

Interfacial Electron-Transfer Kinetics in Metal-Free Organic Dye-Sensitized Solar Cells: Combined Effects of Molecular Structure of Dyes and Electrolytes

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Abstract: Electron diffusion coefficient, lifetime, and density in the TiO₂ electrode of dye-sensitized TiO₂ solar cells (DSCs) employing I⁻/I₃⁻ redox couples were measured with eight different metal-free organic dyes and three Ru complex dyes. At matched electron density, all DSCs using organic dyes (ODSCs) showed shorter electron lifetime with comparable or larger diffusion coefficients in comparison to the DSCs using the Ru dyes (RuDSC). The shorter lifetime was attributed partially to the slower dye cation reduction rate of the organic dyes by I⁻, faster electron diffusion coefficient in the TiO₂, and mostly higher I₃⁻ concentration in the vicinity of the TiO₂ surface. Whereas a slight shift of the conduction band edge potential (E_{cb}) of the TiO₂ was seen with a few organic dyes, no correlation was found with the dipole moment of the adsorbed dyes. This implies that the adsorbed dyes interact with cations in the electrolyte, so the direction of the dipole is altered or simply screened. The increase of [I₃⁻] in the vicinity of the TiO₂ surface was interpreted with partial charge distribution of the dyes. Under one-sun conditions, less electron density due to shorter electron lifetime was found to be the main reason for the lower values of V_{oc} for all ODSCs in comparison to that of RuDSCs. Among the organic dyes, having larger molecular size and alkyl chains showed longer electron lifetime, and thus higher V_{oc} . Toward higher open circuit voltage, a design guide of organic dyes controlling the electron lifetime is discussed.

Introduction

Dye-sensitized solar cells (DSCs) consisting of dye-adsorbed nanoporous semiconductor electrodes immersed in electrolytes have been the subject of intensive study due to relatively high energy conversion efficiency and expectations of low production costs.¹ To date, the highest efficiency is over 11%, achieved by employing a Ru complex dye, TiO₂ electrode, and I⁻/I₃⁻ redox couple.² Replacing the Ru complex dye with metal-free organic dye is one of the strategies that can be used to increase the efficiency. Organic dyes have several advantages in view of extinction coefficients, variations of structure, and material costs. To apply DSCs, various organic dyes, such as merocianine dyes,^{3,4} coumarin dyes,^{5,6} polyene dyes,⁷ indoline dyes,⁸ tetra-

hydroquinoline dyes,⁹ cyanine dyes,¹⁰ oligoene dyes,¹¹ and carbazole dyes,¹² have been synthesized. Initially, the efficiency of organic dye-sensitized solar cells (ODSCs) was low. After making larger efforts, recent reports show 8–9% efficiency under one-sun conditions.^{13,14} The increase of the efficiency is mainly due to the increase of short circuit current (J_{sc}) by expanding the absorption spectrum. In contrast, open circuit

- (5) Hara, K.; Sayama, K.; Ohga, Y.; Shinpo, A.; Suga, S.; Arakawa, H. *Chem. Commun.* **2001**, 569.
- (6) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, *107*, 597.
- (7) Hara, K.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *Chem. Commun.* **2003**, 252.
- (8) Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, *126*, 12218.
- (9) Chen, R.; Yang, X.; Tian, H.; Wang, X.; Hagfeldt, A.; Sun, L. *Chem. Mater.* **2007**, *19*, 4007.
- (10) Ehret, A.; Stuhl, L.; Spitler, M. T. *J. Phys. Chem. B* **2001**, *105*, 9960.
- (11) Kitamura, T.; Ikeda, M.; Shigaki, K.; Inoue, T.; Anderson, N. A.; Ai, X.; Lian, T.; Yanagida, S. *Chem. Mater.* **2004**, *16*, 1806.
- (12) Koumura, N.; Wang, Z. S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256.
- (13) Ito, S.; Zakeeruddin, S. M.; Humphry-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Pechy, P.; Takata, M.; Miura, H.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2006**, *18*, 1202.
- (14) Wang, Z. S.; Cui, Y.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Hara, K. *J. Phys. Chem. C* **2007**, *111*, 7224.

[†] Shinshu University.

[‡] National Institute of Advanced Industrial Science and Technology.

[§] Kobe University.

- (1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.
- (2) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. *Jpn. J. Appl. Phys.* **2006**, *45*, L638.
- (3) Sayama, K.; Tsukagoshi, S.; Hara, K.; Ohga, Y.; Shinpo, A.; Abe, Y.; Suga, S.; Arakawa, H. *J. Phys. Chem. B* **2002**, *106*, 1363.
- (4) Sayama, K.; Tsukagoshi, S.; Mori, T.; Hara, K.; Ohga, Y.; Shinpo, A.; Abe, Y.; Suga, S.; Arakawa, H. *Sol. Energy Mater. Sol. Cells* **2003**, *80*, 47.

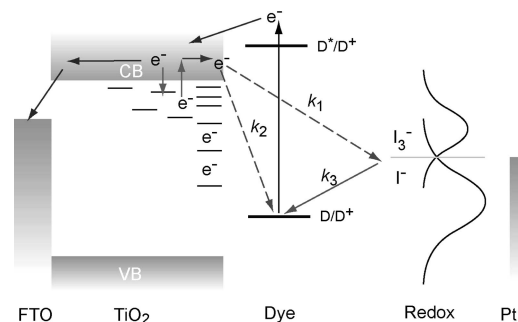


Figure 1. Schematics of electron-transfer processes in DSC. k_1 represents the electron transfer rate constant from TiO_2 to I_3^- , k_2 to dye^+ , and k_3 from I^- to dye^+ .

voltage (V_{oc}) of ODSCs has been lower than that of DSCs employing Ru complex dyes (RuDSCs).

