

Electronic Supplementary Information

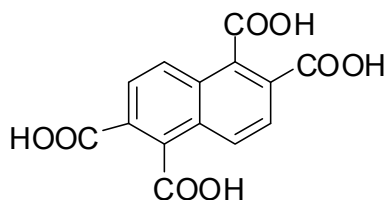
Angular-Shaped Naphthalene Tetracarboxylic Diimides for n-Channel Organic Transistor Semiconductors

5 Shanci Chen, Qikai Zhang, Qingdong Zheng*, Changquan Tang and Can-Zhong Lu*

Experimental

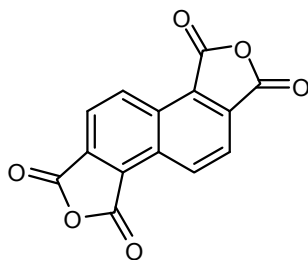
The reagents were purchased from Aldrich Inc. and J&K Chemical Ltd. and used without further
10 purification. 1,5-Dibromo-2,6-dimethylnaphthalene (**1**) was obtained by a bromination reaction from
2,6-dimethylnaphthalene according literature procedures.¹ 1,5-Dicyano-2,6-dimethylnaphthalene (**2**)
was obtained from a reaction between copper cyanide and 1,5-dibromo-2,6-dimethylnaphthalene
according to the method developed by Friedman and Shechter.² Then
1,5-dicyano-2,6-dimethylnaphthalene was oxidized to 1,2,5,6-naphthalenetetracarboxylic acid (**3**) by
15 Dozen's method.³ Melting points were determined on a differential thermal analyzer (Netzsch
DTA404PC). Column chromatography was conducted with silica gel 60 (400 mesh). ¹H NMR spectra
were recorded at 400 MHz. For the field-effect transistors, the devices were measured using an Agilent
4155C semiconductor parameter analyzer with the ICS lite software.

20



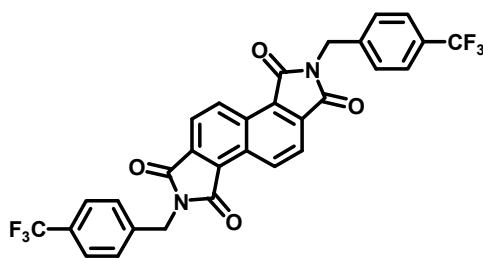
1,2,5,6-naphthalenetetracarboxylic acid (**3**)³

In a 70 mL Teflon liner, 1.05 g of 1,5-dicyano-2,6-dimethylnaphthalene was added to 20 mL of
25 aqueous solution containing K₂Cr₂O₇ (4.4 g) and NaOH (0.4 g). The mixture was stirred for 30 min
and was sealed in a stainless steel autoclave and was then heated for 200 °C for 10 h. After it was
cooled and filtrated, the basic solution was treated with ether. The crude
1,2,5,6-naphthalenetetracarboxylic acid was reprecipitated from the washed water layer by adding the
hydrochloric acid. Yellow precipitate (0.69 g, Yield 45%) was collected by filtration, then applied to
30 the next reaction without further purification.

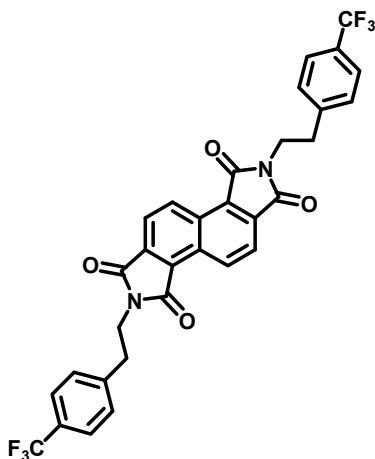


1,2,5,6-naphthalenetetracarboxylic dianhydride (4)

1.0 g of crude compound **3** was stirred in 50 mL of acetic anhydride for 3 h under reflux. After the solvent was distilled off, 1,2,5,6-naphthalenetetracarboxylic dianhydride was obtained by filtration and **5** washed with methanol (0.79 g, Yield: 90 %) .

