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Synthesis and Monolayer Behaviors of Optically Active 1,12-Dimethylbenzo[*c*]phenanthrene-5,8-diamides and the Formation of Chiral Langmuir-Blodgett Films

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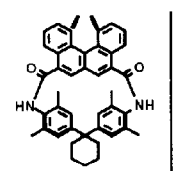
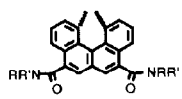
Abstract. We previously reported that an optically active cyclic amide consisting of a helical chiral 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylic acid forms a stable monolayer on the water surface, and that the monolayer can be transferred on a solid support giving optically active Langmuir-Blodgett (LB) films. In this study, several related amides were synthesized, and their monolayer behaviors were investigated with expectation to prepare optically active LB films possessing functional groups. The result indicates that the cyclic amide structure and cyclohexyl moiety are essential for the formation of stable monolayer on the water surface. *N*-Alkylation of the secondary amide does not seriously affect the formation of monolayer, and chiral LB films are obtained by *N,N'*-bis(3-mercaptopropyl) derivative of the cyclic amide.

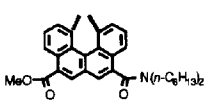
Previously, we reported the formation of Langmuir-Blodgett (LB) films of optically active cycloamide (*P*)-**1**,[1] which is a cyclic amide consisting of the helical chiral unit, 1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylic acid,[2] and a dianiline compound (Figure 1). The unique structure of (*P*)-**1** to form LB films lead us to study the relationships between its structure and the monolayer behavior on the water surface. Described



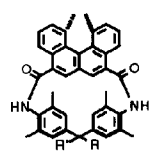
(*P*)-**1**



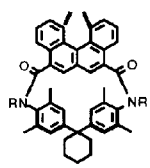
R = *n*-C_6H_{13}, R' = H (*P*)-**3**
R = *n*-$C_{10}H_{21}$, R' = H (*P*)-**4**
R = *n*-$C_{16}H_{33}$, R' = H (*P*)-**5**
R = Ph, R' = H (*P*)-**6**
R = 1-naphthyl, R' = H (*P*)-**7**
R = 2,6-dimethylphenyl R' = H (*P*)-**8**
R = R' = *n*-C_6H_{13} (*P*)-**9**
R = R' = *n*-$C_{10}H_{21}$ (*P*)-**10**
R = Ph, R' = Me (*P*)-**11**



(*P*)-**12**



R = R' = *n*-C_4H_9 (*P*)-**13**
R = Ph, R' = H (*P*)-**14**



R = Me (*P*)-**15**
R = $(CH_2)_3SH$ (*P*)-**16**

Figure 1. Structures of (*P*)-**1** and its derivatives.

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here are the effects of i) the cyclic structure, ii) the substituent on the diphenylmethane moiety, and iii) the substituent on the amide NH. This work is carried out also with the intention of preparing optically active LB films with functional groups, which can be used for asymmetric catalyst, chiral sensor, *etc*. Preparation of optically active LB films by *N,N'*-bis(3-mercaptopropyl) derivative of (*P*)-**1** is described as well.

Acyclic diamides were synthesized in order to reveal the role of the cyclic structure of (*P*)-**1**. Since it is presumed that the benzo[*c*]phenanthrenediamide moiety acts as a hydrophilic group on the water surface,[1] the monolayer behaviors of the acyclic diamides appear interesting. Acid chloride (*P*)-**2** prepared from (*P*)-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylic acid was reacted with several amines giving the corresponding secondary amides (*P*)-**3** to (*P*)-**8** and the tertiary amides (*P*)-**9** to (*P*)-**11**. Notably, these tertiary amides are mixtures of at least two conformers in $CDCl_3$ at room temperature as indicated by NMR, which are assigned to the rotamers concerning the C-C bond of the aromatic carbon and carbonyl carbon. The NMR peaks of the conformers coalesce at about 40 °C in DMSO-d_6. In accordance, monoamide (*P*)-**12** is a mixture of two conformers, and behaves similarly on heating. The amides (*P*)-**3** to (*P*)-**11** are spread from $CHCl_3$ solution on the water surface to measure the surface pressure (π)-area (*A*) isotherms at 20 °C (Figure 2). Extrapolation of the steeply rising part of the π-*A* curve to zero pressure gives the average surface area occupied by a molecule in the monolayer. In all cases, the surface areas of the compounds obtained from the π-*A* isotherms are smaller than those calculated from their CPK models. For example, 0.42 nm^2/molecule is experimentally obtained for (*P*)-**6**, while 1.43 nm^2/molecule is obtained by the calculation of a face-on orientation[1] and 0.75 nm^2 of a edge-on orientation.[1] Probably, these acyclic amides overlap to a certain extent when compressed by the barrier on the water surface because of the good planar structure of the molecule at the benzo[*c*]phenanthrene moiety. The isotherms for the tertiary amides (*P*)-**9** to **11** show larger surface areas, where the alkyl substituents probably

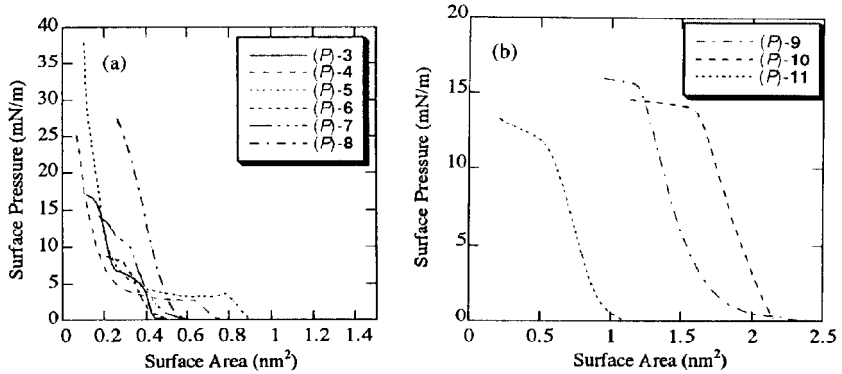


Figure 2. (a) π-*A* isotherms of (*P*)-**3**, (*P*)-**4**, (*P*)-**5**, (*P*)-**6**, (*P*)-**7**, and (*P*)-**8**. (b) π-*A* isotherms of (*P*)-**9**, (*P*)-**10**, and (*P*)-**11**.

form an expanded form. Among these compounds, only 1-naphthyl amide (*P*)-**7** can be transferred to hydrophobic quartz slides under a deposition pressure of 8 mN/m up to 6 strokes. That the monolayer can be transferred upward (1.33) and not downward indicates the formation of Z-type LB films. Meanwhile an absorbance at 311 nm of (*P*)-**7** in the LBfilms increases well with increasing number of deposited layers (Figure 3). CD (circular dichroism) spectra[3] was measured to compare the structure of the optically active LB

