Electronic Supplementary Information for

A Phthalimide-fused Naphthalene Diimide with High Electron

Affinity for High Performance *n*-Channel Field Effect Transistor

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Table of Contents

1.	Materials and characterization	2
2.	UV-vis absorption and emission spectra of NDIIC24	3
3.	Thermal gravity analysis (TGA) curve of NDIIC24	4
4.	Stability of the OFET devices	4
5.	Tapping-mode AFM images of NDIIC24	5
6.	HR MALDI-TOF mass spectra and NMR spectra of NDIIC24	5

1. Materials and characterization

Instrumentation and materials

All NMR spectra were recorded on Bruker AMX500 at 500 MHz spectrometers. ¹H NMR spectrum was recorded in CDCl₃. All chemical shifts are quoted in ppm, using the residual solvent peak as a reference standard. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) analysis was performed on a Bruker Autoflex III MALDI-TOF instrument by using 1,8,9-trihydroxyanthracene as matrix and Pepmix as internal standard or external standard.

UV-vis absorption and fluorescence spectra were recorded on Shimadzu UV-1700 and RF-5301 spectrometers in HPLC pure solvents. Cyclic voltammetry was performed on a CHI 620C electrochemical analyzer with a three-electrode cell in a solution of 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) dissolved in dry DCM at a scan rate of 100 mV s⁻¹. A gold electrode with a diameter of 2 mm, a Pt wire and a Ag/AgCl electrode were used as the working electrode, the counter electrode and the reference electrode, respectively. The potential was calibrated against the ferrocene/ferrocenium couple.

Thermogravimetric analysis (TGA) was carried out on a TA instrument 2960 at a heating rate of 10 °C/min under N₂ flow, differential scanning calorimetry (DSC) was performed on a TA instrument 2920 at a heating/cooling rate of 10 °C/min under N₂ flow. The initial phase transitions and corresponding temperatures for these compounds were determined by the OLYMPUS BX51 polarizing optical microscope (POM) equipped with the Linkam TP94 programmable hot stage. Room temperature XRD measurements were performed on a Bruker-AXS D8 DISCOVER with GADDS Powder X-ray diffractometer, with Cu K α radiation.

2,12-bis(2-decyltetradecyl)benzo[lmn]isoindolo[5',6':4,5]imidazo[2,1-b]isoindolo [5',6':4,5]imidazo[2,1-i][3,8]phenanthroline-1,3,8,11,13,18(2H,12H)-hexaone isomers (**NDIIC24**)

A mixture of 1,4,5,8-naphthalenetetracarboxylic dianhydride (40 mg, 0.15 mmol, 1.0 equiv), and the diamine 5,6-diamino-2-(2-decyltetradecyl)isoindoline-1,3-dione (154 mg, 0.30 mmol, 2.0 equiv) were refluxed in HOAc (15 mL) under nitrogen atmosphere overnight. Upon cooling, the suspension was dissolved with CHCl₃ and water, and extracted with CHCl₃. The combined organic phases were washed with saturated NaCl (aq), and were finally dried over Na₂SO₄, concentrated under reduced pressure to give a residue which precipitated in MeOH. Reprecipitation in MeOH for another two times gave the title compound as an orange solid (170 mg, 93%). ¹H NMR (500 MHz, CDCl₃): δ ppm = 9.16 – 9.02 (m, 5H), 8.94 – 8.91 (m, 1H), 8.37 – 8.33 (m, 2H), 8.66 (d, *J* = 7.0 Hz, 4H), 1.95 (br, 2H), 1.57 – 1.24 (m, 80H), 0.86 – 0.85 (m, 12H). HR-MALDI-TOF-MS (m/z): calcd. for C₇₈H₁₀₆N₆O₆: 1223.7128; found 1224.8325 (error = 2.08 ppm). Elemental Analysis: calcd. for C₇₈H₁₀₆N₆O₆: C, 76.56; H, 8.73; N, 6.87; O, 7.84; found: C, 76.45; H, 8.63; N, 6.57.

Fabrication and characterization of OFET devices

Top-contact, bottom-gate TFTs were prepared. A heavily p+-doped silicon wafer (100, Silicon Quest International, resistivity $< 0.005 \ \Omega \text{cm}^{-1}$) with a 200-nm thermal silicon dioxide (SiO₂) was used as the substrate/gate electrode, with the SiO₂ layer serving as the gate dielectric. The SiO₂/Si substrate was cleaned with acetone, IPA. It was then immersed in a piranha solution $(V(H_2SO_4) : V(H_2O_2) = 2:1)$ for 20 minutes, followed by rinsing with deionized water, and then treated with octadecyltrimethoxysilane (OTMS) spin coated from 10 mM trichloroethylene solution, and treated with ammonia for 7h, or octadecyltrichlorosilane (ODTS) immersed in 3 mM hexadecane solution for 16h in N₂. The semiconductor layer was deposited on top of the modified substrates by spin coating the 0.6-1 wt% solution in chloroform, firstly annealed at 60 °C for 10 min to remove the solvent, then the devices annealed at selective temperatures for 0.5 h. Subsequently, gold source/drain electrode pairs were deposited by thermal evaporation through a metal shadow mask to create a series of TFTs with various channel length ($L = 100/150 \mu m$) and width (W = 1/4 mm) dimensions. The TFT devices were characterized using a Keithley SCS-4200 probe station under N_2 or ambient conditions in the dark.

2. UV-vis absorption and emission spectra of NDIIC24



Fig. S1 UV-vis absorption and emission spectra of NDIIC24.

3. Thermal gravity analysis (TGA) curve of NDIIC24



Fig. S2 TGA curve of NDIIC24 with a heating rate of 10 °C/min in nitrogen.

4. Stability of the OFET devices



Fig. S3 The transfer characteristics of the OFET device tested after storing in N_2 for 6 months.

5. Tapping-mode AFM images of NDIIC24



Fig. S4 Tapping mode AFM images (a) height and (b) phase images of the thin films of **NDIIC24** on OTMS modified SiO₂/Si substrate.

6. HR MALDI-TOF mass spectra and NMR spectra of NDIIC24



Formula	Mass	Error (ppm)	DblEq	N rule	Electron Configuration
C 78 H 108 N 6 O 6	1,224.8325	2.0753	28.00	ok	odd
C 78 H 109 N 6 O 6	1,225.8403	0.0337	27.50	ok	even
C 77 H 108 N 6 O 6 ^13C	1,225.8358	3.6804	28.00	-	odd



¹H NMR spectrum of **NDIIC24** (500 MHZ, CDCl₃)