Tetrahedron 67 (2011) 5972–5978

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Formation of double helix self-assembled monolayers of ethynylhelicene oligomer disulfides on gold surfaces

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ARTICLE INFO

Article history:
Received 4 May 2011
Received in revised form 9 June 2011
Accepted 10 June 2011
Available online 16 June 2011

Keywords:
Ethynylhelicene oligomer
Double helix
Self-assembled monolayer
Thermal stability
Intercomplex interaction

ABSTRACT

Optically active ethynylhelicene pentamers and hexamers linked by disulfide bonds were synthesized. They formed self-assembled monolayers (SAMs) with double helix structure on gold surfaces, which were analyzed by infrared reflection-absorption spectroscopy (IR-RAS), quartz crystal microbalance (QCM), surface plasmon resonance (SPR), and circular dichroism (CD). Double helix SAMs could be formed on gold surfaces either from double helices or random coils in solution. The double helices on the surface were more stable than in solution. This result suggested the presence of strong intercomplex interactions between double helix complexes on the surface.

1. Introduction

Grafting simple small organic molecules, in general alkanethiols, on gold surfaces by metal–sulfide bonds is a well-established method to form self-assembled monolayers (SAMs) on solid surfaces.[1] If SAMs can be formed by multifunctional organic macromolecules possessing thiol groups, surface materials with various functions can be obtained. Attempts have been made using DNA, which reversibly forms double helices. However, electronic repulsions between DNA molecules resulted in low surface densities of the molecules,[2] and densely coated monolayers on gold surfaces have been obtained only in exceptional cases.[3,4] Synthetic oligomers, which can form double helices, have recently been developed,[5,6] and it was of interest to examine functional SAMs made from such macromolecules. The SAM formation study of synthetic double helix macromolecules double helices, however, has been challenging, owing to the difficulty in forming and detecting the double helix structures on solid surfaces.

We previously reported that optically active ethynylhelicene oligomers containing 1,12-dimethylbenzo[*c*]phenanthrene and *m*-phenylene formed double helices in organic solvents.[7,8] Ethynylhelicene oligomers reversibly changed their structures between random coil and double helix, and both the stability of double helix and the unfolding process were affected by temperature, concentration, and solvent. The structural change could be conveniently detected by CD, taking advantage of extremely large changes in $\Delta\varepsilon$ values extending over three orders of magnitude.

It was of interest to determine whether such multifunctional macromolecules can form SAMs on gold surfaces through a single metal thiolate bond, which is a very small part of the macromolecule. Double helix formation on a solid surface may be detected by taking advantage of the very large $\Delta\varepsilon$ values of the double helix itself. Described in this report are the synthesis and SAM formation of the ethynylhelicene oligomers with disulfide linkages. The formation of double helices on gold surfaces was analyzed by CD as well as infrared reflection-absorption spectroscopy (IR-RAS), quartz crystal microbalance (QCM), and surface plasmon resonance (SPR).

2. Results and discussion

2.1. Synthesis

Disulfides (*P*)-**1**, (*P*)-**2**, and (*P*)-**3** were synthesized from trimer (*P*)-**4**, pentamer (*P*)-**5**, and hexamer (*P*)-**6**, respectively, possessing

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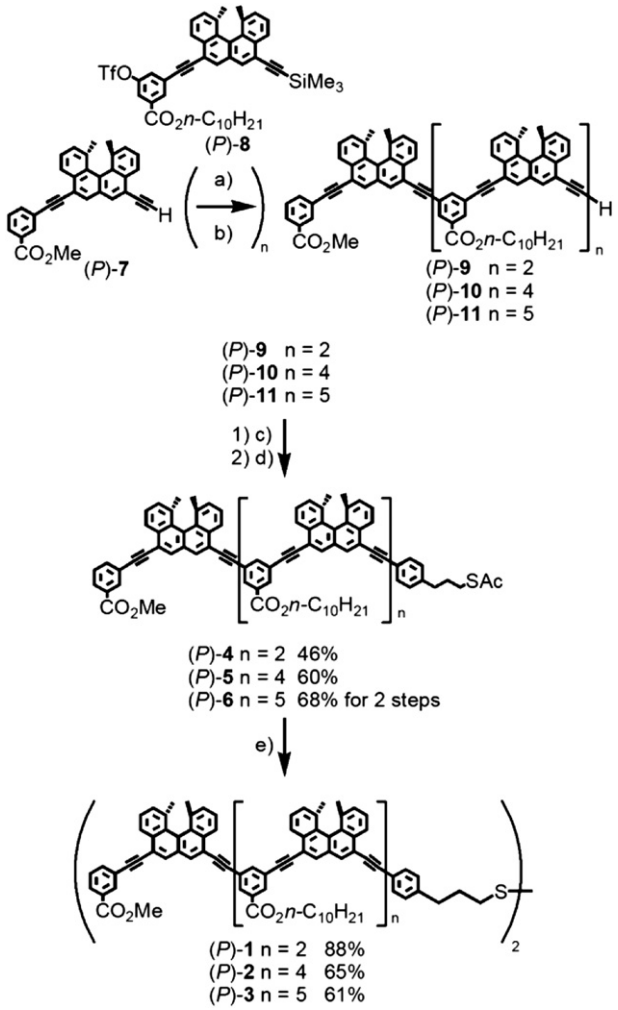
doi:10.1016/j.tet.2011.06.024

organothio terminal groups, which in turn were obtained by a one-direction oligomer synthesis starting from (*P*)-**7** (Scheme 1). The coupling and deprotection sequences of (*P*)-**7** with building block (*P*)-**8** gave trimer (*P*)-**9**, pentamer (*P*)-**10**, and hexamer (*P*)-**11**. Then, the reaction with 1-(3-bromopropyl)-4-iodobenzene **12** converted these oligomers to 3-bromopropylated derivatives, which were reacted with potassium thioacetate, affording thioesters (*P*)-**4**, (*P*)-**5**, and (*P*)-**6**. Dethioacetylation and oxidation to disulfides of the thioesters were conducted by treating the thioesters in toluene/pyrrolidine mixture under oxygen atmosphere at room temperature for 2 h, and (*P*)-**1**, (*P*)-**2**, and (*P*)-**3** were obtained in 88, 65, and 61% yield, respectively.



Scheme 1. Synthesis of (*P*)-**1**, (*P*)-**2**, and (*P*)-**3**. Conditions: (a) (*P*)-**8**, $[Pd_2(dba)_3]\cdot CHCl_3$, CuI, Mes_3P, Ph_3P, *n*-Bu_4NI, NEt_3, DMF/THF, 45 °C; (b) Bu_4NF, THF, 0 °C; (c) 1-(3-bromopropyl)-4-iodobenzene **12**, $[Pd_2(dba)_3]\cdot CHCl_3$, CuI, Mes_3P, Ph_3P, *n*-Bu_4NI, NEt_3, DMF/THF, 45 °C; (d) KSAc, DMA/THF, rt; (e) toluene/pyrrolidine, rt, O_2. dba=dibenzylideneacetone, DMF=*N*,*N*-dimethylformamide, Mes=mesityl, Tf=trifluoromethanesulfonyl, Ac=acetyl, DMA=*N*,*N*-dimethylacetoamide.

The disulfides (*P*)-**2** and (*P*)-**3** formed intramolecular double helices in trifluoromethylbenzene (0.1 mM) as indicated by their typical CD spectra as well as VPO analysis (Figs. S2 and S3), and (*P*)-**1** was likely to be in the random coil state under the same conditions, as indicated by the CD spectra (Fig. S4).

