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EFFECT OF SUBSTITUENTS AT 1,4-POSITIONS OF POLYCYCLIC AROMATIC COMPOUNDS AND PREPARATION OF 2,3-DIFUNCTIONALIZED PENTACENES AND NAPHTHACENES

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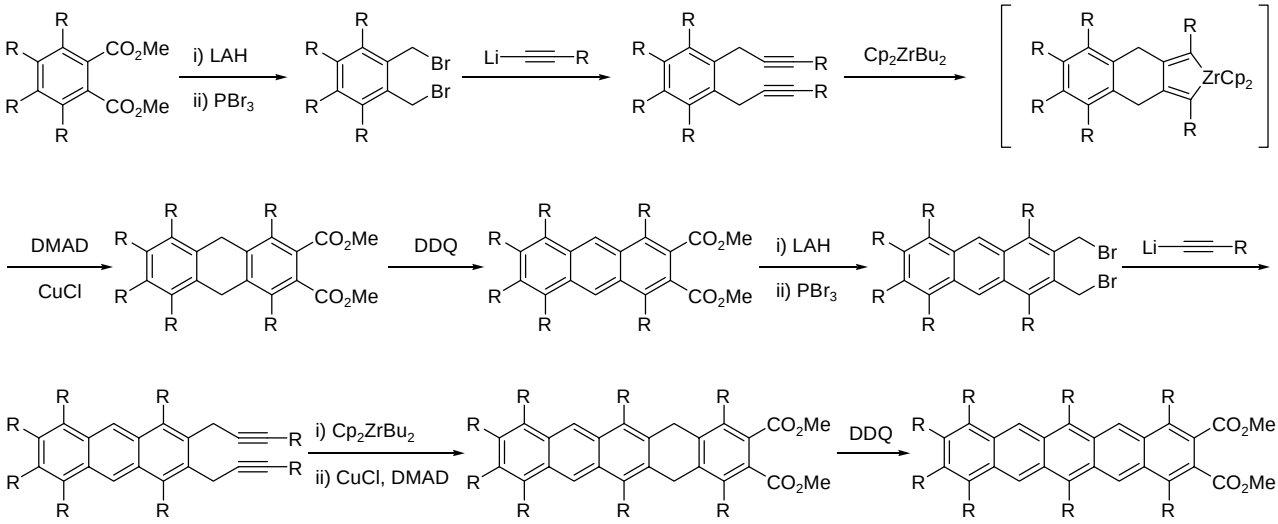
Abstract – Effects of substituents at 1,4-positions of polycyclic aromatic compounds were investigated in the case of reduction of 2,3-bis(alkoxycarbonyl)arenes with the $LiAlH_4/AlCl_3$ system. 2,3-Bis(alkoxycarbonyl)dihydronaphthacenes and dihydropentacenes **1** were treated with a mixture of $LiAlH_4$ and $AlCl_3$. The products were dependent on the substituents at 1,4-positions. Similar type of influence of the substituents at 1,4-positions was observed in the oxidation of diols **2** to dialdehydes **4**. Without substituents at 1,4-positions, dialdehydes **4** were conveniently obtained. However, with substituents at 1,4-positions, dialdehydes **4** were not obtained. Instead, 1,3-dihydroisobenzofuran-1,3-diol or 1,3-dihydroisobenzofuran-1-ol derivatives **5, 6** were obtained in good yields. Preparation of pentacene imides and pentacene carboxylic acid anhydride was also reported.

INTRODUCTION

In 1997, Jackson *et al.* reported that pentacene showed the comparable or higher mobility compared with amorphous silicon as organic semiconductor.[1] Since pentacene is not soluble in organic solvent, we proposed and reported substituted soluble pentacene derivatives (Scheme 1)[2] for wet process fabrication of organic semiconductors.

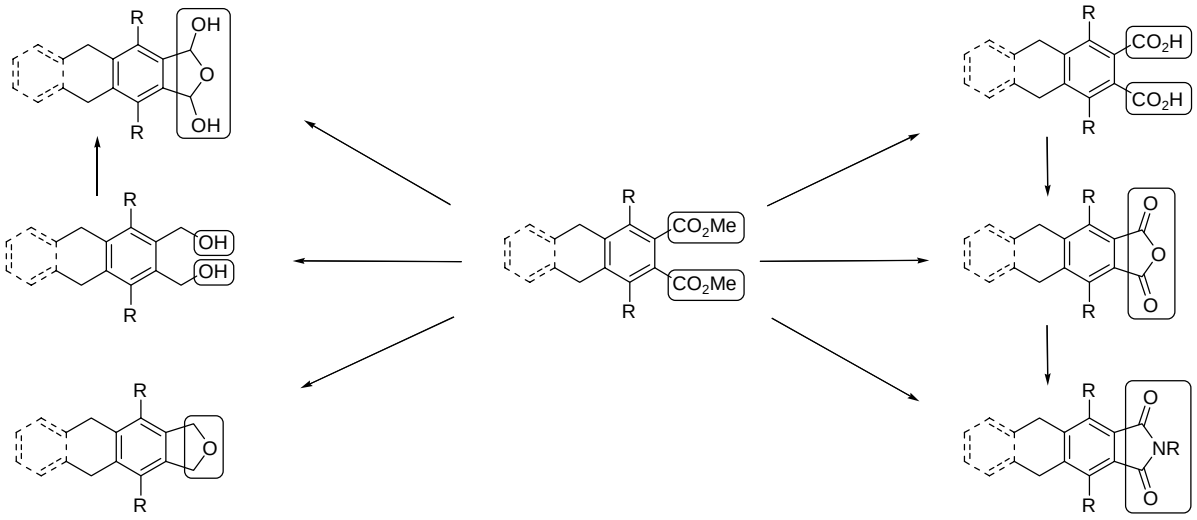
After our report, several groups reported the formation of substituted pentacenes.[3-7] Although various substituted pentacenes have been reported, functionalized pentacenes are still limited. So far alkyl, alkenyl, aryl, alkynyl, silyl, halogeno, cyano, alkoxy, aryloxy, thienyl, alkoxy carbonyl groups have been reported.

Scheme 1. Homologation Method for the Formation of Soluble and Substituted Pentacene Derivatives



During the course of our study on functionalized polycyclic aromatic compound formation such as 2,3-difunctionalized pentacenes and naphthacenes, we found the effects of substituents at 1,4-positions of polycyclic aromatic compounds. In this paper, we would like to report the effects of the substituents at 1,4-positions and the formation of 2,3-difunctionalized pentacene and naphthacene derivatives derived from 2,3-bis(methoxycarbonyl)pentacenes and naphthacenes as shown in Scheme 2.

Scheme 2. Formation of 2,3-Difunctionalized Acene Derivatives



RESULTS AND DISCUSSION

EFFECTS OF SUBSTITUENTS AT 1,4-POSITIONS IN THE REDUCTION OF 2,3-DIESTER GROUPS OF POLYCYCLIC COMPOUNDS WITH ALUMINUM HYDRIDES AND ALUMINUM TRICHLORIDE

The results of reduction of two ester groups of 1,4-bis(trimethylsilyl)-2,3- bis(methoxycarbonyl)-5,12-dihydronaphthacene (**1a**) with a series of aluminum hydrides were shown in Table 1. To obtain the desired diol **2a** in high yield, a suitable choice of an aluminum hydride and a solvent was critical. The reaction of diester **1a** with DIBAL-H was disappointing to afford the desired diol **2a** only in low yield (entry 1), although diester **1a** was consumed completely. With $LiAlH_4$ in THF, the yield was improved but still not satisfactory (entry 2). It was worth noting that just changing the solvent from THF to ether dramatically improved the yield (entry 3). When diester **1a** was mixed with $LiAlH_4$ in THF, the color of the mixture turned to dark red and was kept during the reaction. The color change would indicate electron transfer reaction, which caused undesired side reaction. In contrast, the reaction in ether showed no color change.

