Subscriber access provided by UNIV OF NEW ENGLAND ARMIDALE

Wide-Range Near-Infrared Sensitizing 1H-Benzo[c,d]indol-2ylidene-Based Squaraine Dyes for Dye-Sensitized Solar Cells

YUKI HAISHIMA, Yasuhiro Kubota, Kazuhiro Manseki, Jiye Jin, Yoshiharu Sawada, Toshiyasu Inuzuka, Kazumasa Funabiki, and Masaki Matsui J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.8b00070 • Publication Date (Web): 26 Mar 2018 Downloaded from http://pubs.acs.org on March 26, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.



is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Wide-Range Near-Infrared Sensitizing *H*-Benzo[*c,d*]indol-2-ylidene-Based Squaraine Dyes for Dye-Sensitized Solar Cells

Yuki Haishima,^a Yasuhiro Kubota,^{a,*} Kazuhiro Manseki,^a Jiye Jin,^b Yoshiharu Sawada,^c Toshiyasu Inuzuka,^c Kazumasa Funabiki,^a and Masaki Matsui,^{a,*}

^aDepartment of Chemistry and Biomolecular Scienece, Faculty of Engineering, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan.

^bDepartment of Chemistry, Faculty of Science, Shinshu University, 3-1-1-Asahi, Matsumoto, Nagano 390-8621, Japan.

^cDivision of Instrumental Analysis, Life Science Research Center, Gifu University, 1-1 Yanagido, Gifu 501-1193, Japan.

E-mail : kubota@gifu-u.ac.jp, matsuim@gifu-u.ac.jp



NIR absorbing squaraine dyes **SQ1–SQ7** having 1*H*-benzo[*c*,*d*]indol-2-ylidene as a donor moiety were designed for application in DSSCs. Annulation of the benzene ring to an 3*H*-indolium-based anchor moiety led to a red-shifted and broadened absorption band on TiO₂ film, which were reflected in the improved short-circuit current density of **SQ2** (6.22 mA cm⁻²) compared to the non-benzene fused derivative **SQ1** (4.39 mA cm⁻²). Although the introduction of a butoxy (**SQ4**: 806 nm) or dialkylamino group (**SQ5–SQ7**: 815–820 nm) to the 1*H*-benzo[*c*,*d*]indol-2-ylidene-based donor moiety resulted in red-shifted absorption maxima in ethanol compared to the non-substituted derivative **SQ2** (784 nm), the HOMO energy level of **SQ4–SQ7** gave rise to an undesirable approximation to the redox potential of Γ/I_3^- . Thus, the butoxy (**SQ4**: 0.56) and dialkylamino (**SQ5–SQ7**: 0.25–0.30) derivatives had relatively lower conversion efficiencies. Since the 2-ethylhexyl derivative **SQ3** exhibited red-shifted absorption (λ_{max} : 796 nm), suitable HOMO and LUMO energy levels, and relatively efficient restriction of charge recombination, this dye achieved the highest conversion efficiency (1.31%), along with a high IPCE response of over 20% over a wide range from 640 to 860 nm and an onset of IPCE at 1000 nm.

Introduction

Since first being reported in 1991 by Grätzel and O'Regan, dye-sensitized solar cells (DSSCs) have attracted a great deal of attention as next generation solar cells due to advantages such as their facile fabrication process and low production cost.¹ The light-to-energy conversion efficiency (n) of DSSC cells is strongly affected by the type of sensitizer that is used as an absorber of sunlight. Therefore, the development of new sensitizers is being actively studied. Although metal organic sensitizers such as ruthenium polypyridine complexes² (η : 10–12 %) and zinc porphyrin complexes³ (SM315: $\eta = 13.15$ %) are known to have high conversion efficiencies, the high cost of the metals, relatively low molar extinction coefficients (ε) and difficulty of the syntheses⁴ are considered to be drawbacks. On the other hand, metal-free organic sensitizers have many advantages, including their low cost, high η values, flexibility of molecular design, and easily tunable absorption properties.⁵ Several metal-free organic sensitizers such as tetrathienoacene-based dyes (**TPA-TTART-A**: $\eta = 10.1$ %),⁶ indoline-based dyes (**YA422**: $\eta = 10.65$ %),⁷ and indenopervlene-based dyes (C275: $n = 12.5\%)^4$ have been reported so far. Since these sensitizers show high incident photon-to-current efficiencies (IPCEs) of greater than 90 % in the visible light region (ca. 350-600 nm), their utilization of sunlight in the visible region is already sufficient. To further improve their conversion efficiencies, utilization of sunlight in the near-infrared (NIR) region is required. Co-sensitization⁸ and tandem systems⁹ using NIR dyes are promising approaches to achieve higher η values. In addition, transparent NIR dyes that do not absorb light in the visible region can be applied to transparent solar cells.¹⁰ Lead halide perovskite solar cells (PSCs) have also received increased attention recently due to their excellent conversion efficiency (>20 %).¹¹ As one method to enhance the η values of PSCs, hybridized systems with NIR DSSCs are a useful approach.¹² Thus, the development of efficient NIR sensitizers is very important.

Several NIR sensitizers, such as methyinecyanine,¹³ BODIPY,¹⁴ squaraine (SQ),¹⁵ porphyrin,¹⁶ phthalocyanine,¹⁷ and other dves,¹⁸ have been reported. However, the IPCE response of these NIR sensitizers is still insufficient. The development of efficient NIR dyes with absorption over the entire NIR region (ca. 750–1000 nm) is a challenging task. Among the NIR sensitizers, SO dyes are considered the most promising candidates because of their intense absorption, high photostability, and their ability to extend absorption to longer wavelengths.¹⁹ In order to achieve the sensitization of SQ dyes in the longer wavelength NIR region, oligomerization²⁰ and introduction $(EDOT)^{21}$ the of the ethylenedioxythiophene and 1H-benzo[*c*.*d*]indol-2-vlidene moieties²² have been examined. Notably, in the oligomerization approach, the SO oligomer **TSOa** showed a high IPCE response of over 15 % from 750 nm to 900 nm.^{20d} In the case of EDOT-containing SQ dyes, JYL-SQ5 exhibited a high IPCE response in the NIR region: ca. 40 % at 750 nm, ca. 30 % at 800 nm, ca. 15 % at 850 nm, and ca. 5 % at 900 nm.^{21a} Despite their simple structure, 1H-benzo[c,d]indol-2-ylidene-based SQ dyes also show IPCE response in the NIR region. Among the reported 1*H*-benzo[c,d]indol-2-ylidene-based SQ dyes, VG5 had the highest IPCE value (ca. 30 % at 750 nm, ca. 35 % at 800 nm, ca. 15 % at 850 nm, and ca. 1 % at 900 nm).^{22c}

Recently, we also have reported 1*H*-benzo[c,d]indol-2-ylidene-based SQ dyes with an anchor group on the 3*H*-indolium ring as NIR sensitizers.^{22e} Among the SQ dyes, the highest η and IPCE values were 0.58 % and 14 % at 790 nm, respectively. In this paper, in order to improve the conversion efficiency and

The Journal of Organic Chemistry

achieve greater red-shift of the sensitization region, we report the molecular design and synthesis of novel 1H-benzo[c,d]indol-2-ylidene-based SQ sensitizers. We focused on the following three points: (1) extension of the π -conjugation by annulation of the benzene ring to an 3H-indolium-based anchor moiety for further red-shifted absorption, (2) enhancement of the intramolecular charge transfer property by introducing an electron donating group such as a dialkylamino group into the 1H-benzo[c,d]indol-2-ylidene-based donor moiety to realize further spectral red shift, and (3) introduction of various substituent groups onto the 1H-benzo[c,d]indol-2-ylidene-based donor moiety to adjust the HOMO and LUMO energy levels.

Results and discussion

Synthesis

H-Benzo[*c*,*d*]indol-2-ylidene-based SQ dyes SQ1–SQ7 were synthesized as sensitizers for dye-sensitized solar cells (DSSCs) (Scheme 1). Semisquaric acid $6^{22e}_{,,22e}_{,23H}$ -indolium salt $7a^{23}_{,23}_{,1H}$ -benzo[*e*]indolium salt $7b^{24}_{,24}$ and semisquarine $8^{24}_{,24}$ are known compounds. These compounds were synthesized according to the previously reported method. First, in order to efficiently introduce various types of electron donating groups, bromo-substituted 1*H*-benzo[*c*,*d*]indol-2-ylidene **3** was synthesized from commercially available 1*H*-benzo[*c*,*d*]indol-2-one **1** (Scheme **1a**). 1*H*-Benzo[*c*,*d*]indol-2-one **1** was brominated using bromine to obtain the bromo-substituted derivative **2**. *N*-Alkylation of **2** was carried out with hexyl iodide in the presence of sodium hydride to obtain the *N*-hexylated derivative **3**.

Next, 1*H*-benzo[*c*,*d*]indolium perchlorates **5a**–**5e** were synthesized from **3** (**Scheme 1b**). These reactions were performed according to modified literature procedures.²⁵⁻³⁰ To introduce a 2-ethylhexyl group directly onto the bromo derivative **3** under mild conditions, we carried out a Negishi cross coupling reaction using an organozinc reagent and a Pd catalyst. 2-Ethylhexyl zinc bromide was prepared by the reaction of zinc powder and 2-ethylhexyl bromide in the presence of iodine,²⁵ and was then titrated according to Knochel's method to determine its concentration²⁶ which was 0.42 M. The Negishi cross coupling reaction of **3** with 2-ethylhexyl zinc bromide in the presence of Pd₂(dba)₃ and SPhos gave the 2-ethylhexyl-substituted derivative **4a**.²⁷ The reaction of **3** with sodium butoxide in the presence of CuI gave butoxy-substituted derivative **4b**.²⁸ Dialkylamino-substituted derivatives **4c**–**4e** were obtained by the Buchwald–Hartwig cross coupling reaction of **3** with secondary amines in the presence of Pd₂(dba)₃, XPhos, and LiHMDS.²⁹ The reactions of amides **4a**–**4e** with methylmagnesium chloride, followed by dehydration using perchloric acid, afforded the corresponding 1*H*-benzo[*c*,*d*]indolium perchlorates **5a**–**5e**.³⁰

Finally, the synthesis of squaraine dyes SQ1-SQ7 was carried out by the reaction of semisquarine with the indolium salts (Scheme 1c). Squaraine dyes SQ1 and SQ2 were synthesized from the reactions of semisquarine 6 with 3*H*-indolium salt 7a and 1*H*-benzo[*e*]indolium salt 7b, respectively. Semisquarine 8 was hydrolyzed with aqueous sodium hydroxide, followed by acidification by adding hydrochloric acid to provide the corresponding semisquarine. The obtained semisquaric acid was reacted without further purification with 1*H*-benzo[*c*,*d*]indolium perchlorates 5a–5e to yield the corresponding squaraine dyes SQ3–SQ7.

sQ (a)



ACS Paragon Plus Environment



Scheme 1. Synthesis of 1*H*-benzo[*c*,*d*]indol-2-ylidene-based SQ dyes SQ1–SQ7.

UV/Vis/NIR absorption properties

The UV/Vis/NIR absorption spectra of the SQ dyes in ethanol are shown in Figure 1a. The absorption maximum (λ_{max}) and molar extinction coefficient (ε) values are listed in Table 1. All the

synthesized SQ dyes exhibited intense and weak absorption bands at around 800 nm (λ_{max} : 771–820 nm, ε : 94,100–115,800) and 450 nm (λ_{max} : 412–486 nm, ε : 11,000–15,200), respectively. The λ_{max} value of **SQ2** (784 nm) was slightly red-shifted compared to that of **SQ1** (771 nm) due to the extension of the π -conjugation by the fusion of the benzene ring. The introduction of electron donating groups onto the 1*H*-benzo[*c*,*d*]indol-2-ylidene moiety of **SQ2** led to a further red shift in the λ_{max} values (796–820 nm). The λ_{max} values exhibited greater red-shift as the electron donating ability of the substituent groups increased: **SQ3** (2-ethylhexyl, 796 nm), **SQ4** (butoxy, 806 nm), **SQ5** (dibutylamino, 818 nm), **SQ6** (dioctylamino, 820 nm), **SQ7** (di(2-ethylhexyl)amino, 816 nm). Additionally, the introduction of dialkylamino groups not only caused a significant red shift of λ_{max} , but also broadened the absorption bandwidth. As a result, the absorption edge of the dialkyamino-substituted derivatives reached up to 932 nm (**SQ7**).

The UV/Vis/NIR absorption spectra of the SQ dyes adsorbed on a 4 μ m TiO₂ film are shown in **Figure 1b**. Compared to the corresponding solution spectra, the absorption bands on the TiO₂ films were slightly red-shifted and broadened, probably due to the formation of aggregates and the interaction of the anchor group with the TiO₂ surface.³¹ Furthermore, the intensities of the shorter absorption bands at around 450 nm were relatively higher in the absorption spectra on the TiO₂ films. As observed in the solution measurements, the absorption bands of SQ dyes with strong electron donating groups tended to be more red-shifted. The absorption edges were extended to 1000 nm on the TiO₂ film.



