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A Desirable Hole-Conducting Coadsorbent for Highly Efficient Dye-Sensitized Solar Cells through an Organic Redox Cascade Strategy

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Over the past decade, dye-sensitized solar cells (DSSCs)^[1] based on nanocrystalline mesoporous metal oxides (typically TiO₂) have been intensively studied and developed as a promising, low-cost alternative to conventional silicon photovoltaic devices. The components of such DSSCs are a dye sensitizer, a TiO₂ metal oxide coated on conductive glass, a redox electrolyte couple, and a counter electrode. As illustrated in Scheme 1, the power-conversion efficiency of DSSCs is strongly dependent upon the minimization of charge recombination losses at the TiO₂/dye/electrolyte interface (pathways 3 and 4).^[2] There are two recombination pathways of importance in DSSCs, in which electrons photoinjected into the TiO2 electrode can recombine with either dye cations or with redox electrolytes. Moreover, such charge recombination leads to losses in both the short-circuit photocurrent (J_{sc}) and the open-circuit photovoltage $(V_{\rm oc})$, resulting in a decrease in overall energy conversion efficiency (η) .

To reduce the possible charge recombination pathways occurring at the TiO₂/dye/electrolyte interface, several kinds of additives, such as decylphosophonic acid (DPA), dineohexyl bis(3,3-dimethylbutyl)phosphinic acid (DINHOP), and chenodeoxycholic acid (CDCA) have been introduced to adsorb onto the TiO₂ surface.^[3] Among them, for example, cholic acid (CA) derivatives as coadsorbents in DSSCs, based on a Ru–pyridyl complex,^[4] courmarin,^[5] porphyrin,^[6] phthalocyanine,^[7] and naphthalocyanine dye,^[8] have been investigated well. Deoxycholic acid (DCA) is often used as a coadsorbent to break up organic and Ru–dye aggregates and hence to significantly improve V_{oc} and J_{sc} .^[5,9] Moreover, alternative approaches directed toward the minimization of recombination losses have been extensively studied by not

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only the insertion of a metal oxide blocking layer,^[10] but also by energetic cascades for multistep hole conductors (HC),^[11] as well as superior molecular sensitizer dyes^[12] and the insertion of a barrier layer between the sensitizer dye and the HC.^[2] To date, however, the desired redox intermediate mediators between the dye and I^-/I_3^- redox electro-



Scheme 1. a) Schematic diagram of the ideal charge-transfer processes occurring at a dyed TiO₂/electrolyte interface including organic HC, and b) one of the charge-transfer processes proposed herein. Pathways: (1) Electron injection from the dye or **HC-A** excited state into the conduction band of the TiO₂, (2) dye regeneration by electron transfer from a redox couple, (3,4) charge recombination with dye cation and I_3^- ions. Reaction pathway (5) corresponds to the hole-transfer from the HOMO of the dye cation to the HOMO of the **HC-A**, and (5*) hole transfer from the HOMO of the **HC-A** to redox electrolyte.

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lyte have been intensively looked for to increase the open circuit voltage of $V_{\rm oc}$ and improve the device performance through a cascade-type hole-hopping channel, but these have not yet been developed (see Scheme 1a).^[13] For this, by minimizing the energy difference between the HOMO of the sensitizing dye and the work function of the organic HC, it is possible to develop DSSCs with higher energy conversion efficiency.^[14]

Among the metal-free organic dyes studied in DSSCs, coumarin-based dyes^[15] are somewhat promising sensitizers for DSSCs based on TiO₂ films, because of their good photoresponse in the visible region, good long-term stability under light-soaking conditions (one sun),^[16] appropriate lowest unoccupied molecular orbital (LUMO) levels matching the conduction band of TiO₂, and low cost. However, π - π stacking of organic dye molecules usually occurs, because of the strong intermolecular interaction. The strong π -electron interaction in oligothiophene, in particular, allows easy formation of π stacks or lamellar structure. $^{[17]}$ Although π - π stacking is advantageous to light-harvesting, because of its broad feature in the UV/Vis absorption spectrum, π -stacked aggregates usually lead to inefficient electron injection and thus result in low power-conversion efficiency.^[18] Prohibition of π - π stacking by use of an additive in the dye solution is a typical way to improve efficiency of organic dye-sensitized solar cells suffering from the π - π stacking problem. Coadsorption of the dye with additives and structural modification of the dye molecules has proven to be effective to dissociate π - π stacking or dye aggregation and thus to improve solar-cell efficiency.^[19]

