Chemical Communications

Electronic Supplementary Information (ESI)

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

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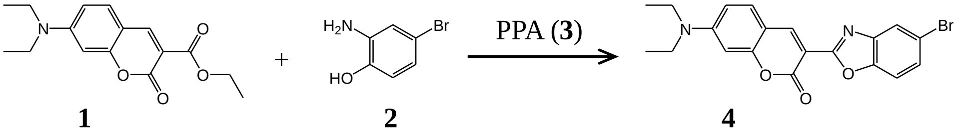
a) Synthesis of SFD-5:

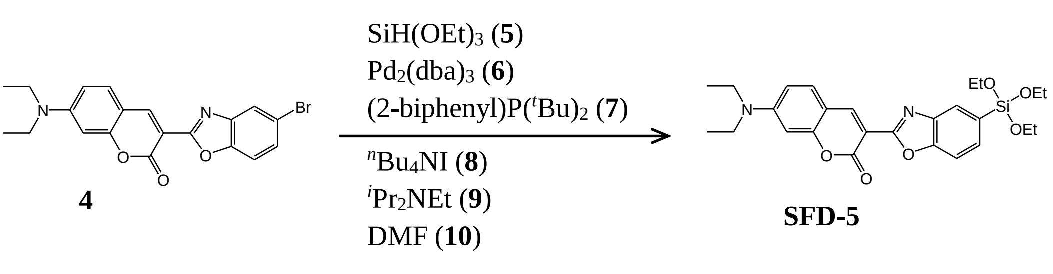
All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted.

A mixture of **1** (2.89 g, 0.0100 mol), **2** (2.26 g, 0.0120 mol) and **3** (24.78 g) was stirred at 160 °C for 2 h. After cooling to 70 °C, the reaction was quenched with water (150 mL). The obtained solid was filtrated, recrystallized [pyridine (50 mL) / water (25 mL)] and dried under vacuum at 40 °C for 1 h to give **4** (2.33 g, 54%) as a yellow solid. ^{1}H NMR (DMSO-d$_6$, 400 MHz) δ_H 8.79 (s, 1H), 7.96 (s, 1H), 7.70 (dd, 2H), 7.53 (d, 1H), 6.81 (d, 1H), 6.60 (s, 1H), 3.51 (q, 4H), 1.17 (t, 6H).



1 **2** **4**

A mixture of **4** (0.827 g, 0.00200 mol), **5** (0.493 g, 0.00300 mol), **6** (0.027 g, 0.000030 mol), **7** (0.036 g, 0.00012 mol), **8** (0.739 g, 0.00200 mol), **9** (0.776 g, 0.00600 mol) and **10** (4.0 mL) was stirred at 40 °C under argon for 3 h and at 60 °C for 9 h. Ethyl acetate and water were added in the reaction. Filtration with celite, oil/water separation, PLC purification (SiO$_2$. Hexane : AcOEt = 1 : 1) and drying under vacuum at 40 °C for 1 h were performed to give **SFD-5** (0.259 g, 26%) as a yellow solid. ^{1}H NMR (CDCl$_3$, 400 MHz) δ_H 8.64 (s, 1H), 8.15 (s, 1H), 7.67 (d, 1H), 7.62 (d, 1H), 7.44 (d, 1H), 6.66 (d, 1H), 6.56 (s, 1H), 3.91 (q, 6H), 3.48 (q, 4H), 1.27 (t, 15H).



4 **SFD-5**

b) Device Fabrication:

