Supporting Information for:

Site-selective Mono-titanation of Dialkynylpyridines and Its Application for Preparation of Highly Fluorescent π-Conjugated Oligomers

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General. Melting points were measured with Yanaco MP-J3 Micro Melting Point Apparatus. ^{1}H and ^{13}C NMR spectra were taken on a Varian Gemini-2000 spectrometer at 300 and 75 MHz, respectively. $CDCl_3$ was used as the solvent. Chemical shifts are reported in parts per million shift (δ value) from Me_4Si (δ 0 ppm for ^{1}H) or based on the middle peak of the solvent ($CDCl_3$) (δ 77.00 ppm for ^{13}C NMR) as an internal standard. Signal patterns are indicated as br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in hertz. Infrared (IR) spectra were recorded on a JASCO FT-IR 230 spectrometer and are reported in wave numbers (cm^{-1}). UV/Vis spectra were obtained with HITACHI U-2000 Spectrophotometer. Fluorescence spectra were obtained with SPEX FLUOROMAX-2. Mass spectra (MS, EI, 70 eV) were measured on a Shimadzu QP-5000 GC mass spectrometer. MALDI-TOF-MS spectra were obtained using a Shimadzu MALDI-TOFMS AXIMA-CFR. 2,5-Dihydroxybenzoic acid (DHB) was used as matrix. Elemental analyses were performed on an Elementar Vario-EL. All reactions were carried out under an argon atmosphere, using flame-dried glassware and were monitored by TLC (Merck, Kieselgel 60 F254); visualization was done with UV light (254 nm) / $KMnO_4$ or Vanillin.

Material. $Ti(O\text{-}i\text{-}Pr)_4$ was distilled and stored under argon. Isopropylmagnesium chloride was prepared in Et_2O as 1.30 – 2.25 M solution from isopropyl chloride and magnesium turnings by the usual procedure, titrated and stocked under an argon atmosphere. Dry solvent (Et_2O, THF, CH_2Cl_2) was purchased from Kanto Chemicals. Degassing of solvents and amines used for Pd-catalyzed coupling reactions was accomplished by vigorously bubbling argon for at least 1 h. Chemicals were purified or dried in a standard manner.

Preparation of Dialkynylpyridines 2.

2,3-Bis[(trimethylsilyl)ethynyl]pyridine (**2a**).

This compound was prepared according to the literature procedure.[1]

2,4-Bis[(trimethylsilyl)ethynyl]pyridine (**2b**).

To a CH_2Cl_2 (27 mL) solution of 2,4-dihydroxypyridine (1.00 g, 9.00 mmol) were added Et_3N (4.60 mL, 33.0 mmol) and trifluoromethanesulfonic anhydride (3.57 mL, 21.2 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 12 h. After removal of the solvent, the residue was chromatographed on silica gel (Wakogel C-200, hexane – Et_2O) to give 2,4-bis(trifluoromethanesulfonyl)pyridine (2.60 g, 77%) as a yellow oil.

To a mixture of 2,4-bis(trifluoromethanesulfonyl)pyridine (1.70 g, 4.53 mmol), CuI (17.3 mg 0.0906 mmol), and $Pd(PPh_3)_4$ (52.2 mg 0.0452 mmol) in diisopropylamine (6.3 mL) was added (trimethylsilyl)acetylene (1.92 mL, 13.6 mmol) and the mixture was stirred for 12 h at 80 °C. Et_2O and a saturated solution of NH_4Cl were added to the mixture at 0 °C and the organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et_2O) to afford the title compound **2b** (0.893 g, 73%) as a brown oil. ^1H NMR □ 8.48 (br d, J = 4.8 Hz, 1H), 7.48 (br s, 1H), 7.20 (br d, J = 4.8 Hz, 1H), 0.24 (s, 9H), 0.23 (s, 9H); ^{13}C NMR □ 149.70, 142.98, 131.43, 129.29, 124.78, 102.95, 101.13, 100.67, 95.50, -0.25, -0.28; IR (neat) 2960, 2160, 1585, 1532, 1461, 1380, 1251, 1163, 947, 863, 760 cm^{-1}; Anal. Calcd. for $C_{15}H_{21}NSi_2$: C, 66.36; H, 7.80; N, 5.16. Found: C, 66.04; H, 7.80; N, 5.57.

2,5-Bis[(trimethylsilyl)ethynyl]pyridine (**2c**).

This compound was prepared according to the literature procedure.[2]

2,6-Bis[(trimethylsilyl)ethynyl]pyridine (**2d**).

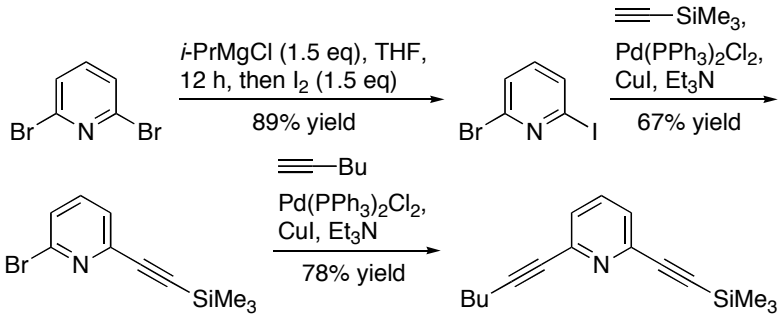
This compound was prepared according to the literature procedure.[2]

3,4-Bis[(trimethylsilyl)ethynyl]pyridine (**2e**).

To a mixture of 3-bromo-4-iodopyridine[3] (1.68 g, 5.92 mmol), CuI (22.5 mg 0.118 mmol), $Pd(PPh_3)_4$ (68.4 mg 0.0592 mmol), and diisopropylamine (16.6 mL, 118 mmol) in THF (8 mL) was added (trimethylsilyl)acetylene (4.18 mL, 29.6 mmol) and the mixture was stirred for 3 days at 90 °C. Et_2O and a saturated solution of NH_4Cl were added to the mixture at 0 °C and the organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et_2O) to afford the title compound **2e** (1.06 g, 66%) as a brown oil. ^{1}H NMR 8.68 (d, J = 0.9 Hz, 1H), 8.44 (d, J = 5.1 Hz, 1H), 7.29 (dd, J = 5.1, 0.9 Hz, 1H), 0.29 (s, 18H); ^{13}C NMR 152.65, 147.91, 133.01, 125.10, 121.71, 104.17, 102.04, 100.38, 99.94, -0.02, -0.16; IR (neat) 2961, 2900, 2161, 1575, 1476, 1400, 1251, 1191, 844, 760, 701 cm^{-1}; Anal. Calcd. for $C_{15}H_{21}NSi_2$: C, 66.36; H, 7.80. Found: C, 66.40; H, 7.62.

6-(1-Hexynyl)-2-[(trimethylsilyl)ethynyl]pyridine (**2f**).

