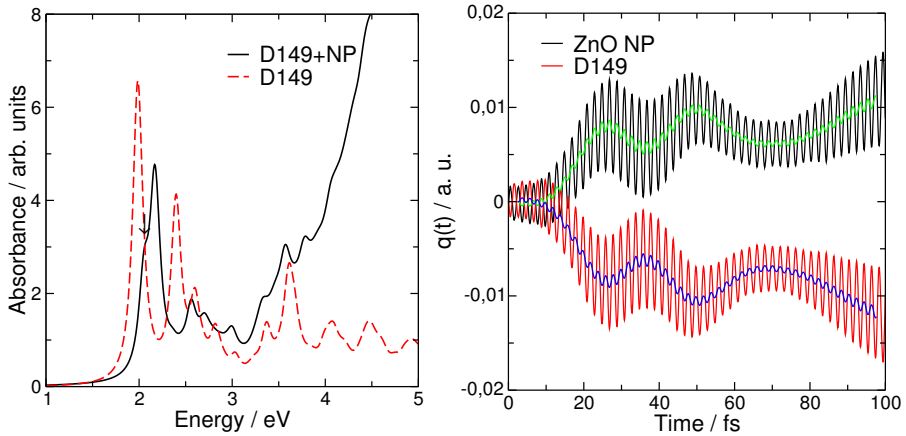


Figure S2: Different conformations of D149 dye and orientations on the ZnO.



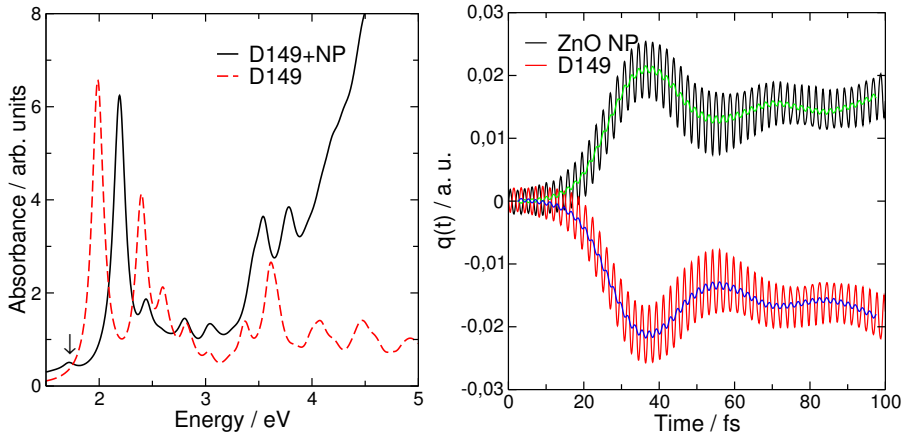
(a) (b)

Figure S3: (a) Spectrum of one conformation and orientation of the D149 dye attached to the NP. (b) Charge transfer for this conformation.



(a) (b)

Figure S4: (a) Spectrum of one conformation and orientation of the D149 dye attached to the NP. (b) Charge transfer for this conformation.



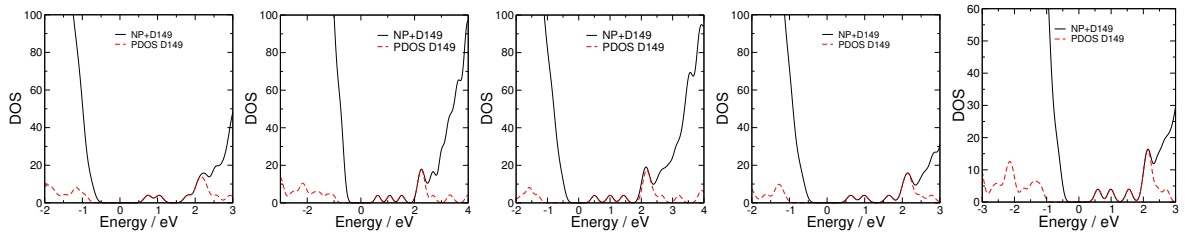
(a) (b)

Figure S5: (a) Spectrum of one conformation and orientation of the D149 dye attached to the NP. (b) Charge transfer for this conformation.