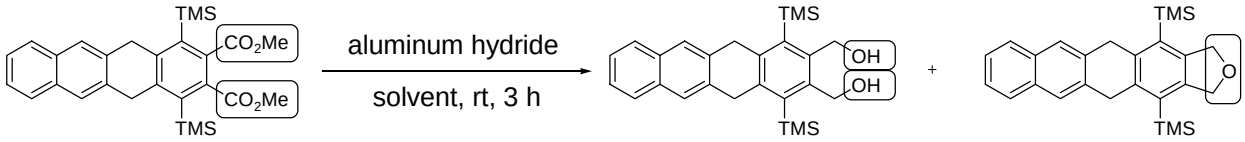
Scheme 3

$$3\ LiAlH_4 + AlCl_3 \longrightarrow 3\ LiCl + 4\ AlH_3$$

$$LiAlH_4 + AlCl_3 \longrightarrow LiCl + 2\ AlH_2Cl$$

$$LiAlH_4 + 3\ AlCl_3 \longrightarrow LiCl + 3\ AlHCl_2$$

Table 1. Reduction of Diester **1a** with Aluminum Hydrides



1a **2a** **3a**

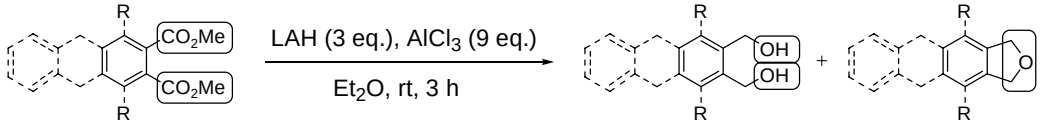
Entry	Reagents	Amount (eq.)	Solvent	Yields[a] of **2a** (%)	Yields[a] of **3a** (%)
1	DIBAL-H[b,c]	6	toluene	6	-
2	$LiAlH_4$[c]	3	THF	67	-
3	$LiAlH_4$	3	Et_2O	100	-
4	$LiAlH_4$: $AlCl_3$ (AlH_3)	3:1	Et_2O	26	74
5	$LiAlH_4$: $AlCl_3$ (AlH_2Cl)	3:3	Et_2O	16	84
6	$LiAlH_4$: $AlCl_3$ ($AlHCl_2$)	3:9	Et_2O	6	94
7	$LiAlH_4$: $AlCl_3$	3:12	Et_2O	7	93

[a] NMR yields. [b] This reaction was carried out at -78 °C. [c] No starting material remained.

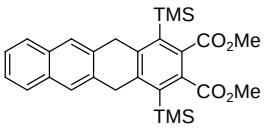
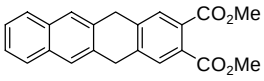
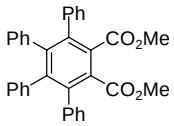
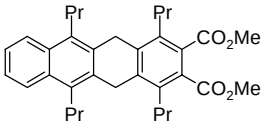
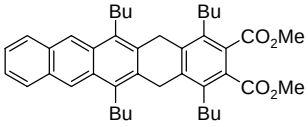
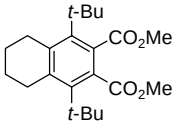
Surprisingly, the cyclic ether derivative **3a** was obtained as a major product when $AlCl_3$ was combined with $LiAlH_4$ in the reduction system (entries 4-7). The combination of $LiAlH_4$ and $AlCl_3$ in different

ratios could provide different types of aluminum hydrides as shown in Scheme 3 as reported in the literature.[8] Thus the reducing ability of the resulting aluminum hydrides could be tuned. The yield of cyclic ether derivative **3a** increased with increase of the ratio of $AlCl_3$ to $LiAlH_4$, and the best yield for **3a** was obtained when the ratio of $LiAlH_4$: $AlCl_3$ was 3:9 (entry 6). Further increasing of the ratio of $AlCl_3$ did not improve the yield of **3a** (entry 7).

Table 2. Substituent Effects in the Reduction of Diester **1** with $LiAlH_4$ and $AlCl_3$



Substrate 1 **Diol 2** **Cyclic Ether 3**

Entry	Substrate **1**	Yields[a] of **2** (%)	Yields[a] of **3** (%)
1	 **a**	6	94
2	 **b**	97[b]	-
3	 **c**	65	35
4	 **d**	45	55
5	 **e**	41	59
6	 **f**	-	85[c]

[a] NMR yields. [b] Isolated yield.

[c] Refluxing in Et_2O for 2 days. Starting material was recovered in 15%.

The tendency for the formation of the cyclic ethers was strongly affected by steric bulkiness of the *ortho*-substituents at 1,4-positions. Table 2 summarizes the results of the reduction of a series of aromatic diester compounds with the $LiAlH_4$-$AlCl_3$ (3:9) mixed reagent. When 3,4,5,6-tetraphenylphthalate dimethyl ester **1c** was reduced with $LiAlH_4$-$AlCl_3$, a mixture of the corresponding diol **2c** and cyclic ether **3c** was obtained in the ratio of 65:35, respectively (entry 3). Similarly, the reductions of *n*-propyl- or *n*-butyl-substituted substrates **1d** and **1e** also afforded mixtures of the corresponding diols and cyclic ethers in comparable ratios (entries 4 and 5). When di-*t*-butyl-substituted substrate **1f** was used for the reduction, cyclic ether **3f** was formed as a single product. No corresponding diol **2f** was formed. At room temperature, the yield of **3f** was 12% and starting material **1f** recovered in 88%. Even after refluxing the reaction mixture in diethyl ether for 2 days, the starting material **1f** still remained in 15% and cyclic ether **3f** was formed in 85% as a single product (entry 6). On the other hand, the reduction of diester **1b** without substituents at 1,4-positions afforded only the corresponding diol **2b** in quantitative yield (entry 2). No cyclic ether **3b** was formed in this case. Probably, increasing of the steric bulkiness of the *ortho*-substituents would induce close proximity of the two aluminoxy moieties of the intermediate, which could cause the formation of the corresponding cyclic ether **2**.

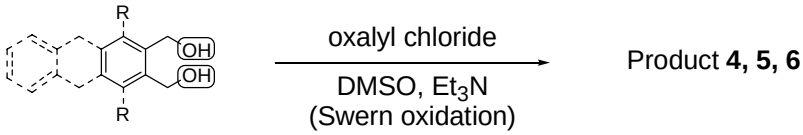
EFFECTS OF SUBSTITUENTS AT 1,4-POSITIONS IN THE OXIDATION OF 2,3-BIS(HYDROXYMETHYL)AROMATIC COMPOUNDS

Oxidation of 2,3-bis(hydroxymethyl)acene derivatives was also strongly affected by sterical bulkiness of *ortho*-substituents at 1,4-positions. The results of Swern oxidation of a series of aromatic diol compounds are summarized in Table 3.[9] When diols **2g-i** having no *ortho*-substituents were oxidized with oxalyl chloride-DMSO-Et_3N, the corresponding dialdehydes **4g-i** were obtained cleanly in 71, 90, and 30%, respectively (entries 1-3). However, *n*-propyl-substituted substrate **2j** was used for the oxidation, 1,3-dihydro-isobenzofuran-1,3-diol derivative **5j** was formed in 55% yield (entry 4). Other two cases **2a,k** having *ortho*-trimethylsilyl- or *n*-propyl groups also could not give corresponding dialdehydes. Their crude NMR spectra suggested that **5a** and **5k** have isobenzofuran-1,3-diol structures, but full characterization of them was failed due to their instability and impurity. Although careful work-up and purification was preformed, all such attempts gave contaminated products. Oxidation of *n*-butyl-substituted substrate **2l** afforded 1,3-dihydro-isobenzofuran-1-ol derivative **6l** in 62% (entry 7). The corresponding dialdehyde was not formed in this case.

