Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Triarylamine-based dual-function coadsorbents with extended π -conjugation aryl linkers for organic dye-sensitized solar cells

In Taek Choi^{a,1}, Ban Seok You^{a,b,1}, Yu Kyung Eom^{a,1}, Myung Jong Ju^a, Won Seok Choi^a, Sung Ho Kang^a, Min Soo Kang^a, Kang Deuk Seo^a, Ji Yeoun Hong^a, Sang Hyun Song^a, Ji-Woon Yang^{b,*}, Hwan Kyu Kim^{a,*}

^a Global GET-Future Laboratory, Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-ro, Sejong 339-700, Republic of Korea ^b Department of Electronics and Information Engineering, Korea University, 2511 Sejong-ro, Sejong 339-700, Republic of Korea

ARTICLE INFO

Article history: Received 10 June 2014 Accepted 6 September 2014 Available online 18 September 2014

Keywords: Dual-function coadsorbents Extended π -conjugation aryl linkers Prevention of dye aggregation Light-harvesting Dye-sensitized solar cells

ABSTRACT

Triarylamine-based dual-function coadsorbents containing a carboxylic acid acceptor linked by extended π -conjugation aryl linkers (e.g., phenylene: **HC-A3**, naphthalene: **HC**-A4 and anthracene: HC-A5) were newly designed and synthesized. They were used as coadsorbents in organic dve-sensitized solar cells (DSSCs) based on a porphyrin dve (hexyloxy-biphenyl-ZnP-CN-COOH (HOP)). For comparison, the π -conjugated phenyl linker (HC-A3) previously developed by our group was also used as a coadsorbent. The structural effects on the photophysical and electrochemical properties and DSSC performance were systematically investigated. As a result, the DSSCs based on HC-A4 and HC-5 displayed power conversion efficiencies (PCEs) of 8.2% and 5.1%, respectively, while the HC-A3-based DSSC achieved a PCE of 7.7%. In the case of HC-A4, both the short-circuit photocurrent densities (I_{sc}) and open-circuit voltages (V_{oc}) of DSSCs were simultaneously improved to a large extent due to the more effective prevention of $\pi - \pi$ stacking of organic dye molecules and the better light-harvesting effect at short wavelengths. The HC-A5based DSSC exhibited a much lower short-circuit current (J_{sc}) and open-circuit voltages (Voc) compared to the HC-A4-based DSSC, due to the fact that the dihedral angle of the π -conjugated linkers was too high for electron injection into the TiO₂ conduction band (CB) level. This had a reduced effect on preventing the $\pi - \pi$ stacking of dye molecules, resulting in lower J_{sc} and V_{oc} values.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been extensively studied as a promising candidate for low-cost, color-

http://dx.doi.org/10.1016/j.orgel.2014.09.008

1566-1199/© 2014 Elsevier B.V. All rights reserved.

ful, and applicable solar cells [1-5]. Until now, high light to power conversion efficiencies surpassing 12% have been achieved co-sensitization with YD2-o-C8 and Y123 organic sensitizer-based DSSCs using cobalt electrolyte [6]. The PCE of DSSCs depends on the sensitizing ability of dyes, and extensive efforts have been made to develop highly efficient dyes for panchromatic sensitization [7,8]. On the other hand, effective enhancement of the conversion efficiency has been achieved through a co-sensitization method using two organic dyes having complementary spectral responses [9,10], an organic dye and multifunctional coadsorbent [11–15], Zn-phthalocyanine



CrossMark



^{*} Corresponding authors at: Global GET-Future Laboratory, Department of Advanced Materials Chemistry, Korea University, 2511 Sejong-ro, Jochiwon, Sejong 339-700, Republic of Korea. Tel.: +82 44 860 1493; fax: +82 44 860 1331 (H.K. Kim), Tel./fax: +82 44 860 1426 (Ji-W. Yang).

E-mail addresses: jyang@korea.ac.kr (Ji.-W. Yang), hkk777@korea.ac.kr (H.K. Kim).

¹ The authors contributed equally to this work.



Scheme 1. Molecular structures of (a) HC-A3, (b) HC-A4, and (c) HC-A5.



Fig. 1. (a) Normalized UV-visible absorption (solid lines) and emission spectra (dashed lines) of **HC-A3**, **HC-A4**, and **HC-A5** in THF solution. (b) Potentiallevel diagram exhibiting the upper (LUMO) and lower (HOMO) potentials for the **HOP** dye and **HC-A** coadsorbents used in this study, the conduction band of TiO₂, and the potential of the I^-/I_3^- redox couple.

Table 1 Optical and electrochemical properties of HOP, HC-A3, HC-A4, and HC-A5.

Dye & coadsorbent	Absorption $\lambda_{max}/nm (\epsilon/M^{-1}cm^{-1})$	$E_{\rm ox}/V(vs. \rm NHE)$	$E_{\rm ox} - E_{\rm o-o} / V(vs. \text{ NHE})$	$E_{\rm o-o}/V$ (vs. eV)
НОР	419 (209,584), 632 (10,732)	0.78	-1.05	1.83
HC-A3	358.5 (42,040)	1.178	-2.042	3.22
HC-A4	359.5 (37,759), 408.5 (9786)	1.18	-1.58	2.76
HC-A5	362 (51,353), 453.5(7104)	1.08	-1.38	2.47

(or Zn-porphyrin) and an organic dye [6,16,17], and a ruthenium complex dye and organic dye [18,19].

The photovoltaic performance of DSSC is also influenced on the low charge recombination at the interface of TiO₂/ dye/electrolyte as well as on the dye regeneration efficiency [20]. Moreover, charge recombination at the interface of the TiO₂/dye/electrolyte results in a decrease of PCE due to losses in both the short-circuit current (J_{sc}) and the open-circuit voltage (V_{oc}). To reduce the possible charge recombination at the TiO₂/dye/electrolyte interface, several kinds of additives have been adapted as coadsorbents onto the TiO₂ surface. Decylphosphonic acid (DPA), dineohexyl bis(3,3-dimethylbutyl)phosphinic acid (DIN-HOP), and chenodeoxycholic acid (CDCA) have been adsorbed onto the TiO₂ surface [21]. Among them, cholic acid (CA) derivatives as coadsorbents in DSSCs, based on a Ru-pyridyl complex [22,23], coumarin [24–26], porphyrin [6,27], phthalocyanine [28,29], and naphthalocyanine dye [30] have been well-studied. Deoxycholic acid (DCA) is commonly used as a coadsorbent to prevent the dye aggregation, thus remarkably improving V_{oc} and J_{sc} [24– 26,31]. Recently, we demonstrated that a newly discovered coadsorbent based on the π -conjugated phenyl linker (**HC**-**A3**) has dual functions, including both harvesting light ability at shorter wavelength to improve J_{sc} and the prevention of dye aggregation to enhance V_{oc} by reducing charge recombination [32].

