

Supplementary Information

Nitro Group as A New Anchoring Group for Organic Dyes in Dye-Sensitized Solar Cells

Jiayan Cong,^a Xichuan Yang,^{*a} Jing Liu,^a Jinxia Zhao,^a Yan Hao,^a Yu Wang^a and Licheng Sun^{*ab}

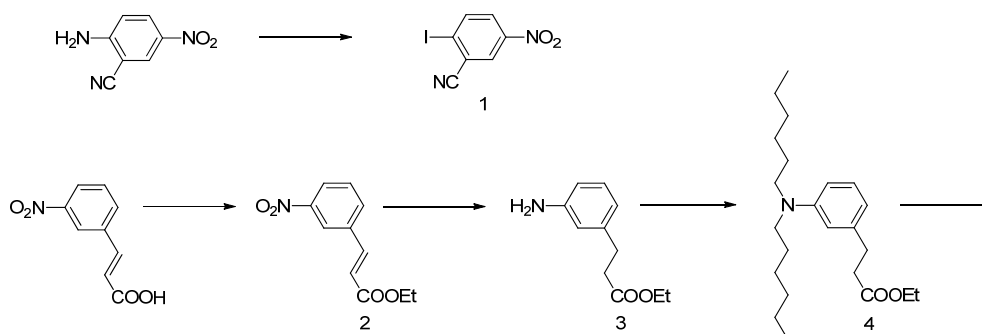
^a State Key Laboratory of Fine Chemicals, DUT-KTH Joint Education and Research Center on Molecular Devices, Dalian University of Technology (DUT), 2[#] Linggong Rd. 116024 Dalian, China;

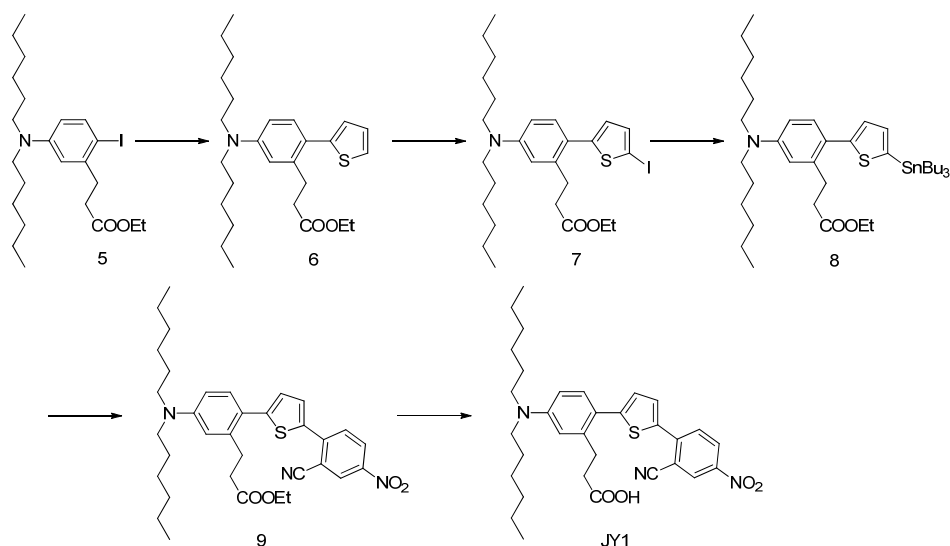
^b School of Chemical Science and Engineering, Center of Molecular Devices, Department of Chemistry, KTH Royal Institute of Technology, Teknikringen 30, 10044 Stockholm, Sweden

General methodology. Solvents were dried by standard procedures. All other chemicals were purchased from commercial sources and used without further purification. ¹H NMR spectra were recorded with a Varian INOVA 400 NMR instrument. MS data were obtained with GCT CA156 (UK) high-resolution mass spectrometer (HRMS) or HP1100 LC/MSD (USA) mass spectrometer. UV-Vis spectra of the dyes in solution were recorded in a quartz cell with 1 cm path length on a HP 8453 spectrophotometer.

Synthesis of the dye JY1

The synthesis and the characterizations of 2-iodo-5-nitrobenzonitrile (1) were previously described by Ozaki et al.¹, then ethyl 3-(3-nitrophenyl)acrylate (2) and ethyl 3-(3-aminophenyl)acrylate (3) were described by Strawn et al.².





