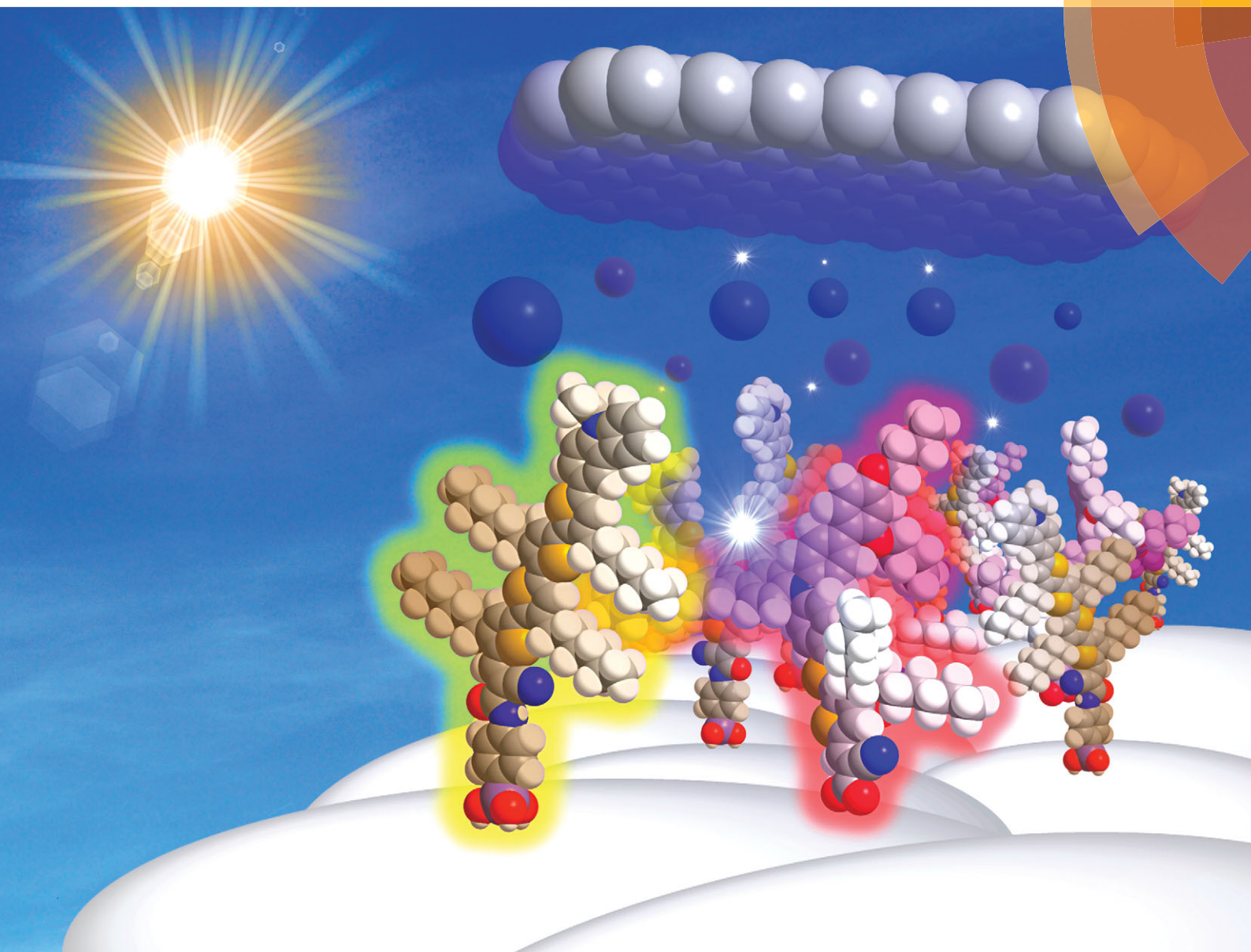


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## Highly-efficient dye-sensitized solar cells with collaborative sensitization by silyl-anchor and carboxy-anchor dyes†

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In dye-sensitized solar cells co-photosensitized with an alkoxy-silyl-anchor dye ADEKA-1 and a carboxy-anchor organic dye LEG4 was revealed to work collaboratively by enhancing the electron injection from the light-excited dyes to the TiO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> payback times, low toxicity of the constituent elements and relatively high light-to-electric energy conversion efficiencies ( $\eta$ ) especially under low-light intensities and scattered light conditions.<sup>1–4</sup> In DSSCs,  $\eta$  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<sub>2</sub>.<sup>1–9</sup>

