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SYNTHESIS AND PROPERTIES OF DICARBOXIMIDE DERIVATIVES OF PERYLENE AND AZAPERYLENE

Yukinori Nagao,* Tatsurou Yoshida, Koji Arimitsu, and Kozo Kozawa

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

Abstract – The *N*-alkyl dicarboximide derivatives of naphthylisoquinoline and binaphthalene were prepared by the hetero coupling reaction of the corresponding *N*-alkyl dicarboximide derivatives of stannylnaphthalene with bromodimethyisoquinoline and bromodimethylnaphthalene, respectively. The ring closing of the *N*-hexyl derivatives of naphthylisoquinoline and binaphthalene produced the *N*-hexyldicarboximide derivatives of azaperylene and perylene having the same substituents, respectively. The absorption spectra and fluorescence spectra of the azaperylene and perylene derivatives were investigated.

INTRODUCTION

Perylene dyes have a high fastness to light and a high stability to heat. Moreover, perylene dyes have absorption in the visible light range in the solid form and an n-type semiconductorcharacter. Recently, some of them are being used not only as pigments, but also as functional dyes for organic photoconductors in electrophotography, organic EL devices, and organic solar cells (photovoltaic cells). Paying attention to the usefulness of perylene dyes, the synthesis of the azaperylene derivative having an N atom in its skeleton is useful because it is assumed that the azaperylene derivatives have analogous properties to the perylene derivatives, and the difference in the perylene properties is very interesting.

≠ Dedicated to Professor Emeritus Akira Suzuki on the occasion of his 80th birthday.

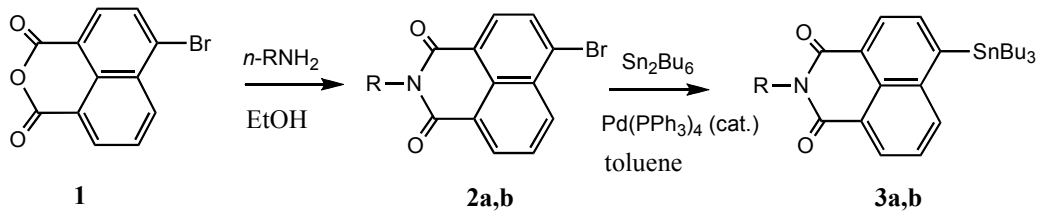
Furthermore, it is expected that replacement of the C-atom in the perylene skeleton by the N atom produces an increasing absorption intensity. Previously, azaperylene derivatives having the *N*-pentyl group were prepared[1], but these derivatives had no adequate solubility. In this study, the synthesis of an azaperylene derivative containing the *N*-hexyl group was investigated and then the synthesis of the corresponding perylene derivatives with the same groups was investigated.

The stannyl substituted naphthalenedicarboximides **3a,b**[2, 3] and isoquinoline bromides **7** [1, 4, 5] were prepared from naphthalic anhydride **1** and acetophenone **4**, respectively (Schemes 1 and 2). The naphthylisoquinoline derivatives **8a,b** [3] that were obtained via the heterocoupling reaction of **3a,b** and **7** in the presence of $Pd(PPh_3)_4$, were cyclized using t-BuOK/DBN to synthsize the azaperylene derivative **9a** (Schemes 3 and 4). In addition, naphthylbromide **12** [7, 8, 9] was prepared from naphthalic anhydride **15** (Scheme 2). The binaphthalene derivatives **13a,b** [3] that were obtained via the heterocoupling reaction of **3a,b** and **12** in the presence of $Pd(PPh_3)_4$, was cyclized using t-BuOK/DBN to synthesize the perylene derivative **14a** (Scheme 4). The optical properties of the prepared azaperylene derivative **9a** and perylene derivative **14a** were compared.

RESULTS AND DISCUSSION

Preparation of stannylnaphthalenedicarboximide 3a,b

The bromo naphthalenedicarboximides **2a,b** and stannylnaphthalenedicarboximides **3a,b** (**a**: alkyl = *n*-hexyl, **b**: alkyl = cyclohexyl) were prepared according to Scheme 1. Compounds **2a,b** (**a:** 90%, **b:** 80%) were synthesized by imidization of the anhydride **1** with n-hexylamine and cyclohexylamine, respectively. **3a,b** (**a:**82%, **b:**71%) were then synthesized by the substitution of **2a,b** with $SnBu_3$.