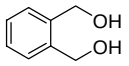
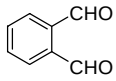
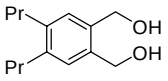
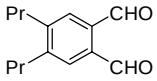
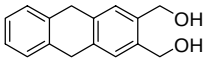
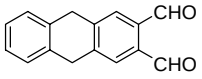
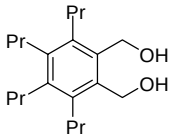
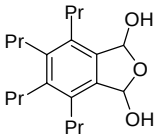
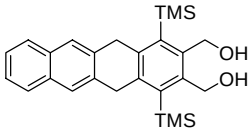
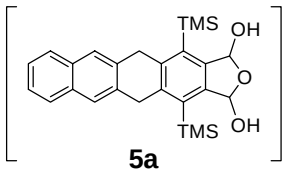
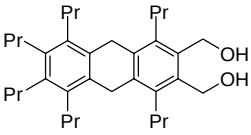
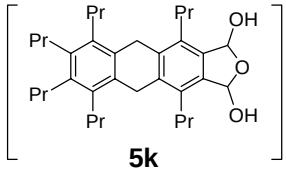
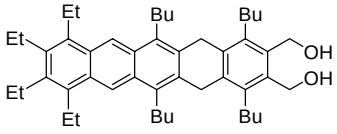
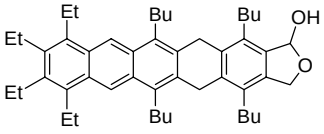
The existence of the *ortho*-substituents would interfere with the coplanar conformation between the aromatic ring and the carbonyl moieties, and it would increase the reactivity of these carbonyl groups due to interception of the π-conjugation with the aromatic ring. Thus destabilized carbonyl groups could

facilitate the cyclization with water or the neighboring hydroxy group to produce the corresponding isobenzofuranols **5** or **6**.

Table 3. Substituent Effects in the Oxidation of 2,3-Bis(hydroxymethyl)acenes **2**



Substrate **2**

Entry	Substrate **2**	Product	Yields[a] (%)
1[b]	 **g**	 **4g**	71
2	 **h**	 **4h**	90
3	 **i**	 **4i**	30
4	 **j**	 **5j**	55
5[c]	 **a**	 **5a**	-
6[c]	 **k**	 **5k**	-
7	 **l**	 **6l**	62

[a] Isolated yields. [b] See Ref. 9. [c] See Experimental Section.

FORMATION OF NAPHTHACENE- AND PENTACENE DICARBOXYLIC ANHYDRIDES AND IMIDES

Preparation of naphthacene- and pentacene dicarboxylic anhydrides **8a,l** from the corresponding

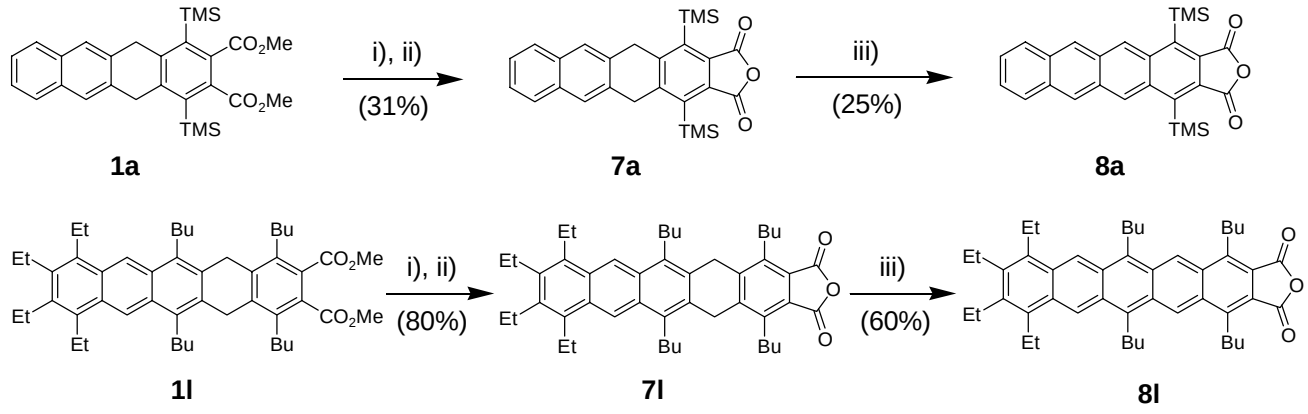
2,3-diester polycyclic compounds **1a,l** was shown in Scheme 4. Diesters **1a,l** reacted with lithium iodide in refluxing pyridine to afford the corresponding dicarboxylic anhydrides **7a,l**.[10] These compounds were aromatized with DDQ at 100 °C in degassed toluene to afford the corresponding naphthacene- and pentacene anhydrides **8a,l** in 25 and 60% yields, respectively.

The formation of pentacene imides was shown in Scheme 5. The dicarboxylic anhydride **7l** was treated with primary amines to give the corresponding imides **9lo,lp** in good yields.[11] Aromatization of **9lo,lp** with DDQ at 100 °C in degassed toluene afforded the corresponding pentacene imides **10lo,lp** in 76 and 68% yields, respectively.

Unexpectedly, solubility of these pentacene imides was relatively lower than that of pentacene diesters, although these were highly alkylated. Probably, this is due to the planarity of the imide moieties in these pentacenes. Such structural changing would cause strong π-π interaction between the pentacene molecules.

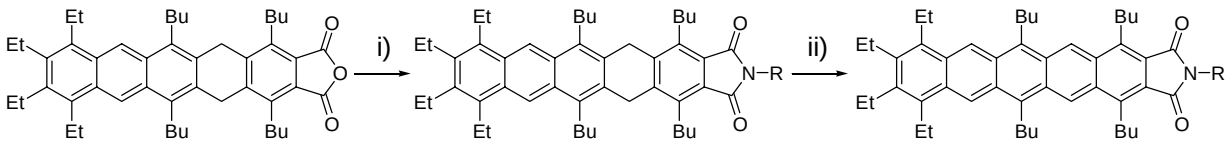
When 1,4-nonsubstituted tetrahydropentacene **1m** reacted with lithium iodide in refluxing pyridine, the two-ester groups were converted to carboxylic ones to afford diacid **11m** in 96% yield. It is different from the reaction of 1,4-dibutyldihydropentacene **1l** to produce the corresponding dicarboxylic anhydride

Scheme 4. Formation of Naphthacene- and Pentacene Dicarboxylic Anhydride



i) 15 eq LiI, reflux, pyridine, 2 h. ii) 3 N HCl iii)1 eq. DDQ, 100 °C, 3 h

Scheme 5. Formation of Pentacene Imides



9lo (R = *n*-hexyl, 96%)
9lp (R = 2-ethylhexyl, 92%)

10lo (R = *n*-hexyl, 76%)
10lp (R = 2-ethylhexyl, 68%)

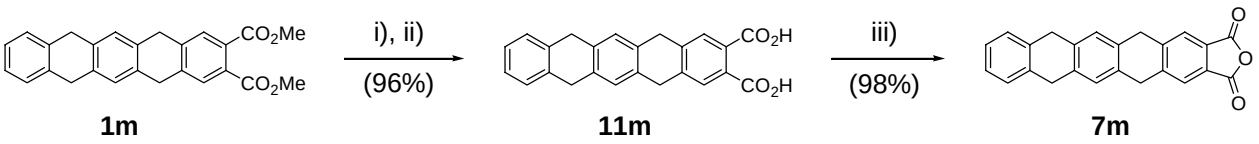
i) $R\text{-}NH_2$ toluene, reflux, 6 h ii) 1 eq. DDQ, toluene, 100 °C, 3 h

7l (Scheme 4). Probably it is also due to the steric effect of *ortho*-substituents same as the cyclic ether formation as mentioned before. The carboxylic acid **11m** was heated at 140 °C in acetic anhydride to give the corresponding dicarboxylic anhydride **7m** in 98% yield.

