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# Photocurrents of solar cells sensitized by aggregate-forming polyenes: Enhancement due to suppression of singlet-triplet annihilation by lowering of dye concentration or light intensity

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### Abstract

Titania-based Grätzel-type solar cells were fabricated by the use of polyene dyes with various transition dipole moments. In the dye having the largest transition dipole among the samples, an aggregate was readily formed through dispersive interaction, and the photocurrent was increased when the dye concentration or the light intensity was lowered. This observation was ascribed to the suppression of the singlet-triplet annihilation reaction. In the dye having the smallest transition dipole, there was no sign of aggregate formation, and the photocurrent was decreased when the dye concentration or the light intensity was lowered.

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### 1. Introduction

The geometrical arrangement and the excited-state dynamics of the dye molecules on the surface of the TiO<sub>2</sub> layer must strongly affect the performance of dye-sensitized solar cells (DSSCs): It is well documented that formation of dye aggregates suppresses the performance [1] and that prevention of aggregate formation by co-adsorption of spacers [2,3] or by structural modification of dye sensitizer [4] can solve this problem. It is also shown that high lightintensity can sometimes suppress the performance of DSSCs [5,6]. All those observations have never been explained systematically, as far as we know.

In our previous study [7], we fabricated TiO<sub>2</sub>-based DSSCs using a series of retinoic acid and carotenoic acids (RA and CAs) as dye sensitizers having the number of conjugated double bonds, n = 5-13. The incident photon-to-

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current conversion efficiency (IPCE) as well as the solar energy-to-electricity conversion efficiency (to be called conversion efficiency,  $\eta$ ) were the highest for the CA having 7 conjugated double bonds (CA7), and the IPCE and the  $\eta$ values declined toward n = 5 and n = 13 (from 1.5% to 1.0% and 0.3%, respectively) (see Table 1 of Supplementary Information of Ref. [7]). For CA7, we examined the effect of dilution with deoxycholic acid as a spacer on the performance. At various concentrations, we scaled the abovementioned values to those per unit concentration and then divided by the value at 100% to obtain the enhancement factors. They monotonically increased with the decreasing concentration and reached a value as high as  $\approx 9-10$  times at the 10% dye concentration (see Fig. 4 of Ref. [7]). The result indicated that isolated excitation was the best to obtain the highest performance per unit dye molecule.

In another study [8], we examined the excited-state dynamics of RA5 and CA6-CA11 bound to TiO2 nanoparticles in suspension by sub-ps and sub-us time-resolved absorption spectroscopy. The electron-injection efficiency

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 $(\Phi)$  immediately after excitation to the 1B<sup>+</sup><sub>u</sub> singlet state was as high as 98% in CA7, and declined toward n = 11 (29%). However, the  $\Phi$  value declined only slightly toward n = 5(92%), contrary to the above-mentioned large decline of  $\eta$ . On the other hand, the efficiency of triplet generation increased systematically from 75% to 92% on going from CA7 to RA5.

Based on these results, we ascribed the decline of the performance of DSSCs from CA7 to RA5 to an increasing singlet-triplet annihilation reaction in the aggregate of the dve molecules [7].

The present investigation has been planned to establish this idea: We have synthesized a series of polyene dyes having various transition-dipole moments, and as a result, different potentials of aggregate formation through the dispersive (van der Waals) interaction. Then, we fabricated DSSCs by the use of those polyenes as sensitizers at various concentrations. In order to prove the idea, we have examined the effect of dilution of each dye sensitizer with deoxycholic acid on the performance of the DSSCs, addressing two questions: First, how does the lowering of the dye concentration (to suppress singlet-triplet annihilation) affect the photocurrent and the conversion efficiency?

To achieve definitive evidence for the mechanism of singlet-triplet annihilation, we have also examined the effect of light intensity. We have addressed the second question: How does the lowering of the light intensity (to suppress singlet-triplet annihilation) affect the photocurrent in the DSSCs using those dye sensitizers?

# 2. Experimental

The set of polyene dyes in Scheme 1 was synthesized starting from commercially available or synthesized [9] benzaldehyde derivatives via the Emmons-Horner reaction with two different kinds of  $C_5$ -phosphonate [10] and a  $C_{10}$ phosphonate [11], as shown in Scheme S-1 in supplementary information, where  $\phi$ -6-CA, MeO- $\phi$ -6-CA, (MeO)<sub>3</sub>- $\phi$ -6-CA and Me<sub>2</sub>N- $\phi$ -6-CA are named **6a**, **6b**, **6c** and **6d**, respectively. The details of syntheses and spectroscopic characterizations of relevant compounds are also described in Supplementary Information.

