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PREPARATION AND SPECTROSCOPIC STUDY OF ALTERNATE *meta*-ETHYNYLPYRIDINE OLIGOMER INVOLVING 2,4,6-TRISUBSTITUTED AND 3,5-DISUBSTITUTED PYRIDINE RINGS

Hajime Abe,* Daiki Suzuki, Ayako Shimizu, and Masahiko Inouye*

Graduate School of Pharmaceutical Sciences, University of Toyama, Sugitani 2630, Toyama 930-0194, Japan. E-mail: abeh@pha.u-toyama.ac.jp

Abstract – A new type of ethynylpyridine cooligomer which consists of 3,5- and 2,6-pyridylene units alternately linked with acetylene bonds was prepared by repeating Sonogashira reaction. ^{1}H NMR study suggested that this cooligomer associates with methanol by hydrogen-bonding at the pyridine units. Intramolecular excimer emission was observed around 540 nm by fluorescence measurement, indicating the formation of helical conformation. Weak induced CD was observed by the addition of octyl glucoside as a guest.

Dedicated to Professor Victor Snieckus on the occasion of his 77th birthday

INTRODUCTION

Helical structures of molecular level have attracted the interests of scientists in various fields. In order to build well-organized helical oligomers and polymers based on a heterocyclic main chain, a number of strategies have been applied.[1] For example, heterohelicenes: very rigid structure can force the helical structure;[2] helicates: the helical structure is held by coordination with metal centers;[3] supramolecules: non-covalent interaction as hydrogen bonding and solvophobic effects can contribute to the helix formation. Intramolecular interaction, intermolecular dimerization (or more), and host−guest interaction can be adopted;[4] and conformers: curving conformation suitable for the helix formation can be stabilized by electrostatic effects. In some cases, two kinds of *N*-heterocycles were alternately oligomerized to form a helix.[5] Without any appropriate strategy, the oligomers and polymers usually tend to form a disordered structure such as random-coil.

So far, our group has developed *meta*-ethynylpyridine oligomers and polymers **1** (Figure 1), which consist

of pyridine rings linked with acetylene bonds at 2,6-positions.[6–8] These polymers and oligomers prefer transoid conformation, because of the local dipole moment at each pyridine ring. The addition of a saccharide guest stabilized the cisoid conformation by multiple hydrogen-bonding, and the resulting helical complex showed induced CD due to the chirality transfer from the guest to the helix.[6a] Recently, we reported heterocyclic cooligomers **2**, which have 1*H*-4-pyridone rings in addition to pyridine rings, and these two kinds of rings were linked alternately by acetylene bonds.[7] Because the pyridine and pyridone rings have the local dipolar moments in the opposite direction, the cisoid conformation could be stabilized in their own right. This situation made the cooligomers favorable in the helical structures without addition of the saccharide guests. The cooligomers **2** proved to have strong saccharide recognition ability by virtue of the helical conformation. Next we planned to make another kind of alternate ethynylpyridine cooligomer **3** to build a helix. This cooligomer consisted of six 2,6-pyridylene and five 3,5-pyridylene groups linked with acetylene bonds. Figure 2 shows comparison between conformers of model compounds **3a** by DFT calculation. The U-shape conformer of **3a** was predicted to be 0.61 kJ/mol more stable than N-shape one, therefore the helical structure of **3** was expected to exist more than the case of **1**. These prospects encouraged us to develop **3** as a helical device. The 3-butenyloxy groups at 2,6-pyridylene moieties were introduced at the aim of improving solubility and fixing the helix afterward by alkene metathesis reaction.

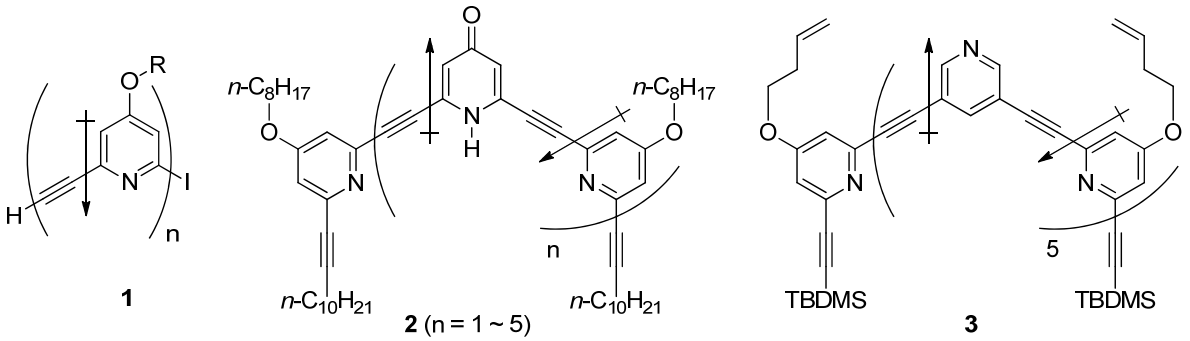


Figure 1. Ethynylpyridine polymers **1** and alternate cooligomers **2** and **3**.

