Electronic Supplementary Information

Structure-Activity Relationship of Naphthalene Based Donor-π-Acceptor Organic Dyes for Dye-Sensitized Solar Cells: Remarkable Improvement of Open-Circuit Photovoltage

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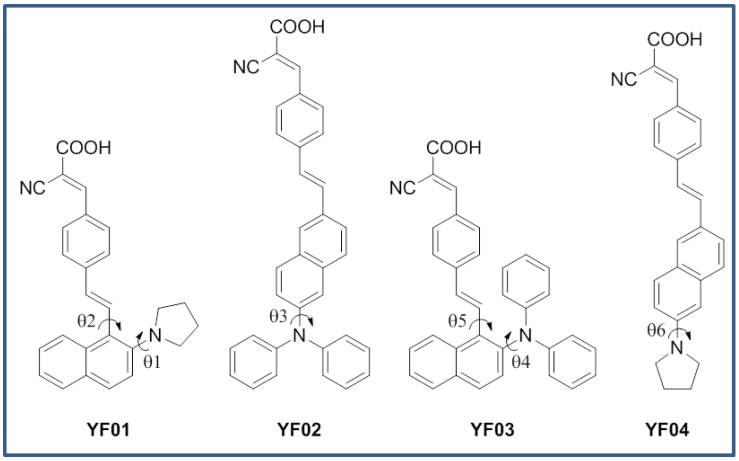
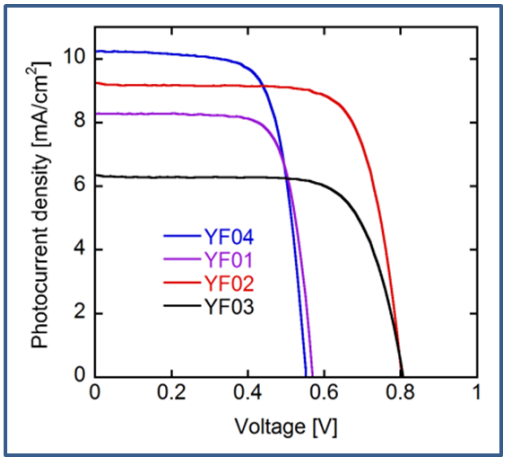




DSCs fabrication process

A double-layer TiO_2 photoelectrode (10+5) μm in thickness with a 10 μm thick nanoporous layer and a 5 μm thick scattering layer (area: 0.25 cm^2) was prepared by screen printing on conducting glass substrate.[1] A dye solution of YF04-01 with 3 x 10^{-4} M concentration in acetonitrile/*tert*-butyl alcohol (1/1, v/v) was used to up take the dye on to the TiO_2 film. Deoxycholic acid (DCA) (20 mM) as a co-adsorbent was added into the dye solution to prevent aggregation of the dye molecules. The TiO_2 films were immersed into the dye solution and then kept at 25 ^oC for 30 h. Photovoltaic measurements were performed in a sandwich type solar cell in conjunction with an electrolyte consisting of a solution of 0.6M dimethylpropyl-imidazolium iodide (DMPII), 0.05M I_2, 0.1M LiI and 0.5M *tert*-butylpyridine (TBP) in acetonitrile (AN). The dye-deposited TiO_2 film and a platinum-coated conducting glass were separated by a Surlyn spacer (40 μm thick) and sealed by heating the polymer frame.

