Electronics Supplementary Information

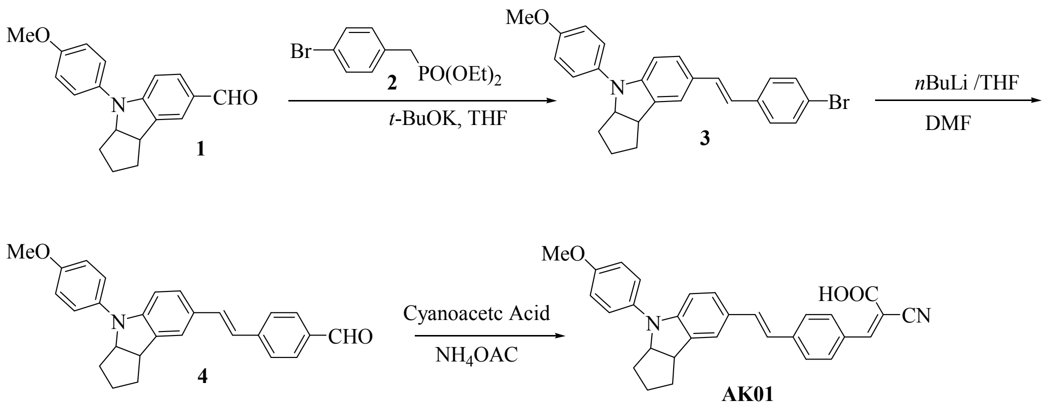
A novel metal-free panchromatic TiO_2 sensitizer based on phenylenevinylene-conjugated unit and indoline derivative for highly efficient dye-sensitized solar cells

Md. Akhtaruzzaman,* [a] **Ashraful Islam,**[c,d] **Fan Yang,**[a] **Naoki Asao,**[b] **Eunsang Kwon,**[e] **Surya Prakash Singh,**[c] **Liyuan Han**[c] **and Yoshinori Yamamoto***[b]

[a]*Department of Chemistry, Graduate School of Science, Tohoku University, Aramaki-Azaaoba 6-3, Aoba-ku, Sendai, 980-8578, Japan. Fax:+81(0)22-795-3899; Tel:+81(0)22-795-3898; E-mail: akhtar@m.tohoku.ac.jp*
[b]*WPI-AIMR, Tohoku University, Katahira 2-1-1, Aobaku, Sendai 980-8577;Tel.:+81-22-217-5130;Fax.:+81-22-217-5129; E-mail:yoshi@m.tohoku.ac.jp*
[c]*Photovoltaic Materials Unit, National Institute for Materials Science , 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan. Fax: +81(0)29 859 2301 Tel: +81(0)29 859 2129; E-mail: ISLAM.Ashraful@nims.go.jp*
[d]*Center of Excellence for Research in Engineering Materials (CEREM), College of Engineering, King Saud University, Riyadh 11421, Saudi Arabia*
[e]*Research and Analytical Center for Gaint Molecules, Graduate School of Science, Tohoku University, 6-3 Aramaki-AzaAoba, Japan 980-8578.*

Synthesis

General Information: ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) and BRUKER (600 MHz) spectrometers. 1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CDCl3 at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet and m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. High-resolution mass spetra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out employing Silica gel 60N (spherical, neutral, 40~100 µm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm precoated plate Kieselgel 60 F254 (Merck). All other reagents and solvents commercially available were used without further purification unless otherwise noted. 4-(4-Methoxyphenyl)-1,2,3,3a,4,8b-Hexahydrocyclopenta[b]indole-7-carboaldehyde **1** was synthesized according to the literature method[1].



Scheme 1. Synthesis procedure for the preparation of AK01

Preparation of compound **3.** To a solution of potassium *tert*-butaoxide (6.2 mmol) in THF (10 ml) was added dropwise a mixture of compound **1** (6.2 mmol) and Diethyl(4-Bromobenzyl)-phosphonste (**2**) (2.74 mmole) in 10 ml THF under nitrogen at room temperature. The reaction mixture was stirred at room temperature for 18 hr and then poured into water. The organic layer was extracted with CH_2Cl_2 and dried over Na_2SO_4. After removal the solvent under reduced pressure, the residue was purified by recrystalization in hexane to give compound **3** as red solid (82 % yield): ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 1.53-1.56 (m 2H), 1.69-1.71 (m, 2H), 1.86-1.88 (m, 2H), 2.02-2.03 (m, 1H), 3.80 (S, 3H), 4.72-4.75 (m, 1H), 6.66 (d, J =8.0 Hz, 1H), 6.81 (d, J = 16.36 Hz, 2H), 6.90 (d, J = 8.8, 2H), 7.01 (d, J = 16.36 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 7.2 (d, J = 9.0 Hz, 2H), 7.24 (s, 1H), 7.31 (d, J = 8.8 Hz, 2H), 7.42(d, J = 8.2 Hz, 2H).

