

Supporting information

New porphyrin dyes containing hydrazide anchor for dye-sensitized solar cells

Hai-Lang Jia,^{*ab} Zhi-Ji Peng^a and Ming-Yun Guan^a

^aSchool of Chemical and Environmental Engineering, Jiangsu University of Technology, Changzhou 213001, P. R. China

^bState Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P. R. China

General information

All solvents were treated by standard methods before use and all chemicals were purchased from commercial suppliers and used without further purification unless indicated otherwise. *N*, *N*-Dimethylformamide (DMF) and tetrahydrofuran (THF) were dried and distilled from CaH_2 .

The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX (300, 400 MHz) NMR spectrometer with tetramethylsilane (TMS) as the internal standard. The mass spectra were measured in ESI Mass Spectrometer (LCQ Fleet).

Experimental

Fabrication of DSSCs

The working electrode (active area is 0.196 cm^2) was prepared by screen printing the TiO_2 paste on Fluorine-doped tin oxide (FTO) glass plates ($15 \Omega / \text{square}$). For preparation of a DSSC, FTO glass plates were cleaned in a detergent solution using an ultrasonic bath for 30 min for two times and then rinsed with water and ethanol. Then, the plates were immersed into 40 mM TiCl_4 (aqueous) at 70°C for 30 min and washed with water and ethanol. The TiO_2 paste consisted of 12 μm thick film (particle size, 20 nm, pore size 32 nm). The TiO_2 films were performed with a programmed procedure: (1) 80°C for 15 min; (2) 135°C for 10 min; (3) 325°C for 30 min; (4) 375°C for 5 min; (5) 450°C for 15 min, and (6) 500°C for 15 min. Then the films were treated again with TiCl_4 at 70°C for 30 min and sintered at 500°C for 30 min. Then the electrode was immersed into 0.2 mM dye (JA4 and JA5) solution (THF/EtOH=1/4) for 18 h at room temperature. The working electrode and the Pt counter electrode were then sealed with a Surlyn film (25 μm) by heating the sandwich-type cell at 110°C . The electrolyte was introduced through pre-drilled holes in the counter electrode and was driven into the cell via vacuum backfilling, and the hole was sealed with a Surlyn film and a thin glass (0.1 mm thickness) cover by heating. The

electrolyte was composed of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 50 mM I₂, 50 mM LiI, 0.5 M tert-butylpyridine and 0.1 M guanidiniumthiocyanate (GuNCS) in acetonitrile.^[81]

Characterizations of DSSCs

The photocurrent-voltage (*I-V*) curves of the DSSCs were measured on a Keithley 2400 source meter under standard global AM 1.5G solar irradiation supplied by a xenon light source (Oriel). The incident photo-to-electron conversion efficiency (IPCE) spectra of the DSSCs were measured by a DC method. The light source was a 300 W xenon lamp (Oriel 6258) coupled with a flux controller to improve the stability of the irradiance. The single wavelength was selected by a monochromator (Cornerstone 260 Oriel74125). Light intensity was measured by a NREL traceable Si detector (Oriel 71030NS) and the short circuit currents of the DSSCs were measured by an optical power meter (Oriel 70310).

Theoretical calculations

Density function theory (DFT) calculations were performed at the DFT-B3LYP/LanL2DZ level with Gaussian 09 suite of programs.

UV-Vis spectroscopy, photoluminescence, electrochemical properties and measurement of dye adsorbed amounts

The UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Fluorescence spectra were recorded on a Perkin Elmer LS55 spectrophotometer. FTIR spectra were recorded on a Vector22 spectrometer. The fluorescence lifetimes of the dyes were measured on a FLS920 spectrometer. The cyclic voltammograms of the dyes were recorded by IM6EX Electrochemical Workstation. Electrochemical Impedance Spectroscopy was studied using a Chenhua CHI660D model Electrochemical Workstation (Shanghai).

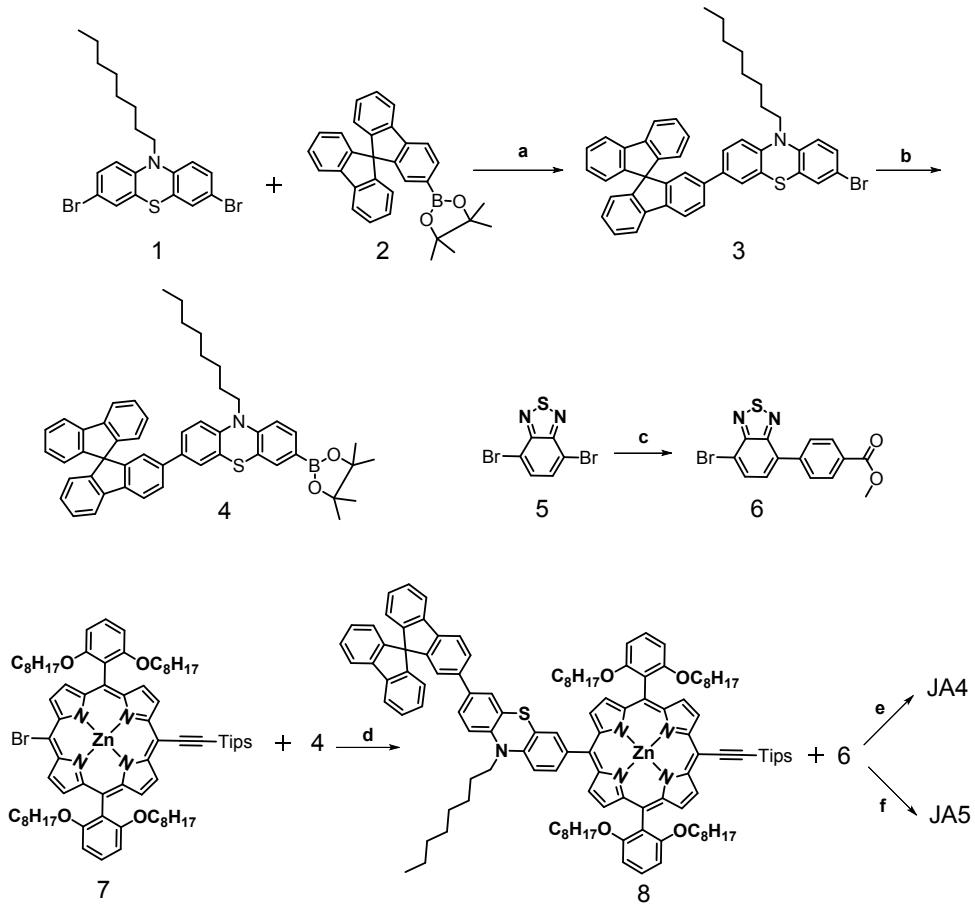
The amounts of dye adsorption on the TiO₂ films were measured by a Shimadzu

UV-3600 spectrometer. The sensitized electrodes were immersed into a 0.1 M NaOH solution in a mixed solvent (H₂O/THF=1/1), which resulted in desorption of each dye.

Water-stability studies of the anchoring group under various aqueous conditions

The water-stability of TiO₂ films sensitized with JA4 and JA5 were investigated under various aqueous conditions for varying amounts of time, including acidic, neutral and alkaline conditions.^[S2] All of the TiO₂ film was prepared from the same batch. Considering the solubility of the dyes, we added THF into the deionized water (H₂O/THF=3/2, V/V). We used deionized water as the neutral condition, the acidic condition was adjusted with AcOH (10 mM), and the alkaline condition was adjusted with K₂CO₃ (pH=11). Once removed from the water solution, the slides were rinsed with additional deionized water and dried under a stream of N₂ gas for 5 min before measuring the amounts of dye adsorption.

Synthesis of the dyes



Scheme S1 synthesis procedure of **JA4** and **JA5**. Reagents and conditions: a) $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , H_2O , 1, 4-dioxane, 90°C ; b) bis(pinacolato)diboron, $\text{Pd}(\text{dppf})\text{Cl}_2$, KOAc , DMF , 80°C ; c) Methyl 4-boronobenzoate, $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , H_2O , 1, 4-dioxane, 90°C ; d) $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , H_2O , 1, 4-dioxane, 90°C ; e) i: $\text{Pd}_2(\text{dba})_3$, AsPh_3 , Et_3N , THF , reflux; ii: NaOH , EtOH , H_2O , 90°C ; f) i: $\text{Pd}_2(\text{dba})_3$, AsPh_3 , Et_3N , THF , reflux; ii: hydrazine hydrate, EtOH , 90°C .

