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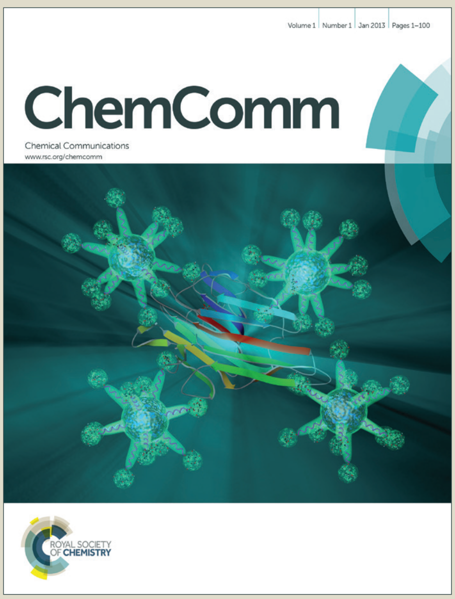

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COMMUNICATION

Fabrication of a high-performance dye-sensitized solar cell with 12.8% conversion efficiency using organic silyl-anchor dyes

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The co-sensitization of organic silyl-anchor dyes in dye-sensitized solar cells (DSSCs) using carbazole and coumarin dyes with organosilicon tethers for binding to titanium dioxide has been examined. We have succeeded in fabricating a high-performance DSSC with a light-to-electric energy conversion efficiency of 12.8% under one sun simulated solar irradiation.

Dye-sensitized solar cells (DSSCs), which are composed of mesoporous nanocrystalline-TiO_2 thin layers modified by photosensitizing dyes as working electrodes, redox electrolytes and counter electrodes, have become a promising alternative photovoltaic technology to conventional inorganic solar cells because of their potential low costs, relatively high solar light-to-electric energy conversion efficiencies (η) and fine photovoltaic properties in low-light intensities.[1-3] In DSSCs, η of 12-13% under the simulated sunlight irradiation at one sun have been reported up to now by the photosensitization using polypyridyl and porphyrin complexes of metals such as ruthenium and zinc.[2-7]

Recently, we have reported a metal-free carbazole/alkyl-functionalized oligothiophene/alkoxysilyl-anchor moiety type compound, **ADEKA-1** (Fig. 1a), as the organic photosensitizing dye for DSSCs. The **ADEKA-1**-sensitized solar cell exhibited the highest η of 12.5% among the cells with organic dyes reported so far with the open-circuit photovoltage (V_{oc}) higher than 1 V by using a cobalt(III/II) tris(5-chloro-1,10-phenanthroline) complex ($[Co(Cl\text{-}phen)_3]^{3+/2+}$) as the redox electrolyte.[4] Besides the high photovoltaic performance, the TiO_2 photoelectrode sensitized with **ADEKA-1** possesses much higher durability to mixed solvents containing nitrile and water than those with conventional carboxy-anchor dyes. In DSSCs co-sensitizations by using two kinds of dyes have been demonstrated to be effective to improve the energy conversion efficiencies,[6-11] and the durability of the photoelectrode allows co-adsorptions of plural sensitizing dyes to the electrode for producing the co-sensitization effect.

In this work, therefore, we examined the co-sensitization in the DSSCs with **ADEKA-1** by using the alkoxysilyl-anchor coumarin dye of **SFD-5** (Fig. 1b) to confirm the possibility of the co-sensitization and to improve the photovoltaic performance of the cells. While **ADEKA-1** has major absorption band in the visible region from 400 to 600 nm with the maximum molar absorption coefficient (ε_{max}) of 43,200 at λ_{max} = 498 nm, **SFD-5** has a strong absorption band due to the π-π^* transition from 370 to 480 nm (ε_{max} = 58,400 at λ_{max} = 440 nm) as shown in Fig. S1. The oxidation potential (E_{ox}: approximately the energy level of

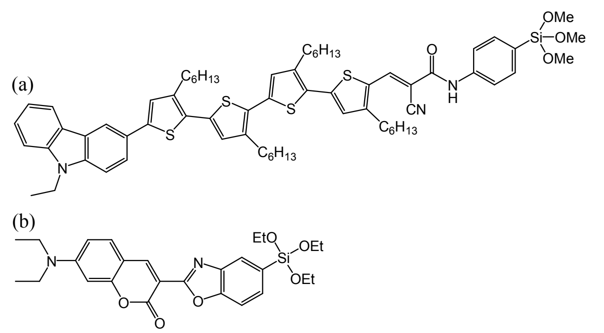

Fig. 1 Molecular structures of metal-free organic silyl-anchor dyes: (a) **ADEKA-1** and (b) **SFD-5**.

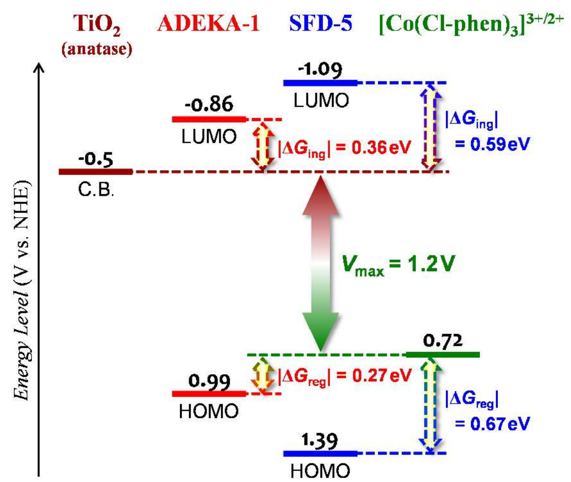

Fig. 2 Schematic energy diagram of the DSSC composed of anatase-TiO_2, **ADEKA-1**, **SFD-5** and $[Co(Cl\text{-}phen)_3]^{3+/2+}$.