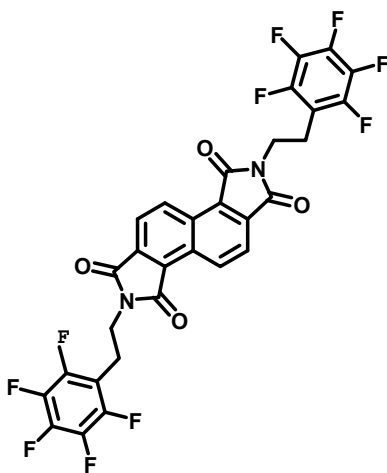


Compound 5a: 1,2,5,6-Naphthalenetetracarboxylic dianhydride (**4**) (0.58g, 2.2 mmol), an excess amount of 4-(trifluoromethyl)benzylamine (6.6mmol), and zinc acetate (0.35, 1.54 mmol) were stirred in 10 mL of quinoline and the temperature was raised above 200 °C for 3 h. The mixture was allowed 10 to cool down, and solids were collected and washed with hot dilute aqueous Na₂CO₃, water, toluene and methanol in that order. 1.06 g of crude solid was obtained (Yield 83%). The crude product was purified by vacuum sublimation. Mp: 317-318 °C. MALDI-TOF/MS, m/z calcd. for C₃₀H₁₆F₆N₂O₄: 582.1, found: 582.1; ¹H NMR (400 MHz, CDCl₃, ppm): δ = 4.97 (s, 4H), 7.60 (s, 8H), 8.12 (d, *J* = 8.4 Hz, 2H), 9.35 (d, *J* = 8.4 Hz, 2H). Elemental analysis: calcd. for C, 61.86; H, 2.77; N, 4.81; found: C, 15 62.03; H, 2.77, N, 4.87.



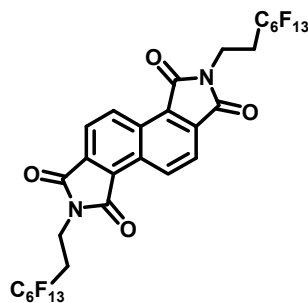
Compound 5b

Compound **5b** was prepared according to the same procedure as that for compound **5a**. Yield, 54 %, Mp: 309-310 °C, ¹H NMR (400 MHz, CDCl₃, ppm): δ = 9.32 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 5 2H), 7.55 (d, *J* = 8.0 Hz, 4H), 7.40 (d, *J* = 8.0 Hz, 4H), 4.03 (t, *J* = 7.6 Hz, 4H), 3.12 (t, *J* = 7.6 Hz, 4H); MALDI-TOF/MS, *m/z* calcd. for C₃₂H₂₀F₆N₂O₄: 610.5, found: 610.2;. Elemental analysis: calcd. for C, 62.96; H, 3.30; N, 4.59; found: C, 63.00; H, 3.59, N, 4.59.



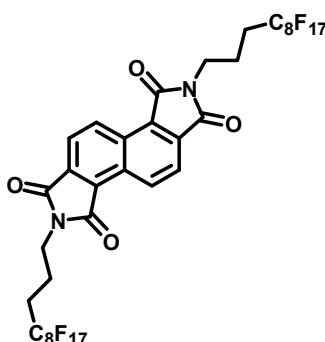
Compound 5c

10 Compound **5c** was prepared according to the same procedure as that for compound **5a**. Yield 51%, Mp: 307-308 °C; ¹H NMR (400 MHz, CDCl₃, ppm): δ = 9.31 (br.s, 2H), 8.11 (br.s, 2H), 4.04 (br.s, 4H), 3.17 (br.s, 4H). MALDI-TOF/MS, *m/z* calcd. for C₃₀H₁₂F₁₀N₂O₄: 654.06, found: 654.0; Elemental analysis: calcd. for C, 55.06; H, 1.85; N, 4.28; found: C, 55.34; H, 2.07, N, 4.46.



