

Supplementary Information

Fluorescent Protein Red Kaede Chromophore; One-Step, High-Yield Synthesis and Potential Application for Solar Cells

Wei-Ti Chuang, Bo-So Chen, Kew-Yu Chen, Cheng-Chih Hsieh and Pi-Tai Chou*

Department of Chemistry, National Taiwan University, Taipei, 106, Taiwan, R.O.C

E-mail: chop@ntu.edu.tw; Tel.: +886-2-33663894; fax: +886-2-23695208

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General Procedures.

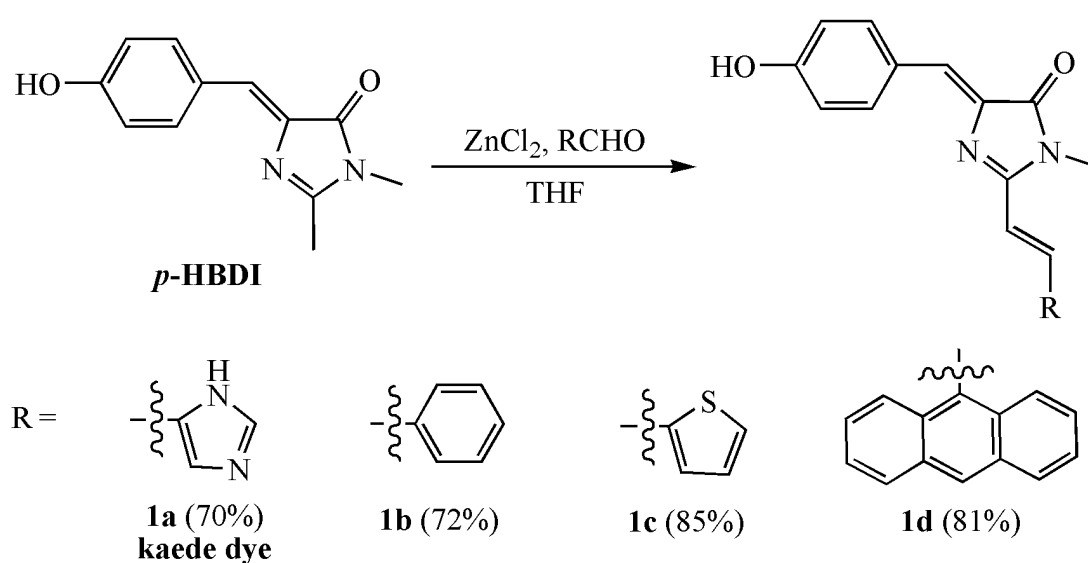
All solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Macherey-Nagel pre-coated glassic sheets (0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV light at 254 nm and 365 nm. Flash column chromatography was carried out using silica gel from Merck (230-400 mesh). Infrared spectra were recorded on a Nicolet Magna II 550 FTIR apparatus with automatic background subtraction. ^1H NMR and ^{13}C NMR spectra were recorded on Varian Unity 400 or Bruker Avance 400 spectrometer at 400 MHz and 100 MHz, respectively. Chemical shifts (δ) are quoted in parts per million (ppm) and coupling constant (J) are recorded in Hertz (Hz). Low and high resolution mass spectra were recorded by Gas Chromatograph-Mass Spectrometer (Finnigan MAT TSQ-46C GC/MS/MS/ DS). Steady-state absorption and emission spectra were recorded on a

Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively. Both the wavelength-dependent excitation and the emission response of the fluorimeter were calibrated. The quantum yield of **1a** in various solvents was compared with the dye DCM in methanol ($\Phi = 0.44$).¹ Lifetime studies were performed with an Edinburgh FL 900 photon-counting system with Spectra Phys Tsunami laser as the excitation source. Data were analyzed using a nonlinear least squares procedure in combination with an iterative convolution method. The nanosecond emission decays were analyzed by the sum of the exponential functions, which allowed partial removal of the instrument time broadening and consequently renders a temporal resolution of ~ 30 ps.

Synthesis.

Red Kaede chromophore (**1a**), Kaede-like chromophores (**1b**, **1c** and **1d**)², **2** and **3** can be prepared according to a synthetic route depicted in Scheme S1, Scheme S2 and Scheme S3.