1 **2a,b** **3a,b**

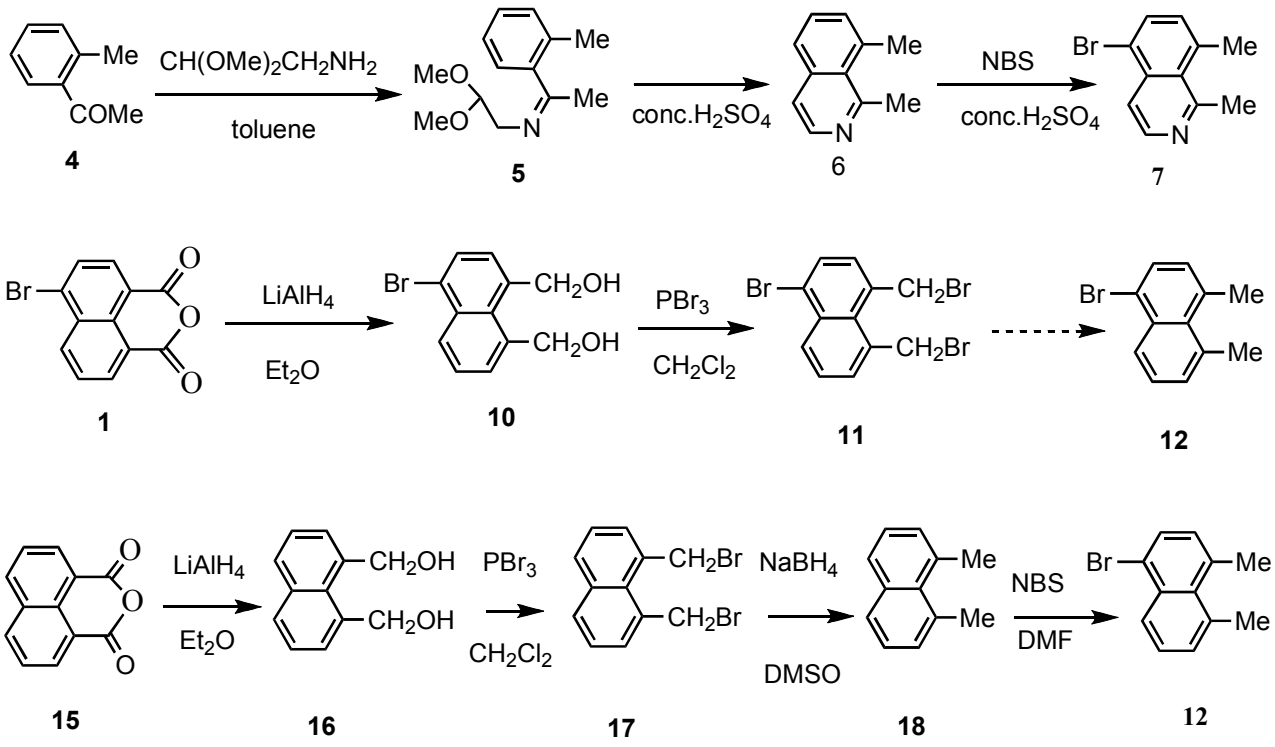
R= **a**: *n*-Hex **b**: c-Hex

Scheme 1

Preparation of bromoisoquinoline 7 and bromonaphthalene 12

Bromoisoquinoline **7** and bromonaphthalene **12** were prepared according to Scheme 2. The imine **5** (90%) was prepared from *O*-methyl acetophenone **(4)**, and isoquinoline **6** (35%) was prepared from **5** using sulfuric acid . The bromoisoquinoline **7** (86%) was then prepared by the bromination of **6** with NBS.

Hydroxymethylbromonaphthalene **10** was prepared from the anhydride **1** in a 64% yield, then the bromomethybromonaphthalene **11** was prepared in a 70% yield by the bromine substitution of the hydroxyl group using PBr_3. After reduction of **11** by $LiAlH_4$, the bromonaphthalene **12** was produced, but a side reaction occurred and purification was very difficult. The starting material was then changed from the anhydride **1** to **15,** and methylnaphthalene **18** was prepared in a 92% yield in 3 steps reaction from **15**. The bromonaphthalene **12** (63%) was then prepared by the bromination of **18** with NBS.

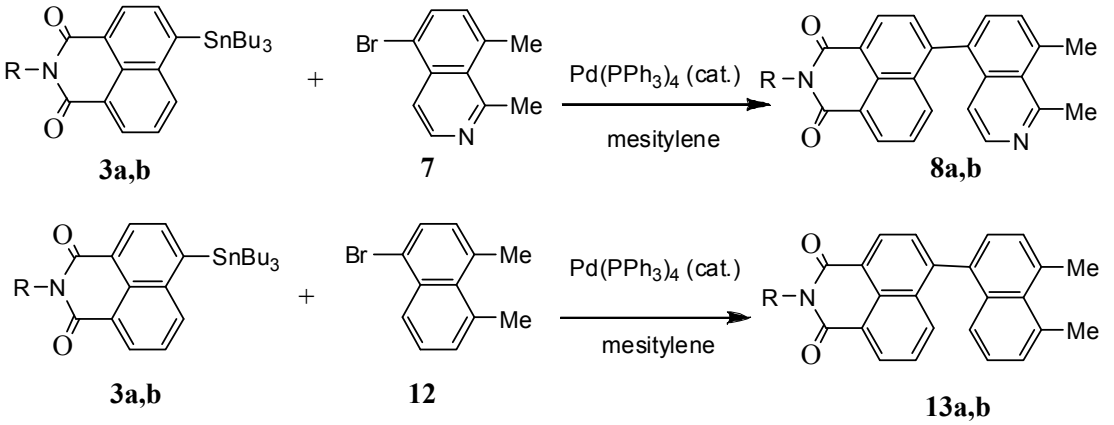


Scheme 2

Palladium-catalyzed coupling reaction of stannylnaphthalenedicarboximide 3a,b with bromoisoquinoline7 and bromonaphthalene 12

The naphthylisoquinolines **8a,b** and binaphthalenes **13a,b** (**a**: alkyl = *n*-hexyl, **b**: alkyl = cyclohexyl)

were prepared according to Scheme 3. **8a,b** and **13a,b** were prepared by the palladium-catalyzed hetero coupling reaction of stannylnaphthalenedicarboximide **3a,b** with bromoisoquinoline **7** and bromonaphthalene **12**, respectively.

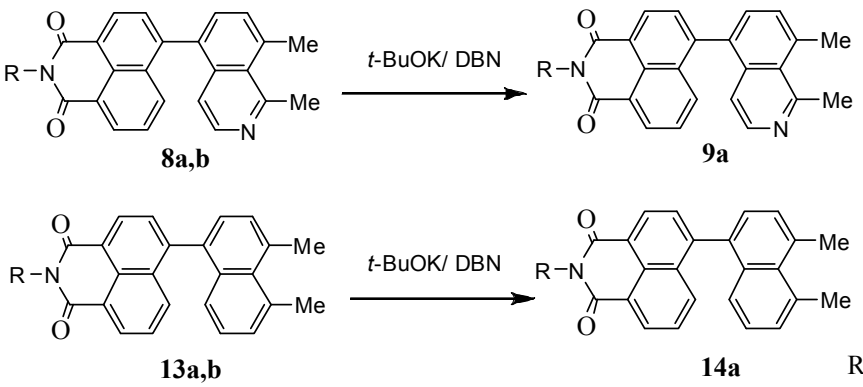


R= **a**: *n*-Hex **b**: c-Hex

Scheme 3

Preparation of azaperylene derivative 9a and perylene derivative 14a

The azaperylene derivative **9a** and perylene derivative **14a** were prepared according to Scheme 4. The ring-closing reactions of the naphthylisoquinolines and binaphthalenes with a complex base reagent (*t*-BuOK/DBN) were investigated. The reaction mechanism of this method is not clear, but an alkyl chain participated in the reaction progress. **9a** (12%) and **14a** (10%) containing a hexyl group were obtained, but **8b** and **13b** containing a cyclohexyl group did not give the corresponding ring-closing products (Table 1). Neither using other ring-closing reaction conditions or bases were reaction successful.



R= **a**: *n*-Hex **b**: c-Hex

Scheme 4

Table 1. Yields and mp of azaperylene and perylene derivatives for the ring-closing reaction with t-BuOK/DBU

Alkyl chain	Products	Yield (%)	mp (℃)
n-C_6H_{13}	**9a**	12	236.1~236.4
c-Hex	**9b**	no reaction	--
n-C_6H_{13}	**14a**	10	254.1~254.4
c-Hex	**14b**	no reaction	--

Photophysical Properties

Absorption spectra in $CHCl_3$ and thin film

The absorption spectra of azaperylene **9a** and perylene **14a** in $CHCl_3$ are presented in Figure 1 and Table 2. The changes in λmax were significantly red shifted due to the change in the absorption spectrum by the ring-closing reaction of naphthylisoquinoline **8a** and binaphthalene **13a**. Because forming the perylene or azaperylene skeleton by a ring-closure reaction extended the π- conjugate system, **9a** from **8a** had about a 150 nm (Figure 1 a) red shift and **14a** from **13a** had about 160 nm (Figure 1 b) red shift. In addition, compared to before the ring-closure, the ε rise was about 2.5 times and 2.0 times, respectively.

