Supporting Information

Synthesis and Metal Complex Formation of Bis(terpyridine) Derivative Having Phenylacetylene Framework

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Experimental

Melting points were determined on a Yanaco micro melting point apparatus. All melting points were uncorrected. Preparative gel permeation chromatography was performed by LC-9201 (Japan Analytical Industry) with JAIGEL 1H+2H columns with CHCl₃ as solvent. ¹H and ¹³C NMR as well as HH COSY and HSQC spectra were measured in CDCl₃ with a Bruker Avance 300 and 400 spectrometers using tetramethylsilane as an internal standard. UV/Vis spectra were recorded on a HITACHI U-3010 spectrophotometer. High resolution mass spectra were recorded on a Thermo Fisher Exactive at Center for Analytical Instrumentation, Chiba University. Elemental analyses were performed by the Instrument Analysis Center in Faculty of Sciences, Toho University.

2-Bromo-5-[(3-iodophenyl)ethynyl]pyridine (**3**)

To a solution of 1, 3-diiodobenzene (907 mg, 2.75 mmol), CuI (15 mg, 0.079 mmol), and Pd(PPh₃)₄ (35 mg, 0.030 mmol) in degassed triethylamine (15 ml) was added a solution of 2-bromo-5-ethynylpyridine **2**^[S1] (200 mg, 1.10 mmol) in degassed triethylamine (2.5 ml) and the reaction mixture was stirred overnight under reflux. After cooled to room temperature, Et₂O was added to the reaction mixture, then the precipitate was filtered off. The solvent was evaporated under reduced pressure and the residue was separated by column chromatography (SiO₂ / hexane:EtOAc = 9:1) to afford compound **3** (310 mg, 0.81 mmol, 74%) as white solid.

Mp 120–122 °C.

¹H NMR (300 MHz, CDCl₃): δ 8.50(d, J =2.0 Hz, 1H), 7.90(t, J =2.0 Hz, 1H), 7.71(d, J =8.1 Hz, 1H), 7.64(dd, J =8.1, 2.0 Hz, 1H), 7.50(d, J =8.1 Hz, 2H), 7.11(t, J =8.1 Hz, 1H).

¹³C NMR (75 MHz, CDCl₃): δ 152.4, 141.5, 140.5, 140.2, 138.1 130.8, 130.0, 127.8, 124.2, 119.3, 93.8, 92.1, 86.0.

HRMS–ESI m/z [M+H]⁺ calcd for C₁₃H₈BrIN: 383.8873; found: 383.8879.

5,5'-({[(2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl)]bis(3,1-phenylene)}bis(ethyne-2,1-diyl))bis(2-bromopyridine) (**4**)

To a solution of 1,4-dibutoxy-2,5-diethynylbenzene^[S2] (440 mg, 1.63 mmol), CuI (16 mg, 0.084 mmol), and Pd(PPh₃)₄ (85 mg, 0.16mmol) in degassed triethylamine (10 ml) was added a solution of compound **3** (1.25 g, 3.26 mmol) in dehydrated THF (5 ml) under argon atmosphere and the reaction mixture was stirred overnight under reflux. After cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was dissolved in CH₂Cl₂ and CH₃Cl and the solution was washed with saturated aqueous ammonium chloride solution, water, and brine. The organic layer was dried over anhydrous MgSO₄, filtered, and the solvent was evaporated under reduced pressure. The residue was separated by column chromatography (SiO₂ / CH₂Cl₂) to afford compound **4** (1.04 g, 1.34 mmol, 82%) as yellow solid.

Mp 174–177 °C.

¹H NMR (300 MHz, CDCl₃): δ 8.52(d, J =2.0 Hz, 2H), 7.71(s, 2H), 7.65(dd, J =8.2, 2.0 Hz, 2H), 7.55-7.48(m, 6H), 7.37(t, J =7.7 Hz, 2H), 7.02(s, 2H), 4.05(t, J =6.4 Hz, 4H), 1.90-1.81(m, 4H), 1.66-1.53(m, 4H), 1.02(t, J =7.4 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃): δ 153.7, 152.4, 140.5, 134.6, 132.0, 131.3, 128.7, 127.7, 125.5, 124.1, 122.5, 119.5, 116.9, 113.9, 93.8, 93.1, 86.9, 85.3, 69.4, 31.4, 19.3, 13.9.

HRMS–ESI m/z [M+H]⁺ calcd for C₄₄H₃₅Br₂N₂O₂: 781.1071; found 781.1060.

