

Indolo[3,2,1-jk]carbazole Derivatives-Sensitized Solar Cells: Effect of π -Bridges on the Performance of Cells

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Synthesis procedure of Indolo[3,2,1-jk]carbazole derivatives

The synthesis route of Indolo[3,2,1-jk]carbazole derivatives (IC-1, IC-2, IC-3 and IC-4) are given in Figure S1. Indolo[3,2,1-jk]carbazole (compound 1) was synthesized by according to the procedure of the previous work¹.

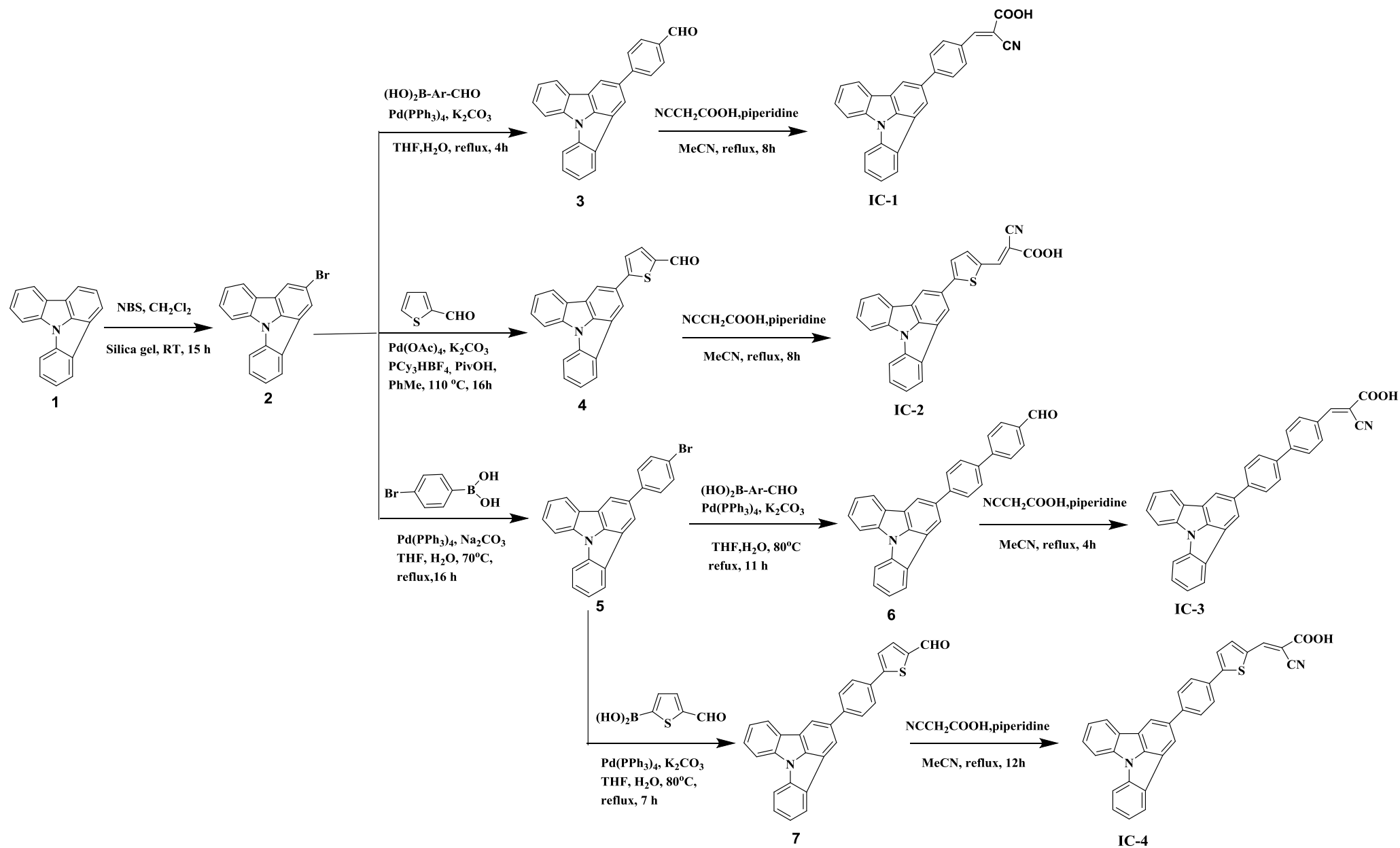


Figure S1 Synthesis route

2-bromoindolo[3,2,1-jk]carbazole (2)