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

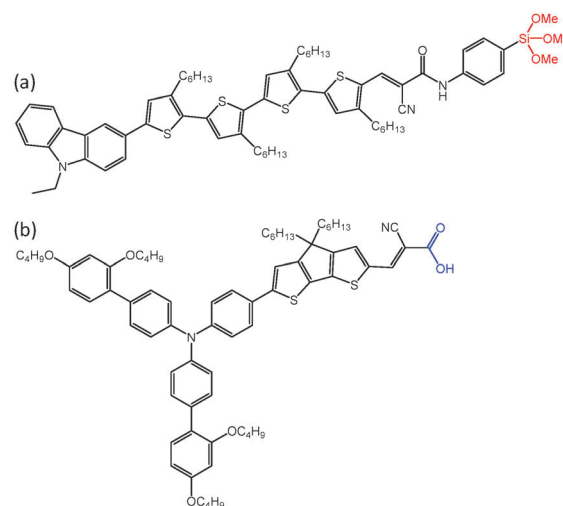


Fig. 1 Molecular structures of photosensitizing dyes: (a) silyl-anchor dye ADEKA-1 and (b) carboxy-anchor dye LEG4.

Besides the high photovoltaic performance, the TiO<sub>2</sub> 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  $\eta$  to 12.8% by means of the co-sensitization of ADEKA-1 and a silyl-anchor coumarin dye SFD-5.<sup>14</sup>

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<sup>15</sup> (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  $\eta$  by a factor of 1.3 under simulated sunlight at one sun (AM-1.5G,  $100 \text{ mW cm}^{-2}$ ; Table S2, ESI†).

In the cell photosensitized by **ADEKA-1** with **LEG4**, in which the relative amount of the dyes adsorbed on the  $\text{TiO}_2$  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  $\text{TiO}_2$ . In **ADEKA-1** the alkoxy-silyl-anchor moiety links to the chromophore (carbazole/alkyl-functionalized oligothiophene moiety) *via* the phenyl-amide 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  $\text{TiO}_2$  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  $\text{Al}_2\text{O}_3$  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  $\text{TiO}_2$  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  $\text{TiO}_2$  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  $99 \pm 2\%$  (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  $\text{TiO}_2$  conduction band estimated from the transient open-circuit voltage decays (Fig. S14, ESI†) observed in the co-sensitization with **LEG4** indicate that the

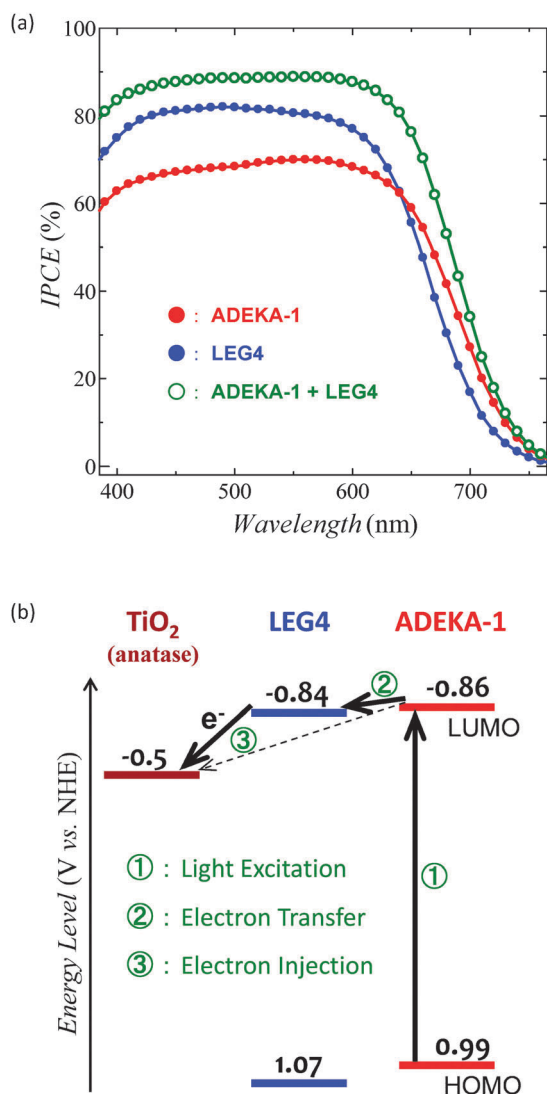


Fig. 2 (a) IPCE spectra of the cells photosensitized by **ADEKA-1**, by **LEG4** and by **ADEKA-1** with **LEG4** (cell-A) and (b) a schematic drawing of the charge separation processes for the  $\text{TiO}_2$  electrode sensitized collaboratively by **ADEKA-1** and **LEG4**.



