An achievement of over 12 percent efficiency in an organic dye-sensitized solar cell

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**General**

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. Chloroform and dimethylformamide were dried over MS4A. Column chromatography was performed on silica gel (YAMAZEN, particle size 70 μm).

**Syntheses of ADEKA-1 and ADEKA-2**

**ADEKA-1**

To a stirred mixture of MK-2\(^1\) (96 mg, 0.10 mmol), oxalyl chloride (14 mg, 0.11 mmol) and chloroform (2 ml) was added dimethylformamide (0.1 ml) at room temperature under argon. After stirring for 1 h, ethyldiisopropylamine (26 mg, 0.20 mmol) and 4-(trimethoxysilyl)aniline (21 mg, 0.10 mmol) were added at 10 °C. After stirring at room temperature for 1 h, the reaction was quenched with water (2 ml). The aqueous layer was removed, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using chloroform/hexane = 1:1 as eluent to give **ADEKA-1** (94 mg, 82%) as a dark green solid. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) H 8.31 (s, 1H), 8.14 (d, 1H), 7.96 (s, 1H), 7.73-7.67 (m, 5H), 7.49 (t, 1H), 7.41 (t, 2H), 7.26 (s, 1H), 7.20 (s, 1H), 7.10 (s, 1H), 7.02 (s, 2H), 4.39 (q, 2H), 3.63 (s, 9H), 2.90-2.81 (m, 8H), 1.76-1.35 (m, 35H), 0.93-0.88 (m, 12H). \(^1\)3C NMR (CDCl\(_3\), 100 MHz) \(\delta\) C 159.5, 155.5, 144.8, 143.5, 143.2, 142.6, 140.8, 140.7, 140.4, 139.5, 139.4, 136.8, 135.8, 135.3, 129.8, 129.2, 129.1, 128.9, 128.5, 128.3, 127.3, 126.0, 125.7, 125.1, 123.8, 123.4, 122.8, 120.6, 119.5, 119.1, 117.8, 117.5, 108.7, 108.7, 96.4, 50.9, 37.7, 31.7, 31.7, 31.6, 31.3, 30.6, 30.4, 30.3, 30.1, 29.8, 29.6, 29.4, 29.3, 29.1, 22.7, 22.7, 22.6, 14.1, 14.1, 13.9.
ADEKA-2 tert-butyl ester (1)

A mixture of MK-2 (382 mg, 0.40 mmol), mesyl chloride (50 mg, 0.44 mmol) and dimethylformamide (20 ml) was stirred at room temperature under argon for 3 h. After warming to 60 °C, tert-butyl 4-aminobenzoate (85 mg, 0.44 mmol) was added, and the solution was stirred for 2 h. After cooling to room temperature, the reaction was quenched with water (20 ml). The mixture was extracted with chloroform (20 ml), and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel) using chloroform as eluent to give 1 (54 mg, 12%) as a dark green solid. $^1$H NMR (CDCl$_3$, 400 MHz) δ$_H$ 8.59 (s, 1H), 8.31 (s, 1H), 8.14 (d, 1H), 8.03-7.99 (m, 3H), 7.73-7.68 (m, 3H), 7.49 (t, 1H), 7.42 (t, 2H), 7.20 (s, 1H), 7.11 (s, 1H), 7.03 (s, 1H), 7.02 (s, 1H), 4.39 (q, 2H), 2.91-2.81 (m, 8H), 1.76-1.68 (m, 8H), 1.61 (s, 9H), 1.48-1.35 (m, 27H), 0.94-0.90 (m, 12H).

ADEKA-2

A mixture of 1 (53 mg, 0.047 mmol) and trifluoroacetic acid (5 ml) was refluxed for 2 h. The solvent was removed under reduced pressure to give ADEKA-2 (51 mg, quant.) as a dark green solid. $^1$H NMR (DMSO-d$_6$, 400 MHz) δ$_H$ 10.43 (s, 1H), 8.45 (s, 1H), 8.32 (s, 1H), 8.22 (d, 1H), 7.93 (d, 2H), 7.79 (d, 2H), 7.73 (d, 1H), 7.61 (t, 2H),...
7.49-7.45 (m, 2H), 7.31 (s, 1H), 7.22 (t, 1H), 7.17 (s, 1H), 7.11 (s, 1H), 4.44 (q, 2H), 2.86-2.77 (m, 8H), 1.73-1.64 (m, 8H), 1.40-1.23 (m, 27H), 0.89-0.84 (m, 12H).