Figure 1. UV/Vis/NIR absorption spectra of SQ dyes (a) in ethanol $(1.0 \times 10^{-5} \text{ M})$ and (b) on TiO₂ (4 µm) film in the presence of CDCA.

Table 1. Photophysical	properties of SQ1-SQ7 ^a
------------------------	------------------------------------

SQ dyes	$\lambda_{\max} \left(\varepsilon \right)^a / \operatorname{nm}$	$\lambda_{\text{onset}}^{a}$ / nm	$\lambda_{\max}{}^b$ / nm
SQ1	412 (11,700), 718 (93,700), 771 (103,000)	827	419, 720, 785

ACS Paragon Plus Environment

SQ2	413 (11,000), 728 (110,000), 784 (103,000)	838	422, 726, 800
SQ3	424 (11,600), 740 (100,000), 796 (116,000)	849	431, 736, 814
SQ4	438 (10,800), 749 (63,800), 806 (94,100)	873	447, 745, 821
SQ5	474 (12,400), 760 (77,900), 818 (102,000)	919	479, 761, 827
SQ6	474 (13,900), 761 (81,600), 820 (110,000)	919	479, 757, 830
SQ7	486 (15,200), 760 (73,600), 815 (97,700)	932	486, 756, 823

^{*a*}Measured in ethanol (1.0×10^{-5} M). ^{*b*}Measured on a 4 µm transparent TiO₂ film which was dipped in 0.12 mM of SQ dye and 6 mM of CDCA in a solution of acetonitrile and chloroform (v : v = 1 : 1) for 30 min at room temperature.

Theoretical calculation

To obtain deeper insight into the absorption properties, density functional theory (DFT) calculations were performed using the Gaussian 09 package.³² The geometries were optimized at the DFT/B3LYP level using the 3-21G basis set. Single-point energy calculations of the optimized structures were then performed using the B3LYP/6-31G(d,p) method (**Figure 2**). Time-dependent DFT (TDDFT) calculations were also performed using the B3LYP/6-31G(d) method. The calculated λ_{max} values, the main orbital transition, the oscillator strength (f) values, and the experimentally obtained λ_{max} and ε values are shown in **Table 2**. The calculated λ_{max} values were in good agreement with the experimental values.

For all the SQ dyes, the $S_0 \rightarrow S_1$ transitions were mainly attributed to HOMO to LUMO transitions, and the λ_{max} and f values were estimated to fall between 653–714 nm and 1.288–1.511, respectively. The HOMO and LUMO orbitals of **SQ1–SQ7** were delocalized from the 1*H*-benzo[c,d]indol-2-ylidene donor moiety to a particular part of the indolium acceptor moiety. Therefore, the observed first absorption bands of **SQ1–SQ7** (λ_{max} : 771–820 nm) were attributed to the $\pi \rightarrow \pi^*$ transition. In the LUMO orbitals of **SQ2–SQ7**, no electron density was observed around the carboxyl group. This indicates that the electron transfer from the excited S₁ state of **SQ2–SQ7** by light absorption to the TiO₂ conduction band was unfavorable.

Although the λ_{max} values of the $S_0 \rightarrow S_2$ transitions of **SQ1–SQ7** were estimated to fall between 558–572 nm, these transitions are forbidden ($f \le 0.001$). Thus, the observed absorption peaks at around 718–761 nm in ethanol were attributed to the vibrational peaks ($S_{0,0} \rightarrow S_{1,1}$ transitions) or absorption by aggregated dyes. In order to reveal the effect of aggregates on the absorption properties, absorption spectra of **SQ3** were measured in ethanol–water mixtures of various ratios (**Figure S1**). When the water content of the mixture reached 40 %, the absorption intensity at around 690 nm increased obviously. The increase in the absorption intensity became more pronounced with increasing water content. The formation of aggregates was confirmed by the Tyndall phenomenon (**Figure S2**). Therefore, the absorption peak at approximately 690 nm was assigned to the aggregates of **SQ3**. Therefore, the absorption peak observed at 740 nm for **SQ3** in ethanol was probably a vibrational peak. These results suggested that the vibrational absorption peak and the absorption peak of the aggregates both appeared at approximately 720 nm.

The λ_{max} and f values of the $S_0 \rightarrow S_3$ transitions were estimated to fall between 439–528 nm and 0.011–0.059, respectively. Therefore, the observed weak absorption peaks at 412–486 nm for **SQ1–SQ7** in ethanol were attributed to the $S_0 \rightarrow S_3$ transitions, which were mainly assigned to the HOMO to LUMO+1 transitions. The LUMO+1 orbitals of **SQ2–SQ7** were located on the 1*H*-benzo[*e*]indolium acceptor moiety. Thus, the HOMO to LUMO+1 transitions of **SQ2–SQ7** were attributed to the intramolecular charge transfer

(ICT) transition. The calculated results indicated that electron transfer from the S_3 states of **SQ2–SQ7** that originated from the absorption at 412–486 nm to the TiO₂ was favorable.

We then focused on the HOMO, LUMO, and LUMO+1 energy levels. DFT calculations suggested that the fusion of benzene to the 3*H*-indolium-based anchor moiety slightly reduced the LUMO energy level (**SQ1**: -2.76 eV, **SQ2**: -2.77 eV) and that the HOMO–LUMO gap became slightly smaller (**SQ1**: 1.84 eV, **SQ2**: 1.83 eV). The introduction of substituent groups to the 1*H*-benzo[*c*,*d*]indol-2-ylidene donor moiety led to an increase in both the HOMO and LUMO energy levels. The changes to the HOMO (**SQ2**: -4.60 eV, **SQ3**: -4.54 eV, **SQ4**: -4.44 eV, **SQ2**: -4.39 eV) and LUMO (**SQ2**: -2.77 eV, **SQ3**: -2.73 eV, **SQ4**: -2.64 eV, **SQ2**: -2.63 eV) energy levels became more pronounced as the electron-donating properties of the substituent groups increased. The calculated HOMO and LUMO energy levels were in good agreement with the experimentally obtained E_{HOMO} and E_{LUMO} values, which will be described below (**Table 3**).



Figure 2. Molecular orbital energy diagram and isodensity surface plots of the HOMO–1, HOMO, LUMO, and LUMO+1 of **SQ1–SQ7** calculated using the B3LYP/6-31G(d,p)//B3LYP/3-21G method.

Table 2. Calculated absorption maxima (λ_{max}), oscillator strengths (*f*), and main orbital transitions and experimentally observed λ_{max} and molar extinction coefficient (ε) values

SQ dyes	Transition	$\lambda_{\max}{}^a$ / nm	Main orbital transition	f	$\lambda_{\max}{}^b$ / nm	$arepsilon^b$

SQ1	$S_0 \mathop{\rightarrow} S_1$	653	HOMO \rightarrow LUMO (0.72)	1.288	718 771	93,700 103.000
	$S_0 \mathop{\rightarrow} S_2$	572	HOMO-1 \rightarrow LUMO (0.70)	0.000	C	c
	$S_0 \rightarrow S_3$	439	HOMO \rightarrow LUMO+1 (0.51) HOMO-2 \rightarrow LUMO (-0.47)	0.059	412	11,700
SQ2	$S_0 \to S_1$	663	HOMO \rightarrow LUMO (0.72)	1.342	728 784	110,000 103,000
	$S_0 \mathop{\rightarrow} S_2$	565	HOMO-1 \rightarrow LUMO (0.70)	0.000	<i>c</i>	
	$S_0 \mathop{\rightarrow} S_3$	503	HOMO \rightarrow LUMO+1 (0.69) HOMO-2 \rightarrow LUMO (0.14)	0.012	413	11,000
SQ3	$S_0 \to S_1$	675	HOMO \rightarrow LUMO (0.71)	1.439	740 796	100,000 116,000
	$S_0 \mathop{\rightarrow} S_2$	563	HOMO-1 \rightarrow LUMO (0.70)	0.000	<i>c</i>	
	$S_0 \mathop{\rightarrow} S_3$	508	HOMO \rightarrow LUMO+1 (0.69) HOMO-2 \rightarrow LUMO (0.14)	0.011	424	11,600
SQ4	$S_0 \mathop{\rightarrow} S_1$	678	HOMO \rightarrow LUMO (0.71)	1.440	749 806	63,800 94,100
	$S_0 \mathop{\rightarrow} S_2$	558	HOMO-1 \rightarrow LUMO (0.70)	0.001		
	$S_0 \mathop{\rightarrow} S_3$	515	HOMO \rightarrow LUMO+1 (0.69) HOMO-2 \rightarrow LUMO (-0.13)	0.012	438	10,800
SQ5	$S_0 \to S_1$	701	HOMO \rightarrow LUMO (0.71)	1.481	760 818	77,900 102,000
	$\mathrm{S}_0 \to \mathrm{S}_2$	559	HOMO-1 \rightarrow LUMO (0.70)	0.001	<i>c</i>	
	$S_0 \rightarrow S_3$	524	HOMO \rightarrow LUMO+1 (0.67) HOMO-2 \rightarrow LUMO (-0.21)	0.011	474	12,400
SQ6	$S_0 \to S_1$	703	HOMO \rightarrow LUMO (0.71)	1.494	761 820	81,600 110,000
	$S_0 \mathop{\rightarrow} S_2$	559	HOMO-1 \rightarrow LUMO (0.70)	0.001		c
	$S_0 \rightarrow S_3$	524	HOMO \rightarrow LUMO+1 (0.67) HOMO-2 \rightarrow LUMO (-0.21)	0.011	474	13,900
SQ7	$S_0 \to S_1$	714	HOMO \rightarrow LUMO (0.71)	1.511	760 815	73,600 97,700
	$S_0 \mathop{\rightarrow} S_2$	559	HOMO-1 \rightarrow LUMO (0.70)	0.000	C	
	$S_0 \rightarrow S_3$	528	HOMO \rightarrow LUMO+1 (0.63) HOMO-2 \rightarrow LUMO (-0.30)	0.011	486	15,200
101 1.1	hr		1.01.1.1			

^aCalculated in vacuum. ^bMeasured in ethanol. ^cNot observed.

Electrochemical properties

Cyclic voltammetry measurements were performed in DMF solution using 0.1 M tetrabutylammonium perchlorate as a supporting electrode and ferrocene (Fc) as an external standard (Figure

3). The first half-wave potential for oxidation ($E_{1/2}$ (ox)) of **SQ1**, corresponding to the HOMO energy level (E_{HOMO}), was observed at 0.07 V vs. Fc/Fc⁺. In DMF, the $E_{1/2}$ (vs. Fc/Fc⁺) value can be converted to the $E_{1/2}$ (vs. NHE) value as follows: $E_{1/2}$ (vs. NHE) = $E_{1/2}$ (vs. Fc/Fc⁺) + 0.72 V.³³ Thus, the E_{HOMO} value of **SQ1** was estimated to be 0.79 V vs NHE. The energy gap between the HOMO and LUMO energy levels ($E_{0.0}$) of **SQ1** obtained from the onset of the UV/Vis/NIR absorption spectrum was 1.50 eV. Thus, the LUMO energy level (E_{LUMO}) of **SQ1** estimated by subtracting the $E_{0.0}$ value from the E_{HOMO} value vs. NHE was -0.71 V. The E_{HOMO} and E_{LUMO} values of the other SQ dyes were determined in a similar manner (**Figure 4**).

The E_{LUMO} values of all the synthesized SQ dyes (-0.91 to -0.71 V vs. NHE) were more negative than the conduction band level of TiO₂ (-0.5 V vs. NHE), which suggested that the electron transfer from the excited SQ dyes to the conduction band of TiO₂ was thermodynamically allowed.³⁴ However, in order for an oxidized dye to undergo thermodynamically allowed regeneration by iodide, the E_{HOMO} value of the dye must be more positive than the redox potential of Γ/I_3^- in the electrolyte (0.4 V vs. NHE).³⁴ Since all the synthesized SQ dyes had positively shifted E_{HOMO} values (0.52 to 0.83 V vs. NHE), regeneration of these SQ dyes was possible.



Figure 3. Cyclic voltamogram of SQ1-SQ7 in DMF.

ACS Paragon Plus Environment



Figure 4. Energy level diagram for SQ1–SQ7.

