A dualistic arrangement of a chiral [1]rotaxane based on the assembly of two rings and two rods

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**ABSTRACT:** We demonstrate the synthesis and chiroptical properties of doubled molecules of a chiral [1]rotaxane, based on the assembly of an achiral ring of phenylacetylene macrocycle (6PAM) and a *p*-phenylene ethynylene rod. Two molecules of [1]rotaxane constituted the doubled molecule through the ring-fusion of 6PAMs to a 10PAM, which assured stationary occupation relative to each optically active unit. Absorption properties of the 10PAM-based doubled molecule and 6PAM-based original unit were consistently characterized by the independent existence of *m*-phenylene ethynylene ring(s) and *p*-phenylene ethynylene rod(s). Thus, molar circular dichroisms (CDs) were directly compared between the doubled molecule (*n* = 2) and the original unit (*n* = 1) to show that molar CDs were increased more than expected by an increase in the number of units, or by an increase in absorbance. Due to the invariance of configuration and the relative occupation of two units arranged adjacent to each other in 10PAM, one more comparison was available with an isomeric molecule of two rings and two rods in a threaded-and-unthreaded form. The additional arrangement of an optically inactive unit in an unthreaded form also led to an increase in molar CDs, compared to the original chiral unit in a threaded form.

**INTRODUCTION**

Chirality is generated through the assembly of achiral elements and so a huge variety of chiral forms have been presented.1 As an approach to considering the molecular chiroptical activity, various oligomeric molecules based on the repetition of an optically active unit have been investigated to reveal how the overall chiroptical activity of such oligomers is related to the original activity of the chiral unit itself.2-14 Some dendrimers3 have revealed a significant change in the molar optical rotation per chiral subunit as the dendrimer size increased, while the magnitude of the Cotton effect was proportional to the number of chromophores.4 In other cases with doubled molecules,5-10 a chiral nanoribbon based on a double-hexahelicene showed a substantial increase in molar circular dichroism (CD) and its dissymmetry relative to a smaller helical analogue.6 For two hexahelicenes aligned in a different configuration, each exhibited a more than two-fold increase in the intensity of molar CD and polarized luminescence, compared to the monomeric hexahelicene.7 A similar amplification of chiroptical activity has been reported with helically-folded secondary structures induced for some linear-chained oligomers of a binaphthyl11 or allene12 unit. Apart from these reports concerning chiral amplification in a three-dimensional arrangement, studies on linearly aligned binaphthyl-based oligomers exhibited that molar optical rotations and molar CDs increased steadily from the monomer to the tetramer, and reached a plateau due to the rotational freedom between units.13 Alternatively, there was little correlation between the molar optical rotation and the number of chiral units when the chiral units were arranged in a cyclic array.14 Crucial points for a comparison of the overall activities of oligomeric molecules to those of the original monomeric unit include (i) a stable configuration around a chiral element, (ii) restricted rotation between units, and (iii) invariant properties of the original unit. In light of this, we were interested in doubled molecules that consist of achiral rings and rods, where a chiral or achiral space was established adjascent to an optically active unit.

We assumed the arrangement of achiral component elements by using two molecules of optically active and/or inactive units based on the assembly of an achiral ring of phenylacetylene macrocycle (PAM)15-19 and an achiral phenylacetylene rod; these achiral elements are doubly bridged to form a molecular unit with or without a mechanical bond (Scheme 1). The configuration of the chiral unit was assured with a suitable ring, rod and bridge (i).20 A doubled form with homochirality could be envisioned by ring fusion of either of the two enantiomeric units. The relative occupation of each unit would be assured in this dualistic arrangement (ii). Ring fusion at the side of 6PAM led to a slight change in 1,3-diethynylphenyl to 1,3,5-triethynylphenyl in 10PAM, which did not originally exist in the unit. Electronic perturbation would not be so great with the additional ethynylene linkage at the 5-position.21 Absorption properties of the original unit (*n* = 1) were based on the coexistence of a ring (*m*-phenylene ethynylenes) and rod (*p*-phenylene ethynylenes), which would remain in the doubled form (*n* = 2) if the fused bicyclic 10PAM could be similar in profile to the original 6PAM (iii).

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**SCHEME 1.** Dualistic arrangements of optically active and/or inactive units through ring fusion.

For the synthesis of these chiral molecules based on 10PAM, we adopted a double ring-closing strategy (Scheme 2). This intramolecular reaction (PAM formation) would produce a mixture of rotational isomers with or without a mechanical bond between the ring and rod that are bridged by covalent bonds. Through the two-fold reaction, homochiral (threaded-and-threaded) form **1** and chiral (threaded-and-unthreaded) form **2** would be generated as racemates, in addition to optically-inactive species (**3** and **4**). In this article, we describe below the synthesis and characterization of four isomers and chiroptical properties of **1** and **2** based on bicyclic 10PAM (**6**) and two rods (**7**) through comparisons of molar CDs as well as molar optical rotations with a chiral (**8**) or achiral (**9**) monomeric unit based on 6PAM (**10**) and one rod (**7**).

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**SCHEME 2.** Abbreviated structures of **1**-**4**, chemical structure of ring-closing precursor **5**, and synthetic strategy based on double ring-closing reactions. Only one enantiomer is depicted for clarity.

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**Chart 1.** Chemical structures of achiral component elements **6** (10PAM), **7**20 (rod) and **10**20 (6PAM), and monomeric references **8**20 and **9**20. The absolute configuration of optically-resolved enantiomers of **1**, **2**, and **8** remains undecided.

**RESULTS AND DISCUSSION**

**Synthesis and characterization of 1-4.** As expected, four isomers (two racemates and two optically inactive species) were obtained in one reaction of the achiral double ring-closing precursor (Scheme 2). These four isomers have identical component elements (C190H146N8O8) of hydrocarbons and amide groups, and were successfully separated by HPLC techniques (Charts S1-S2 in the supporting information).

Ring-closing precursor **5** is composed of a branched *m*-phenylene ethynylene chain and *p*-phenylene ethynylene rod, which were bound in advance with a two-fold terephthaloyl bridge (Scheme 3). The precursor **5** was prepared in steps of Sonogashira coupling reactions by starting with diphenylacetylene **13**,22,23 on which bromo and iodo substituents were placed to be same in the molecular symmetry as that of **5**. A mixture of four species was obtained by the intramolecular double ring-closing reactions of the *α*-iodo-*ω*-ethynyl sequences16 through Sonogashira coupling under pseudo-high dilution conditions. Separation was implemented based mainly on the difference in molecular polarity, which would stem from amide dipoles in the bridge (*R*f value on SiO2 decreased for **1**, **2**~**3**, and **4** in this order). By HPLC separation with a chiral stationary column, racemate (±)-**1** was optically resolved to give (‒)-**1** (first fraction, [*α*]D = ‒752) and (+)-**1** (second fraction, [*α*]D = +760). (±)-**2** and **3** could not be separated due to close *R*f values on SiO2. Instead, a mixture was passed through the chiral stationary column same as above to give (‒)-**2** (first fraction, [*α*]D = ‒558), **3** (second fraction) and (+)-**2** (third fraction, [*α*]D = +562).

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**SCHEME 3.** Synthesis of **1**-**4**. Reagents and yields: (a) Pd(PPh3)4, CuI, THF, Et3N (81%); (b) **14**20, Pd(PPh3)4, CuI, THF, Et3N (86%); (c) trimethylsilylacetylene (TMSA), Pd(PPh3)4, CuI, THF, Et3N (77%); (d) i) K2CO3, MeOH, THF (95%), ii) 1,3-diiodobenzene, Pd(PPh3)4, CuI, THF, Et3N (70%); (e) tetra-*n*butylammonium fluoride (TBAF), THF (84%); (f) Pd(PPh3)4, CuI, THF, Et3N [12% for (±)-**1**, 9% for (±)-**2**, 2% for **3**, and 10% for **4**].

The mass spectra of each isolated isomer **1**-**4** showed an identical value (*m*/*z* = 2667). According to our knowledge regarding the assignment of threaded and unthreaded species based on 6PAM through 1H NMR spectroscopy,20 we could roughly but confidently assign an isomer to a threaded (**1**, **2** and **4**) or unthreaded (**3**) form according to the presence or absence of a distinctive downfield-shift for the central phenylene protons (Hc) in the rod (Figure 1). In the 13C NMR spectra of **1**, **2**, **4** and **8**, we obserbed downfield-shifts for acetylenic carbons close to the central phenylene ring in the rod (Figure 2). An isomer with a threaded-and-unthreaded form (**2**) could be ascertained by a half value for the integral for the downfield-shifted rod protons due to difference in the molecular symmetry, compared with **1** or **4**. Threaded-and-threaded forms of homochiral **1** and heterochiral **4** should not be assigned based solely on the 1H and 13C NMR spectra, although they had both similarities and differences from each other. Instead, the actual results of their passage through a chiral column were determinant. As a reference with two rings, bicyclic 10PAM (**6**) was synthesized with a corresponding double ring-closing precursor, which has no rod (Scheme S2 in the supporting information). Two amide groups in the bridge were replaced by BOC-protected nitrogen atoms arranged at the same positions on 10PAM, to attain the same symmetry and solubility of the hydrocarbon backbone.25

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**FIGURE 1.** Partial 1H NMR spectra (400 MHz) of (a) **1**, **4**, **6**, **7** and **8**; (b) **2**, **3**, **6**, **7** and **9**. All spectra were measured in CDCl3 at room temperature. Nonequivalent protons (six or twelve inner H, two or four HN, two Ho, the remaining outer protons, two or four Ha-c, and four or eight Ht) are not assigned.

