Supplementary Information

Single-molecule rectifiers based on voltage-dependent deformation of molecular orbitals in carbazole oligomers

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Figure S1 | Scheme for the principle of the MCBJ measurement.

Figure S1 shows the experimental setup for the mechanically controllable break junction (MCBJ) measurement. Polished phosphor-bronze plates (1.2 mm × 0.5 mm, thickness: 0.1 mm) were used as bending beams. Polyimide layers with a thickness of 100 µm were formed by spin-coating commercial poly(pyromellitic dianhydride-co-4,4'-oxydianiline) in an amic acid solution (Sigma-Aldrich) followed by baking at 300 °C for 2 h. A pair of Au (30 nm)/Cr (5 nm) electrodes with a spacing of 4 µm were
formed on the polyimide film by conventional photolithography. The spacing between the Au electrodes was narrowed by the electrodeposition of Au from an electrolyte solution (TEMPELEX 8400, Electroplating Engineers of Japan, Ltd.) to form a contact. The formation of the Au contact was detected by the technique reported by Liu et al. [1].

For the MCBJ measurements, the bending beam was bent from below by a pushing rod driven by the piezoelectric stepper motor (ANPz-51, attocube). The displacement of the electrodes induced by a single step of the piezoelectric stepper motor was estimated to be ~0.04 nm from the tunnelling decay constant measured without molecules [2]. Triangular voltage waves were generated from a digital-to-analogue converter (National Instruments, PXI-4461) and applied to the junction to measure the $I-V$ characteristics. The electric current was measured by a current amplifier (FEMTO DLPCA-200). The output of the current amplifier was recorded by an analogue-to-digital converter (National Instruments, PXI-4461). The MCBJ instrument was placed in the variable-temperature insert of a cryostat (Oxford Instruments) and cooled by N$_2$ gas evaporated from liquid N$_2$. The temperature was monitored by a Si diode sensor attached to the variable temperature insert unit.
Figure S2 | Histograms of the conductance for a, HSCBZ1SH; b, HSCBZ2SH; and c, HSCBZ3SH along with the contour maps of the two-dimensional (2D) histograms of \( I_{\text{ratio}} \) calculated at and the conductance for d, HSCBZ1SH; e, HSCBZ2SH; and f, HSCBZ3SH. Note that c is a reproduction of the inset in Fig. 4a. The blue bins represent the histogram of the conductance taken without molecules. To calculate the 2D histograms, the \( I-V \) characteristics were inverted so that the \( I_{\text{ratio}} < 1 \) because the direction of the molecule, i.e. rectification is not controlled.

Figure S2 shows the histograms of the conductance and two-dimensional histograms showing the relation between \( I_{\text{ratio}} \) and the conductance values for HSCBZ1SH and HSCBZ2SH. For HSCBZ1SH, the histogram of the conductance (Fig. S2a) exhibits a peak around \( 1.2 \times 10^{-4} G_0 \) that is attributed to the SHCRZ1SH single-molecule junction. Most of the \( I-V \) characteristics observed around this conductance satisfy \( I_{\text{ratio}} \sim 1 \) (Fig. S2d). Although \( I_{\text{ratio}} < 1 \) appears around \( \sim 10^{-6} G_0 \), the asymmetrical \( I-V \) characteristics with \( 10^{-6} G_0 \) can be attributed to the tunnel junctions formed after breaking the single-molecule junctions. In these tunnel junctions, breaking one of the contacts between a molecule and the electrodes can produce a highly asymmetric junction. For HSCBZ2SH, the histogram of the conductance (Fig. S2b) exhibits peaks around \( 2 \times 10^{-5} G_0 \) and \( 2 \times 10^{-6} G_0 \) (indicated by the arrows in the figure). The lowest conductance peak, i.e. \( 2 \times 10^{-6} G_0 \) can be attributed to the conductance of the HSCBZ2SH single-molecule junctions. The \( I-V \) characteristics observed around \( 2 \times 10^{-6} G_0 \) satisfy \( I_{\text{ratio}} < 0.4 \) (Fig. S2e). For HSCBZ3SH, the histogram of the conductance (Fig. S2c) exhibits a peak around \( 2 \times 10^{-6} G_0 \), and the \( I-V \) characteristics observed around this conductance satisfy \( R_1 < 0.2 \) (Fig. S2f).
Figure S3 | An average $I$-$V$ characteristic obtained from 189 $I$-$V$ characteristics found between $G = 10^{-5.71} G_0$ and $10^{-5.85} G_0$. Asymmetry ratio measured at $V = \pm 1.3$ mV was 0.7. To calculate the average of $I$-$V$ characteristics, the $I$-$V$ characteristics were inverted so that the positive bias voltage becomes forward direction because the direction of the molecule, *i.e.* rectification is not controlled.
Details of synthesis of HSCBZnSH

