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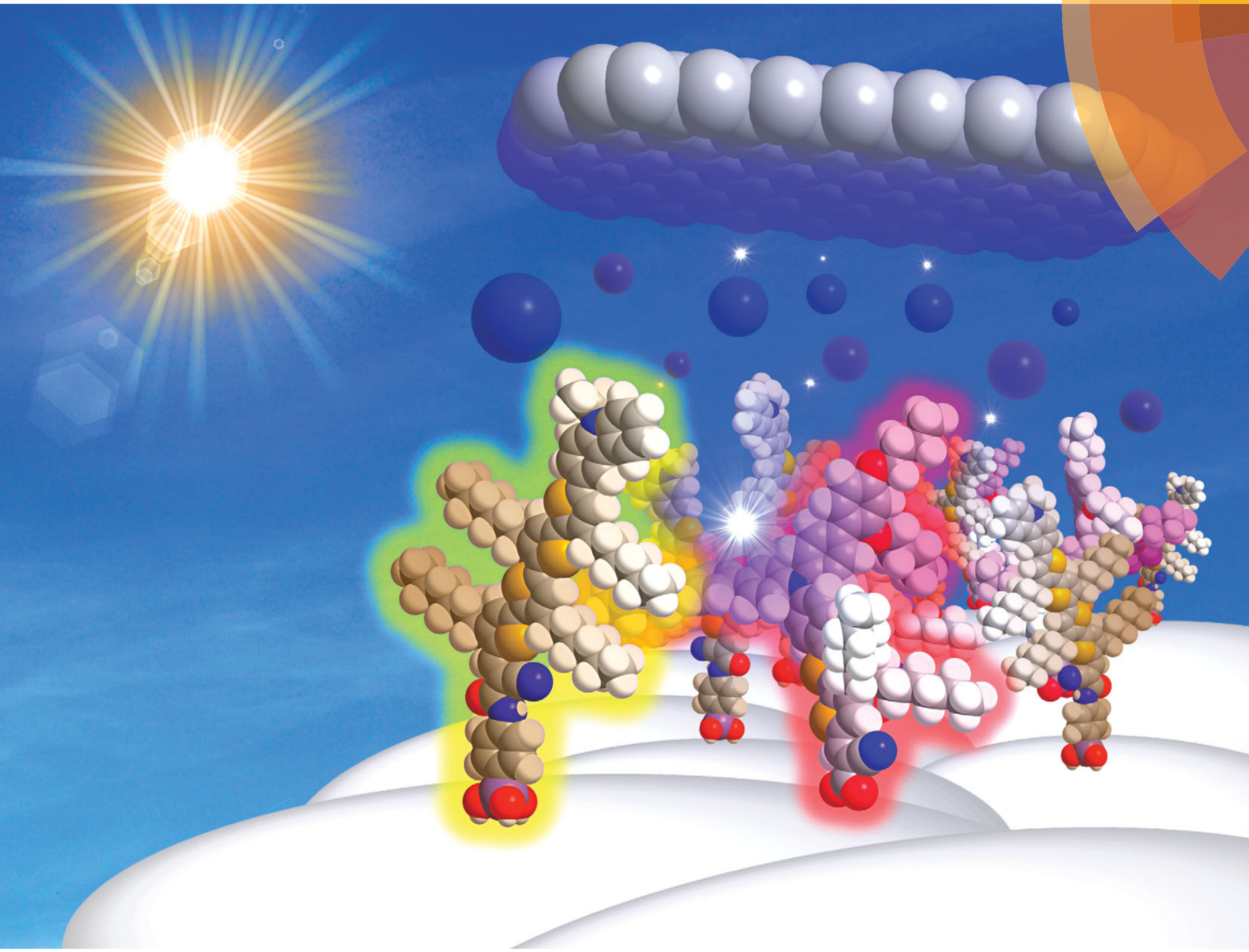

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Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes†

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In dye-sensitized solar cells co-photosensitized with an alkoxysilyl-anchor dye ADEKA-1 and a carboxy-anchor organic dye LEG4, LEG4 was revealed to work collaboratively by enhancing the electron injection from the light-excited dyes to the TiO_2 electrodes, and the cells exhibited a high conversion efficiency of over 14% under one sun illumination.