Scheme S1



(4Z)-2-((E)-2-(1H-imidazol-5-yl)vinyl)-4-(4-hydroxybenzylidene)-1-methyl-1H-imidazol-5(4H)-one (1a).

(4Z)-4-(4-hydroxybenzylidene)-1,2-dimethyl-1H-imidazol-5(4H)-one (*p*-HBDI, 1.00 g, 4.63 mmol), anhydrous zinc chloride³ (0.06 g, 0.44 mmol), 1H-imidazole-5-carbaldehyde (0.45 g, 4.68 mmol) and THF (20 ml) were heated at 80 °C with stirring for 4 hours. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent methanol/dichloromethane (1/15, v/v) to afford free red Kaede chromophore (**1a**). (0.95 g, 70 %). ¹H NMR (DMSO, ppm) 12.41 (br, 1H), 8.14 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 15.3 Hz, 1H), 7.79 (s, 1H), 7.65 (s, 1H), 6.94 (d, *J* = 15.3 Hz, 1H), 6.87 (s, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 3.20 (s, 3H). ¹³C NMR (100 MHz, DMSO, ppm) 171.30, 160.03, 158.99, 137.45, 136.84, 134.36, 133.36, 128.39, 126.99, 126.20, 116.02, 115.37, 109.82, 25.37. MS (EI, 70eV): *m/z* (relative intensity) 294 (*M*⁺, 100); HRMS calcd. for C₁₆H₁₄O₂N₄ 294.1117, found 294.1115.

(4Z)-4-(4-hydroxybenzylidene)-1-methyl-2-styryl-1H-imidazol-5(4H)-one (1b).

(4Z)-4-(4-hydroxybenzylidene)-1,2-dimethyl-1H-imidazol-5(4H)-one (*p*-HBDI, 1.00 g, 4.63 mmol), anhydrous zinc chloride³ (0.06 g, 0.44 mmol), benzaldehyde (0.48 ml, 4.73 mmol) and THF (20 ml) were heated at 80 °C with stirring for 4 hours. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent hexane/dichloromethane (1/1, v/v) to afford (**1b**). (1.36 g, 72 %). ¹H NMR (DMSO, ppm) 10.18 (br, 1H), 8.21 (d, *J* = 8.8 Hz, 2H), 8.00 (d, *J* = 16.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.38-7.45 (m, 3H), 7.24 (d, *J* = 16.0 Hz, 1H), 7.01 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.26 (s, 3H). ¹³C NMR (100 MHz, DMSO, ppm) 170.28, 160.66, 158.99, 138.39, 136.92, 135.28, 127.42, 127.11, 126.46, 126.33, 126.02, 116.22, 115.94, 108.97, 26.02.

MS (EI, 70eV): m/z (relative intensity) 304 (M^+ , 100); HRMS calcd. for $C_{19}H_{16}N_2O_2$ 304.1212, found 304.1209.

(4Z)-4-(4-hydroxybenzylidene)-1-methyl-2-((E)-2-(thiophen-2-yl)vinyl)-1H-imidazol-5(4H)-one **(1c).**