Table 3. Electrochemical	properties of SQ	21–SQ7
--------------------------	------------------	--------

SQ dyes	$E_{1/2}$ (ox) (vs. Fc/Fc ⁺) ^{<i>a</i>} / V	E_{HOMO} (vs. NHE) ^b / V	$E_{0-0}{}^{c} / eV$	$E_{\text{LUMO}} (\text{vs. NHE})^d / \text{V}$
SQ1	0.07	0.79	1.50	-0.71
SQ2	-0.04	0.68	1.48	-0.80
SQ3	-0.04	0.68	1.46	-0.78
SQ4	-0.16	0.56	1.42	-0.86
SQ5	-0.21	0.51	1.35	-0.84
SQ6	-0.28	0.44	1.35	-0.91
SQ7	-0.22	0.50	1.33	-0.83

^{*a*}The first half-wave potential for oxidation was measured in DMF solution using 0.1 M tetrabutylammonium perchlorate as a supporting electrode and ferrocene (Fc) as an external standard. ^{*b*} $E_{1/2}$ (vs. NHE) = $E_{1/2}$ (vs. Fc/Fc⁺) + 0.72 V in DMF. ^{*c*} E_{0-0} (eV) = $1240/\lambda_{onset}$. ^{*d*} E_{LUMO} was calculated as $E_{HOMO} - E_{0-0}$.

Photovoltaic performance

Photovoltaic measurements were carried out on the DSSC cells, which consisted of the TiO_2 photoelectrode (transparent layer: 8 μ m, scattering layer: 4 μ m) with squaraine dyes **SQ1–SQ7** absorbed as a

The Journal of Organic Chemistry

sensitizer and chenodeoxycholic acid (CDCA, 50 equiv.) as a co-adsorbent in acetonitrile/t-butyl alcohol (v : v = 1 : 1), a Pt counter electrode, and an iodine-based electrolyte. The IPCE spectra and I-V curves are shown in **Figure 5**, and the performance parameters are summarized in **Table 4**. For comparison, UV/Vis/NIR absorption and photovoltaic measurements in the absence of CDCA were also conducted (**Figure S3** and **S4**). In the UV/Vis/NIR absorption spectra of without CDCA, the absorption intensities at around 700 nm which correspond to dye aggregates were relatively increased and the spectra were broadened compared to those of with CDCA. In all synthesized SQ dyes, the short-circuit current density (J_{SC}), open-circuit voltage (V_{oc}) and power conversion efficiency (η) values were significantly improved by addition of CDCA due to the inhibition of unfavorable dye aggregation (**Table 4**).

The maximum IPCE value of **SQ2** (17% at 800 nm) was slightly red-shifted compared to that of **SQ1** (17% at 790 nm) (**Figure 5a**). Moreover, **SQ2** showed a higher IPCE value than **SQ1** over the entire wavelength range from 400 nm to 950 nm. Accordingly, the J_{SC} value of **SQ2** (6.22 mA cm⁻²) was larger than that of **SQ1** (4.39 mA cm⁻²). The slightly higher IPCE value of **SQ2** in the longer wavelength region (600–950 nm) was consistent with the broadened absorption spectrum of **SQ2** on TiO₂ (**Figure 1a**). Although both **SQ1** and **SQ2** showed similar absorption spectra on TiO₂, **SQ2** had a significantly higher IPCE value in the shorter wavelength region (400–550 nm). Based on the calculation results discussed above, the absorption peak at around 450 nm was attributed to the HOMO to LUMO+1 transition. The LUMO+1 orbital of **SQ1** was delocalized over the whole molecule, while that of **SQ2** was located around the anchor group (**Figure 2**). This implied the electron transfer from the LUMO+1 to the conduction band of TiO₂ was more effective in **SQ2** than in **SQ1**. The effective electron transfer properties of **SQ2** were probably the reason for the higher IPCE value in the shorter wavelength region. The V_{oc} values of **SQ1** (0.300 V) and **SQ2** (0.303 V) were nearly equal. The fill factor (*FF*) value of **SQ2** (0.47) was smaller than that of **SQ1** (0.56). Consequently, the η value of **SQ2** (0.89) was larger than that of **SQ1** (0.74), due to the improved IPCE response.

In the 2-ethylhexyl derivative **SQ3**, a remarkable enhancement of the IPCE spectrum was observed. The IPCE value of **SQ3** was higher than that of **SQ2** over the whole wavelength range, and the IPCE spectral edge of **SQ3** was significantly red-shifted, reaching 1000 nm. The IPCE response of **SQ3** was as follows: 24 % at 680–840 nm, 22 % at 850 nm, 10 % at 900 nm, and 2 % at 950 nm. Thus, the J_{SC} value of **SQ3** (9.20 mA cm⁻²) was further improved. On the other hand, introduction of a butoxy group caused a decrease in the IPCE value over a wide wavelength range from 400 to 850 nm, and an increase over a narrow wavelength range from 850 to 1000 nm. The overall decrease in the IPCE response led to the relatively low J_{SC} value for **SQ4** (3.81 mA cm⁻²). The dialkylamino-substituted derivatives showed even lower J_{SC} values (**SQ5**: 1.77 mA cm⁻², **SQ6**: 1.45 mA cm⁻², **SQ7**: 2.05 mA cm⁻²), which explains the substantially inferior IPCE responses. Among the dialkylamino-substituted derivatives, the di(2-ethylhexyl)amino derivative **SQ7** had a significantly higher IPCE value in the range from 650 nm to 1000 nm. The difference in the longer wavelength region (850–950 nm), which was probably associated with the broadened absorption peak of **SQ7** on TiO₂ in this region, was especially remarkable.

In addition to efficient electron transfer, appropriate E_{LUMO} and E_{HOMO} values are also desirable. Roughly speaking, the E_{HOMO} and E_{LUMO} values must be more positive than 0.7 vs. NHE and more negative than -0.7 V vs. NHE, respectively.^{15e, 35} In the 1*H*-benzo[*e*]indolium derivatives **SQ2–SQ7**, the E_{HOMO} values increased in the order **SQ6** (0.44 V) < **SQ7** (0.50 V) < **SQ5** (0.51 V) < **SQ4** (0.56 V) < **SQ2** (0.68 V), **SQ3**

(0.68 V) (Figure 4). This was highly consistent with the trend of the increase in the J_{SC} values: SQ6 (1.45 mA cm⁻²) < SQ5 (1.77 mA cm⁻²) < SQ7 (2.05 mA cm⁻²) < SQ4 (3.81 mA cm⁻²) < SQ2 (6.22 mA cm⁻²) < SQ3 (9.20 mA cm⁻²). The E_{HOMO} values of the butoxy- (SQ4: 0.56 V vs NHE) and dialkylamino-substituted derivatives (SQ5–SQ7: 0.44–0.51 V vs. NHE) were obviously close to the Γ/I_3^- redox potential (0.40 V vs. NHE). Therefore, the lower J_{SC} value of SQ4–SQ7 could be ascribed to ineffective regeneration of the oxidized dye by iodide. Due to its suitable E_{LUMO} and E_{HOMO} values, the 2-ethylhexyl derivative SQ3 showed the highest J_{SC} value.

In order to understand the effect of the dye loading of **SQ1–SQ7**, the dyes were desorbed by immersing the TiO₂ photoelectrode in the mixture of 2M HCl and ethanol with the volume ratio of 1 : 9. The UV/Vis/NIR absorption spectra of the desorbed solutions and the dye loading were shown in Figure S6 and Table S1, respectively. In the case of using CDCA (50 equiv.), the dye loading of **SQ1–SQ7** were in the range of 2.80×10^{-8} to 5.80×10^{-8} mol/cm². **SQ2** (4.39×10^{-8} mol/cm²) exhibited a higher dye loading than **SQ1** (2.80×10^{-8} mol/cm²). This also contributes to the improved J_{sc} value by the annulation of a benzene ring to the anchor moiety. Introduction of 2-ethylhexyl group lead to a slightly increase of the dye loading (**SQ3**: 5.41×10^{-8} mol/cm²). This indicates that introduction of the bulky substituent to a separate position from the anchor moiety is associated with the formation of well-packed layers rather than decrease of the dye loading. The dye loading of butoxy (**SQ4**: 3.16×10^{-8} mol/cm²) and dialkylamino (**SQ5–SQ7**: 3.69×10^{-8} to 5.80×10^{-8} mol/cm²) derivatives has no significant differences compared to that of **SQ3**. Thus, the lower J_{sc} values of **SQ4–SQ7** are not due to the difference of the dye loading but due to their higher HOMO energy levels.

The V_{oc} value increased compared to the non-substituted derivative **SQ2** (0.303 V) with the introduction of the 2-ethylhexyl group (**SQ3**: 0.315 V), while it decreased with the butoxy (**SQ4**: 0.266 V) and dialkylamino (**SQ5**: 0.276 V, **SQ6**: 0.289 V, **SQ7**: 0.279 V) groups. On the other hand, no remarkable trend was observed for the *FF* values. Accordingly, the η values followed the order: **SQ6** (0.25) < **SQ5** (0.29) < **SQ7** (0.30) < **SQ4** (0.56) < **SQ2** (0.89) < **SQ3** (1.31).

 $J_{\rm sc}$ / mA cm⁻² CDCA (equiv.) FFSQ dye $V_{\rm oc}$ / V $\eta / \%$ 0 1.84 0.258 0.60 SQ1 0.29 50 4.39 0.300 0.56 0.74 SQ2 0 2.56 0.248 0.56 0.36 50 6.22 0.300 0.47 0.89 0 SQ3 5.11 0.269 0.50 0.69 50 9.20 0.315 0.45 1.31 0 SQ4 1.72 0.197 0.48 0.16 50 3.81 0.266 0.56 0.56 0 0.195 SQ5 1.00 0.45 0.09 50 0.59 1.77 0.276 0.29 0 SQ6 0.226 0.55 0.07 0.58 50 1.45 0.289 0.60 0.25

Table 4. Photovoltaic performance of DSSCs based on $SQ1-SQ7^a$

SQ7	0	1.53	0.186	0.45	0.13
	50	2.05	0.279	0.52	0.30

^{*a*}Conditions: electrode: $8 + 4 \mu m$ (transparent + scattering) layer of TiO₂, electrolyte: 0.05 M I₂, 0.5 M DMPImI, and 0.5 M LiI in acetonitrile/chloroform (v : v = 1 : 1), dye absorption: 0.12 mM of SQ dye in acetonitrile/t-butanol (v : v = 1 : 1), 6.0 mM CDCA (or without CDCA), dipping time: 15 h, measurement: active area of 0.20 cm² using a mask under AM1.5G (100 mW cm⁻²). ^{*b*}Dye absorption: 0.12 mM of **SQ4** in THF, CDCA 6.0 mM (or without CDCA).



Figure 5. (a) IPCE spectra and (b) I-V curve of DSSCs based on SQ1-SQ7 with CDCA.

Electrochemical impedance spectroscopy (EIS)

2-Ethylhexyl-substituted derivative **SQ3** showed the highest performance ($J_{sc} = 9.2 \text{ mA cm}^2$, $V_{oc} = 0.315 \text{ V}$, FF = 0.45, $\eta = 1.31$ %). In order to investigate the effects on the V_{oc} value, electrochemical impedance spectroscopy (EIS) was performed on cells based on **SQ1**, **SQ2**, and **SQ3** with CDCA (50 equiv.) under an illumination of AM 1.5 G (100 mW cm⁻²). The measurement results are summarized in **Table 5**, and the Nyquist plots are shown in **Figure 6a**. The large semicircles in the midfrequency range of the Nyquist plots were assigned to charge transfer at the TiO₂/dye/electrolyte interface.³⁶ The charge recombination resistance (R_{rec}) at the TiO₂ surface can be estimated by fitting Nyquist plots. The R_{rec} of **SQ3** (60 Ω) was obviously larger than that of **SQ1** (49 Ω) and **SQ2** (48 Ω), which indicates a slower charge recombination rate.^{15e, 37} The Bode phase plots are shown in **Figure 6b**. The electron lifetime (τ) was calculated from the peak frequency of the low-frequency peak in the Bode phase plots using the formula $\tau = 1/2\pi f$.^{15e, 15h, 38} The τ value of **SQ3** (15.9 ms) was longer than those of **SQ1** (12.6 ms) and **SQ2** (12.6 ms). These results strongly supported the higher V_{oc} value of **SQ3** (0.315 V) compared to those of **SQ1** (0.300 V) and **SQ2** (0.303 V), which suggested that the introduction of the 2-ethylhexyl group could prevent charge recombination from the TiO₂ surface to triiodide and/or the oxidized dye.

Table 5. EIS measurement data for DSSCs based on SQ1, SQ2, and SQ3 with CDCA (50 equiv.)

SQ dye	$R_{ m rec}/\Omega$	f/Hz	au / ms
SQ1	49	12.6	12.6
SQ2	48	12.6	12.6
SQ3	60	10.0	15.9



Figure 6. EIS characteristics of DSSCs based on **SQ1–SQ3** with CDCA (50 equiv.) under an illumination of AM1.5G (100 mW cm⁻²). (a) Nyquist plot and (b) Bode phase plot.