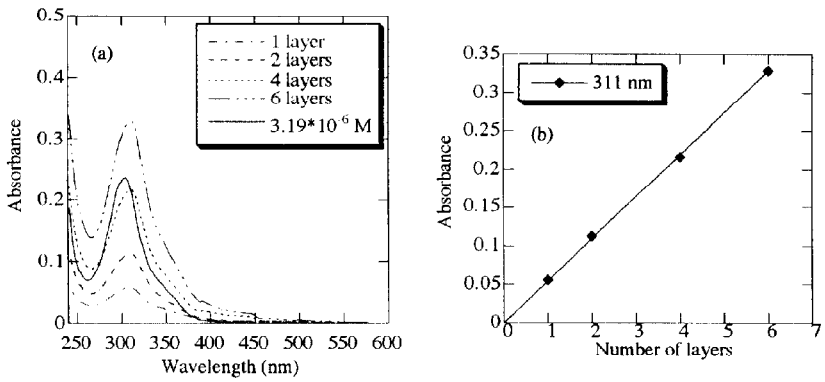


Figure 3. (a)UV absorption spectra of (*P*)-**7** in $CHCl_3$ (3.19×10^{-6} M) and in LB films. (b) Plots of the absorbance of (*P*)-**7** (311 nm) in LB films as a function of the number of layers.

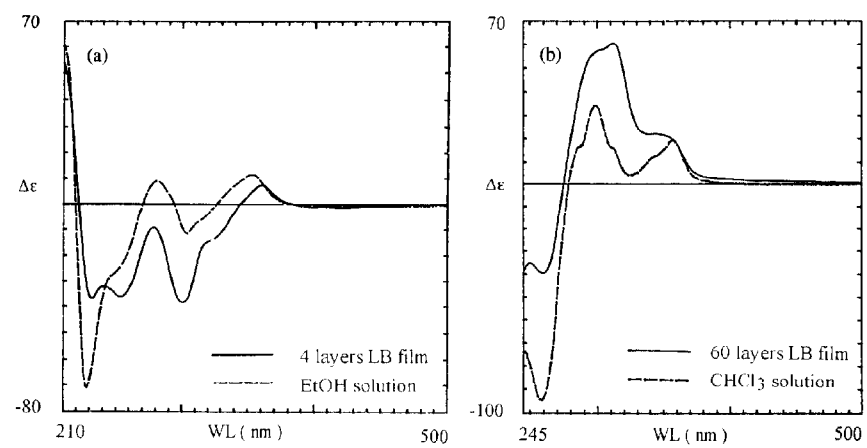
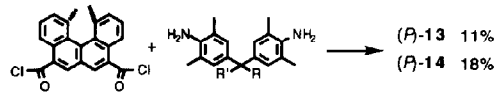


Figure 4. (a) CD spectra of (*P*)-**7** in EtOH (8.5×10^{-6} M) and in LB films with 4 layers. (b) CD spectra of (*P*)-**15** in $CHCl_3$ (2.5×10^{-5} M) and in LB films with 60 layers.

films and that in solution; the Cotton effect of the LB film and solution turned out to be similar (Figure 4a). Although (*P*)-**7** exceptionally forms LB films, it may reasonably be concluded that the cyclic structure of (*P*)-**1** is essential for the formation of stable monolayer on the water surface.

The effect of the dianiline structure is further examined by changing the substituent at the diphenylmethane moiety. While the cyclohexane derivative incorporated in (*P*)-**1** was readily synthesized from cyclohexanone and 2,6-dimethylaniline,[4] the synthesis of the related dianiline **17** from 5-nonanone was problematic. After various trials, a very low yield of **17** was obtained by treatment with CF_3SO_3H in DMSO. In contrast, the reaction of benzaldehyde and the aniline proceeded smoothly giving **17** in a higher yield. The cyclization of **17** and **18** with (*P*)-**2** was conducted under high dilution conditions,[2] and (*P*)-**13** and (*P*)-**14** were obtained in 11% and 18% yield, respectively (Scheme 1). Then, their monolayer behaviors were investigated. (*P*)-**14** shows less steep rise in the surface pressure compared to the parent compound (*P*)-**1** (Figure 5). Although (*P*)-**13** shows relatively steep rise and has a similar shape with (*P*)-**1**, the monolayer can not be kept stable enough to form LB films. It thus appears that the cyclohexane moiety of (*P*)-**1** is critical to form stable monolayer on the water surface.



(*P*)-**2** R = R' = *n*-C_4H_9 **17**
R = Ph, R' = H **18**

Scheme 1.

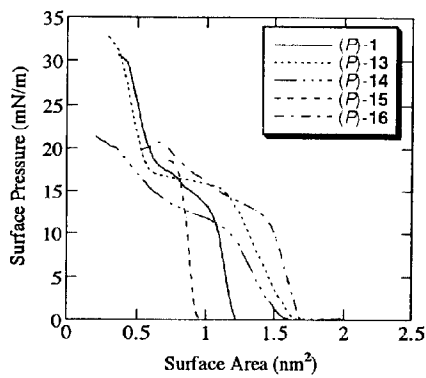
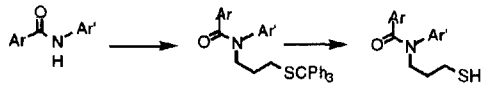


Figure 5. π-*A* isotherms of (*P*)-**1**, (*P*)-**13**, (*P*)-**14**, (*P*)-**15**, and (*P*)-**16**.

Next studied is the effect of *N*-alkylation at the secondary amide in (*P*)-**1**. (*P*)-*N*,*N*'-Dimethyl[1+1]cycloamide (*P*)-**15** previously synthesized[2] shows a sharp rise in the surface pressure on the

water surface owning an area of 0.93 nm^2/molecule (Figure 5). The π-*A* isotherm shape lacking a phase transition from face-on to edge-on orientation, however, differs from (*P*)-**1**,[1] and (*P*)-**15** can not be transferred on a solid support. This result suggesting that *N*-alkylation does not seriously interfere the formation of stable monolayers lead us to investigate another *N*-alkyl derivative: *N,N'*-Bis(3-mercaptopropyl) derivative, (*P*)-**16**. The compound was selected in order to prepare LB films possessing mercapto group, which, if obtained, may be used as an asymmetric catalyst or a chiral sensor. In addition, various functionalized LB films can be obtained by the transformation of thiol to functional groups such as sulfide, disulfide, thioester, sulfone, *etc.* Alkylation of the secondary amide in (*P*)-**1** with a protected 3-halopropanethiol was examined. Bis(3-bromopropyl) disulfide and bis(3-iodopropyl) disulfide were prepared from the known bis[3-(*p*-toluenesulfonyloxy)propyl] disulfide[5] by treating with NaBr in DMF or NaI in acetone, respectively, for 12 h. The latter compound was stable only in the solution, and decomposed when the solvent was removed to dryness. The alkylation of benzanilide **19**, a model compound of (*P*)-**1**, with either of the reagent under phase transfer conditions[6] gave a mixture of the monoalkylated amide, dialkylated amide, and the recovered **19**, even when **19** and the alkylating reagents were reacted in a molar ratio of 2:1. Since the disulfides gave the relatively complex mixtures as their products, triphenylmethyl protected 3-mercaptopropyl iodide[7] was examined. The reagent was readily prepared by reacting triphenylmethylthiol and excess 1,3-diiodopropane. Treatment of **19** with 2 equivalents of the alkylating reagent gave the product **20** in a quantitative yield, and the protecting group was removed again quantitatively by reacting with trifluoroacetic acid and triethylsilane leading



Ar =Ar' = Ph **19** (*P*)-**1** — **20** quant. (*P*)-**22** 90% — **21** quant. (*P*)-**16** 80%

Scheme 2.

