**Electronic Supplementary Information**

# A Synergistic Combination of Local Tight Binding Theory and Second Harmonic Generation Elucidating Surface Properties of ZnO Nanoparticles

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**Calculation of surface vs bulk number density ratio**

Consider a tetrahedron[1] of side $a_T = 1.98 \times 10^{-10} m$. The area of one side of this is

$A_0 = a_T{}^2 \sqrt{3} = 6.79 \times 10^{-20} m^2$. Now consider a cube with a diagonal $d = 2(1.98 \times 10^{-10} m) = 3.96 \times 10^{-20} m$. The side of this cube is $a_C = \frac{d}{\sqrt{3}} = 2.28 \times 10^{-10} m$,

So the volume of this cube is $V_0 = a_C^3 = 1.19 \times 10^{-29} m^3$. Now the surface number density and the volume number density are given by,

$$N_S = \frac{4\pi r^2}{A_0},\ N_B = \frac{4\pi r^3}{3V_0}$$

The ratio of the surface to volume densities is

$$\frac{N_S}{N_V} = \frac{3V_0}{A_0 r} = \frac{5.27 \times 10^{-10} m}{r}$$

This indicates that surface contributions do not dominate until the radius of the nanoparticle is less than 5 Å.

**Calculation of the damping coefficient**

Here we calculate the value of the damping coefficient, $\gamma$, for C343. We assume that the form is given by[2, 3]

$$\gamma = \frac{1}{4\pi\varepsilon_0}\frac{4\omega_0^3 e^2 \left\langle \pi \middle| r \middle| \pi^* \right\rangle^2}{3\hbar c^3}.$$

Here we take the constant terms in MKS units to be,

$$\frac{1}{4\pi\varepsilon_0} = 8.99\times10^9 \frac{N\cdot m^2}{C^2}, c = 3.0\times10^8 m/s, e = 1.6\times10^{-19} C, \hbar = 1.054\times10^{-34} J\cdot s.$$

We take the resonant frequency for the C343 molecule to be $\omega_0 = 4.34\times10^{15} Hz$.
The dipole amplitude is determined by assuming the ionization energy is $E_P = -14.14eV$.[4] We assume the Pi pseudo wave functions can be approximated as $\phi_P \approx re^{-\mu r}\cos(\theta)$. Then we have $-\frac{(\hbar\mu)^2}{2m} = -E_p$, which gives us $\mu = 1.92A^{-1}$. With this in mind we take the dipole amplitude to be $\left\langle \pi \middle| r \middle| \pi^* \right\rangle \approx 8.5\times10^{-8} m$.

This large amplitude on the order of hundreds of Angstroms is due to delocalization of the $\pi^*$ orbital over the area of the coumarin molecule. We realize this crude calculation will mostly serve to obtain the magnitude of $\gamma$ for this process. Substituting all these quantities into the equation above yields $\gamma \approx 6.4\times10^{13} s^{-1}$.

This is in agreement with the values reported previously for various substituted coumarin dyes.[5, 6] This term is far too small to affect the denominator in any of the calculations of $\chi^2_{ijk}$ in the main text.

**Supplementary Data**

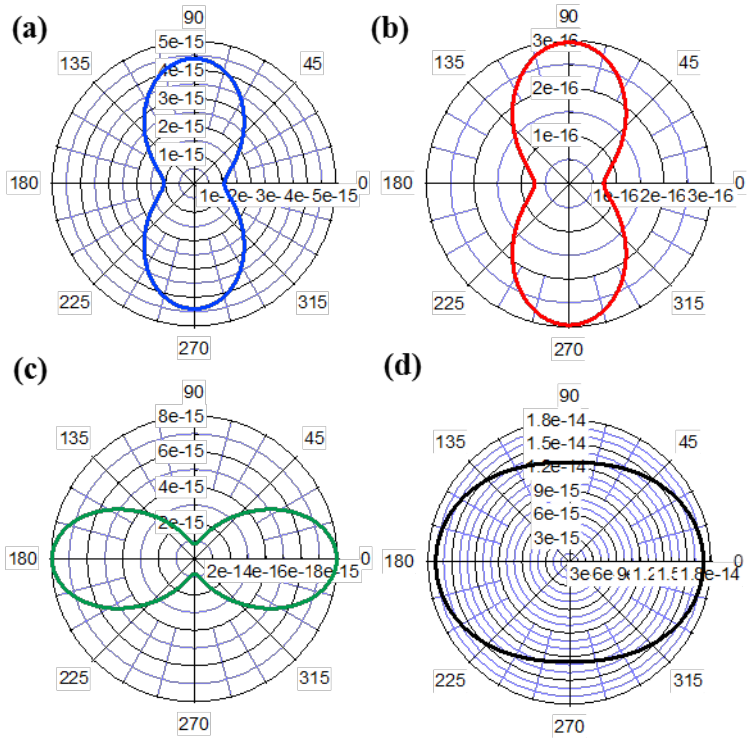


**Figure S1** Plots of $\left|P_z^{(2)}(2\omega)\right|^2$ as a function of polarization angle of the fundamental field (equation 2) as calculated using TB model. These represent SHG contributions from **(a)** Zn-terminated surfaces, **(b)** O-terminated surface, and **(c)** the bulk of ZnO. The overall contribution is shown in **(d)**.