The transition dipole moment,  $\mu_{obs}$ , of each compound was determined spectroscopically from the molar extinction coefficient as a function of energy by [12]

$$\left|\mu_{\rm obs}\right|^2 = 91.86 \times 10^{-4} \cdot n \cdot \int \frac{\varepsilon(\bar{\nu})}{\bar{\nu}} d\bar{\nu},\tag{1}$$

where *n* is the refractive index of solvent,  $\bar{v}$  is the energy in  $cm^{-1}$  and  $\mu_{obs}$  is the transition dipole in debye. The corresponding value,  $\mu_{calc}$ , was calculated by the INDO/S SCI method [13] after the optimization of the molecular geometry by the MOPAC PM3 method [14]. Similar values were also obtained by the INDO/S method.

Each DSSC was fabricated, and its IPCE and *I*–*V* curves were recorded [15]. Concerning the concentration dependence, we assumed that the composition of each dye and



Scheme 1.

deoxycholic acid (spacer) in THF solution was conserved after deposition on the TiO<sub>2</sub> layer.

### 3. Results and discussion

### 3.1. Characterization of dye sensitizers

The dye sensitizers used in this study (Scheme 1) are analogues of carotenoic acids, consisting of a conjugated chain having 6 double bonds, and one of the phenyl, methoxyphenyl, tri-methoxyphenyl and N-dimethylphenyl groups attached to it. According to their chemical structures, we call them ' $\phi$ -6-CA', 'MeO- $\phi$ -6-CA', '(MeO)<sub>3</sub>- $\phi$ -6-CA' and 'Me<sub>2</sub>N- $\phi$ -6-CA', respectively. Table 1 compares the observed and calculated  $\mu$  values. The  $\mu_{obs}$  values increase systematically in the order,  $\phi$ -6-CA  $\leq$  MeO- $\phi$ -6- $CA \leq (MeO)_3 - \phi - 6 - CA \leq Me_2 N - \phi - 6 - CA$ . The  $\mu_{calc}$  values exhibit much smaller differences.

In the electronic spectra of the dye sensitizers in THF solution, shown in Fig. 1a, the  $1B_{\mu}^{+}$  profile manifests a systematic red shift, and its intensity decreases in the order,  $\phi$ -6-CA, MeO- $\phi$ -6-CA, (MeO)<sub>3</sub>- $\phi$ -6-CA and Me<sub>2</sub>N- $\phi$ -6-CA; the absorption maxima are indicated in the figure and listed in Table 1. As for the dye sensitizers deposited on the  $TiO_2$ layer, all the absorption profiles are broadened, as shown in Fig. 1b. The absorption maxima exhibit a systematic red shift and decrease in the case of  $\phi$ -6-CA, MeO- $\phi$ -6-CA and  $(MeO)_3-\phi-6-CA$ ; the profile of Me<sub>2</sub>N- $\phi-6-CA$ may be slightly shifted to the blue due to partial aggregation on the TiO<sub>2</sub> surface. (The aggregated states are expected to give rise to the  $1B_u^+$  absorption below 350 nm.) Fig. 1c shows the absorption spectra of the dyeTable 1

 $1B_u^+$  energies, molar extinction coefficients ( $\varepsilon_{max}$ ) both at absorption maxima, oscillator strengths (*f*), transition dipole moments determined spectroscopically ( $\mu_{obs}$ ), and those determined theoretically ( $\mu_{calc}$ ) for a set of dye sensitizers

Dye	$1 B_u^+$ energy/cm <sup>-1</sup>	$\epsilon_{\rm max}/{ m M}^{-1}$ cm <sup>-1</sup>	$f^{\mathbf{a}}$	$\mu_{\rm obs}/{\rm D}$	$\mu_{\rm calc}/\Gamma$
ф-6-CA	24067	89100	2.3	14.2	15.3
MeO-φ-6-CA	23696	85800	2.5	15.1	15.4
(MeO) <sub>3</sub> -\$-6-CA	22779	75300	2.5	15.2	15.4
Me <sub>2</sub> N- $\phi$ -6-CA	22321	72100	2.6	15.6	15.6

<sup>a</sup> Calculated by  $f = 4.71 \times 10^{-7} \cdot \bar{\nu}_{\text{max}} \cdot |\mu_{\text{obs}}|^2$ .