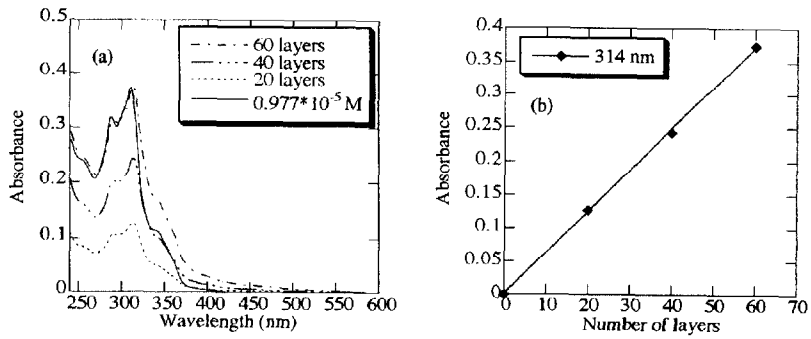


Figure 6. (a) UV absorption spectra of (*P*)-**16** in $CHCl_3$ (0.977×10^{-5} M) and in LB films. (b) Plots of the absorbance of (*P*)-**16** (314 nm) in LB films as a function of the number of layers.

to **21** (Scheme 2). As expected **21** possesses *s-cis* configuration concerning the two phenyl groups, which is shown by the presence of NOE between the *ortho*-protons of the two aromatic rings.[8] This *N*-alkylation method was then applied to (*P*)-**1**, and the corresponding 3-mercaptopropylated product (*P*)-**16** was obtained *via* (*P*)-**22**.

The π-*A* isotherm of (*P*)-**16** shows steep rise in the surface pressure, and exhibits a surface area of 1.68 nm^2/molecule (Figure 5). A calculated surface area of (*P*)-**16** on a face-on orientation, 1.70 nm^2/molecule, coincides with the experimental result. We consider that (*P*)-**16** takes a face-on orientation similar to (*P*)-**1** on the water surface (Figure 7). The phase transition observed in (*P*)-**1**, however, is not seen for (*P*)-**16**. We are pleased to find that the monolayer of (*P*)-**16** can be transferred under a deposit pressure of 7 mN/m onto a hydrophobic quartz slide up to 60 layers, and the films show good linear relationship between an absorption at 314 nm and number of layers (Figure 6). The formation of optically active LB films based on helical chirality is also confirmed by CD spectra measurement; the LB films of (*P*)-**16** exhibited somehow similar Cotton effect[3] with solution as was in the case of (*P*)-**1**[1] (Figure 4b). It should be noted that LB films are prepared by the 3-mercaptopropyl derivative of (*P*)-1. These results now clearly shows that the secondary amide structure in (*P*)-1 is not important. It is rather unexpected since we presumed that the intermolecular hydrogen bonding by the secondary amide would play an important role in the formation of stable monolayers.[1]

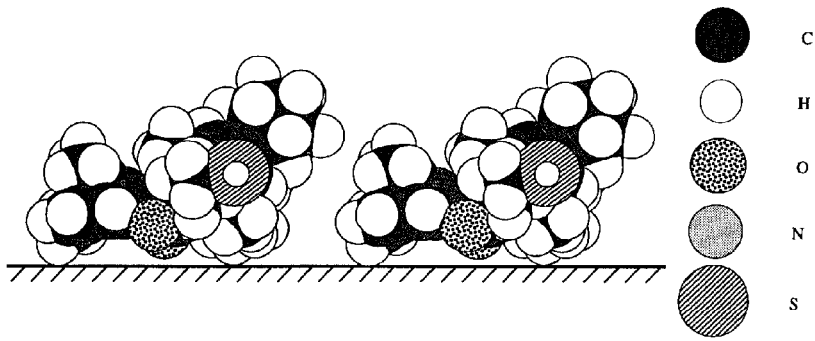


Figure 7. CPK Models of (*P*)-**16** at Face-on Orientation.

To summarize, the cyclic amide structure and the cyclohexyl moiety of (*P*)-**1** are essential for the formation of stable monolayers on the water surface. *N*-Alkylation of the secondary amide does not seriously affect the formation of monolayer, and LB films are obtained by *N,N'*-bis(3-mercaptopropyl) derivative of the cyclic amide. A variety of optically active LB films which exhibit interesting properties may be obtained from (*P*)-**16** and related *N*-alkyl derivatives.

Experimental Section

Melting points were determined with a Yanagimoto micro melting point apparatus without correction. Optical rotations were measured on a JASCO DIP-340 digital polarimeter. IR spectra were measured on JASCO FT/IR-400 spectrophotometer. UV spectra were measured on BECKMAN DU 640 and Hitachi U-3000 UV-VIS spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra

were recorded on a Varian Mercury NMR (400 MHz) or a Brucker AM-600 (600 MHz) with Me_4Si as an internal standard. Mass spectra were recorded on a JEOL JMS-DX-303 or JMS-AX-500 spectrometer. FAB mass spectra were measured using *m*-nitrobenzyl alcohol matrix.

