Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C

Supporting Information

Phase transition, optical and photoconductive properties of bay-substituted benzoporphyrin derivatives

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Chemical Synthesis and Analytical Methods.

Unless stated otherwise, solvents and chemicals were obtained commercially and were used without further purification. Tetrahydrofuran was freshly distilled from purple Na/benzophenone ketyl. Quinoline was dried over KOH followed by distillation under reduced pressure. MeMgBr (3M) was obtained as a solution in diethyl ether from Aldrich. All products have been purified by column chromatography and recrystallization and their structures were characterized by ^{1}HNMR and MS. The polarized light microscope of Optiphot2-pol, Nikon, the hot-stage of FP900 thermo-system was employed for taking optical graphs. The charged carrier mobility was obtained by a TOF technique under controlled temperatures. Photocurrent was measured in the system of steady-state dark and photocurrent. The light source was a Xe lamp of 500w, the wavelength of illuminating light was selected by the color or interference filter and the on-off of light was controlled by the electromagnetic shutter. For the I-V measurement, a source measurement unit, R8340 Ultra High Resistance Meter, Advantest, Tokyo, Japan, was used. The spin coating was carried out using a spin coater (MIKASA MS A100).

1. Synthesis

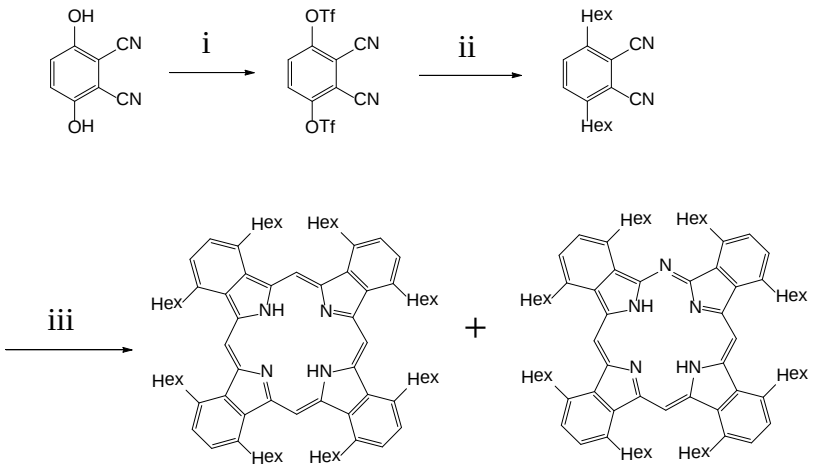

Fig. S1 Synthetic route for TBP and TBMAP i: trifluoromethanesulfonic anhydride, pyridine, dry DCM; ii: $C_6H_{13}B(OH)_2$, $Pd(dppf)Cl_2$, AgO, K_2CO_3, THF, 80℃; iii: a) BrMgMe, THF, reflux,30min; b) quinoline, 200℃, 12h; c) AcOH, reflux

i: Synthesis of 3,6- bis(trifluoromethanesulfonyloxy)phthalonitrile

2,3-dicyanohydroquinone (5.2 g, 0.033 mol) was dissolved in a mixture of dry DCM (30 mL) and triethylamine (5 mL) and the resulting yellow solution was cooled to -20 °C. A solution of trifluoromethanesulfonic anhydride (22.1 g, 0.079 mol) in dry DCM (8 mL) was added dropwise over 30 min. The resulting mixture was allowed to

warm to rt and stirred for 14 h under argon. The resulting brown solution was left in the fridge for 24 h to help the formation of crystals which were filtered off, washed with cold methanol and recrystallised from DCM/petrol to afford 3,6-bis(trifluoromethanesulfonyloxy)phthalonitrile (yield 90%). ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 7.87(s, 2H).

