

OFET performance of low-symmetric 5-TIPS-ethyny-15-TMS-ethynyl-tetrabenzoporphyrins in the single crystal states

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ABSTRACT: To achieve the high charge carrier mobility of small molecular organic semiconductors, a molecular design strategy for controlling the packing structure of two-dimensional (2D) π -extended organic semiconductors in single crystal is essential. Although tetrabenzoporphyrin (**BP**) is one of the promising organic semiconductors, the control of the packing structure is still challenging. To improve the low solubility of 5,15-bis(trimethylsilyl-ethynyl)-tetrabenzoporphyrin (**TMS-BP**) and the crystal polymorph of 5,15-bis(trimethylisopropylsilyl-ethynyl)-tetrabenzoporphyrin (**TIPS-BP**), 5-triisopropylsilylethynyl-15-trimethylsilylethynyl-tetrabenzoporphyrin (**TIPS-TMS-BP**) with different substituents at *meso*-positions was synthesized. **TIPS-TMS-BP** gave herringbone structure of antiparallel slipped-stack dimers in single crystals. The single crystal field effect transistors exhibit a high hole mobility of $1.65 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in parallel to π - π stacking direction and moderate $0.37 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in perpendicular to π - π stacking direction.

KEYWORDS: Benzoporphyrin, Organic semiconductor, Substituent effect, Single crystal structure, Organic field effect transistor

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INTRODUCTION

Organic semiconductors have been expected as light-weight and flexible materials. Especially, small-molecular organic semiconductors are attractive as organic field-effect transistor (OFET) materials with high charge carrier mobility and stability due to its good crystallinity compared to the polymer materials.[1-3] Tetrabenzoporphyrin (**BP**) is one of the promising organic semiconductors with similar framework with phthalocyanine.[4-13] Since the solubility of **BP** in common organic solvents is very low,[14-16] a synthesis route of unsubstituted **BP** via soluble precursor, bicyclo[2.2.2]octadiene-fused porphyrin (**CP**), by retro-Diels–Alder reaction was reported in 1998.[17] Since the retro-Diels–Alder reaction proceeds quantitatively, the spin-coating of **CP** on the substrate, followed by heating to 180–200 °C, gave a polycrystalline film of **BP** with OFET hole carrier mobility (μ_h) of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ order.[4-13]

In 2006, 5,15-bis(trimethylsilyl-ethynyl)-tetrabenzoporphyrin (**TMS-BP**) was designed for the direct solution process (Chart 1), but the solubility in common organic solvents was not enough to fabricate the thin film by direct spin-coating of **TMS-BP**. [18-20] In 2017, 5,15-bis(triisopropylsilyl-ethynyl)-tetrabenzoporphyrin (**TIPS-BP**) was reported as a soluble **BP**. [21] **TIPS-BP** had crystal polymorph to afford two-type of packing structures, brickwork-type and one-dimensional (1D)-packing structure, depending on the deposition condition of the film. The μ_h for the brickwork structure prepared by dip-coating method was $1.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and 1D-packing structure prepared by drop-casting method was $0.018 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. **TIPS-BP** afforded $2.7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as a single crystal (SC)-FET with a 1D-packing structure,[22] and $\mu_h = 6.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with the droplet-pinned crystallization (DPC) method with annealing at 140 °C, whereas TIPS-pentacene showed $3.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at the same condition.[23] Thus, **TIPS-BP** was found to have a comparable potential with TIPS-pentacene.

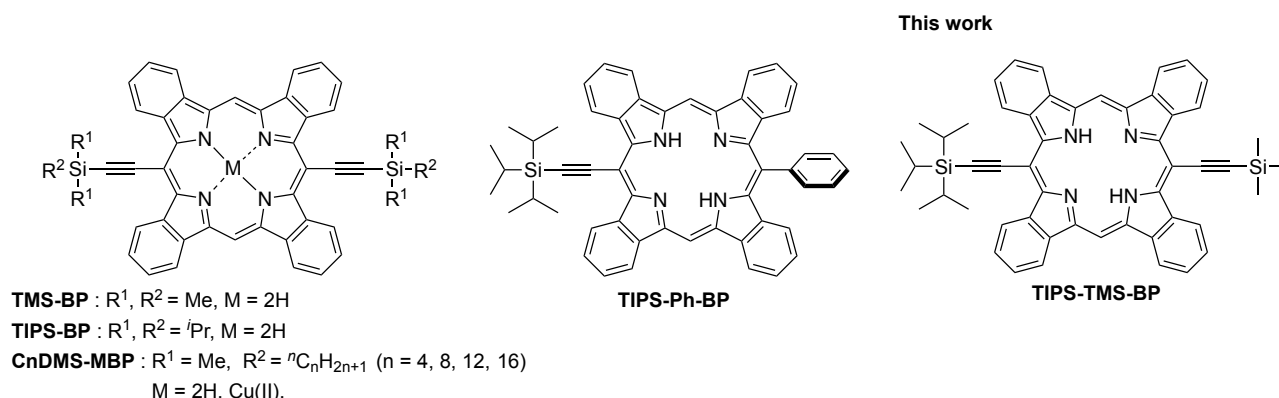


Chart 1 BP-based organic semiconductors

Although **TIPS-BP** is promising organic semiconductor, it is still difficult to control the packing structure of the crystals. To understand the correlation between the OFET performance and the packing structure, several **BP** derivatives with substituents at 5,15-positions have been investigated. 5,15-Bis(dimethyl-*n*-alkylsilyl-ethynyl)-tetrabenzoporphyrin (**CnDMS-BP**), where Cn is C4 (*n*-C₄H₉), C8 (*n*-C₈H₁₇), C12 (*n*-C₁₂H₂₅), and C16 (*n*-C₁₆H₃₃), afforded thermally stable herringbone structure.[24] The best OFET performance of dip-coated film was obtained for copper complexes of **C8-** and **C12DMS-BP** as $4.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Transfer integrals of *b*-axis was close to 100 meV, which suggested the strong interaction between porphyrin planes.

Low-symmetric 5-triisopropylsilylethynyl-15-phenyl-tetrabenzoporphyrin (**TIPS-Ph-BP**) showed the antiparallel dimeric packing with greatly deflected porphyrin rings because of the large size difference of TIPSethynyl and phenyl groups.[25] The aryl groups at *meso*- positions were perpendicular to the porphyrin plane, disturbing the strong π -stacks

of porphyrins, and the overlap of porphyrin planes are small due to the existence of phenyl groups. The transfer integral values in one-direction was alternative that's why the SC-FET charge carrier mobility was $0.71 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Here, 5-triisopropylsilylethynyl-15-trimethylsilylethynyl-tetrabenzoporphyrin (**TIPS-TMS-BP**) was designed to control the packing structure in crystal and to improve the solubility. We selected non-aromatic different substituents at 5- and 15-positions: a combination of TIPS-ethynyl group and TMS-ethynyl group. **TIPS-TMS-BP** is expected to have the advantage of **TMS-BP** and **TIPS-BP**. Because both of the TIPS and TMS groups are attached to the porphyrin backbone via ethyne bridges, there is less imbalance in packing in the crystal than in **TIPS-Ph-BP** to give high charge carrier mobilities. The synthesis, packing structure and charge carrier mobility of **TIPS-TMS-BP** will be discussed in detail.

EXPERIMENTAL

General: All reagents and solvent were purchased from FUJIFILM Wako, Kanto Chemical, Nacalai Tesque, Tokyo Chemical Industry (TCI), or Sigma-Aldrich, and were used without further purification. Thin layer chromatography (TLC), gravity column chromatography, and alumina column chromatography were performed on Art. 105554 (Merck KGaA) silica gel plates, silica gel 60N (Kanto Chemical), and Aluminium oxide 90 active neutral (Sigma-Aldrich) respectively. Recycling preparative GPC-HPLC was performed on a Japan Analytical Industry LC-9225NEXT equipped with a series of JAIGEL-1H and 2H ($\Phi 40 \text{ mm}$, CHCl_3 eluent, flow rate; 6.0 mL/min). ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance NEO 400, or a Bruker Avance III 800 spectrometer at ambient temperature. Chemical shifts of ^1H and ^{13}C signals are quoted to tetramethylsilane ($\delta = 0.00 \text{ ppm}$) as an internal standard). High resolution mass spectra (HR-MS) were collected by a Bruker solarix FT-ICR (MALDI) instrument. UV-Vis absorption spectra were measured using a JASCO UV/Vis/NIR spectrophotometer V-670. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) was performed on an ALS 621E electrochemical analyzer and a three-electrode cell equipped with a glassy carbon electrode, a Pt wire, and an Ag/AgNO_3 (0.1 M in CH_3CN) electrode as a working, a counter, and a reference electrode, respectively. X-ray diffraction (XRD) data were collected on a Rigaku XtaLAB Synergy (1.2 kW), using $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ \AA}$). Out-of-plane XRD measurements of the single crystals for FET were performed using a Rigaku SmartLab X-ray diffractometer with a Cu-K α source ($\lambda = 1.5418 \text{ \AA}$) in the θ - 2θ scan mode at scattering angles of 2 - 30° .

Synthesis:

Bicyclo[2.2.2]octadiene-fused 5-triisopropylsilylethynyl-15-trimethylsilylethynyl-porphyrin (TIPS-TMS-CP): A solution of bicyclo[2.2.2]octadiene-fused dipyrromethane (**1**, 524.8 mg, 1.74 mmol) in MeOH (210 mL) was deoxygenated by bubbling of argon gas for 20 min. After an addition of 3-(triisopropylsilyl)propionaldehyde (**2**, 220.2 mg, 1.05 mmol) and 3-(trimethylsilyl)propionaldehyde (**3**, 134.5 mg, 1.06 mmol), boron trifluoride diethyl ether complex ($\text{BF}_3 \cdot \text{OEt}_2$, 0.065 mL, 0.52 mmol) was added dropwise to the mixture at 0°C . The resulting mixture was stirred for 3 hours at 0°C . 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ, 786 mg, 3.46 mmol) was added to the mixture and the solution was stirred for 9 h at room temperature. Then, the solvent was removed under reduced pressure. The residue was purified by alumina column chromatography (CHCl_3), silica gel column chromatography (CHCl_3) and GPC (CHCl_3) to give **TIPS-TMS-CP** as a purple solid in 4.8% yield (37.5 mg, 41.7 μmol). Note that these products were isolated as a mixture of stereoisomers regarding orientation of the bicyclo[2.2.2]octadieno units. **TIPS-TMS-CP:** ^1H NMR (400 MHz, CDCl_3 , δ): 10.22 (s, 2H), 7.09 – 7.04 (m, 8H; Ar-H), 6.63 (s, 2H; Ar-H), 6.52 (s, 2H; Ar-H), 5.69 (s, 2H; Ar-H), 2.17 – 1.89 (m, 16H; CH_2), 1.70 – 1.62 (m, 3H; CH), 1.51 – 1.50 (m, 18H; CH_3), 0.69 (s, 9H; CH_3), -2.96 (s,

1H; *NH*), −3.01 (s, 1H; *NH*), as shown in Figure S12; ¹³C NMR (200 MHz, CDCl₃, δ): 151.6, 151.5, 151.5, 148.1, 148.1, 148.1, 148.0, 142.1, 141.9, 137.3, 137.3, 137.2, 136.4, 136.4, 136.1, 136.0, 109.0, 107.8, 104.3, 104.2, 100.7, 98.9, 98.8, 98.8, 98.1, 97.6, 96.8, 38.5, 38.4, 38.4, 38.3, 36.2, 36.1, 29.7, 27.3, 27.3, 27.2, 27.0, 26.9, 19.0, 12.0, as shown in Figure S13; Peak of methyl carbon of trimethylsilyl group is not observed because of the presence of tetramethylsilane. HRMS (MALDI) *m/z*: [M]⁺ calcd. for C₆₀H₆₆N₄Si₂, 898.48205; found, 898.48102, as shown in Figure S16.