Scheme S1. Synthetic route of JY1.

Synthesis of ethyl 3-(3-(dihexylamino)phenyl)propanoate (**4**)

Ethyl 3-(3-aminophenyl)propanoate (**3**) (0.80 g, 4 mmol), 1-bromohexane (2.70 g, 16 mmol), tetrabutyl ammonium bromide (157 mg, 0.49 mmol) and anhydrous potassium carbonate (4.40 g, 32 mmol) were added into 30 ml dry DMF and reacted at 120 °C under nitrogen atmosphere for 24 hour. The solvent was removed by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1). Yield: 1.17g, 81%, colourless oil. ¹H NMR (400 MHz, CDCl₃, ppm) δ 7.11 (t, J = 8.0 Hz, 1H), 6.47 (dd, J = 7.4, 5.2 Hz, 3H), 4.14 (q, J = 7.2 Hz, 2H), 3.27 – 3.16 (m, 4H), 2.94 – 2.81 (m, 2H), 2.67 – 2.55 (m, 2H), 1.57 (d, J = 8.0 Hz, 4H), 1.31 (s, 12H), 1.25 (t, J = 7.1 Hz, 3H), 0.90 (t, J = 6.4 Hz, 6H). GCT/TOF HRMS-EI(m/z): [M]⁺ calcd. for C₂₃H₃₉NO₂, 361.2981; found: 361.2982.

Synthesis of ethyl 3-(5-(dihexylamino)-2-iodophenyl)propanoate (**5**)

4 (774 mg, 2.14 mmol) was dissolved in 30ml carbon tetrachloride (CCl₄). N-Iodosuccinimide (NIS, 506 mg, 2.25 mmol) was slowly added to the solution, and stirred at 40 °C for 18h. Pour the reaction solution to Sodium thiosulfate aqueous solution (50 ml), stirred at room temperature until the mixture turned to clear and transparent. The mixture was extracted with dichloromethane (50 ml) for three times. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. The residue was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1). Yield: 972 mg, 81%, colourless oil. ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.51 (d, J = 8.8 Hz, 1H), 6.53 (d, J = 3.1

Hz, 1H), 6.23 (dd, $J = 8.8, 3.1$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.24 – 3.16 (m, 4H), 2.97 (dd, $J = 16.9, 9.3$ Hz, 2H), 2.60 (dd, $J = 9.9, 6.1$ Hz, 2H), 1.54 (dd, $J = 13.2, 7.1$ Hz, 4H), 1.32 (d, $J = 16.2$ Hz, 12H), 1.27 (d, $J = 7.2$ Hz, 3H), 0.92 – 0.85 (m, 6H). GCT/TOF HRMS-EI(m/z): $[M]^+$ calcd. for $C_{23}H_{38}NO_2I$, 487.1947; found: 487.1947.

Synthesis of ethyl 3-(5-(dihexylamino)-2-(thiophen-2-yl)phenyl)propanoate (**6**)

The reaction is a classic Suzuki Cross-Coupling Reaction.³ **5** (725 mg, 1.49 mmol), 2-Thiopheneboronic acid (229 mg, 1.79 mmol), $Pd(PPh_3)_4$ (171mg, 0.15 mmol) and K_2CO_3 aq(2 M, 3ml) was dissolved in pre-dried tetrahydrofuran (THF, 20 ml), and blow nitrogen for 30 min. The solution was stirred and refluxed under nitrogen atmosphere for 24 hours. Deionized water (50 ml) was added, after the reaction solution cooled to room temperature. The solution was extracted with dichloromethane (50 ml) for three times. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. The residue was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1). Yield: 462 mg, 70%, colourless oil. 1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.27 – 7.23 (m, 1H), 7.19 (t, $J = 7.9$ Hz, 1H), 7.04 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.95 (dd, $J = 7.9, 5.4$ Hz, 1H), 6.52 (s, 1H), 6.49 (d, $J = 2.6$ Hz, 1H), 4.10 (q, $J = 7.1$ Hz, 2H), 3.36 – 3.16 (m, 4H), 3.13 – 2.90 (m, 2H), 2.57 – 2.43 (m, 2H), 1.58 (d, $J = 7.7$ Hz, 4H), 1.31 (d, $J = 13.3$ Hz, 12H), 1.22 (t, $J = 7.1$ Hz, 3H), 0.94 – 0.87 (m, 6H). GCT/TOF HRMS-EI(m/z): $[M]^+$ calcd. for $C_{27}H_{41}NO_2S$, 443.2858; found: 443.2863.