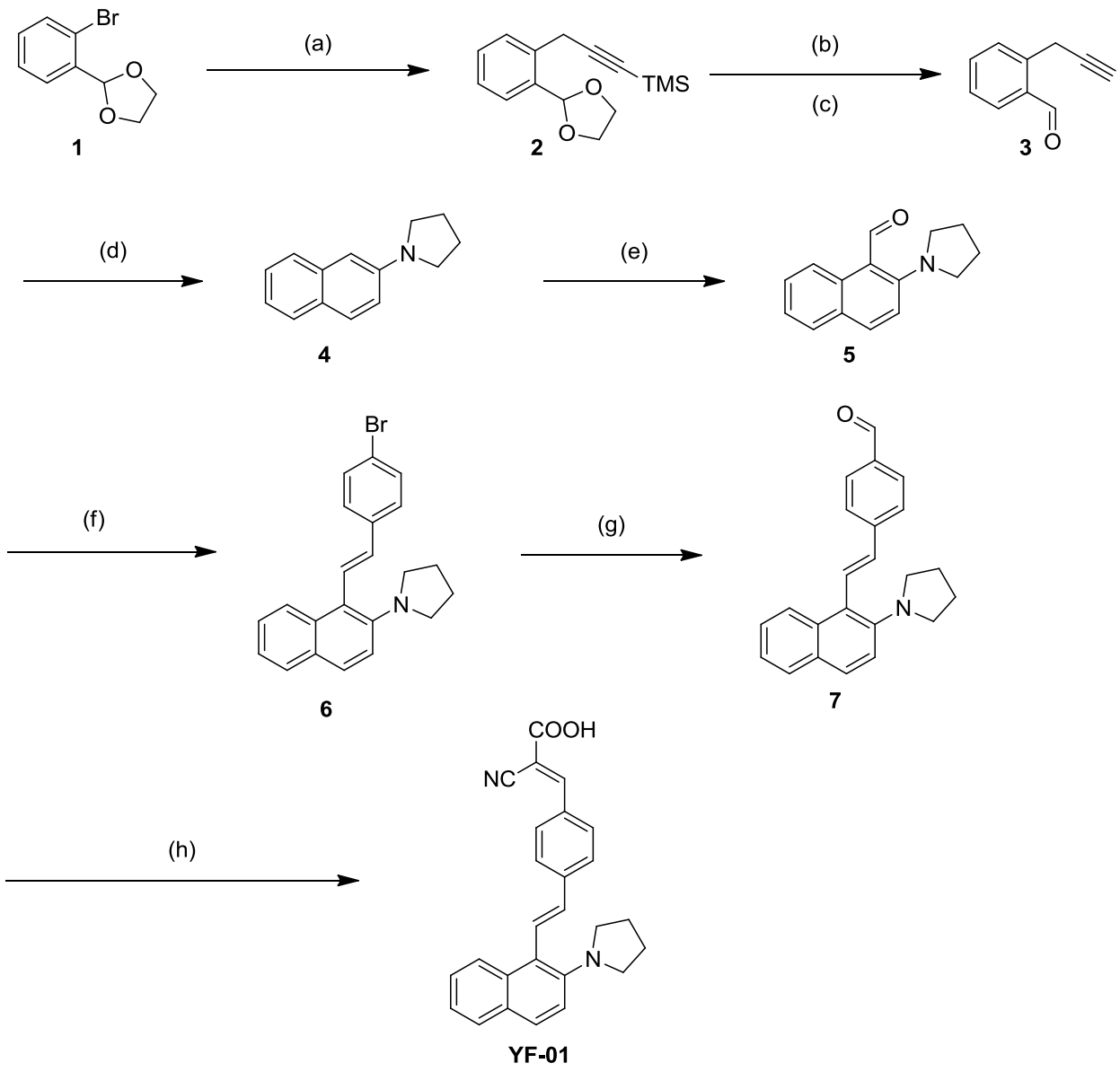
EIS and IMVS measurements

The intensity-modulated photovoltage spectra (IMVS) were measured with a potentiostat (Solartron1287) equipped with a frequency response analyzer (Solartron1255B) at an open-circuit condition based on a monochromatic illumination (420 nm) controlled by Labview system to obtain the photovoltaic response induced by the modulated light. The modulated light was driven with a 10% AC perturbation current super imposed on a DC current in a frequency range from 0.1 to 10^6 Hz. The charge extraction method (CEM) was performed with the same monochromatic light source. The solar cell was illuminated at an open-circuit condition for 5 s to attain a steady state and then the light source was switched off when the device simultaneously switched to a short-circuit condition to extract the charges generated at that light intensity. The electrochemical impedance spectra were measured with an impedance analyzer (Solartron Analytical, 1255B) connected with a potentiostat (Solartron Analytical, 1287) under illumination using a solar simulator (WXS-155S-10: Wacom Denso Co. Japan). EIS spectra were recorded over a frequency range of 10^{-2}–10^6 Hz at 298 K. The applied bias voltage and AC amplitude were set at *V*oc of the DSCs. The electrical impedance spectra were characterized using *Z*-View software (Solartron Analytical).

General Information: ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JMTC-270/54/SS (JASTEC, 400 MHz) and BRUKER (600 MHz) spectrometers. 1H NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of $CDCl_3$ at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet and m = multiple), and coupling constants (Hz). ^{13}C NMR spectra reported in ppm (δ) relative to the central line of triplet for $CDCl_3$ at 77 ppm. High-resolution mass spectra were obtained on a BRUKER APEXIII spectrometer. Column chromatography was carried out employing Silica gel 60N (spherical, neutral, 40~100 μm, KANTO Chemical Co.). Analytical thin-layer chromatography (TLC) was performed on 0.2

mm precoated plate Kieselgel 60 F254 (Merck). All other reagents and solvents commercially available were used without further purification unless otherwise noted.

Synthesis of YF dyes



Scheme S1. Synthesis of **YF-01.** (a) Mg/(3-bromoprop-1-yn-1-yl)trimethylsilane, THF, rt to reflux. (b) K_2CO_3, MeOH, rt. (c) PPTS, EtOH, reflux. (d) Pyrrolidine, MS 4Å, rt. (e) $POCl_3$/DMF, rt, 71%. (f) diethyl 4-bromobenzylphosphonate/KO*t*Bu, THF, 75%. (g) *n*BuLi/DMF, THF, -78°C to rt, 88%. (h) 2-cyanoacetic acid/NH_4OAc, CH_3COOH/CH_3CN, reflux, 92%.

1-(naphthalen-2-yl)pyrrolidine (4)

Compound 4 was synthesized by reported method[1]

2-(pyrrolidin-1-yl)-1-naphthaldehyde (5)

To a solution of 1-(naphthalen-2-yl) pyrrolidine **4** (395 mg, 2 mmol) in DMF (20 mmol, 1.5 mL) was add $POCl_3$ (20 mmol, 1.83 mL) at room temperature for 2 h, and then dilute with water, nutrulized by NaOH and aqueous solution of $NaHCO_3$, extracted with EtOAc. The combined organic phases were dried over anhydrous $MgSO_4$. Solvents were removed by rotary evaporation, and the residue was purified by silica-gel column chromatography with hexane-EtOAc (10:1) as eluent to yield the product **5** as a yellow solid (320mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 8.91 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 9.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 9.2 Hz, 1H), 3.51 (t, *J* = 6.4 Hz, 4H), 1.95 (t, *J* = 6.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.77, 153.12, 134.82, 133.42, 128.63, 127.99, 126.68, 122.66, 122.41, 116.22, 112.02, 53.71, 25.88.

(E)-1-(1-(4-bromostyryl)naphthalen-2-yl)pyrrolidine (6)

Diethyl 4-bromobenzylphosphonate (480 mg, 1.56 mmol) and **5** (320 mg, 1.42 mmol) were dissolved in anhydrous THF 30 mL. *t*-BuOK (191.2 mg,1.7 mmol) was added to the solution, and stirred overnight reflux. After cooling to room temperature, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-EtOAc (80:1) as eluent to yield the product 6 as a yellow solid (510mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.8 Hz, 1H), 8.00 (d, *J* = 5.6 Hz, 1H), 7.95 (d, *J* = 6.8 Hz, 1H), 7.78-7.75 (m, 3H), 7.70-7.66 (m, 3H), 7.55- 7.52 (m, 2H), 6.95 (d, *J* = 13.6 Hz, 1H), 3.61 (t, *J* = 5.2 Hz, 4H), 2.17 (t, *J* = 5.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.21, 137.10, 133.29, 132.00, 131.77, 128.27, 128.14, 128.09, 127.68, 127.60, 126.22, 123.51, 122.41, 120.91, 119.15, 116.92, 52.05, 25.56.

