Supplementary Information for:

Copper(II)-mediated chiral helicity amplification and inversion of
meta-ethynylpyridine polymers with metal coordination sites

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Experimental Section S2
References S13
Figures S1–S12 S13
$^1$H NMR spectra S20
Experimental Section

**General.** NMR spectra were recorded on a Varian Gemini 300 spectrometer using tetramethylsilane (TMS) as an internal reference. ESI-HRMS analyses were carried out on a JEOL JMS-T100LC mass spectrometer. IR, UV-vis, and CD spectra were obtained by a JASCO spectrometers FT/IR-460plus, V-560, J-720WI, respectively. Melting points were determined with Yanako MP-500D and not corrected. THF was freshly distilled from sodium benzophenone ketyl before use. CH₂Cl₂ used for the spectroscopic analyses was purchased from Aldrich (anhydrous grade). 2,6-Dibromo-4-nitropyridine¹ (5) was prepared according to the procedure in the literature. Halogen exchange reactions to obtain 7, 13ᵃᵇ were carried out according to the procedure reported by Buchwald et al.²

### Preparation of Polymer 2

2,6-Dibromo-4-(2-hydroxyethyloxy)pyridine (6). To a suspension of NaH (0.99 g, 23 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) in THF (100 mL) was slowly added ethylene glycol (13 g, 0.21 mol) at 0 °C, and subsequently 5 (6.0 g, 21 mmol) was added to the mixture in one portion at the same temperature. The reaction mixture was stirred for 2
h at 0 °C and additionally for 12 h at room temperature. The resulting mixture was quenched with saturated aqueous NH₄Cl solution and extracted with CH₂Cl₂ (60 mL × 3). The combined organic layer was dried over MgSO₄, and concentrated by a rotary evaporator. The resulting syrup was subjected to silica gel column chromatography (elucent; hexane/AcOEt = 1:1) to yield 6 (4.3 g, 92%) as a white solid. Mp 85−86 °C; ¹H NMR (CDCl₃, 300 MHz) δ 6.99 (s, 2 H), 4.16 (t, J = 4.2 Hz, 2 H), 4.01 (t, J = 4.2 Hz, 2 H), 3.24 (s, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 166.6, 140.7, 113.7, 70.3, 60.3; IR (KBr) νmax 3305, 3116, 3084, 2957, 2925, 2869, 1577, 1537 cm⁻¹; HRMS (ESI−TOF) calcd for C₇H₇Br₂NNaO₂ (M + Na⁺): 319.8721; found: 319.8764.

4-(2-Hydroxyethyloxy)-2,6-diiodopyridine (7). A mixture of 6 (10 g, 35 mmol), CuI (0.67 g, 3.5 mmol), NaI (26 g, 0.18 mol), 1,3-diaminopropane (0.52 g, 7.0 mmol), diglyme (60 mL), and o-xylene (140 mL) was stirred at 110 °C for 24 h. The resulting suspension was allowed to reach room temperature, and then diluted with water (100 mL). The resulting mixture was extracted with AcOEt (100 mL × 3), and the combined organic layer was washed with water and brine subsequently, dried over Na₂SO₄, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography (elucent; hexane/AcOEt = 1:1) to yield 7 (12 g, 85%) as a white solid. Mp 104−106 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.27 (s, 2 H), 4.10 (t, J = 4.5 Hz, 2 H), 3.97 (br s, 2 H), 2.00 (s, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.3, 121.1, 115.8, 69.9, 60.8; IR (KBr) νmax 3323, 3101, 3069, 2966, 2925, 2852, 1563, 1520 cm⁻¹; HRMS (ESI−TOF) calcd for C₇H₈I₂NO₂ (M + H⁺): 391.88644; found: 391.8635.

Tosylate 8. To a CH₂Cl₂ (450 mL) solution of 7 (11 g, 29 mmol) were added p-toluenesulfonyl chloride (15 g, 78 mmol) and triethylamine (91 g, 0.90 mol) at 0 °C. The reaction mixture was stirred for 2 h at that temperature, and additionally stirred for 12 h at room temperature. The resulting mixture was evaporated by a rotary evaporator and the resulting residue was dissolved in CHCl₃ (1 L). This solution was washed with 1N HCl and brine subsequently, dried over Na₂SO₄, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography (elucent; hexane/AcOEt = 3:1) to yield 8 (14.3 g, 89%) as a pale yellow solid. Mp 104−105 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.78 (d, J = 8.3 Hz, 2 H), 7.36 (d, J = 8.3 Hz, 2 H), 7.07
(s, 2 H), 4.37 (t, J = 4.4 Hz, 2 H), 4.15 (t, J = 4.4 Hz, 2 H), 2.48 (s, 3 H); 13C NMR (CDCl3, 75 MHz) δ 163.4, 145.1, 132.4, 129.8, 127.8, 120.9, 115.7, 67.1, 65.8, 21.8; IR (KBr) νmax 3098, 3068, 2955, 2922, 1594, 1559, 1522, 1362, 1174 cm⁻¹; HRMS (ESI–TOF) calcd for C14H14I2NO4S (M + H⁺): 545.8733; found: 545.8734.