This was prepared according to the following scheme. 6-Bromo-2-iodopyridine was synthesized from 2,6-dibromopyridine by the procedure according to the literature.[4a] ^{1}H and ^{13}C spectra of 6-bromo-2-iodopridine thus synthesized were identical with the literature.[4b]



To a mixture of 6-bromo-2-iodopyridine (1.16 g, 4.09 mmol), CuI (31.1 mg, 0.163 mmol), and $Pd(PPh_3)_2Cl_2$ (57.4 mg 0.0817 mmol) in triethylamine (14 mL) was added (trimethylsilyl)acetylene (0.635 mL, 4.49 mmol) at 0 °C and the mixture was stirred for 6 h at room temperature. After filtration, the filtrate was concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et_2O) to afford 6-(trimethylsilyl)ethynyl-2-bromopyridine (0.698 g, 67%). ^{1}H spectrum of 6-(trimethylsilyl)ethynyl-2-bromopyridine thus obtained was identical with the literature.[5]

To a stirred solution of 6-(trimethylsilyl)ethynyl-2-bromopyridine (0.812 g, 3.19 mmol), CuI (24.3 mg, 0.128 mmol), and $Pd(PPh_3)_2Cl_2$ (44.8 mg 0.0639 mmol) in triethylamine (11 mL) was added 1-hexyne (0.734 mL, 6.39 mmol), and the resulting mixture was stirred for 12 h at room temperature. The mixture was filtered and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et_2O) to afford the pure title compound **2f** (0.634 g, 78%) as a brown oil. . ^{1}H NMR δ 7.54 (dd, J = 7.8, 7.8 Hz, 1H), 7.32 (dd, J = 7.8, 0.9 Hz, 1H), 7.27 (dd, J = 7.8, 0.9 Hz, 1H), 2.40 (t, J = 6.9 Hz, 2H), 1.62-1.53 (m, 2H), 1.50-1.38 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H), 0.23 (s, 9H); ^{13}C NMR δ 144.34, 143.24, 136.22, 126.20, 125.91, 103.35, 94.92, 91.67, 79.97, 30.21, 21.92, 18.90, 13.34, -0.492; IR (neat) 2959, 2930, 2870, 2230, 2162, 1560, 1442, 1250, 1216, 847, 810, 761 cm^{-1}; Anal. Calcd. for $C_{16}H_{21}NSi$: C, 75.23; H, 8.29. Found: C, 75.52; H, 8.39.

5-(1-Hexynyl)-2-[(trimethylsilyl)ethynyl]pyridine (**2g**).

To a mixture of 5-bromo-2-[(trimethylsilyl)ethynyl]pyridine[6] (1.00 g, 3.93 mmol), CuI (30.0 mg 0.157 mmol), and $Pd(PPh_3)_2Cl_2$ (55.2 mg 0.0787 mmol) in triethylamine (16 mL) and CH_2Cl_2 (3 mL) was added 1-hexyne (0.678 mL, 5.90 mmol) and the mixture was stirred for 1 day at room temperature. Et_2O and H_2O were added to the mixture at 0 °C and the organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et_2O) to afford the title compound **2g** (0.783 g, 78%) as an orange oil. ^{1}H NMR δ 8.55 (dd, J = 2.1, 0.9 Hz, 1H), 7.60 (dd, J = 8.1, 2.1 Hz, 1H), 7.36 (dd, J = 8.1, 0.9 Hz, 1H), 2.43 (t, J = 6.9 Hz, 2H), 1.65-1.55 (m, 2H), 1.54-1.42 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR δ 152.50, 140.93, 138.45, 126.49, 120.60, 103.50, 96.27, 96.06, 77.27, 30.42, 21.88, 19.09, 13.44, -0.484; IR (neat) 2959, 2933, 2870, 2230, 2164, 1540, 1466, 1363, 1250, 867, 760, 699 cm^{-1}; Anal. Calcd. for $C_{16}H_{21}NSi$: C, 75.23; H, 8.29. Found: C, 75.55; H, 8.56.

4-(1-Hexynyl)-3-[(trimethylsilyl)ethynyl]pyridine (**2h**).

Diisopropylamine (11 mL) was added to a mixture of 3-bromo-4-iodopyridine[3] (1.08 g, 3.80 mmol), $Pd(PPh_3)_4$ (44.0 mg, 0.0380 mmol), and CuI (14.5 mg, 0.0761 mmol) and then 1-hexyne (0.656 mL, 5.71 mmol) was added to the mixture. The reaction was stirred for 12 h at ambient temperature. The mixture was filtered and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – AcOEt) to 3-bromo-4-(1-hexynyl)pyridine (0.658 g, 73%) as a brown oil.

To a stirred solution of to 3-bromo-4-(1-hexynyl)pyridine (0.629 g, 2.64 mmol), CuI (16.9 mg, 0.0886 mmol), and $Pd(PPh_3)_4$ (51.2 mg 0.0443 mmol) in diisopropylamine (6.2 mL) was added (trimethylsilyl)acetylene (0.940 mL, 6.65 mmol), and the resulting mixture was warmed up to 90 °C and stirred for 2 days at this temperature. The mixture was filtered and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – AcOEt) to afford the title compound **2h** (0.372 g, 55%) as a brown oil. ^{1}H NMR δ 8.63 (d, *J* = 0.9 Hz, 1H), 8.38 (d, *J* = 5.1 Hz, 1H), 7.20 (dd, *J* = 5.1, 0.9 Hz, 1H), 2.47 (t, *J* = 6.9 Hz, 2H), 1.66-1.55 (m, 2H), 1.54-1.43 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR δ 152.81, 148.16, 134.50, 125.18, 121.82, 101.45, 100.56, 100.36, 77.36, 30.36, 21.87, 19.24, 13.44, -0.333; IR (neat) 2959, 2933, 2870, 2230, 2160, 1577, 1478, 1400, 1250, 844, 759 cm^{-1}; Anal. Calcd. for $C_{16}H_{21}NSi$: C, 75.23; H, 8.29. Found: C, 75.49; H, 8.20.

General Procedure for Regioselective Mono-titanation of Dialkynylpyridines 2 in Table.

(*Z*)-2-[2-(trimethylsilyl)ethenyl]-3-[(trimethylsilyl)ethynyl]pyridine (**3a**).

To a stirred solution of 2,3-bis[(trimethylsilyl)ethynyl]pyridine (**2a**) (6.00 g, 22.1 mmol) and Ti(O-*i*-Pr)$_4$ (6.52 mL, 22.1 mmol) in 220 mL of Et_2O was added a 2.25 M solution of *i*-PrMgCl in Et_2O (21.6 mL, 48.6 mmol) at –78 °C under argon to give a yellow homogeneous solution. The solution was warmed up to –50 °C over 30 min, during which period its color turned brown. After the solution was stirred at –50 °C for 2 h, H_2O (22 mL) was added at 0 °C. After addition of NaF and Celite, the resulting mixture was filtered through a pad of Celite and concentrated *in vacuo* to give a crude, which was purified by column chromatography (hexane) on silica gel (Wakogel C-200, hexane - Et_2O) to afford the title compound **3a** (5.05 g, 84%) as a yellow solid. M.p. = 33-34 °C; ^{1}H NMR δ 8.45 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.72 (d, *J* = 14.1 Hz, 1H), 7.69 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.08 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.20 (d, *J* = 14.1 Hz, 1H) 0.27 (s, 9H), 0.17 (s, 9H); ^{13}C NMR δ 156.80, 147.02, 141.16, 140.30, 139.77, 121.24, 118.32, 101.73, 101.25, 0.79, 0.01; IR (neat) 2957, 2898, 2157, 1547, 1420, 1250, 1164, 1096, 841 cm^{-1}; Anal. Calcd. for $C_{15}H_{23}NSi_2$: C, 65.87; H, 8.48. Found: C, 65.62; H, 8.25.

(*Z*)-2-[2-(trimethylsilyl)ethenyl]-4-[(trimethylsilyl)ethynyl]pyridine (**3b**).