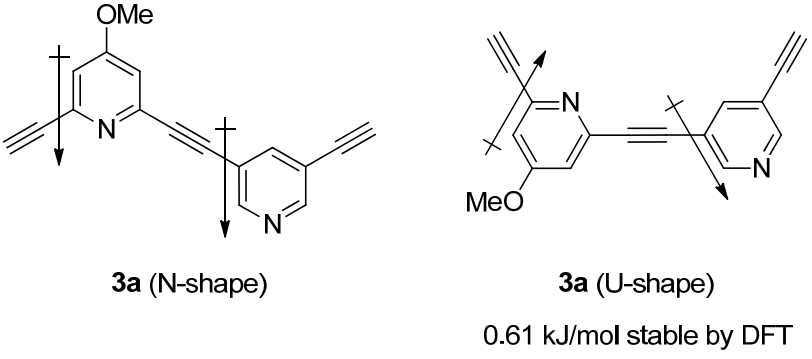
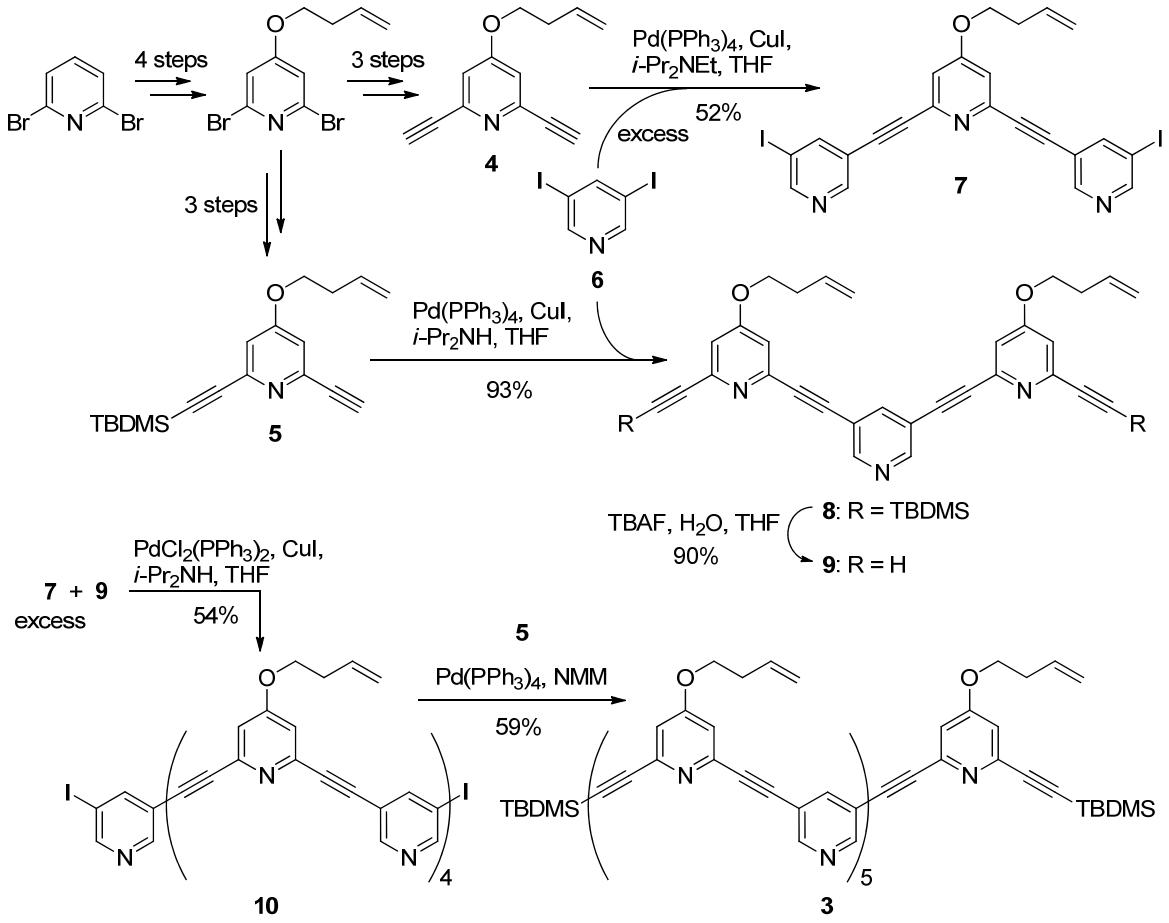