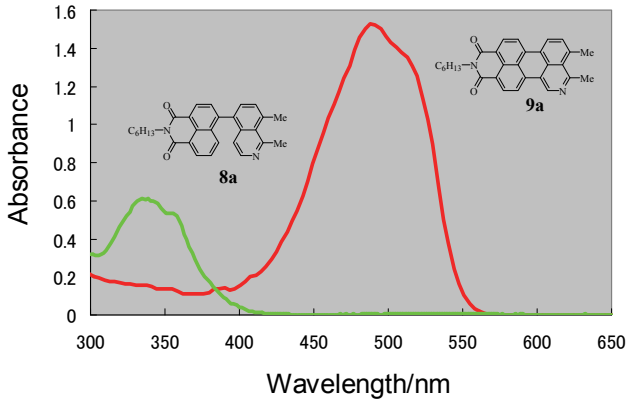


Figure 1. (a) UV/Vis spectra of **8a** and **9a** *Solv.: $CHCl_3$($C=5.0\times10^{-5}$ mol/l)

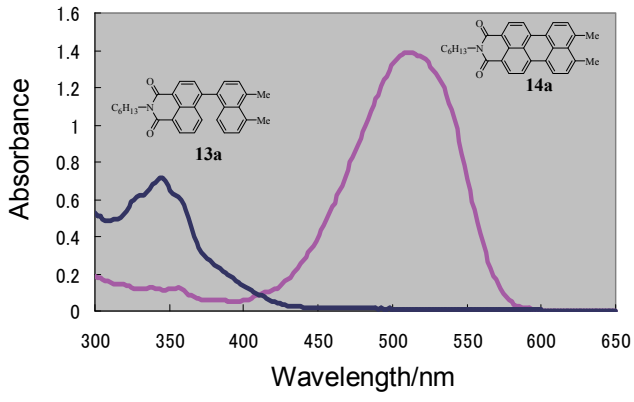


Figure 1. (b) UV/Vis spectra of **13a** and **14a** *Solv.: $CHCl_3$($C=5.0\times10^{-5}$ mol/l)

Table 2. Absorption spectra of **8a** and azaperylenes **9a**, and **13a** and perylene **14a** in $CHCl_3$

Compound	**8a**	**9a**	**13a**	**14a**
λ max/nm [ε]/ l/mol・cm	**336 [1.2×10^4]**	**489 [3.3×10^4]**	**345 [1.4×10^4]**	**510 [3.0×10^4]**

As for λmax, **9a** has a shorter wavelength than **14a** in $CHCl_3$ (Table 2)**.** Maybe the lone pair electron of the N atom had no influence on the π conjugated system. However, introducing the N atom in the perylene skeleton decreased the π-electron density of the perylene skeleton by the electron withdrawing nature of the N atom which lead to the blue shift. According to the molecular orbital calculation, the stabilization of the HOMO is a slightly higher and gave a calculated short wavelength shift. On the other hand, the absorption strength increases by the N atom introduction, deflection occurs in the electronic density of the perylene skeleton and a change occurs in the transition moment. The absorption spectrum in the film state is shown in Figure 2.

In the solid state, the visible absorption spectrum of the thin film is broad compared to the visible absorption spectrum in solution (Figure 2 b). The distance between molecules becomes short in the solid state, a deviation occurs in the electric charge of the molecule by the interaction between molecules, and it is thought that it becomes a broad absorption by affecting the electronic change energy. Maybe two perylene derivatives form H-aggregate, and λmax in the solid showed blue shifts: **9a** (490→458 nm), **14a** (510→446 nm) compared to the values in solution. Different from that in $CHCl_3$, the λmax of **9a** showed a longer wavelength than **14a** in the solid state. Maybe by introducing the N atom, itproduces a deflection in the electronic density of the perylene skeleton, and a change in the aspect or interval of the intermolecular packing compared to perylene.

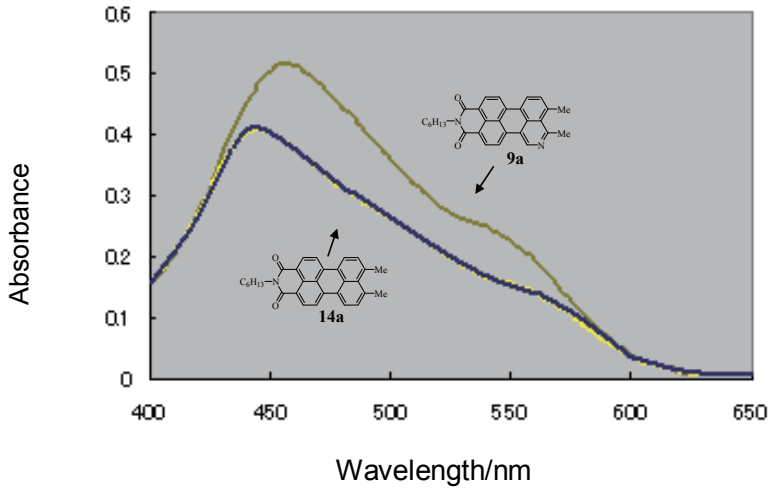


Figure 2. UV/Vis spectra of **9a** and **14a** of thin film (500 Å)

Table 3. The absorption spectrum of **9a** and **14a** in the film state

thin film (500Å)	9a	14a
λmax/nm	458	446

Fluorescence spectra

The fluorescence spectra of azaperylene **9a** and perylene **14a** in $CHCl_3$ are presented in Figure 3. It is generally reported that the fluorescence intensities remarkably decrease by introducing an N atom, such as pyridine or quinoline, for the N-hetero compound compared with benzene and naphthalene. Normally the singlet excitation electron which is in a state returns to the ground state while producing the fluorescence. However, because of the triplet excitation state by the n-π* transition of the lone pair electron, radiationless transition and electron withdrawing of the N atom remarkably decrease the fluorescence intensities. However, **14a** showed a equally strong fluorescence intensity compared to **9a** and it is shown that azaperylene had a sufficient fluorescence intensity equal to perylene. Maybe the dimethyl, which was substituted at the 1,8- position, play a role in preventing the remarkable decrease in fluorescence. Corresponding N-pentylazaperylene derivative[1] previously obtained had poor solubility in $CHCl_3$ and gave no clear ^{1}H-NMR. But this derivative show similar absorption and fluorescence spectra with those of **9a**. The relative quantum yield of the N-pentyl derivative was 0.89 and **9a** have almost equal fluorescence intensity with that.

