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

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Electronic Supplementary Information (ESI)

a) Photosensitizing dyes used in this work:

A carbazole/hexyl-functionalized oligothiophene/trimethoxysilyl-anchor dye (ADEKA-1) was synthesized by using MK-2 as a starting material.\textsuperscript{2,3} Dibiphenylmonophenylamine dyes (LEG4 and D35) were purchased from Dyenamo and a triphenylamine dye (L0) was synthesized by using the general method.\textsuperscript{4-7} An indoline dye (D131) was purchased from Mitsubishi Paper Mills.\textsuperscript{8} Molecular structures of these photosensitizing dyes are shown in Fig. S2.

b) Device fabrication of Cell-A:

The Cell-A is the cell for checking photosensitization properties of the dyes. The nanocrystalline porous TiO\textsubscript{2} film electrodes were prepared by squeegeeing a commercial TiO\textsubscript{2} paste [JGC Catalysts and Chemicals, PST-18NR\textsuperscript{9}] on the washed F-doped SnO\textsubscript{2} (FTO)-coated glass plates (9-11 Ω/sq.; Asahi Glass) followed by sintering the TiO\textsubscript{2} layers at 450 °C. The thickness of the transparent porous TiO\textsubscript{2} film was estimated to be ~4 μm. An adsorption of ADEKA-1 on the TiO\textsubscript{2} electrodes was performed by immersing the electrodes in a toluene solution with 3.0 × 10\textsuperscript{-4} M ADEKA-1 at ~25 °C for 2 h, and then the dye-adsorbed electrodes were washed with toluene and ethanol. Adsorptions of the other photosensitizing dyes (LEG4, D35, L0 and D131) on the TiO\textsubscript{2} electrodes were performed by immersing the electrodes in ethanol solutions with 3.0 × 10\textsuperscript{-4} M dyes at ~25 °C for 2 h, and then the dye-adsorbed electrodes were washed with ethanol. Co-adsorptions of the dyes (LEG4, D35, L0 and D131) on the ADEKA-1-adsorbed TiO\textsubscript{2} electrodes were carried out by immersing the ADEKA-1-adsorbed electrodes in the ethanol solutions containing 3.0 × 10\textsuperscript{-4} M dyes at ~25 °C for 2 h, and then the electrodes were washed with ethanol. Before the immersion in the ADEKA-1 solution, the TiO\textsubscript{2} electrodes were kept in air at 120 °C for 2 h to eliminate adsorbed water on the TiO\textsubscript{2} surface for the efficient dye adsorption.

Photovoltaic measurements were performed for the electrochemical cells of an open sandwich type. A platinum-deposited stainless-steel plate was employed as the counter electrode and a solution with I\textsubscript{3}/I\textsubscript{2} (0.50 M LiI, 0.05 M I\textsubscript{2} in MeCN) was used as the redox electrolyte solution. The dye-adsorbed TiO\textsubscript{2} electrode, the counter electrode and a polyethylene film spacer with ~40 μm thick were assembled into a cell, and the redox electrolyte solution was injected into the space between the electrodes.

c) Device fabrication of Cell-B:

The Cell-B is the cell for a high photovoltaic performance. The nanocrystalline porous TiO\textsubscript{2} film electrodes were prepared on the UV-O\textsubscript{3}, TiCl\textsubscript{4} and Nb(OC\textsubscript{4}H\textsubscript{9})\textsubscript{5}-treated FTO-coated glass plates (9 Ω/sq.; Nippon Sheet Glass) by spin-coating and screen-printing methods with subsequent sintering at 520 °C.\textsuperscript{10,11} The commercial TiO\textsubscript{2} powders (Nippon Aerosil, Ishihara...
Sangyo Kaisha, Tayca Corporation and JGC C&C) were used with purifications. The thickness of the porous TiO₂ film with the multilayer structure was estimated to be ~10 µm (blocking layer ~ 0.2 µm, transparent layer ~ 4 µm, semitransparent layer ~ 2 µm and scattering layer ~ 4 µm). Then, the surface of the TiO₂ electrodes were modified by the TiCl₄, Al[OCH(CH₃)₂]₃ and Mg(OCH₂H₂)₂ treatments to prevent the back-electron transfer. ¹⁰,¹² An adsorption of ADEKA-1 on the TiO₂ electrodes was performed by immersing the electrodes in a toluene-acetonitrile (9:1 in volume) solution with 2.0 × 10⁻⁴ M ADEKA-1 and 1.0 × 10⁻⁴ M coadsorbent of isoctyltrimethoxysilane (Gelest) at 10 °C for 15 h, and then the dye-adsorbed electrodes were washed with toluene, acetonitrile and ethanol.²,³ A co-adsorption of LEG4 on the ADEKA-1-adsorbed TiO₂ electrodes was carried out by immersing the ADEKA-1-adsorbed electrodes in the ethanol solution containing 3.0 × 10⁻⁴ M LEG4 at 25 °C for 2 h, and then the ADEKA-1 + LEG4-co-adsorbed electrodes were washed with ethanol and acetonitrile. Before the immersion in the ADEKA-1 solution, the TiO₂ electrodes were treated with UV-O₃, heated in air at 100 °C for 5 h and then cooled to 80 °C to eliminate adsorbed water on the TiO₂ surface for the efficient dye adsorption. The hierarchical multi-capping treatment was performed to the ADEKA-1 + LEG4-co-adsorbed TiO₂ electrodes by immersing the electrodes in a 1.0 × 10⁻⁴ M toluene-acetonitrile (3:2 in volume) solution at 25 °C of octadecylphosphonic acid (ODPA) for 1 min and in 1.0 × 10⁻³ M toluene-acetonitrile (1:1 in volume) solutions at 25 °C of octadecyltrimethoxysilane (ODTMS) for 10 min, dodecyltrimethoxysilane (DDTMS) for 10 min, octyldimethoxysilane (OMTMS) for 10 min and ethyltrimethoxysilane (ETMS) for 15 min in turn to form the ‘alkyl-thicket’ structure on the TiO₂ photoelectrodes (Figs. S19 and S20).²,³