Preparation of compound **4**. To a solution of compound **3** in dry THF, *n*-BuLi (1.3 mmol, 1.6 M in hexane) at -78 °C under nitrogen. The mixtures was stirred at -78 °C for 2 hrs and DMF (1.3 mmol) was added. After 1h, the mixtures was poured into aqueous HCl (4.5% 100 mL) and stirred at 0 °C for 1h. The organic layer was extracted with CH_2Cl_2 and dried over Na_2SO_4. After removal the solvent under reduced pressure, the residue was purified by column chromatography with CH2Cl2-Ethylacetate as eluent to give compound **4** as red solid (68 % yield): ^{1}H NMR (400 MHz, $CDCl_3$) δppm: 1.53-1.56 (m 2H), 1.69-1.71 (m, 2H), 1.86-1.88 (m, 2H), 2.03-2.05 (m, 1H), 3.81 (S, 3H), 4.76-4.79 (m, 1H), 6.66 (d, *J* =8.3 Hz, 1H), 6.91 (d, *J* = 16.39 Hz, 1H), 6.93 (d, *J* = 8.8, 2H), 7.04 (d, *J* = 16.39 Hz, 1H), 7.15 (d, *J* = 8.52 Hz, 1H), 7.2 (d, *J* = 8.8 Hz, 2H), 7.33 (s, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.81(d, *J* = 8.3 Hz, 2H), 9.93 (s, 1H).

Preparation of compound **Ak01**.To a mixture of **4** (1.0 mmol), 2-cyanuric acid (1.0 mmol) and ammonium acetate (2.6 mmol) in acetonitrile (10 mL) was added 10 mL of glacial acetic. and the mixture was stirred for 3 hr under Ar. After evaporation of the solvent, the crude solid was dissolved into CH_2Cl_2 and washed with water. The organic layer dried over Na_2SO_4. After removal the solvent under reduced pressure, the residue was purified by recrystalization in acetonitrile to give compound **Ak01** as red solid (62 % yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ ppm: 1.53-1.56 (m 2H), 1.69-1.71 (m, 2H), 1.86-1.88 (m, 2H), 2.03-2.05 (m, 1H), 3.81 (S, 3H), 4.76-4.79 (m, 1H), 6.65 (d, *J* =8.0 Hz, 1H), 6.88 (d, *J* = 16.12 Hz, 2H), 6.90 (d, *J* = 8.8, 2H), 7.01 (d, *J* = 16.12 Hz, 1H), 7.11 (d, *J* = 8.6 Hz, 1H), 7.2 (d, *J* = 9.0 Hz, 2H), 7.34 (s, 1H), 7.6 (d, *J* = 8.3 Hz, 2H), 8.0 (d, *J* = 8.1 Hz, 2H), 8.2 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ190.82, 164.74, 155.87, 155.78, 150.07, 144.57, 135.49, 135.39, 133.51, 132.24, 129.07, 128.33, 126.44, 123.32, 122.77, 121.90, 115.77, 114.69, 106.52, 77.63, 77.21, 77.00, 76.78, 70.00, 55.55, 45.25, 35.30, 33.47, 24.33. HRMS Calcd for $C_{30}H_{26}N_2O_3$ $(M-H)^-$ 461.1871. Found 461.1870

Preparation of compound **TA-St-CA**. The compound **TA-St-CA** was synthesized according to the published procedures.[2] ^{1}H NMR (400 MHz, DMSO-d_6) δ ppm: 6.94 (d, *J* =8.0 Hz, 2H), 7.03-7.09 (m, 6H), 7.18 (d, *J* = 16.4 Hz, 1H), 7.31 (dd, *J* = 7.6, 7.6 Hz, 4H), 7.42 (d, *J* = 16.4 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.8 Hz, 2H), 8.28 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δppm: 163.34, 153.48, 147.35, 146.60, 142.23, 131.42, 131.22, 130.26, 129.90, 129.52, 128.05, 126.67, 125.23, 124.37, 123.48, 122.21, 116.33, 101.93. HRMS Calcd for $C_{30}H_{26}N_2O_3$ $(EI^+)^-$ 442.1681. Found 442.1687