1. Experimental

Chemicals. All chemicals were purchased from Kanto Kagaku Co., Ltd., TCI chemicals, Wako Pure Chemical Industries, Ltd., or Aldrich and used without further purification unless otherwise noted (solvents for the reactions were of dehydrated grade).

General. The NMR spectra were obtained using a Bruker AVANCE III 400 (400MHz. 1H NMR and 13C NMR were measured with TMS as internal standard). The HRMS (DirectProbe APCI-TOF-MS) data were obtained using a Bruker micrOTOF II in the positive ion mode. The elemental analysis was performed at the Center for Advanced Materials Analysis, Technical Department, TIT. An automated flash purification system, Isolera (Biotage), was used to isolate each compound. A preparative scale gel permeation chromatograph, LC-908 C60 (Japan Analytical Industry Co., Ltd.), was used to isolate each compound with chloroform as the eluent.

2. Synthesis

9-(tert-butyldimethylsilyl)-3-iodo-9H-carbazole (ICBZTBS)

3-iodo-9H-carbazole (8913 mg, 30.4 mmol) was dissolved in dehydrated DMF (100ml) and cooled to 0 °C. NaH (55% dispersion in paraffin, 1467 mg, 36.6 mmol) was slowly added and stirred for 45 min. tert-Butyldimethylsilyl chloride (5514mg, 36.43mol) was added in one portion. After stirring for 1h, the temperature was raised to room temperature and stirred for 2h. Toluene and NaHCO3(aq) was added to the mixture, and the aqueous layer was extracted with toluene. The organic layers were combined, dried over Na2SO4, and concentrated. The product was isolated by silica gel column chromatography (toluene: hexane= 1: 4). Yield: 26% (3242 mg, 7.96 mmol).

1H NMR (400 MHz, CD2Cl2, 300 K): δ = 8.37 (1H, d, J = 1.8 Hz), 7.99 (1H, dd, J = 7.8, 0.6 Hz), 7.63-7.59 (2H, m), 7.42-7.36 (2H, m), 7.25-7.21 (1H, m), 1.01 (9H, s), 0.74 (6H, s).

13C NMR (100 MHz, CD2Cl2, 302 K): δ = 145.63, 144.81, 133.84, 129.36, 129.02, 126.41, 125.33, 120.39, 120.27, 116.57, 114.69, 82.55, 26.70, 20.88, -1.12.

3-(4-(methylthio)phenyl)-9H-carbazole (HCBZ1SMe)

4-(Methylthio)phenylboronic Acid (518 mg, 3.08 mmol), 3-bromo-9H-carbazole (629 mg, 2.56 mmol), tetrakis(triphenylphosphine)palladium (288 mg, 0.25 mmol), and K$_2$CO$_3$ (702 mg, 5.08 mmol) was placed in a flask. The THF (10 ml), and water (5 ml) was added under nitrogen atomosphere, and stirred at reflux for 4h. The reaction mixture was extracted with toluene. The organic layers were combined, dried over Na$_2$SO$_4$, and concentrated. The product was isolated by silica gel column chromatography (toluene: hexane= 2: 1). Yield: 67% (493 mg, 1.70 mmol).

$^1$H NMR (400 MHz, Acetone-d6, 301 K): δ = 10.38 (1H, br s), 8.42 (1H, d, J = 1.8 Hz), 8.21 (1H, d, J = 7.8 Hz), 7.73-7.68 (3H, m), 7.58 (1H, d, J = 8.5 Hz), 7.53 (1H, d, J = 8.2 Hz), 7.43-7.38 (3H, m), 7.22-7.18 (1H, m), 2.54 (3H, s).

