

Synthesis and Crystal Structures of 5,15-Bis(triisopropylsilylethynyl)-tetrabenzoporphyrins

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1. Introduction

Organic semiconducting materials have attracted much attention as an active layer for organic light emitting diode (OLED), organic thin-film transistor (OTFT) and organic solar cell (OSC) because the organic electronic devices are expected to be flexible, light-weight, large area, and low cost devices [1-4]. To achieve these purposes, various solution processes such as spin-coating, ink-jet printing, slot die coating, and spray coating are considered to be advantageous over the vacuum process. In this sense, the solution processable materials are strongly required. Ono and coworkers have developed the synthesis of insoluble tetrabenzoporphyrin (**BP**) from soluble precursor, bicyclo[2.2.2]octadiene (BCOD)-substituted porphyrin (**CP**), by retro Diels-Alder reaction [5]. This thermal conversion process from **CP** to **BP** only released four ethylene molecules with no other byproduct. This method, thus, could be applied to the fabrication of OTFT and OSC by solution process. In particular, Ono and Kanicki et al. have achieved a carrier mobility of $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for OTFT [6]. Furthermore, Nakamura and coworkers reported an excellent performance of OSC devices based on **BP** and bis(dimethyl phenylsilylmethyl)[60]fullerene (**SIMEF**) with a photo-conversion efficiency of 5.2 % [7].

Pentacene is also one of the most promising organic semiconducting materials [8]. However, the solubility in common organic solvents is very low and the reactivity with oxygen under light is very high. To solve these problems, pentacene attached with solubilizing groups and electron deficient

groups have been reported. Among them, 6,13-bis(triisopropylsilyl-ethynyl)pentacene (**TIPS-PEN**) represented a good solubility and chemical stability [9]. Furthermore, the crystal packing of pentacene to **TIPS-PEN** changed from herringbone structure to a 1D-slip-stacked column structure. In addition, **TIPS-PEN** based OTFT devices exhibited a good carrier mobility of $0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for thin-film [10] and $1.42 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for single crystal nanowire [11]. Since then, various TIPS-substituted acenes were reported and indicated satisfactory device performances [12].

By combining the benefits of benzoporphyrin and **TIPS-PEN**, we have designed a 5,15-triisopropylsilylethynyl-tetrabenzoporphyrin (**TIPS-H₂BP**) and its zinc complex (**TIPS-ZnBP**), assuming that we can control the crystal structure and optical properties. Its bulky TIPS group can improve the solubility and crystallinity to adapt the **TIPS-BPs** as a solution processable semiconducting material for OTFT and OSC. In this paper, we describe the crystal structures and optical properties of these **TIPS-BPs**.

2. Experimental

¹H NMR and ¹³C NMR spectra were recorded on a JEOL ECX 400P spectrometer at ambient temperature using tetramethylsilane as an internal standard. ESI mass spectra were measured on a JEOL JMS-700 spectrometer. UV-vis spectra were measured on a JASCO UV/VIS/NIR spectro-photometer V-570. All solvents and chemicals were reagent grade quality, obtained commercially and used without further purification.

For spectral measurements, spectral grade solvents were purchased from Nacalai Tesque Inc. X-ray crystallographic data were recorded at 103 K on a Rigaku CCD detector (Saturn 724) mounted on a Rigaku rotating anode X-ray generator (MicroMax-007HF) using Mo-K α radiation from the corresponding set of confocal optics. The structures were solved by direct methods and refined on F2 by full-matrix least-squares using the CrystalClear and SHELXS-2000 program.

TIPS-H₂CP

Trifluoroborate etherate (0.10 ml, 0.796 mmol) was added to a solution of dipyrromethane **1** (0.889 g, 2.94 mmol) and 3-triisopropylsilyl-2-propynal (0.80 ml, 3.27 mmol) in methanol (300 ml) and the resulting mixture was stirred for 3 h at 0 °C. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (1.33 g, 5.86 mmol) was added to the solution and the solution was stirred for 30 min at room temperature. Then, triethylamine was added to neutralize the mixture and the solvent was removed under reduced pressure. The residue was purified by alumina column chromatography (CH₂Cl₂) and recrystallization (CHCl₃/MeOH) to give **TIPS-H₂CP** as purple solids in 57% (820 mg, 0.834 mmol). ¹H NMR (400 MHz, CDCl₃) δ = 10.24 (m, 2H), 7.06 (m, 8H), 6.63 (m, 4H), 5.71 (m, 4H), 2.27-1.81 (m, 16H), 1.66 (m, 6H), 1.57-1.46 (m, 36H) ppm; ¹³C NMR (75 MHz, CDCl₃) δ = 151.39, 148.00, 142.06, 137.23, 136.20, 136.02, 109.00, 100.67, 98.75, 97.45, 38.39, 36.25, 27.36, 19.05, 12.13 ppm; HRMS (ESI): m/z = 983.5445. calcd. for C₆₆H₇₉N₄Si₄: 983.5843 [M+H]⁺. Crystallographic data: C₆₆H₇₈N₄Si₂, M_w = 983.54, monoclinic, space group *P*2₁/*c*, a = 12.3216(3), b = 11.3648(2), c = 19.8665(4) Å, β = 93.7137(7)°, V = 2776.11(9) Å³, T = 123 K, Z = 2, R_1 = 0.0754, wR_2 = 0.2038, GOF = 1.049. CCDC No. 930877.

