Supporting Information

Synthesis of pentacene-, tetracene- and anthracene bisimides using double-cyclization reaction mediated by bismuth(III) triflate

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Contents

- 1. Materials and General Methods
- 2. Optimization of the cyclization-reaction
- 3. X-Ray crystallographic structures
- 4. Fluorescence lifetimes
- 5. Electrochemical properties
- 6. OTFT-Devices Fabrication and Measurements
- 7. Syntheses and Characterization of Compounds

1. Materials and General Methods

X-ray Analysis Single crystals of N-*i*Pr-TBI and N-nHx-TBI suitable for X-ray diffraction analysis were obtained by slow evaporation of CHCl₃, from their mother liquids. The crystals were mounted in *LithoLoops* (purchased from Protein Wave Co.). The diffraction data were collected at -173 °C on a Rigaku VariMaxRAPID/ α imaging plate diffractometer equipped graphite-monochromated CuK α radiation or on a Rigaku Mercury-8 diffractometer equipped graphite-monochromated CuK α radiation or on a Rigaku Mercury-8 diffractometer equipped graphite-monochromated NoK α radiation with a CCD detector. The diffraction data were processed with *CrystalStructure* on a Rigaku program, solved with SIR-97^[S1] and refined with SHELX-97.^[S2]

Fluorescence Lifetimes Measurement Fluorescence lifetime of **N-iPr-ABI** and **N-iPr-TBI** in chloroform was measured using time-correlated single-photon counting (TCSPC) technique. As an excitation light, picosecond-pulsed diode laser (465 nm, 80 ps FWHM, 10 MHz, LDH-P-C-470B, picoquant) was used, and the fluorescence was detected by an avalanche single-photon counting modules (APD: SPCM-AQR-14, PerkinElmer). The fluorescence from 490 nm to 750 nm was detected. The signal from the diode laser and the APD were connected to TCSPC module (SPC-630, Becker & Hickl) as a start and a stop signal of the TCSPC module, respectively. The instrumental response function was about 500 ps in this system. All lifetime measurements were analyzed using a deconvolution technique to account for the influence of the instrument response function. Fluorescence decay curves obtained from N-*i*Pr-ABI and N-*i*Pr-TBI in chloroform are shown in Fig S3. Dot lines are the instrument response function. Both decay curves were fitted by a single exponential.

OTFT-Device Fabrication and Measurement An *n*-type heavily doped Si wafer with a SiO₂ layer was used as the gate electrode and dielectric layer. The thin-films (60 nm) of **N-nHx-TBI** were prepared by vapor deposition $(2.0 \times 10^{-5}$ Pa, 0.30 Å/s) onto HMDS treated substrates. Gold source and drain contacts (30 nm in thickness) were deposited by vapor deposition on the active layer. The channel length (*L*) and width (*W*) were 50 µm and 5.5 mm, respectively. Measurements of OTFT devices were carried out using a semiconductor parameter analyzer (Agilent, 4155C) in a nitrogen glove box where the concentrations of H₂O and O₂ are less than 1 ppm. The mobilities were determined in the saturation regime by using the equation of $I_{DS} = (\mu W C_i/2L)(V_G - V_T)^2$, where I_{DS} is the drain-source current, μ is the field-effect mobility, *W* is the channel width, *L* is the channel length, C_i is the capacitance per unit area of the gate dielectric layer, and V_T is the threshold voltage. XRD and AFM image is recorded on Bruker D8 and Veeco Dimension Icon AFM respectively.

Synthesis ¹H NMR and ¹³C NMR spectra were recorded on a JEOL JNM-AL 400 spectrometer using tetramethylsilane as an internal standard. FAB and DI-EI mass spectra were measured on JEOL JMS-MS 700V spectrometer. MALDI-TOF mass spectra were measured on Voyager DE Pro (Applied Biosystems). UV-vis spectra were measured on JASCO UV/VIS/NIR Spectrophotometer V-570. Fluorescence spectra and fluorescence quantum yields were measured on Absolute PL Quantum Yield Measurement System C9920-02. Melting points were measured on J-Science Group RFS-10. Elemental analyses were performed on Yanaco MT-5 elemental analyzer. All solvents and chemicals were

reagent grade quality, obtained commercially and used without further purification except as noted. For spectral measurements, distilled CHCl₃ was used. Thin-layer chromatography (TLC) and column chromatography were performed on Art. 5554 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively. The CH₂Cl₂ used for cyclic voltammetry measurements was distilled over CaH₂.

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2. Optimization of the cyclization-reaction

COCI Pr-NCO Acid o-DCB O N N N O N N N N N N N N N N N N N				
Entry	Acid	Time/h	Temp/ °C	Product (Isolated yield)
1	TfOH (2.0 mmol)	2	120	N-iPr-TBI (trace)
2	AlCl ₃ (0.35 mmol)	0.5	90	None
3	AlCl ₃ (0.7 mmol)	0.25	150	None
4	FeCl ₃ (0.41 mmol)	2	120	None
5	Bi(OTf) ₃ (0.35 mmol)	2	120	N-<i>i</i>Pr-TBI (47)
6	Al(OTf) ₃ (0.35 mmol)	1.5	120	None

Table S1 Screening of Protic- or Lewis-acid for the synthesis of **N-***i***Pr-TBI**. Reaction conditions: Acid chloride (0.1 mmol), isopropyl isocyanate (5.1 mmol), o-DCB (3.0 ml).

