Facile synthesis of picenes incorporating imide moieties at the both edges of the molecule and their application to $n$-channel field-effect transistors

Yuxin Guo, a Kaito Yoshioka, a Shino Hamao, b Yoshihiro Kubozono, * b Fumito Tani, c Kenta Goto c and Hideki Okamoto * a

a Division of Earth, Life, and Molecular Sciences, Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan. E-mail: hokamto@okayama-u.ac.jp
b Research Institute for Interdisciplinary Science, Okayama University, Okayama 700-8530, Japan.
c Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan

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**Fig. S1** Fluorescence spectra of $C_n$-PicDIs in the solid state.
**Fig. S2** Transfer (a) and output (b) curves of $\text{C}_4$-$\text{PicDI}$ thin-film FETs with ZrO$_2$ gate dielectric. This FET refers to device #2 in Table S1.

**Fig. S3** Transfer (a) and output (b) curves of $\text{C}_{12}$-$\text{PicDI}$ thin-film FETs with ZrO$_2$ gate dielectric. This FET refers to device #5 in Table S2.
Table S1 FET parameters of C4-PicDI thin-film FET with ZrO2 gate dielectric. The parameters were determined from the forward transfer curves.

| sample | $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $|V_{th}|$ (V) | on/off (V) | $S$ (V/decade) |
|--------|---------------------------------|-------------|-----------|---------------|
| #1     | $2.4 \times 10^{-4}$            | 19.4        | $1.3 \times 10^2$ | 4.1           |
| #2     | $2.7 \times 10^{-4}$            | 20.0        | $1.2 \times 10^2$ | 3.9           |
| #3     | $1.2 \times 10^{-4}$            | 17.7        | $0.45 \times 10^2$ | 5.3           |
| #4     | $0.75 \times 10^{-4}$           | 17.8        | $1.2 \times 10^2$ | 4.1           |
| average| $2(1)\times 10^{-4}$            | 19(1)       | $1.0(4) \times 10^2$ | 4.3(7)       |

$^a$ The parameters were determined from the forward transfer curves.

Table S2 FET parameters of C12-PicDI thin-film FET with ZrO2 gate dielectric. The parameters were determined from the forward transfer curves.

| sample | $\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$) | $|V_{th}|$ (V) | on/off (V) | $S$ (V/decade) |
|--------|---------------------------------|-------------|-----------|---------------|
| #1     | $1.5 \times 10^{-2}$            | 17.9        | $11 \times 10^4$ | 1.0           |
| #2     | $0.97 \times 10^{-2}$           | 18.0        | $11 \times 10^4$ | 1.7           |
| #3     | $1.1 \times 10^{-2}$            | 18.2        | $1.5 \times 10^4$ | 1.2           |
| #4     | $1.8 \times 10^{-2}$            | 20.2        | $0.56 \times 10^4$ | 2.1           |
| #5     | $1.9 \times 10^{-2}$            | 20.5        | $3.3 \times 10^4$ | 1.6           |
| #6     | $1.4 \times 10^{-2}$            | 20.1        | $3.3 \times 10^4$ | 1.8           |
| #7     | $1.5 \times 10^{-2}$            | 19.5        | $4.2 \times 10^4$ | 1.4           |
| #8     | $1.3 \times 10^{-2}$            | 20.9        | $2.0 \times 10^4$ | 1.7           |
| average| $1.4(3) \times 10^{-2}$         | 19(1)       | $5(4) \times 10^4$ | 1.6(4)       |

$^a$ The parameters were determined from the forward transfer curves.
Experimental

General Information

$^1$H and $^{13}$C NMR spectra were recorded on VARIAN NMR System 600 (600 MHz) and VARIAN 400-MR (400 MHz) and JEOL JNM-ECZ600R (600 MHz) spectrometers. IR spectra were recorded on a JASCO FT/IR-460 Plus spectrophotometer. Absorption spectra in solution were respectively obtained on a JASCO V-530 UV-VIS spectrophotometers. Absorption spectra of thin films of C$_n$-PicDI$_s$, formed on a quartz substrate by thermal deposition under $10^{-7}$ Torr, were collected with a JASCO V-670 iRM EX spectrophotometer. Fluorescence spectra were collected on a JASCO FP-6300 spectrofluorometer.

Elemental analyses were measured on a PERKIN-ELMER 2400II CHN-S analyzer at the Micro Elemental Analysis Laboratory of Okayama University. High-resolution mass spectra (FAB) were recorded on a JEOL JMS-700 MStation spectrometer at Institute for Materials Chemistry and Engineering, Kyushu University.

Photoelectron yield spectroscopy (PYS) of the films of C$_n$-PicDI$_s$ was measured at room temperature using a PYS spectrometer (Bunko-keiki BIP-KV201). For the measurement of the PYS spectra, a 60-nm film of C$_n$-PicDI$_s$ was formed on a SiO$_2$/Si substrate.

The X-ray diffraction (XRD) patterns of thin films of C$_n$-PicDI$_s$ were measured with CuK$\alpha$ radiation (wavelength $\lambda = 1.5418$ Å) using a RIGAKU SMARTLAB-PRO at room temperature. For the XRD measurements, a 60-nm thin-film of C$_n$-PicDI$_s$ was formed on the SiO$_2$/Si substrate by thermal deposition under $10^{-7}$ Torr.