ii: Synthesis of 3,6- dihexylphthalonitrile

A suspension of compound 1(1.5g), Alkyl boronic acid (3 equiv.), Pd(dppf)Cl_2 (10%), powdered K_2CO_3 (3 equiv.),and Ag_2O (2.5 equiv.) in THF (75ml) was stirred under argon at 80°C in a sealed tube. After 48 h, the mixture was cooled to room temperature. The dark solid was filtered, and water was added into the solution. The solution was extracted using $CHCl_3$. After evaporation, chromatography column was carried out to purify the crude product to provide 0.85g white crystal, yield 60.9%. ^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 7.47 (s, 2H), 2.86 (t, J=7.0Hz, 4H,), 1.67(m, 4H), 1.34 (m, 12H), 0.90 (t, 6H).

iii. Synthesis of benzoporphyrin derivatives (refer to reference 1)

Cyclization for bay substituted benzoporphyrin was operated as the reference, 3 (200 mg) A solution of MeMgBr in Et_2O (0.93ml, 2.9M in Et_2O, 4 equiv), dry quinoline (3 mL), Acetic acid (3 mL), green super-pure crystals after repetitive recrystallization in EL-level solvent were obtained (TBP: yield 2.4%; TBMAP: yield3.5%).

TBP: Transition temperature: 149℃ (K – D), 178℃ (D – I);

^{1}H NMR (300 MHz, [D8]THF): d=11.56 (s, 4 H), 7.92 (s, 8H), 4.41 (t, J=7.2 Hz, 16H), 2.25 – 2.44 (m, 16H), 1.5 – 1.8 (m, 16 H), 1.2 – 1.5 (m, 32H),0.75 – 0.95 (m, 24 H), – 2.10 ppm (s, 2H);

TBMAP: Transition temperature: 149℃ (K – D), 177℃ (D – I);

^{1}H NMR (300 MHz, [D_8]THF): d=10.95 (s, 2H), 10.88 (s, 1 H), 7.96(d, J=7.6 Hz, 2 H), 7.84 (d, J=7.6 Hz, 2 H), 7.54 (m, 4H), 5.05 (t, J=7.2 Hz, 4H), 4.08 (t, J=7.2 Hz, 4H), 3.97(t, J=7.2 Hz, 4H), 3.85 (t, J=7.2 Hz, 4H), 2.35 – 2.42 (m, 4 H), 2.23 – 2.30(m, 4 H), 2.1 – 2.23 (m, 8H), 1.75 – 1.83 (m, 4H), 1.56 – 1.65 (m, 12 H), 1.26 – 1.45 (m, 32H), 0.80 – 0.91 (m, 24H), – 1.36 ppm (s, 2H);

2. Electronic spectrum in amorphous state

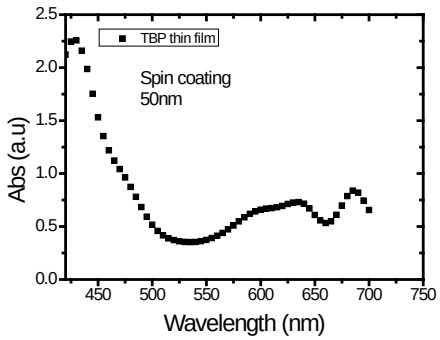

Fig. S2 Electronic spectra of visible region of the film of the representative derivative TBP

