

Electronic structures of quinizarin complexed with TiO₂ clusters

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Electronic structure calculations using the semiempirical method PM3 were performed on quinizarin complexed with TiO₂ clusters. At first, electronic structure calculations of quinizarin complexed with small TiO₂ clusters were performed to check a reliability of the parameters. The calculated transition energies were correlated to the observed absorption spectra. Then, TiO₂ cluster was expanded into rutile type cluster which contained 11 Ti⁴⁺ ions. The LUMO of quinizarin complexed with the cluster was greater than the CB of the matrix. The replacements of Ti⁴⁺ ions by Si⁴⁺ ions changed the density of states of the matrix. The increase of Si⁴⁺ sites shifted the CB to larger energy, and a change of relative energy level of the CB to the LUMO of the dye was observed. This result was consistent with a consideration from the TiO₂ content dependence of the fluorescence lifetimes of quinizarin. © 2000 Kluwer Academic Publishers

1. Introduction

Organic-inorganic composite materials, in which a dye compound forms chemical bonds to an inorganic host, have become of interest in recent years [1–6]. This new class of compounds has a possibility to show unique properties due to strong interaction between organic part and inorganic part. Electron transfer from an excited dye to inorganic matrix is one of the interesting properties, because it was reported that a chemical bond between a dye and inorganic matrix made the efficiency of conversion of light captured by dye into current larger [7]. In addition, this phenomenon is applicable to solar cells [7–12] or frequency-domain optical storage [13].

In the previous study [14], we reported that the fluorescence lifetimes of quinizarin in SiO₂-TiO₂ gels decreased with increasing TiO₂ content. From a comparison of the oxidation reduction potential corresponding to the LUMO of quinizarin [15] and the CB of rutile, electron transfer was proposed as an additive nonradiative process. A further investigation was needed because the oxidation potential corresponding to the LUMO of quinizarin complexes was not necessarily agreed with that of quinizarin itself.

In general, the possibility of electron transfer is examined by a comparison of the oxidation reduction potential [11, 12]. As a new tool to investigate electron transfer, we pay attention to molecular orbital (MO) calculations using the semiempirical method PM3 [16]. MO calculations can provide important information on the relative energy level and on the orbital overlap of the donor and the acceptor. And the optical properties of

unknown combinations of organic and inorganic substances may be predictable.

In this study, electronic structure calculations using PM3 were performed on quinizarin complexed with TiO₂ clusters. The matrix dependence of the fluorescence lifetimes was considered.

2. Technical details

As a first step, electronic structure calculations of quinizarin (1,4-AQ(OH)₂) and 1-hydroxyanthraquinone (1-AQ(OH)) complexed with small TiO₂ clusters (Ti(OH)_{4-n}H₂O: $n = 0-2$) were performed to check a reliability of the parameters. The obtained optimized structures and the transition energies were compared with observed ones. 1-AQ(OH) complexed with TiO₂ gel was prepared in the same manner as in ref. [14].

In a second step, TiO₂ cluster was expanded into rutile type cluster that contained 11 Ti⁴⁺ ions (11r). The cluster was designed based on the rutile structure. The inorganic clusters are saturated by H atoms. Ti-O distances were fixed to 1.95 and 1.98 Å and H atoms on the surface were optimized. A quinizarin was brought close to the cluster, and geometry optimization of the interface was carried out. Then, the changes of the electronic structures due to replacements of Ti⁴⁺ ions by Si⁴⁺ ions were investigated.

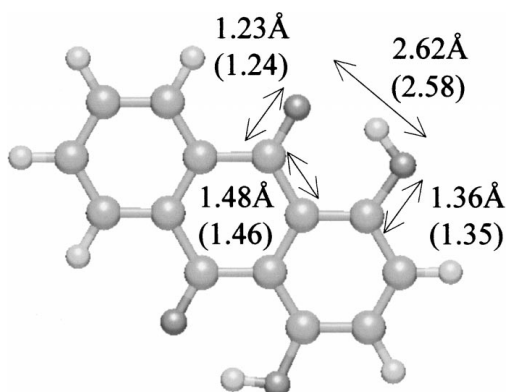
The density of states (DOS) diagrams shown in the figures were constructed directly from the calculated orbital energies, by convoluting the calculated energies with Gaussians with a fwhm of 1.0 eV.