13C NMR (THF-d8, 100 MHz) δC 167.1, 160.6, 155.6, 144.8, 144.2, 143.8, 143.5, 142.7, 141.7, 141.6, 141.5, 140.6, 137.2, 136.3, 131.3, 131.0, 130.3, 130.1, 129.1, 128.4, 127.4, 126.7, 126.0, 125.9, 124.4, 123.9, 121.2, 120.4, 119.8, 118.0, 117.4, 109.8, 109.6, 99.8, 38.2, 32.7, 32.6, 32.3, 31.5, 31.3, 30.9, 30.7, 30.6, 30.3, 30.2, 30.0, 29.6, 24.9, 23.6, 23.5, 14.5, 14.4, 14.1.

**Spectral and Electrochemical Measurements**

The NMR spectra were obtained by using a JEOL JNM-ECA 400 Spectrometer. Chemical shifts were reported as δ units (ppm) relative to the standard material (SiMe₄). The UV-visible absorption spectra of toluene solutions at 25 °C of the carbazole dyes (ADEKA-1, ADEKA-2 and MK-2) were recorded on a JASCO V-650 UV-Vis Spectrophotometer, and an integrating sphere was equipped to the spectrophotometer for the measurements of the various sensitizing-dyes adsorbed on the TiO₂ electrodes. Cyclic voltammetry measurements were carried out at 25 °C in a three-electrode electrochemical cell on an ALS/CH Instruments Electrochemical Analyzer Model 600C to determine the oxidation potentials of the carbazole dyes. Pt, Pt and Ag/Ag⁺ were employed as working, counter and reference electrodes, respectively. The supporting electrolyte was 0.10 M tetrabutylammonium perchlorate (TBAP) in CH₂Cl₂ and the scan rate was set to be 100 mV s⁻¹. The potential of the reference electrode is 0.43 V versus normal hydrogen electrode (NHE) and was calibrated with ferrocene.
Device Fabrication and Photovoltaic Measurement

The nanocrystalline porous TiO$_2$ film electrodes for dye-sensitized solar cells (DSSCs) were prepared on the UV-O$_3$, TiCl$_4$ and Nb(OC$_4$H$_9$)$_5$-treated F-doped SnO$_2$ (FTO)-coated glass plates (9 Ω/sq.; Nippon Sheet Glass) by spin-coating and screen-printing methods with subsequent sintering at 520 °C. The commercial TiO$_2$ powders (Nippon Aerosil, Ishihara Sangyo Kaisha, Tayca Corporation and JGC Catalysts and Chemicals) were used with further purifications. The thickness of the porous TiO$_2$ film was estimated to be 10-11 μm (blocking layer ~ 0.2 μm, transparent layer ~ 4 μm, semitransparent layer ~ 2 μm and scattering layer ~ 4 μm). Then, the TiO$_2$ electrodes were modified by the TiCl$_4$, Al[OCH(CH$_3$)$_3$]$_3$ and Mg(OC$_2$H$_5$)$_2$ treatments to improve the TiO$_2$ surface and prevent the back-electron transfer for the DSSCs.\textsuperscript{2,3} Adsorption of the trimethoxysilyl dye (ADEKA-1) on the TiO$_2$ 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 24 h, and then the dye-adsorbed electrodes were washed with toluene, acetonitrile and ethanol. Adsorption of the carboxy dyes (ADEKA-2 and MK-2) on the TiO$_2$ electrodes was carried out by immersing the electrodes in 2.0 × 10$^{-4}$ M toluene solutions of ADEKA-2 and MK-2 at 25 °C for 24 h, and then the dye-adsorbed electrodes were washed with above solvents. Before the immersions, the TiO$_2$ electrodes were treated with UV-O$_3$ and heated in air at 100 °C for 5 h and then cooled to 80 °C to eliminate excess adsorbed water on the TiO$_2$ surface for efficient dye adsorptions. The dye-adsorbed TiO$_2$ electrodes were immersed in a 1.0 × 10$^{-3}$ M toluene-acetonitrile (1:1 in volume) solution of heptanoic acid (HA) at 25 °C for 30 min as the single-capping treatment. The hierarchical multi-capping treatment was performed to the ADEKA-1-adsorbed TiO$_2$ electrodes by immersing the electrodes in 1.0 × 10$^{-3}$ M toluene-acetonitrile (1:1 in volume) solutions at 25 °C of melissic acid (MeA) for 10 min, octadecylphosphonic acid (OPA) for 5 min, stearic acid (SA) for 10
min, myristic acid (MyA) for 10 min, decylphosphonic acid (DPA) for 5 min, octyl trimethoxysilane (OTMS) for 15 min, HA for 10 min and pivalic acid (PA) for 15 min in sequence (Fig. S8) to form the ‘alkyl-thicket’ structure on the TiO$_2$ photoelectrodes (Fig. S9).