Photovoltaic measurements were performed for the electrochemical cells of an open sandwich type. A platinum-deposited FTO-coated glass plate (FTO/Pt), which was prepared by a rf magnetron sputtering of Pt and the reported H₂PtCl₆ treatment,¹³ and graphene nanoplatelets (GNP) + gold-treated FTO-coated glass plate (FTO/Au/GNP), which was prepared by a vacuum evaporation of Au and the reported GNP treatment,¹⁴,¹⁵ were employed as the counter electrodes. The mixture (1:1 in weight) of a commercial graphene (Cheap Tubes, Grade 3: t ~ 8 nm, d < ~2 µm) and an exfoliated graphene (t ~ 5 nm, d < ~5 µm) prepared by ADEKA was employed as the GNP. As for the redox electrolytes, six redox electrolyte solutions with I₃⁻/I⁻ or cobalt(II/III) complexes were used: A) 0.07 M I₂, 0.05 M NaI, 0.05 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPlmI), 0.10 M 1-ethyl-3-methylimidazolium iodide (EMImI), 0.05 M tetra-n-butylammonium iodide (TBAI), 0.05 M tetra-n-hexylammonium iodide (THAI), 0.40 M 4-tert-butylpyridine (TBP), 0.10 M 4-methylpyridine (MP), 0.10 M guanidinium thiocyanate (GuSCN) in MeCN/valeronitrile (VN)/tetrahydrofuran (THF) (8:1:1 in volume) (Fig. S21),¹⁶⁻¹⁹ B) 0.25 M [Co²⁺(phen)₃]([PF₆]₂), 0.035 M [Co³⁺(phen)₃]([PF₆]₃), 0.10 M LiClO₄, 0.50 M TBP in MeCN,²⁰ C) 0.20 M [Co²⁺(phen)₃]([PF₆]₂), 0.05 M [Co³⁺(phen)₃]([PF₆]₃), 0.10 M LiClO₄, 0.50 M TBP in MeCN, D) 0.20 M [Co²⁺(phen)₃]([TFSI]₂), 0.05 M [Co³⁺(phen)₃]([TFSI]₃), 0.10 M LiClO₄, 0.50 M TBP in MeCN, E) 0.20 M [Co²⁺(phen)₃]([PF₆]₂), 0.05 M [Co³⁺(phen)₃]([PF₆]₃), 0.07 M LiClO₄, 0.02 M NaClO₄, 0.03 M tetrabutylammonium hexafluorophosphate (TBAPF), 0.01 M tetrabutylammonium hexafluorophosphate (TBPPF), 0.01 M 1-hexyl-3-methylimidazolium hexafluorophosphat (HMImPF), 0.30 M TBP, 0.10 M 4-trimethylsilylpyridine (TMSP),²¹ 0.10 M MP in MeCN,²,³ F) 0.20 M [Co²⁺(phen)₃]([PF₆]₂), 0.05 M [Co³⁺(phen)₃]([PF₆]₃), 0.07 M LiClO₄, 0.02 M NaClO₄, 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 4-cyano-4'-propylbiphenyl (CPrBP), 0.10 M 4-cyano-4'-pentylbiphenyl (CPeBP), 0.05 M 4-cyano-4'-octylibiphenyl (COcBP) in MeCN (Fig. S22).²²
The dye-adsorbed TiO$_2$ electrode, the counter electrode and a polyethylene film spacer with ~12 μm thick were assembled into a cell, and the redox electrolyte solution was injected into the space between the electrodes.

