

## Supporting Information

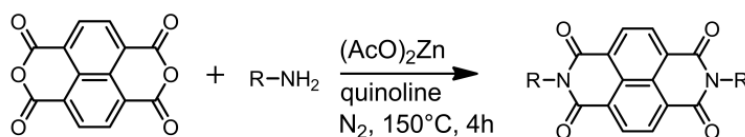
### Correlation of mobility and molecular packing in organic transistors based on cycloalkyl naphthalene diimides

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#### 1. Synthesis



**Scheme S1** Synthesis of NTCDI derivatives.

The *Cyn*-NTCDIs were prepared following the reported procedure (Scheme S1),<sup>1,2</sup> by direct condensation of naphthalene dianhydride with the appropriate amines. Since the products were purified by sublimation, the yields were not estimated.

***N,N'*-Bis(cyclopropyl)naphthalene-1,4,5,8-bis(dicarboximide) (Cy3-NTCDI):** 1,4,5,8-naphthalenetetracarboxylic acid anhydride (0.67 g, 2.5 mmol), cyclopropylamine (0.86 g, 15 mmol) and a catalytic amount (25 mg) of zinc acetate were heated in quinoline (7.5 ml) at 150 °C for four hours. The mixture was cooled and diluted with several volumes of methanol (250 ml). The resulting slurry was filtered, and the collected solid was washed with methanol and dried in air. The crude product was purified by sublimation at 175 °C and  $1 \times 10^{-3}$  Pa. A yellowish brown solid was obtained. <sup>1</sup>H-NMR  $\delta$  0.88-0.92 (m, 4H), 1.25-1.32 (m, 4H), 2.89-2.92 (m, 2H), 8.73 (s, 4H), Mass (EI)  $m/z = 346$  (M<sup>+</sup>). Calcd for C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 69.36; H, 4.07; N, 8.09; O, 18.48. Found: C, 69.35; H, 3.84; N, 8.11; O, 18.21.

***N,N'*-Bis(cyclobutyl)naphthalene-1,4,5,8-bis(dicarboximide) (Cy4-NTCDI):** 1,4,5,8-naphthalenetetracarboxylic acid anhydride (0.67 g, 2.5 mmol), cyclobutylamine (0.86 g, 15 mmol) and a catalytic amount (25 mg) of zinc acetate were heated in quinoline (7.5 ml) at 150 °C for four hours. The mixture was cooled and diluted with several volumes of methanol (250 ml). The resulting slurry was filtered, and the collected solid was washed with methanol and dried in air. The crude product was purified by sublimation at 175 °C and  $1 \times 10^{-3}$  Pa. A light orange solid was obtained.  $^1\text{H-NMR}$   $\delta$  1.82-2.08 (m, 4H), 2.39-2.49 (m, 4H), 2.89-3.02 (t, 4H), 5.35-5.47 (t, 2H), 8.71 (s, 4H), Mass (EI)  $m/z = 374$  ( $\text{M}^+$ ). Calcd for  $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}_4$ : C, 70.58; H, 4.85; N, 7.48; O, 17.09. Found: C, 70.24; H, 4.68; N, 7.47; O, 16.79

***N,N'*-Bis(cyclopentyl)naphthalene-1,4,5,8-bis(dicarboximide) (Cy5-NTCDI):** 1,4,5,8-naphthalenetetracarboxylic acid anhydride (0.67 g, 2.5 mmol), cyclopentylamine (1.28 g, 15 mmol) and a catalytic amount (25 mg) of zinc acetate were heated in quinoline (7.5 ml) at 150 °C for four hours. The mixture was cooled and diluted with several volumes of methanol (250 ml). The resulting slurry was filtered, and the collected solid was washed with methanol and dried in air. The crude product was purified by sublimation at 175 °C and  $1 \times 10^{-3}$  Pa. A pink beige solid was obtained.  $^1\text{H-NMR}$   $\delta$  1.68-1.75 (m, 4H), 1.96-2.24 (m, 12H), 5.50-5.61 (t, 2H), 8.72 (s, 4H), Mass (EI)  $m/z = 402$  ( $\text{M}^+$ ). Calcd for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4$ : C, 71.63; H, 5.51; N, 6.96; O, 15.90. Found: C, 71.62; H, 5.45; N, 7.00; O, 15.84.