2,4-Bis[(trimethylsilyl)ethynyl]pyridine (**2b**) (0.137 g, 0.505 mmol) was mono-titanated with Ti(O-*i*-Pr)$_4$ (0.149 mL, 0.505 mmol) and a 1.61 M solution of *i*-PrMgCl in Et_2O (0.690 mL, 1.11 mmol) in Et_2O (5 mL) as described in the general procedure. Column chromatography (Wakogel C-200, hexane - Et_2O) afforded the title compound **3b** (0.110 g, 80%) as a pale yellow

oil. ^{1}H NMR δ 8.49 (dd, *J* = 4.8, 0.6 Hz, 1H), 7.22-7.20 (m, 1H), 7.16 (d, *J* = 14.4 Hz, 1H), 7.14 (dd, *J* = 4.8, 1.5 Hz, 1H), 6.08 (d, *J* = 14.4 Hz, 1H), 0.26 (s, 9H), 0.16 (s, 9H); ^{13}C NMR δ 156.07, 148.20, 143.00, 139.01, 131.19, 125.54, 123.83, 102.22, 99.16, 0.69, -0.14; IR (neat) 2957, 2159, 1577, 1251, 933, 838, 759 cm^{-1}; Anal. Calcd. for $C_{15}H_{23}NSi_2$: C, 65.87; H, 8.48; N, 5.12. Found: C, 65.93; H, 8.79; N, 4.70.

(*Z*)-2-[2-(Trimethylsilyl)ethenyl]-5-[(trimethylsilyl)ethynyl]pyridine (**3c**).

2,5-Bis[(trimethylsilyl)ethynyl]pyridine (**2c**) (4.00 g, 14.7 mmol) was mono-titanated with Ti(O-*i*-Pr)$_4$ (4.35 mL, 14.7 mmol) and a 1.55 M solution of *i*-PrMgCl in Et$_2$O (20.9 mL, 32.4 mmol) in Et$_2$O (160 mL) as described in the general procedure. Column chromatography (Wakogel C-200, hexane - AcOEt) afforded the title compound **3c** (3.56 g, 88%) as a pale yellow oil. ^{1}H NMR δ 8.63 (d, *J* = 2.1 Hz, 1H), 7.67 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.17 (d, *J* = 14.4 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 6.11 (d, *J* = 14.4 Hz, 1H), 0.28 (s, 9H), 0.19 (s, 9H); ^{13}C NMR δ 154.99, 151.33, 142.94, 139.85, 138.91, 122.62, 118.22, 102.11, 98.24, 0.56, -0.14; IR (neat) 2957, 2159, 1586, 1539, 1475, 1363, 1251, 1024; 839 cm^{-1}; Anal. Calcd. for $C_{15}H_{23}NSi_2$: C, 65.87; H, 8.48. Found: C, 65.88; H, 8.84. If the reaction was terminated by an addition of D$_2$O instead of H$_2$O, (*Z*)-2-[1,2-Bis(deuterio)-2-(trimethylsilyl)ethenyl]-5-[(trimethylsilyl)ethynyl]pyridine was obtained. The peaks at δ 7.17 ppm (alkenyl-H) and 6.11 ppm (alkenyl-H) of **3c** disappeared to show 99% deuterium incorporation in both peaks.

(*Z*)-2-[2-(trimethylsilyl)ethenyl]-6-[(trimethylsilyl)ethynyl]pyridine (**3d**).

2,6-Bis[(trimethylsilyl)ethynyl]pyridine (**2d**) (0.137 g, 0.505 mmol) was mono-titanated with Ti(O-*i*-Pr)$_4$ (0.164 mL, 0.555 mmol) and a 1.95 M solution of *i*-PrMgCl in Et$_2$O (0.626 mL, 1.22 mmol) in Et$_2$O (5 mL) as described in the general procedure. Column chromatography (Wakogel C-200, hexane – Et$_2$O) afforded the title compound **3d** (0.124 g, 90%). ^{1}H NMR δ 7.55 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.25 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.16 (d, *J* = 14.1 Hz, 1H), 7.09 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.10 (d, *J* = 14.1 Hz, 1H), 0.28 (s, 9H), 0.23 (s, 9H); ^{13}C NMR δ 156.02, 142.64, 141.69, 139.57, 136.16, 124.86, 122.59, 103.83, 94.40, 0.54, -0.17; IR (neat) 2957, 2157, 1557, 1443, 1251, 1196, 1151, 1084, 970, 841, 760 cm^{-1}; Anal. Calcd. for $C_{15}H_{23}NSi_2$: C, 65.87; H, 8.48. Found: C, 66.19; H, 8.22.

(*Z*)-4-[2-(trimethylsilyl)ethenyl]-3-[(trimethylsilyl)ethynyl]pyridine (**3e**).

3,4-Bis[(trimethylsilyl)ethynyl]pyridine (**2e**) (0.137 g, 0.505 mmol) was mono-titanated with Ti(O-*i*-Pr)$_4$ (0.298 mL, 1.01 mmol) and a 1.61 M solution of *i*-PrMgCl in Et$_2$O (1.38 mL, 2.22 mmol) in Et$_2$O (5 mL) as described in the general procedure. Column chromatography (Wakogel C-200, hexane – Et$_2$O) afforded the title compound **3e** (0.109 g, 79%) as a brown oil. ^{1}H NMR 8.63 (s, 1H), 8.44 (d, *J* = 5.1 Hz, 1H), 7.39 (d, *J* = 15.3 Hz, 1H), 7.18 (d, *J* = 5.1 Hz, 1H), 6.10 (d, *J* = 15.3, 1H), 0.25 (s, 9H), 0.036 (s, 9H); ^{13}C NMR 153.09, 149.53, 148.18, 142.34, 137.79, 122.20, 119.23, 102.74, 100.29, -0.17, -0.28; IR (neat) 2959, 2158, 1579, 1402, 1251, 1191, 1052, 844, 761 cm^{-1}; Anal. Calcd. for $C_{15}H_{23}NSi_2$: C, 65.87; H, 8.48. Found: C, 66.09; H, 8.47.

(*Z*)-6-(1-Hexenyl)-2-[(trimethylsilyl)ethynyl]pyridine (**3f**).

6-(1-Hexynyl)-2-[(trimethylsilyl)ethynyl]pyridine (**2f**) (58.6 mg, 0.229 mmol) was mono-titanated with Ti(O-*i*-Pr)$_4$ (0.135 mL, 0.459 mmol) and a 1.89 M solution of *i*-PrMgCl in Et$_2$O (0.534 mL, 1.01 mmol) in Et$_2$O (3 mL) as described in the general procedure. After being stirred at -50 °C for 1 h, this reaction was terminated and column chromatography (Wakogel C-200, hexane – Et$_2$O) afforded the title compound **3f** (41.4 mg, 70%) as a pale yellow oil and the site-isomer, 2-(1-hexynyl)-6-[(trimethylsilyl)ethenyl]pyridine, (9.50 mg, 16%) as a pale yellow oil. **3f**: ^{1}H NMR 7.56 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 6.43 (d, *J* = 11.7 Hz, 1H), 5.88 (dt *J* = 11.7, 7.5 Hz, 1H), 2.47 (dt, *J* = 7.5, 7.5 Hz, 2H), 1.50-1.30 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR 157.12, 142.62, 137.81, 135.95, 128.43, 124.87, 123.05, 104.11, 93.98, 31.61, 28.35, 22.24, 13.74, -0.44; IR (neat) 2959, 2927, 2858, 2158, 1641, 1561, 1447, 1405, 1251, 846, 760, 732 cm^{-1}; Anal. Calcd. for $C_{16}H_{23}NSi$: N, 5.44. Found: N, 5.48. The site-isomer, 2-(1-hexynyl)-6-[(trimethylsilyl)ethenyl]pyridine: ^{1}H NMR 7.53 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.18, (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 14.4 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.06 (d, *J* = 14.4 Hz, 1H), 2.44 (t, *J* = 6.9 Hz, 2H), 1.65-1.48 (m, 4H), 0.95 (d, *J* = 7.2 Hz, 3H), 0.21 (s, 9H). ^{13}C NMR 156.27, 143.30, 143.03, 139.21, 136.24, 124.98, 122.01, 90.76, 80,39, 30.46, 21.83, 18.81, 13.44, 0.29; IR (neat) 2957, 2871, 2230, 1564, 1445, 1414, 1241, 1088, 842, 745, 655 cm^{-1}.