The nanocrystalline porous TiO_2 film electrodes for dye-sensitized solar cells (DSSCs) were prepared on the UV-O_3, $TiCl_4$ and $Nb(OC_4H_9)_5$-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 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 $TiCl_4$, $Al[OCH(CH_3)_2]_3$ and $Mg(OC_2H_5)_2$ treatments to improve the TiO_2 surface and prevent the back-electron transfer for the DSSCs [S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613; H. Ozawa, Y. Okuyama and H. Arakawa, *Dalton Trans.*, 2012, **41**, 5137]. Adsorption of the trimethoxysilyl carbazole 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 isooctyltrimethoxysilane (Gelest) at 10 °C for 24 h, and then the dye-adsorbed electrodes were washed with toluene and ethanol. Co-adsorption of the triethoxysilyl coumarin dye (**SFD-5**) on the **ADEKA-1**-adsorbed TiO_2 electrodes was carried out by immersing the **ADEKA-1**-adsorbed electrodes in a toluene-acetonitrile (8:2 in volume) solution containing 2.0×10^{-4} M **SFD-5** and 2.0×10^{-4} M coadsorbent of isooctyltriethoxysilane (Gelest) at 20 °C for 2 h, and then the electrodes were washed with toluene, acetonitrile and ethanol. Before the immersion in the **ADEKA-1** solution, 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 the efficient dye adsorption. The hierarchical multi-capping treatment was performed to the **ADEKA-1**-adsorbed and **ADEKA-1** + **SFD-5**-co-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, heptanoic acid (HA) for 10 min and pivalic acid (PA) for 15 min in sequence (Fig. S2) to form the 'alkyl-thicket' structure on the TiO_2 photoelectrode (Fig. S3) [K. Kakiage, Y. Aoyama, T. Yano, T. Otsuka, T. Kyomen, M. Unno and M. Hanaya, *Chem. Commun.*, 2014, **50**, 6379].

Photovoltaic measurements were performed for the electrochemical cells of an open sandwich type. A Pt-treated FTO-coated glass plate, which was prepared by a rf magnetron sputtering and the reported H_2PtCl_6 treatment [S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516**, 4613], was employed as the counter electrode and a cobalt(III/II) complex solution [0.25 M $[Co(Cl\text{-}phen)_3]^{2+}$ + 0.035 M $[Co(Cl\text{-}phen)_3]^{3+}$ + 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-methyl-imidazolium hexafluorophosphate (HMImPF) + 0.30 M 4-*tert*-butylpyridine (TBP) + 0.10 M 4-trimethylsilylpyridine (TMSP) + 0.10 M 4-methylpyridine (MP) in acetonitrile (Fig. S4)] was used as the redox electrolyte solution. The dye-adsorbed TiO_2 electrode, the counter electrode and a polyethylene film spacer with ~12 μm thick were assembled into the cell, and the cobalt(III/II) complex electrolyte solution was injected into the space between the electrodes (Fig. S5).

c) Photovoltaic Measurements:

The photovoltaic performances of the fabricated DSSCs 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 0.102 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 *J-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 *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.

$IPCE$ (%) = $\{(1240\ [\mathrm{V\ nm}] \times J_{\mathrm{ph}}\ [\mathrm{mA\ cm^{-2}}]) / (\lambda\ [\mathrm{nm}] \times I_{\mathrm{m}}\ [\mathrm{mW\ cm^{-2}}])\} \times 100$

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

η (%) = $\{(J_{\mathrm{sc}}\ [\mathrm{mA\ cm^{-2}}] \times V_{\mathrm{oc}}\ [\mathrm{V}] \times FF) / I_{\mathrm{s}}\ [\mathrm{mW\ cm^{-2}}]\} \times 100$

The overall light-to-electric energy conversion efficiency (η) of the DSSC is determined by the short-circuit photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the fill factor (FF) [= $P_{\mathrm{max}} / (J_{\mathrm{sc}} \times V_{\mathrm{oc}})$] of the solar cell and the intensity of the incident simulated sunlight (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.

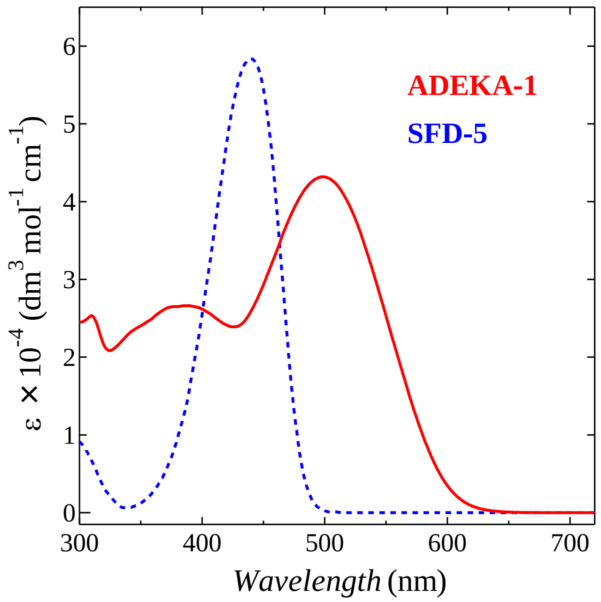


Fig. S1 UV-visible absorption spectra of **ADEKA-1** in a toluene solution and **SFD-5** in an acetonitrile solution.