Fig. 1. Electronic absorption spectra of dye sensitizers (a) in THF solution, and those adsorbed on the  $TiO_2$  layer at the concentrations of (b) 5% and (c) 100%.

sensitizers deposited on the TiO<sub>2</sub> layer without dilution (100%). The profiles are similar to one another, probably reflecting the blue shift of absorption due to the formation of aggregates in (MeO)<sub>3</sub>- $\phi$ -6-CA and Me<sub>2</sub>N- $\phi$ -6-CA. Thus,

the trend is shown that the dyes having larger transition dipoles have higher potentials of aggregate formation in the dyes.

# 3.2. Dependence of photocurrent and conversion efficiency on the dye concentration

Fig. 2 shows the dependence of the IPCE profiles on the dye concentration in DSSCs: These profiles, as action spectra for generation of the photocurrent, indicate that  $\phi$ -6-CA and MeO- $\phi$ -6-CA are rather in the monomeric state, whereas (MeO)<sub>3</sub>- $\phi$ -6-CA and Me<sub>2</sub>N- $\phi$ -6-CA are in the aggregated state at 100%. The latter two transform to the monomeric state at 5%. The effect of dilution can be summarized as follows: (i) The photocurrent systematically decreases in  $\phi$ -6-CA, whereas it increases in Me<sub>2</sub>N- $\phi$ -6-CA on going from 100% to 5%; (ii) MeO- $\phi$ -6-CA and (MeO)<sub>3</sub>- $\phi$ -6-CA exhibit two phases of rise and decay with decreasing dye concentration, and the highest IPCE profiles appear at 70% and 10%, respectively.

Fig. 3 shows the dependence of the I-V curves on the dye concentration in DSSCs: In  $\phi$ -6-CA, the  $J_{\rm sc}$  value decreases monotonically with the dye concentration lowered from 100% to 5%. In MeO- $\phi$ -6-CA, the  $J_{\rm sc}$  value jumps up from 100% to 70% and then declines gradually toward 5%. For these sensitizers, the  $V_{\rm oc}$  values are similar to one another at different concentrations.

For (MeO)<sub>3</sub>- $\phi$ -6-CA, the  $J_{\rm sc}$  value jumps up from 100% to 70% and stays almost unchanged, whereas the  $V_{\rm oc}$  value increases at lower concentrations, which probably reflects an improvement of the molecular packing supported by the spacer, because the bulky head group, (MeO)<sub>3</sub>- $\phi$ , may prevent close packing of the dye molecules by themselves (see Scheme 1). For Me<sub>2</sub>N- $\phi$ -6-CA, however, the  $J_{\rm sc}$  and  $V_{\rm oc}$  values both increase systematically at lower concentrations (except for an anomaly at 30%, which may be an artifact). It is highly likely that the  $J_{\rm sc}$  value increases due to the suppression of singlet–triplet annihilation, while the  $V_{\rm oc}$  value increases due to the better molecular packing supported by the spacer.

Table 2 lists the values relevant to the performance of DSSCs extracted from the *I*–*V* curves. The highest  $\eta$  values, 2.2%, 2.6%, 1.8% and 1.2%, are obtained for  $\phi$ -6-CA, MeO- $\phi$ -6-CA, (MeO)<sub>3</sub>- $\phi$ -6-CA and Me<sub>2</sub>N- $\phi$ -6-CA at the dye concentrations of 100%, 70%, 10% and 5%, respectively. The conversion efficiency scaled to a unit concentration,  $\eta_{\rm u}$ , increases monotonically toward the lowest concentration, 5%, for all the sensitizers. The enhancement factor of the conversion efficiency per unit concentration,  $\eta_{\rm e}$ , with reference to the value at 100%, increases as 12, 17, 31 and 60 times for  $\phi$ -6-CA, respectively.

The conversion efficiency,  $\eta$ , as observed, decreases monotonically with the decreasing dye concentration, as shown in Fig. 4. The trend for  $\phi$ -6-CA is obviously ascribed to the decrease in the number of dye molecules.



Fig. 2. Dependence of the IPCE profiles on the concentration of dye sensitizers in DSSCs.



Fig. 3. Dependence of the I-V curves on the dye concentration in DSSCs.