Synthesis of compound 3

Under an nitrogen, compound **5** (8 g, 17 mmol), compound **2** (7.5 g, 17 mmol), K_2CO_3 (7.1 g, 51 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.98 g, 0.85 mmol) were dissolved in 1, 4-dioxane (100 mL) and H_2O (20 mL). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and extracted by EtOAc (3×100 mL). The combined organic layers were washed with brine, dried over MgSO_4 , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound **3** (4 g, 33%). ^1H NMR (CDCl_3 , 400 MHz) δ_{H} 7.83-7.86 (m, 4H), 7.52-7.54 (m, 1H), 7.38 (t, J = 7.6Hz, 3H), 7.14-7.19 (m, 4H), 7.07-7.12 (m, 3H), 6.85 (s, 1H), 6.70-6.78 (m, 4H), 6.62 (d, J = 8Hz, 1H), 3.72 (s, 2H), 1.67-1.74 (m, 2H), 1.23-1.37 (m, 10H), 0.84 (t, J = 7.2Hz, 3H). MS (ESI): Calcd for $\text{C}_{45}\text{H}_{38}\text{BrNS}$, 703.19; found, 703.75.

Synthesis of compound 4

A mixture of compound **3** (2.5 g, 3.55 mmol), bis(pinacolato)diboron (1.35 g, 5.32 mmol) and KOAc (1.04 g, 10.64 mmol) in DMF (40 mL) was added $\text{Pd}(\text{dppf})\text{Cl}_2$ (0.29 g, 0.35 mmol) under dinitrogen. The mixture was heated under 80°C for overnight. The reaction mixture was cooled to room temperature and H_2O (150 mL) was added, the mixture was extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over MgSO_4 , and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=10/1) to give the compound **4** (2 g, 75%). ^1H NMR (CDCl_3 , 300 MHz) δ_{H} 7.84-7.90 (m, 4H), 7.47-7.59 (m, 2H), 7.40 (t, J = 6.9Hz, 2H), 7.10-7.20 (m, 4H), 6.92-7.06 (m, 3H), 6.89 (s, 1H), 6.73-6.83 (m, 5H), 3.81 (t, J = 6.3Hz, 2H), 1.74-1.78 (m, 2H), 1.26-1.46 (m, 22H), 0.85-0.91 (m, 3H). MS (ESI): Calcd for $\text{C}_{51}\text{H}_{50}\text{BNO}_2\text{S}$, 751.36; found, 752.42.

Synthesis of compound 6

Under an nitrogen, compound **5** (5 g, 17 mmol), Methyl 4-boronobenzoate (3.1 g, 17 mmol), K_2CO_3 (7.1 g, 51 mmol) and $Pd(PPh_3)_4$ (0.98 g, 0.85 mmol) were dissolved in 1, 4-dioxane (100 mL) and H_2O (20 mL). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and extracted by EtOAc (3×50 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/EA=4/1) to give the compound **6** (2 g, 34%). 1H NMR ($CDCl_3$, 400 MHz) δ_H 8.19 (d, J = 8.4Hz, 2H), 7.94-7.99 (m, 3H), 7.64 (d, J = 7.6 Hz, 1H), 3.97 (s, 3H).

Synthesis of compound 8

Under an nitrogen, compound **4** (1 g, 1.33 mmol), compound **7** (1.21 g, 0.93 mmol)^[S3], K_2CO_3 (0.55 g, 3.99 mmol) and $Pd(PPh_3)_4$ (0.15 g, 0.13 mmol) were dissolved in 1, 4-dioxane (50 mL) and H_2O (10 mL). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and extracted by CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and evaporated in vacuo. The residue was purified by silica gel column chromatography (PE/ CH_2Cl_2 = 4/1) to give the compound **8** as a green solid (1.9 g, 78%). 1H NMR ($CDCl_3$, 400 MHz) δ_H 9.63 (d, J = 4.8Hz, 2H), 8.84 (d, J = 4.8Hz, 2H), 8.74 (d, J = 4.8Hz, 2H), 8.70 (d, J = 4.8Hz, 2H), 7.74-7.80 (m, 6H), 7.61 (t, J = 8.4Hz, 2H), 7.50 (d, J = 6.8Hz, 1H), 7.19-7.28 (m, 5H), 7.12 (s, 1H), 7.01 (t, J = 7.2Hz, 4H), 6.83-6.89 (m, 5H), 6.70 (d, J = 7.2Hz, 2H), 6.62 (d, J = 7.6Hz, 1H), 3.94 (s, 2H), 3.72 (s, 8H), 1.90 (s, 2H), 1.44-1.49 (m, 2H), 1.12-1.38 (m, 29H), 0.78-0.86 (m, 11H), 0.63-0.69 (m, 8H), 0.29-0.51 (m, 44H). MS (ESI): Calcd for $C_{120}H_{141}N_5O_4SSiZn$, 1840.97; found, 1841.75.

Synthesis of JA4

To a solution of compound **8** (500 mg, 0.27 mmol) in anhydrous THF (20 mL)

was added TBAF (0.6 mL, 1 M in THF). The solution was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with H₂O and then extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue and compound **6** (284 mg, 0.81 mmol) were dissolved in a mixture of anhydrous THF (50 mL) and Et₃N (12 mL) under dinitrogen, then Pd₂(dba)₃ (75 mg, 0.081 mmol) and AsPh₃ (166 mg, 0.542 mmol) were added to the mixture. The solution was refluxed for 6 h. The solvent was removed under reduced pressure and was purified by silica gel column chromatography (PE/DCM=4/1), then the residue was added in EtOH (10 mL), THF (20 mL) and H₂O (30 mL), and then added NaOH (0.29 g, 7.31 mmol). The mixture was heated under 90°C for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the residue was acidified with diluted HCl, then filtered and recrystallization from MeOH/Ether to give dye **JA4** as a brown solid (200 mg, 38%). ¹H NMR (THF-*d*₈, 300 MHz) δ_H 10.07 (d, *J* = 4.5Hz, 2H), 8.83-8.91 (m, 2H), 8.73-8.80 (m, 2H), 8.62-8.67 (m, 2H), 8.52 (d, *J* = 4.5Hz, 1H), 8.37-8.39 (m, 1H), 8.28-8.33 (m, 2H), 8.21 (d, *J* = 8.1Hz, 2H), 8.11-8.16 (m, 2H), 8.03 (d, *J* = 8.1Hz, 1H), 7.87-7.96 (m, 4H), 7.79-7.84 (m, 3H), 7.63-7.73 (m, 3H), 7.33-7.38 (m, 3H), 7.04-7.13 (m, 8H), 6.73-6.76 (m, 2H), 6.68 (d, *J* = 7.5Hz, 1H), 4.54 (s, 2H), 3.88 (s, 8H), 2.13-2.20 (m, 2H), 1.47-1.51 (m, 2H), 1.30-1.40 (m, 8H), 0.85-0.92 (m, 26H), 0.51-0.72 (m, 37H). ¹³C NMR (THF-*d*₈, 75 MHz) δ_C 161.27, 157.46, 154.51, 153.42, 152.39, 152.17, 151.58, 151.49, 150.93, 150.38, 149.91, 143.08, 142.57, 142.32, 140.44, 138.80, 138.70, 138.29, 136.91, 135.29, 133.06, 131.80, 130.83, 130.15, 129.82, 128.77, 128.08, 127.67, 127.46, 125.71, 125.03, 122.95, 122.16, 121.62, 121.07, 117.49, 115.92, 114.81, 106.76, 105.67, 104.64, 97.84, 92.84, 69.16, 48.70, 32.99, 32.62, 30.52, 29.89, 27.78, 26.45, 23.73, 23.40, 14.66, 14.46. MS (ESI): Calcd for C₁₂₄H₁₂₇N₇O₆S₂Zn, 1938.86; found, 1938.33.