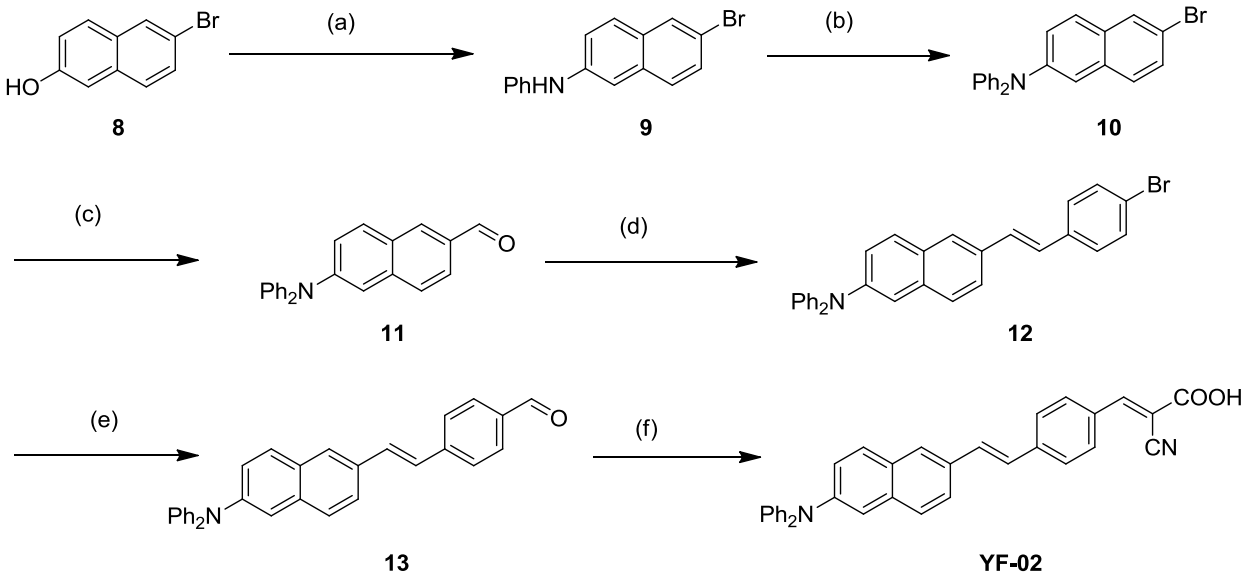
(E)-1-(1-(4-bromostyryl)naphthalen-2-yl)pyrrolidine (7)

The compund **6** (510 mg, 1.35 mmol) was dissolved in anhydrous THF 15 mL, *n*-BuLi (1.65 M in hexane, 1 mL) was added slowly to the solution at -78 °C for 1 h, after that DMF (312 µL,4 mmol) was added, after warmed to room temperature, and react 1 h, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-EtOAc (10:1) as eluent to yield the product **7** as a yellow solid (389mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.78-7.63 (m, 5H), 7.44-7.39 (m, 1H), 7.28-7.20 (m, 2H), 6.78 (d, *J* = 16.8 Hz, 1H), 3.32 (t, *J* = 6.4 Hz, 4H), 1.89 (t, *J* = 6.4 Hz, 4H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ 191.28, 146.25, 144.03, 134.83, 132.99, 131.61, 130.40, 130.07, 128.41, 128.05, 128.02, 126.24, 126.21, 123.08, 122.31, 118.28, 116.74, 52.09, 25.54. HRMS (ESI positive): $[M+H]^+$ calcd for $C_{23}H_{21}NOH$, 328.16959; found, 328.16952.

(*E*)-2-cyano-3-(4-((E)-2-(2-(pyrrolidin-1-yl)naphthalen-1-yl)vinyl)phenyl)acrylic acid (YF-01)

A mixture of **7** (389 mg, 1.2 mmol), 2-cyanoacetic acid (306 mg, 3.6 mmol) and ammonium acetate (46mg, 0.6 mmol) was dissolved in 10 mL acetonitrile and 10 mL acetic acid, and the mixture was stirred for 12 hours under Ar under reflux condition. After evaporation of the solvent, the crude solid was dissolved into CH_2Cl_2 and purification by column chromatography over silica gel to give compound **YF-01** as red solid (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.94 (s, 1H), 8.31 (s, 1H), 8.06 (d, *J* = 8.4 Hz, 3H), 7.90-7.84 (m, 3H), 7.77- 7.72 (m, 2H), 7.40-7.37 (m, 1H), 7.31-7.23 (m, 2H), 6.70 (d, *J* = 16.8 Hz, 1H), 3.30 (bs, 4H), 1.86 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.34, 153.49, 145.83, 142.46, 132.90, 131.22 (x2), 130.17, 130.08, 128.29, 127.91, 127.37, 126.62, 126.31, 122.82, 122.01, 116.97, 116.78, 102.300, 51.83, 25.30. HRMS (ESI positive): $[M+H]^+$ calcd for $C_{26}H_{22}N_2O_2H$, 395.17540; found, 395.17546.



Scheme S2. Synthesis of **YF-02.** (a) aniline, PTSA, xylene, 190 °C. (b) iodobenzene, Cu, K_2CO_3, *o*-DCB, 180 °C. (c) *n*-BuLi/DMF, THF, -78°C to rt, 93%. (d) diethyl 4-bromobenzylphosphonate/KO*t*Bu, THF, 97%. (e) *n*-BuLi/DMF, THF, -78°C to rt, 78%. (f) 2-cyanoacetic acid/NH_4OAc, CH_3COOH/CH_3CN, reflux, 75%.

