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Homologation Method for Preparation of Substituted Pentacenes and Naphthacenes

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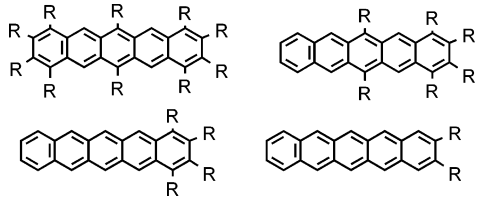

Multi-substituted pentacenes, such as 1,2,3,4,6,8,9,10,11,13-decasubstituted pentacenes (Type I), 1,2,3,4,6,-13-hexasubstituted pentacenes (Type II), 1,2,3,4-tetrasubstituted pentacenes (Type III), and 2,3-disubstituted pentacenes (Type IV), 1,2,3,4,6,11-hexasubstituted naphthacenes (Type V), 1,2,3,4-tetrasubstituted naphthacenes (Type VI), and 2,3-disubstituted naphthacenes (Type VII), were prepared by a homologation method. The homologation method involved the conversion of phthalic acid ester derivatives to two ring extended phthalic acid ester derivatives via diynes and metallacyclopentadienes using transition metals, such as Zr and Rh. For the formation of pentacenes of Type III and Type IV and naphthacenes of Type VII, trimethylsilyl-substituted diynes were used for zirconocene-mediated cyclization. Elimination of the trimethylsilyl groups after the cyclization afforded nonsubstituted position on pentacenes or naphthacenes. Structures of 1,4,6,8,9,10,11,13-octaethyl-2,3-bis(methoxycarbonyl)pentacene (**9a**) and 8,9,10,11-tetraethyl-2,3-bis(methoxycarbonyl)-1,4,6,13-tetrapropylpentacene (**9b**) were determined by X-ray analysis. The structure of **9a** had the herringbone packing system in the crystal like nonsubstituted pentacene. However, **9b**, whose substituents at 1,4,6,13-positions were changed from Et to Pr at 1,4,6,13-positions of **9a**, had the face parallel plane system in the crystal.

Introduction

Acenes, such as pentacene, have attracted much attention as organic materials with high mobility.[1] However, it has a critical limitation in solubility in organic solvents. Introduction of substituents into pentacene is attractive since its property and solubility can be controlled by the substituents. The first substituted pentacene, 6,13-diphenylpentacene, was reported by Allen et al. in 1942.[2] This compound was prepared by the reaction of PhMgBr and pentacenequinone. In 1949, Clar reported 6-methylpentacene.[3a] In 1969, Maulding et al. reported the formation of 6,13-bis(alkynyl)pentacene and 5,7,12,14-tetrakis(alkynyl)pentacene derivatives.[4] These compounds were prepared from pentacenequinone derivatives and alkynylmetal compounds. After these reports, development of a preparation

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¶ Sony Corporation.

(1) (a) Gundlach, D. J.; Lin, Y.-Y.; Jackson, T. N.; Nelson, D. F.; Nelson, S. F.; Schlom, D. G. *IEEE Electron Device Lett.* **1977**, *18*, 87. (b) Lin, Y.-Y.; Gundlach, D. J.; Nelson, D. F.; Jackson, T. N. *IEEE Electron Device Lett.* **1977**, *18*, 606. (c) Lin, Y.-Y.; Gundlach, D. J.; Nelson, S. F.; Jackson, T. N. *IEEE Trans. Electron Devices* **1977**, *44*, 1325. (d) Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854.

(2) Allen, C. F. H.; Bell, A. *J. Am. Chem. Soc.* **1942**, *64*, 1253.

(3) (a) Clar, E. *Chem. Ber.* **1949**, *82*, 495. (b) Clar, E.; Wright, J. W. *Nature* **1949**, *163*, 921.

(4) Maulding, D. R.; Roberts, B. G. *J. Org. Chem.* **1969**, *34*, 1734.

