Electronic structures of TiO₂-TCNE, -TCNQ, and -2,6-TCNAQ surface complexes studied by ionization potential measurements and DFT calculations: mechanism of the shift of interfacial charge-transfer bands

Jun-ichi Fujisawa* and Minoru Hanaya

*Graduate School of Science and Technology, Gunma University, 1-5-1 Tenjin-cho, Kiryu,
Gunma, 376-8515, Japan*

* E-mail: jfujisawa@gunma-u.ac.jp

Interfacial charge-transfer (ICT) transitions between inorganic semiconductors and π -conjugated molecules allow direct charge separation without loss of energy. This feature is potentially useful for efficient photovoltaic conversions. Charge-transferred complexes of TiO₂ nanoparticles with 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its analogues (TCNX) show strong ICT absorption in the visible region. The ICT band was reported to be significantly red-shifted with extension of the π -conjugated system of TCNX. In order to clarify the mechanism of the red-shift, in this work, we systematically study electronic structures of the TiO₂-TCNX surface complexes (TCNX; TCNE, TCNQ, 2,6-TCNAQ) by ionization potential measurements and density functional theory (DFT) calculations.

1. Introduction

Interfacial charge-transfer (ICT) transitions between inorganic semiconductors and π -conjugated organic compounds are characteristic electronic transitions that enable direct photoinduced charge separation with an internal quantum efficiency of unity and without loss of energy, in principle. [1-13] Because of this feature, ICT transitions are applicable to photovoltaic conversions. So far, several surface complexes formed between a wide-band-gap semiconductor titanium dioxide (TiO₂) and enediol compounds such as 1,2-benzenediol (so-called catechol) were reported to show the absorption of visible light due to ICT transitions from the π -conjugated

systems to the conduction band of TiO₂. These surface complexes were used in photovoltaic cells. Contrary to the expectation, the observed photoelectric conversion induced by the ICT transitions was quite inefficient with incident photon-to-current conversion efficiencies (IPCEs) lower than ca. 30%. [4,5] Wang *et al.* reported that the inefficient conversion is attributed to a fast carrier recombination. [6] Another type of surface complex that shows ICT absorption was reported to be formed between TiO₂ and an organic electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ). [7-13] The TiO₂-TCNQ complex is produced by a nucleophilic addition reaction of a surface hydroxy group with TCNQ, in which a negatively charged TCNQ adduct is generated on TiO₂, as shown in Fig. 1(a). The charge-transferred complex shows a broad absorption band due to ICT transitions from the negatively-charged TCNQ adduct to the conduction band of TiO₂, as shown in Fig. 1(b) and 1(c). It was demonstrated that photovoltaic cells based on the TiO₂-TCNQ surface complex exhibit much higher IPCE values (ca. 70%) than those reported for the TiO₂-enediol complexes. [7] In a theoretical study based on Marcus theory, Fujisawa attributed the efficient light-to-current conversion to the suppression of carrier recombination by the reduction in reorganization energy. [14] In addition, Manzhos *et al.* reported dependence of the ICT band on the size of the π -conjugation system of TCNQ, showing a large red-shift of the ICT band with the extension of the π -conjugation system of bis(dicyanomethylene) compounds (TCNX) from tetracyanoethylene (TCNE) to 11,11,12,12-tetracyanonaphtho-2,6-quinodimethane (2,6-TCNAQ), as shown in Fig. 2. [9] The red-shift of the ICT band was well reproduced by time-dependent density functional theory (TD-DFT) calculations using the mono-Ti model complexes. [9] However, the mechanism still remains to be clarified. In order to clarify the mechanism of the red-shift, in this work, we study the electronic structures of the surface complexes of TiO₂ with TCNE, TCNQ, and 2,6-TCNAQ by means of ionization potential measurements and density functional theory (DFT) calculations with TiO₂-cluster model complexes.

