

Structural Modification of Organic Dyes for Efficient Coadsorbent-Free Dye-Sensitized Solar Cells

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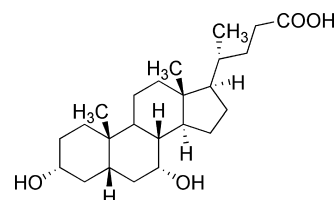
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Three triphenylamine-based organic sensitizers with different electron-donating substituents (butoxyl chains or dimethylamine groups) were examined to investigate the effect of bulky alkoxy donor substituents on the photovoltaic performances of dye-sensitized solar cells (DSCs) in the presence and absence of the coadsorbent chenodeoxycholic acid (CDCA) in dye-bath solutions. The study showed that, using the **D29** dye without bulky alkoxy substituents, the power conversion efficiency of DSC was significantly increased by about 84% in the presence of CDCA as compared to that in the absence of CDCA addition during the sensitization. However, the photovoltaic performance of **D35**-sensitized DSC having four bulky butoxyl substituents was not dependent on CDCA at all, probably due to the inherent structural nature of the **D35** molecule. The DSC based on the **D37** sensitizer with only two bulky butoxyl chains displayed an expected medium performance as compared to **D29** and **D35**. The inclusion of bulky alkoxy electron-donating substituents in dye molecules for efficient DSCs suppressed the electron recombination and reduced the interactions between dye molecules. This emphasizes the importance of designing novel dyes including functional groups that incorporate the properties normally needed from an external coadsorbent. The development of a coadsorbent free system is in particular important for the future economization and simplification of the DSCs' assembly process.

Introduction

The dye-sensitized solar cell (DSC) is a molecular system that consists of a wide band gap semiconductor photoanode, typically TiO₂, an anchored molecular sensitizer, a redox electrolyte, and a platinized photocathode.^{1–5} To increase the light-to-electricity conversion efficiency as well as the stability, all of the elements of the photoelectric device need to be optimized, and there is still substantial potential for further improvement. Among these elements, the sensitizing dye plays a vital role for the light harvesting efficiency providing electron injection into the conduction band of semiconductor upon light excitation. In recent years, metal-free organic sensitizers, such as coumarin,^{6–9} merocyanine,^{10,11} indoline,^{12–17} hemicyanine,^{18,19} fluorene,^{20,21} carbazole,^{22,23} perylene,²⁴ oligoene,^{25–27} quinoxaline,^{28,29} phenothiazine,³⁰ squaraine,^{31,32} and triphenylamine dyes,^{33–39} have attracted a lot of attention due to many virtues as compared to noble metal complexes. Some of the benefits with organic sensitizers are low cost synthesis routes, high molar extinction coefficients, flexible structural modifications, and the absence of noble metals. There are, however, still some major problems for organic dyes used in DSCs, such as dye aggregation, a lack of directionality in the dye excited state on the TiO₂ film,^{40–45} and pronounced recombination of TiO₂ conduction-band electrons with oxidized species as compared to ruthenium dyes.^{46–50} These are all obstacles to obtain higher overall conversion efficiencies (η). As a result, a number of research efforts have been made to overcome these drawbacks and to enhance the

CHART 1: Molecular Structure of Chenodeoxycholic Acid (CDCA)



power conversion efficiency of DSCs based on organic dyes. For example, coadsorbents, such as chenodeoxycholic acid (CDCA, Chart 1), are routinely added in the dye solutions. The exact role of coadsorbents in the DSC is still under discussion; some suggested effects of the coadsorbents are suppressing the dye aggregation, shifting the TiO₂ conduction band edge, and shielding the TiO₂ surface to reduce electron recombination with the oxidized species in redox electrolyte.^{51,52} According to previous studies, addition of CDCA in the dye solution has proved to improve the performance of DSCs, increasing both the short-circuit photocurrent density (J_{sc}) and the open-circuit voltage (V_{oc}).^{46,53} In addition, some works showed that the power conversion efficiency of DSCs based on organic dyes can be further improved by introducing bulky alkyl or alkoxy chains into the dye structure to obtain an insulating effect of dye layer on the TiO₂ surface.^{17,20–22} Recently, alkoxy chains located on the electron-donating part of the dye have resulted in very promising conversion efficiencies.^{39,54,55} As a result, strategic structural modification of organic sensitizers is an effective approach to enhance the dye performance in DSC and hence obtain higher conversion efficiencies.