5-Triisopropylsilylethynyl-15-trimethylsilylethynyl-tetrabenzoporphyrin (TIPS-TMS-BP): TIPS-TMS-CP (13.7 mg, μmol) was heated at 200 °C for 1 hour under vacuum in a glass tube oven to give **TIPS-TMS-BP** as a dark purple solid in 98% yield (11.8 mg, 15 μmol). **TIPS-TMS-BP** was further purified by recrystallization with CHCl₃ and octane to provide a highly pure material for photophysical measurements and fabrications of OFETs. ¹H NMR (400 MHz, CDCl₃, δ): 10.41 (d, *J* = 8 Hz, 2H; Ar-*H*), 10.24 (s, 2H, Ar-*H*), 10.06 (d, *J* = 7 Hz, 2H; Ar-*H*), 9.28 (d, *J* = 7 Hz, 2H; Ar-*H*), 9.24 (d, *J* = 7 Hz, 2H; Ar-*H*), 8.13 – 7.95 (m, 8H; Ar-*H*), 1.80 – 1.71 (m, 3H; *CH*), 1.59 (d, *J* = 7 Hz, 18H; *CH*₃), 0.81 (s, 9H; *CH*₃), −2.19 (s, 1H; *NH*), −2.41 (s, 1H; *NH*), as shown in Figure S14; ¹³C NMR (200 MHz, CDCl₃, δ): 143.2, 142.5, 138.5, 138.2, 137.1, 135.7, 135.3, 127.3, 127.2, 127.2, 126.0, 125.4, 120.7, 120.5, 108.8, 107.4, 106.9, 105.0, 95.3, 94.7, 93.5, 19.3, 12.2, 0.3; Peak of methyl carbon of trimethylsilyl group is not observed because of the presence of tetramethylsilane, as shown in Figure S15. HRMS (MALDI) *m/z*: [M]⁺ calcd. or C₅₂H₅₀N₄Si₂, 786.35685; found, 786.35552, as shown in Figure S17. CCDC 2410764.

Fabrication and evaluation of organic field-effect transistors: All OFET devices were fabricated in a top-contact bottom-gate configuration on a heavily n-doped Si wafer with a 300 nm-thick thermally grown SiO₂ layer (C_i = 11.5 nF cm^{−2}). The Si/SiO₂ substrates were cleaned with deionized water, acetone, and 2-propanol for 10 min each in an ultrasonic bath. Substrates were dried with a flow of N₂ gas and then treated by UV–O₃ cleaner (Filgen UV253V8) for 45 min. Single crystals for FET measurements were prepared as follows: 0.25 mL of chlorobenzene solution (0.25 g L^{−1}) of **TIPS-TMS-BP** was dropped on UV–O₃-treated Si/SiO₂ substrate and kept in *n*-octane vapor for 1 day at room temperature. Then, the source and drain electrode of Au (30 nm) were vacuum-deposited at 0.1 Å s^{−1} under the pressure of 5 × 10^{−4} Pa through a shadow mask on the active layer. The drain–source channel length (*L*) and width (*W*) of each device were measured independently using Zeiss Axio Scope.A1 optical microscope. The output and transfer characteristics of the OFETs were measured using a Thermal Block SB-MCPS-NAT prober system and a Keithley 2400 source measure unit at room temperature under air atmosphere. The field-effect hole mobilities (μ_h) of the OFETs were determined from the forward transfer curve in the saturation regime (*V*_{DS} = −80 V) using the following equation:

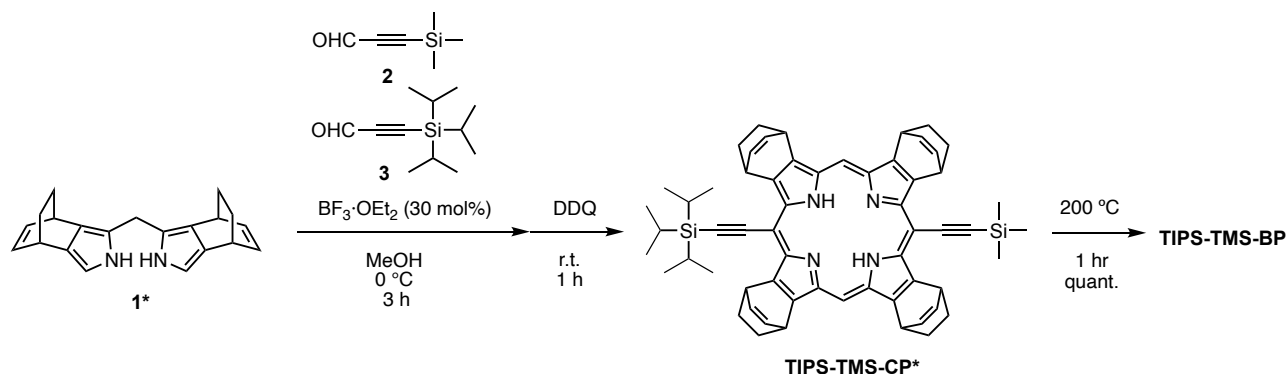
$$I_{DS} = (\mu W C_i / 2L) (V_G - V_{th})^2 \quad (1)$$

where *I*_{DS} is the drain–source current and *V*_{DS}, *V*_G, and *V*_{th} are the drain–source voltage, gate voltage, and threshold voltage, respectively. The on/off current ratios (*I*_{on}/*I*_{off}) were determined from the *I*_{DS} at *V*_G = 0 V (*I*_{off}) and *V*_G = −80 V (*I*_{on}).

RESULTS AND DISCUSSION

Synthesis and Characterization

The precursor, **TIPS-TMS-CP**, was prepared from dipyrromethane **1** and two kinds of aldehydes, **2** and **3**, by acid-catalyzed condensation and oxidation in 4.8% yield as described in Experimental section (Scheme 1). **TIPS-TMS-CP** was heated at 200 °C for 1 hour in a glass tube oven under vacuum to afford **TIPS-TMS-BP**. The obtained derivatives were characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and high-resolution mass spectroscopy (Figures S12–17).



Scheme 1. Synthesis scheme of **TIPS-TMS-BP** via **TIPS-TMS-CP**. * is a mixture of stereoisomers.

The UV-visible absorption spectrum of **TIPS-TMS-BP** was measured in CH_2Cl_2 (Figure 1). The Soret bands in absorption spectrum was observed at 461 nm with shoulder at 451 nm, and Q bands was at 710, 626 and 583 nm for the **TIPS-TMS-BP**. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of **TIPS-TMS-BP** was also measured to reveal the substitution effect on the electrochemical property (Figure 2 and S1). These porphyrins showed two reversible oxidation waves (E_{ox}) and one reduction waves (E_{red}): $E_{\text{ox}} = -0.05$ and 0.41 V (vs. Fc/Fc^+) and $E_{\text{red}} = -1.48$ V (vs. Fc/Fc^+) for **TIPS-TMS-BP**. These values are similar with those of **TIPS-BP**: $E_{\text{ox}} = 0.04$ and 0.33 V (vs. Fc/Fc^+) and $E_{\text{red}} = -1.47$ V (vs. Fc/Fc^+).

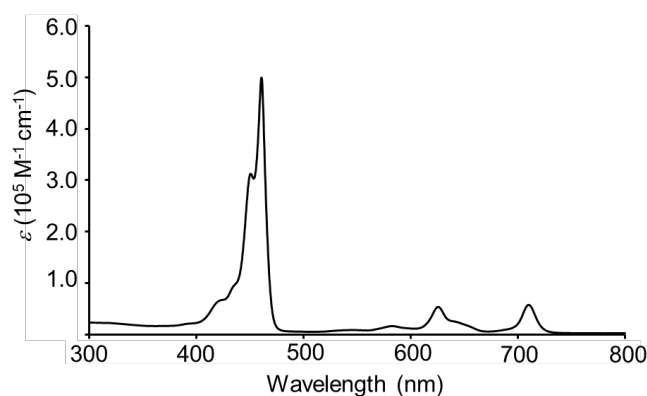


Figure 1. UV-vis absorption spectrum of **TIPS-TMS-BP** in CH_2Cl_2 .

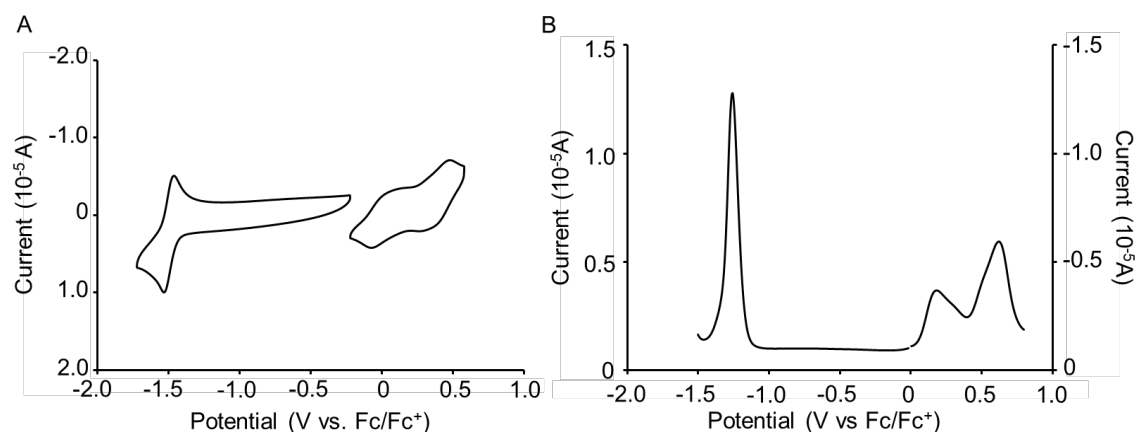


Figure 2. (A) Cyclic voltammogram and (B) DPV of **TIPS-TMS-BP**. Solvent: dichloromethane, electrolyte: 0.1 M *n*-Bu₄NPF₆, working electrode: glassy carbon; counter electrode: Pt wire, reference electrode: Ag/AgNO₃ (0.1M in CH₃CN) electrode; scan rate: 0.1 V s⁻¹.

X-ray single crystal structure analyses of TIPS-TMS-BP.