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**FIGURE 2.** Partial 13C NMR spectra [100 MHz; (left) carbonyl carbons and (right) acetylenic carbons] of **1**, **4**, **8**, **2**, **3**, **9**, **6** (10PAM), **10** (6PAM) and **7** (rod), measured in CDCl3 at room temperature or at 313 K.

**Molecular structures in solution of 1-4.** By NMR and UV spectroscopy (Figures 1-3), we confirmed that each monomeric unit **8** or **9** continued to exist in doubled structures.

Since the molecular symmetry was changed in doubled structures of **1**-**4**, each end of the rod should be nonequivalent in **1**-**4**, while they were equivalent in the monomeric units **8** and **9** (Chart 1). This was distinctively confirmed by four or eight signals for amide carbons in the 13C NMR spectra of **1**-**4**, compared with two signals for **8** and **9** (Figure 2). Although this nonequivalence led to the differentiation of all inner and outer protons regarding half of the molecule, the chemical shifts were close to those of the original unit (Figure 1). It should be noted that the two nonequivalent central phenylene protons (Hc) of the rod in **1** were observed as an apparent singlet. To be exact, they were nonequivalent, and emerged as a pair of two doublet signals at lower temperatures (Figure S1A in the supporting information), and the average chemical shift (8.06 ppm at room temperature) for these two doublets was very close to the chemical shift for the corresponding singlet protons (8.07 ppm at room temperature) in **8**. This resemblance showed that the rod was allowed to accommodate in the cavity of 10PAM, as in the cavity of 6PAM. Similar resemblance in the chamical shift for acetylenic carbons close to the central phenylene ring in the rod (91.5 and 91.6 ppm for **1**, 91.7, 91.7, 90.4 and 90.4 ppm for **2**, 90.4 and 90.1 ppm for **3**, 91.6 and 91.6 ppm for **4**, compared with 91.5 ppm for **8** and 90.3 ppm for **9**) was also confirmed in the 13C NMR spectra (Figure 2). When the temperature was lowered (Figure S1 in the supporting information), rotation of *p*-phenylene groups, located in a narrow space between the rod and bridge, slowed while maintaining values of the chemical shift (Ha, Hb and Ht). Alternatively, several signals for ring protons (both inner and outer) showed a greater shift with a change in temperature. This can be explained by assuming interconversions among several nonplanar conformations of 10PAM in **1** and **2**, since similar changes in the chemical shift for the corresponding ring protons of **6** were observed (Figure S2B in the supporting information).

Regarding absorption properties, first we note that the spectral appearance was consistent with a single ring of 6 PAM (**10**) and fused rings of 10PAM (**6**) (Figure 3a and Table 1). In the UV spectrum of 10PAM, we found two bands characteristic of *m*-phenylene ethynylenes (PEs).15,20,21 The absorption maximum of each band (*λ*1 and *λ*2) was similar to that of 6PAM. The sum of each molar absorption coefficient (*ε*1 and *ε*2) for 10PAM was increased by 1.62-fold compared to that for 6PAM, which seemed close to the quotient 1.67 of 10 PE units and 6 PE units.

The UV spectrum of **1** (10PAM, two rods and four bridges) was remarkably similar to that of **8** (6PAM, one rod and two bridges) (Figure 3b and Table 1). In a shorter-wavelength region regarding rings and bridges, absorption intensities were less than 2-fold different from **8**, as expected from the component elements. In a longer-wavelength region specific to *p*-PEs of the rod, the intensities were doubled. The relationship between **3** and **9** could be explained as described above (Figure 3c and Table 1). Regarding the rod, the spectral shape differed between **8** and **9**, and thus **1** and **3**, which would be caused by some difference in dihedral angles about *p*-phenylene groups in threaded and unthreaded forms.27 The spectrum of **2** was rationalized by the coexistence of threaded and unthreaded forms of **8** and **9**. The spectrum of **4** resembled that of **1**, except that *ε*1 and *ε*2 were slightly attenuated in **4**.

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**FIGURE 3.** UV spectra of (a) **6** (10PAM, solid line), **10** (6PAM, orange dashed line) and **7** (rod, green dashed line); (b) **1** (thick solid line), **4** (thin dashed line) and **8** (thin solid line); (c) **2** (thin dashed line), **3** (thick solid line) and **9** (thin solid line). All spectra wre measured in CH2Cl2 at room temperature.

**TABLE 1.** Wavelengths (*λ*1, *λ*2, *λ*1 > *λ*2, and *λ*rod) of absorption maximum, molar absorption coefficients *ε* [L·mol‒1·cm‒1] (*ε*1, *ε*2 and *ε*rod) and the ratio of *ε*1/*ε*2, measured in CH2Cl2 at room temperature.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | *λ*1/nm | *ε*1/105 | *λ*2/nm | *ε*2/105 | *ε*1/*ε*2 | *λ*rod/nm | *ε*rod/105 |
| 1 | 308 | 4.63 | 292 | 4.92 | 0.942 | 331 | 1.11 |
| 2 | 308 | 4.09 | 291 | 4.53 | 0.902 | 360, 331 | 0.474, 1.01 |
| 3 | 309 | 3.68 | 291 | 4.26 | 0.864 | 360, 333 | 0.699, 0.950 |
| 4 | 307 | 4.38 | 292 | 4.71 | 0.931 | 331 | 1.06 |
| 6 (10PAM) | 308 | 3.42 | 291 | 3.60 | 0.948 | - | - |
| 8 | 305 | 2.28 | 289 | 2.83 | 0.805 | 331 | 0.536 |
| 9 | 303 | 1.76 | 287 | 2.31 | 0.761 | 360, 337 | 0.369, 0.459 |
| 10 (6PAM) | 305 | 1.88 | 287 | 2.45 | 0.766 | - | - |
| 7 (rod) | - | - | - | - | - | 331 | 0.659 |

The ratio of molar absorption coefficients *ε*1/*ε*2 has been used to consider the conformation of *m*-phenylene ethynylene oligomers.28 For linear-chained oligomers, the ratio for the cisoid torsional state is believed to be smaller than that for the transoid state (Cf. 0.6 for the helically-folded state and 0.9 for the random state).29 Though it is unable to similarly interpret the ratio for macrocyclic oligomers (PAMs), where all the chromophores are constrained to adopt a syn orientation, the ratio might reflect a difference in the conformation of a ring. In this regard, we found that the ratio in 10PAM (**6**) was greater than that in 6PAM (**10**). The ratio decreased for 6PAM, 5PAM and 4PAM in this order (Figure S3 in the supporting information). For the assembly of ring(s) and rod(s), the ratio generally seems to be higher for the threaded form than for the unthreaded form in either **1**-**4**, **8**-**9** and other threaded and unthreaded analogs based on 6PAM, 5PAM and 4PAM (Figure S3 in the supporting information).

**Chiroptical properties of 1, 2 and 8.** The CD spectra of isolated enantiomers are shown in Figure 4, where values of Δ*ε*/*ε* are also plotted versus wavelength. The absolute values of a molar CD at extreme wavelengths in the CD spectra of (+)-**1**, (+)-**2** and (+)-**8** are shown in Figure 6, where values of the molar optical rotation [*M*]D are also shown in degrees, measured in a 10-cm cell.

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**FIGURE 4.** CD spectra of (a) (‒)-**1** (thick solid line), (+)-**1** (thick dashed line), (‒)-**8** (thin solid line), (+)-**8** (thin dashed line), (b) (‒)-**2** (thick solid line), (+)-**2** (thick dashed line), (‒)-**8** (thin solid line), (+)-**8** (thin dashed line), and (c) plots of Δ*ε*/*ε* for **1** (thick solid line), **2** (thin solid line) and **8** (thin dashed line) versus wavelength. All spectra were measured in CH2Cl2 at 293 K.

Several compositive Cotton effects were found throughout the absorption region to make the spectra of **1**, **2** and **8** similar in profile. With either 10PAM-based **1** or **2**, the intensity of molar CDs was increased in the absorption regions for both the ring and rod, compared with those for 6PAM-based **8**. The increases in Δ*ε* for **1** were greater than those for **2**, especially in a shorter wavelength region below 340 nm. Alternatively, in a longer wavelength region, there was either almost no difference, or the changes were greater for **2** at 354 nm and above. For both 10PAM-based **1** and **2**, the additional ring and rod were arranged adjacent to the 6PAM-based optically active monomeric unit, and the molar absorption coefficients were increased, as shown in Figure 3. Regarding the increase in molar CDs for **1**, it is not surprising that some chiroptical activity could be changed by the arrangement of an additional chiral unit adjacent to the original chiral unit. Notably, also for **2**, molar CDs were increased throughout the absorption region by the arrangement of an optically inactive unit. This result showed that the achiral fused ring as well as the achiral unthreaded rod could be part of a chiral source to create new chiroptical activity.