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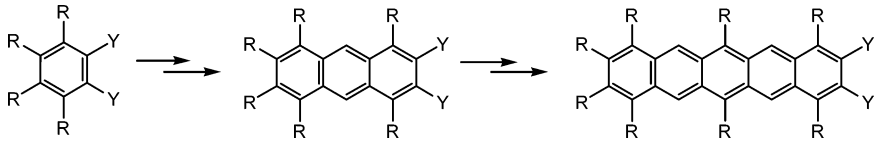
CHART 1. Homologation Method for the Formation of Acenes



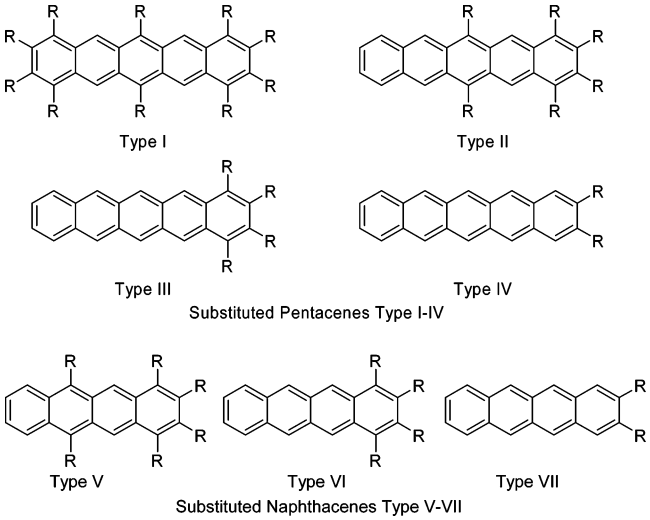
method and characterization of the substituted pentacenes have not been clearly reported in the literature for more than 30 years, although some attempt has been reported.[5]

As mentioned above, in 1997, it was reported that pentacene showed the highest mobility among organic thin film transistor devices, and that it was comparable to the mobility of amorphous silicon.[1] Therefore, we believed that the substituted pentacenes became very important. However, unfortunately, there have been no systematic preparation methods of substituted pentacene derivatives, although, historically, some compounds have been known.[2−4] This situation prompted us to develop a systematic method for the formation of substituted pentacene derivatives. In 2000, we preliminarily reported a novel homologation method for the formation of multi-substituted pentacene derivatives,[6] which was the first report of the systematic preparation method of the substituted pentacenes since 1997. After our reports, several papers on the preparation of substituted pentacenes appeared in the literature.[7−11]

Among substituted pentacene derivatives, alkyl-substituted pentacenes are quite rare. 6-Methylpentacene, as Clar reported, existed as 6-methylene-6,13-dihydropentacene at room temperature.[3b] Theoretical calculation of the energy indicated that 6-methylene-6,13-dihydropentacene is more stable than 6-methylpentacene.[12] This is one reason for the limited number of alkyl-substituted pentacene derivatives. Even after our communication, alkyl-substituted pentacenes are quite limited. Only a few examples, such as 2,3,9,10-tetramethylpentacene derivatives, have been reported.[8] Fully characterized higher alkyl groups, such as Et- or Pr-substituted pentacene derivatives, have not been reported in the literature.

In contrast, our substituted pentacenes reported in a communication could have eight alkyl groups as stable pentacenes. Such stability can be explained by the existence of electron-withdrawing groups, such as methoxycarbonyl groups. It is

CHART 2. Substituted Pentacenes and Naphthacenes



supported by a theoretical study of [1,5]-sigmatropic hydrogen rearrangement in substituted 1,3-pentadiene systems, in which the transition state is destabilized by the introduction of an electron-withdrawing group in the π-system.[13] The tautomerization between 6-methylpentacene and 6-methylene-6,13-dihydropentacene can also be categorized as a [1,5]-sigmatropic hydrogen rearrangement, and the stability of the pentacene form in our reported pentacene can be attributed to the two ester groups at the 2,3-positions.

The concept of our homologation method involves the ring extension of the functionalized aromatic compounds using the reactivity of the functional groups as shown below.In this paper, we would like to report the details of the homologation method to control the position of the substituents of the substituted pentacenes (Types I−IV) and naphthacenes (Types V−VII).

Results and Discussion

Preparation of Type I and Type II Pentacenes by Homologation. We have reported a convenient preparative method of 3,4,5,6-tetrasubstituted phthalate derivative **1** by zirconium-mediated benzene formation.[14] Starting from 3,4,5,6-tetrasubstituted phthalate **1**, reduction of the two ester groups, bromination of the resulting diol, alkynylation of dibromide, and cyclization of diyne with dimethyl acetylenedicarboxylate (DMAD) afforded dihydroanthracene derivatives **4**, as shown in Scheme 1. Thus formed tricyclic compounds **4** are also 3,4,5,6-tetrasubstituted phthalate derivatives, which are the same as **1**. The tricyclic skeleton of **5** can be again extended to pentacyclic compounds **8** by the same combination of the procedures as for **1**. Thus Type I pentacenes were prepared.