$^{13}$C NMR (100 MHz, Acetone-d6, 302K): δ = 141.59, 140.55, 139.94, 137.47, 132.39, 128.25, 127.96, 126.69, 125.55, 124.71, 124.18, 121.13, 119.85, 118.98, 112.10, 112.05, 111.90, 15.85.


Anal. Calcd. for C$_{19}$H$_{15}$NS: C, 78.86; H, 5.22; N, 4.84; S, 11.08; Found: C, 78.86; H, 5.00; N, 4.84; S, 11.16.
HCBZ1SMe (2083 mg, 7.20 mmol), ICBZTBS (3015 mg, 7.40 mmol), CuI (138 mg, 0.72 mmol), and K$_3$PO$_4$ (7961 mg, 37.5 mmol) were added to a flask, and then (±)-trans-1,2-cyclohexanediamine (133 μl, 1.11 mmol) and dioxane (40 ml) were added under a nitrogen atmosphere. After stirring for 4 h at 110 °C, the reaction mixture was cooled to room temperature. TBAF (1M THF solution, 11 ml) was added, and stirred for 20 min. Toluene and NH$_4$Cl(aq) was added to the mixture, the organic layer was separated, and the aqueous layer was extracted with toluene. The organic layers were combined, dried over Na$_2$SO$_4$, filtered through silica gel, and concentrated. The product was isolated by Flash silicagel chromatography (toluene: hexane= 1:5 →10:0). Yield: 87 % (2843 mg, 6.25 mmol).

1H NMR (400 MHz, CD$_2$Cl$_2$, 301 K): δ = 8.39 (2H, d, J = 1.5 Hz), 8.24-8.22 (2H, m), 8.06 (1H, d, J = 7.8 Hz), 7.69-7.63 (4H, m), 7.58-7.53 (2H, m), 7.50-7.46 (1H, m), 7.43-7.41 (3H, m), 7.37 (2H, dt, J = 8.7, 2.1 Hz), 7.32-7.24 (2H, m), 2.53 (3H, s).

13C NMR (100 MHz, CD$_2$Cl$_2$, 302K): δ = 142.85, 141.83, 140.76, 139.27, 139.18,

Anal. Calcd. for C_{31}H_{22}N_{2}S: C, 81.91; H, 4.88; N, 6.16; S, 7.05. Found: C, 81.83; H, 4.62; N, 6.05; S, 6.97.

HCBZ3SMe

As per the general procedure for the N-arylation reaction and TBS cleavage, H2SMe (2307 mg, 5.07 mmol), ICBZTBS (2265 mg, 5.56 mmol), CuI (95.2 mg, 0.50 mmol), K_{3}PO_{4} (5345 mg, 25.2 mmol), (±)-trans-1,2-cyclohexanediamine (91 μl, 0.76 mmol), and dioxane (30 ml) were heated in an oil bath at 110 ºC for 12h. After cooling to room temperature, TBAF (1 M THF solution, 9 ml) were added, and stirred for 15min. The product was isolated by preparative GPC (eluent: chloroform). Yield: 90 % (2836 mg, 4.58 mmol).

1H NMR (400 MHz, CD_{2}Cl_{2}, 301 K): δ = 8.44 (1H, s), 8.40 (1H, d, J = 1.5 Hz), 8.33 (2H, dd, J = 10.9, 1.7 Hz), 8.23 (1H, d, J = 7.8 Hz), 8.17 (1H, d, J = 7.8 Hz), 8.10 (1H, d, J = 7.8 Hz), 7.73-7.63 (5H, m), 7.59-7.56 (3H, m), 7.52-7.41 (6H, m), 7.37 (2H, dt, J = 8.7, 2.1 Hz), 7.33-7.28 (3H, m), 2.54 (3H, s).

13C NMR (100 MHz, CD_{2}Cl_{2}, 302K): δ = 143.13, 142.89, 141.86, 141.57, 140.80, 139.35, 139.30, 137.15, 132.73, 129.89, 129.51, 127.91, 127.56, 127.08, 127.01, 126.55, 125.71, 125.67, 125.46, 124.85, 124.49, 124.07, 123.59, 123.38, 123.12, 120.95, 120.90, 120.68, 120.45, 120.34, 120.19, 119.89, 119.68, 118.69, 112.32, 111.47, 111.42, 110.68, 110.62, 110.47, 16.27.