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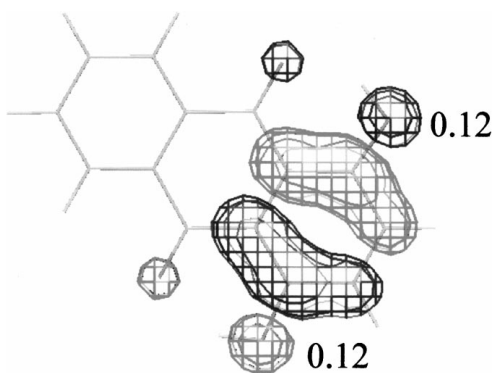
3. Results and discussion

3.1. Electronic structure of quinizarin complexed with small TiO₂ cluster

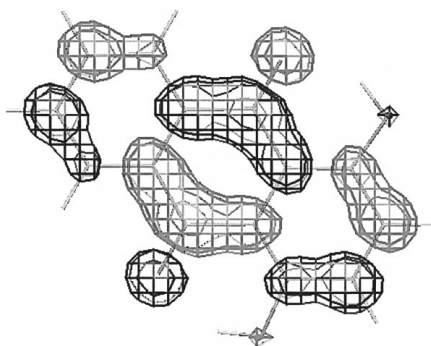
Fig. 1a is the optimized structure of 1,4-AQ(OH)₂ which showed close agreement with the result of X-ray studies [17]. The HOMO and the LUMO of 1,4-AQ(OH)₂ are depicted in Fig. 1b and c. There was a significant concentration on the ring with the substituent groups in the HOMO. In the LUMO the charge was distributed over the anthraquinone ring. The HOMO-LUMO transition corresponded to a typical charge transfer transition as was described in the literature [17, 18]. The DOS of the optimized Ti(OH)_{4-n}H₂O (*n* = 0–2) clusters are shown in Fig. 2. These small clusters represented an initial state of inorganic matrix because a Ti(OPrⁱ)₄ exists in monomer [19]. The VB consisted of O2*p* nonbonding orbitals and the CB was mainly Ti3*d* orbitals. The coordination numbers had little effect on the electronic structure. The band gap



(a)



(b)



(c)

Figure 1 Optimized structure of 1,4-AQ(OH)₂ and its frontier orbitals, (a) Optimized structure of quinizarin with a data from ref. [17] in parentheses, (b) HOMO of quinizarin, and (c) LUMO of quinizarin.

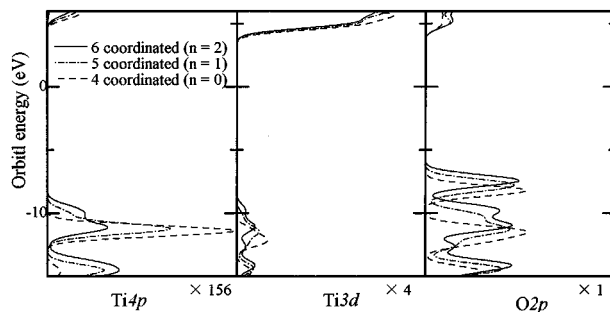


Figure 2 Density of states of Ti(OH)_{4-n}H₂O (*n* = 0, 1, 2).