(5) Hart, H.; Bashir-Hashemi, A.; Luo, J.; Meador, M. A. *Tetrahedron* **1986**, *42*, 1641.

(6) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876.

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(8) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. *Adv. Mater*. **2003**, *15*, 1090.

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(11) For 6- or 6,13-aryl-substituted pentacenes, see: (a) Vets, N.; Smet, M.; Dehaen, W. *Synlett* **2005**, 217. Very recently multi-phenyl-substituted pentacenes were reported. See: (b) Miao, Q.; Chi, X.; Xiao, S.; Zeis, R.; Lefenfeld, M.; Siegrist, T.; Steigerwald, M. L.; Nucholls, C. *J. Am. Chem. Soc.* **2006**, *128*, 1340.

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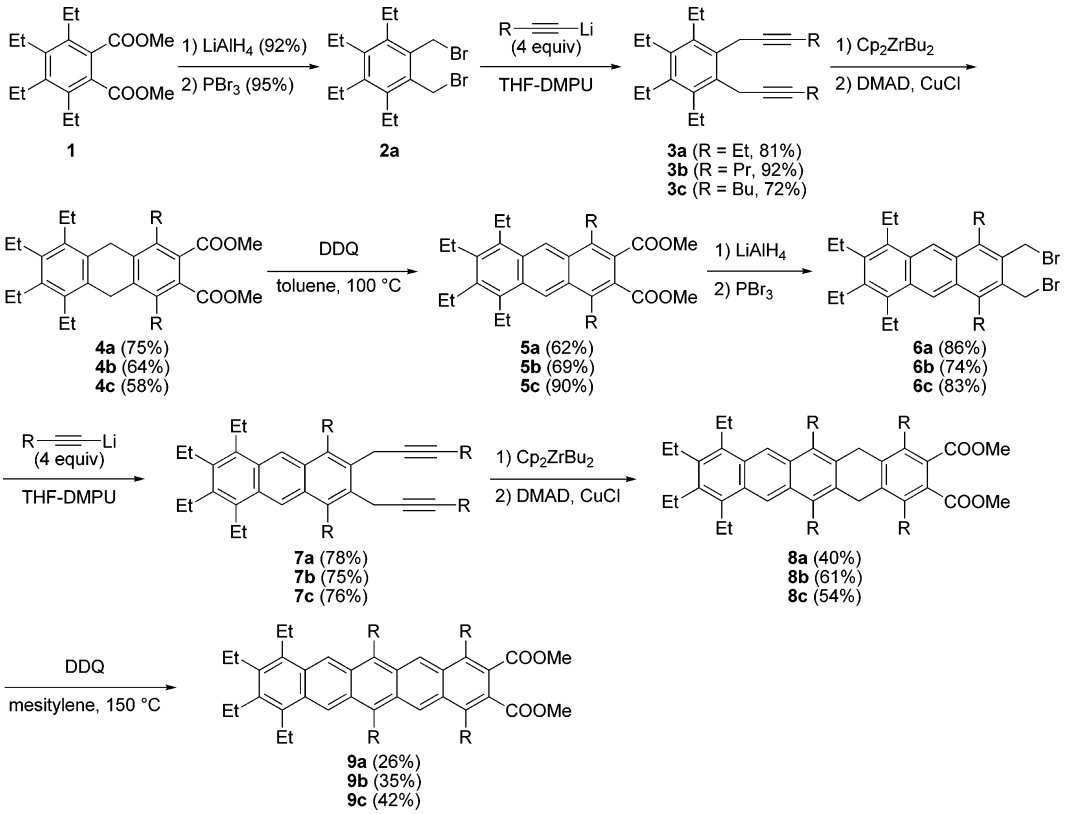
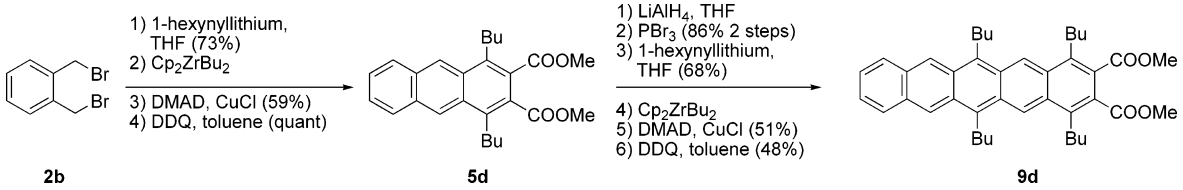
(13) Saettel, N. J.; Wiest, O. *J. Org. Chem.* **2000**, *65*, 2331.