Photovoltaic measurements were performed for the electrochemical cells of an open sandwich type. A Pt-treated FTO-coated glass plate was employed as the counter electrode and three Co$^{3+/2+}$ solutions [electrolyte A with the cobalt(III/II) tris(2,2'-bipyridine) complex ([Co(bpy)$_3$]$^{3+/2+}$), electrolyte A with the cobalt(III/II) tris(5-chloro-1,10-phenanthroline) complex ([Co(Cl-phen)$_3$]$^{3+/2+}$) and electrolyte B] were used as the redox electrolyte solutions; the electrolyte A composed of 0.25 M Co$^{2+}$(PF$_6$)$_2$ + 0.035 M Co$^{3+}$(PF$_6$)$_3$ + 0.10 M LiClO$_4$ + 0.50 M 4-tert-butylpyridine (TBP) in acetonitrile; and the electrolyte B of 0.25 M [Co(Cl-phen)$_3$]$^{2+}$(PF$_6$)$_2$ + 0.035 M [Co(Cl-phen)$_3$]$^{3+}$(PF$_6$)$_3$ + 0.07 M LiClO$_4$ + 0.02 M NaClO$_4$ + 0.03 M tetrabutylammonium hexafluorophosphate (TBAPF) + 0.01 M tetrabutylphosphonium hexafluorophosphate (TBPPF) + 0.01 M 1-hexyl-3-methylimidazolium hexafluorophosphate (HMImPF) + 0.30 M TBP + 0.10 M 4-trimethylsilylpyridine (TMSP)$^4$ + 0.10 M 4-methylpyridine (MP) in acetonitrile (Fig. S10). One of the dye-adsorbed TiO$_2$ electrodes, the counter electrode and a polyethylene film spacer ~12 μm thick were assembled, and one of the redox electrolyte solutions was injected into the space between the electrodes.

The photovoltaic performances of the fabricated cells were assessed from the incident monochromatic photon-to-current conversion efficiency (IPCE) spectra and the photocurrent-voltage (I-V) properties of the cells with maintaining the aperture area of the cells to be 0.102 cm$^2$ by the use of a square shade mask. 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 I-V properties were measured by using a solar simulator of OTENTO-SUN III (Bunkoukeiki) and a source meter of R6240A.
(Advantest) under the simulated sunlight irradiation of AM-1.5G one sun condition (100 mW cm$^{-2}$) at 25 °C. The power of the simulated sunlight was calibrated by the use of a reference Si photodiode for DSSC of BS-520 (Bunkoukeiki). The $I$-$V$ 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.

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

$J_{ph}$ is the short-circuit photocurrent density for the monochromatic light irradiation. $\lambda$ and $\Phi$ are the wavelength and the intensity of the light irradiation, respectively, of the monochromatic light.

