Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

Enhanced performance of dye-sensitized solar cells with Y-shaped organic dyes containing di-anchoring groups

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Synthesis Details

Synthesis of compound 2

A mixture of phenothiazine (10 g, 50.2 mmol), 2-bromo-9,9-dimethylfluorene (20.6 g, 75.3 mmol), NaOBu-t (9.7 g, 100.4 mmol), $Pd(OAc)_2$ (0.56 g, 2.5 mmol) and $Pd(dppf)Cl_2$ (0.7 g, 0.96 mmol) in dry toluene (150 mL) was refluxed for overnight under dinitrogen. The solvent was removed under vacuum. The residue was purified by column chromatography (silica gel) using PE/EA = 10/1 as eluent to give the compound **2** (15.2 g, 77%).^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.97 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 7.0 Hz, 1H), 7.49-7.52 (m, 2H), 7.38-7.44 (m, 3H), 7.07 (d, J = 7.5 Hz, 2H), 6.86-6.88 (m, 4H), 6.31 (d, J = 7.0 Hz, 2H), 1.55 (s, 6H), MS (ESI): Calcd for $C_{27}H_{21}NS$, 391.13; found, 391.50.

Synthesis of compound 3

A mixture of Compound **2** (10.0 g, 25.5 mmol) in DMF (50 mL), then the NBS (9.5 g, 53.6 mmol) in a soultion of DMF (50 mL) was added dropwise for 30 min. The reaction mixture was stirred for overnight at room temperature. The reaction mixture was quenched with ice water and extracted with ethylacetate. The combined organic fractions were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA = 10/1) to give the compound **3** (11.5 g, 82%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.98 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 7.5 Hz, 1H), 7.51-7.52 (m, 1H), 7.43 (s, 3H), 7.33 (d, J = 8.0 Hz, 1H), 7.14 (s, 2H), 6.96 (d, J = 9.0 Hz, 2H), 6.11 (d, J = 9.0 Hz, 2H), 1.55 (s, 6H).

Synthesis of compound 4

Under an nitrogen, compound **3** (10.0 g, 18.2 mmol), 2-thiopheneboronic acid (2.3 g, 18.2 mmol), K_2CO_3 (7.5 g, 54.6 mmol) and $Pd(PPh_3)_4$ (0.80 g, 0.71 mmol) were dissolved in 1, 4-dioxane (100 mL) and H_2O (20 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the mixture was 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 **4** (4.1 g, 41%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 7.99 (d, *J* = 8.0 Hz, 1H), 7.81-7.83 (m, 1H), 7.51-7.52 (m, 1H), 7.39-7.46 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.04-7.27 (m, 6H), 6.93 (d, *J* = 9.0 Hz, 1H), 6.23 (d, *J* = 3.0 Hz, 1H), 6.11 (d, *J* = 3.0 Hz, 1H), 1.56 (s, 6H), MS (ESI): Calcd for $C_{31}H_{22}BrNS_2$, 551.03; found, 551.67.

Synthesis of compound 5

Under an nitrogen, compound **4** (4.0 g, 7.2 mmol), 9,9-dimethyl-9H-fluoren-2-yl-boronic acid, 2-thiopheneboronic acid (3.5 g, 14.5 mmol), K_2CO_3 (3.0 g, 21.7 mmol) and $Pd(PPh_3)_4$ (0.20 g, 0.18 mmol) were dissolved in 1, 4-dioxane (50 mL) and H_2O (10 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, 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 = 8/1) to give the compound **5** (3.7 g, 77%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.01 (s, 1H), 7.85 (d, *J* = 7.0 Hz, 1H), 7.74-7.76 (m, 2H), 7.50-7.53 (m, 4H), 7.41-7.47 (m, 5H), 7.33-7.37 (m, 4H), 7.11-7.23 (m, 2H), 7.06 (s, 2H), 6.26 (s, 2H), 1.58 (s, 6H), 1.54 (s, 6H), MS (ESI): Calcd for $C_{46}H_{35}NS_2$, 665.22; found, 664.08.

Synthesis of compound 6

A mixture of Compound **5** (3.5 g, 5.3 mmol) in DMF (30 mL), then the NBS (1.0 g, 5.8 mmol) in a soultion of DMF (20 mL) was added dropwise for 30 min. The reaction mixture was stirred overnight at room temperature. The reaction mixture was quenched with ice water and extracted with ethylacetate. The combined organic fractions were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (PE/EA = 8/1) to give the compound **6** (2.5 g, 64%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ_H 8.03 (s, 1H), 7.84 (d, *J* = 7.0 Hz, 1H), 7.73-7.77 (m, 2H), 7.40-7.56 (m, 8H), 7.30-7.38 (m, 4H), 7.05-7.26 (m, 3H), 7.00 (s, 2H), 6.32 (s, 1H), 1.58 (s,

6H), 1.54 (s, 6H), MS (ESI): Calcd for $C_{46}H_{34}BrNS_2$, 743.13; found, 744.17.

Synthesis of compound 7

A mixture of compound **6** (2.5 g, 3.4 mmol), trimethylsilylacetylene (0.66 g, 6.8 mmol) and CuI (0.13 g, 0.67 mmol) in THF (30 mL) and TEA (30 mL) was added $Pd(PPh_3)_2Cl_2$ (0.3 g, 0.42 mmol) under dinitrogen. The mixture was heated under 80℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the mixture was 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 = 8/1). After evaporated, the residue was dissolved in MeOH (100 mL), and K_2CO_3 (2.3 g, 16.7 mmol) was then added. The reaction mixture was stirred overnight at room temperature. The mixture was quenched with H_2O and then extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure to give the compound **7** (1.6 g, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 7.99 (d, *J* = 8.0 Hz, 1H), 7.80-7.82 (m, 1H), 7.71-7.73 (m, 2H), 7.53 (s, 1H), 7.37-7.50 (m, 7H), 7.28-7.33 (m, 3H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.18 (d, *J* = 4.0 Hz, 1H), 7.12-7.15 (m, 1H), 7.00-7.05 (m, 2H), 6.32 (d, *J* = 8.4 Hz, 1H), 6.22 (d, *J* = 8.4 Hz, 1H), 3.37 (s, 1H), 1.55 (s, 6H), 1.51 (s, 6H), MS (ESI): Calcd for $C_{48}H_{35}NS_2$, 689.22; found, 688.00.

