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PAPER

# A simple triaryl amine-based dual functioned co-adsorbent for highly efficient dye-sensitized solar cells<sup>†</sup>

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We have developed 4-(bis(9,9-dimethyl-9*H*-flouren-2-yl)amino)benzoic acid (HC-Acid) to use as an alternative co-adsorbent to deoxycholic acid (DCA) in organic dye-sensitized solar cells (DSSCs). It has dual functioned effects, that is, the prevention effect of the  $\pi$ - $\pi$  stacking of organic dye molecules like DCA and the light harvesting effect at shorter-wavelength regions. When the HC-Acid was used as the co-adsorbent onto the TiO<sub>2</sub> surface with the organic dye NKX2677 sensitized solar cell, an extremely high conversion efficiency of 9.09% was achieved under 100 mW cm<sup>-2</sup> AM 1.5G simulated light ( $J_{sc}$  = 18.01 mA cm<sup>-2</sup>,  $V_{oc}$  = 0.663 V, and FF = 76.16). As we herein demonstrate, an increase in short-circuit photocurrent density ( $J_{sc}$ ) of 20%, open-circuit photovoltage ( $V_{oc}$ ) of 11% and overall conversion efficiency ( $\eta$ ) of 38% occurred in comparison to the NKX2677 based solar cell. As a consequence, this new class of a low molecular weight organic co-adsorbent (HC-Acid) is a promising candidate as an alternative co-adsorbent with a new function not seen in DCA or CA derivatives for highly efficient dye-sensitized solar cells.

# Introduction

Dye-sensitized solar cells (DSSCs),<sup>1</sup> mainly composed of dyesensitizer, wide band gap semiconductor oxide, redox electrolyte and counter electrode, have been intensively studied and developed because of their relatively high solar-to-electricity conversion efficiency and low cost.<sup>2-11</sup> DSSCs employing Ru-sensitizers have shown the highest  $\eta$  value of over 11%.<sup>12</sup> However, in view of the cost and environmental demand, organic dyes have attracted much attention due to their many advantages over Rudyes, such as diversity of molecular structures, high molar extinction coefficient, and simple synthesis.<sup>13</sup>

Upon light excitation, initial charge separation occurs in the adsorbed dye molecules and electrons are injected from their excited states into the conduction band (CB) of the semiconductor. However, excited electrons are injected not only into the CB of the semiconductor but also into the trap states and recombine with oxidized dye molecules. In addition, it is possible for free electrons on a semiconductor surface to recombine with acceptors such as  $I_3^-$  ions. Such a charge recombination leads to losses in both the short-circuit current ( $J_{sc}$ ) and the open-circuit photovoltage ( $V_{oc}$ ), resulting in a decrease in  $\eta$ . To reduce the possible charge recombination pathways occurring at the TiO<sub>2</sub>/

dye/electrolyte interface, several kinds of additives have been introduced as co-adsorbents onto the TiO<sub>2</sub> surface to improve the photovoltaic performance of DSSCs. Deoxycholic acid (DCA),<sup>14</sup> hexadecylmalonic acid (HDMA),<sup>15</sup> guanidinium thiocyanate,16 tert-butylpyridine,17 and citric acid18 have been added to dye sensitized solar cells in order to improve the photovoltaic performance of DSSCs. Moreover, many attempts for achieving a high power conversion efficiency in DSSCs, for example, cosensitization by using multilayered dyes,19 the stepwise cosensitization based on organic dyes having complementary spectral absorption in the visible region,<sup>20</sup> molecular cocktails for efficient panchromatic DSSCs using two dyes,21,22 and light harvesting effect by co-sensitization with energy relay dyes,<sup>23,24</sup> have been widely studied and developed. Furthermore, recently, to reduce the dye aggregation, an unsymmetrical starburst triphenylamine-based cyanine organic sensitizer<sup>25</sup> having a bulkyshaped structure, di-branched organic sensitizers<sup>26</sup> with one donor and two anchoring groups has been reported.

Among the metal-free organic dyes studied in DSSCs, coumarin-based dyes<sup>27</sup> are somewhat promising sensitizers for DSSCs based on TiO<sub>2</sub> films because of their good photoresponse in the visible region, good long-term stability under one sun soaking,<sup>28</sup> and appropriate lowest unoccupied molecular orbital (LUMO) levels matching the conduction band of TiO<sub>2</sub>. However,  $\pi$ - $\pi$  stacking of organic dye molecules usually occurs because of the strong intermolecular interaction. The strong  $\pi$ -electron interaction in oligothiophene, in particular, allows easy formation of  $\pi$ -stacks or lamellar structure.<sup>29</sup> Although  $\pi$ - $\pi$ 

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stacking is advantageous to light harvesting because of its broad feature in the UV-vis absorption spectrum,  $\pi$ -stacked aggregates usually lead to inefficient electron injection and thus results in low power conversion efficiency.<sup>30,31</sup> Prohibition of  $\pi$ - $\pi$  stacking with additive in the dye solution is a typical way to improve efficiency of organic dye-sensitized solar cells suffering from the  $\pi$ - $\pi$  stacking problem. Coadsorption of dyes with additives<sup>32</sup> and structural modification of dye molecules<sup>33</sup> are proven to be effective to dissociate  $\pi$ - $\pi$  stacking or dye aggregation and thus to improve solar cell efficiency.