**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)

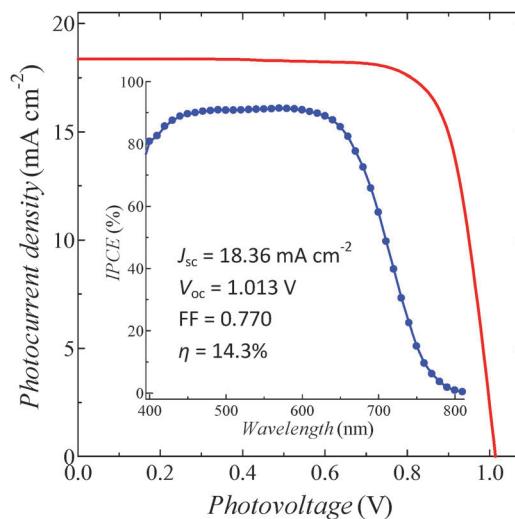
Entry	Electrolyte:redox <sup>a</sup>	Counter electrode	Light intensity (mW cm <sup>-2</sup> )	J <sub>sc</sub> (mA cm <sup>-2</sup> )	V <sub>oc</sub> (V)	FF	η (%)
1	A:I <sub>3</sub> <sup>-</sup> /I <sup>-</sup>	FTO/Pt	100	19.11	0.783	0.748	11.2
2	F:[Co(phen) <sub>3</sub> ] <sup>3+/2+</sup>	FTO/Pt	100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

<sup>a</sup> Electrolyte: (A) 0.07 M I<sub>2</sub>, 0.05 M LiI, 0.05 M NaI, 0.50 M DMPImI, 0.10 M EMImI, 0.05 M TBAl, 0.05 M THAl, 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<sup>2+</sup>(phen)<sub>3</sub>](PF<sub>6</sub><sup>-</sup>)<sub>2</sub>, 0.05 M [Co<sup>3+</sup>(phen)<sub>3</sub>](PF<sub>6</sub><sup>-</sup>)<sub>3</sub>, 0.07 M LiClO<sub>4</sub>, 0.02 M NaClO<sub>4</sub>, 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 CCoBP in MeCN. The data for the cells with other electrolytes (B–E) are listed in Table S6 (ESI). <sup>b</sup> The values are the averages of the results of the four cells which were prepared separately (Table S5, ESI).

adsorbed **LEG4** on the TiO<sub>2</sub> electrode also works as a suppressor, preventing back electron transfer from the TiO<sub>2</sub> electrode to the electrolyte by covering the naked surface of the TiO<sub>2</sub> electrode with its plural alkyl-chain substituents.<sup>15–18</sup> By using an I<sub>3</sub><sup>-</sup>/I<sup>-</sup> 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<sub>max</sub>) obtained in the DSSC is attributed to the energy gap between the quasi-Fermi level of the TiO<sub>2</sub> [approximately the energy level of the conduction-band edge (E<sub>C.B.</sub>)] 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<sub>3</sub><sup>-</sup>/I<sup>-</sup>.<sup>1–4,7–9,11,13–15</sup> The redox potential of the cobalt(III/II) tris(1,10-phenanthroline) complex ([Co(phen)<sub>3</sub>]<sup>3+/2+</sup>) is lower than that of I<sub>3</sub><sup>-</sup>/I<sup>-</sup> by ca. 0.2 V,<sup>19</sup> 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<sup>2+</sup>-complex electrolyte to the oxidized dye.<sup>13–15</sup> Thus we employed [Co(phen)<sub>3</sub>]<sup>3+/2+</sup> 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<sup>2+</sup>/Co<sup>3+</sup> ratio, the kind of cobalt(III/II) complex counter anion and the electrolyte additives, were optimized experimentally according to the literature<sup>7,13,14,20,21</sup> using a platinum-deposited F-doped SnO<sub>2</sub> (FTO)-coated glass plate as the counter electrode. The cell using an electrolyte solution with the optimized composition exhibited a high V<sub>oc</sub> 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)<sub>3</sub>]<sup>3+/2+</sup>. However, a decrease of the J<sub>sc</sub> was also observed in the cell compared to the cell with the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox electrolyte solution. In order to recover the J<sub>sc</sub>, 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



**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<sup>-2</sup>). Inset shows the IPCE spectrum of the cell.

higher J<sub>sc</sub> and fill factor (FF) in photocurrent–voltage properties than the standard platinum electrodes.<sup>8,22,23</sup> Fig. 3 shows an example of the *J*–*V* curve under AM-1.5G one sun illumination (100 mW cm<sup>-2</sup>) 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<sub>sc</sub> was actually improved in the cell from 17.8 to 18.3 ± 0.1 mA cm<sup>-2</sup> 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<sub>oc</sub> 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<sup>-2</sup> intensity (entry 4 in Table 1, and Fig. S16 and S17 in the ESI†).

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<sub>oc</sub> 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<sub>2</sub> 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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