2.2. Double helix monolayer formation

Glass plates (1 mm thick) coated with a 200–250-nm-thick gold layer were immersed in solutions of the disulfides (*P*)-**1** (0.05 mM), (*P*)-**2** (0.1 mM), and (*P*)-**3** (0.1 mM) in trifluoromethylbenzene at room temperature for 24 h. The plates were washed with trifluoromethylbenzene and dried by argon blowing. IR-RAS analyses of (*P*)-**1**, (*P*)-**2**, and (*P*)-**3** grafted plates exhibited C–H bond stretching at 2856, 2927, and 2956 cm^{-1}, and carbonyl absorption at 1728 cm^{-1} (Fig. 1), which confirmed the adsorption of (*P*)-**1**, (*P*)-**2**, and (*P*)-**3** on the surface.

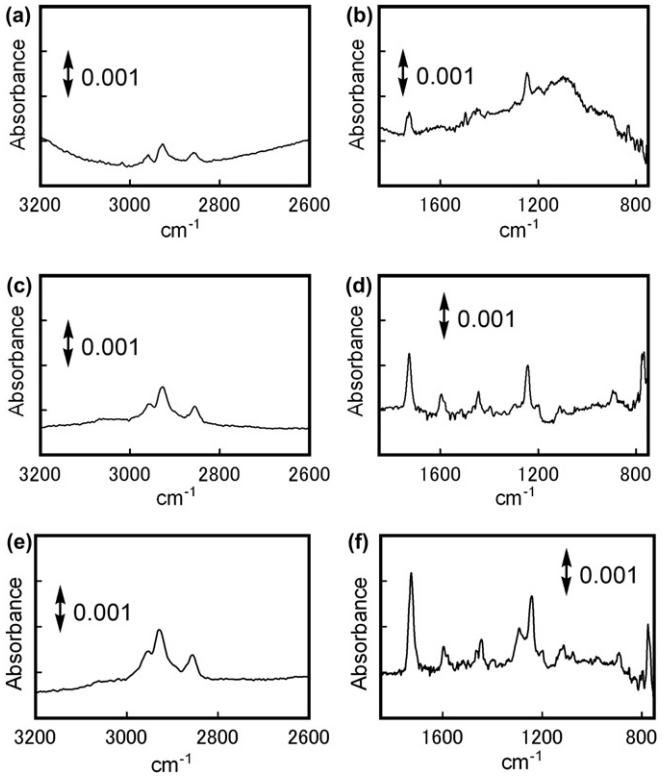


Fig. 1. IR-RAS spectra of monolayers on a gold surface. SAMs were prepared by immersion in solution of (a), (b) (*P*)-**1** (0.1 mM toluene), (c), (d) (*P*)-**2** (0.1 mM trifluoromethylbenzene), and (e) and (f) (*P*)-**3** (0.1 mM trifluoromethylbenzene) at rt for 24 h. After 24 h, the plates were washed with (a), (b) toluene, (c), (d), (e), and (f) trifluoromethylbenzene and dried by nitrogen blowing.

The transmission CD spectra were obtained for quartz plates with an 8-nm-thick gold layer.[9] The plate obtained by immersion in (*P*)-**1** solution did not show appreciable peaks, whereas (*P*)-**2** and (*P*)-**3** plates exhibited a positive Cotton effect at 364 nm and a negative effect at 325 nm (Fig. 2). These spectra were very similar in shape to those of (*P*)-**2** and (*P*)-**3** in trifluoromethylbenzene (Fig. S4), and indicated the formation of double helices on the surface. The lack of

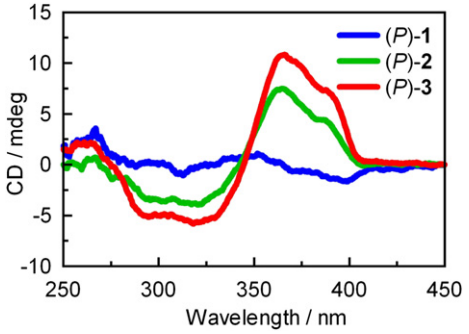


Fig. 2. CD spectra of SAMs of (*P*)-**1**, (*P*)-**2**, and (*P*)-**3** grafted gold-coated quartz plates. SAMs were prepared by immersion in solution of (*P*)-**1** (0.05 mM trifluoromethylbenzene), (*P*)-**2**, and (*P*)-**3** (0.1 mM trifluoromethylbenzene) at rt for 24 h.

a Cotton effect for the (*P*)-**1** plate was due to the random coil state of this compound on the surface as well as in solution. It should be emphasized that the surface double helix structure of (*P*)-**2** and (*P*)-**3** could be detected by CD. Such observation of surface monolayer macromolecules by CD has not been reported before, and the advantage of the extremely strong Cotton effects of (*P*)-**2** and (*P*)-**3** with the double helix form was used in the analysis.

Ethynylhelicene octamer (*P*)-**13** lacking the disulfide group formed double helix in trifluoromethylbenzene at 1 mM.[8] A gold plate was immersed in the trifluoromethylbenzene solution of (*P*)-**13**, and this plate showed no Cotton effect (Fig. S5). The result suggested that oligomers (*P*)-**1**, (*P*)-**2**, and (*P*)-**3** were adsorbed on the gold surface by covalent S–Au bonds.

Quartz crystal microbalance (QCM) analyses were conducted for gold electrodes treated with (*P*)-**2** or (*P*)-**3** in order to determine the amount of compounds on the surface: (*P*)-**2**, 57±6 ng on 0.392 cm^2 plate; (*P*)-**3**, 61±6 ng on 0.392 cm^2 plate. From these results, the values of the area per molecule on the surface were estimated: (*P*)-**2**, 6.5±0.6 nm^2/molecule; (*P*)-**3**, 7.3±0.6 nm^2/molecule. Assuming cylindrical structures of the double helix, diameters were calculated: (*P*)-**2**, 2.8±0.2 nm; (*P*)-**3**, 3.0±0.2 nm. These values were consistent with dense monolayer formation of these compounds on the gold surface (Table 1).

Table 1
Results of QCM analysis. SAMs were prepared by immersion in solution of (*P*)-**2** or (*P*)-**3** (0.1 mM trifluoromethylbenzene) at rt for 24 h. After 24 h, the plates were washed with chloroform

	(*P*)-**2**	(*P*)-**3**
Δf (Hz)	42±5	46±5
Δm (ng/0.392 cm^2)	57±6	61±6
Area per molecule (nm^2/molecule)	6.5±0.6	7.3±0.6
Diameter (nm)	2.8±0.2	3.0±0.2

Surface plasmon resonance (SPR) analyses were conducted to determine the thickness of the double helices on the gold layer (ca. 50 nm) on glass (Fig. 3). The thickness was determined by curve fitting the calculated and experimental SPR reflectivity curve: (*P*)-**2**, 3.9±0.1 nm; (*P*)-**3**, 4.5±0.3 nm. The height of the longer oligomer (*P*)-**3** was slightly greater than that of (*P*)-**2**, which supported the suggestion that a monolayer of double helix (*P*)-**2** and (*P*)-**3** formed on the gold surface.