Figure 1 shows the schematics of DSCs. Charge separation occurs in the adsorbed dyes by the injection of excited electrons into the conduction band of TiO_2 and the reduction of resulting dye cations by I^- in the electrolyte solutions. Then, at short circuit conditions, the electrons and I_3^- diffuse to a transparent conductive oxide (TCO) and to a Pt counter electrode, respectively. Charge collection efficiency is related to electron diffusion coefficients (D) and electron lifetime (τ) in the TiO_2 . Here, the electron lifetime is defined as the average time spent in the TiO_2 electrode. If electron diffusion length, which is $(D\tau)^{0.5}$, is shorter than the thickness of the TiO_2 electrode, the electrons in the TiO_2 recombine with the dye cation and/or I_3^- during the diffusion. High-incident photon to current conversion efficiency of recent ODSCs indicates that the recombination at short circuit is negligible. At open circuit conditions, the injected electrons in the TiO_2 accumulate until the charge injection rate (G) is balanced with the recombination rate. The value of V_{oc} is the difference between the Fermi level of TiO_2 and I^-/I_3^- redox potential,¹⁵ and the Fermi level is determined by the conduction band edge potential (E_{cb}) and electron density (n) in the TiO_2 . The n is determined roughly by the product of G and τ . In the case of coumarin and carbazole dyes, less electron density, induced by short τ , was one of the reasons for the low V_{oc} in the ODSCs.^{12,16}

The electron density in the TiO_2 may be written as

$$\frac{\partial n}{\partial t} = G - k_1 n[\text{I}_3^-] - k_2 n[\text{dye}^+] \quad (1)$$

where k_1 is the rate constant for I_3^- and k_2 is the rate constant for the dye cation. Lifetimes τ_1 and τ_2 are defined as reciprocals of $k_1[\text{I}_3^-]$ and $k_2[\text{dye}^+]$. Since k_1 and k_2 depend on the electron density,^{17,18} eq 1 is valid when Δn is small enough so that $k_{1,2}$ can be approximated as constants. When the electron lifetime is measured by transient response of V_{oc} , which is used to monitor the change of the electron density in TiO_2 , the measured lifetime is the reciprocal of $(1/\tau_1 + 1/\tau_2)$. The rate constant in eq 1 could be expressed as

$$k_i = \frac{2\pi}{\hbar} [H_{ab}]^2 \frac{1}{\sqrt{4\pi\lambda_i k_B T}} \exp\left[-\frac{(-\Delta G_i + \lambda_i)^2}{4\pi\lambda_i k_B T}\right] \quad (2)$$

where ΔG_i is the free energy difference, λ_i the reorganization energy, which is the sum of internal (λ_v) and solvent (λ_s) reorganization energy, k_B Boltzmann's constant, T temperature, and H_{AB} electronic coupling for a second-order reaction.^{19,20} In the case of k_2 , the term of H_{AB}^2 may be written by $H_{AB}^2 e^{-\beta x}$, where β is a constant and x is the spatial distance between the TiO_2 and HOMO of acceptor species.²⁰

For the case of carbazole derivatives, the electron lifetime in the ODSCs was increased by the addition of *n*-hexyl chains to thiophene moieties of the dyes.¹² The mechanism of the increase of the lifetime was postulated as being due to the blocking of reorganization energy of the dye (λ) due to the increase of the molecular size. One of the objectives of this paper is to substantiate the postulations. In addition, whereas the structure of organic dyes has been studied in view of charge injection efficiency, absorption spectrum, and tendency of aggregation, there has been little study on electron lifetime. Thus, the other objective is to elucidate the relationship between the electron lifetime and the structure of organic dyes, which is essential to set the design guide for sensitizing dyes.

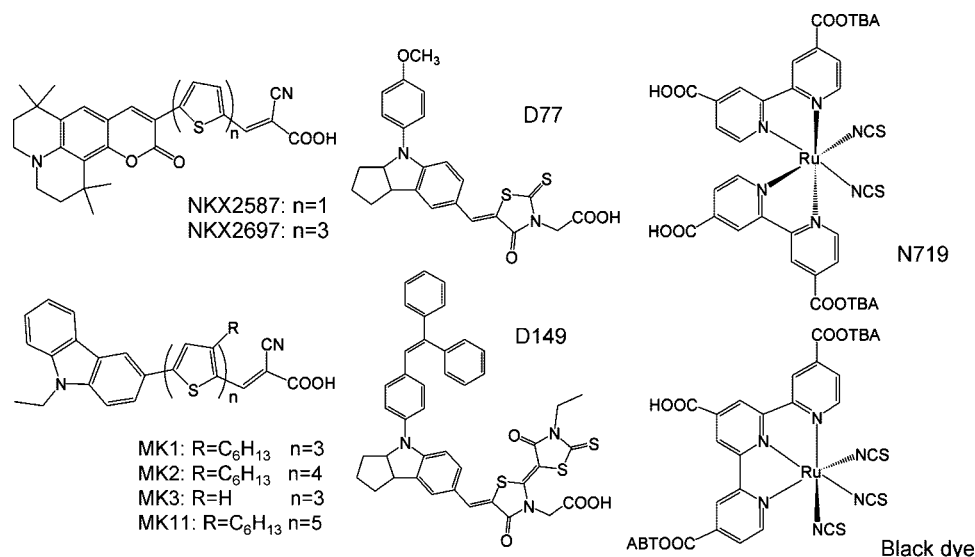
Experimental Section

Nanoporous TiO_2 electrodes were prepared by applying a paste containing nanosized TiO_2 particles (Nanoxide-T, Solaronix) on to TCO (SnO_2/F , FTO, 9.5 Ω/sq , Nippon sheet glass) with doctor blade techniques, and the electrodes were sintered at 550 $^\circ\text{C}$ for 30 min in air. The TCO was cleaned with 2-propanol by super-sonication for 10 min followed by UV/ozone irradiation for 15 min. Structures of sensitizing dyes are shown in Scheme 1. Ru complex dye, $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{Hdcbpy})_2(\text{NCS})_2]$ (known as N719), was purchased from Peccell Technology. Another Ru dye, $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{Htcterpy})(\text{NCS})_3]$ (known as Black dye), was obtained from Solaronix. Indorine dyes (D77 and D149) were supplied from Mitsubishi paper mills. MK and NKX series of dyes were synthesized as described elsewhere.^{12,21} The electrodes were immersed into a solution containing less than 0.5 mM of dye for 16 h, except for D149, which was for 2 h. To reduce the amount of adsorption, the dye solutions were diluted and immersion time was shortened. The uniformity of the dye adsorption was checked by visible inspection from the front and back (substrate) side of the TiO_2 electrode. The solvent was acetonitrile (AN)/4-*tert*-butyl alcohol (*t*-BuOH) (1:1 wt %, denoted as solvent A) for N719, black dye, Ru505, D77, D149, NKX-2587, NKX-2697, and MK1, and AN/*t*-BuOH/toluene (1:1:1 wt %, denoted as solvent B) for MK1, 2, 3, and 11. MK1 solutions were prepared with both mixed solvents, and MK1_B was examined only in Figure 2 and S1 in the Supporting Information. For D149 and black dye solutions, chenodeoxycholic acid (DCA 1.0 and 6.6 mM, respectively) was added. After the electrodes are rinsed with AN for solvent A or toluene for solvent B, they are placed onto a Pt-sputtered TCO and sealed with thermal adhesive film. Electrolytes were introduced from a drilled hole and the hole was again placed with a piece of glass and the film. Standard electrolyte consists of 0.1 M LiI, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.5 M 4-*tert*-butylpyridine (tBP), and 0.05 M I_2 , in dehydrated AN. Thickness of the TiO_2 electrodes was measured by a surface profilometer (Dektak). DSCs were prepared with the TiO_2 film having the thickness between 2.5 and 5 μm . $I-V$ characteristics were measured under simulated one-sun conditions (AM1.5, 100