Table S1 Photovoltaic parameters of the **ADEKA-1**-photosensitized cells with and without **SFD-5** under the irradiation 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 (η)

Entry	Dyes	J_{sc} (mA cm^{-2})	V_{oc} (V)	*FF*	η (%)
1	**ADEKA-1**	15.50	1.036	0.7760	12.46
2	**ADEKA-1**	15.59	1.037	0.7737	12.51
3	**ADEKA-1**	15.52	1.036	0.7747	12.46
4	**ADEKA-1**	15.67	1.034	0.7741	12.54
ave. of 1-4	**ADEKA-1**	15.57	1.036	0.7746	12.49
5	**ADEKA-1** + **SFD-5**	15.94	1.033	0.7754	12.77
6	**ADEKA-1** + **SFD-5**	16.07	1.035	0.7733	12.86
7	**ADEKA-1** + **SFD-5**	15.97	1.035	0.7744	12.80
ave. of 5-7	**ADEKA-1** + **SFD-5**	15.99	1.034	0.7744	12.81

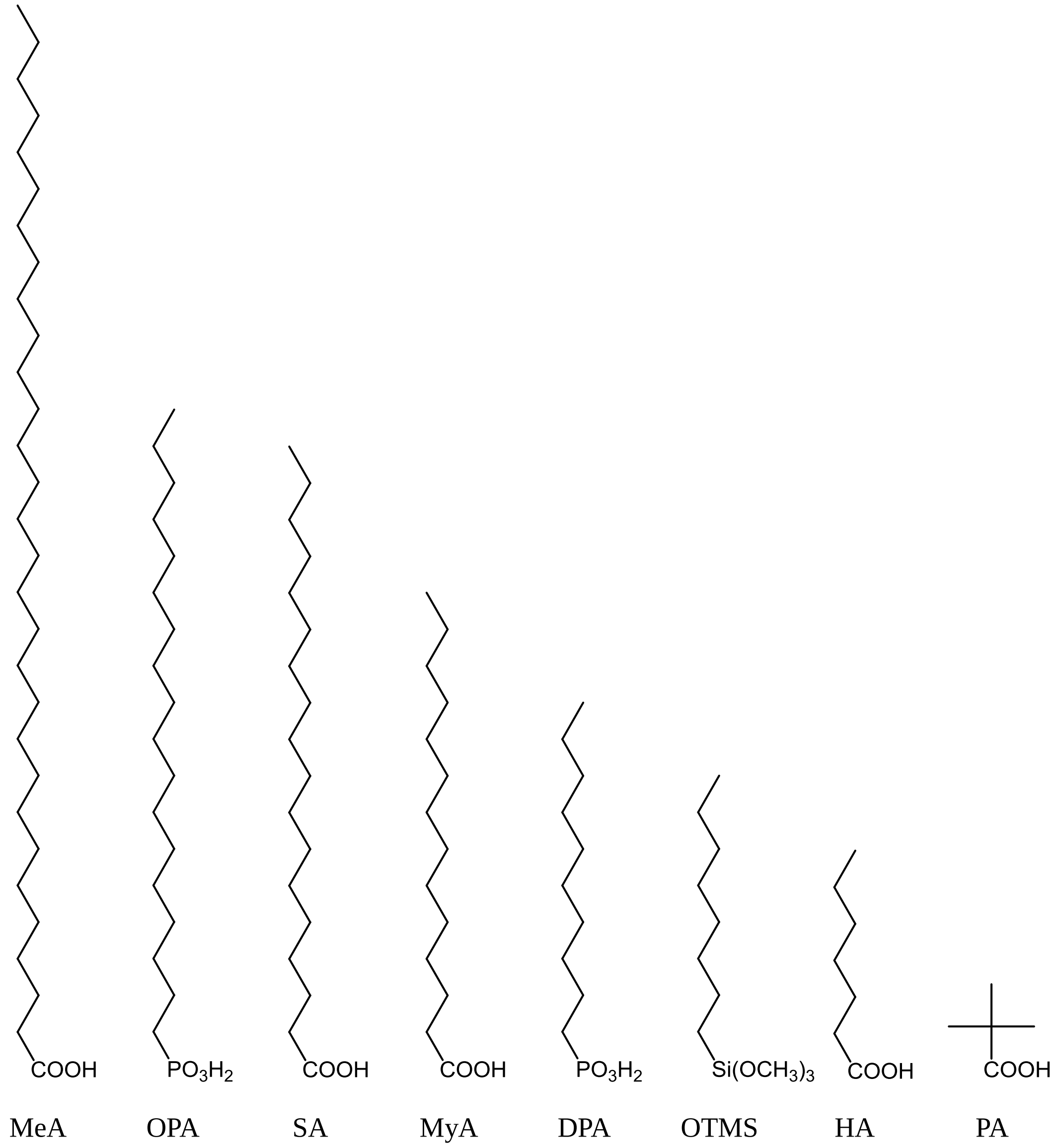


Fig. S2 Molecular structures of compounds (melissic acid: MeA, octadecylphosphonic acid: OPA, stearic acid: SA, myristic acid: MyA, decylphosphonic acid: DPA, octyl trimethoxysilane: OTMS, heptanoic acid: HA and pivalic acid: PA) used in the hierarchical multi-capping treatment.

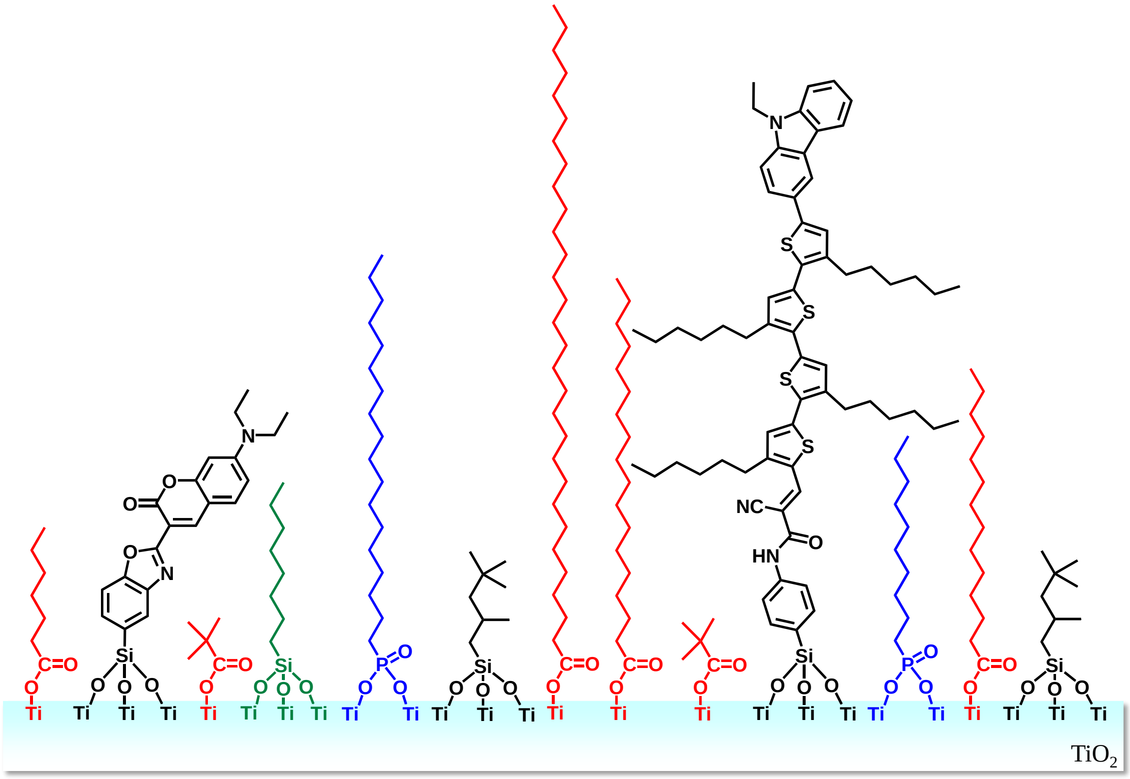
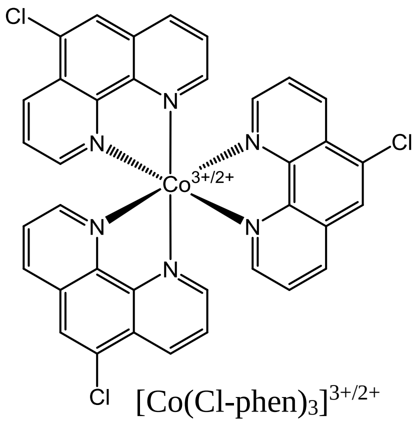
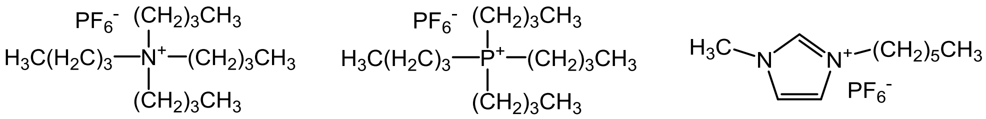