TIPS-ZnCP

A saturated solution of zinc acetate in methanol (5 ml) was added to a solution of **TIPS-H₂CP** (202 mg, 0.206 mmol) in CHCl₃ (25 ml). After stirring for 2 h at room temperature, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography and recrystallization (CHCl₃/MeOH) to give **TIPS-ZnCP** as purple crystals in 94% (202 mg, 0.193 mmol). ¹H NMR (400 MHz, CDCl₃) δ =

10.25 (m, 2H), 7.08 (m, 8H), 6.78 (m, 4H), 5.70 (m, 4H), 2.25-1.85 (m, 16H), 1.68 (m, 6H), 1.51 (m, 36H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 151.93, 151.89, 149.95, 149.90, 144.79, 144.77, 140.74, 140.72, 140.70, 137.66, 137.63, 137.61, 137.58, 136.26, 136.20, 110.12, 100.51, 100.48, 99.57, 99.55, 99.52, 98.62, 98.58, 39.21, 39.19, 36.18, 27.35, 27.29, 18.99, 18.97, 12.15 ppm; HRMS (ESI): m/z = 1045.4977. calcd. for C₆₆H₇₇N₄Si₂Zn: 1045.4978 [M+H]⁺. Crystallographic data: C₆₆H₇₆N₄Si₂Zn, M_w = 1046.90, monoclinic, space group *P*2₁/*c*, a = 12.3027(3), b = 11.4639(2), c = 19.6184(4) Å, β = 94.1046(7)°, V = 2759.81(9) Å³, T = 123 K, Z = 2, R_1 = 0.0469, wR_2 = 0.1306, GOF = 1.072. CCDC No. 930879.

General procedure of synthesis of TIPS-benzoporphyrins by retro Diels-Alder reaction

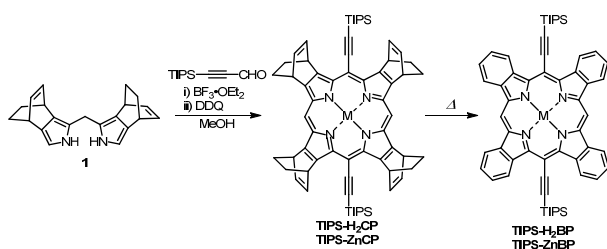
The precursor was heated under vacuum in a glass tube oven to give the **TIPS-BPs** quantitatively.

TIPS-H₂BP: ¹H NMR (400 MHz, CDCl₃) δ = 10.12 (m, 4H), 9.85 (s, 2H), 9.10 (m, 4H), 7.98 (m, 4H), 7.86 (m, 4H), 1.86-1.72 (m, 6H), 1.70-1.59 (m, 36H), -3.53 (s, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 142.30, 137.79, 136.17, 134.82, 126.91, 126.80, 125.50, 120.25, 108.55, 104.06, 94.51, 92.80, 19.30, 12.06 ppm; HRMS (ESI): m/z = 871.4592. calcd. for C₅₈H₆₃N₄Si₂: 871.4591 [M+H]⁺. Crystallographic data: C₅₈H₆₂N₄Si₂, M_w = 871.33, triclinic, space group *P*-1, a = 8.9294(4), b = 15.8338(6), c = 18.7583(7) Å, α = 65.3553(8), β = 78.8503(9), γ = 81.1152(9)°, V = 2356.96(15) Å³, T = 103 K, Z = 2, R_1 = 0.0608, wR_2 = 0.1667, GOF = 1.002. CCDC No. 930876.

TIPS-ZnBP: ¹H NMR (400 MHz, pyridine-*d*₅) δ = 11.34 (m, 2H), 11.09 (m, 4H), 9.85 (m, 4H), 8.27 (m, 8H), 1.79-1.65 (m, 6H), 1.59-1.46 (m, 36H) ppm; ¹³C NMR (100 MHz, pyridine-*d*₅) δ = 146.54, 143.39, 140.49, 138.79, 127.68, 127.39, 127.14, 121.62, 111.75, 105.36, 96.60, 19.30, 12.16 ppm; HRMS (ESI): m/z = 955.3544. calcd. for C₅₈H₆₀N₄Si₂Zn: 955.3546 [M]⁺. Crystallographic data: C₆₁H₆₇N₄OSi₂Zn•C₆H₅Cl, M_w = 1106.34, triclinic, space group *P*-1, a = 11.8702(3), b = 13.5596(3), c = 19.5798(4) Å, α = 81.0943(7), β = 81.6659(7), γ = 68.5772(7)°, V = 2884.94(10) Å³, T = 123 K, Z = 2, R_1 = 0.0593, wR_2 = 0.1729, GOF = 1.067. CCDC No. 930878.