Synthesis of ethyl 3-(5-(dihexylamino)-2-(5-iodothiophen-2-yl)phenyl)propanoate (**7**)

The synthesis process of **7** is similar to that of **5**. **6** (325 mg, 0.73 mmol) was dissolved in 25 ml CCl_4 . NIS (181 mg, 0.81 mmol) was slowly added to the solution, and stirred at 40 °C for 18h. Pour the reaction solution to Sodium thiosulfate aqueous solution (50 ml), stirred at room temperature until the mixture turned to clear and transparent. The mixture was extracted with dichloromethane (50 ml) for three times. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator. The residue was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1). Yield: 299 mg, 72%, colourless oil. 1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.16 (t, $J = 4.4$ Hz, 1H), 7.14 (d, $J = 8.2$ Hz, 1H), 6.63 (d, $J = 3.6$ Hz, 1H), 6.53 – 6.45 (m, 2H), 4.11 (q, $J = 7.1$ Hz, 2H), 3.33 – 3.21 (m, 4H), 2.99 (dd, $J = 16.9, 8.6$ Hz, 2H), 2.54 – 2.47 (m, 2H), 1.59 (d, $J = 9.9$ Hz, 4H), 1.39 – 1.27 (m, 12H), 1.23 (dd, $J = 9.1, 5.3$ Hz, 3H), 0.89 (d, $J = 6.7$ Hz, 6H). GCT/TOF HRMS-EI(m/z): $[M]^+$ calcd. for $C_{27}H_{40}NO_2SI$, 569.1825; found: 569.1828.

Synthesis of ethyl 3-(2-(5-(2-cyano-4-nitrophenyl)thiophen-2-yl)-5-(dihexylamino)phenyl)propanoate (**9**)

The synthesis of organotin intermediate accords to the literature method.⁴ **7** (291 mg, 0.51 mmol) was dissolved in pre-dried THF (20 ml), and cooled the solution to -78 °C. N-butyllithium (2.50 M, 0.25ml, 0.63 mmol) was slowly added to the solution, kept the temperature at -78 °C for 1 hour. Then, tributyltin chloride (0.18ml, 0.66 mmol) was slowly added, and stirred at r.t. for 24 hours. The reaction solution was poured to 30 ml cold water, extracted with dichloromethane (50 ml) for three times. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and concentrated with a rotary evaporator, yellow oil was obtained. Yellow oil (0.51 mmol), Pd(PPh₃)₂Cl₂ (6.2 mg, 0.0088 mmol) and PPh₃ (4.6 mg, 0.0176mmol) were dissolved in pre-dried THF (10 ml), and reacted at 100 °C under nitrogen atmosphere for 24 hours. Cooled the reaction solution to r.t., and concentrated with a rotary evaporator. The residue was purified by chromatography (silica gel, dichloromethane: petroleum ether = 1:1). Yield: 72 mg, 24%, red solid. ¹H NMR (400 MHz, Acetone,ppm) δ 8.71 (d, J = 2.4 Hz, 1H), 8.55 – 8.48 (m, 1H), 8.06 (t, J = 6.6 Hz, 1H), 7.95 (d, J = 3.9 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.22 (d, J = 3.9 Hz, 1H), 6.71 (d, J = 2.6 Hz, 1H), 6.63 (dd, J = 8.7, 2.7 Hz, 1H), 4.07 (dt, J = 10.4, 5.5 Hz, 2H), 3.44 – 3.32 (m, 4H), 3.14 – 3.06 (m, 2H), 2.59 (dd, J = 15.7, 8.1 Hz, 2H), 1.63 (dd, J = 14.1, 6.9 Hz, 4H), 1.40 – 1.32 (m, 12H), 1.18 (dd, J = 9.1, 5.1 Hz, 3H), 0.93 – 0.88 (m, 6H). GCT/TOF HRMS-EI(m/z): [M]⁺ calcd. for C₃₄H₄₃N₃O₄S⁺, 589.2974; found: 589.2970.