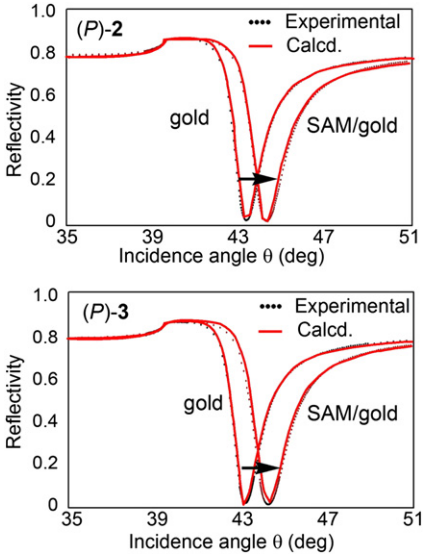


Fig. 3. Calculated (red line) and experimental (dotted line) SPR reflectivity curve for a bare gold layer and a gold layer covered by a (upper) (*P*)-**2** and (bottom) (*P*)-**3** monolayer. SAMs were prepared by immersion in solution of (*P*)-**2** or (*P*)-**3** (0.1 mM trifluoromethylbenzene) at rt for 24 h. After 24 h, the plates were washed with chloroform and dried by nitrogen blowing.

The surface analyses indicated the dense monolayer formation of (*P*)-**2** and (*P*)-**3** with double helix structures on the gold surface. Assuming homogeneous surfaces, the double helix structure was estimated to be 4–5 nm in height with 3 nm in diameter, which are reasonable dimensions for the molecules.

2.3. Grafting of oligomer in random coil state

In these experiments, the grafting of (*P*)-**2** and (*P*)-**3** on gold (*P*)-**2** and (*P*)-**3** formed double helix structures. Then, it was of interest to compare grafting of (*P*)-**2** and (*P*)-**3** in a random coil state. Quartz plates with 8-nm-thick gold layers were immersed in a THF solution of (*P*)-**2** (0.1 mM, 20 °C) for 24 h, in which (*P*)-**2** was in random coil state (Fig. S6a). The CD spectra of the plate was identical to that obtained by grafting in trifluoromethylbenzene, in which (*P*)-**2** adopted a double helix structure. The result showed that (*P*)-**2** was grafted with a double helix structure on the surface from the solution of random coil as well as of double helix (Fig. 4a). Similarly, SAMs of (*P*)-**3** were prepared by immersion in a THF solution of (*P*)-**3** (0.1 mM, 20 °C), in which (*P*)-**3** was an approximately 1:3 mixture of double helix and random coil as indicated by CD (Fig. S6b). The CD spectra of SAMs prepared from THF solution were again identical to that prepared from trifluoromethylbenzene solution (Fig. 4b). Since trimer (*P*)-**1** was adsorbed on the surface in a random coil state, random coils of (*P*)-**2** and (*P*)-**3** could be also grafted. Random coils of (*P*)-**2** and (*P*)-**3** probably converted into a double helix on the surface. Strong interactions between the double helix complexes on the surface might have promoted double helix formation of initially grafted random coils of (*P*)-**2** and (*P*)-**3**.

The presence of such strong intercomplex interactions was also suggested by attempted mixed grafting experiments of these compounds with an alkanethiol. Plates with gold layers were immersed in trifluoromethylbenzene solutions of (*P*)-**2** or (*P*)-**3** (0.1 mM) and 1-decanethiol (20 mM). CD spectra (Fig. 5) and IR-RAS spectra (Figs. 1 and S7) of the plates did not markedly change

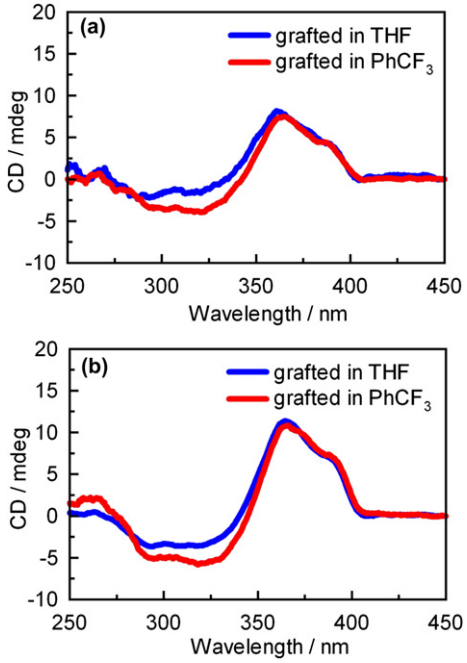


Fig. 4. CD spectra of SAM of (a) (*P*)-**2** and (b) (*P*)-**3** on gold. SAMs were prepared by immersion in solution of (*P*)-**2** (0.1 mM) (a, blue line) in tetrahydrofuran, (a, red line) in trifluoromethylbenzene, or (*P*)-**3** (0.1 mM) (b, blue line) in tetrahydrofuran, (b, red line) in trifluoromethylbenzene at 20 °C for 24 h.

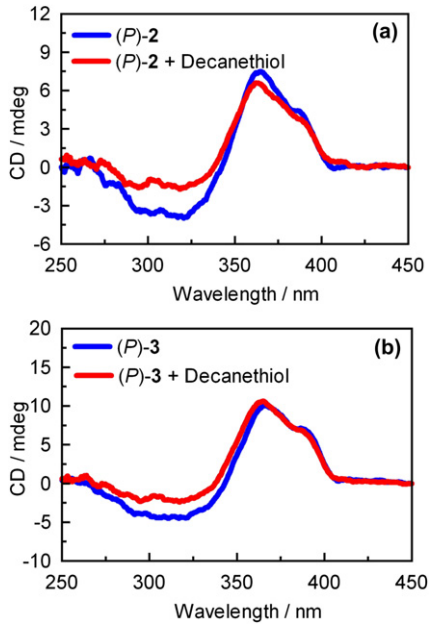


Fig. 5. CD spectra of gold plates prepared by immersion in the mixture of the oligomer (0.1 mM) and 1-decanethiol (x mM) in trifluoromethylbenzene for 24 h at rt (a) (*P*)-**2** (0.1 mM) and 1-decanethiol (blue line) x=0 and (red line) x=20. (b) (*P*)-**3** (0.1 mM) and 1-decanethiol (blue line) x=0 and (red line) x=20.

compared with those of the plates obtained from (*P*)-**2** or (*P*)-**3**. Despite the large difference between the concentration of (*P*)-**2**/(*P*)-**3** and 1-decanethiol, very small amounts of 1-dcanethiol were adsorbed on the surface, if any (Figs. 5 and S6). This could be explained by strong intercomplex interactions between the double helices on the gold surface.

2.4. Thermal stability of double helix on gold surface

Changing the structure of (*P*)-**2** and (*P*)-**3** on the gold surface was attempted. When (*P*)-**2** and (*P*)-**3** on gold were heated at 80 °C for 2 h and 6 h, respectively, the CD spectra showed essentially no change (Fig. 6). On the other hand, in chloroform, toluene, and THF

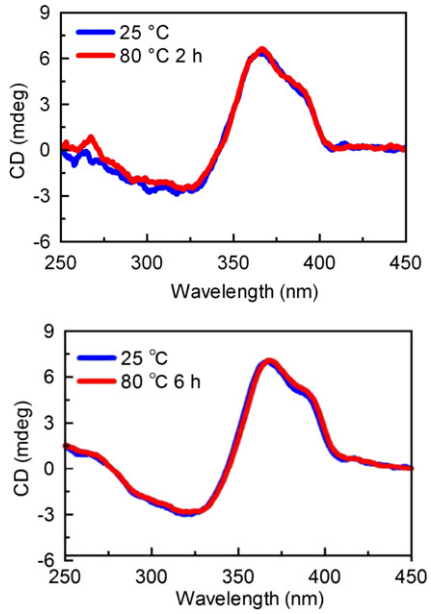


Fig. 6. CD spectra of SAM plates of (*P*)-**2** (upper) and (*P*)-**3** (bottom) on gold surfaces before and after heating at 80 °C.