The platelet crystals of **TIPS-TMS-BP** were obtained by the recrystallization from toluene and *n*-octane using a vapor diffusion method (Figure S1). In Figure 3 and Table S1, the single crystal structure and data of **TIPS-TMS-BP** are shown. There are very similar two types of porphyrins, I and II (Figure S2). Each porphyrin is gently sigmoidal in shape and the angles between benzene rings are 11.1° and 11.4°, respectively (Figure 3, S4 and S5). They are arranged in a unidirectional slip-packed column, column 1 and 2, along the *a*-axis. In each column, TMS and TIPS groups are alternatively arranged along *c*-axis (Figure 3). Each column has two kinds of pairs: pairs A and B for porphyrin I (Figure 3 and S3) and pairs C and D for porphyrin II (Figure S4). The distance and the overlap between the π -planes of the pairs A and B as well as of C and D are different. The distance between the porphyrins are shown in Figure 3B and S5. In Pair A, half of the porphyrin framework is overlapped and the distance is 3.27 Å. In Pair B only a benzopyrrole moiety is overlapped and the distance between the benzopyrrole planes is 3.30 Å. This trend is similar to porphyrin II, and the distance between overlapping part is 3.26 Å for Pair C and 3.30 Å for Pair D. These distances are shorter than those of **TIPS-Ph-BP**, 3.40 and 3.43 Å [25]. The columns I and II are arranged in herringbone packing by CH- π interaction. Therefore the charge carrier mobilities are expected mainly in *a*-axis direction, but also in *b*-axis direction.

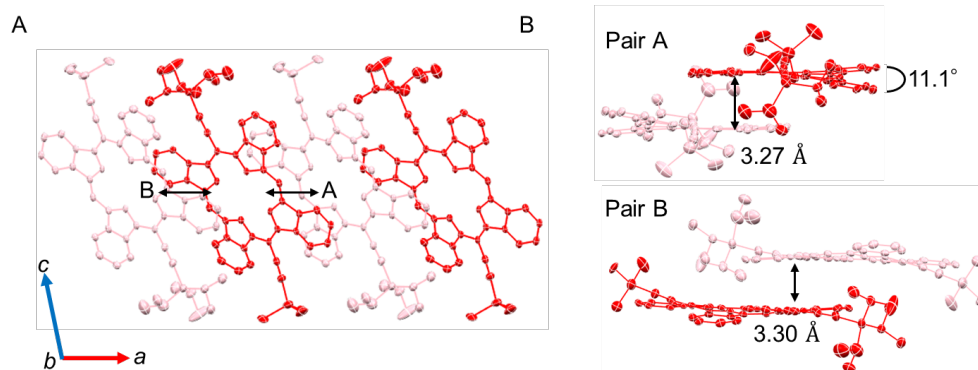


Figure 3. Crystal structures of **TIPS-TMS-BP**: (A) π -stacking structure of porphyrin I viewed along the *b*-axis, and (B) Two types of π -stacking structures of porphyrin I, Pair A and B, observed in column 1 in the crystal of **TIPS-TMS-BP**. Hydrogen atoms are omitted for clarity.

Charge transfer integrals (t_{HOMO}) values were calculated using the single crystal structure data and summarized in Figure S5 and Table S2.[27] The t_{HOMO} values of pairs A and B in column I are 112.6 meV and 32.7 meV, while t_{HOMO} of pairs C and D are 110.6 meV and 33.7 meV, respectively. The t_{HOMO} value between porphyrin I and II is 14.2 meV. Since there are large difference of t_{HOMO} values between intra-column and inter-column, anisotropy of charge carrier mobility is expected.

The packing structure of **TIPS-TMS-BP** is similar to **TIPS-Ph-BP**, an *anti*-parallel dimer, which are packed in herringbone structure. However, in **TIPS-Ph-BP**, TIPS-ethynyl group is largely bended from the porphyrin plane due to the different size of TIPS-ethynyl group and phenyl group at *meso*-position. The t_{HOMO} values of **TIPS-Ph-BP** in the direction in column is 62.3 and 15.9 meV, about half of **TIPS-TMS-BP**. One of the reasons is the distance between porphyrins in column: 3.40 and 3.43 Å for **TIPS-Ph-BP**, while 3.26 or 3.27 and 3.30 Å for **TIPS-TMS-BP**. The distances are similar to that of **TIPS-BP**[23], but due to the asymmetric substitution, the packing is not balanced.

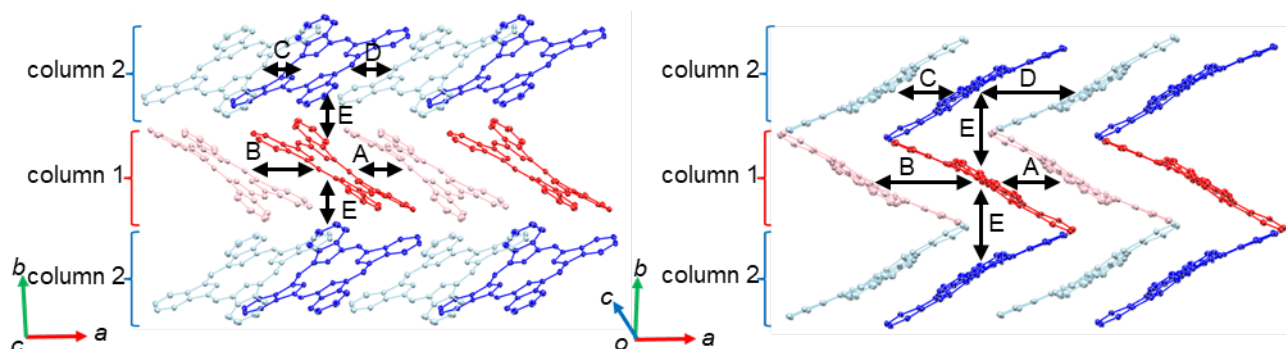


Figure 4. Packing structure of **TIPS-TMS-BP**. Substituents and hydrogen atoms are omitted for clarity.

Out-of-plane XRD

Out-of-plane XRD profiles of single crystals prepared for SC-FET were measured (Figure 5 and S8, 9). **TIPS-TMS-BP** showed clear peaks of (00*l*) with interplanar spacing (d) = 20.0 Å. The peaks agreed well with the simulated (00*l*) peaks from single crystal data with 19.8 Å. Face index analysis of **TIPS-TMS-BP** based on the single crystal X-ray crystallography revealed that the crystal face with the largest area of the platelet crystal corresponds to the (001) face. This result suggests that the crystallographic *ab* plane, which contains π -stacking direction, is parallel to the substrate and current flow direction (Figure S7, S8).

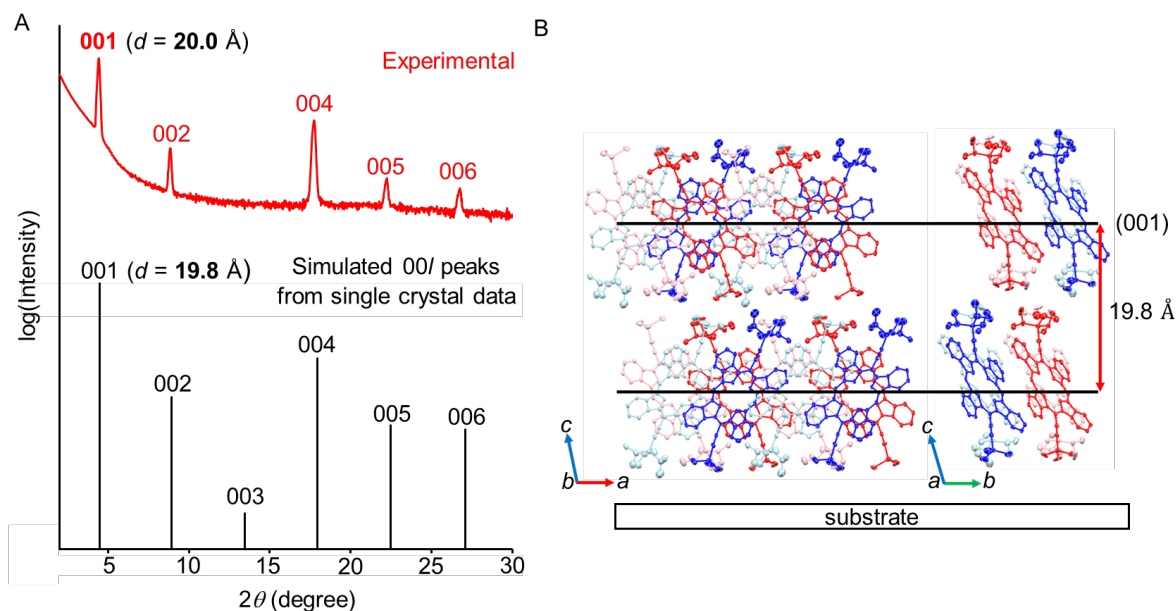


Figure 5. (A) Out-of-plane XRD profiles of single crystals for SC-FET; **TIPS-TMS-BP**, (B) Packing structure of **TIPS-TMS-BP** displaying (001) lattice planes. (Left) Along with *b*-axis; (right) Along with *a*-axis.

Hole mobility in single crystals

The hole transport capability in SC-FETs of **TIPS-TMS-BP** was evaluated with the bottom-gate-top-contact structure. Single crystals of **TIPS-TMS-BP** for FET measurements were prepared as described in Experimental and lozenge-shaped plate-like crystals were obtained. The longer diagonal is perpendicular and the shorter one is parallel to (100) plane. On the obtained single crystal, gold source and drain electrodes were vacuum deposited (30 nm thickness) in perpendicular to longer diagonal (Pair A–D), which is the direction of the strong π - π interaction. (see SI for the details of device fabrication and measurements). Optical microscopy images of the single crystals are shown in Figure S6 and S7. The obtained FET parameters are summarized in Table S3, while the transfer curves and output characteristics of the devices are shown in Figure 6A-C, S10, and S11. **TIPS-TMS-BP** gave $\mu_{h,max}$ ($\mu_{h,ave}$) = 1.65 (1.20) $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (6 devices) with threshold voltage (V_{th}) = -17V and the on/off current ratio (I_{on}/I_{off}) = 5.6×10^3 . Compared to **TIPS-Ph-BP**, **TIPS-TMS-BP** has a 0.1 Å shorter π -stack distance to improve the charge mobility from $\mu_{h,max}$ ($\mu_{h,ave}$) = 0.71 (0.55) $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (5 devices) of **TIPS-Ph-BP** SC-FET prepared in the same method. However, **TIPS-TMS-BP** has a non-equivalent π -stack due to the formation of an antiparallel arrangement similar to that of **TIPS-Ph-BP** and this non-equivalent π -stack inhibits efficient charge transport.

The device anisotropy was also evaluated by changing the orientation of the gold electrode (Figure S8). The gold source and drain electrodes were vacuum deposited (30 nm thickness) in perpendicular to shorter diagonal, which is the direction of the inter-column interaction (Pair E). The $\mu_{h,max}$ ($\mu_{h,ave}$) values of **TIPS-TMS-BP** in shorter diagonal is 0.37 and 0.12 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ (2 devices) with threshold voltage (V_{th}) = -3.6 V and the on/off current ratio (I_{on}/I_{off}) = 1.2×10^3 (Table S4, Figure 6D-F and S12). The charge carrier mobility is 5 times smaller than that of longer diagonal. Of note is the smoothness of the graphs for the transfer and output characteristics. The shorter diagonal has a more pronounced noise than the longer diagonal. This is because the interactions between different columns are weaker and more subject to external influences than between molecules, which may be the cause of the noise in the graph.

