Supplementary Information

Dye-sensitized solar cells based on D- π -A fluorescent dyes with two pyridyl groups as electron-withdrawing-injecting anchoring group

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Experimental Section:

General: Melting points were measured with a Yanaco micro melting point apparatus MP model. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer by ATR method. High-resolution mass spectral data were acquired on a Thermo Fisher Scientific LTQ Orbitrap XL. ¹H NMR spectra were recorded on a Varian-500 (500 MHz) FT NMR spectrometer with tetramethylsilane as an internal standard. Absorption spectra were observed with a Shimadzu UV-3150 spectrophotometer and fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. The fluorescence quantum yields in solution and in the solid state were determined by a Hamamatsu C9920-01 equipped with CCD by using a calibrated integrating sphere system ($\lambda_{ex} = 327$ nm and 378 nm for **YNI-1** and 417 nm for YNI-2, respectively). Cyclic voltammetry (CV) curves were recorded in CH₂Cl₂/Bu₄NClO₄ (0.1M) solution with a three-electrode system consisting of Ag/Ag⁺ as reference electrode, Pt plate as working electrode, and Pt wire as counter electrode by using a Hokuto Denko HAB-151 potentiostat equipped with a function generator. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of two dyes were evaluated from the spectral analyses and the CV data The LUMO energy levels of the dyes were estimated from the onset of the oxidation potential for YNI-1 and $E_{1/2}^{\text{ox}}$ for YNI-2, and an intersection of absorption and fluorescence spectra (355 nm) for YNI-1 and (417 nm) for YNI-2, which correspond to the energy gap between the HOMO and the LUMO.

Preparation of 9-ethyl-3,6-di(pyridin-4-yl)-9H-carbazole (YNI-1)

To a mixture of 3,6-dibromo-9-ethyl-9*H*-carbazole (0.5 g, 1.42 mmol), 4-pyridylboronic acid (0.435 g, 3.54 mmol), and Pd(PPh₃)₄ (0.164 g, 0.14 mmol) under an argon atmosphere was added aqueous 1M Na₂CO₃ (5 mL) and DMF (15 ml) and stirred for 11 h at 100 °C. After

concentrating under reduced pressure, the resulting residue was dissolved in dichloromethane and washed with water. The residue was chromatographed on silica gel (dichloromethane-methanol = 4 : 1 as eluent) to give a crude solid, which was then recrystallized form a mixture of dichloromethane and *n*-hexane to give **YNI-1** (0.08 g, yield 16 %) as a light yellow solid; M.p. 243–244 °C; IR (ATR): $\tilde{v} = 1588$, 1474 cm⁻¹; ¹H NMR (500 MHz, acetone-d₆, TMS) $\delta = 1.48$ (t, J = 7.2 Hz, 3H), 4.60 (q, 2H), 7.78 (d, J = 8.6 Hz, 2H), 7.81 (d, J = 6.2 Hz, 4H), 7.98 (dd, J = 2.0 and 8.6 Hz, 2H), 8.64 (d, J = 6.2 Hz, 4H), 8.82 (d, J = 2.0 Hz, 2H); HRMS (ESI): *m*/*z* (%):[M+H⁺] calcd for C₂₄H₂₀N₃, 350.16517; found 350.16528.

Preparation of 9-butyl-3,6-bis(5-(pyridin-4-yl)thiophen-2-yl)-9H-carbazole (YNI-2)

A solution of 4-(5-tributylstannanyl-thiophen-2-yl)-pyridine (2.5 g, 5.55 mmol), 3,6-dibromo-9-butyl-9*H*-carbazole (1.00 g, 2.62 mmol), and Pd(PPh₃)₄ (0.151 g, 0.13 mmol) in DMF (30 mL) was stirred for 2 h at 90 °C under an argon atmosphere. The reaction mixture was poured into water (200 mL). The resulting precipitate was filtrated. The residue was chromatographed on silica gel (dichloromethane–methanol = 20 : 1 as eluent) to give a crude solid, which was then recrystallized form dichloromethane to give **YNI-2** (0.537 g, yield 38 %) as a yellowish-orange solid; M.p. 236–237 °C; IR (ATR): $\tilde{v} = 1589$, 1481, 1446 cm⁻¹; ¹H NMR (500 MHz, DMSO-d₆) $\delta = 0.89$ (t, J = 7.4 Hz, 3H), 1.28–1.34 (m, 2H), 1.76–1.82 (m, 2H), 4.46 (t, J = 7.0 Hz, 2H), 7.67–7.69 (m, 6H), 7.72 (d, J = 8.6 Hz, 2H), 7.87 (dd, J = 1.8 and 8.6 Hz, 2H), 7.89 (d, J = 3.9 Hz, 2H), 8.60 (d, J = 6.2 Hz, 4H) , 8.72 (d, J = 1.8 Hz, 2H); HRMS (ESI): m/z (%):[M+H⁺] calcd for C₃₄H₂₈N₃S₂, 542.17192; found 542.17163.