Compound 1 (1.17 g, 4.8 mmol) was dissolved in dichloromethane (50 mL) containing 10 g of silica gel. The mixture was kept in an ice bath under dark. N-Bromosuccinimide (NBS, 0.86 g, 4.8 mmol) was added in several times under stirring. After 1 h, the mixture was removed from the ice bath and kept at room temperature for another 15 h. After the reaction, the crude product was collected by filtration. After recrystallization in glacial acetic acid twice, a white solid product was obtained with a yield of 59 %. ¹H NMR(CDCl₃, 300 MHz), δ: 8.13(s, 2H), 8.06(d, *J*=7.8 Hz, 2H), 7.86(d, *J*=7.8 Hz, 2H), 7.57(t, *J*=7.3 Hz, 2H), 7.36(t, *J*=7.3 Hz, 2H).

4-(indolo[3,2,1-jk]carbazol-2-yl)benzaldehyde (3)

Compound 2 (100 mg, 0.312 mmol), (4-formylphenyl)boronic acid (51.5 mg, 0.342 mmol), anhydrous potassium carbonate (86 mg, 0.624 mmol) and tetrakis(triphenylphosphine)palladium (14.4 mg, 8 mmol %) were added into a mixed solvent of THF/H₂O (10 mL, 3:1). The mixture was refluxed under nitrogen for 4 h. The reaction was quenched by adding water. The crude product was extracted by using dichloromethane, which upon purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) gave the light yellow product (3). ¹H NMR(CDCl₃, 300 MHz), δ: 10.11(s, 1H), 8.28(s, 2H), 8.18(d, *J*=7.5 Hz, 2H), 8.03(d, *J*=7.8 Hz, 2H), 7.93(d, *J*=7.2 Hz, 4H), 7.60(t, *J*=7.3 Hz, 2H), 7.40(t, *J*=7.5 Hz, 2H).

(E)-2-cyano-3-(4-(indolo[3,2,1-jk]carbazol-2-yl)phenyl)acrylic acid (IC-1)

Compound 3 (173.5 mg, 0.5 mmol) and cyanoacetic acid (425 mg, 5.0 mmol) were dissolved in acetonitrile (50 mL), followed by the addition of piperidine (5 drops). The mixture was refluxed under nitrogen for 8 h. After cooling to room temperature, the yellow product was collected and washed with ethyl acetate (yield 85.5 %). ¹H NMR(DMSO-*d*₆, 300 MHz), δ: 8.57(s, 2H), 8.32(t, *J*=8.8 Hz, 4H), 8.04(d, *J*=2H), 7.97(d, *J*=7.8 Hz, 3H), 7.64(t, *J*=7.5 Hz, 2H), 7.44(t, *J*=7.5 Hz, 2H).

5-(indolo[3,2,1-jk]carbazol-2-yl)thiophene-2-carbaldehyde (4)

Compound 2 (500 mg, 1.56 mmol) and thiophene-2-carbaldehyde (350 mg, 3.12 mmol) were added into a mixture of tricyclohexylphosphonium tetrafluoroborate (115.5 mg, 0.312 mmol), trimethylacetic acid (47.75 mg, 0.47 mmol), anhydrous potassium carbonate (325 mg, 2.34 mmol), palladium acetate (33.75 mg, 0.15 mmol) in toluene. The mixture was refluxed for 16 h under nitrogen atmosphere. After cooling to room temperature, the reaction was quenched by ice water. The mixture was extracted by using dichloromethane for three times. The combined organic phase was washed by water and dried by anhydrous MgSO₄. The solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give the light yellow solid (4) with a

yield of 40.2%. ¹H NMR(CDCl₃, 300MHz), δ: 9.94 (s, 1H), 8.32(s, 2H), 8.15(d, *J*=8.1Hz, 2H), 7.89(d, *J*=7.5Hz, 2H), 7.81(d, *J*=4.2Hz, 1H), 7.60(t, *J*= 7.5Hz, 2H), 7.53(d, *J*=2.7Hz, 1H), 7.40(t, *J*=7.5Hz, 2H).