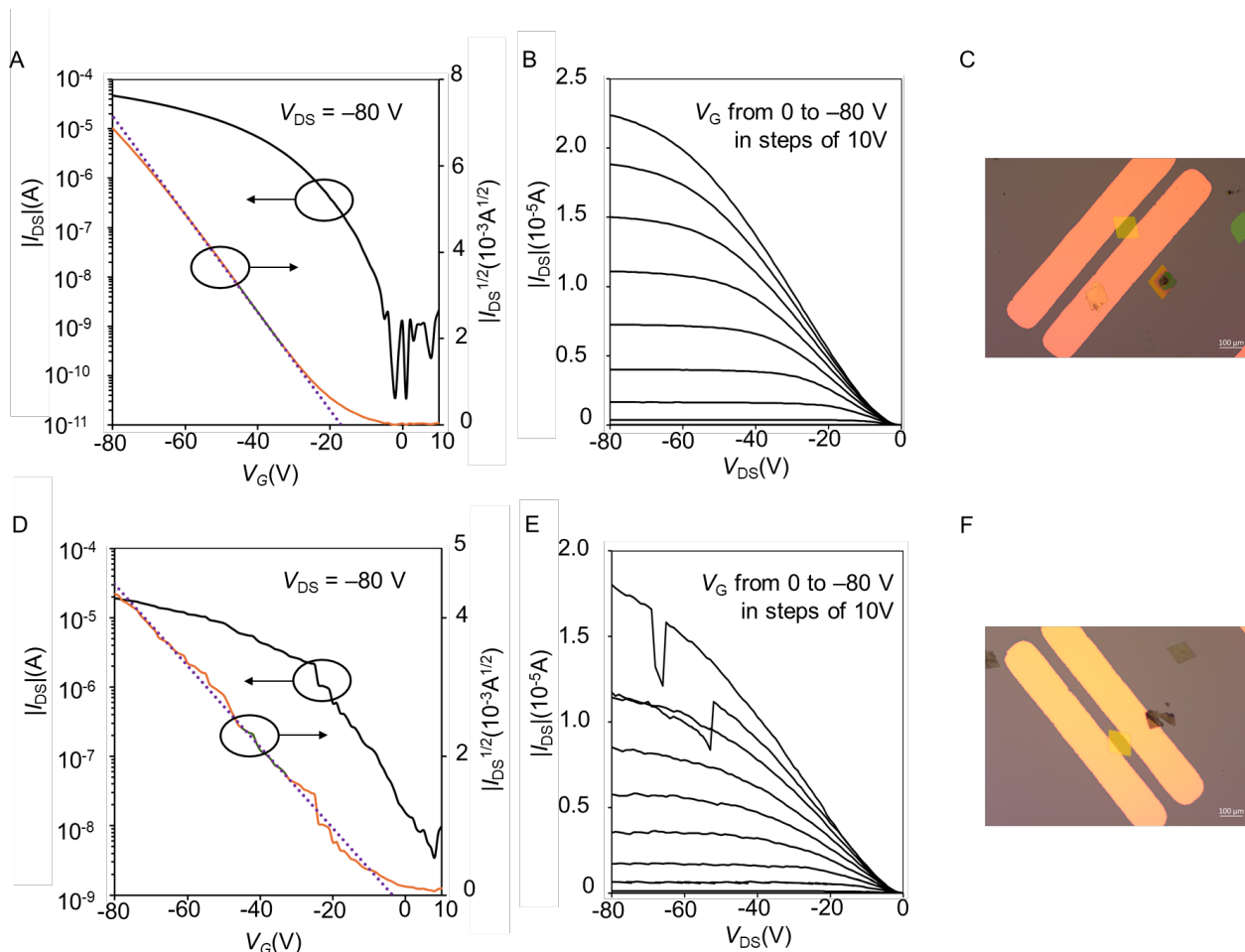


Figure 6. (A) Transfer, (B) output characteristics and (C) optical image of the best-performing OFET (Device 1) using **TIPS-TMS-BP** arranged in longer diagonal. (D) Transfer, (E) output characteristics and (F) optical image of the best-performing OFET (Device 7) using **TIPS-TMS-BP** arranged in shorter diagonal.

CONCLUSION

Low-symmetric benzoporphyrin, **TIPS-TMS-BP**, was synthesized to investigate the packing structure in single crystals and to evaluate the SC-FET performance. **TIPS-TMS-BP** formed herringbone-like packing with antiparallel slipped π -stacking motif. Compared to **TIPS-Ph-BP** with the Ar group substituted in the *meso*-position, the π -stacking distance was significantly reduced and the charge transfer integral values were larger. However, the antiparallel slipped π -stacking motif formed inequivalent π -stacks, which may have inhibited efficient charge transport. **TIPS-TMS-BP**, whose solubility was improved by putting different substituents at *meso*-positions, achieved a hole mobility of $1.65 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The small size of TMS-group compared to Ph group improved the distance between porphyrins, but the antiparallel packing structure induced the unbalanced packing, with charge carrier mobility dominated by the lower interaction.

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OFET performance of low-symmetric 5-TIPS-ethyny-15-TMS-ethynyl-tetrabenzoporphyrins in the single crystal states

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1. X-ray crystallographic analysis

Green platelet crystals of **TIPS-TMS-BP** were obtained by the recrystallization from toluene and *n*-octane using a vapor diffusion method. X-ray diffraction data were collected on a Rigaku XtaLAB Synergy (1.2 kW), using CuK α radiation ($\lambda = 1.54184 \text{ \AA}$). The structure was solved by SHELXT-2018/3^[S1] and refined by least square method on F^2 for all reflections (SHELXL-2018/3).^[S2] All non-hydrogen atoms were refined anisotropically. All calculations were performed by using Yadokari-XG.^[S3] The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication materials. CCDC number is 2410764. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

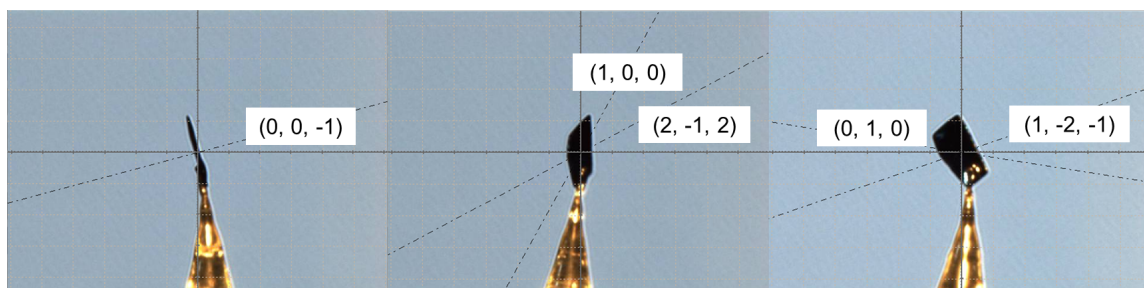


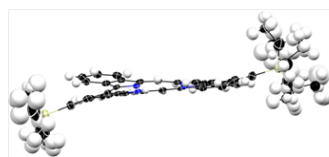
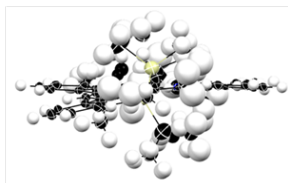
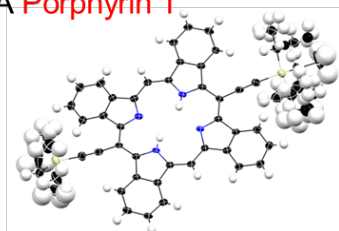
Figure S1. Face index of the single crystal for **TIPS-TMS-BP**.

Table S1. Crystallographic data for **TIPS-TMS-BP**

Parameter	TIPS-TMS-BP
Empirical formula	C52 H50 N4 Si2
FW	787.14
Temperature (K)	86
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> (Å)	14.1064(2)
<i>b</i> (Å)	15.2447(2)
<i>c</i> (Å)	20.9211(5)
α (°)	105.533(2)
β (°)	101.004(2)
γ (°)	90.0660(10)
<i>V</i> (Å ³)	4248.51(14)
<i>Z</i>	4
<i>D</i> _{calcd} (g cm ⁻³)	1.231
μ (mm ⁻¹)	1.068
<i>F</i> (000)	1672
Crystal size (mm)	0.100 × 0.100 × 0.030
θ_{range} (°)	3.1820 to 76.5470
Reflection collected	46250
Independent reflections	13162
<i>R</i> _{int}	0.0759
Completeness to θ_{max}	0.959
Data/restraints/parameters	13162/0/1118
GOF on <i>F</i> ²	1.411
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.1098
<i>wR</i> ₂ (all data)	0.3232
Largest diff. peak and hole (e Å ⁻³)	1.595, -0.849
CCDC	2410764

The Alert B level alerts arise due to the easily overlapped crystals and the disorder of the TIPS and TMS groups. These have been addressed during the refinement process appropriately, and these do not significantly affect the reliability of the structural model.

A Porphyrin I



B Porphyrin II

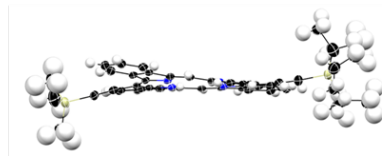
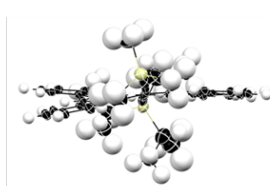
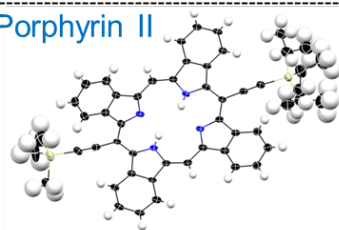


Figure S2. X-ray crystal structure of TIPS-TMS-BP ((A) porphyrin I, (B) porphyrin II).