(0.1 mM), (*P*)-**2** and (*P*)-**3** unfolded to random coils by heating at 60–90 °C (Fig. S8). These results showed that the double helix was more stable on the gold surface than in solution, which may again be ascribed to strong intercomplex interactions between the double helix (*P*)-**2** and (*P*)-**3** on the surface.

3. Conclusion

To summarize, ethynylhelicene trimer, pentamer, and hexamer, all with a disulfide moiety, were synthesized and formed dense double helix monolayers on gold surfaces. These results are a notable example of grafting multifunctional macromolecules by thiolate linkage. CD was effective to probe the structure of these compounds on the solid surface. These compounds formed double helical SAMs on gold surfaces either from double helices or random coils in solution. The presence of strong intercomplex interactions on the surface was suggested.

4. Experimental section

4.1. General methods

Elemental analyses were conducted with a Yanaco CHN CORDER MT-6 and a Yanaco HNS-15/HSU-20. Optical rotations were measured on a JASCO DIP-340 digital polarimeter. IR spectra were measured on a JASCO FT/IR-400 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury (400 MHz), a Brucker AM-600 (600 MHz) or a JEOL JNM-ECA600 (600 MHz) with tetramethylsilane as an internal standard, and the abbreviations of signal patterns are follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet. ^{13}C NMR spectra taken in $CDCl_3$ (δ 77.0) were referenced to the residual solvents. Low- and High-resolution mass spectra were recorded on a JEOL JMS DX-303 or a JEOL JMS AX-700 spectrometer. MALDI-TOF MS spectra were recorded on a Perseptive Biosystems Voyager™ DE using α-cyano-4-hydroxycinnamic acid as the matrix. CD and UV/vis spectra were measured on a JASCO J-720 spectropolarimeter. Vapor pressure osmometry (VPO) was conducted with a Knauer vapor pressure osmometer K-7000 molecular weight apparatus using benzil as a standard. Gel permeation chromatography (GPC) was conducted with Recycling Preparative HPLC LC-908 or LC-918 (Japan Analytical Industry, Co. Ltd.). Vacuum evaporation of gold was conducted by a vacuum evaporator V-KS200 (Osaka vacuum) or small vacuum evaporator VPC-260F (ULVAC kiko, Inc.).

4.2. Synthesis and characterization

4.2.1. 1-(3-Bromopropyl)-4-iodobenzene ***12****.* To a mixture of 3-(4-iodophenyl)propan-1-ol (195 mg, 0.743 mmol), triphenylphosphine (234 mg, 0.892 mmol), and dichloromethane (8 mL) was added carbon tetrabromide (259 mg, 0.780 mmol) at 0 °C, and the mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure, and silica gel chromatography gave the title compound (246 mg, quant.) as colorless oil. LRMS (EI, 70 eV) m/z 326 (M^++2, 75%), 324 (M^+, 76%), 217 (M^+–$(CH_2)_2Br$, 100%). HRMS m/z calcd for $C_9H_{10}BrI$: 323.9011. Found 323.9006. IR (KBr) 2931, 2856 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 (2H, quint, J=6.8 Hz), 2.72 (2H, t, J=7.3 Hz), 3.37 (2H, t, J=6.6 Hz), 6.95 (2H, d, J=8.1 Hz), 7.60 (2H, d, J=8.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.9, 33.5, 33.9, 91.2, 130.5, 137.4, 140.0.

*4.2.2. Acetylthio trimer (P)-****4****.* Under an argon atmosphere, a mixture of tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (11.2 mg, 0.0108 mmol), cuprous iodide (24.6 mg, 0.129 mmol), trimesitylphosphine (25.1 mg, 0.0645 mmol), tetrabutylammonium iodide (317.7 mg, 0.860 mmol), triethylamine (0.3 mL), and

N,*N*-dimethylformamide (3 mL) was freeze-evacuated three times in flask A. In flask B, a mixture of (*P*)-**9**[10] (67.2 mg, 0.0430 mmol) and **12** (15.4 mg, 0.0473 mmol) in tetrahydrofuran (3 mL) was freeze-evacuated three times, and was added dropwise to flask A. The mixture was stirred for 2 h at 45 °C. The reaction was quenched by adding saturated aqueous ammonium chloride, the organic materials were extracted with toluene. The organic layer was washed with brine, and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography gave a mixture. The mixture was dissolved in tetrahydrofuran (2 mL) and *N*,*N*-dimethylacetoamide (2 mL), and potassium thioacetate (75.4 mg, 0.660 mmol) was added. The mixture was stirred for 13 h at room temperature. The reaction was quenched by adding water, and the organic materials were extracted with toluene. The organic solvents were evaporated under reduced pressure, and separation by recycling GPC gave (*P*)-**4** (34.9 mg, 0.0199 mmol, 46% for two steps). Mp 128–130 °C (chloroform/methanol). $[\alpha]_D^{23}$ −549 (*c* 1.00, chloroform). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{124}{}^{13}C_1H_{110}O_7S$: 1755.8. Found: 1755.0. IR (KBr) 1723, 1686 cm^{-1}. Anal. Calcd for $C_{125}H_{110}O_7S$: C, 85.48; H, 6.31%. Found: C, 85.64; H, 6.44%. ^1H NMR (600 MHz, $CDCl_3$) δ 0.86 (6H, t, *J*=6.9 Hz), 1.20–1.45 (24H, m), 1.48–1.55 (4H, m), 1.86 (4H, quint, *J*=7.2 Hz), 1.92 (2H, quint, *J*=7.6 Hz), 1.977 (6H, s), 1.981 (6H, s), 2.00 (6H, s), 2.35 (3H, s), 2.75 (2H, t, *J*=7.6 Hz), 2.92 (2H, t, *J*=7.4 Hz), 3.98 (3H, s), 4.43 (4H, t, *J*=6.5 Hz), 7.24 (2H, d, *J*=7.9 Hz), 7.45–7.55 (7H, m), 7.64 (2H, d, *J*=7.9 Hz), 7.66–7.77 (6H, m), 7.89 (1H, d, *J*=7.6 Hz), 8.03 (1H, d, *J*=7.9 Hz), 8.08 (1H, s), 8.11 (1H, s), 8.13 (1H, s), 8.14 (1H, s), 8.16 (2H, s), 8.20–8.22 (2H, m), 8.36–8.40 (5H, m), 8.51–8.59 (6H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.7, 23.2, 26.1, 28.5, 28.8, 29.31, 29.34, 29.6, 30.7, 30.9, 31.9, 34.8, 52.3, 65.8, 87.3, 88.6, 89.33, 89.35, 89.37, 89.45, 92.9, 92.99, 93.02, 93.04, 93.7, 94.9, 119.7, 119.8, 119.86, 119.88, 120.1, 120.7, 121.0, 123.59, 123.65, 123.75, 123.81, 124.31, 124.33, 124.4, 126.5, 126.7, 126.8, 126.95, 126.98, 127.0, 128.6, 129.1, 129.22, 129.24, 129.28, 129.31, 129.4, 129.7, 129.88, 129.93, 130.6, 130.99, 131.03, 131.07, 131.09, 131.2, 131.5, 131.8, 132.1, 132.17, 132.23, 132.25, 132.4, 132.8, 135.8, 136.8, 136.87, 136.90, 136.95, 138.3, 141.9, 165.4, 166.4, 195.7.