2. Methods

2.1. Experimental

Fig. 1. (a) Formation mechanism of the TiO₂-TCNQ complex, (b) absorption spectra of the TiO₂ (black) and TiO₂-TCNQ (red) thin film samples together with that of TCNQ (blue), and (c) energy level diagram for ICT transitions. The experimental data of the absorption spectra are reported in Ref. 9

TCNE, TCNQ and 2,6-TCNAQ were purchased from Tokyo Chemical Industry and used without further purification. The TiO₂-TCNX samples were prepared by immersing anatase-TiO₂ nanoparticles (P90, Aerosil; particle size: ca. 15 nm, **specific surface area: 96 m²/g**) in the acetonitrile solutions of TCNX ([TCNE] = 3 mM, [TCNQ] = 3 mM, [2,6-TCNAQ] ≤ 0.1 mM) for ca. 24 hours at room temperature. Then, the TiO₂ nanoparticles were filtered and washed with acetonitrile and then vacuum-dried. Ionization potentials of the TiO₂-TCNX samples were measured by means of ultraviolet (UV) photoelectron spectroscopy (AC-3, Riken Keiki) **with a deuterium lamp as a light source. This instrument equipped with an open photoelectron counter allows photoelectron spectroscopy in air without charging-up of samples and has been widely utilized for estimation of ionization potentials of organic materials. [15] Photoelectron quantum yields were calculated from the observed photoemission intensities.**

Fig. 2. Dependence of the wavelength region of the ICT band on the π -conjugated system of TCNX (TCNX: TCNE, TCNQ, 2,6-TCNAQ).

2.1. Computational

For the theoretical analysis of the electronic structures and ionization potentials of the three TiO_2 -TCNX complexes, we constructed model complexes based on an anatase TiO_2 nanocluster, $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$. The TiO_2 cluster was built using the reported X-ray crystallographic data [16,17] of a bulk anatase TiO_2 crystal. The optimized structures and orbital properties (energies and spatial distributions) were calculated with DFT [18] employing a B3LYP functional [19,20] and a 6-31G(d,p) basis set [21,22] taking into account solvation effects of acetonitrile that was used as a solvent of the TCNX solutions by employing a conductor-like polarizable continuum model (CPCM). [23-25] As ICT transitions possess a strong charge-transfer character sensitive to long-range interactions, to account for possible artefacts due to the choice of the functional, we also performed similar DFT calculations using a CAM-B3LYP functional [26] with a long-range correction. [26,27]

During optimization, all atoms of the TCNX moiety and the bridging oxygen atom as well as the hydrogen atoms of the hydroxy groups were relaxed. On the other hand, the coordinations of the atoms of the TiO_2 cluster were frozen to maintain the anatase structure. Ionization potentials of the model complexes were estimated from the total energies of the geometrically optimized $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$ (a total charge: -1, $s = 0$ (singlet)) and ionized $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]$ (a total charge: 0, $s = 1/2$ (doublet)) with the same optimized structure as $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$. We found that the introduction of solvation effects is necessary to obtain the stable structures. The negatively charged TCNX adducts on TiO_2 are considered to be stabilized by interactions with counter cations such as H_3O^+ and physisorbed water molecules on TiO_2 surfaces. However, at present, it is difficult to take into account such intermolecular interactions explicitly in our DFT calculations. In this work, we tentatively take into account the stabilization effect by using solvation effects of acetonitrile. For this reason, in this work we focus on qualitative rather than quantitative trends in the ionization potentials. All the calculations were performed using the Gaussian 09 software. [28] Total and partial densities of states were calculated using the GaussSum software. [29]

3. Results and discussion

3.1. Ionization potentials of TiO_2 -TCNX surface complexes

Fig. 3 shows the UV photoelectron spectra of TiO_2 (blank) and the TiO_2 -TCNE, -TCNQ, and -2,6-TCNAQ samples together with those of TCNE, TCNQ, and 2,6-TCNAQ. TiO_2 shows almost no photoelectron signals. This result is consistent to the fact that the top of the valence band is located at ca. -7.3 eV (vs the vacuum level). The three TCNX acceptors also exhibit almost no signals in the energy range, because the ionization potentials are higher than ca. 7 eV. [30,31] On the other hand, the three TiO_2 -TCNX samples show remarkable photoelectron signals. These photoelectrons originate from the negatively charged TCNX adducts on TiO_2 . The onset energy that corresponds to the ionization potential decreases with the extension of the

Fig. 3. UV photoelectron spectra of TiO₂ (black open circles) and TiO₂-TCNE (blue solid circles), TiO₂-TCNQ (green solid circles), and (c) TiO₂-2,6-TCNAQ (red solid circles) together with those of TCNE (blue open circles), TCNQ (green open circles), and 2,6-TCNAQ (red open circles).