6-bromo-N,N-diphenylnaphthalen-2-amine (10)

Compound **10** was synthesized by reported methodoligy[2]

6-(diphenylamino)-2-naphthaldehyde (11)

The compund **10** (375mg, 1 mmol) was dissolved in anhydrous THF 10 mL, *n*-BuLi (1.65 M in hexane, 0.8 mL) was added slowly to the solution at -78 ^{o}C for 1 h, after that DMF (231 µL, 3 mmol) was added, after warmed to room temperature, and react 1 h, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-EtOAc (10:1) as eluent to yield the product **11** as a yellow solid (300mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.18 (s, 1H), 7.87-7.80 (m, 2H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.38-7.32 (m, 6H), 7.22-7.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.37, 148.31, 146.64, 137.60, 133.85, 132.12, 130.16, 129.35, 127.94, 127.32, 125.22, 124.00, 123.41, 123.24, 116.82.

(E)-6-(4-bromostyryl)-N,N-diphenylnaphthalen-2-amine (12)

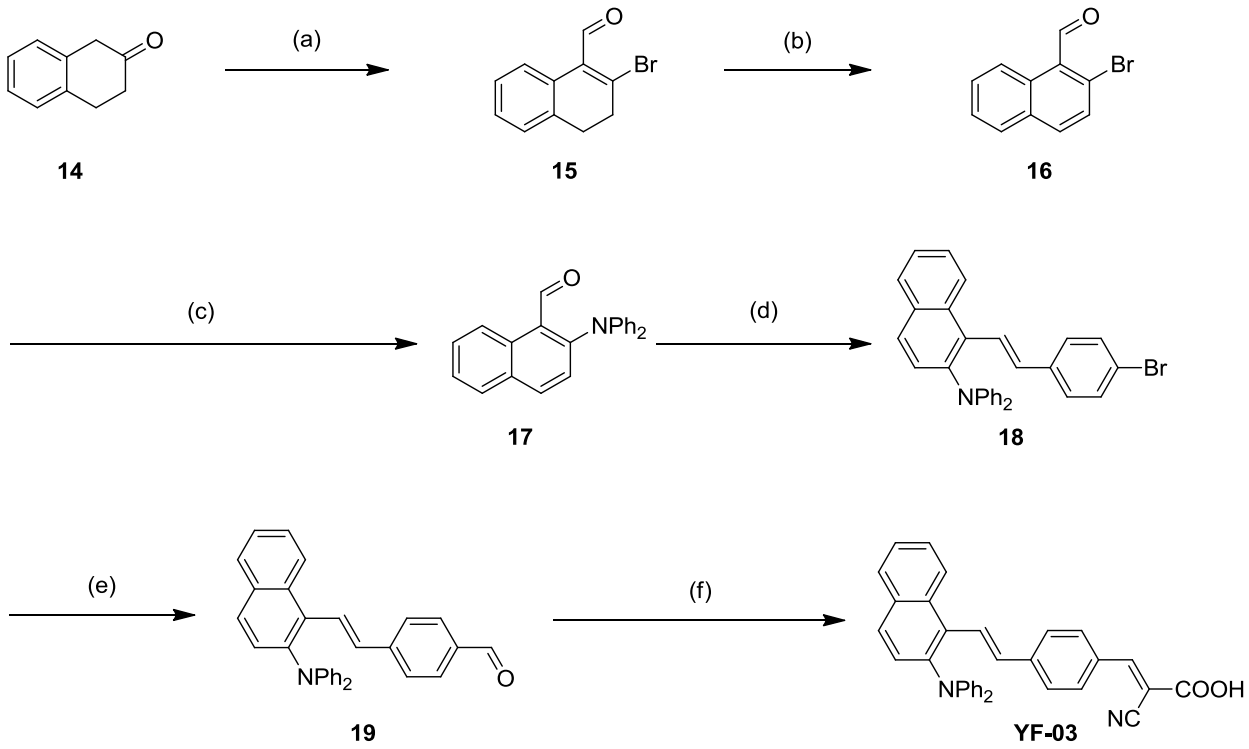
Diethyl 4-bromobenzylphosphonate (314.2 mg, 1.02 mmol) and **11** (300 mg, 0.93 mmol) were dissolved in anhydrous THF 20 mL. *t*-BuOK (125.23 mg, 1.12 mmol) was added to the solution, and stirred overnight reflux. After cooling to room temperature, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-EtOAc (80:1) as eluent to yield the product **12** as a yellow solid (429 mg, 97 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.49 (s, 1H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.39-7.35 (m, 5H), 7.29-7.24 (m, 5H), 7.18-7.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.44, 145.62, 136.23, 134.01, 132.83, 131.62, 129.81, 129.36, 129.21, 128.84, 127.75, 127.22, 126.63, 126.48, 124.46, 124.36, 123.69, 123.04, 121.01, 119.40.

(*E*)-4-(2-(6-(diphenylamino)naphthalen-2-yl)vinyl)benzaldehyde (13)

The compound **12** (429 mg, 0.9 mmol) was dissolved in anhydrous THF 10 mL, *n*BuLi (1.65M in hexane, 0.71 mL) was added slowly to the solution at -78 °C for 1 h, after that DMF (208 µL, 2.7 mmol) was added, after warmed to room temperature, and react 1 h, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-EtOAc (10:1) as eluent to yield the product **13** as a yellow solid (299mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.75 (s, 1H), 7.67-7.60 (m, 4H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.36 (d, *J* = 16.0 Hz, 2H), 7.28-7.24 (m, 5H), 7.17-7.12 (m, 5H), 7.07-7.03 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.29, 147.36, 145.98, 143.41, 134.98, 134.32, 132.36, 132.18, 130.10, 129.65, 129.24, 128.95, 127.31, 127.23, 126.62, 126.46, 124.58, 124.30, 123.67, 123.19, 119.06. HRMS (ESI positive): $[M+H]^+$ calcd for $C_{31}H_{23}NOH$, 426.18524; found, 426.18518.