Anal. Calcd. for C_{43}H_{29}N_{3}S: C, 83.33; H, 4.72; N, 6.78; S, 5.17. Found: C, 83.33; H, 4.63; N, 6.56; S, 5.08.

MeSCBZ1SMe

As per the general procedure for the N-arylation reaction, HCBZ1SMe (207 mg, 0.72 mmol), 4-iodothioanisole (343 mg, 1.37 mmol), CuI (13.4 mg, 0.07 mmol), K_{3}PO_{4} (460 mg, 2.17 mmol), (±)-trans-1,2-cyclohexanediamine (12.4 μl, 0.10 mmol), and dioxane (4 ml) were heated in an oil bath at 110 ºC for 12h. The product was isolated by Flash silicagel chromatography (toluene: hexane= 1:10 →2:1). Yield: 77 % (229 mg, 0.56 mmol).

1H NMR (400 MHz, CD_{2}Cl_{2}, 301K): δ = 8.35 (1H, d, J = 1.6 Hz), 8.18 (1H, d, J = 7.8 Hz), 7.68-7.63 (3H, m), 7.50 (4H, s), 7.45-7.40 (3H, m), 7.37 (2H, dt, J = 8.7, 2.1 Hz), 7.32-7.28 (1H, m), 2.58 (3H, s), 2.53 (3H, s).

13C NMR (100 MHz, CD_{2}Cl_{2}, 302K): δ = 141.88, 140.84, 139.09, 138.74, 137.29,
SMeCBZ2SMe

As per the general procedure for the N-arylation reaction, HCBZ2SMe (311 mg, 0.68 mmol), 4-iodothioanisole (342 mg, 1.37 mmol), CuI (11.9 mg, 0.06 mmol), K,PO₄ (452 mg, 2.13 mmol), (±)-trans-1,2-cyclohexanediamine (11.9 µl, 0.10 mmol), and dioxane (4 ml) were heated in an oil bath at 110 ºC for 12h. The product was isolated by Flash silicagel chromatography (toluene: hexane= 1:8 →10:0). Yield: 56 % (219 mg, 0.38 mmol).

1H NMR (400 MHz, CD₂Cl₂, 300K): δ = 8.39 (1H, d, J = 1.6 Hz), 8.31 (1H, d, J = 1.4 Hz), 8.23 (1H, d, J = 7.8 Hz), 8.13 (1H, d, J = 7.8 Hz), 7.68-7.63 (3H, m), 7.60-7.51 (6H, m), 7.50-7.40 (5H, m), 7.37 (2H, d, J = 8.4 Hz), 7.33-7.29 (2H, m), 2.60 (3H, s), 2.53 (3H, s).

13C NMR (100 MHz, CD₂Cl₂, 301K): δ = 142.80, 142.16, 141.77, 140.58, 139.24, 139.18, 137.16, 134.65, 132.76, 130.19, 128.15, 127.96, 127.89, 127.53, 127.10, 126.55, 125.74, 125.46, 124.76, 124.08, 123.60, 123.32, 120.95, 120.75, 120.68, 120.23, 119.70, 118.69, 111.30, 110.56, 110.51, 110.41, 16.25, 16.09


MeSCBZ3SMe

As per the general procedure for the N-arylation reaction, HCBZ3SMe (311 mg, 0.50 mmol), 4-iodothioanisole (259 mg, 1.04 mmol), CuI (9.58 mg, 0.05 mmol), K,PO₄ (308 mg, 1.45 mmol), (±)-trans-1,2-cyclohexanediamine (8.72 µl, 0.07 mmol), and dioxane (3 ml) were heated in an oil bath at 110 ºC for 12h. The product was isolated by Flash silicagel chromatography (toluene: hexane= 1:8 →10:0). Yield: 68 % (251 mg, 0.34 mmol).