- (15) Pichot, F.; Gregg, B. A. *J. Phys. Chem. B* **2000**, *104*, 6.
 (16) Hara, K.; Miyamoto, K.; Abe, Y.; Yanagida, M. *J. Phys. Chem. B* **2005**, *109*, 23776.
 (17) Haque, S. A.; Tachibana, Y.; Klug, D. R.; Durrant, J. R. *J. Phys. Chem. B* **1998**, *102*, 1745.
 (18) Schlichthörl, G.; Huang, S. Y.; Sprague, J.; Frank, A. J. *J. Phys. Chem. B* **1997**, *101*, 8141.

- (19) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.
 (20) Clifford, J. N.; Palomares, E.; Nazeeruddin, M. K.; Grätzel, M.; Nelson, J.; Li, X.; Long, N. J.; Durrant, J. R. *J. Am. Chem. Soc.* **2004**, *126*, 5225.
 (21) Hara, K.; Wang, Z. S.; Sato, T.; Furube, A.; Katoh, R.; Sugihara, H.; Dan-Oh, Y.; Kasada, C.; Shinpo, A.; Suga, S. *J. Phys. Chem. B* **2005**, *109*, 15476.

Scheme 1. Structures of Dyes Examined in This Work



mW/cm², YSS-100A, Yamashita Denso) without a mask.²² The values of V_{oc} , J_{sc} , FF, and efficiency of examined DSCs are summarized in Table S1 in the Supporting Information.

Electron diffusion coefficients and lifetimes were measured by stepped light-induced photocurrent and voltage transients.²³ In short, DSCs were irradiated by a diode laser (635 nm, 10 mW, Lablaser, Coherent), and less than 10% of the laser intensity was stepped down. The initial and final intensity were controlled by a PC through a D/A converter. At low laser intensity, a set of neutral density filters was used. For the case of the DSCs with a low amount of dye adsorption, white LED was used instead of the diode laser. Note that the influence of the light source wavelength on the measured D and τ was not seen among blue, red, and white LED. This was probably because the thickness of the TiO₂ was thin enough. Induced transients were measured by a fast multimeter having data storage (AD7461A, Advantest). The measurements were repeated under various laser intensities to measure light

intensity-dependent D and τ . Electron densities at open circuit were measured by a charge extraction method.²⁴ In short, under laser irradiation, bias potential was applied to DSC by a potentiostat (HA5001, Hokuto Denko) to have the condition equivalent to open circuit, and the current transients, induced by switching the intensity and bias potential to zero simultaneously, were measured. Measurements were repeated again under various light intensities to obtain the relationship between V_{oc} and n . Electron density was estimated by the charge obtained by numerical integration of the transients divided by the volume of the TiO₂ electrodes. Note that the porosity was not taken into account for the calculation. Cell capacitance was measured by a method used in a paper by O'Regan et al.²⁵ In short, a DSC was irradiated by a small-intensity 100 μ s pulse (635 nm, Cube, Coherent) over continuous laser irradiation of Lablaser at open circuit conditions. The capacitance was obtained by the charges generated by the laser pulse divided by the increase of V_{oc} induced by the pulse. Amplitude of the V_{oc} increase by the pulse

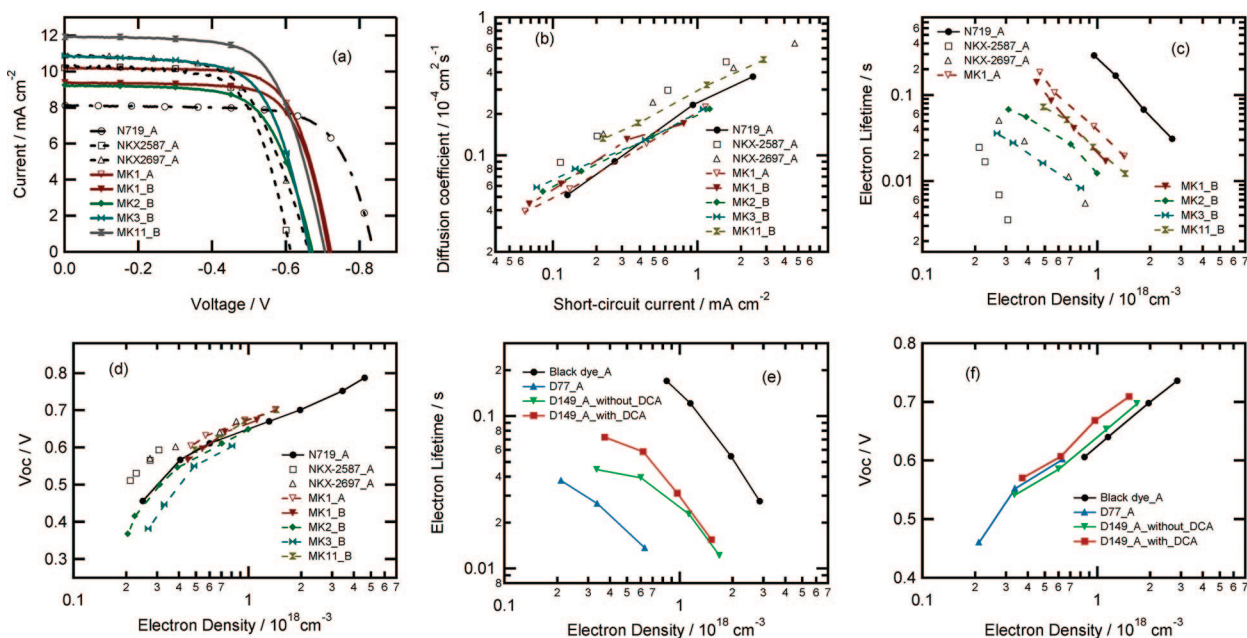


Figure 2. I - V curves under one-sun conditions (a), electron diffusion coefficient in the TiO₂ vs J_{sc} (b), electron lifetime in the TiO₂ vs n (c and e), and V_{oc} vs n (d and f) for the DSCs prepared from the dyes shown in Scheme 1. The letters A and B in parts (a)–(f) denote the cells prepared from dye solution using AN/tBuOH and AN/tBuOH/toluene mixed solvents, respectively. The caption DCA denotes that the DCA was added to the dye solutions. The thickness of the TiO₂ was around 3.5 μ m. Electrolyte consists of 0.1 M LiI, 0.6 M DMPIImI, 0.05 M I₂, and 0.5 M tBP in AN.

was less than 5 mV. All measurements were performed at least with two identical samples. Typical deviation of the value of D was about 15% of the mean values under relatively high light intensity.