Scheme S1. Synthesis of compounds YNI-1 and YNI-2.



Fig. S1 Cyclic voltammograms of (a) **YNI-1** and (b) **YNI-2** in THF containing 0.1 M Bu_4NClO_4 at a scan rate of 50 mV s⁻¹. The arrow denotes the direction of the potential scan.

Table SI Electrochemical properties of YNI-1 and YNI-2.				
Dye	$E_{\rm pa}/{ m V}^{\rm a}$	$E_{\rm pc}/{\rm V}^{\rm b}$	$\Delta E_{\rm p}/{ m V}$	$E_{1/2}^{\rm ox}/{\rm V}$
YNI-1	0.99	_	_	_
YNI-2	0.58	0.48	0.10	0.53
^{a, b} E_{pa} and E_{pc} are the anodic and cathodic peak potentials vs. Fc/Fc ⁺ .				

Computational Methods: The semi-empirical calculations were carried out with the WinMOPAC Ver. 3.9 package (Fujitsu, Chiba, Japan). Geometry calculations in the ground state were made using the AM1 method. All geometries were completely optimized (keyword PRECISE) by the eigenvector following routine (keyword EF). Experimental absorption spectra of the compounds were compared with their absorption data by the semi-empirical method INDO/S (intermediate neglect of differential overlap/spectroscopic). Dipole moments of the compounds were also evaluated from INDO/S calculations. All INDO/S calculations were performed using single excitation full SCF/CI (self-consistent field/configuration interaction), which included the configuration with one electron excited from any occupied orbital to any unoccupied orbital, where 225 configurations were considered [keyword CI (15 15)].



Fig. S2 (a) LUMO and (b) HOMO of **YNI-1** (above) and **YNI-2** (below). The red and blue lobes denote the positive and negative phases, respectively, of the coefficients of the MOs. The size of each lobe is proportional to the MO coefficient. (c) Calculated electron density changes accompanying the first electronic excitation of **YNI-1** (above) and **YNI-2** (below). The black and white lobes signify the decrease and increase in electron density accompanying the electronic transition, respectively. Their areas indicate the magnitude of the electron density change. (Light blue, green, blue, red, and gold balls correspond to hydrogen, carbon, nitrogen, oxygen, and sulfur atoms, respectively.)

Preparation of the Dye-Sensitized Solar Cells Based on Dyes YNI-1 and YNI-2: The TiO₂ paste (JGC Catalysts and Chemicals Ltd., PST-18NR) was deposited on a fluorine-doped-tin-oxide (FTO) substrate by doctor-blading, and sintered for 50 min at 450 °C. The 9 μ m thick TiO₂ electrode (0.5×0.5 cm² in photoactive area) was immersed into a 0.1 mM or 0.02 M dye solution in THF for a number of hours enough to adsorb the photosensitizer. The DSSCs were fabricated by using the TiO₂ electrode thus prepared, Pt-coated glass as a counter electrode, and a solution of 0.05 M iodine, 0.1 M lithium iodide, and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide acetonitrile electrolyte. in as The photocurrent-voltage characteristics were measured using a potentiostat under a simulated solar light (AM 1.5, 100 mW cm⁻²). IPCE spectra were measured under monochromatic irradiation with a tungsten-halogen lamp and a monochromator. The amount of adsorbed dye on TiO₂ nanoparticles was determined by absorption spectral measurement of the concentration change of the dye solution before and after adsorption. Absorption spectra of the dyes adsorbed on TiO₂ nanoparticles were recorded on the dyes-adsorbed TiO₂ film (thickness of 9 µm) in the transmission mode with a calibrated integrating sphere system. The

dye coverage (θ) of TiO₂ surface for **YNI-1** and **YNI-2** is evaluated from the amount (i.e., number of molecules in Table 1 / 1051 cm⁻²) of dyes adsorbed on TiO₂ surface relative to the real surface area (1051 cm⁻²) in 1 cm⁻² geometric area of TiO₂ film and total number of acid sites (2.14×10¹⁴ / cm⁻²) on TiO₂ surface which was obtained by the temperature programmed desorption of ammonia (NH₃-TPD, CAT-B-82 NH₃-TPD, Bel Japan).



Fig. S3 Photovoltaic parameters (J_{sc} , V_{oc} , ff, and η) with **YNI-1** (\bullet) and **YNI-2** (\blacktriangle) during light soaking (AM 1.5, 100 mW cm⁻²).



Fig. S4 Configurations of YNI-1 and YNI-2 on the TiO₂ surface.