Dye-sensitized solar cells (DSSCs), which are composed of mesoporous nanocrystalline-TiO_2 thin layers modified with photosensitizing dyes as working electrodes, redox electrolytes and counter electrodes, have been actively investigated as photovoltaic devices in the next generation of alternatives to conventional silicon-based inorganic solar cells (Fig. S1, ESI†), because of their potentially low production costs, shorter energy and CO_2 payback times, low toxicity of the constituent elements and relatively high light-to-electric energy conversion efficiencies (η) especially under low-light intensities and scattered light conditions.[1–4] In DSSCs, η values of 11–13% under the simulated sunlight of one sun have been reported up to now through photosensitization using polypyridyl and porphyrin complexes of metals such as ruthenium or zinc, and a few metal-free organic dyes with carboxy-anchor moieties for binding to the surface of the TiO_2.[1–9]

Organosilicon compounds such as silanols and alkoxysilanes have high metal-oxide surface bonding abilities by forming strong Si–O–metal bonds. While paying attention to the characteristics of silanols and alkoxysilanes, we have focused on the development of photosensitizing dyes for DSSCs possessing silyl-anchor moieties,[10–12] and recently we succeeded in achieving over 12% conversion efficiency in cells using a carbazole/alkyl-functionalized oligothiophene/alkoxysilyl-anchor moiety type compound, **ADEKA-1** (Fig. 1a), as the photosensitizer.[13]

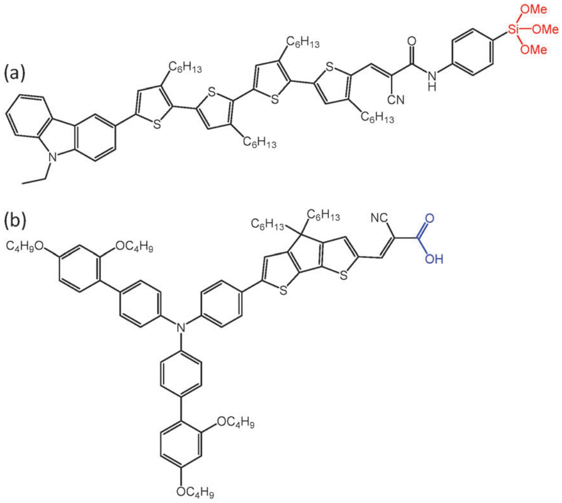

Fig. 1 Molecular structures of photosensitizing dyes: (a) silyl-anchor dye **ADEKA-1** and (b) carboxy-anchor dye **LEG4**.

Besides the high photovoltaic performance, the TiO_2 photoelectrode sensitized with **ADEKA-1** possesses much higher durability to solvents, *e.g.* nitrile, water and mixtures of them, and to surface modification using wet processes than those sensitized with carboxy-anchor dyes. The durability of the photoelectrode allows the co-adsorption of another sensitizing dye to the electrode for production of a co-sensitization effect, and actually we succeeded in improving the η to 12.8% by means of the co-sensitization of **ADEKA-1** and a silyl-anchor coumarin dye **SFD-5**.[14]

For further improvement in the efficiency of **ADEKA-1**-sensitized DSSCs, we expanded the study of co-sensitizers for the cells to widely developed carboxy-anchor dyes, which have been demonstrated to possess high sensitizing properties as photosensitizers in DSSCs. In the investigation we found that the **ADEKA-1**-sensitized cells with the co-sensitizer **LEG4**[15] (Fig. 1b) exhibited a considerably higher photovoltaic performance through collaborative sensitization by the dyes, and succeeded in achieving

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over 14% conversion efficiency in the cells. The efficiency shows the high potential of DSSCs to be practical light-to-electric energy conversion devices in the near future.

As co-sensitizers for the **ADEKA-1**-sensitized DSSCs, we selected carboxy-anchor organic sensitizing dyes which have been reported to have high sensitizing properties and an absorption band in the shorter wavelength region than **ADEKA-1**, *i.e.* **LEG4**, **D35**, **L0** and **D131** (Fig. S2–S6 and Table S1, ESI†). To check the potential of these dyes as co-sensitizers for **ADEKA-1**, we fabricated cells sensitized by **ADEKA-1** and by **ADEKA-1** with the dyes using an electrolyte solution containing an I_3^-/I^- redox mediator (cell-A; the fabrication procedures of the cells are described in the ESI†). Among the cells, a significant and the largest improvement in the incident monochromatic photon-to-current conversion efficiency (IPCE) was observed in the cell photosensitized by **ADEKA-1** with **LEG4** (Fig. 2a and Fig. S7 in the ESI†). The cell exhibited much higher IPCE values of close to 90% compared to the cells sensitized only by **ADEKA-1** and only by **LEG4** in all of the visible region. The increase of the open-circuit photovoltage (V_{oc}) and the short-circuit photocurrent density (J_{sc}) compared to those of the cell sensitized only by **ADEKA-1** resulted in the improvement of the η by a factor of 1.3 under simulated sunlight at one sun (AM-1.5G, 100 mW cm^{-2}; Table S2, ESI†).