(*P*)-*N,N'*-Dihexyl-1,12-dimethylbenzo[*c*]phenanthrere-5,8-diamide, (*P*)-3. Under an argon atmosphere, a mixture of (*P*)-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylic acid (50 mg, 0.15 mmol) and $SOCl_2$ (3 mL) was heated at reflux for 3 h. After cooled to room temperature, the solvent was evaporated under a reduced pressure, and the resulted acid chloride (*P*)-2 was azeotropically dried by adding CH_2Cl_2 (3 mL) and evaporating three times. Then dry CH_2Cl_2 (3 mL), pyridine (0.05 mL), and hexylamine (60 μL, 0.45 mmol) were added, and the mixture was stirred for 3 h at room temperature. The reaction was quenched by adding 2 M HCl, and the organic materials were extracted twice with $CHCl_3$. The combined organic layers were successively washed with 2 M HCl, water, and brine. After being dried over $MgSO_4$, the solvents were removed in vacuo, and the residue was purified by silica gel chromatography giving (*P*)-3 (56 mg, 73%). Mp 150-152 °C (toluene-hexane). Anal. Calcd for $C_{34}H_{42}N_2O_2$: C, 79.94; H, 8.29; N, 5.49. Found: C, 79.55; H, 8.28; N, 5.43. $[\alpha]_D^{27}$ +121 (c 1.00, $CHCl_3$). MS *m/z* 510 (M^+, 100%), 410 (M^+–$C_6H_{13}NH$, 32%). HRMS (EI 70 eV) Calcd for $C_{34}H_{42}N_2O_2$: 510.3246. Found: 510.3256. UV-VIS ($CHCl_3$) λ_{max} (ε) 300 nm ($6.6x10^4$). IR ($CHCl_3$) 3440, 1653 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.92 (6H, t, *J* = 7 Hz), 1.32-1.47 (12H, m), 1.66 (4H, quintet, *J* = 7 Hz), 1.84 (6H, s), 3.45-3.57 (4H, m), 6.44 (2H, t, *J* = 6 Hz), 7.40 (2H, d, *J* = 7 Hz), 7.59 (2H, t, *J* = 8 Hz), 7.71 (2H, s), 8.25 (2H, d, *J* = 8 Hz). ^{13}C-NMR ($CDCl_3$) δ 14.6, 22.7, 23.3, 26.8, 30.0, 31.6, 40.2, 122.2, 122.6, 123.6, 126.7, 127.5, 128.8, 129.4, 130.9, 134.1, 136.6, 169.1.

(*P*)-*N,N'*-Didecyl-1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamide, (*P*)-4. Mp 123–125 °C (toluene-hexane). $[\alpha]_D^{27}$ +102 (c 0.40, $CHCl_3$). MS *m/z* 622 (M^+, 100%), 466 (M^+–$C_{10}H_{21}NH$, 36%). HRMS (EI 70 eV) Calcd for $C_{42}H_{58}N_2O_2$: 622.4498. Found: 622.4498. UV-VIS ($CHCl_3$) λ_{max} (ε) 300 nm ($5.7x10^4$). IR ($CHCl_3$) 3445, 1653 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.89 (6H, t, *J* = 7 Hz), 1.20-1.45 (28H, m), 1.63 (4H, quintet, *J* = 7 Hz), 1.79 (6H, s), 3.40-3.50 (4H, m), 6.61 (2H, t, *J* = 6 Hz), 7.36 (2H, d, *J* = 7 Hz), 7.55 (2H, dd, *J* = 7, 8 Hz), 7.60 (2H, s), 8.23 (2H, d, *J* = 8 Hz). ^{13}C-NMR ($CDCl_3$) δ 14.2, 22.8, 23.3, 27.1, 29.4, 29.4, 29.7, 29.7, 29.8, 32.0, 40.2, 122.7, 123.6, 126.7, 127.5, 128.8, 129.3, 129.5, 131.0, 134.1, 136.6, 169.1.

(*P*)-*N,N'*-Dihexadecyl-1,12-dimethylbenzo[*c*]phenanthrere-5,8-diamide, (*P*)-5. Mp 131–132 °C (toluene-hexane). Anal. Calcd for $C_{54}H_{80}N_2O_2$: C, 81.97; H, 10.37; N, 3.54. Found: C, 81.70; H, 10.33; N, 3.44. $[\alpha]_D^{27}$ +72.2 (c 1.0, $CHCl_3$). MS *m/z* 790 (M^+, 100%), 550 (M^+–$C_{16}H_{33}NH$, 30%). HRMS (EI 70 eV) Calcd for $C_{54}H_{80}N_2O_2$: 790.6376. Found: 790.6371. UV-VIS ($CHCl_3$) λ_{max} (ε) 300 nm ($2.7x10^4$). IR ($CHCl_3$) 3442, 1651 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 0.88 (6H, t, *J* = 7 Hz), 1.20-1.45 (52H, m), 1.63 (4H, quintet, *J* = 7 Hz), 1.80 (6H, s), 3.40-3.50 (4H, m), 6.61 (2H, t, *J* = 7 Hz), 7.38 (2H, d, *J* = 7 Hz), 7.57 (2H, dd, *J* = 7, 8 Hz), 7.63 (2H, s), 8.23 (2H, d, *J* = 8 Hz). ^{13}C-NMR ($CDCl_3$) δ 14.2, 22.8, 23.3, 27.2, 29.4, 29.5, 29.7 (4 carbons), 29.7 (4 carbons), 29.8, 32.0, 40.3, 122.7, 123.7, 126.7, 127.6, 128.8, 129.3, 129.6, 131.0, 134.1, 136.6, 169.2.

(*P*)-*N,N'*-Diphenyl-1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamide, (*P*)-6. Mp >300 °C (toluene). $[\alpha]_D^{27}$ +183 (c 1.0, $CHCl_3$). MS *m/z* 494 (M^+, 33%), 402 (M^+–C_6H_5NH, 100%). HRMS (EI 70 eV) Calcd for $C_{34}H_{26}N_2O_2$: 494.1994. Found: 494.1989. UV-VIS ($CHCl_3$) λ_{max} (ε) 302 nm ($2.8x10^4$). IR ($CHCl_3$) 3411, 1676 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.79 (6H, s), 7.17 (2H, t, *J* = 7 Hz), 7.36 (4H, t, *J* = 8 Hz), 7.38 (2H, d, *J* = 7 Hz), 7.54 (2H, dd, *J* = 7, 8 Hz), 7.65 (2H, s), 7.69 (4H, d, *J* = 8 Hz), 8.29 (2H, d, *J* = 8 Hz), 8.34 (2H, s). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 23.2, 120.2, 122.7, 124.1, 124.7, 127.3, 128.4, 129.1, 129.1, 129.3, 129.6, 131.1, 133.9, 136.9, 138.0, 167.3.

(*P*)-*N,N'*-Bis(1-naphtyl)-1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamide, (*P*)-7. Mp >300 °C (toluene). $[\alpha]_D^{27}$ +46.0 (c 0.10, $CHCl_3$). MS *m/z* 594 (M^+, 22%), 452 (M^+–$C_{10}H_7NH$, 100%). HRMS (EI 70 eV) Calcd for $C_{42}H_{30}N_2O_2$: 594.2307. Found: 594.2303. UV-VIS ($CHCl_3$) λ_{max} (ε) 304 nm ($5.1x10^4$). IR ($CHCl_3$) 3409, 1677 cm^{-1}. ^{1}H-NMR (acetone-d_6) δ 1.99 (6H, s), 7.45-7.60 (8H, m), 7.69 (2H, t, *J* = 7 Hz), 7.81 (2H, d, *J* =7 Hz), 7.93 (2H, d, *J* = 7Hz), 8.08-8.18 (2H, m), 8.23 (2H, d, *J* = 7Hz), 8.42 (2H, s), 8.53 (2H, d, *J* = 8 Hz), 9.82 (2H, s). ^{13}C-NMR (acetone-d_6) δ 22.3, 121.1, 121.2, 122.2, 123.8, 124.6, 125.0, 125.1, 125.2, 126.2, 127.3, 127.4, 128.2, 128.9, 129.2, 130.3, 132.4, 133.3, 133.6, 135.7, 167.4.