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

The overall light-to-electric energy conversion efficiency of the DSSC ($\eta$) is determined by the photocurrent density measured at short-circuit ($J_{sc}$), the open-circuit photovoltage ($V_{oc}$), the fill factor ($FF$) [$= P_{max} / (J_{sc} \times V_{oc})$] of the solar cell and the intensity of the incident light ($I_s$). $P_{max}$ is the product of $J_{max}$ and $V_{max}$, that is photocurrent density and photovoltage at the voltage where the power output of the cell is maximal.
**Fig. S1**  UV-visible absorption spectra of ADEKA-1, ADEKA-2 and MK-2 in toluene solutions.
Fig. S2  Cyclic voltammograms (vs. Ag/Ag⁺) of ADEKA-1, ADEKA-2 and MK-2 in CH₂Cl₂ containing 0.1 M TBAP.
Fig. S3  Schematic drawings of the bonding structures of the trimethoxysilyl dye (ADEKA-1) and carboxy dye (ADEKA-2) on the surface of the TiO₂ electrode: (A) adsorption of ADEKA-1 and (B, C) adsorptions of ADEKA-2.
Fig. S4a  Molecular structures of typical carboxy dyes used in the examination of solvent-stability (Fig. S5).
**Fig. S4b**  Molecular structures of typical carboxy dyes used in the examination of solvent-stability (Fig. S5).
Fig. S5  Changes of the absorbances due to the carbazole and the various carboxy dyes (Fig. 1 and S4) adsorbed on the TiO$_2$ electrodes (~1 μm, transparent) with the soaked time into 3-methoxypropionitrile-water (1:1 in volume) at 85 °C in the dark.
Fig. S6  $I$-$V$ properties of the cells sensitized by ADEKA-1, ADEKA-2 and MK-2 with the Co$^{3+/2+}$ redox electrolytes under the simulated sunlight irradiation of AM-1.5G one-sun condition (100 mW cm$^{-2}$). The entry numbers correspond to those in Table 1.
Fig. S7  Schematic energy diagram of DSSC with anatase-TiO$_2$, ADEKA-1 and redox electrolytes ($\text{I}_3$/I$^-$, [Co(bpy)$_3$]$^{3+/2+}$, [Co(phen)$_3$]$^{3+/2+}$ and [Co(Cl-phen)$_3$]$^{3+/2+}$) and molecular structures of the cobalt(III/II) complexes.
Fig. S8 Molecular structures of compounds (melissic acid: MeA, octadecylphosphonic acid: OPA, stearic acid: SA, myristic acid: MyA, decylphosphonic acid: DPA, octyl trimethoxysilane: OTMS, heptanoic acid: HA and pivalic acid: PA) used in the hierarchical multi-capping treatment.
Fig. S9  Schematic drawing of the ‘alkyl-thicket’ structure on the ADEKA-1-adsorbed TiO$_2$ electrode formed by the hierarchical multi-capping treatment.
**Table S1** Photovoltaic parameters of the ADEKA-1-sensitized cells with various capping treatments 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>Dye</th>
<th>Redox / Electrolyte$^a$</th>
<th>Capping$^b$</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADEKA-1</td>
<td>[Co(bpy)$_3$]$^{3+/2+}$ / A</td>
<td>No</td>
<td>15.1</td>
<td>0.826</td>
<td>0.757</td>
<td>9.44</td>
</tr>
<tr>
<td>ADEKA-1</td>
<td>[Co(bpy)$_3$]$^{3+/2+}$ / A</td>
<td>Single</td>
<td>16.1</td>
<td>0.848</td>
<td>0.762</td>
<td>10.4</td>
</tr>
<tr>
<td>ADEKA-1</td>
<td>[Co(Cl-phen)$_3$]$^{3+/2+}$ / A</td>
<td>Single</td>
<td>15.6</td>
<td>0.897</td>
<td>0.764</td>
<td>10.7</td>
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<tr>
<td>ADEKA-1</td>
<td>[Co(Cl-phen)$_3$]$^{3+/2+}$ / A</td>
<td>Multi</td>
<td>15.8</td>
<td>0.958</td>
<td>0.748</td>
<td>11.3</td>
</tr>
<tr>
<td>ADEKA-1</td>
<td>[Co(Cl-phen)$_3$]$^{3+/2+}$ / A</td>
<td>Reverse-Multi</td>
<td>15.6</td>
<td>0.926</td>
<td>0.756</td>
<td>10.9</td>
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</table>