FET device fabrication and measurements of FET characteristics

60 nm thick thin-films of C$_n$-PicDI$_s$ were formed for an active layer on solid gate dielectrics of 150 nm thick ZrO$_2$ by a thermal deposition of C$_n$-PicDI$_s$ under a vacuum of $10^{-7}$ Torr. The surface of ZrO$_2$ was covered with 50 nm thick parylene. The ZrO$_2$/ Si substrates were heated at 100$^\circ$C during the thermal deposition of C$_8$-PicDI and C$_{12}$-PicDI, and at 80$^\circ$C during the thermal deposition of C$_4$-PicDI. The above temperatures are the general ones in heating the substrate of FETs with phenacene derivatives, and without heating the substrate, the device did not operate. The shape of the thin film...
was determined by use of a metal mask. 3 nm thick 2,3,5,6-tetrafluoro-7,7,8,8-teracyano-quinodimethane (F4TCNQ) was deposited on the C₈-PicDIs’ thin films under vacuum of 10⁻⁷ Torr, and the source and drain electrodes were formed by the thermal deposition of Au under vacuum of 10⁻⁷ Torr. The device structure is top-contact bottom-gate type.

All measurements were made in two-terminal measurement mode at room temperature with an Agilent B1500A semiconductor parametric analyzer; the FET characteristics in FET devices were measured in an Ar-filled glove box. The measured transfer curves were analyzed to determine the FET parameters (μ, threshold voltage (Vₜℎ), on/off ratio and subthreshold swing (S)) using the general formula for a saturation regime:

\[ I_D = \frac{\mu W C_o}{2L} (V_G - V_{th})^2 \]

where \( I_D \), \( V_G \), \( V_{th} \), \( W \), \( L \) and \( C_o \) refer to drain current, gate voltage, threshold voltage, channel width, channel length and capacitance per area of gate dielectric, respectively; the value of drain voltage, \( V_D \), was fixed to 26 V in the measurement of the transfer curve. The capacitance, \( C_o \), was determined by extrapolation of the capacitance recorded at 20 Hz –1.0 kHz to 0 Hz with an AC amplitude of 1 V using LCR meter (Agilent E4980A). The \( C_o \) value for the employed ZrO₂ gate dielectric was 3.89 × 10⁻⁸ F cm⁻². The condition for a saturation regime, \( V_D > V_G - V_{th} \), was completely satisfied in the analysis of the transfer curve. The saturation was completely recorded in the output characteristics of all FET devices fabricated in this study.

Materials

4-Bromo-2,3-naphthalenedicarboxylic anhydride 2

\[
\text{Br}_{2} \quad \text{NaOH} \quad \rightarrow
\]

Compound 2 was prepared according to the method reported for bromination of phthalic anhydride.⁵¹ To a mixture of naphthalene-2,3-dicarboxylic anhydride 1 (2.0 g, 10.1 mmol) in aqueous NaOH (1
M, 20 ml) was dropwise added Br₂ (1 mL, 19.4 mmol). The reaction mixture was refluxed for ca. 16 h. After being cooled to room temperature, the solid formed was collected by suction filtration. The obtained solid was dissolved in a 1:1 mixture of MeOH and H₂O (40 ml) and acidified to pH 1.5 with conc. HCl. The resulting mixture was extracted with ether (4 × 60 ml) and the combined extracts were washed with Na₂S₂O₃ aq., dried over Na₂SO₄, and concentrated. The residue was recrystallized from MeCN to afford anhydride 2 (719 mg, 26%) as colorless crystals, mp 214–216°C. ¹H NMR (600 MHz, CDCl₃), δH 9.00 (s, 1H), 8.55 (s, 1H), 8.14–8.08 (m, 2H), 7.66 (dd, J = 8.1, 7.7 Hz, 1H), ¹³C NMR (151 MHz, CDCl₃), δC 162.71, 162.60, 137.66, 135.28, 134.65, 130.88, 130.41, 128.27, 127.78, 127.31, 126.88, 125.51. IR (neat) νmax 1837, 1793 (C=O), 1236, 1182 (CO) cm⁻¹. HRMS (FAB, m/z, MH⁺) Calcd. for C₁₂H₆BrO₃: 276.9500. Found: 276.9503.

N-Butyl-4-bromonaphthalene-2,3-dicarboximide 3a

![Reaction Diagram]

To a solution of anhydride 2 (76 mg, 0.27 mmol) in acetic acid (2 mL) was added butylamine (50 μl mL, 0.50 mmol) and the mixture was refluxed for 17 h. After being cooled to r.t., the reaction mixture was poured into ice water (100 ml) and extracted with AcOEt (100 ml). The organic layer was washed with NaHCO₃ aq., dried over MgSO₄, and concentrated. The residue was chromatographed on silica gel (AcOEt) followed by recrystallization from a CHCl₃-hexane mixture to afford imide 3a (79 mg, 87%) as colorless needle, mp 123–124°C. ¹H NMR (400 MHz, CDCl₃), δH 8.77 (s, 1H), 8.31 (s, 1H), 8.01(d, J = 8.3 Hz, 1H), 7.98 (dd, J = 7.5, 1.0 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 3.77(t, J = 7.3 Hz, 2H), 1.75–1.67 (m, 2H), 1.40 (sext, J = 7.5 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). ¹³C NMR (100MHz, CDCl₃), δC 167.89, 167.82, 137.02, 134.51, 133.30, 130.15, 129.49, 129.30, 128.80, 125.26, 124.87, 124.26, 38.36, 30.69, 20.28, 13.81. IR (neat) νmax 1696 (C=O), 1400 (C-N) cm⁻¹. Anal. Calcd. for C₁₆H₁₄BrNO₂: C, 57.85; H, 4.25; N, 4.22. Found: C, 57.95; H, 4.08; N, 4.13.
N-octyl-4-bromonaphthalene-2,3-dicarboximide 3b and N-dodecyl-4-bromonaphthalene-2,3-dicarboximide 3c

Compounds 3b and 3c were obtained via the same procedure for preparation of 3a by using octylamine and dodecylamine, respectively.