1. M. Matsui, A. Ito, M. Kotani, Y, Kubota, K, Funabiki, J, Jin, T, Yoshida, H. Minoura, H. Miura., Dyes and Pigments., **80**, (2009), 233.
2. S. Hwang, J. H. Lee, C.Park, H. Lee, C. Kim, C. Park, M-H. Lee, W. Lee, J. Park, K. Kim, N.-G. Park and C. Kim, Chem. Commun., 2007, 4887

Theoretical calculations of **AK01.**

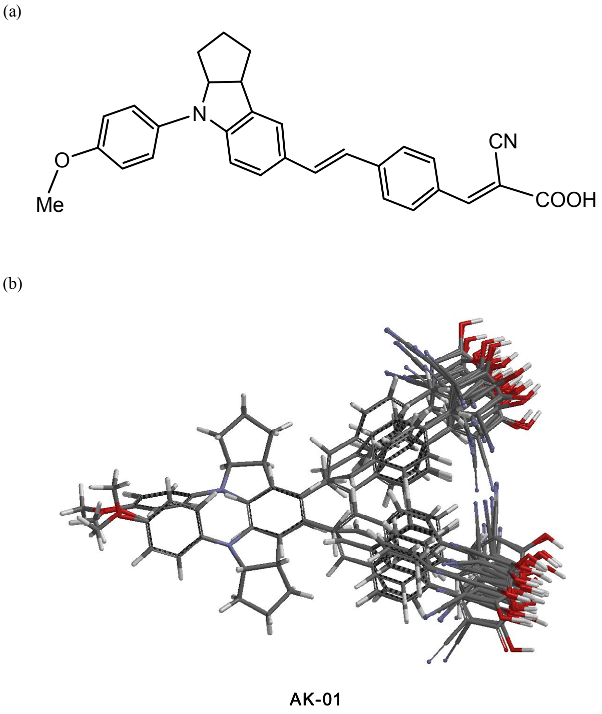


Fig. S1. (a) Molecular structure and (b) conformational analysis of **AK01**.

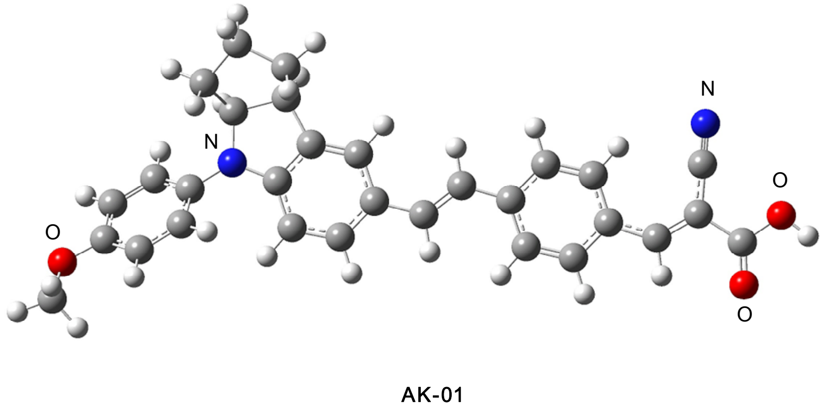


Fig. S2. Optimized geometry (at B3LYP/6-31+G(d) level of theory) of **AK01**.

Table S1. Cartesian coordinates (Angstroms) for **AK01**.

PG: C1

Total energy = -1494.05876197 hartree

Atom	X	Y	Z
H	-6.58735	0.833067	-1.9395
C	-6.68878	0.080574	-1.16309
C	-6.97716	-1.88198	0.801172
C	-5.63929	-0.13308	-0.24932
C	-7.85866	-0.66622	-1.09417
C	-8.011	-1.66116	-0.1167
C	-5.81098	-1.11249	0.737532
H	-8.6668	-0.50069	-1.80056
H	-5.03296	-1.27002	1.478235
H	-7.06814	-2.63147	1.579638
O	-9.1931	-2.34806	-0.14085
N	-4.46165	0.64635	-0.31093
C	-2.99996	2.554203	-0.39438
C	-2.2389	1.254125	-0.2916
C	-3.16017	0.180377	-0.22733
H	-2.67223	3.144983	-1.25803
C	-5.32776	2.924411	0.435345
C	-4.40791	4.089939	0.851488
C	-3.00697	3.456658	0.867406