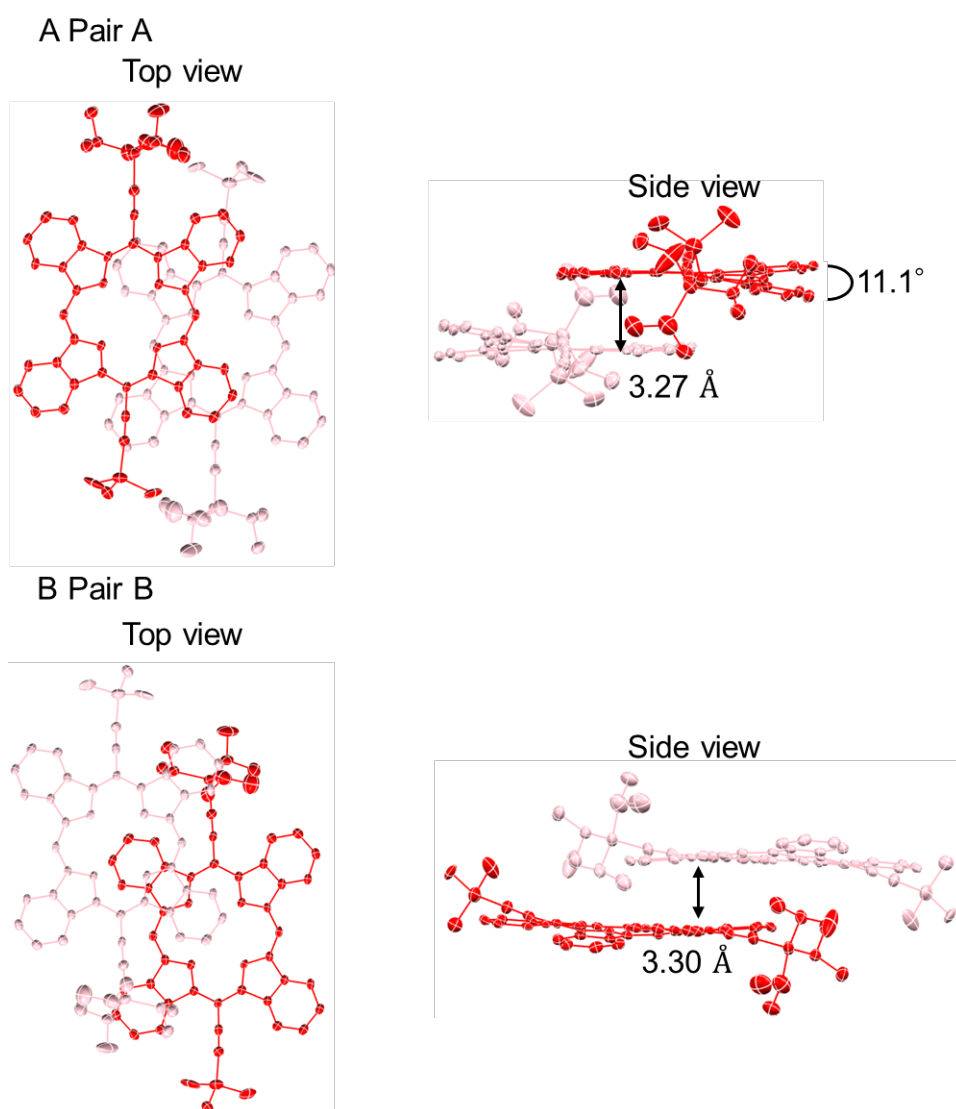


Figure S3. Two types of π -stacking structures of porphyrin I, Pair A and B, observed in column 1 in the crystal of TIPS-TMS-BP. Hydrogen atoms are omitted for clarity.

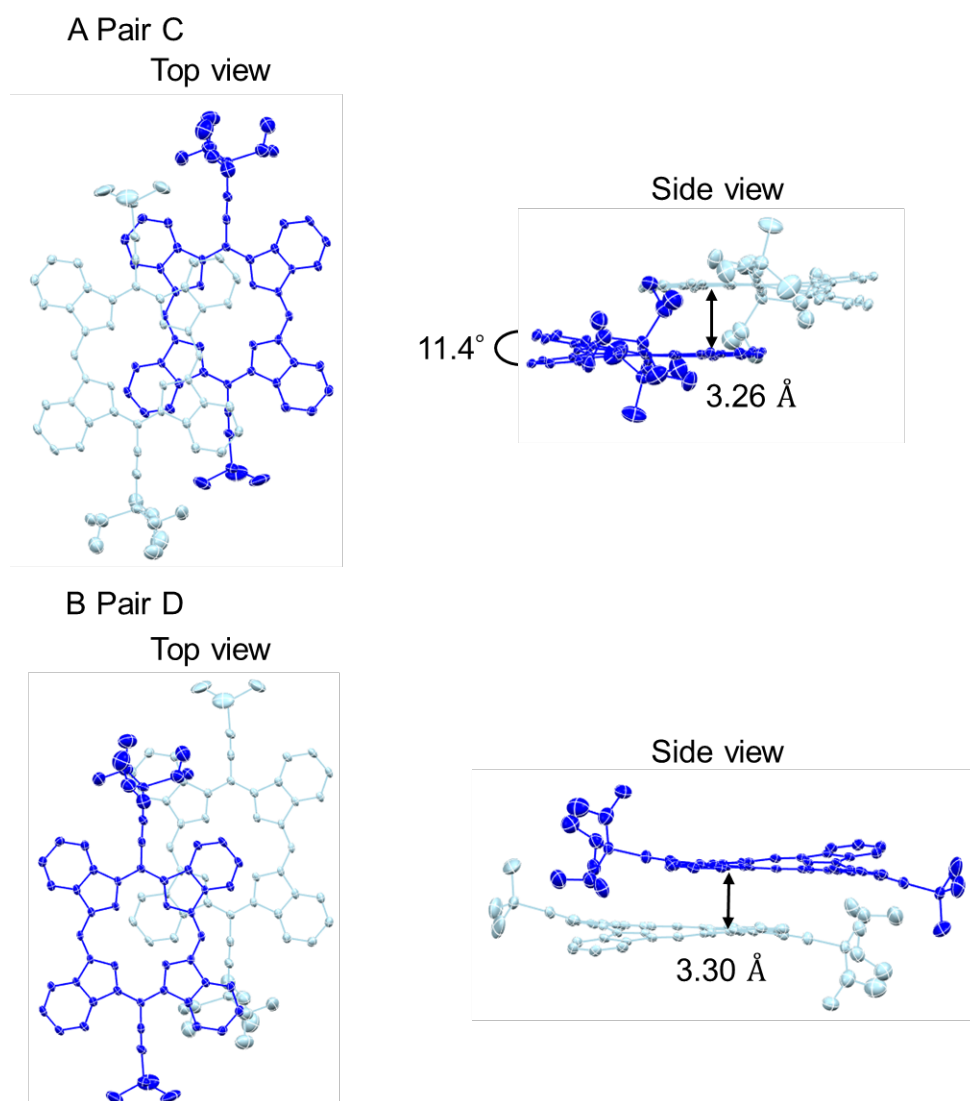


Figure S4. Two types of π -stacking structures of porphyrin II, Pair C and D observed in column 2 in the crystal of **TIPS-TMS-BP**. Hydrogen atoms are omitted for clarity.

2. Charge transfer integral calculations

Charge transfer integrals in the crystal packing structures of **TIPS-TMS-BP** was calculated using the ADF2023 program^[S4] at the PBE/TZ2P level of theory.

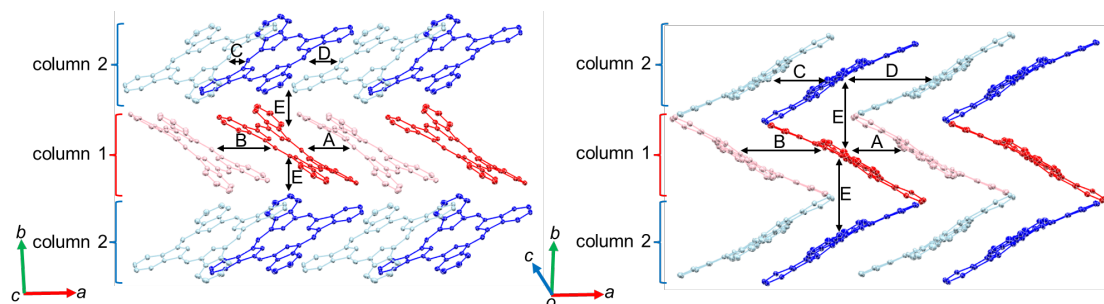


Figure S5. Packing structure of **TIPS-TMS-BP**. Substituents and hydrogen atoms are omitted for clarity.

Table S2. Calculated charge transfer integrals of HOMOs for **TIPS-TMS-BP**.

Pair	t_{HOMO} [meV]
A	112.6
B	32.7
C	110.6
D	33.7
E	14.2

3. Fabrication and evaluation of organic field-effect transistors

All OFET devices were fabricated in a top-contact bottom-gate configuration on a heavily n-doped Si wafer with a 300 nm-thick thermally grown SiO₂ layer ($C_i = 11.5 \text{ nF cm}^{-2}$). The Si/SiO₂ substrates were cleaned with deionized water, acetone, and 2-propanol for 10 min each in an ultrasonic bath. Substrates were dried with a flow of N₂ gas and then treated by UV–O₃ cleaner (Filgen UV253V8) for 45 min. The 0.25 gL⁻¹ chlorobenzene solution of **TIPS-TMS-BP** was drop-casted on the precleaned substrate at room temperature. Then, the substrate was confined in a petri dish filled with octane. The solvent was slowly evaporated at the same temperature to afford sparsely deposited small crystalline films. Then, the source and drain electrode of Au (30 nm) were vacuum-deposited at 0.1 Å s⁻¹ under the pressure of 5×10⁻⁴ Pa through a shadow mask on the active layer. The drain–source channel length (L) and width (W) of each device were measured independently using Zeiss Axio Scope.A1 optical microscope. The output and transfer characteristics of the OFETs were measured using a Thermal Block SB-MCPS-NAT prober system and a Keithley 2400 source measure unit at room temperature under air atmosphere. The field-effect hole mobilities (μ_h) of the OFETs were determined from the forward transfer curve in the saturation regime ($V_{DS} = -80 \text{ V}$) using the following equation:

$$I_{DS} = (\mu WC_i/2L)(V_G - V_{th})^2 \quad (1)$$

where I_{DS} is the drain–source current and V_{DS} , V_G , and V_{th} are the drain–source voltage, gate voltage, and threshold voltage, respectively. The on/off current ratios (I_{on}/I_{off}) were determined from the I_{DS} at $V_G = 0 \text{ V}$ (I_{off}) and $V_G = -80 \text{ V}$ (I_{on}). The averaged μ values (μ_{ave}) were calculated from the 6 devices for **TIPS-TMS-BP** respectively. Out-of-plane XRD measurements of the FET was performed using a Rigaku SmartLab X-ray diffractometer with a Cu-K α source ($\lambda = 1.5418 \text{ Å}$) in the 2θ scan mode at a fixed incidence angle of 0.58°.

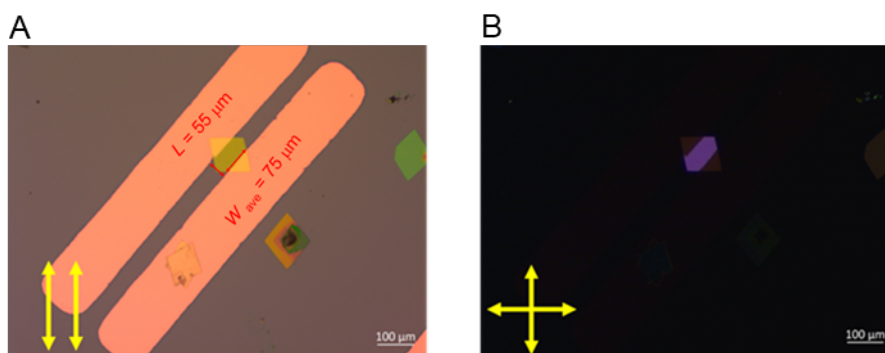


Figure S6. (A) Optical and (B) crossed-Nicols polarized micrographs of the best-performing OFET (Device 1) using **TIPS-TMS-BP** arranged in longer diagonal.