3b: (yield: 83%). Colorless needles, mp 107–108°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)H 8.77 (s, 1H), 8.31 (s, 1H), 8.01 (d, \(J = 8.3\) Hz, 1H), 7.98 (dd, \(J = 7.5, 1.1\) Hz, 1H), 7.53 (dd, \(J = 8.1, 7.6\) Hz, 1H), 3.76 (t, \(J = 7.3\) Hz, 2H), 1.72 (quin, \(J = 7.3\) Hz, 2H), 1.41–1.18 (m, 10H), 0.87 (t, \(J = 6.9\) Hz, 3H).

\(^{13}\)C NMR (100MHz, CDCl\(_3\)), \(\delta\)C 167.89, 167.82, 137.00, 134.49, 133.29, 130.15, 129.49, 129.28, 128.78, 125.25, 124.88, 124.26, 38.62, 31.91, 29.31 (two lines overlap), 28.66, 27.05, 22.77, 14.23.

IR (neat) \(\nu_{\text{max}}\) 2921 (C-H), 1693 (C=O), 1400 (C-N) cm\(^{-1}\). Anal. Calcd. for C\(_{20}\)H\(_{22}\)BrNO\(_2\): C, 61.86; H, 5.71; N, 3.61. Found: C, 61.86; H, 5.65; N, 3.56.

3c (yield: 89%). Colorless needles, mp 104–105°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\)H 8.78 (s, 1H), 8.31 (s, 1H), 8.01 (d, \(J = 8.3\) Hz, 1H), 7.98 (dd, \(J = 7.5, 1.0\) Hz, 1H), 7.53 (t, \(J = 7.8\) Hz, 1H), 3.76 (t, \(J = 7.3\) Hz, 2H), 1.72 (quin, \(J = 7.4\) Hz, 2H), 1.41–1.18 (m, 18H), 0.87 (t, \(J = 6.9\) Hz, 3H).

\(^{13}\)C NMR (100MHz, CDCl\(_3\)), \(\delta\)C 167.91, 167.84, 137.02, 134.51, 133.30, 130.16, 129.51, 129.30, 128.79, 125.27, 124.89, 124.28, 38.64, 32.05, 29.77, 29.76, 29.71, 29.64, 29.49, 29.36, 28.66, 27.06, 22.83, 14.28. IR (neat) \(\nu_{\text{max}}\) 2920 (C-H), 1693 (C=O), 1400 (C-N) cm\(^{-1}\). Anal. Calcd. for C\(_{24}\)H\(_{30}\)BrNO\(_2\): C, 64.86; H, 6.80; N, 3.15. Found: C, 64.85; H, 6.79; N, 3.10.

\((E)\)-1,2-Bis(2-butyl-1,3-dihydro-1,3-dioxobenzo[f]-2H-isooindol-5-yl)ethene 4a
A round flask containing a solution of compound 3a (483.6 mg, 1.44 mmol) and (E)-1,2-bis(tributylstannyl)ethene (411 mg, 0.7 mmol) in 15 ml toluene was deaerated by three evacuation-argon-refill cycles. Pd(PPh₃)₄ (63 mg, 3 mol%) was added to the mixture. The mixture was further purged with argon. The resulting solution was refluxed overnight. After being cooled to r.t., the solvent was removed and the residue was chromatographed on silica gel using a hexane-AcOEt mixture (5:1). The obtained crude product was recrystallized from a MeOH-CHCl₃ mixture to afford compound 4a (312 mg, 84%) as yellow crystals, mp >300°C. ¹H NMR (600 MHz, CDCl₃): δH 8.72 (s, 1H), 8.38 (s, 1H), 8.10 (d, J = 7.3 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H) 7.99 (s, 1H), 7.79 (dd, J = 8.2, 7.4 Hz, 1H), 3.77 (t, J = 7.3 Hz, 2H), 1.75–1.67 (m, 2H), 1.40 (sext, J = 7.5 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃): δC 168.40, 168.17, 137.29, 136.06, 133.55, 130.89, 129.61, 129.17, 128.32, 128.07, 127.37, 125.36, 120.53, 38.30, 30.74, 20.29, 13.81. IR (neat) νmax 2378 (C-H), 1703 (C=C), 1489, 1338, 1057 cm⁻¹. Anal. Calcd. for C₃₄H₃₀N₂O₄: C, 76.96; H, 5.70; N, 5.28%. Found: C, 76.75; H, 5.33; N, 5.20%.