Conclusions

The novel squaraine dyes **SQ1–SQ7**, in which a 1*H*-benzo[$c_{,d}$]indol-2-ylidene moiety bearing various substituent groups acts as a donor moiety, were synthesized, and their application to DSSCs was investigated. Squaraine dyes SQ1–SQ7 exhibited a strong first absorption band (λ_{max} : 771–820 nm, ε : 94,100-116,000) corresponding to the HOMO-LUMO transition, and a relatively weak second absorption band (λ_{max} : 412–486 nm, ε : 10,800–15,200) corresponding to the HOMO–LUMO+1 transition in ethanol. When we investigated the use of different anchor moieties, we found that the 1H-benzo[e]indolium derivative SQ2 (784 nm) showed a more red-shifted λ_{max} value compared to the 3*H*-indolium derivative SQ1 (771 nm) because of the extension of π -conjugation by the annulation of the benzene ring. Due to its broadened absorption band and suitable intramolecular HOMO to LUMO+1 charge transfer transition properties, SQ2 (6.22 mA cm⁻²) exhibited a higher J_{sc} value than SQ1 (4.39 mA cm⁻²). When we focused on the substituent group on the 1*H*-benzo[*c*,*d*]indol-2-ylidene moiety of SQ2, we found that the λ_{max} value showed a bathochromic shift that became more pronounced as the electron-donating properties of the substituent group increased: 2-ethylhexyl (SQ3: 796 nm) < butoxy (SQ4: 806 nm) < dibutylamino (SQ5: 818 nm) < dioctylamino (SQ6: 820 nm) < di(2-ethylhexyl)amino (SQ7: 815 nm). Cyclic voltammetry measurements and DFT calculations indicated that the introduction of butoxy and dialkylamino groups gave rise to a significant increase in the HOMO energy levels (SQ4-SQ7: 0.44 to 0.56 V vs. NHE, -4.44 to -4.37 eV) compared to the non-substituted derivative SQ2 (0.68 V vs. NHE, -4.60 eV), which resulted in the undesirable approximation of the HOMO levels to the redox potential of Γ/I_3^- (0.4 V vs. NHE). Due to the ineffective regeneration of the oxidized dye by iodide, SQ4–SQ7 had lower J_{sc} values (1.45–3.81 mA cm⁻²). Introduction of the 2-ethylhexyl group led to desirable properties such as a spectral red shift, suitable HOMO and LUMO energy levels, and prevention of charge recombination. Therefore, SQ3 showed the highest J_{sc}

(9.20 mA cm⁻²), V_{oc} (0.315), and η (1.31) values among the synthesized SQ dyes.

Experimental section

General information

NMR spectra were recorded on ECX400P or ECA–600 spectrometers. Chemical shifts are referred to TMS (¹H and ¹³C) as internal standards. Infrared (IR) spectra were determined on a Simazu IR–Affinity spectrometer. UV–vis spectra were taken on a Hitachi U4100 spectrophotometer. Mass spectra were recorded on a JEOL JMS–700 spectrometer. High-resolution mass spectroscopy (HRMS) was obtained using a double-focusing magnetic sector mass spectrometer (JEOL JMS–700). Melting points were measured on a Yanagimoto MP–S2 micro–melting–point apparatus. Analytical thin-layer chromatography (TLC) was performed on pre-coated plates (Merck, silica gel 60 F254). Silica gel (Wakogel C–200) was used for column chromatography.

Synthesis of 2: Benz[*c*,*d*]indol-2(1*H*)-one (**1**) (5.01 g, 29.1 mmol) was dissolved in chloroform (120 mL). Bromine (7.10 g, 44.4 mmol) was added to the solution and stirred at room temperature for 60 h. A saturated sodium thiosulfate aqueous solution (100 mL) was poured into the reaction mixture. The resulting precipitate was filtered off and washed with water to give **2** as a yellow solid (6.89 g, 94%). **2**: mp 219.0–220.0°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.91 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.93 (t, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.24 (d, *J* = 7.8 Hz, 1H), 10.9 (s, 1H); ¹³C NMR (100 MHz, DMSO-*d*₆) δ 107.5, 111.9, 124.8, 126.6, 127.3, 128.3, 129.5, 130.4, 131.8, 138.1, 168.2; IR (KBr) 3194, 1705, 1636, 1485, 1462, 1396, 1369, 1258, 1219 cm⁻¹; HRMS (FAB) *m/z* calcd for C₁₁H₇BrNO [M + H]⁺ 247.9711, found 247.9715.

Synthesis of 3: Sodium hydride (60wt% in oil, 1.09 g, 27.2 mmol) was added to a solution of 1 (2.25 g, 9.08 mmol) in anhydrous DMF (40 mL) at 0°C and stirred at 0°C for 5 min. To the solution, hexyl iodide (2.89 g, 13.6 mmol) was added and stirred at room temperature for 2 h. Water was then poured into the mixture, and the mixture was extracted with ethyl acetate. The organic extract was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by column chromatography (silica gel, $R_f = 0.30$, dichloromethane : hexane = 5 : 2) to give **3** as a yellow solid (2.23 g, 76%). **3**: mp 53.0–54.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (t, J = 7.3 Hz, 3H), 1.24-1.46 (m, 6H), 1.76 (quint, J = 7.3 Hz, 2H), 3.89 (t, J = 7.3 Hz, 2H), 6.77 (d, J = 7.3 Hz, 1H), 7.66 (d, J = 7.3 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 8.09 (d, J = 7.7 Hz, 1H), 8.15 (d, J = 7.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.2, 22.7, 26.8, 28.8, 31.6 40.5, 106.1, 114.0, 125.2, 126.3, 127.2, 129.1, 129.8, 130.4, 131.3, 139.4, 167.5; IR (KBr) 1712, 1628, 1493, 1466, 1373, 1308, 1207 cm⁻¹; HRMS (FAB) *m/z* calcd for C₁₇H₁₉BrNO [M + H]⁺ 332.0650, found 332.0647.

Preparation of 2-ethylhexylzinc bromide and synthesis of 4a: Zinc powder (983 mg, 15.0 mmol) was heated to 70 °C under vacuum for 1 h. After back-filling with argon, iodine (127 mg, 0.50 mmol) was added, followed by application of a vacuum and filling with argon. Dry DMA (10 mL) was added, and the resulting mixture was stirred at room temperature until the red color of the iodine disappeared (ca. 2 min). Then, 2-ethylhexyl bromide (1.93 g, 10.0 mmol) was added, and the mixture was stirred at 80 °C for 13 h. The resulting gray solution was cooled to room temperature and then was titrated according to Knochel's method to determine concentration²⁵, which was found to be 0.42 M. The prepared 2-ethylhexylzinc bromide (0.42 M solution in DMA, 3.6 mL, 1.50 mmol), **3** (332 mg, 1.00 mmol), SPhos (10.3 mg, 0.025 mmol, 2.5 mol%) and Pd₂(dba)₃ (9.2 mg, 0.010 mmol, 1.0 mol%) were stirred at 80 °C for 21 h. After completion of the

reaction, 2N HCl (1 mL) was added to the reaction mixture, followed by the addition of water (20 mL). The resulting solution was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄, and concentrated in vacuo. The residue was purified by column chromatography (silica gel, $R_f = 0.25$, hexane : ethyl acetate = 30 : 1) to give **4a** as a yellow oil (345 mg, 94%). **4a**: oil; ¹H NMR (400 MHz, CDCl₃) δ 0.83-0.95 (m, 9H), 1.21-1.46 (m, 14H), 1.65-1.83 (m, 3H), 2.89 (dd, J = 7.2, 7.5 Hz, 1H), 2.93 (dd, J = 7.2, 7.5 Hz, 1H), 3.90 (t, J = 7.4 Hz, 2H), 6.82 (d, J = 7.2 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 7.71 (dd , J = 7.3, 1.4 Hz, 1H), 8.05 (d, J = 7.3 Hz, 1H), 8.11 (d, J = 7.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 10.9, 14.1, 14.2, 22.6, 23.2, 25.7, 26.8, 28.9, 31.6, 32.7, 36.4, 40.3, 41.3, 105.0, 123.8, 125.6, 127.4, 128.1, 128.30, 128.34, 129.0, 132.6, 137.9, 168.0; IR (KBr) 1701, 1628, 1501, 1474, 1377, 1312, 1172 cm⁻¹; HRMS (FAB) *m/z* calcd for C₂₅H₃₆NO [M + H]⁺ 366.2797, found 366.2781.

Synthesis of 4b: Anhydrous *n*-butanol (1.50 g, 20.2 mmol) was added to a suspension of sodium hydride (60 wt% in oil, 200 mg, 5.00 mmol) in anhydrous DMF (2 mL) at room temperature. After stirring at room temperature for 1 h, the resulting solution was added to a suspension of copper (I) iodide (381 mg, 2.00 mmol) and 2 (332 mg, 1.00 mmol) in anhydrous DMF (2 mL). The reaction mixture was stirred at 120 °C for 3 h, and the resulting precipitate was then filtered off and washed with THF to remove copper (I) iodide. The washed THF solution and the filtrate were combined. After concentrating the solution under reduced pressure, the residue was purified by column chromatography (silica gel, $R_f = 0.35$, dichloromethane : hexane = 5 : 4) to give 4b as a yellow oil (320 mg, 98%). 4b: oil; ¹H NMR (400 MHz, CD₃OD) δ 0.88 (t, J = 7.3 Hz, 3H), 1.05 (t, J = 7.3 Hz, 3H), 1.24-1.46 (m, 6H), 1.61 (sext, J = 7.3 Hz, 1H), 1.78 (quint, J = 7.3 Hz, 2H), 1.84-1.95 (m, 2H), 3.91 (t, J = 7.3 Hz, 2H), 4.15 (t, J = 7.3 Hz, 2H), 6.81 (d, J = 7.8 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 7.74 (t, J = 8.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CD₃OD) δ 14.4, 14.5, 20.6, 23.8, 27.8, 30.0, 32.6, 32.8, 41.4, 48.5, 48.7, 48.9, 49.2, 49.4, 49.6, 49.8, 69.6, 107.3, 108.4, 124.2, 125.8, 127.0, 127.5, 128.0, 129.2, 133.2, 153.6, 169.9; IR (KBr) 1693, 1636, 1474, 1450, 1377, 1315, 1219 cm⁻¹; HRMS (FAB) *m/z* calcd for C₂₁H₂₈NO₂ [M + H]⁺ 326.2120, found 326.2099.

Synthesis of 4c: A solution of **3** (498 mg, 1.50 mmol), di-*n*-butylamine (0.30 mL, 1.80 mmol), lithium bis(trimethylsilyl)amide (552 mg, 3.30 mmol), XPhos (17.2 mg, 0.036 mmol, 2.4 mol%) and Pd₂(dba)₃ (13.7 mg, 0.015 mmol, 1.0 mol%) in anhydrous THF (5 mL) was stirred at 65 °C for 24 h. Then, to the solution 2N HCl (3 mL) was added, followed by a saturated aqueous sodium bicarbonate solution (20 mL). The resulting solution was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. Column chromatography of the residue on silica gel (R_f = 0.25, dichloromethane : hexane = 5 : 4) gave **4c** as a yellow oil (191 mg, 34%). **4c**: oil; ¹H NMR (400 MHz, CDCl₃) δ 0.82-0.92 (m, 9H), 1.22-1.55 (m, 8H), 1.36-1.44 (m, 2H), 1.45-1.54 (m, 4H), 1.78 (quint, J = 7.8 Hz, 2H), 3.17 (t, J = 7.8 Hz, 4H), 3.90 (t, J = 7.8 Hz, 2H), 6.80 (d, J = 7.8 Hz, 1H), 6.96 (d, J = 7.8 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 8.03 (d, J = 7.5 Hz, 1H), 8.23 (d, J = 7.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 14.2, 20.6, 22.7, 26.9, 29.0, 29.4, 31.7, 40.4, 54.5, 105.6, 118.5, 124.1, 126.5, 127.5, 127.67, 127.74, 128.4, 134.8, 144.3, 168.2; IR (KBr) 1701, 1628, 1605, 1470, 1450, 1373, 1312, 1215 cm⁻¹; HRMS (FAB) *m/z* calcd for C₂₅H₃₇N₂O [M + H]⁺ 381.2906, found 381.2904.