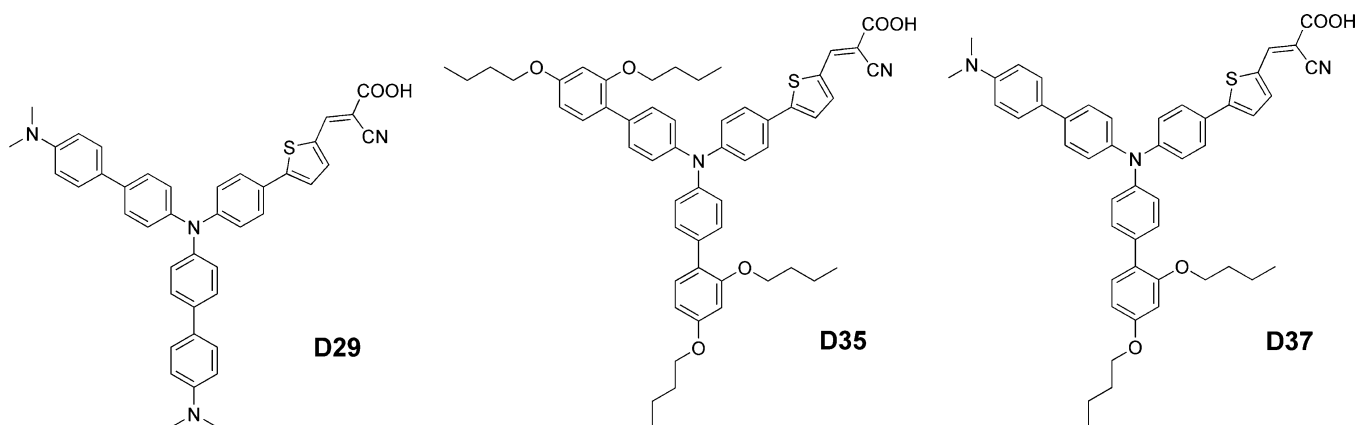
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CHART 2: Molecular Structures of Sensitizers D29, D35, and D37



Among the great number of reported organic dyes mentioned above, sensitizers based on triphenylamine (TPA) moiety have proved to be a promising alternative. This is due to its excellent electron-donating nature and nonplanar configuration. In our recent work, we presented a series of new organic sensitizers based on TPA functionalized with different donor substituents, named **D29**, **D35**, and **D37** (Chart 2).⁵⁶ These dyes have the same conjugated bridge units (thiophene) and electron acceptors (cyanoacrylic acid). The TPA donor was functionalized at the adjacent phenyl rings of the TPA core with either butoxyl groups, short dimethylamine groups, or a combination of both (Chart 2). The different electron donors on respective dye led to very different photovoltaic performances of DSCs. The overall conversion efficiencies increased in the order of **D29** < **D37** < **D35** (Table S1). For the present dyes, the results showed that structural properties are more determinative than spectral properties for the photovoltaic performances of DSCs. Despite the broader and more red-shifted absorption, DSCs based on **D29**, without any bulky chains, showed a comparatively low performance as compared to DSCs based on the less red-shifted **D35** dye with four bulky butoxyl groups. DSCs based on **D37** with two bulky butoxyl chains (as compared to four for **D35**) exhibited medium efficiencies as compared to the other two dyes. It is obvious that the presence of long butoxyl chains contributed to the higher performance of DSCs. It was found that the longer electron lifetimes were mainly responsible for the higher value of V_{oc} , resulting in higher power conversion efficiencies (Figures S1–S3). The reason is probably the insulating effect of the butoxyl chains protecting the surface of TiO_2 from oxidized species in the redox electrolyte.

As previously mentioned, the dye sensitization needs to be done in such way so a protecting insulating dye layer is attained. This is normally done by the introduction of coadsorbents during the sensitization and/or modification of the dye structure with bulky alkyl or alkoxy chains. It is noted that even for dyes capable of leading to respectable conversion efficiencies modified with alkyl or alkoxy chains, the sensitization still requires coadsorbent in the dye bath to gain better photovoltaic performances.^{17,36,54} Thus, the question is how dye modifications (alkyl or alkoxy chains) perform in comparison to the use of external coadsorbents in the role of providing effective surface blocking effect and impeding the electron recombination. Therefore, the aim of the present study is to compare the influence of the bulkiness of the dye donor substituents versus the presence and absence of a coadsorbent (CDCA) during the sensitization in DSCs, and to study the effect on parameters, such as electron recombination, dye loads, semiconductor energy level, and the overall photovoltaic performance. It is noted that

throughout the text the comparisons will be performed for the cases of with and without CDCA addition in the dye bath during the sensitization process.