In this study, in order to enhance the harvesting light at shorter wavelengths with the increased UV–visible absorbance range by introducing extended π -conjugation aryl



Fig. 2. The optimized structures and the dihedral angles between the conjugated linker (anthracene) of (a) HC-A3, (b) HC-A4, and (c) HC-A5, and the electron distribution of the HOMO and LUMO energy levels of three HC-A coadsorbents from DFT calculations.

Table 2

Photovoltaic parameters of the DSSCs with different coadsorbents under one sun illumination (AM 1.5 G (100 mW cm⁻²)).

Device	Adsorbed dye amount/ $(10^{-7} \text{ mol cm}^{-2})$	Adsorbed coadsorbent amount/ $(10^{-7} \text{ mol cm}^{-2})$	$J_{\rm sc}/({\rm mA~cm^{-2}})$	$V_{\rm oc}/({\rm mV})$	FF (%)	η (%)
HC-A3: Device 1	-	2.55	4.15	692	77.5	2.2
HC-A4: Device 2	-	2.29	5.24	711	76.7	2.8
HC-A5: Device 3	-	0.21	0.29	486	74.1	0.1
HOP: Device 4	1.54		11.0	618	71.5	4.9
HOP/HC-A3: Device 5	0.65	2.35	15.0	692	73.0	7.7
HOP/HC-A4: Device 6	0.68	1.82	15.6	703	74.9	8.2
HOP/HC-A5: Device 7	1.32	0.24	11.3	621	72.4	5.1
Y123/CDCA: Device 8	-	-	14.2	630	74.1	6.6
Y123/HC-A4: Device 9	-	-	14.6	711	71.1	7.4

Performance of DSSCs was measured with a black metal mask (0.16 cm^2). Electrolyte composition: 0.6 M DMPII, 0.5 M TBP, 0.05 M I₂ and 0.1 M LiI in CH₃CN. HOP dye concentration was 0.2 mM. Y123 dye concentration was 0.1 mM. **HC-A3**, **HC-A4** and **HC-A5** concentration was 2 mM. CDCA conenetration was 5 mM. TiO₂ nanocrystalline particle size was 20 nm.

linkers, two types of Y-shaped coadsorbents, 4-(bis(9,9dimethyl-9H-flouren-2-yl)amino)-1-naphthoic acid (**HC-A4**) and 4-(10-(bis(9,9-dimethyl-9H-flouren-2-yl)amino) anthracen-9-yl)benzoic acid (**HC-A5**), were newly designed and synthesized for use as coadsorbents in organic DSSCs based on a porphyrin dye (hexyloxy-biphenyl-ZnP-CN-COOH (**HOP**)) previously developed by our group [33]. For comparison, the π -conjugated phenyl linker (**HC-A3**) was also used as a coadsorbent [32]. The structural effects on the photophysical and electrochemical properties and DSSC performance were systematically investigated.



Fig. 3. (a) The UV–visible absorption spectra of dye only or dye with **HC-A** coadsorbents adsorbed onto the TiO₂ surface. (b) The absorption spectra of the dye-desorbed solution, obtained from the treatment of the same TiO₂ films with 0.1 M aqueous NaOH solution, in a 50:50:50 (vol%) EtOH:H₂0:THF mixture. (c) The emission spectra for the dye only and the dye with **HC-A** coadsorbents adsorbed onto ZrO₂ film.

2. Results and discussion

The molecular structures of **HC-A3**, **HC-A4** and **HC-A5** have low molecular weight Y-shaped structures with an anchorable carboxylic acid acceptor linked by various π -conjugated aryl moieties, such as phenylene, naphthalene, and anthracene units (Scheme 1). Fig. 1a exhibits the UV-vis absorption and emission spectra of the three

coadsorbents, e.g., HC-A3, HC-A4 and HC-A5. Their optical and electrochemical properties are summarized in Table 1. HC-A4 and 5 exhibited one strong absorption band at the absorption λ_{max} of 359.5 (ε_{max} = 37,759 M⁻¹ cm⁻¹) and 362 nm (ε_{max} = 51,353 M⁻¹ cm⁻¹) as well as another additional weak absorption band at the absorption λ_{max} $(\varepsilon_{\rm max} = 9786 \,{\rm M}^{-1} \,{\rm cm}^{-1})$ of 408.5 and 453.5 nm $(\varepsilon_{\text{max}} = 7104 \text{ M}^{-1} \text{ cm}^{-1})$, respectively, while **HC-A3** exhibited one strong absorption band at the absorption λ_{max} of 358.5 (ε_{max} = 42,040 M⁻¹ cm⁻¹). The latter weak absorption band in **HC-A4** and **5** corresponds to the naphthalene and anthracene units. In addition, the tailed absorption bands of HC-A3-5 in the edge region of absorbance were at 405, 444 and 512 nm, respectively. As a consequence, the absorbance edge of HC-A4 and HC-A5 was red-shifted due to the extended π -conjugation aryl unit between the amino and carboxylic acid groups. This was attributed to better delocalization of electrons over the whole molecule when naphthalene or anthracene was used as the conjugated linker rather than a phenylene unit. In general, a broader absorption wavelength range is favorable for coadsorbents used in DSSCs based on an organic dye, because of the better light-harvesting effect to increase J_{sc} [9,10,11– 15,32,33].

The HOMO energy levels of the HC-A coadsorbents were measured by cyclic voltammetry (CV) (see Fig. S1). The cyclic voltammograms were obtained from a three-electrode cell, which consisted of a dye-coated TiO₂ electrode as the working electrode, a Pt wire counter electrode, and an Ag/AgCl (saturated KCl) reference electrode (+0.197 V vs. NHE) calibrated with ferrocene, in 0.1 M TBAPF₆ in CH₃CN at a scan rate of 50 mV s⁻¹. All of the measured potentials were converted to the NHE scale. The electrochemical data are presented in Fig. 2b and Table 1. The HOMO energy levels of three coadsorbents exhibited higher potentials than that of the I^-/I_3^- redox couple (ca. 0.35 V vs. NHE) [34] indicating effective regeneration of the oxidized state. The zero-zero excitation energies (E_{0-0}) was calculated from the intersection between absorption and emission spectra, and the lowest unoccupied molecular orbital (LUMO) levels of the dye and coadsorbents were determined using the formula: LUMO = HOMO – E_{0-0} . As a consequence, the band gaps of HC-A4 and HC-A5 were decreased due to the extended π -conjugation aryl unit between the amino donor and carboxylic acid groups, compared to HC-A3.