In the comparison of **1** and **8**, in the absorption regions for the ring and rod, the values of *ε*321 and Δ*ε*321 were increased by 2.3 and 4.1 fold, and *ε*331 and Δ*ε*331 were increased by 2.1 and 4.3 fold, respectively. In the comparison of **2** and **8**, the values of *ε*320 and Δ*ε*320 were increased by 2.1 and 2.1 fold, and *ε*331 and Δ*ε*331 were increased by 1.9 and 2.4 fold, respectively. The increase in Δ*ε* for **1** was greater than expected based on the increase in *ε*, while the increase in Δ*ε* for **2** might have been due to the increase in *ε*. Thus, the increase in Δ*ε*/*ε* was greater for **1** than for **2** (e.g., 0.0030 for **1**, 0.0018 for **2** and 0.0016 for **8** at 323 nm).

VT-CD measurements showed partial changes, not entire changes, in molar CDs at some extreme wavelengths (Figure 5). Since the configuration was assured in both **1** and **2** about the [1]rotaxane unit, partial changes of molar CDs in the absorption region for a ring would be caused by interconversion among conformers based on the nonplanarity of 10PAM in **1** and **2**. The spectra of **2** showed other small changes in a longer wavelength region for rods, which might be due to two diastereomers regarding the locations of the unthreaded rod with respect to the chiral monomeric unit in **2**. These two diastereomeric forms would conformationally interconvert to make the chiroptical properties average based on their populations in solution.

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**FIGURE 5.** VT-CD spectra of (a) (+)-**1** and (b) (+)-**2**, measured in CH2Cl2 at 263-313 K.

The values of [*M*]D increased from (+)-**8** to (+)-**2** (2.6 times) and (+)-**1** (3.5 times) (Figure 6). This increasing pattern was similar to that of Δ*ε* (Cf. Figure S4 in the supporting infromation). These increases for both **1** and **2** were greater than the increase in the number of units.

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**FIGURE 6.** (a) Absolute values of a molar circular dichroism at extreme wavelengths, measured in CH2Cl2 at 293 K, and (b) molar optical rotation [*M*]D (1M, cell length = 10 cm) of (+)-**8** ([*α*]D =+411), (+)-**2** ([*α*]D = +562), and (+)-**1** ([*α*]D = +761), measured in CHCl3 at room temperature.

**CONCLUSION**

We have discussed the synthesis and characterization of four isomers based on 10PAM and two rods. The absorption properties of 6PAM were seen in 10PAM. The absorption intensity was characterized by the number of phenylacetylene units, as shown by the sum of *ε*1 and *ε*2. Thus, the intensity of 10PAM was approximately 10/6-fold that of 6PAM. A conformational consideration, based on the ratio of *ε*1/*ε*2, showed that there were nonplanar conformations of PAMs involved in equilibrium, and the ratio decreased with a decrease in the size of PAMs.

In doubled forms of **1**-**4** (homochiral **1**, chiral **2**, achiral **3** and heterochiral **4**), the relationship between the ring and rod was maintained as in each monomeric unit of threaded **8** or unthreaded **9**, as shown by several similarities in NMR and UV spectra. The intensity of molar CDs (Δ*ε*) of **1** was enhanced throughout the absorption region compared to what was expected based on the increase in absorption (*ε*), compared to **8**. The molar optical rotation ([*M*]D) was also increased more than the increase in the number of units. The overall chiroptical properties, not only Δ*ε* and [*M*]D, of **2** in a threaded-and-unthreaded form changed from the original chiral unit (**8**) by additional arrangements of the achiral ring and rod.

Based on the invariance of configuration, we have demonstrated increases in both molar CDs and molar optical rotations through the dualistic arrangement of chiral units, even though one was optically inactive.

**EXPERIMENTAL SECTION**

**General Information.**

All solvents, reagents and silica for chromatography were obtained from commercial sources and were used without further purification other than the double ring closing reaction, for which triethylamine was distilled prior to use. For reactions that required heating, the heat source was an oil bath. The NMR spectra were collected in a Bruker AscendTM 400 spectrometer using tetramethylsilane (TMS) as the internal standard (*δ* = 0) for recording 1H NMR spectra. The 13C NMR spectra were recorded with CDCl3 as the internal standard (*δ* = 77.0). The splitting pattern of the signals is denoted as follows: s = singlet, br.s = broad singlet, d = doublet, br.d = braod doublet, t = triplet, br.t = broad triplet, dd = doublet of doublet, m = multiplet, and br.m = broad multiplet. IR spectra were taken on a Shimadzu IRAffinity-1S spectrophotometer (as neat) using the attenuated total reflection mode. Absorptions are given in wavenumbers (cm−1). UV and CD spectra were recorded on a Hitachi U-2910 spectrophotometer and a JASCO J-820 spectropolarimeter. Specific optical rotations were recorded on a JASCO P-1020 polarimeter. Low- and High-resolution mass spectra (LRMS and HRMS) were obtained using a JEOL JMS-T100GCV instrument.

**Preparation of 13**

To a solution of **11**22 (20.3 g, 44.6 mmol), Pd(PPh3)4 (1.28 g, 1.11 mmol) and CuI (421 mg, 2.21 mmol) in THF (35 mL) and Et3N (370 mL) was added a solution of **12**23 (1.92 g, 7.39 mmol) in THF (18 mL) at 60 °C via a syringe pump over 6 hours under an argon atmosphere, and the mixture was further stirred at that temperature for 40 min. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, which was washed with 0.1 M aq. HCl, dried over magnesium sulfate and passed through a Celite/SiO2 pad. The filtrate was concentrated on a small amount of SiO2. The resultant solid was put onto a SiO2 column and eluted with hexane to give a mixture of **11** and **13** as a yellowish white solid. The mixture was further purified by GPC (chloroform; JAIGEL-1H & 2H, Japan Analytical Industry Co., Ltd., Japan) to give **13** (3.50 g) as a yellowish white solid in 81% yield. The obtained solid was finally recrystallized from benzene to give colorless crystals. **13**: mp 203-204 °C; Anal. Calcd for C14H6Br2I2: C, 28.61; H, 1.03. Found: C, 28.87; H, 0.92; 1H NMR (400 MHz, CDCl3, TMS) *δ* 8.05 (1H, t, *J* = 1.6 Hz), 7.81 (2H, d, *J* = 1.6 Hz), 7.66 (1H, t, *J* = 1.6 Hz), 7.58 (2H, d, *J* = 1.6 Hz) ppm; 13C{1H} NMR (100 MHz, CDCl3) *δ* 145.5, 139.4, 134.6, 133.1, 125.8, 125.7, 122.8, 94.1, 88.7, 88.3 ppm; IR (neat) 2201, 1575, 1538, 1527, 1437, 1400, 917, 853, 666 cm‒1; LRMS (FD) *m*/*z* 585.7 (M+, 51%), 586.7 ([M+1]+, 9), 587.7 ([M+2]+, 100), 588.7 ([M+3]+, 18), 589.7 ([M+4]+, 51); HRMS (FD) Calcd for C14H6Br2I2 (M+) 585.6926, Found 585.6931.

**Preparation of 15**

To a solution of **13** (98 mg, 0.17 mmol), Pd(PPh3)4 (58 mg, 0.050 mmol) and CuI (12 mg, 0.063 mmol) in Et3N (34 mL) was added a solution of **14**24 (443 mg, 0.339 mmol) in THF (4 mL) at 60 °C via a syringe pump over 6 hours under an argon atmosphere, and the mixture was further stirred at that temperature for 1 hour. After removal of the solvents by evaporation, the residue was dissolved in ethyl acetate, which was washed with 0.2 M aq. HCl, dried over magnesium sulfate, and then purified by column chromatography on SiO2 (ethyl acetate/dichloromethane-tetrahydrofuran/dichloromethane), followed by GPC (chloroform; JAIGEL-2H & 2.5H, Japan Analytical Industry Co., Ltd., Japan) to give **15** (420 mg) as a pale yellowish white solid in 86% yield. An analytical sample was obtained as a white solid by further purification through HPLC with a standard normal-phase column (YMC-Pack SIL, SIL-06, YMC Co., Ltd., Japan, ethanol/tetrahydrofuran/dichloromethane = 20/100/900, flow rate = 7.0 mL/min, detection wavelength (*l*) = 254 nm). **15**: mp 214-217 °C (dec.); 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.72-7.55 (15H, br.m), 7.54-7.46 (5H, br.m), 7.45-7.31 (12H, br.m), 7.31-7.22 (4H, br.m), 7.19-6.98 (2H, br.m), 7.12 (8H, s), 7.10 (8H, s), 6.83 (4H, d, *J* = 8.4 Hz), 6.91-6.98 (6H, br.m), 6.66 (2H, br.s), 4.33-3.47 (16H, br.m), 1.71-1.43 (16H, br.m), 1.42-1.25 (16H, m), 1.16-1.08 (42H, m), 0.95-0.85 (24H, m) ppm; 13C{1H} NMR (100 MHz, CDCl3, 313 K) *δ* 169.8, 169.6, 168.6, 168.5, 143.8, 143.5, 143.4, 143.3, 137.6, 137.3, 136.7, 136.5, 134.7, 134.5, 134.2, 133.0, 132.9, 132.8, 132.4, 132.3, 132.1, 131.6, 131.5, 129.5, 128.7, 128.5, 127.7, 127.5, 127.2, 127.1, 125.8, 124.8, 124.4, 124.3, 123.7, 123.4, 123.3, 123.1, 122.95, 122.89, 122.8, 121.2, 121.1, 105.2, 93.4, 90.8 (br.), 90.3, 89.9, 89.8, 89.6, 89.5, 89.3, 88.9, 88.3, 88.2, 88.0, 49.9, 49.79, 49.75, 49.6, 29.79, 29.76, 29.74, 29.72, 20.10, 20.06, 18.6, 13.71, 13.68, 11.3 ppm; IR (neat) 3051, 2956, 2929, 2863, 2215, 2152, 1646, 1579, 1517, 1378, 1294, 835, 730 cm‒1; LRMS (FD) *m*/*z* 1469.7 (M2+, 7%), 1470.2 ([M+1]2+, 12), 1470.6 ([M+2]2+, 33), 1471.2 ([M+3]2+, 48), 1471.7 ([M+4]2+, 57), 1472.2 ([M+5]2+, 68), 1472.7 ([M+6]2+, 56), 1473.2 ([M+7]2+, 45), 1473.7 ([M+8]2+, 82), 2939.3 (M+, 13), 2940.3 ([M+1]+, 27), 2941.3 ([M+2]+, 56), 2942.3 ([M+3]+, 82), 2943.3 ([M+4]+, 100), 2944.3 ([M+5]+, 98), 2945.3 ([M+6]+, 78), 2946.3 ([M+7]+, 51), 2947.3 ([M+8]+, 37), 2948.3 ([M+9]+, 18); HRMS (FD) Calcd for C192H180Br2N8O8Si2 (M+) 2939.1829, Found 2939.1834.