Experimental Section

General Procedure for Preparation of Solar Cells. Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC8) were cleaned in subsequent order of detergent solution, water, and ethanol using an ultrasonic bath overnight. The conducting glass substrates were immersed into a 40 mM aqueous $TiCl_4$ solution at 70 °C for 30 min and washed with water and ethanol. The screen printing procedure was repeated (layers of $\sim 3 \mu m$) with TiO_2 paste to obtain a transparent nanocrystalline film of thickness around 10 μm and area of 0.25 cm^2 . The preparation of TiO_2 paste (~ 25 nm colloidal particles) is described elsewhere.⁵⁷ A scattering layer ($\sim 3 \mu m$, PST-400C, JGC Catalysts and Chemicals Ltd.) was deposited, and a final thickness of $13.0 \pm 0.2 \mu m$ was attained. The TiO_2 electrodes were gradually heated in an oven (Nabertherm Controller P320) at air atmosphere. The temperature gradient program has four levels at 180 °C (10 min), 320 °C (10 min), 390 °C (10 min), and 500 °C (60 min). After sintering, the electrodes once again passed, as described above, a post- $TiCl_4$ treatment. A second and final sintering, at 500 °C for 30 min, was performed. When the temperature decreased to 70 °C after the sintering, the electrodes were immersed into 0.2 mM dye solutions and kept for 16–17 h in the dark at room temperature. The solvent was ethanol (99.5%) for **D35**, and acetonitrile (99.8%) for **D29** and **D37**, respectively. After the adsorption of the dyes, the electrode was rinsed with the same solvent. The electrodes were assembled with a platinized counter electrode using a hot-melt Surlyn film. The redox electrolyte consisting of 0.1 M LiI (99.9%), 0.6 M tetrabutylammonium iodide (TBAI, 98%), 0.05 M I_2 (99.9%), 0.5 M 4-*tert*-butylpyridine (4-TBP, 99%), and 0.05 M guanidinium thiocyanate (GuSCN, 99.8%) in acetonitrile was introduced through a hole drilled in the back of the counter electrode. Finally, the hole was also sealed with the Surlyn film.

Measurement of Dye-Loading. The preparation of TiO_2 films was the same as the procedure above. The adsorbed dyes were then desorbed in 0.1 M $(CH_3)_4NOH$ in acetonitrile solution, and the dye load on the TiO_2 film was estimated by means of a UV–vis absorption spectroscopy.

Photocurrent Density–Voltage (J – V) Measurements. Prepared solar cells were characterized by current–voltage characteristics and incident photon-to-current conversion efficiency (IPCE). Current–voltage characteristics were carried out with an AM 1.5G solar simulator, 300 W xenon (ozone free). The incident light intensity was 1000 W/m^2 calibrated with a

TABLE 1: Current and Voltage Characteristics of DSCs Based on D29, D35, and D37 Dyes,^a with and without CDCA Addition during the Sensitization Process

dye	CDCA (mM)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	efficiency improvement
D29^b	0	7.98	0.66	0.47	2.22	
	6	11.15	0.71	0.52	4.09	84.2%
D35^c	0	12.02	0.78	0.54	5.07	
	6	11.84	0.77	0.56	5.10	0.6%
D37^b	0	10.52	0.71	0.51	3.77	
	6	11.26	0.69	0.56	4.37	15.9%

^a Photovoltaic performance under AM 1.5 irradiation of DSCs based on **D29**, **D35**, and **D37** dyes. Electrolyte: 0.6 M tetrabutylammonium iodide (TBAI), 0.1 M LiI, 0.05 M I₂, 0.5 M 4-*tert*-butylpyridine (4-TBP), 0.05 M guanidinium thiocyanate (GuSCN) in acetonitrile. ^b Dye bath: acetonitrile solution (2×10^{-4} M) with and without the addition of CDCA. ^c Dye bath: ethanol solution (2×10^{-4} M) with and without the addition of CDCA.

standard Si solar cell. For the J - V curves, the solar cells were evaluated by using a black mask on the cell surface to avoid diffusive light (cell area of 0.25 cm², aperture area of 0.49 cm²).⁵⁸ IPCE measurements were carried out with a computerized setup consisting of a xenon arc lamp (300 W Cemax, ILC Technology), followed by a 1/8 m monochromator (CVI Digikrom CM 110). The data collection was done with a Keithley 2400 source/meter and a Newport 1830-C power meter with 818-UV detector head.

Photophysical Measurements. The UV-vis absorption spectra of the dye-loaded transparent film and the dye solution (1×10^{-5} M, in ethanol) were recorded on a Lambda 750 spectrophotometer by using a normal quartz sample cell (1 cm path length). The fluorescence spectra of dye solution were recorded on a Cary Eclipse fluorescence spectrophotometer using the same concentration as the UV-vis measurement.