***N,N'*-Bis(cyclohexyl)naphthalene-1,4,5,8-bis(dicarboximide) (Cy6-NTCDI):** 1,4,5,8-naphthalenetetracarboxylic acid anhydride (0.67 g, 2.5 mmol), cyclohexylamine (1.49 g, 15 mmol) and a catalytic amount (25 mg) of zinc acetate were heated in quinoline (7.5 ml) at 150 °C for four hours. The mixture was cooled and diluted with several volumes of methanol (250 ml). The resulting slurry was filtered, and the collected solid was washed with methanol and dried in air. The crude product was purified by sublimation at 175 °C and  $1 \times 10^{-3}$  Pa. A pink beige solid was obtained.  $^1\text{H-NMR}$   $\delta$  1.26-1.57 (m, 6H), 1.73-1.77 (d, 6H), 1.89-1.94 (d, 4H), 2.46-2.58 (m, 4H), 4.96-5.07 (t, 2H), 8.71 (s, 4H), Mass (EI)  $m/z = 430$  ( $\text{M}^+$ ), Mass (EI)  $m/z = 430$  ( $\text{M}^+$ ). Calcd for  $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_4$ : C, 72.54; H, 6.09; N, 6.51; O, 14.84. Found: C, 72.65; H, 6.05; N, 6.50; O, 14.70.

***N,N'*-Bis(cycloheptyl)naphthalene-1,4,5,8-bis(dicarboximide) (Cy7-NTCDI):** 1,4,5,8-naphthalenetetracarboxylic acid anhydride (0.67 g, 2.5 mmol), cycloheptylamine (1.70 g, 15 mmol) and a catalytic amount (25 mg) of zinc acetate were heated in quinoline (7.5 ml) at 150 °C for four hours. The mixture was cooled and diluted with several volumes of methanol (250 ml). The resulting slurry was filtered, and the collected solid was washed with methanol and dried in air. The crude

product was purified by sublimation at 175 °C and  $1 \times 10^{-3}$  Pa. A pink beige solid was obtained.  $^1\text{H-NMR}$   $\delta$  1.56-1.69 (m, 12H), 1.84-1.88 (d, 8H), 2.36-2.54 (m, 4H), 5.13-5.20 (t, 2H), 8.71 (s, 4H), Mass (EI)  $m/z = 458$  ( $\text{M}^+$ ). Calcd for  $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_4$ : Found: C, 73.34; H, 6.59; N, 6.11; O, 13.96. Found: C, 73.21; H, 6.63; N, 6.10; O, 13.81.

***N,N'*-Bis(cyclooctyl)naphthalene-1,4,5,8-bis(dicarboximide) (Cy8-NTCDDI):** 1,4,5,8-naphthalenetetracarboxylic acid anhydride (0.40 g, 1.5 mmol), cyclohexylamine (1.14 g, 9 mmol) and a catalytic amount (15 mg) of zinc acetate were heated in quinoline (4.5 ml) at 150 °C for four hours. The mixture was cooled and diluted with several volumes of methanol (150 ml). The resulting slurry was filtered, and the collected solid was washed with methanol and dried in air. The crude product was purified by sublimation at 175 °C and  $1 \times 10^{-3}$  Pa. A pink beige solid was obtained.  $^1\text{H-NMR}$   $\delta$  1.58-1.68 (m, 12H), 1.75-1.88 (m, 12H), 2.43-2.54 (m, 4H), 5.27-5.34 (t, 2H), 8.71 (s, 4H), Mass (EI)  $m/z = 486$  ( $\text{M}^+$ ). Calcd for  $\text{C}_{30}\text{H}_{34}\text{N}_2\text{O}_4$ : Found: C, 74.05; H, 7.04; N, 5.76; O, 13.15. Found: C, 73.22; H, 6.98; N, 5.71; O, 9.31.