Synthesis of dye ZJA1

The compound **7** (0.5 g, 0.72 mmol) and ethyl 4-iodobenzoate (0.4 g, 1.45 mmol) and CuI (28 mg, 0.14 mmol) in TEA (20 mL) and THF (10 mL) was added $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mmol) under dinitrogen. The mixture was heated under 80℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, 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=4/1). After evaporated, the residue was dissolved in EtOH (10 mL) and H_2O (10 mL), then added NaOH (0.15 g, 3.62 mmol). The mixture was heated under 90℃ for overnight. The

reaction mixture was cooled to room temperature and the solvent was evaporated, the residue was acidified with HCl, then filtered and recrystallization from MeOH/Ether to give dye **ZJA1** (0.40 g, 68%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ_H 13.19 (s, 1H), 8.19 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 3H), 7.82-7.85 (m, 3H), 7.74 (s, 1H), 7.62-7.68 (m, 3H), 7.53-7.59 (m, 3H), 7.40-7.47 (m, 6H), 7.31-7.36 (m, 3H), 7.24-7.27 (m, 1H), 6.25 (d, J = 8.4 Hz, 1H), 6.19 (d, J = 8.4 Hz, 1H), 1.52 (s, 6H), 1.47 (s, 6H); ^{13}CNMR (DMSO-d_6, 125 MHz) δ_C 167.11, 157.14, 154.56, 154.34, 154.08, 138.22, 138.14, 138.07, 135.23, 131.63, 130.06, 127.77, 127.51, 125.54, 125.40, 124.96, 123.93, 123.42, 123.20, 123.02, 120.94, 120.86, 120.60, 93.63, 86.03, 47.42, 47.03, 27.30, 27.09; MS (ESI): Calcd for $C_{55}H_{39}NO_2S_2$, 809.24; found, 808.08.

Synthesis of compound 8

The compound **7** (1.00 g, 1.45 mmol), tribromobenzene (0.91 g, 2.90 mmol) and CuI (55 mg, 0.29 mmol) in TEA (20 mL) and THF (10 mL) was added $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mmol) under dinitrogen. The mixture was heated under 80℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the mixture was extracted by EtOAc (3×30 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 **8** (0.80 g, 60%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 8.02 (d, J = 7.8 Hz, 1H), 7.82-7.85 (m, 1H), 7.73-7.76 (m, 2H), 7.63 (t, J = 1.8 Hz, 1H), 7.59 (d, J = 1.8 Hz, 1H), 7.49-7.55 (m, 4H), 7.38-7.47 (m, 5H), 7.30-7.36 (m, 4H), 7.24 (d, J = 3.9 Hz, 1H), 7.15-7.18 (m, 1H), 7.00-7.09 (m, 2H), 6.35 (d, J = 8.7 Hz, 1H), 6.25 (d, J = 8.7 Hz, 1H), 1.57 (s, 6H), 1.53 (s, 6H); MS (ESI): Calcd for $C_{54}H_{37}Br_2NS_2$, 923.07; found, 922.25.

Synthesis of dye ZJA2

Under an nitrogen, compound **8** (0.5 g, 0.54 mmol), 3-methoxycarbonylphenylboronic acid (0.29 g, 1.62 mmol), K_2CO_3 (0.3 g, 2.16 mmol) and $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol) were dissolved in 1, 4-dioxane (20 mL) and H_2O (4 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the mixture was extracted by EtOAc

(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/EA = 4/1). After evaporated, the residue was dissolved in EtOH (10 mL) and H_2O (10 mL), then added NaOH (0.17 g, 4.33 mmol). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the residue was acidified with HCl, then filtered and recrystallization from MeOH/Ether to give dye **ZJA2** (0.30 g, 55%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ_H 8.28 (s, 2H), 8.16 (d, J = 8.1 Hz, 1H), 8.06 (d, J = 7.8 Hz, 2H), 7.92-7.99 (m, 5H), 7.86 (s, 1H), 7.78-7.82 (m, 3H), 7.72 (s, 1H), 7.56-7.63 (m, 4H), 7.50-7.53 (m, 3H), 7.43-7.45 (m, 3H), 7.38-7.40 (m, 2H), 7.29-7.33 (m, 3H), 7.21-7.25 (m, 1H), 6.26 (d, J = 8.4 Hz, 1H), 6.18 (d, J = 8.4 Hz, 1H), 1.50 (s, 6H), 1.45 (s, 6H); ^{13}CNMR (DMSO-d_6, 125 MHz) δ_C 167.82, 157.12, 154.56, 154.33, 154.07, 141.31, 139.71, 138.65, 138.13, 138.06, 131.87, 129.81, 129.34, 129.09, 128.15, 127.75, 127.51, 125.38, 124.94, 123.19, 120.93, 120.83, 120.58, 94.05, 84.05, 47.41, 47.02, 27.29, 27.08; MS (ESI): Calcd for $C_{68}H_{47}NO_4S_2$, 1005.29; found, 1004.50.

Synthesis of dye ZJA3

Under an nitrogen, compound **8** (0.5 g, 0.54 mmol), 3-pyridylboronic acid (0.20 g, 1.62 mmol), K_2CO_3 (0.3 g, 2.16 mmol) and $Pd(PPh_3)_4$ (0.10 g, 0.09 mmol) were dissolved in 1, 4-dioxane (20 mL) and H_2O (4 mL). The mixture was heated under 90℃ for overnight. The reaction mixture was cooled to room temperature and the solvent was evaporated, the mixture was extracted by EtOAc (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 (DCM/MeOH = 30/1) to give dye **ZJA3** (0.25 g, 50%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ_H 8.94 (s, 2H), 8.69 (s, 2H), 7.97-8.02 (m, 3H), 7.82-7.84 (m, 1H), 7.76-7.78 (m, 2H), 7.72-7.76 (m, 3H), 7.65-7.69 (m, 2H), 7.55-7.58 (m, 2H), 7.51-7.52 (m, 2H), 7.48-7.49 (m, 2H), 7.40-7.46 (m, 5H), 7.32-7.35 (m, 3H), 7.28-7.29 (m, 2H), 7.15-7.18 (m, 1H), 7.07-7.11 (m, 2H), 6.35 (d, J = 8.4 Hz, 1H), 6.28 (d, J = 8.4 Hz, 1H), 1.57 (s,

6H), 1.53 (s, 6H); ^{13}CNMR ($CDCl_3$, 125 MHz) δ_C 156.89, 154.30, 154.03, 153.82, 149.05, 148.18, 145.55, 144.14, 143.00, 139.67, 139.28, 139.09, 138.82, 138.31, 138.11, 135.63, 134.65, 133.64, 132.09, 129.52, 128.64, 128.54, 127.21, 127.02, 125.33, 125.06, 123.78, 122.58, 120.56, 120.28, 119.99, 116.12, 115.90, 92.87, 84.46, 47.26, 46.91, 29.70, 27.22; MS (ESI): Calcd for $C_{64}H_{45}N_3S_2$, 919.39; found, 920.58.