*4.2.3. Trimer Disulfide (P)-**1**.* Under an oxygen atmosphere, to a solution of (*P*)-**4** (32.2 mg, 0.0183 mmol) in toluene (2 mL) was added pyrrolidine (2 mL) at room temperature. After being stirred at room temperature for 3.5 h, the reaction was quenched by added 2 M aqueous hydrochloric acid. The organic materials were extracted with toluene. The organic layer was washed with water and brine, dried over magnesium sulfate. The solvents were removed under reduced pressure, and separation by recycling GPC gave (*P*)-**1** (27.7 mg, 0.0081 mmol, 88%). Mp 168–170 °C (chloroform/methanol). $[\alpha]_D^{26}$ −579 (*c* 0.10, chloroform). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{244}{}^{13}C_2H_{214}O_{12}S_2$: 3425.6. Found: 3425.4. UV/vis (trifluoromethylbenzene, 0.05 mM) λ (ε) 341 nm (2.5×10^5). CD (trifluoromethylbenzene, 0.05 mM) λ ($\Delta\varepsilon$) 336 nm (80), 388 nm (−140). IR (KBr) 2202, 1722 cm^{-1}. Anal. Calcd for $C_{246}H_{214}O_{12}S_2$: C, 86.23; H, 6.30%. Found: C, 86.02; H, 6.57%. ^1H NMR (600 MHz, $CDCl_3$) δ 0.83–0.88 (12H, m), 1.20–1.55 (56H, m), 1.82–1.89 (8H, m), 1.94 (9H, m), 1.97 (9H, s), 1.978 (9H, s), 1.986 (9H, s), 2.07 (4H, quint, *J*=7.4 Hz), 2.72 (4H, t, *J*=7.2 Hz), 2.78 (4H, t, *J*=7.8 Hz), 3.97 (6H, s), 4.42 (8H, m), 7.24 (4H, d, *J*=7.2 Hz), 7.42–7.54 (14H, m), 7.62–7.76 (16H, m), 7.88 (2H, dt, *J*=7.6, 1.4 Hz), 8.03 (2H, s), 8.04–8.08 (4H, m), 8.09 (2H, s), 8.11 (3H, s), 8.12 (3H, s), 8.17 (2H, t, *J*=1.6 Hz), 8.19 (2H, t, *J*=1.6 Hz), 8.32–8.39 (10H, m), 8.48–8.57 (12H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.7, 23.2, 26.1, 28.8, 29.31, 29.34, 29.6, 30.4, 31.9, 34.4, 38.1, 52.3, 65.8, 87.4, 88.6, 89.3, 89.36, 89.44, 92.9, 92.99, 93.01, 93.05, 93.7, 94.9, 119.7, 119.8, 119.86, 119.89, 120.1, 120.6, 121.0, 123.57, 123.65, 123.7, 123.8, 124.30, 124.34, 124.36, 126.4, 126.7, 126.8, 126.9, 126.97, 126.99, 127.04, 128.6, 128.7, 129.1, 129.19, 129.24, 129.3, 129.5, 129.7, 129.88, 129.93, 130.6, 131.00, 131.08, 131.11, 131.2, 131.48, 131.52, 131.9, 132.1, 132.18, 132.23, 132.26, 132.4, 132.8, 135.8, 136.8, 136.85, 136.93, 136.95, 138.29, 138.31, 142.0, 165.5, 166.4.

*4.2.4. Acetylthio pentamer (P)-**5**.* Under an argon atmosphere, a mixture of tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (34.2 mg, 0.033 mmol), cuprous iodide (74.3 mg, 0.390 mmol), triphenylphosphine (51.4 mg, 0.196 mmol), trimesitylphosphine (76.2 mg, 0.196 mmol), tetrabutylammonium iodide (960.4 mg, 2.600 mmol), triethylamine (1 mL), and *N*,*N*-dimethylformamide (10 mL) was freeze-evacuated three times in flask A. In flask B, a mixture of (*P*)-**10**[10] (350 mg, 0.173 mmol) and **12** (56.2 mg, 0.173 mmol) in tetrahydrofuran (10 mL) was freeze-evacuated three times, and was added dropwise to flask A. The mixture was stirred for 2 h at 45 °C. The reaction was quenched by adding saturated aqueous ammonium chloride, the organic materials were extracted with toluene. The organic layer was washed with brine, and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography gave a mixture. The mixture was dissolved in tetrahydrofuran (15 mL) and *N*,*N*-dimethylacetoamide (15 mL), and potassium thioacetate (494.0 mg, 4.325 mmol) was added. The mixture was stirred for 12 h at room temperature. The reaction was quenched by adding water, and the organic materials were extracted with toluene. The solvents were removed under reduced pressure, and separation by recycling GPC gave (*P*)-**5** (289.4 mg, 0.133 mmol, 77% for two steps). Mp 154–156 °C (chloroform/methanol). $[\alpha]_D^{23}$ +3807 (*c* 0.10, trifluoromethylbenzene, within 1 h after dissolution). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{205}{}^{13}C_2H_{186}O_{11}S$: 2881.4. Found: 3443.9. UV/vis (trifluoromethylbenzene, 5 μM, within 5 min after dissolution) λ (ε) 335 nm (2.3×10^5). CD (trifluoromethylbenzene, 3 μM, within 5 min after dissolution) λ ($\Delta\varepsilon$) 326 nm (−890), 364 nm (1420), 390 nm (760). IR (KBr) 2204, 1722, 1693 cm^{-1}. Anal. Calcd for $C_{207}H_{186}O_{11}S$: C, 86.27; H, 6.51; S, 1.11%. Found: C, 86.18; H, 6.76; S, 1.21%. ^1H NMR (600 MHz, $CDCl_3$, mM, observed at 60 °C after heated for 15 min) δ 0.83 (12H, t, *J*=6.9 Hz), 1.20–1.42 (48H, m), 1.46–1.52 (8H, m), 1.81–1.86 (8H, m), 1.92 (2H, quint, *J*=7.4 Hz), 1.942 (3H, s), 1.948 (6H, s), 1.952 (3H, s), 1.97 (12H, s), 1.98 (6H, s), 2.33 (3H, s), 2.73 (2H, t, *J*=7.4 Hz), 2.90 (2H, t, *J*=7.5 Hz), 3.95 (3H, s), 4.39–4.42 (8H, m), 7.22 (2H, d, *J*=8.1 Hz), 7.41–7.49 (11H, m), 7.61 (2H, d, *J*=8.1 Hz), 7.64–7.74 (10H, m), 7.86 (1H, ddd, *J*=7.8, 1.8, 1.2 Hz), 8.03 (1H, ddd, *J*=7.8, 1.8, 1.2 Hz), 8.05 (1H, s), 8.08 (1H, s), 8.095 (1H, s), 8.104 (1H, s), 8.131 (2H, s), 8.133 (2H, s), 8.15 (2H, s), 8.18–8.20 (4H, m), 8.33–8.36 (9H, m), 8.49–8.56 (10H, m). ^{13}C NMR (150 MHz, $CDCl_3$ mM, observed at 60 °C after heated for 30 min) δ 14.0, 22.6, 23.1, 26.1, 28.6, 28.9, 29.29, 29.34, 29.6, 30.5, 30.9, 31.9, 34.9, 52.2, 65.8, 87.4, 88.8, 89.5, 89.6, 93.0, 93.08, 93.14, 93.8, 95.0, 119.9, 120.0, 120.1, 120.3, 120.9, 121.2, 123.7, 123.9, 124.0, 124.5, 124.6, 126.6, 126.9, 127.0, 127.1, 128.2, 128.6, 128.7, 129.05, 129.14, 129.2, 129.26, 129.28, 129.33, 129.5, 129.7, 129.96, 130.03, 130.9, 131.17, 131.23, 131.8, 131.9, 132.3, 132.38, 132.44, 132.6, 132.9, 135.8, 136.9, 137.00, 137.03, 137.05, 137.09, 138.3, 142.0, 165.4, 166.4, 195.3.