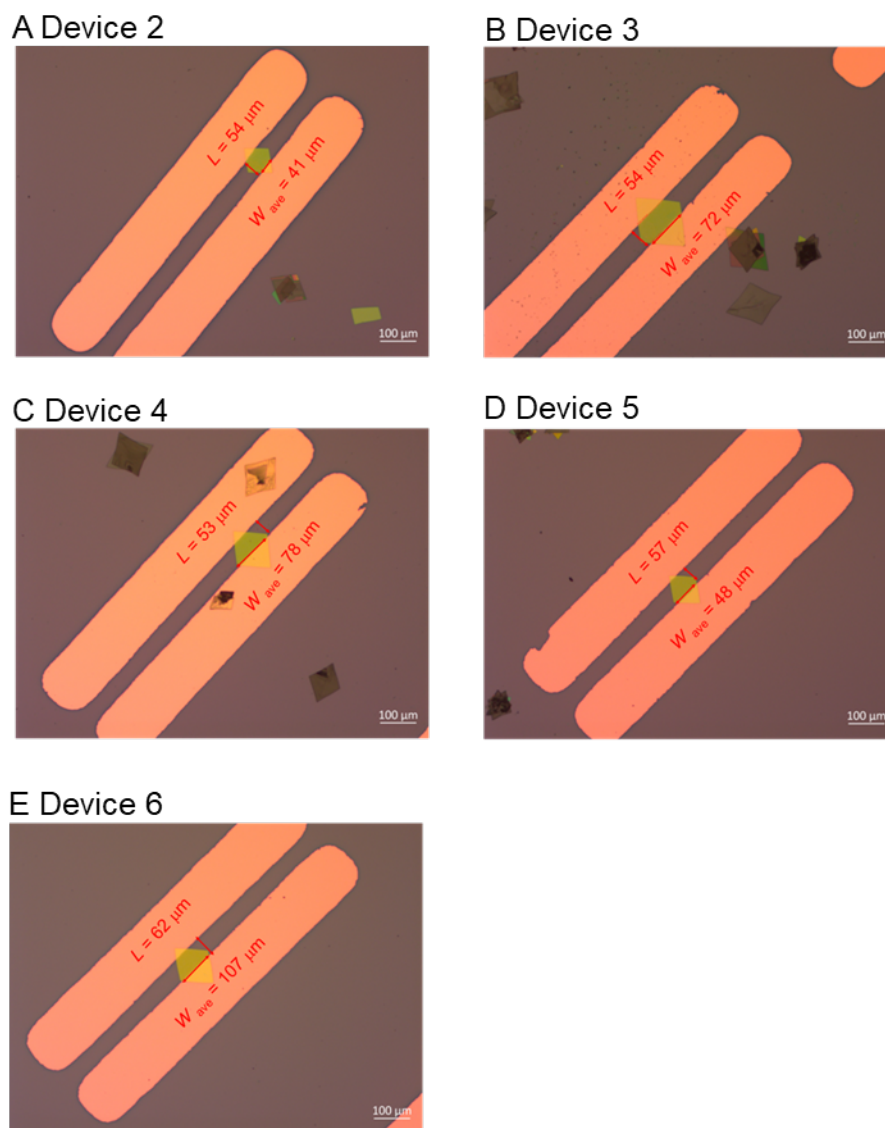
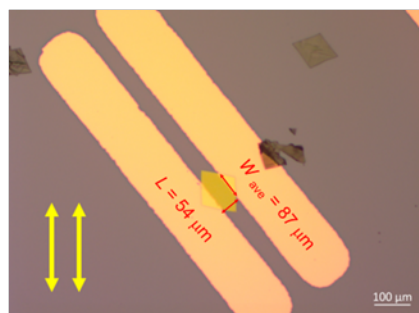
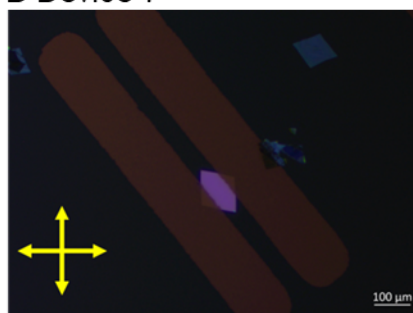


Figure S7. Optical micrographs of the OFETs using **TIPS-TMS-BP** arranged in longer diagonal.

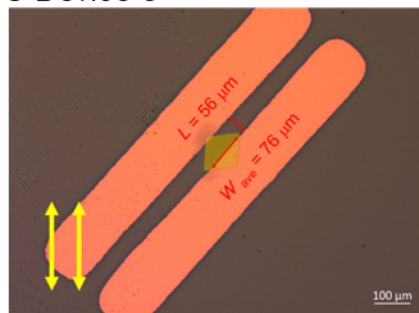
A Device 7



B Device 7



C Device 8



D Device 8

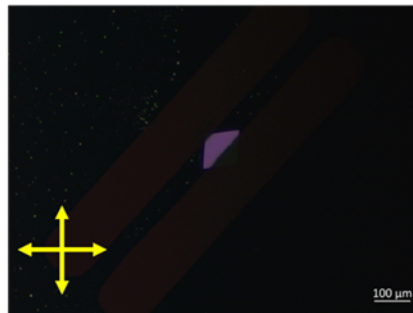


Figure S8. (A, C) Optical and (B, D) crossed-Nicols polarized micrographs of the OFET (Device 7, 8) using **TIPS-TMS-BP** arranged in shorter diagonal.

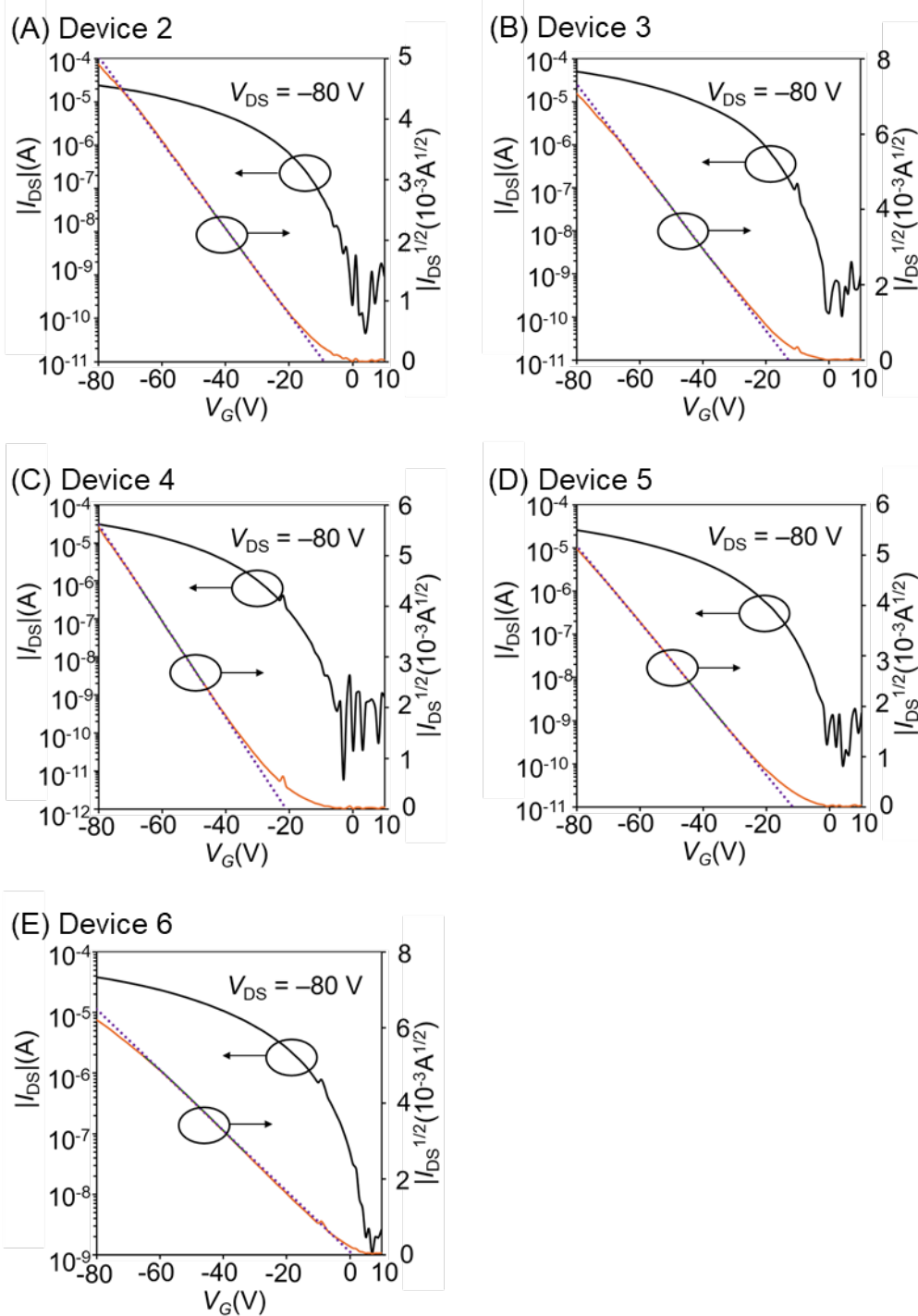


Figure S9. Transfer characteristics of the OFETs using **TIPS-TMS-BP** arranged in longer diagonal.

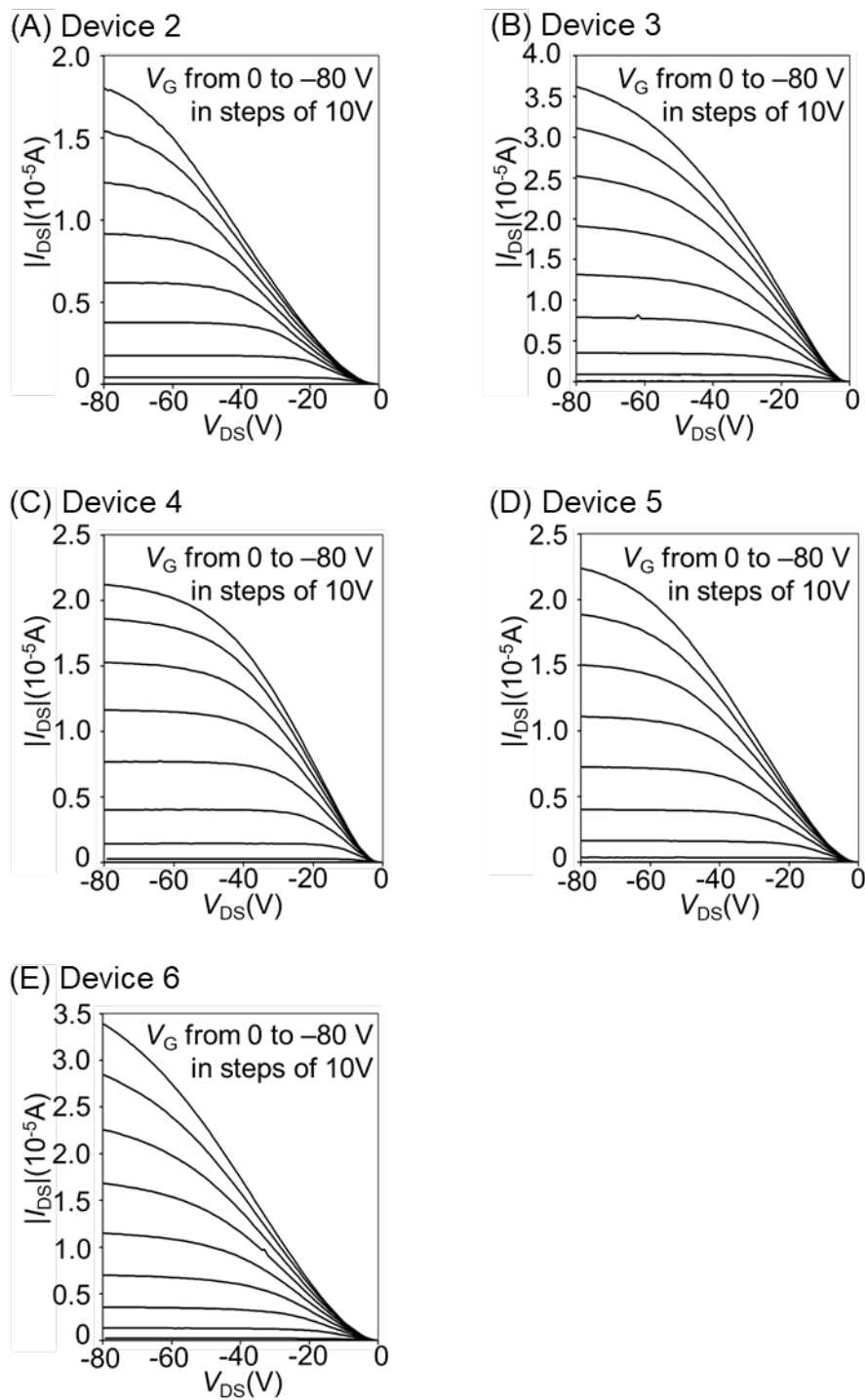


Figure S10. Output characteristics of the OFETs using **TIPS-TMS-BP** arranged in longer diagonal.