In the present study, we have synthesized a carbazole moiety^[20] of 4-{3,6-bis[4-(2-ethylhexyloxy)phenyl]-9*H*-carbazol-9-yl}benzoic acid (*b*EHCBA: hole conductor **HC-A**) as an alternative coadsorbent with a new function not seen in DCA or CA derivatives to enhance the overall conversion efficiency of DSSCs by reducing the possible charge-recombination pathways occurring at the TiO₂/dye/electrolyte interface. Also, we have investigated the charge-transfer process occurring in co-sensitized DSSCs including a processes proposed here that proceeds via an organic hole conductor (Scheme 1b).

As depicted in Figure S2 in the Supporting Information, HC-A with a low molecular weight and Y-shaped structure can strongly absorb UV light, leading to the light-harvesting effect in the shorter wavelength regions. It is anticipated to increase the photocurrent of DSSCs. The introduction of the bulky ethylhexyloxy group into a carbazole-based HC-A was also achieved in order to enhance its solubility in organic solvents, as well as the potential of inserting into the barrier layer to retard recombination losses.^[2] Its oxidation mid-potential was determined from cyclic voltammetry (CV) in DMF containing 0.1 M TBA(PF₆) to be 1.35 V versus NHE. Details of chemical synthesis and characterization of HC-A, cell fabrication, and device performance measurements are described in the Supporting Information. The redox liquid electrolyte contained 0.1 M LiI, 0.05 M I₂, 0.6 м 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPII), and 0.5 M 4-*tert*-butylpyridine (*t*BP) using dehydrated CH₃CN as a solvent. The dye NKX2677 was prepared according to the literature.^[15]

The UV/Vis absorption spectra for the dye-adsorbed TiO_2 films with different coadsorbents are compared in Figure 1. The molar extinction coefficient (ε) of **HC-A** was estimated



Figure 1. UV/Vis absorption spectra for TiO₂ films after immersion for 12 h in 0.3 mm NKX2677 dye (—), 0.3 mm NKX2677 dye + 40 mm DCA (·····), 0.3 mm NKX2677 dye + 10 mm **HC-A** (·····), and 10 mm **HC-A** alone ($-\cdots$ -··). The bare TiO₂ transparent film with the thickness of 8 µm was used as a reference for the spectrum scan.

to be $44200 \text{ m}^{-1} \text{ cm}^{-1}$ at 296 nm. NKX2677 exhibited an absorption maximum peak at 511 nm in ethanol (with $\varepsilon = 64300 \text{ m}^{-1} \text{ cm}^{-1}$),^[16] but the NKX2677-sensitized TiO₂ film exhibited a blue-shifted maximum peak at 501 nm. Such a blue shift was attributed to the solvent effect and deprotonation of carboxylic acid upon adsorption.^[21] The NKX2677/DCA-sensitized TiO₂ film showed a similar absorption peak position, but the absorbance at 501 nm decreased from 3.42 to 2.21, indicating that the amount of dye on the TiO₂ surface decreased by about 35%. The dye/**HC**-**A**-sensitized TiO₂ film showed an absorption peak at around 511 nm and an additional sharp absorption peak at around 355 nm, corresponding to the **HC-A** molecule. This red shift may be caused by the breakup of H-aggregation of NKX2677.

According to Figure 1, the absorbance at maximum peak of NKX2677 decreased from 3.42 to 0.73, indicating an approximate 78% drop in dye adsorption upon coadsorption with **HC-A**. When the dye with DCA and **HC-A** coadsorbed on the TiO₂ film, the deprotonation of the carboxylic acid group in the dye induced less adsorption of NKX2677 onto the TiO₂ surface, owing to the electrostatic repulsion of negatively charged carboxylic groups.^[9] Moreover, less dye adsorption for **HC-A** than DCA coadsorption was mainly attributed to the bigger molecular size of **HC-A**. Thus, The **HC-A** with a Y-shaped bulky structure could be allowed to be more efficient than DCA in decreasing dye adsorption and preventing π - π aggregation between the dye molecules in the pores of TiO₂ films. The amount of the dyes adsorbed on the TiO₂ surface were estimated spectroscopically by de-

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sorbing the dyes with a 0.1 M solution of NaOH in 50:50 (vol%) THF/H₂O, and the surface concentrations were determined to be 2.02×10^{-7} , 1.31×10^{-7} , and 4.1×10^{-8} mol cm⁻² forNKX2677-, NKX2677/DCA-, NKX2677/**HC-A**-based TiO₂ films, respectively (see Figure S4 in the Supporting Information).