*4.2.5. Pentamer disulfide (P)-**2**.* Under an oxygen atmosphere, to a solution of (*P*)-**5** (28.1 mg, 9.8 μmol) in toluene (2 mL) was added pyrrolidine (2 mL) at room temperature. After being stirred at room temperature for 1.5 h, the reaction was quenched by added 2 M aqueous hydrochloric acid, and the organic materials were extracted with toluene. The organic layer was washed with water and brine, dried over magnesium sulfate. The solvents were removed under reduced pressure, and separation by recycling GPC gave (*P*)-**2** (17.9 mg, 6.3 μmol, 65%). Mp 179–181 °C (chloroform/methanol). $[\alpha]_D^{23}$ +4190 (*c* 0.10, trifluoromethylbenzene, within 1 h after dissolution). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{406}{}^{13}C_4H_{366}O_{20}S_2$: 5676.7. Found: 3443.9. UV/vis (trifluoromethylbenzene, 3 μM, within 5 min

after dissolution) λ (ε) 332 nm (4.2×10^5). CD (trifluoromethylbenzene, 3 μM, within 5 min after dissolution) λ (Δε) 326 nm (−2200), 364 nm (3450), 390 nm (1950). IR (KBr) 2205, 1722 cm^{-1}. Anal. Calcd for $C_{410}H_{366}O_{20}S_2$: C, 86.74; H, 6.50; S, 1.13%. Found: C, 86.47; H, 6.53; S, 1.41%. ^1H NMR (600 MHz, $CDCl_3$, mM, observed at 60 °C after heated at 60 °C for 15 min) δ 0.82–0.90 (24H, m), 1.20–1.53 (112H, m), 1.84 (16H, quint, *J*=7.2 Hz), 1.94–1.99 (60H, m), 2.06 (4H, quint, *J*=7.4 Hz), 2.72 (4H, t, *J*=7.2 Hz), 2.78 (4H, t, *J*=7.8 Hz), 3.96 (6H, s), 4.39–4.43 (16H, m), 7.23 (4H, d, *J*=8.4 Hz), 7.43–7.50 (22H, m), 7.62 (4H, d, *J*=8.4 Hz), 7.61–7.72 (20H, m), 7.85 (2H, ddd, *J*=8.4, 1.8, 1.2 Hz), 7.99 (2H, s), 8.03 (2H, s), 8.03 (2H, ddd, *J*=6.6, 1.8, 1.2 Hz), 8.07 (2H, s), 8.09 (2H, s), 8.09 (2H, s), 8.10–8.12 (10H, m), 8.14 (2H, dd, *J*=1.8, 1.2 Hz), 8.17–8.18 (6H, m), 8.31 (2H, t, *J*=1.8, 1.2 Hz), 8.32 (2H, t, *J*=1.8, 1.2 Hz), 8.34–8.35 (12H, m), 8.36 (2H, dd, *J*=1.8, 1.2 Hz), 8.48–8.55 (20H, m). ^{13}C NMR (150 MHz, $CDCl_3$ mM, observed at 60 °C after heated at 60 °C for 30 min) δ 14.0, 22.6, 23.1, 26.1, 28.9, 29.30, 29.34, 29.6, 29.7, 30.4, 31.9, 34.5, 38.4, 52.2, 65.8, 87.5, 88.8, 89.5, 89.6, 93.0, 93.09, 93.14, 93.8, 95.0, 96.2, 119.8, 120.0, 120.1, 120.3, 120.9, 121.2, 123.6, 123.75, 123.84, 124.0, 124.49, 124.53, 126.6, 126.8, 126.9, 127.0, 127.1, 128.6, 128.7, 129.0, 129.1, 129.26, 129.33, 129.5, 129.7, 129.96, 130.01, 131.17, 131.22, 131.3, 131.76, 131.82, 131.9, 132.3, 132.38, 132.44, 132.6, 132.9, 135.8, 136.9, 137.0, 137.1, 138.3, 142.1, 165.4, 166.4.

*4.2.6. Acetylthio hexamer (P)-**6**.* Under an argon atmosphere, a mixture of tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (12.8 mg, 0.0124 mmol), cuprous iodide (28.4 mg, 0.149 mmol), triphenylphosphine (19.5 mg, 0.0743 mmol), trimesitylphosphine (28.9 mg, 0.0743 mmol), tetrabutylammonium iodide (365.7 mg, 0.990 mmol), triethylamine (0.4 mL), and *N*,*N*-dimethylformamide (2 mL) was freeze-evacuated three times in flask A. In flask B, a mixture of (*P*)-**11**[10] (161.1 mg, 0.0495 mmol) and **12** (21.4 mg, 0.0658 mmol) in tetrahydrofuran (6 mL) was freeze-evacuated three times, and was added dropwise to flask A. The mixture was stirred for 2 h at 45 °C. The reaction was quenched by adding saturated aqueous ammonium chloride, the organic materials were extracted with toluene. The organic layer was washed with brine, and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography gave a mixture. The mixture was dissolved in tetrahydrofuran (7 mL) and *N*,*N*-dimethylacetoamide (7 mL), and potassium thioacetate (141.6 mg, 1.24 mmol) was added. The mixture was stirred for 12 h at room temperature. The reaction was quenched by adding water, and the organic materials were extracted with toluene. The organic solvents were evaporated under reduced pressure, and separation by recycling GPC gave (*P*)-**6** (108.6 mg, 0.0317 mmol, 64% for two steps). Mp 152–154 °C (chloroform/methanol). $[\alpha]_D^{23}$ +4038 (*c* 0.10, trifluoromethylbenzene, within 1 h after dissolution). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{246}{}^{13}C_2H_{224}O_{13}S$: 3443.7. Found: 3443.9. UV/vis (trifluoromethylbenzene, 5 μM, within 5 min after dissolution) λ (ε) 332 nm (2.5×10^5). CD (trifluoromethylbenzene, 5 μM, within 5 min after dissolution) λ (Δε) 326 nm (−1380), 365 nm (2130), 390 nm (1280). IR (KBr) 2206, 1722, 1692 cm^{-1}. Anal. Calcd for $C_{248}H_{224}O_{13}S$: C, 86.48; H, 6.55; S, 0.93%. Found: C, 86.51; H, 6.76; S, 1.00%. ^1H NMR (600 MHz, $CDCl_3$, mM, observed at 60 °C after heated for 15 min) δ 0.85 (15H, t, *J*=6.9 Hz), 1.23–1.38 (50H, m), 1.41 (10H, quint, *J*=7.4 Hz), 1.50 (10H, quint, *J*=7.5 Hz), 1.94 (2H, quint, *J*=7.4 Hz), 1.97 (15H, s), 1.99 (21H, s), 2.33 (3H, s), 2.74 (2H, t, *J*=7.4 Hz), 2.92 (2H, t, *J*=7.4 Hz), 3.96 (3H, s), 4.40–4.43 (10H, m), 7.21 (2H, d, *J*=8.1 Hz), 7.44–7.49 (13H, m), 7.61 (2H, d, *J*=8.1 Hz), 7.65 (1H, dd, *J*=7.9, 7.2 Hz), 7.67–7.73 (11H, m), 7.85 (1H, ddd, *J*=7.5, 1.5, 1.3 Hz), 8.03 (1H, s), 8.03 (1H, ddd, *J*=7.7, 1.6, 1.3 Hz), 8.07 (1H, s), 8.09 (1H, s), 8.09 (1H, s), 8.11 (4H, s), 8.12 (4H, s), 8.17–8.18 (5H, m), 8.33–8.35 (10H, m), 8.36 (1H, s), 8.49–8.55 (12H, m). ^{13}C NMR (150 MHz, $CDCl_3$ mM, observed at 60 °C after heated for 30 min) δ 14.0, 22.6, 23.1, 26.1, 28.6, 28.9, 29.29, 29.34, 29.6, 29.7, 30.5, 30.9, 31.9, 34.9, 52.2, 65.8, 87.4, 88.8, 89.5, 89.6, 93.0, 93.1, 93.8, 95.0, 119.9, 120.0, 120.1, 120.3, 120.9, 121.2, 123.7, 123.9, 124.0, 124.5, 124.6, 126.6, 126.9, 127.0, 127.1, 128.6, 128.7, 129.1, 129.23, 129.24, 129.28, 129.32, 129.5, 129.7, 129.96, 130.03, 130.9, 131.2, 131.3, 131.8, 131.9, 132.3, 132.4, 132.6, 132.9, 135.8, 136.9, 136.94, 136.99, 137.04, 137.1, 138.3, 142.0, 165.4, 166.4, 195.3.