(E)-1,2-Bis(2-octyl-1,3-dihydro-1,3-dioxobenzo[f]-2H-isooindol-5-yl)ethene 4b and (E)-1,2-bis(2-dodecyl-1,3-dihydro-1,3-dioxobenzo[f]-2H-isooindol-5-yl)ethene 4c

Compounds 4b and 4c were obtained via the same procedure for preparation of 4a by using substrates 3b and 3c, respectively.
4b: (yield: 79%). Yellow crystals, mp 260–261°C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$H 8.73 (s, 1H), 8.39 (s, 1H), 8.10 (d, $J$ = 7.3 Hz, 1H), 8.08 (d, $J$ = 8.3 Hz, 1H), 8.00 (s, 1H), 7.79 (dd, $J$ = 8.0, 7.3 Hz, 1H), 3.75 (t, $J$ = 7.4 Hz, 2H), 1.71 (quin, $J$ = 7.4 Hz, 2H), 1.42–1.19 (m, 10H), 0.86 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (151MHz, CDCl$_3$) $\delta$C 168.41, 168.16, 137.28, 136.06, 133.54, 130.89, 129.59, 129.17, 128.32, 128.07, 127.37, 125.38, 120.53, 38.57, 31.91, 29.32 (two lines overlap), 28.71, 27.07, 22.77, 14.23. IR (neat) $\nu_{\text{max}}$ 2924 (C-H), 1764, 1707 (C=O), 1384 (C-N) cm$^{-1}$. Anal. Calcd. for C$_{42}$H$_{46}$N$_2$O$_4$: C, 78.47; H, 7.21; N, 4.36. Found: C, 78.62; H, 7.15; N, 4.37.

4c: (yield: 88%). Yellow crystals, mp 237–239°C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$H 8.72 (s, 1H), 8.38 (s, 1H), 8.09 (d, $J$ = 7.4 Hz, 1H), 8.07 (d, $J$ = 8.1 Hz, 1H), 7.99 (s, 1H), 7.79 (t, $J$ = 7.7 Hz, 1H), 3.75 (t, $J$ = 7.4 Hz, 2H), 1.71 (quin, $J$ = 7.3 Hz, 2H), 1.39–1.18 (m, 18H), 0.86 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (151MHz, CDCl$_3$) $\delta$C 168.40, 168.16, 137.29, 136.07, 133.56, 130.89, 129.60, 129.17, 128.34, 128.09, 127.37, 125.37, 120.52, 38.58, 32.05, 29.77, 29.76, 29.71, 29.65, 29.48, 29.37, 28.71, 27.08, 22.82, 14.26. IR (neat) $\nu_{\text{max}}$ 2921 (C-H), 1766, 1710 (C=O), 1384 (C-N) cm$^{-1}$. Anal. Calcd. for C$_{50}$H$_{62}$N$_2$O$_4$: C, 79.54; H, 8.28; N, 3.71. Found: C, 79.55; H, 8.33; N, 3.77.

$N,N'$-Dibutylpicene-2,3,10,11-tetracarboxydiimide $C_4$-PicDI
A solution of compound 4a (217 mg, 0.4 mmol) and iodine (10 mg, 10 mol%) in 400 mL CH$_2$Cl$_2$ was purged with air and irradiated with black-light lamps (352 nm, 6 ×15 W) until TLC analysis revealed the complete consumption of 4a. The solvent was removed under reduced pressure and the residue was dissolved in CH$_2$Cl$_2$ (100 mL). The solution was washed with saturated Na$_2$S$_2$O$_3$ solution 3 times, dried over MgSO$_4$, and concentrated. The residue was recrystallized from chlorobenzene to afford C$_4$-PicDI as pale yellow solid (130 mg, 60%), mp > 300°C. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$H 9.32 (s, 1H), 9.07 (s, 1H), 8.98 (d, $J$ = 9.2 Hz, 1H), 8.48 (s, 1H), 8.25 (d, $J$ = 9.0 Hz, 1H), 3.82 (t, $J$ = 7.4 Hz, 2H), 1.80–1.72 (m, 2H), 1.45 (sext, $J$ = 7.5 Hz, 2H), 1.00 (t, $J$ = 7.4 Hz, 3H). $^{13}$C NMR (151 MHz, 50°C) $\delta$H 168.44, 168.16, 135.38, 133.72, 130.48, 130.20, 129.68, 129.59, 129.06, 124.83, 124.58, 123.37, 119.62, 38.436, 30.852, 20.354, 13.77. IR (neat) $\nu$$_{max}$ 2912 (C-H), 1736 (C=C), 1261, 1120, 781 cm$^{-1}$. Anal. Calcd. for C$_{34}$H$_{28}$N$_2$O$_4$: C, 77.25; H, 5.34; N, 5.16%. Found: C, 77.55; H, 5.06; N, 5.16%.

$N,N'$-Dioctyl-picene-2,3,10,11-tetracarboxydiimide C$_8$-PicDI and $N,N'$-Didodecyl-picene-2,3,10,11-tetracarboxydiimide C$_{12}$-PicDI

C$_8$-PicDI and C$_{12}$-PicDI were prepared by the same procedure for the synthesis of C$_4$-PicDI by using
4b and 4c, respectively.