**Tertiary Amine 9.** A mixture of 8 (14 g, 26 mmol), bis(2-methoxyethyl)amine (4.2 g, 31 mmol), and K2CO3 (4.3 g, 31 mmol) in MeCN (200 mL) was stirred under reflux for 4 days. After cooling to room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: hexane/AcOEt = 1:1) to yield 9 (10 g, 77%) as a yellowish brown oil. 1H NMR (CDCl3, 300 MHz) δ 7.24 (s, 2 H), 4.07 (t, J = 6.0 Hz, 2 H), 3.47 (t, J = 5.6 Hz, 4 H), 3.34 (s, 6 H), 3.01 (t, J = 6.0 Hz, 2 H), 2.81 (t, J = 5.6 Hz, 4 H); 13C NMR (CDCl3, 75 MHz) δ 164.4, 121.0, 115.5, 71.1, 67.4, 58.7, 54.6, 53.3; IR (neat) νmax 3098, 3061, 2924, 2875, 2825, 1560, 1521 cm⁻¹; HRMS (ESI–TOF) calcd for C13H21I2N2O3 (M + H⁺): 506.9642; found: 506.9678.

**Bis(TMS-acetylene) 10.** A mixture of 9 (0.14 g, 0.27 mmol), PdCl2(PPh3)2 (9.5 mg, 14 μmol), and CuI (2.1 mg, 11 μmol) in i-Pr2NH (2 mL) and THF (2 mL) was stirred for 30 min at room temperature. To this mixture was added trimethylsilylacetylene (TMSA, 0.11 g, 1.1 mmol) dropwise, and the reaction mixture was additionally stirred for 3 h at room temperature. The resulting mixture was diluted with ether (5 mL) and filtered. The filtrate was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt) to yield 10 (0.12 g, 98%) as a brown oil. 1H NMR (CDCl3, 300 MHz) δ 6.94 (s, 2 H), 4.10 (t, J = 5.9 Hz, 2 H), 3.48 (t, J = 5.5 Hz, 4 H), 3.35 (s, 6 H), 3.02 (t, J = 5.9 Hz, 2 H), 2.83 (t, J = 5.5 Hz, 4 H), 0.25 (s, 18 H); 13C NMR (CDCl3, 75 MHz) δ 164.7, 144.1, 113.0, 103.1, 94.6, 71.3, 67.0, 58.8, 54.7, 53.4, −0.27; IR (neat) νmax 2957, 2925, 2876, 2823, 2164, 1579, 1550 cm⁻¹; HRMS (ESI–TOF) calcd for C23H39N2O3Si2 (M + H⁺): 447.2499; found: 447.2498.

**Diacetylene 11.** To a THF (4 mL) solution of 10 (0.12 g, 0.26 mmol) were added tetrabutylammonium fluoride (TBAF, 1.0 M solution in THF, 0.52 mL, 0.52 mmol) and a few drops
of water. After stirring for 1 h at room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: hexane/AcOEt = 1:1 to AcOEt) to yield 11 (70 mg, 88%) as a brown oil. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.00 (s, 2 H), 4.11 (t, $J$ = 5.9 Hz, 2 H), 3.48 (t, $J$ = 5.8 Hz, 4 H), 3.34 (s, 6 H), 3.12 (s, 2 H), 3.03 (t, $J$ = 5.9 Hz, 2 H), 2.83 (t, $J$ = 5.8 Hz, 4 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 164.9, 143.4, 114.0, 82.1, 77.1, 71.3, 67.2, 58.8, 54.8, 53.5; IR (neat) $\nu_{\text{max}}$ 3286, 2925, 2874, 2824, 2103, 1578, 1550 cm$^{-1}$; HRMS (ESI−TOF) calcd for C$_{17}$H$_{22}$N$_2$NaO$_3$ (M + Na$^+$): 325.1528; found: 325.1568.

Polymer 2. Co-polymerization of 9 and 11. A mixture of 9 (43 mg, 84 μmol), 11 (32 mg, 0.11 mmol), PdCl$_2$(PPh$_3$)$_2$ (3.7 mg, 5.3 μmol), and Cul (0.8 mg, 4.2 μmol) in $i$-Pr$_2$NH (4 mL) and THF (4 mL) was stirred for 3 days at room temperature. The reaction mixture was concentrated by a rotary evaporator and the resulting residue was treated with a Sephadex LH-20 column (eluent: CHCl$_3$). The crude product of 2 was subjected to GPC (Shodex K-2002 and K-2002.5; eluent: CHCl$_3$) and divided into four fractions as brown oils. The sum of the weights of these fractions was 40 mg (53% yield by weight). One fraction of $M_n$ = 12,700 g/mol (corresponding to 46-mer) was used for the experiments to evaluate additive effects of Cu(II) ion. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.17 (s, 2n H), 4.13 (br s, 2n H), 3.53 (t, $J$ = 5.5 Hz, 4n H), 3.34 (br s, 6n H), 3.12 (br s, 2n H), 2.87 (t, $J$ = 5.5 Hz, 4n H); IR (KBr) $\nu_{\text{max}}$ 2924, 2873, 1579, 1550 cm$^{-1}$. 