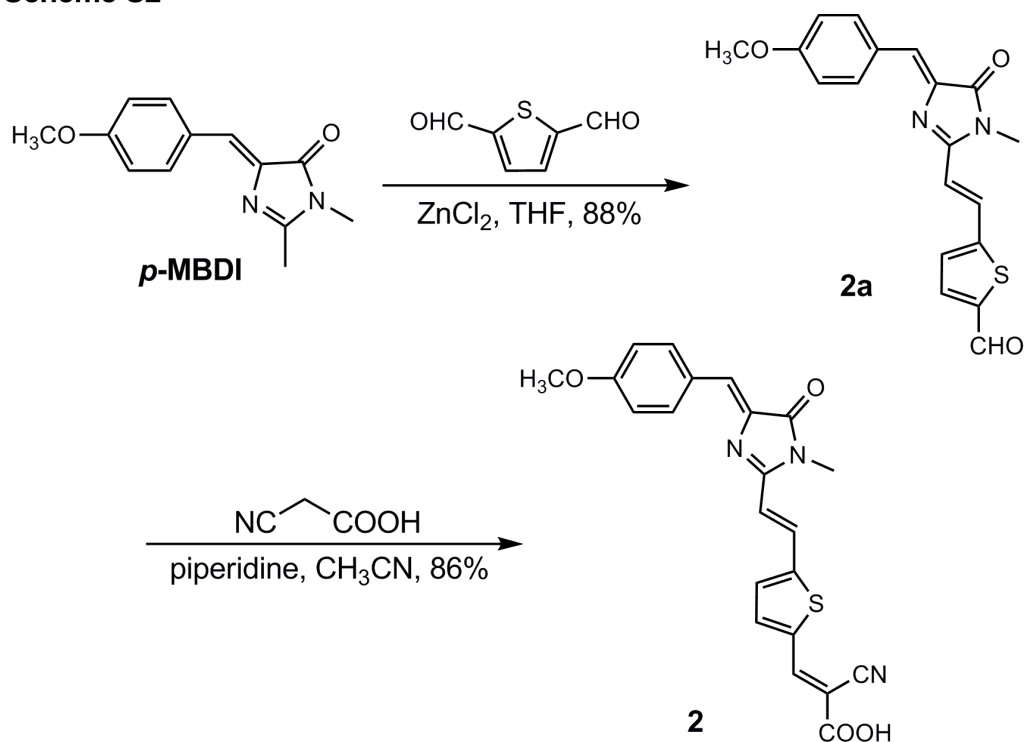
(4Z)-4-(4-hydroxybenzylidene)-1,2-dimethyl-1H-imidazol-5(4H)-one (*p*-HBDI, 1.00 g, 4.63 mmol), anhydrous zinc chloride³ (0.06 g, 0.44 mmol), thiophene-2-carboxaldehyde (0.44 ml, 4.73 mmol) and THF (20 ml) were heated at 80 °C with stirring for 4 hours. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent hexane/dichloromethane (1/1, v/v) to afford **(1c)**. (1.22 g, 85 %). ¹H NMR (DMSO, ppm) 10.20 (br, 1H), 8.15 (d, $J = 8.8$ Hz, 2H), 8.12 (d, $J = 16.0$ Hz, 1H), 7.72 (d, $J = 4.8$ Hz, 1H), 7.62 (d, $J = 3.2$ Hz, 1H), 7.16 (dd, $J = 3.2$ Hz, 4.8 Hz, 1H), 6.93 (s, 1H), 6.84 (d, $J = 8.8$ Hz, 2H), 6.82 (d, $J = 16.0$ Hz, 1H), 3.21 (s, 3H). ¹³C NMR (100 MHz, DMSO, ppm) 170.66, 159.94, 159.05, 136.88, 134.98, 131.02, 128.32, 127.22, 127.15, 126.48, 126.42, 116.10, 115.96, 108.92, 26.05. MS (EI, 70eV): m/z (relative intensity) 310 (M^+ , 100); HRMS calcd. for $C_{17}H_{14}N_2O_2S$ 310.0776, found 310.0774.

(4Z)-4-(4-hydroxybenzylidene)-2-((E)-2-(anthracen-10-yl)vinyl)-1-methyl-1H-imidazol-5(4H)-one **(1d).**

(4Z)-4-(4-hydroxybenzylidene)-1,2-dimethyl-1H-imidazol-5(4H)-one (*p*-HBDI, 1.00 g, 4.34 mmol), anhydrous zinc chloride³ (0.06 g, 0.44 mmol), anthracene-10-carbaldehyde (0.90 g, 4.37 mmol) and THF (20 ml) were heated at 80 °C with stirring for 4 hours. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent methanol/dichloromethane (1/10, v/v) to afford **(1d)**. (1.42 g,

81 %). ^1H NMR (DMSO, ppm) 10.18 (br, 1H), 8.84 (d, $J = 16.0$ Hz, 1H), 8.66 (s, 1H), 8.34 (d, $J = 8.4$ Hz, 2H), 8.25 (d, $J = 8.4$ Hz, 2H), 8.14 (d, $J = 8.0$ Hz, 2H), 7.56-7.61 (m, 4H), 7.07 (s, 1H), 7.02 (d, $J = 16.0$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 2H), 3.23 (s, 3H). ^{13}C NMR (100 MHz, DMSO, ppm) 170.45, 160.32, 158.83, 137.21, 136.29, 135.11, 131.33, 130.49, 129.51, 129.27, 128.48, 127.19, 127.14, 126.19, 126.03, 125.66, 123.71, 116.38, 26.88. MS (EI, 70eV): m/z (relative intensity) 404 (M^+ , 100); HRMS calcd. for $\text{C}_{27}\text{H}_{20}\text{N}_2\text{O}_2$ 404.1525, found 404.1529.