The incident photon conversion efficiency (IPCE) spectrum and J-V curve of **HC-A**-based solar cell under standard test conditions (STC: AM 1.5 G, 100 mW cm⁻² irradiation at 25°C) are shown in Figure S5 in the Supporting Information. The photovoltaic performance of **HC-A**-based solar cell was obtained with a short circuit current (J_{sc}) of 0.885 mA cm⁻², an open circuit voltage (V_{oc}) of 560 mV, a fill factor (FF) of 73.76%, and an overall conversion efficiency (η) of 0.37% under STC. The maximum IPCE of **HC-A**based solar cell was about 50% at 350 nm, indicating that **HC-A** has the same effect as DCA, in addition, it has a light-harvesting effect at short-wavelength regions.

Figure 2 shows the IPCE and J-V characteristics of the DSSCs using different additives under the STC. Their photovoltaic performance is summarized in Table 1. The IPCE of the NKX2677-sensitized solar cell was lower than that of the others and was ascribed to charge recombination caused



Figure 2. a) The IPCE spectra, b) *J*–*V* curves of the DSSCs, and dark-current density of NKX2677 (\Box), NKX2677/DCA (\odot), NKX2677/**HC-A** (\triangle), and film thickness and active area of 16(8+8) µm and 0.16 cm², respectively.

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Table 1. Photovoltaic performance parameters of the DSSCs under the STC (AM 1.5 G, 100 mW cm⁻² irradiation at 25 °C).

	Relative ratio of dye adsorbed	$V_{ m oc}$ [V]	$J_{\rm sc}$ [mA cm ⁻²]	FF [%]	η [%]
NKX2677	1.00	0.579	15.49	74.36	6.68
NKX2677/DCA	0.67	0.608	16.81	74.86	7.67
NKX2677/ HC-A	0.39	0.688	17.25	74.93	8.89
НС-А	_	0.560	0.885	73.76	0.37

by dye molecule aggregation or close π - π stacking. Such aggregate formation has been suggested to cause unwanted intermolecular energy transfer or nonradiative decay pathways, thus reducing the electron injection efficiency.^[22] However, in both the case of DCA and HC-A coadsorption, even though the amount of dye on the TiO₂ surface was remarkably reduced, the maximum IPCE was improved up to 80 and 85%, respectively. Taking the \approx 85% transmittance of the TCO glass into account, the IPCE value for the TiO₂ film loaded with HC-A is 100%, even without an antireflecting coating film. Because the dye monomer can inject electrons to TiO₂ more efficiently than aggregate,^[18] the coabsorbed dye/DCA TiO₂ film obtained from the exposure of TiO₂ 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-A** TiO_2 film obtained from exposure of TiO_2 film to the dye solution with 10 mM HC-A is mainly composed of dye monomer. Upon HC-A coadsorption, the maximum IPCE was remarkably improved up to 65% at 360 nm than that of the other two devices, maybe contributing to increase the photocurrent of the DSSCs. Even with its lower dye adsorption, NKX2677/HC-A exhibited a 5% higher value than the maximum IPCE of NKX2677/DCA. It implies that HC-A can act as a more effective spacer than DCA among dye molecules and thus suppresses the π - π stacking of the dye molecules, which in turn retards the charge recombination and hence improves the device performance significantly. Thus HC-A has the same effect like DCA; in addition, it has a light-harvesting effect at short wavelength as seen in IPCE data. In other words, it has multiple-functioned effects that are the prevention of the π - π stacking of organic dye molecules like DCA and the light-harvesting effect at shorter-wavelength regions. As indicated in Figure 2b and Table 1, the photovoltaic performance of the NKX2677-sensitized DSSC was lower than the others, which influenced the overall conversion efficiency ($\eta = V_{oc} \times J_{sc} \times FF$). For the NKX2677/DCA-sensitized DSSC, compared with NKX2677sensitized DSSC, V_{oc} increased from 0.579 to 0.608 V, J_{sc} increased from 15.49 to 16.81 mA cm⁻², and the overall conversion efficiency increased from 6.68 to 7.67 %.