d) Photovoltaic measurements:

The photovoltaic performances of the fabricated dye-sensitized solar cells (DSSCs) with an antireflection film were assessed from the incident monochromatic photon-to-current conversion efficiency ($IPCE$) spectra and the photocurrent-voltage ($J$-$V$) properties of the cells with maintaining the aperture area of the cells to be $0.320 \times 0.320$ cm$^2$ by the use of a square black shade mask with 30 μm thick (Bunkoukeiki) (Fig. S23). The $IPCE$ spectra were obtained by using a monochromatic light source of SM-25 (Bunkoukeiki) and an electrometer of R8240 (Advantest) at 25 °C. The $J$-$V$ properties were measured by using a solar simulator with Class AAA of OTENTO-SUN III (Bunkoukeiki) and a source meter of R6240A (Advantest) under the simulated sunlight illumination of AM-1.5G one sun condition (100 mW cm$^{-2}$) at 25 °C. Lower light intensities were also applied. The power of the simulated sunlight was calibrated by the use of a reference Si photodiode for DSSCs of BS-520 (Bunkoukeiki). The $J$-$V$ properties were obtained by applying an external bias to the cells and measuring the generated photocurrent with the source meter. The voltage step and delay time for the photocurrent measurements were set to be 5 mV and 250 ms, respectively.

\[
IPCE(\%) = \left\{ \frac{(1240 \text{ [V nm]} \times J_{ph} \text{ [mA cm}^{-2})}{(\lambda \text{ [nm]} \times I_{m} \text{ [mW cm}^{-2})}\right\} \times 100
\]

\[
J_{ph}\text{ is the short-circuit photocurrent density for the monochromatic light irradiation. } \lambda \text{ and } I_{m}\text{ are the wavelength and the intensity of the monochromatic light, respectively.}
\]

\[
\eta(\%) = \left\{ \frac{(J_{sc} \text{ [mA cm}^{-2}) \times V_{oc} \text{ [V]} \times FF)}{I_{s} \text{ [mW cm}^{-2})}\right\} \times 100
\]

The overall light-to-electric energy conversion efficiency ($\eta$) of the DSSC is determined by the short-circuit photocurrent density ($J_{sc}$), the open-circuit photovoltage ($V_{oc}$), the fill factor ($FF$) ($= P_{max}/(J_{sc} \times V_{oc})$) of the cell and the intensity of the incident simulated sunlight ($I_{s}$). $P_{max}$ is the product of $J_{P_{max}}$ and $V_{P_{max}}$, that are photocurrent density and photovoltage at the voltage where the power output of the cell is maximal.

e) Other measurements and calculations:

Optical measurements: The UV-visible absorption spectra of photosensitizing dye solutions were recorded on a HITACHII U-3010 spectrophotometer at ~25 °C. An integrating sphere was equipped to the spectrophotometer for the measurements of the dye-adsorbed TiO$_2$ electrodes. The emission spectra of photosensitizing dye solutions and Al$_2$O$_3$ porous films with ADEKA-1 and/or LEG4 were recorded on a JASCO FP-8300 spectrofluorometer at ~25 °C with the excitations at 475 and 500 nm. The semitransparent Al$_2$O$_3$ porous films with ~3 μm thick on the FTO-coated glass plates (Asahi Glass) were made of AEROXIDE Alu C (Nippon Aerosil) by the use of a screen printing method.

Molecular orbital (MO) calculations: We optimized the molecular structures and calculated the energy levels of frontier orbitals and others for the trimethoxysilyl carbazole dye (ADEKA-1) and the carboxy triarylamine dye (LEG4) on the Gaussian 09 program package by using a density functional theory (DFT).

A Becke’s three-parameter hybrid functional with the LYP correlation functional (B3LYP) and a better hybrid exchange-correlation functional of coulomb-attenuating method-B3LYP (CAM-B3LYP) were employed together with 6-31+G(d,p) basis set. Geometry optimizations and calculations of electronic properties of the dyes were...
performed without any symmetry constraint in the gas phase and by assuming the target molecules to be isolated. Calculated molecular orbitals were visualized by using the Winmoster (X-Ability Co.,Ltd.). In addition, we calculated the lowest 3 singlet transitions of the dyes by using a time-dependent density functional theory (TDDFT) method, and the absorption spectra of the dyes were estimated by applying an artificial Gaussian broadening.

