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Ultra-sensitive boscalid sensors based on β-cyclodextrin modified perfluorinated copper phthalocyanine field-effect transistor

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Preparation method of inclusion compound

Take 50 mL of deionized water in a 100 mL three-necked flask and heat it to 50°C, add β-CD and stir until it is completely dissolved to form a saturated solution. A small amount of guest molecules was dissolved in 15ml of ethanol, and the prepared guest solution was slowly added to the saturated β-CD solution within 2 hours using a constant pressure dropping funnel, and stirred at 50°C for 6 hours. When the reaction was completed, the three-necked flask was placed at 4° C overnight. Rinse the precipitate with a small amount of low-temperature ethanol and water to remove the reactants, the product was then dried in an oven for 12 hours.

Phase solubility

Prepare a series of β-CD aqueous solutions with different concentrations, in which the β-CD concentration is 0, 1, 2, 3, 4, 5 mmol/L, the excess boscalid (100 mg) was added to 20 mL of the above β-CD solution, and then the centrifuge tube was shaken at 25° C for 72 hours until equilibrium. The solution was filtered with a 0.22μm water phase filter membrane and detected by HPLC-MS/MS. Using the measured concentration of the original drug as the vertical axis and the concentration of the β-CD solution as the horizontal axis, calculate the stable equilibrium constant Ks according to formula:

$K_S = L/(S_0 \times (1 - L))$

L represents the slope of the phase solubility curve, and S_0 represents the concentration of the saturated aqueous solution of guest molecules without β-CD.

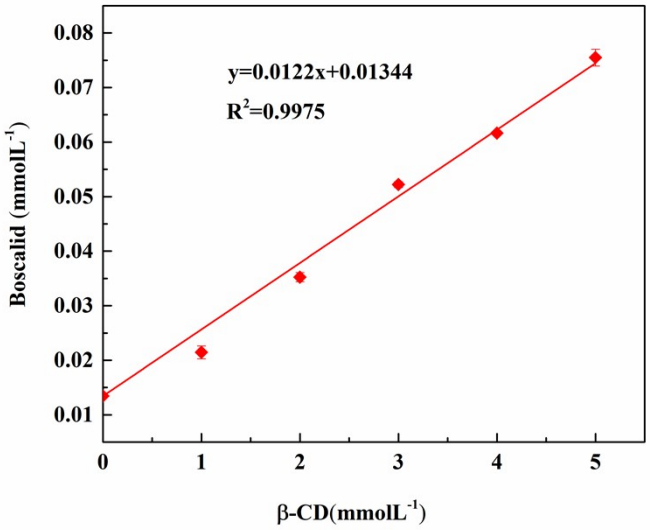

Figure. S1 Phase solubility diagram of β-CD with boscalid.

^{1}H NMR Characterization

In the ^{1}H-NMR spectrum of the inclusion complex of β-CD and boscalid, the imine-

linked hydrogen of boscalid and the hydrogen on pyridine have obvious chemical shift changes. The chemical shift of the corresponding β-CD hydrogen atom in the inclusion compound also changed significantly. The hydrogen split near 5.71 ppm and 4.46 ppm changed significantly, corresponding to the hydroxyl hydrogen and ether bond in the cyclodextrin cavity. These evidences indicate that the pyridine ring and amide bond of boscalid enter the cavity of the β-CD molecule and interact with the hydroxyl and ether oxygen groups on the glucose unit.