(*P*)-*N,N'*-Bis(2,6-dimethylphenyl)-1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamide (*P*)-8. Mp >300 °C (toluene). $[\alpha]_D^{25}$ + 13.5 (c 0.25, $CHCl_3$). MS *m/z* 550 (M^+, 23%), 430 (M^+–C_6H_5NMe, 100%). HRMS (EI 70 eV) Calcd for $C_{38}H_{34}N_2O_2$: 550.2620. Found: 550.2620. IR ($CHCl_3$) 3407, 1672 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 1.90 (6H, s), 2.38 (12H, s), 7.13-7.20 (6H, m), 7.47 (2H, d, *J* = 7 Hz), 7.63 (2H, dd, *J* = 7, 8 Hz), 8.11 (2H, s), 8.41 (2H, d, *J* = 8 Hz). ^{13}C-NMR (150 MHz, $CDCl_3$) δ 18.8, 23.3, 122.8, 124.1, 127.4, 127.7, 128.4, 128.6, 129.3, 129.3, 129.9, 131.3, 133.6, 134.1, 135.5, 137.1, 167.8.

(*P*)-*N,N,N',N'*-Tetrahexyl-1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamide, (*P*)-9. Anal. Calcd for $C_{46}H_{66}N_2O_2$: C; 81.33, H; 9.72, N; 4.12%. Found: C; 81.20, H; 9.88, N; 4.29%. $[\alpha]_D^{27}$ +59.8 (c 1.0, $CHCl_3$). MS *m/z* 678 (M^+, 100%), 494 (M^+–$(C_6H_{13})_2N$, 39%). HRMS (EI 70 eV) Calcd for $C_{46}H_{66}N_2O_2$: 678.5124. Found: 678.5126. UV-VIS ($CHCl_3$) λ_{max} (ε) 300 nm ($5.6x10^4$). IR ($CHCl_3$) 1636 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 80 °C) δ 0.30-0.60 (4H, m), 0.65-1.00 (20H, m), 1.30-1.55 (16H, m), 1.70-1.85 (4H, m), 1.90 (6H, s), 2.95-3.10 (4H, m), 3.45-3.60 (2H, m), 3.60-3.70 (2H, m), 7.50 (2H, d, *J* = 7 Hz), 7.65 (2H, t, *J* = 8 Hz), 7.77 (2H, d, *J* = 8 Hz), 7.85 (2H, s). ^{13}C-NMR (DMSO-d_6, 80 °C) δ 14.8, 15.3, 23.0, 23.6, 24.2, 27.0, 27.9, 28.9, 29.7, 31.8, 32.7, 46.1, 50.0, 123.8, 124.2, 126.5, 128.3, 130.4, 130.5, 131.8, 131.9, 136.7, 137.8, 170.7 .

(*P*)-*N,N,N',N'*-Tetradecyl-1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamide, (*P*)-10. Anal. Calcd for $C_{62}H_{98}N_2O_2$: C; 82.42, H; 10.93, N; 3.10%. Found: C; 81.47, H; 10.51, N; 2.81%. $[\alpha]_D^{27}$ +22.4 (c 0.40, $CHCl_3$). MS *m/z* 902 (M^+, 100%), 606 (M^+–$(C_{10}H_{21})_2N$, 37%). UV-VIS ($CHCl_3$) λ_{max} (ε) 300 nm ($1.9x10^4$). IR ($CHCl_3$) 1636 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 80 °C) δ 0.70-1.60 (72H, m), 1.70-1.80 (4H, m), 1.91 (6H, s), 2.90-3.20 (4H, m), 3.50-3.70 (4H, m), 7.49 (2H, d, *J* = 8 Hz), 7.63 (2H, t, *J* = 8 Hz), 7.77 (2H, d, *J* = 8 Hz), 7.81 (2H, s). ^{13}C-NMR (DMSO-d_6, 80 °C) δ 13.7, 21.2, 22.6, 26.0, 27.0, 27.3, 28.2, 28.6, 28.7, 28.8, 31.2, 44.7, 48.6, 122.1, 122.5, 124.9, 126.6, 128.7, 128.9, 130.1, 130.3, 135.0, 136.2, 169.1 (some peaks overlapped).

(*P*)-*N,N'*-Dimethyl-*N,N'*-diphenyl-1,12-dimethylbenzo[*c*]phenanthrene-5,8-diamide, (*P*)-11. $[\alpha]_D^{27}$ +84.7 (c 0.22, $CHCl_3$). MS *m/z* 522 (M^+, 36%), 416 (M^+–C_6H_5NMe, 100%). HRMS (EI 70 eV) Calcd for $C_{36}H_{30}N_2O_2$: 522.2307. Found: 522.2313. UV-VIS ($CHCl_3$) λ_{max} (ε) 302 nm ($3.0x10^4$). IR ($CHCl_3$) 1646 cm^{-1}. ^{1}H-NMR (DMSO-d_6, 80 °C) δ 1.61 (6H, s), 3.48 (6H, s), 6.84-6.93 (2H, m), 6.93-7.02 (4H, m), 7.07-7.14 (4H, m), 7.35 (2H, d, *J* = 7 Hz), 7.57 (2H, t, *J* = 8 Hz), 7.71 (2H, s), 7.92 (2H, d, *J* = 8 Hz). ^{13}C-NMR (DMSO-d_6, 80 °C) δ 22.2, 37.3, 122.3, 124.2, 125.3, 126.2, 126.4, 126.5, 128.3, 128.4, 128.7, 129.2, 129.7, 134.4, 135.7, 143.5, 168.8 .