Anhydride **7m** was treated with primary amines to give imides **9mp-r.** Thus formed **9mp-r** were aromatized with DDQ at 100 °C in degassed toluene. In this way, three kinds of pentacene imides **10mp-r** were synthesized in high yields (Scheme 6). Surprisingly the solubility of these pentacene imides **10mp-r** were much lower than the corresponding 2,3-bis(methoxycarbonyl)pentacene, although much longer alkyl chains were substituted on the imide nitrogen atom.

For the imide formation step, 1,4-bis-silylated anhydride **7n** did not react with primary amines probably due to the steric hindrance of the bulky trimethylsilyl groups (Scheme 7).

Scheme 6. Formation of Pentacene Imides

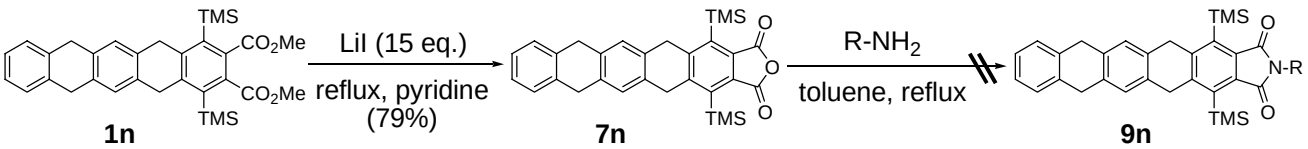


9mp (R = 2-ethylhexyl, 91%)
9mq (R = *n*-octyl, 90%)
9mr (R = *n*-octadecyl, 94%)

10mp (R = 2-ethylhexyl, 91%)
10mq (R = *n*-octyl, 90%)
10mr (R = *n*-octadecyl, 90%)

i) 15 eq. LiI, pyridine, reflux, 2 h. ii) 3 N HCl. iii) Ac_2O, 140 °C, 1 h
iv) R-NH_2, toluene, reflux, 6 h. v) 1 eq. DDQ, toluene, 100 °C, 3 h.

Scheme 7



1n **7n** **9n**

CONCLUSION

Effect of the substituents at 1,4-positions of polycyclic aromatic compounds was remarkable for the functionalization of 2,3-positions. Various functional groups could be introduced into substituted naphthacenes and pentacenes by the functionalization of the corresponding 2,3-bis(alkoxycarbonyl) naphthacenes and pentacenes which were obtained by zirconium-mediated homologation.

EXPERIMENTAL

General Information. Manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Diethyl ether was dried over 4 Å molecular sieves. Lithium aluminum hydride and aluminum trichloride were purchased from KANTO Chemical Co. Ltd. NMR spectra were recorded on a JEOL JNM-AL300 NMR spectrometer. Tetramethylsilane (TMS) was used as the reference for ^{1}H and ^{13}C NMR.

Compounds **1a-n, 2j-l** were prepared according to the literature.[2,12]

A Representative Procedure for the Reduction with $LiAlH_4$ and $AlCl_3$:

1,4-Bis(trimethylsilyl)-2,3-bis(hydroxymethyl)-5,12-dihydronaphthacene (2a).

4,13-Bis(trimethylsilyl)-1,3,5,12-tetrahydro-2-oxacyclopenta[*b*]naphthacene (3a).

To a suspension of $LiAlH_4$ (114 mg, 3.0 mmol) in Et_2O (10 mL), $AlCl_3$ (1.20 g, 9.0 mmol) was added and the mixture was stirred at 0 °C for 0.5 h. Diester **1a** (490 mg, 1.0 mmol) was added to the mixture. After stirring for 3 h at rt, the reaction mixture was carefully quenched with water and 2 N H_2SO_4 at 0 °C. The organic layer was extracted with AcOEt. The extract was washed with saturated aqueous $NaHCO_3$ solution, brine, and dried over Na_2SO_4. After removal of the solvent, the residue was purified by a column chromatography on silica gel (AcOEt: hexane = 1: 10 as eluent) to afford the title compound **3a** as colorless solid (349 mg, 84% isolated yield, 94% NMR yield), and the corresponding diol **2a** as colorless solid (21 mg, 5% isolated yield, 6% NMR yield).

2a: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.60 (s, 18 H), 3.40 (brs, 2 H), 4.18 (s, 4 H), 4.77 (s, 4 H), 7.39-7.42 (m, 2 H), 7.71 (s, 2 H), 7.77-7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 3.6, 38.7, 62.6, 124.1, 125.3, 127.2, 132.4, 136.4, 140.2, 143.3, 144.1; HRMS (EI) calcd for $C_{26}H_{34}O_2Si_2$: 434.2097. Found: 434.2101.

3a: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.48 (s, 18 H), 4.17 (s, 4 H), 5.11 (s, 4 H), 7.41-7.44 (m, 2 H), 7.73 (s, 2 H), 7.78-7.81 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 2.1, 38.3, 74.5, 124.0, 125.3, 127.3, 131.1, 132.4, 136.7, 141.8, 143.1; HRMS (EI) calcd for $C_{26}H_{32}OSi_2$: 416.1992. Found: 416.1987.

Preparation of 2,3-Bis(hydroxymethyl)-5,12-dihydronaphthacene (2b) from 1b.

The title compound was prepared in 97% isolated yield by the same way as described for **2a**.

2b: ^{1}H NMR (DMSO-d_6, Me_4Si) δ: 4.05 (s, 4 H), 4.52 (s, 4 H), 5.08 (brs, 2 H), 7.37 (s, 2 H), 7.41-7.45 (m, 2 H), 7.84 (s, 2 H), 7.82-7.85 (m, 2 H); ^{13}C NMR (DMSO-d_6, Me_4Si) δ: 35.7, 60.3, 124.8, 125.3, 125.9, 127.1, 131.8, 134.9, 136.1, 137.3; HRMS (EI) calcd for $C_{20}H_{18}O_2$: 290.1307. Found: 290.1321.

Preparation of 1,2-Bis(hydroxymethyl)-3,4,5,6-tetraphenylbenzene (2c).

Preparation of 4,5,6,7-Tetraphenyl-1,3-dihydroisobenzofuran (3c).

The compounds **2c** and **3c** were prepared in 65 and 35% NMR yields, respectively, by the same way as

described for **2a, 3a**.

2c: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 2.71 (brs, 2 H), 4.68 (s, 4 H), 6.72-6.82 (m, 10 H), 7.10-7.17 (m, 10 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 61.1, 125.4, 126.5, 126.6, 127.4, 130.4, 130.9, 137.3, 139.7, 140.1, 141.4, 142.0; HRMS (EI) calcd for $C_{32}H_{26}O_2$: 442.1933. Found: 442.1926.