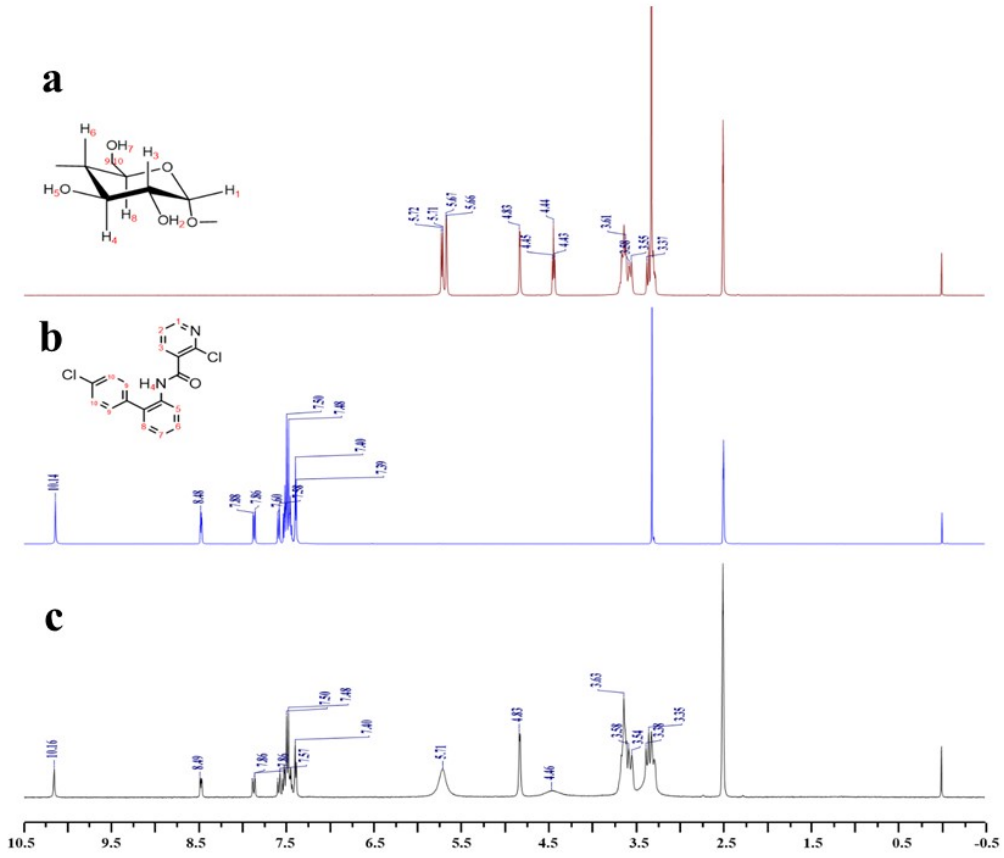

Figure. S2 [1]HNMR of boscalid, β-CD and their inclusion compounds (a) β-CD, (b) boscalid, (c) boscalid + β-CD inclusion compound.

Table S1 Chemical shifts of H protons in β-CD, boscalid and inclusion compound.

H	ppm (DMSO-d6)			
	β-CD	Boscalid	inclusion compound	Δδ[a]
H1	5.72		5.71	–0.01
H2	3.61		3.63	0.02
H5	4.83		4.83	0.00
H7	4.45		4.46	0.01
H′1		8.48	8.49	0.01
H′3		7.88	7.89	0.01
H′4		10.14	10.16	0.02
H′8		7.57	7.58	0.01
H′9		7.50	7.50	0.00
H′10		7.40	7.40	0.00

Contact angle test

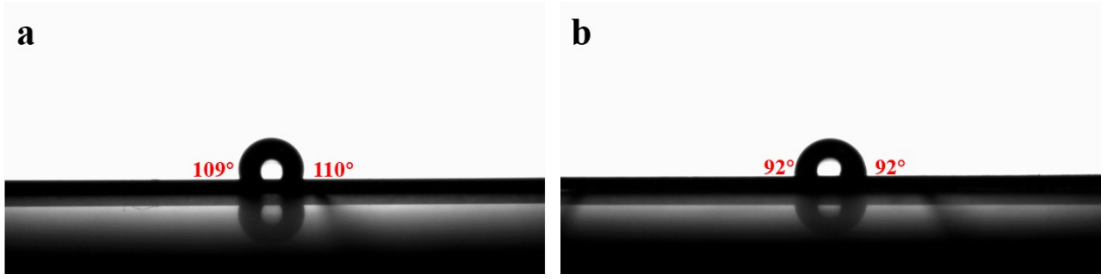

Figure. S3 Surface contact angle of $F_{16}CuPc$ films (a) unmodified and (b) modified β-CD.