Figure 2. Difference of stability between conformers of model compound **3a** predicted by DFT calculation. Conditions: B3LYP/6-31+G(d,p).

RESULTS AND DISCUSSION

The alternate cooligomer **3** was prepared from three kinds of building blocks **4**, **5**, and **6** via sequential Sonogashira coupling reaction. Both the 2,4,6-trisubstituted pyridine blocks **4** and **5** were obtained from 2,6-dibromopyridine,[8] and 3,5-diiodopyridine **6** was obtained from 3,5-dibromopyridine.[9] The Sonogashira reaction using **4** with an excess of **6** gave diiodo-trimer **7**. The coupling of **6** with two equivalents of **5** gave trimer **8**, and the two *tert*-butyldimethylsilyl groups were removed by TBAF to give **9**. This trimer **9** was further extended to nonamer **10** by the treatment with an excess of diiodide **7**. Finally, the two 3-iodopyridyl moieties at the both ends of **10** was coupled with two equivalent of **5** to afford the targeted alternate undecamer **3**, which was identified by ^{1}H NMR in $CDCl_3$ and ESI-TOF-HRMS measurements. Chloroform could dissolve **3** moderately, whereas **3** was practically insoluble in more polar acetonitrile or methanol.



Scheme 1. Preparation of alternate cooligomer **3**. TBAF = tetrabutylammonium fluoride, NMM = *N*-methylmorpholine.

Spectroscopic properties were studied for the cooligomer **3**. A solvent effect was observed in ^{1}H NMR measurements in $CDCl_3$ and $CDCl_3/CD_3OD$ (2:5) as shown in Figure 3. It was found that most of aromatic ^{1}H signals shifted downfield in $CDCl_3/CD_3OD$ compared with that in $CDCl_3$ (Table 1) except the

protons at 2,6-positions of 3,5-disubstituted pyridine rings. On the other hand, remarkable downfield shifts were observed for protons at 4-positions of 3,5-disubstituted pyridine rings. Among the aliphatic protons, -OCH_2- ones at 3-butenyloxy side chains showed about 0.04 ppm downfield shift in $CDCl_3/CD_3OD$, though other aliphatic ones were less affected (< 0.02 ppm shift).