3. X-Ray crystallographic structures



Fig. S1 X-Ray crystallographic structures of N-nHx-TBI. Views along (a) a- (b) b- (c) c-axis.



Fig. S2 X-Ray crystallographic structures of N-*i*Pr-TBI. Views along (a) *a*- (b) *b*- (c) *c*-axis.

4. Fluorescence lifetimes



Fig. S3 Fluorescence decays of (left) N-*i*Pr-ABI at 491 nm and (right) N-*i*Pr-TBI at 653 nm; excited at 465nm in CHCl₃.

5. Electrochemical properties



Fig. S4 Cyclic voltammogram of acene bisimides in dichloromethane (1 mM). 0.1 M Bu_4NPF_6 as supporting electrolyte; Ag/AgNO₃ as a reference electrode; glassy carbon as a working electrode; Pt wire as a counter electrode; scan rate of 0.1 V/s.

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6. OTFT-Devices Fabrication and Measurements



Fig. S5 OFET-response of N-nHx-TBI.



Fig. S6 XRD pattern of N-nHx-TBI on HMDS treated substrate.



Fig. S7 AFM image of **N-nHx-TBI** on HMDS treated substrate.

7. Syntheses and Characterization of Compounds

Pentacene-6, 13-dicarboxylic acid (2a) Under an argon atmosphere, NaClO₂ (44 mg, 0.486 mmol) and NaH₂PO₄ (87.5 mg, 0.759 mmol) in H₂O (5 ml) was added to the stirred suspension of starting material (80 mg, 0.240 mmol), 1,4-dimethoxybenzene (0.48 g, 3.45 mmol) and 2-methyl-2-butene (0.37 ml, 13.94 mmol) in THF (15 ml) over 5 h at 0 $^{\circ}$ C. The reaction was gradually warmed to room temperature. After being stirred for 11 h, THF was evaporated under reduced pressure to give the residue. The residue was diluted with H₂O and filtrated. 1M-HCl was added to the filtrates to precipitate the crude product. The crude product was washed with CHCl₃ to afford the product as blue solid, which was used for next reaction without further purification (30.4 mg, 34%)

¹H NMR (400 MHz, CDCl₃) δ 8.79 (s, 4H), 8.13 (m, 4H), 7.48 (m, 4H); MS (TOF-MS) *m/z* 367 (M⁺+1).



¹H NMR spectrum of **pentacene-6**, 13-dicarboxylic acid (2a) in DMSO-*d*₆

Tetracene-5, 12-dicarboxylic acid (2b) Under an argon atmosphere, NaClO₂ (1.190 g, 13.16 mmol) and NaH₂PO₄ (1.579 g, 13.16 mmol) in H₂O (40 ml) was slowly added to a stirred solution of 5,12-diformyltetracene (1.176 g, 4.136 mmol) and 2-methyl-2-butene (10.0 ml) in THF (250 ml) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 16h. Then THF was removed under reduced pressure. 1M-HCl was added to the remaining residue to precipitate the crude product. Crude product was filtrated off and washed with H₂O then CHCl₃ to afford the product as orange powder, which was then used for next reaction without further purification (1.00 g, 76%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.78 (s, 2H), 8.19 (m, 2H), 8.05 (m, 2H), 7.62 (m, 2H), 7.54 (m, 2H); IR (KBr) v_{max} /cm⁻¹: 2965, 2597, 1686, 1252, 865, 742; m. p. 223.2 °C (decomp.); MS (FAB) *m*/*z* 317 (M⁺+1); HRMS: calculated for C₂₀H₁₂O₄ 316.0736, found 316.0732.



¹H NMR spectrum of tetracene-5, 12-dicarboxylic acid (2b) in DMSO- d_6

General procedure for the synthesis of acid chlorides ($3a \sim 3c$): Reactions were performed in Schlenk-flask. Under an argon atmosphere, *dry*-DMF ($2 \sim 3$ drops) was added to the stirred suspension of starting material (0.0945 mmol) and SOCl₂ (0.3 ml, excess) in *dry*-CH₂Cl₂ (2.0 ml) at 0 °C. After being stirred at same temperature for 10~20 min, all volatiles were removed under reduced pressure to give the product which was used for next reaction without further purification (quant).