Synthesis of JA5

To a solution of compound **8** (500 mg, 0.27 mmol) in anhydrous THF (20 mL)

was added TBAF (0.6 mL, 1 M in THF). The solution was stirred at room temperature for 30 min under dinitrogen. The mixture was quenched with H₂O and then extracted with CH₂Cl₂. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reduced pressure. The residue and compound **6** (284 mg, 0.81 mmol) were dissolved in a mixture of anhydrous THF (50 mL) and Et₃N (12 mL) under dinitrogen, then Pd₂(dba)₃ (75 mg, 0.081 mmol) and AsPh₃ (166 mg, 0.542 mmol) were added to the mixture. The solution was refluxed for 6 h. The solvent was removed under reduced pressure and was purified by silica gel column chromatography (PE/DCM= 4/1), then the residue was added in EtOH (30 mL) and hydrazine hydrate (30 mL). The mixture was heated under 80°C for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the residue was purified by silica gel column chromatography (DCM/MeOH=20/1), and then recrystallization from MeOH/Ether to give dye **JA5** as a brown solid (180 mg, 34%). ¹H NMR (THF-*d*₈, 300Hz) δ_H 10.05 (d, *J* = 4.5Hz, 2H), 8.86-8.90 (m, 2H), 8.73-8.80 (m, 2H), 8.62-8.67 (m, 2H), 8.51 (d, *J* = 4.8Hz, 1H), 8.36-8.38 (m, 2H), 8.28-8.30 (m, 3H), 8.12-8.14 (m, 3H), 8.03-8.07 (m, 1H), 7.88-7.96 (m, 4H), 7.80-7.85 (m, 3H), 7.63-7.73 (m, 3H), 7.33-7.38 (m, 3H), 7.04-7.12 (m, 8H), 6.73-6.75 (m, 2H), 6.67 (d, *J* = 7.5Hz, 1H), 4.54 (s, 2H), 3.89 (s, 8H), 2.31 (m, 2H), 2.07-2.16 (m, 2H), 1.46-1.50 (m, 2H), 1.29-1.39 (m, 8H), 1.12-1.17 (m, 2H), 0.83-0.98 (m, 24H), 0.50-0.72 (m, 37H). ¹³C NMR (THF-*d*₈, 75 MHz) δ_C 161.26, 157.46, 154.53, 153.41, 152.38, 152.16, 151.58, 151.49, 150.93, 150.36, 149.91, 143.07, 142.56, 142.33, 140.40, 138.79, 138.68, 138.25, 136.91, 135.28, 133.02, 131.85, 130.71, 130.01, 129.77, 128.77, 127.94, 127.73, 127.44, 126.00, 125.60, 122.94, 122.17, 121.61, 121.07, 117.50, 115.92, 114.82, 106.78, 105.69, 104.59, 97.89, 92.85, 69.16, 48.70, 32.99, 32.62, 30.51, 29.91, 27.75, 26.44, 23.73, 23.40, 14.66, 14.48. MS (ESI): Calcd for C₁₂₄H₁₂₉N₉O₅S₂Zn, 1952.88; found, 1952.17.

Table S1. Optical and electrochemical properties of dyes

Dye	^a λ_{max} /nm ($\epsilon \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$)	^b λ_{max} /nm	^c E_{OX} /V (vs. NHE)	^d E_{0-0} /eV	^e E^*_{OX} /V (vs. NHE)
JA4	435(1.52), 459(0.92) 576(0.12), 648(0.47)	685	1.04	1.90	-0.86
JA5	435(1.64), 458(1.12) 575(0.15), 647(0.60)	683	1.02	1.91	-0.89

[a] Absorption maximum in THF solution ($1 \times 10^{-6} \text{ M}$), [b] emission maximum in THF solution ($1 \times 10^{-6} \text{ M}$), [c] the ground state oxidation potentials, [d] E_{0-0} was estimated from the intercept of the normalized absorption and emission spectra, [e] E^*_{OX} was calculated by the formula: $E^*_{\text{OX}} = E_{\text{OX}} - E_{0-0}$.

Table S2. Photovoltaic parameters of the DSSCs obtained from the J-V curves

Dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	η (%)	Amounts of dye adsorption ($10^{-7} \text{ mol cm}^{-2}$)
JA4	14.44	0.772	62.77	7.00	1.56
JA5	11.57	0.737	64.38	5.49	1.35

The size of the active area for each cell is 0.196 cm^2 , the DSSCs were all measured under standard global AM 1.5G solar irradiation.

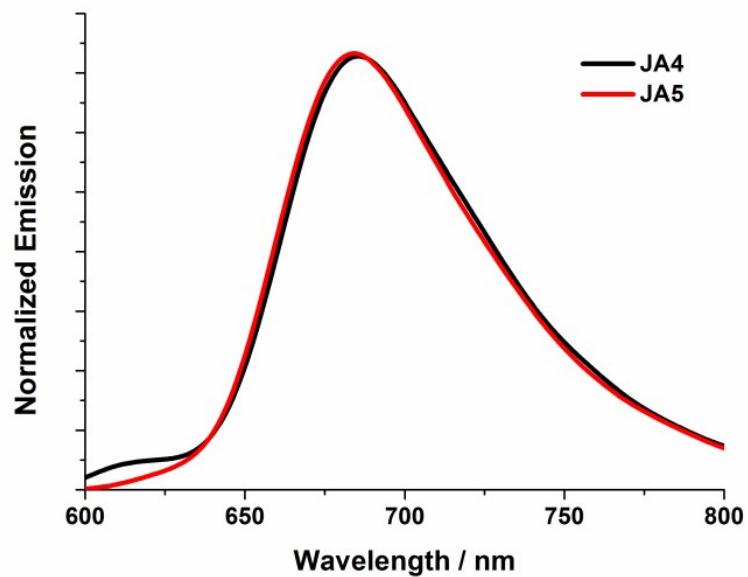


Fig. S1 Emission spectra of **JA4** and **JA5** in THF.

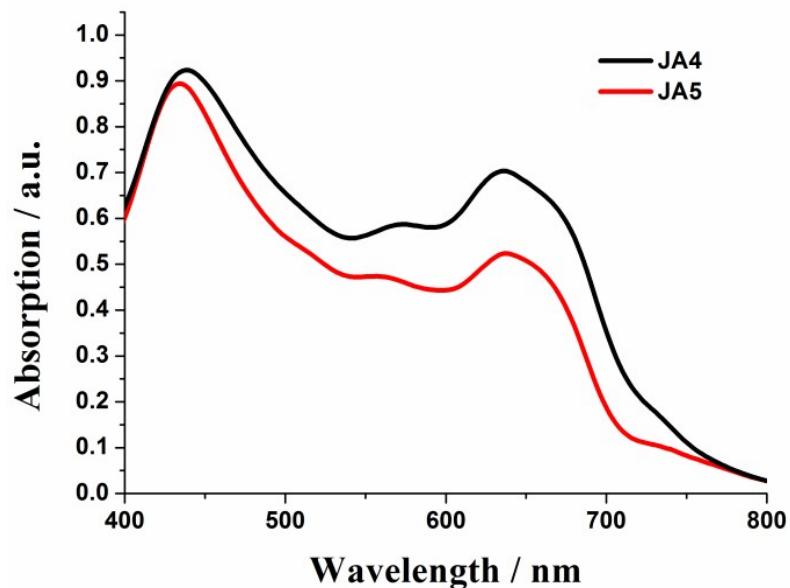


Fig. S2 Absorption spectra of **JA4** and **JA5** anchored on the 12 μm porous TiO_2 nanoparticle films.

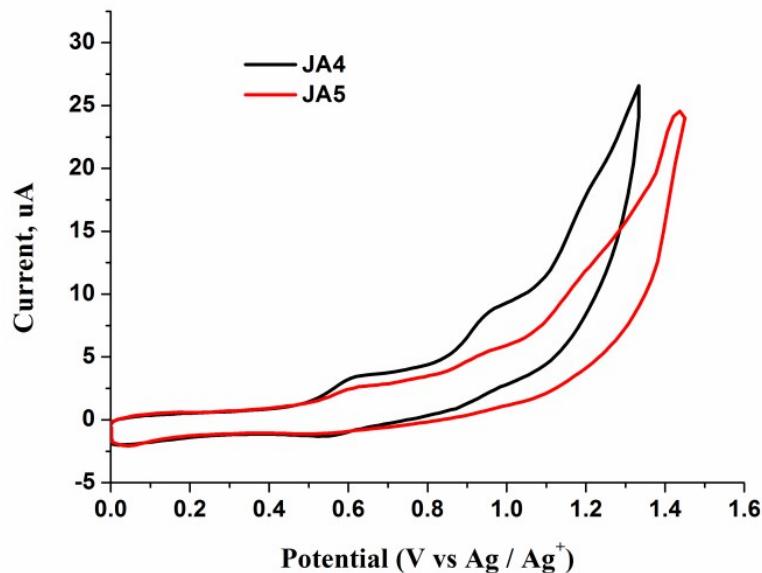


Fig. S3 Cyclic voltammogram of **JA4** and **JA5** in DMF, 0.1 M TBAPF₆, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag^+ as reference electrode, scan rate: 100 mV s⁻¹, calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an external reference.