2-bromo-5-({4-[(*tert*-butyldimethylsilyl)oxy]phenyl}ethynyl)pyridine(**6**)

A solution of 2-bromo-5-ethynylpyridine **2**^[S1] (1.82 g, 10.0 mmol), compound **5**^[S3] (3.34 g, 10.0 mmol), CuI (57 mg, 0.30 mmol), and Pd(PPh₃)₄ (346 mg, 0.30 mmol) in degassed triethylamine (20 ml) was stirred at room temperature for 80 min under argon atmosphere. The reaction mixture was passed through a small amount of SiO₂ to remove precipitate and the solvent was evaporated under reduced pressure. The residue was separated by

column chromatography (SiO₂ / Hexane:Et₂O = 11:1) to afford compound **6** (2.10 g, 5.41 mmol, 54%) as white solid.

Mp 53–55 °C.

¹H NMR (300 MHz, CDCl₃): δ 8.48(d, *J*=2.3 Hz, 1H), 7.62(dd, *J*=8.2, 2.3 Hz, 1H), 7.46(d, *J*=8.2 Hz, 1H), 7.41(d, *J*=8.6 Hz, 2H), 6.83(d, *J*=8.6 Hz, 2H), 0.97(s, 9H), 0.20(s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ 156.7, 152.2, 140.6, 140.4, 133.2, 127.6, 120.4, 120.1, 114.9, 94.2, 83.7, 25.6, 18.2, -4.4.

Anal calcd for C₁₉H₂₂BrNOSi: C, 58.76; H, 5.71; N, 3.61; found C, 58.51; H, 5.66; N, 3.56.

5-({4-[(*tert*-butyldimethylsilyl)oxy]phenyl}ethynyl)-2-(tributylstannyl)pyridine (**7**)

To a solution of compound **6** (1.55 g, 4.00 mmol) in dehydrated THF (15 ml) was added *n*BuLi (2.5 M in THF, 1.76 ml, 4.40 mmol) at -78 °C under argon atmosphere and the reaction mixture was stirred for 20 min. To the reaction mixture was added Bu₃SnCl (1.20 ml, 4.40 mmol) and stirred at room temperature for 30 min. Saturated aqueous ammonium chloride solution was added to the reaction mixture, then the solution was extracted with Et₂O. The organic layer was washed with water and brine, and dried over anhydrous MgSO₄, filtered, and the solvent was evaporated under reduced pressure. The residue was separated by column chromatography (SiO₂ with 10 w/w% of K₂CO₃ / Hexane:Et₂O = 11:1) to afford compound **7** (1.71 g, 2.86 mmol, 72%) as orange oil.

¹H NMR (300 MHz, CDCl₃): δ 8.84(d, *J*=2.1 Hz, 1H), 7.58(dd, *J*=7.7, 2.1 Hz, 1H), 7.42(d, *J*=8.6 Hz, 2H), 7.39(d, *J*=7.7 Hz, 1H), 6.82(d, *J*=8.6 Hz, 2H), 1.61-1.51(m, 6H), 1.39-1.27(m, 6H), 1.16-1.10(m, 6H), 0.99(s, 9H), 0.88(t, *J*=7.2 Hz, 9H), 0.20(s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ 173.6, 156.3, 152.2, 135.1, 133.1, 131.4, 120.3, 118.8, 115.5, 92.4, 85.5, 29.1, 27.3, 25.6, 18.2, 13.7, 9.9, -4.4.

HRMS–ESI *m/z* [M+H]⁺ calcd for C₃₁H₅₀NOSiSn: 600.2670; found 600.2678.

6'-bromo-5-((4-((*tert*-butyldimethylsilyl)oxy)phenyl)ethynyl)-2,2'-bipyridine
(**8**)

To a solution of compound **7** (1.71 g, 2.86 mmol), CuI (70 mg, 0.37 mmol), and Pd(PPh₃)₄ (345 mg, 0.29 mmol) in dehydrated toluene (20 ml) was added a solution of 2-bromo-6-iodopyridine^[S4] (893 mg, 3.15 mmol) in dehydrated THF (5 ml) under argon atmosphere and the reaction mixture was stirred overnight under reflux. After cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was separated by column chromatography (SiO₂ with 10 w/w% of K₂CO₃ / Hexane:Et₂O = 9:1) to afford compound **8** (897 mg, 1.93 mmol, 68%) as white solid.

Mp 149–151 °C.

