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Article

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Development of Helical Aromatic Amide Foldamers with a Diphenylacetylene Backbone

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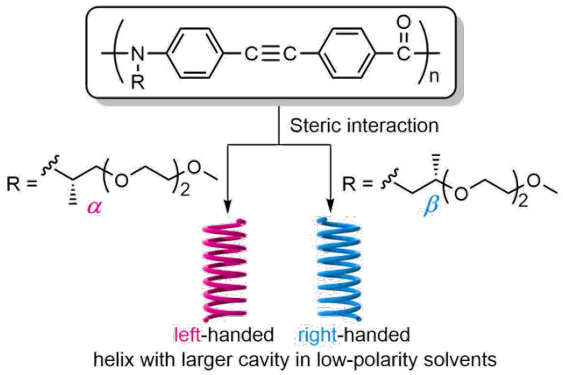


Abstract

We designed and synthesized aromatic polyamides with a diphenylacetylene backbone, **α-DPA** and **β-DPA**, bearing (*S*)-*α*- and (*S*)-*β*-methyl-substituted triethyleneglycol (TEG) side chains, respectively, and examined their conformations in solution. Both polymers exhibit strong, solvent-polarity-dependent CD spectra, which indicated that they take helical conformations in low-polarity solvents. The spectra were mirror images, depending on the chiral position of the side chains. Thus, the polyamide **α-DPA** bearing (*S*)-*α*-methyl-substituted TEG groups takes a left-handed helical conformation, while the polyamide **β-DPA** with (*S*)-*β*-methyl-substituted TEG groups takes a right-handed helical conformation. The difference in the screw sense of **α-DPA** and **β-DPA** would be caused by the steric interaction between the main chain and the side chain, as observed in poly(*p*-benzamide) possessing (*S*)-*β*-methyl-substituted TEG side chains (**β-PA**), since the large cavity of the helical structure of **DPA** would disturb the solvophobically induced helical folding. Detailed conformational analyses of the oligoamides **6** – **12** with *β*-methyl-substituted TEG groups were conducted. Theoretical calculations indicated that the oligoamides with *β*-methyl-substituted TEG groups exist in a helical conformation with a cavity of 7 Å in diameter. The ^{1}H NMR spectra of the oligomers revealed interactions with small anions such as chloride and acetate anions, and with pyridinium cation.

INTRODUCTION

Biological macromolecules such as DNA and proteins adopt unique three-dimensional structures, including helical and β-sheet structures, and are regarded as natural foldamers.[1] Helical foldamers have attracted much attention in the past few decades, both to investigate the relationship of structure to function for natural foldamers, and to develop artificial foldamers that mimic natural foldamers or have unique feature not found in nature.[2] They are classified into two categories, peptidomimetic foldamers and abiotic foldamers, from the viewpoint of design.[3] The study of artificial foldamers begun with aliphatic β-amino acids.[4,5] Then, many abiotic foldamers consisting of aromatic units and torsionally flexible linkers have been reported. They utilize noncovalent interactions such as hydrogen bonding,[6] aromatic-aromatic interaction, metal coordination,[7] donor-acceptor interaction,[8] solvophobic effect, salt-bridges,[9] etc., to build helical structures.

m-Phenylene ethynylene (***m*PE**) oligomers are well-known foldamers that utilize solvophobic effects. ***m*PE** oligomers bearing triethyleneglycol (TEG) side chain take random coil structure in nonpolar solvents such as chloroform, while they fold into helical structures in polar solvents such as acetonitrile.[10] The helical structure of ***m*PE** oligomers is stabilized by aromatic stacking, and one helical turn consists of six monomer units.[11] ***m*PE** oligomers with alkyl side chains take helical structure in heptane.[12] However, they still exist as random coils in chloroform, and it remains unclear whether van der Waals interaction or the solvophobic effect plays the predominant role in helix formation.

The basic skeleton of ***m*PE** oligomers has been widely applied, with various modifications of the main chain or side chains.[13] As an example of main chain modification, Yamaguchi introduced helicene into ***m*PE** oligomers and showed that the products formed a double helix.[14] On the other hand, Hecht inserted azo units to control helical structure formation by photoirradiation.[15] As for side chain modification, Yashima developed ***m*PE** polymer bearing chiral TEG side chains via amide bonds and reported that it adopted a stable helical conformation in chloroform via intramolecular hydrogen bonding.[16] They were able to observe the helical sense directly by means of atomic force microscopy (AFM). Furthermore, it was reported by Zhao[17] and Yashima,[18] respectively, that not only **PE** linked at the *m*-position, but also **PE** linked alternately at the *o*- and *p*-positions adopts helical structure.

We previously reported that *N*-substituted aromatic amides show cis preference in the crystalline state and in solution.[19] The dihedral angle of tertiary *cis*-amide is about 60

degrees, and by utilizing this folded *cis*-amide moiety repeatedly, we can construct helical foldamers.[20] Among them, poly(*p*-benzamide) possessing (*S*)-β-methyl-substituted TEG side chains (**β-PA**, Figure 1) was shown by exciton model analysis to adopt a dynamic helical conformation with three monomer units per turn and a right-handed form.[21] The conformation of **β-PA** was independent of the solvent. Poly(*p*-benzamide) with (*S*)-α-methyl-substituted TEG side chains (**α-PA**) was also synthesized in the expectation of a larger bias to one helical handedness, compared with **β-PA**. However, **α-PA** adopted a right-handed helical conformation in polar solvents, such as water and methanol, and a random structure in chloroform.[22] These results indicate that the solvophobic effect plays a significant role in the helical folding of **α-PA**. An attempt to synthesize **α-PA** by amide bond formation between the monomer units using potassium hexamethyldisilazide (KHMDS) and 18-crown-6 was unsuccessful, because of preferential formation of cyclic trimer. The synthesis was finally achieved by the use of Et_3SiH, CsF and 18-crown-6. Formation of cyclic trimer indicated that the high planarity of the amide linkages causes the two end groups of the trimer to be located close to each other in a triangular conformation. If this is the case, we anticipated that elongation of the monomer unit would increase the distance between the two terminals of the trimer and thus should favor polymer formation rather than cyclization.

In addition, **α-** and **β-PA** have small cavities, which are difficult to apply for guest encapsulation. Our previous study showed that the cavity size of macrocycles with folded *cis*-amide bonds could be controlled by using two aromatic molecules linked by various bonds as the monomer unit.[23] Recently, we have developed alternately *N*-alkylated amide oligomers and succeeded in expanding the helical cavity.[24]

Here, we describe the synthesis and helical structure of polyamides **α-DPA** and **β-DPA** (Figure 1), which have a diphenylacetylene backbone with (*S*)-α- and (*S*)-β-methyl-substituted TEG side chains, respectively, based on the idea that changing the benzene moiety of **PA** to diphenylacetylene would afford **α-DPA** and **β-DPA** with a larger helical cavity than **α-** and **β-PA**. In addition, we systematically synthesized a series of oligomers and conducted detailed conformational analyses.

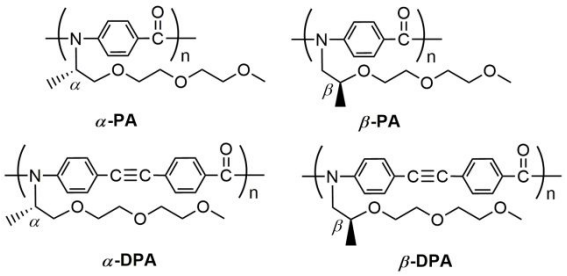
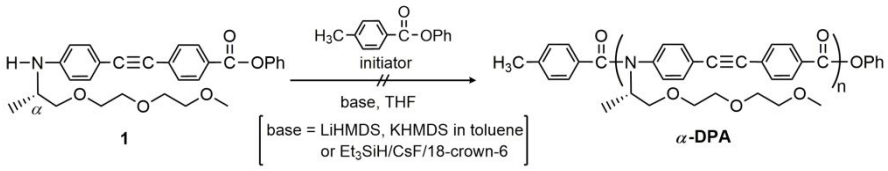


Figure 1. Structures of the polyamides.

RESULTS AND DISCUSSION

1. Syntheses of Polyamides α-DPA and β-DPA.

We initially tried to synthesize **α-DPA** by polymerization of monomer **1** (Scheme 1), which was derived from 1-bromo-4-iodobenzene in 5 steps (see Experimental Section). The condensation polymerization of **1** using lithium hexamethyldisilazide (LiHMDS) as a base and phenyl 4-methylbenzoate as an initiator did not proceed in a chain-growth manner, but afforded the cyclic trimer as the major product. The reaction of **1** using KHMDS and 18-crown-6 at 50 °C afforded the polymer (M_n = 9210, M_w/M_n = 6.18). However, the purified polymer (M_n = 6230, M_w/M_n = 1.40) incorporated undesired structures, as deduced from the ^{1}H NMR spectrum. The polymerization using the combination of Et_3SiH, CsF, and 18-crown-6 in the absence of initiator, as optimized for the synthesis of **β-PA**,[21] afforded only oligoamides (7−9-mers). Therefore, **α-DPA** could not be obtained by the condensation of **1** using base.

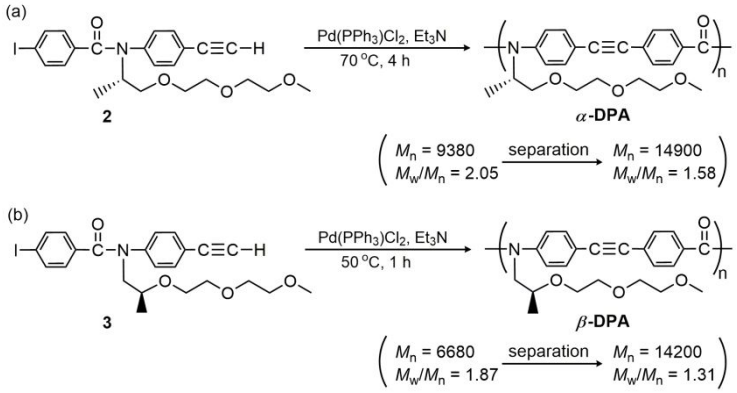


Scheme 1. Condensation polymerization of **1**.

Therefore, we examined the preparation of **α-DPA** by repeated Sonogashira reaction (Scheme 2a). Monomer **2** was prepared from 4-iodobenzoyl chloride in 2 steps (see Experimental Section). Sonogashira reaction of **2** was performed without a copper catalyst to prevent acetylene homocoupling,[25] and afforded **α-DPA** (M_n = 14900, M_w/M_n = 1.58).

To investigate the influence of chiral position on the helical conformation, **β-DPA** was also synthesized in the same manner as **α-DPA**. (*S*)-β-Methyl-substituted TEG was

prepared in 6 steps according to the reported method,[26] and converted to monomer **3** (see Experimental Section). The Sonogashira coupling condensation of **3** afforded ***β*-DPA** (M_n = 14200, M_w/M_n = 1.31) (Scheme 2b).



Scheme 2. Polymerization of (a) **2** and (b) **3** by Sonogashira reaction.

2. CD Spectra of Polymers.

The CD spectra of ***α*-DPA** were measured in various solvents (Figure 2a). Split-type signals, in which the negative Cotton effects appeared at 330–335 nm and the positive Cotton effects appeared at 280–290 nm, were observed in low-polarity solvents such as chloroform and THF, while the negative Cotton effect at 330–335 nm was not observed in mixtures of THF with high-polarity solvents such as acetonitrile, methanol, and water. The chiral monomeric unit **4** showed only a broad positive Cotton effect at around 290 nm (Figure 2b), which suggested that the negative Cotton effect of ***α*-DPA** was derived from secondary structures. Thus, chiral secondary structure appeared to be induced as the solvent polarity was decreased.

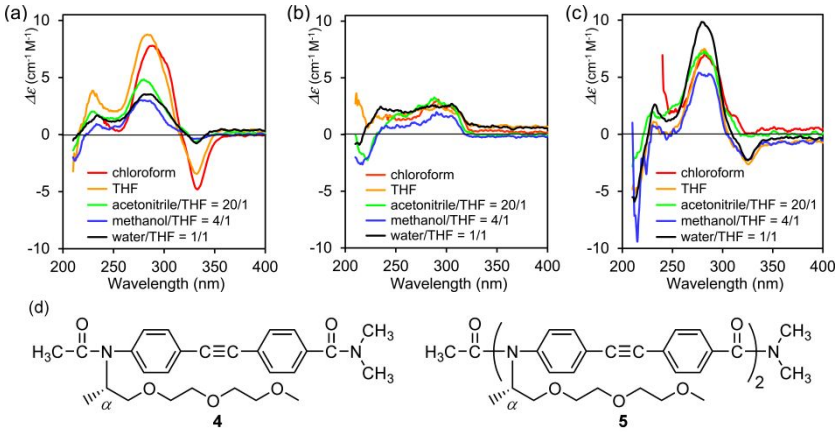


Figure 2. CD spectra of (a) ***α*-DPA**, (b) model compounds **4** and (c) **5** in various

solvents at 0 °C (0.01 g/L). (d) Structures of compounds **4** and **5**.

We next synthesized compound **5**, which has only two diphenylacetylene units linked by a *cis*-amide bond with a chiral side chain, and could not form helical structure, and we measured its CD spectrum (Figure 2c). A strong positive Cotton effect was observed at around 280 nm in all solvents examined. In contrast, the negative Cotton effect at around 330 nm was not observed in chloroform or acetonitrile/THF (20:1), though it was observed in THF, methanol/THF (4:1) or water/THF (1:1). These results indicated that the positive Cotton effect at 280–290 nm of **α-DPA** represents the sum of the contributions of the local structure around the amide bond and the helical structure, and that the strong negative Cotton effect at 330–335 nm of **α-DPA** in chloroform arises mainly from the helical structure. Therefore, **α-DPA** takes the helical structure in less polar solvents, such as chloroform.

Because the monomeric chromophore of **α-DPA** is 4-[[4-(alkylamino)phenyl]ethynyl]benzoyl unit, the chromophore behaves as a typical donor-acceptor diphenylacetylenes whose transition moment lies along the molecular axis,[27] as in the case of 4-(alkylamino)benzoyl unit, a monomeric chromophore of **β-PA** (Figure 1).[21] Therefore, the CD spectrum of **α-DPA** can be interpreted in a similar manner to those of **α-PA** and **β-PA**. Since the CD spectrum of **α-DPA** was a mirror-image of that of **α-PA**,[22] **α-DPA** takes a left-handed helical structure, opposite to that of **α-PA**.

The difference of screw senses was probably due to the different driving forces to induce the helical structure of **α-DPA** and **α-PA**. As described in the previous report,[22] the helical folding of **α-PA** needed solvophobic interactions. In contrast, as for **α-DPA**, the main chain and the side chain of **α-DPA** were solvated similarly in chloroform and THF, and the preference of left-handed helical conformation of **α-DPA** would be determined by the steric interaction between the main chain and the side chain, not by solvophobic interactions. As we expected, the helical folding of **α-DPA** without solvophobic interactions would come about by the elongation of the monomer unit compared to **α-PA**. Since the helical cavity of **α-DPA** will be larger than that of **α-PA**, it should be solvated. However, because polar solvents such as acetonitrile, methanol and water could not solvate the hydrophobic cavity, **α-DPA** could not adopt helical structure in acetonitrile/THF (20:1), methanol/THF (4:1), and water/THF (1:1).

β-DPA also showed a similar solvent-dependency of the CD spectra to **α-DPA** (Figure 3a). The split-type CD signal of **β-DPA** was observed in low-polarity solvents such as chloroform and THF, and the intensity was larger in chloroform than in THF. In

methanol/THF (4:1), the positive Cotton effect at 340–350 nm was not observed, and the negative Cotton effect was blue-shifted. These results suggested that **β-DPA** and **α-DPA** were folded into helical structure in low-polarity solvent independently of the chiral position in the side chain. The absorption peaks of **α-DPA** and **β-DPA** were observed in the range of 295–305 nm with shoulders at ca. 320 nm and ca. 330 nm, respectively (Figure 3b). These results also support that the CD spectra of **α-DPA** and **β-DPA** can be interpreted by the coupling of electric transition dipole moments of helically arranged chromophore units in a similar manner to **β-PA**.[21] The opposite sign of the Cotton effect between **α-DPA** and **β-DPA** indicates that the helicity is also opposite, and **β-DPA** takes right-handed helical structure as in the case of **β-PA** (Figure 3b). These results indicate that the screw sense of the polyamide was determined by the steric interaction between the polymer main chain and the β-substituted side chain. In addition, the *g* value of **β-DPA** was 2.8 times larger than that of **α-DPA** in chloroform, which indicates that the helical conformation of **β-DPA** is more strongly biased to one helical sense than that of **α-DPA**. Because the α-methyl group of the side chain interacts sterically with the amide bond, the planarity of the amide linkage is higher in the case of **α-DPA**, which might interfere with helical folding.

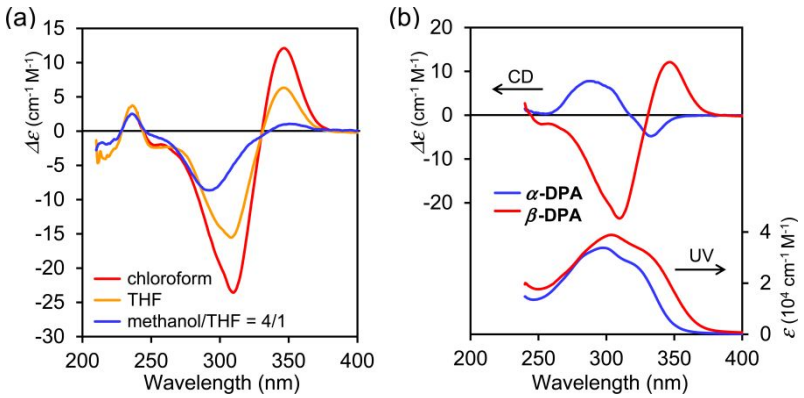


Figure 3. (a) CD spectra of **β-DPA** in various solvents at 0 °C and (b) comparison of UV (lower) and CD (upper) spectra of **α-** and **β-DPA** in chloroform at 0 °C.

The effect of temperature on the helical conformation was next examined (Figure S1). The CD signal intensities of **α-** and **β-DPA** decreased with increasing temperature. These results reflect the thermodynamical nature of the helical folding process of these polyamides.

3. Syntheses of Oligoamides.

In order to understand why **β-DPA** has a stable helical structure with a stronger handedness bias than **α-DPA**, we synthesized a series of oligoamides **6c** – **12c** with (*S*)-*β*-methyl-substituted TEG side chains (Figure 4). We also synthesized oligoamides **6a** – **7a** with *N*-methyl groups and **6b** – **12b** with achiral TEG groups as *N*-substituents for X-ray crystallographic analysis and for the chiral induction experiments, respectively.

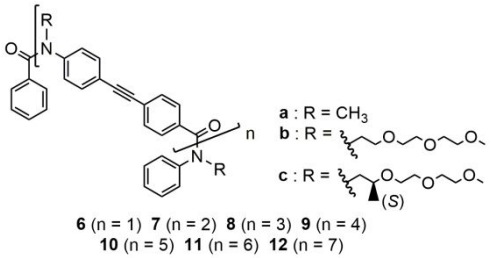


Figure 4. Structures of oligoamides **6** – **12**.

Monomer **6a** and dimer **7a** were synthesized as shown in Scheme S6. However, elongation of oligomers bearing chiral or achiral TEG side chains via this strategy requires many steps, and the introduction of TEG side chains after the synthesis of the main chain is difficult. Therefore, the oligomers **6b** – **12b** and **6c** – **12c** were synthesized by means of sequential Sonogashira reactions (see Experimental Section).

4. X-ray Crystallographic Analysis.

Single crystals were obtained only for monomer **6a** and for **13**, the synthetic intermediate of dimer **7a** (Figures S4-S6, and Table S1). The tertiary amide bond exists in cis form in both compounds. The dihedral angle of the two benzene units of diphenylacetylene is 66.88° for **6a**, and 88.08° and 87.86° for **13**. Intermolecular CH-O and CH-π interactions were observed in the packing structure of **13** (Figure S6), which may generate the zig-zag conformation of **13**. These results suggested that *cis*-form tertiary amide bonds are preferable to enable oligomers to form well-ordered folded conformations.