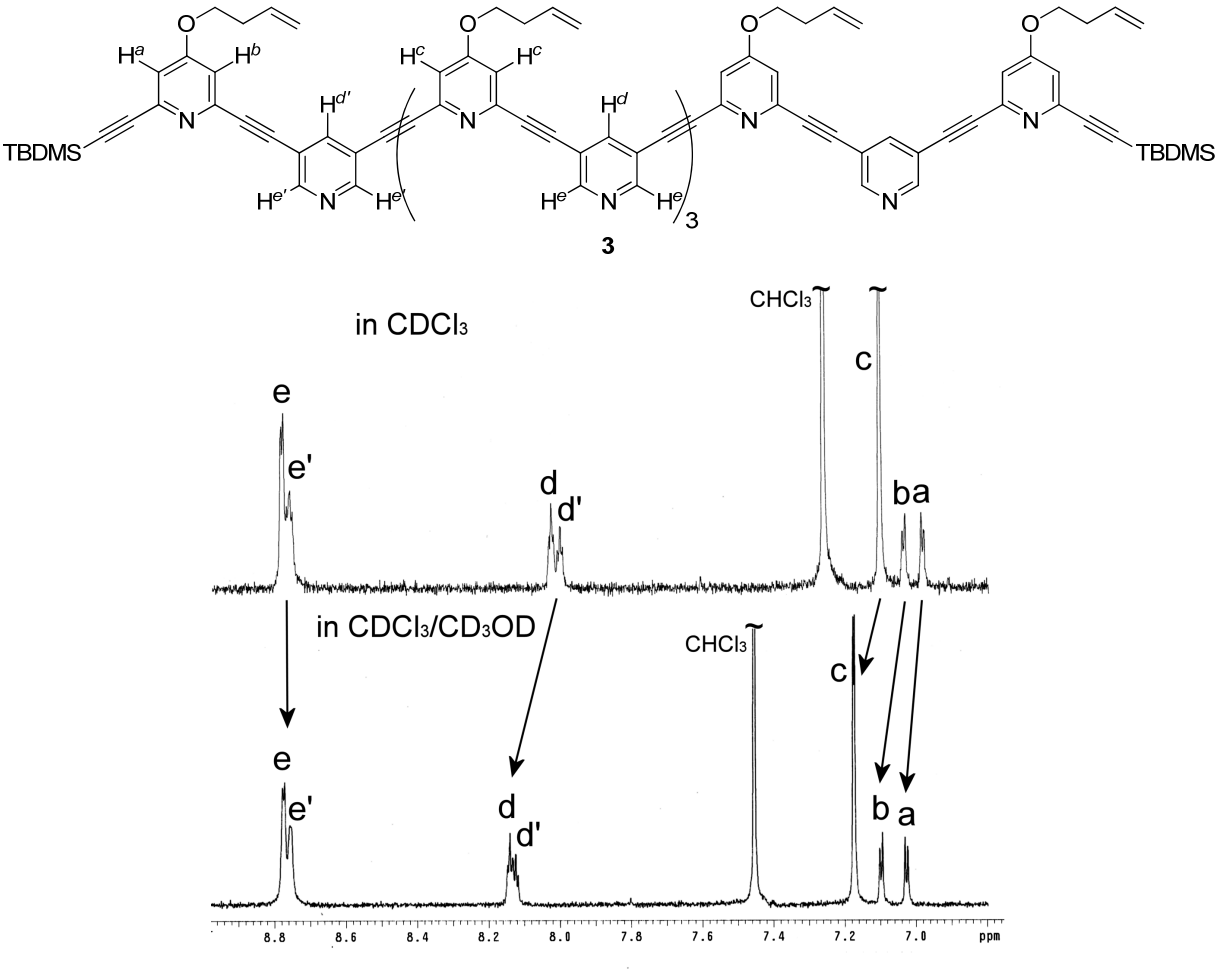


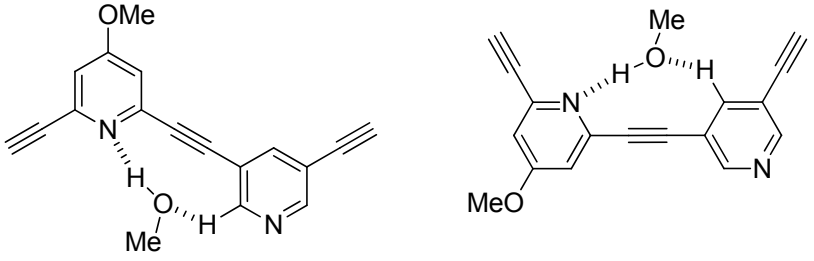
Figure 3. ^{1}H NMR spectra of aromatic region for **3** (top) in $CDCl_3$, (bottom) in $CDCl_3/CD_3OD$ (2:5). Conditions: **3** (1.0×10^{-3} M), 300 MHz, 23 °C.

Table 1. Chemical shifts and differences for aromatic ^{1}H NMR signals shown in Figure 3.[a]

	pyridine unit	3,5-disubstituted				2,4,6-trisubstituted		
	position	H^e	$H^{e'}$	H^d	$H^{d'}$	H^c	H^b	H^a
	number of H	6	4	3	2	8	1	1
in $CDCl_3$		8.78	8.76	8.03	8.00	7.10	7.03	6.98
in $CDCl_3/CD_3OD$ (2:5)		8.78	8.76	8.14	8.12	7.17	7.10	7.03
difference		0.00	0.00	0.11	0.12	0.07	0.07	0.05

[a] δ values were shown as ppm. For conditions, see footnote of Figure 3.

These position-depended downfield shifts could be rationalized by considering hydrogen-bonding of two adjacent pyridine units with methanol. Figure 4 represents hydrogen-bonding of the expected push-pull manner between N-/U-shape model **3a** and methanol, of which stability was evaluated by DFT study. There have been supramolecular helical structures in which hydrogen-bonding of C-H hydrogen atoms on *N*-containing heterocycles are important.[1,4] When the hydrogen atom of the hydroxy group in methanol associated with 4-alkoxypyridine unit of **3a**, the oxygen atom of the hydroxy group is able to approach the 2- and 4-H atoms of 3,5-disubstituted pyridine unit, according to the conformation. The ^{1}H NMR observation and DFT calculation would suggest the advantage of **3a** of U-shape conformation, in which the 4-H atom of 3,5-disubstututed pyridine unit is more affected by hydrogen-bonding.