3c: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 5.11 (s, 4 H), 6.79-6.91 (m, 10 H), 7.07-7.21 (m, 10 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 74.4, 125.5, 126.6, 126.8, 127.8, 129.3, 131.4, 134.7, 137.6, 139.3, 139.5, 140.5; HRMS (EI) calcd for $C_{32}H_{24}O$: 424.1827. Found: 424.1832.

1,4,6,11-Tetrapropyl-2,3-bis(hydroxymethyl)-5,12-dihydronaphthacene (2d).
4,6,11,13-Tetrapropyl-1,3,5,12-tetrahydro-2-oxacyclopenta[*b*]naphthacene (3d).

The compounds **2d** and **3d** were prepared in 45 and 55% NMR yields, respectively, by the same way as described for **2a**, **3a**.

2d: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.15 (t, J = 7.2 Hz, 6 H), 1.17 (t, J = 7.2 Hz, 6 H), 1.59-1.77 (m, 8 H), 2.56 (brs, 2 H), 2.88-2.94 (m, 4 H), 3.17-3.23 (m, 4 H), 4.09 (s, 4 H), 4.83 (s, 4 H), 7.43-7.46 (m, 2 H), 8.04-8.07 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.8, 14.9, 24.3, 25.3, 30.6, 30.9, 31.8, 59.8, 124.5, 124.7, 131.0, 132.2, 133.4, 135.9, 136.3, 137.1; HRMS (EI) calcd for $C_{32}H_{42}O_2$: 458.3185. Found: 458.3187.

3d: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.08 (t, J = 7.2 Hz, 6 H), 1.17 (t, J = 7.2 Hz, 6 H), 1.60-1.77 (m, 8 H), 2.63-2.68 (m, 4 H), 3.17-3.23 (m, 4 H), 4.06 (s, 4 H), 5.15 (s, 4 H), 7.42-7.46 (m, 2 H), 8.04-8.08 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.6, 14.8, 23.8, 24.3, 29.7, 30.9, 33.0, 73.8, 124.5, 124.7, 130.0, 131.0, 132.1, 133.7, 135.5, 135.9; HRMS (EI) calcd for $C_{32}H_{40}O$: 440.3079. Found: 440.3078.

1,4,6,13-Tetrabutyl-2,3-bis(hydroxymethyl)-5,14-dihydropentacene (2e).
4,6,13,15-Tetrabutyl-1,3,5,14-tetrahydro-2-oxacyclopenta[*b*]pentacene (3e).

The compounds **2e** and **3e** were prepared in 41% and 59% NMR yields, respectively, from **1e** by the same way as described for **2a**, **3a**.

2e: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.08 (t, J = 7.2 Hz, 6 H), 1.11 (t, J = 7.2 Hz, 6 H), 1.61-1.82 (m, 16 H), 2.30 (brs, 2 H), 2.95-3.00 (m, 4 H), 3.35-3.40 (m, 4 H), 4.16 (s, 4 H), 4.88 (s, 4 H), 7.42-7.47 (m, 2 H), 8.00-8.03 (m, 2 H), 8.60 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.0, 14.1, 23.4, 23.6, 28.7, 29.4, 30.7, 33.1, 34.2, 59.9, 122.9, 124.9, 128.2, 130.1, 130.8, 131.6, 132.8, 136.0, 136.4, 137.1; HRMS (EI) calcd for $C_{40}H_{52}O_2$: 564.3967. Found: 564.3958.

3e: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.03 (t, J = 7.2 Hz, 6 H), 1.09 (t, J = 7.2 Hz, 6 H), 1.50-1.78 (m, 16 H), 2.66-2.72 (m, 4 H), 3.33-3.37 (m, 4 H), 4.11 (s, 4 H), 5.16 (s, 4 H), 7.41-7.44 (m, 2 H), 7.99-8.02 (m, 2 H), 8.59 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.0, 14.1, 23.2, 23.5, 28.7, 29.8, 30.6, 32.7, 33.1, 73.8,

122.9, 124.9, 128.2, 130.1, 130.1, 130.8, 131.6, 133.1, 135.5, 135.8; HRMS (EI) calcd for $C_{40}H_{50}O$: 546.3862. Found: 546.3860.

Preparation of 4,9-Di-*tert*-butyl-1,3,5,6,7,8-hexahydronaphtho[2,3-*c*]furan (3f) from 1f.

$LiAlH_4$ (114 mg, 3.0 mmol) was mixed with $AlCl_3$ (1.20 g, 9.0 mmol) in anhydrous Et_2O (10 mL) at 0 °C for 0.5 h. Diester **1f** (360 mg, 1.0 mmol) was added to the mixture. After refluxing for 2 days, hydrolysis with water and 2 N H_2SO_4 was performed carefully at 0 °C. The mixture was extracted with AcOEt. The extract was washed with saturated aqueous $NaHCO_3$ and brine then dried over Na_2SO_4. Column chromatography on silica gel (AcOEt: hexane = 1: 10 as eluent), 212 mg of title compound was obtained as white crystals in 74% isolated yield (85% NMR yield).

3f: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.45 (s, 18 H), 1.58-1.63 (m, 4 H), 2.80-2.84 (m, 4 H), 5.19 (s, 4 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 20.0, 27.6, 32.6, 37.0, 73.4, 134.6, 139.3, 141.2; HRMS (EI) calcd for $C_{20}H_{30}O$: 286.2297. Found: 286.2274.

A Representative Procedure for the Swern Oxidation:

Preparation of Benzene-1,2-dialdehyde (4g) from 2g.

To a 20 mL Schlenk tube, oxalyl chloride 0.22 mL (2.5 mmol) was added into 3 mL of dry CH_2Cl_2 under nitrogen. Then 0.35 mL (5 mmol) of DMSO in 1 mL of dry CH_2Cl_2 was added dropwise at -78 °C. After 5 min, to a solution of 1 mmol of diol **2g** in 1 mL of dry CH_2Cl_2 was dropwisely added 0.5 mL of DMSO. The reaction mixture was stirred for 1 h, and then 3 mL of Et_3N was added slowly at -78 °C. Then it was warmed to rt. After 1 h, the reaction mixture was poured into water and extracted with AcOEt. The combined organic layer was dried over Na_2SO_4, filtered, and evaporated to give the crude products. Chromatography on Aluminium Oxide 90 active neutral (hexane: AcOEt = 3:1) gave 95 mg of the title compound as a pale yellow solid in 71% isolated yield.

All spectral data were identical to the reported ones.[9]

Preparation of 3,4-Dipropylbenzene-1,2-dialdehyde (4h) from 2h.

The title compound was prepared in 90% isolated yield as a white solid from **2h** by the same way as described for **4g**.

4h: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.01 (t, J = 7.5 Hz, 6 H), 1.60-1.70 (m, 4 H), 2.71 (t, J = 7.5 Hz, 4 H), 7.74 (s, 2 H), 10.49 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.0, 23.8, 34.6, 132.2, 134.1, 147.3, 192.4; HRMS (EI) calcd for $C_{14}H_{18}O_2$: 218.1307. Found: 218.1307.

Preparation of 9,10-Dihydroanthracene-2,3-dialdehyde (4i) from 2i.

The title compound was prepared in 30% isolated yield as a white solid from **2i** by the same way as described for **4g**.

4i: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 4.07 (s, 4 H), 7.25-7.32 (m, 4 H), 7.88 (s, 2 H), 10.53 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 36.1, 126.8, 127.5, 130.3, 134.5, 134.6, 143.3, 192.1; HRMS calcd for $C_{16}H_{12}O_2$: 236.0837. Found: 236.0837.

Preparation of 4,5,6,7-Tetrapropyl-1,3-dihydroisobenzofuran-1,3-diol (5j) from 2j.