(E)-2-cyano-3-(5-(indolo[3,2,1-jk]carbazol-2-yl)thiophen-2-yl)acrylic acid (IC-2)

The synthesis procedure of IC-2 is same as that of IC-1. The yield is 76.2 %. ¹H NMR(DMSO-d₆, 300MHz), δ: 8.58(s, 2H), 8.37(d, *J*=7.5Hz, 2H), 8.28(d, *J*=7.5Hz, 2H), 8.09(s, 1H), 7.74(d, *J*= 3.3Hz, 2H), 7.64(s, 2H), 7.44(d, *J*=7.2Hz, 2H).

2-(4-bromophenyl)indolo[3,2,1-jk]carbazole (5)

Compound 2(500 mg , 1.56 mmol) , (4-bromophenyl)boronic acid (473.8 mg, 2.34 mmol) , anhydrous sodium carbonate (661 mg, 6.24 mmol) and tetrakis(triphenylphosphine)palladium((90 mg) were added into a mixed solvent of THF/H₂O(10 mL, 3:1). The mixture was refluxed for 16 h under nitrogen atmosphere. After cooling to the room temperature, the reaction was quenched by water. The crude product was extracted by using dichloromethane, which upon purification by column chromatography on silica gel (petroleum ether /ethyl acetate = 20:1) gave the white product (5) with a yield of 21.7%. ¹H NMR(CDCl₃, 300MHz), δ: 8.21(s, 2H), 8.18(d, *J*=8.1Hz, 2H), 7.94(d, *J*=7.5Hz, 2H), 7.65(s, 4H), 7.60(t, *J*=8.0Hz, 2H), 7.40(t, *J*=7.5Hz, 2H).

4'-(indolo[3,2,1-jk]carbazol-2-yl)-[1,1'-biphenyl]-4-carbaldehyde (6)

Compound 5(95 mg, 0.24 mmol), (4-formylphenyl)boronic acid (107.8 mg, 0.72 mmol), anhydrous potassium carbonate (105.8 mg, 0.72 mmol) and tetrakis(triphenylphosphine)palladium (11 mg) were added into a mixed solvent of THF/H₂O(60 mL, 2:1). The mixture was refluxed at 80 °C for 11 h under nitrogen. After cooling to the room temperature, the reaction was quenched by ice water. The crude product was extracted by using dichloromethane, which upon purification by column chromatography on silica gel (petroleum ether /ethyl acetate = 10:1) gave the blue yellow product (6) with a yield of 59.4%. ¹H NMR(DMSO-d₆, 300MHz), δ: 10.10(s, 1H), 8.31(s, 2H), 8.21(d, *J*=7.8Hz, 2H), 7.91(m, 10H), 7.61(t, *J*=7.5Hz, 2H), 7.41(t, *J*=7.5Hz, 2H).

(E)-2-cyano-3-(5-(indolo[3,2,1-jk]carbazol-2-yl)thiophen-2-yl)acrylic acid (IC-3)

Compound 6 (130mg , 0.31 mmol) and cyanoacetic acid (264 mg , 3.1 mmol) were dissolved in acetonitrile (50 mL), followed by the addition of piperidine(6 drops). The mixture was refluxed at 80 °C for 8 h under nitrogen. After cooling to room temperature, the precipitate was collected and purified by column chromatography on silica gel (DCM:EtOH=2:1) to give the yellow product IC-3 with a yield of 68.9%. ¹H NMR(DMSO-d₆, 300MHz), δ: 8.48(s, 2H), 8.25(m, 4H), 8.05(s, 1H), 7.99(d, *J*=8.1Hz, 2H), 7.89(m, 6H), 7.60(t, *J*=7.5Hz, 2H), 7.37(t, *J*=7.5Hz, 2H).