Scheme S2



5-((1*E*)-2-((4*Z*)-4-(4-methoxybenzylidene)-4,5-dihydro-1-methyl-5-oxo-1*H*-imidazol-2-yl)vinyl)thiophene-2-carbaldehyde (2a).

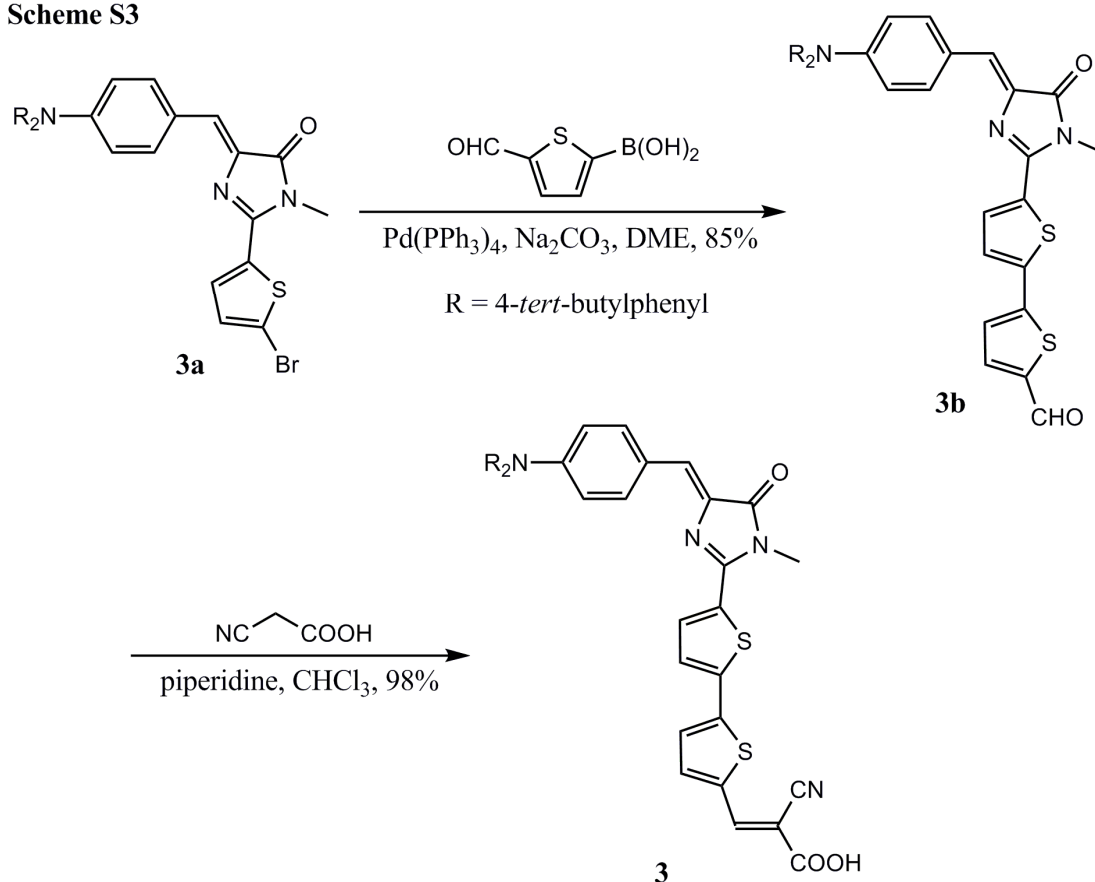
(4*Z*)-4-(4-hydroxybenzylidene)-1,2-dimethyl-1*H*-imidazol-5(4*H*)-one (*p*-HBDI, 1.00 g, 4.34 mmol), anhydrous zinc chloride³ (0.06 g, 0.44 mmol), thiophene-2,5-dicarbaldehyde