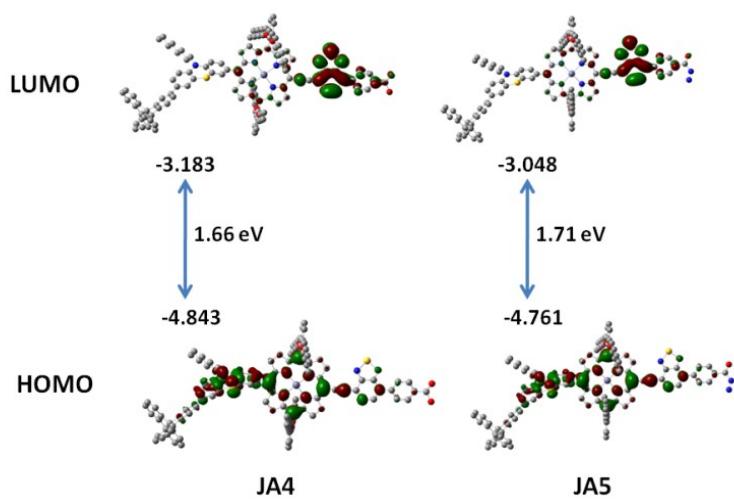


Fig. S4 The HOMO and LUMO frontier molecular orbitals of JA4 and JA5 calculated at the DFT-B3LYP/LanL2DZ level with the Gaussian 09 suite of programs.

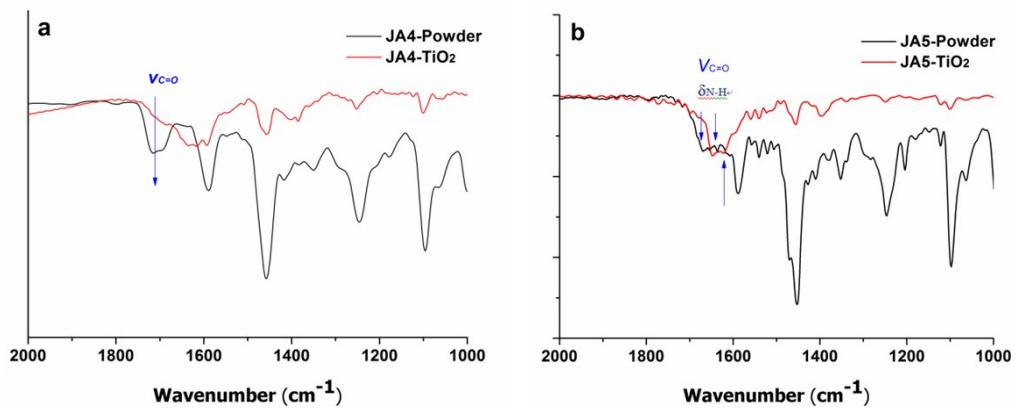


Fig. S5 FTIR spectra of dye powders (black line) and dyes adsorbed on TiO_2 films (red line) for dye **JA4** (a) and **JA5** (b).

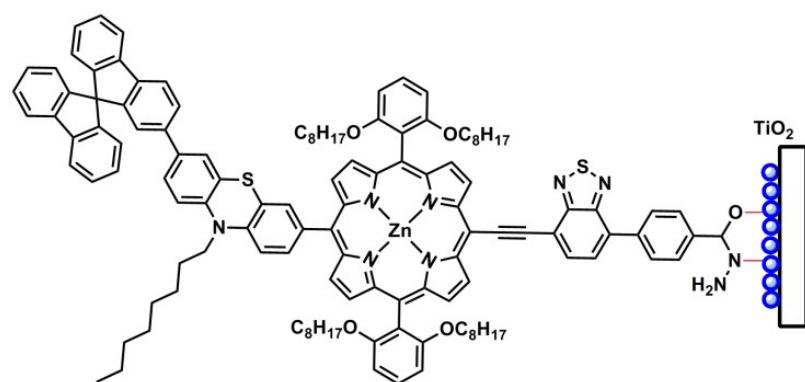


Fig. S6 Configuration of **JA5** adsorbed on TiO_2 surface.

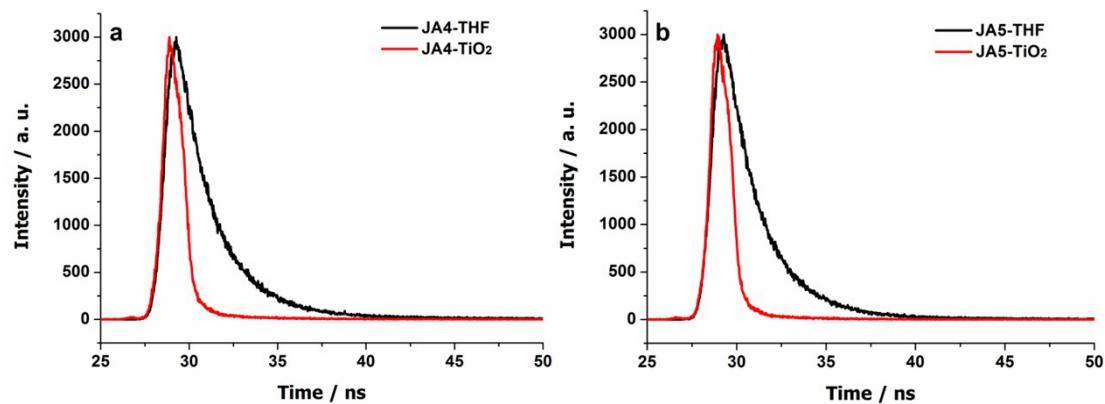


Fig. S7 Fluorescence decay curves of dyes in THF (black line) and dyes adsorbed onto TiO_2 surface (red line), (a) JA4, (b) JA5.

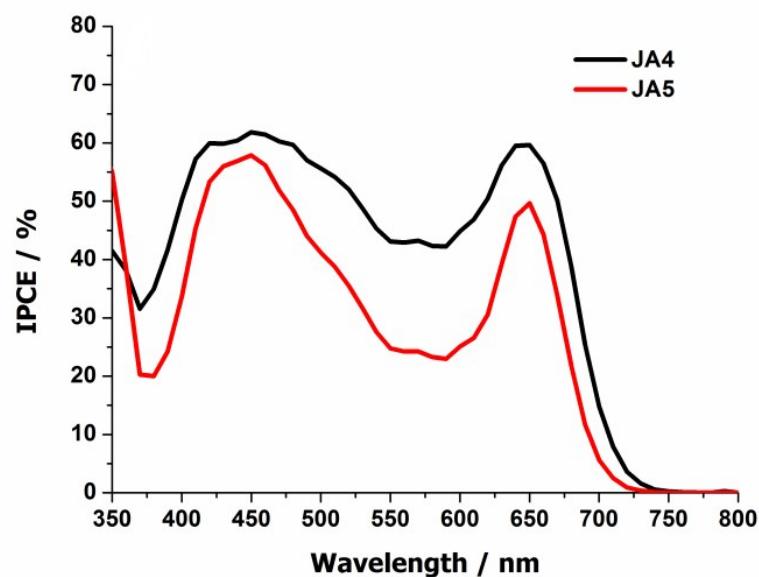


Fig. S8 The IPCE curves of DSSCs based on JA4 and JA5.