Very recently, we also reported that a carbazole-based low molecular weight co-adsorbent<sup>34</sup> having multiple functioned effects, that is, the prevention effect of the  $\pi$ - $\pi$  stacking, the light harvesting effect at shorter-wavelength regions and the hole conducting function through a redox cascade process, was studied for improving the photovoltaic performance of DSSCs.<sup>34</sup>

In order to reduce the possible charge recombination pathways occurring at the TiO<sub>2</sub>/dye/electrolyte interface, in this study, we synthesized a triaryl amine-based 4-(bis(9,9-dimethyl-9*H*-flouren-2-yl)amino)benzoic acid (hole conductor-acidified co-adsorbent: HC-Acid) as an alternative co-adsorbent to DCA. HC-Acid has a low molecular Y-shaped structure (Scheme 1) and can also absorb the shorter-wavelength regions so that the light harvesting effect at shorter-wavelength regions is anticipated to increase the photocurrent of DSSCs. Also, we propose possible energy or charge transfer processes of HC-Acid in the TiO<sub>2</sub> film (Scheme 2) used as the co-adsorbent onto the TiO<sub>2</sub> surface with the organic dye NKX2677 sensitized solar cell.

# Experimental

## Characterizations

<sup>1</sup>H-NMR spectra were recorded at room temperature with a Varian Oxford 300 spectrometer and chemical shifts were reported in ppm units with tetramethylsilane as an internal standard. <sup>13</sup>C NMR spectra were recorded with a BRUKER DRX 300 instrument. Mass spectra were obtained with a JEOL JMS-700 spectrometer in EI mode. UV-vis absorption spectra of dye-loaded films were recorded with a Shimadzu UV-2401PC spectrophotometer. Cyclic voltammetry (CV) measurements



Scheme 2 Schematic diagram of the possible charge or energy transfer pathways occurring at a dyed  $TiO_2/HC$ -Acid/electrolyte interface. ET1 means a direct injection of electron from the HC-Acid to the  $TiO_2$  surface. ET2 and ET3 correspond to the energy transfer from the HC-Acid to the dye, and quenching of the HC-Acid by triiodide, respectively.

were carried out with a *VersaSTAT* 3 (AMETEK) using a typical three electrode electrochemical cell in a solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte in water-free THF at a scan rate of 50 mV s<sup>-1</sup> at room temperature, which was degassed with argon gas for 10 min prior to the scan. Dye-adsorbed TiO<sub>2</sub> on conductive glass was used as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. The potential of the reference electrode was calibrated by ferrocene, and all potentials mentioned in this study are against the normal hydrogen electrode (NHE). The dye adsorption amount on the TiO<sub>2</sub> surface was estimated spectroscopically after the dye had been desorbed in a 0.1 M NaOH in 50 : 50 (vol%) EtOH : H<sub>2</sub>O.

#### Materials

2-Iodo-9,9-dimethylfluorene was easily prepared according to the methods in the literature.<sup>35,36</sup> 4-Aminobenzonitrile,



Scheme 1 Molecular structures of (a) HC-Acid, (b) DCA, and (c) NKX2677, and the right is a snapshot of HC-Acid derived from a semi-empirical method (AM1). F: front view and S: side view.

1,10-penanthroline and copper iodide were purchased from Sigma-Aldrich inc. NKX2677 was synthesized according to the literature.<sup>27</sup> Other reagents and chemicals were purchased from Samchun Chemical Co. Tetrahydrofuran (THF) was dried over and distilled from sodium and benzophenone under an atmosphere of dry nitrogen, and *p*-xylene was dried over and distilled from CaH<sub>2</sub> under an atmosphere of dry nitrogen. Other chemicals and reagents were used as-received without further purification.

# Synthesis of 4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino) benzonitrile (1)

A mixture of 2-iodo-9,9-dimethylfluorene (7.45 g, 23.28 mmol), 4-aminobenzonitrile (1.25 g, 10.58 mmol), 1,10-penanthroline (0.19 g, 1.06 mmol), CuI (0.2 g, 1.06 mmol), and K<sub>2</sub>CO<sub>3</sub> (4.39 g, 31.74 mmol) in dry *p*-xylene (13 ml) was refluxed for 48 h under a N<sub>2</sub> atmosphere. The reaction mixture was quenched with water and extracted with ethyl acetate. The organic layer was collected, and the aqueous layer was washed with ethyl acetate. The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography (*n*-hexane/DCM = 2/3) to afford the title compound (1) (3.5 g, 66%): 'H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.69– 7.65 (m, 4H), 7.48–7.11 (m, 14H).

# Synthesis of 4-(bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzoic acid (2)

4-(Bis(9,9-dimethyl-9*H*-fluoren-2-yl)amino)benzonitrile (2 g, 3.98 mmol) and potassium hydroxide (2.3 g, 41 mmol) in 2ethoxyethanol/THF/H<sub>2</sub>O (2 : 1 : 2, 50 ml) were refluxed for 24 h. The reaction mixture was allowed to cool at room temperature and then acidified with 6 M HCl solution until white precipitate appeared. The precipitates were filtered and dissolved again with dichloromethane and washed several times with distilled water. The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by gravity column chromatography (DCM/MeOH = 1/1) to afford the title compound HC-Acid (1.8 g, 87%): <sup>1</sup>H NMR (300 MHz, DMSO) δ 12.58 (b, 1H), 7.83–7.77 (m, 6H), 7.5 (d, J 6 Hz, 2H), 7.35–7.25 (m, 6H), 7.13 (d, J 6 Hz, 2H), 7.07-6.99 (m, 2H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta = 167.31, 154.97, 153.27, 151.46, 146.09, 145.68,$ 138.06, 135.08, 134.57, 130.86, 126.97, 124.37, 123.80, 122.89, 121.26, 119.83, 54.87, 46.49, 26.61 ppm. EI-mass (m/z): calculated: 521.24 (M + H<sup>+</sup>), found: 521 (M<sup>+</sup>).