(3.04 g, 21.7 mmol) and THF (20 ml) were heated at 80 °C with stirring for 6 hours. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent hexane/dichloromethane (2/1, v/v) to afford **(2a)**. (1.35 g, 88 %). ¹H NMR (CDCl₃, ppm) 9.92 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 16.0 Hz, 1H), 7.73 (d, *J* = 3.6 Hz, 1H), 7.40 (d, *J* = 3.6 Hz, 1H), 7.18 (s, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 16.0 Hz, 1H), 3.87 (s, 3H), 3.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm) 182.60, 170.52, 161.64, 157.39, 149.14, 148.99, 144.20, 138.62, 137.64, 136.65, 134.98, 131.55, 130.37, 128.61, 127.51, 115.98, 114.41, 55.38, 26.55. MS (EI, 70eV): *m/z* (relative intensity) 352 (M⁺, 100); HRMS calcd. for C₁₉H₁₆N₂O₃S 352.0882, found 352.0886.

(2E)-3-(5-((1E)-2-((4Z)-4-(4-methoxybenzylidene)-4,5-dihydro-1-methyl-5-oxo-1H-imidazol-2-yl)vinyl)thiophen-2-yl)-2-cyanoacrylic acid (2).

5-((1E)-2-((4Z)-4-(4-methoxybenzylidene)-4,5-dihydro-1-methyl-5-oxo-1H-imidazol-2-yl)vinyl)thiophene-2-carbaldehyde (0.50 g, 1.42 mmol), 2-cyanoacetic acid (0.24 g, 2.82 mmol), piperidine (1.0 mL) and acetonitrile (10 ml) were heated at 80 °C with stirring for 4 hours. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent methanol/dichloromethane (1/5, v/v) to afford **(2)**. (0.52 g, 86 %). ¹H NMR (DMSO, ppm) 8.27 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 16.0 Hz, 1H), 8.11 (s, 1H), 7.73 (s, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 7.01 (s, 1H), 6.99 (d, *J* = 16.0 Hz, 1H), 3.82 (s, 3H), 3.25 (s, 3H). ¹³C NMR (100 MHz, DMSO, ppm) 169.80, 161.06, 160.54, 158.64, 137.70, 134.37, 131.10, 127.29, 126.01, 125.24, 116.23, 116.18, 114.50, 108.99, 55.38, 26.41. MS (EI, 70eV): *m/z* (relative intensity) 419 (M⁺, 100); HRMS calcd. for C₂₂H₁₇N₃O₄S 419.0940, found 419.0936.

Scheme S3



(4Z)-4-(4-(bis(4-*tert*-butylphenyl)amino)benzylidene)-2-(5-bromothiophen-2-yl)-1-methyl-1*H*-imidazol-5(4*H*)-one (**3a**).

(4Z)-4-(4-(bis(4-*tert*-butylphenyl)amino)benzylidene)-2-(5-bromothiophen-2-yl)-1-methyl-1*H*-imidazol-5(4*H*)-one was synthesized following the general synthesis of GFP core.⁴

¹H NMR (CDCl_3 , ppm) 8.01 (d, $J = 8.8$ Hz, 2H), 7.38 (d, $J = 4.0$ Hz, 1H), 7.29 (d, $J = 8.5$ Hz, 4H), 7.13 (s, 1H), 7.09 (d, $J = 4.0$ Hz, 1H), 7.07 (d, $J = 8.5$ Hz, 4H), 6.96 (d, $J = 8.8$ Hz, 2H), 3.46 (s, 3H), 1.30 (s, 18H). ¹³C NMR (100 MHz, CDCl_3 , ppm) 170.70, 152.75, 150.47, 147.50, 143.72, 135.86, 135.02, 134.00, 131.15, 129.03, 126.55, 126.34, 125.55, 119.83, 118.69, 34.44, 31.40, 28.44. MS (EI, 70eV): m/z (relative intensity) 625 (M^+ , 100); HRMS calcd. for $\text{C}_{35}\text{H}_{36}\text{BrN}_3\text{OS}$ 625.1762, found 625.1765.