(*Z*)-5-(1-Hexynyl)-2-[(trimethylsilyl)ethenyl]pyridine (**3g**).

5-(1-Hexynyl)-2-[(trimethylsilyl)ethynyl]pyridine (**2g**) (0.103 g, 0.403 mmol) was mono-titanated with Ti(O-*i*-Pr)$_4$ (0.119 mL, 0.403 mmol) and a 1.62 M solution of *i*-PrMgCl in Et$_2$O (0.548 mL, 0.887 mmol) in Et$_2$O (4 mL) as described in the general procedure. Column chromatography (Wakogel C-200, hexane – Et$_2$O) afforded the title compound **3g** (0.0771 g, 74%)

as a pale yellow oil. ^{1}H NMR δ 8.57 (d, *J* = 1.8 Hz, 1H), 7.59 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.17 (d, *J* = 14.4 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.07 (d *J* = 14.4 Hz, 1H), 2.43 (t, *J* = 6.9 Hz, 2H), 1.64-1.42 (m, 4H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR δ 154.42, 151.12, 143.28, 138.99, 138.60, 122.74, 119.27, 94.20, 77.81, 30.59, 21.90, 19.09, 13.50, 0.42; IR (neat) 2957, 2870, 2230, 1588, 1534, 1483, 1364, 1240, 1212, 847, 765, 664 cm^{-1}; Anal. Calcd. for $C_{16}H_{23}NSi$: C, 74.65; H, 9.00. Found: C, 74.37; H, 9.01.

(*Z*)-4-(1-Hexenyl)-3-[(trimethylsilyl)ethenyl]pyridine (**3h**).

4-(1-Hexynyl)-3-[(trimethylsilyl)ethynyl]pyridine (**2h**) (58.7 mg, 0.230 mmol) was mono-titanated with Ti(O-*i*-Pr)$_4$ (0.136 mL, 0.460 mmol) and a 1.89 M solution of *i*-PrMgCl in Et_2O (0.535 mL, 1.01 mmol) in Et_2O (3 mL) as described in the general procedure. Column chromatography (Wakogel C-200, hexane – Et_2O) afforded the title compound **3h** (49.3 mg, 83%) as a yellow oil. ^{1}H NMR δ 8.65 (s, 1H), 8.43 (d, *J* = 5.1 Hz, 1H), 7.19 (d, *J* = 5.1 Hz, 1H), 6.56 (d, *J* = 12.0 Hz, 1H), 5.91 (dt *J* = 12.0, 7.5 Hz, 1H), 2.25 (dt, *J* = 7.5, 7.5 Hz, 2H), 1.50-1.28 (m, 4H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.24 (s, 9H); ^{13}C NMR δ 153.41, 148.20, 147.08, 137.87, 125.15, 122.64, 119.44, 102.25, 100.59, 31.59, 28.57, 22.18, 13.72, -0.30; IR (neat) 3017, 2959, 2928, 2861, 2157, 1581, 1472, 1401, 1250, 843, 761, 658 cm^{-1}; Anal. Calcd. for $C_{16}H_{23}NSi$: C, 74.65; H, 9.00. Found: C, 74.58; H, 8.76.

Synthesis of Conjugated Oligomers in Scheme 1.

(*E*)-2-(2-Bromoethenyl)-5-[(trimethylsilyl)ethynyl]pyridine (**4**).

To a stirred solution of (*Z*)-2-[2-(trimethylsilyl)ethenyl]-5-[(trimethylsilyl)ethynyl]pyridine (**3c**) (6.75 g, 24.7 mmol) in CH_2Cl_2 (50 mL), cooled to –78 °C, was added slowly a solution of Br_2 (1.58 mL, 30.8 mmol) in CH_2Cl_2 (15 mL). To the resulting orange / red solution were added MeOH (250 mL) and Na_2SO_3 (12.3 g), and the resulting mixture was stirred until it became light yellow. While still at –78 °C, the reaction mixture was poured into 10% Na_2SO_3 solution, and shaken until all color had disappeared. After separation, the aqueous layer was extracted thoroughly with pentane, and the combined organic extracts dried. The solution was concentrated *in vacuo* to give the crude of 2-[1,2-di(bromo)ethyl]-5-[(trimethylsilyl)ethynyl]pyridine, which was used immediately.

The crude was dissolved in MeOH (250 mL) and THF (60 mL), and treated with MeONa (2.00 g, 37.0 mmol) at 0 °C. The resulting mixture was stirred at this temperature for 1 h, and then at ambient temperature for 2 h. It was then partitioned between pentane and H_2O, and the

aqueous layer was extracted thoroughly with pentane. The combined organic extracts were dried and concentrated *in vacuo* to give acrude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – AcOEt) to afford (*E*)-2-(2-Bromoethenyl)-5-ethynylpyridine (3.49 g, 68% overall yield from **3c**).

To a stirred solution of (*E*)-2-(2-Bromoethenyl)-5-ethynylpyridine (1.51 g, 7.26 mmol) in THF (24 mL) was added $NaN[SiMe_3]_2$ (9.44 mL, 1.00 mol/L in THF, 9.44 mmol) at –78 °C. After being stirred for 1 h, Me_3SiCl (1.38 mL, 10.9 mmol) was added to the reaction mixture. And then the mixture was warmed up to room temperature and stirred for 12 h. The reaction was terminated by an addition of H_2O. The resulting mixture was extracted with Et_2O, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et_2O) to afford the title compound **4** (1.74 g, 86%) as a yellow oil. ^{1}H NMR 8.59 (dd, *J* = 2.4, 0.6 Hz, 1H), 7.68 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.41 (d, *J* = 13.8, Hz, 1H), 7.11 (d, *J* = 13.8 Hz, 1H), 7.09 (dd, *J* = 8.1, 0.6 Hz, 1H), 0.26 (s, 9H); ^{13}C NMR 152.75, 152.52, 139.44, 135.94, 120.77, 119.08, 113.98, 101.54, 99.07, 0.23; IR (neat) 2959, 2159, 1473, 1250, 1163, 1023, 936, 843 cm^{-1}; Anal. Calcd. for $C_{12}H_{14}BrNSi$: C, 51.43; H, 5.04; N, 5.00. Found: C, 51.48; H, 5.05. N, 5.06.

(*E*)-2-(1-Tetradecen-3-yn-1-yl)-5-[(trimethylsilyl)ethynyl]pyridine (**Monomer 5**).

To a mixture of **4** (1.07 g, 3.80 mmol), $Pd(PPh_3)_2Cl_2$ (53.4 mg, 0.0761 mmol), CuI (29.0 mg, 0.152 mmol), and triethylamine (4.98 mL, 35.7 mmol) in THF (40 mL) was added 1-dodecyne (1.05 mL, 4.94 mmol) at 0 °C and the reaction mixture was stirred at this temperature for 30 min. Et_2O and water were added to the mixture and the organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et_2O) to afford the title compound **5** (1.24 g, 90%) as a brown oil. ^{1}H NMR 8.58 (d, *J* = 1.8 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 15.6 Hz, 1H), 6.72 (dt, *J* = 15.6, 2.1 Hz, 1H), 2.37 (dt, *J* = 2.1, 6.9 Hz, 2H), 1.61-1.51 (m, 2H), 1.46-1.34 (m, 2H), 1.33-1.22 (m, 12H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR 153.54, 152.52, 139.16, 138.18, 120.79, 118.84, 114.75, 101.90, 98.81, 96.50, 79.69, 31.89, 29.56, 29.51, 29.30, 29.13, 28.89, 28.65, 22.66, 19.79, 14.08, -0.18; IR (neat) 2926, 2855, 2210, 2158, 1615, 1582, 1471, 1371, 1250, 955, 863, 760 cm^{-1}. UV/Vis ($CHCl_3$) λ_{abs} ( ) [nm] = 294 (21 500), 325 (37 100); MS (EI) *m/z* (relative intensity), 365 (30.7, M^+), 252 (100), 226 (61.9); Anal. Calcd for $C_{24}H_{35}NSi$: C, 78.84; H, 9.65. Found: C, 78.64; H, 9.62.