(14) (a) Takahashi, T.; Kotora, M.; Xi, Z. *J. Chem. Soc., Chem. Commun.* **1995**, 361. (b) Takahashi, T.; Xi, Z.; Yamazaki, A.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1998**, *120*, 1672. (c) Takahashi, T.; Tsai, F.-Y.; Li, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **1999**, *121*, 11093.

SCHEME 1



SCHEME 2



When **8a**−**c** were treated with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) at 100−150 °C, some amounts of DDQ adducts of the desired pentacene derivatives **9a**−**c** were formed as byproducts[14] along with the desired pentacenes **9a**−**c** and some unidentified species. The unidentified species could not be separated by column chromatography in some cases. Fortunately, these byproducts and the unidentified species were soluble in methanol, but the products **9a**−**c** were not soluble in methanol. Therefore, addition of methanol to the reaction mixture of **8a**−**c** with DDQ afforded blue precipitates of **9a**−**c**. In the sequence of the pentacene synthesis of Type I, the aromatization of the corresponding 5,7,12,14-tetrahydropentacene with 2 equiv of DDQ was attempted. The amount of the byproducts, however, increased and resulted in failure for isolation of the desired pentacene. Then, the stepwise procedure of DDQ aromatization was chosen in the synthesis.

The alkyl-substituted pentacenes **9a**−**c** prepared here were stable under nitrogen[15] and did not show any conversion to its tautomer, 6-alkylidene-6,13-dihydropentacene, at room temperature as described above. Structures of **9a**,**b** were determined by X-ray analysis (vide infra).

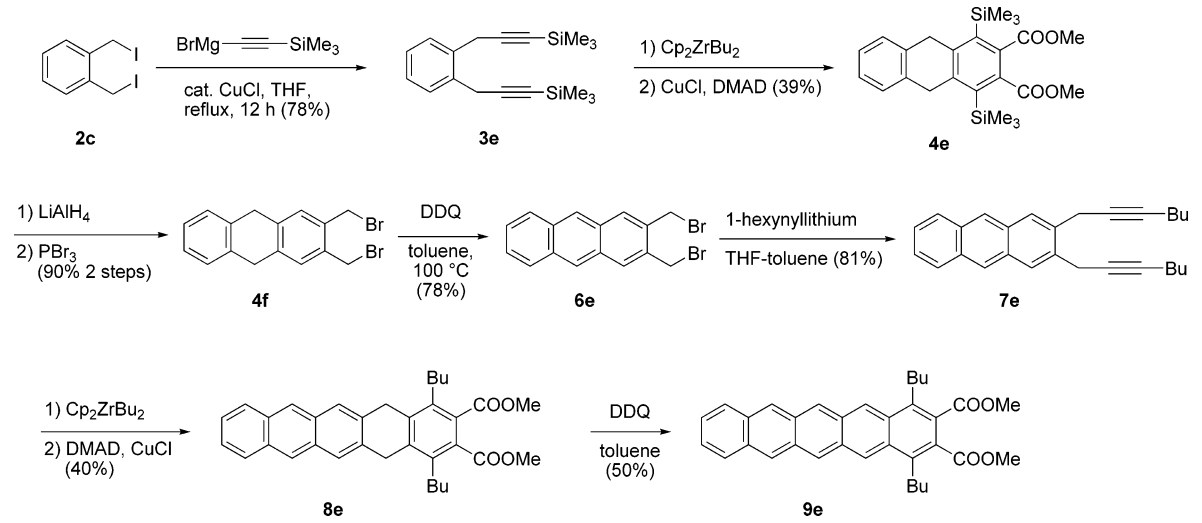
Type II pentacene derivatives could be prepared using dibromo-*o*-xylene which is commercially available as the starting material in a similar way to Type I pentacene derivatives, as shown in Scheme 2. The product **9d** was obtained as a blue solid.