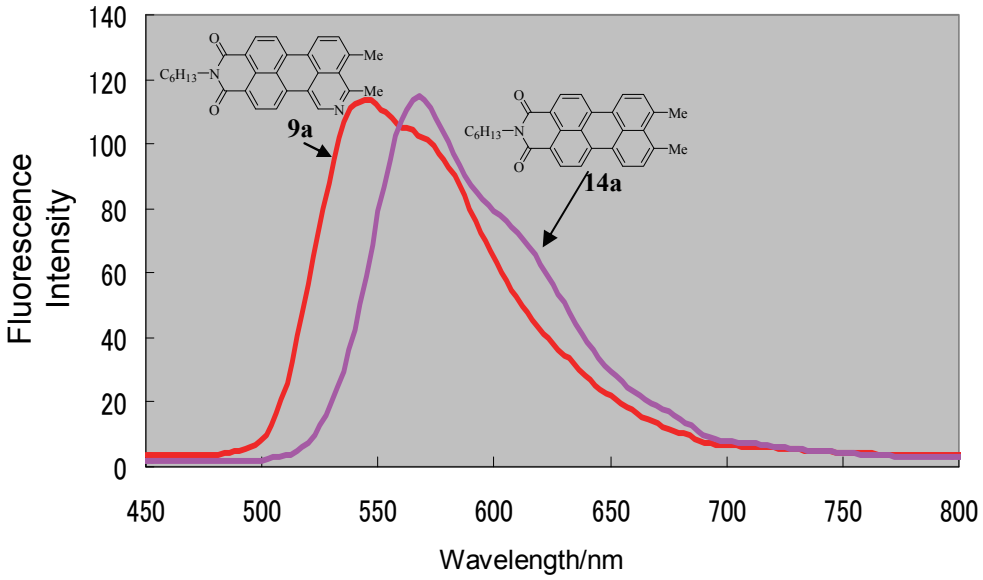


Figure 3. Fluorescence spectra of **9a** (green) and **14a** (red) *Solv.: $CHCl_3$ ($C=2.0\times10^{-5}$mol/l)

Table 4. Fluorescence spectra of azaperylene **9a** and perylene **14a**

Compound	9a	14a
Emission λmax/nm	550	573
Fluorescence (relative intensity)	116.3	120.9

CONCLUSION

N-Hexyl-1,8-dimethylazaperylene-8,9-dicarboximide (**9a**) and *N*-hexyl-1,8-dimethylperylene- 8,9-dicarboximide (**14a**) were synthesized via the hetero coupling reaction of the corresponding stannylnaphthalenedicarboximide **3a** with isoquinoline bromide **7** and naphthyl bromide **12** in the presence of $Pd(PPh_3)_4$, and ring-cyclization of these coupling products using *t*-BuOK/DBN, respectively. The absorption strength increases by the N atom introduction into the perylene skeleton for deflection to the electronic density in azaperylene skeleton. The azaperylene indicate sufficient intensity of fluorescence equal to perylene.

EXPERIMENTAL

Instrument Melting points were determined using an MRK MP-MG. The IR spectra were recorded by a JASCO FT/IR-410 using a potassium bromide pellet. The ^{1}H-NMR and ^{13}C-NMR spectra were acquired by a JEOL JNM-ECP300 at 300 and 75 MHz in $CDCl_3$. The ^{1}H-NMR coupling constants are given in Hz and all chemical shifts are relative to the internal standard of tetramethylsilane. Low-resolution electron impact mass spectra were obtained using a JEOL MS station.

Manufacture of thin film

The Manufacturing of the thin films were performed by a vacuum deposition method using a high vacuum vapor deposition device, EBH-6 (Ulvac Co., Ltd.). The film thickness was measured using an Alpha-Step500 (Tencor Company) surface shape measuring instrument and CRT -5000 (Ulvc Co., Ltd.) film thickness counter . The vacuum degree was measured by a GI-TL2 ionization gauge.

A sample first put it in the vacuum bottom of 10^{-5} Torr, and heated and after vapor deposition speed became constant, objective thickness of film was obtained by vapor deposition.

Synthesis of materials

1,8-*N*-Alkyl-4-bromonaphthalenedicarboximide (2a,b) (a: alkyl = *n*-hexyl, b: alkyl = cyclohexyl)

A solution of compound **1** (5.0 g , 1.8×10^{-2} mol), *n*-hexylamine (10.0 mL , 7.0×10^{-2} mol) in EtOH (300 mL) were heated to 78 °C for 5 h with stirring. After the reaction, the mixture was cooled to rt and removed **1** by filtration. After evaporation of the filtrate, the solid was washed with water and dried. Recrystallization from EtOH yielded **2a** (6.0 g, 90%) as yellow needles. Similarly, cyclohexylamine produced **2b** (5.2 g, 80%)

(2a): mp 65.0~65.4 °C (lit.,[2] 65.3~65.7 °C), IR (KBr) $\nu_{C=O}$ imide/cm^{-1} : 1662, 1701 MS(FAB) (m/z): 360{M+H}$^+$,362{M+H+2}$^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.65 (d, *J*=7.5 Hz, 1H, arom.H), 8.56 (d, *J*=7.5 Hz, 1H, arom.H), 8.43 (d, *J*=8.0 Hz, 1H, arom.H), 8.05 (d, *J*=8.0 Hz, 1H, arom.H), 7.85 (t, *J*=7.5 Hz, 1H, arom.H), 4.16 (t, *J*=8.0 Hz, 2H, -NCH_2), 1.74 (d, *J*=7.5 Hz, 2H, -CH_2-), 1.43 (d, *J*=7.5 Hz, 2H, -CH_2-), 1.33~1.35 (m, 4H, -CH_2CH_2-), 0.89 （t, *J*=7.5 Hz, 3H, CH_3）. ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 14.27, 22.53, 26.75, 27.99, 31.51, 40.59, 122.24, 123.09, 128.01, 128.91, 130.01, 130.53, 131.02, 131.12, 131.92, 133.10, 163.50, 163.52