Synthesis of 3-(2-(5-(2-cyano-4-nitrophenyl)thiophen-2-yl)-5-(dihexylamino)phenyl)propanoic acid (**JY1**)

9 (137 mg, 0.23 mmol) was dissolved in anhydrous alcohol (20 ml), and a solution of LiOH (5.6 mg, 2.3 mmol) in water (2-3 ml) was added slowly. The reaction solution was stirred at r.t. for 48 hours, and then the solution was adjusted to acid with dilute hydrochloric acid. Solid particles were formed, when the solution was poured into deionized water. The particles were filtered, washed with deionized water and dried. The residue was purified by chromatography (silica gel, dichloromethane: methanol = 50:1). Yield: 68 mg, 53%, red solid. ¹H NMR (400 MHz, Acetone,ppm) δ 8.71 (s, 1H), 8.52 (d, J = 8.9 Hz, 1H), 8.06 (d, J = 8.7 Hz, 1H), 7.95 (d, J = 3.7 Hz, 1H), 7.29 (d, J = 8.6 Hz, 1H), 7.23 (d, J = 3.8 Hz, 1H), 6.74 (s, 1H), 6.64 (d, J = 8.7 Hz, 1H), 3.43 – 3.34 (m, 4H), 3.10 (t, J = 7.9 Hz, 2H), 2.61 (t, J = 7.8 Hz, 2H), 1.64 (s, 4H), 1.36 (s, 12H), 0.91 (d, J = 6.6 Hz, 6H). GCT/TOF HRMS-EI(m/z): [M]⁺ calcd. for C₃₂H₃₉N₃O₄S, 561.2661; found: 561.2672.

Absorption spectra of dye JY1:

The absorption spectra of dye **JY1** in acetonitrile and on TiO₂ film are shown in Fig. S1 and the photophysical data are collected in Table S1. Two strong absorption peaks were observed in the UV-Vis spectra, and the maximum absorption wavelengths of the two peaks of **JY1** are 322 nm and 448 nm. The molar extinction coefficient of **JY1** is $1.18 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 448 nm in acetonitrile. On TiO₂ film, the maximum absorption wavelength of peak (>400 nm) for **JY1** red shifted to 476 nm. J-aggregation might be the reason of the red shifts.⁵ Since mono layer adsorption could benefit to light-induce electron transfer⁶, chenodeoxycholic acid (CDCA) was added to the dye bath to prevent the dye aggregation.

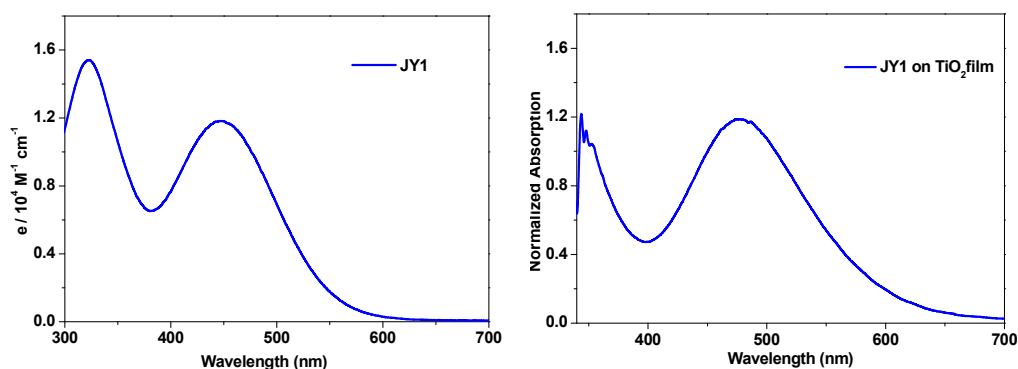


Fig. S1 UV-Vis absorption spectra of the dye JY1 in CH₃CN (left) and on TiO₂ film (right)

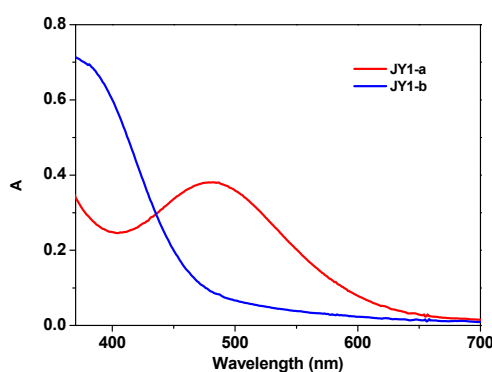


Fig. S2 UV-Vis absorption spectra of the dyes JY1 on TiO₂ film before (a) and after iterative testing (b), respectively.