3. Results and Discussion

Synthetic routes of **TIPS-H₂BP** and **TIPS-ZnBP** are shown in Scheme 1. **TIPS-H₂CP** was synthesized by [2+2] McDonald type condensation reaction. Dipyrrrolylmethane **1** was reacted with TIPS-propyne in the presence of borontrifluoride etherate to afford **TIPS-H₂CP** in 57% yield. The zinc complex was prepared from **TIPS-H₂CP** with Zn(OAc)₂ according to previously reported methods [13]. Thermogravimetric analysis was performed to investigate the elimination of four ethylene molecules by the retro Diels-Alder reaction. The weight-loss of **TIPS-H₂CP** and **TIPS-ZnCP** were started around 120 °C and finished around 210 °C. The observed weight losses of 11.4% for **TIPS-H₂CP** and 10.8% for **TIPS-ZnCP** were in agreement with the calculated value of 11.4% and 10.7%, respectively. When **TIPS-H₂CP** and **TIPS-ZnCP** were heated as a solid at 200 °C in a glass tube oven under vacuum, **TIPS-H₂BP** and **TIPS-ZnBP** were obtained quantitatively. They showed good solubility in halogenated solvents. The single crystals of **TIPS-H₂CP** and **TIPS-ZnCP** suitable for X-ray diffraction were obtained by a slow diffusion of methanol and hexane into a chloroform solution, respectively (Figure 1). The crystal parameters were very similar to **TIPS-H₂CP** and **TIPS-ZnCP**. Two TIPS-ethynyl groups bended from the porphyrin plane sigmoidally.



Scheme 1. Synthesis of **TIPS-H₂BP** and **TIPS-ZnBP**.

The single crystal of **TIPS-H₂BP** was also obtained by a slow diffusion of methanol into a chloroform solution. For **TIPS-ZnBP**, it was obtained by a slow diffusion of isopropanol into a chlorobenzene solution (Figure 2).

The crystal structure of **TIPS-H₂BP** consisted of two crystallographically independent molecules in a unit cell. These molecules roughly formed orthogonal positions to each other and made an

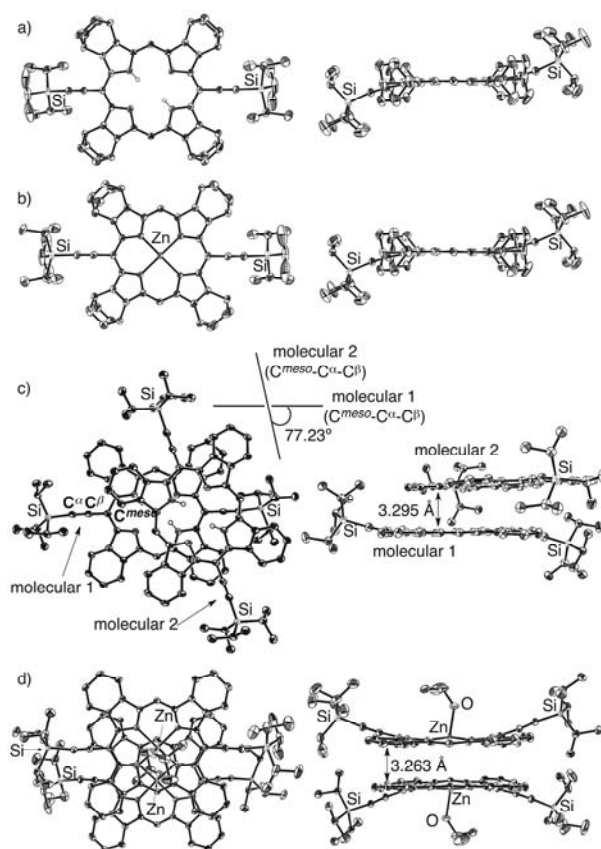


Figure 1. Crystal structures of a) **TIPS-H₂CP**, b) **TIPS-ZnCP**, c) **TIPS-H₂BP**, and d) **TIPS-ZnBP**. Hydrogen atoms, except for the inner N-H hydrogen, were omitted for clarity. Thermal ellipsoids represent 50% probability.

angle of 77.23°. **TIPS-H₂BP** showed highly planar structures and these two species were alternately packed to form a 1D-slip-stacked structure with a minimum interplanar spacing of 3.295 Å. In the case of **TIPS-ZnBP**, isopropanol was coordinated with zinc atom at the axis position. The porphyrin framework was ruffled and two ethynyl groups formed a *syn*-conformation structure. **TIPS-ZnBP** was packed to form a dimeric structure while avoiding the mutual bulky TIPS-groups. Their minimum interplanar distance was 3.263 Å.