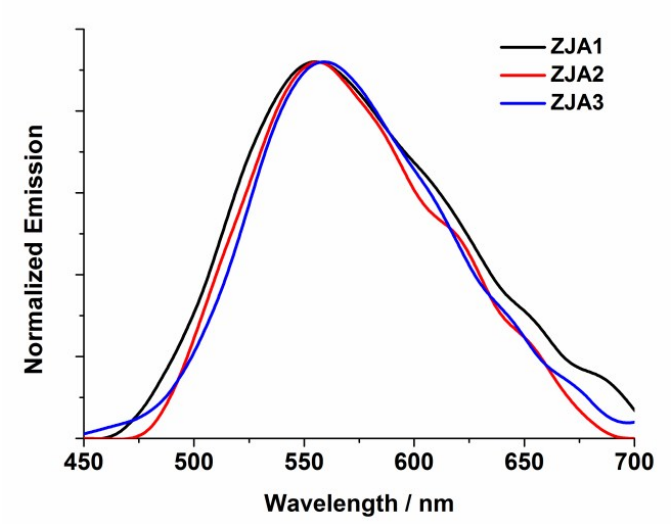

Fig. S1 Emission spectra of **ZJA1, ZJA2** and **ZJA3** in DMF

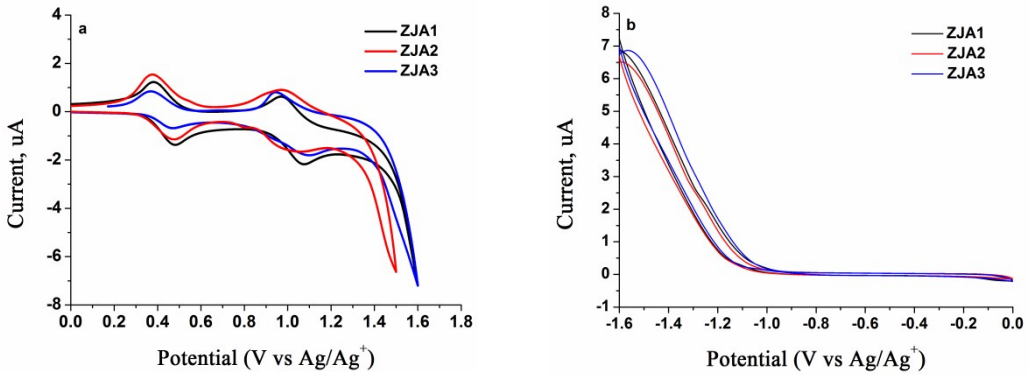

Fig. S2 Cyclic voltammogram of **ZJA1**, **ZJA2** and **ZJA3** in DMF (0.1 M $TBAPF_6$, glassy carbon electrode as working electrode, Pt as counter electrode, Ag/Ag^+ as reference electrode, the ferrocene (+0.63 V vs. NHE) as an external reference, scan rate: 100 mV s^{-1})

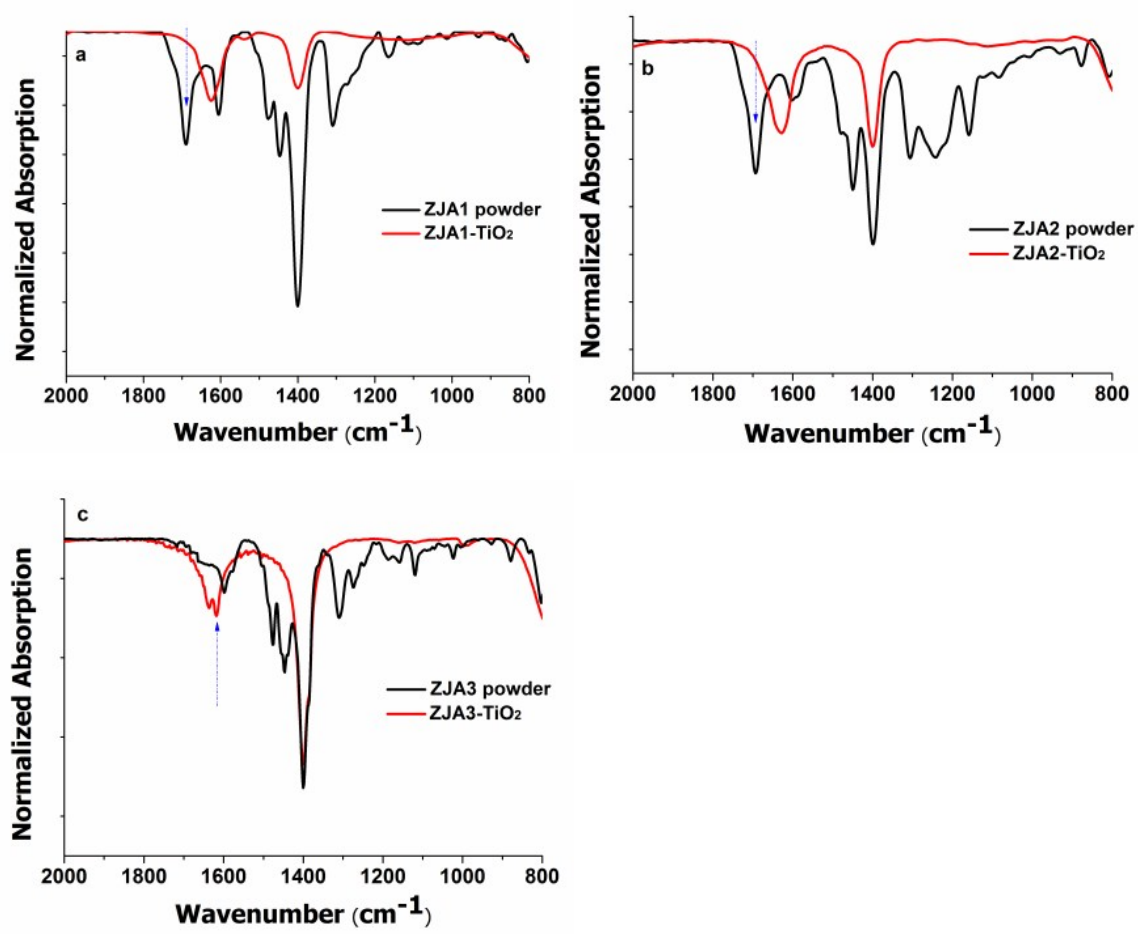

Fig. S3 FTIR spectra of the dye powders and dyes adsorbed on TiO_2 for (a) **ZJA1**, (b) **ZJA2** and (c) **ZJA3**.

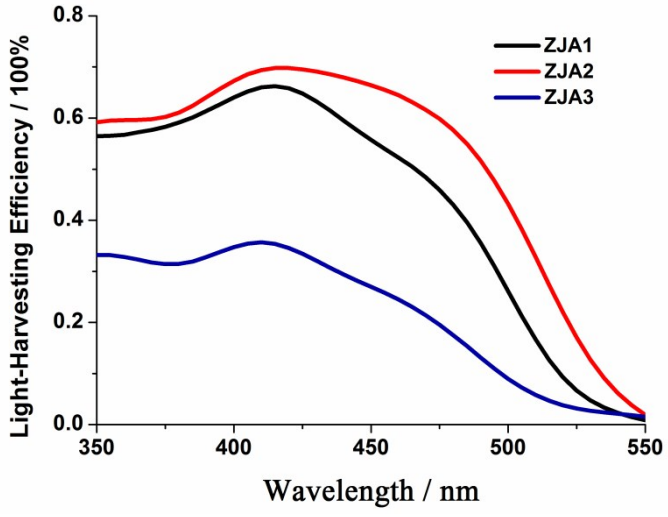

Fig. S4 Light-Harvesting Efficiency of **ZJA1**, **ZJA2** and **ZJA3** on 12 μm porous TiO_2 nanoparticle films (LHE (λ)=1-10$^{-Abs\ (\lambda)}$, where Abs (λ) is the optical absorbance of the dye adsorbed to TiO_2)