(*E*)-2-cyano-3-(4-((E)-2-(6-(diphenylamino)naphthalen-2-yl)vinyl)phenyl)acrylic acid (YF-02)

A mixture of **13** (149mg, 0.35 mmol), 2-cyanoacetic acid (89mg, 1.05 mmol) and ammonium acetate (20mg,0.25 mmol) was dissolved in 7 mL acetonitrile and 7 mL acetic acid, and the mixture was stirred for 12 hours under Ar under reflux condition. After evaporation of the solvent, the crude solid was dissolved into CH_2Cl_2 and purification by column chromatography over silica gel to give compound **YF-02** as red solid (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.06 (d, *J* = 8.8 Hz, 2H), 7.96 (s, 1H), 7.82-7.77 (m, 4H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 16.4 Hz, 1H), 7.42 (d, *J* = 16.4 Hz, 1H), 7.34-7.30 (m, 5H), 7.18 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 7.10-7.06 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.30, 153.33, 146.85, 145.39, 141.95, 133.89, 132.58, 131.88, 131.21, 130.21, 129.53, 129.32, 129.27, 127.24, 127.01, 126.87, 126.71, 124.21, 124.04, 123.79, 123.36, 118.56, 116.38, 102.27. HRMS (ESI positive): $[M+Na]^+$ calcd for $C_{34}H_{24}N_2O_2Na$, 515.17300; found, 515.17291.



Scheme S3. Synthesis of **YF-03.** (a) PBr_3/DMF, CH_3Cl, 0 °C to rt, 50%. (b) DDQ, toluene, reflux, 72%. (c) $Pd(OAc)_2$/(o-biphenyl)P(*t*-Bu)$_2$/K_3PO_4, toluene, 110 °C, 57%. (d) diethyl 4-bromobenzylphospho-nate/KO*t*Bu, THF, 90%. (e) *n*-BuLi/DMF, THF, -78°C to rt, 80%. (f) 2-cyanoacetic acid/NH_4OAc, CH_3COOH/CH_3CN, reflux, 70%.

2-bromo-1-naphthaldehyde (16)

Compound **16** was synthesized by reported method[3]

2-(diphenylamino)-1-naphthaldehyde (17)

A toluene (8 mL) solution of **16** (940.4mg, 4 mmol), diphenylamine (694 mg, 4.1 mmol), K_3PO_4 (1.2g, 5.6mg), $Pd(OAc)_2$ (45 mg, 0.2 mmol) and (*o*-biphenyl)P(*t*-Bu)$_2$ (120mg, 0.4 mmol) was stirred at 110 °C for 3 days. After cooling, the solution filtered through celite, wash with CH_2Cl_2, the combined organic phases were removed by rotary evaporation, and the residue was purified by silica-gel column chromatography with hexane-CH_2Cl_2 to give compound **17** (730mg, 57%).

(*E*)-1-(4-bromostyryl)-N,N-diphenylnaphthalen-2-amine (18)

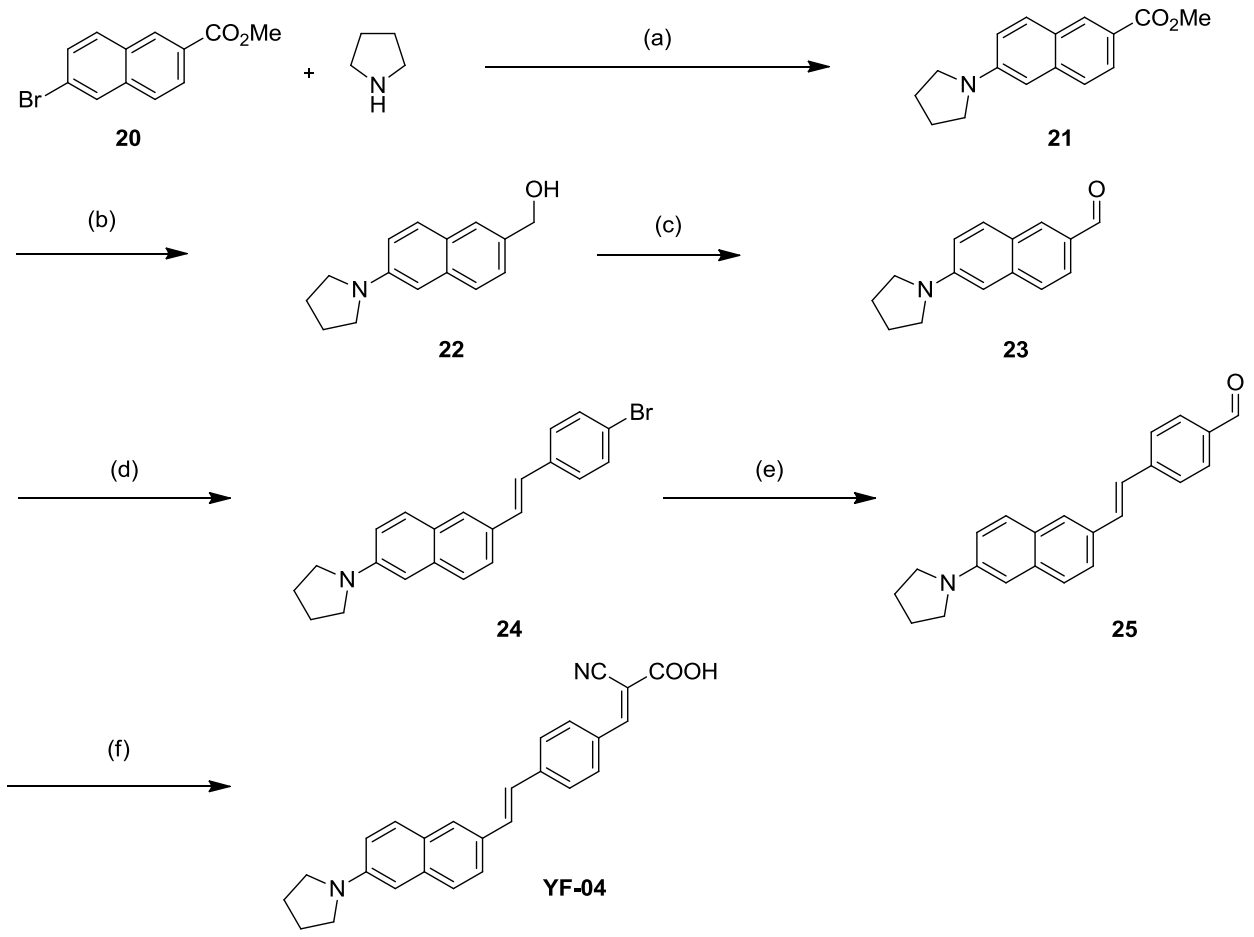
Diethyl 4-bromobenzylphosphonate (74 3mg, 2.4 mmol) and **17** (711 mg, 2.2 mmol) were dissolved in anhydrous THF 22 mL. *t*-BuOK (296mg, 2.64 mmol) was added to the solution, and stirred 3 h reflux. After cooling to room temperature, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-CH_2Cl_2 (100:1-10:1) as eluent to yield the product **18** as a yellow solid (943 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.23 (m, 1H), 7.95-7.86 (m, 2H), 7.57- 7.55 (m, 2H), 7.46 (d, *J* = 7.2 Hz, 3H), 7.28-7.24 (m, 4H), 7.17-7.10 (m, 4H), 7.02-6.98 (m, 2H), 6.79 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.38, 142.13, 136.28, 133.31, 133.06, 131.89, 131.72, 131.32, 128.94, 128.19, 127.77, 127.73, 126.29, 125.38, 125.07, 124.95, 122.09, 121.65, 121.14.