¹H NMR (300 MHz, CDCl₃): δ 8.78(d, *J*=2.0 Hz, 1H), 8.41(dd, *J*=8.0, 2.0 Hz, 2H), 7.92(dd, *J*=8.0, 2.0 Hz, 1H), 7.70(t, *J*=8.0 Hz, 1H), 7.51(d, *J*=8.0 Hz, 1H), 7.48(d, *J*=8.5 Hz, 2H), 6.86(d, *J*=8.5 Hz, 2H), 1.01(s, 9H), 0.24(s, 6H).

¹³C NMR (75 MHz, CDCl₃): δ 156.8, 156.6, 152.8, 151.5, 141.7, 139.22, 139.17, 133.3, 128.1, 121.3, 120.7, 120.4, 119.9, 115.2, 94.2, 85.2, 25.6, 18.2, -4.4.

HRMS–ESI *m/z* [M+H]⁺ calcd for C₂₄H₂₆BrN₂OSi: 465.0988; found 465.0992.

UV/Vis titration

UV/Vis spectra were measured using a solution of compound **1** in CHCl₃ (4.50 μ M, 3 ml). Solutions of ZnCl₂, CoCl₂, and FeCl₂ (0.14 mM) were added to the bis(terpyridine) solution. UV/Vis spectra were measured after addition of a 20 μ l of metal chloride solution, and repeated this procedure until 2 eq. of metal chlorides were added.

NMR titration

NMR spectra were measured using a solution of compound **1** (12.08 mg, 8.67 μ mol) in CDCl₃. A Solution of ZnCl₂ in CD₃OD (86.7 mM) was added to the

bis(terpyridine) solution. NMR spectra were measured after addition of a 20 μ l of ZnCl_2 solution, and repeated this procedure until 2 eq. of ZnCl_2 was added.

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Figure S1. ^1H NMR Spectra of Compound **3**

Figure S2. ^{13}C NMR Spectra of Compound **3**

Figure S3. ^1H NMR Spectra of Compound **4**

Figure S4. ^{13}C NMR Spectra of Compound **4**

Figure S5. ^1H NMR Spectra of
Compound **6**

Figure S6. ^{13}C NMR Spectra of

Compound **6**

Figure S7. ^1H NMR Spectra of Compound **7**

Figure S8. ^{13}C NMR Spectra of
Compound **7**

Figure S9. ^1H NMR Spectra of Compound **8**

Figure S10. ^{13}C NMR Spectra of

8

Compound

Figure S11. ^1H NMR Spectra of Compound **1**

Chemical structure of compound 10 is shown. The structure features a central 1,3-dibutoxyphenylene core linked via ethynyl groups to two 4-(4-(tert-butyldimethylsilyloxy)phenyl)pyridine-2-yl groups.

¹³C NMR spectrum (ppm) is displayed, showing peaks corresponding to the structure. The spectrum includes peaks for the aromatic region (110-155 ppm), the tert-butyl groups (18-26 ppm), and the dimethylsilyl groups (-4.38 and 69.40 ppm).

Peak list (ppm): 154.77, 154.45, 153.78, 151.69, 151.53, 139.29, 139.05, 137.97, 134.70, 133.25, 131.75, 131.34, 128.61, 124.04, 123.00, 121.51, 121.45, 120.80, 120.43, 120.37, 120.14, 117.00, 115.33, 113.96, 93.93, 93.79, 92.73, 87.02, 86.88, 85.39, 77.34, 77.23, 77.03, 76.71, 69.40, 31.43, 25.64, 19.35, 18.25, 13.97, -4.38.

Figure S13. ^{13}C NMR Spectra of Compound **1** (DEPT135)

Figure S14. HH COSY Spectra of Compound **1**

Figure S15. HSQC Spectra of Compound **1**

Figure S16. UV/Vis Titration of Compound **1** with CoCl_2

Figure S17. UV/Vis Titration of Compound **1** with FeCl₂

Figure S18. NMR Titration of Compound **1** with ZnCl_2

Figure S19. ESI-MS Spectra of Compound **1** with ZnCl₂

131211_watanabe_06 #6-14 RT: 0.11-0.21 AV: 4 NL: 3.21E6

T: FTMS {1,1} + p ESI Full ms [200.00-3000.00]

131211_watanabe_06 #6-14 RT: 0.11-0.21 AV: 4 NL: 4.73E4

T: FTMS {1,1} + p ESI Full ms [200.00-3000.00]