5. UV and CD spectra of Oligomers.

The UV and CD spectra of oligoamides **6c** – **12c** bearing chiral (*S*)-methyl-substituted TEG side chains were measured to investigate their conformations. The CD intensity of the oligomers increased with elongation of the chain length (Figure 5). In addition, the intensity showed temperature dependency (Figure S2). The shapes of the UV and CD

spectra were different between monomer **6c** and oligoamides **7c** – **12c**. In the CD spectra, monomer **6c** showed a weak, broad negative Cotton effect at around 290 nm, while oligoamides **7c** – **12c** gave sharp split-type spectra (a negative Cotton effect at 315 nm and a positive Cotton effect at 350 nm), like ***β*-DPA**. In the UV spectra, the absorption maximum of **6c** was at 315 nm, whereas those of oligoamides **7c** – **12c** were at 305 nm, with a shoulder at 330 nm as in the case of ***α*-DPA** and ***β*-DPA**.

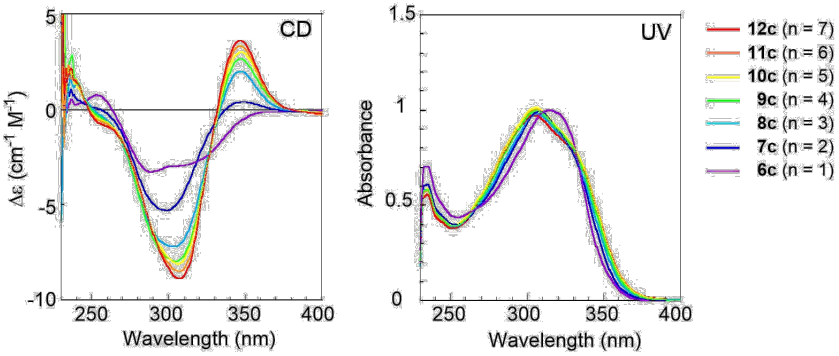


Figure 5. UV and CD spectra of the oligomers **6c** – **12c** in chloroform at 20 °C.

Like the polymer ***β*-DPA**, the oligomer **12c** showed solvent-dependent CD spectra (Figures 6 and S3). In low-polarity solvents such as THF, chloroform and dichloromethane, the oligomer **12c** showed bisignate CD spectra. In high-polarity solvents such as methanol and acetonitrile, only a negative Cotton effect was observed with a blue shift. Not only the shape, but also the intensity was correlated with solvent polarity, especially dielectric constant, and the intensity was high in low-polarity solvents. Similar tendencies were observed in the CD spectra of the dimer **7c**, though the intensity of the positive Cotton effect at 350 nm was very weak, even in low-polarity solvent. These results indicated that oligomers bearing (*S*)-methyl-substituted TEG side chains exist in helical conformation only in low-polarity solvents, and adopt other structures in high-polarity solvents, probably because the solvation of the helical cavity with polar solvents is difficult due to the solvophobic nature of the cavity. These oligomers have a diphenylacetylene moiety as the monomer unit, like ***m*PE** oligomers, but the solvent dependency of their properties is quite different. The major difference is that our oligomers have *cis*-form tertiary amide bonds, and this results in a difference in the direction of the benzene units with respect to the helical axis. In the case of ***m*PE**, the benzene units are perpendicular to the axis, and the helical structure is further stabilized by strong π-π stacking interactions. Furthermore, our oligomers are linked at the para position, while ***m*PE** linkages are at

the meta position. This may lead to a difference of cavity size.

We examined the solution structures of oligomers **6c** – **12c** by means of NMR spectroscopy. However, the ^{1}H NMR spectra of the oligomers did not show any significant dependence on oligomer length or solvent polarity, in contrast to the UV/CD spectra (Figures S7-S8).

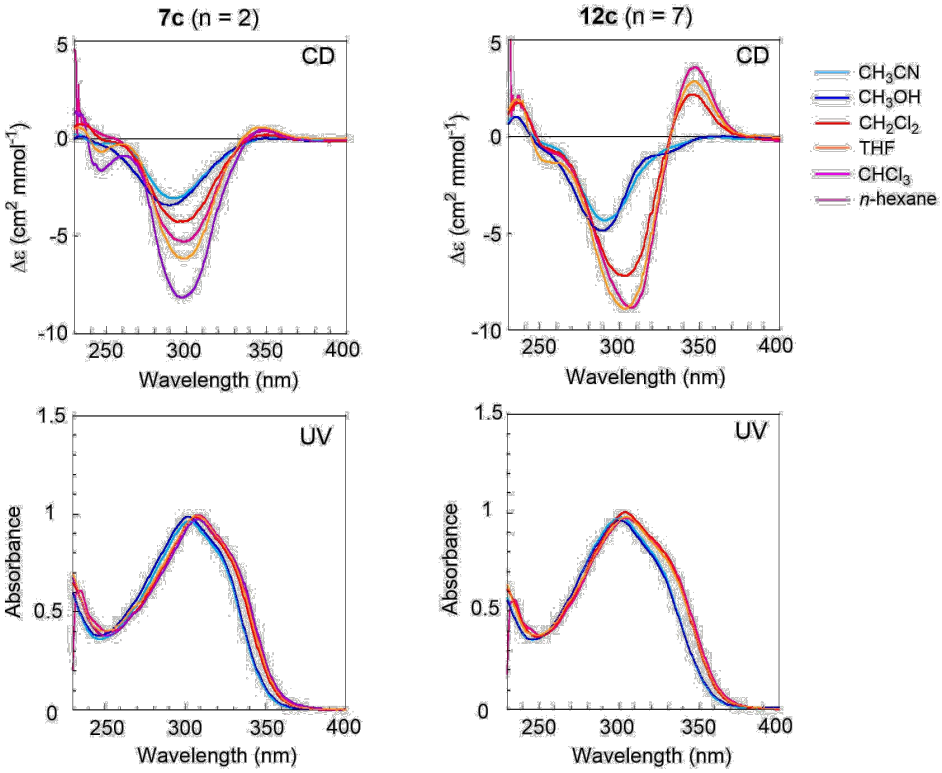


Figure 6. CD and UV spectra of oligomers **7c** and **12c** in various solvents at 20 °C. (**12c** was insoluble in *n*-hexane.).

6. Theoretical Study of the Structural and Spectral Properties of Oligomers.

To understand the relationship between the helical structure of oligomers and the spectral features, we performed geometry optimization calculations on oligoamides **8a**, **10a**, and **12a** at the RI-DFT-D B-LYP/def-SV(P) level after optimization by the PM3 method with Gaussian03, based on the crystal structure of monomer **6a**. The optimized conformations are helical and possess a cavity of approximately 7 Å (Figure 7). Geometry optimization was also done at the RI-DFT B-LYP/def-SV(P) level. The result also indicated helical conformation, but the aromatic rings along the helical axis are divergent, suggesting that van der Waals interactions strongly influence the helical

conformation of these oligoamides.

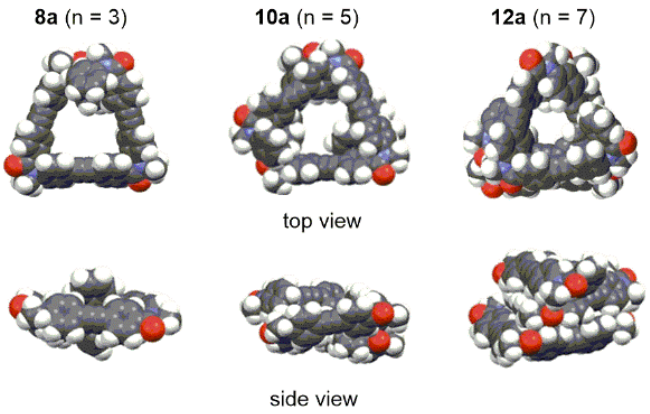


Figure 7. Optimized conformations of **8a**, **10a**, and **12a**.

We also employed time-dependent DFT at the RI-B-LYP/def-SV(P) level to calculate the UV and CD spectra of the optimized conformations of monomer **6a**, and oligomers **8a** and **10a** (Figure S14). The calculated UV spectra show a similar tendency to the experimental UV spectra as regards the blue shift from monomer **6** to oligomer **8**. In addition, the shape of the calculated CD spectra resembles that of the experimental spectra. These results support the idea that the oligomers take helical conformation in low-polarity solvents.

7. Guest Recognition Ability of Oligomers.

The binding interaction between oligomers **8a** and various kinds of chiral molecules was examined by computational study, and the chiral induction of oligomers **8b**, **10b**, and **12b** with achiral TEG side chains was investigated by means of CD and UV measurements. However, addition of any chiral molecule to solutions of these oligomers did not affect the spectra. Thus, any structural change induced by interaction with guest molecules may be too modest to detect by means of CD and UV measurements.

Cyclic derivatives of diphenylacetylene linked by cis-amide bonds were reported to show high binding affinity for Cl^- and I^- anions.[28] Energy minimization calculation using the MM2 force field revealed that the diameter of the macrocycle cavity is about 7.5 Å, and the driving force for anion binding can be attributed to weak C-H···Cl or C-H···I hydrogen bonding.

Taking account of previous findings on cyclic derivatives, the anion recognition abilities of oligomers **6b** – **12b** bearing achiral TEG side chains were evaluated by means of NMR study. When tetrabutylammonium chloride (TBACl, 1 equiv) was added

to a solution of oligomers **6b** – **12b**, no chemical shift change was observed up to trimer **8b** (Figures S9 and 8a). In tetramer **9b**, the chemical shift and the signal shape were slightly but significantly changed by addition of TBACl. The aromatic proton signal at 7.20 ppm was shifted upfield by about 0.01 ppm, and the signals of TEG side chain were also shifted. The addition of excess TBACl (3 and 5 equiv) did not induce further changes in the chemical shifts (data not shown). TBACl also induced smaller changes in the chemical shifts of pentamer **10b**. The relationship between the oligomer length and the chemical shift change (Δδ) of the signal at 7.20 ppm is plotted in Figure 8b. The biggest change was observed in tetramer **9b**, which exhibits 1.5 helical turns, and the change was diminished in longer oligomers. In the case of longer oligomers, it may be difficult for an anion to approach the cavity, or the helical structure may be increasingly stabilized, so that the effect of anion encapsulation on the NMR spectra would be small.

Furthermore, the signals of the TEG side chains were also shifted by addition of TBACl, depending on the oligomer length. Alteration of the helical conformation induced by anion encapsulation would induce a change in the conformation of the TEG side chain.

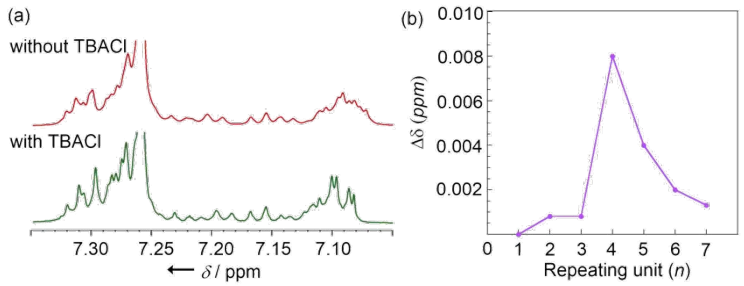


Figure 8. (a) ^{1}H NMR (600 MHz, $CDCl_3$) spectral changes of **9b** (1 mM) with 1 equiv of TBACl in $CDCl_3$ at 25 °C. (b) Chemical shifts of the aromatic proton signal at around 7.20 ppm of **6b** – **12b** when complexed with 1 equiv of TBACl in $CDCl_3$ at 25 °C.

Next, the solvent effect was examined with a mixture of tetramer **9b** and 1 equiv of TBACl (Figure S10). A similar tendency was observed in CD_2Cl_2, while there was no change in CD_3OD and CD_3CN, in which the helical conformation of the oligomer was not stable. In addition, VT-NMR spectra of **9b** were measured in CD_2Cl_2 in the presence and absence of TBACl (Figure S11). The aromatic signals became broader at low temperature in the absence of TBACl. In the presence of TBACl, they were broad at 263 K, but became sharp at lower temperatures. These results suggest that the complex between oligomer and Cl^- anion is stable, and the helical conformation is fixed.

Anion selectivity was also examined with tetramer **9b** in $CDCl_3$ (Figure S12). The chemical shift change upon addition of tetrabutylammonium bromide and acetate was similar to that in the case of TBACl. However, there was no change in the case of tetrabutylammonium iodide. The ionic radii increase in the order of Cl^- (1.81 Å), AcO^- (1.86 Å), Br^- (1.96 Å), and I^- (2.20 Å),[29] suggesting that the selectivity is determined by the ion size. Anion-π interaction rather than CH-halogen interaction may cause these changes, because they were observed with not only halogen anion, but also acetate anion.

Since we expected that encapsulation could occur via cation-π interaction, we examined the effect of addition of some pyridinium cations to a solution of tetramer **9b** by means of NMR measurements (Figure S13). In the case of pyridinium *p*-toluenesulfonate, the chemical shifts of **9b** changed, similarly to the case of Cl^- anion. Although the signals of sulfonate anion did not change, those of pyridinium cation were slightly shifted (*o*-H: +0.047 ppm, *m*-H: −0.024 ppm, *p*-H: −0.017 ppm), suggesting that the oligomer interacted with pyridinium cation.

CONCLUSIONS

We synthesized polyamides and oligoamides consisting of a diphenyl acetylene backbone linked by *cis*-amide bonds, and found that they formed helical structures in low-polarity solvents such as chloroform and THF. The solvent-dependent CD spectra of the polyamides indicates that the screw sense of **α-DPA** and **β-DPA** would be determined by the steric interaction between the main chain and the side chain, as in the case of **β-PA**, and that the solvophobic property is less significant in **DPA** with the longer monomer unit and the large helical cavity, unlike the case of **α-PA**. Theoretical study of the oligoamides suggested these molecules take helical structures with a larger cavity than that of **PA**. With respect to guest recognition, NMR study revealed that the oligomers interact with anions and cations.

EXPERIMENTAL SECTION

General Information. All reagents were purchased from Sigma-Aldrich Chemical Co., Wako Pure Chemical Industries, Tokyo Chemical Industry Co., and Kanto Chemical Co., Inc. Silica Gel 60 N (spherical, neutral) and Kieselgel 60 (230–400 mesh) for column chromatography were purchased from Kanto Chemical Co., Inc. and Merck, respectively. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-ECS400, JNM-ECA500, and JNM-ECA600 spectrometers, and Bruker Avance 600 spectrometer by using solvent molecules such as chloroform (7.26 ppm), methylene chloride (5.32

ppm), methanol (3.31 ppm) or DMSO (2.50 ppm) as the internal standard peak. Infrared (IR) spectra were recorded on a JASCO FT/IR-410. Mass spectral data were obtained on a Shimadzu Biotech Axima CFRplus in the linear and reflectron modes using a laser (λ = 337 nm), a Bruker Daltonics micro TOF-2focus in the positive ion detection mode, and a Thermo Fisher Scientific Q Exactive Hybrid Quadrupole-Orbitrap Mass Spectrometer. Gel permeation chromatography (GPC) profiles were obtained on a Shodex GPC-101 equipped with Shodex UV-41 and RI-71S detectors, and two Shodex KF-804L columns (bead size = 7 μm, pore size = 200 Å). Tetrahydrofuran (THF) was used as the eluent (temperature = 40 °C, flow rate = 2 mL/min), and calibration was carried out using polystyrene standards. Isolation of the oligomer and polymer was carried out with a Japan Analytical Industry (JAI) LC-908 recycling preparative HPLC (eluent: chloroform) using two TSK-gel columns (2 x G2000HHR) and a JAI LC-9201 recycling preparative HPLC (eluent: chloroform) using JAIGEL-1H and -2H columns. Preparative thin layer chromatography (PTLC) was performed on silica gel 60 F254 plates (Merck, Germany). X-ray crystallographic data on compounds **6a** and **13** were collected on a Bruker SMART APEX II ULTRA diffractometer attached with a CCD detector and graphite-monochromated Mokα (λ = 0.71073 Å) radiation. Data were corrected for absorption by the multiscan semiemprical method implemented in SADABS and their crystal structures were solved by intrinsic phasing method SHELXT and refined by SHELXL.[30] Full-matrix least-squares refinement was performed on F^2 for all unique reflections with anisotropic displacement parameters for non-hydrogen atoms. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included as their calculated positions. UV spectra were recorded with JASCO V-650 and Shimadzu UV-1800, and CD spectra were recorded with JASCO J-820 spectropolarimeter using 2 mm and 10 mm quartz cells. The concentration of each solution of CD experiments was adjusted so that the absorbance of the oligomer was 1 at the maximum absorption wavelength in the examined solvents.

Synthesis of Monomer 1. The monomer **1** was synthesized as shown in Scheme S1.

*((4-Bromophenyl)ethynyl)triisopropylsilane (**14**).*[23] In a round bottom flask with a three-way stopcock, 1-bromo-4-iodobenzene (604 mg, 2.14 mmol), $Pd(PPh_3)_2Cl_2$ (151 mg, 0.215 mmol), and CuI (38 mg, 0.20 mmol) were added, and the flask was degassed under reduced pressure and filled with argon. A dry DMF (21 mL) was added, and the atmosphere in the flask was replaced with argon again. Then distilled Et_3N (0.75 mL, 5.4 mmol) and (triisopropylsilyl)acetylene (0.50 mL, 2.2 mmol) were added via syringes from the three-way stopcock with a stream of nitrogen. After stirred at room

temperature for 6 h, the mixture was diluted with AcOEt, washed with 1 M hydrochloric acid and brine, and dried over anhydrous $MgSO_4$. Purification with silica gel column chromatography (hexane) gave a colorless liquid (719 mg) which was a mixture of **14** (yield: 92%), 1-bromo-4-iodobenzene (recovery: 1%), (triisopropylsilyl)acetylene (recovery: 1%), and its dimer (yield: 3%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 9.0 Hz, 2H), 7.33 (d, J = 9.0 Hz, 2H), 1.13–1.12 (m, 21H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 133.4, 131.4, 122.5, 122.4, 105.8, 92.0, 18.6, 11.2; IR (neat) 3081, 3054, 2891, 2864, 2158, 1585, 1485, 1384, 1071, 824 cm^{-1}.

*(S)-N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)-4-((triisopropylsilyl)ethynyl)aniline (**16**)*.[31] $Pd(P^tBu_3)_2$ (0.325 g, 0.636 mmol), ^{t}BuONa (3.00 g, 31.2 mmol) and **15**[22] (3.70 g, 20.9 mmol) were placed in a round bottom flask with a three-way stopcock, and the flask was degassed under reduced pressure and filled with argon. A degassed solution of **14** containing a small amount of 1-bromo-4-iodobenzene, (triisopropylsilyl)acetylene, and its dimer (7.06 g, **14** = 18.6 mmol) in dry toluene (64 mL) was added to the flask via syringes from the three-way stopcock with a stream of nitrogen. The flask was cooled to 0 °C, degassed under reduced pressure, and filled with argon. Then, the mixture was stirred at 90 °C in an oil bath for 2 h, cooled to room temperature, diluted with CH_2Cl_2, and filtered with Celite. The filtrate was washed with 1 M hydrochloric acid and water, and dried over anhydrous Na_2SO_4. The crude product was purified with silica gel column chromatography (AcOEt/hexane = 1/2) to give **16** as a light brown syrup (6.93 g, 86%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, J = 9.0 Hz, 2H), 6.51 (d, J = 9.0 Hz, 2H), 4.10 (br m, 1H), 3.68–3.59 (m, 7H), 3.55–3.47 (m, 4H), 3.38 (s, 3H), 1.21 (d, J = 7.0 Hz, 3H), 1.11–1.10 (m, 21H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.5, 133.3, 112.7, 111.4, 108.3, 87.0, 74.3, 71.9, 70.7, 70.6, 70.5, 59.0, 48.1, 18.7, 17.7, 11.4; IR (neat) 3360, 2941, 2865, 2361, 2145, 1608, 1518, 1365, 1104, 1017 cm^{-1}.