(E)-4-(2-(2-(diphenylamino)naphthalen-1-yl)vinyl)benzaldehyde (19)

The compound **18** (429 mg, 0.9 mmol) was dissolved in anhydrous THF 10 mL, *n*-BuLi (1.65M in hexane, 0.71 mL) was added slowly to the solution at -78 °C for 1 h, after that DMF (208 µL, 2.7 mmol) was added, after warmed to room temperature, and react 1 h, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-EtOAc (10:1) as eluent to yield the product **19** as a yellow solid (306.36 mg, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.00 (s, 1H), 8.20-8.17 (m, 1H), 7.90-7.80 (m, 4H), 7.54- 7.52 (m, 2H), 7.42-7.37 (m, 3H), 7.29-7.18 (m, 5H), 7.05 (d, *J* = 7.2 Hz, 4H), 6.94 (t, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.51, 147.36, 143.40, 142.45, 135.12, 133.31, 132.92, 131.85, 131.10, 129.83, 129.31, 128.98, 128.28, 127.91, 127.64, 126.67, 126.46, 125.45, 124.89, 122.18, 121.79. HRMS (ESI positive): $[M+H]^+$ calcd for $C_{31}H_{23}NOH$, 426.18524; found, 426.18518.

(E)-2-cyano-3-(4-((E)-2-(2-(diphenylamino)naphthalen-1-yl)vinyl)phenyl)acrylic acid (YF-03)

A mixture of **19** (149 mg, 0.35 mmol), 2-cyanoacetic acid (89 mg, 1.05 mmol) and ammonium acetate (20 mg,0.25 mmol) was dissolved in 7 mL acetonitrile and 7 mL acetic acid, and the mixture was stirred for 12 hours under Ar under reflux condition. After evaporation of the solvent, the crude solid was dissolved into CH_2Cl_2 and purification by column chromatography over silica gel to give compound **YF-03** as red solid (92 % yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.94 (s, 1H), 8.26 (s, 1H), 8.19-8.16 (m, 1H), 7.96- 7.92 (m, 4H), 7.54-7.49 (m, 4H), 7.39 (d, J = 16.4 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 7.20-7.16 (m, 4H), 6.92 -6.86 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.22, 153.44, 146.92, 141.90, 141.56, 132.86, 132.33, 131.53, 130.93, 130.64, 130.42, 129.54, 129.13, 128.28, 127.47, 126.81, 126.76, 125.64, 124.70, 121.77, 121.68, 116.22, 102.58. HRMS (ESI positive): $[M+H]^+$ calcd for $C_{34}H_{24}N_2O_2H$, 493.19105; found, 493.19106.



Scheme S4. Synthesis of **YF-04.** (a) $Pd(OAc)_2$/(*o*-biphenyl)P(t-Bu)$_2$/K_3PO_4, toluene, 85 °C, 43%. (b) $LiAlH_4$, THF, 96%. (c) MnO_2, CH_2Cl_2, rt, 75%. (d) diethyl 4-bromobenzylphosphonate /KO*t*Bu, THF, 83%. (e) *n*-BuLi/DMF, THF, -78°C to rt, 85%. (f) 2-cyanoacetic acid/NH_4OAc, CH_3COOH/CH_3CN, reflux, 76%.

methyl 6-(pyrrolidin-1-yl)-2-naphthoate (21)

A toluene (8 mL) solution of **20** (1 g, 4 mmol), pyrrolidine (418 µL, 5 mmol), K_3PO_4 (1.2g, 5.6 mg), $Pd(OAc)_2$ (45 mg, 0.2 mmol) and (*o*-biphenyl)P(*t*-Bu)$_2$ (120 mg, 0.4 mmol) was stirred at 80 °C for 18 hours. After cooling, the solution filtered through celite, wash with CH_2Cl_2, the combined organic phases were removed by rotary evaporation, and the residue was purified by silica-gel column chromatography with hexane-CH_2Cl_2 to give compound **21** (433.5 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 6.72 (s, 1H), 3.94 (s, 3H), 3.43 (t, *J* = 6.0 Hz, 4H), 2.07 (t, *J* = 6.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.61, 147.36, 137.66, 131.11, 130.47, 125.68, 125.42, 124.75, 122.19, 116.09, 104.11, 51.84, 47.71, 25.56.