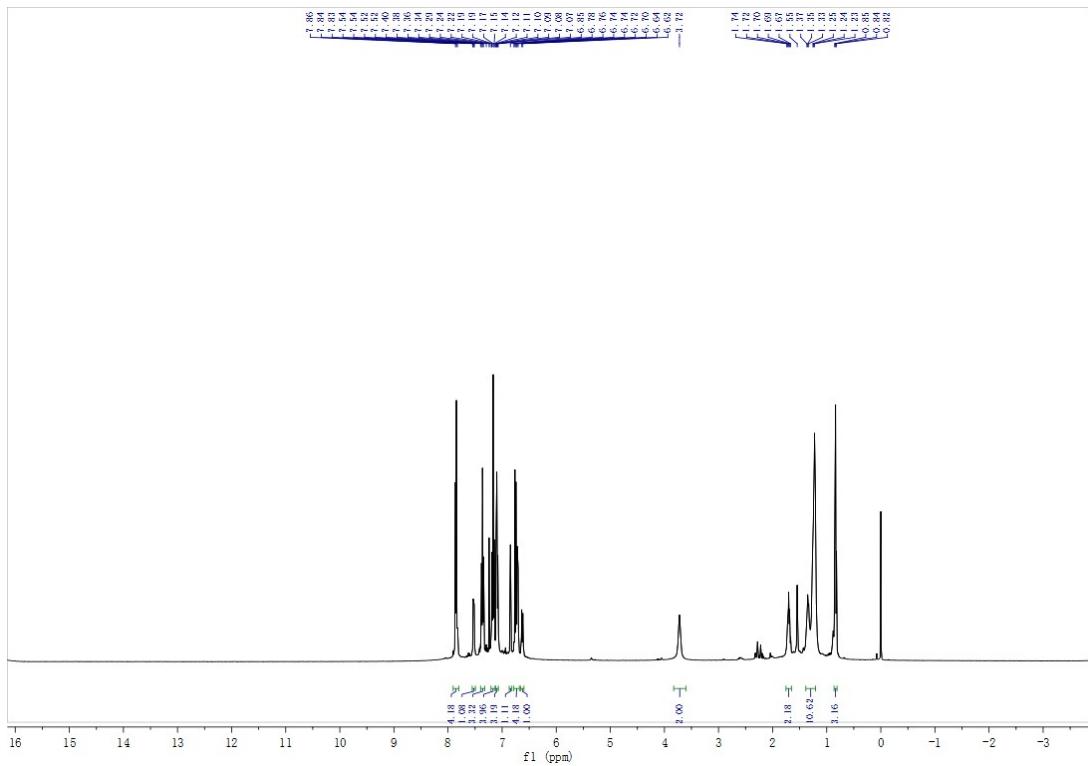


Fig. S9 ^1H NMR of compound 3 (CDCl_3)

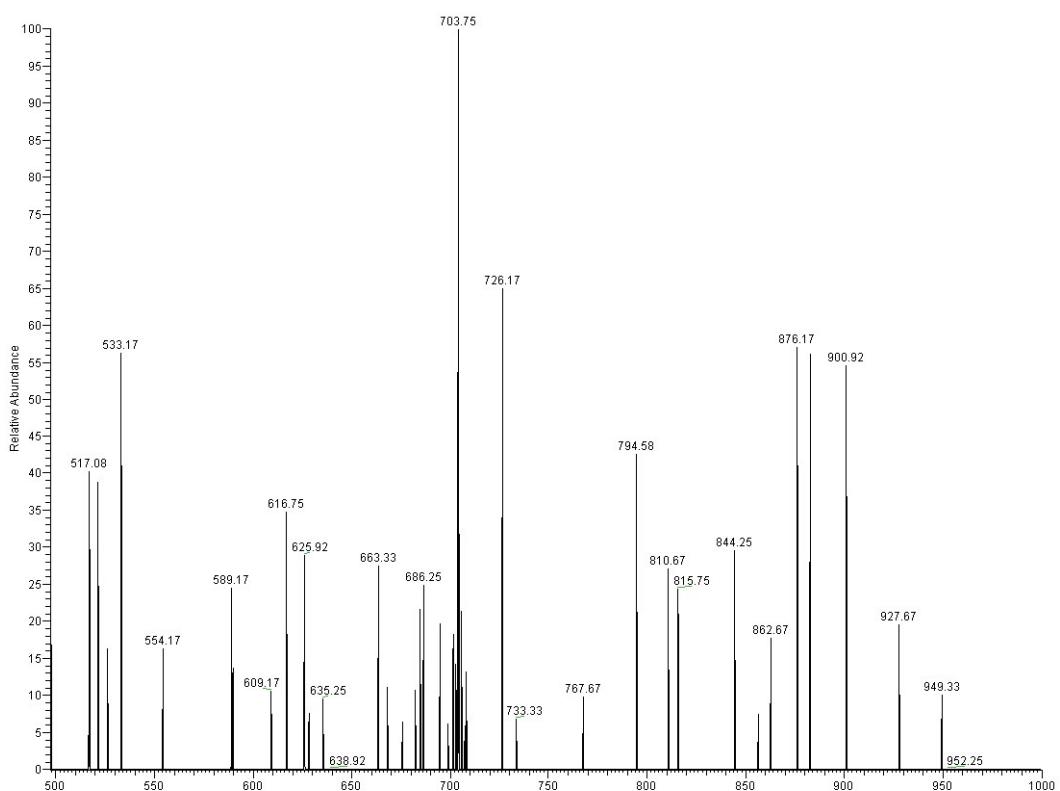


Fig. S10 ESI-MS of compound 3, found 703.75.

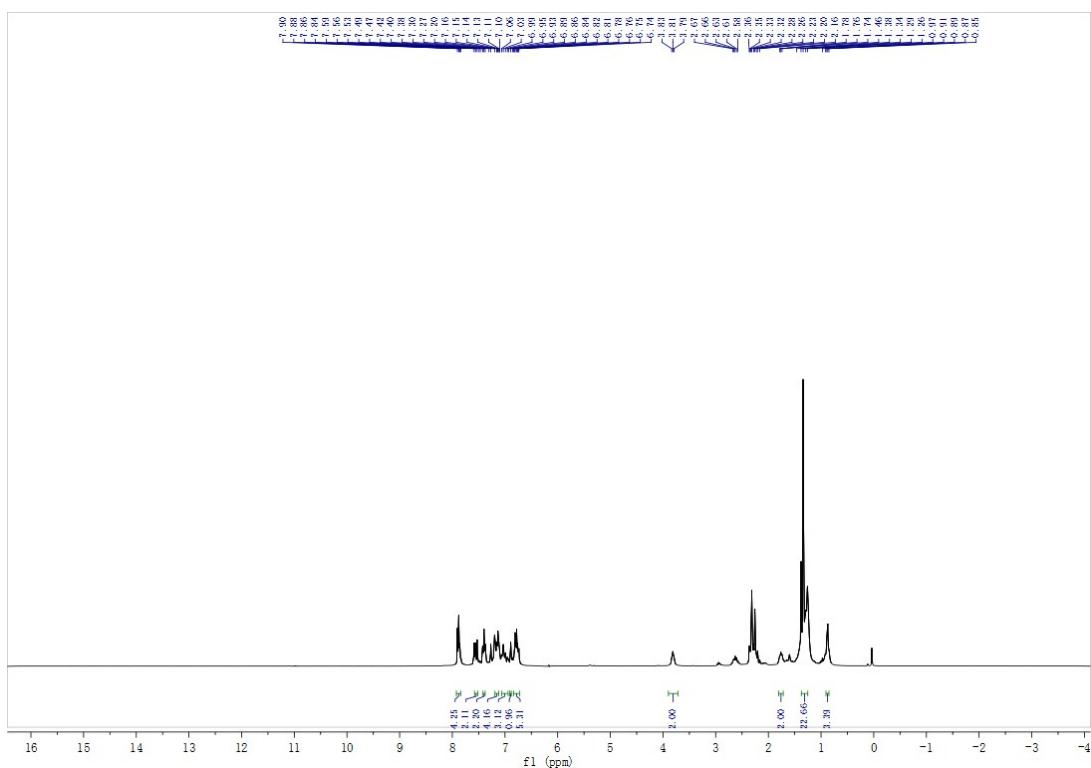


Fig. S11 ^1H NMR of compound 4 (CDCl_3)