# Fabrication of the dye-sensitized solar cells

FTO glass plates (Pilkington) were cleaned in a detergent solution using an ultrasonic bath for 1 h, rinsed with water and ethanol. The FTO glass plates were immersed in an aqueous solution of 40 mM TiCl<sub>4</sub> at 70 °C for 30 min and washed with water and ethanol. The first TiO<sub>2</sub> layer of 8  $\mu$ m thickness was prepared by doctor blade printing TiO<sub>2</sub> paste (Solaronix, Ti-Nanoxide T/SP) and then dried for 2 h at 25 °C. The TiO<sub>2</sub> electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min. A paste for the scattering layer containing 400 nm sized anatase particles (CCIC, PST-400C) was deposited by doctor

blade printing and then dried for 2 h at 25 °C. The scattering layer coated TiO<sub>2</sub> electrodes were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min. The resulting layer was composed of an 8 µm thick transparent layer and an 8 µm thick scattering layer, which were treated again by TiCl<sub>4</sub> at 70 °C for 30 min and sintered at 500 °C for 30 min. The  $TiO_2$  electrodes were immersed into a 0.3 mM NKX2677 dve solution (with 40 mM DCA or 10 mM HC-Acid added) in a mixture of EtOH and THF (v/v, 2 : 1) and kept at room temperature for 24 h to complete the sensitizer uptake. Counter electrodes were prepared by coating with a drop of H<sub>2</sub>PtCl<sub>6</sub> solution (2 mg of Pt in 1 ml of ethanol) on an FTO plate. The dye-adsorbed TiO<sub>2</sub> electrode and Pt-counter electrode were assembled into a sealed sandwich-type cell. A drop of the electrolyte was then introduced into the cell, which was composed of 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.5 mM tert-butylpyridine in CH<sub>3</sub>CN. It was introduced into the inter-electrode space from the counter electrode side through predrilled holes. The drilled holes were sealed with a microscope cover glass slide and Surlyn to avoid leakage of the electrolyte solution.

# Photovoltaic measurements of the solar cells

Photoelectrochemical data were measured using a 1000 W xenon light source (Oriel, 91193) that was focused to give 1000 W m<sup>-2</sup>, the equivalent of one sun at Air Mass (AM) 1.5G, at the surface of the cell. The light intensity was adjusted with a Si solar cell that was double-checked with an NREL-calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current-voltage characteristics of the cell with the active area of 0.16 cm<sup>2</sup> under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software. Electrochemical impedance spectroscopy (EIS) measurements were performed using an impedance analyzer (VersaSTAT 3, AMETEK) connected to a potentiostat under dark conditions at room temperature. The spectra were scanned in a frequency range of 0.1-105 Hz and ac amplitude of 10 mV at room temperature. The EIS results were analyzed using ZSimpWin 3.21 software.

# **Results and discussion**

# Dye absorption behaviors

Fig. 1 shows the absorption and emission spectra of the HC-Acid in THF solution. The absorption peak ( $\lambda_{max}$ ) was observed at 359 nm and the emission peak ( $\lambda_{max}$ ) was observed at 450 nm. The molar extinction coefficient  $\varepsilon$  of HC-Acid was estimated to be 36 700 M<sup>-1</sup> cm<sup>-1</sup> at 359 nm. Fig. 2(a) shows the UV-visible absorption spectra of 0.3 mM NKX2677, 0.3 mM NKX2677 + 40 mM DCA, NKX2677 + 10 mM HC-Acid in 8 µm TiO<sub>2</sub> films. NKX2677 exhibited an absorption maximum at 511 nm in ethanol solution,<sup>29</sup> but the absorption peak was blue-shifted to 474 nm for a dye-loaded TiO<sub>2</sub> film, obtained by exposing the thin TiO<sub>2</sub> film in dye solution (0.3 mM) until the saturation of dye adsorption on the TiO<sub>2</sub> surface was reached. Such a blue shift is attributed to the solvent effect and deprotonation of carboxylic



Fig. 1 Absorption and emission spectra of  $3.5 \times 10^{-5}$  M HC-Acid in THF.



**Fig. 2** (a) The absorption spectra of NKX2677 (dotted line), NKX2677/ DCA (dashed dotted line) and NKX2677/HC-Acid (straight line) on the TiO<sub>2</sub> film (thickness 8  $\mu$ m). The inset is the absorption spectrum of the TiO<sub>2</sub> film loaded with HC-Acid alone. (b) The absorption spectra of the dye desorbed solution in a 0.1 M NaOH in 50 : 50 (vol%) EtOH : H<sub>2</sub>O.

acid upon adsorption.<sup>32</sup> When 40 mM DCA was included in the dye solution, the dye-sensitized  $TiO_2$  film co-grafted with DCA showed a similar absorption peak position. When 10 mM HC-Acid was substituted for DCA on the  $TiO_2$  surface, the absorption peak was red-shifted from 474 to 511 nm compared with

those of NKX2677 and NKX2677/HC-Acid-based devices, which may be effectively caused by the breakup of H-aggregation of NKX2677.