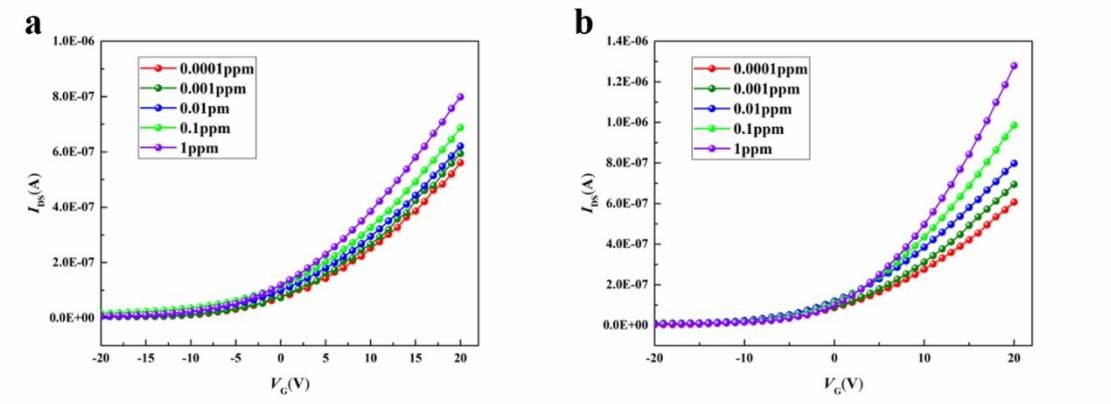

Figure. S4 (a) Transfer characteristics of $F_{16}CuPc$ sensor treated with various concentration of boscalid. (b) Transfer characteristics of $F_{16}CuPc$ + β-CD sensor treated with various concentration of boscalid.

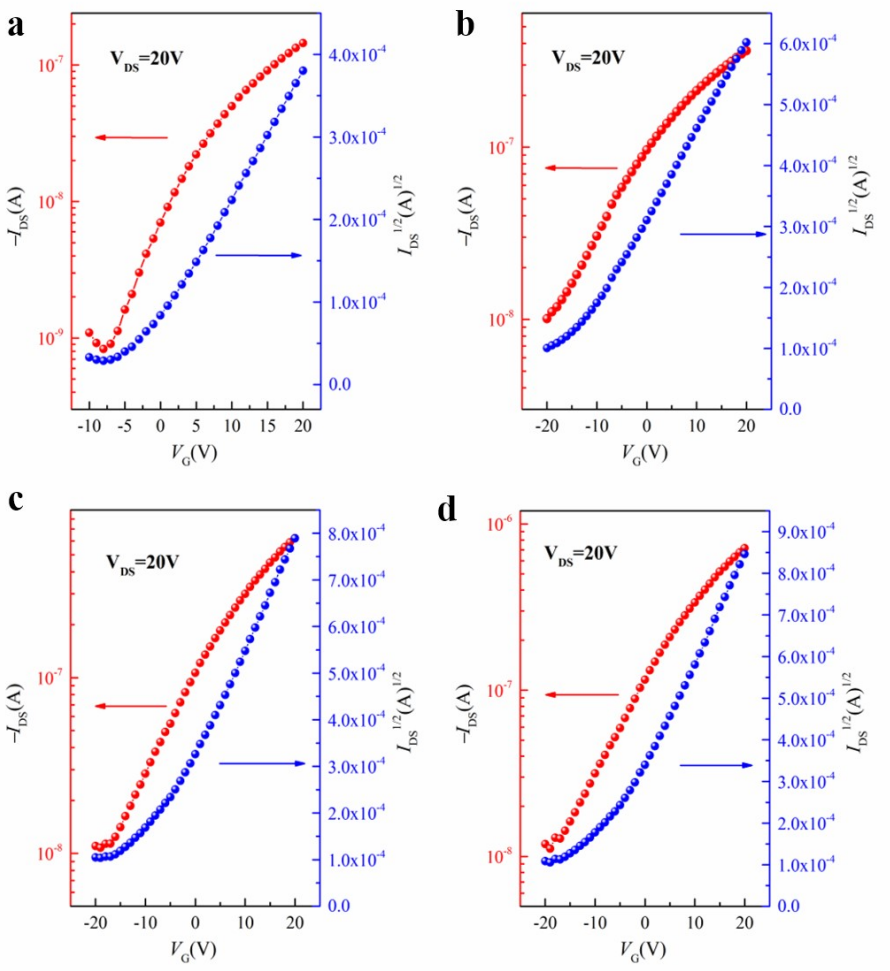

Figure. S5 Transfer characteristics of (a) F_{16}CuPc, (b) F_{16}CuPc + ethanol, (c) F_{16}CuPc + ethanol + boscalid, (d) F_{16}CuPc + β-CD + ethanol + boscalid.