3a (N-shape)-MeOH **3a** (U-shape)-MeOH

2.41 kJ/mol stable by DFT

Figure 4. Possible push-pull binding of methanol by pyridine nitrogen and 2- or 4-pyridine C-H represented by model compound **3a** with difference of stability predicted by DFT calculation. Conditions: B3LYP/6-31+G(d,p).

UV-vis and fluorescence spectra were measured in CH_2Cl_2 solutions of undecamer **3** and trimer **8** in order to study the length effect. On comparison of UV-vis spectra for **3** and **8** (Figure 5), no remarkable movement of λ_{max} was observed. The difference of absorption strength would be due to the difference of the number of pyridine rings. On the other hand, in fluorescence spectrum of **3** (λ_{ex} = 320 nm) a structureless broad band was observed around 540 nm (Figure 6). Because the corresponding emission was not observed in the case of **8**, this band could be attributed to intramolecular excimer emission. Appearance of the intramolecular excimer emission in **3** indicates the interaction of the both ends of the longer cooligomer at the excited state. A similar emission was also observed in the case of *meta*-ethynylpyridine oligomers and polymers in our early work,[6a] and in those cases shorter cooligomers also showed no excimer emission. The much smaller Storks shift for **3** than that for **8** would be due to the rigidity of **3** brought by its higher-order structure.

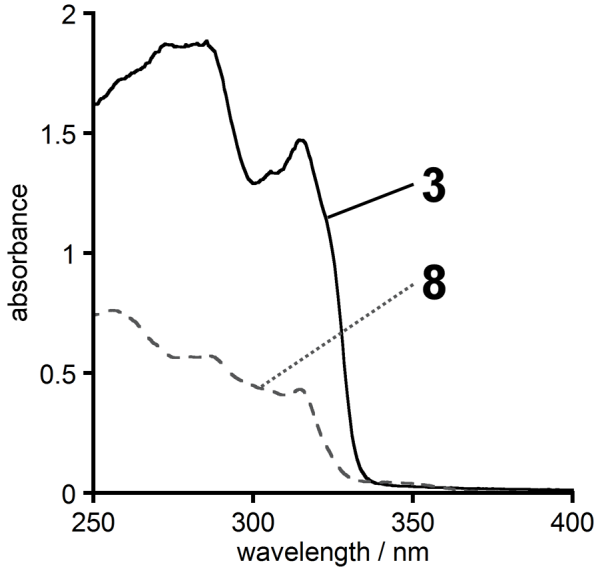


Figure 5. UV-vis spectra of **3** and **8**. Conditions: **3** (1.0×10^{-5} M) or **8** (1.0×10^{-5} M), CH_2Cl_2, 25 °C. Path length = 10 mm.

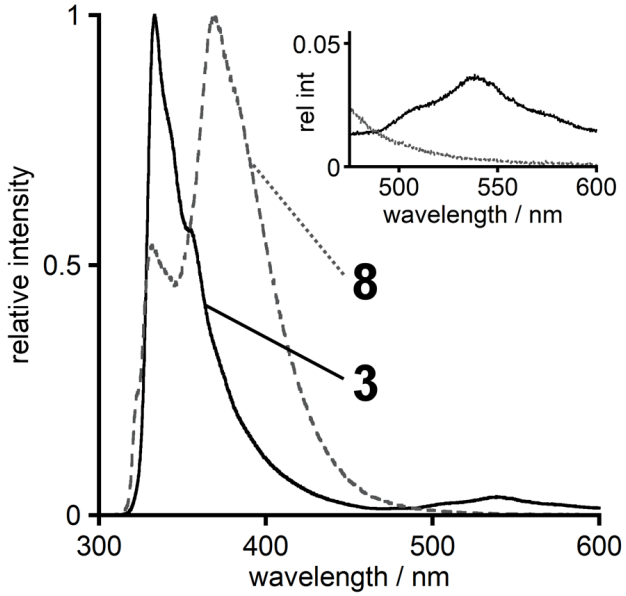


Figure 6. Normalized fluorescence spectra of **3** and **8**. Conditions: **3** (1.0×10^{-5} M) or **8** (1.0×10^{-5} M), CH_2Cl_2, 25 °C, λ_{ex} = 320 nm. Path length = 10 mm. Inset shows an expansion of the region 475 - 600 nm.