S5
Preparation of Polymers 3 and 4

2,6-Dibromo-4-[2-(2-hydroxyethyloxy)ethyloxy]pyridine (12a). To a suspension of NaH (94 mg, 3.9 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) in THF (20 mL) was slowly added diethylene glycol (7.5 g, 71 mmol) at 0 °C, and subsequently 5 (1.0 g, 3.5 mmol) was added to the mixture in one portion at the same temperature. The reaction mixture was stirred for 2 h at 0 °C and additionally for 12 h at room temperature. The reaction mixture was quenched with saturated aqueous NH₄Cl solution and extracted with CH₂Cl₂ (10 mL × 3). The combined organic layer was dried over MgSO₄, and concentrated by a rotary evaporator. The resulting syrup was subjected to silica gel column chromatography (eluent; CH₂Cl₂ to hexane/AcOEt = 1:1) to yield 12a (1.1 g, 95%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.01 (s, 2 H), 4.20 (t, J = 4.4 Hz, 2 H), 3.86 (t, J = 4.4 Hz, 2 H), 3.76 (t, J = 4.6 Hz, 2 H), 3.65 (t, J = 4.6 Hz, 2 H), 2.63 (s, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 166.4, 140.7, 113.6, 72.6, 68.7, 68.2, 61.5; IR (neat) νmax 3414, 3115, 3081, 2932, 2874, 1574, 1536 cm⁻¹; HRMS (ESI−TOF) calcd for C₉H₁₁Br₂NNaO₃ (M + Na⁺): 363.8983; found: 363.8971.
2,6-Dibromo-4-[2-(2-hydroxyethyloxy)ethyloxy]ethyloxy|pyridine (12b). To a suspension of NaH (0.38 g, 15 mmol; commercial 60% dispersion was washed thoroughly with hexane prior to use) in THF (60 mL) was slowly added triethylene glycol (42 g, 0.28 mol) at 0 °C, and subsequently 5 (4.0 g, 14 mmol) was added to the mixture in one portion at the same temperature. The reaction mixture was stirred for 2 h at 0 °C and additionally for 12 h at room temperature. The resulting mixture was quenched with saturated aqueous NH₄Cl solution and extracted with CH₂Cl₂ (40 mL × 3). The combined organic layer was dried over MgSO₄, and concentrated by a rotary evaporator. The resulting syrup was subjected to silica gel column chromatography (eluent; CH₂Cl₂ to CH₂Cl₂/MeOH = 100:3) to yield 12b (5.0 g, 92%) as a pale yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.03 (s, 2 H), 4.20 (t, J = 4.4 Hz, 2 H), 3.86 (t, J = 4.4 Hz, 2 H), 3.76–3.63 (m, 6 H), 3.60 (t, J = 4.5 Hz, 2 H), 3.35 (s, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 166.4, 140.6, 113.6, 72.3, 70.6, 69.9, 68.7, 68.2, 61.3; IR (neat) νₘₐₓ 3414, 3115, 3081, 2875, 1575, 1536 cm⁻¹; HRMS (ESI–TOF) calcd for C₁₁H₁₅Br₂NNaO₄ (M + Na⁺): 407.9246; found: 407.9279.

4-[2-(2-Hydroxyethyloxy)ethyloxy]-2,6-diiodopyridine (13a). A mixture of 12a (2.6 g, 7.6 mmol), CuI (0.14 g, 0.76 mmol), NaI (5.7 g, 38 mmol), 1,3-diaminopropane (0.11 g, 1.5 mmol), diglyme (18 mL), and o-xylene (42 mL) was stirred at 110 °C for 24 h. The resulting suspension was allowed to reach room temperature, and then diluted with water (50 mL). The resulting mixture was extracted with AcOEt (50 mL × 3), and the combined organic layer was washed with water and brine, subsequently, dried over Na₂SO₄, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield 13a (2.7 g, 83%) as a yellow solid. Mp 63–66 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.27 (s, 2 H), 4.17 (t, J = 4.3 Hz, 2 H), 3.85 (t, J = 4.3 Hz, 2 H), 3.76 (br s, 2 H), 3.70–3.62 (br m, 2 H), 3.01 (br s, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.1, 120.9, 115.6, 72.5, 68.6, 67.9, 61.3; IR (KBr) νₘₐₓ 3370, 3107, 3075, 2952, 2920, 2872, 2852, 1565, 1532 cm⁻¹; HRMS (ESI–TOF) calcd for C₉H₁₁I₂NNaO₃ (M + Na⁺): 457.8726; found: 457.8713.

