Supporting information for

Substitution Effect on Molecular Packing and Transistor Performance of Indolo[3,2-*b*]carbazole Derivatives

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Scheme S1. Synthetic route of CICZ and CHICZ compounds

Materials Synthesis:

2,8-dichloro-indolo[3,2-*b***]carbazole (CICZ):** The solution of (4-chlorophenyl) hydrazine hydrochloride (15.75 g, 88 mmol) in AcOH (100 ml) was dropped into a solution of cyclohexane-1, 4-dione (4.48 g, 40 mmol) in AcOH (80ml). The resulting mixture solution was heated to 40° C and kept for 1.5 h before cooling to room temperature. The final solution was filtered and the filter residue was washed by cold ethanol, and (4-chlorophenyl) hydrazine hydrochloride (12 mmol) was added into the mixture solution of AcOH (32 ml) and H₂SO₄ (8 ml). The resulting solution was firstly heated to 60° C quickly and then heated to reflux slowly. When the color of the mixture solution was turned from brown to yellow after 5 min, the solution was cooled to

room temperature. Solvents was removed under vacuum and afforded a yellow solid, which was further recrystallized from the ethanol/DMF () mixture solvents and gave CICZ as light-yellow crystalline solid (yield: 20%). ¹H-NMR (400 MHz, DMSO-d6): δ [ppm] 11.26 (s, 2H), 8.33 (d, J = 2.0 Hz, 2H), 8.21 (s, 2H), 7.47-7.45 (m, 2H), 7.39 (d, J = 2.1 Hz, 1H), 7.37 (d, J = 2.1 Hz, 1H). MS (EI): 324 (calcd. 324.02 for C18H10Cl2N2).

2,8-dichloro-5,11,-dihexyl-indolo[3,2-*b***]carbazole (CHICZ): NaH (198 mg, 8.25 mmol) was added to a solution of CICZ (1.079 g, 3.3 mmol) in dry DMF (25 ml) under the argon protection and kept the reaction for 3h. Then 1-bromohexane (1.4 ml, 10 mmol) was added into the reacted solution and the resulting solution was stirred for 12 h at room temperature. The final solution was poured into water and extracted by CH₂Cl₂, then the organic layer was further purified by column chromatography (SiO₂, Petroleum:CH₂Cl₂=4:1) to give CHICZ as yellow solid (yield: 90%). ¹H-NMR (400 MHz, CDCl₃): \delta [ppm] 8.15 (s, 2H), 7.94 (s, 2H), 7.42 (d,** *J* **= 0.86 Hz, 2H), 7.32 (d,** *J* **= 0.86 Hz, 2H), 4.34-4.38 (t,** *J* **= 0.72Hz, 4H), 1.88-1.94 (m, 4H), 1.27-1.43 (m, 12H), 0.85-0.89 (m, 6H). MS (EI): 492 (calcd. 492 for C₃₀H₃₄Cl₂N₂).**



Fig. S1 Typical output and transfer curves of top-contact field-effect transistors based on vacuum-evaporated CHICZ thin films on OTS-modified Si/SiO₂ substrates at different temperatures : (a,b) 40 $^{\circ}$ C, (c,d) 60 $^{\circ}$ C.



Fig. S2 Optical microscopy images of CHICZ single crystals grown from different experimental conditions.