The inset in Fig. 2(a) shows the absorption maxima peak  $(\lambda_{max})$  at 385 nm for the TiO<sub>2</sub> film solely loaded with HC-Acid. Compared to the absorption peak of HC-Acid in THF solution, TiO<sub>2</sub> film loaded with HC-Acid shows the maximum absorption peak to be red-shifted by  $\sim 24$  nm. This red-shift, favourable for light harvesting in the longer wavelength of the UV region, can be anticipated to increase the photocurrent of DSSCs. We also measured the dye adsorption amount by the dye desorption into a basic solution followed by spectroscopic determination. As seen in Fig. 2(b), the dye amount on the  $TiO_2$  film decreased from  $2.50 \times 10^{-7} \mbox{ mol cm}^{-2}$  to  $1.80 \times 10^{-7} \mbox{ mol cm}^{-2}$  and  $1.49 \times 10^{-7}$ mol cm<sup>-2</sup>, leading to a 28% and 41% drop in dye adsorption with DCA and HC-Acid, respectively. As a result, the Y-shaped structure of HC-Acid is allowed to be more efficient than DCA in decreasing dye adsorption. Moreover, as shown in Fig. 2(b), it indicates that, when comparing the dye amount adsorbed, HC-Acid adsorbed about 7 times more. Judging by the difference of structure between DCA and HC-Acid, a coadditive with a bulky structure may be necessary for effective spacing of adjacent organic dye molecules. As seen in Scheme 1, the molecular sizes from the side view of NKX2677, DCA and HC-Acid were estimated to be 8.98 Å, 6.0 Å and 13.37 Å, respectively. In the case of HC-Acid, the dihedral angles of the phenyl group and the fluorene unit with a nitrogen atom as the central, using a semiempirical method (AM1), are estimated to be 54°.

# **Electrochemical properties**

Fig. 3 shows the typical CV of NKX2677 on the TiO<sub>2</sub> surface using 0.1 M TBAPF<sub>6</sub> in water-free THF. For comparison, different dye-loaded films were obtained by dipping the TiO<sub>2</sub> films in (a) 0.3 mM NKX2677, (b) 0.3 mM NKX2677 + 40 mM DCA, and (c) 0.3 mM NKX2677 + 10 mM HC-Acid in THF overnight, and the inset in Fig. 3 is 10 mM HC-Acid only. NKX2677 displayed two reversible one-electron anodic



Fig. 3 Cyclic voltammograms of the TiO<sub>2</sub> films after immersion for 12 h in different solutions: (a) 0.3 mM NKX2677, (b) 0.3 mM NKX2677 + 40 mM DCA and (c) 0.3 mM NKX2677 + 10 mM HC-Acid. The inset is CV of the TiO<sub>2</sub> film after immersion for 12 h in 10 mM HC-Acid.

Table 1 Energy levels of the NKX2677, NKX2677/DCA, NKX2677/ HC-Acid and HC-Acid alone adsorbed TiO<sub>2</sub> electrodes

Electrode	HOMO/V <sup>a</sup>	LUMO/V	Gap/eV <sup>b</sup>
NKX2677	0.92	-0.90	1.82
NKX2677/DCA	0.92	-0.91	1.85
NKX2677/HC-Acid	0.91	-0.89	1.85
HC-Acid	1.11	-1.06	2.17

<sup>a</sup> The first oxidation potential vs. NHE in Fig. 3 was adopted as the HOMO. <sup>b</sup> The absorption threshold in Fig. 2(a) was taken as the gap between the HOMO and the LUMO.

oxidation steps at half-wave potentials of 0.92 and 1.39 V. Similar to NKX2677, a co-adsorbent DCA electrode exhibits two reversible couples at 0.89 and 1.33 V. In the case of HC-Acid coadsorption, the first oxidation potential is 1.12 V and the second is 1.84 V, which is similar to HC-Acid alone. The lowest unoccupied molecular orbital (LUMO) level is determined by using the expression LUMO = HOMO - gap, where the gap is estimated from the absorption threshold in Fig. 2(a). The energy levels of these three electrodes are summarized in Table 1. The NKX2677 adsorbed to the TiO<sub>2</sub> films can be electrochemically oxidized and reduced in a reversible pattern. Generally, initial oxidation of NKX2677 molecules followed by the electron hopping across the TiO<sub>2</sub> nanoparticle surface is one accepted mechanism,<sup>37-40</sup> for charge transfer in a working electrode. The formation of  $\pi$ - $\pi$  stacking of NKX2677, due to the increase of the dye adsorbed amount, was also evidenced by the strong current intensity signal as shown in Fig. 3. That is, after the coadsorption of HC-Acid with the dye on the TiO<sub>2</sub> surface, the significant decrease in current intensity in the CV signal suggests that HC-Acid more effectively decreases the dye adsorbed amount than DCA. This different behavior in electrochemical activity between the two electrodes, i.e., NKX2677/DCA and NKX2677/HC-Acid, indicates that the coadsorption of HC-Acid would be more favorable than DCA for suppressing the recombination of electrons with electron acceptors in the electrolyte  $I_3^{-}/I_2$  or preventing possible intermolecular electron losses between two neighboring dye molecules in a DSSC device. In other words, the coadsorption of HC-Acid would be more effective than DCA for forming an insulting spacer among dye molecules, which blocked the recombination of injected electrons with  $I_3^-$  ions in the electrolyte and/or the oxidized dye cations generated after electron injection in a DSSC device.