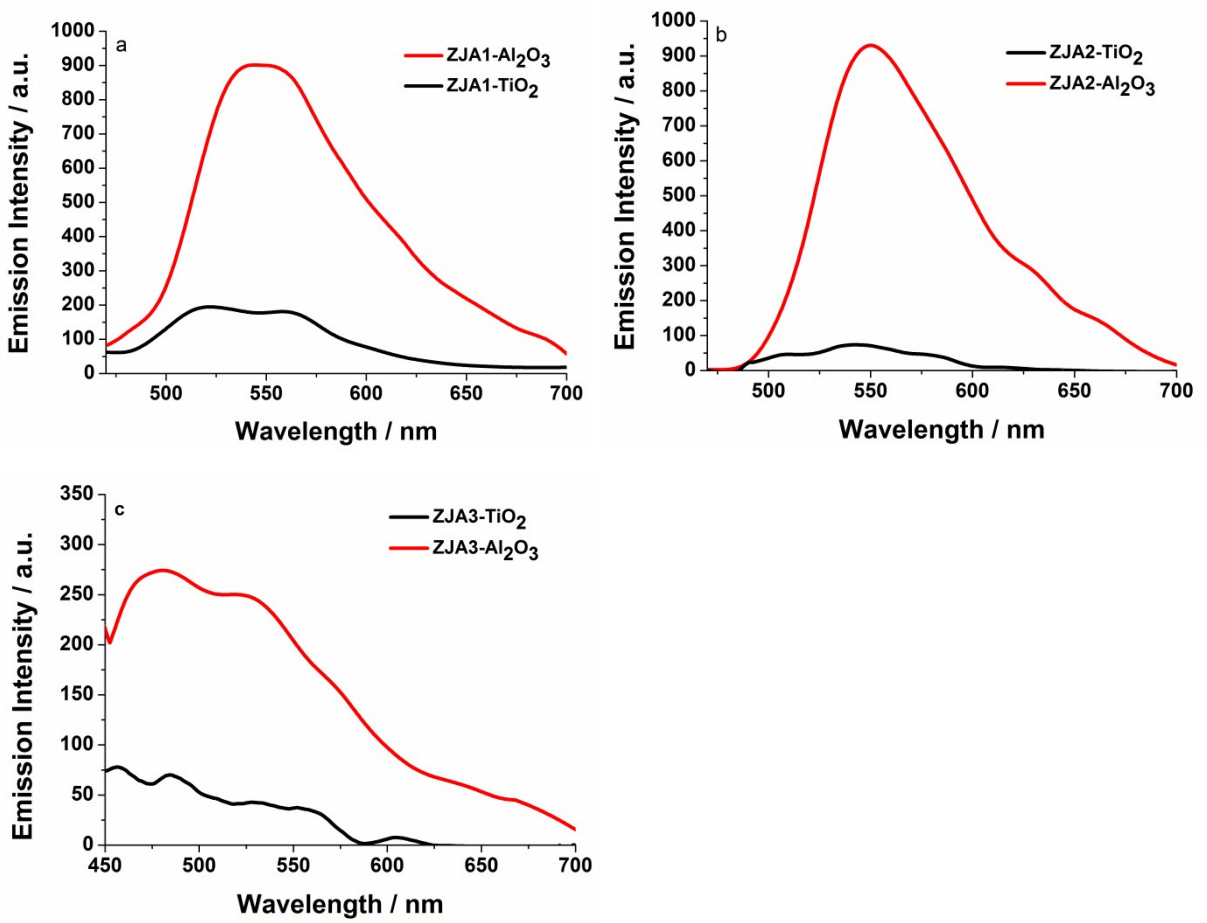

Fig. S5 Comparison of emission quenching **ZJA1, ZJA2** and **ZJA3** loaded on TiO_2 and Al_2O_3.