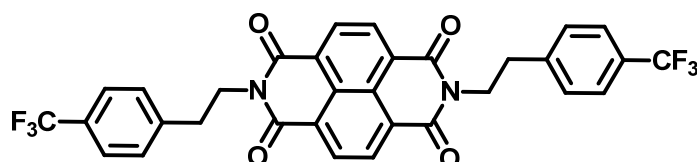
Compound 5d

Compound **5d** was prepared according to the same procedure as that for compound **5a**. Yield 62%; Mp: 227-228 °C; MALDI-TOF/MS, *m/z* calcd. for C₃₀H₁₂F₂₆N₂O₄: 958.04, found: 958.5; Elemental analysis: calcd. for C, 37.60; H, 1.26, N, 2.92; found: C, 37.64; H, 1.25, N, 2.90.



Compound 5e

Compound **5e** was prepared according to the same procedure as that for compound **5a**. Yield 68%; Mp: 238-239 °C; MALDI-TOF/MS, *m/z* calcd. for C₃₀H₁₂F₂₆N₂O₄: 1186.06, found: 1186.1. Elemental analysis: calcd. for C, 36.44; H, 1.36, N, 2.36; found: C, 36.74; H, 1.44, N, 2.36.



Compound 5f

Compound **5f** was prepared from 1,4,5,8-Naphthalenetetracarboxylic dianhydride according to the same procedure as that for compound **5b**. Yield 69%; ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.78 (s, 4H), 7.58 (d, *J* = 8.4 Hz, 4H), 7.37 (d, *J* = 8.4 Hz, 4H), 4.45 (t, *J* = 8.4 Hz, 4H), 3.12 (t, *J* = 8.0 Hz, 4H).

20 Differential Scanning Calorimetry (DSC)

DSC measurements were carried out by using Netzsch DTA404PC with from 5 to 10 mg of samples at a heating and cooling rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere.