In order to evaluate the electron distribution of the HOMO and LUMO energy levels of the **HC-A** coadsorbents, density functional theory (DFT) calculations were achieved by employing Becke's three parameterized Lee–Yang–Parr (B3LYP) exchange correlation functional and 6-31G^{*} basis sets using a suite of Gaussian 09 programs (see Table S2) [35]. Fig. 2 shows the dominant electron transfer from the donor unit to the acceptor one for the HOMO–LUMO transition. The HOMO energy levels were localized on the bis(dimethylfluorenyl)amino donor and π -conjugated linker. The LUMO energy levels of **HC-A3** and **HC-A4** were delocalized across the π -conjugated linker and acceptor system, whereas the LUMO energy levels of **HC-A5** were not concentrated on the acceptor unit but rather distributed over a range of the π -conjugated anthracene linker.



Fig. 4. (a) IPCE action spectra and (b) *J*–V curves of the DSSCs based on various **HC-A** coadsorbents. HOP only (black), HOP/**HC-A3** (red), HOP/**HC-A4** (green), and HOP/**HC-A5** (blue). The IPCE and J–V curves of **HC-A3**, **HC-A4**, and **HC-A5** only are shown in the insets. (C) J–V curves of the DSSCs based on Y123/CDCA and Y123/**HC-A4**. The TiO₂ film thickness is 16 (12 + 4) µm. All cells were tested with a metal shadow mask having an aperture area of 0.16 cm². (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The theoretical calculation of **HC-A5** suggests that the dihedral angle between anthracene and phenyl is too large, which is unfavorable for intramolecular charge transfer from the HOMO to the LUMO orbitals [36,37]. This means that the electron distribution from the donor unit to the anchoring moiety is expected to be less susceptible to excitation from the HOMO to the LUMO orbitals, such that charge transfer in **HC-A5** is expected to be less effective than any other HC-As, leading to less electron injection from the excited coadsorbents into the CB of TiO₂ in the DSSC.

We obtained the dye desorption solution to investigate the dye adsorption amount on the TiO_2 surface by UV–vis absorption spectra (Table 2 and Table S1). Fig. 3a exhibits the UV–visible spectra of the **HOP** dye only or the **HOP** dye with coadsorbents adsorbed onto a TiO_2 surface. The UV–visible spectrum of the TiO_2 film adsorbed with dye only showed a much broader absorption than the TiO_2 films adsorbed with both dye and coadsorbents. This phenomenon comes from the strong intermolecular interactions among the dye molecules aggregated on the TiO_2 surface. When the dye with coadsorbents was adsorbed onto the TiO_2 film, the deprotonation of the carboxylic acid group in the dye induced the electrostatic repulsion of negatively charged carboxylic groups onto the TiO₂ surface, leading to the reduction of the adsorption of the HOP dye onto the TiO₂ surface [31,32]. In this study, we confirmed that coadsorbents prevent dye aggregation in another way as well. Fig. 3c shows the PL emission spectra at the excitation wavelength (λ_{ex}) of 500 nm on a nanocrystalline ZrO₂ thin film. ZrO₂ film was employed to prevent electron injection from the excited dye state [38]. We noted that the emission intensity for the ZrO₂/HOP film was much lower than those for $ZrO_2/HOP/HC-A3$ and $ZrO_2/HOP/HC-A4$ films, consistent with the much higher aggregation of HOP only. This aggregation has been suggested to promote intermolecular interactions which compete with charge separation [39,40] and/or form a layer of non-injecting dves [41].

The amount of adsorption of the coadsorbents on the TiO₂ film was determined to be 2.35×10^{-7} , 1.82×10^{-7} , and 0.24×10^{-7} mol cm⁻² for **HC-A3**, **HC-A4**, and **HC-A5**, respectively (see Table 2). The adsorption amount of dye on the TiO₂ film decreased from 1.54×10^{-7} to 0.65×10^{-7} , 0.68×10^{-7} , and 1.32×10^{-7} mol cm⁻², leading to a 58%, 57%, and 14.28% drop with **HCA3**, **HC-A4**,



Fig. 5. (a) Nyquist and (b) Bode plots of the DSSCs measured at -0.62 V from 10^6 Hz to 0.1 Hz under dark condition. (c) The η_{cc} and R_{rec} , and (d) dark currents measured by EIS for the same DSSCs.

and **HC-A5**, respectively. Judging by the differences in the amount of dye adsorption, coadsorbents with Y-shaped structures may be necessary for effective spacing of adjacent **HOP** dye molecules. The prevention of π – π stacking with an additive in the dye solution is a typical method to enhance the PCE efficiency of organic DSSCs. The advantage of π – π stacking is to have a better light harvesting due to broad absorption in the UV–vis absorption spectrum, but π – π stacked aggregates usually lead to low short-circuit (J_{sc}) current and low PCE, due to inefficient electron injection [33].

Fig. 4a exhibits the incident photon to current conversion efficiency (IPCE) action spectra as a function of the light wavelength and the corresponding current–voltage (J-V) characteristics for the DSSCs using various coadsorbents under one sun illumination (AM 1.5G, 100 mW cm⁻² irradiation at 25 °C). The inset in Fig. 4a shows the IPCE

spectra for the TiO₂ film loaded with the HC-A coadsorbent series alone. As shown in Fig. 4, the maximum IPCE was only ~59% for HOP-sensitized solar cells. It was much lower than 85%, taking into account the light loss (\sim 15%) by the reflection and absorption of the TCO glass. Upon coadsorption of the **HC-A** coadsorbent in the dye solution, except for HC-A5, which had the lowest light-harvesting effect in UV-visible regions, due to the less effective charge transfer caused by the large dihedral angle between anthracene and phenyl, the IPCE was increased remarkably, even with relatively lower dye adsorption. This indicates that the better light harvesting effect in shorter-wavelength regions induces an increased photocurrent of the DSSCs. The maximum IPCE increased from 59% to 73% when HC-A4 was added to the dye solution, and increased from 59% to 66% with HC-A3 in the dye solution. Upon HC-A coadsorption, except for HC-A5, the