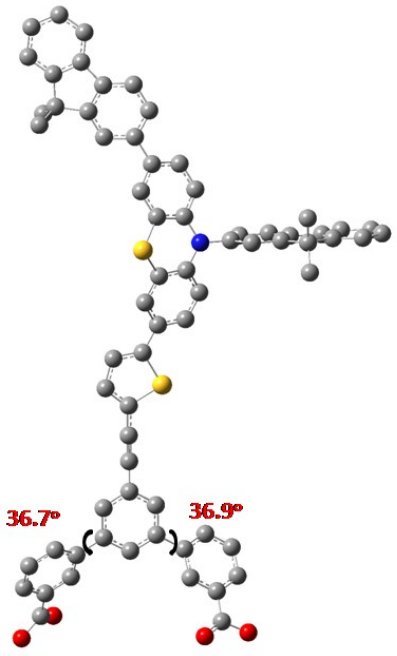

Fig. S6 The geometry optimized ground state molecular structure of dye **ZJA2.**

^{1}H NMR

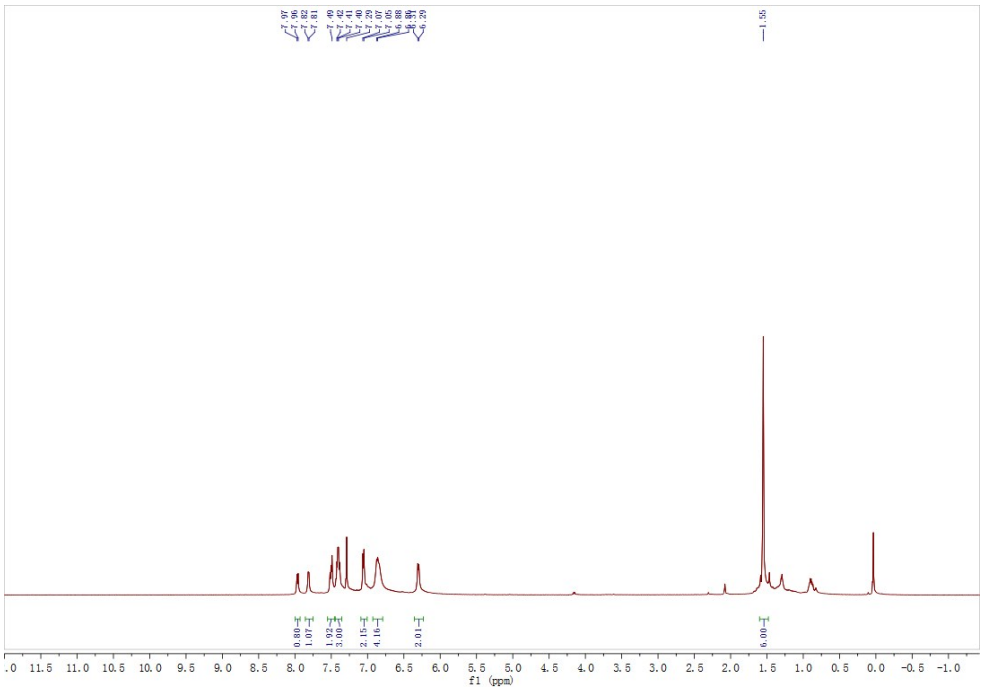

Fig. S7 ^{1}H NMR ($CDCl_3$, 500 MHz) of **compound 2**

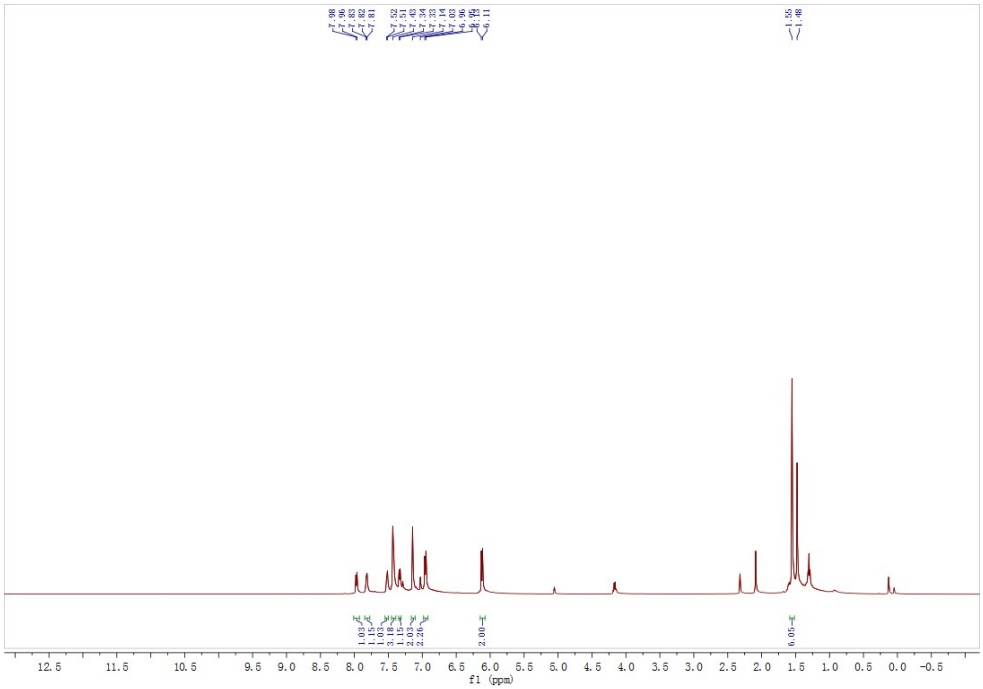

Fig. S8 ^{1}H NMR ($CDCl_3$, 500 MHz) of **compound 3**