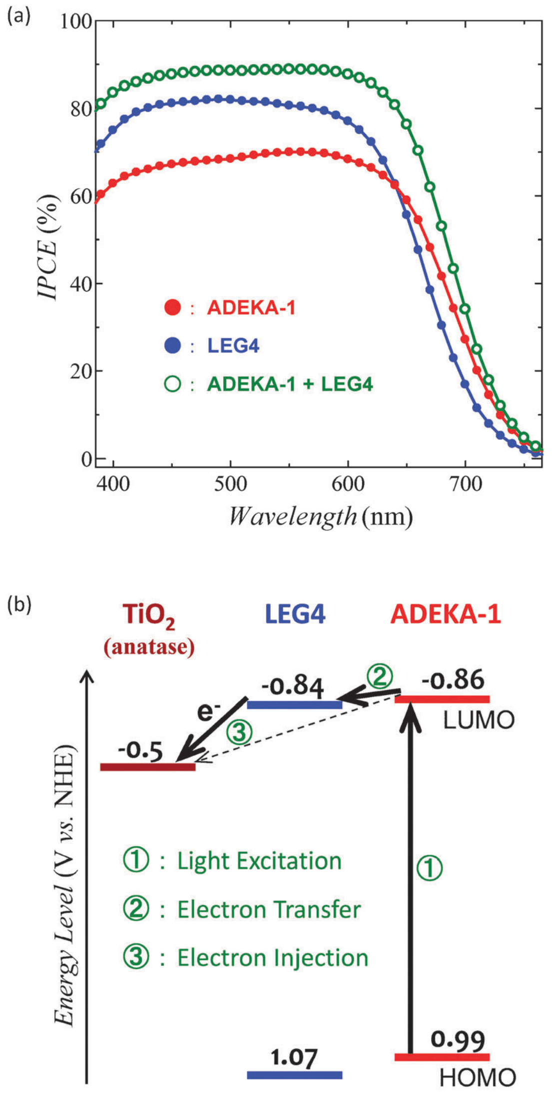

Fig. 2 (a) IPCE spectra of the cells photosensitized by **ADEKA-1**, by **LEG4** and by **ADEKA-1** with **LEG4** (cell-A) and (b) a schematic drawing of the charge separation processes for the TiO_2 electrode sensitized collaboratively by **ADEKA-1** and **LEG4**.

In the cell photosensitized by **ADEKA-1** with **LEG4**, in which the relative amount of the dyes adsorbed on the TiO_2 electrode was estimated to be 1.0 : 0.25 for **ADEKA-1 : LEG4**, the improvement of the IPCE values compared to those of the **ADEKA-1**-sensitized cell was observed not only in the light-absorption wavelength region of **LEG4** but also in the longer wavelength region where the light absorption by **LEG4** was absent (Fig. S8, ESI†), which is different to the other co-sensitized cells. In order to clarify the origin of the peculiar and large improvement in the IPCE by the co-sensitization with **LEG4**, we examined MO calculations of the dyes (Fig. S9 and S10, and Tables S3 and S4 in the ESI†).