Internal quantum efficiency (IQE) measurements: The IQE spectra of the cells photosensitized by ADEKA-1 and/or LEG4 were estimated by using cells, which were fabricated in the same procedures as Cell-A but changing only the thickness of the TiO$_2$ films to be $\sim$1 $\mu$m, based on a following equation. The hyper monolight of SM-25 (Bunkoukeiki) was used as the monochromatic light source in the measurements.

$$IQE\; (\%) \approx \Phi_{dye} = (J_{ph} / e) / \{ I \times 10^{-Abs.(TiO_2)} \times (1 - 10^{-Abs.(Dye)}) \} , \; I = (W_\lambda / hc)$$

$\Phi_{dye}$ is the photocurrent generation efficiency (quantum yield). $J_{ph}$ is the short-circuit photocurrent density for monochromatic irradiation, $e$ is the elementary charge, $I$ is the number of photons per unit area and unit time, $\lambda$ is the wavelength of the light irradiation, $Abs.(TiO_2)$ is the absorbance of the TiO$_2$ electrode, $Abs.(Dye)$ is the absorbance of the dyes adsorbed on the TiO$_2$ electrode, $W$ is the irradiated light power, $h$ is the Planck’s constant and $c$ is the light velocity.

Open-circuit voltage decay (OCVD) measurements: The cells photosensitized by ADEKA-1 with/without LEG4 (Cell-A) were used to measure OCVDs. The cells were illuminated at an open-circuit condition under the AM-1.5G one sun simulated sunlight (100 mW cm$^{-2}$) at 25 °C by using the solar simulator (OTENTO-SUN III, Bunkoukeiki). After the open-circuit photovoltages ($V_{oc}$) indicated steady values, the illumination was turned off with a shutter, and OCVDs were plotted with the measurement step of 200 ms. The lifetimes of the electrons in the TiO$_2$ conduction band were calculated by using the results of the OCVD measurements based on a following equation.

$$\tau_n = -(k_B T / e) \times (dV_{oc} / dt)^{-1}$$

$\tau_n$ is the lifetime of an electron in the TiO$_2$ conduction band, $k_B$ is the Boltzmann constant, $T$ is temperature, $e$ is the elementary charge and $t$ is time after turning off the simulated sunlight.
Figure S1. Schematic illustrations of the structure and the operation principle for DSSCs.
Figure S2. Molecular structures of ADEKA-1 and the dyes employed as the co-photosensitizers in this work (LEG4, D35, L0 and D131).
Figure S3. Normalized absorption spectra of the solutions containing ADEKA-1 and the dyes employed as the co-photosensitizers in this work. Chloroform for ADEKA-1 and ethanol for the others were used as the solvents.
**Figure S4.** Normalized absorption spectra of the transparent TiO$_2$ films with ADEKA-1 and the dyes employed as the co-photosensitizers in this work.
Figure S5. (a) Absorption spectra and (b) normalized absorption spectra (solid lines) and emission spectra with $\lambda_{\text{ex}} = 475$ nm (dashed lines) of ADEKA-1 in a chloroform solution and LEG4 in an ethanol solution.
Table S1. Optical and electrochemical data for ADEKA-1 and LEG4.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Absorption&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Emission&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Potential vs NHE&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Driving Force&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm)</td>
<td>ε&lt;sub&gt;max&lt;/sub&gt; (dm&lt;sup&gt;3&lt;/sup&gt; mol&lt;sup&gt;-1&lt;/sup&gt; cm&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>λ&lt;sub&gt;max&lt;/sub&gt; (nm) on TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>E&lt;sub&gt;ox&lt;/sub&gt; (V)</td>
</tr>
<tr>
<td>ADEKA-1</td>
<td>507</td>
<td>43,500</td>
<td>708</td>
<td>1.85</td>
</tr>
<tr>
<td>LEG4</td>
<td>483</td>
<td>47,500</td>
<td>645</td>
<td>1.91</td>
</tr>
</tbody>
</table>