From figure 3, we can see that the absorption at about 470 nm dropped, and the absorption at about 400 nm rose after colour change. This is caused by the decrease of electron-withdrawing ability of nitro group, after the structure changed. In D- π -A (Donor- π conjugation-Acceptor) system, the drop of electron-withdrawing ability of acceptor will make LUMO (lowest unoccupied molecular orbital) more positive, and E₀₋₀ (zero-zero transition

energy) of dye will decrease. This makes the λ_{max} of dye blue shifted. Therefore, the loss of the visible absorption feature at about 470 nm is caused by the λ_{max} blue shift of dye **JY1**.

Electrochemical characterization of dye **JY1**:

The potentials of **JY1** were obtained by cyclic voltammetry using a three electrode cell and an electrochemical workstation (BAS100B, USA). The working electrode was a glass carbon electrode (HCH Instruments, Inc., Part Number: MF-2012), the auxiliary electrode was a Pt wire (HCH Instruments, Inc., Part Number: CHI115), and Non-Aqueous Ag/Ag^+ reference (HCH Instruments, Inc., Part Number: CHI112) was used as reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF_6) 0.01 M was used as supporting electrolyte in CH_3CN , and ferrocenium/ferrocene (Fc^+/Fc) redox couple was used as an internal potential reference. CV experiments were carried out at 22 °C over the potential range 1.0 V to -1.0 V vs. Ag/Ag^+ at a scan rate of 100 mV s^{-1} .

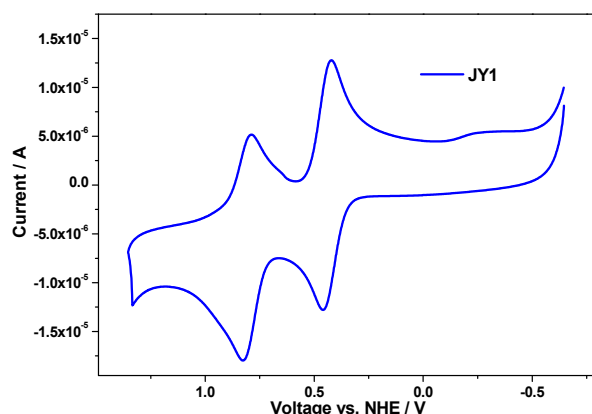


Fig. S3 CV-curve of dyes **JY1 in acetonitrile solution.** The working electrode was a glassy carbon electrode, the auxiliary electrode was a Pt wire, and non-aqueous Ag/Ag^+ reference were used as reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF_6) of 0.01 M concentration was used as supporting electrolyte in acetonitrile.

The electrochemical properties of **JY1** are also measured and shown in Table S1. Cyclic voltammetry (CV) was employed to measure the first oxidation potential (E_{ox}). The first oxidation potential versus normal hydrogen electrode (vs. NHE) calibrated by Fc/Fc^+ (with 440 mV vs. NHE) corresponds to the highest occupied molecular orbital (HOMO) levels of the dye. The HOMO level for **JY1** is found to locate at 0.83 V (vs. NHE). It is more positive than the reducing potential of iodine/iodide (0.4 V vs. NHE) pair, ensuring regeneration of the oxidized dyes after electron injection. The lowest unoccupied molecular orbital (LUMO) level of the **JY1** is estimated from the E_{ox} and the zero-zero transition energy (E_{0-0}) estimated from the absorption spectrum of the dye **JY1** on TiO_2 film. The LUMO level is more negative than

the conduction band edge (CB) of TiO₂ (approximately -0.5 V vs. NHE)⁶, indicating that the electrons could be efficiently injected into the TiO₂ conduction band from the excited dyes. Therefore, the dye **JY1** was considered to have suitable electronic energy levels for TiO₂-based DSCs.