The title compound was prepared in 55% isolated yield as a pale yellow solid from **2j** by the same way as described for **4g**.

5j: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.99-1.07 (m, 12 H), 1.44-1.66 (m, 8 H), 2.47-2.59 (m, 6 H), 2.67-2.77 (m, 2 H), 3.82 (s, 2 H), 6.15 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.8, 14.9, 24.4, 25.0, 31.3 (2C), 99.5, 134.2, 135.9, 141.2; HRMS (EI) calcd for $C_{20}H_{32}O_3$: 320.2351. Found: 320.2351.

Swern Oxidation of 2a.

Swern oxidation of **2a** was carried out as described above. Before poured into water, the reaction mixture was concentrated *in vacuo* and the reaction was checked by NMR study. NMR study clearly indicated no formation of dialdehyde derivatives. Furthermore, the characteristic peak at 98.7 ppm on ^{13}C NMR spectrum suggest the structure of anthra[2,3-*c*]furan-1,3-diol derivative analogized to **5j**. The selected data are listed below. After column separation, it was found that the product was contaminated with Et_3N and undefined compounds.

5a: ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 1.4, 37.9, 98.7, 123.2, 124.9, 126.5, 131.6, 132.9, 136.1, 143.1, 144.6.

Swern Oxidation of 2k.

The reaction of **2a** was carried out in the same way as described above. After column separation, the product was contaminated with Et_3N and undefined products. Its NMR data of reaction mixture indicated the formation of 4,6,7,8,9,11-hexapropyl-1,3,5,10-tetrahydro-anthra[2,3-*c*]furan-1,3-diol (**5k**).

5k: ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.7, 15.0, 15.1, 24.1, 24.5, 25.0, 29.3, 31.3, 32.2, 32.3, 99.6, 132.2, 133.4, 135.1, 135.6, 136.6, 138.9.

Preparation of 8,9,10,11-Tetraethyl-4,6,13,15-tetrabutyl-1,3,5,14-tetrahydro-penta[2,3-*c*]furan-1-ol (6l) from 2l.

The title compound was prepared in 62% isolated yield as a pale green solid from **2l** by the same way as described for **4g**.

6l: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.03 (t, J = 7.2 Hz, 6 H), 1.10 (t, J = 7.2 Hz, 6 H), 1.29 (t, J = 7.5 Hz, 6 H), 1.43 (t, J = 7.5 Hz, 6 H), 1.52-1.71 (m, 12 H), 1.77-1.83 (m, 4 H), 2.67-2.73 (m, 3 H), 2.89-2.93 (m, 5

H), 3.27 (q, *J* = 7.2 Hz, 4 H), 3.37 (t, *J* = 6.9 Hz, 4 H), 4.12 (s, 4 H), 5.02 (d, *J* = 13 Hz, 1H), 5.28 (d, *J* = 13 Hz, 1H) 6.54 (dd, *J* = 12.0 and 1.8 Hz, 1 H), 8.77 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 13.94, 13.97, 14.00, 15.4, 15.9, 22.1, 23.0, 23.2, 23.4, 23.5, 28.7, 29.2, 29.8, 29.9, 30.3, 32.6, 33.1, 33.4, 71.6, 102.1, 119.46, 119.49, 128.8, 128.9, 130.1, 131.6, 132.0, 132.1, 132.6, 134.70, 134.73, 135.20, 135.9, 136.9, 137.1, 138.3; HRMS (EI) calcd for $C_{48}H_{66}O_2$: 674.5063. Found: 674.5076.

A Representative Procedure for Cleavage of Carboxylic Esters with Lithium Iodide:

Preparation of 1,4-Bis(trimethylsilyl)-5,12-dihydronaphthacene-2,3-dicarboxylic Anhydride (7a) from 1a.

1,4-Bis(trimethylsilyl)-2,3-bis(methoxycarbonyl)-5,12-dihydronaphthacene **1a** (490 mg, 1.0 mmol) and LiI (2 g, 15.0 mmol) were added to 30 mL of anhydrous pyridine. Under nitrogen atmosphere, the solution was heated to reflux for 3 h. After cooling to rt, the solvent was removed *in vacuo*. The residue was acidified with aqueous 3 N HCl (pH = 1) and extracted with $CHCl_3$. After removal of the solvent, the residue was dissolved in 3 mL of $CHCl_3$ and it was put into 10 mL of MeOH. The resulting precipitate was collected by filtration, and dried *in vacuo* to afford the title compound 138 mg as a yellow solid in 31 % isolated yield.

7a: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.59 (s, 18 H), 4.33 (s, 4 H), 7.43-7.45 (m, 2 H), 7.74 (s, 2 H), 7.81-7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 2.2, 39.0, 124.7, 125.8, 127.3, 132.6, 134.5, 135.1, 141.2, 152.3, 164.1; HRMS (EI) calcd for $C_{26}H_{28}Si_2$: 444.1577. Found: 444.1572.

Preparation of 1,4-Bis(trimethylsilyl)pentacene-2,3-dicarboxylic Anhydride (8a) from 7a.

DDQ (13.6 mg, 0.06 mmol) in 2 mL of toluene was dropwisely added to **7a** (26.6 mg, 0.06 mmol) in 1 mL of toluene at 100 °C over 3 h. After cooling to rt, the precipitate was removed by filtration, and the filtrate was concentrated *in vacuo*. The residue was dissolved in $CHCl_3$ (30 mL) and filtered to remove the remaining hydroquinone. The solvent was removed in vacuo, the residue was dissolved in 1 mL of $CHCl_3$, and the mixture was put into 10 mL of degassed MeOH. The mixture was stirred for 10 min to produce precipitate of the title compound as red solid, which was collected by filtration (6.6 mg, 25% yield).

8a: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.72 (s, 18 H), 7.51-7.53 (m, 2 H), 8.06-8.08 (m, 2 H), 8.71 (s, 2 H), 9.35 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 2.4, 126.5, 127.2, 128.4, 129.9, 130.4, 132.3, 132.9, 135.1, 150.6, 164.0; HRMS (EI) calcd for $C_{26}H_{26}Si_2$ 442.1420. Found: 442.1421.

Preparation of 1,4,6,13-Tetrabutyl-8,9,10,11-tetraethyl-5,14-dihydropentacene-2,3-dicarboxylic Anhydride (7l) from 1l.

The title compound was prepared in 80% isolated yield as a yellow solid from **1l** by the same way as described for **7a**.

7l: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.06 (t, J = 7.3 Hz, 6 H), 1.11 (t, J = 7.3 Hz, 6 H), 1.30 (t, J = 7.5 Hz, 6 H), 1.43 (t, J = 7.5 Hz, 6 H), 1.59-1.72 (m, 12 H), 1.74-1.86 (m, 4 H), 2.90 (q, J = 7.5 Hz, 4 H), 3.24-3.41 (m, 12 H), 4.25 (s, 4 H), 8.80 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 13.9, 14.0, 15.4, 15.9, 22.0, 23.0, 23.1, 23.5, 27.6, 28.7, 30.3, 32.9, 33.1, 119.7, 126.3, 128.8, 129.1, 129.6, 132.4, 134.8, 137.4, 139.3, 146.7, 163.5; HRMS (ESI) calcd for $C_{48}H_{62}O_3$: 686.4699. Found: 686.4669.

Preparation of 1,4,6,13-Tetrabutyl-8,9,10,11-tetraethylpentacene-2,3-dicarboxylic Anhydride (8l) from 7l.