Preparation of Type III and Type IV Pentacenes by Introduction and Elimination of the Trimethylsilyl Group. To obtain Types III and IV pentacenes, it was necessary to consider the solubility of the intermediates. Zirconium-mediated cyclization usually requires the existence of substituents on diynes. Therefore, silylated diynes were used, and after cyclization, the silyl groups were removed.

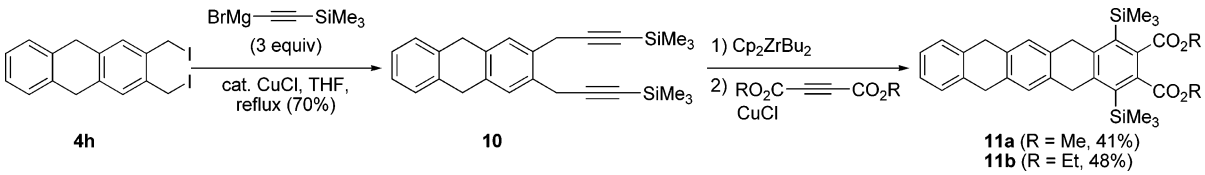
Reaction of dibromo-*o*-xylene (**2b**) with trimethylsilylethynyllithium or magnesium halide did not lead to the clean formation of the desired diyne **3e**. Therefore, **2b** was converted to diiodo-*o*-xylene **2c**. Diiodo-*o*-xylene (**2c**) cleanly reacted with trimethylsilylethynylmagnesium bromide in the presence of CuCl to give the desired diyne **3e**. The diyne **3e** was treated with Cp_2ZrBu_2 (Negishi reagent) followed by the reaction with DMAD in the presence of CuCl to afford dihydroanthracene derivative **4e**. The structure of **4e** was verified by X-ray analysis. Desilylation of **4e** with Bu_4NF in THF gave a mixture of

(15) In general, naphthacenes and pentacenes should be treated in the absence of oxygen because they react with molecular oxygen in the presence of light to afford the corresponding endoperoxides. We previously reported such oxidation reactions with substituted pentacenes. See: Zhou, X.; Kitamura, M.; Shen, B.; Nakajima, K.; Takahashi, T. *Chem. Lett.* **2004**, *33*, 410.

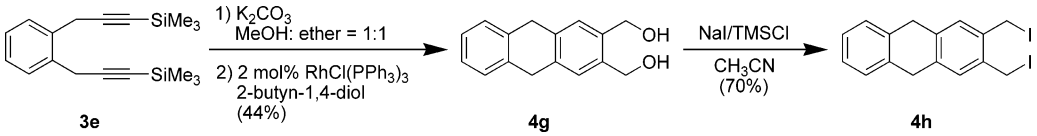
SCHEME 3



SCHEME 4



SCHEME 5



desilylated dihydroanthracene and its aromatized one. Fortunately, reduction of **4e** with $LiAlH_4$, hydrolysis, and successive bromination with PBr_3 gave cleanly 2,3-bis(bromomethyl)-9,-10-dihydroanthracene (**4f**) as a separable major product. The NMR analyses of these steps showed that the protodesilylation occurred at the bromination step, probably due to HBr generated from the reaction of the alcohol with PBr_3 or contaminated in it. Aromatization of **4f** with DDQ gave **6e**. Further reactions from **6e** for preparation of **9e** were the same as described for the formation of **9d**. Alkynylation of **6e** with 1-hexynyllithium afforded **7e**. Aromatization of dihydroanthracene **4e** gave the corresponding anthracene **5e**. Cyclization of **7e** using Cp_2ZrBu_2 and DMAD in the presence of CuCl produced **8e**, which was aromatized with DDQ to give **9e**.

To prepare Type IV pentacenes, **4f** was converted to diiodide **4h**. Aromatization of **4h** caused a problem for the second desilylation step at the dihydropentacene stage. Therefore, the alkynylation of **4h** was carried out without aromatization of **4h**, as shown in Scheme 4. The zirconium-mediated cycloadditions of diyne **10** with dimethyl or diethyl acetylenedicarboxylates afforded the corresponding tetrahydropentacenes **11a**,**b**.