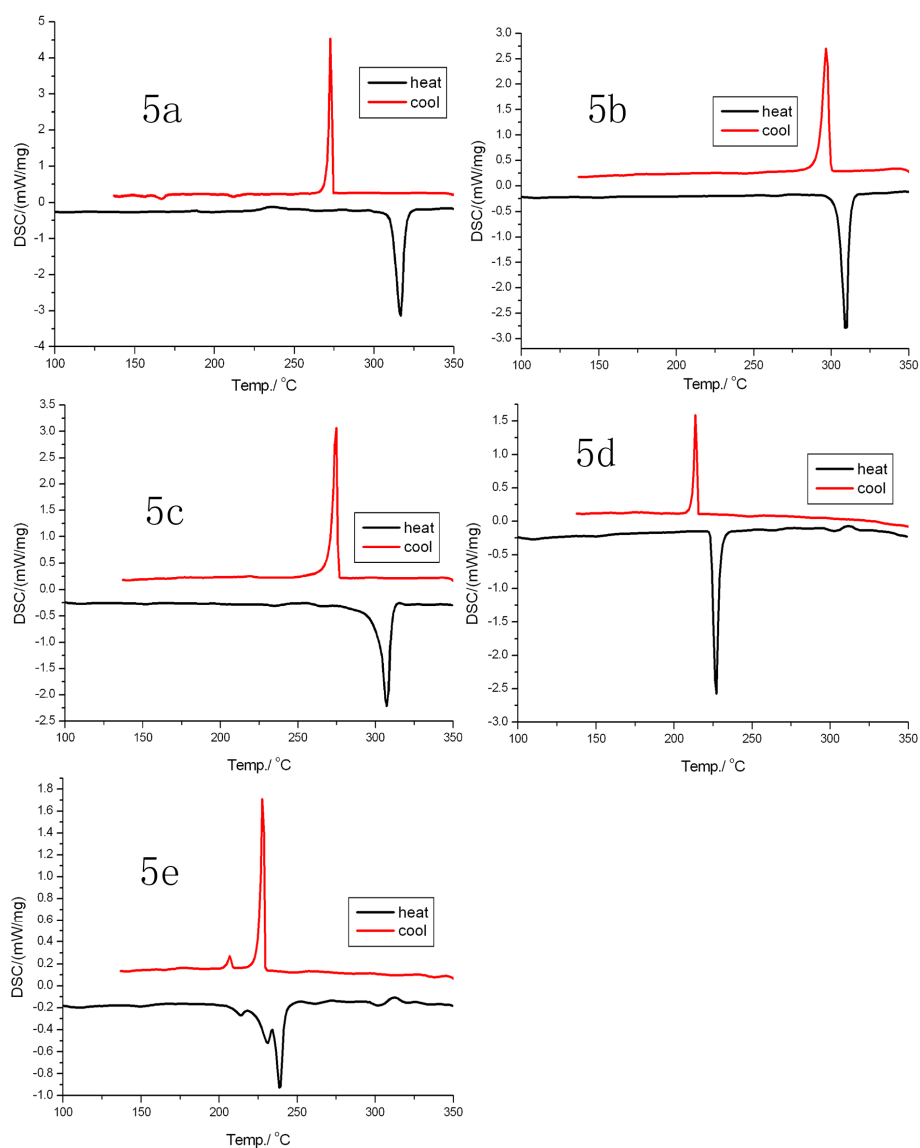


Figure S1. DSC thermograms of 5a-5e.

X-ray Diffraction.

X-ray diffraction scans were acquired in the Bragg-Brentano (θ - 2θ) geometry using a MiniFlex II X-ray diffraction system. Scan parameters were: step size 0.02° and a time per step of 0.1 s. The beam wavelength was 1.5406 \AA operated at 30 KV and 15 mA.

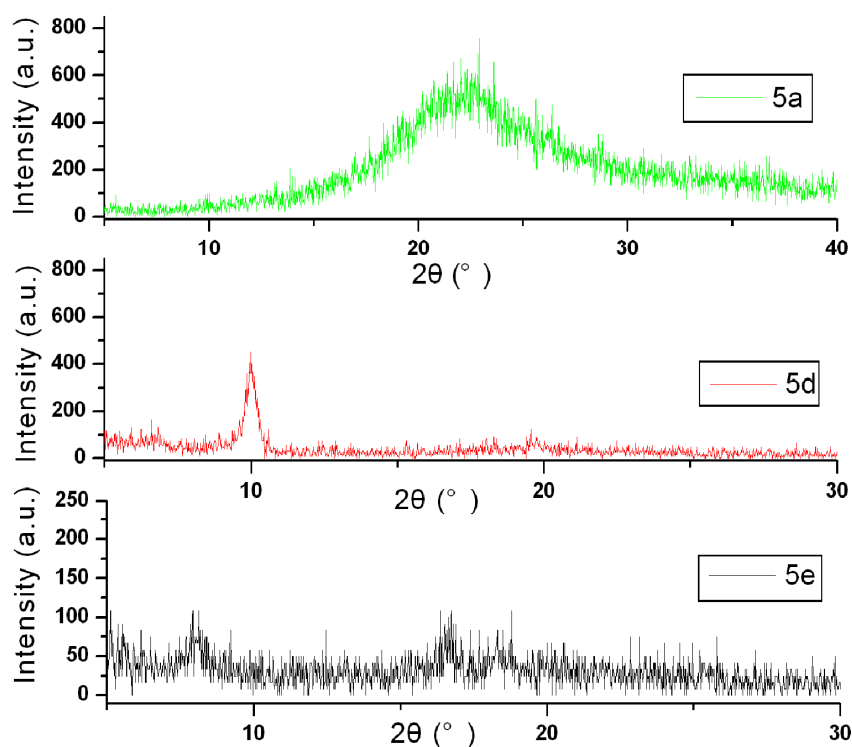


Figure S2. X-ray diffraction patterns of 5a, 5d, 5e.