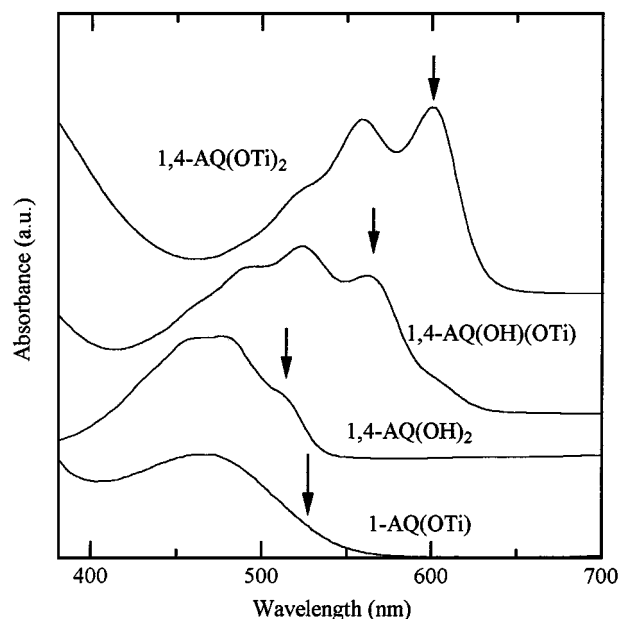


Figure 3 Absorption spectra for Ti complexes. Transition energies in Fig. 5 are shown with arrows.

was rather large, approximately 10 eV, compared to the experimentally observed 3.5 eV. As was reported in the INDO calculations [20] and in the *ab initio* calculations [21], it was an effect of cluster size. A decrease of the band gap with the growth of the matrix was observed experimentally [22].

1,4-AQ(OH)₂ and 1-AQ(OH) form complexes with Ti⁴⁺ ion, i.e., 1,4-AQ(OH)(OTi), 1,4-AQ(OTi)₂, and 1-AQ(OTi). The absorption spectra of the complexes are shown in Fig. 3. As the complexations occurred immediately after mixing the dye solution and the alkoxide [14], the electronic structures of quinizarin in the TiO₂ gels can be considered with quinizarin complexed with these small clusters.

The optimized structures of the complexes are depicted in Fig. 4. An additive H₂O coordinated to the Ti⁴⁺ ion, but another H₂O was repelled as shown in Fig. 4b and c. The relationship between the observed excitation energy and the calculated HOMO-LUMO transition energy was given in Fig. 5. The calculated transition energies were correlated to the observed absorption spectra. It was considered that a reliability of the parameters for this system was checked. In Fig. 6, the HOMOs and the LUMOs of 1,4-AQ(OH)(OTi) and 1,4-AQ(OTi)₂ were depicted. From a comparison with those for 1,4-AQ(OH)₂ shown in Fig. 1b and c, it was