Synthesis of 4d: A solution of 3 (665 mg, 2.00 mmol), di-*n*-octylamine (0.73 mL, 2.40 mmol), lithium bis(trimethylsilyl)amide (736 mg, 4.40 mmol), XPhos (23.0 mg, 0.048 mmol, 2.4 mol%) and $Pd_2(dba)_3$ (18.3 mg, 0.020 mmol, 1.0 mol%) in anhydrous THF (10 mL) was stirred at 65 °C for 24 h. Then, to the solution

2N HCl (6 mL) was added, followed by a saturated aqueous sodium bicarbonate solution (40 mL). The resulting solution was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. Column chromatography of the residue on silica gel ($R_f = 0.20$, hexane : ethyl acetate = 30 : 1) gave **4d** as an orange oil (548 mg, 56%). **4d**: oil; ¹H NMR (400 MHz, CDCl₃) δ 0.80-0.92 (m, 9H), 1.15-1.37 (m, 24H), 1.38-1.46 (m, 2H), 1.51 (quint, J = 7.3 Hz, 4H), 1.77 (quint, J = 7.3 Hz, 2H), 3.16 (t, J = 7.3 Hz, 4H), 3.88 (t, J = 7.3 Hz, 2H), 6.80 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 7.66 (t, J = 7.5 Hz, 1H), 8.03 (d, J = 7.5 Hz, 1H), 8.22 (d, J = 7.5 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.1 14.2, 22.6, 22.7, 26.8, 27.1, 27.4, 29.0, 29.4, 29.5, 31.6, 31.9, 40.3, 54.6, 105.5, 118.4, 124.0, 126.4, 127.4, 127.57, 127.64, 128.3, 134.7, 144.2, 168.1; IR (KBr) 1694, 1632, 1605, 1470, 1450, 1377, 1312, 1219 cm⁻¹; HRMS (FAB) *m/z* calcd for C₃₃H₅₃N₂O [M + H]⁺ 493.4158, found 493.4173.

Synthesis of 4e: A solution of **3** (997 mg, 3.00 mmol), di-*n*-(2-ethylhexyl)amine (1.1 mL, 3.60 mmol), lithium bis(trimethylsilyl)amide (1.10 g, 6.60 mmol), XPhos (34.3 mg, 0.072 mmol, 2.4 mol%) and Pd₂(dba)₃ (27.5 mg, 0.030 mmol, 1.0 mol%) in anhydrous THF (7 mL) was stirred at 65 °C for 24 h. Then, to the solution HCl (9 ml) was added, followed by a saturated aqueous sodium bicarbonate solution (60 mL). The resulting solution was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄ and concentrated in vacuo. Column chromatography of the residue on silica gel ($R_f = 0.20$, hexane : ethyl acetate = 30 : 1) gave **4e** as an orange oil (167 mg, 11%). **4e**: oil; ¹H NMR (400 MHz, (CD₃)₂CO) δ 0.77-0.92 (m, 15H), 1.12-1.52 (m, 22H), 1.55-1.64 (m, 2H), 1.77 (quint, *J* = 7.3 Hz, 2H), 3.10 (t, *J* = 7.3 Hz, 4H), 3.90 (t, *J* = 7.3 Hz, 2H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.78 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 8.38 (d, *J* = 7.9 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 10.75, 10.81, 14.17, 14.21, 22.7, 23.3, 24.47, 24.50, 26.8, 28.7, 28.8, 29.0, 31.17, 31.21, 31.7, 37.3, 40.4, 59.4, 105.7, 119.6, 124.1, 126.3, 127.4, 127.6, 127.8, 128.4, 134.4, 134.9, 145.7, 168.2; IR (KBr) 1690, 1628, 1605, 1474, 1443, 1377, 1312, 1219 cm⁻¹; HRMS (FAB) *m/z* calcd for C₃₃H₅₃N₂O [M + H]⁺ 493.4158, found 493.4130.

Synthesis of 5a: Methylmagnesium chloride (1.0 mL, 3 M solution in THF, 3.08 mmol) was added to a solution of **4a** (280 mg, 0.766 mmol) in anhydrous THF (2.0 mL) at 0°C. The mixture was stirred at 60°C for 2 h. After cooling to 0°C, water (0.5 mL) was added, and then perchloric acid (60%, 0.6 mL) was added to the reaction mixture. Ice water (90 mL) was added to the obtained yellow solution. The resulting yellow precipitate was collected by vacuum filtration and washed with water to yield **5a** as a yellow solid (350 mg, 98%). **5a**: mp 110.0–111.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.81-0.96 (m, 9H), 1.19-1.43 (m, 10H), 1.44-1.52 (m, 2H), 1.70-1.79 (m, 1H), 2.0 (quint, *J* = 7.3 Hz, 2H), 3.07-3.17 (m, 2H), 3.25 (s, 3H), 4.68 (t, *J* = 7.3 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 8.01-8.08 (m, 2H), 8.61 (d, *J* = 7.8 Hz, 1H), 8.74 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 10.6, 12.8, 13.8, 13.9, 22.2, 22.8, 25.5, 26.3, 28.6, 30.3, 31.1, 32.4, 36.5, 42.7, 47.4, 121.1, 123.0, 128.7, 129.3, 129.9, 130.6, 135.1, 136.1, 136.7, 146.8, 169.2; IR (KBr) 1593, 1512, 1477, 1443, 1342, 1219 cm⁻¹; HRMS (FAB) *m/z* calcd for C₂₆H₃₉N⁺ [M + H]⁺ 365.3078, found 365.3090.

Synthesis of 5b: Methylmagnesium chloride (0.8 mL, 3 M solution in THF, 2.44 mmol) was added to a solution of 4b (198 mg, 0.608 mmol) in anhydrous THF (2.0 mL) at 0°C. The mixture was stirred at 60°C for 2 h. After cooling to 0°C, water (0.4 mL) was added, and then perchloric acid (60%, 0.8 mL) was added to the reaction mixture. Ice water (90 mL) was added to the obtained orange solution. The resulting orange precipitate was collected by vacuum filtration and washed with water to yield 5b as an orange solid (220 mg, 90%). 5b: mp 93.0–94.0°C; ¹H NMR (400 MHz, DMSO-*d*₆) δ 0.86 (t, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 7.3 Hz), 1.00 (t, J = 7.3 Hz), 1.00

3H), 1.21-1.36 (m, 4H), 1.37-1.48 (m, 2H), 1.57 (sext, J = 7.3 Hz, 2H), 1.85-1.96 (m, 4H), 3.15 (s, 3H), 4.40 (t, J = 7.3 Hz, 2H), 4.63 (t, J = 7.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 1H), 8.11 (t, J = 7.7 Hz, 1H), 8.47 (d, J = 8.2 Hz, 1H), 8.77 (d, J = 7.7 Hz, 1H), 8.94 (d, J = 7.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 13.87, 13.93, 14.0, 19.4, 22.5, 26.6, 30.7, 31.0, 31.4, 47.7, 70.1, 108.5, 122.3, 123.9, 124.9, 128.5, 129.7, 131.3, 134.3, 134.5, 161.7, 165.5; IR (KBr) 1740, 1447, 1366, 1215 cm⁻¹; HRMS (FAB) *m/z* calcd for C₂₂H₃₁NO⁺ [M + H]⁺ 325.2401, found 325.2381.

Synthesis of 5c: Methylmagnesium chloride (0.6 mL, 3 M solution in THF, 1.88 mmol) was added to a solution of **4c** (179 mg, 0.470 mmol) in anhydrous THF (1.5 mL) at 0°C. The mixture was stirred at 60°C for 2 h. After cooling to 0°C, water (0.3 mL) was added, and then perchloric acid (60%, 0.6 mL) was added to the reaction mixture. Ice water (90 mL) was added to the obtained blue purple solution. The resulting blue purple precipitate was collected by vacuum filtration and washed with water to yield **5c** as a blue purple solid (217 mg, 97%). **5c**: mp 82.0–83.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (t, *J* = 7.3 Hz, 3H), 1.04 (t, *J* = 7.3 Hz, 3H), 1.41-1.53 (m, 4H), 1.80-1.91 (m, 4H), 1.97 (quint, *J* = 7.3 Hz, 2H), 3.05 (s, 3H), 3.78 (t, *J* = 7.3 Hz, 4H), 4.60 (t, *J* = 7.3 Hz, 2H), 6.87 (d, *J* = 9.2 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 9.2 Hz, 1H), 8.51 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 12.7, 14.0, 14.1, 20.3, 22.5, 26.6, 28.7, 31.1, 31.4, 47.0, 55.1, 111.7, 121.4, 124.0, 124.6, 126.7, 127.4, 128.0, 132.6, 135.8, 153.0, 154.0; IR (KBr) 1709, 1628, 1466, 1369, 1312, 1285, 1207 cm⁻¹; HRMS (FAB) *m/z* calcd for C₂₆H₄₀N₂⁺ [M + H]⁺ 380.3186, found 380.3192.

Synthesis of 5d: Methylmagnesium chloride (0.8 mL, 3 M solution in THF, 2.40 mmol) was added to a solution of **4d** (296 mg, 0.60 mmol) in anhydrous THF (2.0 mL) at 0°C. The mixture was stirred at 60°C for 2 h. After cooling to 0°C, water (0.5 mL) was added, and then perchloric acid (60%, 0.5 mL) was added to the reaction mixture. Ice water (90 mL) was added to the obtained blue purple solution. The resulting blue purple precipitate was collected by vacuum filtration and washed with water to yield **5d** as a blue purple solid (325 mg, 92%). **5d**: mp 81.0–82.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.80-0.94 (m, 9H), 1.22-1.50 (m, 26H), 1.79-1.90 (m, 4H), 1.96 (quint, *J* = 7.3 Hz, 2H), 3.04 (s, 3H), 3.76 (t, *J* = 7.3 Hz, 4H), 4.60 (t, *J* = 7.3 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 1H), 7.87 (t, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 8.50 (d, *J* = 7.8 Hz, 1H), 8.55 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 12.6, 14.0, 14.2, 22.5, 22.7, 26.56, 26.62, 26.9, 29.3, 29.4, 31.1, 31.4, 31.8, 46.9, 55.3, 111.5, 121.3, 123.9, 124.5, 126.5, 127.4, 127.9, 132.7, 135.8, 152.8, 153.9; IR (KBr) 1631, 1570, 1466, 1312, 1219 cm⁻¹; HRMS (FAB) *m/z* calcd for C₃₄H₅₆N₂⁺ [M + H]⁺ 492.4438, found 492.4437.

Synthesis of 5e: Methylmagnesium chloride (0.52 mL, 3 M solution in THF, 1.56 mmol) was added to a solution of **4e** (190 mg, 0.386 mmol) in anhydrous THF (2.0 mL) at 0°C. The mixture was stirred at 60°C for 2 h. After cooling to 0°C, water (0.2 mL) was added, and then perchloric acid (60%, 0.4 mL) was added to the reaction mixture. Ice water (90 mL) was added to the obtained blue solution. The resulting blue precipitate was collected by vacuum filtration and washed with water to yield **5e** as a blue solid (210 mg, 91%). **5e**: mp 52.0–53.0°C; ¹H NMR (400 MHz, CD₃OD) δ 0.73-0.95 (m, 15H), 1.10-1.54 (m, 22H), 1.90-2.05 (m, 4H), 3.06 (s, 3H), 3.85 (d, *J* = 7.3 Hz, 4H), 4.60 (t, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 1H), 7.96 (t, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 8.7 Hz, 1H), 8.70 (d, *J* = 7.8 Hz, 1H), 8.90 (d, *J* = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 10.4, 12.7, 13.8, 13.9, 22.3, 22.9, 23.8, 26.3, 28.3, 30.5, 30.8, 31.2, 37.4, 46.8, 58.6, 114.3, 122.8, 123.8, 124.9, 127.6, 127.8, 128.3, 133.2, 135.7, 155.8, 156.3; IR (KBr) 1681, 1601, 1512,

1477, 1427, 1219 cm⁻¹; HRMS (FAB) m/z calcd for C₃₄H₅₆N₂⁺ [M + H]⁺ 492.4438, found 492.4460.

Synthesis of SQ1: A solution of semisquaric acid **6** (191 mg, 0.550 mmol) and **7a** (253 mg, 0.550 mmol) in toluene (5 mL) and *n*-butanol (5 mL) was heated to reflux in a Dean-Stark apparatus for 16 h. After completion of the reaction, the mixture was concentrated in vacuo to give a residue. The residue was purified by column chromatography (silica gel, $R_f = 0.35$, chloroform : methanol = 15 : 1) to yield **SQ1** (67 mg, 18%) as a brown solid. **SQ1**: mp 219.0–220.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.80-0.92 (m, 6 H), 1.16-1.51 (m, 16 H), 1.72-1.95 (m, 10 H), 4.15 (br s, 2H), 4.18 (br s, 2H), 6.10 (s, 1H), 6.37 (s, 1H), 7.03 (d, J = 7.9 Hz, 1H), 7.07 (d, J = 7.9 Hz, 1H), 7.51 (t, J = 7.9 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.85 (t, J = 7.9 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 8.08 (s, 1H), 8.13 (dd, J = 8.3, 1.8 Hz, 1H), 9.20 (brs, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 14.1, 14.2, 22.67, 22.72, 27.0, 27.15, 27.19, 27.4, 28.9, 29.3, 29.5, 31.7, 31.9, 44.2, 49.2, 89.0, 91.3, 107.2, 109.1, 121.8, 124.2, 125.6, 125.8, 128.5, 129.8, 129.9, 130.5, 131.2, 132.0, 141.7, 142.4, 146.6, 152.0, 170.3, 170.54, 177.9, 179.9, 183.2; IR (KBr) 1731, 1693, 1566, 1501, 1354, 1285, 1223 cm⁻¹; HRMS (FAB) *m/z* calcd for C₄₂H₄₉N₂O₄ [M + H]⁺ 645.3692, found 645.3722.