As shown in Figure 2, J_{sc} increased in the same order of integrated photocurrent from the IPCE spectrum. For the NKX2677/**HC-A**-sensitized DSSC, compared to the NKX2677-sensitized DSSC, V_{oc} increased from 0.579 to 0.688 V, J_{sc} increased from 15.49 to 17.25 mA cm⁻², and the overall conversion efficiency increased from 6.68 to 8.89%.

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It was observed that the coadsorption of either DCA or **HC-A** improved J_{sc} and V_{oc} , simultaneously, but coadsorption with **HC-A** enhanced V_{oc} more significantly than with DCA, even with the lower dye adsorption. Also, V_{oc} increased to 29 mV for DCA and 107 mV for **HC-A** coadsorption. These results indicate that **HC-A** is more efficient than DCA for retarding charge recombination and hence improves photovoltaic performance, that is, J_{sc} and V_{oc} , significantly.

To further clarify the effect of HC-A on the V_{oc} , electrochemical impedance spectroscopy (EIS), which is a powerful tool to elucidate the electronic and ionic transporting processes in DSSCs, was measured under dark conditions. EIS can provide valuable information for the understanding of photovoltaic performance parameters (J_{sc} , V_{oc} , FF, and η) in DSSCs. The enhancement of $V_{\rm oc}$ is usually associated with the negative shift of conduction band edge or the suppression of charge recombination. The value of $V_{\rm oc}$ is determined by the potential difference between the Fermi level of TiO₂ and the chemical potential of the redox species $(E_{\rm red})$ in the electrolyte, which can be described as Equation (1),^[23] in which γ is characteristic constant of TiO₂ tailing states, $k_{\rm B}$ is the Boltzmann constant, T is temperature, e is the elementary charge, and $N_{\rm e}$ is the effective density of states at the TiO₂ conduction band edge.

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

Considering that $E_{\rm red}$ would not change strongly in DSSCs fabricated under similar conditions, $V_{\rm oc}$ is determined by the potential of the conduction band edge ($E_{\rm CB}$) and the electron density (*n*) in TiO₂. These two parameters are closely related to the surface charge and charge recombination, respectively. Possible factors influencing $V_{\rm oc}$ for DSSCs involve the TiO₂ surface blocking, conduction band movement, and electrolyte-dye interaction.

Typical EIS Nyquist plots and Bode phase plots measured under dark conditions at a forward bias of -0.65 V for DSSCs based on NKX2677, NKX2677/DCA and NKX2677/ HC-A are shown in Figure 3. The equivalent circuit presented in Figure 3b 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_{μ} and $R_{\rm ct}$ are the chemical capacitance and the charge recombination resistance at the dyed TiO₂/electrolyte interface, respectively. C_{Pt} and R_{Pt} are the interfacial capacitance and charge transport resistance at the Pt/electrolyte interface, respectively. The larger semicircle at lower frequencies represents the interfacial charge transfer resistance (R_{ct}) at the dyed TiO_2 /electrolyte interface. The fitted R_{ct} increased in the order of NKX2677 (14 Ω) <NKX2677/DCA (33 Ω) <NKX2677/**HC-A** (106 Ω), which were consistent with the sequence of $V_{\rm oc}$ values in the devices.

The smaller $R_{\rm ct}$ value means that the electron recombination from the conduction band to the electrolyte occurs more easily, thus resulting in lower $V_{\rm oc}$. Clearly, the electron



Figure 3. a) Nyquist plots and b) fitted Bode-phase plots of electrochemical impedance spectra for the DSSCs based on NKX2677 (\Box), NKX2677/DCA (\odot), and NKX2677/**HC-A** (\triangle); the inset is an equivalent circuit (see text for explanation).

recombination in devices based on NKX2677 and NKX2677/DCA is faster than that of NKX2677/**HC-A**. The results could be cross-checked by measuring the *J*–*V* characteristics of the DSSCs in the dark (Figure 2b). The onset potentials at the dark current value of -1 mA cm^{-2} for the three different devices were in the order of NKX2677/(453 mV) <NKX2677/DCA (469 mV) <NKX2677/**HC-A** (533 mV). Their sequence was in accordance with that of $R_{\rm ct}$ values. This dark current change indicates that the coadsorption of **HC-A** leads to the suppression of the charge recombination between injected electron and I_3^- ions in the electrolyte, favorable for $V_{\rm oc}$ gain.