(2b) mp 265.7~266.1 °C (lit.,[10] 265.0 °C) IR (KBr) $\nu_{C=O}$ imide/cm^{-1} : 1663, 1703 MS(FAB) (m/z): 358 {M+H}$^+$, 360{M+H+2}$^+$ ^{1}H-NMR (300 MHZ, Solv.: $CDCl_3$, Ref.:TMS) δ: 8.58 (d, *J*=6.9Hz, 1H,arom.H), 8.47 (d, *J*=6.9Hz, 1H, arom.H), 8.08 (d, *J*=7.5Hz, 1H, arom.H), 7.88 (d, *J*=7.5Hz, 1H, arom.H), 7.34 (t, *J*=7.5Hz, 1H, arom.H), 4.95~4.99 (m, 1H, -NCH-), 1.87~1.92 (m, 2H), 1.74~1.71 (m, 3H), 1.25~1.30 (m, 18H), 0.84~0.94 (m, 12H) ppm. ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ : 25.40, 26.50, 29.05, 53.92, 122.81, 123.66,128.02, 128.96, 129.72, 130.41, 131.01, 131.07, 131.83, 132.79, 163.97, 163.99

1,8-*N*-Alkyl-4-tributylstannylnaphthalene-dicarboximide (3a,b)(a: alkyl = *n*-hexyl, b: alkyl = cyclohexyl)

Each compound **2a,b** (2.5 g, $6.94\sim6.98\times10^{-3}$ mol), hexabutylditin (7.5 g, 1.3×10^{-3} mol), and $Pd(PPh_3)_4$ (0.050 g (4.3×10^{-5} mol) in toluene (150 mL) was refluxed for 48 h under a nitrogen atmosphere. After the reaction, the solvent was removed by evaporation and the residue was purified by column

chromatography on silica gel using toluene as the eluent, affording the product as a yellow viscous liquid **3a** (3.1 g, 82%) and yellowish-green viscous liquid **3b** (2.8 g, 71%)

(3a): IR (KBr) $\nu_{C=O}$ imide/cm^{-1} : 1694 MS(FAB) (m/z): 568{M-2}$^+$, 570{M}$^+$, 572{M+2}$^+$^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.65 (d, *J*=7.5 Hz, 1H, arom.H), 8.56 (d, *J*=7.5 Hz, 1H, arom.H), 8.43 (d, *J*=8.0 Hz, 1H, arom.H), 8.05 (d, *J*=8.0 Hz, 1H, arom.H), 7.85 (t, *J*=7.5 Hz, 1H, arom.H), 4.16 (t, *J*=8.0Hz, 2H, -NCH_2), 1.25~1.34 (m, 9H), 1.33~1.35 (m, 15H), 0.89（m, 14H）. ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 10.57, 13.39, 22.38, 26.66, 27.06, 28.76, 28.89, 29.02, 31.37, 40.12, 122.43, 123.31, 126.23, 127.85, 129.22, 130.41,135.62, 135.76, 137.27, 153.84,163.70, 164.20

(3b): IR (KBr) $\nu_{C=O}$ imide/cm^{-1} : 1694 MS(FAB) (m/z): 566{M-2}$^+$, 568{M}$^+$, 570{M+2}$^+$ ^{1}H-NMR (300 MHZ, Solv.: $CDCl_3$, Ref.:TMS) δ: 8.58 (d, *J*=6.9 Hz, 1H, arom.H), 8.47 (d, *J*=6.9 Hz, 1H, arom.H), 8.08 (d, *J*=7.5 Hz, 1H, arom.H), 7.88 (d, *J*=7.5 Hz, 1H, arom.H), 7.34 (t, *J*=7.5 Hz, 1H, arom.H), 4.95~4.99 (m, 1H, -NCH-), 1.87~1.92 (m, 2H), 1.74~1.71 (m, 3H), 1.25~1.30 (m, 20H), 0.84~0.94 (m, 12H). ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 10.75, 13.36, 17.25, 26.73, 27.22, 28.24, 29.04, 53.62, 124.04, 126.47, 128.09, 128.17, 129.37, 130.55, 135.67, 135.87, 137.31, 153.67, 164.53, 165.03

***N*-Acetaldehyde dimethyl acetal-α-(*o*-toluyl)ethane imine (5)**

Compound **4** (30 g, 2.2×10^{-3} mol), 2,2-dimethoxyethylamine (30 g, 2.3×10^{-1} mol), and *p*-toluene sulfonic acid monohydrate (0.2 g, 1.2×10^{-3} mol) in toluene (150 mL) were refluxed for 48 h using a Dean-Stark. trap. After the reaction, the solvent was removed by evaporation and purified by distillation under reduced pressure affording the product as a colorless liquid **5** (45 g, 89%)

(5): bp 94.1 °C/ 1.5 mmHg, MS (FAB) (m/z): 222{M+1}$^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 7.11~7.21 (m, 3H, arom.H), 6.87 (d, *J*=7.5 Hz, 1H, arom.H), 4.56 (t, *J*=4.0 Hz, 1H, CH), 3.30 (s, 6H, OCH_3), 3.10 (d, *J*=6.0 Hz, 2H, N-CH_2-), 2.26 (s, 3H, CH_3), 2.20 (s, 3H, CH_3).

1,8-Dimethylisoquinoline (6)

To a 500 mL, 4-necked flask equipped with a condenser was charged 95% conc.H_2SO_4 (250 mL). After heating at 130 °C, compound **5** (50 g, 2.2×10^{-1} mol) was added portionwise over 30 min and stirred for 1 h. After the reaction, the solution was neutralized with 50% aq.KOH. The solution was filtered off under reduced pressure. The salt after was washing with Et_2O, the water layer was abstracted with Et_2O.

The organic liquid was dried (KOH) for 24 h.

The dried solution was evaporated under reduced pressure. The residual solid was purified by distillation under reduced pressure to give a white solid **6** (12 g, 35%)

(6): mp 48.5~49.0 °C (48.5~50.0 °C)[5] IR (KBr) $\nu_{C=N}$ /cm^{-1} **:** 1429, 1462, 1492 MS(FAB) (m/z): 158 {M+1}$^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.36 (d, *J*=6.0Hz, 1H, arom.H), 7.90 (d, *J*=6.0Hz, 1H, arom.H), 7.65 (t, *J*=7.5Hz, 1H, arom.H), 7.20 (d, *J*=7.5Hz, 1H, arom.H), 3.12 (s, 3H, -CH_3), 2.84 (s, 3H, -CH_3), ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 22.44, 25.98, 115.51, 117.01, 126.20, 127.33, 129.78, 132.82, 133.09, 138.88, 155.62

5-Bromo-1,8-dimethylisoquinoline (7)

Compound **6** (8.0 g, 3.4×10^{-2} mol), NBS (9.4 g, 5.3×10^{-2} mol) 95% conc.H_2SO_4 (80 mL) were added under a nitrogen atmosphere, and heated to 65 °C with stirring for 6 h. After the reaction, the reacted solution was mixed with 10% aq.$NaNO_2$ (100 mL) and neutralized with 50% aq.KOH. The solution was filtered off under reduced pressure. The salt was washed with $CHCl_3$ and the water layer was extracted with $CHCl_3$. The organic liquid was dried (KOH) for 24 h. The dried solution was evaporated under reduced pressure to remove the solvent. The residual solid was purified by distillation under reduced pressure to give a white powder **7** (10 g, 81%)