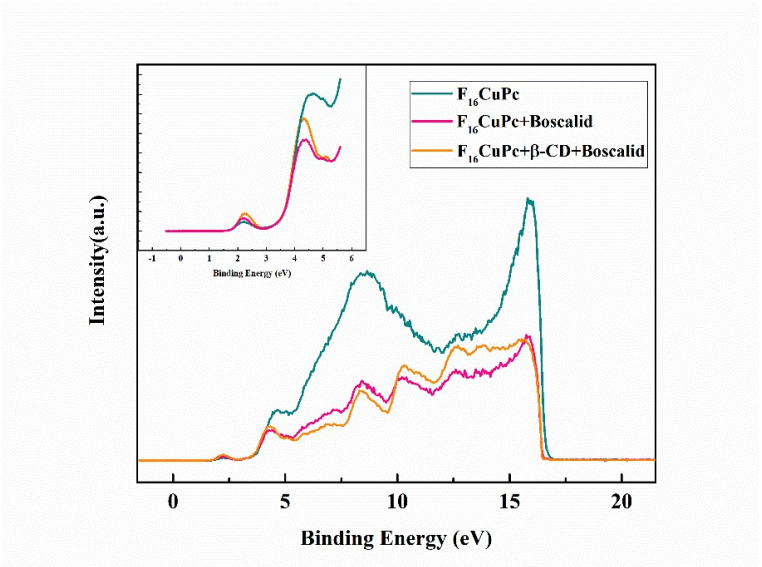

Figure. S6 Ultraviolet Photoelectron Spectroscopy (UPS) of F_{16}CuPc, F_{16}CuPc + boscalid, F_{16}CuPc + β-CD + boscalid.

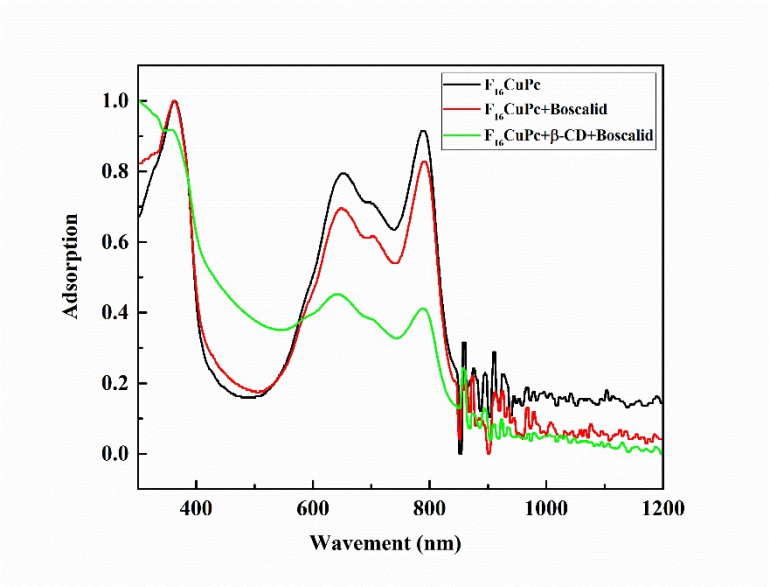

Figure. S7 UV absorption spectrum (UV) of F_{16}CuPc, F_{16}CuPc+boscalid, F_{16}CuPc + β-CD + boscalid.

Table S2 Energy lever of F_{16}CuPc, F_{16}CuPc + boscalid, F_{16}CuPc + β-CD + boscalid.

	F_{16}CuPc	F_{16}CuPc + boscalid	F_{16}CuPc + β-CD + boscalid
UPS(HOMO)	−6.31	−6.46	−6.57
UV(Bandgap)	−1.45	−1.45	−1.47
LUMO (Calculation)	−4.86	−5.01	−5.1