<sup>a</sup> Steady-state absorption and emission data were observed by using a chloroform solution of ADEKA-1 and an ethanol solution of LEG4.  
<sup>b</sup> Lowest transition energies (E<sub>0,0</sub>) were estimated from absorption onsets in the absorption spectra of the dye-adsorbed TiO<sub>2</sub> electrodes (Fig. S4).  
<sup>c</sup> Oxidation potentials (E<sub>ox</sub> vs. NHE) are literature values. Excited state oxidation potentials (E<sub>ox</sub><sup>*</sup> vs. NHE) were estimated from E<sub>ox</sub><sup>*</sup> = E<sub>ox</sub> - E<sub>0,0</sub>).  
<sup>d</sup> Driving forces for electron transfer processes. ΔG<sub>inj</sub>: Driving forces for the electron injection from the singlet excited state (E<sub>ox</sub><sup>*</sup>) of the dye to the TiO<sub>2</sub> conduction band (−0.5 V vs. NHE). ΔG<sub>reg</sub>: Driving forces for the regeneration process of the dyes in the radical cation state (E<sub>ox</sub>) by the I<sup>−</sup>/I<sup>−</sup> redox in the state of +0.4 V vs. NHE.
Figure S6. Energy levels of the frontier orbitals of ADEKA-1 and the dyes employed as the co-photosensitizers in this work.²⁴,⁷,³⁰
Figure S7. IPCE spectra of the cells photosensitized by ADEKA-1 and/or LEG4, D35, L0, D131 (Cell-A).
Table S2. Relative photovoltaic parameters of the cells photosensitized by ADEKA-1 and/or LEG4, D35, L0, D131 (Cell-A) under the illumination of the simulated sunlight (AM-1.5G, 100 mW cm\(^{-2}\)): short-circuit photocurrent density (\(J_{sc}\)), open-circuit photovoltage (\(V_{oc}\)), fill factor (\(FF\)) and light-to-electric energy conversion efficiency (\(\eta\)).

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Rel. (J_{sc})</th>
<th>Rel. (V_{oc})</th>
<th>Rel. (FF)</th>
<th>Rel. (\eta)</th>
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</thead>
<tbody>
<tr>
<td>ADEKA-1</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>LEG4</td>
<td>1.04</td>
<td>0.79</td>
<td>0.89</td>
<td>0.73</td>
</tr>
<tr>
<td>D35</td>
<td>0.85</td>
<td>0.78</td>
<td>0.92</td>
<td>0.61</td>
</tr>
<tr>
<td>L0</td>
<td>0.52</td>
<td>0.72</td>
<td>1.02</td>
<td>0.38</td>
</tr>
<tr>
<td>D131</td>
<td>0.63</td>
<td>0.75</td>
<td>1.04</td>
<td>0.50</td>
</tr>
<tr>
<td>ADEKA-1 + LEG4</td>
<td>1.27</td>
<td>1.07</td>
<td>0.97</td>
<td>1.29</td>
</tr>
<tr>
<td>ADEKA-1 + D35</td>
<td>1.14</td>
<td>1.07</td>
<td>0.93</td>
<td>1.14</td>
</tr>
<tr>
<td>ADEKA-1 + L0</td>
<td>1.04</td>
<td>1.02</td>
<td>0.96</td>
<td>1.01</td>
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<tr>
<td>ADEKA-1 + D131</td>
<td>1.06</td>
<td>1.04</td>
<td>0.93</td>
<td>1.01</td>
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</table>
Figure S8. (a) Absorption spectra of ADEKA-1, LEG4 and ADEKA-1 + LEG4 adsorbed TiO₂ electrodes (t ~ 4 μm). Insets show the photographs of the dye-adsorbed TiO₂ electrodes. (b) Absorption spectra in visible region of ADEKA-1 and ADEKA-1 + LEG4 adsorbed on TiO₂ electrodes (t ~ 1 μm). Dotted lines represent the result of the spectral decomposition into the components by ADEKA-1 and LEG4. The relative amount of the dyes adsorbed on the TiO₂ electrode was estimated to be 1.0 : 0.25 for ADEKA-1 : LEG4.
Figure S9. Molecular orbitals (HOMO-1, HOMO, LUMO and LUMO+1) of ADEKA-1 and LEG4 calculated by DFT at the CAM-B3LYP/6-31+G(d,p) // B3LYP/6-31+G(d,p) levels.
Table S3. Energy levels of HOMO-1, HOMO, LUMO and LUMO+1 for **ADEKA-1** and **LEG4** calculated by DFT at the CAM-B3LYP/6-31+G(d,p) // B3LYP/6-31+G(d,p) levels.

<table>
<thead>
<tr>
<th>Dye</th>
<th>HOMO-1 (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>LUMO+1 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADEKA-1</td>
<td>-6.8058</td>
<td>-6.1258</td>
<td>-1.8498</td>
<td>-0.3644</td>
</tr>
<tr>
<td>LEG4</td>
<td>-6.8643</td>
<td>-6.1528</td>
<td>-1.8994</td>
<td>-0.9138</td>
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</table>
Table S4. Calculated excited energies, oscillator strengths ($f$) and compositions in terms of molecular orbital contributions for **ADEKA-1** and **LEG4** (TDDFT: CAM-B3LYP/6-31+G(d,p) // B3LYP/6-31+G(d,p) levels).