π -conjugated system. The ionization potentials of the TiO₂-TCNE, -TCNQ, and -2,6-TCNAQ complexes are estimated to be 6.00 – 6.10 eV, 5.70 – 5.80 eV, and 5.55 – 5.65 eV, respectively, as shown in Table 1. Since the ionization potentials are attributed to the negatively charged TCNX adducts, the onset energies of the ICT bands in the surface complexes are calculated from the ionization potentials and the energy (E_{CBB} = ca. -4.1 eV versus the vacuum level [32-34]) of the bottom of the conduction band of TiO₂ by the following equation:

$$E_{\text{onset}} = IP + E_{CBB} \quad (1)$$

The onset energies of the ICT transitions in the TiO₂-TCNE, -TCNQ, and -2,6-TCNAQ complexes are estimated to be 1.90 – 2.00 eV (620 – 650 nm), 1.60 – 1.70 eV (730 – 780 nm), and 1.45 – 1.55 eV (800 – 860 nm), respectively. The estimated onset energies are in good agreement with the experimental data within experimental errors, as shown in Table 1. Therefore, the above-mentioned red-shift of the ICT band with the

Table 1. Ionization potentials of the TiO_2 -TCNE, -TCNQ, and -2,6-TCNAQ complexes and calculated onset energies of the ICT transitions from the ionization potentials together with experimental data of ICT onset energies estimated from absorption spectra reported in Ref. [9].

Complex	Ionization potential (<i>IP</i>)	Onset energy estimated from <i>IP</i> (wavelength)	Experimental onset energy (wavelength)
TiO_2 -TCNE	6.00 – 6.10 eV	1.90 – 2.00 eV (620 – 650 nm)	1.9 eV (ca. 640 nm)
TiO_2 -TCNQ	5.70 – 5.80 eV	1.60 – 1.70 eV (730 – 780 nm)	1.7 eV (ca. 725 nm)
TiO_2 -2,6-TCNAQ	5.55 – 5.65 eV	1.45 – 1.55 eV (800 – 860 nm)	1.4 eV (ca. 900 nm)

Fig. 4. Optimized structures of [$\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}$] complexes (TCNX: TCNE, TCNQ, 2,6-TCNAQ) calculated with (a) B3LYP and (b) CAM-B3LYP functional.

Table 2. Calculated ionization potentials of $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$ complexes (TCNX: TCNE, TCNQ, 2,6-TCNAQ).

Functional	Model complex	Calculated ionization potential (eV)
B3LYP	$[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})_2\text{-O-TCNE}]^-$	5.14
B3LYP	$[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})_2\text{-O-TCNQ}]^-$	4.53
B3LYP	$[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})_2\text{-O-2,6-TCNAQ}]^-$	4.41
CAM-B3LYP	$[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})_2\text{-O-TCNE}]^-$	5.18
CAM-B3LYP	$[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})_2\text{-O-TCNQ}]^-$	4.55
CAM-B3LYP	$[\text{Ti}(\text{OH})_3(\text{H}_2\text{O})_2\text{-O-2,6-TCNAQ}]^-$	4.44

extension of the π -conjugated system of TCNX is attributed to the reduction in the ionization potential.

3.2. DFT analysis

In order to investigate the reduction in the ionization potential, we theoretically examined the electronic structures of the TiO_2 -TCNE, -TCNQ, and -2,6-TCNAQ complexes by DFT calculations using the corresponding three model complexes $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$ (TCNX: TCNE, TCNQ, TCNAQ), as described in Computational. Fig. 4 shows the optimized structures calculated by DFT with B3LYP and CAM-B3LYP. As shown in this figure, there are little differences in the $\text{Ti-O}_{\text{bridge}}$ and $\text{C-O}_{\text{bridge}}$ among the three TCNX compounds. All the structures have a sp^3 -type tetragonal configuration at the carbon atom bonded to the bridging oxygen atom. For $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNAQ}]^-$, the coplanar naphthalene ring and dicyanomethylene group are tilted as compared to $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNE}]^-$ and $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNQ}]^-$. Based on the optimized structures, we calculated the total energies of the $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$ complexes and the ionized $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]$ complexes (charge: 0, $s = 1/2$). The ionization potentials of the $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$ complexes were calculated by subtracting the total energies of $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$ from those of $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]$, as shown in Table 2. The calculated ionization potentials are remarkably smaller than the experimental data

Fig. 5. Total and partial densities of states of $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]$ complexes (TCNX: TCNE, TCNQ, 2,6-TCNAQ) calculated with (a) B3LYP and (b) CAM-B3LYP functional. Large white: titanium, small white: hydrogen, gray: carbon, blue: nitrogen, and red: oxygen atom. Green and brown isosurfaces stand for signs opposite in amplitude.