# Solar cell performances

Incident photon-to-electron conversion efficiency (IPCE) as a function of wavelength was measured to evaluate the photoresponse of the photoelectrodes in the whole spectral region. Fig. 4 shows the IPCE spectra for  $TiO_2$  films before and after coadsorption with DCA or HC-Acid. The inset in Fig. 4 shows the IPCE spectrum for TiO<sub>2</sub> film loaded HC-Acid alone. The photovoltaic performance of the HC-Acid-based solar cell was obtained with a short circuit current  $(J_{sc})$  of 2.57 mA cm<sup>-2</sup>, an open circuit voltage ( $V_{oc}$ ) of 655 mV, a fill factor (FF) of 71%, and an overall energy conversion efficiency ( $\eta$ ) of 1.21% under standard AM 1.5 conditions. The maximum IPCE of the HC-



Fig. 4 IPCE spectra of DSSCs based on (a) NKX2677, (b) NKX2677/ DCA and (c) NKX2677/HC-Acid. The inset is the IPCE spectrum of the TiO<sub>2</sub> film loaded with HC-Acid alone.

Acid-based solar cell was ca. 45% at 360 nm. These results indicate that it has the good light harvesting effect at shorterwavelength regions (see Table 2). As shown in Fig. 4, the maximum IPCE is only ~77% for NKX2677 sensitized solar cells. It is much lower than 85%, taking into account the light loss  $(\sim 15\%)$  by the reflection and absorption of the TCO glass. Upon addition of DCA or HC-Acid in the dye solution, IPCE was increased remarkably. The maximum IPCE increased from 73% to 77% when 40 mM DCA was added in the dye solution, and increased to 83% with 10 mM HC-Acid in the dye solution. Upon HC-Acid coadsorption, the maximum IPCE improved remarkably, up to 67% at 360 nm, compared to those of the other two devices, which could be contributed to the increased photocurrent of the DSSCs. Taking the  $\sim$ 85% transmittance of the TCO glass into account, the IPCE value for TiO<sub>2</sub> film HC-Acid is almost 100%, even without anti-reflecting coating film. Because dye monomer can inject electrons into TiO<sub>2</sub> more efficiently than aggregate,31 the coadsorbed dye/DCA TiO2 film obtained from the exposure of TiO<sub>2</sub> film to the dye solution with 40 mM DCA may contain a mixture of aggregate and dye monomer judged from the IPCE spectrum. On the other hand, the coadsorbed dye/ HC-Acid TiO<sub>2</sub> film obtained from exposure of TiO<sub>2</sub> film to the dye solution with 10 mM HC-Acid is mainly composed of dye monomer, as judged from the high IPCE. Moreover, a plateau from 500 to 600 nm was observed in the IPCE action spectrum with IPCE of ~85% on the dye/HC-Acid TiO<sub>2</sub> film. It is evidenced that HC-Acid is effective to dissociate formation of  $\pi$ - $\pi$ stacking by the strong intermolecular interaction. This high IPCE value means that all the three efficiencies, such as electron injection, light harvesting, and electron-collection efficiency, are unity.

The lower charge collection efficiency or lower IPCE is ascribed to charge recombination caused by dye aggregation or close  $\pi$ - $\pi$  stacking.<sup>40,41</sup> Wang *et al.* reported that the coadsorption of DPA40,42 or HDMA43 with ruthenium polypyridine dyes could improve both  $J_{sc}$  and  $V_{oc}$ . However, DPA or HDMA coadsorbs parallelly to the dye molecules and the linear alkyl chain cannot separate adjacent molecules efficiently and thus

Device	Dye adsorbed amount/10 <sup>-7</sup> mol cm <sup>-2</sup>	$J_{\rm sc}/{ m mA~cm^{-2}}$	V <sub>oc</sub> /mV	FF (%)	η (%)
NKX2677	2.51	14.96	595	74.05	6.59
NKX2677/DCA	1.81	15.54	640	74.47	7.41
NKX2677/HC-Acid <sup>b</sup>	1.72	17.61	663	75.70	8.83
NKX2677/HC-Acid <sup>c</sup>	1.49	18.01	663	76.16	9.09
HC-Acid <sup>c</sup>	3.41	2.57	655	71.47	1.21
<sup><i>a</i></sup> Performance of DSSCs wa	5.41 s measured with a black metal mask ((	2.57 0.16 cm²). Electrolyte: 0.6 N	655 I DMPII, 0.05 M I2, at	/1.4/ nd 0.1 M LiI in CH <sub>2</sub> CN	1.21 N. <sup>b</sup> HC-Acid

Table 2 Photovoltaic performance parameters of the DSSCs with different co-adsorbents under AM 1.5G (100 mW cm<sup>-2</sup>)<sup>a</sup>

cannot prohibit the  $\pi$ - $\pi$  stacking. Because of this, it was revealed that they could not work on coumarin dye of NKX2700 in terms of efficiency improvement contrary to the DCA.<sup>38</sup> Moreover, recently, di-branched organic sensitizers<sup>26</sup> constituted by one donor and two anchoring groups having a bulky-shaped structure and a novel unsymmetrical organic cyanine sensitizer<sup>25</sup> that contain the tailored starburst triphenylamine moiety acting as an electron donor have been reported for suppressing aggregation, disfavouring molecular stacking between dye molecules resulted in improving the photovoltaic performance in DSSCs. As mentioned above, for effective spacing of adjacent molecules and efficiently prohibiting the  $\pi$ - $\pi$  stacking, a coadditive having a bulky-shaped structure may be necessary. As illustrated in Scheme 1, the chemical structure of HC-Acid has a more bulkyshaped structure than DCA. Thus, HC-Acid can act as a more effective spacer than DCA among dye molecules and thus suppresses the  $\pi$ - $\pi$  interaction of the dye molecules, which retards charge recombination and hence significantly improves the performance of the DSSCs. Moreover, as shown in Table 1, the LUMO of HC-Acid is slightly higher than that of NKX2677, the electron from excited NKX2677 dye cannot directly move to HC-Acid, in addition, it has a light harvesting effect at shorterwavelength regions as seen in IPCE data. In other words, it has dual functioned effects, in which it can act as spacers between the dye molecules and have the light harvesting effect in the shorterwavelength regions.

concentration was 5 mM. <sup>c</sup> HC-Acid concentration was 10 mM.