**C₈-PicDI** (yield: 54%). Pale yellow solid, mp >300°C. ¹H NMR (600 MHz, CDCl₃) δH 9.08 (s, 1H), 8.88 (d, J = 9.4 Hz, 1H), 8.80 (s, 1H), 8.35 (s, 1H), 8.16 (d, J = 9.0 Hz, 1H), 3.77 (t, J = 7.5 Hz, 2H), 1.76 (quin, J = 7.4 Hz, 2H), 1.44–1.22 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δC 168.33, 167.99, 135.01, 133.25, 129.99, 129.78, 129.27, 129.18, 128.90, 124.64, 124.33, 122.95, 119.29, 38.61, 31.95, 29.36 (two lines overlap), 28.78, 27.13, 22.80, 14.25. IR (neat) νmax 2924 (C-H), 1763, 1711 (C=O), 1388 (C-N) cm⁻¹. HRMS (FAB, m/z, M⁺) Calcd. for C₄₂H₄₄N₂O₄: 640.3301. Found: 640.3277.

**C₁₂-PicDI** (yield: 82%). Pale yellow solid, mp >300°C. ¹H NMR (600 MHz, CDCl₃) δH 9.11 (s, 1H), 8.89 (d, J = 9.4 Hz, 1H), 8.84 (s, 1H), 8.37 (s, 1H), 8.18 (d, J = 9.0 Hz, 1H), 3.78 (t, J = 7.4 Hz, 2H), 1.75 (quin, J = 7.4 Hz, 2H), 1.43–1.18 (m, 18H), 0.86 (t, J = 7.0 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δC 168.36, 168.03, 135.02, 133.26, 130.00, 129.80, 129.25, 129.17, 128.91, 124.66, 124.36, 122.98, 119.33, 38.61, 32.06, 29.80, 29.78, 29.75, 29.70, 29.51, 29.40, 28.78, 27.13, 22.84, 14.29. IR (neat) νmax 2917 (C-H), 1765, 1698 (C=O), 1391 (C-N) cm⁻¹. Anal. Calcd. for C₅₀H₆₀N₂O₄: C, 79.75; H, 8.03; N, 3.72. Found: C, 79.64; H, 8.03; N, 3.74.
Theoretical calculations

Theoretical calculations were performed by using GAUSSIAN 09 Revision C. 01 package. The ground-state geometry of picene and Cₙ-PicDI (n = 4, 8, 12) were optimized by density functional theory (DFT) using B3LYP functional with 6-31+G(d) basis set. The optimized atomic coordinates were listed in Tables S3–S6.

The inclined angles (Fig. 3(b)) were evaluated by using the calculated geometries of Cₙ-PicDIs.

Fig. S4 Calculated molecular structure of C₈-PicDI: (a) Top view; (b), (c) side views.

Calculated coordinates

Table S3 Optimized ground state geometry of picene
(Total energy = -846.85214037 au)

| atom | x (angstrom) | y (angstrom) | z (angstrom) |
|------|--------------|--------------|--------------|
| C    | 0.00000000   | 5.73131500   | -0.38378400  |
| C    | 0.00000000   | 5.00891100   | 0.79315700   |
| C    | 0.00000000   | 3.59200300   | 0.77954500   |
| C    | 0.00000000   | 2.89201600   | -0.46367200  |
Table S4 Optimized ground state geometry of C₄-PicDI  
(Total energy $-1723.10764212$ au)

| atom | x       | y       | z       |
|------|---------|---------|---------|
|      | (angstrom) |         |         |
| C    | 0.02161300 | -5.69925600 | 0.90722400 |
| C    | 0.03274800 | -5.01352500 | 2.09485900 |
| C    | 0.02456500 | -3.59044300 | 2.05776700 |
| C    | 0.00773400 | -2.88805500 | 0.80800100 |
| C    | -0.00701800 | -3.64432000 | -0.39910000 |
| C    | -0.00009100 | -5.01570500 | -0.32580500 |
| C    | 0.03228100 | -2.84146040 | 3.27220300 |
| C    | 0.00406300 | -1.43527100 | 0.81356900 |
| C    | 0.00552800 | -0.72503600 | 2.04548500 |
| C    | -0.00552800 | 0.72503600 | 2.04548500 |
| C    | -0.00406300 | 1.43527100 | 0.81356900 |
| C    | 0.00009100 | 0.68465300 | -0.39721600 |
| C    | 0.00084500 | -0.68465300 | 0.39721600 |
| H    | 0.04664000 | -3.38051700 | 4.21563700 |
| H    | 0.04660400 | -5.53038400 | 3.05059000 |
| H    | -0.02582300 | -3.16519400 | -1.37062500 |
| H    | 0.02783700 | -0.96174000 | 4.21937800 |
| H    | -0.00235300 | 1.19308000 | -1.35370500 |
| H    | 0.00235300 | -1.19308000 | -1.35370500 |
Table S5 Optimized ground state geometry of C₈-PicDI (Total energy \(-2037.60841182\) au)