2. Procedures of fabricating devices

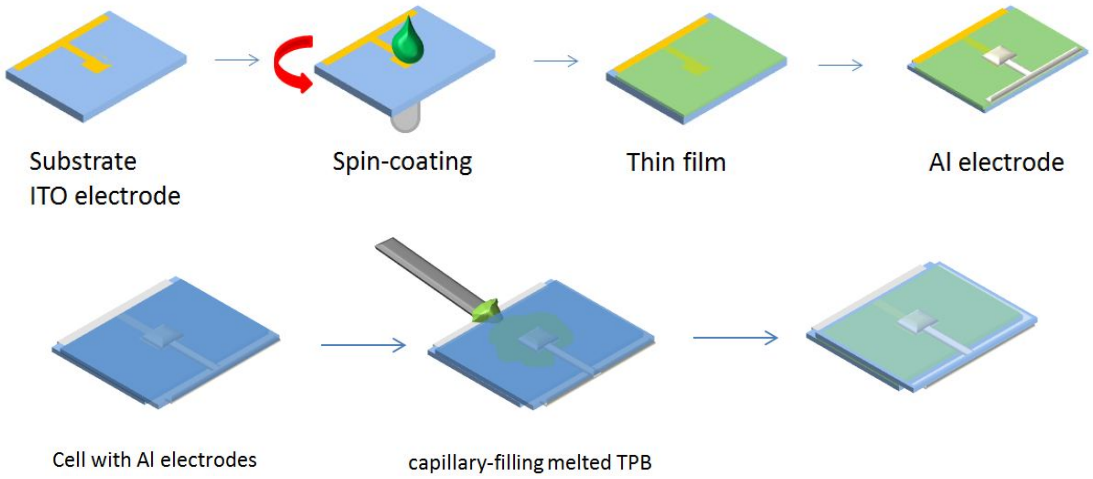

Fig S3 Schematic diagram of fabricating devices (above: thin film; below: thick film)

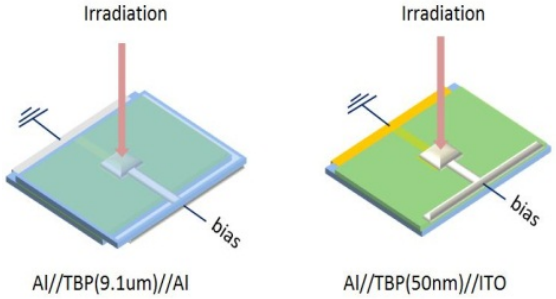

Fig S4 Schematic diagram of devices used on photocurrent experiments

3. Steady state photocurrent measurement

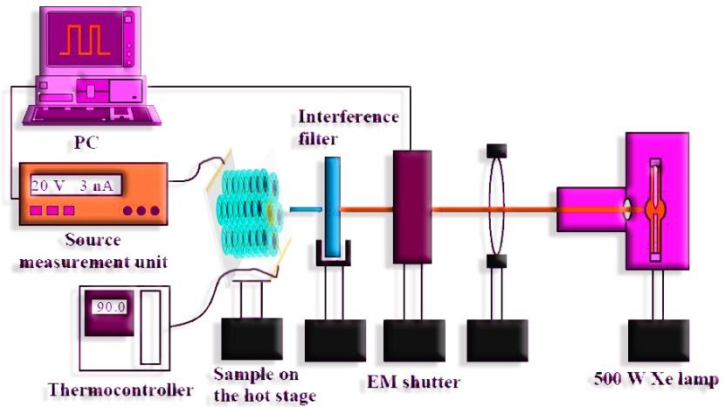

Fig S5 Setup for steady state photocurrent measurement, which consists of 500 W Xe lamp as an excitation light source, source measurement unit, electromagnetic shutter controlled by personal computer, and hot stage with PID thermocontroller.

4. Time of flight measurement

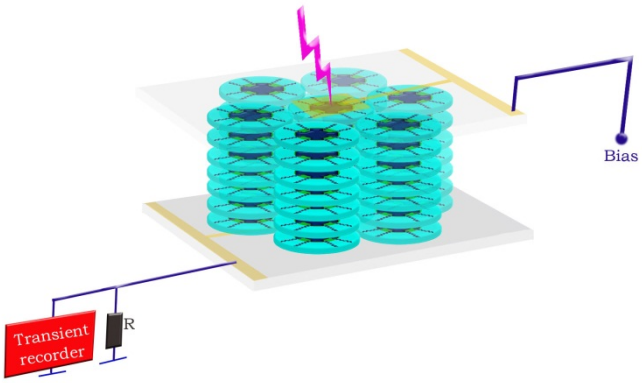

Fig S6 TOF setup for this study, which consists of N_2-dye pulse laser (wavelength = 337 nm, pulse width = 600 ps, and intensity = 90 μJ/pulse), DC voltage source, preamplifier with 100 Ω resistor, digital oscilloscope, and hot stage with PID thermocontroller

Reference

1 A. N. Cammidge, I. Chambrier, M. J. Cook, D. L. Hughes, M. Rahman, and L. Sosa-Vargas, Chem. Eur. J. 2011. 17. 3136