Electron Lifetime and Extraction Charge Measurements. Electron lifetimes in the complete dye-sensitized solar cell devices were measured in a system using a red-light emitting diode (Luxeon Star 1W, $\lambda_{max} = 640$ nm) as light source. Voltage and current traces were recorded using a 16-bit resolution data acquisition board (DAQ National Instruments) in combination with a current amplifier (Stanford Research Systems SR570) and a custom-made system using electromagnetic relay switches. The relation between potential and charge was investigated by combining the voltage decay and charge extraction methods. Extraction charge measurements were performed in the following way: the solar cell was illuminated for 5 s under open-circuit conditions, and then the light was shut off and the voltage was let to decay to a voltage V . At a certain voltage V , the cell was short-circuited, and the current was measured under 10 s and then integrated to obtain Q_{oc} (V). Electron lifetimes were determined by monitoring the transient voltage responses after a small light intensity modulation (square wave modulation, <10% intensity of 0.5 Hz), and the step response was recorded by the DAQ board. The voltage response was well fitted to first-order decay, and time constants were hence obtained.

Results and Discussion

1. Effects of Coadsorbent CDCA on the Photovoltaic Performance of D29-Sensitized DSCs. The photovoltaic performance characteristics of DSCs based on **D29**, **D35**, and **D37** sensitizers with and without the addition of CDCA during the sensitization, under standard global AM 1.5 illumination, 100 mW cm⁻², are summarized in Table 1. As seen from Table 1, **D29**-sensitized DSC without CDCA addition showed very

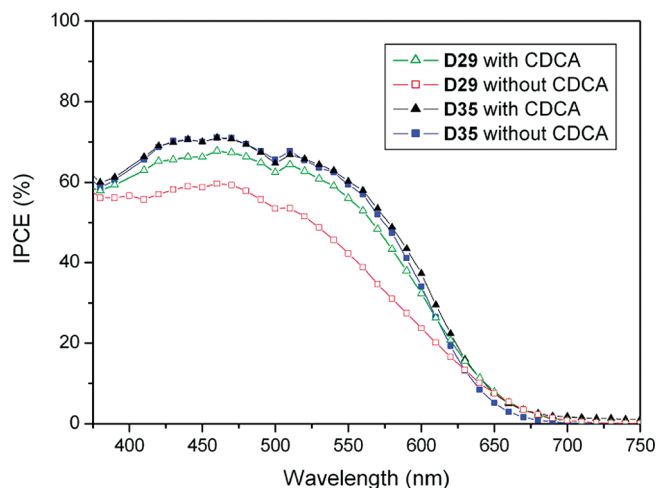
TABLE 2: Adsorbed Amount of D29, D35, and D37 Dyes, Respectively, on the TiO₂ Film with and without CDCA Addition during the Sensitization Process

dyes	ϵ (10^4 M ⁻¹ cm ⁻¹)	dye load (10^{-8} mol/cm ²)	
		with CDCA	without CDCA
D29	7.02	4.10	7.51
D35	7.01	4.57	5.24
D37	3.72	8.47	12.33

low conversion efficiency. In contrast, the DSC with addition of CDCA gave a pronounced efficiency enhancement of 84% by increasing both values of J_{sc} and V_{oc} as compared to the case without CDCA addition.

The adsorbed amount of dye on the TiO₂ film (determined by dye desorption) with and without CDCA was listed in Table 2. It was found that the dye amount of **D29** sensitizer adsorbed onto the TiO₂ surface was reduced to 54% in the presence of CDCA, as compared to that without CDCA in the dye bath. Despite this, higher J_{sc} was observed (Table 1). The main possible explanation is that the coadsorption of CDCA prevents dye aggregation, which can cause intermolecular energy transfer and sequentially result in the excited-state quenching of the dyes.⁵⁹⁻⁶⁵ As a result, the reduction of dye load on the TiO₂ surface in the presence of CDCA in the dye bath consequently results in more efficient electron injection from the excited dyes to the TiO₂ conduction band.^{52,66} A more efficient electron injection thus compensates for the less amount of dye adsorption. It is noted that there was no direct evidence to support the coadsorption of CDCA with dyes on the surface, but indirect results, indicating that it might most probably be present on the surface.⁵² The observed changes in J_{sc} agreed well with the corresponding incident photon-to-current conversion efficiency (IPCE) spectra for **D29**-sensitized DSC with and without the addition of CDCA during the sensitization process (Figure 1).