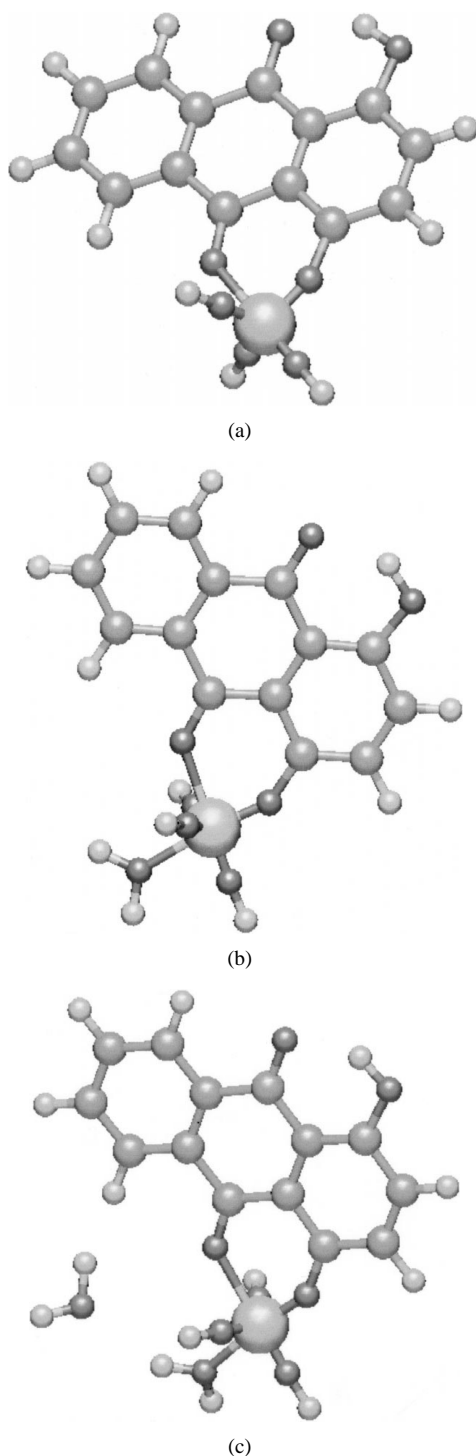


Figure 4 Optimized structures of 1,4-AQ(OH)(OTi) clusters. (a) 1,4-AQ(OH)(OTi)(OH)₃, (b) 1,4-AQ(OH)(OTi)(OH)₃-H₂O, and (c) 1,4-AQ(OH)(OTi)(OH)₃-2H₂O

considered that the charge transfer character of the dye did not change significantly after complexation. This result was consistent with that of the quinizarin complexed with Al³⁺ ion [23, 24]. The electronic structures of the complexes are presented in Fig. 7. The orbital energies of the HOMO and the LUMO changed 1.67 eV and 0.94 eV for 1,4-AQ(OH)(OTi), and 2.93 eV and 1.77 eV for 1,4-AQ(OTi)₂, respectively. The changes of the orbital energies due to complexation were larger for the HOMO for both complexes. Such a character is the same as the other substituted anthraquinones [25, 26]. The distribution of the frontier orbitals could be responsible for it. While the charge

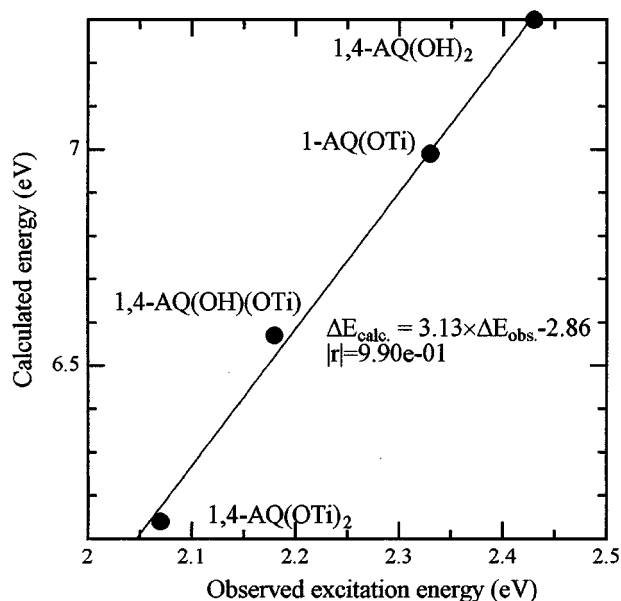


Figure 5 Relationship between observed excitation energy and calculated energy.

density of O atom connected with Ti atom was small for the LUMO, that for the HOMO was over 0.10 for each bond. The character of the HOMO was antibonding with respect to the bonds between the ring and the O atom. As shown in Figs 1 and 6, the orbital energy of the HOMO increased with the increase of the total charge density of the O atom, namely 0.13×2 , $0.18 + 0.07$, and 0.12×2 . This tendency was consistent with the result that the larger the electron donating power of an O²⁻ ion in the oxides was, the more the absorption band of quinizarin red-shifted [27]. It was assumed that the changes of absorption spectra were mainly caused by the degree of the antibonding character of the HOMO.