The light-to-electric energy conversion in DSSCs proceeds by light excitation of the sensitizing dye followed by charge separation produced through electron injection from the LUMO of the light-excited dye to the conduction band of TiO_2. In **ADEKA-1** the alkoxysilyl-anchor moiety links to the chromophore (carbazole/alkyl-functionalized oligothiophene moiety) *via* the phenylamide moiety, and the LUMO has a small electron distribution around the silyl-anchor moiety. On the other hand, the LUMO of **LEG4** has a large electron distribution around the carboxy-anchor moiety and thus **LEG4** is expected to have a higher electron injection efficiency from the LUMO to the TiO_2 conduction band than **ADEKA-1** (Fig. S9, ESI†). When comparing the energy levels of the LUMOs of the dyes, only **LEG4** has a lower LUMO than **ADEKA-1** which is different to the other dyes, **D35**, **L0** and **D131** (Fig. S6, ESI†), and emission analyses using an Al_2O_3 porous film modified by **ADEKA-1** with **LEG4** showed that the emission from **ADEKA-1** was quenched almost completely by the existence of **LEG4** as the co-adsorbent (Fig. S11, ESI†). From the MO properties and the results of the emission analyses, the large improvement of the photovoltaic performance in the cell photosensitized by **ADEKA-1** with **LEG4** is considered to be brought about by the collaborative sensitization by the dyes through an electron-injection enhancement effect due to the existence of the **LEG4** molecules near the **ADEKA-1** molecules on the TiO_2 electrode; the electron transfers from the light-excited **ADEKA-1** to the co-adsorbent **LEG4** and immediate electron injection occurs from **LEG4** to the conduction band of the TiO_2 with much higher efficiency than the direct electron injection from the light-excited **ADEKA-1** (Fig. 2b). Internal quantum efficiency (IQE) measurements revealed a considerably higher electron injection efficiency in the cell photosensitized by **ADEKA-1** with **LEG4**, and the maximum IQE was evaluated to be 99 ± 2% (Fig. S12, ESI†). The increase of the V_{oc} (Table S2, ESI†), the decrease of the dark-current (Fig. S13, ESI†) and the elongation of the electron lifetime in the TiO_2 conduction band estimated from the transient open-circuit voltage decays (Fig. S14, ESI†) observed in the co-sensitization with **LEG4** indicate that the

Table 1 Photovoltaic parameters of the cells sensitized collaboratively by **ADEKA-1** and **LEG4** (cell-B) under the illuminations of the simulated sunlight (AM-1.5G)

Entry	Electrolyte:redox[a]	Counter electrode	Light intensity (mW cm^{-2})	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
1	A:I_3^-/I^-	FTO/Pt	100	19.11	0.783	0.748	11.2
2	F:$[Co(phen)_3]^{3+/2+}$	FTO/Pt	100	17.77	1.018	0.765	13.8
3[b]	F:$[Co(phen)_3]^{3+/2+}$	FTO/Au/GNP	100	18.27	1.014	0.771	14.3
4	F:$[Co(phen)_3]^{3+/2+}$	FTO/Au/GNP	50	9.55	0.994	0.776	14.7

[a] Electrolyte: (A) 0.07 M I_2, 0.05 M LiI, 0.05 M NaI, 0.50 M DMPImI, 0.10 M EMImI, 0.05 M TBAI, 0.05 M THAI, 0.40 M TBP, 0.10 M MP, and 0.10 M GuSCN in MeCN/VN/THF (8 : 1 : 1 in volume); (F) 0.20 M $[Co^{2+}(phen)_3](PF_6^-)_2$, 0.05 M $[Co^{3+}(phen)_3](PF_6^-)_3$, 0.07 M $LiClO_4$, 0.02 M $NaClO_4$, 0.03 M TBAPF, 0.01 M TBPPF, 0.01 M HMImPF, 0.30 M TBP, 0.10 M TMSP, 0.10 M MP, 0.05 M CPrBP, 0.10 M CPeBP, and 0.05 M COcBP in MeCN. The data for the cells with other electrolytes (B–E) are listed in Table S6 (ESI). [b] The values are the averages of the results of the four cells which were prepared separately (Table S5, ESI).

adsorbed **LEG4** on the TiO_2 electrode also works as a suppressor, preventing back electron transfer from the TiO_2 electrode to the electrolyte by covering the naked surface of the TiO_2 electrode with its plural alkyl-chain substituents.[15–18] By using an I_3^-/I^- redox electrolyte solution with an experimentally optimized composition, the cell photosensitized collaboratively by **ADEKA-1** and **LEG4** (cell-B; the fabrication procedures of the cell are described in the ESI†) exhibited the η of 11.2% under AM-1.5G one sun illumination (entry 1 in Table 1).

The maximum photovoltage (V_{max}) obtained in the DSSC is attributed to the energy gap between the quasi-Fermi level of the TiO_2 [approximately the energy level of the conduction-band edge ($E_{C.B.}$)] and the redox potential of the electrolyte, and the improvement of the efficiency of DSSCs is possible by the increase of the photovoltage through using an electrolyte having a more positive (lower) redox potential than I_3^-/I^-.[1–4,7–9,11,13–15] The redox potential of the cobalt(III/II) tris(1,10-phenanthroline) complex ($[Co(phen)_3]^{3+/2+}$) is lower than that of I_3^-/I^- by *ca.* 0.2 V,[19] and the values of the HOMO levels of **ADEKA-1** and **LEG4** are still more positive than the redox potential of the cobalt(III/II) complex (Fig. S15, ESI†), which provides the thermodynamic driving force for the dye regeneration reaction by electron transfer from the Co^{2+}-complex electrolyte to the oxidized dye.[13–15] Thus we employed $[Co(phen)_3]^{3+/2+}$ as the redox electrolyte for the **ADEKA-1** and **LEG4** co-sensitized cell for further improvement of the η of the cells.