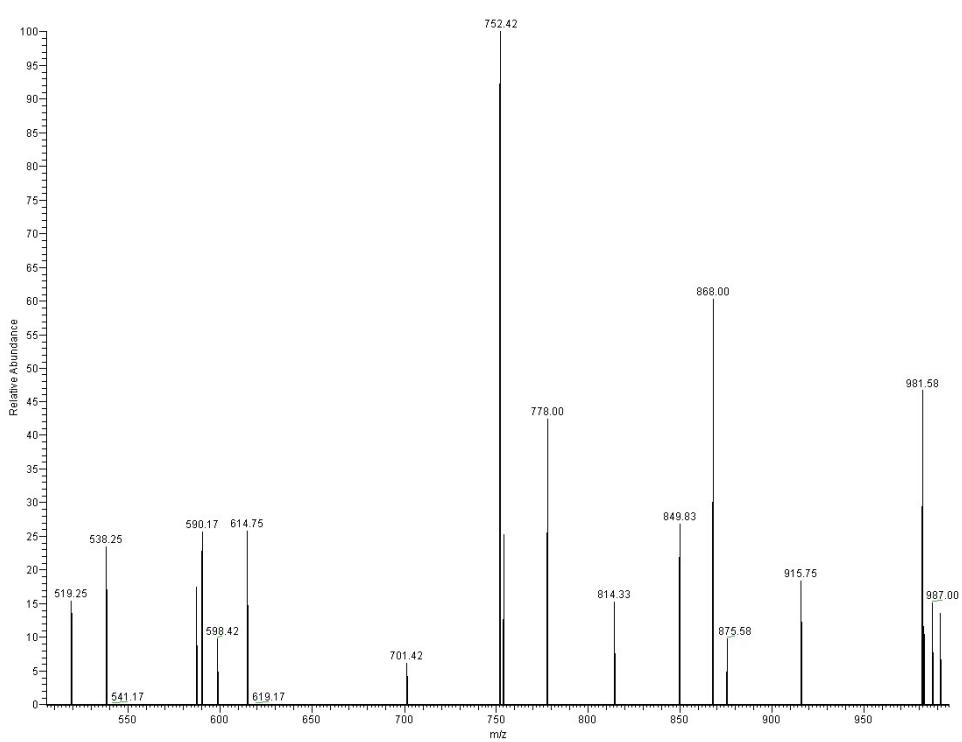


Fig. S12 ESI-MS of compound 4, found 752.42.

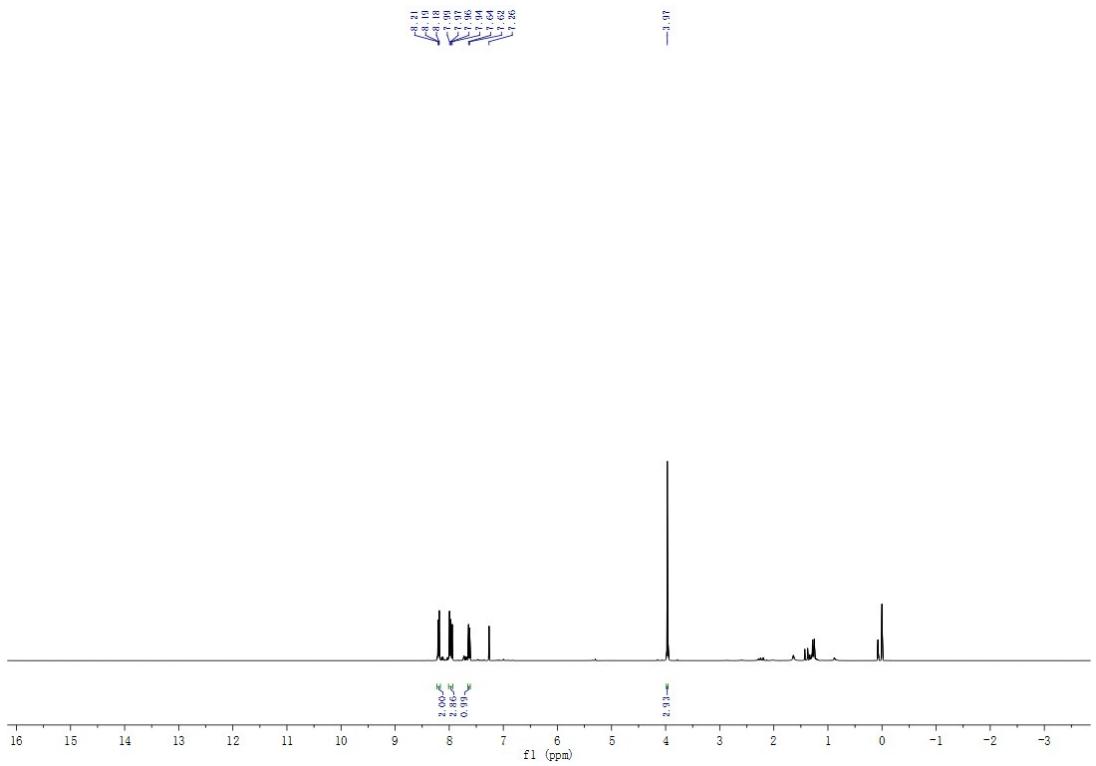


Fig. S13 ^1H NMR of compound 6 (CDCl_3)

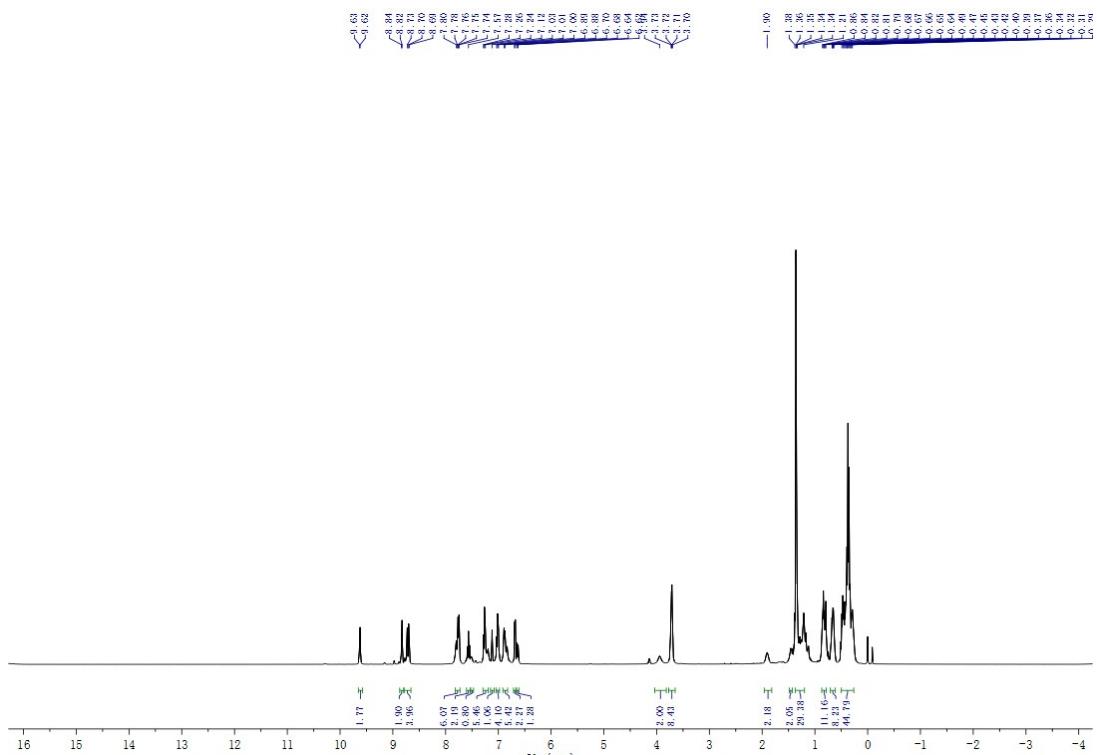


Fig. S14 ^1H NMR of compound 8 (CDCl_3)

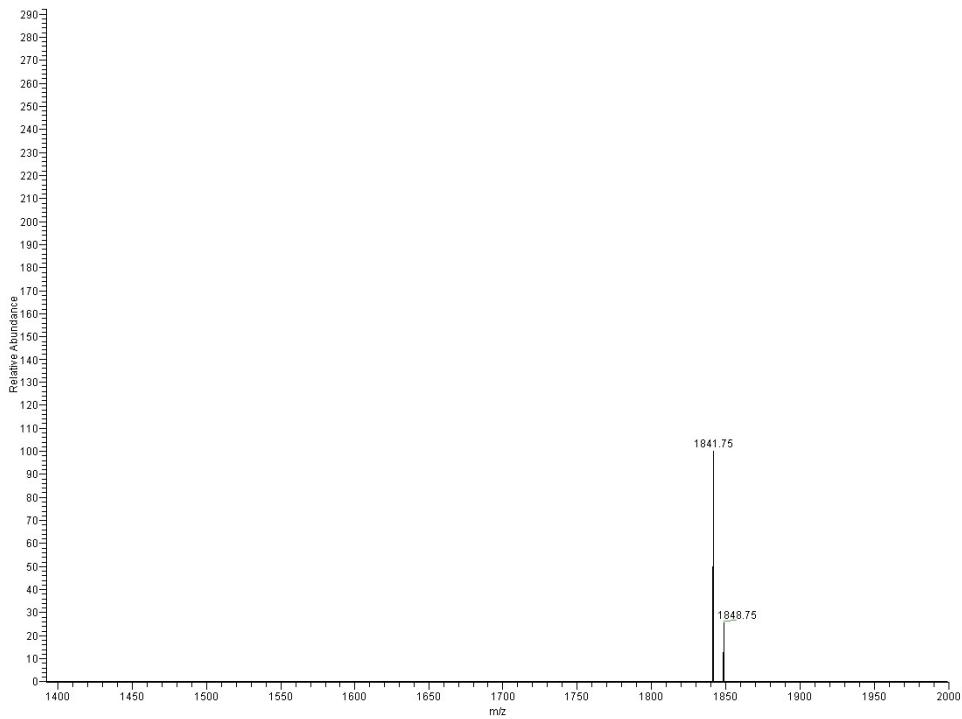


Fig. S15 ESI-MS of compound 8, found 1841.75.