## 2. Redox properties

Cyclic voltammograms were measured on a BI-POTENTIOSTAT ALS/DY2323 in 0.1 M tetrabutylammonium hexafluoro-phosphate ( $n\text{-Bu}_4\text{N}^+\text{PF}_6^-$ ) solutions of benzonitrile at a scan rate of 100 mV/s. The reference electrode was Ag/AgNO<sub>3</sub> with using a glassy carbon working electrode and a Pt supporting electrode. The LUMO levels measured from the vacuum levels are estimated by the relation,  $E_{\text{LUMO}} = -5.24 \text{ eV} - E_{\text{red}}$ .<sup>3</sup>

## 3. UV-vis spectra

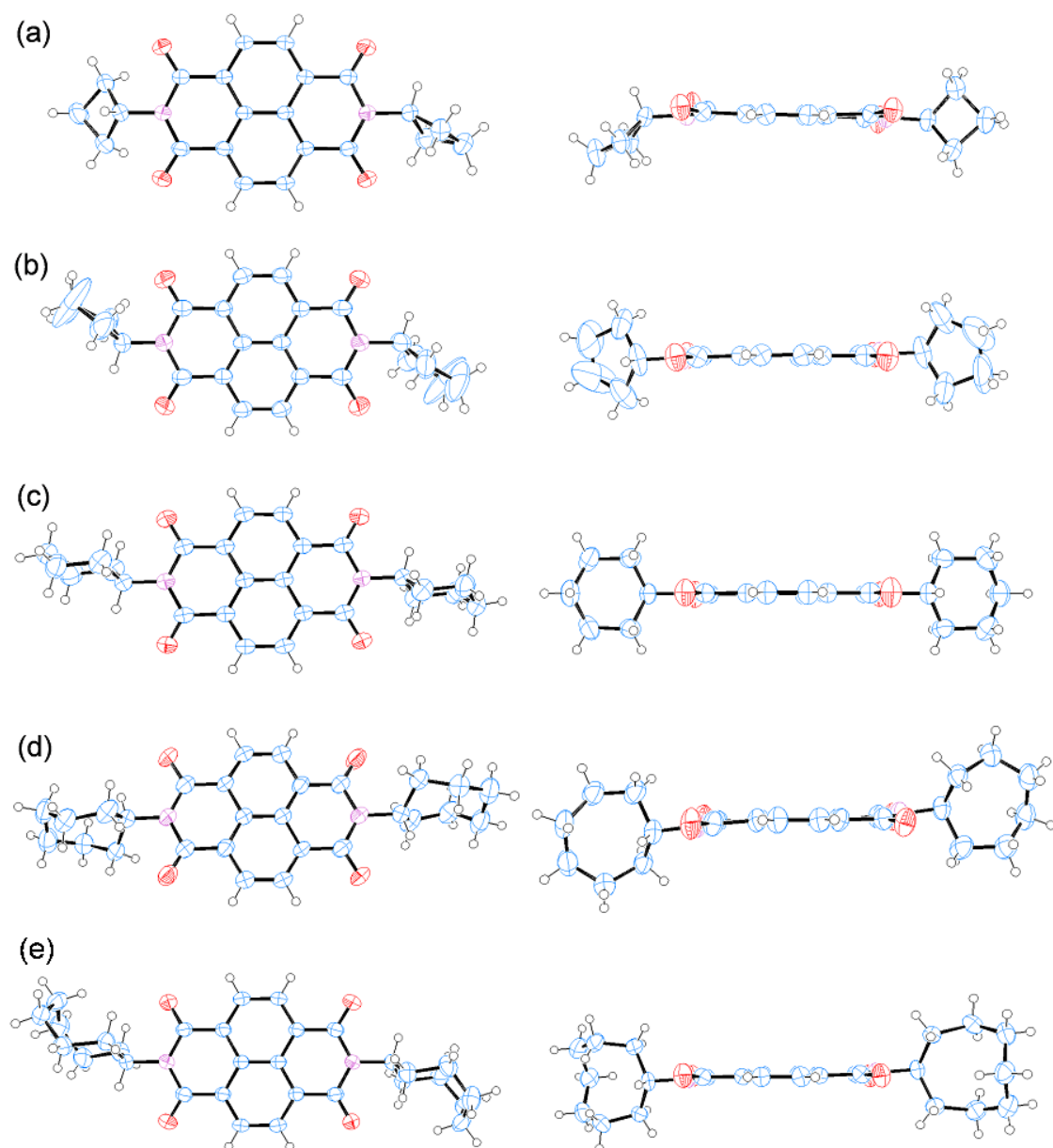
UV-vis absorption spectra in dichloromethane were measured on a Hitachi U-2800 UV-vis double beam spectrophotometer at room temperature using a quartz cuvette with a path of 1 cm. Optical bandgaps (HOMO-LUMO gaps) were calculated from the edge of the visible-absorption bands.