(*P*)-*N,N*-Dihexyl-8-methoxycarbonyl-1,12-dimethylbenzo[*c*]phenanthrene-5-amide, (*P*)-12. Under an argon atmosphere, a mixture of (*P*)-8-methoxycarbonyl-1,12-dimethylbenzo[*c*]phenanthrene-5-carboxylic acid[9] (36 mg, 0.10 mmol) and thionyl chloride (2 mL) was heated at reflux for 3 h. Then, excess thionyl chloride was evaporated under reduced pressure, and residue was azeotropically dried by adding and evaporating toluene (1 mL) twice. CH_2Cl_2 (1 mL) and dihexylamine (75 μL, 0.3 mmol) were successively added, and stirring was continued for 1 h. After the solvent was evaporated, the mixture was chromatographed over silica gel giving (*P*)-**12** (45 mg, 86%). $[\alpha]_D^{27}$ +145 (c 2.2, $CHCl_3$). MS *m/z* 525 (M^+, 75%), 341 (M^+–$N(C_6H_{13})_2$, 100%). HRMS (EI 70 eV) Calcd for $C_{35}H_{43}NO_3$: 525.3243. Found: 525.3251. IR ($CHCl_3$) 2986, 2958, 2930, 2859, 1714 cm^{-1}. ^{1}H-NMR (400 MHz, DMSO-d_6 at 80 °C) δ 0.30-0.50 (2H, br), 0.65-1.00 (10H, br), 1.30-1.55 (8H, br), 1.70-1.80 (2H, br), 1.86 (3H, s), 1.88 (3H, s), 2.90-3.10 (2H, m), 3.45-3.60 (1H, m), 3.60-3.75 (1H, m), 4.02 (3H, s), 7.50 (1H, d, *J* = 7Hz), 7.51 (1H, d, *J* = 7Hz), 7.68 (1H, dd, *J* = 7, 8Hz), 7.69 (1H, dd, *J* = 7, 8Hz), 7.80 (1H, d, *J* = 8Hz), 7.93 (1H, s), 8.55 (1H, s), 8.66 (1H, d, *J* = 8Hz). ^{1}H-NMR (400 MHz, $CDCl_3$ at 23 °C) about 1:1 mixture of conformer A and B (selected data) δ 0.49 (3H, t, *J* = 7Hz, C<u>H</u>$_3$), 0.66-0.74 (3H, br, C<u>H</u>$_3$), 0.96 (6H, t, *J* = 7Hz, C<u>H</u>$_3$), 1.88-1.96 (6H, brs, ArC<u>H</u>$_3$), 2.99 (2H, m, NC<u>H</u>$_2$), 3.05-3.25 (2H, m, NC<u>H</u>$_2$), 3.40-3.50 (1H, m, NC<u>H</u>$_2$), 3.55-3.65 (1H, m, NC<u>H</u>$_2$), 3.75-3.82 (1H, m, NC<u>H</u>$_2$), 3.82-3.92 (1H, m, NC<u>H</u>$_2$), 4.08 (3H, s, COOC<u>H</u>$_3$), 7.44 (2H, d, *J* = 7Hz, Ar<u>H</u> 2,11-position), 7.62 (1H, t, *J* = 8Hz, Ar<u>H</u> 3-position), 7.66 (1H, t, *J* = 8Hz, Ar<u>H</u> 10-position), 7.66 (1H, s, Ar<u>H</u> 6-position), 7.81 (1H, s, Ar<u>H</u> 6-position), 7.85 (1H, d, *J* = 7Hz, Ar<u>H</u> 4-position), 8.46 (1H, s, Ar<u>H</u> 7-position), 8.82 (1H, d, *J* = 9Hz, Ar<u>H</u> 9-position). ^{13}C-NMR (100MHz, DMSO-d_6 at 80 °C) δ 13.3, 13.8, 21.5, 22.1, 22.6, 22.8, 25.5, 26.4, 27.3, 28.1, 30.3, 31.1, 44.5, 48.4, 52.3, 122.1, 122.6, 126.7, 127.2, 127.3, 128.6, 128.7, 128.9, 129.1, 129.4, 129.9, 130.6, 135.1, 135.8, 136.4, 167.0, 168.7.

5,5-Bis(4-amino-3,5-dimethylphenyl)nonane 17. Under an argon atmosphere, a mixture of CF_3SO_3H (7 mL) and DMSO (7 mL) was added to 5-nonanone (7.8 mL, 45 mmol) and 2,6-dimethylaniline (13.6 mL, 110 mmol) at 0 °C. After heated at 150 °C for 1 day, the mixture was cooled to room temperature, and saturated aqueous $NaHCO_3$ was added. The organic materials were extracted with $CHCl_3$ twice, and the combined organic layers were washed with water and brine. The solution was dried over $MgSO_4$, and was concentrated *in vacuo*. The residue was purified by silica gel chromatography and recycling GPC ($CHCl_3$) giving **17** (139 mg, 1%). Mp 157–158 °C (toluene). IR (KBr) 3437 (br), 3363 (br) cm^{-1}. MS *m/z* 366 (M^+, 16%), 309 (M^+–C_4H_9, 100%). HRMS (EI 70 eV) Calcd for $C_{25}H_{38}N_2$: 366.3035. Found: 366.3033. ^{1}H-NMR ($CDCl_3$) δ 0.82 (6H, t, *J* = 7Hz), 0.86-0.96 (4H, m), 1.23 (4H, quintet, *J* = 7Hz), 1.92 (4H, dt, *J* = 4, 8Hz), 2.10 (6H, s), 3.35 (4H, brs), 6.72 (4H, s). ^{13}C-NMR ($CDCl_3$) δ 14.2, 18.0, 23.6, 26.3, 37.6, 47.3, 120.6, 127.6, 139.2, 139.3.

α,α-Bis(4-amino-3,5-dimethylphenyl)toluene 18. Under an argon atmosphere concentrated HCl (2 mL) was added to benzaldehyde (0.6 g, 5 mmol) and 2,6-dimethylaniline (1.4 mL, 11 mmol) at 0 °C. The mixture was heated at reflux for 1 day. After cooled to room temperature, saturated aqueous $NaHCO_3$ was added. The organic materials were extracted with $CHCl_3$ twice, and the combined organic layers were washed with water and brine. The solution was dried over $MgSO_4$, and was concentrated *in*

vacuo. The residue was purified by silica gel chromatography giving **18** (1.0 g, 61%). Mp 157–158 °C (acetone). Anal. Calcd for $C_{23}H_{26}N_2$: C, 83.59; H, 7.93; N, 8.48. Found: C, 83.49; H, 8.03; N, 8.40. IR (KBr) 3430 (br), 3395 (br) cm^{-1}. MS *m/z* 330 (M^+, 100%), 315 (M^+–Me, 57%). HRMS (EI 70 eV) Calcd for $C_{23}H_{26}N_2$: 330.2096. Found: 330.2097. ^{1}H-NMR ($CDCl_3$) δ 2.07 (12H, s), 3.43 (4H, brs), 5.25 (1H, s), 6.67 (4H, s), 7.08-7.25 (5H, m). ^{13}C-NMR ($CDCl_3$) δ 17.7, 60.2, 121.2, 125.4, 127.7, 128.9, 129.1, 133.8, 140.4, 145.2.