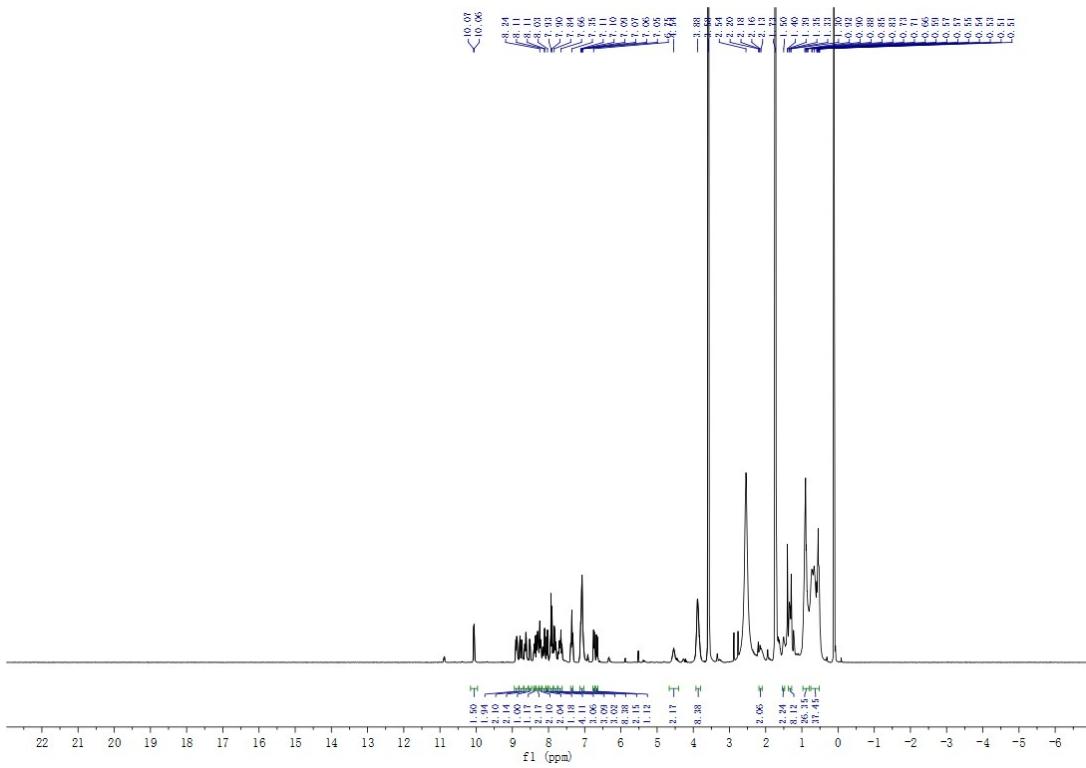


Fig. S16 ^1H NMR of JA4 (THF- d_8)

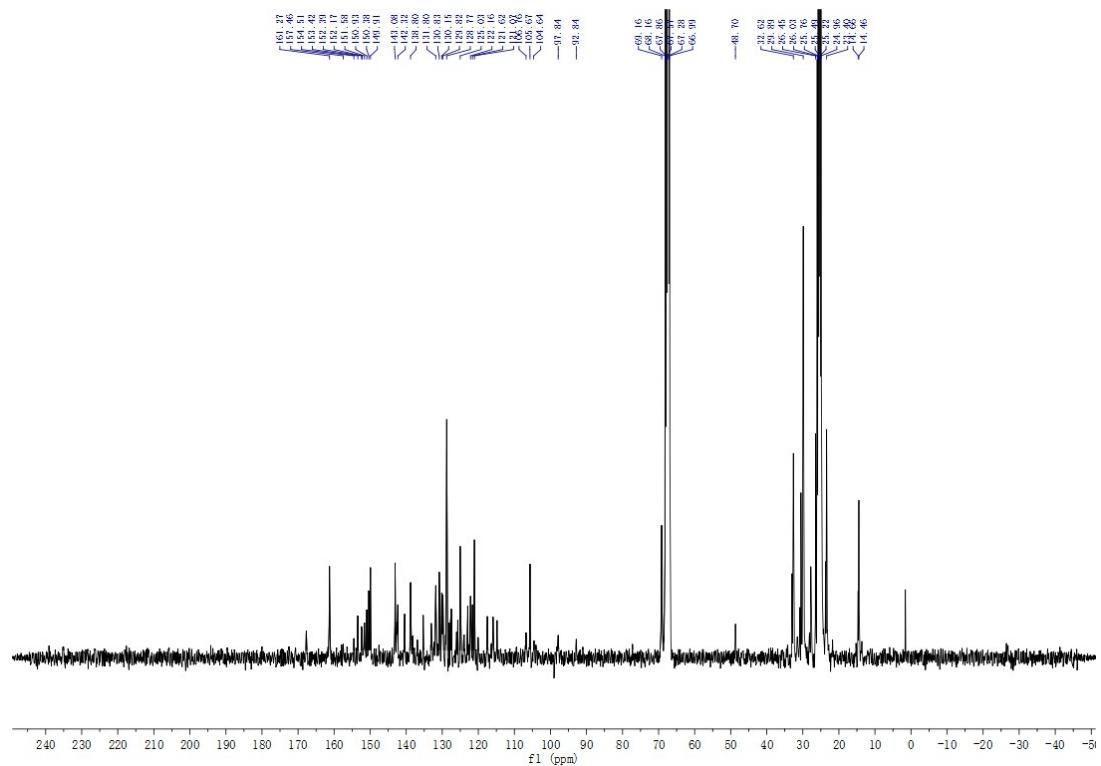


Fig. S17 ^{13}C NMR of JA4 (THF- d_8)

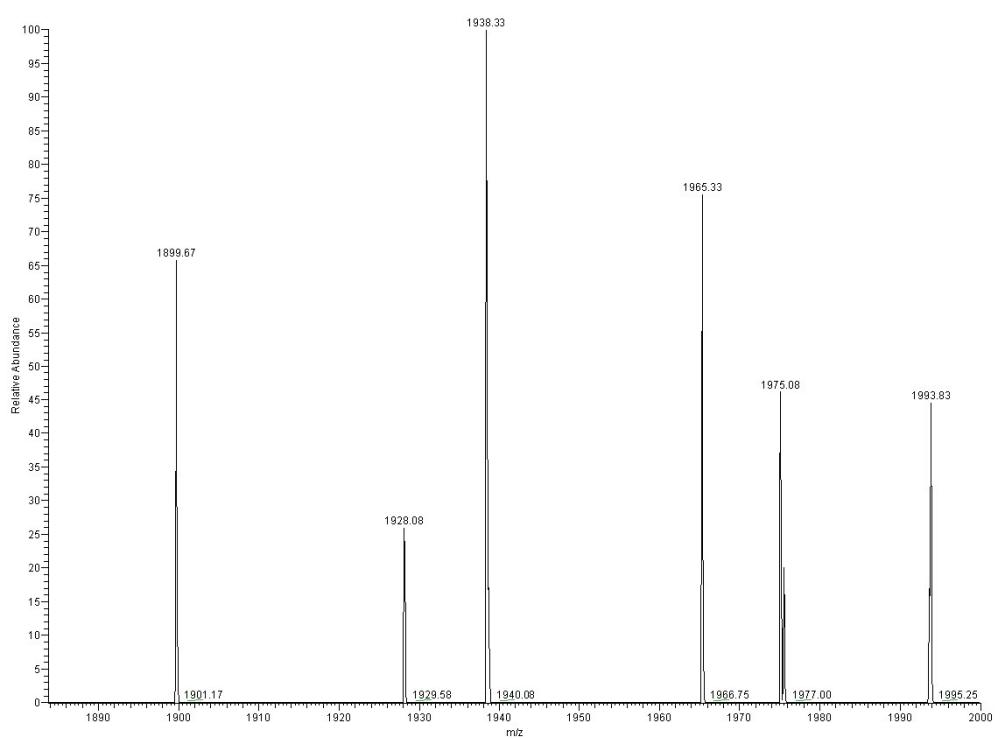


Fig. S18 ESI-MS of JA4, found 1938.33.