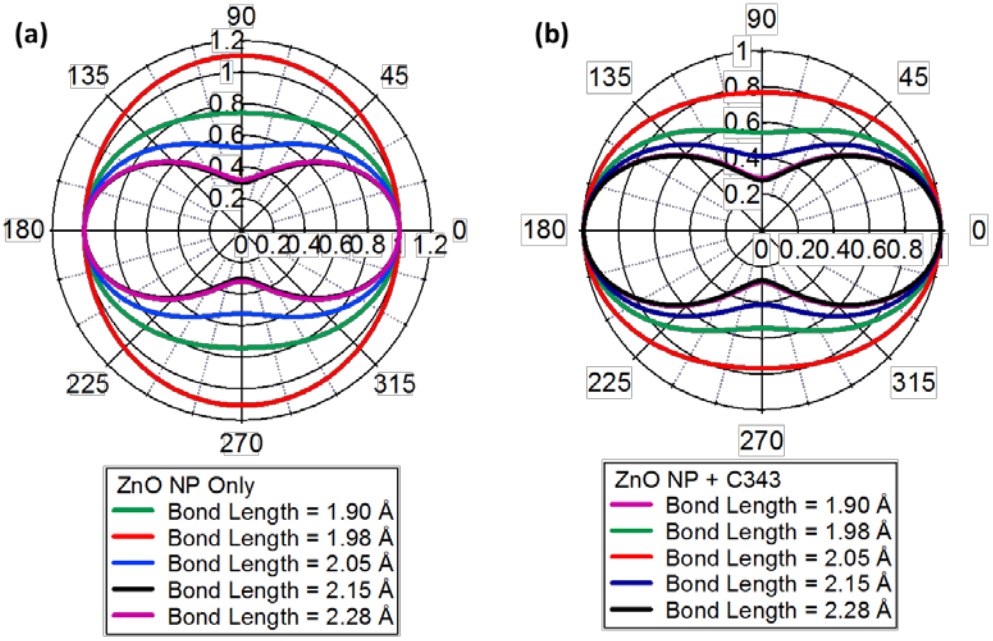


**Figure S2** Effect of surface relaxation, as explored by varying the Zn–O bond length, on the plots of $\left|P_z^{(2)}(2\omega)\right|^2$ as a function of polarization angle of the fundamental field (equation 2) as calculated using TB model. These represent SHG contributions from **(a)** ZnO NP only, without C343 and **(b)** ZnO NP and C343.