Dimer (**6**).

To a stirred solution of the monomer **5** (1.14 g, 3.13 mmol) in THF (10 mL) was added TBAF (3.13 mL, 1.0 mol/L in THF, 3.13 mmol) and the mixture was stirred for 1 h at 0 °C. The reaction mixture was extracted with Et_2O, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude of the desilylated monomer. The terminal acetylene derivative was used for the next step without further purification.

To a mixture of **4** (1.05 g 3.75 mmol), $Pd(PPh_3)_4$ (72.2 mg, 0.0625 mmol), and CuI (23.8 mg, 0.125 mmol) in degassed *i*-Pr_2NH (1.97 mL, 14.1 mmol) was added a solution of the desilylated monomer in degassed THF (16 mL). The reaction mixture was stirred at room temperature for 1 h and extracted with Et_2O, washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford a crude product, which was chromatographed on silica gel (Wakogel C-200, hexane - Et_2O) to yield the dimer **6** (1.20 g, 78% overall yield from the monomer **5**) as a yellow solid. M.p. = 125-126 °C; ^{1}H NMR □ 8.63 (d, *J* = 2.1 Hz, 1H) 8.62 (d, *J* = 2.4 Hz, 1H), 7.68 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.67 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.05 (d, *J* = 15.9 Hz, 1H), 6.98 (d, *J* = 15.9 Hz, 1H), 6.86 (d, *J* = 15.9 Hz, 1H), 6.75 (dt, *J* = 15.9, 2.1 Hz, 1H), 2.38 (dt, *J* = 2.1, 6.9 Hz, 2H), 1.62-1.51 (m, 2H), 1.48-1.22 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.26 (s, 9H); ^{13}C NMR □ 153.53, 152.76, 152.67, 152.22, 140.00, 139.30, 138.80, 138.17, 121.59, 121.06, 119.45, 118.87, 114.79, 113.07, 101.72, 99.41, 96.69, 92.60, 91.48, 79.72, 31.88, 29.56, 29.51, 29.30, 29.13, 28.90, 28.64, 22.67, 19.80, 14.10, -0.20; IR (KBr) 2922, 2852, 2188, 2154, 1575, 1469, 1369, 1250, 954, 858, 758 cm^{-1}; UV/Vis ($CHCl_3$) □$_{abs}$ (□) [nm] = 256 (15 700), 294 (17 600), 367 (66 300), 389 (51 100); MALDI-TOF-MS (DHB) 492.9 (Calcd for $C_{33}H_{40}N_2Si$: 492.3); Anal. Calcd for $C_{33}H_{40}N_2Si$: C, 80.43; H, 8.18; N, 5.68. Found: C, 80.54; H, 8.11; N, 5.98.

Trimer (**7**).

The dimer **6** (1.10 g, 2.23 mmol) was desilylated with TBAF (2.23 mL, 1.0 mol/L in THF, 2.23 mmol) and the resulting terminal acetylene was cross-coupled with vinyl bromide **4** (0.751 g, 2.68 mmol) in degassed $CHCl_3$ (22 mL) in the presence of $Pd(PPh_3)_4$ (77.4 mg, 0.0670 mmol), CuI (25.5 mg, 0.134 mmol), and degassed *i*-Pr_2NH (2.03 mL, 14.5 mmol) for 1 h as described in the procedure for synthesis of **6**. The reaction was extracted with $CHCl_3$ and recrystallization from $CHCl_3$ - hexane afforded the trimer **7** (1.00 g, 73% overall yield from the dimer **6**) as a yellow solid. M.p. = >220 °C (decoloration from yellow to brown); ^{1}H NMR □ 8.68-8.64 (m, 1H), 8.64-8.61 (m, 2H), 7.71 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.70 (dd, *J* = 7.8, 2.4 Hz, 1H), 7.68 (dd, *J* = 7.8, 2.1 Hz, 1H), 7.26-7.17 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.073 (d, *J* = 15.9 Hz, 1H), 7.070 (d, *J* = 15.9 Hz, 1H),

7.00 (d, *J* = 15.9 Hz, 1H), 6.99 (d, *J* = 15.9 Hz, 1H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.75 (dt, *J* = 15.9, 2.1 Hz, 1H), 2.39 (dt, *J* = 2.1, 6.6 Hz, 2H), 1.63-1.51 (m, 2H), 1.47-1.22 (m, 14H), 0.88 (t, *J* = 7.2 Hz, 3H), 0.27 (s, 9H); ^{13}C NMR □ 153.70, 152.94, 152.83 (x2), 152.52, 152.36, 140.33, 140.11, 139.43, 139.03, 138.93, 138.28, 121.89, 121.71, 121.13, 119.60 (x2), 118.96, 114.90, 113.20, 113.06, 101.75, 99.55, 96.75, 93.10, 92.71, 91.65, 91.37, 79.74, 31.81, 29.48, 29.43, 29.22, 29.05, 28.82, 28.56, 22.57, 19.72, 13.98, -0.33; IR (KBr) 2922, 2852, 2203, 2152, 1572, 1468, 1367, 1250, 956, 855, 757 cm^{-1}. UV/Vis ($CHCl_3$) □$_{abs}$ (□) [nm] = 282 (22 200), 391 (86 400); MALDI-TOF-MS (DHB) 619.8 (Calcd for $C_{42}H_{45}N_3Si$: 619.3); Anal. Calcd for $C_{42}H_{45}N_3Si$: C, 81.37; H, 7.32. Found: C, 81.46; H, 7.32.

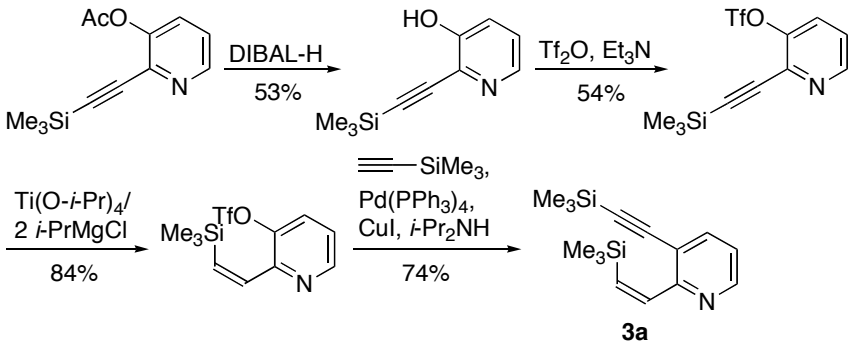
Tetramer (**8**).