S3 PDOS of ZnO+D149 and ZnO+Catechol for 2 nm and 3 nm of different adsorption sites

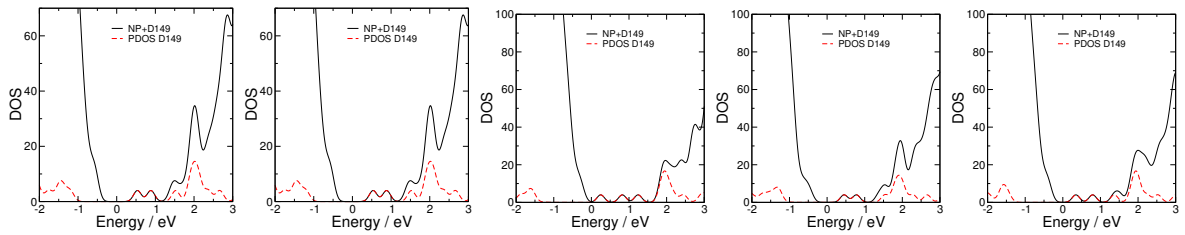
The density of states (DOS) of the complexes NP+D149 indoline and NP+Catechol of two different size of ZnO nanoparticle (2 nm and 3 nm) has been calculated. Also the projected density of states projected over the dye (PDOS) were calculated (see figure S6 to S8). In figure S6 and S7 the DOS and PDOS are shown for different adsorption sites of 2 nm-ZnO+D149 indoline and 3 nm-ZnO+D149 indoline respectively.

The states are similarly distributed around of the Fermi energy for all adsorption sites. The same is observed in figure S7 for 3 nm-ZnO+D149 indoline, where the figure S7e (site 5) is the graph presented in the manuscript. In all cases the dye states are located above the Fermi energy, which indicate that these complexes present a hole injection from the dye to the nanoparticle.



(a) (b) (c) (d) (e)

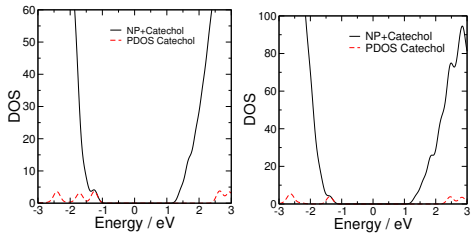
Figure S6: Total DOS of 2 nm-ZnO+D149 indoline and PDOS of dye. (a) site 1, (b) site 2, (c) site 3 (d) site 4 and (e) site 5.



(a) (b) (c) (d) (e)

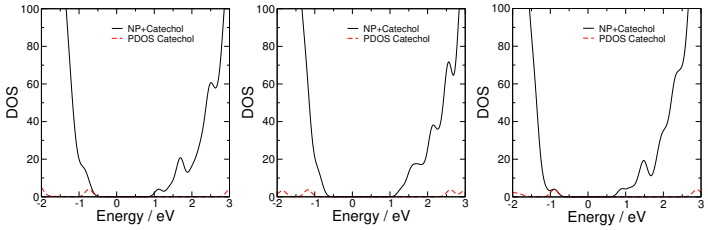
Figure S7: Total DOS of 3nm nanoparticle and PDOS of dye D149 indoline. (a) site 1, (b) site 2, (c) site 3 (d) site 4 and (e) site 5.

In figure S8 and figure S9 the DOS and PDOS for the complexes ZnO+Catechol of 2 nm and 3 nm are shown, respectively. As in the case of ZnO+D149, the distribution of states is similar for each site in both complexes (2 nm ZnO+Dye and 3 nm ZnO+Dye). It is worth noting that there are states of catechol in the edge of the ZnO valence band. In these cases, catechol inject electrons into the nanoparticle. The figure S9c is the graph presented in the manuscript.