*(S)-4-Ethynyl-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)aniline (**17**)*.[32] A 1.0 M solution of tetrabutylammonium fluoride in THF (18 mL, 18 mmol) was added to a solution of **16** (6.50 g, 15.0 mmol) in dry THF (14.8 mL) stirred at 0 °C, and the mixture was stirred at 0 °C for 2.5 h. A saturated aqueous solution of ammonium chloride and water was added successively, and the mixture was extracted with Et_2O. The organic layer was washed with brine and dried over anhydrous Na_2SO_4. Purification with silica gel column chromatography (AcOEt/hexane = 1/1) gave **17** as a light brown syrup (3.96 g, 95%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, J = 9.0 Hz, 2H), 6.52 (d, J = 9.0 Hz, 2H), 4.15 (br m, 1H), 3.69–3.61 (m, 7H), 3.55–3.47 (m, 4H), 3.38 (s,

3H), 2.94 (s, 1H), 1.22 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 147.9, 133.4, 112.7, 109.6, 84.7, 74.5, 74.3, 71.9, 70.7, 70.53, 70.50, 59.0, 48.0, 17.7; IR (neat) 3490, 2873, 2097, 1351, 1328, 1259, 1199, 1174, 1028, 825 cm^{-1}.

*Phenyl 4-iodobenzoate (**18**)*. A mixture of 4-iodobenzoic acid (7.00 g, 28.2 mmol) in thionyl chloride (17 mL, 23 mmol) was refluxed in an oil bath for 12 h under an argon atmosphere, and then concentrated under reduced pressure. To the residue was added dry CH_2Cl_2 (96 mL), a solution of phenol (2.64 g, 28.1 mmol) in dry CH_2Cl_2 (9 mL), and Et_3N (4.40 mL, 31.7 mmol), successively, and the mixture was stirred at room temperature for 3 h. After addition of water, the mixture was extracted with CH_2Cl_2. The organic layer was washed with 1 M hydrochloric acid, water, and a saturated aqueous solution of $NaHCO_3$, and dried over anhydrous $MgSO_4$. Recrystallization of the crude product from AcOEt-hexane gave **18** as colorless plates (7.46 g, 82%); mp 131.6−135.1 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 2H), 7.88 (d, J = 8.5 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 2H); IR (KBr) 1732, 1582, 1281, 1203, 1179, 1075, 1054, 1001, 750, 702, 510 cm^{-1}.

*Phenyl (S)-4-((4-((1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)amino)phenyl)ethynyl)benzoate (**1**)*.[33] In a round bottom flask equipped with a three-way stopcock, **18** (4.29 g, 13.2 mmol), $Pd(PPh_3)_4$ (0.705 g, 0.610 mmol), and CuI (0.232 g, 1.22 mmol) were placed, and the flask was degassed under reduced pressure and filled with argon. Distilled Et_3N (126 mL, 908 mmol) and a solution of **17** (3.49 g, 12.6 mmol, dried azeotropically twice with toluene) in dry THF (126 mL) were added successively via syringes from the three-way stopcock with a stream of nitrogen, and the atmosphere in the flask was replaced with argon again. After stirred at room temperature for 2.5 h, a saturated aqueous solution of ammonium chloride was added, and the mixture was extracted with AcOEt. The organic layer was washed water and brine, and dried over anhydrous Na_2SO_4. Purification with silica gel column chromatography (AcOEt/hexane = 1/1) afforded **1** as a yellow syrup (5.58 g, 94%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.3 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.27 (t, J = 7.7 Hz, 1H), 7.22 (d, J = 7.7 Hz, 2H), 6.58 (d, J = 8.6 Hz, 2H), 4.24 (d, J = 7.7 Hz, 1H), 3.74–3.61 (m, 7H), 3.57–3.51 (m, 4H), 3.39 (s, 3H), 1.25 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 164.8, 150.9, 148.1, 133.2, 131.1, 130.0, 129.7, 129.5, 127.9, 125.9, 121.7, 112.8, 110.0, 94.7, 86.8, 74.3, 71.9, 70.7, 70.6, 70.5, 59.0, 48.1, 17.7; IR (neat) 2874, 2206, 1734, 1370, 1332, 1263, 1198, 1072, 824 cm^{-1}.

Polymerization of 1.

Polymerization with LiHMDS. All glass apparatus was dried prior to use. Addition of reagents into the reaction flask was conducted via a syringe from the three-way stopcock with a stream of nitrogen. A round bottom flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. A 1 M solution of LiHMDS in THF (0.40 mL, 0.40 mmol) was placed in the flask, and the atmosphere in the flask was replaced with argon. A solution of the monomer **1** (187 mg, 0.396 mmol, dried at 50 °C under reduced pressure overnight prior to use) and phenyl 4-methylbenzoate[34] (2.3 mg, 0.011 mmol) in dry THF (0.5 mL) was added at room temperature, and the mixture was stirred at room temperature for 8 days. An aqueous saturated solution of ammonium chloride was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give the crude product (111 mg) as a deep yellow syrup. Separation of the crude product by preparative HPLC afforded the cyclic trimer; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26–7.25 (m, 6H), 7.20 (d, J = 8.3 Hz, 6H), 7.14 (d, J = 8.3 Hz, 6H), 7.11–7.05 (br m, 6H), 5.12 (sext, J = 7.2 Hz, 3H), 3.75-3.47 (m, 30H), 3.39 (s, 9H), 1.18 (d, J = 7.2 Hz, 9H); MALDI-TOF MS (dithranol) calcd for $C_{69}H_{75}N_3O_{12}$ $[M + Na]^+$ 1160.53, found 1160.40.

Polymerization with KHMDS. All glass apparatus was dried prior to use. Addition of reagents into the reaction flask was conducted via a syringe from the three-way stopcock with a stream of nitrogen. A round bottom flask equipped with a three-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. To a 0.5 M solution of KHMDS in toluene (0.80 mL, 0.40 mmol) in the flask was added a solution of 18-crown-6 (520 mg, 1.97 mmol, dried at 50 °C under reduced pressure overnight prior to use) in dry THF (0.25 mL), and the solution was stirred at 50 °C in an oil bath. A solution of the monomer **1** (191 mg, 0.402 mmol, dried azeotropically twice with toluene prior to use) and phenyl 4-methylbenzoate (2.7 mg, 0.013 mmol) in dry THF (0.25 mL) was added, and the mixture was stirred at 50 °C in an oil bath for 26 h. After the mixture was cooled to room temperature, an aqueous saturated solution of ammonium chloride was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give the crude product as a light brown syrup (382 mg, M_n = 9210, M_w/M_n = 6.18). Purification of the crude product by silica gel column chromatography (MeOH), followed by preparative HPLC afforded the product (12 mg, M_n = 6230, M_w/M_n = 1.40).

Polymerization with Et_3SiH, CsF, and 18-crown-6. All glass apparatus was dried

prior to use. Addition of reagents into the reaction flask was conducted via a syringe from the three-way stopcock with a stream of nitrogen. Cesium fluoride (91.0 mg, 0.599 mmol) was placed in a round bottom flask equipped with a three-way stopcock, and dried at 250 °C under reduced pressure. Then, the flask was cooled to room temperature under an argon atmosphere. A solution of **1** (189 mg, 0.399 mmol, dried azeotropically twice with toluene prior to use), triethylsilane (67.5 mg, 0.580 mmol), and 18-crown-6 (320 mg, 1.21 mmol, dried at 50 °C under reduced pressure overnight prior to use) in dry THF (0.2 mL) was added to the flask at room temperature, and the mixture was stirred at 50 °C in an oil bath for 36 h. After the mixture was cooled to room temperature, an aqueous saturated solution of ammonium chloride was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give the crude product (M_n = 2490, M_w/M_n = 1.24).

Synthesis of Monomer 2. The monomer **2** was synthesized as shown in Scheme S2.

*(S)-4-Iodo-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)-N-(4-((triisopropylsilyl) ethynyl)phenyl)benzamide (**19**)*. To a round bottom flask was added a solution of 4-iodobenzoyl chloride (4.62 g, 20.4 mmol) in dry CH_2Cl_2 (17 mL), Et_3N (1.4 mL, 10 mmol), and a solution of **16** (3.50 g, 8.08 mmol) in dry CH_2Cl_2 (16 mL), and the mixture was stirred at room temperature for 17 h under an argon atmosphere. After addition of water, the mixture was extracted with CH_2Cl_2, and the organic layer was washed with 1 M hydrochloric acid, water, and a saturated aqueous solution of $NaHCO_3$, and dried over anhydrous Na_2SO_4. Silica gel column chromatography (AcOEt/CH_2Cl_2 = 6/1) gave **19** as a brown syrup (4.63 g, 94%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 6.9 Hz, 2H), 7.33 (d, J = 7.7 Hz, 2H), 7.06 (d, J = 7.2 Hz, 2H), 7.03–6.89 (m, 2H), 5.05 (br m, 1H), 3.71–3.62 (m, 5H), 3.59–3.53 (m, 3H), 3.47 (br m, 2H), 3.37 (s, 3H), 1.14–1.08 (m, 24H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.1, 139.7, 136.9, 136.4, 132.6, 130.2, 130.0, 122.8, 106.0, 95.7, 92.0, 72.0, 71.8, 70.6, 70.5, 70.2, 59.0, 52.2, 18.6, 15.3, 11.2; IR (neat) 2942, 2864, 2155, 1646, 1221, 1118, 1040, 882, 823, 501 cm^{-1}. HRMS (ESI$^+$) m/z calcd for $C_{32}H_{47}INO_4Si$ $[M + H]^+$ 664.2314, found 664.2308.

*(S)-N-(4-Ethynylphenyl)-4-iodo-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)b enzamide (**2**)*.[32] In a round bottom flask, **19** (4.30 g, 6.48 mmol) was dissolved in dry THF (6.2 mL), and the solution was stirred at 0 °C. A 1.0 M solution of tetrabutylammonium fluoride in THF (8.4 mL, 8.4 mmol) was added, and the mixture

was stirred at 0 °C for 24 h under an argon atmosphere. After addition of a saturated aqueous solution of ammonium chloride and water, the mixture was extracted with Et_2O, and the organic layer was washed with brine and dried over anhydrous Na_2SO_4. The crude product was purified with silica gel column chromatography (AcOEt/hexane = 1/1), which afforded **2** as a pale yellow syrup (2.97 g, 90%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 7.7 Hz, 2H), 7.04–6.84 (br m, 2H), 5.03 (br m, 1H), 3.71–3.61 (m, 5H), 3.59–3.42 (m, 5H), 3.37 (s, 3H), 3.09 (s, 1H), 1.14 (d, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.1, 140.3, 136.9, 136.3, 132.7, 130.3, 129.9, 121.4, 95.7, 82.6, 78.4, 71.9, 71.8, 70.6, 70.5, 70.2, 59.0, 52.4, 15.4; IR (neat) 3287, 2976, 2875, 1645, 1456, 1199, 1076, 1107, 1058, 822 cm^{-1}.

Polymerization of Monomer 2.[25] The monomer **2** (153 mg, 0.302 mmol) was placed in a round bottom flask and dried azeotropically twice with toluene. $Pd(PPh_3)_2Cl_2$ (8.9 mg, 0.013 mmol) was added, and the flask was degassed under reduced pressure and filled with argon. Then Et_3N (0.14 mL, 1.0 mmol) was added via a syringe from the three-way stopcock with a stream of nitrogen, and the mixture was stirred at 70 °C in an oil bath for 4 h and then cooled to room temperature. Water was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 1 M hydrochloric acid and waster, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude product (M_n = 9380, M_w/M_n = 2.05). Purification of the crude product by reprecipitation (CH_2Cl_2-hexane) followed by preparative HPLC gave the polymer ***α*-DPA** (51.6 mg, M_n = 14900, M_w/M_n = 1.58); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–6.97 (m, 8H), 5.04 (br m, 1H), 3.72–3.41 (m, 10H), 3.35 (s, 3H), 1.14 (d, J = 6.3 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.2, 140.0, 136.8, 132.0, 130.9, 130.3, 128.2, 123.7, 122.1, 89.8, 89.6, 71.9, 71.8, 70.6, 70.5, 70.1, 59.0, 52.3, 15.4.

Synthesis of Monomer 3. The monomer **3** was synthesized as shown in Scheme S3.

4-((Triisopropylsilyl)ethynyl)aniline (**20**).[33] In a round bottom flask equipped with a three-way stopcock, 4-iodoaniline (110 mg, 0.502 mmol), $Pd(PPh_3)_4$ (29.8 mg, 0.0258 mmol), and CuI (10.1 mg, 0.0530 mmol) were placed, and the flask was degassed under reduced pressure and filled with argon. Dry THF (5.0 mL) was added via a syringe from the three-way stopcock with a stream of nitrogen, and the atmosphere in the flask was replaced with argon again. Then (triisopropylsilyl)acetylene (0.13 mL, 0.58 mmol) and distilled Et_3N (5.0 mL, 36 mmol) were added via syringes from the three-way stopcock with a stream of nitrogen, and the atmosphere in the flask was replaced with argon again.

After stirred at room temperature for 3 h, AcOEt was added, and the mixture was filtered with Celite. The filtrate was washed with 1 M hydrochloric acid, water, and brine, and dried over anhydrous $MgSO_4$. Purification with silica gel column chromatography (AcOEt/hexane = 1/7) afforded **20** as a brown syrup (122 mg, 89%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.3 Hz, 2H), 6.58 (d, *J* = 8.3 Hz, 2H), 3.78 (br s, 2H), 1.13–1.11 (m, 21H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 146.6, 133.4, 114.5, 113.1, 107.9, 87.5, 18.7, 11.4; IR (neat) 3480, 2148, 1886, 1621, 1606, 1512, 1463, 1230, 1174, 1126 cm^{-1}.

*2-Nitro-N-(4-((triisopropylsilyl)ethynyl)phenyl)benzenesulfonamide (**21**).*[35] A mixture of **20** (12.0 g, 42.8 mmol) in pyridine (125 mL, 1.55 mol) was stirred at 0 °C, and 2-nitrobenzenesulfonyl chloride (12.7 g, 57.2 mmol) was added. The mixture was stirred at room temperature for 1 day, and 1 M hydrochloric acid was added. The mixture was extracted with CH_2Cl_2, and the organic layer was washed with water and dried over anhydrous Na_2SO_4. The crude product was purified successively with silica gel column chromatography (CH_2Cl_2/hexane = 1/1) and recrystallization from CH_2Cl_2-hexane to give **21** as pale yellow needles (16.1 g, 83%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86–7.84 (m, 2H), 7.70 (dt, *J* = 1.4 and 7.9 Hz, 1H), 7.58 (dt, *J* = 1.4 and 7.9 Hz, 1H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.31 (br s, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 1.12–1.04 (m, 21H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.2, 135.3, 134.1, 133.2, 132.7, 132.0, 131.9, 125.4, 122.5, 121.7, 105.8, 91.7, 18.6, 11.2.

*(S)-N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)-2-nitro-N-(4-((triisopropylsilyl) ethynyl)phenyl)benzenesulfonamide (**22**).*[35] To a mixture of **21** (15.0 g, 34.0 mmol), (*S*)-2-(methoxyethoxyethoxy)propanol[21,36] (3.99 g, 22.4 mmol), and triphenylphosphine (9.49 g, 36.2 mmol) in dry THF (150 mL) stirred at 0 °C was added a 2.2 M solution of diethyl azodicarboxylate in toluene (17 mL, 37 mmol). The mixture was stirred at room temperature for 1 day and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (AcOEt/hexane = 1/2) to afford **22** as a yellow syrup (13.8 g, 99%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64–7.58 (m, 2H), 7.52 (dd, *J* = 1.4 and 7.9 Hz, 1H), 7.47 (ddd, *J* = 1.4, 6.8, and 8.2 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 3.85 (dd, *J* = 7.2 and 14.4 Hz, 1H), 3.76 (dd, *J* = 4.8 and 14.4 Hz, 1H), 3.62–3.57 (m, 3H), 3.54–3.49 (m, 5H), 3.43–3.40 (m, 1H), 3.36 (s, 3H), 1.17 (d, *J* = 6.2 Hz, 3H), 1.12–1.10 (m, 21H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 147.9, 138.8, 133.6, 132.9, 132.1, 131.9, 131.1, 129.0, 123.8, 123.4, 105.9, 92.4, 74.5, 71.9, 70.6, 70.5, 68.2, 59.0, 56.9, 18.6, 17.3, 11.2.

*(S)-N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)-4-((triisopropylsilyl)ethynyl)aniline (**23**).*[35] Thiophenol (113 mg, 1.03 mmol) and Cs_2CO_3 (1.44 g, 4.42 mmol) were added to a mixture of **22** (501 mg, 0.810 mmol) in acetonitrile (8.5 mL), and the mixture was stirred at 70 °C in an oil bath for 4 h, poured into water, and extracted with CH_2Cl_2. The organic layer was washed with water and dried over anhydrous $MgSO_4$. Silica gel column chromatography (AcOEt/hexane = 1/3) gave **23** as a yellow syrup (311 mg, 89%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.51 (d, *J* = 8.6 Hz, 2H), 4.51 (br m, 1H), 3.76–3.68 (m, 2H), 3.67–3.61 (m, 4H), 3.59–3.53 (m, 3H), 3.38 (s, 3H), 3.21 (br d, *J* = 12.4 Hz 1H), 3.03 (dd, *J* = 7.9 and 12.7 Hz, 1H) 1.21 (d, *J* = 6.2 Hz, 3H), 1.12-1.10 (m, 21H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.5, 133.3, 112.4, 111.4, 108.3, 87.0, 74.2, 71.9, 70.7, 70.5, 68.0, 59.0, 48.8, 18.7, 17.8, 11.4.

*(S)-4-Iodo-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)-N-(4-((triisopropylsilyl)ethynyl)phenyl)benzamide (**24**).* To a round bottom flask was added a solution of 4-iodobenzoyl chloride (221 mg, 0.829 mmol) in dry CH_2Cl_2 (1.2 mL), Et_3N (0.12 mL, 0.87 mmol), and a solution of **23** (302 mg, 0.696 mmol) in dry CH_2Cl_2 (1.1 mL), and the mixture was stirred at room temperature for 2.5 h under an argon atmosphere. After addition of water, the mixture was extracted with CH_2Cl_2, and the organic layer was washed with 1 M hydrochloric acid, water, and a saturated aqueous solution of $NaHCO_3$, and dried over anhydrous Na_2SO_4. Silica gel column chromatography (AcOEt/hexane = 1/2) gave **24** as a yellow syrup (405 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 7.05 (d, *J* = 8.6 Hz, 2H), 4.05 (d, *J* = 11.7 Hz, 1H), 3.90 (br m, 1H), 3.71 (ddd, *J* = 3.8, 5.5, and 10.3 Hz, 1H), 3.64 (dd, *J* = 8.6 and 14.1 Hz, 1H), 3.62–3.54 (m, 4H), 3.52–3.47 (m, 3H), 3.35 (s, 3H), 1.18 (d, *J* = 6.2 Hz, 3H), 1.12–1.09 (m, 21H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.6, 144.3, 137.1, 135.5, 132.7, 130.5, 127.4, 121.6, 106.1, 96.5, 91.5, 73.5, 71.9, 70.8, 70.5, 68.2, 59.0, 56.6, 18.6, 17.5, 11.2. HRMS (ESI$^+$) m/z calcd for $C_{32}H_{47}INO_4Si$ $[M + H]^+$ 664.2314, found 664.2305.

*(S)-N-(4-Ethynylphenyl)-4-iodo-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)benzamide (**3**).*[32] In a round bottom flask, **24** (5.00 g, 7.53 mmol) was dissolved in dry THF (7.1 mL), and the solution was stirred at 0 °C. A 1.0 M solution of tetrabutylammonium fluoride in THF (9.8 mL, 9.8 mmol) was added, and the mixture was stirred at room temperature for 10 h under an argon atmosphere. After addition of a saturated aqueous solution of ammonium chloride and water, the mixture was extracted with Et_2O, and the organic layer was washed with brine and dried over anhydrous

Na_2SO_4. The crude product was purified with silica gel column chromatography (AcOEt/hexane = 2/1), which afforded **3** as a yellow syrup (3.38 g, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.12 (d, J = 8.6 Hz, 2H), 7.03 (d, J = 8.6 Hz, 2H), 4.13–4.04 (m, 1H), 3.96–3.89 (m, 1H), 3.73–3.70 (m, 1H), 3.64–3.53 (m, 5H), 3.52–3.47 (m, 3H), 3.35 (s, 3H), 3.06 (s, 1H), 1.19 (d, J = 6.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.6, 144.8, 137.0, 135.4, 132.8, 130.4, 127.5, 120.1, 96.5, 82.8, 77.9, 73.4, 71.9, 70.7, 70.4, 68.2, 59.0, 56.6, 17.4.