4-[2-(2-Hydroxyethyloxy)ethyloxy]-2,6-diiodopyridine (13b). A mixture of 12b (0.1 g, 0.26 mmol), CuI (4.9 mg, 26 μmol), NaI (0.19 g, 1.3 mmol), 1,3-diaminopropane (3.9 mg, 52
μmol), diglyme (0.6 mL) and o-xylene (1.4 mL) was stirred at 110 °C for 24 h. The resulting suspension was allowed to reach room temperature, and then diluted with water (2 mL). The resulting mixture was extracted with AcOEt (2 mL × 3), and the combined organic layer was washed with water and brine, subsequently, dried over Na₂SO₄, and concentrated by a rotary evaporator. The crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield 13b (96 mg, 77%) as a yellow oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.26 (s, 2 H), 4.12 (t, J = 4.6 Hz, 2 H), 3.83 (t, J = 4.6 Hz, 2 H), 3.79–3.65 (m, 6 H), 3.61 (t, J = 4.5 Hz, 2 H), 2.41 (br s, 1 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.3, 121.1, 115.6, 72.4, 70.7, 70.1, 68.8, 67.9, 61.5; IR (neat) ν max 3420, 3098, 3064, 2875, 1561, 1520 cm⁻¹; HRMS (ESI–TOF) calcd for C₁₁H₁₅I₂NNaO₄ (M + Na⁺): 501.8988; found: 501.8976.

Tosylate 14a. A water (5 mL) solution of NaOH (1.0 g, 26 mmol) and a THF (5 mL) solution of 13a (1.1 g, 2.6 mmol) were mixed and cooled to 0 °C. To this mixture was added a THF (5 mL) solution of p-toluenesulfonyl chloride (0.6 g, 3.1 mmol) dropwise and the reaction mixture was stirred for 2 h, being kept at the same temperature. The resulting mixture was poured into ice-water (50 mL) and extracted with CH₂Cl₂ (25 mL × 3). The combined organic layer was dried over MgSO₄, and concentrated by a rotary evaporator, and the crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 3:2) to yield 14a (1.3 g, 87%) as a white solid. Mp 110–111 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.79 (d, J = 8.3 Hz, 2 H), 7.33 (d, J = 8.3 Hz, 2 H), 7.22 (s, 2 H), 4.18 (t, J = 4.6 Hz, 2 H), 4.05 (t, J = 4.6 Hz, 2 H), 3.80–3.71 (m, 4 H), 2.45 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.2, 144.7, 129.7, 127.7, 121.0, 115.6, 69.0, 68.9, 67.8, 21.7; IR (KBr) ν max 3100, 3068, 2995, 2895, 2870, 1597, 1559, 1522, 1357, 1175 cm⁻¹; HRMS (ESI–TOF) calcd for C₁₆H₁₇I₂NNaO₅S (M + Na⁺): 611.8814; found: 611.8846.

Tosylate 14b. A water (25 mL) solution of NaOH (3.3 g, 82 mmol) and a THF (25 mL) solution of 13b (13 g, 2.6 mmol) were mixed and cooled to 0 °C. To this mixture was added a THF (25 mL) solution of p-toluenesulfonyl chloride (7.8 g, 41 mmol) dropwise and the reaction mixture was stirred for 2 h, being kept at the same temperature. The resulting mixture was poured into ice-water (250 mL) and extracted with CH₂Cl₂ (100 mL × 3). The combined organic layer was dried over
MgSO₄, and concentrated by a rotary evaporator, and the crude product was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1) to yield 14b (16 g, 94%) as a colorless oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.79 (d, J = 8.1 Hz, 2 H), 7.34 (d, J = 8.1 Hz, 2 H), 7.25 (s, 2 H), 4.18–4.10 (m, 4 H), 3.80 (t, J = 4.5 Hz, 2 H), 3.69 (t, J = 4.5 Hz, 2 H), 3.62 (s, 4 H), 2.45 (s, 3 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.4, 144.7, 132.7, 129.7, 127.7, 121.2, 115.6, 70.7, 69.2, 69.1, 68.7, 68.1, 21.7; IR (neat) νmax 3101, 3065, 2878, 1597, 1560, 1522, 1362, 1175 cm⁻¹; HRMS (ESI−TOF) calcd for C₁₉H₂₁I₂NNaO₆S (M + Na⁺): 655.9077; found: 655.9052.

Tertiary Amine 15a. A mixture of 14a (1.3 g, 2.3 mmol), bis(2-methoxyethyl)amine (0.37 g, 2.7 mmol), and K₂CO₃ (0.38 g, 2.7 mmol) in MeCN (60 mL) was stirred under reflux for 4 days. After cooling to room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1 to AcOEt) to yield 15a (0.98 g, 77%) as a yellowish brown oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.26 (s, 2 H), 4.12 (t, J = 4.5 Hz, 2 H), 3.78 (t, J = 4.5 Hz, 2 H), 3.61 (t, J = 6.0 Hz, 2 H), 3.46 (t, J = 6.0 Hz, 4 H), 3.33 (s, 6 H), 2.84–2.76 (m, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.4, 121.1, 115.6, 70.9, 70.0, 68.7, 68.0, 58.8, 54.4, 54.3; IR (neat) νmax 3102, 3060, 2925, 2875, 2822, 1561, 1523 cm⁻¹; HRMS (ESI−TOF) calcd for C₁₅H₂₄I₂N₂NaO₄ (M + Na⁺): 572.9723; found: 572.9677.