<table>
<thead>
<tr>
<th>Dye</th>
<th>State</th>
<th>Major Excitation (Coefficient : Contribution)*,**</th>
<th>Character</th>
<th>Energy (eV)</th>
<th>$f$ ***</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_0 \rightarrow S_1$</td>
<td>H $\rightarrow$ L (0.61865 : 77%) , H-1 $\rightarrow$ L (-0.23782 : 11%)</td>
<td>$\pi^-\pi^*$</td>
<td>2.4504 (506.03 nm)</td>
<td>2.3502</td>
</tr>
<tr>
<td><strong>ADEKA-1</strong></td>
<td>$S_0 \rightarrow S_2$</td>
<td>H $\rightarrow$ L+1 (0.52972 : 56%) , H-1 $\rightarrow$ L (-0.35061 : 25%)</td>
<td></td>
<td>3.2810 (377.93 nm)</td>
<td>0.1317</td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_3$</td>
<td>H-1 $\rightarrow$ L (0.40218 : 32%) , H $\rightarrow$ L+1 (0.36720 : 27%)</td>
<td></td>
<td>3.7078 (334.43 nm)</td>
<td>0.0912</td>
</tr>
<tr>
<td></td>
<td>$S_0 \rightarrow S_1$</td>
<td>H $\rightarrow$ L (0.56471 : 64%) , H-1 $\rightarrow$ L (0.36745 : 27%)</td>
<td>$\pi^-\pi^*$</td>
<td>3.5037 (353.91 nm)</td>
<td>1.7820</td>
</tr>
<tr>
<td><strong>LEG4</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>$S_0 \rightarrow S_2$</td>
<td>H-1 $\rightarrow$ L (0.48550 : 47%) , H $\rightarrow$ L (-0.28628 : 16%)</td>
<td></td>
<td>3.9280 (315.68 nm)</td>
<td>0.1954</td>
</tr>
</tbody>
</table>

$^*H = \text{HOMO}, L = \text{LUMO}$  
$^{**}|\text{CI coeff.}| > 0.1$  
$^{***}\text{Oscillator strength $[4.319\times10^{-9}\cdot \int \varepsilon(\nu) d\nu]$}$
**Figure S10.** Calculated UV-visible absorption spectra (Dotted lines) of ADEKA-1 and LEG4 (TDDFT: CAM-B3LYP/6-31+G(d,p) // B3LYP/6-31+G(d,p) levels). All spectra were obtained by applying an artificial Gaussian broadening of 3,500 cm$^{-1}$ FWHM to the intensities calculated with TDDFT for the visualization purpose. Solid lines show the experimental data of the dye solutions (CHCl$_3$ solution for ADEKA-1 and EtOH solution for LEG4; Fig. S5).
Figure S11. (a) Absorption spectra in visible region of ADEKA-1, LEG4 and ADEKA-1 + LEG4 adsorbed on Al₂O₃ porous films. Dotted lines represent the result of the spectral decomposition into the components by ADEKA-1 and LEG4. The relative amount of the dyes adsorbed on the Al₂O₃ porous film was estimated to be 1.0 : 0.27 for ADEKA-1 : LEG4. (b) Normalized emission spectra of the Al₂O₃ porous films modified by ADEKA-1, LEG4 and ADEKA-1 + LEG4. The emission spectra were obtained by the excitation at 500 nm.
Figure S12. (a) Absorption spectra of the dyes adsorbed on the TiO$_2$ electrodes, (b) IPCE spectra of the cells used for the estimation of IQEs and (c) the estimated IQE spectra of the cells photosensitized by ADEKA-1 and/or LEG4.
Figure S13. Dark $J-V$ properties of the cells sensitized by ADEKA-1 with/without LEG4 (Cell-A).
Figure S14. (a) Open-circuit voltage decays (OCVDs) of the cells photosensitized by ADEKA-1 with/without LEG4 (Cell-A). (b) Lifetime of the electrons in the TiO$_2$ conduction band plotted as a function of the open-circuit voltage.
Figure S15. Schematic energy diagram of the DSSC composed of the anatase-TiO$_2$, the photosensitizing dyes of ADEKA-1 and LEG4, and the redox electrolytes of I$_3^{-}$/I$^-$ and [Co(phen)$_3$]$^{3+/2+}$ couples.$^{2,4,31}$ Molecular structure of the [Co(phen)$_3$]$^{3+/2+}$ is also shown.
Table S5. Photovoltaic parameters of the cells with the same composition as the best-performance cell of Entry 3 in Table 1; photosensitized collaboratively by ADEKA-1 and LEG4 using the [Co(phen)3]3+/2+ redox electrolyte (Electrolyte F) and the FTO/Au/GNP counter electrode under the illumination of the simulated sunlight (AM-1.5G, 100 mW cm\(^{-2}\)).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dyes</th>
<th>Electrolyte : Redox</th>
<th>Counter Electrode</th>
<th>Light Intensity</th>
<th>(J_{sc}) (mA cm(^{-2}))</th>
<th>(V_{oc}) (V)</th>
<th>FF</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>ADEKA-1 + LEG4</td>
<td>F : [Co(phen)(_3)]^{3+/2+}</td>
<td>FTO/Au/GNP</td>
<td>100 mW cm(^{-2})</td>
<td>18.36</td>
<td>1.013</td>
<td>0.770</td>
<td>14.3</td>
</tr>
<tr>
<td>3b</td>
<td>ADEKA-1 + LEG4</td>
<td>F : [Co(phen)(_3)]^{3+/2+}</td>
<td>FTO/Au/GNP</td>
<td>100 mW cm(^{-2})</td>
<td>18.19</td>
<td>1.014</td>
<td>0.771</td>
<td>14.2</td>
</tr>
<tr>
<td>3c</td>
<td>ADEKA-1 + LEG4</td>
<td>F : [Co(phen)(_3)]^{3+/2+}</td>
<td>FTO/Au/GNP</td>
<td>100 mW cm(^{-2})</td>
<td>18.16</td>
<td>1.013</td>
<td>0.768</td>
<td>14.1</td>
</tr>
<tr>
<td>3d</td>
<td>ADEKA-1 + LEG4</td>
<td>F : [Co(phen)(_3)]^{3+/2+}</td>
<td>FTO/Au/GNP</td>
<td>100 mW cm(^{-2})</td>
<td>18.37</td>
<td>1.014</td>
<td>0.776</td>
<td>14.5</td>
</tr>
<tr>
<td>3 (Av.)</td>
<td>ADEKA-1 + LEG4</td>
<td>F : [Co(phen)(_3)]^{3+/2+}</td>
<td>FTO/Au/GNP</td>
<td>100 mW cm(^{-2})</td>
<td>18.27</td>
<td>1.014</td>
<td>0.771</td>
<td>14.3</td>
</tr>
</tbody>
</table>