(7) : mp 89.1~89.6 °C (lit.,[1] 89.2~91.0 °C), IR (KBr) $\nu_{C=N}$ /cm^{-1} : 1428, 1482 MS(FAB) (m/z): 236 {M-1}$^+$,238{M+1}$^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.25 (d, *J*=6.0 Hz, 1H, arom.H), 7.57 (d, *J*=7.5 Hz, 1H, arom.H), 7.43 (d, *J*=7.5 Hz, 1H, arom.H), 7.31 (d, *J*=6.0 Hz, 1H, arom.H), 7.29 (d, *J*=7.5 Hz, 1H, arom.H), 3.08 (s, 3H, -CH_3), 2.88(s, 3H, -CH_3). ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 22.61, 26.92, 117.05, 122.98, 126.03, 127.29, 129.98, 131.69, 132.97, 134.81, 137.73

5-(1,8-*N*-Alkyl-dicarboximidenaphthyl)-1,8-dimethylisoquinoline (8a,b)(a: alkyl = *n*-hexyl, b: alkyl = cyclohexyl)

Each compound **3a,b** (3.3 g, 5.8×10^{-3} mol), **7** (2.0 g, 8.4×10^{-3} mol), and $Pd(PPh_3)_4$ (0.050 g, 4.3×10^{-5} mol) in mesitylene (50 mL) were refluxed for 72 h under a nitrogen atmosphere. After the reaction, the solvent was removed by evaporation and the residue was purified by column chromatography on silica gel using AcOEt as the eluent. The crude solid was recrystallized from methanol affording the product

as a white powder **8a** (0.89 g, 35%) and light brown powder **8b** (0.95 g, 39%)

(8a): mp 158.0~158.4 °C IR (KBr) $\nu_{C=N}$ /cm^{-1} : 1655 $\nu_{C=O}$ /cm^{-1} : 1694 MS(FAB) (m/z): 437{M+1}$^{+}$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.71 (d, *J*=7.0 Hz, 1H, arom.H), 8.60 (d, *J*=7.0 Hz, 1H, arom.H), 8.08 (d, *J*=6.0 Hz, 1H, arom.H), 7.59~7.69 (m, 5H, arom.H), 6.94 (d, *J*=6.0 Hz 1H, arom.H), 4.17(t, *J*=7.5 Hz, 2H, -CH_2), 3.17 (s, 3H, -CH_3), 3.01 (s, 3H, -CH_3), 1.72 (m, 2H, -CH_2-), 1.10~1.19 (m, 6H, -$CH_2CH_2CH_2$-), 0.89 (m, 3H, -CH_3) . ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 14.01, 22.60, 26.23, 26.83, 28.10, 29.82, 31.58, 40.56, 117.91, 122.54, 127.05, 128.38, 128.96, 129.99, 130.71, 131.00, 131.14, 131.32, 132.49, 134.38, 136.84, 137.26, 141.53, 144.53, 159.16, 164.02, 164.17 HRMS [m/z] Found:437.2235 Calcd.:437.2229 {M+1}$^{+}$

(8b) mp 265.1~265.4 °C IR (KBr) $\nu_{C=N}$ /cm^{-1} : 1654 $\nu_{C=O}$ /cm^{-1} : 1694 MS(FAB) (m/z): 435{M+1}$^{+}$ ^{1}H-NMR (300 MHZ , solv.: $CDCl_3$, Ref.:TMS) δ: 8.69 (d, *J*=7.5 Hz, 1H, arom.H), 8.59 (d, *J*=8.4 Hz, 1H, arom.H), 8.16 (d, *J*=7.5 Hz, 1H, arom.H), 7.65~7.71 (m, 5H, arom.H), 7.27 (d, *J*=7.5 Hz, 1H, arom.H), 4.95~4.99 (m, 1H, -NCH-), 3.23 (s, 3H, -CH_3), 3.07 (s, 3H, -CH_3), 2.55~2.60 (m, 2H), 1.87~1.92 (m, 2H), 1.75~1.80 (m, 3H), 1.28~1.31 (m, 3H) . ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 14.21, 21.08, 25.47, 26.23, 26.56, 29.13, 29.85, 58.82, 117.89, 123.07, 123.53, 127.06, 128.39, 128.94, 129.96, 130.60, 130.74, 130.95, 131.00, 131.19, 132.15, 134.42, 136.83, 137.19, 141.57, 144.18, 159.15, 164.45, 164.61 . HRMS [m/z] Found:435.2075 Calcd.:435.2073 {M+1}$^{+}$

***N*-Hexyl-1,8-dimethylazaperylene-8,9-dicarboximide (9a)**

To a 100 mL, 4-necked flask equipped with a condenser was charged with *t*-BuOK (1.0 g, 8.9×10^{-3} mol) and DBN (2.0 g, 1.6×10^{-2} mol) that was heated to 140 ℃ for 1 h with stirring. Each compound **8a,b** (0.50 g, 1.2×10^{-3} mol) was added and stirred for 7 h. After the reaction, 100 mL of water was added and the solution was filtered off under reduced pressure. The solid was washed with MeOHmethanol and purified by column chromatography on silica gel using AcOEt as the eluent. The crude solid was recrystallized from MeOH affording the product as a red solid **9a** (0.051 g, 12%). **8b** did not give the corresponding product.

(9a): mp 236.1~236.4 °C IR (KBr) $\nu_{C=N}$ /cm^{-1} : 1655 $\nu_{C=O}$ /cm^{-1} : 1693 MS(FAB) (m/z): 435{M+1}$^{+}$ ^{1}H-NMR (300 MHz,Solv.:$CDCl_3$, Ref.:TMS) δ: 8.84 (s, 1H, arom.H), 7.80~8.26 (m, 6H, arom.H), 4.16

(t, *J*=7.5 Hz, 2H, -CH_2), 3.03 (s, 3H, -CH_3), 2.75 (s, 3H, -CH_3), 1.78~1.74 (m, 2H, -CH_2-), 1.65~1.71 (m, 6H, -$CH_2CH_2CH_2$-), 1.39 (t, 3H, -CH_2CH_3). ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 14.09, 22.61, 26.25, 26.87, 28.04, 29.90, 31.58, 40.47, 118.87, 119.26, 120.45, 120.91, 125.26, 125.74, 126.47, 127.76, 130.66, 130.92, 131.25, 131.33, 134.35, 134.89, 135.74, 138.23, 139.12, 139.45, 160.60, 163.36, 163.39 . HRMS [m/z] Found:435.2073 Calcd.:435.2072 $\{M+1\}^+$

4-Bromo-1,8-bis(hydroxymethyl)naphthalene (10)

To a 500 mL, 4-necked flask equipped with a condenser was charged Et_2O (100 mL) and lithium aluminum hydride (5.0 g, 1.3×10^{-1} mol) Compound **1** (5.0 g, 1.8×10^{-2} mol) was slowly added and stirred 48 h. After the reaction, AcOEt (200 mL) was added portionwise over 30 min and stirred 1 h.The solution was neutralized with 10% aq.HCl. The organic layer was evaporated and purified by recrystallization from acetone to yield white needles **10** (3.1 g, 64%).