| atom | x     | y     | z     |
|------|-------|-------|-------|
|      | (angstrom) |       |       |
| C    | 0.02103100 | 1.47501400 | 3.26603900 |
| C    | -0.03228100 | 2.84140400 | 3.27220300 |
| H    | -0.04664000 | 3.38051700 | 4.21563700 |
| C    | -0.02456500 | 3.59044300 | 2.05776700 |
| C    | -0.00773400 | 2.88805500 | 0.80800100 |
| H    | -0.02783700 | 0.96174000 | 4.21937800 |
| C    | -0.03724800 | 5.01352500 | 0.96722400 |
| C    | -0.02161300 | 5.69925600 | 0.96722400 |
| C    | 0.00089100  | 5.01570500 | -0.32580500 |
| C    | 0.00701800  | 3.64432000 | -0.39910000 |
| H    | -0.04660400 | 5.53038400 | 3.05059000 |
| C    | -0.02305200 | 7.16942200 | 0.62361000 |
| C    | 0.02305200  | -7.16942200 | 0.62361000 |
| C    | 0.01678300  | 6.03298500 | -1.41211900 |
| C    | -0.01678300 | -6.03298500 | -1.41211900 |
| O    | -0.03527100 | 8.09739700 | 1.40612400 |
| O    | 0.03527100  | -8.09739700 | 1.40612400 |
| O    | -0.04595400 | 5.86675100 | -2.62214600 |
| O    | 0.04595400  | -5.86675100 | -2.62214600 |
| N    | -0.00084500 | 7.28194100 | -0.77424000 |
| N    | 0.00084500  | -7.28194100 | -0.77424000 |
| C    | -0.00230100 | 8.56059300 | -1.48363300 |
| H    | -0.52476400 | 9.27836100 | -0.84677000 |
| H    | 0.52476400  | -9.27836100 | -0.84677000 |
| H    | -0.58996000 | 8.41968700 | -2.39556000 |
| C    | 1.40862300  | 9.06160800 | -1.82103900 |
| H    | -1.91949900 | 8.30791700 | -2.43942400 |
| H    | -1.98488700 | 9.16427400 | -0.89176300 |
| C    | 1.40862300  | -9.06160800 | -1.82103900 |
| H    | -1.91949900 | -8.30791700 | -2.43942400 |
| H    | 1.98488700  | -9.16427400 | -0.89176300 |
| C    | -1.38051700 | 10.40348800 | -2.56492500 |
| H    | -0.86125000 | 11.15047800 | -1.94775200 |
| H    | -0.78891500 | 10.29650800 | -3.48531700 |
| C    | 1.38051700  | -10.40348800 | -2.56492500 |
| H    | 0.86125000  | 11.15047800 | -1.94775200 |
| H    | 0.78891500  | -10.29650800 | -3.48531700 |
| C    | -2.78204300 | 10.91680000 | -2.91606800 |
| H    | -3.38795500 | 11.06213800 | -2.01257700 |
| H    | -2.73183100 | 11.87698100 | -3.44313400 |
| H    | -3.31268500 | 10.26948000 | -3.56333600 |
| C    | 2.78204300  | -10.91680000 | -2.91606800 |
| H    | 3.38795500  | -11.06213800 | -2.01257700 |
| H    | 2.73183100  | -11.87698100 | -3.44313400 |
| H    | 3.31268500  | -10.26948000 | -3.56333600 |
| X       | Y       | Z       |
|---------|---------|---------|
| C -0.28733401 | -3.57901153 | 2.05776706 |
| C -0.24310368 | -3.87781551 | 0.80800106 |
| C -0.32347655 | -3.62994221 | -0.39909994 |
| C -0.43567143 | -4.99674765 | -0.32580494 |
| C -0.21459809 | -2.83347250 | 3.27220306 |
| C -0.12059614 | -1.43020136 | 0.81356906 |
| C -0.05745746 | -0.72277687 | 2.04548506 |
| C -0.10714366 | -1.47126777 | 3.26639306 |
| C 0.05745746  | 0.72277687  | 2.04548506 |
| C 0.12059614  | 1.43020136  | 0.81356906 |
| C 0.05861577  | 0.68213975  | -0.39721594 |
| C -0.05861577 | -0.68213975 | -0.39721594 |
| H -0.24711173 | -3.37179570 | 4.21563706 |
| H -0.43384931 | -5.51353733 | 3.05059006 |
| H -0.3060159 | -3.15099327 | -1.37062494 |
| H -0.0578892 | -0.96052398 | 4.21937806 |
| H 0.10126699 | 1.18877686 | -1.35370494 |
| H -0.18126699 | -1.18877686 | -1.35370494 |
| C 0.10714366  | 1.47126777  | 3.26639306 |
| C 0.21459809  | 2.83347250  | 3.27220306 |
| H 0.24711173  | 3.37179570  | 4.21563706 |
| C 0.28733401  | 3.57901153  | 2.05776706 |
| C 0.24310368  | 2.87781551  | 0.80800106 |
| H 0.05861577  | 0.72277687  | 2.04548506 |
| C 0.40276718  | 4.99742773  | 2.09485306 |
| C 0.47341131  | 5.67960103  | 0.90722406 |
| C 0.3567143  | 4.99674765  | -0.32580494 |
| C 0.32347655  | 3.62942221  | -0.39909994 |
| H 0.3060159  | 3.15099327  | -1.37062494 |
| C 0.43384931  | 5.51353733  | 3.05059006 |
| C 0.59887034  | 7.13537167  | 0.62236106 |
| C -0.59887034 | -7.13537167 | 0.62236106 |
| C 0.54064440  | 6.00887347  | -1.41211894 |
| C -0.54064440 | -6.00887347 | -1.41211894 |
| O 0.66806758  | 8.06968790  | 1.40612406 |
| O -0.66806758 | -8.06968790 | 1.40612406 |
| O 0.55526887  | 5.84059548  | -2.62214594 |
| O -0.55526887 | -5.84059548 | -2.62214594 |
| N 0.63154656  | 7.25450304  | -0.77423994 |
| N -0.63154656 | -7.25450304 | -0.77423994 |
| C 0.74572314  | 8.52805106  | -1.48363294 |
| H 1.32854566  | 9.19773486  | -0.84467694 |
| H 1.31887140  | 8.33664780  | -2.39556594 |
| C -0.74572314 | -8.52805106 | -1.48363294 |
| H -1.32854566 | -9.19773486 | -0.84467694 |
| H -1.31887140 | -8.33664780 | -2.39556594 |
| C -0.61636052 | 9.14970262  | -1.82103894 |
| H -1.19075949 | 8.44322528  | -2.43492394 |
| H -1.18153152 | 9.30202546  | -0.89176294 |
| C 0.61636052  | -9.14970262 | -1.82103894 |
| H 1.19075949  | -8.44322528 | -2.43492394 |
| H 1.18153152  | -9.30202546 | -0.89176294 |
| C -0.47182731 | 10.48407215 | -2.56492494 |
| H 0.11834903  | 11.18314510 | -1.94775194 |
| H 0.18824910  | 10.32611960 | -3.48531694 |
| C 0.47182731  | -10.48407215 | -2.56492494 |
| H -0.11834903 | -11.18314510 | -1.94775194 |
| H -0.18824910 | -10.32611960 | -3.48531694 |
| C -1.82348039 | 11.11716009 | 2.91606794 |
| H -2.41448177 | 11.31456645 | 2.01257694 |
| H -2.41376373 | 10.45607068 | -3.56333594 |
| C 1.82348039  | -11.11716009 | -2.91606794 |
| atom | x      | y      | z      |
|------|--------|--------|--------|
| C    | 0.01038400 | 5.70074800 | -2.74700600 |
| C    | 0.01500000 | 5.01495300 | -3.93484700 |
| C    | 0.01017000 | 3.59254500 | -3.89903800 |
| C    | 0.00178100 | 2.88858500 | -2.64998000 |
| C    | -0.00629900 | 3.64452700 | -1.44343900 |
| C    | -0.00177700 | 5.01582400 | -1.51580300 |
| C    | 0.01310600 | 2.84226800 | -5.11299900 |
| C    | 0.00082600 | 1.43562600 | -2.65708900 |
| C    | 0.00197200 | 0.72485500 | -3.88810400 |
| C    | 0.00795200 | 1.47654000 | -5.10776400 |
| C    | -0.00197200 | -0.72485500 | -3.88810400 |
| C    | -0.00082600 | -1.43562600 | -2.65708900 |
| C    | 0.00009400 | -0.68452100 | -1.44718500 |
| C    | 0.00009400 | 0.68452100 | -1.44718500 |
| H    | 0.01913200 | 3.38227000 | -6.05653200 |
| H    | 0.02191800 | 5.53670800 | -4.88830100 |
| H    | -0.01702500 | 3.16957100 | -0.49548400 |
| H    | 0.00979300 | 0.96281800 | -6.06120100 |
| H    | -0.00054300 | -1.19478500 | -0.49137700 |
| H    | 0.00054300 | 1.19478500 | -0.49137700 |
| C    | -0.00795200 | -1.47654000 | -5.10776400 |
| C    | -0.01310600 | -2.84226800 | -5.11299900 |
| H    | -0.01913200 | -3.38227000 | -6.05653200 |
| C    | -0.01017000 | -3.59254500 | -3.89903800 |