Tertiary Amine 15b. A mixture of 14b (2.6 g, 4.1 mmol), bis(2-methoxyethyl)amine (0.61 g, 4.6 mmol), and K₂CO₃ (0.63 g, 4.6 mmol) in MeCN (110 mL) was stirred under reflux for 5 days. After cooling to room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent; hexane/AcOEt = 1:1 to AcOEt) to yield 15b (1.7 g, 70%) as a yellowish brown oil. ¹H NMR (CDCl₃, 300 MHz) δ 7.27 (s, 2 H), 4.15 (t, J = 4.4 Hz, 2 H), 3.83 (t, J = 4.4 Hz, 2 H), 3.71–3.52 (m, 6 H), 3.47 (t, J = 5.7 Hz, 4 H), 3.33 (s, 6 H), 2.82–2.74 (m, 6 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.3, 121.0, 115.5, 70.8, 70.7, 70.2, 69.5, 68.9, 68.0, 58.7, 54.3, 54.2; IR (neat) νmax 3100, 3061, 2923, 2873, 1560, 1523 cm⁻¹; HRMS (ESI−TOF) calcd for C₁₇H₂₈I₂N₂NaO₅ (M + Na⁺): 616.9985; found: 616.9973.

Bis(TMS-acetylene) 16a. A mixture of 15a (0.21 g, 0.39 mmol), PdCl₂(PPh₃)₂ (14 mg, 19 μmol),
and Cul (3.0 mg, 16 μmol) in i-Pr₂NH (3 mL) and THF (3 mL) was stirred for 30 min at room temperature. To this mixture was added TMSA (0.15 g, 1.6 mmol) dropwise, and the reaction mixture was additionally stirred for 3 h at room temperature. The resulting mixture was diluted with ether (10 mL) and filtered. The filtrate was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt to AcOEt/MeOH = 50:1) to yield 16a (0.17 g, 88%) as a brown oil. ¹H NMR (CDCl₃, 300 MHz) δ 6.94 (s, 2 H), 4.15 (t, J = 4.6 Hz, 2 H), 3.79 (t, J = 4.6 Hz, 2 H), 3.62 (t, J = 5.9 Hz, 2 H), 3.47 (t, J = 5.9 Hz, 4 H), 3.33 (s, 6 H), 2.86–2.76 (m, 6 H), 0.24 (s, 18 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.66, 144.15, 113.52, 103.0, 94.7, 71.0, 70.0, 68.8, 67.6, 58.8, 54.5, 54.4, −0.26; IR (neat) νmax 2957, 2926, 2875, 2165, 1579, 1550 cm⁻¹; HRMS (ESI–TOF) calcd for C$_{25}$H$_{42}$N$_2$NaO$_4$Si$_2$ (M + Na⁺): 513.2581; found: 513.2617.

Bis(TMS-acetylene) 16b. A mixture of 15b (0.12 g, 0.20 mmol), PdCl₂(PPh₃)₂ (6.9 mg, 9.8 μmol), and Cul (1.5 mg, 7.8 μmol) in i-Pr₂NH (2 mL) and THF (2 mL) was stirred for 30 min at room temperature. To this mixture was added TMSA (77 mg, 0.78 mmol) dropwise, and the reaction mixture was additionally stirred for 3 h at room temperature. The resulting mixture was diluted with ether (5 mL) and filtered. The filtrate was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt to AcOEt/MeOH = 50:1) to yield 16b (98 mg, 94%) as a brown oil. ¹H NMR (CDCl₃, 300 MHz) δ 6.95 (s, 2 H), 4.17 (t, J = 4.8 Hz, 2 H), 3.85 (t, J = 4.8 Hz, 2 H), 3.72–3.50 (m, 6 H), 3.47 (t, J = 5.9 Hz, 4 H), 3.33 (s, 6 H), 2.84–2.76 (m, 6 H), 0.24 (s, 18 H); ¹³C NMR (CDCl₃, 75 MHz) δ 164.5, 144.0, 113.4, 102.9, 94.6, 70.9, 70.8, 70.3, 69.5, 69.0, 67.6, 58.7, 54.4, 54.3, −0.35; IR (neat) νmax 2956, 2926, 2875, 2165, 1580, 1551 cm⁻¹; HRMS (ESI–TOF) calcd for C$_{27}$H$_{47}$N$_2$O$_5$Si$_2$ (M + H⁺): 535.3023; found: 535.3045.