**Fig. 5** J-V curves of DSSCs based on (a) NKX2677, (b) NKX2677/ DCA and (c) NKX2677/HC-Acid. The inset is the J-V curve of HC-Acid alone, and the TiO<sub>2</sub> film thickness and active area of 16(8 + 8) µm and 0.16 cm<sup>2</sup>, respectively.

The current density-voltage (J-V) curves are shown in Fig. 5. Their photovoltaic performance is summarized in Table 2. The photocurrent density  $(J_{sc})$  increased in the same order of integrated photocurrent as the IPCE action spectra in Fig. 4. The NKX2677-based DSSC produced  $\eta = 6.59\%$ ,  $J_{sc} = 14.96$  mA  $cm^{-2}$ ,  $V_{oc} = 0.595$  V, and FF = 74.05. The NKX2677/DCAbased DSSC produced  $\eta = 7.41\%$ ,  $J_{\rm sc} = 15.54$  mA cm<sup>-2</sup>,  $V_{\rm oc} =$ 0.640 V, and FF = 74.47. NKX2677/HC-Acid-based produced  $\eta = 9.09\%$ ,  $J_{sc} = 18.01$  mA cm<sup>-2</sup>,  $V_{oc} = 0.663$  V and FF = 76.16. HC-Acid only provides  $\eta = 1.21\%$ ,  $J_{sc} = 2.57$  mA cm<sup>-2</sup>,  $V_{oc} =$ 0.656 V, and FF = 71.47. Obviously, coadditive exchange from DCA to HC-Acid results in high efficiency, which is attributed to the significant enhancement of  $J_{sc}$  and  $V_{oc}$  mainly originating from its dual functioned effect. The above photovoltaic performance results indicate that coadsorption with HC-Acid is more effective in improving solar cell performance than DCA.

#### Effect of co-additives on the open-circuit voltage of DSSCs

Generally, in the DSSCs,  $V_{oc}$  is defined as the voltage difference between the chemical potential of the electrolyte redox ( $E_{red}$ ) and quasi-Fermi potential of electrons ( $E_{Fn}$ ) in the semiconductor, TiO<sub>2</sub>, which could be described as eqn (1) (ref. 44):

$$V_{\rm oc} = E_{\rm red} - E_{\rm CB} - \gamma \frac{k_{\rm B}T}{e} \ln\left(\frac{N_{\rm e}}{n}\right) \tag{1}$$

where  $\gamma$  is the characteristic constant of TiO<sub>2</sub> tailing states,  $k_{\rm B}$  is the Boltzmann constant, T is the temperature, e is the elementary charge, and  $N_{\rm e}$  is the effective density of states at the TiO<sub>2</sub> conduction band edge. Assuming that  $E_{red}$  is constant,  $V_{oc}$  will be determined by the position of the conduction band edge  $(E_{CB})$ and the concentration of electrons (n) in TiO<sub>2</sub>. These two parameters are closely related to the surface charge and charge recombination, respectively. The position of the conduction band edge will be determined by the surface charge supplied by interface species such as ions, additives, and dye molecules. Any change in the surface charge will shift the conduction band edge position and influence the  $V_{oc}$ . The number of electrons (n) in  $TiO_2$  is determined by the balance between electron injection and electron recombination. Possible factors influencing  $V_{oc}$  for DSSCs based on NKX2677/DCA and NKX2677/HC-Acid involve the TiO<sub>2</sub> surface blocking and conduction band edge shift, which will be discussed in detail in the following sections.

Electrochemical impedance spectroscopy (EIS) is a powerful tool for identifying electronic and ionic transport processes in DSSCs, which provides valuable information for the





**Fig. 6** (a) Nyquist plots and (b) Bode phase plots of electrochemical impedance spectra for the DSSCs based on NKX2677 (open squares), NKX2677/DCA (open circles) and NKX2677/HC-Acid (open triangles). The inset is the equivalent circuit used to fit the impedance spectra.

understanding of photovoltaic parameters.<sup>45–47</sup> Fig. 6 shows the typical EIS Nyquist and Bode phase plots measured under the dark conditions at a forward bias of -0.65 V. The equivalent circuit (inset) in Fig. 6(b) was used to fit the experimental data of all of the samples.  $R_s$  is the series resistance accounting for the transport resistance of the TCO and the electrolyte.  $C_{\mu}$  and  $R_{ct}$  are the chemical capacitance and the charge recombination resistance at the TiO<sub>2</sub>/electrolyte interface, respectively.  $C_{Pt}$  and  $R_{Pt}$  are the interface capacitance and charge transport resistance at the Pt/electrolyte interface, respectively. The larger semicircle at the middle frequency range represents the interfacial charge transfer resistance ( $R_{ct}$ ) at the dyed TiO<sub>2</sub>/electrolyte interface. The fitted  $R_{ct}$  increased in the order of NKX2677 (21  $\Omega$ ) <