Device Fabrication and Characterization

10 Top-contact/bottom-gate OTFT devices were fabricated using vapor deposited thin films of the semiconducting material on the Si substrate with 300 nm-thick SiO_2 dielectrics. Then gold top contact source and drain electrodes were evaporated onto the films. The substrates were subjected to cleaning using ultrasonication in piranha ($\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2=3/1$), deionized water, acetone, and *iso*-propanol, and dried in oven. To optimize device properties, the substrates were modified with 15 octadecyltrimethoxysilane (OTS) to form a self-assembled monolayer (SAM). Compounds for self-assembled monolayer surface treatment, OTS was used as received. Depositions took place under vacuum at pressures of 4×10^{-4} to 2×10^{-3} Pa. The thickness of semiconductors films and gold electrodes are fixed at 45 nm and 60 nm, respectively. The OTFT devices had a channel length (L) of 300 μm and a channel width (W) of 6 mm.

The evaluations of the OTFTs were carried out under a nitrogen atmosphere using an Agilent 4155C semiconductor parameter analyzer with the ICS lite software. The carrier mobility, μ , was calculated from the data in the saturated regime according to the equation $(I_d)_{\text{sat}} = (W/2L)\mu C_i (V_g - V_{\text{th}})^2$, where $(I_d)_{\text{sat}}$ is the drain current in the saturated regime, W and L are the semiconductor channel width and length respectively, C_i ($C_i = 10$ nF) is the capacitance of the gate dielectric layer, and V_g and V_{th} are the gate voltage and the threshold voltage, respectively.

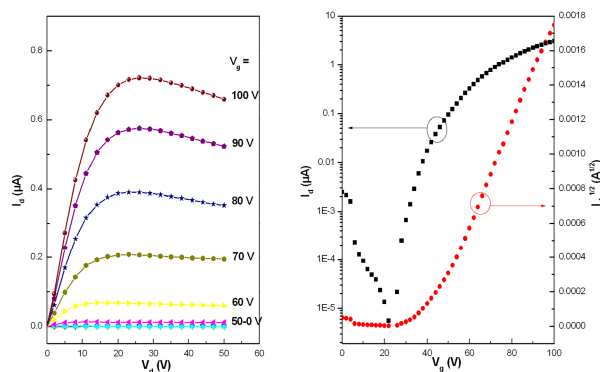


Figure S3. Current-voltage characteristics of **5c**. a) A plot of I_d versus V_d for **5c** (left); b) A plot of $I_{d\text{-sat}}$ versus V_g for **5c** (right).

10

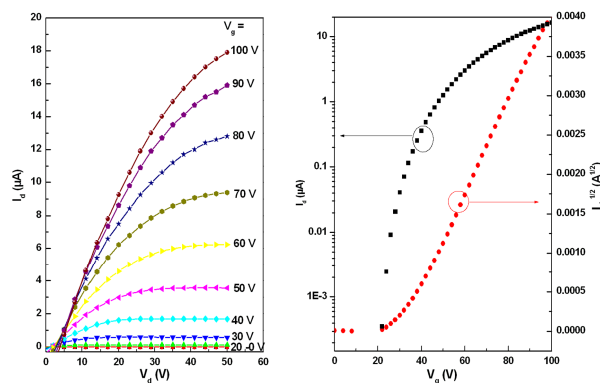


Figure S4. Current-voltage characteristics of **5f**. a) A plot of I_d versus V_d for **5f** (left). b) A plot of $I_{d\text{-sat}}$ versus V_g for **5f** (right).

15

References

1. R. T. Arnold and R. W. Liggett, *J. Am. Chem. Soc.* 1942, **64**, 2875.
- 20 2. L. Friedman and H. Shechter, *J. Org. Chem.* 1961, **26**, 2522.
3. Y. Dozen and S. Fujishima, *Yukigoseigaku* 1972, **30** 964.(Japanese)