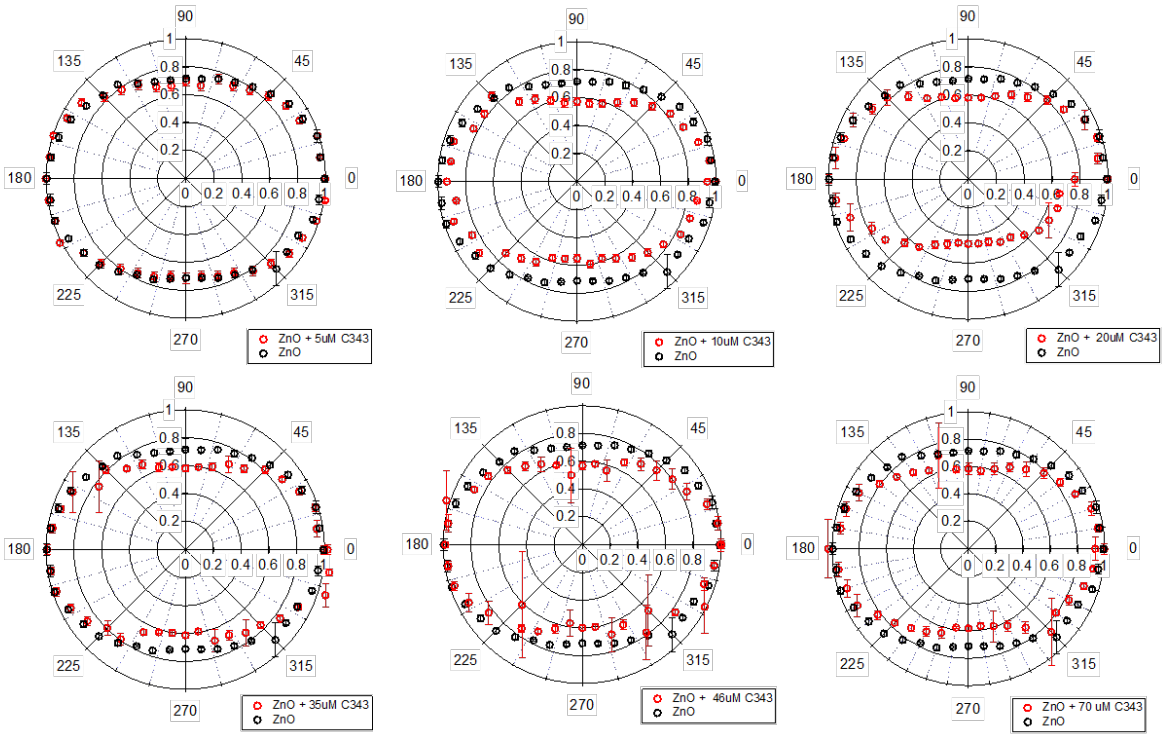


**Figure S3** Plots of experimental SHG $\left|P_z^{(2)}(2\omega)\right|^2$ as a function of polarization angle of the fundamental field for ZnO NPs with varying concentration of C343 dye (5uM, 10uM, 20uM, 35uM, 46uM, and 70uM). The $\left|P_z^{(2)}(2\omega)\right|^2$ of ZnO NP (no dye) is also shown as black markers.

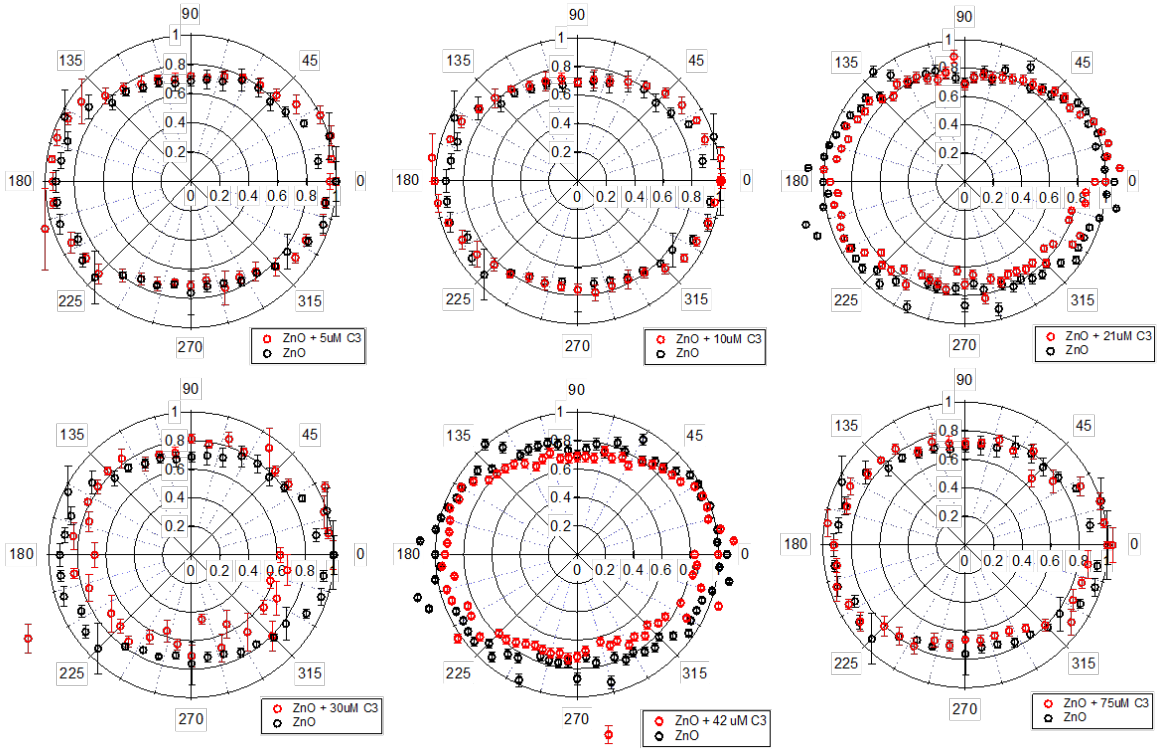


**Figure S4** Plots of experimental SHG $\left|P_z^{(2)}(2\omega)\right|^2$ as a function of polarization angle of the fundamental field for ZnO NPs with varying concentration of C3 dye (5uM, 10uM, 21uM, 30uM, 42uM, and 75uM). The $\left|P_z^{(2)}(2\omega)\right|^2$ of ZnO NP (no dye) is also shown as black markers.

**References**


1. A. Jeffrey, in *Handbook of Mathematical Formulas and Integrals (Third Edition)*, Academic Press, Burlington, 2004, pp. 1-24.
2. M. L. Skully and M. Zubairy, *Quantum Optics*, Cambridge University Press, New York, 2006.
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4. W. A. Harrison, *Elemetary Electronic Structure*, World Scientific, 2004.
5. J. Cerezo, F. J. Avila Ferrer, G. Prampolini and F. Santoro, *Journal of Chemical Theory and Computation*, 2015, **11**, 5810-5825.
6. J. Cerezo, F. J. Avila Ferrer and F. Santoro, *Physical Chemistry Chemical Physics*, 2015, **17**, 11401-11411.