(*P*)-Dibutyl[1+1]cycloamide, (*P*)-13. Under an argon atmosphere a mixture of (*P*)-1,12-dimethylbenzo[*c*]phenanthrene-5,8-dicarboxylic acid (34 mg, 0.10 mmol) and $SOCl_2$ (2 mL) was heated at reflux for 3 h. After cooled to room temperature the solvent was evaporated, and the resulted acid chloride (*P*)-**2** was azeotropically dried by adding CH_2Cl_2 (3 mL) and evaporating three times. Under an argon atmosphere, (*P*)-**2** was dissolved in dry 1,2-dichloroethane (5 mL), and the solution was charged in a syringe. A solution of **17** (36 mg, 0.10 mmol) in 1,2-dichloroethane (5 mL) was charged in another syringe. The two solutions were simultaneously added dropwise to a solution of pyridine (1 mL) in 1,2-dichloroethane (100 mL) over 3 h at reflux. After being refluxed for another 12 h, the reaction mixture was cooled to room temperature, and saturated aqueous $KHSO_4$ was added. The organic materials were extracted with $CHCl_3$, and washed with water and brine. After being dried over $MgSO_4$ the solvents were removed in vacuo, and purification by silica gel chromatography and recycling GPC ($CHCl_3$) gave (*P*)-**13** (7.5 mg, 11%). Mp 201–203 °C (toluene). $[\alpha]_D^{27}$ –46.3 (c 0.19, $CHCl_3$). MS *m/z* 675 (M^++H, 53%), 674 (M^+, 100%), 617 (M^+–C_4H_9, 8%), 561 (M^+–$2C_4H_9$, 8%). HRMS (EI 70 eV) Calcd for $C_{47}H_{50}N_2O_2$: 674.3872. Found: 674.3867. UV-VIS ($CHCl_3$) λ_{max} (ε) 294 nm (4.8×10^4). IR ($CHCl_3$) 3409, 1677 cm^{-1}. ^{1}H-NMR (600 MHz, $CDCl_3$) δ 0.90 (6H, t, *J*= 7Hz), 1.03-1.13 (2H, m), 1.25-1.30 (2H, m), 1.30-1.40 (4H, m), 1.80 (6H, s), 1.87 (6H, s), 2.05-2.15 (8H, m), 2.25-2.30 (2H, m), 6.39 (2H, s), 6.74 (2H, s), 6.99 (2H, s), 7.35 (2H, s), 7.40 (2H, d, *J*=7Hz), 7.64 (2H, dd, *J*=7, 8Hz), 8.49 (2H, d, *J*=8Hz). ^{13}C-NMR (150MHz, $CDCl_3$) δ 14.1, 18.7, 19.2, 23.4, 23.5, 26.3, 31.3, 47.6, 123.4, 124.5, 124.9, 126.2, 127.0, 127.4, 127.6, 128.6, 128.9, 129.9, 131.0, 132.4, 134.2, 134.3, 136.8, 148.2, 169.8.

(*P*)-Phenyl[1+1]cycloamide (*P*)-14. Mp >300 °C (toluene). $[\alpha]_D^{23}$ +6.1 (c 0.6, $CHCl_3$). MS *m/z* 639 (M^++H, 49%), 638 (M^+, 100%). HRMS (EI 70 eV) Calcd for $C_{47}H_{50}N_2O_2$: 638.2933. Found: 638.2930. IR (KBr) 3180 (br), 1647 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.68 (3H, s), 1.78 (3H, s), 1.80 (3H, s), 1.82 (3H, s), 2.26 (3H, s), 2.27 (3H, s), 5.00 (1H, s), 6.36 (1H, s), 6.40 (1H, s), 6.64 (1H, s), 6.75 (1H, s), 6.97 (1H, s), 6.98 (1H, s), 7.26-7.35 (5H, m), 7.40 (1H, d, *J*=7Hz), 7.43 (1H, d, *J*=7Hz), 7.59 (1H, s), 7.65 (1H, dd, *J*=7, 8Hz), 7.65 (1H, dd, *J*=7, 8Hz), 7.67 (1H, s), 8.45 (1H, d, *J*=8Hz), 8.57 (1H, d, *J*=8Hz). ^{13}C-NMR ($CDCl_3$) δ 18.2, 18.7, 19.0, 19.2, 23.2, 23.7, 57.2, 123.4, 123.4, 124.3, 125.2, 126.3, 126.4, 126.8, 126.9, 127.2, 127.4, 127.6, 128.0, 128.3, 128.4, 128.6, 129.0, 129.2, 129.5, 129.5, 129.7, 129.8, 130.7, 131.2, 133.2, 133.3, 134.3, 134.3, 135.1, 135.6, 136.7, 136.7, 141.2, 145.0, 145.8, 169.2, 170.2.

3-Triphenylmethylthio-1-iodopropane. Under an argon atmosphere, NaOH (1.2 g, 30 mmol) dissolved in water (25 mL) was added to a solution of triphenylmethylmercaptan (5.5 g, 20 mmol) in THF (10 mL). The mixture was then added to a solution of 1,3-diiodopropane (25 g, 84 mmol) in THF (10 mL) at room temperature over a period of 30 min. The reaction was completed in 30 min as judged by TLC. Then water was added, and the organic materials were extracted with hexane. The organic layer was washed with water and brine. After being dried over $MgSO_4$ the solvents were removed under a reduced pressure, and silica gel chromatography gave 3-triphenylmethylthio-1-iodopropane (6.86 g, 70%). Anal. Calcd for $C_{22}H_{21}IS$: C; 59.46, H; 4.78, S; 7.22; I; 28.56%. Found: C; 59.77, H; 4.87, S; 7.36, I; 23.34%. MS (EI, 70eV) *m/z* 367 (M^+–C_6H_5, 0.1%), 275 (M^+–C_3H_6I, 1%), 243 (M^+– C_3H_6IS, 100%). IR (KBr) 1594, 1489, 1443, 1156, 742, 699 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.77 (2H, quinted, *J* = 7 Hz), 2.27 (2H, t, *J* = 7 Hz), 3.09 (2H, t, *J* = 7 Hz), 7.19-7.30 (9H, m), 7.39-7.43 (6H, m). ^{13}C-NMR ($CDCl_3$) δ 5.2, 32.4, 32.6, 66.7, 126.5, 127.8, 129.4, 144,5.