(a) (b)

Figure S8: Total DOS of 2nm nanoparticle and PDOS of dye Catechol. (a) site 1, (b) site 2.



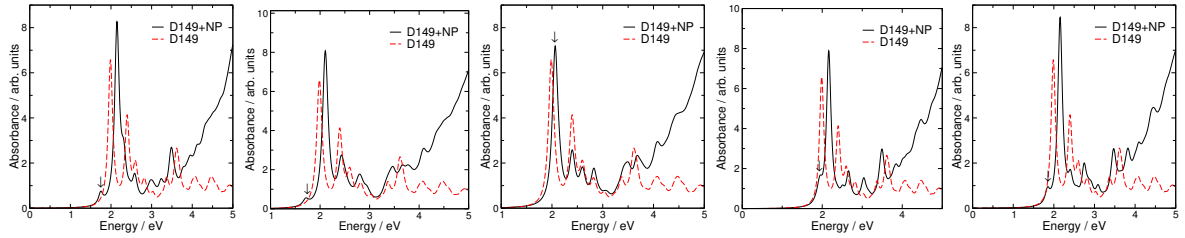
(a) (b) (c)

Figure S9: Total DOS of 3nm nanoparticle and PDOS of dye Catechol. (a) site 1, (b) site 2, (c) site 3.

S4 Spectra of ZnO+D149 and ZnO+Catechol for 2 nm and 3 nm of different adsorption sites

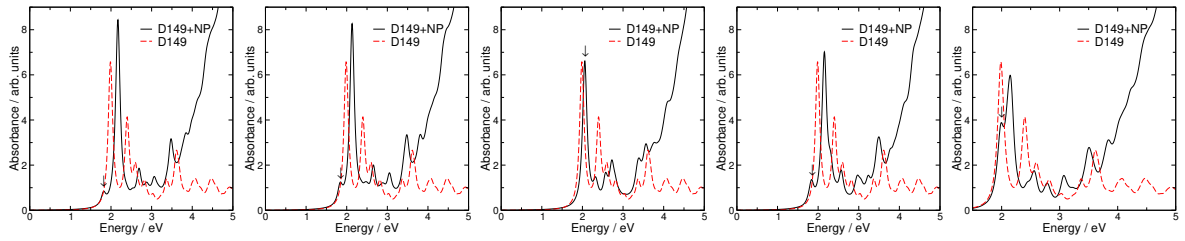
In figure S10 and S11 the absorption spectra of the complexes ZnO+D149 indoline (solid line) and free D149 indoline (dashed line) for different adsorption sites for 2 nm and 3 nm ZnO nanoparticle are shown, respectively. The same absorptions bands present in the spectrum of free dye appear in the spectrum of the complex ZnO+D149 indoline, in all cases. This indicates that the photoinjection process is type I. It is worth noting that the intensity ratio, of the first and second absorption band of the complexes, changes according to the anchor site.

The figure S11 e (site 5) corresponds to the spectrum present in the paper. In the figure S10 c, S11 c and S11 e the intensity of the first absorption band is considerable compared to the others adsorption sites.



(a) (b) (c) (d) (e)

Figure S10: Spectra of 2nm NP+D149 indoline of different adsorption site. (a) site 1, (b) site 2, (c) site 3 (d) site 4 and (e) site 5.

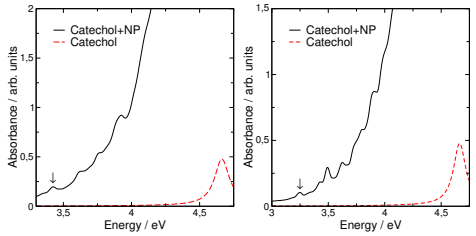


(a) (b) (c) (d) (e)

Figure S11: Spectra of 3nm NP+D149 indoline of different adsorption site. (a) site 1, (b) site 2, (c) site 3 (d) site 4 and (e) site 5.