HOMO) of **SFD-5** was estimated to be 1.39 V vs. NHE, which is more positive enough than the redox potential of 0.72 V vs. NHE of $[Co(Cl\text{-}phen)_3]^{3+/2+}$ as is same in **ADEKA-1**.[4,12,13] Schematic energy diagram of the DSSC is shown in Fig. 2. The positive E_{ox} of **SFD-5** allows the utilization of $[Co(Cl\text{-}phen)_3]^{3+/2+}$ as the redox electrolyte in the cells to produce a high photovoltage. From the difference in the absorption characteristics and the positive E_{ox}, **SFD-5** is considered as an appropriate co-sensitizer for **ADEKA-1**.

We fabricated the cells, equipped with an antireflection film, composed of the TiO_2 electrodes photosensitized by **ADEKA-1** with/without **SFD-5** and an experimentally optimized [Co(Cl-phen)$_3$]$^{3+/2+}$ electrolyte solution. The *IPCE* spectra of the **ADEKA-1**-sensitized cells with and without **SFD-5** are shown in Fig. 3a. The cell with **SFD-5** exhibited better *IPCE* values than the cell without **SFD-5** in the range between 400 and 530 nm which is the light-absorption region of **SFD-5** (Fig. S1), and a maximum *IPCE* value of the cell with **SFD-5** was reached to 88%. On the other hand, *IPCE* values from 550 to 800 nm were almost same in the two cells. While in **ADEKA-1** the alkoxysilyl-anchor moiety links to the chromophore (carbazole/alkyl-functionalized oligothiophene) via the phenyl-amide moiety, **SFD-5** has the alkoxysilyl-anchor moiety bound directly to the coumarin-based chromophore and a higher excited-state oxidation potential (E_{ox}^*: approximately the energy level of LUMO) of -1.09 V vs. NHE than that of **ADEKA-1** (-0.86 V vs. NHE) (Fig. 1 and 2). Thus **SFD-5** is expected to have a higher electron injection efficiency from the light-excited state to the TiO_2 conduction band than **ADEKA-1**, and the improvement of the *IPCE* observed in the light-absorption region of **SFD-5** is considered as the result of the co-sensitization effect by **SFD-5**. The obtained results indicate also that the co-sensitization with **ADEKA-1** and **SFD-5** functioned effectively without the negative interaction between the two organic silyl-anchor dyes for the improvement of the photovoltaic performance of the cell.

The photovoltaic parameters, short-circuit photocurrent density (J_{sc}), V_{oc}, fill factor (*FF*) and η, of the **ADEKA-1**-sensitized cells with and without **SFD-5** were assessed from the photocurrent-voltage (*J*-*V*) curves under the simulated AM-1.5G solar irradiation with the one sun intensity of 100 mW cm^{-2} (Fig. 3b). The results of the *J*-*V* measurements are summarized in Table S1. As expected from the *IPCE* spectra (Fig. 3a), the J_{sc} of the cells co-sensitized by **ADEKA-1** and **SFD-5** was improved to 16.0±0.1 mA cm^{-2} from that of the cells photosensitized only by **ADEKA-1** of 15.6±0.1 mA cm^{-2}. The V_{oc} and *FF* values were almost the same in the two kinds of cells showing that **SFD-5** did not affect those photovoltaic properties. Due to the increment of the photocurrent, the η was improved from 12.5% to 12.8% by the co-sensitization of **ADEKA-1** and **SFD-5** under the one sun irradiation (AM-1.5G, 100 mW cm^{-2}).

In conclusion, the examination of the co-sensitization using two metal-free organic silyl-anchor dyes of **ADEKA-1** and **SFD-5** showed that **SFD-5** works as co-sensitizer to **ADEKA-1** and we succeeded in obtaining the high *IPCE* up to 88%, V_{oc} over 1 V and 12.8% conversion efficiency in the DSSC containing the cobalt(III/II) complex electrolyte. The energy conversion efficiency achieved here is the highest among those reported so far for the DSSCs using metal-free organic photosensitizing dyes.[2-7,14-16] The result shows the potential of organic silyl-anchor dyes[4,12,13,17-19] as the photosensitizers for DSSCs and a possibility of co-sensitization by plural organic silyl-anchor dyes for further improvement of the photovoltaic performance of DSSCs. Detailed molecular design of organic silyl-anchor dyes and co-sensitization using those dyes are a promising way to obtain higher energy conversion performance in DSSCs, and such investigations are currently underway in our group.

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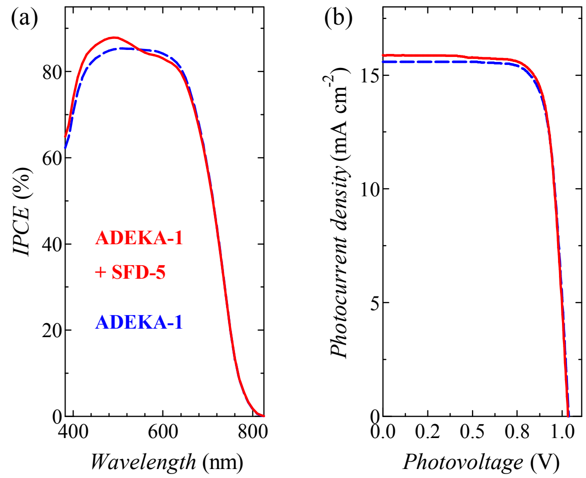

Fig. 3 (a) *IPCE* spectra and (b) *J*-*V* properties under the simulated one sun irradiation (AM-1.5G, 100 mW cm^{-2}) of the cells photosensitized by **ADEKA-1** with/without **SFD-5**.

Notes and references

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