3.2. Electron transfer

The electronic structure of quinizarin in the TiO₂ matrix could be understood qualitatively with the small complexes. But, the bandwidth, the band-gap energy, and the Madelung potential of the inorganic clusters are size dependent [20, 21]. Thus the relative energy level of the HOMO of quinizarin to the CB is variable with cluster size. From a comparison of the oxidation reduction potential and [TiO₂] content dependence of the fluorescence lifetimes, the relative energy levels of the HOMO of the quinizarin to the CB of the SiO₂-TiO₂ matrix were assumed as illustrated in Fig. 8 [14]. The assumed relative energy level of the HOMO of the dye to the CB of TiO₂ was different from that presented in Fig. 7. To study electron transfer, TiO₂ cluster was expanded into rutile type cluster which contained 11 Ti⁴⁺ ions (11r).

Fig. 9 is the optimized structure of 1,4-AQ(OH)(OTi)/11r. Its electronic structure is shown in Fig. 10a. As to the matrix part, the band-gap energy decreased and the bandwidth increased compared to those of the small clusters. Though this cluster was not regarded as a bulk [19, 20], the LUMO of quinizarin was greater than the bottom of the CB of 11r.

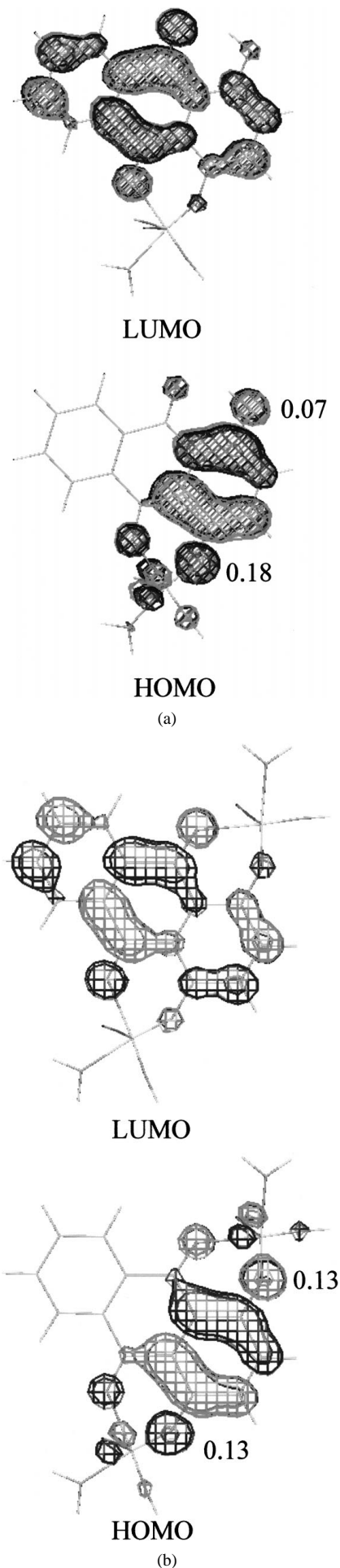


Figure 6 Frontier orbitals of (a) 1,4-AQ(OH)(OTi) and (b) 1,4-AQ(OTi)₂.