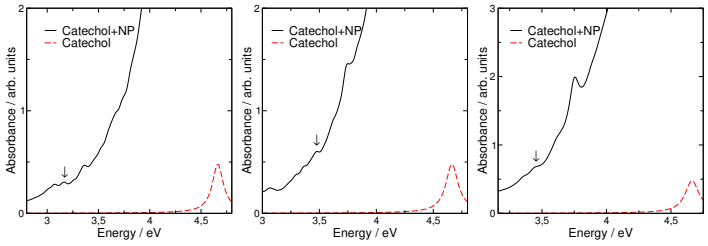
In figure S12 and S13 the spectrum of ZnO+Catechol (solid line) and free catechol dye (dashed line) for 2 nm and 3 nm ZnO size are shown, and different adsorption sites. The spectra show new bands, which indicate a type II photoinjection process. The figure S13 c is also in the manuscript.

For both ZnO+D149 and for ZnO+Catechol, the photoinjection process is the same, regardless of the size of the nanoparticle as of the adsorption site.



(a) (b)

Figure S12: Spectra of 2nm NP+Catechol indoline of different adsorption site. (a) site 1, (b) site 2.



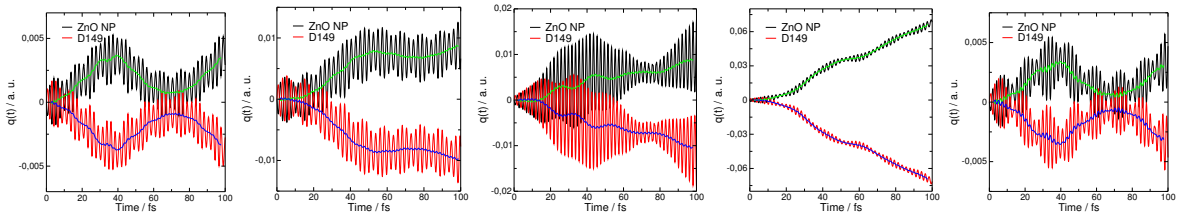
(a) (b) (c)

Figure S13: Spectra of 3nm NP+D149 indoline of different adsorption site. (a) site 1, (b) site 2, (c) site 3.

S5 Charge Transfer of ZnO+D149 and ZnO+Catechol for 2 nm and 3 nm of different adsorption sites

The charge transfer for ZnO+D149 and ZnO+Catechol complexes, was calculated applying a sinusoidal perturbation tuned to the low energy peak of the spectra (indicated with an arrow in figure S10, S11, S12 and S13) and in the maximal polarization direction, for 100 fs.

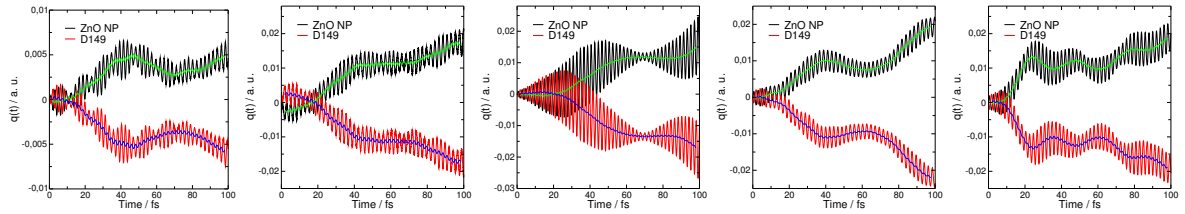
In figure S14 and S15 the charge transfer for ZnO+D149 for 2 nm and 3 nm ZnO nanoparticle respectively are shown. It can be observed that, regardless of the adsorption site, the dye injects holes into the ZnO nanoparticle both for 2 nm and for 3 nm size. On the other hand, the magnitude of the charge transfer varies according to the anchor site. These changes are more evident for the 2 nm ZnO nanoparticle. The figure S15 e is also in the paper.