H	-5.55619	2.296944	1.30538
H	-4.44846	4.893713	0.103146
H	-4.69326	4.528311	1.814433
H	-2.88245	2.839303	1.766786
H	-2.19467	4.191734	0.858031
H	-6.28247	3.260769	0.01784
C	-2.69165	-1.13846	-0.13479
H	-3.37467	-1.98048	-0.11229
H	-0.948	-2.37418	-0.04092
C	-1.31404	-1.35123	-0.10222
C	-0.37531	-0.29916	-0.15337
H	-0.1945	1.8659	-0.3135
C	-0.87995	1.024138	-0.25483
C	1.042096	-0.61999	-0.1118
H	1.253665	-1.68763	-0.06101
C	2.090435	0.243779	-0.12524
H	1.891106	1.313397	-0.16411
C	3.502652	-0.10574	-0.08723
C	6.311006	-0.64851	-0.01227
C	4.4637	0.933729	-0.0746
C	3.991128	-1.43372	-0.06341
C	5.349834	-1.69164	-0.02683

C	5.825437	0.680978	-0.03772
H	4.119814	1.965403	-0.09337
H	3.299146	-2.27017	-0.07684
H	5.695373	-2.72299	-0.01016
H	6.513547	1.517525	-0.0286
C	7.701223	-1.03459	0.026158
H	7.877188	-2.10899	0.039299
C	8.860984	-0.30529	0.050177
C	8.925514	1.120339	0.040816
N	8.971034	2.28473	0.033144
C	10.14054	-1.06233	0.089275
O	10.23492	-2.27646	0.101461
O	11.22231	-0.24808	0.11076
H	12.00949	-0.82314	0.135782
C	-4.48828	2.102017	-0.57676
H	-4.82773	2.27936	-1.6061
C	-9.4057	-3.3665	0.827782
H	-10.3943	-3.77642	0.614668
H	-9.3923	-2.95766	1.84681
H	-8.65409	-4.16237	0.741437

Theoretical calculations of **TA-St-CA.**

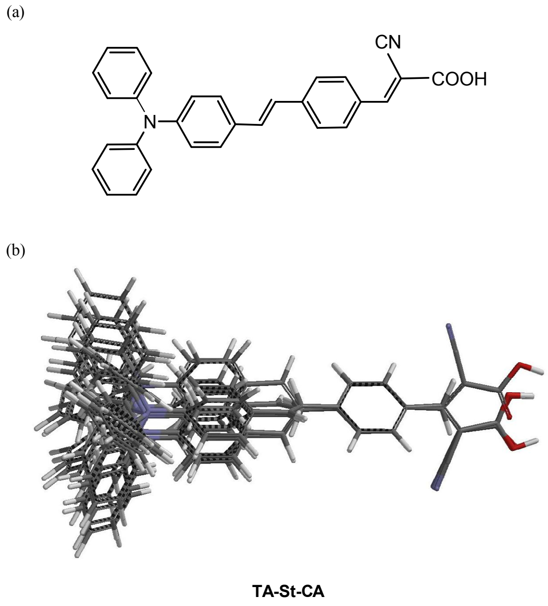


Fig. S3. (a) Molecular structure and (b) conformational analysis of **TA-St-CA**.

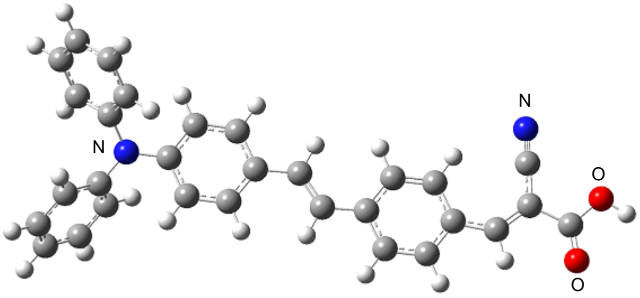


Fig. S4. Optimized geometry (at B3LYP/6-31+G(d) level of theory) of **TA-St-CA**.

Table S2. Cartesian coordinates (Angstroms) for **TA-ST-CA**.