Finally, saccharide recognition ability[10] of **3** was tried by using octyl β-D-glucopyranoside (**Glc**) as a guest. When an excess of **Glc** was added to a CH_2Cl_2 solution of **3**, a typical CD band was induced around 335 nm (Figure 7), which indicate the translation of the chirality of the glucoside into the chirality of higher-order structure of **3**, as well as *meta*-ethynylpyridine oligomers and polymers we have reported so far.[6–8] The strength of induced CD shown in Figure 7 was much weaker compared to that in the cases of usual poly- and oligo(ethynylpyridines) **1** with a glucoside guest. When **3** makes a helix as expected, the nitrogen

atoms of 2,6-pyridylene units direct to inside of the helix and will behave as hydrogen-bonding sites. On the hand, the nitrogen atoms of 3,5-pyridylene units direct to outside and are useless for incorporating a guest. Thus, the alternation in the structure of **3** brought an advantage for forming a helix by a dipole effect, whereas brought a disadvantage for decreasing the number of recognition sites.

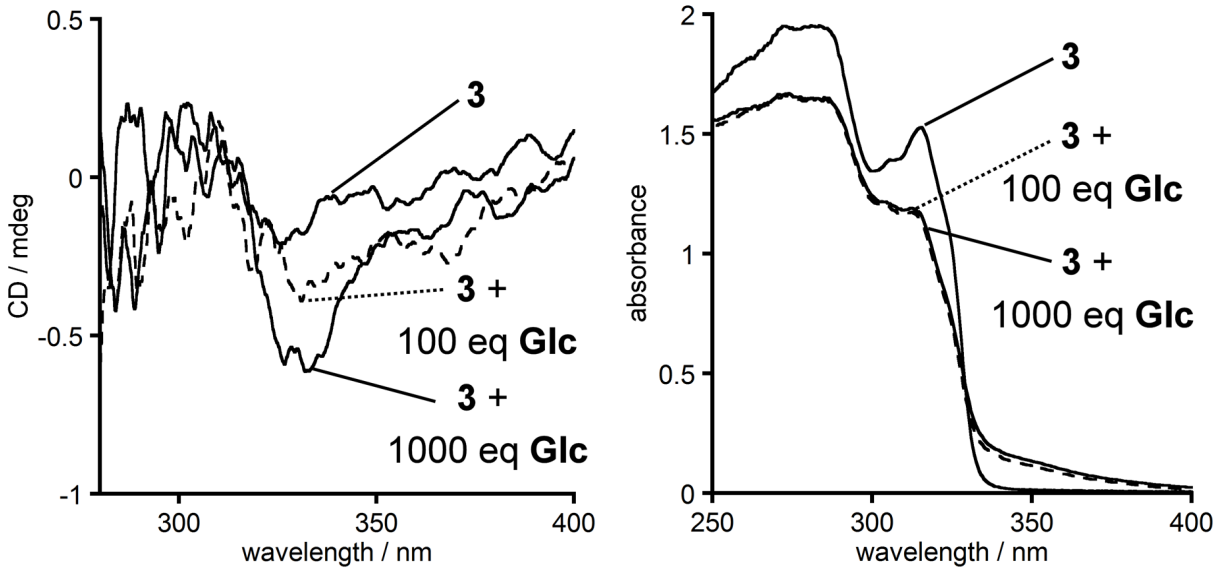


Figure 7. (left) CD and (right) UV-vis spectra of mixtures of **3** and glucoside. Conditions: **3** (1.0×10^{-5} M), octyl β-D-glucopyranoside (**Glc**, 0 M, 1.0×10^{-3} M, or 1.0×10^{-2} M), CH_2Cl_2, 25 °C. Path length = 10 mm.

In conclusion, we designed and prepared a new type of ethynylpyridine cooligomer **3** which consists of 3,5- and 2,6-pyridylene units alternately linked with acetylene bonds. ^{1}H NMR experiments of $CDCl_3$ and $CDCl_3/CD_3OD$ solutions and DFT calculation suggested that cooligomer **3** associates with methanol by hydrogen-bonding in a push-pull manner by adjacent pyridine units. Fluorescence spectra showed an intramolecular excimer emission as a broad band around 540 nm, which supported the formation of helical conformation. Weak glucoside recognition ability was observed by an induced CD measurement, though the CD was much weaker due to the alternation in the structure of **3**.