(*P*)-*N*-(3-Triphenylmethylthiopropyl)-[1+1]cycloamide (*P*)-22. Under an argon atmosphere, a mixture of (*P*)-**1** (630 mg, 1 mmol), 1,4-dioxane (10 mL), powdered KOH (450 mg, 8 mmol), anhydrous K_2CO_3 (280 mg, 2 mmol), and *n*-Bu_4NHSO_3 (680 mg, 2 mmol) was stirred at room temperature for 1 h. During stirring, gelatinous mass was formed. Then, 3-triphenylmethylthio-1-iodopropane (3.92 g, 8 mmol) was added to the stirred mass at 80 °C over a period of 30 min. The reaction mixture was stirred for 12 h at 80 °C to obtain a clear solution. Inorganic materials were removed by filtration, and washed with ethyl acetate. The combined organic layers were washed with 2 M HCl and water. After dried over anhydrous $MgSO_4$ the solvents were removed under a reduced pressure, and silica gel chromatography gave (*P*)-**22** (1.13 g, 90%). Anal. Calcd for $C_{88}H_{82}N_2O_2S_2$: C; 83.64, H; 6.54, N; 2.22; S; 5.07%. Found: C; 82.03, H; 6.20, N; 2.15, S; 5.00%. $[\alpha]_D^{24}$ +9.27 (c 1.4, $CHCl_3$). FABMS *m/z* 1262 (M^+). IR (KBr) 1633, 1593, 1487, 1442, 746, 700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.40-1.60 (6H, m), 1.72 (6H, s), 1.75-1.95 (16H, m), 2.20-2.35 (8H, m), 3.60-4.00 (4H, br), 6.16 (2H, s), 6.70-6.85 (2H, br), 6.85-7.00(2H, br), 7.16-7.21(6H, m), 7.22-7.29 (12H, m), 7.32 (2H, d, *J* = 7 Hz), 7.40-7.45 (12H,m), 7.52 (2H, dd, *J* = 8, 7 Hz), 8.15 (2H, d, *J* = 8 Hz). ^{13}C-NMR ($CDCl_3$) δ 18.9, 19.2, 22.9, 23.5, 26.3, 27.4, 29.8, 33.4, 44.8, 49.0, 66.6, 123.2, 123.4, 125.2, 125.6, 125.9, 126.1, 126.5, 127.5, 127.7, 128.0, 129.4, 129.8, 130.6, 130.9, 135.1, 135.4, 136.4, 137.5, 144.6, 148.6, 168.1.

***N*-(3-Triphenylmethylthiopropyl)benzanilide 20.** MS (EI, 70eV) *m/z* 513 (M^+, 0.2%), 270 (M^+–Tr, 6%), 243 (Tr-H, 100%). Anal. Calcd for $C_{35}H_{31}NOS$: C; 81.83, H; 6.08, N; 2.73; S; 6.24%. Found: C; 80.17, H; 6.21, N; 2.65, S; 4.15%. IR (KBr) 1643, 1594, 1578, 1493, 1444, 741, 699 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.69 (2H, quintet, *J* = 7 Hz), 2.20 (2H, t, *J* = 8 Hz), 3.83 (2H, t, *J* = 7 Hz), 6.85 (2H, d, *J* = 7 Hz), 7.07-7.28 (17H, m), 7.35-7.42 (6H, m). ^{13}C-NMR ($CDCl_3$) δ 26.8, 29.5, 49.6, 66.6, 126.4, 126.4, 127.4, 127.6, 127.7, 128.4, 128.9, 129.2, 129.4, 135.9, 142.9, 144.6, 170.0.

***(P)*-*N*-(3-Mercaptopropyl)-[1+1]cycloamide *(P)*-16.** Under an argon atmosphere, to a solution of *(P)*-**22** (126 mg, 0.1 mmol) and triethylsilane (47 mg, 0.4 mmol) in CH_2Cl_2 (2 mL) was added 10% CF_3CO_2H in dichloroethane (154 μL). The mixture was stirred for 1 h at room temperature. After removing the volatile materials under a reduced pressure, silica gel chromatography gave *(P)*-**16** (62 mg, 80%). Anal. Calcd for $C_{50}H_{54}N_2O_2S_2$: C; 77.08, H; 6.99, N; 3.60, S; 8.23%. Found: C; 76.32, H; 7.14, N; 3.27, S; 9.07%. $[\alpha]_D^{27}$ +6.99 (c 1.4, $CHCl_3$). MS (EI, 70eV) *m/z* 778 (M^+, 52%), 745 (M^+–SH, 24%), 704 (M^+–C_3H_6S, 15%), 671 (M^+–SH–C_3H_6S, 8%), 630 (M^+– 2(C_3H_6S), 100%), 521(M^+– 2(C_3H_6S), 12%). FABMS *m/z* 779 (M^++H). HRMS (EI 70 eV) Calcd for $C_{50}H_{54}N_2O_2S_2$: 778.3627. Found: 778.3621. IR (KBr) 1637 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.40-1.60 (8H, m), 1.74 (6H, s), 1.80-2.00 (12H, m), 2.00-2.20 (4H, m), 2.20-2.35 (4H, m), 2.69 (4H, q, *J* = 8 Hz), 3.80-4.20 (4H, br), 6.23 (2H, s), 6.80-6.90 (2H, br), 6.90-7.00(2H, br), 7.36 (2H, d, *J* = 7 Hz), 7.59 (2H, dd, *J* = 7, 8 Hz), 8.24 (2H, d, *J* = 8 Hz). ^{13}C-NMR ($CDCl_3$) δ 18.9, 19.2, 22.5, 22.8, 23.3, 26.8, 32.6, 33.3, 44.8, 48.5, 123.3, 125.3, 125.7, 126.0, 126.2, 127.4, 128.0, 129.8, 130.6, 130.7, 135.0, 135.3, 136.4, 137.4, 148.7, 168.3.

***N*-(3-Mercaptopropyl)benzanilide 21.** Anal. Calcd for $C_{16}H_{17}NOS$: C; 70.81, H; 6.31, N; 5.16; S; 11.82%. Found: C; 70.13, H; 6.47, N; 5.10, S; 9.30%. MS (EI, 70eV) *m/z* 271 (M^+, 30%), 238 (M^+–SH, 12%), 210 (M^+-C_2H_4SH, 5%). HRMS *m/z* Calcd for $C_{16}H_{17}NOS$: 271.1031. Found: 271.1021. IR (KBr) 2550, 1639, 1595, 1577, 1494, 1446, 699 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ 1.53 (1H, t, *J* = 8 Hz), 1.95 (2H, quinted, *J* = 7 Hz), 2.58 (2H, q, *J* = 8 Hz), 4.05 (2H, t, *J* = 7 Hz), 7.01 (2H, d, *J* = 8 Hz), 7.12-7.18 (3H, m), 7.18-7.25 (3H, m), 7.25-7.28 (2H, m). ^{13}C-NMR ($CDCl_3$) δ 22.1, 32.1, 48.9, 126.6, 127.5, 127.5, 128.5, 129.1, 129.4, 135.8, 143.0, 170.3.

Surface pressure-area (*π*-*A*) Isotherms and Monolayer Deposition. Measurement of surface pressure-area (*π*-*A*) isotherms and monolayer deposition were carried out at 20 °C with use of an automatic Langmuir trough (Kyouwa Kaimen Kagaku HBM-AP) equipped with a Wilhelmy balance. The compounds were spread from a 1 mM $CHCl_3$ solution on a pure water (Milli-Q II, Millipore) surface for the measurement of *π*-*A* isotherms at a compress rate of 14 cm^2/min. The quartz slides on which LB multilayers were deposited were cleaned in boiling concentrated HNO_3, washed with pure water, and made hydrophobic with octadecyltrichlorosilane.

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