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Alkyl-Functionalized Organic Dyes for Efficient Molecular Photovoltaics

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Recently there has been a considerable increase in interest in organic devices such as light-emitting diodes, field effect transistors, and photovoltaic cells.[1] The performances of these devices depend mainly on the properties of functionalized organic molecules. In a dye-sensitized nanocrystalline TiO_2 solar cell (DSSC),[2] which is a promising type of molecular photovoltaics, the properties of photosensitizer such as absorption spectrum and electron-transfer rate are important factors determining the photovoltaic performance. For example, Ru-polypyridyl-complex dyes, such as *cis*-dithiocyanato bis(4,4′-dicarboxy-2,2′-bipyridine)ruthenium(II) (called N3 dye), developed by Grätzel and co-workers, satisfy the criteria, and the DSSCs based on the Ru dyes can produce solar energy-to-electricity conversion efficiency (η) of up to 11% under AM 1.5 G irradiation.[2]

Besides Ru dyes, metal-free organic dyes have been also utilized in DSSCs because of their wide variety of the structures, facile modification, and high molar absorption coefficient. Various organic dyes for DSSCs have been developed, such as coumarin dyes,[3] merocyanine derivatives,[4] and polyene dyes,[5] and high η values of up to 9% under AM 1.5 G irradiation have been attained so far. The performance of DSSCs based on organic dyes, however, have not exceeded those on Ru dyes yet. According to our recent report, it was observed that the electron lifetimes (τ) for the DSSCs with coumarin dyes were shorter than with N719, a Ru dye. The shorter values of τ are probably the cause of the observed lower open-circuit voltage (V_{oc}) from the DSSCs using the coumarin dyes.[6] The dye aggregation, which causes intermolecular energy transfer, is also considered to be one of the factors decreasing photovoltaic performance of DSSCs based on organic dyes.[3d]

Taking these points into account, further strategical molecular design of organic dyes is required to achieve higher η values. Our concept toward the high photovoltaic performance of organic-dye-sensitized solar cells is based on the interface engineering of a dye-adsorbed TiO_2 surface, which can be controlled by the structural modification of the dye molecule to diminish the charge recombination between the electrons and acceptors, that is, dye cation and I_3^- ions, and the aggregation of dye molecules. In addition, since the synthetic schemes for dye molecules should be simplified to facilitate developing dyes for DSSCs, we designed new organic dyes having three separated functional parts: donor, linkage, and acceptor groups shown in Figure 1. The design allows us to examine different molecules systematically for the three parts. The most important feature of the new dye structure (**MK-1** and **MK-2**) is the existence of *n*-hexyl groups substituted at the oligothiophene linkage. With the long alkyl chains, an increase of the electron lifetimes (τ) can be expected by preventing the approach of acceptors (i.e., I_3^- ion) to the TiO_2 surface and/or by reducing the reorganization energy of the dye, resulting in the desired situation for the kinetic competition for the reduction of the dye cation.[7] The aggregation of dye molecules would be also suppressed by the steric hindrance due to the long alkyl chains. **MK-3** dye, which has no alkyl groups at the oligothiophene part, was also synthesized in order to compare with **MK-1**. (Syntheses of dyes **MK-1**, **2**, and **3**, in detail, are described in Supporting Information.)

The inset in Figure 2 shows the absorption spectra of new dyes **MK-1**, **2**, and **3** in chloroform. Absorption maxima (λ_{max}) were observed at 463 nm for **MK-1**, 473 nm for **MK-2**, and 443 nm for **MK-3**, respectively, and the molar absorption coefficient (ϵ) at λ_{max} was 41 400 M^{-1} cm^{-1} for **MK-1**, 35 800 M^{-1} cm^{-1} for **MK-2**, and 42 100 M^{-1} cm^{-1} for **MK-3**, respectively. These results indicate that these dyes could be suitable for DSSCs because of the wide wavelength range of absorption and the relatively high molar absorption coefficient compared with N3 dye (ca. 16 000 M^{-1} cm^{-1}).[2b] The LUMO levels of the dyes adsorbed on a nanocrystalline TiO_2 film, which were estimated from the oxidation potentials and the maximum wavelengths of the UV−visible absorption spectra, were more negative than −0.84 V (vs NHE), suggesting that efficient electron transfer from the dyes to TiO_2 should occur.

Action spectrum of incident photon-to-current conversion efficiency (IPCE) for a DSSC based on **MK-2** is shown in Figure 2. The onset wavelength of the IPCE spectrum was 800 nm. This value is almost equal to that for a DSSC based on N3 dye.[2e] IPCE values around 70% were observed in the range of 400 to 650 nm with a maximum value of 72% at 500 nm for the DSSC based on **MK-2**, showing the highly efficient performance of the solar cells.

The photovoltaic performance of the DSSCs based on N719 dye and MK dyes are summarized in Table S1 (Supporting Information). It is noteworthy that the V_{oc} (0.71−0.72 V) for DSSCs based on **MK-1** and **MK-2** dyes, which have long alkyl chains, were higher than that for **MK-3** (0.63−0.64 V) in the same condition. The V_{oc}, however, was lower with **MK-1** and **MK-2** than with N719 dye (0.79 V). The maximum η value of 7.7% (short-circuit current density $J_{sc} = 14.0$ mA cm^{-2}, $V_{oc} = 0.74$ V, and fill factor FF = 0.74) was obtained with a DSSC using **MK-2** under AM 1.5 G irradiation (100 mW cm^{-2}) with an aperture mask but no antireflection film.