However, it is interesting to find that there were almost no changes between the maximum absorption wavelengths of **D29** on the TiO₂ film with and without CDCA addition during the sensitization process (Figure 2). It should be noted that the TiO₂ film is thinner in the case of UV-vis measurement as compared to the actual DSCs condition. To explain this observation, we propose the following possibilities: (i) The amount of dye was insufficient to form aggregates, and therefore no spectral shift was observed, but "aggregates" might form at higher dye load

**Figure 1.** Spectra of incident photon-to-current conversion efficiency (IPCE) for DSCs based on **D29** and **D35**, respectively, with and without CDCA addition during the sensitization process.

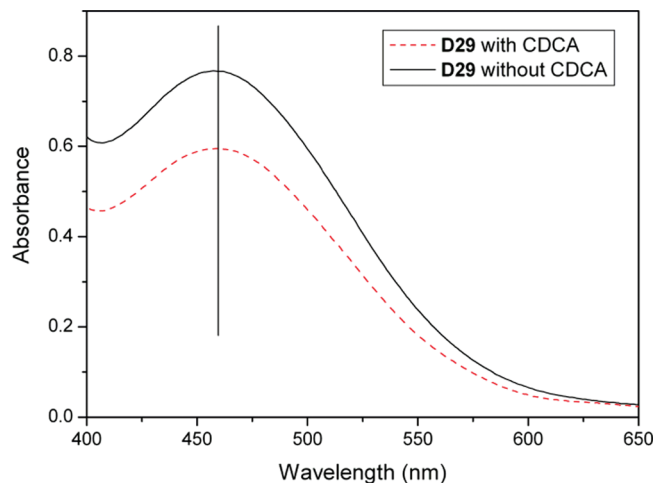


Figure 2. Absorption spectra of **D29** on the TiO_2 film with and without CDCA addition during the sensitization process.

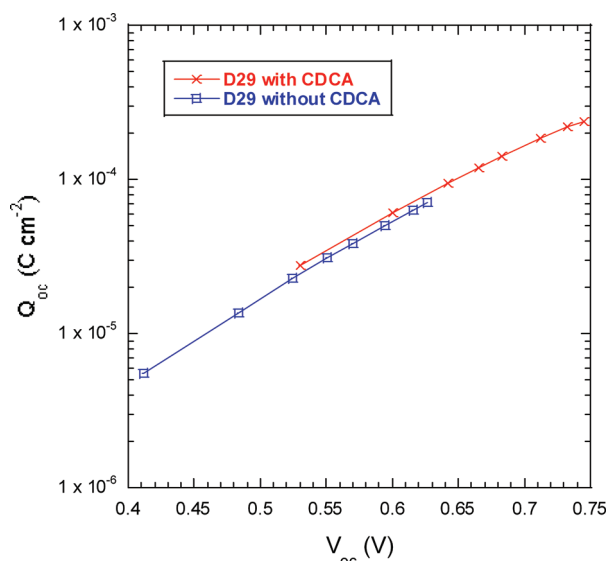


Figure 3. Extracted charge as a function of open-circuit voltage for DSCs based on **D29** sensitizer with and without CDCA addition during the sensitization process.

conditions for thicker TiO_2 films. (ii) The formed “aggregates” were of a different character as compared to the well-known H or J aggregates capable of causing a spectral shift.^{42–44,67–69} So, even if there are complexes of dyes formed on the TiO_2 surface without CDCA addition, they might not be detectable in the absorption spectra. (iii) In the absence of CDCA, there was a certain amount of excess dyes, not necessarily forming aggregates, and thus no spectral shift was observed.

The open-circuit voltage (V_{oc}) of DSCs is determined by the difference between the quasi-Fermi level of TiO_2 and the potential of the redox couple (I^-/I_3^-) in the electrolyte. The quasi-Fermi level is dependent on both the conduction band edge position of TiO_2 and the electron concentration in TiO_2 .^{45,70,71} The electron concentration is strongly dependent on the rate of electron recombination often referred to as the electron lifetime. Figure 3 shows the relation between open-circuit voltage and extracted charge.^{72,73} A possible shift in this relation can be interpreted as a shift of the conduction band edge position of the TiO_2 . Almost no TiO_2 conduction band shift was found for **D29**-sensitized DSCs upon addition of CDCA in the dye bath, indicating that the conduction band edge of TiO_2 was unaffected by the presence of CDCA. Electron