DDQ (114 mg, 0.5 mmol) in 2 mL of toluene was dropwisely added to **7l** (343 mg, 0.5 mmol) in 1 mL of toluene at 100 °C over 3 h. After cooling to rt, the resulting reaction mixture was purified by a flash chromatography under N_2 (silica gel, $CHCl_3$ as eluent) to afford the title compound as blue solid (205 mg, 60% yield).

8l: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 1.08 (t, J = 7.2 Hz, 6 H), 1.14 (t, J = 7.2 Hz, 6 H), 1.33 (t, J = 7.6 Hz, 6 H), 1.51 (t, J = 7.6 Hz, 6 H), 1.64-1.81 (m, 8 H), 1.85-1.93 (m, 4 H), 2.00-2.07 (m, 4 H), 2.92 (q, J = 7.2 Hz, 4 H), 3.34 (q, J = 7.2 Hz, 4 H), 3.78 (t, J = 7.6 Hz, 4 H), 4.01 (t, J = 7.6 Hz, 4 H), 9.20 (s, 2 H), 9.42 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.0, 14.1, 15.3, 15.7, 22.1, 23.1, 23.4, 23.7, 27.3, 28.8, 33.3, 34.1, 119.0, 120.4, 125.4, 127.7, 128.3, 129.6, 130.3, 134.7, 135.3, 138.4, 146.3, 163.5; HRMS (EI) calcd for $C_{48}H_{60}O_3$: 684.4542. Found: 684.4546.

Preparation of 1,4,6,13-Tetrabutyl-8,9,10,11-tetraethyl-5,14-dihydro-(*N*-*n*-hexyl)pentacene-2,3-dicarboxylic Imide (9lo) from 7l.

In a 50 mL flask fitted with a water separator and a refluxing condenser were placed anhydride **7l** (686 mg, 1.0 mmol), *n*-hexylamine (159 μL, 1.2 mmol) and 15 mL of toluene. The flask was heated to maintain a vigorous reflux for 6 h. After cooling to rt, the mixture was washed with aqueous 3 N HCl, saturated aqueous $NaHCO_3$, brine and dried over Na_2SO_4. After evaporation of the solvent, 738 mg of title compound was obtained as a yellow solid in 96% isolated yield.

9lo: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.86 (t, J = 6.9 Hz, 3 H), 1.06 (t, J = 6.9 Hz, 6 H), 1.11 (t, J = 6.9 Hz, 6 H), 1.30 (t, J = 7.2 Hz, 12 H), 1.41-1.45 (m, 8 H), 1.59-1.74 (m, 12 H), 1.76-1.83 (m, 4 H), 2.90 (q, J = 7.5 Hz, 4 H), 3.28 (q, J = 7.5 Hz, 4 H), 3.34-3.41 (m, 8 H), 3.62 (m, 2 H), 4.20 (s, 4 H), 8.79 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 13.9, 14.0 (2C), 15.4, 15.7, 22.1, 22.5, 23.0, 23.3, 23.5, 26.6, 27.3, 28.6, 28.7, 30.0, 31.4, 33.1 (2C), 37.7, 119.6, 126.8, 128.8, 129.0, 130.6, 132.1, 134.8, 137.2, 137.7, 144.0, 169.4; HRMS (FAB) calcd for $C_{54}H_{75}NO_2$: 769.5798. Found: 769.5794.

Preparation of 1,4,6,13-Tetrabutyl-8,9,10,11-tetraethyl-5,14-dihydro-(*N*-2-ethylhexyl)-pentacene-2,3-dicarboxylic Imide (9lp) from 7l.

The title compound was prepared in 92% isolated yield from **7l** as a yellow solid by the same way as described for **9lo**.

9lp: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.86 (t, J = 6.9 Hz, 3 H), 0.90 (t, J = 7.2 Hz, 3 H), 1.06 (t, J = 7.2 Hz, 6 H), 1.11 (t, J = 7.2 Hz, 6 H), 1.30 (t, J = 7.5 Hz, 12 H), 1.43 (t, J = 7.5 Hz, 8 H), 1.62-1.72 (m, 12 H), 1.74-1.86 (m, 5 H), 2.91 (q, J = 7.2 Hz, 4 H), 3.29 (q, J = 7.5 Hz, 4 H), 3.36-3.41 (m, 8 H), 3.53 (d, J = 7.2 Hz, 2 H), 4.20 (s, 4 H), 8.79 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 10.6, 13.9, 14.0, 14.1, 15.4, 15.7, 22.1, 23.0, 23.1, 23.2, 23.5, 24.0, 27.3, 28.5, 28.7, 30.0, 30.6, 33.1, 33.1, 38.3, 41.6, 119.6, 126.7, 128.8, 129.0, 130.6, 132.1, 134.7, 137.2, 137.2, 144.0, 169.6; HRMS (EI) calcd for $C_{56}H_{79}O_2N$: 797.6111. Found: 797.6093.

Preparation of 1,4,6,13-Tetrabutyl-8,9,10,11-tetraethyl-(*N*-*n*-hexyl)pentacene-2,3-dicarboxylic Imide (10lo) from 9lo.

The title compound was prepared in 76% yield from **9lo** as blue solid by the same way as described for **8l**.

10lo: ^{1}H NMR ($CDCl_3$, 323 K, Me_4Si) δ: 0.90 (t, J = 6.9 Hz, 3 H), 1.08 (t, J = 7.2 Hz, 6 H), 1.13 (t, J = 7.2 Hz, 6 H), 1.33 (t, J = 7.2 Hz, 12 H), 1.48-1.53 (m, 6 H), 1.62-1.79 (m, 10 H), 1.82-1.92 (m, 4 H), 1.97-2.07 (m, 4 H), 2.92 (q, J = 7.5 Hz, 4 H), 3.33 (q, J = 7.5 Hz, 4 H), 3.71-3.81 (m, 6 H), 3.96 (m, 4 H), 9.16 (s, 2 H), 9.29 (s, 2 H); ^{13}C NMR ($CDCl_3$, 323 K, Me_4Si) δ: 14.0, 14.1 (2C), 15.3, 15.8, 22.1, 22.6, 23.1, 23.5, 23.7, 26.8, 26.8, 28.5, 28.8, 31.5, 33.3, 34.1, 38.1, 120.3, 121.2, 124.5, 127.5, 128.1, 129.6, 129.9, 134.7, 134.7, 138.0, 142.0, 168.4; HRMS (FAB) calcd for $C_{54}H_{73}NO_2$: 767.5641. Found: 767.5635.

Preparation of 1,4,6,13-Tetrabutyl-8,9,10,11-tetraethyl-(*N*-2-ethylhexyl)pentacene-2,3-dicarboxylic Imide (10lp) from 9lp.

The title compound was prepared in 68% isolated yield from **9lp** as blue solid by the same way as described for **8l**.

10lp: ^{1}H NMR ($CDCl_3$, 323 K, Me_4Si) δ: 0.91 (t, J = 6.9 Hz, 3 H), 0.98 (t, J = 7.2 Hz, 3 H), 1.08 (t, J = 7.2 Hz, 6 H), 1.15 (t, J = 7.2 Hz, 6 H), 1.34 (t, J = 7.2 Hz, 6 H), 1.52 (t, J = 7.2 Hz, 6 H), 1.30-1.44 (m, 9 H), 1.65-1.80 (m, 8 H), 1.84-1.95 (m, 4 H), 2.00-2.10 (m, 4 H), 2.94 (q, J = 7.5 Hz, 4 H), 3.34 (q, J = 7.5 Hz, 4 H), 3.66 (d, J = 6.9 Hz, 2 H), 3.79-3.84 (m, 4 H), 3.96-4.01 (m, 4 H), 9.17 (s, 2 H), 9.32 (s, 2 H); ^{13}C NMR ($CDCl_3$, 323 K, Me_4Si) δ: 10.7, 14.0, 14.1 (2C), 15.3, 15.7, 22.1, 23.1, 23.2, 23.5, 23.7, 24.4, 26.8, 28.7, 28.8, 30.9, 33.4, 34.1, 38.3, 42.1, 120.3, 121.4, 124.6, 127.7, 128.2, 130.1, 130.1, 134.7, 134.8, 138.1, 142.0, 168.6; HRMS (FAB) calcd for $C_{56}H_{77}NO_2$: 795.5954. Found: 795.5950.

