

Electronic Supplementary Information

Fabrication and Characterization of Molecular Scale Field-Effect Transistors

Lingchao Cao,^{ab} Shiyang Chen,^a Dacheng Wei,^a Yunqi Liu,^{*a} Lei Fu,^a Gui Yu,^a Hongming Liu,^c
5 Xinyu Liu,^c and Dexing Wu^c

^aBeijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. Fax: +86-10-62559373; Tel: +86-10-62613253; E-mail:

liuyq@iccas.ac.cn

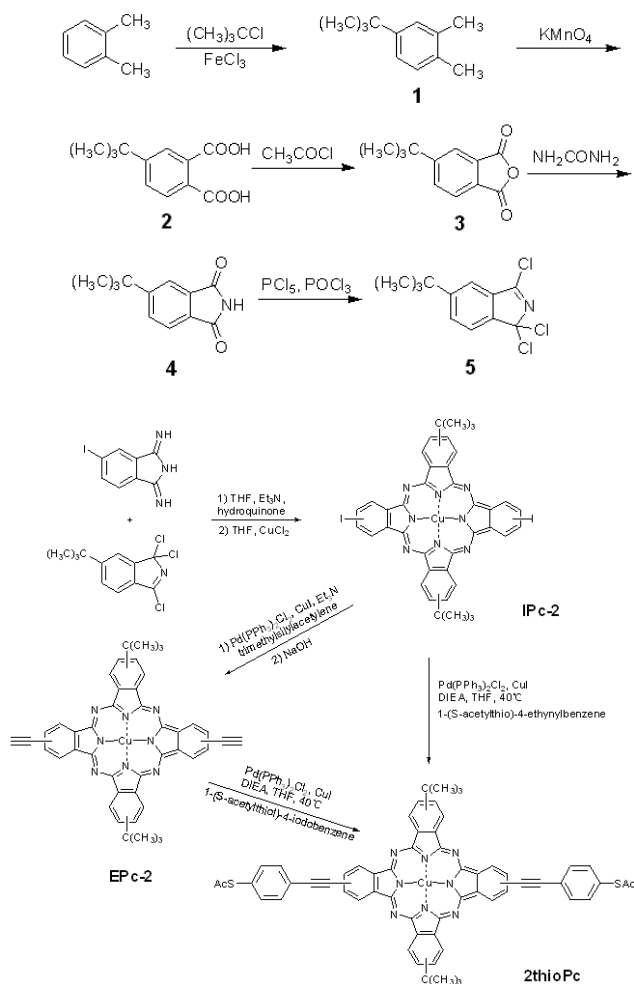
^bGraduate University of the Chinese Academy of Sciences, Beijing 100039, China

10 ^cInstitute of Microelectronics, Chinese Academy of Sciences, Beijing 100029, P. R. China

1. Synthesis

Several methods have been reported to synthesize substituted Pcs. Condensation of corresponding phthalonitriles is one of the most successful methods usually used. Scheme S1 shows the synthetic route to {di-[1-(S-acetylthio)-4-ethynylphenyl]-di-(*tert*-butyl)phthalocyanato}copper(II) (**2thioPc**). Solubility is the key factor to be considerate, so we successfully synthesized 6/7-*t*-butyl-1,3,3-trichloroisoindolenine as one of the precursor which synthetic route is outlined in Scheme S1. Firstly, the *tert*-butyl group was incorporated onto benzene by Friedel-Crafts alkylation, and then the methyl groups were oxidized by potassium permanganate. The obtained 4-*tert*-butyl-phthalic acid (**2**) was converted to 5-*tert*-butyl-isoindole-1,3-dione (**4**) by dehydration and aminization. Finally, after treatment **4** with POCl₃ and PCl₅ for over 60 h, 6/7-*t*-butyl-1,3,3-trichloroisoindolenine (**5**) was distilled at 144–146 °C under 2 mmHg. The *tert*-butyl groups serve to greatly increase the solubility of

the Pc. Our initial synthetic strategy (Method 1) toward the **2thioPc** outlined in Scheme S1: [di-iodo-di-(*tert*-butyl)phthalocyanato]copper(II) (**IPc-2**) by two-step method converted to [di-ethynyl-di-(*tert*-butyl)phthalocyanato]copper(II) (**EPc-2**), and then **EPc-2** reacted with 1-thioacetyl-4-iodobenzene to give the target product **2thioPc**. But the very low yield (overall yield 11.7% from **IPc-2**) makes the route inefficient because of the formation of nonsoluble by-product. It is possible that homo-coupling of ethynes yields the butadiyne species in the Sonogashira reaction in the presence of copper. We overcome this problem by employing 1-(*S*-acetylthio)-4-ethynylbenzene as the precursor to react with **IPc-2** to afford the target product in a higher yield of 46% (Method 2).