Fig. 6. Distribution ratio of HOMO on the two cyano groups of the negatively charged dicyanomethylene group in $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$ (TCNX: TCNE, TCNQ, 2,6-TCNAQ) calculated with (a) B3LYP and (b) CAM-B3LYP.

(Table 1). As mentioned in Computational, this underestimation is caused by the lack of the consideration of interactions of the negatively charge TCNX adducts with counter cations in our calculations. However, the DFT calculations with B3LYP and CAM-B3LYP show a similar tendency that the ionization potential decreases with the extension of the π -conjugation system, which is consistent with the experimental result. (Fig. 3 and Table 1) The ionization potential calculated with B3LYP decreases by 0.61 eV for $\text{TCNE} \Rightarrow \text{TCNQ}$ and 0.12 eV for $\text{TCNQ} \Rightarrow 2,6\text{-TCNAQ}$ and the values calculated with CAM-B3LYP decreases by 0.63 and 0.11 eV, respectively.

These amounts are comparable to the experimental values (0.30 and 0.15 eV, respectively) (Table 1). Hence, the reduction of the ionization potential was well reproduced by the DFT calculations.

Fig. 5 shows the total and partial densities of states (DOSs) of the $[\text{Ti}_8\text{O}_{14}(\text{OH})_3\text{-O-TCNX}]^-$ complexes. For the both functionals, the highest occupied molecular orbital (HOMO) is distributed on the TCNX moiety and the lowest unoccupied molecular orbital (LUMO) is located in the TiO_2 cluster consistently with the reported results. [7-13] The CAM-B3LYP functional shows larger HOMO-LUMO gaps due to the long-range correction as compared to B3LYP. With the extension of the π -conjugation system of TCNX from TCNE to TCNQ, TCNAQ, the HOMO energy increases from -5.14 eV to -4.60 eV, -4.49 eV for B3LYP and from -6.52 eV to -5.82 eV, -5.69 eV for CAM-B3LYP. From this result, the reduction in the ionization potential is explained by the elevation of the HOMO level of the TCNX adduct. As shown in Fig. 5, the HOMOs are remarkably distributed on the negatively charged dicyanomethylene group far from the TiO_2 surface. Thus, the HOMOs of the model complexes are stabilized by the two electron-withdrawing cyano groups in the dicyanomethylene moiety. We calculated the distribution ratios of the HOMOs on the two cyano groups. As shown in Fig. 6, the calculated distribution ratio of the HOMO on the two cyano groups decreases from 44 to 32, 30 for B3LYP and from 43 to 30, 28 for CAM-B3LYP with the extension of the π -conjugation system of TCNX. Therefore, the elevation of the HOMO level that induces the red-shift of the ICT band is attributed to a weaker stabilization due to the two cyano groups in the negatively charged dicyanomethylene moiety.

4. Conclusion

We have studied the electronic structures of the TiO_2 -TCNE, -TCNQ, and -2,6-TCNAQ complexes by means of the ionization potential measurements and DFT calculations in order to clarify the mechanism of the red-shift of the ICT band with the extension of the π -conjugation system. We observed the reduction in the ionization potential with the extension of the π -conjugation system. This result indicates that the red-shift of the ICT band

is caused by the reduction in the ionization potential. Our DFT analysis revealed that the reduction of the ionization potential is attributed to a weaker stabilization of HOMO by the two electron-withdrawing cyano groups in the negatively charged dicyanomethylene group far from TiO_2 surfaces.

Acknowledgements

This research was partially supported by the Precursory Research for Embryonic Science and Technology (PRESTO) program of the Japan Science and Technology Agency (JST) and Grant-in-Aid for Exploratory Research (Grant Number: 25620054) of Japan Society for the Promotion of Science (JSPS). The author (JF) thanks Prof. Sergei Manzhos of National University of Singapore for his comments on an earlier version of this paper.