Quantum chemical calculations were carried out using Gaussian 03²⁶ and CAChe (ver 6.1, Fujitsu). The structures of organic dyes, which were roughly optimized by a semiempirical AM1 level of theory, were fully optimized at the B3LYP/6-31G(d) level of theory. ISCF calculations with optimized geometries were performed at the B3LYP/6-311+G(d) level of theory. HOMO and LUMO were drawn by Winmostar.²⁷ Partial charge distribution of a Ru complex dye (N3) and optimized NKX2587 on a singlet excitation state were estimated at the ZINDO-CI level of theory using CAChe. Polarizabilities of N3 and the optimized NKX2587 and 2697 dyes were calculated at the B3LYP/LANL2DZ level of theory. A choice of an effective-core potential basis, LANL2DZ, was due to Ru atom in N3 molecule. The structure of N3 was referred from a paper by Shklover et al.²⁸

Results

DSC Using Standard Electrolytes. Figure 2 shows $I-V$ curves, D vs J_{sc} , τ vs n , and V_{oc} vs n of DSCs using standard electrolytes. Under one-sun conditions, all ODSCs showed lower V_{oc} and higher values of J_{sc} in comparison to RuDSCs (Figure 2a). At matched electron density, the ODSCs showed comparable or higher D (Figure 2b) and shorter τ (Figure 2c,e) in comparison to the RuDSCs. The DSC/N719 and /black dye showed comparable τ , which is consistent with a previous report.²⁹ The τ of the DSC/MK1 prepared from dye solvent A, which is used for the Ru dyes, was longer in comparison to that of solvent B, but the τ is still lower than τ in the RuDSC.³⁰ Between the coumarin dyes and between the indoline dyes, larger molecule sized dyes (NKX2697, Figure 2c, and D149, Figure 2e) showed a longer electron lifetime. Among carbazole dyes, having alkyl chains (MK1 in comparison to MK3 in Figure 2c) resulted in longer τ , whereas direct correlation between the number of thiophenes and τ was not seen.

The lower values of V_{oc} for ODSCs under one-sun conditions can be caused by less electron density in the TiO₂ due to shorter τ and positive shift of TiO₂ E_{CB} . Figure 2d shows that, at the matched electron density, V_{oc} differs within 25 mV in comparison to N719, when n is larger than $5 \times 10^{17} \text{ cm}^{-3}$, showing that the E_{CB} is shifted within tens of millivolts. To confirm the shift, the capacitances of the DSCs were measured (Figure 3). The capacitance is related to the density of states of TiO₂ and, thus, can be used to check the shift.^{25,31,32} In comparison to the

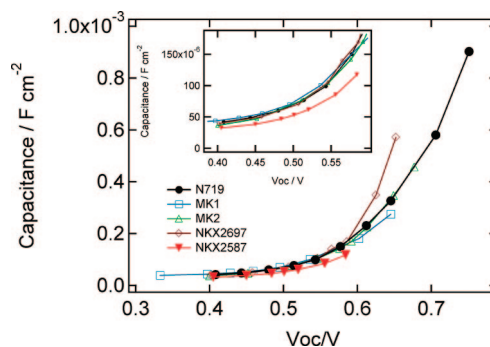


Figure 3. Capacitance of DSCs with various dyes. The electrolyte was the same as that used in Figure 2. Inset shows the same but magnified plot.

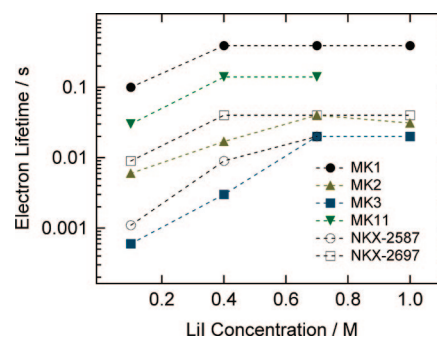


Figure 4. Electron lifetime in DSCs with various concentrations of LiI in AN at an electron density of $1.0 \times 10^{18} \text{ cm}^{-3}$. The concentration of I₂ was fixed at 50 mM for all the electrolytes.

RuDSCs, the result shows that MK1 and 2 showed little influence on the E_{CB} , whereas NKX series causes up to 40 mV negative shift of the E_{CB} . This suggests that the lower V_{oc} for ODSCs in Figure 2a is mainly due to the shorter τ , but not due to the shift of E_{CB} . For the case of the coumarin dyes (Figure 2b), and the indoline dyes (Figure S1–2, Supporting Information), the shorter τ in ODSCs may be partially explained by the observed larger values of D , on the basis of electron-transport limited recombination model.^{33,34} However, the 2 orders of magnitude difference in τ cannot be explained only by the difference of D . The increase of D could be due to the decreased trap density³⁵ and/or different interaction with cations in the electrolyte through ambipolar diffusion mechanism.³⁶ Other possible causes of the short lifetime are the non-negligible recombination to dye cations and/or faster transfer rate to I₃⁻ induced by the adsorption of the organic dyes.