*4.2.7. Hexamer disulfide (P)-**3**.* Under an oxygen atmosphere, to a solution of (*P*)-**6** (56.9 mg, 0.0165 μmol) in toluene (3 mL) was added pyrrolidine (3 mL) at room temperature. After being stirred at room temperature for 3 h, the reaction was quenched by added 2 M aqueous hydrochloric acid, and the organic materials were extracted with toluene. The organic layer was washed with water and brine, dried over magnesium sulfate. The solvents were removed under reduced pressure, and separation by recycling GPC gave (*P*)-**3** (34.1 mg, 0.0101 mmol, 61%). Mp 184–186 °C (chloroform/methanol). $[\alpha]_D^{23}$ +4873 (*c* 0.10, trifluoromethylbenzene, within 1 h after dissolution). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{488}{}^{13}C_4H_{442}O_{24}S_2$: 6801.3. Found: 3443.9. UV/vis (trifluoromethylbenzene, 3 μM, within 5 min after dissolution) λ (ε) 331 nm (4.8×10^5). CD (trifluoromethylbenzene, 3 μM, within 5 min after dissolution) λ (Δε) 326 nm (−2180), 366 nm (4310), 390 nm (2610). IR (KBr) 2208, 1724 cm^{-1}. Anal. Calcd for $C_{488}H_{442}O_{20}S_2$: C, 86.86; H, 6.55; S, 0.94%. Found: C, 86.88; H, 6.73; S, 1.00%. ^1H NMR (600 MHz, $CDCl_3$, 2 mM, observed at 60 °C after heated for 3 h) δ 0.82–0.90 (30H, m), 1.20–1.70 (140H, m), 1.84 (20H, quint, *J*=7.4 Hz), 1.94–2.01 (72H, m), 2.05 (4H, quint, *J*=7.4 Hz), 2.72 (4H, t, *J*=7.2 Hz), 2.77 (4H, t, *J*=7.6 Hz), 3.95 (3H, s), 4.41 (20H, t, *J*=6.8 Hz), 7.22 (4H, d, *J*=8.1 Hz), 7.40–7.51 (26H, m), 7.62 (4H, d, *J*=8.1 Hz), 7.63–7.72 (24H, m), 7.85 (2H, ddd, *J*=7.7, 1.5, 1.3 Hz), 7.99 (2H, s), 8.02 (2H, s), 8.03 (2H, ddd, *J*=7.9, 1.6, 1.2 Hz), 8.06 (2H, s), 8.07 (2H, s), 8.08 (2H, s), 8.10 (12H, s), 8.13 (2H, dd, *J*=1.8, 1.6 Hz), 8.16–8.17 (8H, m), 8.30–8.35 (22H, m), 8.48–8.54 (24H, m). ^{13}C NMR (150 MHz, $CDCl_3$ 2 mM, observed at 60 °C after heated for 3 h) δ 14.0, 22.7, 23.1, 26.1, 28.9, 29.3, 29.4, 29.6, 29.7, 30.5, 31.9, 34.5, 38.4, 52.2, 65.8, 88.8, 89.5, 93.09, 93.14, 93.8, 95.0, 120.0, 120.1, 120.3, 123.7, 124.0, 124.5, 126.6, 126.8, 126.9, 127.0, 127.1, 128.6, 128.7, 129.1, 129.2, 129.26, 129.32, 129.5, 129.7, 130.0, 130.9, 131.15, 131.22, 131.8, 131.9, 132.38, 132.43, 132.9, 135.8, 136.9, 137.0, 138.3, 142.1, 165.4, 166.4.

4.3. Preparation of gold substrate

Gold substrates for IR-RAS measurements were prepared by vapor deposition of chromium (5–7 nm) as adhesion layer and then gold (99.99%, 200–250 nm) on a slide glass. Gold substrates for SPR measurements were prepared by vapor deposition of gold (ca. 50 nm) on a slide glass. In the case of gold substrates for CD measurements, gold (8 nm) was deposited on a quartz substrate.

4.4. Preparation of self-assembled monolayer of (*P*)-1 on gold

The gold substrate (for IR-RAS or CD measurement) was immersed in 0.05 mM trifluoromethylbenzene solution of (*P*)-**1** at 20 °C for 24 h. The substrate was removed from the solution, immediately rinsed with trifluoromethylbenzene, and blown dried with argon or nitrogen.

4.5. Preparation of self-assembled monolayer of (*P*)-2 or (*P*)-3 on gold

Gold substrate (for IR-RAS or CD measurement) was immersed in 0.1 mM trifluoromethylbenzene solution of the (*P*)-**2** or (*P*)-**3** at 20 °C for 24 h. The substrate was removed from the solution, immediately rinsed with trifluoromethylbenzene, and blown dried

with argon or nitrogen. No change of CD spectra was observed by washing (Fig. S1).

4.6. Infrared reflection-absorption spectroscopy (IR-RAS)

Analysis was performed on an FTIR Spectrum One (Perkin–Elmer) with a mercury/cadmium/tellurium (MCT) detector. The IR-RAS measurements used 100 scans of interferogram accumulations with the bare gold substrate as reference. The optical path was purged with dry air before and during measurements. A reflection attachment, at an incident angle of 70°, together with a polarizer was used.

4.7. Surface plasmon resonance (SPR) spectroscopy

Surface plasmon resonance spectra were taken with SPR spectrometer (JEL-001, R-DEC Co., Ltd.). The SPR setup was based on the configuration introduced by Kretschmann and Raether.[11] Normal refractive index glass (n=1.52) slides was used. The substrate was pressed against a 45° prism (n=1.52) with index-matching oil between the substrate glass and prism. Using a p-polarized HeNe laser (λ=632.8 nm) as the light source, the intensity of the beam reflected at the gold interface was detected by a photodiode detector, and recorded as a function of the incidence angle for 'angular-scan' measurements. All sample cells and tubes were made of Teflon, which was resistant to most organic solvents. Fitting of SPR data was performed with the program Winspall (version 3.0.2.0 release: 0.1, Max-Planck-Institut fuer Polymerforschung). The thickness and the complex refractive index of gold layer were determined by curve fitting of the SPR data of bare gold in air. SAM formation was initiated by injection of (*P*)-**2** or (*P*)-**3** solution (0.1 mM trifluoromethylbenzene solution) into the cell. The adsorption was continued for 24 h, after which the surface was rinsed with chloroform, and blown dried with nitrogen. The SPR measurements were carried out in air for determination of the thickness of the SAMs. All measurements were performed at room temperature.