We are now surveying the suitable reaction conditions to bridge the 3-butenyl side chains of **3** by alkene metathesis procedure to fix the helical conformation, which is expected as an saccharide recognition host or a chiral reaction environment.

EXPERIMENTAL

General. NMR spectra were recorded on a 300 MHz NMR spectrometer using tetramethylsilane (TMS) as an internal reference. Melting points were not corrected. THF was freshly distilled from sodium

benzophenone ketyl before use.

Starting Materials. 4-(3-Butenyloxy)-2,6-diethynylpyridine (**4**),[8] 4-(3-butenyloxy)-2-(*tert*-butyldimethylsilylethynyl)-6-ethynylpyridine (**5**),[8] and 3,5-diiodopyridine (**6**)[9] were prepared as reported in the literature. All reactions were carried out under an argon atmosphere.

4-(3-Butenyloxy)-2,6-bis(5-iodo-3-pyridylethynyl)pyridine (7). To a mixture of 4-(3-butenyloxy)-2,6-diethynylpyridine (**4**, 0.10 g, 0.51 mmol), 3,5-diiodopyridine (**6**, 0.63 g, 2.0 mmol), $Pd(PPh_3)_4$ (24 mg, 21 μmol), *i*-Pr_2NH (2.5 mL), and THF (20 mL) was added CuI (3.9 mg, 20 μmol), and the mixture was stirred for 5 h at room temperature. The resulting mixture was treated with a Florisil bed and given a rinse with AcOEt. The filtrate was concentrated by a rotary evaporator and the resulting residue was subjected to silica gel column chromatography (eluent: $CHCl_3$ to $CHCl_3$/MeOH = 50:1) to give **7** as a colorless solid (0.16 g, 52%). Mp 196−198 °C; IR (KBr) ν 3047, 2925, 2222, 1582, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.57−2.64 (m, 2 H), 4.13 (t, J = 6.6 Hz, 2 H), 5.15−5.23 (m, 2 H), 5.82−5.95 (m, 1 H), 7.07 (s, 2 H), 8.21 (s, 2 H), 8.73 (s, 2 H), 8.81 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.2, 67.8, 84.0, 92.1, 92.4, 113.9, 117.9, 120.8, 133.1, 143.8, 146.6, 150.7, 155.2, 165.1; HRMS (ESI-TOF) calcd for $C_{23}H_{16}I_2N_3O$ ($M + H^+$): 603.9383; *m*/*z* found: 603.9362.

3,5-Bis(4-(3-butenyloxy)-6-(*tert*-butydimethylsilylethynyl)-2-pyridylethynyl)pyridine (8). To a mixture of 3,5-diiodopyridine (**6**, 0.28 g, 0.83 mmol), $Pd(PPh_3)_4$ (39 mg, 33 μmol), CuI (6.3 mg, 33 μmol), *i*-Pr_2NH (2.5 mL), and THF (10 mL) was added 4-(3-butenyloxy)-2-(*tert*-butyldimethylsilylethynyl)-6-ethynylpyridine (**5**, 0.52 g, 1.7 mmol), and the mixture was stirred for 4 h at room temperature. The resulting mixture was treated with a Florisil bed and given a rinse with THF. The filtrate was concentrated by a rotary evaporator and the resulting residue was subjected to silica gel column chromatography (eluent: hexane/AcOEt = 8:1 to 4:1) to give **8** as a yellow solid (0.54 g, 93%). Mp 79−81 °C; IR (KBr) ν 3078, 2953, 2928, 2857, 2225, 2164, 1579, 1552 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.20 (s, 12 H), 1.00 (s, 18 H), 2.54−2.61 (m, 4 H), 4.11 (t, J = 6.6 Hz, 4 H), 5.13−5.23 (m, 4 H), 5.81−5.94 (m, 2 H), 6.98 (s, 2 H), 7.03 (s, 2 H), 7.98 (s, 1 H), 8.74 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.7, 16.7, 33.1, 67.6, 84.2, 92.0, 93.6, 103.6, 113.5, 114.0, 117.6, 119.0, 133.2, 141.1, 143.5, 144.5, 151.6, 164.8; HRMS (ESI-TOF) *m*/*z* calcd for $C_{43}H_{52}N_3O_2Si_2$ ($M + H^+$): 698.3598; found: 698.3598.