Scheme S1 Synthetic route to **2thioPc**

2. Characterization

2thioPc was characterized by various spectroscopies. In IR spectra the characteristic absorptions of **2thioPc** is described as follows. The bands at 2958 cm^{-1} and 2955 cm^{-1} are attributed to the asymmetric vibration of $-\text{CH}_3$, the bands at 2190 cm^{-1} , 2150 cm^{-1} and $2190, 2149\text{ cm}^{-1}$ are attributed to the asymmetric vibration of $\text{C}\equiv\text{C}$, the bands at 1711 cm^{-1} and 1709 cm^{-1} are attributed to the asymmetric vibration of $\text{C}=\text{O}$, the bands at 1613 cm^{-1} , 1490 cm^{-1} , 1392 cm^{-1} and 1611 cm^{-1} , 1504 cm^{-1} , 1396 cm^{-1} are attributed to the asymmetric vibration of $\text{C}=\text{C}$, respectively. The strong band at 1090 cm^{-1} observed is attributed to the characteristic of Pc ring vibration.²⁶ ^1H NMR spectroscopy is not particularly useful for characterizing complexes containing the *tert*-butylphthalocyanine due to presence of Pc regioisomers. The protons on *tert*-butyl appear as broad band at the highest field, the CH_3 link to $\text{C}=\text{O}$ is a single peak at about $\delta = 2.5$, and aromatic protons appear at the lowest field as multiple peaks. The mass spectra of **2thioPc** displays an intense isotopic cluster peaking assignable to their molecular ion and the relative abundance of the isotopic cluster is in good agreement with the simulated spectrum of M^+ .

3. Voltammetric measurements

The electronic properties of the **2thioPc** was gained by investigating their electrochemical behaviors in THF. Table S1 lists the redox potentials of **2thioPc** together with those of the reference **4t-BuPc** for comparison. As a general feature, two reductive processes were observed in this compound. These two couples were assigned to $\text{MPc}(-2)/[\text{MPc}(-3)]^-$ and $[\text{MPc}(-3)]^-/[\text{MPc}(-4)]^{2-}$, respectively. Moreover, the difference between the first and the second reduction processes decreased from 0.50 V to 0.37 V with introducing the rigid group, which can be attributed to the enlargement of the π -conjugation. Accordingly, the electrochemical band gaps can be estimated as 1.47 eV , and 1.35 eV from the onset of the oxidation and reduction potential. The result is in line with the electronic absorption spectral studies mentioned above.

Table S1. Redox potentials of **4t-BuPc** and **2thioPc** (potentials vs. Ag/AgCl, work electrode Pt, supporting electrolyte TBAP in THF, scan rate 0.05 V/s) a quasi-reversible wave.

Compound	$E_{1/2}$ (V)	$E_{1/2}$ (V)	$E_{1/2}$ (V)	E_{gap} (V)
4t-BuPc	0.85	-1.08	-1.58	1.47
2thioPc	1.08 ^a	-0.75 ^a	-1.12 ^a	1.35

4. Experimental section

4.1 Synthesis of 1,2-dimethyl-4-t-butylbenzene (1)

A mixture of o-xylene (88.8 mL, 0.75 mol), t-butyl chloride was stirred at room temperature and anhydrous ferric chloride was added in small portions over 30 min. After stirring one another hour, the mixture was heated to reflux for 30 min, and then cooled to room temperature. The reaction mixture was washed with saturated NaHCO₃, brine and dried over anhydrous CaCl₂. The product was obtained as colorless oil collecting the fraction of 70–72 °C/5 mmHg by fractionation (85 g, 70% yield). ¹H NMR (300 MHz, CDCl₃) δ = 1.47 (s, 9H), 2.39 (s, 3H), 2.42 (s, 3H), 7.24–7.32 (m, 3H)