1H NMR (400 MHz, CD₂Cl₂, 301K): δ = 8.40-8.38 (2H, m), 8.36 (1H, d, J = 1.8 Hz), 8.23 (1H, d, J = 7.8 Hz), 8.17 (2H, dt, J = 7.8, 0.9 Hz), 7.70-7.63 (5H, m), 7.62-7.52 (6H, m), 7.47-7.44 (7H, m), 7.39-7.29 (5H, m), 2.61 (3H, s), 2.54 (3H, s).

13C NMR (100 MHz, CD₂Cl₂, 302K): δ = 143.10, 142.89, 142.23, 141.86, 141.53, 140.77, 139.30, 139.28, 137.15, 134.63, 132.74, 129.97, 129.95, 128.18, 128.00, 127.90, 127.56, 127.19, 127.04, 126.55, 125.79, 125.70, 125.47, 124.86, 124.53, 124.07, 123.60, 123.32, 123.16, 120.98, 120.92, 120.82, 120.68, 120.50, 120.20,
119.85, 119.71, 118.69, 111.44, 111.42, 110.66, 110.61, 110.57, 110.47, 16.27, 16.10.

Anal. Calcd. for C_{50}H_{35}N_{3}S_{2}: C, 80.94; H, 4.75; N, 5.66; S, 8.64. Found: C, 80.95; H, 4.43; N, 5.61; S, 8.89.

HSCBZ1SH (General procedure for deprotection of S-methyl group).

NeSCBZ1SMe (79.7 mg, 0.19 mmol), t-BuSNa (102 mg, 0.91 mmol), DMF (2 ml) were heated for 4 h at 165 °C. 3M HCl (aq., 4 ml) was added under nitrogen flow at 0 °C. The reaction mixture was extracted with chloroform, dried over Na_{2}SO_{4}, and concentrated. The product was isolated by Flash silicagel chromatography (toluene: hexane= 1:12 →1:1 with 5% AcOH). Yield: 58 % (29 mg, 0.11 mmol).

^{1}H NMR (400 MHz, CDCl_{3}, 302K): δ = 8.29 (1H, d, J = 1.8 Hz), 8.16 (1H, d, J = 7.7 Hz), 7.61-7.56 (3H, m), 7.51 (2H, dt, J = 8.7, 2.2 Hz), 7.45-7.36 (7H, m), 7.32-7.28 (1H, m), 3.62 (1H, s), 3.49 (1H, s).

^{13}C NMR (100 MHz, CDCl_{3}, 302K): δ = 141.35, 140.37, 139.62, 135.42, 132.74, 130.91, 130.41, 130.11, 128.71, 127.92, 127.76, 126.28, 125.24, 124.00, 123.48, 120.42, 120.25, 118.56, 109.97, 109.85.

Anal. Calcd. for C_{24}H_{17}NS_{2}: C, 75.16; H, 4.47; N, 3.65; S, 16.72. Found: C, 75.00; H, 4.48; N, 3.52; S, 16.89.

HSCBZ2SH

As per the general procedure for the N-arylation reaction, NeSCBZ2SMe (92.8 mg, 0.16 mmol), t-BuSNa (87.3 mg, 0.78 mmol), were added to a flask, and then DMF (2 ml) were added under a nitrogen atmosphere. After stirring for 4 h at 165 °C, the reaction mixture was cooled to 0 °C and stirred for 45 minutes. Then, 3M HCl (aq., 2.7 ml) was added under nitrogen flow. The product was isolated by Flash silicagel chromatography (toluene: hexane= 1:9 →4:1 with 5% AcOH). Yield: 65 % (57 mg, 0.10 mmol).

^{1}H NMR (400 MHz, CD_{2}Cl_{2}, 301K): δ = 8.37 (1H, d, J = 1.5 Hz), 8.29 (1H, dd, J = 1.6, 0.8 Hz), 8.21 (1H, d, J = 7.7 Hz), 8.11 (1H, d, J = 7.8 Hz), 7.61 (3H, dt, J = 8.6, 2.0 Hz), 7.57-7.49 (6H, m), 7.47-7.36 (7H, m), 7.31-7.29 (2H, m), 3.74 (1H, s), 3.57 (1H, s).