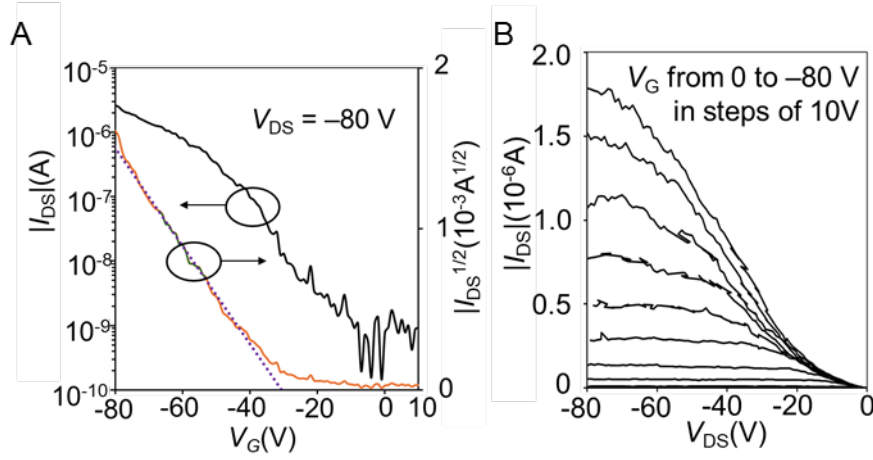


Figure S11. (A) Transfer and (B) output characteristics of the OFET (Device 8) using **TIPS-TMS-BP** arranged in shorter diagonal.

Table S3. Characteristics of OFETs using **TIPS-TMS-BP** arranged in longer diagonal.

Device	μ_{th} [cm ² V ⁻¹ s ⁻¹]	V_{th} [V]	I_{on}/I_{off} [-]
1	1.65	-16.8	5.6×10^3
2	1.15	-8.9	2.4×10^4
3	0.90	-0.5	2.1×10^2
4	1.10	-21.6	9.9×10^4
5	1.19	-11.7	5.5×10^3
6	1.22	-13.3	7.1×10^4
average	1.20	-	-

Table S4. Characteristics of OFET using **TIPS-TMS-BP** arranged in shorter diagonal.

Device	μ_{th} [cm ² V ⁻¹ s ⁻¹]	V_{th} [V]	I_{on}/I_{off} [-]
7	0.37	-3.6	1.2×10^3
8	0.12	-30.7	3.3×10^3
average	0.25	-	-

4. ^1H and ^{13}C NMR spectral data

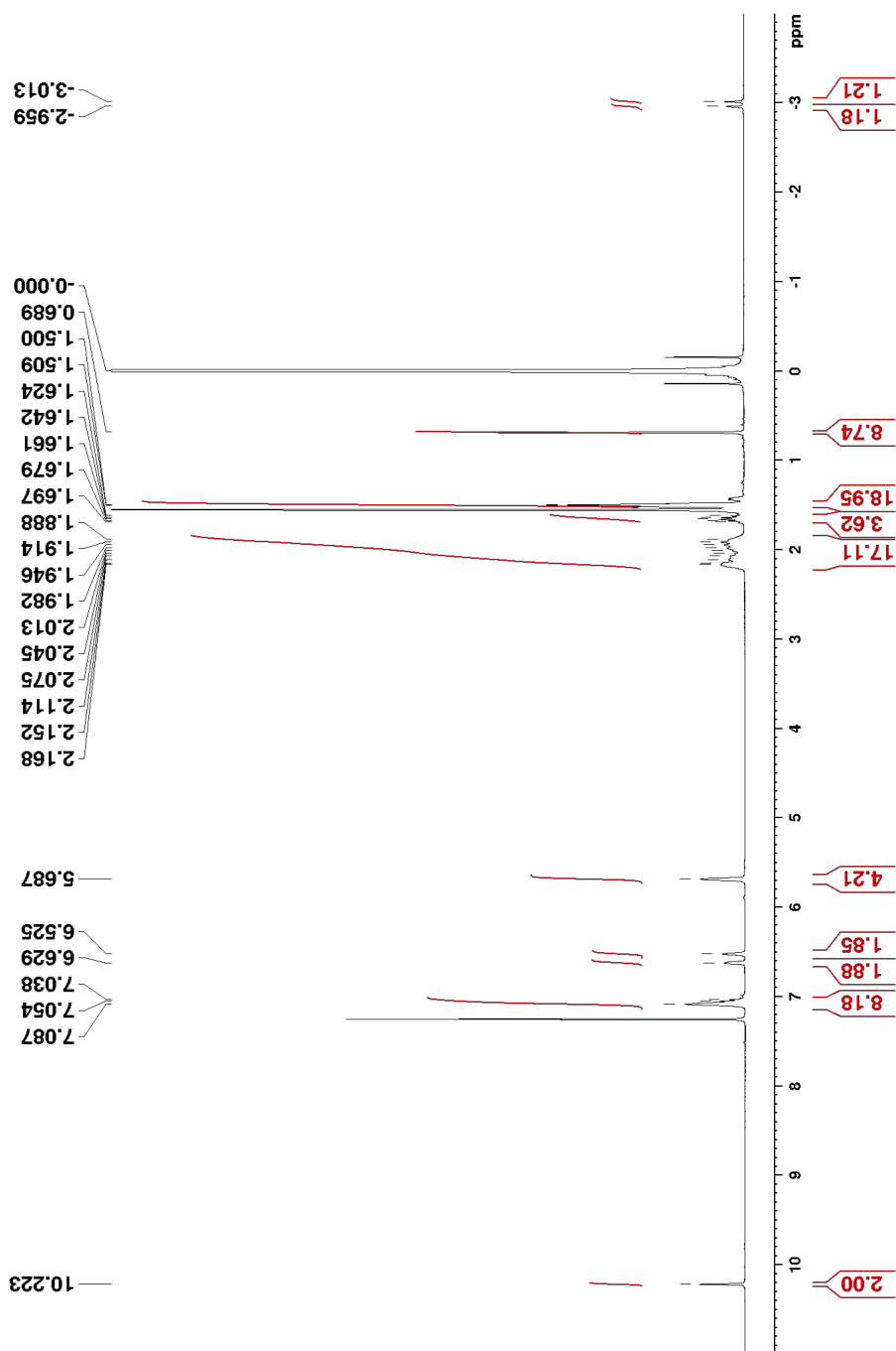


Figure S12. ^1H NMR spectrum of TIPS-TMS-CP (400 MHz).

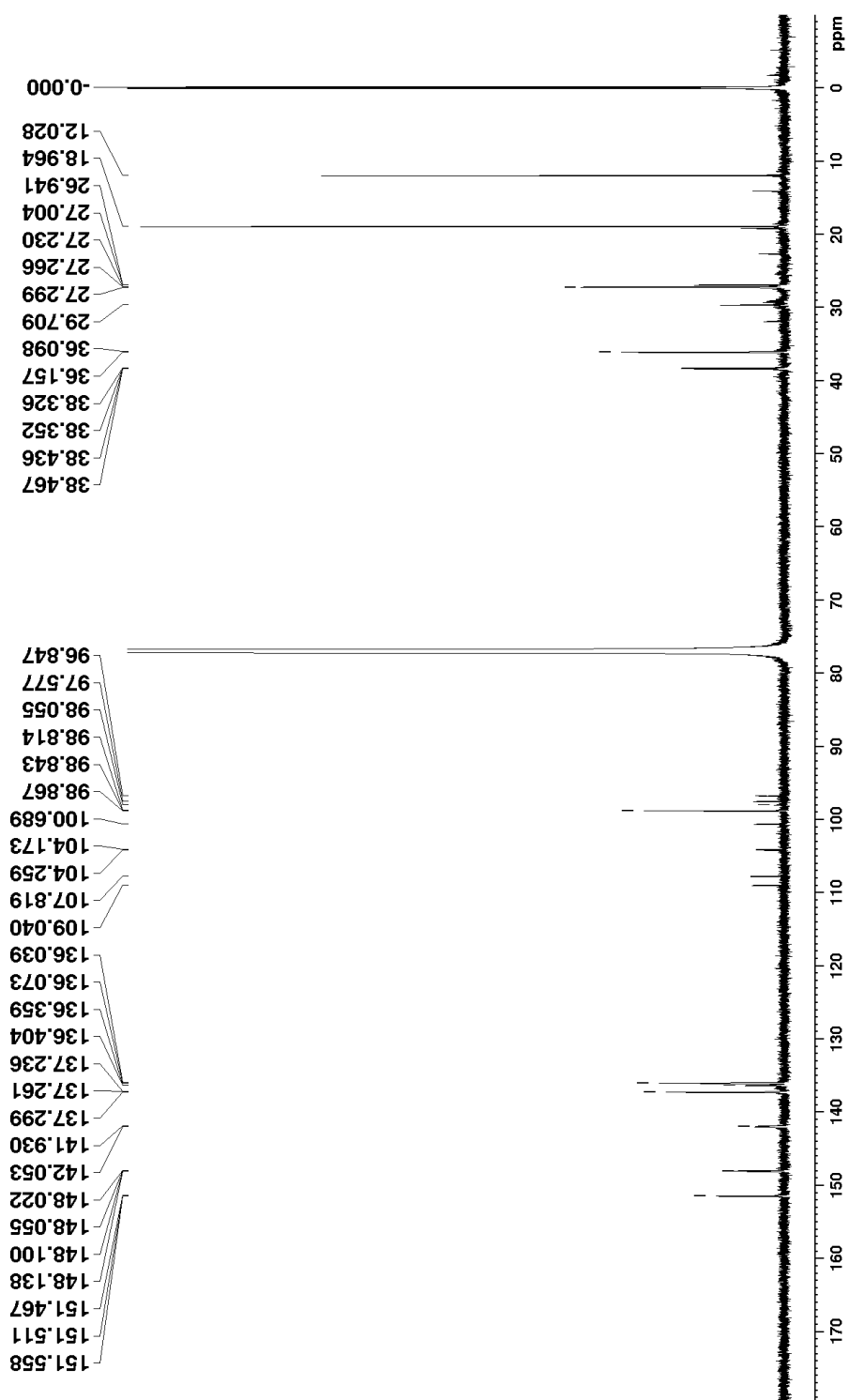


Figure S13. ¹³C NMR spectrum of TIPS-TMS-CP (200 MHz).