4.2 Synthesis of 4-t-butyl-phthalic acid (2)

A mixture of 1,2-dimethyl-4-t-butylbenzene (64.8 g, 0.4 mol), pyridine (430 mL), H₂O (830 mL) was heated to reflux under vigorous stirring with potassium permanganate (320 g, 2 mol) was added slowly. The reaction continued for more 4 h. After cooled to room temperature, the reaction mixture was filtered to remove manganese oxide and the filter cake was washed with 3 × 100 mL hot water. The filtrate was distilled to remove pyridine and water, the resulting pale yellow oil was poured into ice-cold water and neutralized by HCl to pH = 4–5, white solid formed and was separated by filtration

affording the product 84.5 g. Yield: 92%. MS m/z: 222 (M^+); ^1H NMR (300MHz, DMSO) δ = 1.30 (s, 9H), 7.31 (s, 1H) 7.58, 7.59 (d, 1H) 7.86, 7.87 (d, 1H)

4.3 Synthesis of 4-t-butyl-phthalic anhydride (3)

4-t-butyl-phthalic acid (22.2 g, 0.1 mol) was dissolved in 30 mL acetyl chloride and heated to reflux for 3 h. The redundant acetyl chloride was removed under reduced pressure, and then the compound was precipitated as white solid by addition of 40 mL petroleum ether. After filtrated, washed with petroleum ether and dried in vacuo, the pure product (16.9 g) was obtained in 83% yield. Mp 73–75 °C. MS m/z: 204 (M^+); ^1H NMR (300MHz, DMSO) δ = 1.30 (s, 9H), 7.58, 7.61 (d, 1H), 7.58, 7.68 (d, 1H), 7.68 (d, 1H)

4.4 Synthesis of 4-t-butyl-phthalimide (4)

A mixture of 4-t-butyl-phthalic anhydride (19 g, 0.093 mol) and urea (6 g, 0.1 mol) was heated gradually to 170 °C and kept reaction for additional 2 h. After the reaction mixture was cooled to the room temperature, 20 mL ethanol was added and refluxed to separate the solid, and then the mixture was poured into 300 mL water. The crude product was obtained by filtration and washed with water for several times. Recrystallization of the crude product from 95% ethanol gave pale yellow flat crystals (14.0 g). Yield: 74%. Mp 128–130 °C. EI-MS m/z: 204 ($M^+ + 1$); ^1H NMR (300MHz, CDCl_3) δ = 1.42 (s, 9H), 7.81–7.93 (m, 3H); Elemental analysis (%): calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_2$: C 70.90, H 6.45, N 6.89; found: C 70.48, H 6.54, N 7.10.

4.5 Synthesis of 6/7-t-butyl-1,3,3-trichloroisindolenine (5)

A mixture of 4-t-butyl-phthalimide (14.2 g, 0.07 mol), phosphorus pentachloride (32 g, 0.15 mol) and phosphorus oxychloride (30 mL) was stirred and heated to 110 °C. A clear solution was obtained within 30 min. After the reaction mixture was stirred continuously at the same temperature for another 60 h, phosphorus oxychloride was distilled off in vacuo. Subsequently, light yellow viscous oil was

obtained by collecting the fraction of 144–145 °C/2 mmHg which solidified to a yellow solid upon standing (6.0 g, 30%). EI-MS m/z : 275 (M^+), 240, 205. 1H NMR (300 MHz, $CDCl_3$) δ = 1.38, 1.40 (2s, 9H), 7.53–7.81 (m, 3H).