Preparation of 5,7,12,14-Tetrahydropentacene-2,3-dicarboxylic Acid (11m) from 1m.

The title compound was prepared in 96% yield from diester **1m** as a gray white solid by the same way as described for **7a**.

11m: ^{1}H NMR (DMSO-d_6, Me_4Si) δ: 3.88 (s, 4 H), 3.96 (s, 4 H), 7.16-7.18 (m, 2 H), 7.26 (s, 2 H), 7.30-7.32 (m, 2 H), 7.62 (s, 2 H), 12.96 (brs, 2 H); ^{13}C NMR (DMSO-d_6, Me_4Si) δ: 34.6, 35.0, 125.9 126.1, 127.2, 127.3, 130.7, 133.1, 134.4, 136.7, 139.8, 168.8; HRMS (FAB) calcd for $C_{24}H_{18}O_4Na$ ($M+Na^+$): 393.1103. Found: 393.1099.

Preparation of 5,7,12,14-Tetrahydropentacene-2,3-dicarboxylic Anhydride (7m) from 11m.

5,7,12,14-Tetrahydropentacene-2,3-dicarboxylic acid **11m** (370 mg, 1.0 mmol) in 5 mL Ac_2O was refluxed for 2 h. After evaporation of the solvent, 345 mg of title compound was obtained as a white solid in 98% isolated yield.

7m: ^{1}H NMR (DMSO-d_6, Me_4Si) δ: 3.87 (s, 4 H), 3.94 (s, 4 H), 7.14-7.17 (m, 2 H), 7.26 (s, 2 H), 7.29-7.32 (m, 2 H), 8.11 (s, 2 H); ^{13}C NMR (DMSO-d_6, Me_4Si) δ: 34.5, 35.0, 125.9, 126.2, 127.2, 131.6, 132.8, 133.5, 134.3, 136.8, 139.0, 168.0; HRMS (ESI) calcd for $C_{24}H_{16}O_3$: 352.1099. Found: 352.1099.

Preparation of *N*-2-Ethylhexyl-5,7,12,14-tetrahydropentacene-2,3-dicarboxylic Imide (9mp) from 7m.

The title compound was prepared in 91% isolated yield from **7m** by the same way as described for **9lo**.

9mp: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.87 (t, J = 6.9 Hz, 3 H), 0.90 (t, J = 7.2 Hz, 3 H), 1.26-1.36 (m, 8 H), 1.78-1.86 (m, 1 H), 3.55 (d, J = 7.2 Hz, 2 H), 3.93 (s, 4 H), 4.03 (s, 4 H), 7.17-7.21 (m, 2 H), 7.25 (s, 2 H), 7.27-7.30 (m, 2 H), 7.73 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 10.4, 14.0, 22.9, 23.8, 28.4, 30.4, 35.7, 36.4, 38.2, 41.8, 122.1, 126.1, 126.2, 127.3, 130.2, 132.6, 135.1, 136.5, 143.8, 168.8; HRMS (EI) calcd for $C_{32}H_{33}O_2N$: 463.2511. Found: 463.2505.

Preparation of *N*-*n*-Octyl-5,7,12,14-tetrahydropentacene-2,3-dicarboxylic Imide (9mq) from 7m.

The title compound was prepared in 90% isolated yield from **7m** by the same way as described for **9lo**.

9mq: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.86 (t, J = 6.9 Hz, 3 H), 1.25-1.31 (m, 10 H), 1.63-1.68 (m, 2 H), 3.65 (t, J = 7.2 Hz, 2 H), 3.94 (s, 4 H), 4.04 (s, 4 H), 7.17-7.22 (m, 2 H), 7.26 (s, 2 H), 7.28-7.31 (m, 2 H), 7.73 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.1, 22.6, 26.9, 28.6, 29.1 (2C), 31.7, 35.8, 36.5, 38.1, 122.2, 126.1, 126.3, 127.4, 130.4, 132.7, 135.3, 136.6, 143.9, 168.7; HRMS (EI) calcd for $C_{32}H_{33}O_2N$: 463.2511. Found: 463.2512.

Preparation of *N*-*n*-Octadecyl-5,7,12,14-tetrahydropentacene-2,3-dicarboxylic Imide (9mr) from

7m.

The title compound was prepared in 94% isolated yield from **7m** by the same way as described for **9lo**.

9mr: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.88 (t, J = 6.9 Hz, 3 H), 1.23-1.31 (m, 30 H), 1.60-1.67 (m, 2 H), 3.64 (t, J = 7.2 Hz, 2 H), 3.92 (s, 4 H), 4.02 (s, 4 H), 7.17-7.21 (m, 2 H), 7.24 (s, 2 H), 7.27-7.30 (m, 2 H), 7.71 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 14.1, 22.7, 26.9, 28.6, 29.2, 29.3, 29.5, 29.6, 29.6, 29.7 (7C), 31.9, 35.8, 36.5, 38.0, 122.1, 126.1, 126.3, 127.4, 130.4, 132.7, 135.2, 136.5, 143.8, 168.7; HRMS (EI) calcd for $C_{42}H_{53}O_2N$: 603.4076. Found: 603.4088.

Preparation of *N*-2-Ethylhexylpentacene-2,3-dicarboxylic Imide (10mp) from 9mp.

The title compound was prepared in 91% isolated yield from **10mp** as a blue solid by the same way as described for **8a**. Due to its low solubility, NMR measurements were failed.

10mp: HRMS (EI) calcd for $C_{32}H_{29}NO_2$: 459.2198. Found: 459.2198.

Preparation of *N*-*n*-Octylpentacene-2,3-dicarboxylic Imide (10mq) from 9mq.

The title compound was prepared in 90% isolated yield from **9mq** as a blue solid by the same way as described for **8a**. Due to its low solubility, NMR measurements were failed.

10mq: HRMS (EI) calcd for $C_{32}H_{29}NO_2$: 459.2198. Found: 459.2199.

Preparation of *N*-*n*-Octadecylpentacene-2,3-dicarboxylic Imide (10mr) from 9mr.

The title compound was prepared in 90% isolated yield from **9mr** as a blue solid by the same way as described for **8a**.

10mr: HRMS (EI) calcd for $C_{42}H_{49}NO_2$: 599.3763. Found: 599.3770.

Preparation of 1,4-Bis(trimethylsilyl)-5,7,12,14-tetrahydropentacene-2,3-dicarboxylic Anhydride (7n) from 1n.

The title compound was prepared in 79% yield from **1n** by the same way as described for **7a**.

7n: ^{1}H NMR ($CDCl_3$, Me_4Si) δ: 0.57 (s, 18 H), 3.94 (s, 4 H), 4.15 (s, 4 H), 7.17-7.21 (m, 2 H), 7.25 (s, 2 H), 7.27-7.30 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ: 2.1, 35.9, 38.6, 125.6, 126.2, 127.3, 134.0, 134.9, 135.6, 136.5, 141.2, 152.5, 164.2; HRMS (FAB) calcd for $C_{30}H_{32}O_3Si_2Na$ ($M+Na^+$): 519.1788. Found: 519.1788.

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