5-(5-((4Z)-4-(4-(bis(4-*tert*-butylphenyl)amino)benzylidene)-4,5-dihydro-1-methyl-5-oxo-1*H*-imidazol-2-yl)thiophen-2-yl)thiophene-2-carbaldehyde (3b).

(4Z)-4-(4-(bis(4-*tert*-butylphenyl)amino)benzylidene)-2-(5-bromothiophen-2-yl)-1-methyl-1*H*-imidazol-5(4*H*)-one (0.50 g, 0.80 mmol), 5-Formyl-2-thienylboronic acid (0.24 g, 0.96 mmol), Tetrakis(triphenylphosphine)palladium(0) (0.05 g, 0.04 mmol), 2M Na₂CO₃ solution (5.0 mL) and dimethoxyethane (20 ml) were heated at 80 °C with stirring for 12 hours. After solvent was removed, the crude product was purified by silica gel column chromatography with eluent dichloromethane to afford (3b). (0.45 g, 85 %). ¹H NMR (CDCl₃, ppm) 9.86 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 3.9 Hz, 1H), 7.59 (d, *J* = 4.0 Hz, 1H), 7.36 (d, *J* = 4.0 Hz, 1H), 7.35 (d, *J* = 3.9 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 4H), 7.15 (s, 1H), 7.08 (d, *J* = 8.6 Hz, 4H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.51 (s, 3H), 1.31 (s, 18H). ¹³C NMR (100 MHz, CDCl₃, ppm) 182.40, 170.70, 152.94, 150.55, 147.57, 145.42, 143.70, 142.97, 140.28, 136.99, 135.98, 134.30, 134.09, 129.64, 129.25, 126.72, 126.59, 126.35, 125.63, 125.58, 119.86, 34.44, 31.40, 28.58. MS (EI, 70eV): *m/z* (relative intensity) 657 (M⁺, 100); HRMS calcd. for C₄₀H₃₉N₃O₂S₂ 657.2484, found 657.2482.

(2E)-3-(5-(5-((4Z)-4-(4-(bis(4-*tert*-butylphenyl)amino)benzylidene)-4,5-dihydro-1-methyl-5-oxo-1*H*-imidazol-2-yl)thiophen-2-yl)thiophen-2-yl)-2-cyanoacrylic acid (3).

5-(5-((4Z)-4-(4-(bis(4-*tert*-butylphenyl)amino)benzylidene)-4,5-dihydro-1-methyl-5-oxo-1*H*-imidazol-2-yl)thiophen-2-yl)thiophene-2-carbaldehyde (0.10 g, 0.15 mmol), 2-cyanoacetic acid (0.02 g, 0.24 mmol), piperidine (1.0 mL) and chloroform (10 ml) were heated at 80 °C with stirring for 6 hours. After solvent was removed, the crude product was purified by washing with ethanol for several times to afford (3). (0.108 g, 98 %). ¹H

NMR (CD₃OD + 2% TBAOH, ppm) 8.07 (s, 1H), 7.94 (d, $J = 8.8$ Hz, 2H), 7.68 (d, $J = 4.0$ Hz, 1H), 7.53 (d, $J = 4.0$ Hz, 1H), 7.36 (d, $J = 4.0$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 4H), 6.99 (d, $J = 8.4$ Hz, 4H), 6.92 (s, 1H), 6.80 (d, $J = 8.8$ Hz, 2H), 3.41 (s, 3H), 1.29 (s, 18H). MS (EI, 70eV): m/z (relative intensity) 724 (M^+ , 100); HRMS calcd. for C₄₃H₄₀N₄O₃S₂ 724.2542, found 724.2545.

Ultrafast Fluorescence Measurements.

The fluorescence upconversion measurements were performed with a femtosecond optically gated system (FOG100, CDP, Moscow, Russia) which has been described in our previous paper.⁵ In brief, the sample was excited using the second harmonic (SH) of a mode-locked Ti-sapphire laser (750-850 nm, Tsunami, Spectra Physics) pumped by a 10W diode laser (Millennia, Spectra Physics). The resulting fluorescence emitted from the sample was upconverted in a nonlinear crystal (0.5 mm BBO) using a gate pulse of the fundamental beam. The upconverted light was then separated an F/4.9 ($f = 380$ mm) single monochromator (CDP2022) and detected via a photon counting PMT (R1527P, Hamamatsu). The cross correlation between SH and the fundamental had a full width at half-maximum (fwhm) of ~ 150 fs, which was chosen as a response function of the system. All measurements were made under magic angle (54.7°) condition to eliminate the fluorescence anisotropy.

