Please update you figure number as shown in the attached manuscript. You figure numbers start with Figure 2 ???

# ➢ updated

a) They authors seem to have taken some commercial software, which usually provides the user

with fool-proof settings, provided they have enough computing power. I cannot see anything

exotic here concerning the settings.

Commercial software has been used by many researchers in theoretical and Computational studies

## Some published papers were authors use commercial software

- Mahmood, T., Cao, C., Saeed, M. A., Ahmed, M., & Hussain, T. (2012, January). A DFT+ U calculations: Band structural and equation of states for anatase and rutile TiO 2. In 2012 International Conference on Enabling Science and Nanotechnology (pp. 1-2). IEEE.
- Junkaew, A., Meeprasert, J., Jansang, B., Kungwan, N., & Namuangruk, S. (2017). Mechanistic study of NO oxidation on Cr-phthalocyanine: theoretical insight. *RSC advances*, 7(15), 8858-8865.
- Kunaseth, M., Mudchimo, T., Namuangruk, S., Kungwan, N., Promarak, V., & Jungsuttiwong, S. (2016). A DFT study of arsine adsorption on palladium doped graphene: effects of palladium cluster size. *Applied Surface Science*, 367, 552-558.

b) The equation they gave to calculate the band gap is inconsistent with the values given for the HOMO and LUMO energies.

## > The value for equation has been rectified

c) The statement that an electron in a semiconductor moves from the valence band to the

conduction band, then does not find the "right" state and therefore recombines with the hole is

extremely "naïve" and shows an embarrassing ignorance of basic solid state physics. I wonder how this could have survived the proof-reading by the supervisors.

## > The statement has been re-visited and written in a proper way

d) The equation for the light harvesting efficiency is not referenced, not explained and thus falls from the sky. A simple statement like the LHE becoming 0 for zero oscillator strength and 1 for infinite oscillator strength makes sense and would have been enough motivation for this equation. It is also not very helpful to operate with two LHE values, one being a number smaller than 1, the other being a percentage.

### > The equation is now referenced and motivated

e) The authors do not describe how they obtained the spectrum in Fig. 4 using DFT, which in my eyes would be the only interesting methodological issue that has to be explained. At one point they talk about absorption, and the next moment they talk about oscillator strengths. These are two different things.

- In the methodology there is a line "The ground state structures obtained through geometrical optimization was imported into a new 3D atomic window and the optical absorption properties were calculated using Material Studio of BIOVIA Vulnerability Analysis Methodology Program (VAMP)" it explains how Fig 4 was obtained.
- > Absorption is also called oscillator strength and denosted by f on the figure

## Some published paper supporting the statement

- Puyad K.R Chitumella, And K Bhanuprakash. Adsorption Of Croconate Dyes On Tio<sub>2</sub> Anatase (101) Surface: A Periodic Dft Study To Understand The Binding Of Diketo Groups, *Journal Of Chemical Sciences*, **124**, 1, 301-310, (2012).
- Chitumalla, R. K., Lim, M., & Jang, J. (2015). Substituent Effects On The Croconate Dyes In Dye Sensitized Solar Cell Applications: A Density Functional Theory Study. *Journal Of Molecular Modeling*, 21(11), 297

f) With respect to Fig. 4 it would have been interesting to know if any of these peaks has anything to do with the orbitals plotted in Fig. 3, and if so, what do all the sidebands mean. Why is the curve smeared out and does not consist of discrete peaks, given the fact that we talk about transitions in a molecule? Bottom line is, they must explain the concept of an oscillator strength, at least to the degree that their Figures and Table make sense.

#### > The relationship has been clearly shown/stated on the paper

g) Fig. 6 is in complete disagreement with what is said in the text. If I take zero eV as the Fermi level like in the case of the anatase DOS shown in this figure (i.e. the dotted line), then there is no sharp MO level located in the band gap, but the band gap of the anatase has completely disappeared when the dye is added to the system, which therefore becomes metallic (red curve).I am not an expert in this field, but I guess this is exactly what should NOT happen in a dye sensitized solar cell, because the losses would be tremendous. My guess is that they have not properly put the two figures on top of each other. Also there should be strong similarities between the DOS with/without the dye, which I cannot really see in this Figure, and I do not really understand why this is so.

- Once the dye has been adsorbed on the semiconductor the valance band moves towards the fermi level, and more electrons appears near the fermi level
- > If you check carefully the band gap did not disappear, it just become smaller