Polymerization of Monomer 3.[25] The monomer **3** (152 mg, 0.300 mmol) and $Pd(PPh_3)_2Cl_2$ (10.4 mg, 0.0148 mmol) were placed in a round bottom flask, and the flask was degassed under reduced pressure and filled with argon. Dry THF (0.4 mL) and Et_3N (0.13 mL, 0.94 mmol) were added successively via syringes from the three-way stopcock with a stream of nitrogen, and the mixture was stirred at 50 °C in an oil bath for 1 h and then cooled to room temperature. Water was added, and the mixture was extracted with CH_2Cl_2. The organic layer was washed with 1 M hydrochloric acid and waster, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give the crude product (M_n = 6680, M_w/M_n = 1.87). Purification of the crude product by preparative HPLC gave the polymer ***β*-DPA** (34.3 mg, M_n = 14200, M_w/M_n = 1.31); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34–7.27 (m, 6H), 7.14 (d, J = 8.3 Hz, 2H), 4.16–4.03 (m, 1H), 3.94 (m, 1H), 3.74–3.46 (m, 9H), 3.35–3.27 (m, 3H), 1.20 (d, J = 6.2 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.7, 144.6, 135.7, 132.2, 131.0, 128.8, 127.6, 124.5, 120.8, 90.2, 89.4, 73.5, 71.9, 70.8, 70.5, 68.3, 59.0, 56.5, 17.5.

Synthesis of 4. The compound **4** was synthesized as shown in Scheme S4.

*(S)-4-((4-((1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)amino)phenyl)ethynyl)-N, N-dimethylbenzamide (**25**).*[22,37] Dimethylamine hydrochloride (173 mg, 2.12 mmol) and dry toluene (3.3 mL) were placed in a round bottom flask. The flask was degassed under reduced pressure and filled with argon, and the mixture was stirred at 0 °C. A 2 M solution of trimethylaluminum in toluene (1.1 mL, 2.2 mmol) was added dropwise, and the mixture was stirred at room temperature for 1 h. Then, a solution of **1** (75.4 mg, 0.159 mmol) in dry toluene (0.5 mL) was added, and the mixture was stirred at room temperature for 40.5 h. After addition of 1 M hydrochloric acid, the mixture was neutralized with a saturated aqueous solution of $NaHCO_3$ and extracted with AcOEt. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The crude product was purified with silica gel column chromatography (AcOEt) to give **25** as a yellow solid (380 mg, 84%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.9 Hz, 2H), 6.56 (d, J = 8.9 Hz, 2H), 4.32–4.10

(br m, 1H), 3.72–3.60 (m, 7H), 3.56–3.49 (m, 4H), 3.39 (s, 3H), 3.11 (br s, 3H), 2.99 (br s, 3H), 1.24 (d, J = 6.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 171.2, 147.8, 134.9, 133.0, 131.1, 127.1, 125.6, 112.8, 110.4, 92.1, 86.6, 74.3, 71.9, 70.7, 70.6, 70.5, 59.0, 48.1, 39.5, 35.4, 17.7; IR (KBr) 3449, 2925, 2878, 2204, 1636, 1598, 1389, 1136, 1109, 824 cm^{-1}.

*(S)-4-((4-(N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)acetamido)phenyl)ethynyl)-N,N-dimethylbenzamide (**4**).* The compound **25** (39.8 mg, 0.0938 mmol) and dry pyridine (19.1 mg, 0.241 mmol) were dissolved in dry CH_2Cl_2 (0.24 mL) in a round bottom flask equipped with a three-way stopcock, and the flask was degassed under reduced pressure and filled with argon. The mixture was stirred at 0 °C, and a solution of acetyl chloride (18 mg, 0.23 mmol) in dry CH_2Cl_2 (2.2 mL) was added dropwise via a syringe from the three-way stopcock with a stream of nitrogen. After the mixture was stirred at room temperature for 1.5 h, water was added, and mixture was extracted with CH_2Cl_2. The organic layer was washed with 1 M hydrochloric acid and a saturated aqueous solution of $NaHCO_3$ and dried over anhydrous $MgSO_4$. Silica gel column chromatography (MeOH/AcOEt = 1/10) of the crude product afforded **4** as a yellow syrup (29.5 mg, 67%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.57–7.55 (m, 4H), 7.41 (d, J = 8.3 Hz, 2H), 7.23 (br m, 2H), 5.12–5.05 (m, 1H), 3.68–3.60 (m, 5H), 3.56–3.49 (m, 3H), 3.38 (s, 3H), 3.33 (dd, J = 4.9 and 10.6 Hz, 1H), 3.27–3.23 (m, 1H), 3.11 (br s, 3H), 2.99 (br s, 3H), 1.76 (s, 3H), 1.02 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 170.8, 170.4, 139.3, 136.1, 132.5, 131.5, 130.4, 127.2, 124.1, 123.1, 89.9, 89.5, 71.9, 71.8, 70.51, 70.46, 70.0, 59.0, 49.4, 39.5, 35.3, 23.5, 15.5; IR (neat) 2961, 2925, 2873, 2218, 1656, 1637, 1451, 1327, 1102, 801 cm^{-1}.

Synthesis of 5. The compound **5** was synthesized as shown in Scheme S5.

*Phenyl (S)-4-((4-(N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)acetamido)phenyl)ethynyl)benzoate (**26**)*. The compound **1** (449 mg, 0.948 mmol) and dry pyridine (0.15 mL, 1.9 mmol) were dissolved in dry CH_2Cl_2 (2.8 mL) in a round bottom flask equipped with a three-way stopcock, and the flask was degassed under reduced pressure and filled with argon. The mixture was stirred at 0 °C, and a solution of acetyl chloride (153 mg, 1.95 mmol) in dry CH_2Cl_2 (1.9 mL) was added dropwise via a syringe from the three-way stopcock with a stream of nitrogen. After the mixture was stirred at room temperature for 14 h, water was added, and mixture was extracted with CH_2Cl_2. The organic layer was washed with 1 M hydrochloric acid and a saturated aqueous solution of $NaHCO_3$ and dried over anhydrous $MgSO_4$. Silica gel column chromatography

(AcOEt) of the crude product afforded **26** as a brown syrup (436 mg, 89%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.9 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.40–7.07 (br m, 2H), 5.10 (sext, *J* = 6.9 Hz, 1H), 3.68–3.64 (m, 5H), 3.57–3.51 (m, 3H), 3.39 (s, 3H), 3.35 (br dd, *J* = 4.8 and 10.3 Hz, 1H), 3.27 (br t, *J* = 9.6 Hz, 1H), 1.78 (s, 3H), 1.04 (d, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.3, 164.6, 150.8, 139.7, 132.7, 131.7, 130.6, 130.1, 129.5, 129.1, 128.2, 126.0, 122.8, 121.6, 91.6, 89.7, 72.0, 71.8, 70.6, 70.5, 70.0, 59.0, 49.5, 23.6, 15.5; IR (neat) 2976, 2928, 2875, 2218, 1736, 1655, 1599, 1016, 763, 690 cm^{-1}. HRMS (ESI$^+$) m/z calcd for $C_{31}H_{34}NO_6$ $[M + H]^+$ 516.2381, found 516.2374.

*(S)-4-((4-(N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)acetamido)phenyl)ethynyl)benzoic acid (**27**).* A mixture of **26** (193 mg, 0.375 mmol) and ground NaOH (88.8 mg, 2.22 mmol) in dry THF (1.5 mL) in a round bottom flask was stirred at room temperature for 11 h. The mixture was acidified by the addition of 2 M hydrochloric acid and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$. Purification of the crude product by silica gel column chromatography (MeOH/AcOEt = 3/10) gave **27** as a colorless solid (164 mg, quant); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (br d, *J* = 8.0 Hz, 2H), 7.51 (br d, *J* = 8.9 Hz, 2H), 7.48 (br d, *J* = 8.0 Hz, 2H), 7.12 (br m, 2H), 5.11–5.05 (m, 1H), 3.70–3.60 (m, 5H), 3.57–3.48 (m, 3H), 3.34 (s, 3H), 3.30–3.20 (m, 2H), 1.69 (s, 3H), 0.94 (br d, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 172.9, 170.7, 138.9, 136.2, 132.5, 130.9, 130.3, 129.7, 124.8, 123.3, 90.7, 89.5, 71.9, 71.7, 70.2, 69.8, 58.9, 49.2, 23.4, 15.4; IR (KBr) 3423, 2878, 2217, 1701, 1655, 1499, 1458, 1383, 1276, 789 cm^{-1}. HRMS (ESI$^-$) m/z calcd for $C_{25}H_{28}NO_6$ $[M - H]^-$ 438.1922, found 438.1926.

*The dimer **5***. A mixture of **27** (65.7 mg, 0.149 mmol) in thionyl chloride (0.8 mL, 11 mmol) was stirred at room temperature for 1 day, and then concentrated under reduced pressure. Dry CH_2Cl_2 (0.22 mL) was added to the residue, and the mixture was stirred at 0 °C. Then, a solution of **25** (70.6 mg, 0.166 mmol) and dry pyridine (61.0 mg, 0.771 mmol) in dry CH_2Cl_2 (0.54 mL) was added and the mixture was stirred at room temperature for 2.5 h. After addition of water, the mixture was extracted with CH_2Cl_2. The organic layer was washed with 1 M hydrochloric acid and a saturated aqueous solution of $NaHCO_3$, and dried over anhydrous $MgSO_4$. Silica gel column chromatography (MeOH/AcOEt = 1/9) of the crude product afforded **5** as a yellow solid (35 mg, 28%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52–7.50 (m, 4H), 7.40–7.38 (m, 4H), 7.35–7.03 (br m, 8H), 5.11–5.04 (m, 2H), 3.76–3.46 (m, 18H), 3.39 (s, 3H), 3.37 (s, 3H),

3.32 (br dd, J = 5.2 and 10.3 Hz, 1H), 3.26–3.22 (br m, 1H), 3.11 (br s, 3H), 2.98 (br s, 3H), 1.75 (s, 3H), 1.19 (br d, J = 6.9 Hz, 3H), 1.01 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (126 MHz, THF-d_8, 60 °C) δ 170.2, 169.7, 169.0, 142.2, 141.6, 138.6, 138.0, 132.8, 132.5, 131.7, 131.5, 131.4, 131.3, 129.3, 128.1, 124.8, 124.4, 123.6, 122.7, 90.4, 90.27, 90.26, 90.2, 72.91, 72.86, 72.85, 72.82, 71.4, 71.3, 71.24, 71.20, 71.1, 70.9, 58.75, 58.70, 54.0, 51.2, 30.4, 25.6, 23.1, 15.7, 15.5; IR (KBr) 2929, 2873, 2216, 1655, 1638, 1398, 1341, 1262, 1104, 1019 cm^{-1}.

Synthesis of 6a and 7a. The compounds **6a** and **7a** were synthesized as shown in Scheme S6.

*Methyl 4-((trimethylsilyl)ethynyl)benzoate (**28**).*[23c] Methyl *p*-iodobenzoate (205.4 mg, 0.78 mmol), $Pd(PPh_3)_2Cl_2$ (26.8 mg, 5 mol%), triphenylphosphine (20.3 mg, 10 mol%), CuI (15.7 mg, 10 mol%), and DMF (8 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature was added Et_3N (0.3 mL, 2.8 equiv) and (trimethylsilyl)acetylene (0.14 mL, 1.3 equiv), and the mixture was stirred at room temperature for 3 h. Then saturated aqueous ammonium chloride was added, and the mixture was extracted with Et_2O. The organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (CH_2Cl_2/hexane = 1/2) to give **28** as a pale yellow solid (200.4 mg, quant.); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 2H), 7.52 (d, J = 8.2 Hz, 2H), 3.91 (s, 3H), 0.26 (s, 9H).

*Methyl 4-ethynylbenzoate (**29**).*[23c] A 1.0 M solution of tetrabutylammonium fluoride in THF (1 mL, 1 mmol) was added to a stirred solution of **28** (182.1 mg, 0.78 mmol) in THF (7 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with AcOEt, washed with water three times and brine, and dried over anhydrous Na_2SO_4. Purification with silica gel column chromatography (AcOEt/hexane = 1/2) afforded **29** as a colorless solid (96.4 mg, 78%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 2H), 7.55 (d, J = 8.2 Hz, 2H), 3.92 (s, 3H), 3.23 (s, 1H).

*Methyl 4-((4-aminophenyl)ethynyl)benzoate (**30**).* Sonogashira coupling reaction of **29** with *p*-iodoaniline was carried out in a manner similar to the synthesis of **28** by addition of Et_3N (0.23 mL, 2.8 equiv) and *p*-iodoaniline (171.3 mg, 1.3 equiv) to a degassed stirred mixture of **29** (96.4 mg, 0.60 mmol), $Pd(PPh_3)_2Cl_2$ (20.9 mg, 5 mol%), triphenylphosphine (15.6 mg, 10 mol%), and CuI (12.0 mg, 10 mol%) in DMF (7 mL) at room temperature, followed by stirring at that temperature for 3 h. Then saturated aqueous ammonium chloride was added, and the mixture was extracted with Et_2O. The

organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (AcOEt/hexane = 1/4) to give **30** as a yellow solid (107.8 mg, 71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 3.92 (s, 3H), 3.87 (br, 2H).

*Methyl 4-((4-benzamidophenyl)ethynyl)benzoate (**31**).* Triethylamine (0.07 mL, 1.2 equiv) was added to a solution of **30** (107.8 mg, 0.43 mmol) in dichloromethane (5 mL), and the mixture was stirred at 0 °C. Benzoyl chloride (0.05 mL, 1.0 equiv) was added to the cold amine solution and the mixture was stirred at room temperature for 4 h. The white precipitates were collected and dried to give **31** (132.3 mg, 87%) as a white powder; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.88 (br, 3H), 7.68 (m, 2H), 7.59 (m, 5H), 7.53 (m, 2H), 3.93 (s, 3H).

*4-((4-Benzamidophenyl)ethynyl)benzoic acid (**32**).* **31** (107.6 mg, 0.30 mmol) and $LiOH{\cdot}H_2O$ (23.5 mg, 7 equiv) were dissolved in a mixture of THF (10 mL), methanol (4 mL), and water (4 mL). The mixture was stirred for 3 h at room temperature, acidified with 2 M HCl, and extracted with AcOEt. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give **32** (85.0 mg, 82%) as a white solid; ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.48 (s, 3H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 7.3 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.62-7.53 (m, 5H). ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 166.8, 165.9, 140.2, 134.8, 132.3, 131.9, 131.5, 129.7, 128.6, 127.8, 126.9, 120.2, 116.5, 92.4, 88.2. HRMS (ESI$^+$) m/z calcd for $C_{22}H_{16}NO_3$ $[M + H]^+$ 342.1125, found 342.1121.

*4-((4-Benzamidophenyl)ethynyl)-N-phenylbenzamide (**33**).* 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (97.5 mg, 2.0 equiv) and *N,N*-dimethyl-4-aminopyridine (61.9 mg, 2.0 equiv) were added to a solution of **32** (85.0 mg, 0.25 mmol) and aniline (0.03 mL, 1.3 equiv) in DMF (3.5 mL). The resulting mixture was stirred for 18 h at room temperature. After removal of the solvent *in vacuo*, 2 M HCl was added and the white precipitates were collected and dried to give **33** (96.8 mg, 93%); ^{1}H NMR (600 MHz, DMSO-d_6) δ 10.48 (s, 1H), 10.34 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.63–7.58 (m, 3H), 7.55 (t, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6) δ 165.8, 164.7, 140.0, 139.0, 134.7, 134.4, 132.1, 131.7, 131.2, 128.6, 128.4, 128.0, 127.7, 125.6, 123.8, 120.4, 120.1, 116.6, 91.8, 88.2. HRMS (ESI$^+$) m/z calcd for $C_{28}H_{21}N_2O_2$ $[M + H]^+$ 417.1598, found 417.1592.

*The monomer **6a**.* A solution of **33** (120.7 mg, 0.29 mmol) in DMF (3.5 mL) was

added at 0 °C to a suspension of NaH (60 %, 38.4 mg, 3.3 equiv, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at room temperature for 15 min, and iodomethane (0.05 mL, 2.8 equiv) was added at 0 °C. The resulting solution was stirred at room temperature for 2.5 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt/*n*-hexane = 1/1) to give **6a** (96.0 mg, 74%) as a white solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.30–7.27 (m, 6H), 7.25–7.22 (m, 3H), 7.19–7.14 (m, 3H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 3.50 (s ,6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 170.0, 145.1, 144.8, 135.9, 135.7, 132.5, 131.0, 130.0, 129.4, 129.0, 128.9, 128.0, 127.0, 126.8, 126.8, 124.3, 121.0, 90.0, 89.6, 38.5, 38.3. HRMS (ESI$^+$) m/z calcd for $C_{30}H_{25}N_2O_2$ $[M + H]^+$ 445.1911, found 445.1904.

*Methyl 4-((4-(N-methylbenzamido)phenyl)ethynyl)benzoate (**34**).* A solution of **31** (200 mg, 0.56 mmol) in DMF (8 mL) was added at 0 °C to a suspension of NaH (60 %, 27.1 mg, 1.2 equiv, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at room temperature for 15 min, and iodomethane (0.05 mL, 1.4 equiv) was added at 0 °C. The resulting solution was stirred at room temperature for 1.5 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt/*n*-hexane = 1/1) to give **34** (191 mg, 91%) as a pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 3H), 3.51 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 166.6, 145.3, 135.7, 132.6, 131.6, 130.1, 129.7, 128.9, 128.1, 127.7, 126.8, 120.7, 119.9, 91.5, 89.4, 52.4, 38.3. HRMS (ESI$^+$) m/z calcd for $C_{24}H_{20}NO_3$ $[M + H]^+$ 370.1438, found 370.1434.

*4-((4-(N-Methylbenzamido)phenyl)ethynyl)benzoic acid (**35**).* **34** (829 mg, 2.2 mmol) and $LiOH·H_2O$ (567 mg, 6 equiv) were dissolved in a mixture of THF (60 mL), methanol (24 mL), and water (24 mL). The mixture was stirred for 3 h at room temperature, acidified with 2 M HCl, and extracted with AcOEt. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give **35** (757 mg, 95%) as a pale yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.30 (m, 3H), 7.20 (t, *J* = 7.2 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.53 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.8, 169.8, 145.4,

135.7, 132.7, 131.7, 130.3, 130.1, 128.9, 128.6, 128.1, 126.9, 120.6, 92.0, 89.4, 38.3. HRMS (ESI$^+$) m/z calcd for $C_{23}H_{18}NO_3$ $[M + H]^+$ 356.1281, found 356.1272.

*Methyl 4-((4-(4-((4-(N-methylbenzamido)phenyl)ethynyl)benzamido)phenyl)ethynyl)benzoate (**36**).* 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (61.6 mg, 1.9 equiv) and *N,N*-dimethyl-4-aminopyridine (1.4 mg, 5 mol%) were added to a solution of **35** (61.3 mg, 0.17 mmol) and **30** (43.4 mg, 1.0 equiv) in DMF (2 mL). The resulting mixture was stirred for 2 days at room temperature. After removal of the solvent *in vacuo*, 2 M HCl was added and the white precipitates were collected and dried to give **36** (67.0 mg, 66%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 2H), 7.86 (d, J = 6.0 Hz, 3H), 7.68 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 9.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 6.6 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 7.21 (m, 3H), 7.03 (d, J = 8.4 Hz, 2H), 3.93 (s, 3H), 3.53 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.8, 166.7, 164.9, 145.4, 138.4, 135.8, 134.2, 132.9, 132.7, 132.1, 131.7, 131.6, 130.1, 129.7, 129.6, 128.9, 128.2, 128.1, 127.3, 127.1, 126.9, 120.7, 120.0, 118.9, 92.2, 91.5, 89.2, 88.8, 52.4, 38.3. HRMS (ESI$^+$) m/z calcd for $C_{39}H_{29}N_2O_4$ $[M + H]^+$ 589.2122, found 589.2107.