General procedure for the synthesis of acene bisimides: Reactions were performed in Schlenk-flask. Under argon atmosphere, starting material (0.0945 mmol) and N-alkyl-isocyanate (0.5 ml, excess) in dry-1, 2-dichlorobenzene (2.0 ml) was heated to 80 °C. To this flask, Bi(OTf)₃ (0.125 g, 0.1905 mmol) was added at one portion, then the reaction was heated to 120 °C. After being stirred at same temperature for 2h, all volatiles were removed under reduced pressure to give the residue. The residue was dissolved in CHCl₃ and filtrated with Celite. The filtrates were concentrated under reduced pressure to give the crude product. The crude product was purified by column chromatography on silica gel (CHCl₃) to afford the product. Further purification (if necessary) was conducted by gel permeation chromatography.

N-iPr-PBI

¹H NMR (400 MHz, CDCl₃) δ 10.91 (s, 2H), 9.82 (m, 2H), 8.24 (m, 2H), 7.83 (m, 2H), 7.62 (m, 2H), 5.66 (m, 2H), 1.80 (d, *J* = 6.9 Hz, 12H); IR (KBr) v_{max} /cm⁻¹: 3098, 2971, 2929, 1679, 1640, 1290; m. p. 330.6 °C (sublimation); MS (MALDI-TOF) *m/z* 500 (M⁺); HRMS: calculated for C₃₂H₂₄N₂O₄ 500.1736, found 500.1735.



¹H NMR spectrum of **N-***i***Pr-PBI** in CDCl₃

N-*i*Pr-TBI

¹H NMR (400 MHz, CDCl₃) δ 9.72 (m, 4H), 7.78 (m, 4H), 5.56 (m, 2H), 1.76 (d, J = 6.9 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 164.29, 133.91, 130.31, 127.08, 123.37, 121.97, 46.83, 20.22; IR (KBr) v_{max}/cm^{-1} : 3120, 2972, 2933, 1641, 1428, 1288, 1234, 1118, 801, 748; m. p. 356.3 °C (sublimation); MS (FAB) m/z 451 (M⁺+1); Anal. Calculated for C₂₈H₁₂N₂O₄: C, 74.65; H, 4.92; N, 6.22. Found: C, 73.16; H, 4.52; N, 6.13.



¹H NMR spectrum of **N-***i***Pr-TBI** in CDCl₃



¹³C NMR spectrum of N-*i*Pr-TBI in CDCl₃

N-*n*Hx-TBI

¹H NMR (400 MHz, CDCl₃) δ 9.79 (m, 4H), 7.78 (m, 4H), 4.35 (t, J = 7.7 Hz, 4H), 1.92-1.84(m, 4H), 1.46-1.32 (m, 12H), 0.92 (t, J = 7.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.59, 133.90, 130.54, 127.02, 123.56, 121.24, 41.80, 31.64, 28.30, 27.05, 22.71, 14.15; IR (KBr) v_{max} /cm⁻¹: 2959, 2929, 2853, 1683, 1641, 1440, 1304, 1135, 802; m. p. 251.7-252.1 °C; MS (FAB) m/z 535 (M⁺+1); Anal. Calculated for C₃₄H₃₄N₂O₄: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.19; H, 6.13; N, 5.20.



¹H NMR spectrum of **N-***n***Hx-TBI** in CDCl₃



¹³C NMR spectrum of **N-***n***Hx-TBI** in CDCl₃

N-iPr-ABI

¹H NMR (400 MHz, CDCl₃) δ 10.21 (dd, J = 9.1, 1.2 Hz, 2H), 8.81 (dd, J = 7.0, 1.2 Hz, 2H), 7.99 (dd, J = 9.1, 7.0 Hz, 2H), 5.49 (m, 2H), 1.68 (d, J = 7.0 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 164.69, 163.27, 133.49, 133.24, 130.25, 129.55, 128.63, 123.16, 122.61, 46.28, 19.91; IR (KBr) v_{max} /cm⁻¹: 2942, 1696, 1650, 1233, 793, 734; m. p. 259 °C (sublimination); MS (FAB) m/z 401 (M⁺+1); Anal. Calculated for C₂₄H₂₀N₂O₄: C, 71.99; H, 5.03; N, 7.00. Found: C, 70.51; H, 5.04; N, 7.50.



¹H NMR spectrum of N-*i*Pr-ABI in CDCl₃



¹³C NMR spectrum of N-*i*Pr-ABI in CDCl₃

N-nHx-ABI

¹H NMR (400 MHz, CDCl₃) δ 10.23 (m, 2H), 8.76 (m, 2H), 7.94 (m, 2H), 4.24 (t, J = 7.7, 4H), 1.84-1.76 (m, 4H) 1.51-1.30 (m, 12H), 0.92 (t, J = 7.1, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 164.00, 162.80, 133.66, 133.40, 130.35, 129.62, 128.48, 122.49, 121.81, 41.21, 31.60, 28.07, 26.95, 22.66, 14.14; IR (KBr) v_{max}/cm^{-1} : 2945, 2922, 2858, 1692, 1647, 1613, 1541, 1195; m. p. 208.5-208.9 °C; MS (FAB) m/z 485 (M⁺+1); HRMS: calculated for C₃₀H₃₂N₂O₄+Na⁺ 507.2260, found 507.2256.



¹³C NMR spectrum of **N-***n***Hx-ABI** in CDCl₃

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