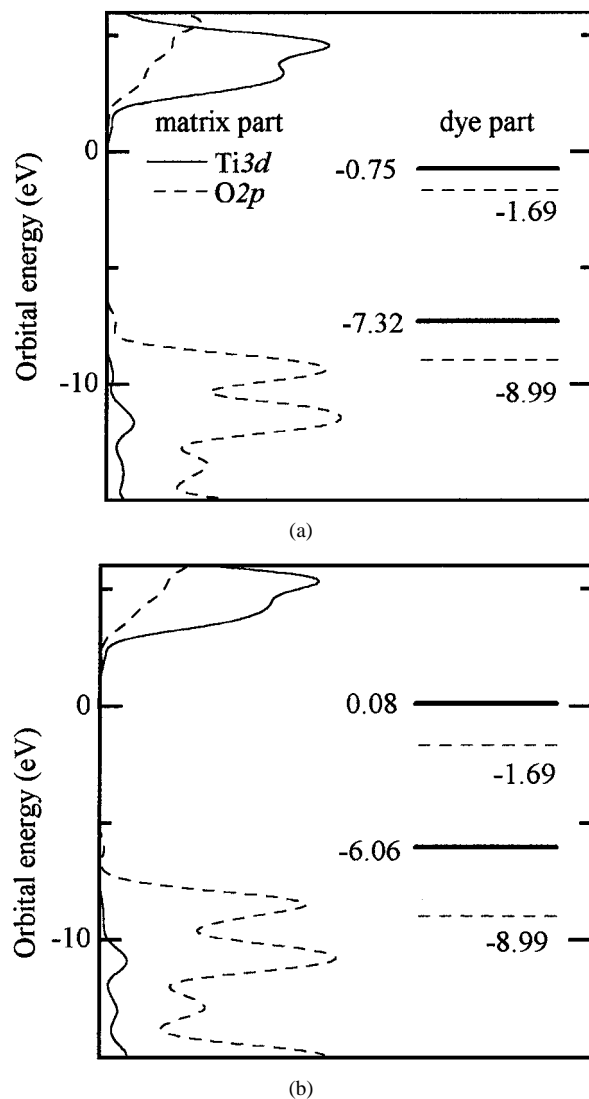


Figure 7 Electronic structures of (a) 1,4-AQ(OH)(OTi) and (b) 1,4-AQ(OTi)₂. The broken line in dye part is orbital energy of 1,4-AQ(OH)₂.

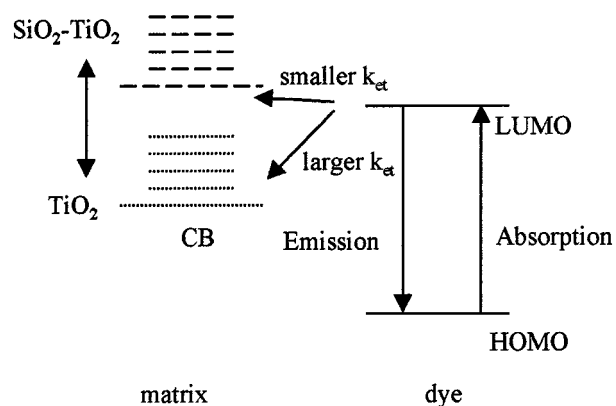


Figure 8 Scheme of relaxation process of S₁ state.

Then, the changes of the electronic structures due to replacements of Ti⁴⁺ ions by Si⁴⁺ ions were investigated. As shown in Fig. 11, the increase of Si⁴⁺ sites shifted the CB to larger energy, and resulted in changes of the relative energy level of the LUMO of the dye to the CB. As an example of small [TiO₂] content matrix, the electronic structure of 1,4-AQ(OH)(OTi)/1r which contained only one Ti⁴⁺ ion was shown in Fig. 10b. It

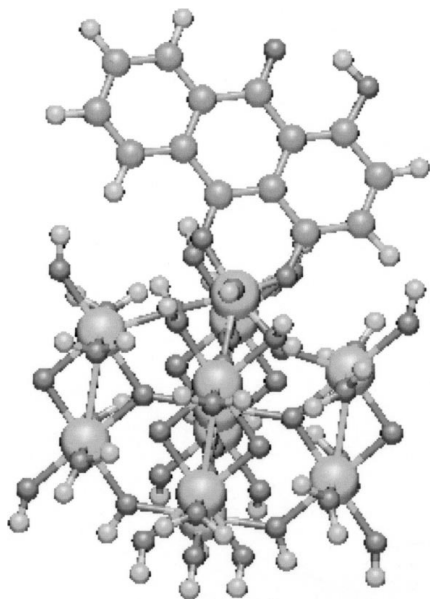


Figure 9 Optimized structure of 1,4-AQ(OH)(OTi)/11r.