Fig. S3 Schematic drawing of the 'alkyl-thicket' structure on the **ADEKA-1** + **SFD-5**-co-adsorbed TiO_2 electrode formed by the hierarchical multi-capping treatment.

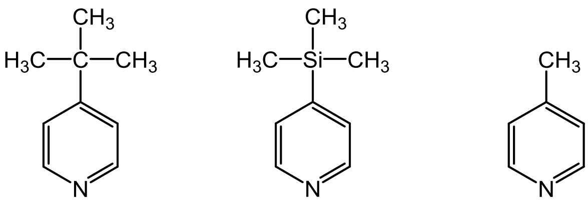


$[Co(Cl\text{-}phen)_3]^{3+/2+}$

$LiClO_4$ $NaClO_4$

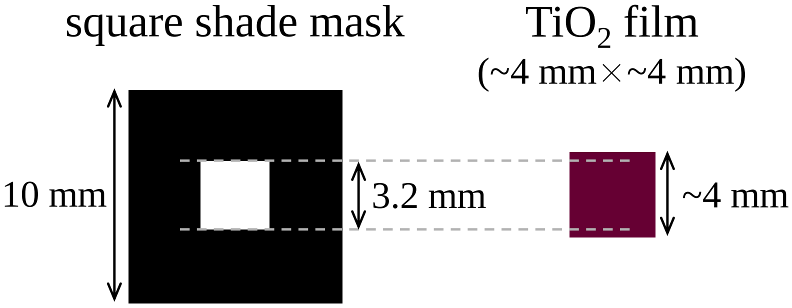


TBAPF TBPPF HMImPF



TBP TMSP MP

Fig. S4 Molecular structures of $[Co(Cl\text{-}phen)_3]^{3+/2+}$ and additives (lithium perchlorate: $LiClO_4$, sodium perchlorate: $NaClO_4$, tetrabutylammonium hexafluorophosphate: TBAPF, tetrabutylphosphonium hexafluorophosphate: TBPPF, 1-hexyl-3-methyl-imidazolium hexafluorophosphate: HMImPF, 4-*tert*-butylpyridine: TBP, 4-trimethyl-silylpyridine: TMSP and 4-methylpyridine: MP) used in the redox electrolyte solution.



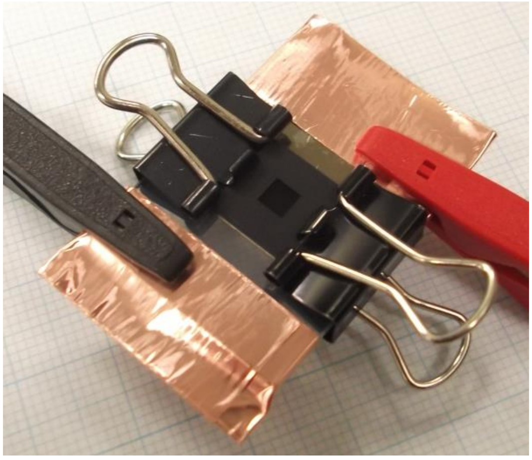


Fig. S5 Schematic drawings of the square shade mask and the TiO_2 film with the sensitizing dyes and a photograph of the electrochemical cell of the open sandwich type used in this work. In the photovoltaic measurements, the spaces between the shade mask and the Cu conduction tapes were also shaded to avoid light scatter and other undesirable effects producing uncertainties in the measurements.