*Methyl 4-((4-(N-methyl-4-((4-(N-methylbenzamido)phenyl)ethynyl)benzamido)phenyl)ethynyl)benzoate (**13**).* A solution of **36** (124 mg, 0.21 mmol) in DMF (3 mL) was added at 0 °C to a suspension of NaH (60 %, 22.4 mg, 2.6 equiv, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at room temperature for 15 min, and iodomethane (123.1 mg, 4.1 equiv) was added at 0 °C. The resulting solution was stirred at room temperature for 1.5 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt/*n*-hexane = 1/1) to give **13** (54.7 mg, 43%) as a yellow solid; ^{1}H NMR (600 MHz, CD_3OD) δ 8.00 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 6.6 Hz, 2H), 7.46 (d, J = 9.0 Hz, 2H), 7.37 (m, 4H), 7.30 (m, 5H), 7.23 (t, J = 7.2 Hz, 2H), 7.19 (d, J = 9.0 Hz, 2H), 7.14 (d, J = 9.0 Hz, 2H), 3.92 (s, 3H), 3.50 (s, 3H), 3.47 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 166.6, 145.1, 144.9, 135.7, 135.4, 132.7, 132.5, 131.6, 131.2, 130.0, 129.8, 129.7, 129.0, 128.9, 128.0, 127.7, 126.8, 126.8, 124.7, 121.0, 120.8, 91.3, 90.3, 89.6, 89.4, 52.4, 38.3. HRMS (ESI$^+$) m/z calcd for $C_{40}H_{31}N_2O_4$ $[M + H]^+$ 603.2278, found 603.2264.

4-((4-(N-Methyl-4-((4-(N-methylbenzamido)phenyl)ethynyl)benzamido)phenyl)et

*hynyl)benzoic acid (**37**).* **13** (44.6 mg, 0.07 mmol) and $LiOH·H_2O$ (20.5 mg, 7 equiv) were dissolved in a mixture of THF (2.5 mL), methanol (1 mL), and water (1 mL). The mixture was stirred for 7 h at room temperature and acidified with 2 M HCl, and the yellow precipitates were collected and dried to give **37** (39.2 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.8 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.33-7.16 (m, 11H), 7.03 (m, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 3.52 (s, 3H), 3.50 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.8, 170.1, 170.0, 145.1, 145.0, 135.6, 135.4, 132.8, 132.7, 132.5, 131.7, 131.2, 130.3, 130.1, 130.1, 129.0, 128.9, 128.9, 128.5, 128.1, 128.1, 126.9, 126.8, 124.7, 121.0, 120.9, 91.8, 90.3, 89.6, 89.5, 38.3, 38.3. HRMS (ESI^+) m/z calcd for $C_{39}H_{29}N_2O_4$ $[M + H]^+$ 589.2122, found 589.2108.

*N-Methyl-4-((4-(N-methylbenzamido)phenyl)ethynyl)-N-(4-((4-(phenylcarbamoyl)phenyl)ethynyl)phenyl)benzamide (**38**).* 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (63.8 mg, 1.9 equiv) and *N,N*-dimethyl-4-aminopyridine (1.1 mg, 5 mol%) were added to a solution of **37** (99.0 mg, 0.17 mmol) and aniline (41.3 mg, 2.6 equiv) in DMF (2 mL). The resulting mixture was stirred overnight at room temperature. After removal of the solvent *in vacuo*, 2 M HCl was added and the pale yellow precipitates were collected and dried to give **38** (87.2 mg, 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (m, 3H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.40 (m, 4H), 7.33–7.24 (m, 8H), 7.17 (m, 3H), 7.02 (m, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 3.52 (s, 3H), 3.49 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 165.0, 145.1, 144.9, 137.8, 135.6, 135.4, 134.6, 132.7, 132.6, 132.5, 132.0, 132.0, 131.2, 130.1, 130.0, 129.3, 129.0, 128.9, 128.9, 128.1, 128.0, 127.3, 126.9, 126.8, 126.7, 126.7, 124.9, 124.7, 121.0, 120.9, 120.7, 120.3, 91.1, 90.3, 89.5, 89.4, 38.3. HRMS (ESI^+) m/z calcd for $C_{45}H_{34}N_3O_3$ $[M + H]^+$ 664.2595, found 664.2580.

*The dimer **7a**.* A solution of **38** (84.4 mg, 0.13 mmol) in DMF (3 mL) was added at 0 °C to a suspension of NaH (60 %, 17.3 mg, 3.3 equiv, washed with *n*-hexane twice) in DMF (1 mL). The solution was stirred at room temperature for 15 min, and iodomethane (55.8 mg, 3.0 equiv) was added at 0 °C. The resulting solution was stirred at room temperature for 1 h. After removal of the solvent *in vacuo*, the residue was poured into water, and extracted with AcOEt. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (AcOEt/*n*-hexane = 2/1) to give **7a** (50.4 mg, 58%) as a yellow solid; ^{1}H NMR (600 MHz, CD_3OD) δ 7.39–7.34 (m, 6H), 7.31–7.26 (m, 11H), 7.24–8.18 (m, 3H), 7.13 (m, 6H), 3.43 (m, 9H); ^{13}C{^{1}H} NMR (151 MHz,

$CDCl_3$) δ 170.7, 170.0, 169.9, 145.1, 144.8, 144.8, 135.9, 135.7, 135.5, 132.6, 132.5, 131.2, 131.0, 130.0, 129.4, 129.0, 128.9, 128.0, 127.0, 126.8, 124.7, 124.2, 121.3, 120.9, 90.3, 89.9, 89.8, 89.5, 38.5, 38.3, 38.3. HRMS (ESI^+) m/z calcd for $C_{46}H_{36}N_3O_3$ $[M + H]^+$ 678.2751, found 678.2734.

Syntheses of 43, 45, and 49. The compounds **43**, **45**, and **49** were synthesized as shown in Scheme S7.

*N-(4-Iodophenyl)-2-nitrobenzenesulfonamide (**39**).*[38] 2-Nitrobenzenesulfonyl chloride (20.2 g, 91.2 mmol) was added to a solution of 4-iodoaniline (20.0 g, 91.3 mmol) in dry pyridine (55 mL) at 0 °C, and the reaction mixture was stirred for 2 h at room temperature. After the solvent was removed *in vacuo*, the residue was poured into 2 M hydrochloric acid, and extracted with chloroform. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated to give **39** (31.4 g, 77.7 mmol, 85%) as a brown solid; ^1H NMR (400 MHz, DMSO-d_6) δ 10.87 (s, 1H), 8.07–7.95 (m, 2H), 7.87–7.81 (m, 2H), 7.62 (d, J = 8.9 Hz, 2H), 6.94 (d, J = 8.6 Hz, 2H).

*N-(4-Iodophenyl)-N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2-nitrobenzenesulfonamide (**40b**).* Diisopropyl azodicarboxylate (10.03 g, 49.6 mmol) in dry THF (20 mL) was added to a mixture of **39** (9.96 g, 24.6 mmol), triethylene glycol monomethyl ether (4.1 g, 25.2 mmol), and triphenylphosphine (12.89 g, 49.1 mmol) in dry THF (130 mL) under an argon atmosphere at 0 °C. The reaction mixture was stirred for 8 h at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **40b** (9.91 g, 18.0 mmol, 73%) as a yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.67–7.58 (m, 5H), 7.52 (t, J = 6.6 Hz, 1H), 7.00 (d, J = 6.6 Hz, 2H), 3.94 (t, J = 5.4 Hz, 2H), 3.61–3.52 (m, 10H), 3.38 (s, 3H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 148.1, 138.7, 138.2, 133.8, 132.1, 132.1, 131.8, 131.4, 124.1, 94.3, 72.0, 70.7, 70.6, 70.4, 68.9, 59.2, 51.7. HRMS (ESI^+) m/z calcd for $C_{19}H_{23}IN_2NaO_7S$ $[M + Na]^+$ 573.0163, found 573.0157.

*(S)-N-(4-Iodophenyl)-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)-2-nitrobenzenesulfonamide (**40c**).* Diisopropyl azodicarboxylate (208 mg, 1.0 mmol) in dry THF (4 mL) was added to a mixture of **39** (200 mg, 0.49 mmol), (*S*)-2-(methoxyethoxyethoxy)propanol (110 mg, 0.62 mmol), and triphenylphosphine (260 mg, 1.0 mmol) in dry THF (3 mL) under an argon atmosphere at 0 °C. The reaction mixture was stirred for 1 h at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl

acetate/*n*-hexane = 1/1) to give **40c** (233 mg, 0.41 mmol, 86%) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65–7.60 (m, 4H), 7.53 (dd, *J* = 7.8 and 1.5 Hz, 1H), 7.49 (dt, *J* = 7.2 and 1.2 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 2H), 3.81 (dd, *J* = 16.2 and 7.2 Hz, 1H), 3.76 (dd, *J* = 13.8 and 4.8 Hz, 1H), 3.64–3.48 (m, 8H), 3.43–3.39 (m, 1H), 3.38 (s, 3H), 1.17 (d, *J* = 6.0 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.0, 139.0, 138.5, 133.7, 132.1, 131.8, 131.3, 131.3, 123.9, 93.8, 74.6, 71.9, 70.6, 68.1, 59.1, 57.0, 17.3. HRMS (ESI$^+$) m/z calcd for $C_{20}H_{25}IN_2NaO_7S$ [M + Na]$^+$ 587.0319, found 587.0312.

*N-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-2-nitro-N-(4-((trimethylsilyl)ethynyl)phenyl)benzenesulfonamide (**41b**).* **40b** (11.4 g, 20.8 mmol), $Pd(PPh_3)_2Cl_2$ (650 mg, 4 mol%), triphenylphosphine (600 mg, 11 mol%), CuI (360 mg, 9 mol%), and acetonitrile (90 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature was added Et_3N (8.3 mL, 2.8 equiv) and (trimethylsilyl)acetylene (3.4 mL, 1.2 equiv), and the mixture was stirred at room temperature for 3 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **41b** (8.13 g, 75%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63–7.61 (m, 2H), 7.52 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.46 (dt, *J* = 7.2 and 1.8 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 3.61–3.52 (m, 10H), 3.38 (s, 3H), 0.24 (s, 9H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.1, 138.3, 133.7, 133.0, 132.2, 131.3, 129.6, 124.0, 123.5, 103.9, 96.2, 72.1, 70.7, 70.7, 70.4, 69.0, 59.2, 51.7, −0.01. HRMS (ESI$^+$) m/z calcd for $C_{24}H_{32}N_2NaO_7SSi$ [M + Na]$^+$ 543.1592, found 543.1581.

*(S)-N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)-2-nitro-N-(4-((trimethylsilyl)ethynyl)phenyl)benzenesulfonamide (**41c**).* **40c** (300 mg, 0.53 mmol), $Pd(PPh_3)_2Cl_2$ (19.0 mg, 5 mol%), triphenylphosphine (16.7 mg, 12 mol%), CuI (10.5 mg, 10 mol%), and acetonitrile (7 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature was added Et_3N (0.22 mL, 3.0 equiv) and (trimethylsilyl)acetylene (0.09 mL, 1.2 equiv), and the mixture was stirred at room temperature for 2 h. Then the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/2) to give **41c** as a yellow oil (283 mg, quant.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62–7.59 (m, 2H), 7.47 (d, *J* = 6.9 Hz, 1H), 7.43 (dt, *J* = 7.2 and 1.8 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 3.85 (dd, *J* = 14.4 and 7.2 Hz, 1H), 3.78 (dd, *J* = 14.4 and 4.8 Hz, 1H), 3.60–3.48 (m, 8H),

3.42–3.38 (m, 1H), 3.37 (s, 3H), 1.17 (d, J = 6.6 Hz, 3H), 0.23 (s, 9H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 147.9, 139.0, 133.6, 132.9, 132.1, 131.8, 131.2, 129.1, 123.9, 123.0, 103.8, 95.9, 74.7, 71.9, 70.6, 70.6, 68.2, 59.1, 56.9, 17.4. HRMS (ESI^+) m/z calcd for $C_{25}H_{34}N_2NaO_7SSi$ $[M + Na]^+$ 557.1748, found 557.1732.

*N-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-4-((trimethylsilyl)ethynyl)aniline (**42b**).* A solution of **41b** (8.10 g, 15.6 mmol) in dry acetonitrile (100 mL) and cesium carbonate (5.69 g, 17.5 mmol) were added to benzenethiol (2.2 mL, 21.6 mmol). The mixture was stirred for 7 h at 45 °C in an oil bath, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/1) to give **42b** (3.57 g, 68%) as a yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 8.4 Hz, 2H), 6.50 (d, J = 8.4 Hz, 2H), 4.39 (br, 1H), 3.69 (t, J = 5.4 Hz, 2H), 3.65–3.64 (m, 6H), 3.56–3.55 (m, 2H), 3.38 (s, 3H), 3.29 (t, J = 5.4 Hz, 2H), 0.22 (s, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 148.5, 133.4, 112.5, 111.1, 106.5, 91.2, 72.0, 70.7, 70.4, 69.5, 59.2, 43.2, 0.31. HRMS (ESI^+) m/z calcd for $C_{18}H_{30}NO_3Si$ $[M + H]^+$ 336.1989, found 336.1982.

*(S)-N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)-4-((trimethylsilyl)ethynyl)aniline (**42c**).* A solution of **41c** (280 mg, 0.52 mmol) in dry acetonitrile (6 mL) and cesium carbonate (211 mg, 0.64 mmol) were added to a solution of benzenethiol (91 mg, 0.82 mmol) in acetonitrile (1 mL). The mixture was stirred for 2 h at 45 °C in an oil bath, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/2) to give **42c** (158 mg, 0.45 mmol, 86%) as a yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, J = 8.8 Hz, 2H), 6.51 (d, J = 8.8 Hz, 2H), 4.55 (br, 1H), 3.76–3.70 (m, 2H), 3.66–3.62 (m, 4H), 3.57–3.54 (m, 3H), 3.38 (s, 3H), 3.21 (m, 1H), 3.02 (dd, J = 12.4 and 8.0 Hz, 1H), 1.21 (d, J = 6.2 Hz, 3H), 0.22 (s, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 148.8, 133.4, 112.5, 110.9, 106.6, 91.1, 74.4, 72.1, 70.9, 70.6, 68.1, 59.2, 48.8, 17.9. HRMS (ESI^+) m/z calcd for $C_{19}H_{31}NNaO_3Si$ $[M + Na]^+$ 372.1965, found 372.1962.

*4-Iodo-N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-N-(4-((trimethylsilyl)ethynyl)phenyl)benzamide (**43b**).* Triethylamine (1.25 mL, 8.97 mmol) was added to a solution of **42b** (1.50 g, 4.47 mmol) in dichloromethane (32 mL), and the mixture was stirred at 0 °C. 4-Iodobenzoyl chloride (1.19 g, 4.46 mmol) in dichloromethane (6 mL) was added to the cold amine solution and the mixture was stirred overnight at room temperature.

The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq., and brine, and dried over $MgSO_4$, filtered, and evaporated to give **43b** as a yellow oil (2.49 g, 99%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 9.0 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 4.05 (t, J = 6.0 Hz, 2H), 3.74 (t, J = 5.4 Hz, 2H), 3.60 (m, 6H), 3.54–3.52 (m, 2H), 3.37 (s, 3H), 0.21 (s, 9H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.5, 137.1, 135.3, 132.8, 130.5, 127.5, 121.4, 104.0, 96.6, 95.3, 71.9, 70.6, 70.6, 70.3, 68.1, 59.1, 50.5, −0.1. HRMS (ESI$^+$) m/z calcd for $C_{25}H_{32}INNaO_4Si$ $[M + Na]^+$ 588.1037, found 588.1036.

*(S)-4-Iodo-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)-N-(4-((trimethylsilyl)ethynyl)phenyl)benzamide (**43c**).* Triethylamine (53.4 mg, 0.53 mmol) was added to a solution of **42c** (80.0 mg, 0.23 mmol) in dichloromethane (4 mL), and the mixture was stirred at 0 °C. 4-Iodobenzoyl chloride (67.3 mg, 0.25 mmol) was added to the cold amine solution and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq., and brine, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/2) to give **43c** as a yellow oil (113.6 mg, 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 9.0 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 7.8 Hz, 2H), 4.05 (dd, J = 13.8 and 3.0 Hz, 1H), 3.91 (m, 1H), 3.71– 3.61 (m, 2H), 3.60–3.56 (m, 4H), 3.51–3.50 (m, 3H), 3.36 (s, 3H), 1.18 (d, J = 6.0 Hz, 3H), 0.21 (s, 9H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.8, 137.2, 135.7, 132.8, 130.6, 127.6, 121.4, 104.3, 96.6, 95.3, 73.8, 72.1, 70.9, 70.6, 68.4, 59.2, 56.6, 17.7, 0.0. HRMS (ESI$^+$) m/z calcd for $C_{26}H_{34}INNaO_4Si$ $[M + Na]^+$ 602.1194, found 602.1184.

*N-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-N-(4-((trimethylsilyl)ethynyl)phenyl)benzamide (**44b**).* Triethylamine (0.83 mL, 6.0 mmol) was added to a solution of **42b** (1.00 g, 2.98 mmol) in dichloromethane (25 mL), and the mixture was stirred at 0 °C. Benzoyl chloride (0.35 mL, 3.0 mmol) was added to the cold amine solution and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq., and brine, dried over $MgSO_4$, filtered, and evaporated. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/2) to give **44b** as a yellow oil (1.34 g, quant.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27–7.25 (m, 4H), 7.22 (tt, J = 6.6 and 1.2 Hz, 1H), 7.14 (t, J = 7.2 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 4.06 (t, J = 5.4 Hz, 2H), 3.75 (t, J = 5.4 Hz, 2H), 3.61–3.60 (m, 6H), 3.53–3.51 (m, 2H), 3.36 (s, 3H), 0.20 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 170.6, 144.4, 135.9, 132.7, 129.9, 128.9, 128.0, 127.6, 121.1, 104.3, 95.0, 72.0, 70.7, 70.7, 70.4, 68.3, 59.2, 50.5, 0.0. HRMS (ESI^+) m/z calcd for $C_{25}H_{33}NNaO_4Si$ $[M + Na]^+$ 462.2071, found 462.2063.

*(S)-N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)-N-(4-((trimethylsilyl)ethynyl)phenyl)benzamide (**44c**).* Triethylamine (50.4 mg, 0.50 mmol) was added to a solution of **42c** (70.0 mg, 0.20 mmol) in dichloromethane (4 mL), and the mixture was stirred at 0 °C. Benzoyl chloride (35.6 mg, 0.25 mmol) was added to the cold amine solution and the mixture was stirred overnight at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq., and brine, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/2) to give **44c** as a yellow oil (88.4 mg, 97%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (m, 3H), 7.23 (t, *J* =7.8 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.08 (dd, *J* = 13.8 and 3.6 Hz, 1H), 3.93 (m, 1H), 3.72–3.65 (m, 2H), 3.60–3.57 (m, 4H), 3.52–3.51 (m, 3H), 3.36 (s, 3H), 1.19 (d, *J* = 6.6 Hz, 3H), 0.22 (s, 9H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 136.2, 132.6, 129.9, 128.9, 128.0, 127.6, 121.0, 104.5, 95.0, 73.8, 72.1, 71.0, 70.6, 68.5, 59.2, 56.6, 17.7, 0.0. HRMS (ESI^+) m/z calcd for $C_{26}H_{35}NNaO_4Si$ $[M + Na]^+$ 476.2228, found 476.2224.

*N-(4-Ethynylphenyl)-N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)benzamide (**45b**).* A 1.0 M solution of tetrabutylammonium fluoride in THF (3 mL, 3 mmol) was added to a stirred solution of **44b** (1.32 g, 3.0 mmol) in THF (25 mL) at room temperature. After stirred at room temperature for 1 h, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **45b** as a yellow oil (990 mg, 90%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.08 (t, *J* = 6.0 Hz, 2H), 3.77 (t, *J* = 5.4 Hz, 2H), 3.62–3.61 (m, 6H), 3.54–3.52 (m, 2H), 3.37 (s, 3H), 3.05 (s, 1H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 170.6, 144.8, 135.9, 132.9, 130.0, 128.9, 128.0, 127.8, 120.1, 83.0, 77.9, 72.1, 70.7, 70.7, 70.5, 68.4, 59.2, 50.6. HRMS (ESI^+) m/z calcd for $C_{22}H_{25}NNaO_4$ $[M + Na]^+$ 390.1676, found 390.1686.