Notes and references

- [1] J. Moser, S. Punchihewa, P. P. Infelta, M. Grätzel, *Langmuir* 7 (1991) 3012.
- [2] T. Rajh, J. M. Nedeljkovic, L. X. Chen, O. Poluektov, M. C. Thurnauer, *J. Phys. Chem. B* 103 (1999) 3515.
- [3] P. Persson, R. Bergström, S. Lunell, *J. Phys. Chem. B* 104 (2000) 10348.
- [4] A. P. Xagas, M. C. Bernard, A. H.-L. Goff, N. Spyrellis, Z. Loizos, P Falaras, *J. Photochem. Photobiol: A* 132 (2000) 115.
- [5] E. L. Tae, S. H. Lee, J. K. Lee, S. S. Yoo, E. J. Kang, K. B. Yoon, *J. Phys. Chem. B* 109 (2005) 22513.
- [6] Y. Wang, K. Hang, N. A. Anderson, T. Lian, *J. Phys. Chem. B* 107 (2003) 9434.
- [7] T. Kubo, J. Fujisawa, H. Segawa, *Electrochemistry* 2009, **77**, 977.
- [8] R. Jono, J. Fujisawa, H. Segawa, K. Yamashita, *J. Phys. Chem. Letters* 2 (2011) 1167.
- [9] S. Manzhos, R. Jono, K. Yamashita, J. Fujisawa, M. Nagata, H. Segawa, *J. Phys. Chem. C* 115 (2011) 21487.
- [10] S. Manzhos, J. Fujisawa, H. Segawa and K. Yamashita, *Jpn. J. Appl. Phys.*, 51 (2012) 10NE03-1-6.
- [11] R. Jono, J. Fujisawa, H. Segawa, K. Yamashita, *Phys. Chem. Chem. Phys.* 15 (2013) 18584.
- [12] J. Fujisawa, M. Nagata, M. Hanaya, *Phys. Chem. Chem. Phys.* 17 (2015) 27343.
- [13] J. Fujisawa, M. Hanaya, *Phys. Chem. Chem. Phys.* 17 (2015) 16285.
- [14] J. Fujisawa, *Phys.Chem.Chem.Phys.* 17 (2015) 12228.

[15] C. Adachi, T. Oyamada, Data book on HOMO levels of organic thin films in organic semiconductor devices, CMC publishing Co., Ltd, 2005.

[16] R. W. G. Wyckoff, Crystal structures, Vol. 1, John Wiley & sons, New York, London (1963).

[17] H. Nakai, J. Heyd, G. E. Scuseria, J. Comput. Chem. Jpn. 5 (2006) 7.

[18] W. Kohn, L. J. Sham, Phys. Rev. 140 (1965) A1133.

[19] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[20] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 37 (1988) 785.

[21] R. Ditchfield, W. Hehre, J. Pople, J. Chem. Phys. 54 (1971) 724.

[22] W. Hehre, R. Ditchfield, J. Pople, J. Chem. Phys. 56 (1972) 2257.

[23] V. Barone, M. Cossi, J. Phys. Chem. A 102 (1998) 1995.

[24] M. Cossi, N. Rega, G. Scalmani, V. Barone, J. Comput. Chem. 24 (2003) 669.

[25] Y. Takano, K. N. Houk, J. Chem. Theory Comput. 1 (2005) 70.

[26] T. Yanai, D. P. Tew, N. C. Handy, Chem. Phys. Lett., 393 (2004) 51.

[27] M. J. G. Peach, P. Benfield, T. Helgaker, D. J. Tozer, J. Chem. Phys. 128 (2008) 044118.

[28] M. J. Frisch et al. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

[29] N. M. O'boyle, A. L. Tenderholt, K. M. Langner, J. Comput. Chem. 29 (2008) 839.

[30] I. Ikemoto, K. Samizo, T. Fujikawa, K. Ishii, T. Ohta, H. Kuroda, Chem. Lett. 3 (1974) 785.

- [31] I. Ikemoto, Y. Sato, T. Sugano, N. Kosugi, H. Kuroda, K. Ishii, N. Sato, K. Seki, H. Inokuchi, T. Takahashi, Y. Harada, Chem. Phys. Lett. 61 (1979) 50.
- [32] I. Chung, B. Lee, J. He, R. P. H. Chang, M. G. Kanatzidis, Nature 485 (2012) 486.
- [33] H.-S. Kim, C.-R. Lee, J.-H. Im, K.-B. Lee, T. Moehl, A. Marchioro, S.-J. Moon, R. Humphry-Baker, J.-H. Yum, J. E. Moser, M. Grätzel, N.-G. Park, Sci. Rep. 2 (2012) 591.
- [34] J. Zhang, C. Yu, L. Wang, Y. Li, Y. Ren, K. Shum, Sci. Rep. 4 (2014) 6954.

Interfacial charge-transfer transition