Table 3

EIS	values	and	charge	collection	efficiency	of	the	DSSCs
-----	--------	-----	--------	------------	------------	----	-----	-------

Device	$R_{\rm t}/\Omega$	$R_{ m rec}/\Omega$	C_u/mF	τ_t/ms	τ_n/ms	$\eta_{\rm cc}$
HOP: Device 4	4.2	34.2	0.69	2.93	23.6	0.89
HOP/HC-A3: Device 5	9.3	148.3	0.97	9.06	144.2	0.94
HOP/HC-A4: Device 6	10.6	160.1	0.90	9.65	145.2	0.93
HOP/HC-A5: Device 7	7.1	40.6	0.67	4.88	27.6	0.85

Calculated values from EIS data measured at a forward bias of -0.62 V under dark conditions.

maximum IPCE improved significantly, up to 55% at 360 nm than that of the HOP-sensitized solar cell, which could have contributed to the increased photocurrent of the DSSCs, due to the better light harvesting ability in the UV wavelength regions of 350-400 nm. Moreover, a plateau from 550 to 650 nm was observed in the IPCE action spectrum with an IPCE of \sim 55% on the dye/HC-A TiO₂ film. This demonstrated that the HC-A coadsorbent is effective in dissociating $\pi - \pi$ stacking by strong intermolecular interactions. This higher IPCE value from 550 to 650 nm implies that a bulky coadsorbent can act as a more effective spacer, suppressing the dye aggregation and thereby retarding the charge recombination. Thus, it significantly improves device performance. As a result, they have dual functions, i.e. both the prevention of the π - π stacking of organic dye molecules such as DCA and the light harvesting in shorter-wavelength regions. Thus, the IPCE of the **HOP**-sensitized solar cell was lower than that of the others.

Table 2. summarizes the photovoltaic properties of the DSSCs with HC-A3, HC-A4, or HC-A5 only. The results were as follows: a J_{sc} of 4.15, 5.24 and 0.29 mA cm⁻²; a V_{oc} of 692, 711, and 486 mV; a fill factor (FF) of 77.5, 76.7 and 74.1%; and a PCE (η) of 2.20%, 2.80% and 0.11%, respectively. Among them, HC-A4 showed the best cell performance because of its highest light harvesting effect at shorter wavelengths. The IPCE and I-V spectra for the DSSCs with HC-A3, HC-A4, and HC-A5 alone are presented in the insets in Fig. 4. The HC-A4-based solar cell exhibited slightly higher maximum IPCE from 300 nm to 550 nm than that of HC-A3. These results indicate that it had a better light harvesting effect in shorter wavelength regions for co-sensitization. UV-visible spectra and molar extinction coefficients were broadened and increased with the increased π -conjugated extension of coadsorbents. However, HC-A5 exhibited the lowest cell performance compared with the HC-A3 and HC-A4, probably due to lower electron injection efficiency into the TiO₂ CB due to its higher dihedral angle, while its UV-visible spectra and molar extinction coefficients were broadened and increased. The dihedral angle between anthracene and phenyl was too large in HC-A5, which is unfavorable for intramolecular charge transfer from the HOMO to the LUMO orbitals [36,37]. Fig. S2 shows the UV-visible



Fig. 6. The density of states (DOS) for the HOP-coated TiO_2 films with different coadsorbents as a function of applied potential.

spectra of the **HC-A3-5** only desorbed on TiO₂ film. The adsorption amounts of the **HCA3-5** on the TiO₂ film were determined to be 2.55×10^{-7} , 2.29×10^{-7} and 0.21×10^{-7} mol cm⁻² for **HC-A3**, **HC-A4**, and **HC-A5**, respectively (see Table 2). Among the **HC-A** series, since the amount of **HC-A5** adsorption is the lowest, its prevention effect of π - π stacking to dyes is the lowest so that **HC-A5** shows the lowest cell performance.

The DSSC with **HOP** only displayed a J_{sc} of 11.0 mA cm⁻², a V_{0c} of 618 mV, an FF of 71.50%, and PCE of 4.9%. The Isc of the DSSCs fabricated with the dye and different coadsorbents gradually enhanced in the this order: HOP/HC-A5 < HOP/HC-A3 < HOP/HC-A4. The Isc strongly relied on the light harvesting efficiency, charge separation (such as charge injection, dye regeneration and recombination) and charge collection. In particular, in the DSSC with **HC-A4**, the J_{sc} and V_{oc} were significantly enhanced compared to the others. Moreover, it is noteworthy that the DSSC with HC-A4 improved approximately 41.8% and 13.8% for both J_{sc} and V_{oc} , respectively, despite a 26% lower HOP dye coverage, and enhanced around 67% for a PCE compared to the DSSC with HOP only. Also, typical organic dye (Y123)-based DSSCs with CDCA and HC-A4 were also fabricated to explore the cell performance enhancement by HC-A4, according to a previously published report [42]. The Y123-based DSSCs with CDCA and HC-A4 gave a J_{sc} of 14.25 and 14.61 mA cm⁻²; a V_{oc} of 630 and 711 mV; a fill factor (FF) of 74.1% and 71.1%; and a PCE (η) of 6.6 and 7.4%, respectively (see Fig. 4 and Table 2). It indicates that The HC-A4 coadsorbent enhanced the cell performance of other organic dye-sensitized solar cells.

To further elucidate the photovoltaic results and gain more information on electron transfer and charge recombination in the TiO₂ photoanode in the DSSCs, electrochemical impedance spectroscopy (EIS) was studied in the dark under a forward bias of -0.62 V. The Nyquist and Bode plots for the DSSCs with various coadsorbents are shown in Fig. 5a and b, respectively. A greater recombination resistance and longer electron lifetime on the TiO₂ film($\tau_n = C_u \cdot R_{rec}$) [43–51] were obtained for the DSSC with **HOP/HC-A4** (160.1 Ω , 145.2 ms) compared to those for **HOP/HC-A3** (148.3 Ω, 144.2 ms) and **HOP/HC-A5** (40.6 Ω, 27.6 ms). HOP/HC-A3 and HOP/HC-A4 had almost the same electron lifetime. The photovoltaic performance depended on the charge collection efficiency derived from $\eta_{\rm cc} = (1 + R_t/R_{\rm rec})^{-1}$ [52]. The charge collection efficiencies evaluated from the EIS parameters with the transmission line model [50,51] are summarized in Table 3, and the fitted Nyquist plots are shown in Fig. S3. The η_{cc} of the DSSCs with HC-A3 and HC-A4 was almost same, but the charge recombination resistance of the DSSC with HC-A4 was greater than that of **HC-A3**. It resulted in an increased $V_{\rm oc}$ of the DSSC (Fig. 5c). Coadsorbents may induce both the adsorption state of the dye and the electronic state of the dye-sensitized TiO₂ to be changed, thereby influencing the electron injection rate and efficiency [53–55]. Wenger and co-workers [56] reported that the charge injection rate of non-aggregated dyes, from the excited dye to the CB of the TiO₂ electrode, was faster than that of aggregated dyes by three orders of magnitude.