NKX2677/DCA (34  $\Omega$ ) < NKX2677/HC-Acid (39  $\Omega$ ), which is consistent with the  $V_{\rm oc}$  values measured in the devices. The smaller  $R_{\rm ct}$  value means the electron recombination from the TiO<sub>2</sub> to electron acceptors in the electrolyte occurring more easily, and thus results in lower  $V_{\rm oc}$ . Clearly, electron recombination based on NKX2677 is faster than that of NKX2677/DCA and NKX2677/HC-Acid. The coadsorption leads to the formation of a more compact monolayer, comprised of the dye and DCA or HC-Acid as the co-adsorbent, than the adsorption of dye alone. This insulating molecular layer effectively shields the back electron transfer from the TiO<sub>2</sub> to I<sub>3</sub><sup>-</sup> ions and gives a higher  $V_{\rm oc}$ . In this study, a coumarin organic sensitizer NKX2677 is coadsorbed with HC-Acid, a combination that enhances the  $V_{\rm oc}$  by 68 mV and increases the overall conversion efficiency by 38%.

To investigate the influences of the shift in the TiO<sub>2</sub> conduction band edge and charge recombination on  $V_{\rm oc}$ , impedance spectra were also measured by varying the applied potential at equal intervals in the vicinity of  $V_{\rm oc}$ . By fitting the EIS curves, another important parameter for DSSCs, electron lifetime ( $\tau$ ), could be extracted from the  $C_{\mu}$  and  $R_{\rm ct}$  using  $\tau = C_{\mu}R_{\rm ct}$ .<sup>48,49</sup> The fitted  $C_{\mu}$  and  $R_{\rm ct}$  values together with  $\tau$  are plotted in Fig. 7. This exponential rise with the increase of forward bias is a typical behaviour of  $C_{\mu}$  that is described by eqn (2) (ref. 50):

$$C_{\mu} = \frac{e^2}{k_{\rm B}T} \exp\left[\frac{\alpha}{k_{\rm B}T} (E_{\rm red} + eV_{\rm a} - E_{\rm CB})\right]$$
(2)

where e is the elementary charge,  $k_{\rm B}$  is the Boltzmann constant, Tis the temperature (298 K),  $\alpha$  is a constant related to the distribution of electronic states below the conduction band, and  $E_{red}$  is the chemical redox potential of the redox couples in the electrolyte. Assuming that  $E_{\rm red}$  is constant,  $C_{\mu}$  is governed by the forward bias  $(V_a)$  and  $E_{CB}$ . As shown in Fig. 7(a), at a given value of  $V_{\rm a}$  the  $C_{\mu}$  for both NKX2677/HC-Acid and NKX2677/DCA is higher than that of NKX2677, indicating a negative shift of the conduction band edge. Generally, the negative shift of  $E_{CB}$  leads to improvement of  $V_{\rm oc}$  of DSSCs.  $C_{\mu}$  between the NKX2677/ HC-Acid and the NKX2677/DCA has almost similar value, but  $R_{\rm ct}$  of the NKX2677/HC-Acid is slightly higher than that of the NKX2677/DCA. This means that it is charge recombination, rather than the position of conduction band edge, that governs  $V_{\rm oc}$ . At the forward bias of -0.65 V, the fitted  $\tau$  increases in the order of NKX2677/HC-Acid (21 ms) > NKX2677/DCA (34 ms) > NKX2677 (39 ms), giving an explanation of the different  $V_{\rm oc}$ yielded by DSSCs based on the three devices. One electron loss



Fig. 7 (a) Chemical capacitance ( $C_{\mu}$ ), (b) interfacial charge transfer resistance ( $R_{ct}$ ), and (c) electron lifetime ( $\tau$ ) fitted from impedance spectra under a series of different forward bias: NKX2677 (filled squares), NKX2677/DCA (open circles) and NKX2677/HC-Acid (filled triangles).

channel is the electron capture by electron acceptors, *i.e.*,  $I_3^{-}/I_2$  ions in the electrolyte. The insertion of HC-Acid, forming an insulating layer, blocks the electron recombination to the  $I_3^-$  ions and thus enhances the electron lifetime. The longer electron lifetime contributed to a higher  $V_{\rm oc}$ . However, the electron lifetime in TiO<sub>2</sub> was not significantly enhanced, compared to that of another HC-Acid in previous article reported by our group,<sup>34</sup> which has multiple functioned effects, such as the prevention effect of the  $\pi$ - $\pi$  stacking, the light harvesting effect at shorter-wavelength regions and the hole conducting function through a redox cascade process. It indicates that the present HC-acid has dual-functioned effects, such as the prevention effect of the  $\pi$ - $\pi$  stacking and the light harvesting effect at shorter-wavelength regions.