**Preparation of 16**

To a solution of **15** (975 mg, 0.331 mmol), Pd(PPh3)4 (33 mg, 0.029 mmol) and CuI (11 mg, 0.058 mmol) in THF (6 mL) and Et3N (12 mL) was added TMSA (0.56 mL, 4.0 mmol) at 78 °C under an argon atmosphere, and the mixture was further stirred at 76-83 °C for 18 hours. After removal of the solvents by evaporation, the residue was dissolved in ethyl acetate, which was washed with 0.1M aq. HCl, dried over magnesium sulfate, and then purified by column chromatography on SiO2 (ethyl acetate/dichloromethane-tetrahydrofuran/dichloromethane), followed by HPLC with a standard normal-phase column (ethanol/tetrahydrofuran/dichloromethane = 5/86/914, flow rate = 7.0 mL/min, *l* = 254 nm) to give **16** (762 mg) as a pale yellowish white solid in 77% yield. An analytical sample was obtained as a white solid by further purification through HPLC with a standard normal-phase column (ethanol/tetrahydrofuran/dichloromethane = 5/86/914). **16**: mp 220-222 °C (dec.); 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.71-7.53 (15H, br.m), 7.52-7.48 (5H, br.m), 7.44-7.32 (12H, br.m), 7.31-7.22 (4H, br.m), 7.19-6.91 (2H, br.m), 7.12 (8H, s), 7.09 (8H, s), 6.83 (4H, d, *J* = 8.4 Hz), 6.89-6.74 (6H, br.m), 6.66 (2H, br.s), 4.35-3.45 (16H, br.m), 1.73-1.40 (16H, br.m), 1.42-1.24 (16H, m), 1.19-1.05 (42H, m), 0.95-0.85 (24H, m), 0.22 (18H, s) ppm; 13C{1H} NMR (100 MHz, CDCl3, 313 K) *δ* 169.8, 169.6, 168.6, 168.5, 143.8, 143.5, 143.4, 143.3, 137.6, 137.3, 136.7, 136.5, 135.3, 134.7, 134.5, 134.0, 132.9, 132.7, 132.4, 132.3, 132.2, 131.5, 129.5, 128.7, 128.5, 127.7, 127.4, 127.2, 127.1, 124.7, 124.4, 124.2, 124.0, 123.6, 123.4, 123.3, 123.1, 122.96, 122.90, 122.87, 121.2, 121.1, 105.2, 102.9, 96.1, 93.4, 90.8 (br.), 90.3, 89.9, 89.8, 89.7, 89.6, 89.1, 89.0, 88.3, 88.1, 49.9, 49.8, 49.7, 49.6, 29.78, 29.76, 29.73, 29.70, 20.1, 20.0, 18.6, 13.70, 13.67, 11.3 ppm; IR (neat) 3062, 2957, 2930, 2864, 2218, 2152, 1653, 1581, 1518, 1379, 1295, 842, 682 cm‒1; LRMS (FD) *m*/*z* 1467.7 ([M+2‒(*i*Pr)+H]2+, 13%), 1487.7 (M2+, 11), 1488.2 ([M+1]2+, 28), 1488.7 ([M+2]2+, 40), 1489.2 ([M+3]2+, 44), 1489.7 ([M+4]2+, 38), 1490.2 ([M+5]2+, 28), 1490.7 ([M+6]2+, 49), 2935.4 ([M+2‒(*i*Pr)+H]+, 13), 2975.5 (M+, 29), 2976.5 ([M+1]+, 73), 2977.5 ([M+2]+, 100), 2978.5 ([M+3]+, 94), 2979.5 ([M+4]+, 73), 2980.5 ([M+5]+, 49), 2981.5 ([M+6]+, 30); HRMS (FD) Calcd for C202H198N8O8Si4 (M+) 2975.4410, Found 2975.4395.

**Preparation of 17**

i) To a solution of **16** (3.47 g, 1.16 mmol) in THF (36 mL) and MeOH (36 mL) was added K2CO3 (967 mg, 7.01 mmol) at room temperature, and the mixture was stirred at that temperature for 40 min. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, which was washed with aq. 0.2 M HCl, dried over magnesium sulfate, and then purified by column chromatography on SiO2 (ethyl acetate/dichloromethane-tetrahydrofuran/dichloromethane) to give **16'** (3.14 g) as a white solid in 95% yield. **16'**: 1H NMR (400 MHz, CDCl3, TMS) *δ* = 7.70 (4H, s), 7.65-7.53 (10H, br.m), 7.53-7.44 (6H, br.m), 7.41-7.32 (12H, br.m), 7.30-7.19 (4H, br.m), 7.19-7.01 (2H, br.m), 7.12 (8H, s), 7.09 (8H, s), 6.82 (4H, d, *J* = 8.4 Hz), 6.93-6.72 (6H, br.m), 6.67 (2H, br.s), 4.34-3.52 (16H, br.m), 3.08 (2H, s), 1.70-1.44 (16H, br.m), 1.41-1.27 (16H, m), 1.19-1.11 (42H, m), 0.95-0.85 (24H, m) ppm.

ii) To a solution of 1,3-diiodobenzene (1.69 g, 5.13 mmol), Pd(PPh3)4 (101 mg, 0.0874 mmol) and CuI (34 mg, 0.18 mmol) in Et3N (63 mL) was added a solution of **16'** (1.20 g, 0.423 mmol) in THF (13 mL) at 60 °C via a syringe pump over 6 hours under an argon atmosphere, and the mixture was further stirred at that temperature for 1 hour. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated and purified by column chromatography on SiO2 (ethyl acetate/dichloromethane), followed by GPC (chloroform; JAIGEL-2H & 2.5H) to give **17** (956 mg) as a yellow amorphous solid in 70% yield. An analytical sample was obtained as a white solid by further purification through HPLC with a standard normal-phase column (ethanol/tetrahydrofuran/dichloromethane = 18/100/800, flow rate = 7.0 mL/min, *l* = 254 nm). **17**: mp 192-196 °C (dec.); 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.87 (2H, t, *J* = 1.6 Hz), 7.73-7.55 (17H, br.m), 7.52-7.45 (7H, br.m), 7.41-7.32 (12H, br.m), 7.31-7.22 (4H, br.m), 7.19-7.00 (4H, br.m), 7.12 (8H, s), 7.09 (8H, s), 6.83 (4H, d, *J* = 8.4 Hz), 6.9-6.7 (6H, br.m), 6.66 (2H, br.s), 4.32-3.40 (16H, br.m), 1.72-1.44 (16H, br.m), 1.43-1.23 (16H, m), 1.17-1.03 (42H, m), 0.95-0.84 (24H, m) ppm; 113C{1H} NMR (100 MHz, CDCl3, 313 K) *δ* 169.9, 169.6, 168.7, 168.6, 143.9, 143.6, 143.5, 143.4, 140.3, 137.8, 137.6, 137.3, 136.8, 136.6, 134.8, 134.7, 134.3, 134.1, 133.0, 132.8, 132.4, 132.3, 132.2, 131.6, 130.7, 129.9, 129.6, 128.8, 128.5, 127.8, 127.5, 127.3, 127.2, 124.8, 124.7, 124.4, 124.3, 124.2, 124.0, 123.7, 123.5, 123.4, 123.3, 123.1, 123.01, 122.96, 121.2, 121.1, 105.2, 93.7, 93.5, 90.9 (br.), 90.3, 90.0, 89.9, 89.7, 89.5, 89.2, 89.1, 88.7, 88.5, 88.4, 88.1, 49.94, 49.86, 49.7, 29.86, 29.83, 29.81, 29.79, 20.2, 20.1, 18.7, 13.77, 13.74, 11.3 ppm; IR (neat) 3057, 2956, 2929, 2863, 2216, 2152, 1646, 1579, 1517, 1378, 1294, 836, 730, 680 cm‒1; LRMS (FD) *m*/*z* 1597.5 ([M+2‒(*i*Pr)+H]2+, 13%), 1617.5 (M2+, 22), 1618.0 ([M+1]2+, 56), 1618.5 ([M+2]2+, 79), 1619.1 ([M+3]2+, 79), 1619.6 ([M+4]2+, 71), 1620.0 ([M+5]2+, 53), 1620.5 ([M+6]2+, 78), 3194.1 ([M+1‒(*i*Pr)+H]+, 8), 3235.1 (M+, 29), 3236.2 ([M+1]+, 70), 3237.2 ([M+2]+, 100), 3238.1 ([M+3]+, 87), 3239.1 ([M+4]+, 66), 3240.1 ([M+5]+, 42), 3241.1 ([M+6]+, 26); HRMS (FD) Calcd for C208H188I2N8O8Si2 (M+) 3235.2178, Found 3235.2188.