To further investigate the influences of the shift in the TiO₂ 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 $V_{\rm oc}$. The charge-transfer resistance at the dyed TiO₂/electrolyte interface ($R_{\rm cl}$), the film capacitance (C_{μ}) and the electron lifetime ($\tau = C_{\mu}R_{\rm el}$) were derived from EIS by fitting the experimental data through an appropriate equivalent circuit.^[24] The fitted C_{μ} and $R_{\rm ct}$ values together with τ are plotted in



Figure 4. a) Chemical capacitance (C_{μ}) , b) interfacial charge transfer resistance $(R_{\rm cl})$, and c) electron lifetime (τ) fitted from impedance spectra under a series of applied potentials. NKX2677 (•), NKX2677/DCA (•) and NKX2677/HC-A (•).

Figure 4. This exponential rise with the increase of forward bias is a behavior typical of C_{μ} that is described by Equation (2),^[25] in which *e* is elementary charge, $k_{\rm B}$ is the Boltzmann constant, *T* is temperature (298 K in this study), α is a constant related to the distribution of electronic states below the conduction, $E_{\rm red}$ is the chemical redox potential of the redox couples in the electrolyte.

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

Considering that $E_{\rm red}$ would not change strongly in DSSCs fabricated under similar conditions,^[26] therefore, C_{μ} is governed by the applied potential ($V_{\rm a}$) and $E_{\rm CB}$.

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As shown in Figure 4a, at the given whole potential range of V_a , C_μ for NKX2677/HC-A and NKX2677/DCA was not changed significantly, but was increased compared to NKX2677. It indicates a sequential negative shift of the conduction band edge: NKX2677/HC-A > NKX2677/DCA > NKX2677. Generally, the negative shifts of $E_{\rm CB}$ lead to improvement of $V_{\rm oc}$ of DSSCs. As shown in Figure 4b, the increased $V_{\rm oc}$ was mainly ascribed to the major increase in $R_{\rm ct}$ for NKX2677/HC-A compared to NKX2677/DCA. At the forward bias of -0.65 V, the device based on NKX2677/HC-A showed a similar value of C_{μ} (678 to 665 μ F), but an increased value of $R_{\rm ct}$ (from 33 to 106 Ω), compared to that of NKX2677/DCA, yielding a higher τ of 72 ms. The fitted τ increased in the order of NKX2677 (6 ms) < NKX2677/DCA (22 ms) <NKX2677/HC-A (72 ms). It gives an explanation of the different values of $V_{\rm oc}$ from three DSSCs. In the range of potentials studied, the order of τ was in good accordance with that of V_{oc} . It implies that the charge recombination rather than the position of CB governs V_{∞} . From these results, the use of HC-A in DSSCs decreases the charge recombination between injected electrons and the oxidized dye or the redox couple, and explains the large open circuit voltage of Voc obtained for NKX2677/HC-Asensitized device.

Furthermore, to clarify the additional role of hole-conducting coadsorbent as proposed in Scheme 1b, the detailed kinetic studies should be systematically and thoroughly achieved. However, these kinetic studies are extremely complicated and constitute another big research area to be progressively undertaken. These studies are out of the scope of this study, in which we just demonstrated a new class of a low-molecular-weight and multiple-functioned coadsorbents for highly efficient dye-sensitized solar cells. Figure 5 shows that the transient absorption spectra (TAS) for the



Figure 5. Transient absorption spectra for a) the NKX2677-, b) the NKX2677/DCA-, and c) the NKX2677/**HC-A**-based TiO_2 films in the absence of redox electrolytes were investigated with a nanosecond pulse laser at 504 nm, and d) and e) the **HC-A**-based TiO_2 films in the absence of redox electrolytes were investigated with a nanosecond pulse laser at 504 and 355 nm, respectively. * corresponds to the spectrum originating from **HC-A** radical cation.