To understand the high V_{oc} observed with **MK-1** and **MK-2**, we measured electron lifetimes in the conduction band of TiO_2. As shown in Figure 3, it is remarkable that the values of τ for the DSSCs with **MK-1** and **MK-2** were larger than with coumarin dyes, **NKX-2587** and **NKX-2697**, which have oligothiophene moiety without alkyl chains.[3f,6] In addition, the τ for the DSSC with **MK-3**, having no alkyl chain, was much shorter than those with **MK-1** and **MK-2**. These results obviously indicate that alkyl chains are markedly effective in increasing the electron lifetimes. The longer electron lifetime may be realized by two possible mechanisms: one is that the alkyl chains block the I_3^- or cations approaching the TiO_2 surface, decreasing the I_3^- concentrations at the vicinity of the TiO_2, and the other is that the alkyl chains reduce the reorganization energy of the dyes, increasing the rate of dye-cation reduction. The latter implies that shorter values of τ for **MK-3** could be due to the recombination between the conduction band electrons and dye cations, because of the slower electron-transfer process

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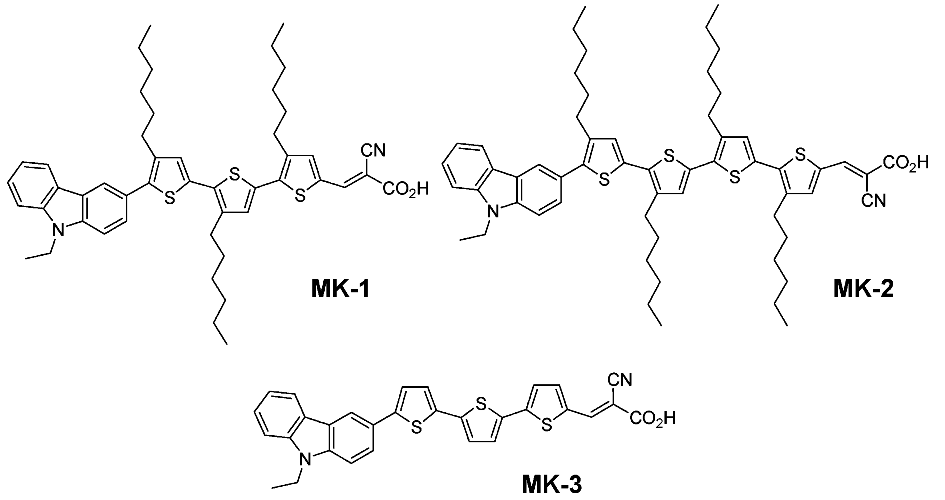

Figure 1. Molecular structures of **MK-1**, **MK-2**, and **MK-3** dyes.

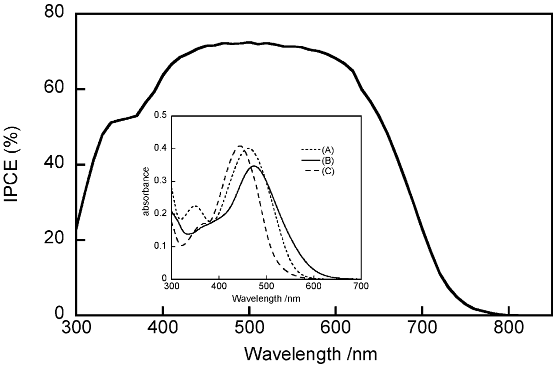

Figure 2. Action spectrum of monochromatic incident photon-to-current conversion efficiency (IPCE) for a DSSC based on **MK-2** dye. Thickness of the TiO_2 electrode was 30 μm. The inset is absorption spectra of dyes (A) **MK-1**, (B) **MK-2**, and (C) **MK-3** in chloroform.

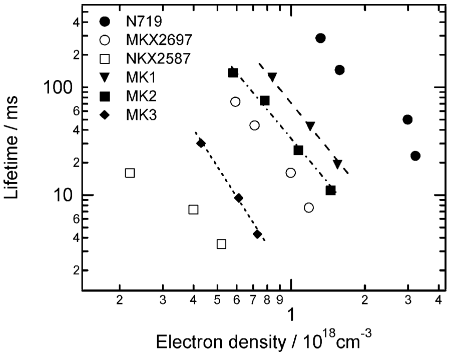

Figure 3. Electron lifetimes in the DSSCs using various dyes as a function of electron density in the DSSCs. The lifetimes were measured at open circuit conditions, and the electron densities were estimated by the charge extraction method.

between I^- ion and the dye cation. Certainly, the longer electron lifetime based on **MK-1** and **MK-2** dyes should be responsible for the improved V_{oc} of the DSSCs.[8] Additionally, it is supposed that the dye aggregation could be inhibited by the existence of alkyl chains, because the high performance of DSSCs with **MK-1** and **MK-2** was achieved without any coadsorption, which is commonly applied for organic dyes to prevent aggregation. To confirm these points, further investigation will be needed.

In conclusion, we succeeded in increasing the electron lifetime in DSSCs using organic dyes by the addition of long alkyl groups at the oligothiophene linkage and have demonstrated the highly efficient performance of the DSSCs using the dyes. Our molecular design of alkyl-functionalized dyes strongly suggests the promising performance of molecular photovoltaics based on organic dyes. To achieve similar photovoltaic performance of DSSCs based on Ru dyes, we are now synthesizing new organic dyes with further molecular designs.

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Supporting Information Available: Synthesis procedures, characterization of all compounds, the DSSCs cell preparation method, all fundamental data of DSSCs, and lifetime measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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