PG: C1

Total energy = -1416.42809083 hartree

Atom	X	Y	Z
C	-9.80983	-0.14795	-0.08361
O	-10.1701	-1.18256	-0.61415
O	-10.6816	0.773734	0.386837
H	-11.5787	0.433765	0.211237
C	-8.39147	0.254759	0.125231
C	-8.13702	1.505002	0.765481
N	-7.92308	2.524386	1.287562
C	-7.42494	-0.60871	-0.31475
H	-7.83617	-1.50588	-0.77449
C	-5.981	-0.55055	-0.28262
C	-5.27872	-1.64467	-0.83999
C	-5.21191	0.509836	0.259576
C	-3.89305	-1.68081	-0.85713
H	-5.84126	-2.47355	-1.26345
C	-3.82849	0.468645	0.239571
H	-5.70118	1.370655	0.698661
C	-3.12426	-0.6255	-0.31846
H	-3.38499	-2.53752	-1.29363
H	-3.28213	1.303827	0.666687

C	-1.67014	-0.71882	-0.3653
H	-1.29149	-1.62952	-0.82665
C	-0.78488	0.196805	0.099922
H	-1.17008	1.104259	0.563092
C	0.670624	0.120811	0.05906
C	1.39005	-0.95255	-0.51067
C	1.428006	1.17281	0.614316
C	2.776709	-0.9713	-0.52519
H	0.858474	-1.78253	-0.96735
C	2.8179	1.160485	0.614388
H	0.910224	2.014335	1.070001
C	3.52151	0.085085	0.041549
H	3.298316	-1.80563	-0.98336
H	3.365431	1.983383	1.062663
N	4.932469	0.062116	0.02758
C	5.672529	1.271289	-0.12894
C	5.308915	2.20585	-1.11205
C	6.780493	1.536481	0.691433
C	6.03475	3.388266	-1.2603
H	4.458519	2.00131	-1.75592
C	7.511328	2.714029	0.526046
H	7.065611	0.817265	1.453562

C	7.141196	3.64877	-0.44563
H	5.74077	4.102017	-2.02581
H	8.366784	2.905243	1.169053
H	7.708392	4.567457	-0.56771
C	5.635351	-1.1687	0.183334
C	6.728635	-1.47051	-0.6444
C	5.250055	-2.08933	1.171388
C	7.423004	-2.67012	-0.48175
H	7.030625	-0.76212	-1.41016
C	5.939321	-3.29394	1.316891
H	4.412064	-1.8567	1.821994
C	7.030791	-3.59093	0.49477
H	8.267372	-2.88943	-1.13043
H	5.628901	-3.99623	2.086512
H	7.569849	-4.52667	0.614876
C	-9.80983	-0.14795	-0.08361
O	-10.1701	-1.18256	-0.61415
O	-10.6816	0.773734	0.386837
H	-11.5787	0.433765	0.211237
C	-8.39147	0.254759	0.125231