On the other hand, the monotonic increase in  $\eta$  for Me<sub>2</sub>N- $\phi$ -6-CA is most probably due to the suppression of singlet-triplet annihilation. For MeO- $\phi$ -6-CA and (MeO)<sub>3</sub>- $\phi$ -6-CA, the effect of lowering concentration consists of two phases: at an early rising phase of  $\eta$  by the sup-

pression of singlet-triplet annihilation, and a later declining phase due to the decreasing number of dye molecules available for excitation. As a result, they reach maxima at 70% and 10%, respectively. Table 2

	Concentration%	$J_{\rm sc}/{\rm mAcm^{-2}}$	$V_{\rm oc}/{ m V}$	FF	$\eta\%$	$\eta_{ m u}{}^{ m a}$	$\eta_e^{b}$
φ-6-CA	100	7.0	0.54	0.59	2.2	2.2	1
	70	6.2	0.57	0.60	2.1	3.0	1.4
	50	6.1	0.57	0.55	1.9	3.8	1.7
	30	5.9	0.55	0.50	1.6	5.3	2.4
	10	4.7	0.55	0.59	1.5	15	6.8
	5	4.2	0.57	0.55	1.3	26	12
MeO-φ-6-CA	100	5.9	0.59	0.63	2.2	2.2	1
	70	7.4	0.59	0.61	2.6	3.7	1.7
	50	6.3	0.59	0.62	2.3	4.6	2.1
	30	6.5	0.57	0.62	2.3	7.7	3.5
	10	6.0	0.59	0.61	2.2	22	10
	5	5.3	0.59	0.63	1.9	38	17
(MeO) <sub>3</sub> -φ-6-CA	100	3.6	0.51	0.60	1.1	1.1	1
	70	4.9	0.52	0.59	1.5	2.1	1.9
	50	4.6	0.55	0.61	1.6	3.2	2.9
	30	4.7	0.56	0.61	1.6	5.3	4.8
	10	5.3	0.57	0.60	1.8	18	16
	5	4.7	0.59	0.61	1.7	34	31
Me <sub>2</sub> N-φ-6-CA	100	1.8	0.41	0.55	0.4	0.4	1
	70	2.7	0.45	0.59	0.7	1.0	2.5
	50	3.2	0.45	0.59	0.8	1.6	4.0
	30	3.0	0.48	0.61	0.9	3.0	7.5
	10	3.4	0.49	0.60	1.0	10	25
	5	3.7	0.50	0.63	1.2	24	60

Concentration dependence of parameters relevant to photo-conversion efficiency, inclusing the values of short-circuit photocurrent ( $J_{sc}$ ), open-circuit photovoltage ( $V_{oc}$ ), Fill factor (*FF*) and conversion efficiency ( $\eta$ )

<sup>a</sup>  $\eta_{\rm u} = 100\eta/\text{concn.}$ 

<sup>b</sup>  $\eta_{\rm e} (x^{\rm 0}) = \eta_{\rm u}(x^{\rm 0})/\eta_{\rm u}(100^{\rm 0}).$ 

As for the enhancement factor,  $\eta_e$ , the monotonic increase with the concentration, shown in Table 2, suggests that the conversion efficiency is strongly suppressed by *aggregate formation*, and the resultant *singlet-triplet annihilation*, in the order:  $\phi$ -6-CA  $\leq$  MeO- $\phi$ -6-CA  $\leq$  (MeO)<sub>3</sub>- $\phi$ -6-CA  $\leq$  Me<sub>2</sub>N- $\phi$ -6-CA.

# 3.3. Dependence of the photocurrent on the light intensity

The observed effect at the dye concentrations of 100% and 5%, shown in Fig. 5, can be summarized as follows: (i) The  $V_{oc}$  value systematically decreases in all the dye sensitizers tested at these concentrations; (ii) Most importantly, the  $J_{sc}$  value systematically decreases for  $\phi$ -6-CA, but it increases for Me<sub>2</sub>N- $\phi$ -6-CA at both concentrations; (iii) For both MeO- $\phi$ -6-CA and (MeO)<sub>3</sub>- $\phi$ -6-CA, the  $J_{sc}$  values increase even at 100%. At 5%, however, the  $J_{sc}$  value for the former decreases, whereas that for the latter stays unchanged. The dependence on the light intensity is hardly affected by the concentration in  $\phi$ -6-CA and Me<sub>2</sub>N- $\phi$ -6-CA, but it is slightly affected in MeO- $\phi$ -6-CA and (MeO)<sub>3</sub>- $\phi$ -6-CA.

On lowering the light intensity, a decrease in the photocurrent is clearly observed for  $\phi$ -6-CA having a small transition dipole (naturally expected), whereas an increase in the photocurrent is seen for Me<sub>2</sub>N- $\phi$ -6-CA, which has a large transition dipole (rather unexpected, see Table 1). The latter trend can be explained in terms of much higher potential of *aggregate formation*, and the resultant *singlet*-*triplet annihilation*.