**Table S6** Optimized ground state geometry of C$_{12}$-PicDI (Total energy $-2037.60841182$ au)
C  -0.00178100  -2.88858500  -2.64998000
H  -0.00979300  -0.96281800  -6.06120100
C  -0.01038400  -5.01495300  -3.93484700
C  -0.01038400  -5.70074800  -2.74700600
C   0.00177700  -5.01582400  -1.51580300
C   0.00629900  -3.64452700  -1.44343900
H   0.01702500  -3.16957100  -0.46948400
H  -0.02191800  -5.53670800  -4.88830100
C  -0.01391400  -7.16520000  -2.46254000
C   0.01391400   7.16520000  -2.46254000
C   0.01017000  -6.03037800  -0.42320500
C  -0.01017000   6.03037800  -0.42320500
O  -0.02084800  -8.09861200  -3.24465200
O   0.02084800   8.09861200  -3.24465200
O   0.02779600  -5.85863000   0.78259100
O  -0.02779600   5.85863000   0.78259100
N  -0.00082600  -7.28097200  -1.06266200
N   0.00082600   7.28097200  -1.06266200
C  -0.00752500  -8.55572800  -0.34902700
H   0.50800200  -9.28015800  -0.98663800
H   0.57735400  -8.41284400   0.56486500
C   0.00752500   8.55572800  -0.34902700
H  -0.50800200   9.28015800  -0.98663800
H  -0.57735400   8.41284400   0.56486500
C  -1.42280100  -9.04370200  -0.00968900
H  -1.93148000  -8.27229400   0.58342200
H  -1.99148200  -9.16463800  -0.94135800
C   1.42280100   9.04370200  -0.00968900
H   1.93148000   8.27229400   0.58342200
H   1.99148200   9.16463800  -0.94135800
C  -2.80952800 -10.36657800   0.76757200
H  -3.39400800 -11.13362600   0.17416200
H  -3.33317400 -10.23846400  1.68922600
C  -2.80952800 -10.87152400  1.13022300
H  -3.39400800 -11.01169900   0.20842000
H  -3.33317400 -10.96609000  1.71007800
C   2.80952800 -10.87152400  1.13022300
H   3.39400800 -11.01169900   0.20842000
H   3.33317400 -10.96609000  1.71007800
C  -4.20272600 -12.68360700  2.30039300
H  -2.12192000 -12.03926800  2.84975100
H  -2.27759600 -12.95781300  1.35080600
C  -4.19393700 -13.98461600  3.11500600
H  -4.72766600 -13.90259100  2.87137900
H  -4.78663200 -13.83473100  1.38090200
C  -6.59596400 -14.48381300  3.49111000
H  -3.67123000 -14.76713600  2.54399200
H  -3.60545300 -13.83288100  4.83281200
C  -5.59596400 -14.48381300  3.49111000
H  -6.11994700 -13.69869100  4.85739900
H  -6.18347800 -14.64106400  2.57363000
C   2.80016500  12.18145500  1.93018400
C   4.20272600  12.68360700  2.30039300
H   2.21219200  12.03926800  2.84975100
H   2.27759600  12.95781300  1.35080600
C   4.19393700  13.98461600  3.11500600
H   4.72766600  11.90259100  2.87137900
H   4.78863200  12.34731000  1.38090200
C   5.59596400  14.48381300  3.49111000
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 3.67123000 | 14.76713600 | 2.54399200 |
| H    | 3.60545300  | 13.83288100  | 4.03281200  |
| H    | 6.11994700  | 13.69869100  | 2.54399200  |
| H    | 6.18347800  | 14.64106400  | 2.57363000  |
| C    | 5.58692200  | 15.77946800  | 4.31426400  |
| C    | 6.98855300  | 16.27679100  | 4.69377900  |
| H    | 4.99798500  | 15.62199700  | 5.23083800  |
| H    | 5.06441900  | 16.56558000  | 3.74791800  |
| C    | 6.98081500  | 17.57026800  | 5.52030800  |
| C    | 7.51230800  | 15.49031900  | 5.25869300  |
| H    | 7.57773800  | 16.43691200  | 3.77764400  |
| C    | 8.38554900  | 18.05821100  | 5.89475800  |
| H    | 6.45878000  | 18.35698800  | 4.95612300  |
| H    | 6.39306000  | 17.41076600  | 6.43621900  |
| H    | 8.34557700  | 18.98289700  | 6.48324000  |
| H    | 8.92042500  | 17.38705700  | 6.49039300  |
| H    | 8.98722300  | 18.25920900  | 4.99880000  |
| C    | -5.58692200 | -15.77946800 | 4.31426400 |
| C    | -6.98855300 | -16.27679100 | 4.69377900 |
| H    | -4.99798500 | -15.62199700 | 5.23083800 |
| H    | -5.06441900 | -16.56558000 | 3.74791800 |
| C    | -6.98081500 | -17.57026800 | 5.52030800 |
| H    | -7.51230800 | -15.49031900 | 5.25869300 |
| H    | -7.57773800 | -16.43691200 | 3.77764400 |
| C    | -8.38554900 | -18.05821100 | 5.89475800 |
| H    | -6.45878000 | -18.35698800 | 4.95612300 |
| H    | -6.39306000 | -17.41076600 | 6.43621900 |
| H    | -8.34557700 | -18.98289700 | 6.48324000 |
| H    | -8.92042500 | -17.38705700 | 6.49039300 |
| H    | -8.98722300 | -18.25920900 | 4.99880000 |
Additional References