**Preparation of 5**

To a solution of **17** (956 mg, 0.295 mmol) in THF (17 mL) was added TBAF (1 M in THF, 0.63 mL, 0.63 mmol) at room temperature, and the mixture was stirred at that temperature for 35 min. After dilution with ethyl acetate, the mixture was washed with 0.1 M aq. HCl and separated. The organic layer was dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO2 (ethyl acetate/dichloromethane), followed by GPC (chloroform; JAIGEL-2H & 2.5H) to give **5** (730 mg) as a white solid in 84% yield. **5**: 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.88 (2H, t, *J* = 1.6 Hz), 7.82-7.28 (40H, br.m), 7.20-6.94 (20H, m), 6.94-6.59 (12H, br.m), 4.43-3.38 (16H, br.m), 3.22 (2H, s), 1.72-1.44 (16H, br.m), 1.43-1.23 (16H, m), 0.95-0.84 (24H, m) ppm.

**Preparation of 1-4**

To a solution of Pd(PPh3)4 (262, 266, 270, 265 mg, 0.22-0.23 mmol) and CuI (45, 44, 45, 48 mg, 0.23-0.25 mmol) in Et3N (113 mL) was added a solution of **5** (730/4 mg, 0.250/4 mmol) in THF (40 mL×4 batches) via a syringe pump over 15.6 hours at 80 °C under an argon atmosphere. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated. The combined crude products were dissolved in dichloromethane, which was washed with water, dried over magnesium sulfate, and then concentrated. The residue was purified by column chromatography on SiO2 (tetrahydrofuran/dichloromethane), followed by GPC (chloroform; JAIGEL-2H & 2.5H) and HPLC0 with a standard normal-phase column, to give a mixture containing **1**-**4** (See Chart S1 and Chart S2 in the supporting information). The mixture was further purified by HPLC1-4 with a standard normal-phase column to give (±)-**1** (77 mg, 12%, HPLC4), (±)-**2** and **3** (104 mg, 16%, HPLC3) and **4** (66 mg, 10%, HPLC2). Optical resolution was implemented by HPLC with a chiral stationary column (IF6 and IF7, CHIRALPAK IF, DAICEL Co., Japan) to give (‒)-**1** (1st fraction) and (+)-**1** (2nd fraction) in this order (IF7) as white solids in pure form, and (‒)-**2** (1st fraction, 32 mg, 5%, IF6-1 and IF6-2), **3** (2nd fraction, 10 mg, 2%, IF6-2), and (+)-**2** (3rd fraction, 29 mg, 4%, IF6-1) in this order (IF6) as white solids in pure form. Each analytical sample of (‒)-**1**, (+)-**1**, (‒)-**2**, (+)-**2**, **3** and **4** was obtained as a white solid by reprecipitation from ethyl acetate and hexane (1:20).

(±)-**1**: 13C{1H} NMR (100 MHz, CDCl3) *δ* 169.16, 169.13, 169.06, 143.9, 143.8, 143.1, 137.40, 137.38, 136.57, 136.56, 135.0, 134.8, 134.3, 134.1, 133.9, 133.2, 133.1, 132.33, 132.30, 132.1, 132.0, 131.9, 131.8, 131.7, 131.6, 129.0, 128.8, 128.7, 128.45, 128.35, 128.2, 127.3, 124.5, 124.4, 124.0, 123.8, 123.62, 123.60, 123.3, 123.2, 123.1, 123.0, 122.9, 120.75, 120.73, 91.6, 91.5, 90.1, 90.0, 89.9, 89.3, 89.0, 89.0, 89.0, 88.8, 88.6, 88.5, 88.3, 50.1, 49.4, 29.65, 29.61, 29.59, 20.12, 20.10, 19.99, 19.98, 13.8, 13.7, 13.6 ppm; IR (neat) 3060, 2957, 2930, 2871, 2217, 1652, 1594, 1517, 1418, 1378, 1295, 836, 684 cm‒1.

(‒)-**1**: mp >300 °C; [*α*]D24 = ‒752 (*c* 0.109, chloroform); LRMS (FD) *m*/*z* 1333.6 (M2+, 13%), 1334.1 ([M+1]2+, 30), 1334.6 ([M+2]2+, 43), 1335.1 ([M+3]2+, 39), 1335.6 ([M+4]2+, 29), 1336.1 ([M+5]2+, 16), 1336.6 ([M+6]2+, 10), 1337.1 ([M+7]2+, 6), 2667.3 (M+, 29), 2668.3 ([M+1]+, 78), 2669.3 ([M+2]+, 100), 2670.3 ([M+3]+, 84), 2671.3 ([M+4]+, 54), 2672.3 ([M+5]+, 28), 2673.3 ([M+6]+, 14), 2674.3 ([M+7]+, 5); HRMS (FD) Calcd for C190H146N8O8 (M+) 2667.1264, Found 2667.1273; CD (CH2Cl2) *λ* 331 (Δ*ε* shoulder ‒270), 321 (‒407), 314 (‒92), 309 (‒284), 288 (+158), 267 (+23) nm.

(+)-**1**: [*α*]D24 = +760 (*c* 0.113, chloroform); 1H NMR (400 MHz, CDCl3, TMS) *δ* 8.06 (8H, s), 7.88 (2H, br.t), 7.85 (2H, d, *J* = 1.2 Hz), 7.733 (1H, t, *J* = 1.2 Hz), 7.729 (1H, t, *J* = 1.2 Hz), 7.72 (2H, br.t), 7.68 (2H, t, *J* = 1.6 Hz), 7.65-7.62 (6H, m), 7.59 (2H, d, *J* = 1.2 Hz), 7.56-7.52 (4H, m), 7.48-7.39 (8H, m), 7.37 (4H, d, *J* = 8.4 Hz), 7.35 (4H, d, *J* = 8.4 Hz), 7.21-7.03 (16H, br.m), 6.79 (8H, br.d), 6.67 (2H, t, *J* = 1.6 Hz), 6.63 (2H, t, *J* = 1.6 Hz), 4.31-4.03 (8H, m), 3.69-3.49 (8H, m), 1.76-1.63 (4H, br.m), 1.62-1.49 (12H, br.m), 1.48-1.36 (8H, m), 1.36-1.21 (8H, m), 1.00 (6H, t, *J* = 7.2 Hz), 0.95 (6H, t, *J* = 7.2 Hz), 0.84 (6H, t, *J* = 7.2 Hz), 0.81 (6H, t, *J* = 7.2 Hz) ppm; LRMS (FD) *m*/*z* 1333.7 (M2+, 30%), 1334.2 ([M+1]2+, 64), 1334.7 ([M+2]2+, 74), 1335.2 ([M+3]2+, 60), 1335.7 ([M+4]2+, 40), 1336.2 ([M+5]2+, 22), 1336.6 ([M+6]2+, 13), 1337.2 ([M+7]2+, 9), 2667.3 (M+, 34), 2668.3 ([M+1]+, 79), 2669.3 ([M+2]+, 100), 2670.3 ([M+3]+, 84), 2671.3 ([M+4]+, 57), 2672.3 ([M+5]+, 31), 2673.4 ([M+6]+, 13), 2674.3 ([M+7]+, 5); HRMS (FD) Calcd for C190H146N8O8 (M+) 2667.1264, Found 2667.1286; UV *λ*max (CH2Cl2) 331 (log *ε* sh. 5.05), 308 (5.67), 292 (5.69), 273 (sh. 5.40) nm; CD *λ* (CH2Cl2) 331 (Δ*ε* sh. +275), 321 (+415), 314 (+97), 309 (+293), 288 (‒156), 267 (‒23) nm.

(‒)-**2**: mp >300 °C; [*α*]D24 = ‒558 (*c* 0.116, chloroform); LRMS (FD) *m*/*z* 1333.7 (M2+, 10%), 1334.1 ([M+1]2+, 26), 1334.6 ([M+2]2+, 42), 1335.1 ([M+3]2+, 42), 1335.6 ([M+4]2+, 30), 1336.1 ([M+5]2+, 16), 1336.6 ([M+6]2+, 11), 1337.1 ([M+7]2+, 6), 2667.3 (M+, 34), 2668.3 ([M+1]+, 77), 2669.3 ([M+2]+, 100), 2670.3 ([M+3]+, 75), 2671.3 ([M+4]+, 50), 2672.3 ([M+5]+, 27), 2673.3 ([M+6]+, 11), 2674.3 ([M+7]+, 5); HRMS (FD) Calcd for C190H146N8O8 (M+) 2667.1264, Found 2667.1243; CD λ (CH2Cl2) 331 (Δ*ε* sh. ‒154), 320 (‒210), 314 (‒68), 310 (‒187), 285 (+98), 264 (+25) nm.