$^a$Electrolyte A: 0.25 M Co$^{3+}$ + 0.035 M Co$^{3+}$ + 0.10 M LiClO$_4$ + 0.50 M TBP in acetonitrile. $^b$No: The no-capping. Single: The single-capping. Multi: The hierarchical multi-capping. Reverse-Multi: The reverse-order multi-capping.

The single-capping: performed by immersing the ADEKA-1-adsorbed TiO$_2$ electrodes in a $1.0 \times 10^{-3}$ M toluene-acetonitrile (1:1 in volume) solution of HA at 25 °C for 30 min.

The hierarchical multi-capping: performed by immersing the ADEKA-1-adsorbed TiO$_2$ electrodes in $1.0 \times 10^{-3}$ M toluene-acetonitrile (1:1 in volume) solutions at 25 °C of MeA for 10 min, OPA for 5 min, SA for 10 min, MyA for 10 min, DPA for 5 min, OTMS for 15 min, HA for 10 min, and PA for 15 min in sequence.

The reverse-order multi-capping: performed by immersing the ADEKA-1-adsorbed TiO$_2$ electrodes in $1.0 \times 10^{-3}$ M toluene-acetonitrile (1:1 in volume) solutions at 25 °C of PA for 15 min, HA for 10 min, OTMS for 15 min, DPA for 5 min, MyA for 10 min, SA for 10 min, OPA for 5 min, and MeA for 10 min in sequence.
**Fig. S10** Molecular structures of additives (lithium perchlorate: LiClO₄, sodium perchlorate: NaClO₄, tetrabutylammonium hexafluorophosphate: TBAPF, tetrabutylphosphonium hexafluorophosphate: TBPPF, 1-hexyl-3-methylimidazolium hexafluorophosphate: HMImPF, 4-tert-butylpyridine: TBP, 4-trimethylsilylpyridine: TMSP and 4-methylpyridine: MP) used in the electrolyte B.
**Table S2** Photovoltaic parameters of the ADEKA-1-sensitized cells using the \([\text{Co(Cl-phen)}_3]^{3+/2+}\) redox electrolyte with the hierarchical multi-capping treatment 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>Entry</th>
<th>Dye</th>
<th>Redox / Electrolyte (^a)</th>
<th>Capping (^b)</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>S8a(^c)</td>
<td>ADEKA-1</td>
<td>([\text{Co(Cl-phen)}_3]^{3+/2+}) / B</td>
<td>Multi</td>
<td>15.59</td>
<td>1.037</td>
<td>0.7737</td>
<td>12.51</td>
</tr>
<tr>
<td>S8b(^c)</td>
<td>ADEKA-1</td>
<td>([\text{Co(Cl-phen)}_3]^{3+/2+}) / B</td>
<td>Multi</td>
<td>15.52</td>
<td>1.036</td>
<td>0.7747</td>
<td>12.46</td>
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<tr>
<td>S8c(^c)</td>
<td>ADEKA-1</td>
<td>([\text{Co(Cl-phen)}_3]^{3+/2+}) / B</td>
<td>Multi</td>
<td>15.67</td>
<td>1.034</td>
<td>0.7741</td>
<td>12.54</td>
</tr>
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</table>

\(^a\)Electrolyte B : 0.25 M \([\text{Co(Cl-phen)}_3]^{2+}\) + 0.035 M \([\text{Co(Cl-phen)}_3]^{3+}\) + 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 acetonitrile.

\(^b\)Multi: The hierarchical multi-capping.

\(^c\)The results for the cell attached an antireflection film on the surface of the photoanode.
References