The trimer **7** (100 mg, 0.161 mmol) was desilylated with TBAF (0.161 mL, 1.0 mol/L in THF, 0.161 mmol) and the resulting terminal acetylene was cross-coupled with vinyl bromide **4** (54.2 mg g, 0.194 mmol) in degassed $CHCl_3$ (40 mL) in the presence of $Pd(PPh_3)_4$ (37.3 mg, 0.0323 mmol), CuI (12.3 mg, 0.0645 mmol), and degassed *i*-Pr_2NH (0.147 mL, 1.05 mmol) for 1 h as described in the procedure for synthesis of **6**. The reaction was extracted with $CHCl_3$ and column chromatography on silica gel (Wakogel C-200, hexane – $CHCl_3$) and the following recrystallization from $CHCl_3$ - hexane afforded the tetramer **8** (62.2 mg, 52% overall yield from the trimer **7**) as a yellow solid. M.p. = >250 °C (decoloration from yellow to brown); ^{1}H NMR □ 8.70-8.66 (m, 2H), 8.65-8.60 (m, 2H), 7.76-7.64 (m, 4H), 7.26-7.20 (m, 3H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.12-6.98 (m, 5H), 7.00 (d, *J* = 15.9 Hz, 1H), 6.87 (d, *J* = 15.3 Hz, 1H), 6.82-6.72 (m, 1H), 2.44-2.34 (m, 2H), 1.62-1.46 (m, 2H), 1.36-1.18 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.27 (s, 9H); IR (KBr) 2923, 2852, 2190, 2153, 1570, 1543, 1468, 1368, 1251, 957, 859 cm^{-1}. UV/Vis ($CHCl_3$) □$_{abs}$ (□) [nm] =285 (24 600), 329 (35 300), 398 (108 700); MALDI-TOF-MS (DHB) 747.2 (Calcd for $C_{51}H_{50}N_4Si$: 746.4); Anal. Calcd for $C_{51}H_{50}N_4Si$: N, 7.50. Found: N, 7.57. Solubility was too low to measure the ^{13}C NMR spectrum.

Determination of the Structure of 3a-c and 3e.

The structures of **3a**-**c** and **3e** were confirmed in comparison with the corresponding authentic sample prepared according to the following schemes. The yields are not necessarily optimized.

For 3a



3-[(Trifluoromethane)sulfonyl]oxy-2-[(trimethylsilyl)ethynyl]pyridine.

To 3-acetoxy-2-[(trimethylsilyl)ethynyl]pyridine[7] (1.29 g, 5.53 mmol) in Et_2O (18 mL) was added DIBAL-H (14.0 mL, 0.95 mol/L in hexane, 13.3 mmol) at -78 °C and warmed up to 0 °C over 2 h and then the reaction mixture was stirred for 30 min at this temperature. After H_2O (1.5 mL) was cautiously added to the mixture, NaF (1.7 g) and Celite (1.4 g) were successively added to the resulting mixture. The mixture was filtered through Celite pad, and then the filtrate was evaporated to give a crude, which was recrystallized from Et_2O – hexane to afford 3-hydroxy-2-[(trimethylsilyl)ethynyl]pyridine (0.558 g, 53%). ^{1}H spectrum of this product was identical with the literature.[8]

To a stirred solution of 3-hydroxy-2-[(trimethylsilyl)ethynyl]pyridine (0.549 g, 2.87 mmol) and Et_3N (0.880 mL, 6.31 mmol) in CH_2Cl_2 (9 mL) was added trifluoromethanesulfonic anhydride (0.579 mL, 3.44 mmol) at 0 °C and the reaction mixture was stirred for 8 h at room temperature. H_2O was added to the mixture at 0 °C and the organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – AcOEt) to afford the title compound (0.499 g, 54%). ^{1}H NMR δ 8.54 (dd, J = 4.5, 1.2 Hz, 1H), 7.59 (dd, J = 8.4, 1.2 Hz, 1H), 7.32 (dd, J = 8.4, 4.5 Hz, 1H), 0.25 (s, 9H); ^{13}C NMR δ 149.30, 147.92, 137.33, 129.31, 124.03, 118.64 (q, $J_{C\text{-}F}$ = 319.3 Hz), 104.27, 96.94, -0.90.

3-[(Trifluoromethane)sulfonyl]oxy-2-[(trimethylsilyl)ethenyl]pyridine.

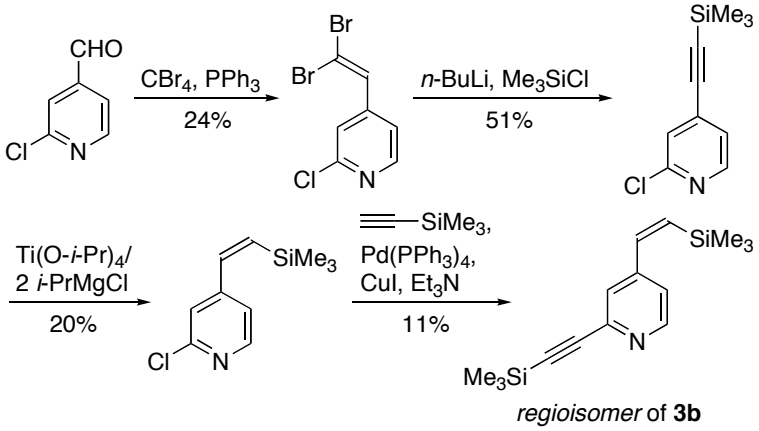
To a stirred solution of 3-[(Trifluoromethane)sulfonyl]oxy-2-[(trimethylsilyl)ethynyl]pyridine (0.513 g, 1.59 mmol) and Ti(O-*i*-Pr)$_4$ (0.702 mL, 2.38 mmol) in 16 mL of Et_2O was added a 1.38 M solution of *i*-PrMgCl in Et_2O (3.45 mL, 4.76 mmol) at –78 °C. The solution was warmed up to –50 °C over 30 min and stirred at this temperature for 2 h. The reaction was terminated by an addition of H_2O (2.4 mL). After addition of NaF and Celite, the resulting mixture was filtered through a pad of Celite and concentrated *in vacuo* to give a crude, which was purified by column chromatography on silica gel (Wakogel C-200, hexane - Et_2O) to

afford the title compound (0.434 g, 84%). ^{1}H NMR δ 8.55 (dd, *J* = 4.2, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.43 (d, *J* = 14.7 Hz, 1H), 7.26 (dd, *J* = 8.1, 4.2 Hz, 1H), 6.35 (d, *J* = 14.7 Hz, 1H), 0.16 (s, 9H); ^{13}C NMR δ 149.07, 147.66, 144.28, 143.67, 135.11, 129.23, 123.31, 118.51 (q, $J_{C\text{-}F}$ = 318.4 Hz), 0.30.

(*Z*)-2-[2-(trimethylsilyl)ethenyl]-3-[(trimethylsilyl)ethynyl]pyridine (**3a**).

To a mixture of 3-[(Trifluoromethane)sulfonyl]oxy-2-[(trimethylsilyl)ethenyl]pyridine (0.349 g, 1.07 mmol), CuI (25.7 mg 0.135 mmol), and $Pd(PPh_3)_4$ (78.0 mg 0.0675 mmol) in diisopropylamine (1.8 mL) was added (trimethylsilyl)acetylene (0.420 mL, 2.97 mmol) and the mixture was stirred for 3 day at 80 °C. Et_2O and H_2O were added to the mixture and the organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et_2O) to afford the title compound **3a** (0.278 g, 95%). Physical properties of the authentic sample thus synthesized were identical with those of **3a** obtained by the mono-titanation of **2a**.

For 3b



regioisomer of **3b**

2-Chloro-4-(2,2-dibromoethenyl)pyridine.

To a solution of CBr_4 (13.1 g, 39.4 mmol) in CH_2Cl_2 (41 mL) was added a CH_2Cl_2 (30 mL) solution of PPh_3 (20.7 g, 78.8 mmol) at 0 °C. After being stirred for 5 min, a solution of 2-chloro-4-pyridinecarboxaldehyde[9] (1.86 g, 13.1 mmol) in CH_2Cl_2 (30 mL) was introduced to the mixture and the resulting mixture was stirred for 20 min at room temperature. H_2O was added to the mixture at 0 °C and the organic layer was separated with CH_2Cl_2, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – AcOEt) to afford the title compound (0.948 g, 24%). ^{1}H NMR δ 8.40 (dd, *J* = 5.1, 0.6 Hz, 1H), 7.47 (ddd, *J* = 1.5, 0.75, 0.6 Hz, 1H),

7.39 (dd, J = 0.75, 0.6 Hz, 1H), 7.36 (ddd, J = 5.1, 1.5, 0.6 Hz, 1H); ^{13}C NMR □ 152.12, 150.03, 145.58, 133.34, 123.01, 121.26, 95.88.