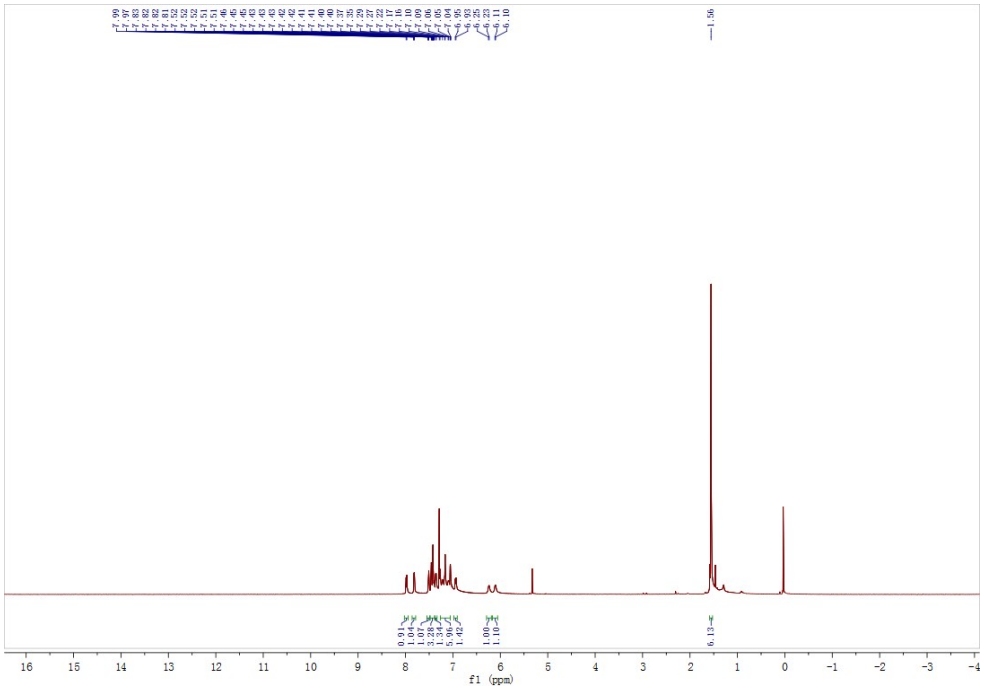

Fig. S9 ^{1}H NMR ($CDCl_3$, 500 MHz) of **compound 4**

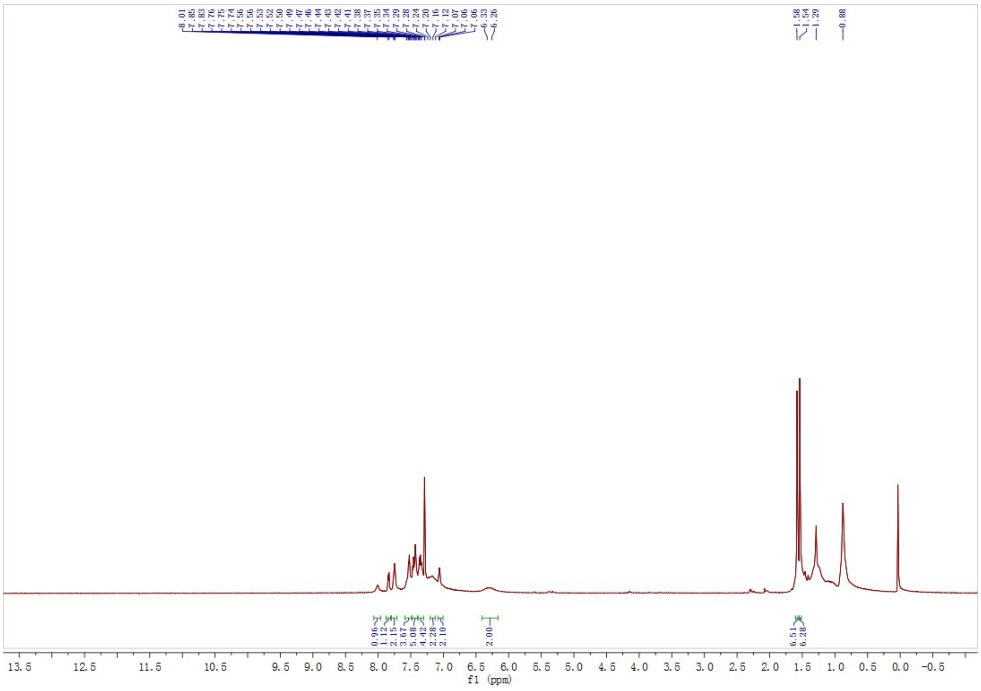

Fig. S10 ^{1}H NMR ($CDCl_3$, 500 MHz) of **compound 5**

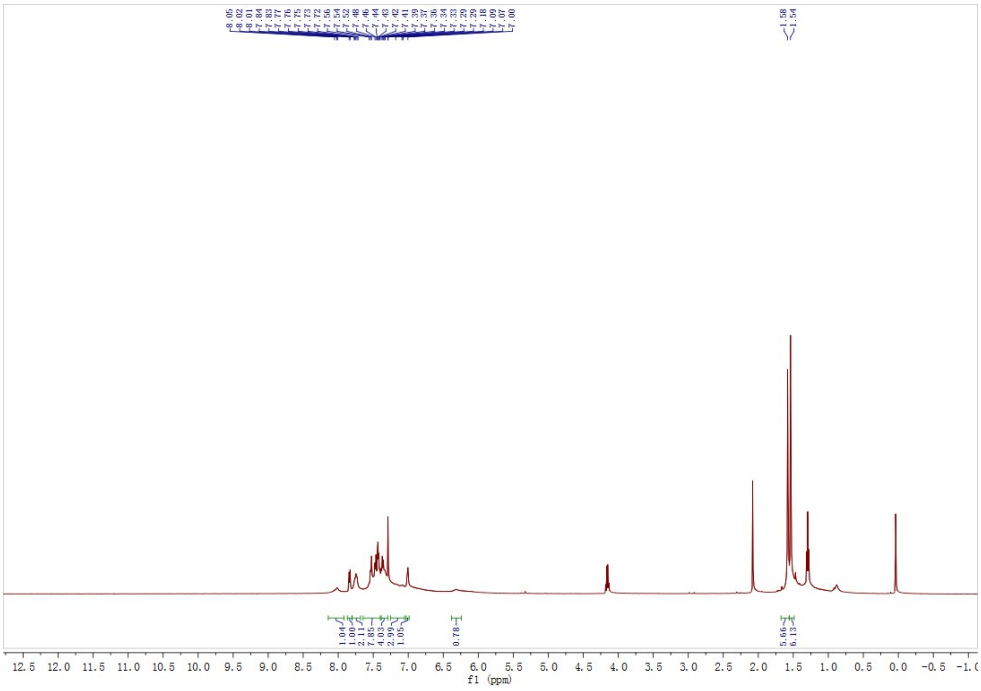

Fig. S11 ^{1}H NMR ($CDCl_3$, 500 MHz) of **compound 6**

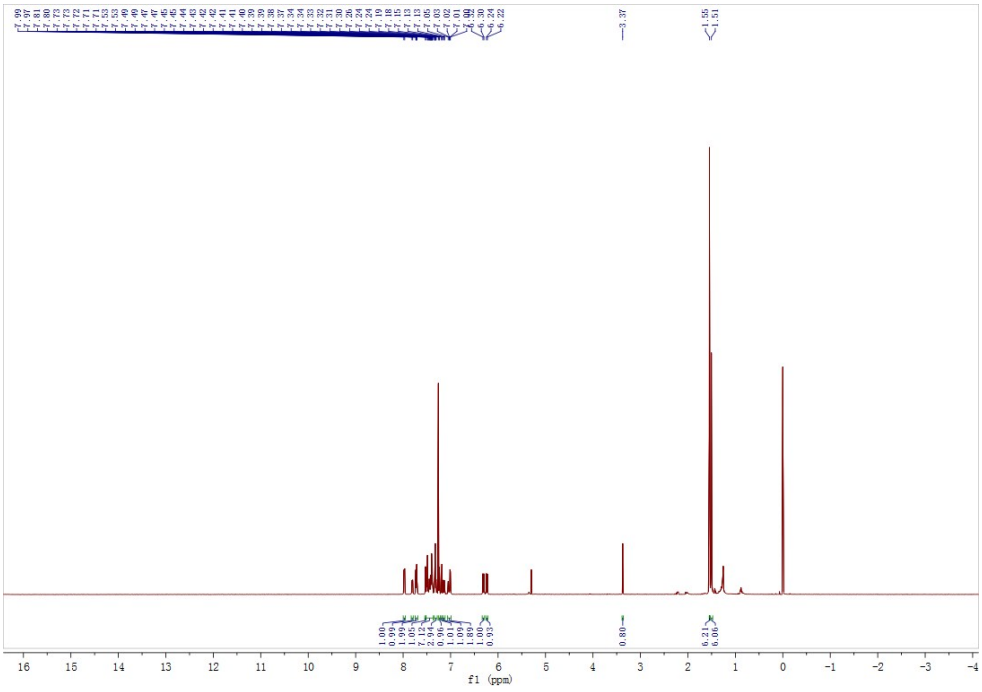

Fig. S12 ^{1}H NMR ($CDCl_3$, 400 MHz) of **compound 7**