The absorption spectra of these **TIPS-CPs** and **BPs** are shown in Figure 2. The shape of the absorption spectrum of **TIPS-H₂CP** was similar to the previously reported **TMS-H₂CP** [13]. The Soret-band was observed at 423 nm and the longest

wavelength of Q-band was observed at 661 nm. By converting to **TIPS-H₂BP**, Soret and Q-band showed red-shifts of 39 nm and 50 nm, respectively, due to π -expansion. The Soret and the longest Q bands of **TIPS-ZnBP** were observed at 468 and 681 nm, respectively. Also, they showed red-shifts of 32 and 71 nm, respectively, from the corresponding peaks of **TIPS-ZnCP**.

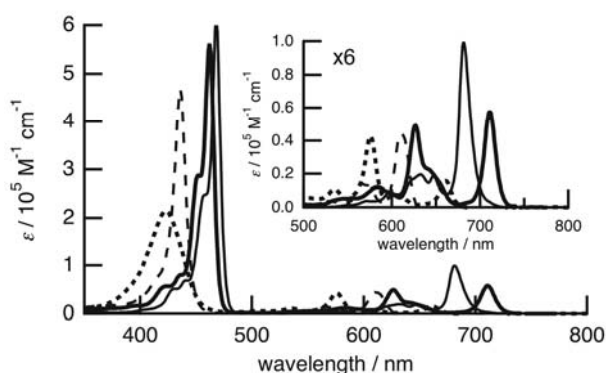


Figure 2. Absorption spectra of **TIPS-H₂CP** (bold dotted line) and **TIPS-ZnBP** (thin-line) in CH₂Cl₂ and **TIPS-ZnCP** (dotted thin-line) and **TIPS-H₂BP** (bold line) in THF.

4. Conclusion

We have succeeded in the preparation of TIPS-ethynyl group substituted benzoporphyrins from BCOD-precursors by the retro Diels-Alder reaction. These compounds exhibited good solubility in common organic solvents due to the introduction of bulky TIPS groups. Absorption spectra of **TIPS-BPs** were red-shifted from **TIPS-CPs** and have relatively strong absorbance at 500-750 nm, which are potentially suitable for good organic solar cells. The crystal structure of **TIPS-H₂BP** revealed a 1D-slip-stacked structure, while that of **TIPS-ZnBP** made a dimeric structure due to coordination with isopropanol on zinc atom. Further investigation of these **TIPS-BPs** for OTFT

and OSC are underway.

5. Acknowledgement

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6. References

1. H. Yamada, T. Okujima, N. Ono, *Chem. Commun.*, (2008) 2957.
2. A. Operamolla, M. Farinola, *Eur. J. Org. Chem.*, (2011) 423.
3. X.-H. Zhu, J. Peng, Y. Cao, J. Roncali, *Chem. Soc. Rev.*, **40** (2011) 3509.
4. A. Mishra, P. Bäuerle, *Angew. Chem. Int. Ed.*, **51** (2012), 2020.
5. S. Ito, T. Murashima, N. Ono, H. Uno, *Chem. Commun.*, (1998), 1661.
6. P. B. Shea, J. Kanicki, L. R. Pattison, P. Petroff, M. Kawano, H. Yamada, N. Ono, *J. Appl. Phys.*, **100** (2006) 034502.
7. Y. Matsuo, Y. Sato, T. Niinomi, I. Soga, H. Tanaka, E. Nakamura, *J. Am. Chem. Soc.*, **131** (2009) 16048.
8. Y. Y. Lin, D. J. Gundlach, S. Nelson, T. N. Jackson, *IEEE Trans. Electron. Dev.*, **44** (1997) 1325.
9. J. E. Anthony, J. S. Brooks, D. L. Eaton, S. R. Parkin, *J. Am. Chem. Soc.*, **123** (2001) 9482.
10. C. D. Sheraw, T. N. Jackson, D. L. Eaton, J. E. Anthony, *Adv. Mater.*, **15** (2003) 2009
11. D. H. Kim, D. Y. Lee, H. S. Lee, W. H. Lee, Y. H. Kim, J. I. Han, K. Cho, *Adv. Mater.*, **19** (2007) 678.
12. C. Wang, H. Dong, W. Hu, Y. Liu, D. Zhu, *Chem. Rev.*, **112** (2012) 2208.
13. H. Yamada, K. Kushibe, T. Okujima, H. Uno, N. Ono, *Chem. Commun.*, (2006) 383.