(+)-**2**: [*α*]D24 = +562 (*c* 0.121, chloroform); 1H NMR (400 MHz, CDCl3, TMS)30 *δ* 8.07 (4H, s), 7.88 (1H, br.s), 7.86 (1H, br.t), 7.75 (1H, br.t), 7.74 (1H, br.t), 7.73-7.68 (4H, br.m), 7.67-7.28 (12H+18H, m), 7.24-7.06 (16H, br.m), 6.92-6.76 (8H, br.m), 6.76-6.68 (3H, br.m), 6.66 (1H, t, *J* = 1.6 Hz), 4.28-3.97 (8H, br.m), 3.84-3.45 (8H, br.m), 1.78-1.49 (16H, br.m), 1.48-1.25 (16H, br.m), 1.00 (6H, t, *J* = 7.2 Hz), 0.96 (6H, *J* = 7.2 Hz), 0.90 (6H, *J* = 7.2 Hz), 0.87 (6H, *J* = 7.2 Hz) ppm; 13C{1H} NMR (100 MHz, CDCl3, 313 K) *δ* 169.8, 169.7, 169.3, 169.1, 169.1, 168.5 (br.), 144.1, 144.0, 143.8, 143.42, 143.35, 143.27, 137.6, 137.53, 137.47, 136.76 (sh.), 136.75, 136.5, 136.2, 135.3, 135.2, 135.1, 134.8, 134.3, 134.08 (sh.), 134.06, 133.4, 133.3, 132.41, 132.37, 132.3, 132.2, 132.0, 131.9, 131.9, 131.7, 131.5, 131.5, 130.9, 129.00, 128.94, 128.91, 128.88 (sh.), 128.6, 128.52, 128.48, 128.4, 128.3, 128.2, 127.6 (br.), 127.5, 127.4, 127.2, 124.9, 124.7, 124.6, 124.5, 124.11, 124.06, 124.04, 123.92, 123.91, 123.7, 123.6, 123.5, 123.4, 123.34, 123.29, 123.23, 123.16, 123.09, 123.08, 123.05, 123.02, 122.9, 121.30, 121.25, 120.88, 120.84, 91.71, 91.66, 90.44, 90.40, 90.19, 90.17, 90.15, 89.97, 89.95 (sh.), 89.8, 89.5, 89.19, 89.14, 89.08, 88.9, 88.78, 88.75, 88.6, 88.49, 88.46, 88.4, 88.2, 88.1, 50.3, 50.2, 49.9, 49.8, 49.5, 29.82, 29.79, 29.77, 29.7, 20.22, 20.19, 20.13, 20.08, 13.81, 13.76, 13.74, 13.71, 13.68, 13.66 ppm; IR (neat) 3060, 2957, 2930, 2872, 2217, 1653, 1594, 1518, 1419, 1379, 1295, 837, 684 cm‒1; LRMS (FD) *m*/*z* 1333.6 (M2+, 23%), 1334.0 ([M+1]2+, 46), 1334.6 ([M+2]2+, 52), 1335.0 ([M+3]2+, 51), 1335.6 ([M+4]2+, 35), 1336.1 ([M+5]2+, 22), 1336.6 ([M+6]2+, 14), 1337.0 ([M+7]2+, 8), 2667.1 (M+, 29), 2668.1 ([M+1]+, 77), 2669.1 ([M+2]+, 100), 2670.1 ([M+3]+, 89), 2671.1 ([M+4]+, 57), 2672.1 ([M+5]+, 30), 2673.1 ([M+6]+, 12), 2674.1 ([M+7]+, 3); HRMS (FD) Calcd for C190H146N8O8 (M+) 2667.1264, Found 2667.1261; UV *λ*max (CH2Cl2) 360 (log *ε* sh. 4.68), 331 (sh. 5.00), 308 (5.61), 291 (5.66), 273 (sh. 5.40) nm; CD *λ* (CH2Cl2) 331 (Δ*ε* sh. +156), 320 (+214), 314 (+73), 310 (+193), 285 (‒98), 264 (‒25) nm.

**3**: mp >300 °C; 1H NMR (400 MHz, CDCl3, TMS)30 *δ* 7.76 (2H, br.t), 7.74 (2H, d, *J* = 1.2 Hz), 7.69 (4H, s), 7.61 (2H, br.t), 7.60 (2H, br.s), 7.56-7.47 (8H, br.m), 7.46-7.29 (22H, br.m), 7.22 (4H, d, *J* = 8.8 Hz), 7.19 (4H, d, *J* = 8.8 Hz), 7.18 (4H, d, *J* = 8.8 Hz), 7.14 (4H, d, *J* = 8.8 Hz), 6.89-6.75 (2H, br.m), 6.83 (4H, d, *J* = 8.4 Hz), 6.80 (4H, d, *J* = 8.4 Hz), 6.73 (2H, br.s), 4.32-3.52 (16H, br.m), 1.73-1.44 (16H, br.m), 1.41-1.25 (16H, br.m), 0.97 (6H, t, *J* = 7.2 Hz), 0.95-0.86 (24H, m) ppm; 13C{1H} NMR (100 MHz, CDCl3, 313 K) *δ* 169.9, 169.6, 168.6, 168.5, 144.0, 143.8, 143.45, 143.37, 137.6, 137.5 (br.), 136.5, 136.1, 135.5, 135.3, 134.8, 133.7, 133.43, 133.35, 132.4, 132.3, 132.0, 131.7, 131.5, 131.0, 129.0, 128.9, 128.6, 128.3 (br.), 127.7, 127.5, 127.2, 124.8, 124.7, 124.03, 124.01 (sh.), 123.8, 123.63, 123.57, 123.4, 123.3, 123.1, 123.0, 122.9, 121.33, 121.25, 90.4, 90.1, 90.0, 89.9, 89.8, 89.5, 89.02, 88.98, 88.65, 88.58, 88.4, 88.2, 88.1, 50.0, 49.9, 49.8, 29.86, 29.81, 29.79, 20.17, 20.14, 13.76, 13.73, 13.71 ppm; IR (neat) 3061, 2956, 2930, 2871, 2215, 1646, 1591, 1578, 1517, 1419, 1378, 1294, 836, 684 cm‒1; LRMS (FD) *m*/*z* 1333.6 (M2+, 17%), 1334.0 ([M+1]2+, 40), 1334.6 ([M+2]2+, 54), 1335.0 ([M+3]2+, 52), 1335.5 ([M+4]2+, 41), 1336.0 ([M+5]2+, 27), 1336.5 ([M+6]2+, 16), 1337.0 ([M+7]2+, 14), 2667.1 (M+, 34), 2668.1 ([M+1]+, 79), 2669.1 ([M+2]+, 100), 2670.1 ([M+3]+, 84), 2671.1 ([M+4]+, 55), 2672.1 ([M+5]+, 28), 2673.1 ([M+6]+, 14), 2674.1 ([M+7]+, 8); HRMS (FD) Calcd for C190H146N8O8 (M+) 2667.1264, Found 2667.1232; UV *λ*max (CH2Cl2) 360 (log *ε* sh. 4.84), 333 (4.98), 309 (5.57), 291 (5.63), 273 (sh. 5.41) nm.

