Excited State Relaxation Processes of Naphthalocyanatovanadium(IV) oxide in Polymer Films for Ultrafast All-optical Modulation in the Near-infrared Region

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Excited state relaxation process of naphthalocyanatovanadium(IV) oxide (VONc) in solutions and in polymer films was studied by transient absorption measurements. The transient absorption decay of VONc in polymer films is faster than that in toluene solution. The excitation power dependence and weight fraction dependence of the excited state dynamics and absorption spectrum suggests that the aggregation of VONcs contributes to faster decay from singlet excited state. The aggregation of VONc is concluded to be useful to ultrafast all-optical light modulation in the near-infrared region.

Phthalocyanines (Pcs) and metallophthalocyanines (MPcs) have received great interests as useful compounds for organic photoreceptor,[1] optical memory,[2] photodynamic therapy,[3] optical limiting,[4] and so on. They show high chemical and thermal stability together with characteristic strong absorption bands from the visible to near-infrared (NIR) region. We have been studying photoresponsive materials for ultrafast all-optical light modulation devices and optical switching by the use of absorption and/or refractive index changes in guided wave mode geometry in the NIR region including telecommunication wavelength.[5,6]

Naphthalocyanines (Ncs) have more expanded π-conjugated structures compared with Pcs, which will shift the steady-state and transient absorption to a longer wavelength region. Therefore, Ncs are expected to work as photoresponsive materials for the ultrafast light modulation in the NIR region. To our best knowledge, there are no reports on the excited state dynamics of naphthalocyanatovanadium(IV) oxide (VONc). In this letter, we report the excited state relaxation processes of VONc in the NIR region in solutions and in polymer films studied by femtosecond transient absorption measurements.

Tetra-*tert*-butylnaphthalocyanatovanadium(IV) oxide (VONc, Sigma-Aldrich) was used without further purification. A tricyclodecane polymer, an ARTON® (JSR Co., Ltd.) was used as a matrix. These structures are shown in Figure 1. Thin films containing VONc were prepared by casting toluene solutions on glass slides. VONc was dispersed in ARTON® with various weight fractions of 1/10–1/20000 (VONc/ARTON®). Experimental details of spectral measurements were reported previously.[5–7]

Figure 2 shows the steady-state UV–vis absorption and fluorescence spectra of VONc in a toluene solution and in ARTON® polymer films with several weight fractions from 1/10 to 1/20000. The absorption spectra are normalized at 810 nm, which is assigned to the Q band. The absorption spectra in polymer films showed a new peak around 745 nm and a shoulder around 925 nm in addition to the sharp peak at 810 nm. These new absorptions became larger with increasing the weight fractions of VONc up to about 5%, after which absorbance values relative to that at 810 nm were almost constant. The fluorescence spectra excited at 800 nm showed a peak at 885 nm as shown in Figure 2b. The fluorescence intensity became weaker with increasing the weight fraction of VONc in ARTON®. The changes of absorption spectra originate from the aggregation of VONc in polymer films, which is explained by the exciton coupling theory.[8] The energy for the VONc monomer was estimated as 12300 cm^{-1}. The split energy levels at 13400 and 10800 cm^{-1} can be attributed to transition dipole moments aligned in a similar way as those in H- and J-like aggregates, respectively.

Figure 3a shows the transient absorption spectra of VONc in toluene solutions excited by 800-nm femtosecond laser. A broad transient absorption band with a peak around 980 nm was observed in the NIR region just after excitation. The excited singlet and triplet state of VONc becomes singdoublet ($^2S_1$) and tripdoublet (^2T) or tripquartet (^4T) state by the coupling between the unpaired d-electron of VO^{2+} and the coordinated Nc^{2-}.[9] Thus, the transient absorption at $t = 0$ and 70 ps were assigned to $^2S_1 \rightarrow {}^2S_n$ and $^2T_1 \rightarrow {}^2T_n$ or $^4T_1 \rightarrow {}^4T_n$ absorption. The time profile of the transient absorbance monitored at 980 nm is shown in Figure 3b, which can be analyzed by taking rise and decay into accounts, $\Delta A = A_1 \exp(-t/\tau_1) + A_2(1 - \exp(-t/\tau_2))$. Both time constants were estimated to be 13 ±

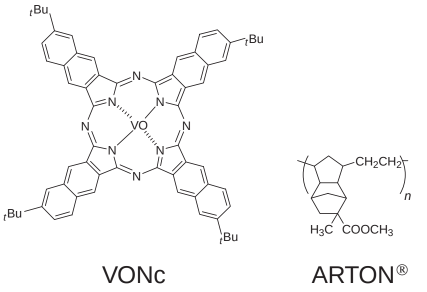

Figure 1. Chemical structure of VONc and ARTON®.

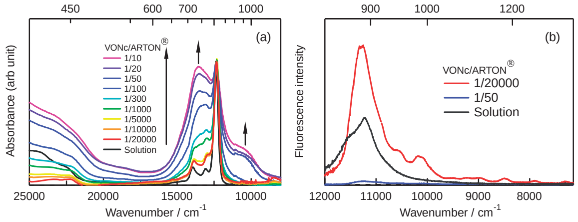

Figure 2. Absorption (a) and fluorescence (b) spectra of VONc in toluene solution (12 μM) and in ARTON® films as a function of weight fraction. The fluorescence was excited at $\lambda = 800$ nm.