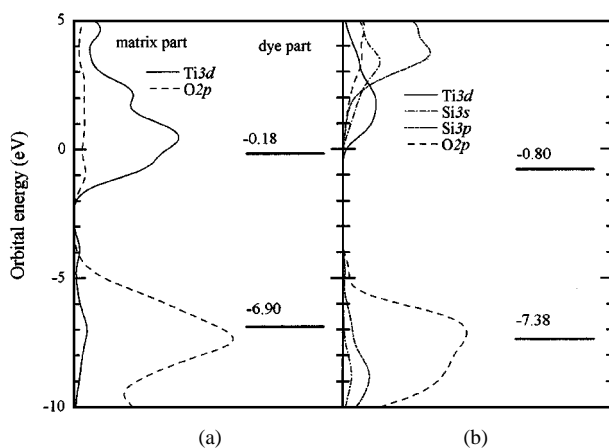


Figure 10 Electronic structures of (a) 1,4-AQ(OH)(OTi)/11r and (b) 1,4-AQ(OH)(OTi)/1r.

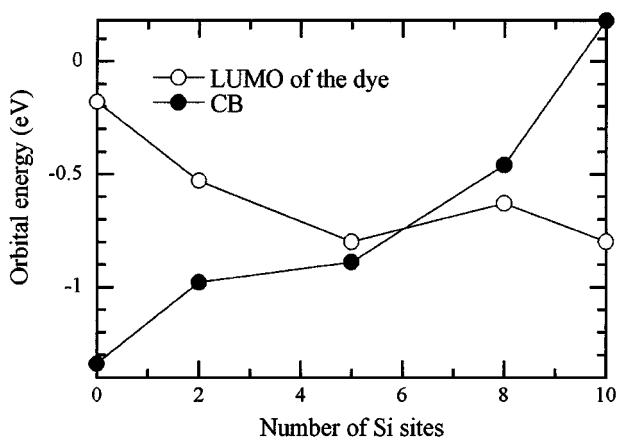


Figure 11 Changes of relative energy level due to substitution from Ti^{4+} ions to Si^{4+} ions.

can be seen from Figs 10 and 11 that the state density of $\text{Ti}3d$ around the same energy as the HOMO of the quinizarin decreased with $[\text{SiO}_2]$ content. This result was consistent with a consideration from the $[\text{TiO}_2]$ content dependence of the fluorescence lifetimes of quinizarin in the SiO_2 - TiO_2 gels [14].

Furthermore, the electronic structure calculations gave an important information on the orbital overlap of the donor and the acceptor. In the previous study [14], the rates of electron transfer from quinizarin to TiO_2 matrices were calculated to be $0.6\text{--}3.0 \times 10^8 \text{ s}^{-1}$, which was small in the range of general values, i.e., $10^7\text{--}10^{13} \text{ s}^{-1}$. We assumed that these small values were caused by the charge distribution of the LUMO shown in Fig. 6. In this system, an electron was thought to migrate via the O atom of the quinone [14, 28]. The small charge density on the O atom could make the orbital overlap between the donor and the acceptor small.

It was considered that the relaxation process including electron transfer could be understood by the use of PM3 calculations.

4. Conclusions

Electronic structure calculations using the semiempirical method PM3 were performed on quinizarin complexes with TiO_2 clusters.

The calculated transition energies of quinizarin complexed with small TiO_2 clusters were correlated to the observed absorption spectra. Then, to investigate electron transfer TiO_2 cluster was expanded into rutile type cluster which contained 11 Ti^{4+} ions. For the cluster, the LUMO of quinizarin was greater than the CB of the matrix. The replacements of Ti^{4+} ions by Si^{4+} ions changed the density of states of the matrix. The increase of Si^{4+} sites shifted the CB to larger energy, and resulted in changes of relative energy levels of the LUMO of the dye to the CB. This result was consistent with a consideration from the TiO_2 content dependence of the fluorescence lifetimes of quinizarin.

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