2-Chloro-4-[(trimethylsilyl)ethynyl]pyridine.

To a stirred solution of 2-Chloro-4-(2,2-dibromoethenyl)pyridine (0.726 g, 2.44 mmol) in THF (8 mL) was added *n*-BuLi (3.22 mL, 1.59 mol/L in hexane, 5.12 mmol) at -78 °C After stirring for 30 min, chlorotrimethylsilane (0.465 mL, 3.66 mmol) was added. After stirring at -78 °C for 1 h, the reaction mixture was warmed up to room temperature and stirred for 30 min. The reaction was terminated by an addition of H_2O. The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated to give a crude, which was chromatographed on silica gel (Wakogel C-200, hexane – AcOEt) to afford the title compound (0.261 g, 51%). ^{1}H NMR □ 8.32 (dd, J = 5.1, 0.9 Hz, 1H), 7.35 (dd, J = 1.2, 0.9 Hz, 1H), 7.21 (dd, J = 5.1, 1.2 Hz, 1H), 0.25 (s, 9H); ^{13}C NMR □ 151.76, 149.63, 134.14, 126.45, 124.49, 101.87, 100.55, -0.59.

2-Chloro-4-[(trimethylsilyl)ethenyl]pyridine.

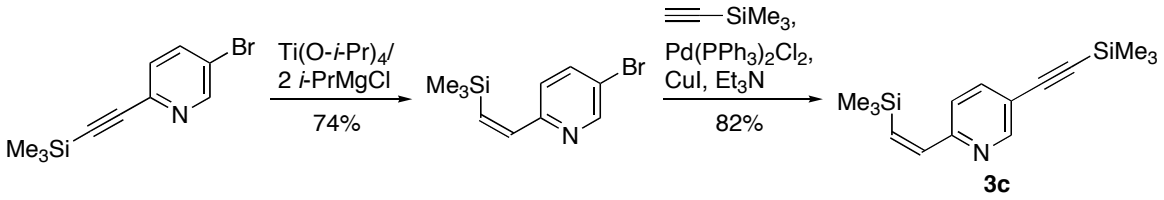
To a stirred solution 2-Chloro-4-[(trimethylsilyl)ethynyl]pyridine (0.233 g, 1.11 mmol) and Ti(O-*i*-Pr)$_4$ (0.492 mL, 1.67 mmol) in 11 mL of Et_2O was added a 1.30 M solution of *i*-PrMgCl in Et_2O (2.56 mL, 3.33 mmol) at –78 °C. The solution was warmed up to –50 °C over 30 min and stirred at this temperature for 2 h. The reaction was terminated by an addition of H_2O (1.7 mL). After addition of NaF and celite, the resulting mixture was filtered through a pad of Celite and concentrated *in vacuo* to give a crude, which was purified by column chromatography on silica gel (Wakogel C-200, hexane - AcOEt) to afford the title compound (0.0461 g, 20%). ^{1}H NMR □ 8.32 (dd, J = 5.1, 0.6 Hz, 1H), 7.20 (dd, J = 1.5, 0.6 Hz, 1H), 7.18 (d, J = 15.0 Hz, 1H), 7.08 (dd, J = 5.1, 1.5 Hz, 1H), 6.11 (d, J = 15.0 Hz, 1H), 0.077 (s, 9H); ^{13}C NMR □ 151.62, 150.81, 149.40, 142.16, 139.22, 123.30, 121.64, -0.17.

4-(Trimethylsilyl)ethenyl-2-[(trimethylsilyl)ethynyl]pyridine.

To a mixture of 2-Chloro-4-[(trimethylsilyl)ethenyl]pyridine (43.8 mg, 0.207 mmol), CuI (15.8 mg 0.0827 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (29.0 mg 0.0414 mmol) in triethylamine (1 mL) was added (trimethylsilyl)acetylene (87.7 □L, 0.621 mmol) and the mixture was stirred for 3 days at 110 °C The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – AcOEt) to afford the title compound (6.40 mg, 11%) which is the site-isomer of **3b** obtained by the mono-titanation of **2b**. ^{1}H NMR □ 8.50 (dd, J = 5.1, 0.9 Hz, 1H), 7.33 (dd, J = 1.5, 0.9 Hz, 1H), 7.19 (d, J = 15.3 Hz, 1H), 7.10 (dd, J = 5.1, 1.5 Hz, 1H), 6.07 (d, J = 15.3 Hz, 1H), 0.27 (s,

9H), 0.067 (s, 9H); ^{13}C NMR 149.76, 147.98, 143.00, 142.90, 138.37, 126.63, 122.14, 103.73, 94.83, -0.11, -0.44; IR (neat) 2960, 2901, 2162, 1583, 1538, 1463, 1389, 1251, 844, 763, 657 cm^{-1}.

For 3c

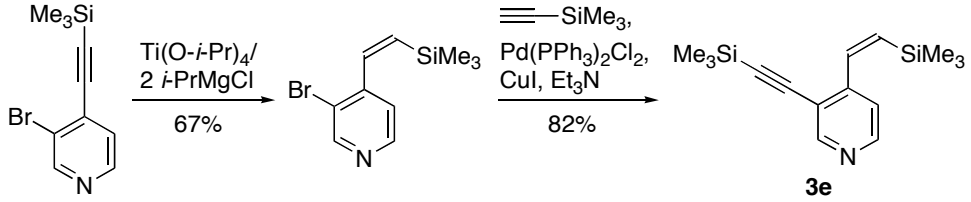


(*Z*)-2-[2-(trimethylsilyl)ethenyl]-5-[(trimethylsilyl)ethynyl]pyridine (**3c**).

To a stirred solution 5-bromo-2-[(trimethylsilyl)ethynyl]pyridine[6] (0.298 g, 1.17 mmol) and Ti(O-*i*-Pr)$_4$ (0.415 mL, 1.41 mmol) in 10 mL of Et$_2$O was added a 1.61 M solution of *i*-PrMgCl in Et$_2$O (1.75 mL, 2.81 mmol) at –78 °C. The solution was warmed up to –50 °C over 30 min and stirred at this temperature for 2 h. The reaction was terminated by an addition of H$_2$O (1.4 mL). After addition of NaF and Celite, the resulting mixture was filtered through a pad of Celite and concentrated *in vacuo* to give a crude, which was purified by column chromatography on silica gel (Wakogel C-200, hexane - Et$_2$O) to afford 5-bromo-2-[(trimethylsilyl)ethenyl]pyridine (0.222 g, 74%).

To a mixture of 5-bromo-2-[(trimethylsilyl)ethenyl]pyridine (0.206 g, 0.804 mmol), CuI (30.6 mg 0.161 mmol), and Pd(PPh$_3$)$_2$Cl$_2$ (56.4 mg 0.0804 mmol) in triethylamine (3.2 mL) and CH$_2$Cl$_2$ (0.6 mL) was added (trimethylsilyl)acetylene (0.170 mL, 1.21 mmol) and the mixture was stirred for 6 h at room temperature. Et$_2$O and H$_2$O were added to the mixture and the organic layer was separated, washed with brine, dried over MgSO$_4$, and concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – Et$_2$O) to afford the title compound **3c** (0.180 g, 82%). Physical properties of the authentic sample thus synthesized were identical with those of **3c** obtained by the mono-titanation of **2c**.