**4**: mp >300 °C; 1H NMR (400 MHz, CDCl3, TMS) *δ* 8.06 (8H, s), 7.91 (2H, br.t), 7.82 (2H, d, *J* = 1.6 Hz), 7.74 (1H, t, *J* = 1.6 Hz), 7.72 (1H, t, *J* = 1.6 Hz), 7.71-7.69 (4H, m), 7.64-7.61 (6H, m), 7.60 (2H, d, *J* = 1.6 Hz), 7.56-7.52 (4H, m), 7.48-7.39 (8H, m), 7.37 (4H, d, *J* = 8.4 Hz), 7.35 (4H, d, *J* = 8.4 Hz), 7.22-7.01 (16H, br.m), 6.82 (4H, br.d), 6.78 (4H, br.d), 6.661 (2H, t, *J* = 1.6 Hz), 6.657 (2H, t, *J* = 1.6 Hz), 4.30-4.04 (8H, m), 3.69-3.49 (8H, m), 1.76-1.62 (4H, br.m), 1.62-1.51 (12H, br.m), 1.48-1.36 (8H, m), 1.36-1.21 (8H, m), 0.97 (6H, t, *J* = 7.2 Hz), 0.96 (6H, t, *J* = 7.2 Hz), 0.85 (6H, t, *J* = 7.2 Hz), 0.82 (6H, t, *J* = 7.2 Hz) ppm; 13C{1H} NMR (100 MHz, CDCl3) *δ* 169.18, 169.14, 169.08, 169.01, 143.9, 143.8, 143.2, 143.1, 137.4, 137.4, 136.6, 136.5, 135.1, 135.0, 134.3, 134.2, 133.8, 133.31, 133.25, 132.3, 132.11, 132.09, 131.90, 131.87, 131.6, 131.5, 129.09, 128.98, 128.87, 128.43, 128.38, 128.25, 128.20, 127.36, 127.32, 124.6, 124.4, 124.02, 123.96, 123.79, 123.64, 123.61, 123.4, 123.3, 123.2, 123.1, 123.0, 122.9, 120.8, 120.7, 91.62, 91.58, 90.10, 90.09, 89.9, 89.8, 89.3, 89.2, 89.09, 89.05, 89.02, 88.8, 88.7, 88.5, 88.3, 50.2, 49.4, 29.65, 29.61, 20.1, 20.0, 13.79, 13.77, 13.68, 13.64 ppm; IR (neat) 3061, 2956, 2930, 2871, 2218, 1653, 1594, 1517, 1420, 1378, 1294, 835, 684 cm‒1; LRMS (FD) *m*/*z* 1333.6 (M2+, 38%), 1334.1 ([M+1]2+, 84), 1334.6 ([M+2]2+, 99), 1335.1 ([M+3]2+, 83), 1335.6 ([M+4]2+, 52), 1336.1 ([M+5]2+, 31), 1336.6 ([M+6]2+, 17), 2667.2 (M+, 36), 2668.2 ([M+1]+, 80), 2669.2 ([M+2]+, 100), 2670.2 ([M+3]+, 82), 2671.2 ([M+4]+, 56), 2672.2 ([M+5]+, 30), 2673.2 ([M+6]+, 14), 2674.1 ([M+7]+, 8); HRMS (FD) Calcd for C190H146N8O8 (M+) 2667.1264, Found 2667.1280; UV *λ*max (CH2Cl2) 331 (log *ε* sh. 5.03), 307 (5.64), 292 (5.67), 273 (sh. 5.39) nm.

**Preparation of 19**

To a solution of **13** (151 mg, 0.257 mmol), Pd(PPh3)4 (36 mg, 0.031 mmol) and CuI (15 mg, 0.079 mmol) in THF (2 mL) and iPr2NH (5 mL) was added a solution of **18** (439 mg, 0.532 mmol) in THF (5 mL) at 50 °C via a syringe pump over 2 hours under an argon atmosphere, and the mixture was further stirred at that temperature for 1.5 hours. After dilution with ethyl acetate, the organic layer was washed with water, separated, and then dried over magnesium sulfate. The crude product was purified by column chromatography on SiO2 (dichloromethane/hexane), followed by GPC (chloroform; JAIGEL-2H & 2.5H) to give **19** (378 mg) as a yellow amorphous solid in 74% yield. **19**: 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.71 (2H, t, *J* = 1.6 Hz), 7.69 (1H, t, *J* = 1.6 Hz), 7.67 (1H, t, *J* = 1.6 Hz), 7.65 (2H, d, *J* = 1.6 Hz), 7.62 (2H, d, *J* = 1.6 Hz), 7.55 (2H, t, *J* = 1.6 Hz), 7.510 (2H, dd, *J* = 8.0, 1.6 Hz), 7.506 (2H, dd, *J* = 8.0, 1.6 Hz), 7.48 (2H, t, *J* = 1.6 Hz), 7.41-7.35 (4H, br.m), 7.36 (2H, t, *J* = 8.0 Hz), 7.31 (2H, br.t), 7.27 (2H, t, *J* = 1.6 Hz), 3.68-3.61 (8H, m), 1.62-1.46 (8H, m), 1.47 (18H, s), 1.45 (18H, s), 1.39-1.27 (8H, m), 1.14 (42H, s), 0.93 (6H, t, *J* = 7.2 Hz), 0.92 (6H, t, *J* = 7.2 Hz) ppm; 13C{1H} NMR (100 MHz, CDCl3) *δ* 154.3, 143.1, 142.8, 134.7, 134.40, 134.35, 133.1, 132.6, 132.1, 131.63, 131.58, 130.5, 130.3, 130.2, 128.6, 126.1, 124.4, 124.0, 123.9, 123.6, 123.5, 123.3, 123.23, 123.20, 122.7, 105.6, 91.9, 90.0, 89.6, 89.4, 89.1, 88.9, 88.6, 88.2, 87.6, 80.6, 80.5, 49.6, 30.63, 30.57, 28.33, 28.30, 19.91, 19.89, 18.6, 13.77, 13.75, 11.3 ppm; IR (neat) 3066, 2959, 2930, 2863, 2221, 2154, 1699, 1582, 1366, 1144, 879, 680 cm‒1; LRMS (FD) *m*/*z* 1978.8 (M+, 24%), 1979.8 ([M+1]+, 38), 1980.8 ([M+2]+, 79), 1981.8 ([M+3]+, 95), 1982.8 ([M+4]+, 100), 1983.8 ([M+5]+, 84), 1984.8 ([M+6]+, 61), 1985.8 ([M+7]+, 34), 1986.8 ([M+8]+, 19), 1987.8 ([M+9]+, 16); HRMS (FD) Calcd for C120H140Br2N4O8Si2 (M+): 1978.8576, Found 1978.8595.

**Preparation of 20**

To a solution of **19** (320 mg, 0.161 mmol), Pd(PPh3)4 (58 mg, 0.050 mmol) and CuI (20 mg, 0.11 mmol) in Et3N (32 mL) was added TMSA (1.0 mL, 7.1 mmol) at 80-85 °C under an argon atmosphere, and the mixture was further stirred at that temperature for 3 days. After dilution with ethyl acetate, the organic layer was washed with water, separated, and then dried over magnesium sulfate. The crude product was purified by column chromatography on SiO2 (dichloromethane/hexane), followed by GPC (chloroform; JAIGEL-2H & 2.5H) to give **20** (240 mg) as a yellow amorphous solid in 74% yield. An analytical sample was obtained as a yellow waxy solid by further purification through HPLC with a standard normal-phase column (ethanol/dichloromethane = 5/1000, flow rate = 7.0 mL/min, *l* = 254 nm). **20**: 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.71 (2H, t, *J* = 1.6 Hz), 7.67 (1H, t, *J* = 1.6 Hz), 7.64 (2H, d, *J* = 1.6 Hz), 7.57 (2H, d, *J* = 1.6 Hz), 7.548 (1H, t, *J* = 1.6 Hz), 7.547 (2H, t, *J* = 1.6 Hz), 7.52-7.49 (4H, m), 7.48 (2H, t, *J* = 1.6 Hz), 7.41-7.35 (4H, br.m), 7.36 (2H, t, *J* = 8.0 Hz), 7.31 (2H, br.t), 7.27 (2H, t, *J* = 1.6 Hz), 3.68-3.60 (8H, m), 1.62-1.48 (8H, m), 1.47 (18H, s), 1.45 (18H, s), 1.39-1.27 (8H, m), 1.13 (42H, s), 0.93 (6H, t, *J* = 7.2 Hz), 0.92 (6H, t, *J* = 7.2 Hz), 0.25 (18H, s) ppm; 13C{1H} NMR (100 MHz, CDCl3) *δ* 154.3, 143.0, 142.8, 135.2, 134.7, 134.6, 134.4, 132.6, 132.1, 131.62, 131.60, 130.5, 130.3, 130.2, 128.6, 124.4, 124.0, 123.9, 123.8, 123.7, 123.60, 123.59, 123.34, 123.25, 123.2, 105.6, 103.0, 95.9, 91.9, 89.42, 89.35, 89.1, 89.0, 88.8, 88.7, 88.6, 88.4, 80.6, 80.5, 49.6, 30.62, 30.57, 28.33, 28.30, 19.91, 19.89, 18.6, 13.77, 13.75, 11.3, ‒0.2 ppm; IR (neat) 3063, 2959, 2930, 2864, 2221, 2156, 1700, 1582, 1366, 1145, 842, 679 cm‒1; LRMS (FD) *m*/*z* 2015.1 (M+, 59%), 2016.1 ([M+1]+, 100), 2017.1 ([M+2]+, 100), 2018.1 ([M+3]+, 76), 2019.1 ([M+4]+, 45), 2020.1 ([M+5]+, 28); HRMS (FD) Calcd for C130H158N4O8Si4 (M+) 2015.1157, Found 2015.1161.