Scheme 2. Schematic diagram of the possible charge or energy transfer pathways taking place at the dyed $TiO_2/HC-A$ series/electrolyte interface. **ET1** indicates the direct injection of an electron from the **HC-A** series to the TiO_2 surface. **ET2** and **ET3** correspond to the energy transfer from the **HC-A** series to the dye and to I_3 ions, respectively.

The difference in $V_{\rm oc}$ for the DSSCs with various coadsorbents was plotted as a function of the I-V curve obtained from the EIS measurements (Fig. 5d). The dark current, measured by EIS, decreased in the following order: HOP, HOP/HC-A5, HOP/HC-A3, and HOP/HC-A4. A higher dark current could reduce V_{oc} because it is governed by back electron transfer from the TiO₂ surface into the redox couple. In particular, among the coadsorbents used in this study, it was obvious that **HC-A4** had the highest V_{oc} value with the lowest dark current. The Y-shaped bulky and robust insulating layer of HC-A4 induced fewer recombination reactions at the interface between the HOP-sensitized TiO₂ and the electrolytes. Therefore, **HC-A4** might be more effective than **HC-A3** and **HC-A5** in screening I_2 or I_3^- , which resulted in the simultaneous improvements in J_{sc} and V_{oc} in the DSSC with HC-A4.

To investigate the change in the trap state caused by the **HC-A** coadsorbents and to reveal the change in V_{oc} , cyclic voltammetry was achieved on each TiO₂ electrode HOPsensitized with HC-A4 and HC-A5 together with LiClO₄ (see Fig. S3). The capacitive currents of different electrodes at the TiO₂/LiClO₄ interface, which exhibited gradual onsets under a forward potential, were shown in Fig. 6. The distribution of the trap states can be estimated from the density of states (DOS) calculated from DOS = dQ/d $dV \times (N_A/F)$ [55], where Q is the total number of surface trapping sites, N_A is Avogadro's number, F is Faraday's constant, and V is the potential applied to the electrode. As shown in Fig. 6, the onsets of the capacitive currents were around -0.194 V for the TiO₂ electrode covered with HOP and HC-A5, whereas the TiO_2 electrode covered with HOP and HC-A4 together demonstrated onsets of around -0.335 V, which indicates that the edge of the TiO₂ CB shifted to lower values (toward the vacuum level). In particular, the TiO₂ electrode with HC-A4 gave a more negative shift in the onset than that evaluated with HC-A5. The $V_{\rm oc}$ is estimated by the difference between the quasi-Fermi level and the redox potential of the I_3/I^- couple in



Fig. 7. PL emission spectra for (a) 3.0×10^{-6} M **HC-A3** (black line), 2.0×10^{-6} M **HOP** (red line), 4.0×10^{-6} M I₂ (green line), 3.0×10^{-6} M **HC-A3** + 2.0×10^{-6} M **HOP** (blue line), 3.0×10^{-6} M **HC-A3** + 2.0×10^{-6} M **HOP** + 4.0×10^{-6} M I₂ (cyan line) at the λ_{ex} of 358 nm in THF and (b) 3.0×10^{-6} M **HC-A4** (black line), 2.0×10^{-6} M **HOP** (red line), 4.0×10^{-6} M I₂ (green line), 3.0×10^{-6} M **HC-A4** + 2.0×10^{-6} M **HC** + 4.0×10^{-6} M I₂ (green line), 3.0×10^{-6} M **HC-A4** + 2.0×10^{-6} M **HC** + 4.0×10^{-6} M **HC** + 4.0×10^{-6} M **HC** + 4.0×10^{-6} M **HC** + 2.0×10^{-6} M **HC** (blue line), 3.0×10^{-6} M **HC** + 4.0×10^{-6} M I₂ (cyan line) at the λ_{ex} of 359 nm in THF solution. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the electrolyte; therefore, the bigger negative shift of the quasi-Fermi level of TiO_2 photoanode with **HOP** and **HC-A4** induced higher V_{oc} .

Furthermore, in order to understand the role of these coadsorbents on cell performance enhancement, the photophysical properties of HC-A3, HC-A4 and HOP dye were investigated in the solution state (see the ESI for extended discussion). Scheme 2 shows the schematic diagram of the possible charge or energy transfer pathways taking place at a dyed TiO₂/HC-A/electrolyte interface. ET1 means a direct injection of electron from the HC-A coadsorbent to the TiO₂ surface. ET2 and ET3 correspond to the energy transfer from the HC-A to the dye, and quenching of the HC-A by triiodide, respectively. Fig. 7a and b show the photoluminescence (PL) spectra with different conditions at the excitation wavelengths (λ_{ex}) of 358 nm and 359 mm in THF, respectively. Each solution was made to similar concentrations estimated from real DSSCs fabricated here (the molar ratio of HC-A3,4/HOP/ $I_2 = 1.5/1/2$). Upon photoexcitation at 358 and 359 nm for HC-A3/HOP/I₂ and HC-A4/HOP/I₂, the emission maximum of HC-A3, HOP and I_2 in the HC-A3/HOP/I₂ system appeared at 462, 689 and 456 nm, and those of HC-A4, HOP and I₂ in the HC-A4/HOP/I₂ system appeared at 516, 691, and 461 nm, respectively. The emission intensities of both HOP and I_2 were much lower than those of HC-A3 and HC-A4. As shown in Fig. 7a and b, the emission intensity of HC-A was significantly decreased for the HC-A/HOP and HC-A/HOP/I₂ systems. The reduction in the HC-A/HOP system was similar to the value for HC-A3 (48%) and HC-A4 (49%), while the reduction for the HC-A/HOP/I₂ system was different from that of HC-A3 (70%) and HC-A4 (67%). From these results, it seems that energy transfer occurred from HC-A3 and HC-A4 to the HOP dye [57]. Once excited, HC-A3 and HC-A4 can transfer their excited energy to a certain acceptor [6,9,10,16,17,58,59], and the energy transfer rate strongly depends on the separation distance (r)between the coadsorbent and the nearby acceptor molecule [60]. Both HC-A3 and HC-A4 were assumed to be within the Förster radius (R_o) of the HOP dye (see Fig. S6), and the separation distance between the donor of HC-A3/4 and the acceptor of HOP dye may be sufficiently close in the solution state. In this investigation, with a similar concentration of each solution estimated from the real DSSCs fabricated here, an increase in the emission spectrum of HOP over 600 nm was not observed, probably due to the fact that the molar excitation coefficient of HOP has an extremely low value of 11,650 M⁻¹ cm⁻¹ and 11,700 M⁻¹ cm⁻¹ at 358 and 359 nm, respectively, and its PL quantum efficiency is also