(a) (b) (c) (d) (e)

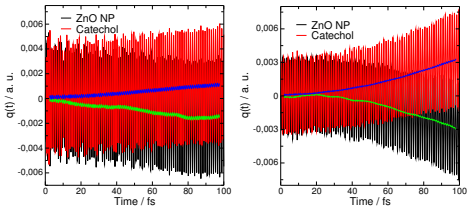
Figure S14: Charge Transfer of 2nm NP+D149 indoline of different adsorption site. (a) site 1, (b) site 2, (c) site 3 (d) site 4 and (e) site 5.

Figure S16 and S17 show the charge transfer for ZnO+Catechol for two ZnO size. In all cases Catechol injects electrons into the ZnO nanoparticle as it was shown in the manuscript. The magnitude of the charge transfer for 3 nm ZnO+Catechol is roughly equal in the three adsorption site. The figure S17 c is the graph presented in the manuscript.



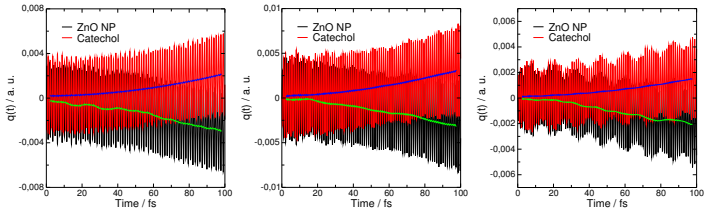
(a) (b) (c) (d) (e)

Figure S15: Charge Transfer of 3nm NP+D149 indoline of different adsorption site. (a) site 1, (b) site 2, (c) site 3 (d) site 4 and (e) site 5.



(a) (b)

Figure S16: Charge Transfer of 2nm NP+D149 indoline of different adsorption site. (a) site 1, (b) site 2.



(a) (b) (c)

Figure S17: Charge Transfer of 3nm NP+D149 indoline of different adsorption site. (a) site 1, (b) site 2, (c) site 3.

S6 Molecular dynamics of 3nm ZnO nanoparticle

The potential energy versus time of the molecular dynamic for the generation of the 3nm ZnO nanoparticle, is shown in figure S18. It can be observed that the energy is stabilized after 2 ns of dynamics. In figure S19 a histogram is plotted of the potential energy of the figure S18, in which the energy of the nanoparticle chosen to perform the optical calculations is indicated by an arrow. Although it is not the most stable structure of production, it is not the most unstable either. In this work the procedure for the generation of the nanoparticle presented in "Journal of Physics. Condensed Matter: An Institute of Physics Journal, 25(11), 115304 (2013)" was reproduced.

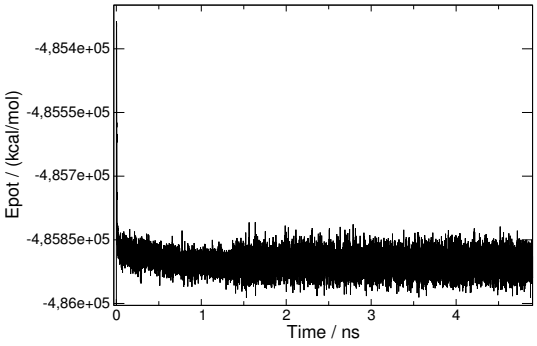


Figure S18: Potential energy vs time of the molecular dynamics of 3nm ZnO nanoparticle.

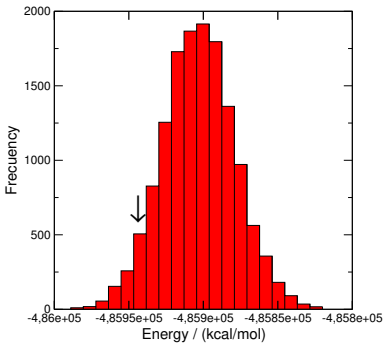


Figure S19: Potential energy histogram.