In the fabrication of the cells using the cobalt(III/II) complex redox electrolytes (cell-B), the compositions of the electrolyte solutions, *i.e.* the Co^{2+}/Co^{3+} ratio, the kind of cobalt(III/II) complex counter anion and the electrolyte additives, were optimized experimentally according to the literature[7,13,14,20,21] using a platinum-deposited F-doped SnO_2 (FTO)-coated glass plate as the counter electrode. The cell using an electrolyte solution with the optimized composition exhibited a high V_{oc} of above 1 V and the η was improved to 13.8% under AM-1.5G one sun illumination (entry 2 in Table 1) as was expected from the more positive redox potential of $[Co(phen)_3]^{3+/2+}$. However, a decrease of the J_{sc} was also observed in the cell compared to the cell with the I_3^-/I^- redox electrolyte solution. In order to recover the J_{sc}, we employed graphene nanoplatelets (GNPs) as the material for the counter electrode and prepared the counter electrode on a FTO-coated glass plate with a structure of FTO/Au/GNP, because the counter electrode has been reported to produce higher J_{sc} and fill factor (FF) in photocurrent–voltage properties than the standard platinum electrodes.[8,22,23] Fig. 3 shows an example of the *J–V* curve under AM-1.5G one sun illumination (100 mW cm^{-2}) and the IPCE spectrum of the cell co-sensitized by **ADEKA-1** and **LEG4.** The photovoltaic parameters, assessed as the averaged values from the *J–V* curves of the four separately prepared cells, are listed in Table 1 as entry 3 (Table S5, ESI†). The J_{sc} was actually improved in the cell from 17.8 to 18.3 ± 0.1 mA cm^{-2} by using the FTO/Au/GNP counter electrode and the maximum value in the IPCE spectrum reached 91%, resulting in the η of 14.3% with the V_{oc} above 1 V. The better photovoltaic performance in the lower light intensity is a characteristic of DSSCs. This is also observed in the present cell and the cell exhibited an η of close to 15% under simulated sunlight with a 50 mW cm^{-2} intensity (entry 4 in Table 1, and Fig. S16 and S17 in the ESI†).

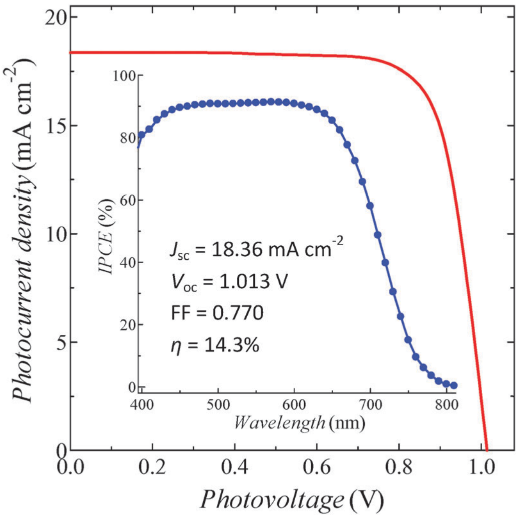

Fig. 3 A typical *J–V* curve of the cell photosensitized collaboratively by **ADEKA-1** and **LEG4** with an efficiency of over 14% (entry 3a in Table S5, ESI†) under the illumination of simulated sunlight (AM-1.5G, 100 mW cm^{-2}). Inset shows the IPCE spectrum of the cell.

In conclusion, a carboxy-anchor organic dye **LEG4** was revealed to work effectively as the collaborative sensitizer to the silyl-anchor dye **ADEKA-1** in DSSCs, and we succeeded in obtaining a high IPCE of up to 91%, V_{oc} of above 1 V and 14.3% conversion efficiency in the cell with the optimized cobalt(III/II) complex redox electrolyte solution and the GNP counter electrode.

The result is attributed basically to the strong adsorption properties of **ADEKA-1** to the TiO_2 electrode and shows the validity of silyl-anchor dyes as photosensitizers for DSSCs. The observation of conversion efficiencies of over 14% in these DSSCs indicates the high potential of DSSCs as light-to-electric energy conversion devices. The collaborative sensitization by plural organic dyes including silyl-anchor dyes, which would bring a further improvement in the photovoltaic performance of DSSCs, is considered as a promising way to produce practical DSSCs.

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