(6-(pyrrolidin-1-yl)naphthalen-2-yl)methanol (22)

A THF (4 mL) solution of **21** (433.5 mg, 1.7 mmol), $LiAlH_4$ (200mg, 5.3 mmol) was added slowly at 0 °C. After warmed to room temperature, and react 1 hour, water was added, and the mixture was treated extracted with EtOAc. The combined extract was dried over anhydrous $MgSO_4$ and filtered. Solvents were removed by rotary evaporation, and the residue **22** was used next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.62 (m, 3H), 7.36 (d, *J* = 8.8 Hz, 1H), 7.00 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 6.75 (s, 1H), 4.77 (s, 2H), 3.41 (t, *J* = 6.0 Hz, 4H), 2.06 (t, *J* = 6.0 Hz, 4H), 1.62 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.92, 134.76, 133.35, 128.72 (x2), 126.19 (x2), 125.80, 115.87, 104.50, 65.92, 47.81, 25.55.

6-(pyrrolidin-1-yl)-2-naphthaldehyde (23)

A CH_2Cl_2 (10 mL) solution of **22,** MnO_2 (1.5 g, 17 mmol) was added, after react 12 hours at room temperature, the solution filtered through celite wash with CH_2Cl_2, the combined organic phases were removed by rotary evaporation, and the residue was purified by silica-gel column chromatography with hexane-CH_2Cl_2 to give compound **23** (276 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.08 (s, 1H), 7.80-7.74 (m, 2H), 7.60 (d, *J* = 8.8 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.69 (s, 1H), 3.40 (t, *J* = 6.0 Hz, 1H), 2.05 (t, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.42, 147.92, 138.68, 134.93, 130.71, 129.85, 126.22, 124.53, 123.26, 116.16, 104.40, 47.62, 25.44.

(E)-1-(6-(4-bromostyryl)naphthalen-2-yl)pyrrolidine (24)

Diethyl 4-bromobenzylphosphonate (153.6 mg, 0.5 mmol) and **23** (100 mg, 0.45 mmol) were dissolved in anhydrous THF 20 mL. *t*-BuOK (68 mg, 0.6 mmol) was added to the solution, and stirred overnight reflux. After cooling to room temperature, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-EtOAc (80:1) as eluent to yield the product

24 as a yellow solid (157 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.8 Hz, 2H), 7.60 (s, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 16.4 Hz, 1H), 7.06-6.97 (m, 2H), 6.73 (s, 1H), 3.42 (bs, 4H), 2.07 (bs, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.06, 136.81, 135.03, 131.62, 130.05, 129.77, 129.04, 127.62, 126.98, 126.20, 126.03, 124.94, 123.64, 120.52, 115.91, 104.71, 47.81, 25.58.

(*E*)-4-(2-(6-(pyrrolidin-1-yl)naphthalen-2-yl)vinyl)benzaldehyde (25)

The compound **25** (151 mg, 0.4 mmol) was dissolved in anhydrous THF 10 mL, *n*BuLi (1.65M in hexane, 0.3 mL) was added slowly to the solution at -78 °C for 1 h, after that DMF (92 µL, 1.2 mmol) was added, after warmed to room temperature, and react 1 h, water was added, and the mixture was treated extracted with CH_2Cl_2. The combined extract was dried over anhydrous Na_2SO_4 and filtered. Solvents were removed by rotary evaporation, and the residue was purification by column chromatography over silica gel with hexane-EtOAc (10:1) as eluent to yield the product **25** as a yellow solid (111 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.74-7.63 (m, 6H), 7.80 (d, *J* = 16.4 Hz, 1H), 7.14 (d, *J* = 16.4 Hz, 1H), 6.99 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.74 (s, 1H), 3.43 (t, *J* = 6.4 Hz, 4H), 2.07 (t, *J* = 6.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.47, 146.29, 144.10, 135.38, 134.73, 132.95, 130.20, 129.35, 129.24, 127.85, 126.46, 126.30, 125.92, 124.76, 123.64, 115.99, 104.71, 47.797, 25.589. HRMS (ESI positive): $[M+H]^+$ calcd for $C_{23}H_{21}NOH$, 328.16959; found, 328.16953.

(*E*)-2-cyano-3-(4-((E)-2-(6-(pyrrolidin-1-yl)naphthalen-2-yl)vinyl)phenyl)acrylic acid (YF-04)

A mixture of **25** (149 mg, 0.34 mmol), 2-cyanoacetic acid (89 mg, 1.05 mmol) and ammonium acetate (20 mg,0.25 mmol) was dissolved in 7 mL acetonitrile and 7 mL acetic acid, and the mixture was stirred for 12 hours under Ar under reflux condition. After evaporation of the solvent, the crude solid was dissolved into CH_2Cl_2 and purification by column chromatography over silica gel to give compound **YF-02** as red solid (76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.83 (s, 1H), 7.77-7.69 (m, 4H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 16.4 Hz, 1H), 7.29 (d, *J* = 16.4 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.75 (s, 1H), 3.35 (bs, 4H), 1.99 (bs, 4H). HRMS (ESI positive): $[M+H]^+$ calcd for $C_{26}H_{22}N_2O_2H$, 395.17540; found, 395.17547.