4.8. Quartz crystal microbalance (QCM) measurement

A quartz crystal microbalance (QCM; 400A Electrochemical Quartz Crystal Microbalances, BAS Co., Tokyo, Japan) was employed for the gravimetric analysis of (*P*)-**2** or (*P*)-**3** SAMs. An 8 MHz AT-cut quartz resonator coated with a thin gold layer (geometric surface area, one side: 0.196 cm^2) was used as a probe, in which the adsorption of 1 ng of substrate induces a −0.75 Hz change in the resonance frequency. The both sides of the Au electrode of the QCM were washed with a piranha solution in order to remove organic adsorbate impurities from the gold surfaces. The QCM was rinsed with distillated water, and dried in a vacuum. The QCM was immersed into trifluoromethylbenzene solution of (*P*)-**2** or (*P*)-**3** (0.1 mM) for 24 h. After washing with chloroform, the QCM was dried in a vacuum, and the mass change was calculated from the frequency shift.

4.9. Preparation of self-assembled monolayer of (*P*)-2 and (*P*)-3 on gold from THF solution

Gold substrate (for CD measurement) was immersed in 0.1 mM tetrahydrofuran solution of the (*P*)-**2** or (*P*)-**3** at 20 °C for 24 h. The substrate was removed from the solution, immediately rinsed with trifluoromethylbenzene, and blown dried with argon.

4.10. Attempted preparation of the mixed monolayer on gold

The gold substrate (for IR-RAS or CD measurement) was immersed in the mixture of (*P*)-**2** or (*P*)-**3** (0.1 mM) and decanethiol (20 mM) in trifluoromethylbenzene at 20 °C for 24 h. The substrate was removed from the solution, immediately rinsed with trifluoromethylbenzene, and blown dried with argon or nitrogen. Trifluoromethylbenzene used in this experiment was degassed by freeze-evacuation three times before preparation of the thiol solution.

Acknowledgements

This work was financially supported by a Grant-in-Aid for Scientific Research (No. 22790003), the GCOE program, and the WPI Initiative from JSPS. K.Y. and Z.A. express their appreciation for financial support from WPI-AIMR. H.A. expresses his appreciation for the financial support from International Advanced Research and Education Organization.

Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.06.024. These data include MOL file and InChIKey of the most important compounds described in this article.

References and notes

1. Ulman, A. *Chem. Rev.* **1996**, *96*, 1533–1554.
2. (a) Okahata, Y.; Matsunobu, Y.; Ijiro, K.; Mukae, M.; Murakami, A.; Makino, K. *J. Am. Chem. Soc.* **1992**, *114*, 8299–8300; (b) Hegner, M.; Wagner, P.; Semenza, G. *FEBS Lett.* **1993**, *336*, 452–456; (c) Herne, T. M.; Tarlov, M. J. *J. Am. Chem. Soc.* **1997**, *119*, 8916–8920; (d) Huang, E.; Satjapipat, M.; Han, S.; Zhou, F. *Langmuir* **2001**, *17*, 1215–1224; (e) Demers, L. M.; Mirkin, C. A.; Mucic, R. C.; Reynolds, R. A., III; Letsinger, R. L.; Elghanian, R.; Viswanadham, G. *Anal. Chem.* **2000**, *72*, 5535–5541; (f) Lee, C. Y.; Gong, P.; Harbers, G. M.; Grainger, D. W.; Castner, D. G.; Gamble, L. J. *Anal. Chem.* **2006**, *78*, 3316–3325; (g) Peterlinz, K. A.; Georgiadis, R. M.; Herne, T. M.; Tarlov, M. J. *J. Am. Chem. Soc.* **1997**, *119*, 3401–3402; (h) Levicky, R.; Herne, T. M.; Tarlov, M. J.; Satija, S. K. *J. Am. Chem. Soc.* **1998**, *120*, 9787–9792; (i) Steel, A. B.; Herne, T. M.; Tarlov, M. J. *Anal. Chem.* **1998**, *70*, 4670–4677.
3. (a) Kelly, S. O.; Barton, J. K.; Jackson, N. M.; Hill, M. G. *Bioconjugate Chem.* **1997**, *8*, 31–37; (b) Kelly, S. O.; Barton, J. K.; Jackson, N. M.; McPherson, L. D.; Potter, A. B.; Spain, E. M.; Allen, M. J.; Hill, M. G. *Langmuir* **1998**, *14*, 6781–6784.
4. Zhang, Z. L.; Pang, D. W.; Zhang, R. Y.; Yan, J. W.; Mao, B. W.; Qi, Y. P. *Bioconjugate Chem.* **2002**, *13*, 104–109.
5. Reviews: (a) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101*, 3893–4011; (b) Albecht, M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6448–6451; (c) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102–6211.
6. Examples of synthetic double helices. (a) Berl, V.; Huc, I.; G Khoury, R.; Krische, M. J.; Lehn, J.-M. *Nature* **2000**, *407*, 720–723; (b) Baptiste, B.; Zhu, J.; Halder, D.; Kauffmann, B.; Légar, J.-M.; Huc, I. *Chem.—Asian. J.* **2010**, *5*, 1364–1375; (c) Zhan, C.; Légar, J.-M.; Huc, I. *Angew. Chem., Int. Ed.* **2006**, *45*, 4625–4628; (d) Goto, H.; Furusho, Y.; Miwa, K.; Yashima, E. *J. Am. Chem. Soc.* **2009**, *131*, 4710–4720; (e) Yamada, H.; Maeda, K.; Yashima, E. *Chem.—Eur. J.* **2009**, *15*, 6794–6798; (f) Abe, H.; Machiguchi, H.; Matsumoto, S.; Inoue, M. *J. Org. Chem.* **2008**, *73*, 4650–4661; (g) Sugimoto, T.; Suzuki, T.; Shinkai, S.; Sada, K. *J. Am. Chem. Soc.* **2007**, *129*, 270–271; (h) Li, J.; Wisner, J. A.; Jennings, M. C. *Org. Lett.* **2007**, *9*, 3267–3269; (i) Yang, H.-C.; Lin, S.-Y.; Yang, H.-C.; Lin, C.-L.; Tsai, L.; Hunag, S.-L.; Chen, W.-P.; Chen, C.-H.; Jin, B.-Y.; Lur, T.-Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 726–730; (j) Gao, Q.; Li, F.; Li, G.; Kauffmann, B.; Xiang, J.; Jiang, H. *Chem. Commun.* **2010**, 297–299.
7. Amemiya, R.; Yamaguchi, M. *Chem. Rec.* **2008**, *8*, 116–127.
8. (a) Sugiura, H.; Nigorikawa, Y.; Saiki, Y.; Nakamura, K.; Yamaguchi, M. *J. Am. Chem. Soc.* **2004**, *126*, 14858–14864; (b) Sugiura, H.; Yamaguchi, M. *Chem. Lett.* **2007**, *36*, 58–59.
9. Huang, X.; Liu, Y.; Wang, S.; Zhou, S.; Zhu, D. *Chem.—Eur. J.* **2002**, *8*, 4179–4184.
10. Sugiura, H.; Amemiya, R.; Yamaguchi, M. *Chem.—Asian. J.* **2008**, *3*, 244–260.
11. Kretschmann, E.; Raether, H. *Z. Naturforsch., A: Phys. Sci.* **1968**, *23*, 2135–2136.