^{13}C NMR (100 MHz, CD_{2}Cl_{2}, 301K): δ = 142.79, 142.04, 141.81, 140.46, 139.92, 135.42, 132.55, 131.46, 131.16, 130.29, 130.23, 129.19, 128.20, 128.15, 127.14, 126.58, 125.75, 125.43, 124.81, 124.07, 123.58, 123.36, 120.96, 120.83, 120.68, 120.26, 119.71, 118.72, 111.25, 110.56, 110.46, 110.41.

Anal. Calcd. for C_{36}H_{24}N_{2}S_{2}: C, 78.80; H, 4.41; N, 5.11; S, 11.69. Found: C, 78.40; H, 4.61; N, 4.77; S, 11.45.
HSCBZ3SH

As per the general procedure for the N-arylation reaction, MeSCBZ3SMe (47.8 mg, 0.064 mmol), t-BuSNa (37.8 mg, 0.34 mmol), were added to a flask, and then DMF (1 ml) were added under a nitrogen atmosphere. After stirring for 4 h at 165 °C, the reaction mixture was cooled to 0 °C and stirred for 45 minutes. Then, 3M HCl (aq., 4 ml) was added under nitrogen flow. The product was isolated by reprecipitation of the chloroform solution of the extracts from MeOH. Yield: 77 % (35 mg, 0.049 mmol).

$^1$H NMR (400 MHz, CD$_2$Cl$_2$, 301K): $\delta = 8.38$ (2H, d, $J = 1.4$ Hz), 8.35 (1H, d, $J = 1.8$ Hz), 8.23 (1H, d, $J = 7.7$ Hz), 8.16 (2H, dd, $J = 7.7$, 2.8 Hz), 7.66-7.53 (11H, m), 7.51-7.43 (7H, m), 7.39 (2H, d, $J = 8.3$ Hz), 7.35-7.29 (3H, m), 3.76 (1H, s), 3.59 (1H, s).

$^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, 302K): $\delta = 143.07$, 142.88, 142.11, 141.91, 141.51, 140.65, 139.98, 135.42, 132.52, 131.56, 131.20, 130.31, 130.03, 129.92, 129.17, 128.25, 128.17, 127.23, 127.04, 126.58, 125.81, 125.69, 125.44, 124.92, 124.53, 124.07, 123.57, 123.36, 123.15, 121.00, 120.92, 120.90, 120.68, 120.51, 120.22, 119.86, 119.70, 118.73, 111.40, 110.64, 110.62, 110.52, 110.47.


Anal. Calcd. for C$_{48}$H$_{31}$N$_3$S$_2$: C, 80.76; H, 4.38; N, 5.89; S, 8.98 Found: C, 80.73; H, 4.47; N, 5.75; S, 9.20.
3. NMR spectra

Figure S1. $^1$H NMR spectrum of ICBZTBS.
Figure S2. $^{13}$C NMR spectrum of ICBZTBS.
Figure S3. $^1$H NMR spectrum of HCBZ1SMe.
Figure S4. $^{13}$C NMR spectrum of HCBZ2SMe.
Figure S5. $^1$H NMR spectrum of HCBZ2SMe.
Figure S6. $^{13}$C NMR spectrum of HCBZ2SMe.
Figure S7. $^1$H NMR spectrum of HCBZ3SMe.
Figure S8. $^{13}$C NMR spectrum of HCBZ3SMe.
Figure S9. $^1$H NMR spectrum of MeSCBZ1SMe.
Figure S10. $^{13}$C NMR spectrum of MeSCBZ1SMe.
Figure S11. $^1$H NMR spectrum of MeSCBZ2SMe.
Figure S12. $^{13}$C NMR spectrum of MeSCBZ2SMe.
Figure S13. $^1$H NMR spectrum of MeSCBZ3SMe.
Figure S14. $^{13}$C NMR spectrum of MeSCBZ3SMe.
Figure S15. $^1$H NMR spectrum of HSCBZ1SH.
Figure S16. $^{13}$C NMR spectrum of HSCBZ1SH.
Figure S17. $^1$H NMR spectrum of HSCBZ2SH.
Figure S18. $^{13}$C NMR spectrum of HSCBZ2SH.
Figure S19. $^1$H NMR spectrum of HSCBZ3SH.
Figure S20. $^{13}$C NMR spectrum of HSCBZ3SH.
References