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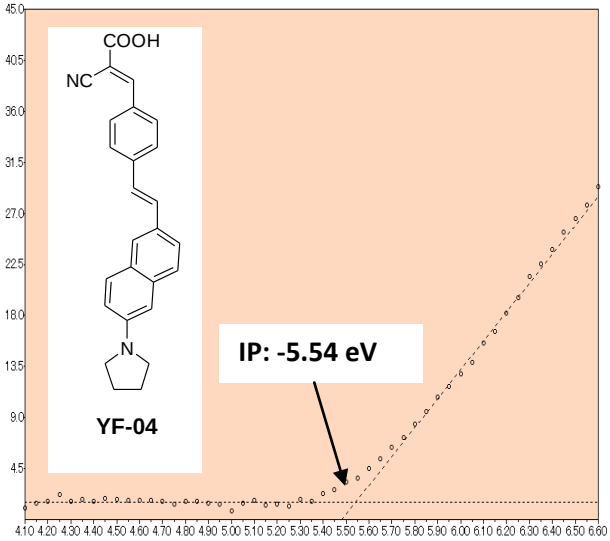
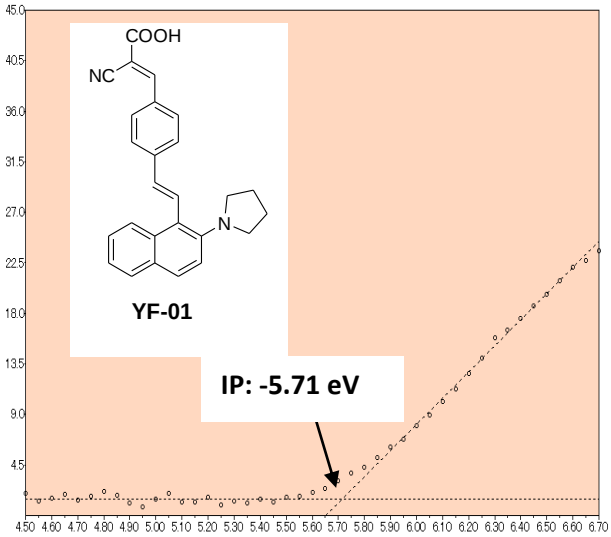
Ionization Potential (IP)





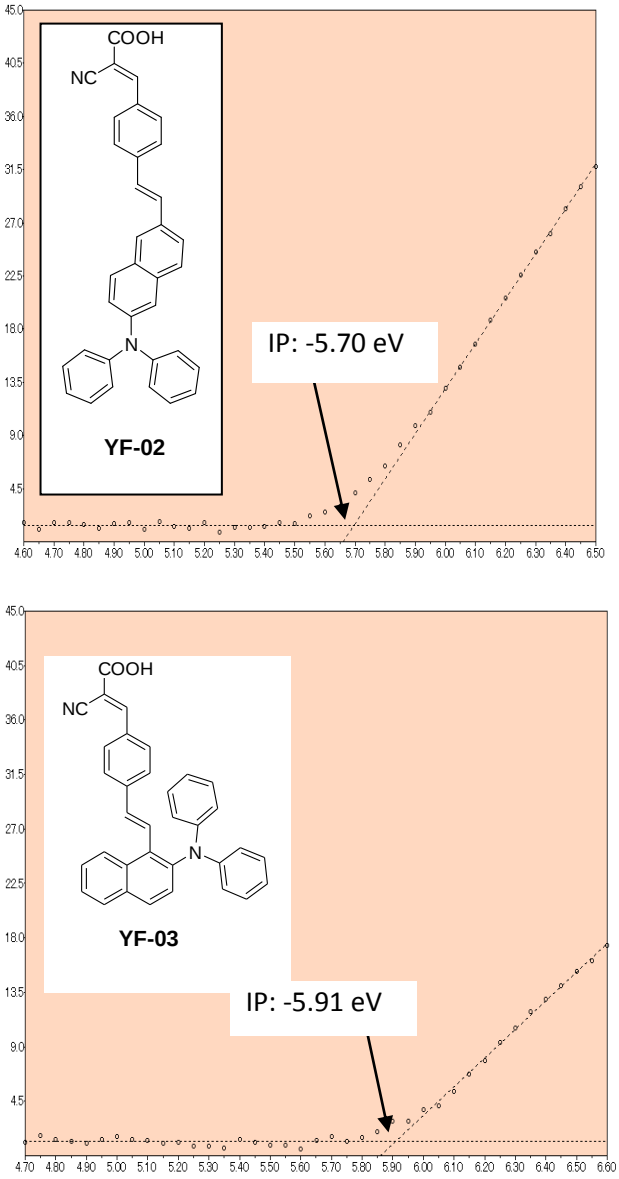


Fig. S1 Ionization potential (IP) of dyes **YF04-01** bound to nanocrystalline TiO_2 film was determined by using the photoemission yield spectrometer (Riken Keiki, AC-3E).

Table S1. Photophysical properties of dyes **YF01-04**.

Dye	$^{a}\lambda_{max}$ (nm)	ε ($M^{-1}cm^{-1}$)	$\lambda_{on\text{-}set}$ on TiO_2 film (nm)	$E_{0\text{-}0}$ (eV)	Ionization Potential (IP)(eV)	$S^{+/*c}$ (eV)
YF-04	316, 423	21110	650	1.91	-5.54	-3.63
YF-01	309, 407	10816	575	2.16	-5.71	-3.55

YF-02	298, 406	32193	550	2.25	-5.70	-3.45
YF-03	324	27349	520	2.39	-5.91	-3.52

[a] Absorption maxima, measured in ethanol at room temperature; [b] $E_{0\text{-}0}$ was estimated from the absorption onset of dye loaded TiO_2 film; [c] The excited-state oxidation potential, $S^{+/*}$ levels were calculated from the expression of $S^{+/*}$ = IP - $E_{0\text{-}0}$.

Table S 2. The photovoltaic data of DSSCs based on **YF 01-04** dyes.

Dye	J_{sc}[mA cm^{-2}]	V_{oc}[V]	Fill factor *[ff]*	η [%]
YF-04	10.24	0.552	0.712	4.03
YF-01	8.33	0.574	0.747	3.57
YF-02	9.19	0.799	0.721	5.29
YF-03	6.494	0.807	0.700	3.67

Measurements were performed under AM 1.5 irradiation on the DSCs devices with 0.25 cm^2 active surface area defined by a metal mask. J_{SC}: short circuit current; V_{OC}: open circuit voltage; *ff*: fill factor; η: conversion efficiency.