3,5-Bis(4-(3-butenyloxy)-6-ethynyl-2-pyridylethynyl)pyridine (9). A mixture of **8** (0.12 g, 0.17 mmol), tetrabutylammonium fluoride (TBAF, 1.0 M in THF, 0.50 mL, 0.50 mmol), THF (10 mL), and three drops of water was stirred for 1 h at room temperature. The resulting mixture was concentrated by a rotary evaporator and the resulting residue was subjected to silica gel column chromatography (eluent: $CHCl_3$/MeOH = 60:1) to give **9** as a brown solid (70 mg, 90%). Mp 74−77 °C; IR (KBr) ν 3289, 3075, 2936, 2225, 2108, 1581, 1551 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.55−2.62 (m, 4 H), 3.15 (s, 2 H), 4.11 (t, J = 6.6

Hz, 4 H), 5.13−5.23 (m, 4 H), 5.81−5.94 (m, 2 H), 7.01 (s, 2 H), 7.07 (s, 2 H), 7.99 (s, 1 H), 8.75 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 33.2, 67.7, 82.1, 84.4, 91.8, 113.9, 114.0, 117.8, 119.0, 133.2, 141.1, 143.7, 151.8, 165.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{31}H_{24}N_3O_2$ ($M + H^+$): 470.1869; found: 470.1862.

Diiodo-nonamer 10. A mixture of tandem diyne **9** (58 mg, 0.12 mmol), diiodide **7** (0.21 g, 0.34 mmol), $PdCl_2(PPh_3)_2$ (3.5 mg, 5.0 μmol), CuI (0.9 mg, 5.0 μmol), *i*-Pr_2NH (2.5 mL), and THF (30 mL) was stirred for 5.5 h at 50 °C. The resulting mixture was treated with a Florisil bed and given a rinse with $CHCl_3$. The filtrate was concentrated by a rotary evaporator and the resulting residue was subjected to silica gel column chromatography (eluent: $CHCl_3$/MeOH = 75:1 to 10:1) to give **10** as a red solid (95 mg, 54%). Mp 178−179 °C; IR (KBr) ν 3072, 2923, 2850, 2222, 1581, 1549 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.57−2.64 (m, 8 H), 4.12−4.18 (m, 8 H), 5.15−5.24 (m, 8 H), 5.82−5.95 (m, 4 H), 7.07−7.11 (m, 8 H), 8.01−8.03 (m, 3 H), 8.22 (s, 2 H), 8.73−8.81 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 33.0, 67.7, 84.5, 91.7, 92.0, 113.8, 117.7, 118.8, 133.0, 141.1, 143.7, 143.8, 146.5, 150.6, 151.7, 155.1, 165.0; HRMS (ESI-TOF) *m*/*z* calcd for $C_{77}H_{52}I_2N_9O_4$ ($M + H^+$): 1420.2232; found: 1420.2231.

Bis(TBDMS-ethynyl)-undecamer 3. A mixture of **5** (40 mg, 0.13 mmol), diiodide **10** (38 g, 27 μmol), $Pd(PPh_3)_4$ (6.2 mg, 5.3 μmol), and *N*-methylmorpholine (NMM, 15 mL) was stirred for 7 h at 55 °C and additionally for 17 h at 65 °C. The resulting mixture was treated with a Florisil bed and given a rinse with $CHCl_3$. The filtrate was concentrated by a rotary evaporator and the resulting residue was subjected to silica gel column chromatography (eluent: $CHCl_3$ to $CHCl_3$/MeOH = 100:1) to give **3** as a pink solid (28 mg, 59%). Mp 139−140 °C; IR (KBr) ν 3074, 2928, 2855, 2224, 2162, 1581, 1550 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 12 H), 1.00 (s, 18 H), 2.55−2.64 (m, 12 H), 4.08−4.18 (m, 12 H), 5.13−5.25 (m, 12 H), 5.81−5.94 (m, 6 H), 6.98 (s, 2 H), 7.01 (s, 8 H), 8.00−8.03 (m, 5 H), 8.73−8.79 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ −4.7, 16.7, 26.2, 33.2, 67.6, 67.8, 84.2, 84.6, 84.7, 91.7, 91.8, 92.0, 93.7, 103.7, 113.6, 113.9, 114.0, 117.7, 117.8, 119.0, 119.1, 133.2, 133.3, 141.2, 143.5, 143.9, 144.6, 151.7, 151.8, 164.9, 165.1; HRMS (ESI-TOF) *m*/*z* calcd for $C_{115}H_{100}N_{11}O_6Si_2$ ($M + H^+$): 1786.7397; found: 1786.7391.

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