*(S)-N-(4-Ethynylphenyl)-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)benzamide (**45c**).* A 1.0 M solution of tetrabutylammonium fluoride in THF (1.84 mL, 1.84 mmol) was added to a stirred solution of **44c** (700 mg, 1.54 mmol) in THF (10 mL) at room temperature. After stirred at room temperature for 15 min, the mixture was diluted

with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **45c** as a yellow oil (555 mg, 94%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.28 (m, 4H), 7.23 (tt, *J* =7.2 and 1.2 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.10 (m, 1H), 3.95 (m, 1H), 3.74–3.71 (m, 1H), 3.68–3.64 (m, 1H), 3.61–3.56 (m, 4H), 3.53–3.51 (m, 3H), 3.36 (s, 3H), 3.04 (s, 1H), 1.20 (d, *J* = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.8, 145.3, 136.0, 132.8, 130.0, 128.9, 128.0, 127.7, 119.9, 83.1, 77.8, 73.8, 72.0, 70.9, 70.6, 68.4, 59.2, 56.6, 17.7. HRMS (ESI^+) m/z calcd for $C_{23}H_{27}NNaO_4$ $[M + Na]^+$ 404.1832, found 404.1831.

*2-Nitro-N-phenylbenzenesulfonamide (**46**).*[39] 2-Nitrobenzenesulfonyl chloride (755 mg, 3.41 mmol) in dry dichloromethane (8 mL) was added to a solution of aniline (320 mg, 3.43 mmol) and pyridine (350 mg, 4.44 mmol) in dry dichloromethane (2 mL) at 0 °C, and the reaction mixture was stirred for 1 h 30 min at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., dried over $MgSO_4$, filtered, and evaporated to give **46** as a red solid (912 mg, 96%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.82 (dd, *J* = 7.8 and 1.8 Hz, 1H), 7.69 (dt, *J* = 7.8 and 1.2 Hz, 1H), 7.57 (dt, *J* = 7.8 and 1.2 Hz, 1H), 7.27 (t, *J* = 8.4 Hz, 2H), 7.25 (br, 1H), 7.20–7.18 (m, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.3, 135.6, 134.1, 132.7, 132.3, 132.0, 129.6, 126.8, 125.5, 123.4.

*N-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)-2-nitro-N-phenylbenzenesulfonamide (**47b**).* Diisopropyl azodicarboxylate (724 mg, 3.58 mmol) in dry THF (5 mL) was added to a mixture of **46** (504 mg, 1.81 mmol), triethylene glycol monomethyl ether (325 mg, 1.98 mmol), and triphenylphosphine (947 mg, 3.61 mmol) in dry THF (10 mL) under an argon atmosphere at 0 °C. The reaction mixture was stirred overnight at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 2/1) to give **47b** (770 mg, quant.) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (m, 2H), 7.52 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.45 (dt, *J* = 7.2 and 1.2 Hz, 1H), 7.30 (m, 3H), 7.23 (m, 2H), 3.97 (t, *J* = 6.0 Hz, 2H), 3.63–3.53 (m, 10H), 3.37 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.1, 138.2, 133.6, 132.3, 132.1, 131.2, 129.9, 129.5, 128.7, 123.9, 72.0, 70.7, 70.6, 70.3, 68.8, 59.2, 51.7. HRMS (ESI^+) m/z calcd for $C_{19}H_{24}N_2NaO_7S$ $[M + Na]^+$ 447.1196, found 447.1191.

*(S)-N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)-2-nitro-N-phenylbenzenesulfonamide (**47c**).* Diisopropyl azodicarboxylate (364 mg, 1.80 mmol) in dry THF (5 mL) was added to a mixture of **46** (250 mg, 0.90 mmol),

(*S*)-2-(methoxyethoxyethoxy)propanol (170 mg, 0.94 mmol), and triphenylphosphine (470 mg, 1.80 mmol) in dry THF (5 mL) under an argon atmosphere at 0 °C. The reaction mixture was stirred for 3 h at room temperature, then the solvent was removed *in vacuo*, and the residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 2/1) to give **47c** (455 mg, quant.) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61–7.59 (m, 2H), 7.48 (dd, *J* = 7.8 and 1.2 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.30–7.25 (m, 5H), 3.88 (dd, *J* = 14.4 and 7.2 Hz, 1H), 3.77 (dd, *J* = 15.0 and 5.4 Hz, 1H), 3.62–3.41 (m, 9H), 3.37 (s, 3H), 1.19 (d, *J* = 6.0 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.1, 139.0, 133.6, 132.2, 132.1, 131.1, 129.5, 129.4, 128.4, 123.8, 74.5, 72.0, 70.7, 70.6, 68.2, 59.2, 57.0, 17.5. HRMS (ESI$^+$) m/z calcd for $C_{20}H_{27}N_2O_7S$ $[M + H]^+$ 439.1533, found 439.1521.

*N-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)aniline (**48b**).* A solution of **47b** (740 mg, 1.74 mmol) in dry acetonitrile (12 mL) and cesium carbonate (681 mg, 2.09 mmol) were added to a solution of benzenethiol (0.27 mL, 2.64 mmol) in dry acetonitrile (2 mL). The mixture was stirred for 4 h at 45 °C in an oil bath, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/1) to give **48b** (271 mg, 65%) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (dt, *J* =7.8 and 1.2 Hz, 2H), 6.70 (tt, *J* = 7.2 and 1.2 Hz, 1H), 6.63 (dt, *J* = 7.8 and 1.2 Hz, 2H), 3.71 (t, *J* = 4.8 Hz, 2H), 3.66 (m, 6H), 3.56 (m, 2H), 3.39 (s, 3H), 3.30 (t, *J* = 5.4 Hz, 2H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.4, 129.3, 117.6, 113.2, 72.1, 70.7, 70.4, 69.7, 59.2, 43.6. HRMS (ESI$^+$) m/z calcd for $C_{13}H_{21}NNaO_3$ $[M + Na]^+$ 262.1414, found 262.1418.

*(S)-N-(1-(2-(2-Methoxyethoxy)ethoxy)propan-2-yl)aniline (**48c**).* A solution of **47c** (425 mg, 0.97 mmol) in dry acetonitrile (6 mL) and cesium carbonate (353 mg, 1.09 mmol) were added to a solution of benzenethiol (151.2 mg, 1.37 mmol) in dry acetonitrile (4 mL). The mixture was stirred for 9 h at 45 °C in an oil bath, then poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (silica gel, ethyl acetate/*n*-hexane = 1/1) to give **48c** (154 mg, 63%) as a yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.16 (dt, *J* =7.8 and 1.2 Hz, 2H), 6.69 (tt, *J* = 7.2 and 1.2 Hz, 1H), 6.62 (dt, *J* = 7.8 and 1.2 Hz, 2H), 4.28 (br, 1H), 3.75–3.56 (m, 9H), 3.39 (s, 3H), 3.22 (dd, *J* = 12.6 and 3.6 Hz, 1H), 3.04 (dd, *J* = 12.6 and 7.8 Hz, 1H), 1.22 (d, *J* = 6.0 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 148.6, 129.3, 117.4, 113.2, 74.5, 72.1, 70.9, 70.7, 68.1, 59.2, 49.3, 18.0. HRMS (ESI$^+$) m/z calcd for $C_{14}H_{23}NNaO_3$ $[M + Na]^+$ 276.1570, found 276.1564.

*4-Iodo-N-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-N-phenylbenzamide (**49b**).* Triethylamine (0.3 mL, 2.15 mmol) was added to a solution of **48b** (271 mg, 1.13 mmol) in dichloromethane (5 mL), and the mixture was stirred at 0 °C. 4-Iodobenzoyl chloride (290 mg, 1.09 mmol) in dichloromethane (5 mL) was added to the cold amine solution and the mixture was stirred for 6 h at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq., and brine, dried over $MgSO_4$, filtered, and evaporated to give **49b** as a yellow oil (463 mg, 87%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 7.8 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.8 Hz, 2H), 7.01 (d, J = 7.8 Hz, 2H), 4.07 (t, J = 5.4 Hz, 2H), 3.74 (t, J = 5.4 Hz, 2H), 3.61 (m, 6H), 3.52 (m, 2H), 3.36 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 169.7, 137.0, 135.7, 130.6, 129.3, 128.0, 126.9, 96.3, 72.1, 70.7, 70.7, 70.4, 68.1, 59.2, 50.5. HRMS (ESI$^+$) m/z calcd for $C_{20}H_{24}INNaO_4$ $[M + Na]^+$ 492.0642, found 492.0640.

*(S)-4-Iodo-N-(1-(2-(2-methoxyethoxy)ethoxy)propan-2-yl)-N-phenylbenzamide (**49c**).* Triethylamine (114 mg, 1.12 mmol) was added to a solution of **48c** (140 mg, 0.55 mmol) in dichloromethane (2 mL), and the mixture was stirred at 0 °C. 4-Iodobenzoyl chloride (150 mg, 0.56 mmol) in dichloromethane (6 mL) was added to the cold amine solution and the mixture was stirred for 5 h at room temperature. The mixture was diluted with dichloromethane, washed with 2 M HCl aq., 2 M NaOH aq., and brine, dried over $MgSO_4$, filtered, and evaporated to give **49c** as a yellow oil (265 mg, 99%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (d, J = 8.4 Hz, 2H), 7.20 (m, 2H), 7.14 (m, 3H), 7.02 (d, J = 7.8 Hz, 2H), 4.04 (br, 1H), 3.92 (br, 1H), 3.73–3.50 (m, 9H), 3.36 (s, 3H), 1.19 (d, J = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 137.0, 136.0, 130.6, 129.2, 127.9, 126.7, 96.3, 73.6, 72.1, 70.9, 70.6, 68.3, 59.2, 56.6, 17.7. HRMS (ESI$^+$) m/z calcd for $C_{21}H_{26}INNaO_4$ $[M + Na]^+$ 506.0799, found 506.0788.

Syntheses of oligoamides 6 – 12. The oligoamides **6** – **12** were synthesized as shown in Scheme S8.

*The monomer **6b**.* **49b** (49.3 mg, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 5 mol%), triphenylphosphine (2.6 mg, 10 mol%), CuI (1.9 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (29.8 mg, 2.9 equiv) and **45b** (38.0 mg, 0.10 mmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel

column chromatography (ethyl acetate/methanol = 10/1) to give **6b** (60.0 mg, 82%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.08 (m, 18H), 4.08 (m, 4H), 3.76 (m, 4H), 3.62 (m, 12H), 3.53 (m, 4H), 3.36 (s, 3H), 3.36 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 170.0, 144.4, 143.8, 136.0, 135.9, 133.2, 132.3, 130.9, 130.1, 130.0, 129.2, 128.9, 128.9, 128.0, 128.0, 127.8, 126.8, 124.2, 120.9, 90.1, 89.5, 72.0, 70.7, 70.6, 70.6, 70.4, 70.4, 68.3, 68.1, 59.2, 50.5, 50.4. HRMS (ESI$^+$) m/z calcd for $C_{42}H_{48}N_2NaO_8$ $[M + Na]^+$ 731.3303, found 731.3282.

*The monomer **6c**.* **49c** (25.7 mg, 53 μmol), $Pd(PPh_3)_2Cl_2$ (2.0 mg, 5 mol%), triphenylphosphine (1.4 mg, 10 mol%), CuI (1.0 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (12.4 mg, 2.3 equiv) and **45c** (20.2 mg, 1.0 equiv) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature for 9 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 10/1 to methanol 10%) to give **6c** (31.8 mg, 82%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.27 (m, 5H), 7.25–7.23 (m, 4H), 7.19–7.11 (m, 9H), 4.12–4.06 (m, 2H), 3.94 (br, 2H), 3.75–3.50 (m, 18H), 3.36 (s, 3H), 3.35 (s, 3H), 1.20 (d, J = 5.4 Hz, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 170.1, 145.0, 136.2, 136.1, 133.1, 132.2, 130.9, 129.9, 129.1, 128.9, 128.0, 128.0, 127.9, 127.7, 126.6, 124.2, 120.6, 90.2, 89.4, 73.8, 73.6, 72.0, 70.9, 70.6, 68.4, 68.3, 59.2, 59.2, 56.6, 56.5, 17.7, 17.7, 17.6. HRMS (ESI$^+$) m/z calcd for $C_{44}H_{52}N_2NaO_8$ $[M + Na]^+$ 759.3616, found 759.3616.

*The monomer derivative **50b**.* **43b** (707 mg, 1.25 mmol), $Pd(PPh_3)_2Cl_2$ (43.7 mg, 5 mol%), triphenylphosphine (37.1 mg, 10 mol%), CuI (23.6 mg, 10 mol%), and acetonitrile (6 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature Et_3N (0.3 mL, 1.7 equiv) and **45b** (463 mg, 1.26 mmol) in acetonitrile (4 mL) was added, and the mixture was stirred at room temperature for 7 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **50b** (1.25 g, quant.) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.23 (m, 11H), 7.17 (t, J = 8.0 Hz, 1H), 7.16 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 4.08 (m, 4H), 3.76 (m, 4H), 3.61 (m, 12H), 3.53 (m, 4H), 3.37 (m, 6H), 0.22 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.0, 135.9, 135.8, 135.7, 133.2, 133.1, 132.8, 132.3, 131.1, 130.1, 130.0, 129.0, 128.9, 128.9, 128.0, 128.0, 127.8, 127.6, 124.5, 121.4, 120.9, 119.5, 104.2, 95.3, 90.4, 89.4, 72.0, 70.7, 70.7,

70.5, 70.4, 68.4, 68.3, 68.2, 59.2, 50.6, 50.5, 0.0. HRMS (ESI^+) m/z calcd for $C_{47}H_{56}N_2NaO_8Si$ $[M + Na]^+$ 827.3698, found 827.3714.

*The monomer derivative **50c**.* **43c** (70.2 mg, 0.12 mmol), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 5 mol%), triphenylphosphine (2.6 mg, 10 mol%), CuI (1.9 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (35.6 mg, 3.5 equiv) and **45c** (38.4 mg, 0.12 mmol) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature for 5 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane = 1/1) to give **50c** (70.5 mg, 84%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.30–7.28 (m, 6H), 7.25–7.24 (m, 4H), 7.18–7.13 (m, 5H), 7.08 (d, J = 8.4 Hz, 2H), 4.10 (m, 2H), 3.94 (m, 2H), 3.73–3.51 (m, 18H), 3.36 (s, 3H), 3.35 (s, 3H), 1.20 (d, J = 6.5 Hz, 3H), 1.19 (d, J = 6.9 Hz, 3H), 0.22 (s, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 170.0, 145.1, 144.7, 136.1, 135.8, 133.1, 132.7, 132.3, 132.2, 132.1, 131.1, 130.0, 129.0, 128.9, 128.7, 128.6, 128.1, 128.0, 127.7, 127.6, 124.6, 121.2, 120.6, 104.3, 95.2, 90.5, 89.3, 73.8, 73.7, 72.0, 70.9, 70.9, 70.6, 68.5, 68.4, 60.6, 59.2, 56.7, 56.5, 21.2, 17.7, 17.7, 14.3, 0.0. HRMS (ESI^+) m/z calcd for $C_{49}H_{60}N_2NaO_8Si$ $[M + Na]^+$ 855.4011, found 855.4005.

*The monomer derivative **51b**.* A 1.0 M solution of tetrabutylammonium fluoride in THF (1.5 mL, 1.5 mmol) was added to a stirred solution of **50b** (1.15 g, 1.43 mmol) in THF (10 mL) at room temperature. After stirred at room temperature for 45 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 20/5/1) to give **51b** as a yellow oil (728 mg, 69%); ^1H NMR (600 MHz, $CDCl_3$) δ 7.32–7.28 (m, 9H), 7.25–7.24 (m, 2H), 7.16 (t, J = 7.8 Hz, 2H), 7.10–7.08 (m, 4H), 4.08 (m, 4H), 3.77 (m, 4H), 3.62 (m, 12H), 3.53 (m, 4H), 3.37 (s, 3H), 3.37 (s, 3H), 3.06 (s, 1H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.5, 169.7, 144.4, 135.9, 135.6, 133.2, 132.9, 132.3, 131.0, 129.9, 128.9, 128.8, 127.9, 127.8, 127.7, 124.6, 120.8, 120.4, 90.4, 89.4, 82.8, 78.1, 72.0, 70.6, 70.6, 70.4, 68.3, 68.2, 59.1, 50.6, 50.5. HRMS (ESI^+) m/z calcd for $C_{44}H_{48}N_2NaO_8$ $[M + Na]^+$ 755.3303, found 755.3299.

*The monomer derivative **51c**.* A 1.0 M solution of tetrabutylammonium fluoride in THF (1.34 mL, 1.34 mmol) was added to a stirred solution of **50c** (945 mg, 1.13 mmol) in THF (7 mL) at room temperature. After stirred at room temperature for 1 h, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column

chromatography (ethyl acetate/*n*-hexane = 2/1) to give **51c** as a yellow oil (860 mg, 99%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.23 (m, 11H), 7.18–7.12 (m, 6H), 4.11 (m, 2H), 3.95 (br, 2H), 3.74–3.51 (m, 18H), 3.36 (s, 3H), 3.35 (s, 3H), 3.05 (s, 1H), 1.20 (m, 6H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 170.0, 145.1, 136.1, 135.8, 132.9, 132.3, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.7, 124.7, 120.6, 120.2, 90.5, 89.3, 83.0, 78.0, 73.8, 73.7, 72.1, 70.9, 70.9, 70.6, 68.5, 68.4, 59.2, 56.6, 17.7, 17.6. HRMS (ESI$^+$) m/z calcd for $C_{46}H_{52}N_2NaO_8$ $[M + Na]^+$ 783.3616, found 783.3639.

*The dimer **7b**.* **49b** (47.5 mg, 0.10 mmol), $Pd(PPh_3)_2Cl_2$ (3.5 mg, 5 mol%), triphenylphosphine (2.6 mg, 10 mol%), CuI (1.9 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (29.9 mg, 3.0 equiv) and **51b** (73.3 mg, 0.10 mmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **7b** (82.1 mg, 76%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.27 (m, 8H), 7.25–7.08 (m, 18H), 4.08 (m, 6H), 3.77 (m, 6H), 3.62–3.60 (m, 18H), 3.53 (m, 6H), 3.36 (s, 3H), 3.36 (s, 3H), 3.36 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.9, 169.8, 144.5, 144.1, 136.0, 135.9, 135.6, 132.4, 132.3, 131.1, 131.0, 130.0, 129.2, 129.0, 129.0, 128.9, 128.0, 127.8, 126.8, 124.6, 124.2, 121.2, 120.8, 90.4, 90.0, 89.7, 89.4, 72.0, 70.7, 70.7, 70.5, 70.4, 68.3, 68.3, 68.1, 59.2, 50.6, 50.4. HRMS (ESI$^+$) m/z calcd for $C_{64}H_{71}N_3NaO_{12}$ $[M + Na]^+$ 1096.4930, found 1096.4932.

*The dimer **7c**.* **49c** (41.0 mg, 85 μmol), $Pd(PPh_3)_2Cl_2$ (2.9 mg, 5 mol%), triphenylphosphine (2.2 mg, 10 mol%), CuI (1.6 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (20.5 mg, 2.4 equiv) and **51c** (62.1 mg, 82 μmol) in acetonitrile (2 mL) was added, and the mixture was stirred at room temperature for 9 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform = 1/1) to give **7c** (74.3 mg, 82%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.27 (m, 13H), 7.25–7.24 (m, 2H), 7.18–7.12 (m, 11H), 4.11 (m, 3H), 3.95 (br, 3H), 3.73–3.50 (m, 27H), 3.36 (s, 3H), 3.35 (s, 3H), 3.35 (s, 3H), 1.20 (d, J = 6.0 Hz, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 145.1, 144.7, 144.5, 136.2, 136.1, 135.8, 132.3, 132.2, 131.1, 131.0, 129.9, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 126.6, 124.6, 124.2, 120.9, 120.6, 90.4, 90.1, 89.6, 89.3, 73.8, 73.7, 73.6, 72.0, 70.9, 70.6, 68.4, 68.4, 68.3, 59.2, 56.6, 56.5,

17.7, 17.7, 17.6. HRMS (ESI$^+$) m/z calcd for $C_{67}H_{77}N_3NaO_{12}$ [M + Na]$^+$ 1138.5399, found 1138.5391.