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NKX2677 \pm DCA- and NKX2677/HC-A-based TiO₂ films in the absence of the redox electrolyte were investigated with a nanosecond pulse laser of 504 nm. The absorption maxima for NKX2677 \pm DCA-based TiO₂ films were observed around 700 nm, which can be assigned to NKX2677 radical cation absorption according to an article reported by Durrant and co-workers,^[27] indicating that the electron-transfer process efficiently occurred from the dye to TiO_2 [Eq. (3)]. Two distinct transient absorption spectra for the NKX2677/ HC-A-based TiO₂ film were observed around 700 and 830 nm. Though the electrochemical interactions between the NKX2677 and HC-A are energetically unfavorable (see Scheme 1b), this hole-transfer mechanism may strongly depend on the energetic overlap between the oxidized dye and HC-A.^[28] The latter absorption could be assigned to HC-A radical cation of the carbazole cation radical species,^[29] because it cannot absorb the 504 nm pulse laser directly. On the other hand, the transient absorption spectrum originating from the organic HC-A radical cation around 830 nm could not be observed from the HC-A-based film as depicted in Figure 5. Thus, HC-A radical cation should be generated through the hole-transfer [Eq. (4) and see pathway (5) in Scheme 1b] from NKX2677 radical cation, as shown below [Eqs. (3)–(8)]:

$$NKX2677^* \rightarrow NKX2677^+ + TiO_2(e^-)$$
(3)

$$\mathbf{HC} \cdot \mathbf{A} + \mathbf{NKX2677^+} \to \mathbf{NKX2677} + \mathbf{HC} \cdot \mathbf{A^+}$$
(4)

$$\text{TiO}_2(e^-) + \text{NKX2677}^+ \rightarrow \text{NKX2677}$$
(5)

$$\operatorname{TiO}_2(\mathbf{e}^-) + \mathbf{HC} \cdot \mathbf{A}^+ \to \mathbf{HC} \cdot \mathbf{A}$$
 (6)

 $NKX2677^+ + 3I^- \rightarrow NKX2677 + I_3^-$ (7)

$$2\mathbf{H}\mathbf{C}\cdot\mathbf{A}^{+} + 3\mathbf{I}^{-} \to 2\mathbf{H}\mathbf{C}\cdot\mathbf{A} + \mathbf{I}_{3}^{-}$$
(8)

Transient absorption spectra for the NKX2677±DCAand NKX2677/**HC-A**-sensitized TiO₂ films in the presence of a redox electrolyte and also the transient absorption traces for the **HC-A**-based TiO₂ films in the presence of electrolyte were investigated with a nanosecond pulse laser at 504 and 355 nm, respectively (see Figure S6 in the Supporting Information). The TAS amplitude of the carbazole cation radical species was somewhat reduced in the presence of a redox electrolyte, while **HC-A** radical cation could not be observed from the **HC-A**-based film. It implies that electron migration could occur from a redox electrolyte to the carbazole cation radical species in Scheme 1b.

To conclude, we just demonstrated that **HC-A** has multiple functions, such as the light-harvesting function as a short-wavelength light absorption dye molecule to increase J_{sc} , the prevention effect of the π - π stacking of organic dye to enhance V_{oc} by reducing the charge recombination, and the hole-conducting function, evidenced from EIS and TAS experiments for the formation of carbazole cation radical species, to enhance V_{oc} and J_{sc} . As a result, the NKX2677/**HC-A**-based DSSC exhibited remarkably enhanced the con-

version efficiency by a factor of 1.33, compared to the NKX2677-based DSSC under STC. The photovoltaic performance of its device exhibited a remarkably high $J_{\rm sc}$ of 17.25 mA cm⁻², $V_{\rm oc}$ of 688 mV, FF of 74.93%, and a conversion efficiency of 8.89% at 100 mW cm⁻², which is the best result ever reported for a DSSC employing the organic dye NKX2677. The detailed kinetics for a cascade-type hole-hopping process proposed here is very complicated and constitutes another big research area to be progressively undertaken.

Experimental Section

Details of the chemical synthesis and characterization as well as the cell fabrication methods, photochemical measurements, and laser flash photolysis are described in the Supporting Information. UV/Vis spectra were recorded with a SHIMADZU (UV-2401 PC) instrument. The FT-IR and NMR spectra were recorded with a JASCO-4200 spectrophotometer and a BRUKER AC-500 instrument. The corrected fluorescence emission spectra were measured on a VARIAN CARY Eclipse fluorescence spectrophotometer. The mass spectra were taken by a JEOL JMS-600W mass spectrometer. Electrochemical impedance spectra (EIS) of DSSCs were measured with 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 10 mV at room temperature.

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