Synthesis of SQ2: A solution of semisquaric acid **6** (167 mg, 0.480 mmol) and **7b** (245 mg, 0.480 mmol) in toluene (5 mL) and *n*-butanol (5 mL) was heated to reflux in a Dean-Stark apparatus for 16 h. After completion of the reaction, the mixture was concentrated in vacuo to give a residue. The residue was purified by column chromatography (silica gel, $R_f = 0.30$, chloroform : methanol = 15 : 1) to yield **SQ2** (46 mg, 13%) as a brown solid. **SQ2**: mp 261.0–262.0°C; ¹H NMR (400 MHz, THF- d_8) δ 0.85-0.94 (m, 6 H), 1.26-1.46 (m, 16 H),1.48-1.57 (m, 4 H), 1.86-1.94 (m, 4 H), 2.10 (s, 6H), 4.22 (t, J = 7.3 Hz, 2H), 4.32 (t, J = 7.3 Hz, 2H), 6.22 (s, 1H), 6.30 (s, 4H), 7.07 (dd, J = 7.6, 2.1 Hz, 1H), 7.42-7.48 (m, 2H), 7.63 (d, J = 8.0 Hz, 1H), 7.74 (t, J = 8.60 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 8.16 (dd, J = 8.9, 1.4 Hz, 1H), 8.39 (d, J = 8.9 Hz, 1H), 8.68 (s, 1H), 9.58 (d, J = 8.0 Hz, 1H); ¹³C NMR (150 MHz, THF- d_8) δ 14.06, 14.11, 23.2, 26.7, 27.4, 27.6, 28.2, 29.2, 29.9, 30.0, 32.3, 32.5, 43.9, 44.5, 52.2, 89.4, 92.2, 105.9, 112.1, 120.4, 123.3, 126.8, 127.6, 127.7, 128.6, 128.9, 129.8, 130.9, 131.3, 131.6, 132.0, 133.3, 135.6, 142.4, 143.1, 150.1, 167.3, 173.2, 180.8, 181.9, 183.6, 201.0, 201.2, 201.3; IR (KBr) 1728, 1690, 1555, 1501, 1470, 1431, 1254, 1219, cm⁻¹; HRMS (FAB) *m/z* calcd for C₄₂H₄₉N₂O₄ [M + H]⁺ 645.3692, found 645.3722.

Synthesis of SQ3: Semisquarine **8** (293 mg, 0.600 mmmol) was dissolved in a mixed solution of 40 wt% aqueous NaOH solution (0.1 mL) and EtOH (3 mL). The solution was refluxed for 5 min. The reaction mixture was neutralized with 2N HCl, and the resulting organic layer was concentrated in vacuo. The residue was then mixed with a solution of **5a** (278 mg, 0.600 mmol) in toluene (6 mL) and *n*-butanol (6 mL). The mixture was heated to reflux in a Dean-Stark apparatus for 17 h. After completion of the reaction, the mixture was concentrated in vacuo to give a residue. The residue was purified by column chromatography (silica gel, $R_f = 0.36$, chloroform : methanol = 20 : 1) to yield **SQ3** (108 mg, 22%) as a brown solid. **SQ3**: mp 232.0–233.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.82-0.90 (m, 12H), 1.18-1.39 (m, 20 H), 1.40-1.51 (m, 4H), 1.67-1.76 (m, 1H), 1.83-1.94 (m, 4 H), 2.10 (s, 6H), 2.94 (d, J = 6.4 Hz, 1H), 4.04-4.24 (m, 4H), 6.13 (s, 1H), 6.33 (s, 1H), 6.95 (d, J = 7.6 Hz, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.36 (d, J = 9.0 Hz, 1H), 7.85 (t, J = 8.1 Hz, 1H), 8.01 (d, J = 9.0 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 8.18-8.29 (m, 2H), 8.74 (s, 1H), 9.15 (brs, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 11.0, 14.16, 14.21, 14.3, 22.7, 23.3, 25.9, 26.9, 27.0, 27.2, 27.7, 29.96, 29.03, 29.3, 29.5, 31.7, 31.9, 32.8, 36.6, 41.8, 44.1, 44.2, 51.3, 88.1, 90.8, 106.8, 111.2, 122.9, 125.5, 126.0, 127.2, 128.7, 129.4, 129.5, 130.4, 131.1, 131.7, 133.7, 134.7, 134.8, 134.8, 140.20, 140.23, 142.0, 151.4, 170.3, 128.7, 129.4, 129.5, 130.4, 131.1, 131.7, 133.7, 134.7, 134.8, 134.8, 140.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.20, 140.23, 142.0, 151.4, 170.3, 180.20, 140.20, 140.23, 142.0, 151.4, 17

171.6, 176.3, 177.7, 183.3; IR (KBr) 1728, 1690, 1574, 1493, 1250, 1219 cm⁻¹; HRMS (FAB) m/z calcd for C₅₄H₆₇N₂O₄ [M + H]⁺ 807.5101, found 807.5079.

Synthesis of SQ4: Semisquarine 8 (195 mg, 0.400 mmmol) was dissolved in a mixed solution of 40 wt% aqueous NaOH solution (0.07 mL) and EtOH (2 mL). The solution was refluxed for 5 min. The reaction mixture was neutralized with 2N HCl, and the resulting organic layer was concentrated in vacuo. The residue was then mixed with a solution of **5b** (170 mg, 0.400 mmol) in toluene (6 mL) and *n*-butanol (6 mL). The mixture was heated to reflux in a Dean-Stark apparatus for 17 h. After completion of the reaction, the mixture was concentrated in vacuo to give a residue. The residue was purified by column chromatography (silica gel, $R_f = 0.41$, dichloromethane : methanol = 15 : 1) to yield **SQ4** (146 mg, 48%) as a brown solid. **SO4**: mp 226.0–227.0°C; ¹H NMR (600 MHz, DMSO- d_6) δ 0.82 (t, J = 6.9 Hz, 3H), 0.86 (t, J = 7.6 Hz, 3H), 1.01 (t, J = 7.6 Hz, 3H), 1.20-1.38 (m, 12H), 1.40-1.47 (m, 4H), 1.57 (sext, J = 7.6 Hz, 2H), 1.78-1.89 (m, 6 H), 2.00 (s, 6H), 4.22 (t, J = 6.9 Hz, 2H), 4.25-4.30 (m, 4H), 5.97 (s, 1H), 6.16 (s, 1H), 7.00 (d, J = 8.3 Hz, 1H), 7.29 (d, J = 8.3 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.82 (t, J = 8.7 Hz, 1H), 8.08 (dd, J = 8.6, 2.1 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.7 Hz, 1H), 8.30 (d, J = 8.7 Hz, 1H), 8.65 (d, J = 2.0 Hz, 1H), 9.15 (d, J = 8.0 Hz, 1H); ¹³C NMR (150 MHz, DMSO- d_6) δ 14.1, 14.18, 14.24, 19.4, 22.4, 26.5, 26.67, 26.70, 27.4, 28.7, 29.0, 29.1, 31.3, 31.4, 31.6, 40.0, 44.0, 51.0, 69.2, 88.0, 90.4, 109.5, 112.7, 122.9, 123.0, 125.2, 126.0, 126.8, 127.2, 129.1, 130.4, 130.5, 130.6, 131.3, 132.1, 132.8, 133.9, 135.4, 142.3, 150.0, 152.8, 167.7, 170.9, 176.6, 177.4, 181.9; IR (KBr) 1728, 1682, 1551, 1477, 1443, 1369, 1250, 1207 cm⁻¹; HRMS (FAB) m/z calcd for C₅₀H₅₉N₂O₅ [M + H]⁺ 767.4424, found 767.4393.

Synthesis of SQ5: Semisquarine 8 (98 mg, 0.200 mmmol) was dissolved in a mixture solution of 40wt% aqueous NaOH solution (0.07 mL) and EtOH (2 mL). The solution was refluxed for 5 min. The reaction mixture was neutralized with 2N HCl and the resulting organic layer was concentrated in vacuo. The residue was then mixed with a solution of 5c (96 mg, 0.200 mmol) in toluene (6 mL) and *n*-butanol (6 mL). The mixture was heated to reflux in a Dean-Stark apparatus for 17 h. After completion of the reaction, the mixture was concentrated in vacuo to give a residue. The residue was purified by column chromatography (silica gel, $R_f = 0.35$, chloroform : methanol = 15 : 1) to yield **SO5** (19 mg, 12%) as a dark green solid. **SO5**: mp 250.0-251.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.80-0.94 (m, 12H), 1.14-1.39 (m, 16H), 1.40-1.50 (m, 4H), 1.56 (quint, J = 7.3 Hz, 4H), 1.78-1.94 (m, 4H), 2.10 (s, 6H), 3.29 (t, J = 7.3 Hz, 4H), 4.04-4.24 (m, 4H), 6.06 (s, 1H), 6.32 (s, 1H), 6.93 (d, J = 7.8 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 7.32 (d, J = 8.7 Hz, 1H), 7.82 (t, J = 8.5 Hz, 1H), 7.98 (d, J = 8.7 Hz, 1H), 8.16-8.20 (m, 2H), 8.24 (d, J = 8.5 Hz, 1H), 8.72 (s, 1H), 9.11 (d, J = 7.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 14.1, 14.16, 14.21, 19.4, 20.6, 22.70, 22.73, 26.95, 27.00, 27.2, 27.6, 29.1, 29.3, 29.45, 29.54, 29.9, 31.7, 31.9, 44.3, 50.9, 54.3, 87.68, 87.71, 90.3, 108.6, 111.1, 117.4, 122.8, 125.1, 126.8, 126.9, 127.1, 127.7, 128.6, 130.1, 131.0, 131.2, 131.6, 133.8, 136.0, 142.3, 146.7, 151.4, 169.83, 170.3, 173.5, 177.4, 183.4; IR (KBr) 1709, 1605, 1566, 1493, 1439, 1331, 1250, 1200 cm⁻¹; HRMS (FAB) m/z calcd for C₅₄H₆₈N₃O₄ [M + H]⁺ 822.5210, found 822.5233.

Synthesis of SQ6: Semisquarine **8** (230 mg, 0.470 mmmol) was dissolved in a mixture solution of 40wt% aqueous NaOH solution (0.07 mL) and EtOH (2 mL). The solution was refluxed for 5 min. The reaction mixture was neutralized with 2N HCl and the resulting organic layer was concentrated in vacuo. The residue was then mixed with a solution of **5d** (278 mg, 0.470 mmol) in toluene (6 mL) and *n*-butanol (6 mL). The mixture was heated to reflux in a Dean-Stark apparatus for 17 h. After completion of the reaction, the

mixture was concentrated in vacuo to give a residue. The residue was purified by column chromatography (silica gel, $R_f = 0.40$, chloroform : methanol = 20 : 1) to yield **SQ6** (59 mg, 13%) as a dark green solid. **SQ6**: mp 209.0–210.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.80-0.94 (m, 12H), 1.14-1.39 (m, 32H), 1.40-1.51 (m, 4H), 1.57 (quint, J = 7.3 Hz, 4H), 1.79-1.94 (m, 4H), 2.11 (s, 6H), 3.28 (t, J = 7.3 Hz, 4H), 4.04-4.24 (m, 4H), 6.07 (s, 1H), 6.33 (s, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.99 (d, J = 7.8 Hz, 1H), 7.33 (d, J = 9.0 Hz, 1H), 7.82 (t, J = 8.0 Hz, 1H), 7.98 (d, J = 9.0 Hz, 1H), 8.16-8.20 (m, 2H), 8.24 (d, J = 8.0 Hz, 1H), 8.72 (s, 1H), 9.12 (d, J = 7.3 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 14.16, 14.23, 22.69, 22.71, 22.8, 26.9, 27.0, 27.2, 27.3, 27.4, 27.6, 29.1, 29.3, 29.4, 29.5, 29.6, 31.7, 31.86, 31.93, 43.9, 44.3, 50.9, 54.5, 87.7, 90.3, 108.6, 111.0, 117.2, 122.7, 125.3, 126.7, 126.8, 127.1, 127.8, 128.6, 130.1, 130.9, 131.1, 131.6, 132.0, 133.7, 134.3, 135.9, 142.2, 146.7, 151.4, 169.8, 170.4, 173.1, 177.1, 183.7; IR (KBr) 1735, 1690, 1550, 1493, 1443, 1250, 1219 cm⁻¹; HRMS (FAB) *m/z* calcd for C₆₂H₈₄N₃O₄ [M + H]⁺ 934.6462, found 934.6436.