Analysis data: **(10):** mp 161.7~162.2 °C (lit.,[8] 162.0~163.0 °C) IR (KBr) ν_{OH}: 3233, 3346 MS(FAB) (m/z): 265$\{M\}^+$, 267$\{M+2\}^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.14 (d, *J*=7.5 Hz, 1H, arom.H), 8.04 (d, *J*=8.5 Hz, 1H, arom.H), 7.89 (d, *J*=8.0 Hz, 1H, arom.H), 7.52 (t, *J*=8.0 Hz, 1H, arom.H), 7.39 (d, *J*=7.5 Hz, 1H, arom.H), 5.76 (s, 2H, -OH), 5.01 (s, 4H, -CH_2-). ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 63.12, 63.48, 122.41, 126.79, 127.36, 128.17, 129.20, 129.52, 131.53, 132.42, 139.41, 139.56

4-Bromo-1,8-bis(bromomethyl)naphthalene (11)

To a 500 mL 4-necked flask equipped with a condenser was charged Et_2O (200 mL) CH_2Cl_2 and compound **10** (5.0 g, 1.8×10^{-2} mol) and stirred . PBr_3 was added slowly and stirred 12 h. After the reaction, the reacted solution was filled with 10% aq.$NaNO_2$ (100 mL) and organic liquid was dried ($MgSO_4$) 12 h. The dried solution was evaporated under reduced pressure. Crude solid was recrystallized from ethanol affording the product as pink solid **11** (5.2 g, 70%)

Analysis data: **(11):** mp 123.1~123.4 °C (lit.,[8] 122.0~123.6 °C) IR (KBr) $\nu_{C\text{-}Br}$: 1200 ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.41 (d, *J*=7.2 Hz, 1H, arom.H), 7.72 (d, *J*=7.8 Hz, 1H, arom.H), 7.45~7.55 (m, 2H, arom.H), 7.38 (d, *J*=7.8 Hz, 1H, arom.H), 5.27 (s, 2H, -CH_2-), 5.27 (s, 2H, -CH_2-) . ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 36.50, 36.52, 125.68, 126.44, 127.06, 130.27, 130.32,

130.97, 132.78, 133.54, 133.87, 133.98

1,8-Bis(hydroxymethyl)naphthalene (16)

To a 500 mL 4-necked flask equipped with a condenser was charged Et_2O (100 mL) and lithium aluminum hydride (5.0 g, 1.3×10^{-1} mol). Compound **15** (5.0 g, 1.8×10^{-2} mol) was added slowly and stirred 48 h. After the reaction, AcOEt (200 mL) was added portionwise over 30 min and stirred 1 h. The solution was neutralized with 10% aq.HCl. The organic layer was evaporated and purified by recrystallization from acetone yielded white needle **16** (3.4 g, 70%).

(16): mp 159.6~160.2 °C (lit.,[8] 160.0~161.0 °C) IR (KBr) ν_{OH}: 3230, 3346 MS(FAB) (m/z): 188{M}$^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 7.81 (d, *J*=8.1Hz, 1H, arom.H), 7.50 (d, *J*=8.1 Hz, 1H, arom.H), 7.40 (t, *J*=8.1 Hz, 1H, arom.H), 5.23 (s, 2H, -CH_2-), 2.94 (s, 1H, -OH). ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 63.65, 124.89, 128.08, 129.00, 130.03, 135.07, 138.50

1,8-Bis(bromomethyl)naphthalene (17)

To a 500 mL 4-necked flask equipped with a condenser was charged Et_2O (200 mL), CH_2Cl_2 and Compound **16** (4.0 g, 1.5×10^{-2} mol) then stirred. PBr_3 was slowly added and stirred for 12 h. After the reaction, to the reacted solution was added 10% aq.$NaNO_2$ (100 mL) and the organic liquid was dried ($MgSO_4$) for 12 h. The dried solution was evaporated under reduced pressure. The crude solid was recrystallized from EtOH affording the product as a pink solid **17** (7.1 g, 85%)

(17): mp 130.6~131.0 °C (lit.,[8] 130.0~131.5 °C) IR (KBr) $\nu_{C\text{-}Br}$: 1202 ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.14 (d, *J*=8.1 Hz, 1H, arom.H), 7.89 (d, *J*=8.1 Hz, 1H, arom.H), 7.52 (t, *J*=8.1 Hz, 1H, arom.H), 5.30 (s, 2H, -CH_2-) ^{13}C-NMR(75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 37.14, 119.96, 121.51, 125.68, 126.56, 131.90, 133.38

1,8-Dimethylnaphthalene (18)

Compound **17** (3.0 g, 7.5×10^{-3} mol), $NaBH_4$ (2.4 g, 9.0×10^{-2} mol) , and DMSO (40 mL) were heated to 80 °C for 48 h with stirring. After the reaction, the mixture was cooled to rt and abstracted with water and $CHCl_3$. The organic liquid was evaporated under reduced pressure. The crude solid was purified by column chromatography on silica gel using hexane as the eluent, affording the product as a white powder **18** (1.5 g, 94%)

(18): mp 79.9~80.4 °C (lit.,[9] 80.0~81.0 °C) MS(FAB) (m/z): 156 {M}$^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 7.56 (d, *J*=6.9 Hz, 1H, arom.H), 7.32 (d, *J*=6.9 Hz, 1H, arom.H), 7.19 (t, *J*=6.9 Hz, 1H, arom.H), 2.81 (s, 3H, -CH_3) . ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 22.58, 124.95, 127.18, 129.51, 133.03, 135.36, 135.54

4-Bromo-1,8-dimethylnaphthalene (12)

Compound **18** (5.0 g, 1.8×10^{-2} mol), NBS (0.75 g, 3.3×10^{-3} mol) , and DMF (30 mL) were stirred at rt for 30 h. After the reaction ended, the mixture was washed with water and extracted with $CHCl_3$. The organic liquid was evaporated under reduced pressure to remove the solvent. The crude solid was purified by column chromatography on silica gel using hexane as the eluent, affording the product as a white solid **12** (0.53 g, 70%)