## 4. Single crystal structures and intermolecular overlap integral calculations

Crystal structures were determined by single crystal X-ray diffraction. Intensity data of Cyn-NTCDIs were measured by a Rigaku four-circle diffractometer AFC-7R with graphite monochromatized MoK $\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ ) radiation ( $2\theta < 60^\circ$ ). The crystal structures were solved by the direct method, SIR-92. The structures were refined by the full-matrix least-squares refinement by applying anisotropic temperature factors for all non-hydrogen atoms. The hydrogen atoms were determined from the calculation.

Molecular structures of Cy4~Cy8-NTCDIs are shown in Fig. S1. Cy4-NTCDI has one crystallographically independent molecule in a unit cell (Fig. S1a). One of the cyclobutane rings is

flat and about 35° tilted from the NTCDI plane, but another is perpendicular to the naphthalene diimide part. The Cy5~Cy8-NTCDIs molecules are located on inversion centers so that half the molecule is crystallographically independent (Figs. S1b-e). The naphthalene diimide is located at the equatorial positions of the cycloalkyl rings. The cycloalkane rings are located approximately perpendicular to the NTCDI parts.



**Fig. S1** ORTEP drawings of (a) Cy4-, (b) Cy5-, (c) Cy6-, (d) Cy7-, and (e) Cy8-NTCDIs.

## 5. Device fabrication

The organic field-effect transistor (OFET) devices were fabricated on a heavily doped  $n^+$ -Si wafer

with a 300 nm thermally grown SiO<sub>2</sub> (13.8 nF cm<sup>-2</sup>) as the gate dielectric. The substrates were washed in an ultrasonic bath successively with acetone and ultrapure water respectively for 10 min. After washing, the substrates were dried in an oven at 150 °C for 10 min, and then exposed to O<sub>3</sub> by using a UV-O<sub>3</sub> Cleaning System Model 203 (Technovision Inc.). The washed substrates were dipped in a toluene solution of 50 mM *n*-octyltrichlorosilane (OTS) at 70 °C for 12 h under Ar atmosphere. The substrates were washed three times with toluene and acetone respectively for 20 min to remove the excess OTS on the substrate.

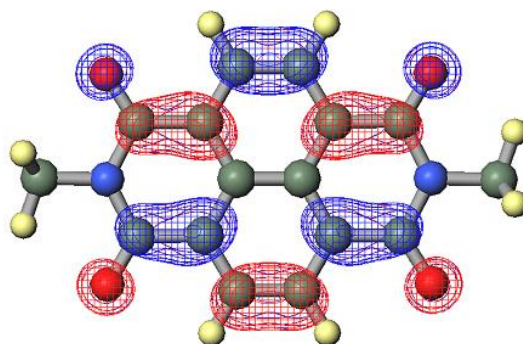
Organic transistors with top-contact (TC) Au source and drain (S/D) electrodes were fabricated. The deposition temperature of Cyn-NTCDI was 175 °C under the vacuum of  $1.0 \times 10^{-4}$  Pa. The Au electrodes were deposited under the vacuum of  $1.0 \times 10^{-3}$  Pa on the top of the organic thin film through a metal mask. The channel length ( $L$ ) was changed from 50 μm to 200 μm with an interval of 50 μm, and the width ( $W$ ) was 1 mm. Characteristics of the OFET devices were measured by a Keithley 4200 semiconductor parameter analyzer at room temperature in vacuum and in air. The field-effect mobility ( $\mu$ ) was calculated in the saturation region using an equation,  $I_D = \mu(WC_i/2L)(V_G - V_{TH})^2$ , where  $I_D$  was the drain current,  $C_i$  was the capacitance of the SiO<sub>2</sub> dielectric layer, and  $V_G$  and  $V_{TH}$  were the gate and threshold voltages, respectively. Current on/off ratio ( $I_{on}/I_{off}$ ) was determined from the maximum and the minimum of  $I_D$ .