Synthesis of SQ7: Semisquarine **8** (157 mg, 0.320 mmmol) was dissolved in a mixture solution of 40wt% aqueous NaOH solution (0.07 mL) and EtOH (2 mL). The solution was refluxed for 5 min. The reaction mixture was neutralized with 2N HCl and the resulting organic layer was concentrated in vacuo. The residue was then mixed with a solution of **5e** (189 mg, 0.320 mmol) in toluene (6 mL) and *n*-butanol (6 mL). The mixture was heated to reflux in a Dean-Stark apparatus for 17 h. After completion of the reaction, the mixture was concentrated in vacuo to give a residue. The residue was purified by column chromatography (silica gel, $R_f = 0.40$, chloroform : methanol = 20 : 1) to yield **SQ7** (34 mg, 11%) as a dark green solid. **SQ7**: mp 234.0–235.0°C; ¹H NMR (400 MHz, CDCl₃) δ 0.75-0.92 (m, 18H), 1.14-1.51 (m, 32H), 1.62-1.73 (m, 2H), 1.80-1.94 (m, 4H), 2.11 (s, 6H), 3.24 (d, J = 6.9 Hz, 4H), 4.04-4.24 (m, 4H), 6.05 (s, 1H), 6.31 (s, 1H), 6.95-7.01 (m, 2H), 7.32 (d, J = 8.8 Hz, 1H), 7.81 (t, J = 7.8 Hz, 1H), 7.98 (d, J = 8.8 Hz, 1H), 8.14-8.28 (m, 3H), 8.72 (s, 1H), 9.10 (d, J = 6.4 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 10.8, 14.2, 22.7, 23.3, 24.4, 27.0, 27.2, 28.7, 28.8, 29.2, 29.3, 29.5, 31.08, 31.11, 31.3, 31.7, 31.9, 37.5, 43.9, 44.3, 50.8, 58.5, 87.7, 90.3, 109.0, 111.1, 117.9, 122.8, 125.1, 126.66, 126.73, 127.1, 128.1, 128.5, 130.1, 131.0, 131.2, 131.6, 133.8, 135.6, 142.4, 148.2, 151.3, 169.5, 170.4, 172.8, 177.2, 183.6; IR (KBr) 1733, 1705, 1570, 1493, 1443, 1250, 1200 cm⁻¹; HRMS (FAB) *m/z* calcd for C₆₂H₈₄N₃O₄ [M + H]⁺ 934.6462, found 934.6479.

Fabrication and measurement of the dye-sensitized solar cell: The dye-sensitized solar cells were fabricated according to the previously reported method of Ito *et al.*³⁹ FTO (F-doped tin oxide; 4 mm thickness, 13 Ω \Box^{-1} , Nippon Sheet Glass) glass substrate was washed for 15 min each with an aqueous detergent solution, distilled water, and ethanol using an ultrasonic bath. The FTO glass substrate was immersed in a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min, and then washed with distilled water and ethanol. A commercial TiO₂ paste (PST-18NR, JGC Catalysts and Chemicals Ltd.) was deposited onto the FTO glass substrate by the squeegee method using mending tape (4 μ m thickness) twice to obtain a 8 μ m transparent TiO₂ film. After drying the FTO glass substrate at 125 °C in air for 10 min, a commercial TiO₂ paste (PST-400C, JGC Catalysts and Chemicals Ltd.) was deposited once to obtain a 4 μ m scattering layer. The resulting substrate was sintered at 500 °C for 15 min. After cooling to room temperature, the sintered TiO₂ film was immersed in a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min, and then washed with distilled water and ethanol. After drying, the TiO₂ film was sintered at 500 °C for 30 min to obtain a μ m thickness) and a scattering layer (4 μ m thickness). The TiO₂ photoelectrode consisting of a transparent layer (8 μ m thickness) and a scattering layer (4 μ m thickness). The TiO₂ electrode was then immersed in a solution of SQ dye (0.12 mM) and

chenodeoxycholic acid (6 mM) in acetonitrile/t-butyl alcohol (v : v = 1 : 1). The dye adsorption was performed in the dark at room temperature for 15 h, washed with ethanol to remove any non-adsorbed dye, and dried. The dye-coated TiO₂ electrode and Pt-sputtered FTO glass counter electrode were assembled into a sandwich type cell (active area: 5 mm \times 4 mm). An electrolyte composed of 0.5 M DMPImI (1,2-dimethyl-3-*n*-propylimidazolium iodide), 0.05 M I₂, and 0.5 M LiI in a mixed solution of acetonitrile and chloroform (v : v = 1 : 1) was added to the cell. After assembling the cell, silver paint was applied to the edges of the TiO₂ photoelectrode and counter electrode of the cells to reduce series resistance. The I–V curves of the cells were measured under illumination with a simulated sunlight condition at AM1.5 (100 mW cm⁻²) generated by a Bunko-Keiki CEP-2000 system. A mask was used to regulate the active area to 0.2 cm². IPCE spectra were measured on a Bunko-Keiki CEP-2000 system under monochromatic light illumination. Electrochemical impedance spectra were measured using VersaSTAT3 potentiostat at open circuit conditions under 1 sun light intensity (25°C). The spectra were fitted using Zview software (Scribner).

Deposition studies of SQ dyes

A TiO₂ photoelectrode (transparent layer: 8 μ m, cell area: 1.0 cm × 1.0 cm, 1.0 cm²) was immersed in a solution of SQ dye (0.12 mM) and chenodeoxycholic acid (6 mM) in acetonitrile/*t*-butyl alcohol (v : v = 1 : 1) (SQ1, SQ2, SQ3, SQ5, SQ6 and SQ7) or in THF (SQ4) for 15 h. The dye-adsorbed TiO₂ photoelectrode was washed with ethanol and dried. Then the adsorbed SQ dye was desorbed by using 4.0 mL (SQ1, SQ4, SQ5, SQ6 and SQ7) or 8.0 mL (SQ2 and SQ3) of a mixture solution of 2M HCl and ethanol at 1 : 9 ratio by volume. After that, the UV/Vis/NIR absorption spectra of the desorbed solution were measured (Figure S6). In order to obtain the ε values, the UV/Vis/NIR absorption spectra of the SQ dyes with reliable concentration values (SQ1, SQ2, SQ4–SQ7: 1.0×10^{-5} M, SQ3: 5.0×10^{-6} M) were measured in the mixture of 2M HCl and ethanol in the ratio of 1 : 9 (v : v) were as follows: SQ1 ($\lambda_{max} = 767$ nm, $\varepsilon = 109,000$), SQ2 ($\lambda_{max} = 781$ nm, $\varepsilon = 123,000$), SQ3 ($\lambda_{max} = 792$ nm, $\varepsilon = 132,000$), SQ4 ($\lambda_{max} = 727$ nm, $\varepsilon = 23,000$).

Supporting Information Available: ¹H and ¹³C NMR spectra of new compounds. This material is available free of charge via the internet at http://pubs.acs.org.

Acknowledgements: This work was partially supported by JSPS KAKENHI Grant Number JP16K05894, the Koshiyama Research Grant, the Research Foundation for the Electrotechnology of Chubu and the Strategic Core Technology Advancement Program, "Supporting Industry Program".

References

(1) (a) O'Regan, B.; Grätzel, M. *Nature* 1991, *353*, 737–740. (b) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* 2010, *110*, 6595–6663. (c) Ooyama, Y.; Yutaka, H. *ChemPhysChem* 2012, *13*, 4032–4080. (d) Wu, Y.; Zhu, W. *Chem. Soc. Rev.* 2013, *42*, 2039–2058. (e) Al-Alwani, M. A. M.; Mohamad, A. B.; Ludin, N. A.; Kadhum, A. A. H.; Sopian, K. *Renew. Sust.*

	Energy Rev. 2016, 65, 183–213. (f) Chaurasia, S.; Lin, J. T. Chem. Rec. 2016, 16, 1311–1336.
(2)	(a) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. Jpn. J. Appl. Phys. 2006, 45,
	638-640. (b) Gao, F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M.; Jing, X.; Humphry-baker, R.; Wang,
	P.; Zakeeruddin, S. M.; Grätzel, M. J. Am. Chem. Soc. 2008, 130, 10720-10728. (c) Chen, C. Y.;
	Wang, M.; Li, J. Y.; Pootrakulchote, N.; Alibabaei, L.; Ngoc-Le, C. H.; Decoppet, J. D.; Tsai, J. H.;
	Grätzel, C.; Wu, C. G.; Zakeeruddin, S. M.; Grätzel, M. ACS Nano 2009, 3, 3103–3109. (d) Yu, Q. J.;
	Wang, Y. H.; Yi, Z. H.; Zu, N. N.; Zhang, J.; Zhang, M.; Wang, P. ACS Nano 2010, 4, 6032–6038.
	(e) Pashaei, B.; Shahroosvand, Graetzel, M. Nazeeruddin, N. K. Chem. Rev. 2016, 116, 9485–9564.
(3)	Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B. F. E.; Ashari-Astani, N.; Tavernelli,
	I.; Rothlisberger, U.; Nazeeruddin, M. K.; Grätzel, M. Nat. Chem. 2014, 6, 242–247.
(4)	Yao, Z.; Zhang, M.; Wu, H.; Yang, L.; Li, R.; Wang, P. J. Am. Chem. Soc. 2015, 137, 3799–3802.
(5)	Mishra, A.; Fischer, M. K. R.; Bäuerle, P. Angew. Chem. Int. Ed. 2009, 48, 2474–2499.
(6)	Zhou, N.; Prabakaran, K.; Lee, B.; Chang, S. H.; Harutyunyan, B.; Guo, P.; Butler, M. R.; Timalsina,
	A.; Bedzyk, M. J.; Ratner, M. A.; Vegiraju, S.; Yau, S.; Wu, C. G.; Chang, R. P. H.; Facchetti, A.;
	Chen, M. C.; Marks, T. J. J. Am. Chem. Soc. 2015, 137, 4414–4423
(7)	Yang, J.; Ganesan, P.; Teuscher, J.; Moehl, T.; Kım, Y. J.; Yı, C.; Comte, P.; Peı, K.; Holcombe, T.
	W.; Nazeeruddin, M. K.; Hua, J.; Zakeeruddin, S. M.; Tian, H.; Grätzel, M. J. Am. Chem. Soc. 2014,
(0)	136, 5722-5730.
(8)	(a) Yum, JH.; Jang, SR.; Walter, P.; Geiger, I.; Nuesch, F.; Kim, S.; Ko, J.; Gratzel, M.;
	Nazeeruddin, M. K. Chem. Commun. 2007, 4680–4682. (b) Choi, H.; Kim, S.; Kang, S. O.; Ko, J.;
	Kang, MS.; Clifford, J. N.; Forneli, A.; Palomares, E.; Nazeeruddin, M. K.; Gratzel, M. Angew.
	Chem. Int. Ed. 2008, 47, 8259–8263. (c) Qin, C.; Numata, Y.; Zhang, S.; Islam, A.; Yang, X.;
	Sodeyama, K.; Tateyama, Y.; Han, L. <i>Adv. Funct. Mater.</i> 2013, 23, $3/82-3/89$. (d) Pei, K.; Wu, Y.;
	Li, H.; Geng, Z.; Tian, H.; Zhu, W. H. ACS Appl. Mater. Interfaces 2015, 7, 5296–5304. (e) Hua, Y.;
	Lin Lee, L. I.; Znang, C.; Znao, J.; Cnen, I.; Wong, WY.; Wong, WK.; Znu, X. J. Mater. Chem.
	A 2015, 5, 15848–15855. (1) Islam, A.; Akntaruzzaman, M.; Chowdnury, T. H.; Qin, C.; Han, L.;
	4623.
(9)	(a) Yum, JH.; Baranoff, E.; Wenger, S.; Nazeeruddin, M. K.; Grätzel, M. Energy Environ. Sci. 2011,
	4, 842-857. (b) Balasingam, S. K.; Lee, M.; Kang, M. G.; Jun, Y. Chem. Commun. 2013, 49, 1471-
	1487.
(10)	Zhang, K.; Qin, C.; Yang, X.; Islam, A.; Zhang, S.; Chen, H.; Han, L. Adv. Energy Mater. 2014, 4,
	1301966.
(11)	(a) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. J. Am. Chem. Soc. 2009, 131, 6050-6051 (b)
	Yang, W. S.; Noh, J. H.; Jeon, N, J; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. Science 2015, 348, 1234-
	1237.
(12)	Kinoshita, T.; Nonomura, K.; Jeon, N. J.; Giordano, F.; Abate, A.; Uchida, S.; Kubo, T.; Seok, S. II;
	Nazeeruddin, M. K.; Hagfeldt, A.; Segawa, H.; Grätzel, M. Nat. Commun. 2015, 5, 1-8.
(13)	(a) Matsui, M.; Hashimoto, Y.; Funabiki, K.; Jin, J. Y.; Yoshida, T.; Minoura, H. Synth. Met. 2005,
	148, 147-153. (b) Otsuka, A.; Funabiki, K.; Sugiyama, N.; Mase, H.; Yoshida, T.; Minoura, H.;

Matsui, M. *Chem. Lett.* **2008**, *37*, 176–177. (c) Ono, T.; Yamaguchi, T.; Arakawa, H. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 831–835. (d) Tang, J.; Wu, W. J.; Hua, J. L.; Li, J.; Li, X.; Tian, H. *Energy Environ. Sci.* **2009**, *2*, 982–990. (e) Funabiki, K.; Mase, H.; Hibino, A.; Tanaka, N.; Mizuhata, N.; Sakuragi, Y.; Nakashima, A.; Yoshida, T.; Kubota, Y.; Matsui, M. *Energy Environ. Sci.* **2011**, *4*, 2186–2192.