Diacetylene 17a. To a THF (4 mL) solution of 16a (0.17 g, 0.34 mmol) we re added TBAF (1.0 M solution in THF, 0.68 mL, 0.68 mmol) and a few drops of water. After stirring for 1 h at room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt/MeOH = 50:1 to 20:1) to yield
17a (86 mg, 75%) as a brown oil.  $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.01 (s, 2 H), 4.16 (t, $J = 4.7$ Hz, 2 H), 3.81 (t, $J = 4.7$ Hz, 2 H), 3.62 (t, $J = 5.9$ Hz, 2 H), 3.46 (t, $J = 5.9$ Hz, 4 H), 3.33 (s, 6 H), 3.10 (s, 2 H), 2.86–2.76 (m, 6 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 164.9, 143.5, 114.0, 82.1, 77.2, 71.0, 70.1, 68.9, 67.8, 58.8, 54.5, 54.4; IR (neat) $\nu_{\text{max}}$ 3249, 2956, 2929, 2873, 2112, 1580, 1556 cm$^{-1}$; HRMS (ESI–TOF) calcd for C$_{19}$H$_{26}$N$_2$NaO$_4$ (M + Na$^+$): 369.1790; found: 369.1785.

**Diacetylene 17b.** To a THF (4 mL) solution of 16b (0.17 g, 0.34 mmol) were added TBAF (1.0 M solution in THF, 0.63 mL, 0.63 mmol) and a few drops of water. After stirring for 1 h at room temperature, the reaction mixture was concentrated by a rotary evaporator and the resulting residue was purified by silica gel column chromatography (eluent: AcOEt/MeOH = 50:1 to 20:1) to yield 17b (82 mg, 67%) as a brown oil. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.01 (s, 2 H), 4.18 (t, $J = 4.5$ Hz, 2 H), 3.86 (t, $J = 4.4$ Hz, 2 H), 3.72–3.55 (m, 6 H), 3.46 (t, $J = 5.9$ Hz, 4 H), 3.33 (s, 6 H), 3.11 (s, 2 H), 2.86–2.76 (m, 6 H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 164.8, 143.5, 114.0, 82.1, 77.2, 71.0, 70.9, 70.4, 69.7, 69.1, 67.8, 58.8, 54.5, 54.4; IR (neat) $\nu_{\text{max}}$ 3229, 2926, 2875, 2111, 1581, 1556 cm$^{-1}$; HRMS (ESI–TOF) calcd for C$_{21}$H$_{30}$N$_2$NaO$_5$ (M + Na$^+$): 413.2052; found: 413.2063.

**Polymer 3. Co-polymerization of 15a and 17a.** A mixture of 15a (57 mg, 0.10 mmol), 17a (45 mg, 0.13 mmol), PdCl$_2$(PPh$_3$)$_2$ (4.5 mg, 6.5 $\mu$mol), and CuI (1.0 mg, 5.2 $\mu$mol) in i-Pr$_2$NH (4 mL) and THF (4 mL) was stirred for 3 days at room temperature. The reaction mixture was concentrated by a rotary evaporator and the resulting residue was treated with a Sephadex LH-20 column (eluent: CHCl$_3$). The crude product of 3 was subjected to GPC (Shodex K-2002 and K-2002.5; eluent: CHCl$_3$) and divided into four fractions as brown oils. The sum of the weights of these fractions was 24 mg (24% yield by weight). One fraction of $M_n = 12,500$ g/mol (corresponding to 39-mer) was used for the experiments to evaluate additive effects of Cu(II) ion. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.19 (s, 2n H), 4.19 (br s, 2n H), 3.84 (br s, 2n H), 3.64 (s, 2n H), 3.48 (t, $J = 5.6$ Hz, 4n H), 3.34 (s, 6n H), 2.88–2.76 (m, 6n H); IR (KBr) $\nu_{\text{max}}$ 2924, 2853, 1578, 1559 cm$^{-1}$.

**Polymer 4. Co-polymerization of 15b and 17b.** A mixture of 15b (57 mg, 95 $\mu$mol), 17b (46

S11
mg, 0.12 mmol), PdCl₂(PPh₃)₂ (4.2 mg, 5.9 μmol), and Cul (0.9 mg, 4.8 μmol) in i-Pr₂NH (4 mL) and THF (4 mL) was stirred for 3 days at room temperature. The reaction mixture was concentrated by a rotary evaporator and the resulting residue was treated with a Sephadex LH-20 column (eluent: CHCl₃). The crude product was subjected to GPC (Shodex K-2002 and K-2002.5; eluent: CHCl₃) and divided into four fractions as brown oils. The sum of the weights of these fractions was 69 mg (67% yield by weight). One fraction of \( M_n = 16,200 \) g/mol (corresponding to 45-mer) was used for the experiments to evaluate additive effects of Cu(II) ion. ¹H NMR (CDCl₃, 300 MHz) δ 7.19 (s, 2n H), 4.22 (br s, 2n H), 3.90 (br s, 2n H), 3.82–3.46 (m, 10n H), 3.33 (s, 6n H), 2.95 (br s, 6n H); IR (neat) \( ν_{\text{max}} \) 2923, 2852, 1578, 1541 cm⁻¹.