Fig. 8. (a) and (b) Emission spectra for the **HC-A3**, dye, the dye with CDCA and the dye with **HC-A3** adsorbed onto ZrO_2 film at a λ_{ex} of 358 nm. (c) and (d) Emission spectra for the **HC-A4** dye, the dye with CDCA and the dye with **HC-A4** adsorbed onto ZrO_2 film at a λ_{ex} of 359 nm.

very low at 358 and 359 nm (see Fig. S7). From these results, it is presumed that the energy transfer from **HC-A3** and **HC-A4** to **HOP** happens to be low as well. In other words, the molar extinction coefficient of **HOP** is very low from $12,825 \text{ M}^{-1} \text{ cm}^{-1}$ to $11,000 \text{ M}^{-1} \text{ cm}^{-1}$ in the UV wavelength region of 350–375 nm (see Fig. S7), such that the energy transfer efficiency from **HC-A3** and **HC-A4** to **HOP** could be low.

We also examined no direct energy transfer from HC-A to the HOP dye. Fig. 8a and c show the photoluminescence spectra of HC-A3, HC-A4, HOP, HOP/CDCA, HOP/HC-A3, and HOP/HC-A4 at the excitation wavelengths (λ_{ex}) of 358 nm and 359 nm on nanocrystalline ZrO₂ thin films. ZrO₂ films were employed to prevent electron injection from the excited dye state [38]. It is interesting that the emission intensity for the ZrO₂/HOP film is much less than those for ZrO₂/HC-A3 and ZrO₂/HC-A4 films, indicating that it is not effective to excite the **HOP** at the λ_{ex} of 358 nm and 359 nm. On the other hand, ZrO₂/HC-A3 and ZrO₂/HC-A4 films have effective emission intensity at the λ_{ex} of 358 nm and 359 nm. This result is similar to the result observed in the real solution state with the DSSCs fabricated here. Therefore, if energy transfer happens from HC-A to the dye, the photoluminescence spectra of HOP with HC-A3, HCA4 on the ZrO₂ film should exhibit stronger intensity than the emission of HOP itself. As expected, the emission intensities of HOP with both HC-A and CDCA were increased (Fig. 8b and d).

CDCA is often adapted as a coadsorbent to prevent the dye aggregation [24–26,31], thereby remarkably increasing $V_{\rm oc}$ and $J_{\rm sc}$, as the aggregation of the dye has been suggested to promote intermolecular interactions which compete with charge separation [39,40] and/or form a layer of non-injecting dyes[41]. An increasing tendency in PL intensity was observed, even with a lower adsorption amount of dye from the dye load amount determination from the absorption spectra of the dye-desorbed solution with the ZrO₂ films, obtained from the treatment of in 0.1 M aqueous NaOH solution, in 0.1 M NaOH in a 50:50:50 (vol%) EtOH:H₂O:THF mixture: 1.92×10^{-8} for HOP; 1.09×10^{-8} for HOP/CDCA; 0.91×10^{-8} for HOP/ **HC-A3**; 0.96×10^{-8} mol cm⁻² for **HOP/HC-A4** (Fig. S8). This can be attributed to the prevention of dye aggregation, because CDCA has no absorption band. Consequentially, the increase in emission intensity of HOP by coadsorption with HC-A and CDCA might be ascribed to the prevention of dye aggregates (Fig. 8 and Fig. S8) rather than the ET2 pathway (Scheme 2).

On the basis of the results described above, it can be concluded that the energy transfer efficiency from **HC-A** to **HOP** is expected to be low or to not occur (**ET2** pathway in Scheme 2). Furthermore, triiodide is a highly mobile ion that is known as a "perfect quencher" and it means that its collisions with **HC-A** have a near unity probability of quenching the excited state of HC-A [57,61]. Thus, **HC-A** cannot influence photovoltaic performance enhancement through the energy transfer pathways of **HC-A** into **HOP** in real DSSCs with I^-/I_3 systems. In other words, the **ET1** electron injection pathway is dominant compared to the other energy transfer pathways, i.e. **ET2** and **ET3** (Scheme 2).

3. Conclusions

We have designed and synthesized multi-functional coadsorbents with naphthalene and anthracene as an extended π -conjugated aryl unit. Co-adsorption of HC-A coadsorbents with HOP broke up dye aggregates and improved the light harvesting effect in UV-vis wavelength regions, leading to a significant enhancement in the photocurrent density (I_{sc}) and the open circuit voltage (V_{oc}) by suppressing charge recombination and increasing electron lifetime. The HOP/HC-A4-based DSSC exhibited higher Voc and Isc values than the HC-A3- and HC-A5-based DSSCs. According to the EIS and IPCE analyses, HC-A4-based DSSC showed greater charge resistance, longer electron lifetime and a higher IPCE value compared to the HC-A3 and HC-A5-based DSSCs. As a consequence, we can conclude that coadsorbents have a better light-harvesting effect with a more extended π -conjugated aryl unit, a smaller dihedral angle for efficient electron injection into the CB of TiO₂, a molecular structure preventing the π - π stacking of dye molecules, and a compact blocking layer on the TiO₂ surface for reducing charge recombination, simultaneously. Particularly, HC-A4-based DSSC showed a higher PCE of up to 8.2% than those of the HC-A3-based DSSC (7.7%) and HC-A5-based DSSC (5.1%).