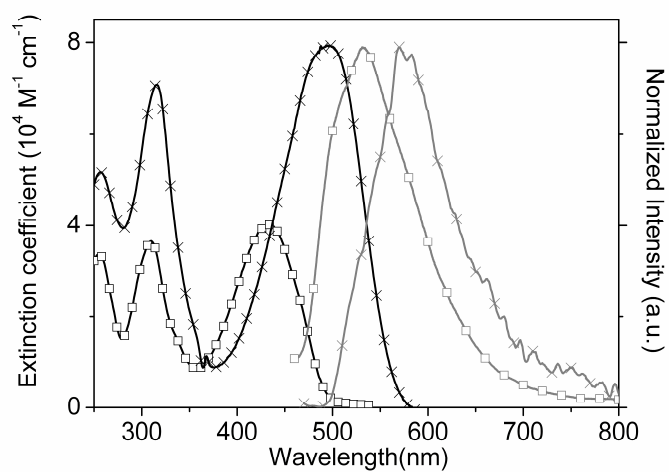


Figure S1. Absorption and emission spectra of neutral ($-\square-$, pH \sim 6.2) and anionic ($-x-$, with 0.1 M KOH) red Kaede core chromophore **1a** in water.

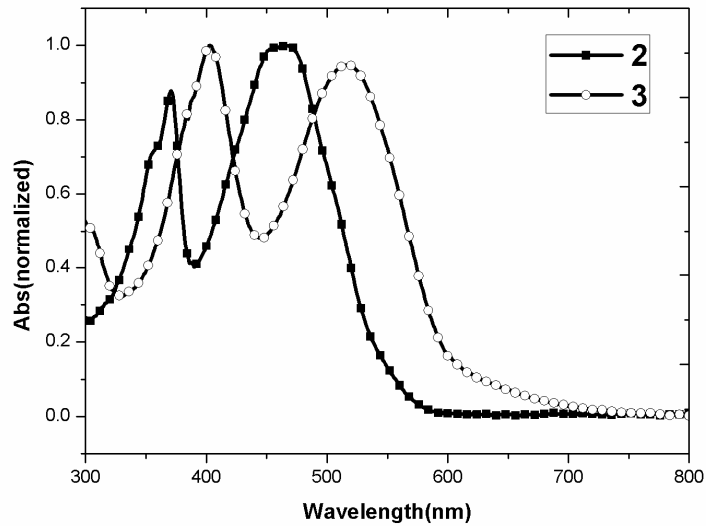


Figure S2. Absorption spectra of **2** and **3** in DMF.

Fabrication of DSSC and Photovoltaic Measurements.

TiO₂ anatase nanoparticles of 20 nm were prepared using published procedures.⁶ TiO₂ particles were dispersed in α -terpineol with ethyl cellulose as a binder. The TiO₂ thin films of 12 μ m were prepared by a doctor-blade method on a transparent conducting oxide (F-doped SnO₂, FTO). These films were dried at 150 °C for 15 min and then a 4 μ m thick layer of 200 nm TiO₂ particles (ST-41, particles were obtained from Ishihara Sangyo, Japan) was deposited again by a doctor-blade method with a dimension of 0.4 \times 0.4 cm². Afterwards, the double-layered films were sintered at 500 °C for 30 min. After sintering, the TiO₂ films were treated with 50mM TiCl₄ solution, rinsed with water and ethanol, and sintered at 500 °C for 30 min. After cooling to 80 °C, the TiO₂ electrode was coated with dyes by dipping the film in a solution of 3×10^{-4} M dye and 10 mM deoxycholic acid in methanol overnight. After being rinsed with methanol, the dye-coated TiO₂ electrode was incorporated into a thin-layer sandwich-type cell with a Pt-coated FTO as counter electrode, a spacer film (Surlyn 1702, 25 μ m), and an organic electrolyte was then injected into the space. Lastly, the cell sealed with Torr Seal cement (Varian, MA) to measure the solar cell performance. The Pt counterelectrode was prepared by spin-coating a 0.05M H₂PtCl₆ in isopropyl alcohol solution on FTO glass followed by sintering at 385 °C for 15–30 min. The electrolyte contained 0.6 M 1-propyl-3-methylimidazolium iodide (PMII), 0.1 M LiI, 0.05 M I₂, 0.5 M 4-*tert*-butylpyridine (TBP) in acetonitrile solvent. Light-to-electricity conversion efficiency values were measured using a standard AM1.5 solar simulator-Oriel 66 924 Arc lamp source with a 6266 450 W Xe lamp, an Oriel 81088 Air Mass 1.5 Global Filter and a digital source meter purchased from Keithley Instruments Inc. The incident light

