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Carbazole Dyes with Alkyl-functionalized Thiophenes for Dye-sensitized Solar Cells: Relation between Alkyl Chain Length and Photovoltaic Performance

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Carbazole dyes with different lengths of alkyl group on oligothiophene were newly synthesized to study the influence of the chain length on photovoltaic performance of dye-sensitized solar cells. It was found that the amount of adsorbed dyes increased with the decrease of the alkyl chain length, while the charge recombination rate was comparable between the dyes with *n*-propyl and *n*-hexyl chains but prompt with dodecyl chains.

Dye-sensitized solar cells[1] (DSSCs) have attracted many researchers because of the high photoenergy conversion efficiency. Efficiencies of DSSCs were achieved over 11% by using ruthenium complex dyes.[2] To date, many kinds of metal-free organic dyes[3–8] have been developed to increase the efficiency. However, most DSSCs based on organic dyes have shown lower open-circuit voltages (V_{oc}) than DSSCs based on ruthenium complex dyes. This is mainly due to faster charge recombination between the injected electron in a nanoporous TiO_2 electrode and I_3^- in an electrolyte.[9]

Previously we reported various carbazole dyes (MK dyes) with oligothiophenes as a π-conjugation linker.[10–12] The addition of *n*-hexyl chains to oligothiophenes suppressed electron recombination in DSSCs by blocking the approach of I_3^- to the TiO_2 surface. On the other hand, although the alkyl chains were added to cover the exposed TiO_2 surface among the adsorbed dyes, depending on the length, the alkyl chains would reduce the density of adsorbed dyes resulting in larger exposed surface area and less retardation of recombination. Therefore, to obtain a design guide for sensitizers, it is important to study how the length of the alkyl chains influence the amount of the adsorbed dyes in relation to the degree of retardation. In this study, we investigated the relation between the photovoltaic performances of MK dyes and the alkyl chain length (*n*-propyl, *n*-hexyl, and dodecyl, in Figure 1).

Carbazole dyes with propyl chains and dodecyl chains (MK-24 and MK-25) were synthesized by using a similar procedure described in previous literature[10] starting from 3-bromocarbazole and 3-propylthiophene or 3-dodecylthiophene (see Supporting Information; SI[13]). Nanoporous TiO_2 electrodes (without $TiCl_4$ treatment) were prepared from TiO_2 paste (18NR, JGC Catalysts and Chemicals Ltd.) by annealing at 550 °C for 30 min. The TiO_2 electrodes were immersed into a 0.3 mM toluene solution of each MK dye and 0.3 mM acetonitrile/*t*-BuOH = 1/1 (volume ratio) solution of N719 dye for 18 h, respectively. An electrolyte was prepared by mixing 0.1 M LiI, 0.6 M DMPImI, 0.05 M I_2, and 0.5 M tBP in acetonitrile.

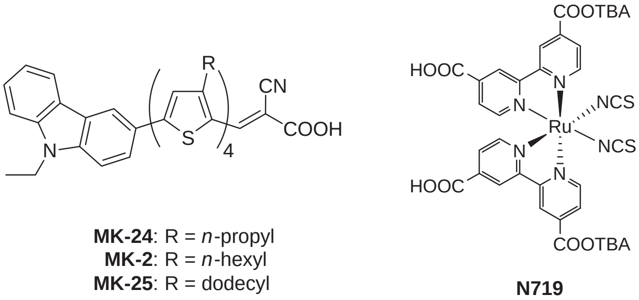

Figure 1. Molecular structures of MK dyes with the different lengths of alkyl chains (MK-24, MK-2, and MK-25) and N719 dye.

Table 1. Absorption properties of dyes and adsorbed dye amount on TiO_2 films

Dye	Alkyl chain	$\lambda_{abs}{}^{a}$/nm (ε/$10^4\,M^{-1}\,cm^{-1}$)	Γ^{b} /10^{-4} mol cm^{-3}
MK-24	C3	470 (4.0)	2.5
MK-2	C6	473 (3.8)	1.9
MK-25	C12	480 (4.0)	0.7

[a]UV spectrum of each dye was measured in a 20%THF–toluene solution through an 1 mm cell. [b]Γ is the density of the dye adsorbed on the TiO_2 film.

As shown in Table 1, similar values of absorption maxima and absorption coefficients (ε) of the MK dyes were observed. When these were adsorbed on the TiO_2 surface, the amounts of the adsorbed dyes decreased with the increase of the alkyl chains.

Figure 2a shows the IPCE (incident-photon-to-current conversion efficiency) spectra of the DSSCs with MK-24, MK-2, MK-25, and a ruthenium dye, N719. The maximum values of the IPCE were varied: MK-24 ≈ MK-2 (≈70%) > MK-25 (≈60%), while the absorption ranges did not change among these three dyes (300 to 800 nm).