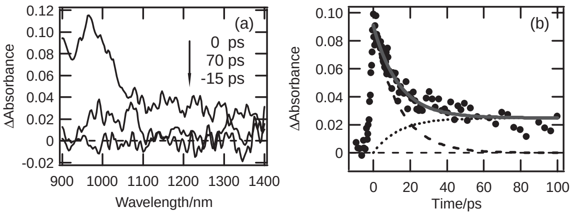

Figure 3. (a) Transient absorption spectra of VONc in toluene solution excited by 800-nm femtosecond laser. (b) Time profiles of transient absorbance at 980 nm.

2 ps, which are shown in dotted and dashed line in Figure 3b. The calculated fluorescence lifetime ($\tau_f{}^c$) and the rate constant of a radiative process (k_f) were 30 ps and $6.3 \times 10^7\,\mathrm{s}^{-1}$ from the intrinsic radiative lifetime (16 ns) obtained from the modified Strickler–Berg relation[10] and the fluorescence quantum yield ($\Phi_f = 0.002$).[11] The $\tau_f{}^c$ value is comparable to the time constant (13 ± 2 ps) of the transient absorption. The total rate constant for deactivation of the $^2S_1$ (k_s) was calculated to be $8.3 \times 10^{10}\,\mathrm{s}^{-1}$ from $\tau = 13 \pm 2$ ps. The rate constants of the internal conversion (k_{IC}) was calculated to be $6.8 \times 10^9\,\mathrm{s}^{-1}$ from $k_{IC} \approx 10^{13} \exp(-\alpha\Delta E)$,[13] where α (eV^{-1}) is the order of $5\,\mathrm{eV}^{-1}$ for rigid aromatic hydrocarbons,[14] $\Delta E = 1.46$ eV is the energy gap between two electronic states. From these values, we can estimate the quantum yield of the fluorescence, IC and ISC, which were calculated to be 0.002, 0.076, and 0.922, respectively. The k_f and k_{IC} are much smaller than k_{ISC}. From these results, the relaxation paths from the $^2S_1$ state of VONc are concluded to be dominated by the ISC, which is similar to that of VOPc reported by Terasaki et al.[15] The ISC will be accelerated by the spin–orbit coupling.

Next, we measured the transient absorption spectra of VONc doped in polymer films. Figure 4a shows time profiles of the transient absorbance observed at two excitation conditions at 1060 nm for the VONc-doped ARTON® film with the weight fraction of 1/100. Analysis showed the decay includes a bimolecular process due to exiton–exiton annihilation, too. The time-dependence of exciton density n for such a case including long-range dipole–dipole interaction is expressed by the following equation,[15] where τ and n_0 are 1st order decay time constant and initial exciton density, respectively. The term of $n_0\gamma$ denotes the bimolecular decay.

$$\frac{n}{n_0} = \frac{\exp(-t/\tau)}{1 + (2n_0\gamma\sqrt{\tau})\,\mathrm{erf}(\sqrt{t/\tau})} \qquad (1)$$

From the best fitting, the same τ-value of 11 ± 2 ps was estimated with $(n_0\gamma)^{-1} = 5.5 \times 10^{-7}$ and $3.0 \times 10^{-6}\,\mathrm{s}^{1/2}$ for excitation at 280 and 75 µJ/pulse, respectively, corresponding to more excitons generated at higher energy.

Figure 4b shows time profiles of transient absorbance at 1200 nm with the weight ratio of VONc in ARTON® films of 1/100 and 1/50. The time profiles were analyzed by eq 1 with $(n_0\gamma)^{-1} = 4.3 \times 10^{-6}\,\mathrm{s}^{1/2}$ and time constants of $\tau = 11 \pm 2$ ps for 1/100, and 1.8 ± 0.9 ps for 1/50 mixtures, respectively. This result is in contrast to Figure 4a. In the case of silicon Pc dimers, the quantum yield of the dimer fluorescence relative to the monomer fluorescence is extremely low ($\Phi_F(D)/\Phi_F(M) = 10^{-3}$) and the decay of the dimer is dominated by nonradiative deactivation.[16] The weight fraction dependence of VONc can be thus ascribed to the increased contribution of the nonradiative deactivation by aggregates in the polymer films. Since VONc is very stable against repeated photoexcitation and shows ultrafast photoresponses in polymer films, it is expected to make a great deal of contribution for such purpose.

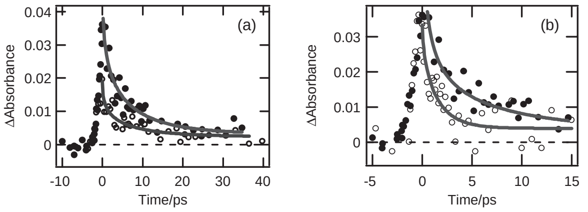

Figure 4. (a) Time profiles of transient absorbance of VONc in ARTON® films (1/100) excited by 800-nm femtosecond laser monitored at 1060 nm. Closed and open circles correspond to the excitation power of 280 and 75 µJ/pulse, respectively. (b) The weight fraction dependence of time profiles of VONc dispersed into ARTON® film. The closed and open circles correspond to the weight fraction of VONc/ARTON® = 1/100 and 1/50, respectively.

In summary, the relaxation process of VONc from $^2S_1$ was dominated by the ISC. The ultrafast relaxation of VONc observed in polymer films was attributed to the exiton–exiton annihilation or nonradiative path due to the formation of aggregates was increased. The present results suggest that the ultrafast deactivation of the VONc in polymer films is useful as all-optical ultrafast modulation materials. Detailed studies on molecular aggregation of VONc and its application to guided wave mode devices will be reported elsewhere.

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