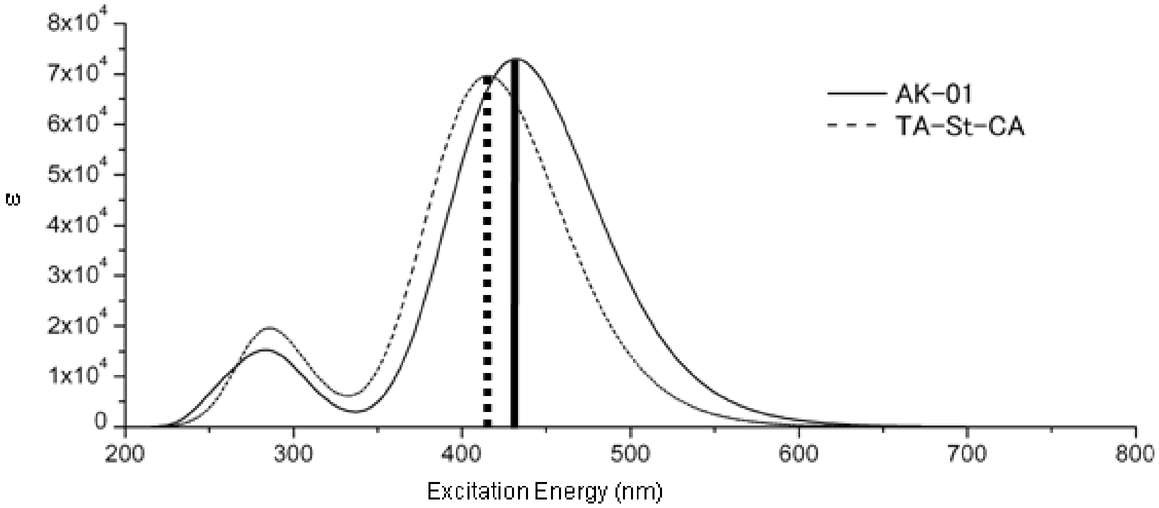


Fig. S5. The lowest energy HOMO→LUMO transitions calculated with the TD-DFT method for **AK01** (solid line) and **TA-St-CA** (dotted line) at the CAM-B3LYP/6-311+G(d,p) level on the B3LYP/6-311+G(d,p) optimized geometry.

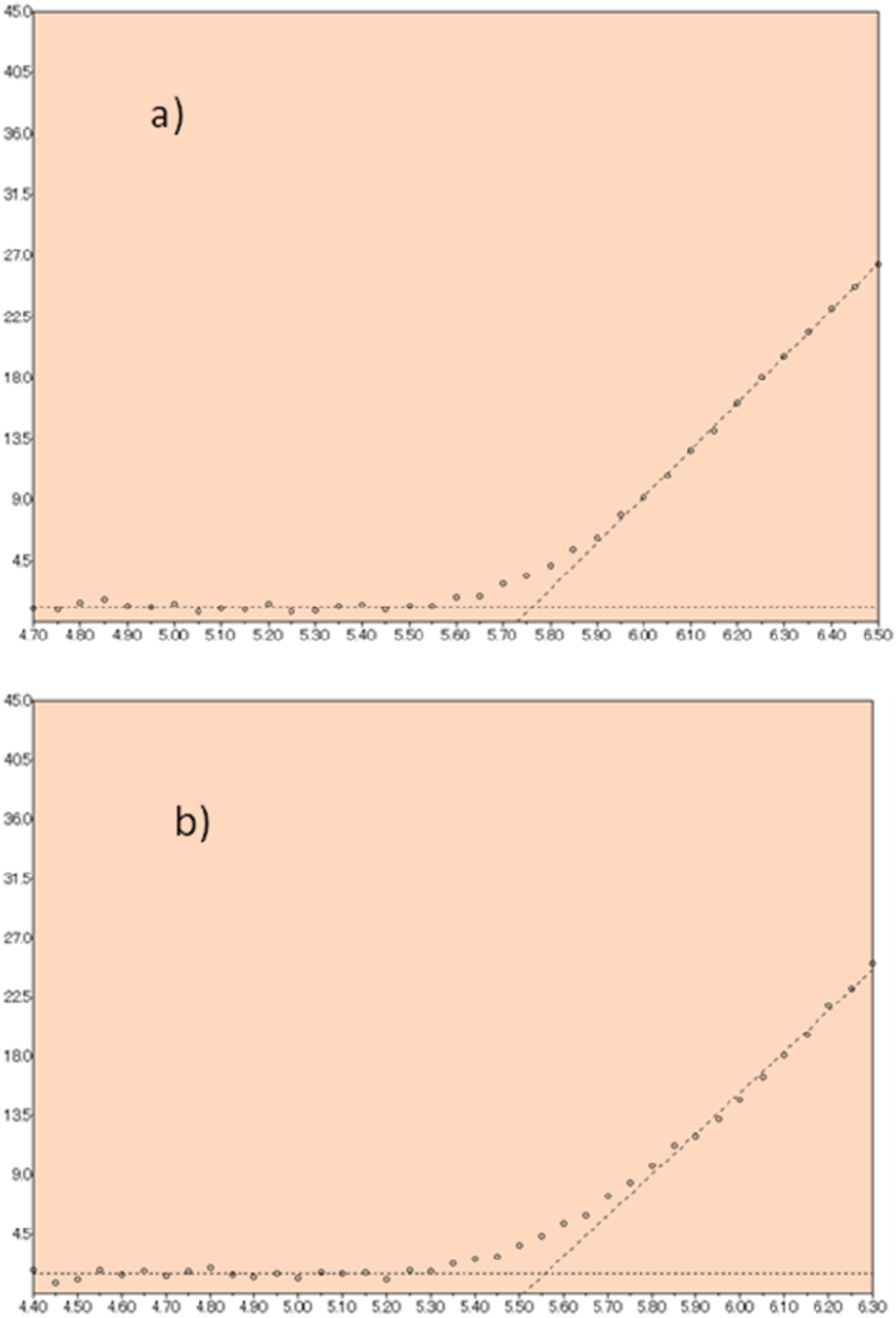


Fig. S6 Ionization potential (IP) of a) **TA-St-CA** (IP = -5.76 eV) and b) **AK01 (**IP = -5.56eV) bound to nanocrystalline TiO_2 film was determined by using the photoemission yield spectrometer (Riken Keiki, AC-3E).