Influence of I⁻ Concentration. Reduction of a dye cation is a competitive process between the electrons in the TiO₂ and I⁻. If the recombination with the dye cation is the origin of short τ , it should be increased with the increase of [I⁻]. Figure 4 shows the τ in ODSCs as a function of LiI concentrations at the electron density of $1 \times 10^{18} \text{ cm}^{-3}$. With the increase of LiI, the τ increased and leveled off. The DSCs/D77 and /D149

- (22) With a mask having the same aperture size as the TiO₂ electrode, typically, 10–20% of the energy conversion efficiency is decreased.
 (23) Nakade, S.; Kanzaki, T.; Wada, Y.; Yanagida, S. *Langmuir* **2005**, *21*, 10803.
 (24) Duffy, N. W.; Peter, L. M.; Rajapakse, R. M. G.; Wijayantha, K. G. U. *Electrochem. Commun.* **2000**, *2*, 658.
 (25) O'Regan, B. C.; Bakker, K.; Kroeze, J.; Smit, H.; Sommeling, P.; Durrant, J. R. *J. Phys. Chem. B* **2006**, *110*, 17155.
 (26) Frisch, M. J.; et al. *Gaussian 03, Revision D.01*; Gaussian, Inc.: Wallingford CT, 2004.
 (27) Senda, N. *Idemitsu Tech. Rep.* **2006**, *49*, 106.
 (28) Shklover, V.; Ovchinnikov, Y. E.; Braginsky, L. S.; Zakeeruddin, S. M.; Grätzel, M. *Chem. Mater.* **1998**, *10*, 2533.
 (29) Miyamoto, K.; Yanagida, M.; Sayama, K.; Sucrihara, H.; Abe, Y. *Chem. Lett.* **2006**, *35*, 336.
 (30) DSCs were prepared also with a dyed TiO₂ with solvent A and rinsed by toluene, the τ of the DSC was shorter than that rinsed by AN. The result implies that the shorter τ is not due to the different adsorption conditions of the dyes. This topic will be addressed further elsewhere.
 (31) O'Regan, B. C.; Lopez-Duarte, I.; Martinez-Diaz, M. V.; Forneli, A.; Albero, J.; Morandeira, A.; Palomares, E.; Torres, T.; Durrant, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 2906.

- (32) This is valid if at least the DOS is not altered by the dye adsorption. The capacitance is also related to the plot of electron density vs V_{oc} , though the integration of capacitance with respect to voltage.
 (33) Nelson, J. *Phys. Rev. B* **1999**, *59*, 15374.
 (34) Kopidakis, N.; Benkstein, K. D.; van de Lagemaat, J.; Frank, A. J. *J. Phys. Chem. B* **2003**, *107*, 11307.
 (35) Nakade, S.; Saito, Y.; Kubo, W.; Kanzaki, T.; Kitamura, T.; Wada, Y.; Yanagida, S. *Electrochem. Commun.* **2003**, *5*, 804.
 (36) Kambe, S.; Nakade, S.; Kitamura, T.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2002**, *106*, 2967.

also showed the same trend. Sufficient LiI concentration giving the constant τ depends on the nature of organic dye. Smaller molecular size dyes tend to show the needs of higher $[I^-]$. This trend seems consistent with Figure 2c; that is, the ODSCs showing shorter τ requires higher $[I^-]$. The results are consistent with the postulation of the recombination with dye⁺ in the ODSCs. However, with high $[I^-]$, the differences in τ still exists among organic dyes and between the Ru dye and organic dyes. In other words, at high $[I^-]$, the recombination with the dye cation is not the major reason for the short lifetime in the ODSCs.

Note that with the increase of LiI concentration, the V_{oc} decreased at the matched electron density (Figure S2, Supporting Information). The decrease was caused by the positive shift of TiO₂ E_{CB} due to the adsorption of Li⁺.³⁷ The positive shift decreases the $\Delta G_{1,2}$, that is, the driving force of electron transfer. Due to the large reorganization energy for I^-/I_3^- ,³⁸ the transfer probably occurs in the Marcus normal region, and thus the decrease of ΔG is expected to decrease the charge-transfer rate. For the case of MK3, when the LiI concentration was increased from 0.4 to 0.7 M, the V_{oc} decreased by only 30 mV, whereas τ was increased by three times. This suggests that the increase of the dye⁺ reduction rate by the increase of $[I^-]$ has significant influence on the electron lifetime.

If the recombination with the dye cation is not the major reason for the short lifetime, the short lifetime should be induced by accelerated recombination with I_3^- . Further experiments were performed by measuring τ by open circuit voltage decay at dark conditions.³⁹ At dark, by applying negative potential by a potentiostat, electrons were injected from the FTO to the TiO₂ in the DSC. Then, it was switched from the potentiostat to the electrometer (high impedance) mode, and transient response of DSC's voltage was monitored.⁴⁰ Since there is no dye cation, the difference of the lifetime must be related to the rate of the recombination with I_3^- . The results are shown in Figure S3, Supporting Information. Shorter lifetime with the DSCs/MK3 was seen in comparison to that of DSCs/N719, supporting the faster recombination with I_3^- for the case of MK3.

Influence of Adsorbed Dye Concentration. It has been reported that adsorption of N719 would decrease the $[I_3^-]$ in the vicinity of the TiO₂ surface.⁴¹ Among organic dyes, the longer lifetime observed with MK1 seems to be explained by the alkyl chains attached to the carbazole dyes, blocking the approaches of I_3^- and/or cations to the surface of TiO₂, and the shorter lifetime with MK3 could be due to the lack of the blocking function. This possibility can be checked by reducing the amount of adsorbed dyes. Figure 5 shows τ vs n in the DSCs having full and half to one-fifth of the amount of adsorbed dyes, where the amounts were estimated from the values of J_{sc} under one-sun conditions (Figure S4, Supporting Information). In the case of N719, and MK1, τ decreased with the reduction of the adsorbed dyes, suggesting the blocking effect. On the other hand, MK3 and NKX2587 showed a little decrease or the same τ with the decrease of the amount of the dyes, respectively, suggesting inefficient blocking effect for these dyes. Between the DSCs/

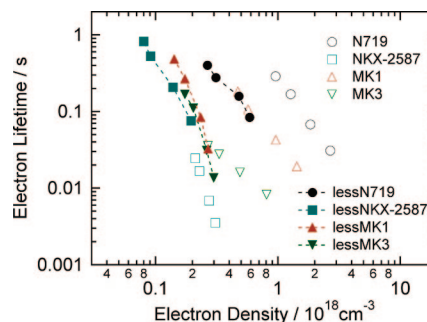


Figure 5. Electron lifetime in DSCs with full and partial (denoted as less) dye loading. The amounts of dyes were about $1/5$, $1/3$, $1/2$, and $1/6$ of those of the fully loaded DSCs/N719, MK1, MK3, and NKX2587, respectively. The amount of adsorbed dyes for the fully loaded DSCs/MK3 was about 2 times higher than that of the fully loaded DSCs/N719. The light source of the measurement was a diode laser.