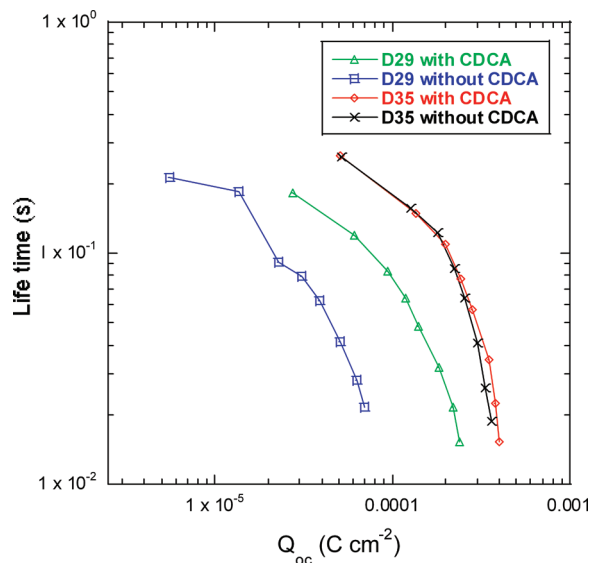


Figure 4. Electron lifetime as a function of extracted charge under open-circuit conditions for DSCs based on **D29** and **D35**, respectively, with and without CDCA addition during the sensitization process.

lifetime measurement was subsequently performed to reveal the influence of CDCA on the electron recombination. Figure 4 shows the electron lifetime as a function of extracted charge of DSCs based on **D29** with and without CDCA addition.^{74,75} At a given charge, longer electron lifetime was obtained for **D29**-sensitized DSC with CDCA addition (Figure S4). This implies that the recombination reaction between electrons in the TiO_2 film and the oxidized species in the redox electrolyte is inhibited by the addition of CDCA in the solar cell. A possible explanation is that the coadsorption of CDCA with dyes on the TiO_2 surface produces surface passivation, resulting in less recombination and longer electron lifetimes. Therefore, it can be concluded that the increased V_{oc} for **D29**-sensitized DSC was mainly caused by the longer electron lifetime due to the presence of CDCA.

On the basis of the above results, it was suggested that the presence of CDCA in the dye solution during the sensitization resulted in shielding of the surface against electron recombination and provided a higher concentration of functional dyes on the TiO_2 surface contributing to an efficient electron injection into the TiO_2 conduction band.

2. Effects of Coadsorbent CDCA on the Photovoltaic Performance of D35-Sensitized DSCs. From Table 1, it is interesting to find that **D35**-sensitized DSCs, with and without the CDCA addition, gave very similar values of J_{sc} , V_{oc} , and power conversion efficiency. This means that the photovoltaic performance of DSCs based on **D35** was not dependent on CDCA. This was further investigated by electron lifetime and extracted charge measurements. As shown in Figure 4, at a given charge, almost no differences in electron lifetimes were found for DSCs based on **D35** independent of the presence of coadsorbent CDCA. This indicates that the recombination of electrons in the TiO_2 film with the oxidized species in the redox electrolyte is unaffected in **D35**-sensitized DSCs with and without CDCA addition. The relation between open-circuit voltage and charge of **D35**-sensitized DSCs with and without CDCA addition is exhibited in Figure 5. For a given charge, a slight decrease in V_{oc} was found when CDCA was present in the dye solution, which means that the conduction band-edge of the TiO_2 film was slightly shifted to a more positive potential.

The amount of adsorbed **D35** on TiO_2 surface with and without CDCA addition is shown in Table 2. Unlike **D29**, the

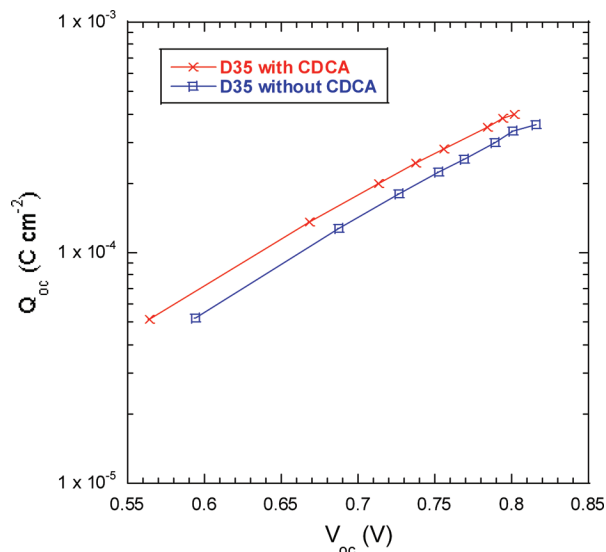


Figure 5. Extracted charge as a function of open-circuit voltage for DSCs based on **D35** sensitizer with and without CDCA addition during the sensitization process.