Table S1. UV-Vis absorption and electrochemical properties of the dyes JY1 and JY2

Dye	$\lambda_{\max}$ (nm) ^a	ε ($\times 10^4$ M ⁻¹ cm ⁻¹) at $\lambda_{\max}$	$\lambda_{\max}$ on TiO ₂ film (nm) ^b	E_{0-0} (V) ^c	E_{ox} (V) (vs. NHE) ^d	$E_{\text{ox}}-E_{0-0}$ (V) (vs. NHE)
JY1	448	1.18	476	2.04	0.83	-1.21

^a Absorption spectrum was measured in CH₃CN solution (2×10^{-5} M) at room temperature. ^b Absorption spectrum on TiO₂ was obtained through measuring the dye adsorbed on TiO₂ film in CH₃CN. ^c E_{0-0} was estimated from the abscissa axis and intersection of the tangent of absorption on TiO₂ film by $1240/\lambda$. ^d The oxidation potential of the dye was measured in CH₃CN with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as electrolyte (working electrode: glassy carbon; reference electrode: Ag/Ag⁺; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference and converted to NHE by addition of 440 mV, counter electrode: Pt).

Device fabrication:

TiO₂ film fabrication: Fluorine-doped tin oxide (FTO) glass plates (Pilkington-TEC8) were cleaned (in the order of detergent water solution, and ethanol) using an ultrasonic bath. A layer of compact TiO₂ was deposited to conducting glass substrate by an electrochemical method. The deposition bath was an alkaline (pH = 10) aqueous solution (250 ml) containing 40 mmol titanium tetrachloride TiCl₄ (Aladdin Chemistry Co., Ltd., 99.9 %), 40 mmol ethylenediaminetetraacetic acid EDTA (China Harbin Chemical Reagent Plant, 99.5 %) and 25 mmol Sodium chloride NaCl (Tianjin Damao Chemical Reagent Factory, 99.5 %). The depositions were performed at room temperature (22 °C) in a 250 ml beaker using a three-electrode configuration. The substrate was a 25*75 mm FTO substrate film previously cleaned by ultrasonic washer. A platinum wire electrode (HCH Instruments, Inc., Part Number: CHI115) served as the counter electrode and an Ag/AgCl electrode (HCH Instruments, Inc., Part Number: CHI111) was used as the reference. The deposition potential was -0.8 V vs. Ag/AgCl, and deposition time was set at 30 min. An electrochemical workstation (Shanghai Huachen Instruments, model CH1630D) interfaced with a PC was employed for the depositions. A layer of 13 nm (DHS-TPP3, Heptachroma, China) paste (ca. 2.4 μ m) was coated on the deposited FTO glass by screen printing and then dried for 6 min at 125 °C. This procedure was repeated for 5 times (ca. 12 μ m), then a layer of 300 nm (DHS-SLP1, Heptachroma, China) titania paste (ca. 4 μ m) was coated as scattering layer. The double-layer TiO₂ electrodes (area: 6×6 mm) were gradually heated under an air flow at 520 °C for 30 min. The sintered film was further treated with 40 mM TiCl₄ aqueous solution at 70 °C for 30 min, then washed with water and ethanol, and annealed at 500 °C for 60 min. After the film was cooled to

80 °C, it was immersed into a 2×10^{-4} M dye **JY1** and 7×10^{-6} M CDCA solution in acetonitrile and maintained under dark for 4 h. The sensitized TiO₂ electrode was then rinsed with the ethanol and dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and sputtered Pt/FTO counter electrode separated with a hot-melt Surlyn 1702 film (25 μm, Dupont).

The photoelectric properties of the DSCs fabricated with dye **JY1**

Table S2. Photovoltaic performance of DSCs based on dyes **JY1 and **JY2**^a**

	Dye ^b	J_{sc} (mA·cm ⁻²)	V_{oc} (V)	ff	η (%)
JY1	JY1-a ^c	0.54	0.446	0.627	0.15
	JY1-b ^d	2.12	0.585	0.656	0.81

^a Light intensity: AM 1.5G illumination (100 mW·cm⁻²); TiO₂ thickness 8 μm (active layer) + 4 μm (scattering layer); working area: 0.159 cm²; electrolyte: 0.60 M DMPII, 0.40 M LiI, 0.04 M I₂, 0.10 M TBAI in acetonitrile solution. ^b 2×10^{-4} M of dye and 7×10^{-6} M of CDCA was dissolved in acetonitrile; sensitized time: 4 h. ^c The colour-unchanged DSCs. ^d The colour-changed DSCs.

IPCE spectrum of initial **JY1**-sensitized DSCs and colour-changed DSCs.