#### 4. Concluding remarks

To the questions addressed in Section 1, the following answers have been obtained:

As for the first question: As we expected, the photocurrent and the conversion efficiency increases (decreases) for Me<sub>2</sub>N- $\phi$ -6-CA ( $\phi$ -6-CA), which has the largest (the smallest) transition dipole. For the dyes having medium transition dipoles, the optimum dye concentration is found to be determined by two factors: one, the singlet-triplet annihilation reaction to quench singlet excitation, and the other, the number of dye molecules to be excited. The former factor becomes predominant for (MeO)<sub>3</sub>- $\phi$ -6-CA, which has the second largest transition dipole, whereas the latter factor becomes predominant for MeO- $\phi$ -6-CA, which has the second smallest transition dipole (see Fig. 4).

As for the second question: In Me<sub>2</sub>N- $\phi$ -6-CA, which has the largest transition dipole, the lowering of light intensity increases the photocurrent, whereas in  $\phi$ -6-CA, which has the smallest transition dipole the lowering light intensity, decreases the photocurrent. The former observation can be ascribed to the suppression of the singlet-triplet annihilation reaction in the dye aggregate, whereas the latter observation can be ascribed to the suppression of the singlet excitation in the dye monomers.





Fig. 4. Dependence of the conversion efficiency  $(\eta)$  on the dye concentration in DSSCs.

In summary, the dependence of the conversion efficiency and the photocurrent on the dye concentration and the light intensity observed in the present study have established the mechanism of singlet-triplet annihilation that lowers the performance of DSSCs.

For making the best use of the potential of polyene sensitizers to build a high-performance DSSC, we need further

Fig. 5. Effect of light intensity on the I-V curves of DSSCs, at the dye concentration of 100% and 5%, after the scaling shown in inset: AM 1.5, 100 mW cm<sup>-2</sup>, is defined as the light intensity of 100%.

Photo-voltage / V

0.4

0.6

<100%>

0.2

0

characterization of the dye systems, e.g. by precise measurements of the efficiencies of electron-injection and triplet-generation, the one-electron oxidation potentials etc., and exploration of well-designed  $TiO_2$  surfaces to accommodate a large number of the dye and spacer molecules.

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# Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2006. 01.003.

### References

- K. Kalyanasundaram, M. Grätzel, Coord. Chem. Rev. 77 (1998) 347.
- [2] A. Kay, M. Grätzel, J. Phys. Chem. 97 (1993) 6272.
- [3] K. Hara, H. Sugihara, Y. Tachibana, A. Islam, M. Yanagida, K. Sayama, H. Arakawa, Langmuir 17 (2001) 5992.

- [4] Z.-S. Wang, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, H. Arakawa, H. Sugihara, J. Phys. Chem. B 109 (2005) 3907.
- [5] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382.
- [6] T. Trupke, P. Würfel, I. Uhlendorf, J. Phys. Chem. B 104 (2000) 11484.
- [7] X.-F. Wang, R. Fujii, S. Ito, Y. Koyama, Y. Yamano, M. Ito, T. Kitamura, S. Yanagida, Chem. Phys. Lett. 416 (2005) 1.
- [8] J. Xiang, F.S. Rondonuwu, Y. Kakitani, R. Fujii, Y. Watanabe, Y. Koyama, H. Nagae, Y. Yamano, M. Ito, J. Phys. Chem. B 109 (2005) 17066.
- [9] N. Kann, T. Rein, B. Åkermark, P. Helquist, J. Org. Chem. 55 (1990) 5312.
- [10] F.J. Jansen, J. Lugtenburg, in: G. Briton, S. Liaaen-Jensen, H. Pfander (Eds.), Carotenoids, Synthesis, vol. 2, Birkhäuser Verlag, Basel, 1996, p. 232.
- [11] Y. Yamano, M. Yoshizawa, M. Ito, J. Nutr. Sci. Vitaminol. 45(1999) 49.
- [12] W. Liptay, Z. Naturforsch. 21A (1966) 1605.
- [13] J. Ridley, M. Zerner, Theort. Chim. Acta. 32 (1973) 111.
- [14] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209.
- [15] X.-F. Wang, J. Xiang, P. Wang, Y. Koyama, S. Yanagida, Y. Wada, K. Hamada, S. Sasaki, H. Tamiaki, Chem. Phys. Lett. 408 (2005) 409.