For 3e



3-Bromo-4-[(trimethylsilyl)ethenyl]pyridine.

To a stirred solution 3-bromo-4-[(trimethylsilyl)ethynyl]pyridine[3] (0.670 g, 2.64 mmol) and Ti(O-*i*-Pr)$_4$ (1.01 mL, 3.43 mmol) in 26 mL of Et_2O was added a 1.30 M solution of *i*-PrMgCl in Et_2O (5.27 mL, 6.85 mmol) at –78 °C. The solution was warmed up to –50 °C over 30 min and stirred at this temperature for 2 h. The reaction was terminated by an addition of H_2O (3.4 mL). After addition of NaF and Celite, the resulting mixture was filtered through a pad of Celite and concentrated *in vacuo* to give a crude, which was purified by column chromatography on silica gel (Wakogel C-200, hexane - Et_2O) to afford the title compound (0.452 g, 67%). ^{1}H NMR 8.68 (s, 1H), 8.45 (d, *J* = 5.1 Hz, 1H), 7.182 (d, *J* = 14.7 Hz, 1H), 7.181 (d, *J* = 5.1 Hz, 1H), 6.11 (d, *J* = 14.7 Hz, 1H), -0.014 (s, 9H); ^{13}C NMR 151.72, 148.22, 147.88, 142.87, 137.90, 124.61, 121.57, -0.28.

(*Z*)-4-[2-(trimethylsilyl)ethenyl]-3-[(trimethylsilyl)ethynyl]pyridine (**3e**).

To a mixture of 3-bromo-4-[(trimethylsilyl)ethenyl]pyridine (0.422 g, 1.65 mmol), CuI (21.9 mg 0.115 mmol), and $Pd(PPh_3)_2Cl_2$ (40.3 mg 0.0574 mmol) in triethylamine (7.7 mL) was added (trimethylsilane)acetylene (0.406 mL, 2.87 mmol) and the mixture was stirred for 3 days at 110 °C. The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to give a crude. The crude was purified by column chromatography on silica gel (Wakogel C-200, hexane – AcOEt) to afford the title compound **3e** (0.371 g, 82%). Physical properties of the authentic sample thus synthesized were identical with those of **3e** obtained by the mono-titanation of **2e**.

Figure 1. Electronic Absorption Spectra of 5-8.

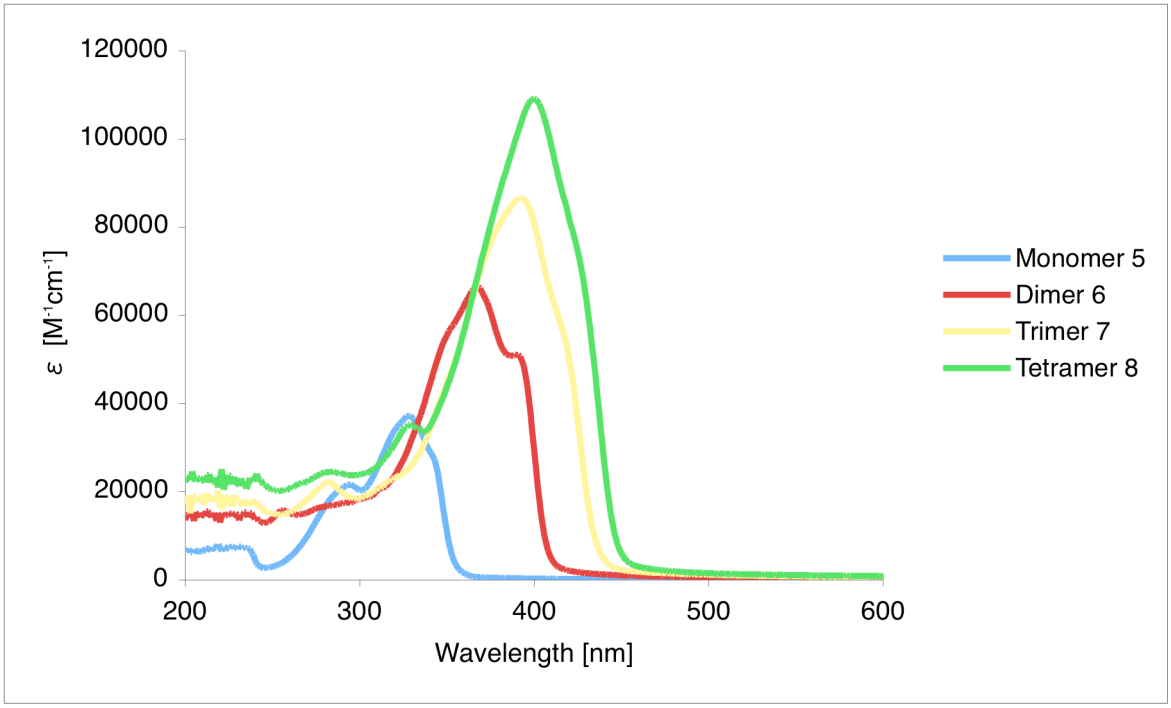
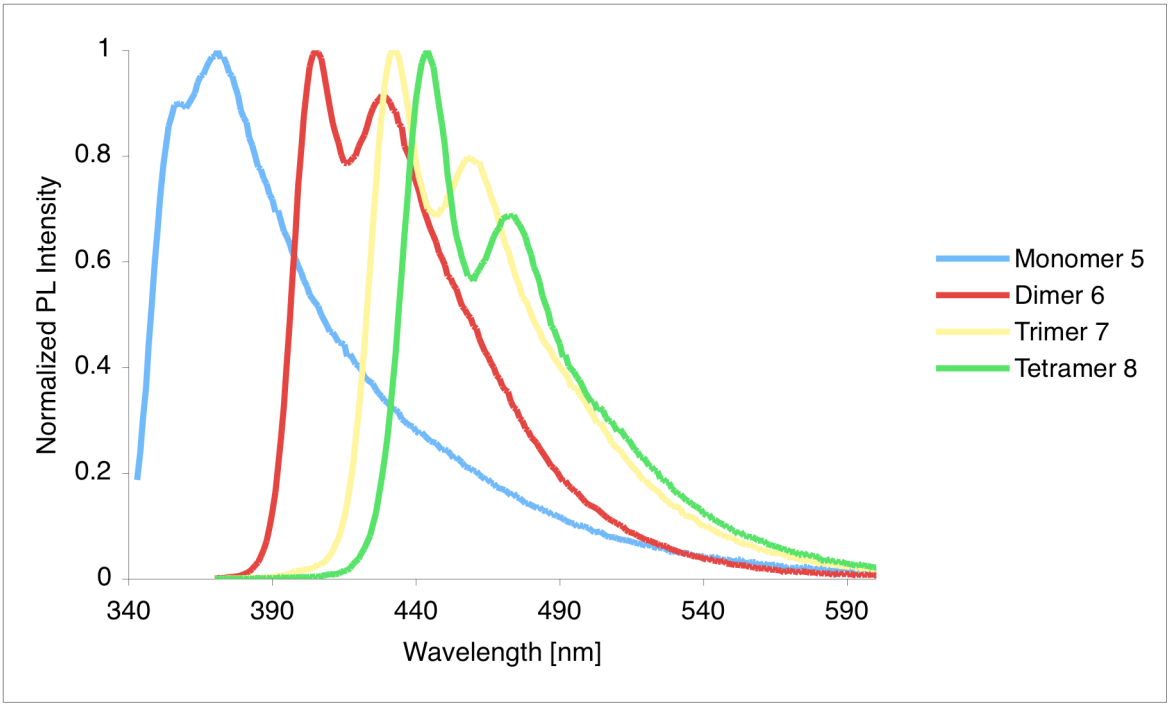


Figure 2. Fluorescence spectra of 5-8.



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