dye load of **D35** on the TiO_2 surface was less dependent on the CDCA. There was a small decrease in dye load when CDCA was added into the dye bath. As previously mentioned, the **D29** dye load on the TiO_2 surface was decreased by about 50% in the presence of CDCA, whereas the **D35** dye load was reduced only about 10%. When using CDCA, the exact ratio of dye/CDCA on the TiO_2 surface is unknown,⁵² but the dye load reduction in the presence of CDCA implies that the competitive coadsorption of CDCA with **D35** sensitizer on the TiO_2 film is weaker than that with **D29** sensitizer. In other words, it is suggested that **D35** forms an ordered dye layer on TiO_2 surface and binds more strongly to the TiO_2 surface than CDCA. Thus, **D35** shows less dependence on the presence of CDCA. Generally, one would expect that a self-assembly property of the dye during the sensitization of TiO_2 film is important to obtain efficient surface coverage and efficient electron injection and thus obtain high photovoltaic performance of DSCs.

The essential reason for higher DSCs performance based on the **D35** sensitizer can be ascribed to its intrinsic structural properties. As shown in Chart 2, the **D35** sensitizer contains four long butoxyl chains in ortho and para positions of the phenyl rings, which are further linked in para position with the TPA phenyl rings by single bonds, allowing free rotation. These rotatable bulky groups may produce surface blocking through steric hindrance, preventing the access of electrons to the redox electrolyte, which will be in favor of higher V_{oc} . On the other hand, the twisted three-dimensional structure may not only facilitate the ordered molecular arrangement on the TiO_2 surface, but also keep dye molecules at a distance, which may suppress possibly intermolecular dye interaction, favoring higher J_{sc} . Even when comparing the results of complete DSC devices based on only **D35** dye (no CDCA) with the DSCs based on **D29** dye and CDCA, **D35**-based DSCs still resulted in better performance. The main difference is still the significantly longer electron lifetimes observed for DSCs based on **D35** resulting in higher V_{oc} . The protection by the butoxyl chains is proven to be more efficient as compared to the coadsorption of CDCA under the examined conditions. However, the less efficient surface protection due to the small donating groups in **D29** sensitizer directly resulted in relatively poor photovoltaic performance. In conclusion, markedly higher power conversion efficiencies were obtained for DSCs based on **D35** with

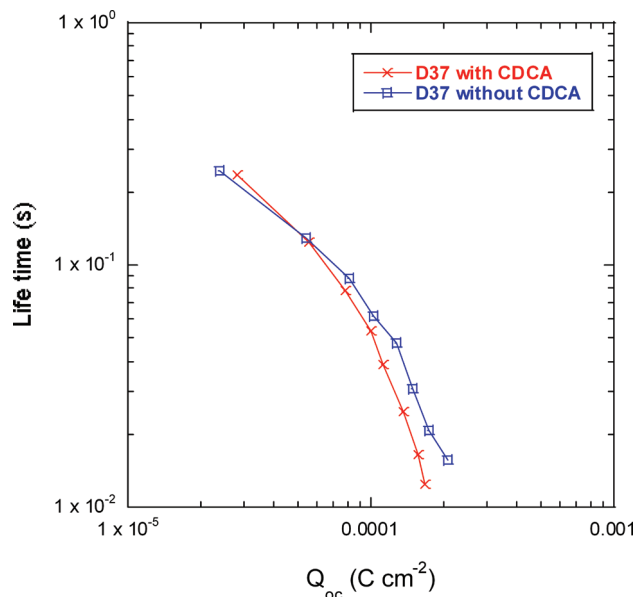


Figure 6. Electron lifetime as a function of extracted charge under open-circuit conditions for DSCs based on **D37** with and without CDCA addition during the sensitization process.

multibulky butoxyl donor substituents due to the inherent properties of the dye molecule.

3. Effects of Coadsorbent CDCA on the Photovoltaic Performance of D37-Sensitized DSCs. **D37** sensitizer is a good example to consolidate the above conclusions. As illustrated in Chart 1, the structure of **D37** is a combination of the two parent chromophores for **D29** and **D35**. There are two bulky butoxyl groups and one small amino group. Thus, an expected intermediate performance for **D37**-sensitized DSC was obtained in comparison with **D29** and **D35** under both conditions, with and without the CDCA addition. The changes in the values of J_{sc} and V_{oc} (Table 1) can also be explained by electron lifetime measurement and extracted charge measurement. We found that the decrease in V_{oc} , when adding CDCA, was a result of collective effects of a slightly increased electron recombination and a small positive band-edge shift of TiO_2 (Figures 6 and 7).