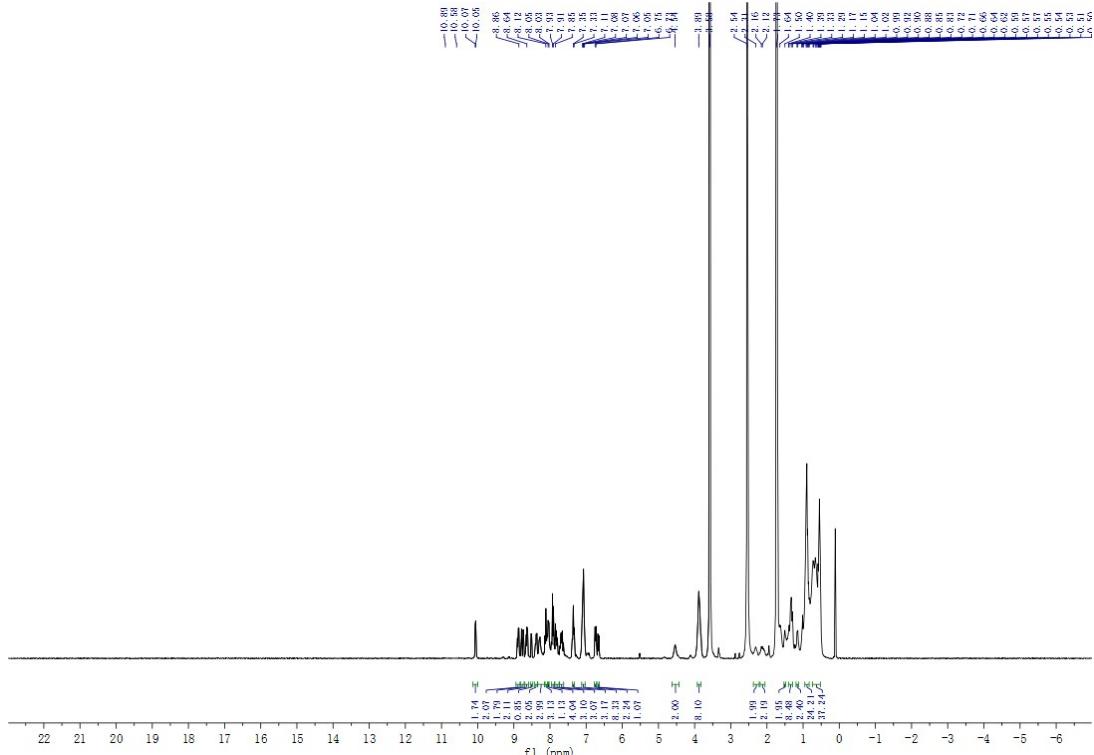


Fig. S19 ^1H NMR of JA5 (THF- d_8)

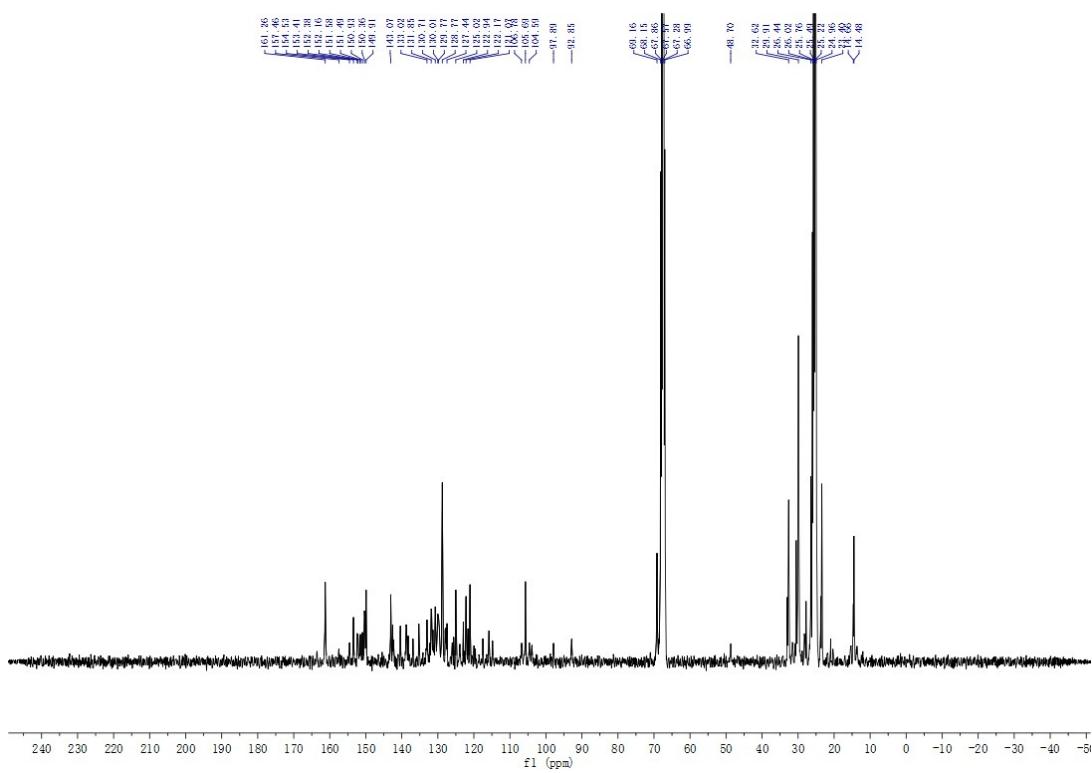


Fig. S20 ^{13}C NMR of JA5 (THF- d_8)

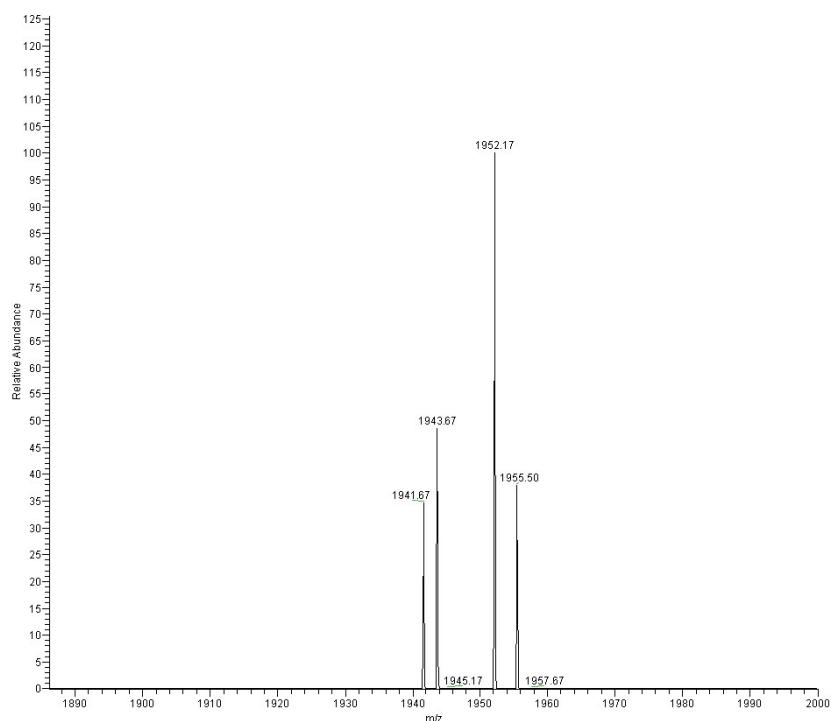


Fig. S21 ESI-MS of JA5, found 1952.17.

References

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