The photovoltaic performances of solar cells based on these dyes, MK-24, MK-2, MK-25, and N719 are summarized in Table 2 (and Table S1, SI[13]). Figure 2b shows *I*–*V* curves of the DSSCs. The J_{sc} value of the DSSC with MK-24 was similar to that of the DSSC with MK-2, although the amount of adsorbed MK-24 on the TiO_2 electrode was higher than that of MK-2. This is because the light absorption in the cells with these two dyes were saturated, as indicated by the fact that the IPCE values were leveled off between 400 and 600 nm.

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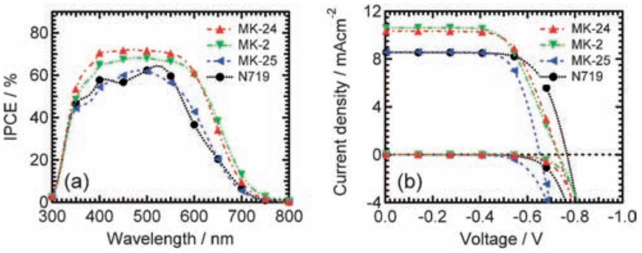

Figure 2. Photovoltaic performances of DSSCs using MK dyes having different lengths of alkyl chains, (a) IPCE spectra of the DSSCs, (b) *I–V* curves of the DSSCs measured under one sun conditions (100 mW cm^{-2}).

Table 2. Photovoltaic performances of DSSCs[a]

Dye	w[b] /µm	J_{SC} /mA cm^{-2}	V_{OC} /V	*FF*	η /%
MK-24	4.5	10.3	0.729	0.65	4.9
MK-2	4.8	10.6	0.733	0.62	4.8
MK-25	4.3	8.57	0.652	0.72	4.0
N719	4.4	8.56	0.764	0.70	4.6

[a] Incident light: AM 1.5G (100 mW cm^{-2}) with a mask (0.17 cm^2) and without an anti-reflection film. [b] TiO_2 thickness.

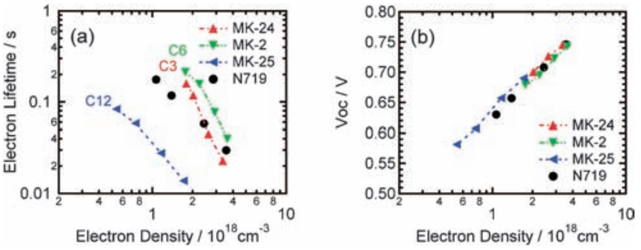

Figure 3. Electron lifetimes (a) and open circuit voltage (b) as a function of electron density in DSSCs. Electron lifetimes and electron densities were measured by stepped light-induced measurement of photocurrent and voltage[14] (SLIM-PCV) and charge extraction method,[15] respectively.

The trends of the V_{oc} values were also similar among the dyes: MK-24 $\approx$ MK-2 > MK-25. The difference of the V_{oc} values is simply explained by the difference of the electron lifetimes in the DSSCs (Figure 3a), because the potential difference between the conduction band edge of TiO_2 (E_{CB}) and I^-/I_3^- (E_{redox}), was not changed by these three dyes (Figure 3b). Note that the lifetime was measured under light intensity lower than one sun, and the slope for the cell with N719 was less steep than these for MK-24 and MK-2. The electron lifetime in the DSSC/MK-25 was much lower than that in the DSSC/MK-2, while the electron lifetime in the DSSC/MK-24 was comparable with that in the DSSC/MK-2. For the case of an MK dye without alkyl chains (MK-3), the DSSCs with the dye have shown shorter electron lifetime and lower V_{oc} than those of the DSSCs with MK-2, although the adsorbed amount of MK-3 was nearly three times higher than that of MK-2.[12] Therefore, in the terms of electron lifetime, the important criterion is not the adsorbed density but the surface coverage. In other words, the length of the alkyl chains needs to be designed to cover the exposed TiO_2 surface between the dyes, and the shape and area of the exposed surface depends on the shape of the dyes. For MK-25, the long alkyl chains decreased the dye amount excessively so that the alkyl chains could not cover the surface enough. We expect that the excessive decrease of the amount of dyes was due to the planar structure of the dyes. Similar effect may be seen for porphyrin and phthalocyanine dyes. For MK-24, the effect of the decreased length of the alkyl chains was balanced with the effect of the increased amount of the dyes, resulting in the similar electron lifetime with MK-2. In view of solar cell performance, higher adsorbed dye density can decrease the thickness of the TiO_2, giving other benefits such as higher V_{oc} and FF.

In summary, we studied the relation of the photovoltaic performances of MK dyes with the different length of alkyl chains, *n*-propyl, *n*-hexyl, and dodecyl. The density of MK dye molecules on TiO_2 surface was increased by decreasing the length of alkyl chains without decreasing the electron lifetime. These demonstrate that the adsorbed density of dyes and the degree of TiO_2 coverage can be controlled by changing the alkyl length. In other words, the addition of alkyl chains does not always improve the solar cell performance if the alkyl chains did not help to cover the TiO_2 surface, especially for the dyes having a planar shape. This finding is particularly important for DSSCs with different redox couples because the required TiO_2 surface coverage to retard charge recombination depends on the molecular size of the acceptor species.[16]

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