5-(4-(indolo[3,2,1-jk]carbazol-2-yl)phenyl)thiophene-2-carbaldehyde (7)

Compound 5 (95 mg, 0.24 mmol), (5-formylthiophen-2-yl)boronic acid (12 mg, 0.72 mmol), anhydrous potassium carbonate (66 mg, 0.48 mmol) and tetrakis(triphenylphosphine)palladium (22 mg) were added into a mixed solvent of THF/H₂O (60 mL, 2:1). The mixture was refluxed at 80 °C for 7 h under nitrogen. After cooling to the room temperature, the reaction was quenched by ice water. The crude product was extracted by using anhydrous ethyl ether. The combined organic phase was washed by water and dried by anhydrous MgSO₄. The solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give the yellow solid (7) with a yield of 61.9%. ¹H NMR(DMSO-d₆, 300MHz), δ : 9.95(s, 1H), 8.57(s, 2H), 8.36(d, *J*=8.4Hz, 2H), 8.32(d, *J*=8.4Hz, 2H), 8.10(s, 1H), 7.99(s, 4H), 7.86(d, *J*=3.9Hz, 1H), 7.66(t, *J*=7.5Hz, 2H), 7.46(t, *J*=7.5Hz, 2H).

(E)-2-cyano-3-(5-(4-(indolo[3,2,1-jk]carbazol-2-yl)phenyl)thiophen-2-yl)acrylic acid (IC-4)

Compound 7 (42.7 mg, 0.1 mmol) and cyanoacetic acid (85 mg, 1.0 mmol) were dissolved in a mixture of acetonitrile (20 mL) and THF (20 mL), followed by the addition of piperidine (4 drops). The mixture was refluxed at 80 °C for 12 h under nitrogen. After cooling to room temperature, the precipitate was collected and purified by column chromatography on silica gel (DCM:EtOH=10:1) to give the orange product IC-4 with a yield of 55%. ¹H NMR(DMSO-d₆, 300MHz), δ : 8.51(s, 2H), 8.29(m, 4H), 8.14(s, 1H), 7.91(m, 4H), 7.74(d, *J*=3.9Hz, 2H), 7.62(t, *J*=7.5Hz, 2H), 7.42(d, *J*=7.5Hz, 2H).

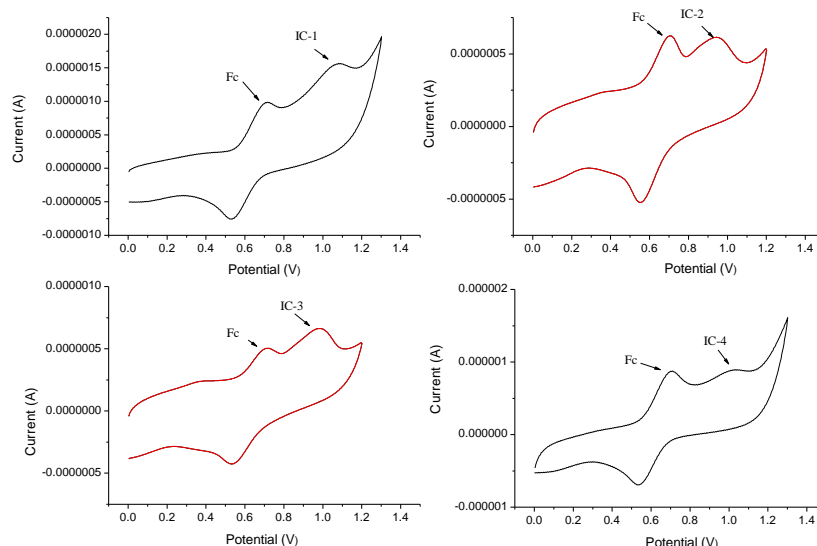


Figure S2 Cyclic voltammograms of IC-1, IC-2, IC-3 and IC-4 with ferrocene as an internal reference recorded in 0.1 M tetrabutylammonium hexafluorophosphate in CH₂Cl₂ at a sweeping rate of 10 mV.s⁻¹ using an Ag/AgCl reference electrode.

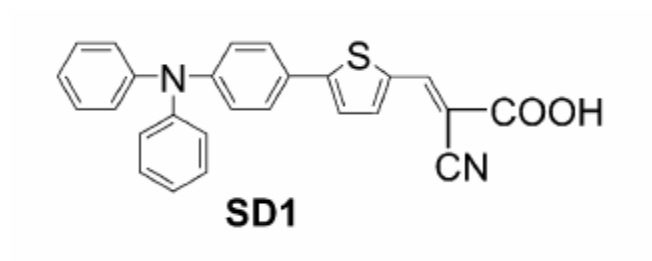


Figure S3 Molecular structure of SD1

reference

- (1) Lv, J.; Liu, Q.; Tang, J.; Perdih, F.; Kranjc, K. *Tetrahedron Lett.* **2012**, *53*, 5248.