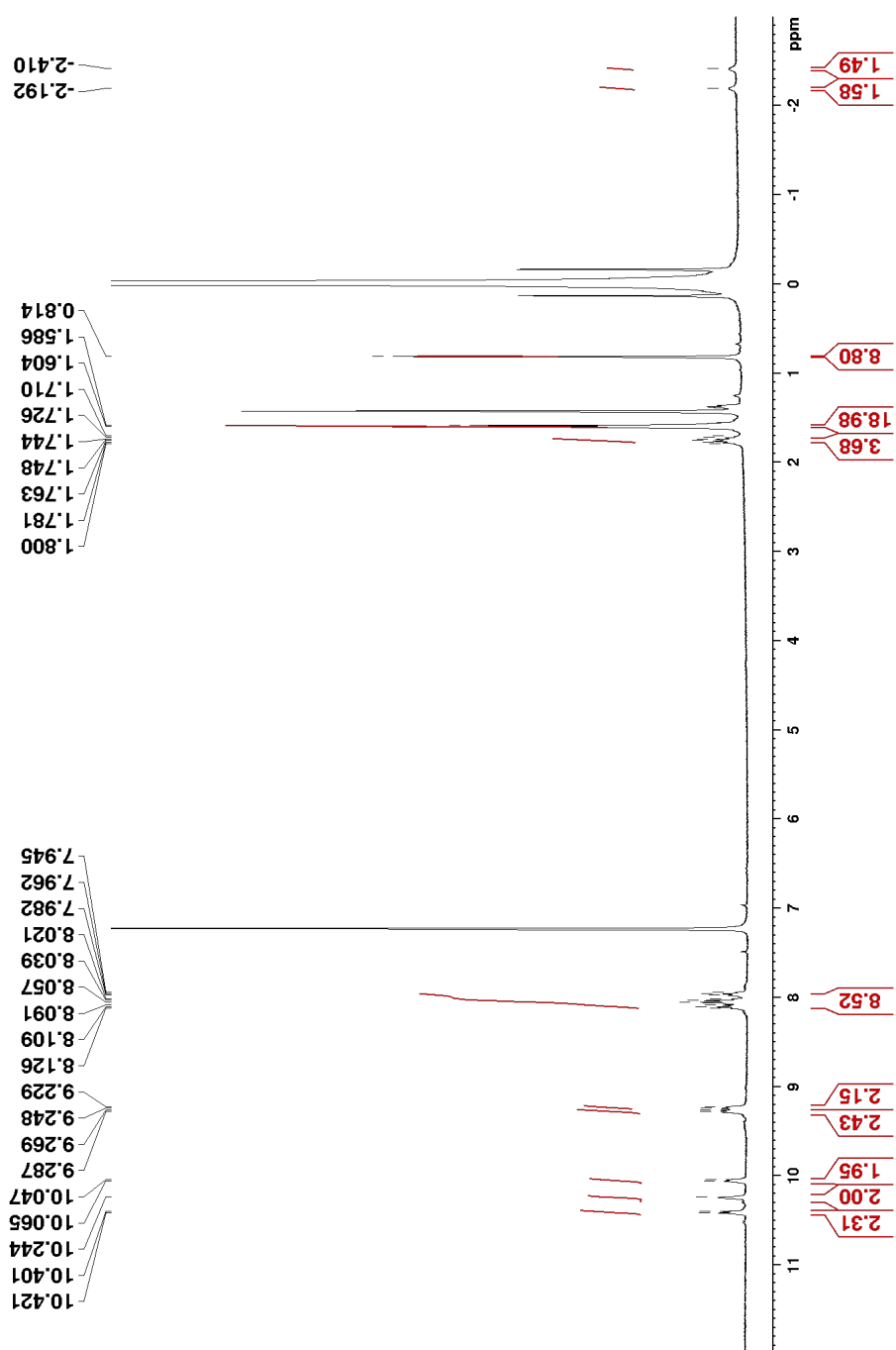


Figure S14. ^1H NMR spectrum of **TIPS-TMS-BP** (400 MHz).

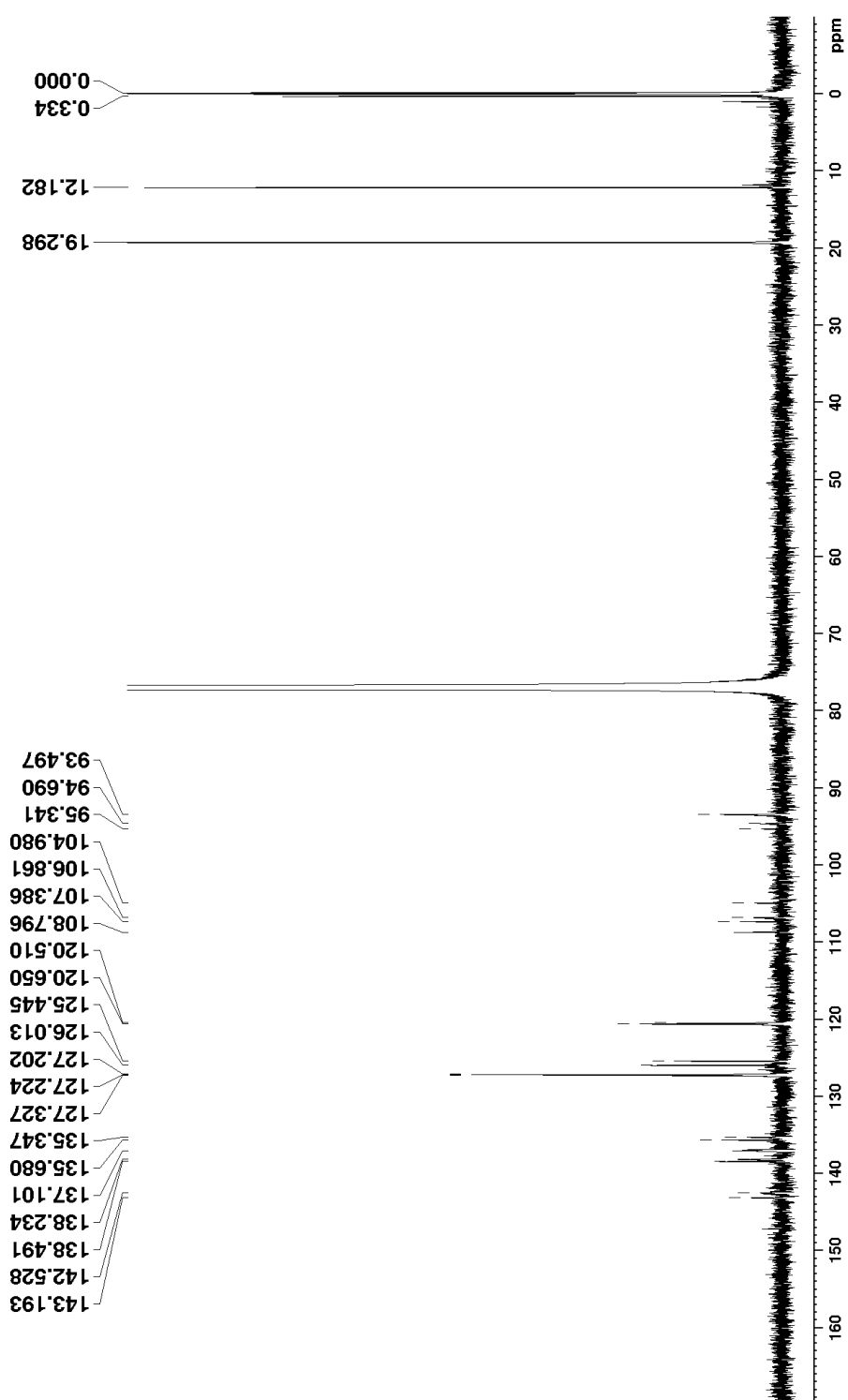


Figure S15. ¹³C NMR spectrum of TIPS-TMS-BP (200 MHz).

5. HR-Mass data

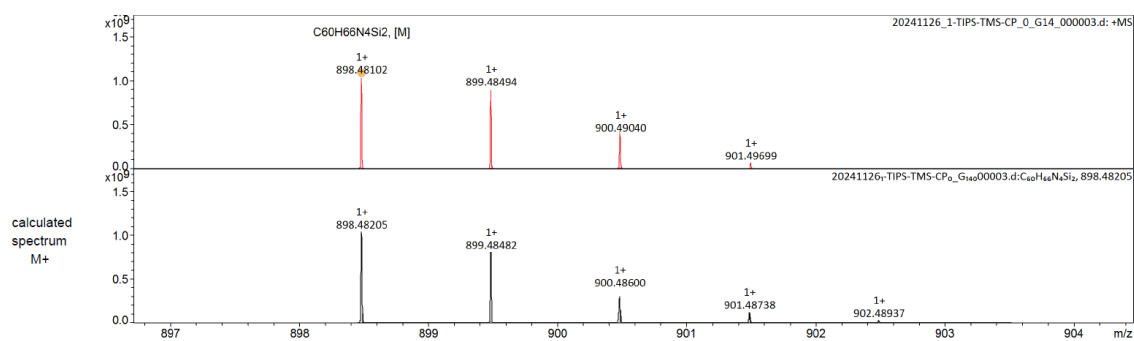


Figure S16. HR-MALDI-FT-ICR mass spectrum of TIPS-TMS-CP.

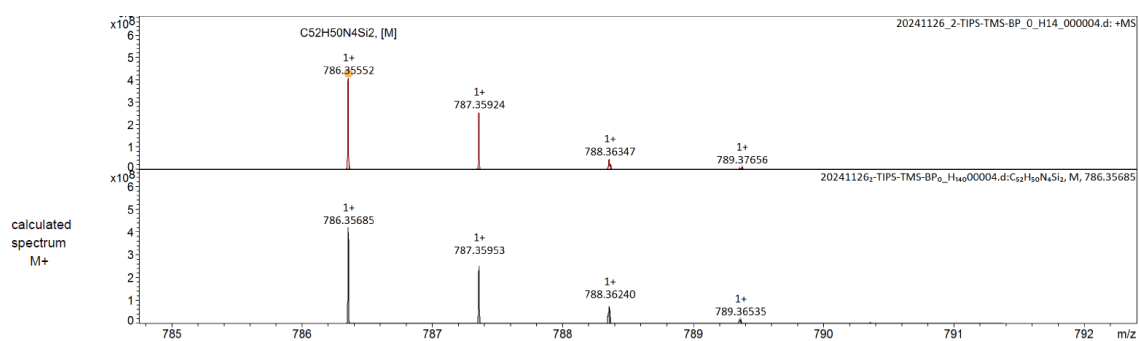


Figure S17. HR-MALDI-FT-ICR mass spectrum of TIPS-TMS-BP.

6. References

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- S3. Kabuto C, Akine S, Kwon E, *J. Cryst. Soc. Jpn.*, 2009; **51**, 218.
- S4. ADF2023, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>.