S1. Z. Zhang, X. Li, T. Song, Y. Zhao and Y. Feng, *J. Med. Chem.*, **2012**, 55, 10735.

S2. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

S3. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

S4. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
Fig. S5 $^1$H (600 MHz, upper) and $^{13}$C (151 MHz, lower) NMR spectra of compound 2 in CDCl$_3$. 
Fig. S6 $^1$H (400 MHz, upper) and $^{13}$C (100 MHz, lower) NMR spectra of compound 3a in CDCl$_3$. 
Fig. S7 $^1$H (400 MHz, upper) and $^{13}$C (100 MHz, lower) NMR spectra of compound 3b in CDCl$_3$. 
Fig. S8 $^1$H (400 MHz, upper) and $^{13}$C (100 MHz, lower) NMR spectra of compound 3c in CDCl$_3$. 

3c
Fig. S9 $^1$H (600 MHz, upper) and $^{13}$C (151 MHz, lower) NMR spectra of compound 4a in CDCl$_3$. 
Fig. S10 $^1$H (600 MHz, upper) and $^{13}$C (151 MHz, lower) NMR spectra of compound 4b in CDCl$_3$. 
Fig. S11 $^1$H (600 MHz, upper) and $^{13}$C (151 MHz, lower) NMR spectra of compound 4c in CDCl$_3$. 
**Fig. S12** $^1$H (600 MHz) and $^{13}$C (151 MHz, 50°C, lower) NMR spectra of $C_4$-PicDI in CDCl$_3$. 

$C_4$-PicDI
Fig. S13 $^1$H (600 MHz, upper) and $^{13}$C (151 MHz, lower) NMR spectra of $C_8$-PicDI in CDCl$_3$. 

$C_8$-PicDI
Fig. S14 $^1$H (600 MHz, upper) and $^{13}$C (151 MHz, lower) NMR spectra of C$_{12}$-PicDI in CDCl$_3$. 

C$_{12}$-PicDI