- (14) (a) Kumaresan, D.; Thummel, R. P.; Bura, T.; Ulrich, G.; Ziessel, R. *Chem. Eur. J.* 2009, *15*, 6335–6339. (b) Kolemen, S.; Bozdemir, O. A.; Cakmak, Y.; Barin, G.; Erten-Ela, S.; Marszalek, M.; Yum, J.-H.; Zakeeruddin, S. M.; Nazeeruddin, M. K.; Grätzel, M.; Akkaya, E. U. *Chem. Sci.* 2011, *2*, 949–954. (c) Kubo, Y.; Eguchi, D.; Matsumoto, A.; Nishiyabu, R.; Yakushiji, H.; Shigaki, K.; Kaneko, M. *J. Mater. Chem. A* 2014, *2*, 5204–5211. (d) Singh, S. P.; Gayathri, T. *Eur. J. Org. Chem.* 2014, 4689–4707. (e) Mao, M.; Song, Q.-H. *Chem. Rec.* 2016, *16*, 719–733. (f) Ooyama, Y.; Kanda, M.; EnoKi, T.; Adachi, Y.; Ohshita, J. *RSC Adv.* 2017, *7*, 13072–13081. (g) Shi, W.-J.; Kinoshita, T.; Ng, D. K. P. *Asian J. Org. Chem.* 2017, *6*, 1476–1485.
- (15) (a) Shi, Y.; Hill, R. B. M.; Yum, J.-H.; Dualeh, A.; Barlow, S.; Grätzel, M.; Marder, S. R.; Nazeeruddin, M. K. Angew. Chem. Int. Ed. 2011, 50, 6619–6621. (b) Paek, S.; Choi, H.; Kim, C.; Cho, N.; So, S.; Song, K.; Nazeeruddin, M. K.; Ko, J. Chem. Commun. 2011, 47, 2874–2876. (c) Delcamp, J. H.; Shi, Y.; Yum, J.-H.; Sajoto, T.; Dell'Orto, E.; Barlow, S.; Nazeeruddin, M. K.; Marder, S. R.; Grätzel, M. Chem. Eur. J. 2013, 19, 1819–1827. (d) Qin, C.; Numata, Y.; Zhang, S.; Yang, X.; Islam, A.; Zhang, K.; Chen, H.; Han, L. Adv. Funct. Mater. 2014, 24, 3059–3066. (e) Jradi, F. M.; Kang, X.; Oneil, D.; Pajares, G.; Getmanenko, Y. A.; Szymanski, P.; Parker, T. C.; El-Sayed, M. A.; Marder, S. R. Chem. Mater. 2015, 27, 2480–2487. (f) Jradi, F. M.; O'Neil, D.; Kang, X.; Wong, J.; Szymanski, P.; Parker, T. C.; Anderson, H. L.; El-Sayed, M. A.; Marder, S. R. Chem. Mater. 1015, 27, 6305–6313. (g) Alagumalai, A.; Munavvar, M. F.; Vellimalai, P.; Sil, M. C.; Nithyanandhan, J. ACS Appl. Mater. Interfaces 2016, 8, 35353–35367. (h) Bisht, R.; Munavvar, F. K.; Singh, A. K.; Nithyanandhan, J. J. Org. Chem. 2017, 82, 1920–1930.
- (16) (a) Bessho, T.; Zakeeruddin, S. M.; Yeh, C.-Y.; Diau, E. W.-G.; Grätzel, M. Angew. Chem. 2010, 122, 6796–6799. (b) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. Science. 2011, 334, 629–634. (c) Yella, A.; Mai, C.-L.; Zakeeruddin, S. M.; Chang, S.-N.; Hsieh, C. H.; Yeh, C.-Y.; Grätzel, M. Angew. Chem. Int. Ed. 2014, 53, 2973–2977. (d) Higashinoa, T.; Imahori, H. Dalton Trans. 2015, 44, 448–463.
- (17) (a) Kimura, M.; Nomoto, H.; Masaki, N.; Mori, S. *Angew. Chem. Int. Ed.* 2012, *51*, 4371–4374. (b) Lim, B.; Margulis, G. Y.; Yum, J.-H.; Unger, E. L.; Hardin, B. E.; Grätzel, M.; McGehee, M. D.; Sellinger, A. *Org. Lett.* 2013, *15*, 784–787. (c) Wu, C.-H.; Chen, M.-C.; Su, P.-C.; Kuo, H.-H.; Wang, C.-L.; Lu, C.-Y.; Tsai, C.-H.; Wu, C.-C.; Lin, C.-Y. *J. Mater. Chem. A* 2014, *2*, 991–999. (d) Tejerina, L.; Martínez-Díaz, M. V.; Nazeeruddin, M. K.; Torres, T. *Chem. Eur. J.* 2016, *22*, 4369–4373.
- (18) (a) Huo, L.; Chen, H.-Y.; Hou, J.; Chen, T. L.; Yang, Y. Chem. Commun. 2009, 5570–5572. (b) Qin, C.; Islam, A.; Han, L. Dyes Pigm. 2012, 94, 553–560. (c) Shen, Z.; Chen, J.; Li, X.; Li, X.; Zhou, Y.; Yu, Y.; Ding, H.; Li, J.; Zhu, L.; Hua, J. ACS Sustain. Chem. Eng. 2016, 4, 3518–3525. (d) Adachi, Y.; Ooyama, Y.; Shibayama, N.; Ohshita, J. Chem. Lett. 2017, 46, 310–312.

2 3

4

5 6

7

8

9 10

11

12 13

14

15

16 17

18

19 20

21

22 23

24

25

26 27

28

29 30

31

32

33 34

35

36 37

38

39

40 41

42

43 44

45

46

47 48

49

50 51

52

53 54

55

56

57 58 59

60

(19) (a) Kim, S.-H.; Han, S.-K. Color. Technol. 2001, 117, 61–67. (b) Yagi, S.; Nakazumi, H. Functional Dves. 2006, 215-255. (c) Yagi, S.; Nakazumi, H. Top. Heterocycl. Chem. 2008, 14, 133-181. (d) Sreejith, S.; Carol, P.; Chithra, P.; Ajayaghosh, A. J. Mater. Chem. 2008, 18, 264-274. (e) Beverina, L.; Salice, P. Eur. J. Org. Chem. 2010, 1207–1225. (f) Hu, L.; Yan, Z.; Xu, H. RSC. Adv. 2013, 3, 7667-7676. (g) Qin, C.; Wong, W. Y.; Han, L. Chem. Asian J. 2013, 8, 1706-1719. (h) Kubota, Y.; Tsukamoto, M.; Ohnishi, K.; Jin, J.; Funabiki, K.; Matsui, M. Org. Chem. Front. 2017, 4, 1522–1527. (20)(a) Kuster, S.; Sauvage, F.; Nazeeruddin, M. K.; Grätzel, M.; Nüesch, F. A.; Geiger, T. Dyes Pigm. 2010, 87, 30–38. (b) Maeda, T.; Hamamura, Y.; Miyanaga, K.; Shima, N.; Yagi, S.; Nakazumi, H. Org. Lett. 2011, 13, 5994–5997. (c) Nakao, H.; Maeda, T.; Nakazumi, H. Chem. Lett. 2013, 42, 25– 27. (d) Maeda, T.; Arikawa, S.; Nakao, H.; Yagi, S.; Nakazumi, H. New J. Chem. 2013, 37, 701-708. (21) (a) Li, J.-Y.; Chen, C.-Y.; Lee, C.-P; Chen, S.-C.; Lin, T.-H.; Tsai, H.-H.; Ho, K.-C.; Wu, C.-G. Org. Lett. 2010, 12, 5454-5457. (b) Li, J.-Y.; Chen, C.-Y.; Ho, W.-C.; Chen, S.-H.; Wu, C.-G. Org. Lett. 2012, 14, 5420-5423. (a) Maeda, T.; Shima, N.; Tsukamoto, T.; Yagi, S.; Nakazumi, H. Synth. Met. 2011, 161, 2481–2487. (22)(b) Pandey, S. S.; Watanabe, R.; Fujikawa, N.; Shivashimpi, G. M.; Ogomi, Y.; Yamaguchi, Y.; Hayase, S. Tetrahedron 2013, 69, 2633–2639. (c) Magistris, C.; Martiniani, S.; Barbero, N.; Park, J.; Benzi, C.; Anderson, A.; Law, C. H.; Barolo, C.; O'Regan, B. Renew. Energy 2013, 60, 672-678. (d) Maeda, T.; Nitta, S.; Sano, Y.; Tanaka, S.; Yagi, S.; Nakazumi, H. Dyes Pigm. 2015, 122, 160-167. (e) Matsui, M.; Haishima, Y.; Kubota, Y.; Funabiki, K.; Jin, J.; Kim, T. H.; Manseki, K. Dyes Pigm. **2017**, *141*, 457–462. (23)Yum, J.-H.; Walter, P.; Huber, S.; Rentsch, D.; Geiger, T.; Nüesch, F.; Angelis, F. D.; Grätzel, M.; Nazeeruddin, M. K. J. Am. Chem. Soc. 2007, 129, 10320-10321. Park, J.; Barbero, N.; Yoon, J.; Dell'Orto, E.; Galliano, S.; Borrelli, R.; Yum, J.-H.; Di Censo, D.; (24)Grätzel, M.; Nazeeruddin, M. K.; Barolo, C.; Viscardi, G. Phys. Chem. Chem. Phys. 2014, 16, 24173-24177. (a) Huo, S. Org. Lett. 2003, 5, 423–425. (b) Son, S.; Fu, G. C. J. Am. Chem. Soc. 2008, 130, 2756– (25)2757. (c) Liang, Y.; Fu, G. C. Angew. Chem. Int. Ed. 2015, 54, 9047-9051. Krasovskiv, A.; Knochel, P. Svnthesis 2006, 5, 890-891. (26)(27)(a) Ackermann, L.; Kapdi, A. R.; Schulzke, C. Org. Lett. 2010, 12, 2298–2301. (b) Yamaguchi, S.; Okamoto, T. 2012, WO 2012096360. Limberg, F. R. P.; Schneider, T.; Höfle, S.; Reisbeck, F.; Janietz, S.; Colsmann, A.; Krüger, H. Adv. (28)Funct. Mater. 2016, 26, 8505-8513. (29)Charles, M. D.; Schultz, P.; Buchwald, S. L. Org. Lett. 2005, 7, 3965-3968. (30)Henary, M.; Mojzych, M.; Say, M.; Strekowski, L. J. Heterocycl. Chem. 2009, 46, 84-87. (31) Mulhern, K. R.; Detty, M. R.; Watson, D. F. J. Phys. Chem. C 2011, 115, 6010-6018. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; (32)Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.;

Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 09, Revision A. 02*; Gaussian, Inc.: Wallingford, CT, 2009.

- (33) Zoski C. G. (Ed.) Handbook of Electrochemistry, Elsevier, 2007.
- (34) Oyama, Y.; Harima, Y. Eur. J. Org. Chem. 2009, 2903–2934.
- (35) (a) Boschloo, G.; Hagfeldt, A. Acc. Chem. Res. 2009, 42, 1819–1826. (b) de Miguel, G.; Marchena, M.; Cohen, B.; Pandey, S. S.; Hayase, S.; Douhal, A. J. Phys. Chem. C 2012, 116, 22157–22168.
- (36) (a) Wang, Z.-S.; Sayama, K.; Sugihara, H. J. Phys. Chem. B 2005, 109, 22449–22455. (b) Kozma, E.; Concina, I.; Braga, A.; Borgese, L.; Depero, L. E.; Vomiero, A.; Sberveglieri, G.; Catellani, M. J. Mater. Chem. 2011, 21, 13785–13788. (c) Maeda, T.; Nitta, S.; Nakao, H.; Yagi, S.; Nakazumi, H. J. Phys. Chem. C 2014, 118, 16618–16625.
- (37) Fabregat-Santiago, F.; Garcia-Belmonte, G.; Mora-Sero, I.; Bisquert. J. Phys. Chem. Chem. Phys. 2011, 13, 9083–9118.
- (38) Pei, K.; Wu, Y.; Islam, A.; Zhang, Q.; Han, L.; Tian, H.; Zhu, W. ACS Appl. Mater. Interfaces 2013, 5, 4986–4995.
- (39) Ito, S.; Murakami, T. N.; Comte, P.; Liska, P.; Grätzel, C.; Nazeeruddin, M. K.; Grätzel, M. *Thin Solid Films* 2008, 516, 4613–4619.