The dimer derivative ***52b***. **43b** (501 mg, 0.89 mmol), $Pd(PPh_3)_2Cl_2$ (31.8 mg, 5 mol%), triphenylphosphine (23.8 mg, 10 mol%), CuI (20.3 mg, 10 mol%), and acetonitrile (2.5 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (0.25 mL 2.0 equiv) and **51b** (650 mg, 1.0 equiv) in acetonitrile (5.5 mL) was added, and the mixture was stirred at room temperature for 8 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **52b** (916 mg, 88%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.22 (m, 17H), 7.15 (t, J = 7.8 Hz, 2H), 7.09 (m, 4H), 7.04 (d, J = 8.4 Hz, 2H), 4.08 (m, 6H), 3.76 (m, 6H), 3.63–3.60 (m, 18H), 3.52 (m, 6H), 3.36 (s, 3H), 3.36 (s, 3H), 3.35 (s, 3H), 0.21 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.1, 144.0, 135.9, 135.7, 135.6, 133.1, 132.8, 132.4, 132.3, 131.1, 130.0, 129.0, 128.9, 128.9, 128.0, 127.8, 127.6, 124.6, 124.5, 121.4, 121.1, 120.8, 104.2, 95.3, 90.4, 90.2, 89.6, 89.4, 72.0, 70.7, 70.7, 70.4, 70.4, 68.3, 68.2, 59.2, 50.6, 50.6, 50.5, 0.0. HRMS (ESI$^+$) m/z calcd for $C_{69}H_{79}N_3NaO_{12}Si$ [M + Na]$^+$ 1192.5325, found 1192.5299.

The dimer derivative ***52c***. **43c** (582 mg, 1.0 mmol), $Pd(PPh_3)_2Cl_2$ (35.7 mg, 5 mol%), triphenylphosphine (28.9 mg, 10 mol%), CuI (20.0 mg, 10 mol%), and acetonitrile (5 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (0.3 mL 2 equiv) and **51c** (765 mg, 1.0 equiv) in acetonitrile (6 mL) was added, and the mixture was stirred at room temperature for 5 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform = 2/1) to give **52c** (1.05 mg, 86%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28–7.22 (m, 17H), 7.17–7.07 (m, 8H), 4.07 (m, 3H), 3.92 (br, 3H), 3.73–3.49 (m, 27H), 3.35 (s, 3H), 3.34 (s, 3H), 3.34 (s, 3H), 1.19 (m, 9H), 0.20 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 144.7, 136.1, 135.9, 135.8, 132.7, 132.3, 132.2, 131.1, 129.9, 129.0, 128.9, 128.9, 128.0, 127.7, 127.6, 124.6, 124.5, 121.2, 120.9, 120.6, 104.3, 95.1, 90.5, 90.3, 89.5, 89.3, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 68.4, 59.1, 56.6, 56.5, 17.7, 17.7, 17.6, 0.0. HRMS (ESI$^+$) m/z calcd for $C_{72}H_{85}N_3NaO_{12}Si$ [M + Na]$^+$ 1234.5795, found 1234.5762.

The dimer derivative ***53b***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.8 mL, 0.8 mmol) was added to a stirred solution of **52b** (875 mg, 0.75 mmol) in

THF (8 mL) at room temperature. After stirred at room temperature for 30 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **53b** as a yellow oil (723 mg, 88%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.22 (m, 17H), 7.16 (t, J = 7.8 Hz, 2H), 7.10–7.08 (m, 6H), 4.08 (m, 6H), 3.76 (m, 6H), 3.63–3.61 (m, 18H), 3.53 (m, 6H), 3.37 (s, 3H), 3.36 (s, 3H), 3.36 (s, 3H), 3.06 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.2, 135.9, 135.7, 135.6, 133.1, 133.0, 132.4, 132.3, 131.1, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.7, 124.6, 124.6, 121.1, 120.8, 120.4, 90.4, 90.3, 89.6, 89.4, 82.8, 78.2, 72.0, 70.7, 70.7, 70.5, 68.3, 68.3, 59.2, 50.6, 50.6, 50.6. HRMS (ESI$^+$) m/z calcd for $C_{66}H_{71}N_3NaO_{12}$ [M + Na]$^+$ 1120.4930, found 1120.4896.

*The dimer derivative **53c***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.83 mL, 0.83 mmol) was added to a stirred solution of **52c** (1.01 g, 0.83 mmol) in THF (7 mL) at room temperature. After stirred at room temperature for 30 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/methanol = 20/1) to give **53c** as a yellow oil (888 mg, 93%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.22 (m, 17H), 7.17–7.11 (m, 8H), 4.10 (br, 3H), 3.94 (br, 3H), 3.73–3.49 (m, 27H), 3.35 (s, 3H), 3.34 (s, 3H), 3.34 (s, 3H), 3.05 (s, 1H), 1.19 (m, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.0, 144.8, 136.1, 135.8, 132.8, 132.3, 132.2, 131.1, 131.1, 129.9, 129.0, 128.9, 128.0, 127.7, 127.7, 124.6, 124.6, 120.9, 120.6, 120.2, 90.5, 90.3, 89.5, 89.3, 82.9, 78.0, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 59.2, 56.6, 17,7, 17,6, 17.6. HRMS (ESI$^+$) m/z calcd for $C_{69}H_{77}N_3NaO_{12}$ [M + Na]$^+$ 1162.5399, found 1162.5396.

*The trimer **8b***. **49b** (31.9 mg, 68 μmol), $Pd(PPh_3)_2Cl_2$ (2.1 mg, 5 mol%), triphenylphosphine (1.6 mg, 10 mol%), CuI (1.1 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (17.5 mg, 2.7 equiv) and **53b** (69.5 mg, 63 μmol) in acetonitrile (1 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative TLC (silica gel, ethyl acetate/methanol = 10/1) to give **8b** (53.0 mg, 58%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29–7.08 (m, 34H), 4.07 (m, 8H), 3.76 (m, 8H), 3.61 (m, 24H), 3.52 (m, 8H), 3.35 (m, 12H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.9, 169.8, 169.7, 144.4, 144.1, 143.8, 136.0, 135.9, 135.6, 135.6, 133.1, 132.4,

132.4, 132.3, 131.1, 130.9, 130.8, 130.0, 129.2, 129.0, 128.9, 128.9, 127.9, 127.8, 126.8, 124.6, 124.5, 124.1, 121.1, 121.1, 120.8, 90.4, 90.2, 90.0, 89.7, 89.5, 89.4, 72.4, 72.0, 70.7, 70.6, 70.4, 70.4, 68.3, 68.2, 68.1, 61.9, 59.2, 50.6, 50.5, 50.4. HRMS (ESI^+) m/z calcd for $C_{86}H_{94}N_4NaO_{16}$ $[M + Na]^+$ 1461.6557, found 1461.6559.

*The trimer **8c***. **49c** (39.1 mg, 81 μmol), $Pd(PPh_3)_2Cl_2$ (3.2 mg, 5 mol%), triphenylphosphine (2.2 mg, 10 mol%), CuI (1.6 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (18.3 mg, 2.1 equiv) in acetonitrile (1 mL) and **53c** (95.4 mg, 84 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative TLC (silica gel, ethyl acetate/methanol = 10/1) to give **8c** (69.4 mg, 57%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.29–7.12 (m, 34H), 4.11 (br, 4H), 3.94 (br, 4H), 3.73–3.49 (m, 36H), 3.34 (m, 12H), 1.19 (d, J = 6.6 Hz, 12H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 169.8, 145.0, 144.7, 144.5, 136.2, 136.0, 135.8, 135.7, 132.3, 132.3, 132.2, 131.1, 130.9, 129.9, 129.0, 128.9, 128.9, 127.9, 127.9, 127.7, 126.6, 124.6, 124.5, 124.1, 120.9, 120.8, 120.5, 90.4, 90.3, 90.0, 89.6, 89.4, 89.3, 73.7, 73.6, 72.0, 70.9, 70.6, 68.4, 68.4, 68.3, 59.1, 56.6, 56.6, 56.5, 17.7, 17.6, 17.6. HRMS (ESI^+) m/z calcd for $C_{90}H_{102}N_4NaO_{16}$ $[M + Na]^+$ 1517.7183, found 1517.7152.

*The trimer derivative **54b***. **43b** (329 mg, 0.58 mmol), $Pd(PPh_3)_2Cl_2$ (20.3 mg, 5 mol%), triphenylphosphine (15.2 mg, 10 mol%), CuI (11.2 mg, 10 mol%), and acetonitrile (3 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (117.4 mg, 2.0 equiv) in acetonitrile (1 mL) and **53b** (639 mg, 1.0 equiv) in acetonitrile (3 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **54b** (606 mg, 68%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.33–7.22 (m, 23H), 7.16 (t, J = 7.8 Hz, 2H), 7.09 (m, 6H), 7.05 (d, J = 8.4 Hz, 2H), 4.07 (m, 8H), 3.75 (m, 8H), 3.61 (m, 24H), 3.53 (m, 8H), 3.36 (m, 12H), 0.21 (s, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.1, 144.0, 135.9, 135.7, 135.6, 135.6, 132.8, 132.5, 132.4, 132.3, 131.1, 131.1, 130.0, 129.0, 129.0, 129.0, 128.9, 128.0, 127.8, 127.8, 127.6, 124.6, 124.6, 124.5, 121.4, 121.1, 121.1, 120.8, 104.2, 95.3, 90.4, 90.2, 90.2, 89.6, 89.6, 89.4, 72.0, 70.7, 70.7, 70.4, 70.4, 68.3, 68.2, 59.2, 50.7, 50.6, 50.6, 50.5, 0.0. HRMS (ESI^+) m/z calcd for

$C_{91}H_{102}N_4NaO_{16}Si$ $[M+ Na]^+$ 1557.6952, found 1557.6995.

The trimer derivative ***54c***. **43c** (380 mg, 0.65 mmol), $Pd(PPh_3)_2Cl_2$ (23.3 mg, 5 mol%), triphenylphosphine (17.0 mg, 10 mol%), CuI (12.4 mg, 10 mol%), and acetonitrile (2 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (0.20 mL, 2.0 equiv) and **53c** (740 mg, 1.0 equiv) in acetonitrile (6 mL) was added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **54c** (776 mg, 75%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.23 (m, 22H), 7.16–7.08 (m, 11H), 4.10 (br, 4H), 3.92 (br, 4H), 3.73–3.50 (m, 36H), 3.35 (m, 12H), 1.20 (m, 12H), 0.21 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 144.7, 144.7, 136.1, 135.9, 135.8, 132.7, 132.4, 132.3, 132.2, 132.1, 131.1, 131.1, 130.0, 129,0, 129.0, 129.0, 128.9, 128.7, 128.6, 128.0, 127.7, 127.6, 124.7, 124.5, 121.2, 120.9, 120.6, 104.3, 90.5, 90.3, 90.3, 89.5, 89.3, 73.8, 73.7, 72.1, 70.9, 70.6, 68.4, 68.4, 59.2, 56.7, 56.6, 56.5, 17.7, 17.7, 0.0. HRMS (ESI^+) m/z calcd for $C_{95}H_{110}N_4NaO_{16}Si$ $[M + Na]^+$ 1613.7578, found 1613.7577.

The trimer derivative ***55b***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.4 mL, 0.4 mmol) was added to a stirred solution of **54b** (592 mg, 0.39 mmol) in THF (4 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **55b** as a yellow oil (503 mg, 89%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.22 (m, 22H), 7.15 (t, J = 7.8 Hz, 2H), 7.10–7.08 (m, 8H), 4.08 (m, 8H), 3.77 (m, 8H), 3.61 (m, 24H), 3.53 (m, 8H), 3.36 (m, 12H), 3.06 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.2, 135.9, 135.7, 135.6, 133.1, 133.0, 132.5, 132.3, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.7, 124.6, 124.6, 124.6, 121.1, 120.8, 120.4, 90.4, 90.3, 90.2, 89.6, 89.4, 82.9, 78.2, 72.0, 70.7, 70.7, 70.5, 68.3, 68.3, 59.2, 50.6, 50.6. HRMS (ESI^+) m/z calcd for $C_{88}H_{94}N_4NaO_{16}$ $[M + Na]^+$ 1485.6563, found 1485.6546.

The trimer derivative ***55c***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.5 mL, 0.5 mmol) was added to a stirred solution of **54c** (767.7 mg, 0.48 mmol) in THF (5 mL) at room temperature. After stirred at room temperature for 2 h, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **55c** as a yellow

oil (625.6 mg, 85%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.22 (m, 23H), 7.17–7.12 (m, 10H), 4.11 (br, 4H), 3.95 (br, 4H), 3.73–3.50 (m, 36H), 3.35 (m, 12H), 3.05 (s, 1H), 1.20 (m, 12H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.1, 135.8, 135.8, 132,9, 132.4, 132.3, 131.1, 130.0, 129.0, 129.0, 128.9, 128.0, 127.7, 127.7, 124.6, 124.6, 124.6, 120.9, 120.6, 120.1, 90.5, 90.3, 89.5, 89.5, 89.3, 82.9, 78.1, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 68.4, 59.2, 56.7, 56.6, 17.7, 17.7. HRMS (ESI$^+$) m/z calcd for $C_{92}H_{102}N_4NaO_{16}$ $[M + Na]^+$ 1541.7183, found 1541.7136.

*The tetramer **9b***. **49b** (24.4 mg, 50 μmol), $Pd(PPh_3)_2Cl_2$ (1.8 mg, 5 mol%), triphenylphosphine (1.3 mg, 10 mol%), CuI (1.0 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (10.1 mg, 2.0 equiv) in acetonitrile (1 mL) and **55b** (73.2 mg, 50 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **9b** (61.9 mg, 69%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.08 (m, 42H), 4.08 (br, 10H), 3.75 (br, 10H), 3.60 (br, 30H), 3.53 (m, 10H), 3.56 (m, 15H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 169.8, 144.3, 144.0, 143.7, 136.0, 135.8, 135.6, 135.6, 132.4, 132.4, 131.1, 131.0, 130.0, 129.3, 129.0, 128.9, 128.9, 128.0, 127.8, 126.9, 124.6, 124.6, 124,2, 124.2, 121.1, 120.9, 90.4, 90.2, 90.0, 89.7, 89.6, 89.4, 72.0, 70.6, 70.6, 70.6, 70.4, 70.3, 68.3, 68.2, 68.1, 59.2, 50.6, 50.6, 50.5, 50.4. HRMS (ESI$^+$) m/z calcd for $C_{108}H_{117}N_5NaO_{20}$ $[M + Na]^+$ 1826.8184, found 1826.8201.

*The tetramer **9c***. **49c** (33.6 mg, 70 μmol), $Pd(PPh_3)_2Cl_2$ (2.5 mg, 5 mol%), triphenylphosphine (1.8 mg, 10 mol%), CuI (1.3 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (16.2 mg, 2.3 equiv) in acetonitrile (1 mL) and **55c** (106.4 mg, 70 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative TLC (silica gel, ethyl acetate/methanol = 10/1) to give **9c** (87.5 mg, 67%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.22 (m, 27H), 7.16–7.11 (m, 15H), 4.10 (br, 5H), 3.94 (br, 5H), 3.73–3.49 (m, 45H), 3.34 (m, 15H), 1.19 (d, J = 6.6 Hz, 15H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 169.9, 145.1, 144.8, 136.2, 136.1, 135.8, 135.8, 132.3, 132.2, 131.1, 131.0, 129.9, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 126.6, 124.6, 124.6, 124.2, 120.9, 120.8, 120.6, 90.5, 90.3, 90.3, 90.1, 89.6, 89.5, 89.3, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 68.3, 59.2,

56.7, 56.7, 56.6, 56.6, 56.5, 17.7, 17.7, 17.6. HRMS (ESI^+) m/z calcd for $C_{113}H_{127}N_5NaO_{20}$ $[M + Na]^+$ 1896.8967, found 1896.8966.

*The tetramer derivative **56b***. **43b** (160.5 mg, 0.28 mmol), $Pd(PPh_3)_2Cl_2$ (10.2 mg, 5 mol%), triphenylphosphine (7.6 mg, 10 mol%), CuI (5.5 mg, 10 mol%), and acetonitrile (3 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (59.3 mg, 2.1 equiv) in acetonitrile (1 mL) and **55b** (415.3 mg, 1.0 equiv) in acetonitrile (2 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **56b** (435.2 mg, 81%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.31–7.22 (m, 29H), 7.16 (t, J = 7.2 Hz, 2H), 7.11 (m, 8H), 7.05 (d, J = 8.4 Hz, 2H), 4.08 (m , 10H), 3.76 (m, 10H), 3.61 (m, 30H), 3.53 (m, 10H), 3.37 (m, 15H), 0.21 (s, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.2, 135.9, 135.7, 135.7, 133.1, 132.8, 132.5, 132.3, 131.1, 131.1, 131.0, 130.0, 129.0, 120.0, 128.9, 128.0, 127.8, 127.6, 124.6, 124.5, 121.4, 121.1, 120.8, 104.2, 95.3, 90.4, 90.2, 89.6, 89.6, 89.6, 89.4, 72.0, 70.7, 70.7, 70.5, 68.3, 68.3, 59.2, 50.7, 50.6, 50.6, 50.5, 0.0. HRMS (ESI^+) m/z calcd for $C_{113}H_{125}N_5NaO_{20}Si$ $[M + Na]^+$ 1922.8579, found 1922.8529.

*The tetramer derivative **56c***. **43c** (191.2 mg, 0.33 mmol), $Pd(PPh_3)_2Cl_2$ (11.6 mg, 5 mol%), triphenylphosphine (8.7 mg, 10 mol%), CuI (6.3 mg, 10 mol%), and acetonitrile (2 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (67.5 mg, 2.0 equiv) in acetonitrile (1 mL) and **55c** (494.0 mg, 1.0 equiv) in acetonitrile (2 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **56c** (496.1 mg, 77%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.30–7.20 (m, 28H), 7.14–7.05 (m, 13H), 4.09 (br, 5H), 3.92 (br, 5H), 3.71–3.48 (m, 45H), 3.33 (m, 15H), 1.18 (m, 15H), 0.19 (s, 9H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.7, 136.1, 135.8, 135.8, 135.8, 133.2, 132.7, 132.3, 132.2, 131.1, 131.1, 129.9, 129.0, 129.0, 128.9, 128.0, 127.7, 127.5, 124.6, 124.6, 124.5, 121.1, 120.9, 120.8, 120.5, 104.3, 95.3, 90.5, 90.3, 90.3, 90.3, 89.5, 89.5, 89.4, 89.3, 73.8, 73.7, 73.6, 72.0, 70.9, 70.6, 68.4, 68.4, 68.4, 59.2, 56.7, 56.7, 56.6, 56.5, 17.7, 17.6, 0.0. HRMS (ESI^+) m/z calcd for $C_{118}H_{135}N_5NaO_{20}Si$ $[M + Na]^+$ 1992.9362, found 1992.9314.

*The tetramer derivative **57b***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.25 mL, 0.25 mmol) was added to a stirred solution of **56b** (425 mg, 0.22 mmol) in THF (4 mL) at room temperature. After stirred at room temperature for 15 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **57b** as a yellow oil (216 mg, 53%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.21 (m, 29H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.09-7.07 (m, 10H), 4.07 (m, 10H), 3.75 (m, 10H), 3.61 (m, 30H), 3.52 (m, 10H), 3.35 (m, 15H), 3.06 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.5, 169.7, 144.3, 144.0, 135.8, 135.6, 133.0, 132.9, 132.4, 132.2, 131.0, 130.6, 129.9, 128.9, 128.9, 128.8, 127.9, 127.7, 127.7, 124.5, 124.5, 124.4, 121.0, 120.7, 120.3, 90.3, 90.2, 89.5, 89.3, 82.7, 78.1, 71.9, 70.6, 70.6, 70.3, 68.2, 68.2, 59.1, 50.5, 50.4. HRMS (ESI$^+$) m/z calcd for $C_{110}H_{117}N_5NaO_{20}$ $[M + Na]^+$ 1850.8184, found 1850.8207.