**Preparation of 21**

i) To a solution of **20** (1.48 g, 0.733 mmol) in THF (4 mL) and MeOH (4 mL) was added K2CO3 (114 mg, 0.826 mmol) at room temperature, and the mixture was stirred at that temperature for 40 min. After removal of the solvents by evaporation, the residue was dissolved in dichloromethane, which was washed with water and dried over magnesium sulfate. The crude product was purified by column chromatography on SiO2 (dichloromethane/hexane) to give **20'** (1.15 g) as a yellow amorphous solid in 84% yield. **20'**: 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.71 (2H, t, *J* = 1.6 Hz), 7.68 (1H, t, *J* = 1.6 Hz), 7.66 (2H, d, *J* = 1.6 Hz), 7.63 (2H, d, *J* = 1.6 Hz), 7.58 (1H, t, *J* = 1.6 Hz), 7.55 (2H, t, *J* = 1.6 Hz), 7.52-7.49 (4H, m), 7.48 (2H, t, *J* = 1.6 Hz), 7.41-7.35 (4H, br.m), 7.36 (2H, t, *J* = 8.0 Hz), 7.31 (2H, br.t), 7.27 (2H, t, *J* = 1.6 Hz), 3.68-3.61 (8H, m), 3.13 (2H, s), 1.62-1.47 (8H, m), 1.47 (18H, s), 1.45 (18H, s), 1.39-1.27 (8H, m), 1.14 (42H, s), 0.93 (6H, t, *J* = 7.2 Hz), 0.92 (6H, t, *J* = 7.2 Hz) ppm.

ii) To a solution of 1,3-diiodobenzene (843 mg, 2.56 mmol), Pd(PPh3)4 (57 mg, 0.049 mmol) and CuI (20 mg, 0.11 mmol) in Et3N (32 mL) was added a solution of **20'** (593 mg, 0.317 mmol) in THF (3.2 mL) at 60 °C via a syringe pump over 6 hours under an argon atmosphere, and the mixture was further stirred at that temperature for 30 min. After removal of the solvents by evaporation, the residue was dissolved in ethyl acetate, which was washed with water and dried over magnesium sulfate. The crude product was purified by column chromatography on SiO2 (dichloromethane/hexane) to give **21** (494 mg) as a yellow amorphous solid in 69% yield. An analytical sample was obtained as a yellow waxy solid by further purification through HPLC with a standard normal-phase column (ethanol/dichloromethane = 5/1000, flow rate = 7.0 mL/min, *l* = 254 nm). **21**: 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.91 (2H, t, *J* = 1.6 Hz), 7.73-7.64 (10H, m), 7.56 (2H, t, *J* = 1.6 Hz), 7.54-7.46 (8H, m), 7.41-7.35 (4H, br.m), 7.36 (2H, t, *J* = 7.6 Hz), 7.31 (2H, br.t), 7.27 (2H, br.t), 7.10 (2H, t, *J* = 8.0 Hz), 3.68-3.60 (8H, m), 1.63-1.46 (8H, m), 1.48 (18H, s), 1.45 (18H, s), 1.39-1.27 (8H, m), 1.13 (42H, s), 0.94 (6H, t, *J* = 7.2 Hz), 0.91 (6H, t, *J* = 7.2 Hz) ppm; 13C{1H} NMR (100 MHz, CDCl3) *δ* 154.29, 154.28, 143.0, 142.8, 140.3, 137.7, 134.7, 134.43, 134.37, 132.6, 132.1, 131.63, 131.60, 130.8, 130.5, 130.3, 130.2, 129.9, 128.6, 124.7, 124.4, 124.0, 123.9, 123.8, 123.65, 123.60, 123.58, 123.34, 123.25, 105.6, 93.7, 91.9, 89.5, 89.4, 89.1, 89.03, 88.96, 88.90, 88.86, 88.8, 88.7, 88.4, 80.6, 80.5, 49.6, 30.63, 30.57, 28.34, 28.31, 19.92, 19.89, 18.6, 13.78, 13.76, 11.3 ppm; IR (neat) 3059, 2958, 2930, 2863, 2220, 2156, 1700, 1582, 1366, 1144, 878, 679 cm‒1; LRMS (FD) *m*/*z* 1010.4 ([M+2‒(BOC)‒(TIPS)+2H]2+, 37%), 1037.9 ([M+1‒(BOC)2+2H]2+, 55), 1087.9 ([M+1‒(BOC)+H]2+, 15), 1138.5 ([M+2]2+, 17), 2119.7 ([M+1‒(TIPS)+H]+, 10), 2175.8 ([M+1‒(BOC)+H]+, 14), 2274.9 (M+, 57), 2275.9 ([M+1]+, 100), 2276.9 ([M+2]+, 95), 2277.9 ([M+3]+, 71), 2278.9 ([M+4]+, 42); HRMS (FD) Calcd for C136H148I2N4O8Si2 (M+) 2274.8925, Found 2274.8906.

**Preparation of 22**

To a solution of **21** (360 mg, 0.158 mmol) in THF (9 mL) was added TBAF (1 M in THF, 0.34 mL, 0.34 mmol) at room temperature, and the mixture was stirred at that temperature for 80 min. After dilution with ethyl acetate, the mixture was washed with water and separated. The organic layer was dried over magnesium sulfate, concentrated, and then purified by column chromatography on SiO2 (dichloromethane/hexane), followed by GPC (chloroform; JAIGEL-2H & 2.5H) to give **22** (189 mg) as a white amorphous solid in 61% yield. **22**: 1H NMR (400 MHz, CDCl3, TMS) *δ* 7.91 (2H, t, *J* = 1.6 Hz), 7.73-7.64 (10H, m), 7.56 (2H, t, *J* = 1.6 Hz), 7.54-7.47 (8H, m), 7.41-7.33 (8H, br.m), 7.31 (2H, br.t), 7.10 (2H, t, *J* = 8.0 Hz), 3.68-3.60 (8H, m), 3.10 (2H, s), 1.63-1.47 (8H, m), 1.48 (18H, s), 1.45 (18H, s), 1.39-1.27 (8H, m), 0.94 (6H, t, *J* = 7.2 Hz), 0.91 (6H, t, *J* = 7.2 Hz) ppm.

**Preparation of 6**

To a solution of Pd(PPh3)4 (141 mg, 0.122 mmol) and CuI (28 mg, 0.15 mmol) in Et3N (29 mL) was added a solution of **22** (189 mg, 0.0962 mmol) in THF (15 mL) via a syringe pump over 18 hours at 75-80 °C under an argon atmosphere. After removal of a solid by filtration through a Celite pad, the filtrate was concentrated. The crude product was dissolved in dichloromethane, which was washed with water, dried over magnesium sulfate, and then concentrated. The residue was purified by column chromatography on SiO2 (ethyl acetate/dichloromethane), followed by GPC (chloroform; JAIGEL-2H & 2.5H) to give **6** (33 mg) as a white solid in 20% yield. **6**: mp 200-220 °C (dec.); 1H NMR (400 MHz, CDCl3, TMS, [**6**] = 2.2 mM, 303 K) *δ* 7.77 (2H, t, *J* = 1.6 Hz), 7.75 (2H, t, *J* = 1.6 Hz), 7.72-7.69 (6H, m), 7.592 (2H, t, *J* = 1.6 Hz), 7.585 (2H, t, *J* = 1.6 Hz), 7.55-7.50 (8H, m), 7.40-7.33 (12H, m), 3.69-3.65 (8H, m), 1.62-1.52 (8H, m), 1.484 (18H, s), 1.475 (18H, s), 1.40-1.30 (8H, m), 0.94 (6H, t, *J* = 7.2 Hz), 0.94 (6H, t, *J* = 7.2 Hz) ppm; 13C{1H} NMR (100 MHz, CDCl3) *δ* 154.3, 143.1, 143.0, 135.3, 135.2, 134.7, 134.6, 133.8, 132.7, 132.6, 131.5, 131.43, 131.38, 131.0, 130.1, 130.04, 130.02, 128.7, 128.6, 124.01, 123.97, 123.92, 123.85, 123.7, 123.63, 123.61, 123.38, 123.36, 123.3, 123.2, 89.9, 89.54, 89.49, 89.4, 89.1, 88.96, 88.94, 88.9, 88.8, 88.6, 88.5, 80.62, 80.56, 49.7, 30.7, 28.4, 19.9, 13.8 ppm; IR (neat) 3065, 2960, 2929, 2861, 2221, 1700, 1145, 873, 678, 527 cm‒1; LRMS (FD) *m*/*z* 1506.7 ([M‒(BOC)2+2H]+, 31%), 1507.7 ([M+1‒(BOC)2+2H]+, 45), 1508.7 ([M+2‒(BOC)2+2H]+, 35), 1509.7 ([M+3‒(BOC)2+2H]+, 15), 1606.7 ([M‒(BOC)+H]+, 68), 1607.7 ([M+1‒(BOC)+H]+, 100), 1608.7 ([M+2‒(BOC)+H]+, 83), 1609.7 ([M+3‒(BOC)+H]+, 37), 1706.8 (M+, 27), 1707.8 ([M+1]+, 38), 1708.8 ([M+2]+, 31), 1709.8 ([M+3]+, 18); HRMS (FD) Calcd for C118H106N4O8 (M+) 1706.8011, Found 1706.8010; UV *λ*max (CH2Cl2) 308 (log *ε* 5.53), 291 (5.56), 273 (sh. 5.27) nm.

**ASSOCIATED CONTENT:**

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information Statement

The supporting information for this article including supplementary figures and schemes (VT-NMR spectra, UV spectra, and chromatograms), and copies of 1H/13C NMR and LRMS spectra of new compounds [**1**-**6**, **13**, **15**-**17**, **19**-**22**] is available free of charge via the Internet at http://pubs.acs.org. FAIR Data is available as Supporting Information for Publication and includes the primary NMR FID files for compounds [**1**-**6**, **13**, **15**-**17**, **19**-**22**].

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27. The disparity in the absorption profile and the intensity of the rod in a threaded or unthreaded form was specific to a pair of **8** and **9** (and thus, **1** and **3**). There was no difference in absorption properties for the corresponding rod in either a threaded or unthreaded form in cases with other 6PAM and 5PAM.20
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30. Either of the two rods (Hc, 4H) in **2** (above 283 K) and **3** was not assigned due to broadening.