less N719 and DSCs/full MK3, the amount of MK3 was estimated to be about nine times higher than that of N719. However, DSCs/MK3 still showed shorter τ , implying increased $[I_3^-]$ in the vicinity of TiO₂ with MK3. Under less dye concentrations, the same values of τ regardless of the structure of dyes may be expected. This is because, from the viewpoint of accessibility for I_3^- to approach the TiO₂ surface, the same conditions of the exposed TiO₂ surface are expected. Thus, for DSCs/N719 and MK3, the amount of the dyes was further decreased, and the lifetime was measured (Figure 6). In the case of N719, the lifetime decreased with the decrease of the dye amount. On the other hand, DSCs/MK3 showed a decrease when the amount was reduced from full to $1/5$ and an increase when the amount was decreased further to $1/30$. At the low amount, the lifetimes in both DSCs became close in value as expected. On the other hand, the increase of the lifetime for the DSCs/MK3, observed when the dye was reduced from $1/5$ to $1/30$, suggests that the dye has two effects: one is the blocking effect and another is the attraction of I_3^- . For the case of porphyrin dye, complex formation with I_3^- has been reported by Splan et al.,⁴² consistent with the latter effect. The inset of Figure 6 shows the dark $I-V$ for the DSCs. For N719, the overpotential decreased, approaching the values of the cell without dye (bare cell). On the other hand, the DSCs/full and $1/5$ amounts of MK3 show lower overpotential in comparison to that of the bare cell, and the overpotential increased with the further decrease of the amount of dye. The results are again consistent with the postulation that the MK3 increases the $[I_3^-]$ at the surface. Such lower overpotential was also seen with other organic dyes examined here. Similar results were reported also with other organic dyes,^{43,44} Os complex dyes,⁴⁵ and phthalocyanine dyes.³¹

Discussions

Electron Transfer to I_3^- . Experimental results suggest that all the ODSCs examined here suffer from the increased rate of recombination with I_3^- . The parameters influencing this transfer rate are ΔG_1 , λ_1 , and $[I_3^-]$. Since ΔG_1 and λ_1 are expected to be independent from the amount of the adsorbed dyes, the results in Figures 5 and 6 suggest that $[I_3^-]$ in the vicinity of TiO₂

(37) Watson, D. F.; Meyer, G. J. *Coord. Chem. Rev.* **2004**, *248*, 1391.

(38) Martinson, A. B. F.; Hamann, T. W.; Pellin, M. J.; Hupp, J. T. *Chem.-Eur. J.* **2008**, *14*, 4458.

(39) Zaban, A.; Greenshtein, M.; Bisquert, J. *ChemPhysChem* **2003**, *4*, 859.

(40) Bisquert, J.; Zaban, A.; Greenshtein, M.; Mora-Sero, I. *J. Am. Chem. Soc.* **2004**, *126*, 13550.

(41) Nakade, S.; Kanzaki, T.; Kubo, W.; Kitamura, T.; Wada, Y.; Yanagida, S. *J. Phys. Chem. B* **2005**, *109*, 3480.

(42) Splan, K. E.; Massari, A. M.; Hupp, J. T. *J. Phys. Chem. B* **2004**, *108*, 4111.

(43) Burke, A.; Ito, S.; Snaith, H.; Bach, U.; Kwiatkowski, J.; Gratzel, M. *Nano Lett.* **2008**, *8*, 977.

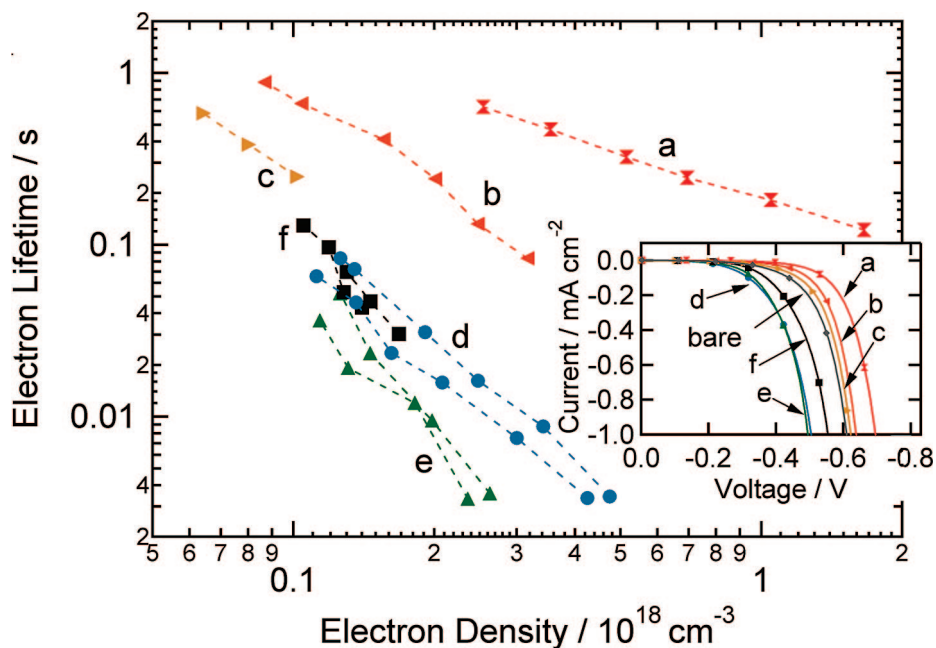


Figure 6. Electron lifetime in DSCs with various amounts of N719 (a,b,c), and MK3 (d,e,f). Inset shows dark $I-V$ curves of the DSCs and a DSC without dye adsorption (bare). The amounts of adsorbed dyes were full (a), $1/4$ (b), $1/13$ (c), full (d), $1/5$ (e), and $1/30$ (f). The light source of the measurement was a white LED.

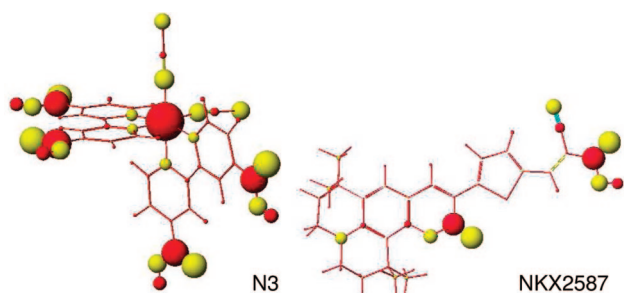


Figure 7. Partial charge distribution of N3 and NKX2587 dyes. Yellow (light) and red (dark) spheres represents negative and positive charges, respectively.

surface depends on the structure of adsorbed dyes. To examine the difference among the dyes, the dipole moment, polarizability, and partial charge distribution of the dyes were calculated. Figure 7 shows the partial charges of N3 and NKX2587. Both show negative charges at the carboxyl group. Besides, a negative charge is at the oxygen in the coumarin framework in NKX2587, whereas large positive charge is at the Ru atom and negative charges are at the NCS ligands. Furube et al. has reported that the energy of NKX2311, which is a coumarin derivative having the same adsorption site as NKX2587, is lowered when Li^+

exists close to the oxygen in the carboxyl group.⁴⁶ Such interaction turns the charges at the absorption site to positive, and starts attracting anions such as I_3^- , resulting in a close proximity to the TiO_2 surface.

