

Theoretical study on interfacial charge transfer transitions of the surface complex between TiO_2 and TCNTQ

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Dye-sensitized solar cells (DSSCs) attract many researchers' attention as new rechargeable batteries. Since not only the production methods were carried out easily and the materials are obtained at a low-cost, but also DSSCs have a performance as highly efficient approach to the direct conversion of light into electrical power. In this mechanism, unlike the case in almost all photovoltaic devices, photo-induced charge separation can take place directly by charge transfer transitions at the interface between the dye molecule and TiO_2 . Interfacial charge transfer transitions are expected to be useful for efficient photoelectric conversion reactions due to the nature of the one-step charge separation¹.

In our previous research¹, the structure of the surface complex of anatase TiO_2 (110) modeled with a $\text{Ti}_9\text{O}_{18}\text{H-OH}$ nanocluster and 7,7,8,8-tetracyanoquinodimethane (TCNQ) was optimized using density functional theory (DFT) calculations. Based on this optimized structure, we investigated the excitation spectra using time-dependent DFT (TD-DFT) calculations and demonstrated that the interfacial charge transfer transitions from the HOMO of the surface-bound TCNQ molecule to the unoccupied levels of the TiO_2 nanocluster occur in the visible to near-infrared (IR) region. A substance of these materials does not show absorption in the visible region, the TiO_2 -TCNQ surface complex for DSSC is therefore important for improving the energy conversion efficiency.

In the present work, we introduce a new dye molecule similar to TCNQ which is considered to promote light absorption in the visible to near-IR region due to interfacial charge transfer transitions when adsorbing onto TiO_2 , and report on the structure, vibrational and excitation spectrum using DFT and TD-DFT calculations. Moreover, we report the optimized structure and absorption spectrum of the surface complex of anatase TiO_2 (110) and of the dye molecule using a $\text{Ti}_9\text{O}_{18}\text{H-OH}$ nanocluster.

Methods

For the new dye molecule, we take 5,5,6,6-tetracyanophenylquinodimethane (TCNTQ). Since the chemical species containing dicyanomethylene compounds (TCNX) react to a surface hydroxyl group on TiO_2 via a nucleophilic addition², TCNTQ replaces to oxide of the hydroxyl group of our $\text{Ti}_9\text{O}_{18}\text{H-OH}$ nanocluster as hydrogen in our calculations. This bonding state is assumed to be the same state of previously reported $\text{Ti}_9\text{O}_{18}\text{H-O-TCNQ}^{-1}$.¹ All calculations were performed at the B3LYP/6-31G* level of theory using the Gaussian09 software. The optimized structure and vibrational spectra were obtained using DFT calculations, and the absorption spectra were calculated with TD-DFT.

Results and discussion

The optimized structure of TCNTQ and $\text{Ti}_9\text{O}_{18}\text{H-O-TCNTQ}^{-1}$ surface complex are shown in Fig. 1, and these vibrational and excitation spectra are shown in Fig. 2 and 3. In Fig. 1, TCNTQ⁻¹ in TiO_2 is parallel configuration except one cyano-group at a bond side

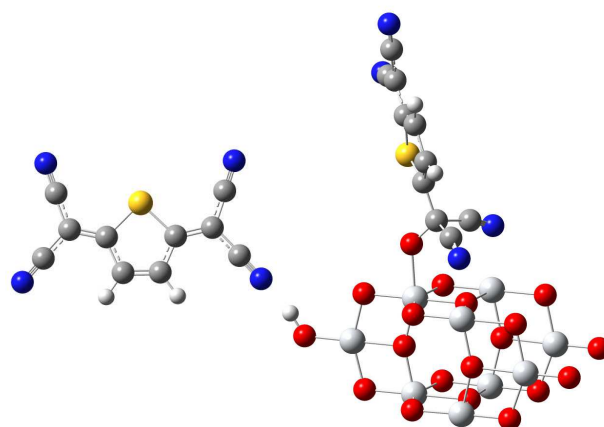


Figure 1. Optimized structures of TCNTQ (left side) and $\text{Ti}_9\text{O}_{18}\text{H-O-TCNTQ}^{-1}$ surface complex (right side). Symbols: black = C, white = H, blue = N, yellow = S, red = O, and silver = Ti.

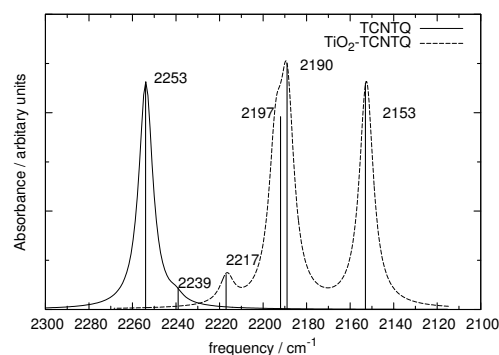


Figure 2. Calculated vibrational spectra of TCNTQ and $\text{Ti}_9\text{O}_{18}\text{H-O-TCNTQ}^{-1}$ surface complex around the CN stretching modes.

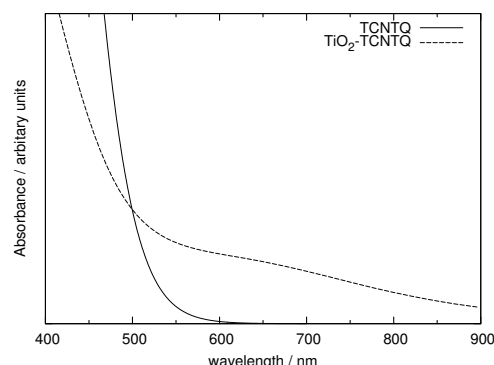


Figure 3. Calculated absorption spectra of TCNTQ and $\text{Ti}_9\text{O}_{18}\text{H-O-TCNTQ}^{-1}$ surface complex.

with TiO_2 . This structure is different from the previous result of $\text{Ti}_9\text{O}_{18}\text{H-O-TCNQ}^{-1}$, and the vibrational spectra shown in Fig. 2 are also obtained from the different CN stretching modes. However, the peaks of the spectra have different values of frequency lower than experimentally observed values. Since the interfacial charge transfer transition of $\text{Ti}_9\text{O}_{18}\text{H-O-TCNTQ}^{-1}$ can be confirmed as the absorption spectra in Fig. 3 and the trend at the experimental measurement, we investigate moreover this material to reproduce accurately the experimentally observed results.

References

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2. S. Manzhos, R. Jono, K. Yamashita, J. Fujisawa, M. Nagata, and H. Segawa, *J. Phys. Chem. C*, **115**, 21487-93 (2011).