4.6 Synthesis of [di-iodo-di-(*tert*-butyl)phthalocyanato]copper(II) (IPc-2)

In a dried 100 mL round-bottom flask equipped with a magnetic stirrer and sealed with a septum were placed 135 mg (0.5 mmol) of 5-iodine-1,3-diiminoisoindolnine and 100 mg (1 mmol) of triethylamine. Dry nitrogen was swept through the flask by the two-needle method, 40 mL of freshly dried THF was added with a syringe, and the mixture was stirred to dissolve the diiminoisoindolnine. The mixture was then cooled to 0 °C in a salt and ice bath. A solution of 138 mg (0.5 mmol) of 6/7-*t*-butyl-1,3,3-trichloroisoindolenine in 10 mL of dry THF was gradually added by syringe over a 15-min period. The reaction was then stirred for 1 h at approximately 0 °C and allowed to slowly warm to room temperature with stirring over a 10-h period. During this time, the reaction turned from its initially formed yellow to a yellow-green. The reaction was then filtered to remove the triethylamine hydrochloride and returned to the reaction flask; 55 mg (0.5 mmol) of hydroquinone was added to the reaction vessel, which was equipped with a reflux condenser. It was then refluxed under nitrogen for 12 h. The reaction was cooled to room temperature and filtered, and the solvent was stripped from the filtrate leaving a dark blue-black residue. The residue was washed with boiling water and methanol until the filtrate was clear. The crude product with anhydrous copper chloride was dissolved in THF at the temperature of 60 °C with stirring for 24 h. Upon removal of the solvent, the remaining black blue solid was further purified by chromatography using CH_2Cl_2 as eluent to give the target product **IPc-2** 46 mg. Yield: 19.6%. MALDI-TOF-MS: m/z calcd. for $C_{40}H_{30}CuI_2N_8$ 939.01, found 938.8 (M^+). 1H NMR (300 MHz, $CDCl_3$) δ = 2.5 (br, 18H), 6.91–13.7(br, 12H).

4.7 Synthesis of [di-ethynyl-di-(*tert*-butyl)phthalocyanato]copper(II) (EPc-2)

Following a general procedure, **IPc-2** (94 mg, 0.1 mmol) and trimethylsilylacetylene (0.56 mL, 0.4 mmol) in the solution of toluene (10 mL) and triethylamine (10 mL) were stirred at room temperature for a day with the catalyst CuI (1.9 mg, 0.01 mmol) and Pd(PPh₃)₂Cl₂ (7 mg, 0.01 mmol). After the solvent was removed under the reduced pressure, the product (82 mg) was obtained as a blue solid after purification by silica gel column chromatography (dichloromethane as eluent) in 93% yield. Trimethylsilylacetylene-disubstituted copperphthalocyanine (82 mg, 0.09 mmol) and 1 mL 1M KOH in 10 mL THF were stirred at room temperature over night. We got the product 48 mg in 72.7% yield. MALDI-TOF-MS: $m/z = 735.2$ (calcd for C₄₄H₃₂CuN₈: 735.21). H NMR (300 MHz, CDCl₃) $\delta = 1.81$ (br, 18H), 3.50 (br, 2H), 7.36–8.44 (br, 12H).

4.8 Synthesis of 2thioPc

Method 1: The standard Schlenk technique was adopted. Sample of **EPc-2** (74 mg, 0.1 mmol), 1-thioacetyl-4-iodobenzene (70 mg, 0.25 mmol), Pd(PPh₃)₂Cl₂ (7 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) were added to a 25 mL Schlenk flask. The flask was evacuated and purged with nitrogen three times, and then deaerated THF (8 mL) and deaerated DIEA (8 mL) were added by syringe. The flask was immersed in an oil bath at 40 °C and stirred under nitrogen for 48 h. The crude product was purified by silica gel column chromatography (eluent: CH₂Cl₂/CH₃OH 50:1) to give 18 mg (17.3% yield) of **2thioPc** as a dark green solid. MALDI-TOF-MS: $m/z = 1035.3$ (calcd for C₆₀H₄₄CuN₈O₂S₂: 1035.24). HR SIMS, calcd for C₆₀H₄₄CuN₈O₂S₂: 1035.2419, observed: 1035.2388: H NMR (300 MHz, CDCl₃) $\delta = 1.16$ – 1.86 (br, 18H), 2.5 (s, 6H), 7.27–11.37 (br, 22H). FT-IR (KBr, cm⁻¹) ν 2955 (CH₃), 2190, 2149 (C≡C), 1709 (C=O), 1611, 1504, 1396 (C=C), 1090 (Pc ring). UV-Vis (THF): λ_{\max}/nm , 694, 676, 636, 615, 351.

Method 2: The procedure was the same as method 1. Yield: 46%.

4.9 Electrochemical characterization

Cyclic voltammetric measurements were carried out on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. A three-electrode cell assembly was used in electrochemical measurements with Pt working platinum, a platinum wire as the counter electrode, and a Ag/AgCl as the reference electrode, respectively. The measurement was performed in freshly distilled THF solution containing 1 mM Pc and 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte. Before measurements, a platinum button electrode was polished before each experiment with a 0.05 μm alumina paste, N_2 bubbling was used to remove oxygen from the electrolyte solutions in the electrochemical cell.