Acknowledgments

This work was supported by the Converging Research Program through the Korean Government Ministry of Education, Science and Technology Science, ICT and Future Planning (2013K000203) and by the New and Renewable Energy R&D Program (20123010010070) of the Korean Institute of Energy Technology Evaluation and Planning (KETEP) grant through the Korean Government Ministry of Trade, Industry and Energy. It would be also acknowledged that Mr. BS You is a visiting graduate student in the GET-future Lab at KU.

Appendix A. Supplementary material

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See doi:http://dx.doi.org/10.1039/ b000000x/http://dx.doi.org/10.1016/j.orgel.2014.09.008.

References

- [1] B. O'Regan, M. Grätzel, Nature 353 (1991) 737-740.
- [2] M. Grätzel, Acc. Chem. Res. 42 (2009) 1788–1798.
- [3] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 110 (2010) 6595–6636.
- [4] M. Grätzel, Nature 414 (2001) 338–344.
- [5] N.S. Baek, J.-H. Yum, X. Zhang, H.K. Kim, M.K. Nazeerudin, M. Grätzel, Energy Environ. Sci. 2 (2009) 1082–1087.
- [6] A. Yella, H.W. Lee, H.N. Tsao, C. Yi, A.K. Chandiran, M.K. Nazeeruddin, E.W.G. Diau, C.Y. Yeh, S.M. Zakeeruddin, M. Grätzel, Science 334 (2011) 629–633.
- [7] S. Paek, H. Choi, C. Kim, N. Cho, S. So, K. Song, M.K. Nazeeruddin, J. Ko, Chem. Commun. 47 (2011) 2874–2876.
- [8] T. Kinoshita, J.T. Dy, S. Uchida, T. Kubo, H. Segawa, Nat. Photonics 7 (2013) 535–539.

- [9] D. Kuang, P. Walter, F. Nüesch, S. Kim, J. Ko, P. Comte, S.M. Zakeeruddin, M.K. Nazeeruddin, M. Grätzel, Langmuir 23 (2007) 10906–10909.
- [10] J.-H. Yum, S.-R. Jang, P. Walter, T. Geiger, F. Nüesch, S. Kim, J. Ko, M. Grätzel, M.K. Nazeeruddin, Chem. Commun. (2007) 4680–4682.
- [11] B.J. Song, H.M. Song, I.T. Choi, S.K. Kim, K.D. Seo, M.S. Kang, M.J. Lee, D.W. Cho, M.J. Ju, H.K. Kim, Chem.-Eur. J. 17 (2011) 11115–11121.
- [12] M.J. Ju, J.C. Kim, H.-J. Choi, I.T. Choi, S.G. Kim, K. Lim, J. Ko, J.-J. Lee, I.-Y. Jeon, J.-B. Baek, H.K. Kim, ACS Nano 7 (2013) 5243–5250.
- [13] I.T. Choi, M.J. Ju, S.H. Kang, M.S. Kang, B.S. You, J.Y. Hong, Y.K. Eom, S.H. Song, H.K. Kim, J. Mater. Chem. A 1 (2013) 9114–9121.
- [14] K.D. Seo, B.S. You, I.T. Choi, M.J. Ju, M. You, H.S. Kang, H.K. Kim, J. Mater. Chem. A 1 (2013) 9947–9953.
- [15] K.D. Seo, B.S. You, H.S. Kang, H.K. Kim, Dyes Pigm. 99 (2013) 599-606.
- [16] J.-J. Cid, J.-H. Yum, S.-R. Jang, M.K. Nazeeruddin, E. Martinez-Ferrero, E. Palomares, J. Ko, M. Grätzel, T. Torres, *Angew. Chem. Int. Ed.* 46 (2007) 8358–8362.
- [17] T. Bessho, S.M. Zakeeruddin, C.-Y. Yeh, E.W.-G. Diau, M. Grätzel, Angew. Chem., Int. Ed. 49 (2010) 6646–6649.
- [18] R. Ogura, S. Nakane, M. Morooka, M. Orihashi, Y. Suzuki, K. Noda, *Appl. Phys. Lett.* 94 (2009) 073308–073311.
- [19] S.-Q. Fan, C. Kim, B. Fang, K.-X. Liao, G.-J. Yang, C.-J. Li, J.-J. Kim, J. Ko, J. Phys. Chem. C 115 (2011) 7747–7754.
- [20] J.E. Kroeze, N. Hirata, S.E. Koops, M.K. Nazeeruddin, L. Schmidt-Mende, M. Grätzel, J.R. Durrant, Alkyl Chain Barriers for Kinetic Optimization in Dye-Sensitized Solar Cells, J. Am. Chem. Soc. 128 (2006) 16376–16383.
- [21] T. Marinado, M. Hahlin, X. Jiang, M. Quintana, E.M.J. Johansson, E. Gabrielsson, S. Plogmaker, D.P. Hagberg, G. Boschloo, S.M. Zakeeruddin, M. Grätzel, H. Siegbahn, L. Sun, A. Hagfeldt, H. Rensmo, J. Phys. Chem. C 114 (2010) (1910) 11903–11910.
- [22] M.K. Nazeeruddin, P. Péchy, T. Renouard, S.M. Zakeeruddin, R. Humphry-Baker, P. Comte, P. Liska, L. Cevey, E. Costa, V. Shklover, L. Spiccia, G.B. Deacon, C.A. Bignozzi, M. Grätzel, J. Am. Chem. Soc. 123 (2001) 1613–1624.
- [23] C. Bauer, G. Boschloo, E. Mukhtar, A. Hagfeldt, J. Phys. Chem. B 106 (2002) 12693–12704.
- [24] K. Hara, Y. Dan-oh, C. Kasada, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, Langmuir 20 (2004) 4205–4210.
- [25] K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, New J. Chem. 27 (2003) 783–785.
- [26] Z.-S. Wang, Y. Cui, K. Hara, Y. Dan-oh, C. Kasada, A. Shinpo, Adv. Mater. 19 (2007) 1138–1141.
- [27] (a) F. Odobel, E. Blart, M. Lagreé, M. Villieras, H. Boujtita, N.E. Murr, S. Caramori, C.A. Bignozzi, J. Mater. Chem. 13 (2003) 502–510; (b) W. Zhou, Z. Cao, S. Jiang, H. Huang, L. Deng, Y. Liu, P. Shen, B. Zhao, S. Tan, X. Zhang, Org. Electron. 13 (2012) 560–569.
- [28] M.K. Nazeeruddin, R. Humphry-Baker, M. Grätzel, B.A. Murrer, Chem. Commun. (1998) 719–720.
- [29] J. He, G. Benkc, F. Korodi, T. Polívka, R. Lomoth, B. Åkermark, L. Sun, A. Hagfeldt, V. Sundstrcm, J. Am. Chem. Soc. 124 (2002) 4922–4932.
- [30] X. Li, N.J. Long, J.N. Clifford, C.J. Campbell, J.R. Durrant, New J. Chem. 26 (2002) 1076–1080.
- [31] X. Ren, Q. Feng, G. Zhou, C.H. Huang, Z.S. Wang, J. Phys. Chem. C 114 (2010) 7190-7195.
- [32] H.M. Song, K.D. Seo, M.S. Kang, I.T. Choi, S.K. Kim, Y.K. Eom, J.H. Ryu, M.J. Ju, H.K. Kim, J. Mater. Chem. 22 (2012) 3786–3794.
- [33] S.H. Kang, I.T. Choi, M.S. Kang, Y.K. Eom, M.J. Ju, J.Y. Hong, H.S. Kang, H.K. Kim, J. Mater. Chem. A 1 (2013) 3977–3982.
- [34] T.W. Hamann, J.W. Ondersma, Energy Environ. Sci. 4 (2011) 370– 381.
- [35] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J.

Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cisolowski, D.J. Fox, Gaussian 09, Revision B.01, Gaussian Inc, Wallingford CT, 2010.

- [36] J. Yang, F. Guo, J. Hua, X. Li, W. Wu, Y. Qu, H. Tian, J. Mater. Chem. 22 (2012) 24356–24365.
- [37] C. Sakong, S.H. Kim, S.B. Yuk, J.Y. Kim, S.W. Park, M.J. Ko, J. P Kim, Bull. Korean Chem. Soc. 32 (2011) 2553–2559.
- [38] A. Kay, R. Humphrybaker, M. Grätzel, J. Phys. Chem. 98 (1994) 952– 959.
- [39] A.C. Khazraji, S. Hotchandani, S. Das, P.V. Kamat, J. Phys. Chem. B 103 (1999) 4693–4700.
- [40] A. Kay, M. Grätzel, J. Phys. Chem. 97 (1993) 6272-6277.
- [41] K. Keis, J. Lindgren, S.E. Lindquist, A. Hagfeldt, Langmuir 16 (2000) 4688-4694.
- [42] H.N. Tsao, C. Yi, T. Moehl, J.-H. Yum, S.M. Zakeeruddin, M.K. Nazeeruddin, M. Grätzel, ChemSusChem 4 (2011) 591–594.
- [43] J. Bisquert, Phys. Chem. Chem. Phys. 5 (2003) 5360-5364.
- [44] F. Fabregat-Santiago, J. Bisquert, L. Cevey, P. Chen, M. Wang, S.M. Zakeeruddin, M. Grätzel, J. Am. Chem. Soc. 131 (2009) 558–562.
- [45] R. Kern, R. Sastrawan, J. Ferber, R. Stangl, J. Luther, Electrochim. Acta 47 (2002) 4213–4225.
- [46] J. Bisquert, J. Phys. Chem. B 106 (2002) 325-333.
- [47] F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, A. Hagfeldt, Sol. Energy Mater. Sol. Cells. 87 (2005) 117–131.
- [48] Q. Wang, S. Ito, M. Grätzel, F. Fabregat-Santiago, I. Mora-Sero, J. Bisquert, T. Bessho, H. Imai, J. Phys. Chem. B 110 (2006) 25210– 25221.
- [49] J. Bisquert, F. Fabregat-Santiago, I. Mora-Sero, G. Garcia-Belmonte, S. Gimenez, J. Phys. Chem. C 113 (2009) 17278–17290.
- [50] J. Nissfolk, K. Fredin, A. Hagfeldt, G. Boschloo, J. Phys. Chem. B 110 (2006) 17715–17718.
- [51] Q. Wang, Z. Zhang, S.M. Zakeeruddin, M. Grätzel, J. Phys. Chem. C 112 (2008) 7084–7092.
- [52] (a) J.-H. Yum, E. Baranoff, F. Kessler, T. Moehl, S. Ahmad, T. Bessho, A. Marchioro, E. Ghadiri, J.-E. Moser, C. Yi, M.K. Nazeeruddin, M. Grätzel, Nat. Commun. 3 (2012) 631–637; (b) G.D. Sharma, G.E. Zervaki, P.A. Angaridis, A. Vatikioti, K.S.V. Gupta, T. Gayathri, P. Nagarjuna, S.P. Singh, M. Chandrasekharam, A. Banthiya, K. Bhanuprakash, A. Petrou, A.G. Coutsolelos, Org. Electron. 15 (2014) 1324–1337.
- [53] N.R. Neale, N. Kopidakis, J. van de Lagemaat, M. Grätzel, A.J. Frank, J. Phys. Chem. B 109 (2005) 23183–23189.
- [54] P. Wang, S.M. Zakeeruddin, R. Humphry-Baker, J.-E. Moser, M. Grätzel, J. Phys. Chem. B 107 (2003) 14336–14341.
- [55] Z. Zhang, S.M. Zakeeruddin, B. O'Regan, R. Humphry-Baker, M. Grätzel, J. Phys. Chem. B 109 (2005) (1824) 21818–21824.
- [56] B. Wenger, M. Grätzel, J.-E. Moser, J. Am. Chem. Soc. 127 (2005) 12150–12151.
- [57] B.E. Hardin, E.T. Hoke1, P.B. Armstrong, J.-H. Yum, P. Comte, T. Torres, J.M.J. Fréchet, M.K. Nazeeruddin, M. Grätzel, M.D. McGehee, Nat. Photonics 3 (2009) 406–411.
- [58] Y. Chen, Z. Zeng, C. Li, W. Wang, X. Wang, B. Zhang, New J. Chem. 29 (2005) 773-776.
- [59] X.-F. Wang, Y. Koyamaa, O. Kitaob, Y. Wadad, S.-I. Sasakie, H. Tamiakie, H. Zhou, *Biosens. Bioelectron*. 25 (2010) 1970–1976.
- [60] T. Förster, Discuss. Faraday Soc. 27 (1959) 7–17.
- [61] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Kluwer Academic/Plenum Publishers, New York, 1999.