Electrolyte: 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, 0.05 M COcBP in MeCN.
Figure S16. Photocurrent density transient dynamics of the cell photosensitized collaboratively by ADEKA-1 and LEG4 with the redox electrolyte containing [Co(phen)$_3$]$^{3+/2+}$ (Cell-B) at various simulated sunlight intensities. The initial decline of the photocurrent signal at the 100 mW cm$^{-2}$ intensity would be due to a mass transfer limitation of [Co(phen)$_3$]$^{3+/2+}$. 
Figure S17. Dependences of the (a) $J_{sc}$ and (b) $V_{oc}$ on the light intensity for the best-performance cell photosensitized collaboratively by ADEKA-1 and LEG4 using the $[Co(phen)_3]^{3+/2+}$ redox electrolyte (Electrolyte F) and the FTO/Au/GNP counter electrode. The data include the results of Entries 3 and 4 in Table 1.
Table S6. Photovoltaic parameters of the cells photosensitized collaboratively by ADEKA-1 and LEG4 (Cell-B) under the illuminations of the simulated sunlight (AM-1.5G).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Dyes</th>
<th>Electrolyte : Redox</th>
<th>Counter Electrode</th>
<th>Light Intensity</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>ADEKA-1 + LEG4 A : I$_2$</td>
<td>FTO/Pt</td>
<td>100 mW cm$^{-2}$</td>
<td>19.11</td>
<td>0.783</td>
<td>0.748</td>
<td>11.2</td>
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<td>S5</td>
<td>ADEKA-1 + LEG4 B : [Co(phen)$_3$]$^{3+/2+}$</td>
<td>FTO/Pt</td>
<td>100 mW cm$^{-2}$</td>
<td>17.62</td>
<td>0.969</td>
<td>0.761</td>
<td>13.0</td>
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</tr>
<tr>
<td>S6</td>
<td>ADEKA-1 + LEG4 C : [Co(phen)$_3$]$^{3+/2+}$</td>
<td>FTO/Pt</td>
<td>100 mW cm$^{-2}$</td>
<td>18.08</td>
<td>0.963</td>
<td>0.760</td>
<td>13.2</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>ADEKA-1 + LEG4 D : [Co(phen)$_3$]$^{3+/2+}$</td>
<td>FTO/Pt</td>
<td>100 mW cm$^{-2}$</td>
<td>17.66</td>
<td>0.957</td>
<td>0.759</td>
<td>12.8</td>
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<tr>
<td>S8</td>
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<td>FTO/Pt</td>
<td>100 mW cm$^{-2}$</td>
<td>17.43</td>
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<td>13.4</td>
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<td>ADEKA-1 + LEG4 F : [Co(phen)$_3$]$^{3+/2+}$</td>
<td>FTO/Pt</td>
<td>100 mW cm$^{-2}$</td>
<td>17.77</td>
<td>1.018</td>
<td>0.765</td>
<td>13.8</td>
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</tr>
<tr>
<td>3a</td>
<td>ADEKA-1 + LEG4 F : [Co(phen)$_3$]$^{3+/2+}$</td>
<td>FTO/Au/GNP</td>
<td>100 mW cm$^{-2}$</td>
<td>18.36</td>
<td>1.013</td>
<td>0.770</td>
<td>14.3</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ADEKA-1 + LEG4 F : [Co(phen)$_3$]$^{3+/2+}$</td>
<td>FTO/Au/GNP</td>
<td>50 mW cm$^{-2}$</td>
<td>9.55</td>
<td>0.994</td>
<td>0.776</td>
<td>14.7</td>
<td></td>
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</table>