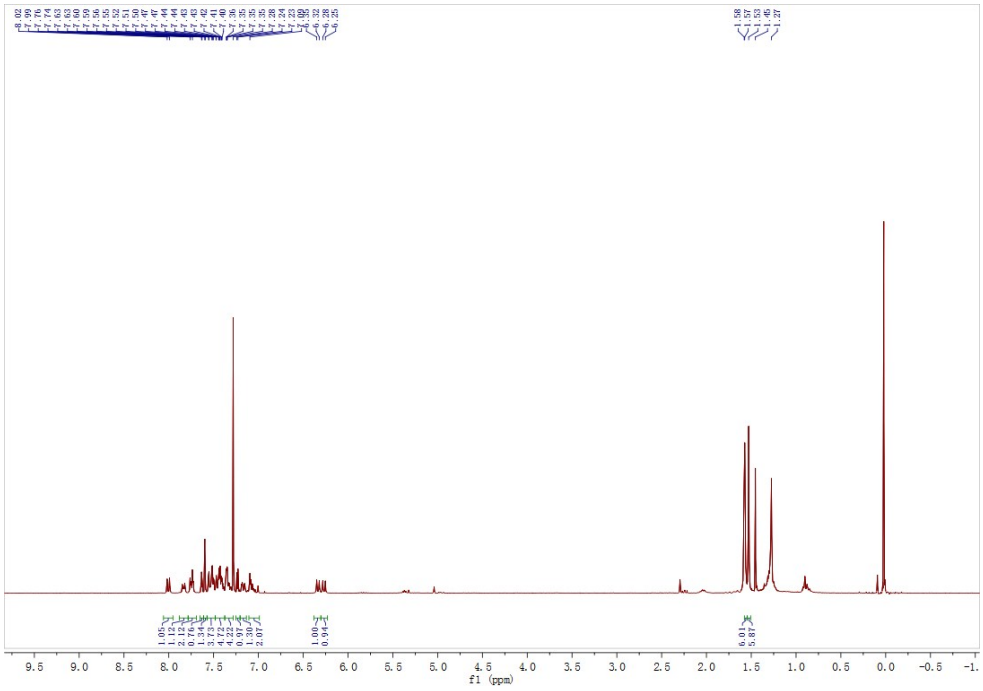

Fig. S13 ^{1}H NMR ($CDCl_3$, 300 MHz) of **compound 8**

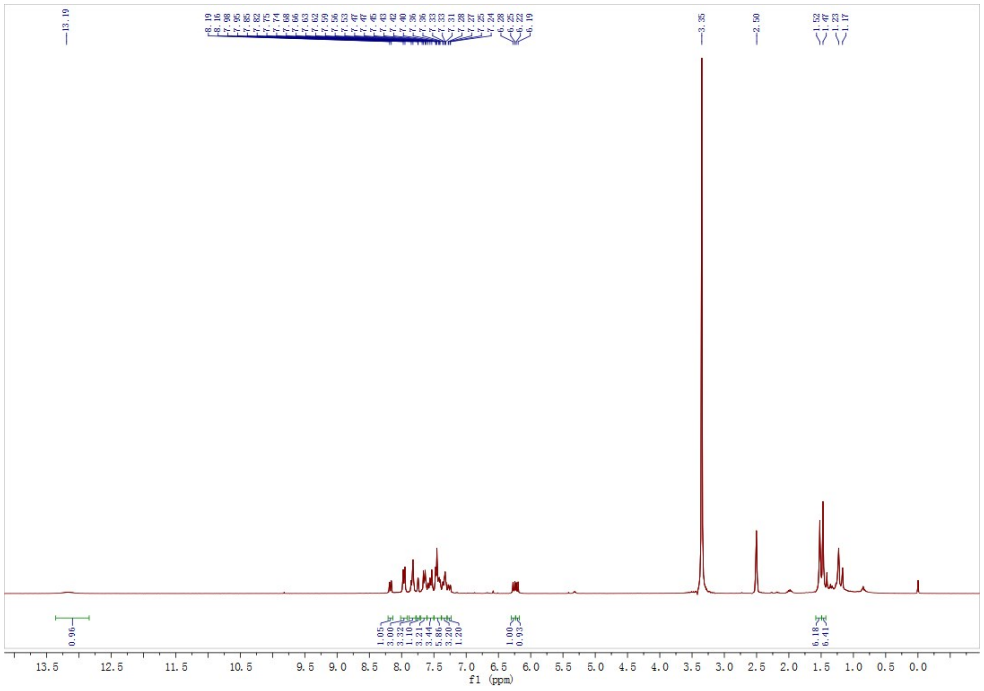

Fig. S14 ^{1}H NMR (DMSO-d_6, 300 MHz) of **ZJA1**

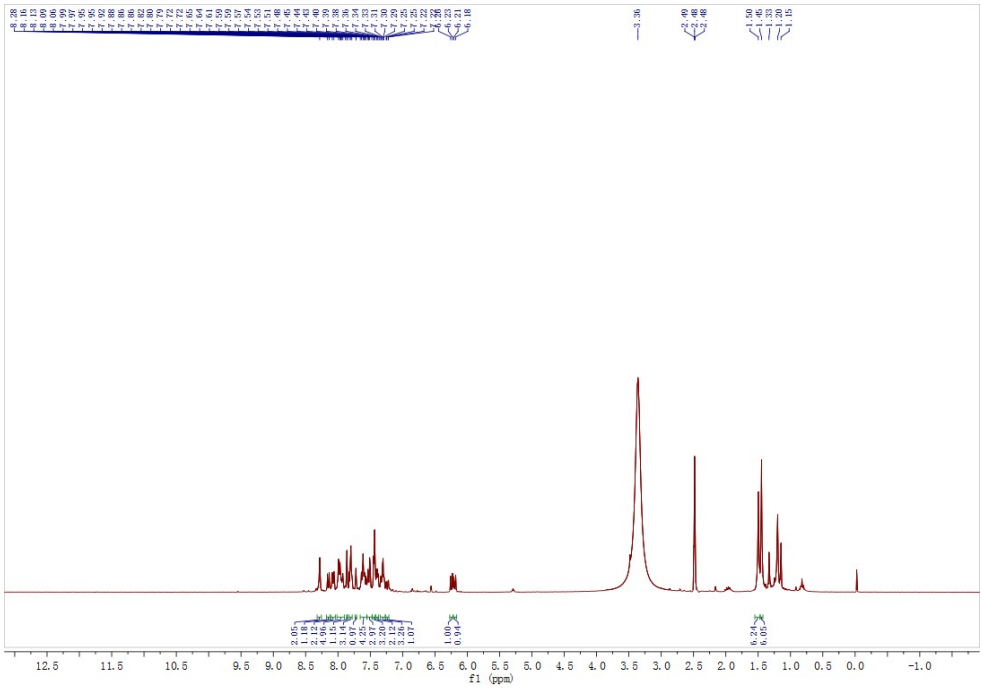

Fig. S15 ^{1}H NMR (DMSO-d_6, 300 MHz) of **ZJA2**

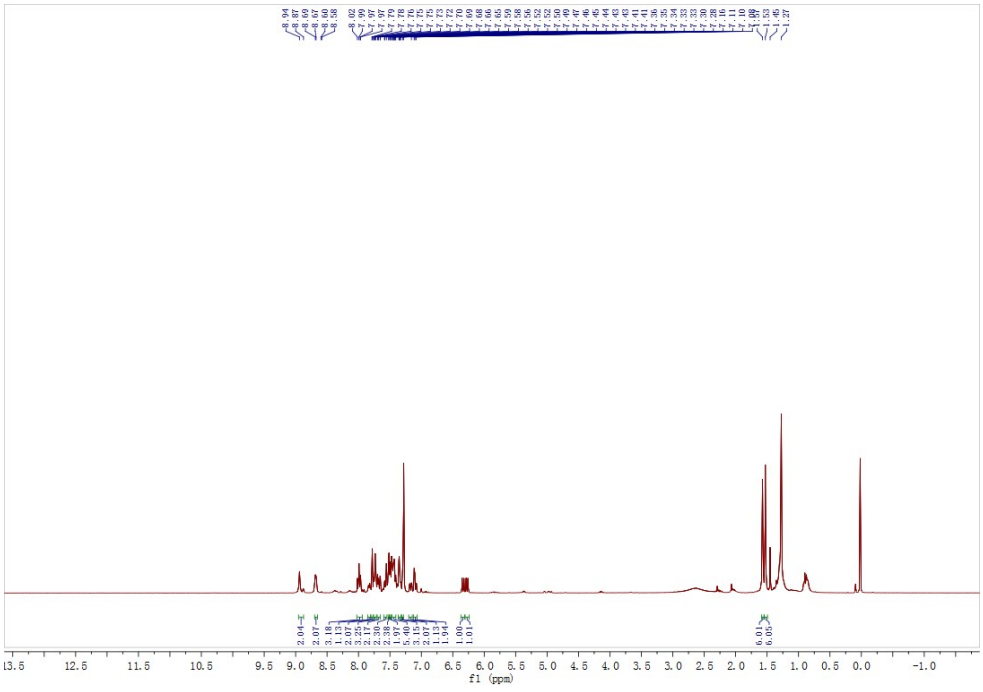