From Table 2, it is clear that the dye load of **D37** dropped by about 30% (about 50% for **D29**, 10% for **D35**) due to the addition of CDCA in the dye bath. However, like **D29**, the value of J_{sc} increased with decreasing dye coverage, probably due to the same reason as mentioned for **D29**.

It is interesting and noticeable that the molar extinction coefficient of **D37** is only about one-half of **D29** and **D35**, although these three dyes have similar structures. The lower molar extinction coefficient is possibly due to the breakage of symmetry of the molecule.^{56,76} As a result, although there is a higher dye load in the **D37** system relative to the other two cases (twice as much as **D35** and **D29**), only a medium performance was obtained due to the poor molar extinction coefficient and relatively few bulky electron-donating groups (two butoxyl groups as compared to four for **D35**) in the molecule.

Conclusions

According to previous reports, the addition of coadsorbent in dye bath and/or functionalization of organic dyes with bulky alkyl/alkoxy electron-donating chains can effectively enhance the photovoltaic performances of DSCs. The role of bulky substituents in dye molecules and the use of coadsorbents have

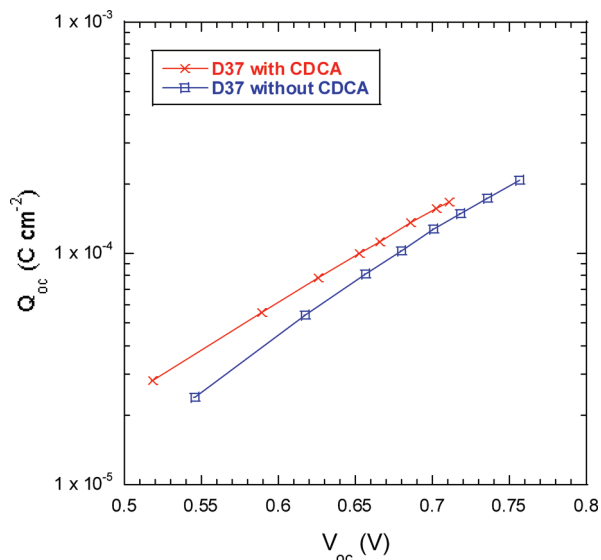


Figure 7. Extracted charge as a function of open-circuit voltage for DSCs based on **D37** sensitizer with and without CDCA addition during the sensitization process.

common purposes: reducing the presence of aggregated dyes and providing surface protection suppressing electron recombination. Three dyes **D29**, **D35**, and **D37**, with different electron-donating substituents (butoxyl chains or dimethylamine groups), showed gradually enhanced photovoltaic performance with increasing the length and the number of electron-donating chains. To better understand the influence of the bulky electron-donating butoxyl dye substituents on the photovoltaic performance of DSCs, we investigated the photovoltaic performances of **D29**-, **D35**-, and **D37**-sensitized DSCs with and without CDCA addition in the dye bath. The studies showed that the photovoltaic performance of **D35**-sensitized DSC containing four bulky butoxyl chains was independent of the coadsorbent CDCA. By comparison, the **D37** bearing two bulky butoxyl chains and **D29** without butoxyl chains showed 16% and 84%, respectively, improvement in photovoltaic performance in the presence of the coadsorbent CDCA. In the absence of CDCA, **D35**-based DSCs were still superior to both **D37** and **D29** in the presence of CDCA. This is probably due to the inherently structural nature of **D35** molecule, functionalized with four bulky butoxyl electron-donating substituents, which resulted in excellent photovoltaic performance. The aims of the bulky butoxyl substituents are proven to be 2-fold. The first is to provide self-assembly and aggregate-free dye layer on the TiO₂ surface. Second, an insulating hydrophobic dye layer will keep oxidized species in the redox electrolyte at a distance from the TiO₂ surface suppressing the electron recombination. This study elucidates the role and the importance of bulky alkoxy electron-donating substituents in dye molecules for efficient dye-sensitized solar cells. The protection by the butoxyl chains is proven to be more efficient as compared to the coadsorption of CDCA under the examined conditions. Additionally, improved dye design incorporating the properties of coadsorbent into the dye structure is important for future economization of cost and simplification of the coadsorbent-free DSCs assembly process.

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Supporting Information Available: Current and voltage characteristics of DSCs based on **D29**, **D35**, and **D37**. Electron lifetime and extracted charge measurements for DSCs based on **D29**, **D35**, and **D37**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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