**Evaluation of binding affinity of 2 with glucosides.** Polymer 2 (1.0 × 10⁻³ M, unit concentration) was dissolved in CH₂Cl₂ (commercially available anhydrous grade). This solution was titrated with a solution of β-D-glucopyranoside (β-D-Glc), and the observed ellipticity was plotted versus the concentration of the β-D-Glc. The formal binding constants were obtained by curve fitting measurements based on the equation³ and the assumption that the molecular weight of the polymer 2 was uniform in length and that the polymer and the guest associate in a 1:1 ratio.

Equation:

\[
\frac{θ_{\text{obs}}}{θ_{11}} = \frac{1 + K_{11}[2]_0 + K_{11}[G]_0 - \left(1 + K_{11}[2]_0 + K_{11}[G]_0\right)^2 - 4K_{11}^2[2]_0[G]_0 \left[1 + K_{11}[2]_0 + K_{11}[G]_0\right]}{2K_{11}[2]_0} \]

\( K_{11} \): 1:1 binding constant of 2 with glycosides

\( θ_{\text{obs}} \): observed ellipticity

\( θ_{11} \): ellipticity of the 1:1 host-guest complex (at the saturation point)

\( [2]_0 \): total concentration of 2

\( [G]_0 \): total concentration of guest glycoside
References


Figures S1 – S12

**Fig S1**  \( n \)-Octyl glycosides subjected as a guest saccharide

**Fig S2** The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the ICDs of host polymer 3 and 4 associated with octyl \( \beta \)-D-glucopyranoside (\( \beta \)-D-Glc).  (A) host polymer: 3  (B) host polymer: 4.  Blue: host polymer; red: host polymer + \( \beta \)-D-Glc; green: host polymer + \( \beta \)-D-Glc
+ Cu(OTf)₂; purple: host polymer + β-D-Glc + Cu(OTf)₂ + EDA. Conditions: host polymer (1.0 × 10⁻³ M, unit conc.), β-D-Glc (2.0 × 10⁻³ M), Cu(OTf)₂ (5.0 × 10⁻⁴ M), EDA (5.0 × 10⁻⁴ M), CH₂Cl₂, 25 °C, path length = 1 mm. Cu(OTf)₂ was added as a DMSO solution of a 1/300 amount to the sample solution.

**Fig S3** The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the ICDs of host polymer 3 associated with (A) octyl β-fructopyranoside (β-D-Fru) and (B) octyl β-mannopyranoside (β-D-Man). Blue: 3; red: 3 + glycoside; green: 3 + glycoside + Cu(OTf)₂; purple: 3 + glycoside + Cu(OTf)₂ + EDA. Conditions: 3 (1.0 × 10⁻³ M, unit conc.), glycoside (2.0 × 10⁻³ M), Cu(OTf)₂ (5.0 × 10⁻⁴ M), EDA (5.0 × 10⁻⁴ M), CH₂Cl₂, 25 °C, path length = 1 mm. Cu(OTf)₂ was added as a DMSO solution of a 1/300 amount to the sample solution.
Fig S4  The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the ICDs of host polymer 4 associated with (A) octyl β-fructopyranoside (β-D-Fru) and (B) octyl β-mannopyranoside (β-D-Man). Blue: 4; red: 4 + glycoside; green: 4 + glycoside + Cu(OTf)$_2$; purple: 4 + glycoside + Cu(OTf)$_2$ + EDA. Conditions: 4 (1.0 × 10$^{-3}$ M, unit conc.), glycoside (2.0 × 10$^{-3}$ M), Cu(OTf)$_2$ (5.0 × 10$^{-4}$ M), EDA (5.0 × 10$^{-4}$ M), CH$_2$Cl$_2$, 25 °C, path length = 1 mm. Cu(OTf)$_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

Fig S5  The additive effect of Cu(II) triflate on the $^1$H NMR (300 MHz) spectrum of tertiary amine 9. The chemical shifts for the side chains shifted upfield by the addition of Cu(OTf)$_2$. a) 9 (1.0 × 10$^{-3}$ M); b) 9 (1.0 × 10$^{-3}$ M) + Cu(OTf)$_2$ (5.0 × 10$^{-4}$ M); c) 9 (1.0 × 10$^{-3}$ M) + Cu(OTf)$_2$ (1.0 × 10$^{-3}$ M). Conditions: 300 MHz, CDCl$_3$/DMSO-d$_6$ = 300:1, 22 °C.
Fig S6 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectrum of host polymer 2 associated with octyl β-D-glucopyranoside (β-D-Glc). Blue: 2; red: 2 + β-D-Glc; green: 2 + β-D-Glc + Cu(OTf)$_2$; purple: 2 + β-D-Glc + Cu(OTf)$_2$ + EDA. Conditions: 2 (1.0 × 10$^{-3}$ M, unit conc.), β-D-Glc (2.0 × 10$^{-3}$ M), Cu(OTf)$_2$ (5.0 × 10$^{-4}$ M), EDA (5.0 × 10$^{-4}$ M), CH$_2$Cl$_2$, 25 °C, path length = 1 mm. Cu(OTf)$_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.