AFM images were obtained with a Seiko Instruments SPA-300 and SPI3800 probe system by using a Si<sub>3</sub>N<sub>4</sub> cantilever. XRD measurements of the thin films were carried out by Phillips X'Pert-MPD-OEC PW3050 with a monochromated Cu-K $\alpha$  radiation ( $\lambda = 1.542512$  Å).

## 6. Theoretical calculation

The used atomic coordinates were optimized by DFT calculations using the B3LYP functional and 6-31G(d,p) basis set implemented by Gaussian 09 software package.<sup>4</sup> The LUMO spreads over the whole NTCDI core, but does not have population on the atoms located on the long axis because of the orbital symmetry (Fig. S2).

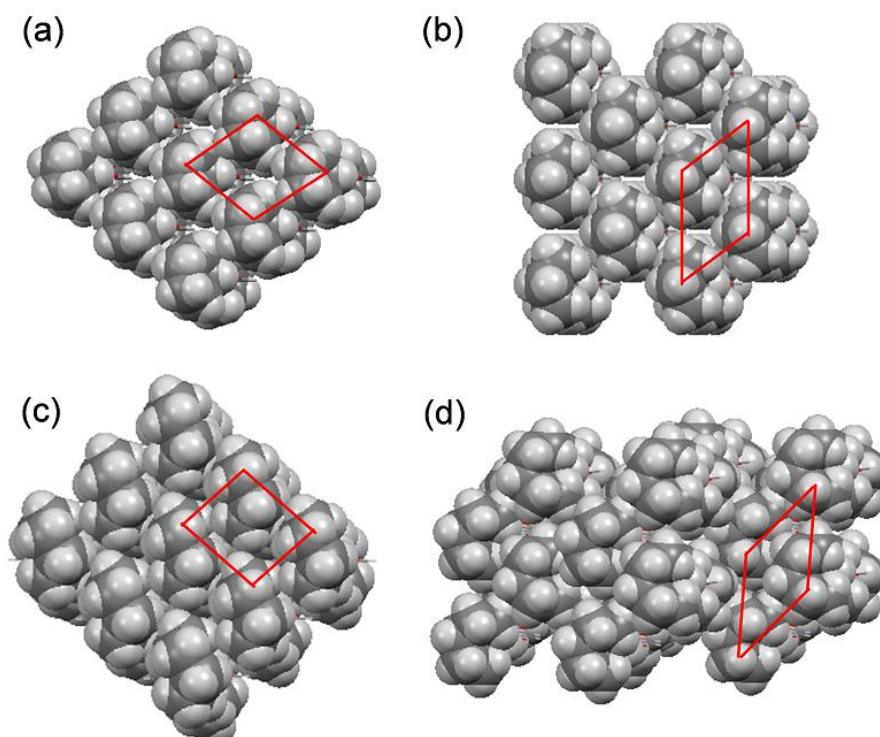
To investigate the variation of the transfer integral depending on the intermolecular packing motifs, the transfer integral was calculated for parallel dimers of methyl NTCDIs by changing the molecular long- and short-axis displacements, in which the interplanar distance is fixed to 3.4 Å. The transfer integrals were calculated by the Slater orbitals used in the extended Hückel method.<sup>5,6</sup>



**Fig. S2** Illustration of the LUMO for methyl NTCDI calculated by Gaussian 09 program at the B3LYP/6-31G(d,p) level.

### 7. Packing of the cycloalkyl groups

Fig. S3 shows the cycloalkyl groups viewed from the molecular long axis. The cross sectional area for the cyclohexyl group ( $28.52 \text{ \AA}^2$ ) is smaller than the others ( $30\text{-}32 \text{ \AA}^2$ ), implying that Cy6-NTCDI is most densely packed.



**Fig. S3** Arrangement of cycloalkyl groups in (a) Cy5-, (b) Cy6-, (c) Cy7-, and (d) Cy8-NTCDI. The cross sectional areas are  $30.64 \text{ \AA}^2$  for Cy5-,  $28.52 \text{ \AA}^2$  for Cy6-,  $31.95 \text{ \AA}^2$  for Cy7-, and  $31.79 \text{ \AA}^2$  for Cy8-NTCDI.

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