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, 0.10 M GuSCN in MeCN/VN/THF (8:1:1 in volume).

Electrolyte: B) 0.25 M [Co$^{2+}$(phen)$_3$](PF$_6$)$_2$, 0.035 M [Co$^{3+}$(phen)$_3$](PF$_6$)$_3$, 0.10 M LiClO$_4$, 0.50 M TBP in MeCN.

Electrolyte: C) 0.20 M [Co$^{2+}$(phen)$_3$](PF$_6$)$_2$, 0.05 M [Co$^{3+}$(phen)$_3$](PF$_6$)$_3$, 0.10 M LiClO$_4$, 0.50 M TBP in MeCN.

Electrolyte: D) 0.20 M [Co$^{2+}$(phen)$_3$](TFSI)$_2$, 0.05 M [Co$^{3+}$(phen)$_3$](TFSI)$_3$, 0.10 M LiClO$_4$, 0.50 M TBP in MeCN.

Electrolyte: E) 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 in MeCN.

Electrolyte: 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, 0.05 M COcBP in MeCN.
Figure S18. $J$-$V$ properties of the cells photosensitized collaboratively by ADEKA-1 and LEG4 (Cell-B) using I$_3^-$/$I^-$ and Co$^{3+/2+}$ redox electrolytes under the illumination of the simulated sunlight (AM-1.5G, 100 mW cm$^{-2}$ and 50 mW cm$^{-2}$ only for Entry 4). The entry numbers correspond to those in Tables 1 and S6.
**Figure S19.** Molecular structures of alkyl compounds with anchor-moieties (octadecylphosphonic acid: ODPA, octadecyltrimethoxysilane: ODTMOS, dodecyltrimethoxysilane: DDTMOS, octyltrimethoxysilane: OTMOS, isoocetyltrimethoxysilane: IOTMOS and ethyltrimethoxysilane: ETMOS) used in the hierarchical multi-capping treatment.
Figure S20. Schematic drawing of the ‘alkyl-thicket’ structure on the ADEKA-1 + LEG4-co-adsorbed TiO$_2$ photoelectrode formed by the hierarchical multi-capping treatment.
**Figure S21.** Molecular structures of additives (1,2-dimethyl-3-\(n\)-propylimidazolium iodide: DMPImI, 1-ethyl-3-methylimidazolium iodide: EMImI, tetra-\(n\)-butylammonium iodide: TBAI, tetra-\(n\)-hexylammonium iodide: THAI, 4-\(\text{tert}\) -butylpyridine: TBP, 4-methylpyridine: MP and guanidinium thiocyanate: GuSCN) used in the \(\text{I}_3^- / \text{I}^-\) redox electrolyte (Electrolyte A).
**Figure S22.** Molecular structures of additives (tetrabutylammonium hexafluorophosphate: TBAPF, tetrabutylphosphonium hexafluorophosphate: TBPPF, 1-hexyl-3-methylimidazolium hexafluorophosphate: HMImPF, 4-*tert*-butylpyridine: TBP, 4-trimethylsilylpyridine: TMSP, 4-methylpyridine: MP, 4-cyano-4'-propylbiphenyl: CPrBP, 4-cyano-4'-pentylbiphenyl: CPeBP and 4-cyano-4'-octylbiphenyl: COcBP) used in the cobalt(III/II) complex redox electrolytes (Electrolytes B-F).
Figure S23. (a) Schematic drawing for size of the square black shade mask and the TiO$_2$ porous film with the photosensitizing dyes. (b) Photograph of the electrochemical cell of the open sandwich type used in this work (Cell-B). In the photovoltaic measurements, the spaces between the shade mask and the Cu conduction tapes were also shaded to avoid light scatter and other undesirable effects producing uncertainties in the measurements.
References (Electronic Supplementary Information)


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