Fig S7 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectra of host polymer 2 associated with (A) octyl β-fructopyranoside (β-D-Fru) and (B) octyl β-mannopyranoside (β-D-Man). Blue: 2; red: 2 + glycoside; green: 2 + glycoside + Cu(OTf)$_2$; purple: 2 + glycoside + Cu(OTf)$_2$ + EDA. Conditions: 2 (1.0 × 10$^{-3}$ M, unit conc.), glycoside (2.0 × 10$^{-3}$ M), Cu(OTf)$_2$ (5.0 × 10$^{-4}$ M), EDA (5.0 × 10$^{-4}$ M), CH$_2$Cl$_2$, 25 °C, path length = 1 mm. Cu(OTf)$_2$ was added as a DMSO solution of a 1/300 amount to the sample solution.
Fig S8 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectra of host polymer 3 and 4 associated with octyl β-D-glucopyranoside (β-D-Glc). (A) host polymer: 3 (B) host polymer: 4. Blue: host polymer; red: host polymer + β-D-Glc; green: host polymer + β-D-Glc + Cu(OTf)₂; purple: host polymer + β-D-Glc + Cu(OTf)₂ + EDA. Conditions: host polymer (1.0 × 10⁻³ M, unit conc.), β-D-Glc (2.0 × 10⁻³ M), Cu(OTf)₂ (5.0 × 10⁻⁴ M), EDA (5.0 × 10⁻⁴ M), CH₂Cl₂, 25 °C, path length = 1 mm. Cu(OTf)₂ was added as a DMSO solution of a 1/300 amount to the sample solution.

Fig S9 The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectra of host polymer 3 associated with (A) octyl β-fructopyranoside (β-D-Fru) and (B) octyl β-mannopyranoside (β-D-Man). Blue: 3; red: 3 + glycoside; green: 3 + glycoside + Cu(OTf)₂; purple: 3 + glycoside + Cu(OTf)₂ + EDA. Conditions: 3 (1.0 × 10⁻³ M, unit conc.), glycoside (2.0
× 10^{-3} \text{ M}), \text{Cu(OTf)}_2 (5.0 \times 10^{-4} \text{ M}), \text{EDA} (5.0 \times 10^{-4} \text{ M}), \text{CH}_2\text{Cl}_2, \text{25 °C, path length = 1 mm.} \)

\text{Cu(OTf)}_2 \text{ was added as a DMSO solution of a 1/300 amount to the sample solution.}

**Fig S10** The additive effect of Cu(II) triflate and ethylenediamine (EDA) on the UV/Vis spectra of host polymer 4 associated with (A) octyl β-fructopyranoside (β-D-Fru) and (B) octyl β-mannopyranoside (β-D-Man). Blue: 4; red: 4 + glycoside; green: 4 + glycoside + Cu(OTf)$_2$; purple: 4 + glycoside + Cu(OTf)$_2$ + EDA. Conditions: 4 (1.0 × 10$^{-3}$ \text{ M, unit conc.}), glycoside (2.0 × 10$^{-3}$ \text{ M}), Cu(OTf)$_2$ (5.0 × 10$^{-4}$ \text{ M}), EDA (5.0 × 10$^{-4}$ \text{ M}), \text{CH}_2\text{Cl}_2, \text{25 °C, path length = 1 mm.} \)

\text{Cu(OTf)}_2 \text{ was added as a DMSO solution of a 1/300 amount to the sample solution.}

**Fig S11** The titration curve for CD at 339 nm of the mixture of 2 and β-D-glucopyranoside (β-D-Glc). β-D-Glc was used as titrant. The formal binding constant $K'$ was obtained by curve fitting measurements based on the equation mentioned above and the assumption that the molecular
weight of the polymer 2 was uniform in length and that the polymer and the guest associate in a 1:1 ratio. Conditions: 2 (1.0 × 10^{-3} M, unit conc.), β-D-Glc, CH₂Cl₂, 25 °C, path length = 1 mm.

Fig S12 A CD spectral change in the reverse-order experiment. β-D-glucopyranoside (β-D-Glc) was added to the mixture of host polymer 2 and Cu(II) triflate. A small ICD band was retained even after reaching equilibrium in four hours upon the addition of β-D-Glc. The ICD was five times smaller than that shown in Fig. 3. Conditions: 2 (1.0 × 10^{-3} M, unit conc.), β-D-Glc (2.0 × 10^{-3} M), Cu(OTf)₂ (5.0 × 10^{-4} M), CH₂Cl₂:DMSO = 300:1, 25 °C, path length = 1 mm.
$^1$H NMR spectra (300 MHz in CDCl$_3$)