*The tetramer derivative **57c***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.3 mL, 0.3 mmol) was added to a stirred solution of **56c** (483.1 g, 0.25 mmol) in THF (3 mL) at room temperature. After stirred at room temperature for 15 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 10/10/1) to give **57c** as a yellow oil (356.0 mg, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.21 (m, 29H), 7.16–7.12 (m, 12H), 4.10 (br, 5H), 3.94 (br, 5H), 3.73–3.56 (m, 45H), 3.34 (m, 15H), 3.05 (s, 1H), 1.19 (m, 15H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 145.0, 144.7, 136.0, 135.7, 133.1, 132.8, 132.3, 132.2, 131.0, 129.9, 128.9, 128.8, 127.9, 127.6, 127.6, 124.7, 124.5, 124.5, 124.5, 120.8, 120.5, 120.0, 90.4, 90.3, 89.4, 89.4, 89.2, 82.8, 78.0, 73.7, 73.6, 71.9, 70.8, 70.5, 68.3, 68.3, 68.3, 59.1, 56.6, 56.6, 56.5, 17.6, 17.6. HRMS (ESI$^+$) m/z calcd for $C_{115}H_{127}N_5NaO_{20}$ $[M + Na]^+$ 1920.8967, found 1920.8920.

*The pentamer **10b***. **49b** (9.4 mg, 20 μmol), $Pd(PPh_3)_2Cl_2$ (0.7 mg, 5 mol%), triphenylphosphine (0.5 mg, 10 mol%), CuI (0.4 mg, 10 mol%) and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (7.2 mg, 3.5 equiv) in acetonitrile (1 mL) and **57b** (36.6 mg, 20 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature for 9 h. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative TLC (silica gel, ethyl acetate/methanol = 10/1) to give **10b** (17.0 mg, 39%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.07 (m, 50H), 4.08 (m, 12H), 3.75 (m, 12H), 3.61 (m, 36H), 3.53 (m, 12H), 3.36 (m, 18H); ^{13}C{^{1}H} NMR (151 MHz,

$CDCl_3$) δ 170.7, 170.0, 169.9, 169.8, 144.3, 144.0, 136.0, 135.8, 135.6, 133.1, 132.5, 132.4, 131.1, 131.0, 130.0, 129.2, 129.0, 128.9, 128.9, 128.0, 127.8, 126.9, 124.6, 124.2, 121.2, 121.1, 120.9, 90.4, 90.3, 90.0, 89.7, 89.6, 89.4, 72.0, 70.6, 70.6, 70.6, 70.4, 70.3, 68.3, 68.3, 68.1, 59.2, 50.6, 50.6, 50.5, 50.4. HRMS (ESI^+) m/z calcd for $C_{130}H_{140}N_6NaO_{24}$ $[M + Na]^+$ 2191.9811, found 2191.9821.

*The pentamer **10c***. **49c** (14.5 mg, 30 μmol), $Pd(PPh_3)_2Cl_2$ (1.1 mg, 5 mol%), triphenylphosphine (0.8 mg, 10 mol%), CuI (0.6 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (6.5 mg, 2.1 equiv) in acetonitrile (1 mL) and **57c** (57.9 mg, 30 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by recycle GPC to give **10c** (42.0 mg, 61%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.30–7.21 (m, 32H), 7.17–7.11 (m, 18H), 4.09 (br, 6H), 3.94 (br, 6H), 3.75–3.49 (m, 54H), 3.34 (m, 18H), 1.19 (d, J = 5.4 Hz, 18H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 170.0, 169.9, 145.1, 144.7, 136.2, 136.1, 135.8, 132.3, 132.2, 131.1, 131.0, 129.9, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 126.6, 124.6, 124.6, 124.2, 120.9, 120.8, 120.6, 90.5, 90.3, 90.3, 90.1, 89.6, 89.5, 89.3, 73.8, 74.6, 70.9, 70.6, 68.4, 68.4, 68.3, 59.2, 56.7, 56.6, 56.6, 56.5, 17.7, 17.6. HRMS (ESI^+) m/z calcd for $C_{136}H_{152}N_6NaO_{24}$ $[M + Na]^+$ 2276.0750, found 2276.0744.

*The pentamer derivative **58b***. **43b** (54.3 mg, 98 μmol), $Pd(PPh_3)_2Cl_2$ (3.4 mg, 5 mol%), triphenylphosphine (2.5 mg, 10 mol%), CuI (1.8 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (19.5 mg, 2.0 equiv) in acetonitrile (1 mL) and **57b** (174.8 mg, 1.0 equiv) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **58b** (159.7 mg, 74%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.32–7.20 (m, 35H), 7.14 (t, J = 7.8 Hz, 2H), 7.08 (m, 10H), 7.04 (d, J = 8.4 Hz, 2H), 4.06 (m, 12H), 3.75 (m, 12H), 3.60 (m, 36H), 3.52 (m, 12H), 3.35 (m, 18H), 0.20 (s, 9 H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.1, 135.9, 135.7, 135.7, 132.8, 132.5, 132.4, 132.1, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.6, 124.6, 124.5, 121.4, 121.1, 120.8, 104.2, 95.3, 90.4, 90.3, 90.2, 89.6, 89.4, 72.0, 70.7, 70.7, 70.5, 68.3, 68.3, 59.2, 50.7, 50.6, 50.6, 50.5, 0.0. HRMS (ESI^+) m/z calcd for $C_{135}H_{148}N_6NaO_{24}Si$ $[M + Na]^+$ 2288.0206, found 2288.0178.

*The pentamer derivative **58c***. **43c** (86.9mg, 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (5.3 mg, 5 mol%), triphenylphosphine (3.9 mg, 10 mol%), CuI (2.8 mg, 10 mol%), and acetonitrile (2 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (30.4 mg, 2.0 equiv) in acetonitrile (1 mL) and **57c** (286.6 mg, 1.0 equiv) in acetonitrile (2 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **58c** (275.1 mg, 78%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.21 (m, 34H), 7.15–7.07 (m, 15H), 4.10 (br, 6H), 3.92 (br, 6H), 3.74–3.49 (m, 54H), 3.34 (m, 18H), 1.19 (m, 18H), 0.20 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.1, 135.9, 135.8, 133.2, 132.7, 132.4, 132.2, 131.1, 131.1, 130.0, 129.0, 129.0, 128.0, 127.7, 127.5, 124.6, 124.5, 121.1, 120.9, 120.6, 104.3, 95.1, 90.5, 90.3, 90.3, 89.5, 89.3, 73.8, 73.7, 73.7, 72.0, 80.9, 80.6, 68.4, 68.4, 68.4, 59.2, 56.7, 56.7, 56.6, 56.5, 17.7, 17.6, 0.0. HRMS (ESI$^+$) m/z calcd for $C_{141}H_{160}N_6NaO_{24}Si$ $[M + Na]^+$ 2372.1145, found 2372.1126.

*The pentamer derivative **59b***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.1 mL, 0.1 mmol) was added to a stirred solution of **58b** (153.1 mg, 68 μmol) in THF (1.5 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by recycle GPC (chloroform) to give **59b** as a yellow oil (105.5 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32–7.21 (m, 35H), 7.15 (t, J = 7.8 Hz, 2H), 7.10–7.07 (m, 12H), 4.07 (m, 12H), 3.75 (m, 12H), 3.61 (m, 36H), 3.52 (m, 12H), 3.35 (m, 18H), 3.06 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.5, 169.7, 144.4, 144.1, 135.9, 135.6, 132.9, 132.4, 132.3, 131.1, 130.0, 129.0, 128.9, 128.9, 128.0, 127.8, 127.7, 124.6, 124.5, 124.5, 121.1, 120.8, 120.4, 90.4, 90.2, 89.6, 89.4, 82.8, 78.2, 72.0, 70.7, 70.6, 70.4, 68.3, 68.2, 59.2, 50.6, 50.6, 50.5. HRMS (ESI$^+$) m/z calcd for $C_{132}H_{140}N_6NaO_{24}$ $[M + Na]^+$ 2215.9811, found 2215.9751.

*The pentamer derivative **59c***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.15 mL, 0.15 mmol) was added to a stirred solution of **58c** (265.1 mg, 0.11 mmol) in THF (3 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **59c** as a yellow oil (195.0 mg, 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.21 (m, 34H), 7.17–7.12 (m, 15H), 4.11 (br, 6H), 3.94 (br, 6H), 3.74–3.49 (m, 54H), 3.34 (m, 18H), 3.05 (s, 1H),

1.19 (m, 18H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.1, 135.8, 132.9, 132.4, 132.2, 131.1, 129.9, 129.0, 128.9, 128.0, 127.7, 127.7, 124.6, 124.5, 120.9, 120.6, 120.1, 90.5, 90.4, 89.5, 89.3, 82.9, 78.1, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 59.2, 56.7, 56.6, 56.6, 17.7, 17.6. HRMS (ESI^+) m/z calcd for $C_{138}H_{152}N_6NaO_{24}$ $[M + Na]^+$ 2300.0750, found 2300.0700.

*The hexamer **11b***. **49b** (8.0 mg, 17 μmol), $Pd(PPh_3)_2Cl_2$ (0.6 mg, 5 mol%), triphenylphosphine (0.5 mg, 10 mol%), CuI (0.4 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (9.8 mg, 6 equiv) in acetonitrile (1 mL) and **59b** (34.6 mg, 16 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative TLC (silica gel, ethyl acetate/methanol = 10/1) to give **11b** (18.1 mg, 45%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.31–7.07 (m, 58H), 4.07 (m, 14H), 3.76 (m, 14H), 3.62 (m, 42H), 3.52 (m, 14H), 3.35 (m, 21H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 170.6, 169.9, 169.8, 144.5, 144.2, 136.1, 136.0, 135.7, 135.7, 132.5, 132.4, 131.1, 131.0, 130.0, 129.2, 129.0, 128.9, 128.9, 128.0, 128.0, 127.8, 126.9, 124.6, 124.6, 124.2, 124.2, 121.2, 121.2, 120.9, 90.4, 90.3, 90.0, 89.8, 89.6, 89.4, 72.1, 70.7, 70.7, 70.5, 70.4, 68.4, 68.3, 68.2, 59.2, 50.7, 50.7, 50.6, 50.5. HRMS (ESI^+) m/z calcd for $C_{152}H_{163}N_7NaO_{28}$ $[M + Na]^+$ 2557.1438, found 2557.1429.

*The hexamer **11c***. **49c** (14.7 mg, 30 μmol), $Pd(PPh_3)_2Cl_2$ (1.1 mg, 5 mol%), triphenylphosphine (0.8 mg, 10 mol%), CuI (0.6 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (9.3 mg, 3.1 equiv) in acetonitrile (1 mL) and **59c** (68.3 mg, 30 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative TLC (silica gel, ethyl acetate/methanol = 10/1) to give **11c** (32.8 mg, 42%) as a pale yellow oil; ^1H NMR (600 MHz, $CDCl_3$) δ 7.29–7.21 (m, 39H), 7.18–7.10 (m, 19H), 4.10 (br, 7H), 3.94 (br, 7H), 3.75–3.49 (m, 63H), 3.34 (m, 21H), 1.19 (m, 21H); $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.2, 136.1, 135.8, 132.4, 132.2, 131.1, 131.0, 130.0, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 126.6, 124.6, 124.2, 120.9, 120.9, 120.6, 90.5, 90.3, 90.1, 89.6, 89.5, 89.3, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 68.3, 59.2, 56.7, 56.6, 56.5, 17.6. HRMS (ESI^+) m/z calcd for $C_{159}H_{177}N_7NaO_{28}$ $[M + Na]^+$ 2655.2534, found 2655.2526.

*The hexamer derivative **60b***. **43b** (15.0 mg, 0.27 mmol), $Pd(PPh_3)_2Cl_2$ (0.9 mg, 5

mol%), triphenylphosphine (0.7 mg, 10 mol%), CuI (0.5 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (5.2 mL 2.0 equiv) in acetonitrile (1 mL) and **59b** (58.0 mg, 1.0 equiv) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **60b** (39.7 mg, 57%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.23 (m, 39H), 7.15 (t, *J* = 7.2 Hz, 4H), 7.09 (m, 12H), 7.05 (d, *J* = 8.4 Hz, 2H), 4.08 (m, 14H), 3.76 (m, 14H), 3.62 (m, 42H), 3.52 (m, 14H), 3.36 (m, 21H), 0.21 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.7, 144.5, 144.1, 136.0, 135.8, 135.7, 132.8, 132.4, 132.3, 131.1, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.6, 124.6, 124.5, 121.4, 121.1, 120.8, 104.2, 95.3, 90.4, 90.3, 90.2, 89.6, 89.4, 72.0, 70.7, 70.7, 70.5, 68.4, 68.3, 59.2, 50.7, 50.6, 50.5, 0.0. HRMS (ESI$^+$) m/z calcd for $C_{157}H_{171}N_7NaO_{28}Si$ $[M + Na]^+$ 2653.1834, found 2653.1801.

*The hexamer derivative **60c***. **43c** (34.8 mg, 0.06 mmol), $Pd(PPh_3)_2Cl_2$ (2.1 mg, 5 mol%), triphenylphosphine (1.6 mg, 10 mol%), CuI (1.1 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (12.1 mg 2.0 equiv) in acetonitrile (1 mL) and **59c** (137.7 mg, 1.0 equiv) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by silica gel column chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **60c** (135.9 mg, 82%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.21 (m, 40H), 7.17–7.08 (m, 17H), 4.11 (br, 7H), 3.92 (br, 7H), 3.74–3.50 (m, 63H), 3.34 (m, 21H), 1.19 (m, 21H), 0.21 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.8, 136.1, 135.9, 135.8, 133.2, 132.7, 132.4, 132.2, 131.1, 131.1, 130.0, 129.0, 129.0, 128.9, 128.0, 127.7, 127.6, 124.6, 124.5, 121.2, 120.9, 120.6, 104.3, 95.1, 90.5, 90.3, 90.3, 89.5, 89.3, 73.8, 73.7, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 59.2, 56.7, 56.6, 56.5, 17.7, 17.6, 0.0. HRMS (ESI$^+$) m/z calcd for $C_{164}H_{185}N_7NaO_{28}Si$ $[M + Na]^+$ 2751.2929, found 2751.2900.

*The hexamer derivative **61b***. A 1.0 M solution of tetrabutylammonium fluoride in THF (14.5 mg, 0.016 mmol) was added to a stirred solution of **60b** (37.7 mg, 0.014 mmol) in THF (1.5 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column

chromatography (ethyl acetate/chloroform/methanol = 5/5/1) to give **61b** as a yellow oil (28.9 mg, 79%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31–7.21 (m, 41H), 7.14 (t, J = 7.8 Hz, 2H), 7.07 (m, 14H), 4.07 (m, 14H), 3.75 (m, 14H), 3.60 (m, 42H), 3.52 (m, 14H), 3.35 (m, 21H), 3.05 (s, 1H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.5, 144.1, 135.9, 135.7, 133.4, 133.0, 132.5, 132.3, 131.1, 130.0, 129.0, 128.9, 128.0, 127.8, 127.8, 124.6, 121.1, 120.8, 120.4, 90.4, 90.3, 89.6, 89.4, 82.8, 78.2, 72.0, 70.7, 70.7, 70.4, 68.3, 68.3, 59.2, 50.7, 50.6, 50.6. HRMS (ESI$^+$) m/z calcd for $C_{154}H_{163}N_7NaO_{28}$ $[M + Na]^+$ 2581.1438, found 2581.1402.

*The hexamer derivative **61c***. A 1.0 M solution of tetrabutylammonium fluoride in THF (0.1 mL, 0.1 mmol) was added to a stirred solution of **60c** (129.5 mg, 0.047 mmol) in THF (1.5 mL) at room temperature. After stirred at room temperature for 10 min, the mixture was diluted with ethyl acetate, washed with water three times and brine, and dried over $MgSO_4$. The crude product was purified by silica gel column chromatography (ethyl acetate/methanol = 10/1) to give **61c** as a yellow oil (61.2 mg, 49%); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.21 (m, 41H), 7.16–7.11 (m, 16H), 4.10 (br, 7H), 3.92 (br, 7H), 3.73–3.49 (m, 63H), 3.33 (m, 21H), 3.05 (s, 1H), 1.18 (m, 21H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.0, 144.7, 136.0, 135.8, 133.2, 132.8, 132.3, 132.2, 131.1, 129.9, 129.0, 128.9, 128.0, 127.7, 127.7, 124.6, 124.5, 120.8, 120.6, 120.1, 90.5, 90.3, 89.5, 89.3, 82.9, 78.1, 73.8, 73.7, 72.0, 70.9, 70.6, 68.4, 68.4, 59.2, 56.7, 56.6, 56.6, 17.7, 17.6. HRMS (ESI$^+$) m/z calcd for $C_{161}H_{177}N_7NaO_{28}$ $[M + Na]^+$ 2679.2534, found 2679.2560.

*The heptamer **12b***. **49b** (5.4 mg, 12 μmol), $Pd(PPh_3)_2Cl_2$ (0.4 mg, 5 mol%), triphenylphosphine (0.3 mg, 10 mol%), CuI (0.3 mg, 15 mol%), and acetonitrile (3 drops) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature. Et_3N (5.8 mg, 5.2 equiv) in acetonitrile (0.5 mL) and **61b** (28.9 mg, 11 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by recycle GPC (chloroform) to give **12b** (8.1 mg, 25%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24–7.07 (m, 66H), 4.07 (m, 16H), 3.76 (m, 16H), 3.60 (m, 48H), 3.52 (m, 16H), 3.35 (m, 24H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 170.6, 169.8, 144.2, 136.1, 135.9, 135.7, 132.5, 132.3, 131.1, 131.0, 130.0, 129.2, 129.0, 128.9, 128.9, 128.7, 128.6, 128.0, 127.8, 126.9, 124.6, 124.2, 121.1, 120.8, 90.4, 90.3, 90.0, 89.7, 89.6, 89.4, 72.0, 70.7, 70.7, 70.5, 70.4, 68.3, 68.3, 68.1, 59.2, 50.7, 50.6, 50.4. HRMS (ESI$^+$) m/z calcd for $C_{174}H_{186}N_8NaO_{32}$ $[M + Na]^+$ 2922.3065, found 2922.3048.

The heptamer ***12c***. **49c** (10.2 mg, 21 μmol), $Pd(PPh_3)_2Cl_2$ (0.7 mg, 5 mol%), triphenylphosphine (0.6 mg, 10 mol%), CuI (0.4 mg, 10 mol%), and acetonitrile (1 mL) were placed in a two-neck round bottom flask. Then, vacuum was applied, which was cancelled with argon (five times). Into the stirred mixture at room temperature, Et_3N (9.3 mg, 4.4 equiv) in acetonitrile (1 mL) and **61c** (55.9 mg, 21 μmol) in acetonitrile (1 mL) were added, and the mixture was stirred at room temperature overnight. The reaction mixture was filtered and the solvent was removed *in vacuo*. The residue was purified by preparative TLC (silica gel, ethyl acetate/methanol = 10/1) to give **12c** (22.1 mg, 35%) as a pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30–7.11 (m, 66H), 4.10 (br, 8H), 3.93 (br, 8H), 3.72–3.49 (m, 72H), 3.34 (m, 24H), 1.19 (m, 24); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 170.7, 169.9, 145.1, 144.7, 136.2, 136.1, 135.8, 135.8, 132.4, 132.2, 132.2, 131.1, 131.0, 130.0, 129.1, 129.0, 128.9, 128.7, 128.6, 128.0, 127.9, 127.7, 126.6, 124.6, 124.2, 120.9, 120.9, 120.6, 90.5, 90.3, 90.1, 89.6, 89.5, 89.3, 73.8, 73.7, 72.1, 70.9, 70.6, 68.4, 68.3, 59.2, 56.7, 56.6, 56.5, 17.6. HRMS (ESI^+) m/z calcd for $C_{182}H_{202}N_8NaO_{32}$ $[M + Na]^+$ 3034.4317, found 3034.4345.

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Supporting Information

Synthetic schemes, CD and UV spectra of polymers and oligomers, crystallographic data of compounds **6a** and **13**, ^{1}H NMR spectra of oligomers, Cartesian coordinates of compounds **6a**, **8a**, **10a**, and **12a**, ^{1}H and ^{13}C NMR spectra of new compounds, and ^{1}H NMR spectra of known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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