From fig. S4, we can see that the IPCE of initial **JY1**-sensitized DSCs have only one peak at about 330 nm, and the colour-changed DSCs have two peaks at about 330 nm and 420 nm. The peak of IPCE at about 330 nm is corresponding to the injection of LUMO+1. From table S3, we can see that a part of electrons moved to cyano group at LUMO+1. Although the injection of cyano group has not been well studied yet, we can see possibility from the high efficiency of DSC sensitized by dye HY113 with three cyano groups⁷. The reason of 400 nm peak loss could be ascribed as follows. In initial **JY1**-sensitized DSCs, dye **JY1** absorbed light at about 470 nm, and the electrons were excited to LUMO. The LUMO of **JY1** is around the nitro group, which can be seen from the DFT calculation in the manuscript. The nitro group cannot efficiently inject the electron to the conduction band of TiO₂. Although dye **JY1** has absorbed the light at about 470 nm, the IPCE at 400-500 nm are very low. This is also the reason that the efficiencies of initial DSCs are comparably low. After colour change, the reduced nitro group connected to the surface of TiO₂, and this make the electrons can be injected to the conduction band of TiO₂. Therefore, there is a high peak at about 420 nm. The reason for a wider IPCE than UV-Vis absorption on TiO₂ is the containing of Li⁺ in electrolyte. The Li⁺ can lower the conduction band of TiO₂, and this made a wider IPCE.⁸ Our electrolyte contains more lithium salt than conventional electrolyte, and this made the phenomenon obviously.

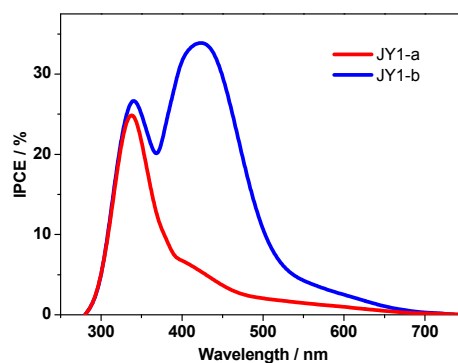
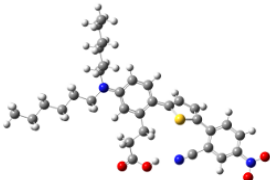
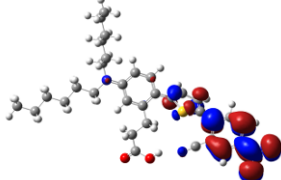
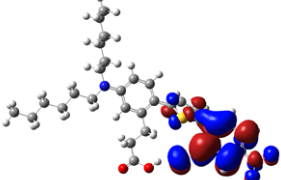


Fig. S4 IPCE spectrum of initial JY1-sensitized DSCs (a) and colour-changed DSCs (b).

Table S3. The optimized structures and electron distribution in LUMO and LUMO+1 levels of the JY1.

Dye	Optimized structure	LUMO	LUMO+1
JY1			

1. H. Ozaki, T. Setaka, S. Tsuchiya, T. Kawai, M. Kuwahara and H. Sawai, *Nucleic Acids Symposium Series*, 2007, **51**, 137-138.
2. L. M. Strawn, R. E. Martell, R. U. Simpson, K. L. Leach and R. E. Counsell, *Journal of Medicinal Chemistry*, 1989, **32**, 2104-2110.
3. P. Vachal and L. M. Toth, *Tetrahedron Letters*, 2004, **45**, 7157-7161.
4. C. Zhao, X. Chen, C. Gao, M.-K. Ng, H. Ding, K. Park and Y. Gao, *Synthetic Metals*, 2009, **159**, 995-1001.
5. K. Sayama, K. Hara, N. Mori, M. Satsuki, S. Suga, S. Tsukagoshi, Y. Abe, H. Sugihara and H. Arakawa, *Chemical Communications*, 2000, 1173-1174.
6. A. Hagfeldt and M. Grätzel, *Chemical Reviews*, 1995, **95**, 49-68.
7. Y. Hao, X. Yang, M. Zhou, J. Cong, X. Wang, A. Hagfeldt and L. Sun, *ChemSusChem*, 2011, **4**, 1601-1605.
8. A. Furube, R. Katoh, K. Hara, T. Sato, S. Murata, H. Arakawa and M. Tachiya, *The Journal of Physical Chemistry B*, 2005, **109**, 16406-16414.