(12): mp 29.7~30.1 °C (lit.,[9] 29.8~30.0 °C) MS(FAB) (m/z): 233{M-1}$^+$,235{M+1}$^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 7.53 (d, *J*=7.7 Hz, 1H, arom.H), 7.33 (t, *J*=8.3 Hz, 1H, arom.H), 7.23 (d, *J*=8.3 Hz, 1H, arom.H), 7.00 (d, *J*=7.7 Hz, 1H, arom.H), 2.86 (s, 3H, -CH_3), 2.84 (s, 3H, -CH_3). ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 21.38, 21.43, 117.31, 121.77, 122.29, 124.78, 124.91, 125.80, 128.64, 129.80, 131.11, 131.38

5-(1,8-*N*-Alkyldicarboximidenaphthyl)-1,8-dimethylnaphthalene (13a,b)(a: alkyl = *n*-hexyl, b: alkyl = cyclohexyl)

Each compound **3a,b** (3.3 g, 5.8×10^{-3} mol), and **12** (2.0 g, 8.4×10^{-3} mol), and $Pd(PPh_3)_4$ (0.050 g, 4.3×10^{-5} mol) in mesitylene (50 mL) were refluxed for 72 h under nitrogen atmosphere. After the reaction, the solvent was evaporated and the residue purified by column chromatography on silica gel using toluene as the eluent, affording the product as a yellowish white powder **13a** (0.65 g, 26%) and white powder **13b** (0.83 g, 33%)

(13a): mp 171.0~171.3 °C IR (KBr) $\nu_{C=O}$ imide/cm^{-1} : 1698 MS(FAB) (m/z): 436{M+1}$^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.69 (d, *J*=7.2 Hz, 1H, arom.H), 8.68 (d, *J*=7.2 Hz, 1H, arom.H), 7.70~7.73 (m, 2H, arom.H), 7.52 (t, *J*=8.2 Hz, 1H, arom.H), 7.38 (t, *J*=7.2 Hz, 1H, arom.H), 7.29 (d, *J*=7.2 Hz, 1H, arom.H), 7.26 (d, *J*=7.2 Hz, 1H, arom.H), 7.12 (d, *J*=8.2 Hz, 1H, arom.H), 7.08 (d, *J*=8.2 Hz, 1H, arom.H), 4.22 (t, *J*=7.5 Hz, 2H, -NCH_2), 3.05 (s, 3H, -CH_3), 3.02 (s, 3H, -CH_3), 1.72~1.79 (m, 2H, -CH_2-), 1.34~1.41 (m, 6H, -$CH_2CH_2CH_2$-), 0.92 (t, 3H, -CH_3) . ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$,

Ref.:TMS) δ 14.07, 22.56, 26.28, 26.36, 26.80, 28.08, 31.36, 40.47, 122.04, 122.81, 125.54, 125.66, 126.71, 127.11, 128.75, 129.75, 130.74, 131.12, 131.36, 132.98, 133.17, 134.08, 135.42, 135.97, 136.60, 146.51, 164.12, 164.28. HRMS [m/z] Found:436.2280 Calcd.:436.2276 $\{M+1\}^+$

(13b) mp 255.0~255.3 °C IR (KBr) $\nu_{C=O}$ imide/cm^{-1} : 1695 MS(FAB) (m/z): 433$\{M+1\}^+$ ^{1}H-NMR (300 MHZ, solv.: $CDCl_3$, Ref.:TMS) δ: 8.67 (d, *J*=7.5 Hz, 1H, arom.H), 8.57 (d, *J*=6.6 Hz, 1H, arom.H), 7.68~7.73 (m, 2H, arom.H), 7.53 (d, *J*=7.5 Hz, 1H, arom.H), 7.41 (d, *J*=7.5 Hz, 1H, arom.H), 7.26~7.29 (m, 2H, arom.H), 7.14~7.19 (m, 2H, arom.H), 5.12 (m, 1H, -NCH), 3.05 (s, 3H, $-CH_3$), 3.02 (s, 3H, $-CH_3$), 2.54~2.62 (m, 2H), 1.89~1.94 (m, 2H), 1.76~1.80 (m, 3H), 1.37~1.46 (m, 3H). ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 25.45, 26.27, 26.35, 26.55, 29.10, 53.72, 122.59, 123.36, 125.51, 125.67, 126.73, 127.08, 128.32, 128.78, 129.74, 130.62, 131.00, 131.22, 132.63, 133.17, 134.09, 135.47, 135.95, 136.55, 146.16, 164.56, 164.72 . HRMS [m/z] Found:434.2123 Calcd.:434.2120 $\{M+1\}^+$

***N*-Hexyl-1,8-dimethylperylene-8,9-dicarboximide (14a)**

To a 100 mL, 4-necked flask equipped with a condenser was charged with *t*-BuOK (1.0g, 8.9×10^{-3} mol), and DBN (2.0g, 1.6×10^{-2} mol) then heated to 140 °C for 1 h and stirred. Each compound **13a,b** (0.50 g, 1.2×10^{-3} mol) was added and stirred for 7 h. After the reaction ended, 100 mL of water was added and the solution was filtered off under reduced pressure.The solid was washed with methanol and purified by column chromatography on silica gel using $CHCl_3$ as the eluent. The crude solid was recrystallized from methanol affording the product as a red solid **14a** (0.050 g, 10%). **13b** did not give the corresponding product.

(14a): mp 254.1~254.4 °C IR (KBr) $\nu_{C=O}$ imide/cm^{-1} : 1688 MS(FAB) (m/z): 434$\{M+1\}^+$ ^{1}H-NMR (300 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ: 8.41 (d, *J*=8.0 Hz, 2H, arom.H), 8.11~8.16 (m, 4H, arom.H), 7.54 (d, *J*=7.7 Hz, 2H, arom.H), 4.16 (t, *J*=7.3Hz, 2H, $-NCH_2$), 2.87 (s, 3H, $-CH_3$-CH_3), 1.61~1.65 (m, 2H, $-CH_2$-), 1.25~1.29 (m, 6H, $-CH_2CH_2$, CH_2-), 0.89 (t, 3H, $-CH_3$) . ^{13}C-NMR (75 MHz, Solv.:$CDCl_3$, Ref.:TMS) δ 14.11, 22.61, 26.88, 28.09, 29.69, 31.61, 40.39, 119.22, 119.84, 123.62, 125.70, 127.54, 128.82, 129.27, 130.71, 131.13, 137.49, 139.61, 149.63, 163.93 HRMS [m/z] Found.:433.2036 Calcd.:433.2042 $\{M\}^+$

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