#### Photophysical properties and possible charge transfer mechanism

For further understanding on the cell performance enhancement by HC-acid, we have investigated the photophysical properties of HC-Acid and NKX2677 in the solution state (see the ESI† for details). Fig. 8 shows the PL emission spectra with different conditions at the excitation wavelength ( $\lambda_{ex}$ ) of 354 nm in acetonitrile. Each solution was made to similar concentrations estimated from real dye-sensitized solar cells fabricated here (the mole ratio of HC-Acid/NKX2677/ $I_2 = 1.5/1/2$ ). Upon the photoexcitation at 354 nm, the PL maximum wavelength of HC-Acid, NKX2677 and I<sub>2</sub> appeared at 419, 430 and 428 nm, respectively. The PL emission intensities of both NKX2677 and I<sub>2</sub> are extremely lower than that of HC-Acid. As shown in Fig. 8, the PL emission maxima of both the mixture of HC-Acid/ NKX2677 and the mixture of HC-Acid/NKX2677/I<sub>2</sub> appeared around 490 nm, and the PL emission intensity of HC-Acid was significantly diminished about 51% and 56% in the system of HC-Acid/NKX2677 and HC-Acid/NKX2677/I2, respectively.

Once excited, the HC-Acid can transfer its excited energy to a certain acceptor,<sup>21,22</sup> and the energy transfer rate is affected as a function of the separation distance (*r*) between HC-Acid and a nearby acceptor molecule (SD).<sup>23,51</sup> HC-Acid is assumed to be within the Förster radius ( $R_0$ ) of the NKX2677 dye (see



Fig. 8 PL emission spectra for (a)  $9.9 \times 10^{-6}$  M HC-Acid, (b)  $6.6 \times 10^{-6}$  M NKX2677, (c)  $1.25 \times 10^{-5}$  M I<sub>2</sub>, (d)  $9.9 \times 10^{-6}$  M HC-Acid +  $6.6 \times 10^{-6}$  M NKX2677, and (e)  $9.9 \times 10^{-6}$  M HC-Acid +  $6.6 \times 10^{-6}$  M NKX2677 +  $1.25 \times 10^{-5}$  M I<sub>2</sub> at  $\lambda_{ex}$  of 354 nm in acetonitrile.

Fig. S1<sup>†</sup>), and the separation distance between the donor of HC-Acid and the acceptor of NKX2677 dye may be sufficiently nearby in the solution state.

In this study, under the similar solution concentrations of each solution estimated from real dye-sensitized solar cells fabricated here, as depicted in Fig. 8, the increase of the emission spectrum of NKX2677 over 600 nm was not observed, may be due to the fact that the molar excitation coefficient of NKX2677 has an extremely low value of 1800 M<sup>-1</sup> cm<sup>-1</sup> at 354 nm, and its PL quantum efficiency is also very low at 354 nm (see Fig. S2<sup>†</sup>). The excitation spectrum profile of a mixture of HC-Acid and NKX2677 ( $\lambda_{em} = 670$  nm) is similar to those of HC-Acid and NKX2677 (see Fig. S3<sup>†</sup>). From this result, it is presumed that the energy transfer from HC-Acid to NKX2677 happens to be low as follows: the molar excitation coefficient of NKX2677 is very low in the range of 1800–7400 M<sup>-1</sup> cm<sup>-1</sup> at the wavelength region of 350-390 nm (see Fig. S2<sup>†</sup>), so that the energy transfer efficiency from HC-Acid to NKX2677 should be expected to be low (pathway ET2 in Scheme 2). Triiodide is a highly mobile ion that is known as a 'perfect quencher', meaning that collisions with the HC-Acid have a near unity probability of quenching the excited state.<sup>23,52</sup> This quenching effect by I<sub>3</sub><sup>-</sup> ions appeared to be relatively lower about 5% in our system (pathway ET3 in Scheme 2). For a real dye-sensitized solar cell based on HC-Acid, the energy transfer efficiencies of ET2 and ET3 seem to be very low, due to the molecular size difference between NKX2677 and HC-Acid. Thus, HC-Acid cannot extremely influence the photovoltaic performance enhancement through the energy transfer pathways of HC-Acid into NKX2677 and I<sup>-</sup>/I<sub>3</sub><sup>-</sup> in the real dye-sensitized solar cell systems. In other words, the electron injection pathway of ET1 is dominant over the other energy transfer pathways of ET2 and ET3 in Scheme 2.

# Conclusions

The role of 4-(bis(9,9-dimethyl-9H-flouren-2-yl)amino)benzoic acid as the co-adsorbent on the TiO<sub>2</sub> surface with NKX2677 sensitizer was investigated. To confirm the role of HC-Acid, we compared it with a deoxycholic acid (DCA). Co-grafted DCA or HC-Acid on the TiO<sub>2</sub> surface reduced the adsorption amount of NKX2677 and diminished the H-aggregation formation between the dye molecules onto TiO2 as seen from the IPCE and absorption spectral data on the TiO<sub>2</sub> film. HC-Acid reduced the recombination process at the TiO2 surface acting like a blocking layer to improve  $V_{oc}$  by slowing recombination, which manifested itself in a longer electron lifetime. Moreover, the breakup of  $\pi$ -stacked aggregates might improve the electron injection yield, thus increasing  $J_{sc}$ . In other words, it has dual functioned effects, which are the prevention effect of the  $\pi$ - $\pi$  stacking of organic dye molecules such as the DCA and the light harvesting effect at shorter-wavelength regions. With the HC-Acid used as the co-adsorbent for the organic dye NKX2677 sensitized solar cell, an extremely high power conversion efficiency of 9.09% was achieved under 100 mW cm<sup>-2</sup> AM 1.5G simulated light ( $J_{sc}$  = 18.01 mA cm<sup>-2</sup>,  $V_{\rm oc} = 0.663$  V, and FF = 76.16). Thus, the dual functioned coadsorbent is a promising candidate as a new coadditive for highly efficient dye-sensitized solar cells to improve UV light harvesting through a charge transfer process.

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