The TiO_2 conduction band can be shifted due to the formation of the surface dipole layer. The relationship between the dipole moment of co-adsorbants and V_{oc} has been studied systematically, showing that the negative dipole moment, that is, the negatively charged part of a molecule that is located close to the TiO_2 surface, results in larger V_{oc} .⁴⁷ The dipole moments of the dyes examined here are negative for organic dyes and positive for the Ru dye. This means that larger V_{oc} can be expected with the organic dyes, whereas the experimental results showed the opposite. The results can be interpreted as follows: the negatively charged carboxyl group, which is the origin of the negative dipole moment of the examined organic dyes, interacts with electrolyte cations.

In the case of N719, Li^+ and DMPIm^+ in electrolytes would feel attractive force from the NCS ligands or nonbonded carboxyl groups at the bipyridine moieties, and then, I_3^- would feel attractive force from the cations, increasing the mean distance between I_3^- and the TiO_2 . The long τ observed in the DSCs using other Ru dyes; black dyes and Ru505 (Figure S9, Supporting Information), can also be explained with this model. These results show that the effect depends on the location of negatively charged atoms in the dye molecule and the structure and size of electrolyte cations. The atomic/molecular size of the cation is an important factor because the size would limit the accessibility to the negatively charged atoms.⁴⁸

(44) Reference 43 reports that electron transfer from FTO to I_3^- is significant for DSC using organic dyes, and it was suppressed largely by introducing a compact layer on the FTO. We have checked the influence of TiCl_4 treatment on nanoporous TiO_2 electrode, and a similar effect was seen between MK3 and N719 (Figure S7, Supporting Information), suggesting the recombination from FTO is not the reason for the lower V_{oc} in the case of DSC/MK3. We have checked also the effect of the compact layer for our samples and observed the non-negligible recombination from the FTO when the electron density becomes lower than $2 \times 10^{17} \text{ cm}^{-3}$. Under these conditions, the electron lifetime and Fermi level are underestimated. Above the electron concentration, little influence was seen.

(45) Sauvè, G.; Cass, M. E.; Coia, G.; Doig, S. J.; Lauermaun, I.; Pomykal, K. E.; Lewis, N. S. *J. Phys. Chem. B* **2000**, *104*, 6821.

(46) Furube, A.; Katoh, R.; Hara, K.; Sato, T.; Murata, S.; Arakawa, H.; Tachiya, M. *J. Phys. Chem. B* **2005**, *109*, 16406.

(47) Ruhle, S.; Greenshtein, M.; Chen, S. G.; Merson, A.; Pizem, H.; Sukenik, C. S.; Cahen, D.; Zaban, A. *J. Phys. Chem. B* **2005**, *109*, 18907.

(48) Among organic dyes, NKX2587 showed the lowest V_{oc} with shortest lifetime under the standard electrolyte, whereas MK3 showed the lowest V_{oc} with electrolyte containing only LiI (Table S1, Supporting Information). These show different interactions of these dyes with electrolytes. Influence of tBP for the case of organic dyes is also interesting but this topic will be addressed elsewhere.

Intermolecular force between the dyes and I_3^- could also increase the $[I_3^-]$ in the vicinity of the TiO_2 ,⁴⁹ without the aid of the electrolyte cations. London dispersion force is related to the polarizability of the molecules.⁵⁰ The calculated polarizabilities were 106, 68, and 112 Å³ for N719, NKX2587, and NKX2697, respectively. Since the difference among the dyes seems to be too small for explaining the large difference of the electron lifetime, at least for these organic dyes, the dispersion force is less likely to be the reason for the high $[I_3^-]$. On the other hand, for the case of oligoene dyes,^{11,51} an increase of the molecular size seems to decrease the electron lifetime, and for these dyes, the dispersion force may have a more important role.

Blocking Effect by Adsorbed Dye. In Figure 5, with the decrease of the amount of adsorbed dyes, the DSC/N719 and /MK1 showed the decreases of τ , whereas DSC/MK3 and /NKX2587 showed a little and no decrease, respectively. When the electrolyte containing only TBAI and I_2 was used, τ in the DSC/MK1 became shorter than that in the DSC/MK1 using only LiI and I_2 (Figure S6, Supporting Information). This is opposite from the case of N719.⁴¹ These results suggest that the adsorbed MK1 layers block the approaches of I_3^- , but not the cations. It was shown by AFM that the MK2 aggregates on the TiO_2 surface, despite the expectation that the alkyl chain could suppress the aggregation.⁵² The case of MK2 suggests that MK1 is also aggregated. Another report showed that the alkyl chain itself would not increase the lifetime when I^-/I_3^- containing electrolyte solutions were employed.⁵³ Here, the blocking effect by MK1 would be caused by the aggregation of the dyes and not by the blocking effect of the alkyl chain itself. There was no clear trend for the lifetime among DSCs using MK1, 2, and 11, and this may be explained by the different conditions of aggregation.

Dye Cation Reduction Rate. Figure 4 shows that organic dyes need a higher concentration of I^- , suggesting that the dye cation reduction rates are slower than that of N719. The parameters influencing the reduction rate is ΔG_3 , λ_3 , and $[I^-]$. Organic dyes having similar ground-state oxidation potentials, e.g., NKX 2587 and 2697 dyes,²¹ showed different $[I^-]$ -dependent τ . This could be related to the difference in the reorganization energy, λ_3 , and/or the difference in the manner of complex formation with I^- .⁵⁴