intensity was calibrated by using a standard solar cell composed of a crystalline silicon solar cell and an IR cutoff filter (Schott, KG-5), giving the photoresponse range of amorphous silicon solar cell.

Table S1. Photophysical, electrochemical and photovoltaic performance data of organic dyes

Dye	Absorption	Emission	Potentials and Energy levels			Photovoltaic performance data ^d			
	λ_{abs} ^a nm (ϵ , M ⁻¹ cm ⁻¹)	λ_{em} ^a nm	E_{ox} ^b V	E_{0-0} ^c V	$E_{ox}-E_{0-0}$ V	J_{sc} mA/cm ²	V_{oc} mV	FF	η (%)
1a	495(53000)	570	0.89	2.31	-1.42	6.6	640	0.72	3.04

^a Absorption, emission spectra were measured in methanol at room temperature. ^b Oxidation potential of dyes on TiO₂ was measured in CH₃CN with 0.1 M TBAP with a scan rate of 50 mV s⁻¹ (vs. NHE). ^c E_{0-0} was determined from intersection of absorption and emission spectra. ^d The concentration was maintained at 3 × 10⁻⁴ M in methanol and 0.6 M 1-propyl-3-methylimidazolium iodide (PMII), 0.1 M LiI, 0.05 M I₂, 0.5 M 4-*tert*-butylpyridine (TBP) in dry acetonitrile as electrolyte. Performances of DSSCs were measured with 0.16 cm² working area.

Stability Test.

The photoanodes of the device employed in this study were composed of a 7 μm transparent TiO₂ thin film and 4 μm thick layer of 400 nm TiO₂ particles. A 405 nm cut-off long pass filter was put on the cell surface during illumination. The cell were irradiated under a Suntest CPS plus lamp (ATLAS GmbH, 100Mw cm⁻²) during visible-light soaking at 60 °C. Electrolyte was switched to 3-methoxy-propionitril based low-volatile solvent consisting of a mixture of BMII/I₂/NBB/GNCS in molar ratio of 1/0.15/0.5/0.1.

1-butyl-3methyl imidazolium iodide (BMII) was purchased from TCI.

Iodine was purchased from Merck.

3-methoxy-propionitril and Guanidinium thiocyanate (GNCS) were purchased from Fluka.

N-butylbenzimidazole (NBB) was synthesized according to the literature method.⁷

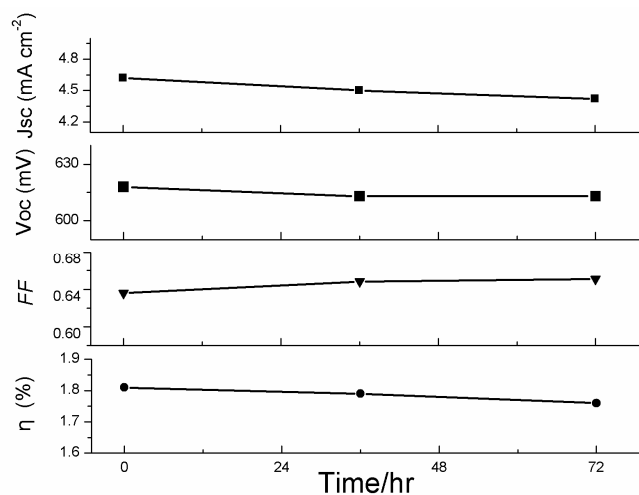


Figure S3. Evolution of photovoltaic parameters of compound **1a** measured under the irradiance of AM 1.5G sunlight during light-soaking at 60 °C.

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