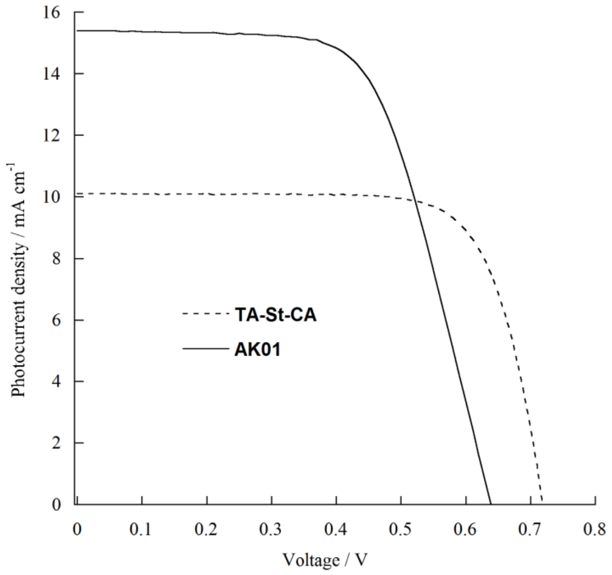


Fig. S7 Photocurrent-voltage characteristics of **TA-St-CA** and **Ak01**

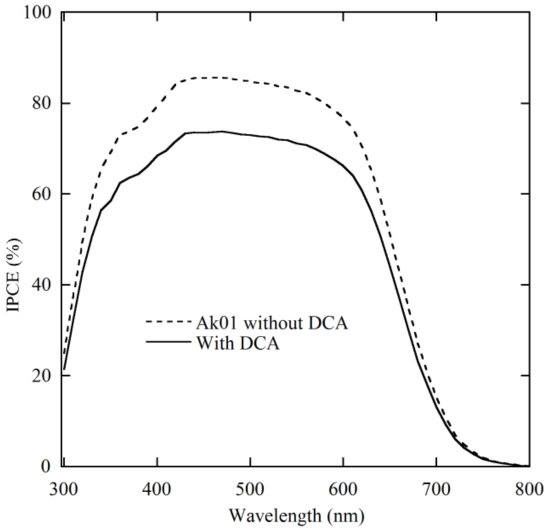


Fig. S8 Photocurrent action spectra (IPCE) of nanocrystalline TiO_2 film sensitized by AK01 with and without DCA. The redox electrolyte solution was a mixture of 0.6M DMPII, 0.05M I2, 0.1M LiI and 0.3M TBP in acetonitrile.

Table S3. Photophysical Physical properties of **AK-01** and **TA-St-CA**

Dye	Absorption[a] λ_{max}/nm ($\varepsilon \times 10^4$/M^{-1}cm^{-1})	Absorb on TiO_2 film (λ_{max}/nm)	Ionization Potential (IP) (eV)	E_{0-0}[b] (eV)	$S^{+/*}$[c] (eV)
AK01	440 (3.4)	426	-5.56	2.03	-3.53
TA-St-CA	412 (3.1)	407	-5.76	2.25	-3.50

[a]Measured in ethanol at room temperature; [b] E_{0-0} was estimated from the absorption onset of dye loaded TiO_2 film; [c] The excited-state oxidation potential, $S^{+/*}$ levels were calculated from the expression of $S^{+/*}$ = IP - E_{0-0}.

Table S4. DSCs performance of dye **AK-01** and **TA-St-CA**

Dye	**Jsc[mA]**	**Voc[V]**	**F.F.**	**Eff.[%]**
AK01	15.4	0.639	0.631	6.20
TA-St-CA	10.1	0.718	0.746	5.41

Measurements were performed under AM 1.5 irradiation on the DSCs devices with 0.25 cm^2 active surface area defined by a metal mask. J_{SC}, short circuit current; V_{OC}, open circuit voltage; *FF*, fill factor; η, conversion efficiency.