The λ_s for dye⁺ having ellipsoidal structure may be written as

$$\lambda_s = \frac{1}{4\pi\epsilon_0 ab^2} \left(\frac{1}{n_r^2} - \frac{1}{\epsilon} \right) \sum_{n=0}^{\infty} \frac{1}{2} [1 - (-1)^n] (2n+1) \lambda_0 (\lambda_0^2 - 1) Q_n(\lambda_0) / P_n(\lambda_0) \quad (3)$$

where r is a distance between donor and acceptor, n_r is the refractive index, a and b are the radii of the ellipsoid, $\lambda_0^2 = a^2/(a^2 - b^2)$.⁵⁵ The λ_s was calculated for NKX2587, NKX2697,

and a Ru dye without TBA⁺ (N3 dye) in AN. The results show lower λ_s for NKX2697 than for NKX2587 (Table S2, Supporting Information), consistent with the postulation. However, we cannot exclude the possible effect of complex formation with electrolytes, and this needs to be substantiated further by other experiments such as transient absorption of these dye⁺. The calculation also shows comparable values between N3 and NKX2587, which cannot explain the fast reduction of N719 cation. In the case of λ for Ru complex dyes, a recent paper shows that the λ is decreased by its adsorption on the TiO_2 surface.⁵⁶ The mechanism of the decrease is not clear yet, and it was addressed to be the increase of rigidity of the dye molecule and/or inaccessibility of solutions between the TiO_2 surface and dyes. For the case of organic dyes examined here, they have only one adsorption site, i.e., one carboxyl group, and have ellipsoidal structures. Thus, when they are adsorbed onto TiO_2 , the difference of λ between the Ru dyes and organic dyes may be much larger than the values obtained by eq 3, which do not include the effect of adsorption. In other words, the τ in ODESCs would be increased by adding another adsorption site to these organic dyes.

Implications to DSCs. To increase the efficiency of ODESCs, an increase of the electron lifetime is essential. Our results suggest that the high concentration of I_3^- at the TiO_2 surface was induced by the adsorption of the organic dyes. This was interpreted with undesired distribution of negatively charged atoms in the organic dyes. Whereas the increased $[I_3^-]$ was suggested as the most critical factor, larger λ of the dyes and higher D would also decrease the electron lifetime. Inefficient reduction of organic dye cation by I^-/I_3^- redox couple has been pointed out also by another group recently.⁵⁷ A comparison among the examined dyes suggests that larger molecular size and aggregation of dyes are effective at increasing the dye⁺ reduction rate and obtaining blocking effect, respectively, and consequently increasing the lifetime. In the MK series, there was no simple correlation with the number of thiophenes and the lifetime, in spite of the expectation of the increase of τ_2 due to the longer distance to donor moiety. However, molecular orbital calculations show that HOMO is delocalized with the increase of thiophene, and thus, the distance was probably not increased as expected. In addition, eq 3 shows that the increase of radius along the major axis does not decrease λ very much, implying the limitation of the strategy. These considerations show that a spherical molecular structure would be desired.

In a comparison between NKX2697 and MK3, the only difference in the molecular structure is the donor moiety. However, there was a large difference in the electron lifetime. Spatial locations of HOMO and LUMO are similar between the dyes (Figure S8, Supporting Information). The difference seems to be related to λ (Table S2, Supporting Information), in addition to the partial charge distribution of the molecules. Locating negatively charged oxygen far from the adsorption site would be beneficial in view of the distance between the TiO_2 surface and I_3^- . This trend is seen also between D77 and D149.

Electron lifetimes in dye-sensitized solar cells have been measured with various metal complex dyes. Among Ru complex dyes, N719 has shown superior performance and it has been interpreted with the packing density of the adsorbed dyes.⁵³ On the other hand, biquinoline Ru complex dyes have shown fast

(49) This was pointed out during the reviewing process.

(50) London, F. *Trans. Faraday Soc.* **1937**, *33*, 8.

(51) Hagberg, D. P.; Marinado, T.; Karlsson, K. M.; Nonomura, K.; Qin, P.; Boschloo, G.; Brinck, T.; Hagfeldt, A.; Sun, L. *J. Org. Chem.* **2007**, *72*, 9550.

(52) Wang, Z.-S.; Koumura, N.; Cui, Y.; Takahashi, M.; Sekiguchi, H.; Mori, A.; Kubo, T.; Furube, A.; Hara, K. *Chem. Mater.* **2008**, *20*, 3993.

(53) Mori, S. N.; Kubo, W.; Kanzaki, T.; Masaki, N.; Wada, Y.; Yanagida, S. *J. Phys. Chem. C* **2007**, *111*, 3522.

(54) Clifford, J. N.; Palomares, E.; Nazeeruddin, M. K.; Gratzel, M.; Durrant, J. R. *J. Phys. Chem. C* **2007**, *111*, 6561.

(55) Cannon, R. D. *Chem. Phys. Lett.* **1977**, *49*, 299.

(56) Shoute, L. C. T.; Loppnow, G. R. *J. Am. Chem. Soc.* **2003**, *125*, 15636.

(57) Tatay, S.; Haque, S. A.; O'Regan, B.; Durrant, J. R.; Verhees, W. J. H.; Kroon, J. M.; Vidal-Ferran, A.; Gavina, P.; Palomares, E. *J. Mater. Chem.* **2007**, *17*, 3037.

charge recombination.⁵⁸ So far, phthalocyanine³¹ and porphyrin⁵⁹ dyes have also shown shorter electron lifetimes than those of N719. These results suggest that employing the metal complex itself does not have an advantage in view of electron recombination in DSCs, but the structure and packing density of sensitizing dyes are essential. The structure here is meant to screen the positively charged metal center, and to increase the adsorption density at the TiO₂ surface.

Conclusions

To investigate the influence of organic dye structure on the electron lifetime in the TiO₂ electrode of DSCs, eight organic dyes and three Ru complex dyes were examined with various electrolytes. All organic dyes showed shorter electron lifetime in comparison to the Ru dyes. Among organic dyes, those having larger molecular size and alkyl chain showed longer lifetime.

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- (58) Yanagida, M.; Miyamoto, K.; Sayama, K.; Kasuga, K.; Kurashige, M.; Abe, Y.; Sugihara, H. *J. Phys. Chem. C* **2007**, *111*, 201.
(59) Mozer, A. J.; Wagner, P.; Officer, D. L.; Wallace, G. G.; Campbell, W. M.; Miyashita, M.; Sunahara, K.; Mori, S. *Chem. Commun.* **2008**, 4741.

The results were attributed to the difference in reorganization energy, electron transport rate in the TiO₂, degree of blocking effect, and most importantly, high I₃⁻ concentration in the vicinity of the TiO₂ surface. This was interpreted with the difference in the partial charge distribution in the dye molecules. To increase the electron lifetime further for ODSCs, the results suggest that spherical and large molecular structure and two adsorption sites to decrease the reorganization energy, wider distribution of charged atoms to control I₃⁻ concentration at the TiO₂ surface, and packing density of dyes to block the approaches of I₃⁻ are essential.

Supporting Information Available: *I*-*V* characteristics, electron lifetime, electron diffusion coefficients, electron density, and comparisons of lifetimes at dark conditions for DSC with Ru and organic dyes with various electrolytes, and with and without TiCl₄ treatment, and molecular orbital calculations; complete reference 26. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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