Fig. S16 ^{1}H NMR ($CDCl_3$, 300 MHz) of **ZJA3**

^{13}C NMR

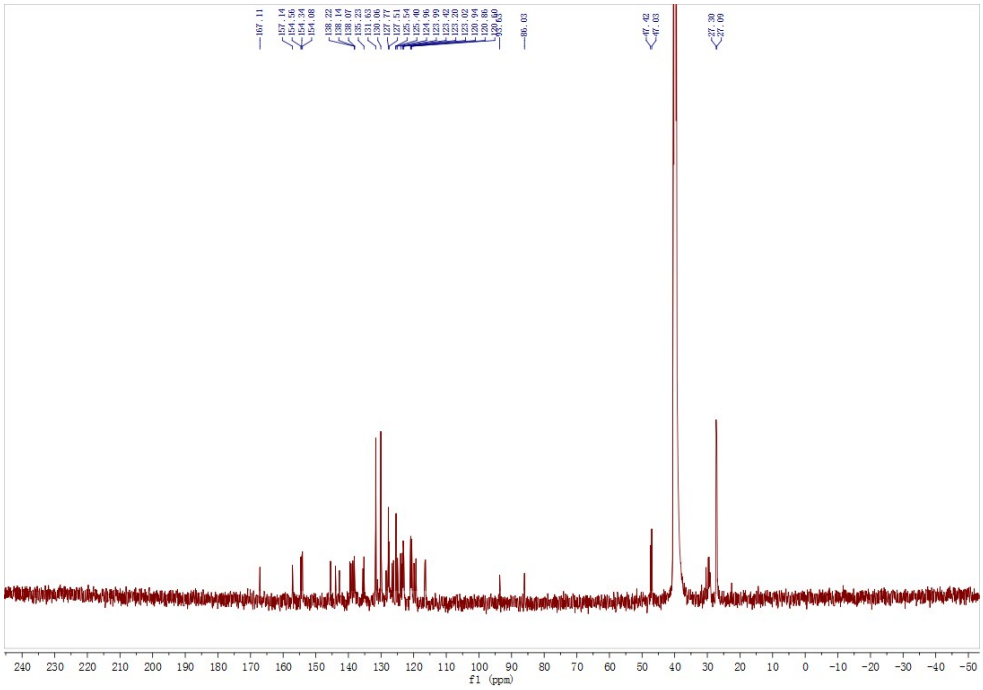

Fig. S17 ^{13}C NMR (DMSO-d_6, 125 MHz) of **ZJA1**

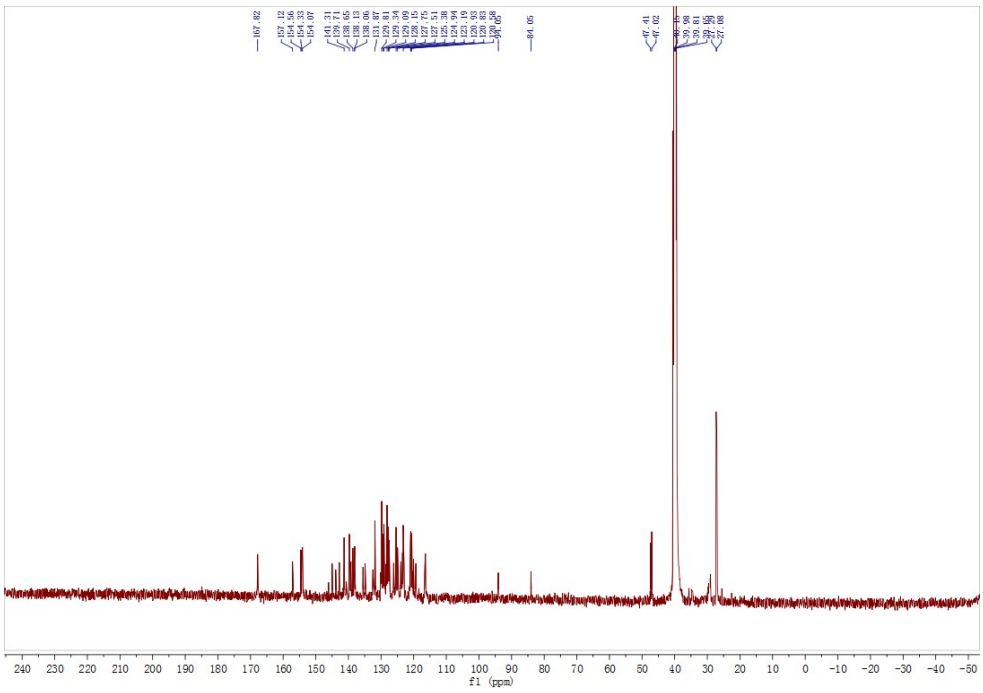

Fig. S18 ^{13}C NMR (DMSO-d_6, 125 MHz) of **ZJA2**

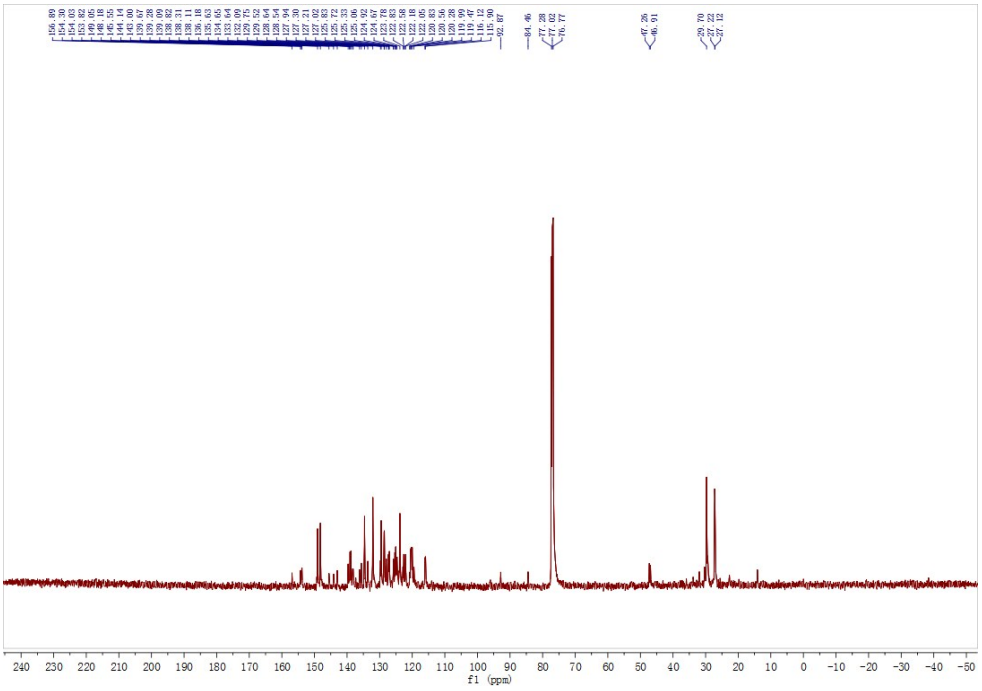

Fig. S19 ^{13}C NMR ($CDCl_3$, 125 MHz) of **ZJA3**