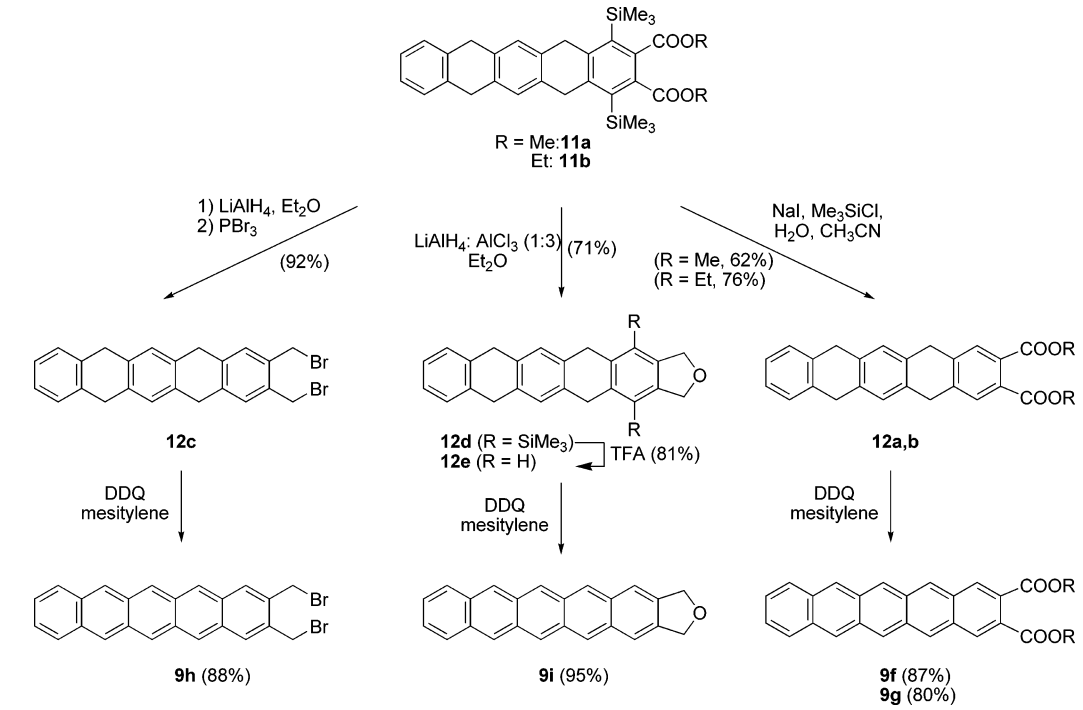
It is well-known that cyclization of diyne derivatives can be done with other transition metal catalysts. In Scheme 5, Rh-catalyzed transformation of **3e** to **4h** is demonstrated.

The product **11a**,**b** could be converted into various pentacene derivatives of Type IV, as shown in Scheme 6. The direct desilylation of **11a**,**b** was successful with the combination of Me_3SiCl, NaI, and H_2O in CH_3CN.[16] 2,3-Bis(methoxy- or ethoxycarbonyl)tetrahydropentacenes **12a**,**b** were obtained. Treatment of **11a** with TBAF instead of the combination of Me_3SiCl, NaI, and H_2O in CH_3CN resulted in the formation of a 1:1 mixture of **12a** and its dihydropentacene derivative, which was partially the aromatized product of **12a**. Fortunately, in contrast to the synthesis of Types I−III pentacenes shown in Schemes 1−3, the double aromatization of the tetrahydropentacenes **12** worked well, and the desired pentacenes were able to be isolated in good yields. Aromatization of **12a**,**b** with 2 equiv of DDQ afforded the desired pentacene diesters **9f**,**g**, as shown in Scheme 6. When **11a** was treated with a 1:3 mixture of $LiAlH_4$ and $AlCl_3$, benzofuran derivative **12d** was obtained. After desilylation of **12d** with trifluoroacetic acid, thus formed tetrahydropentacene **12e** was aromatized in the similar way to afford the pentacene **9i** having a cyclic ether moiety. Reduction of **11a** with LAH and bromination with PBr_3 afforded bis(bromomethyl)tetrahydropentacene **12c**, which was aromatized with DDQ in a manner similar manner to produce bis(bromomethyl)pentacene in high yield.

Preparation of Hexa- (Type V), Tetra- (Type VI), and Disubstituted Naphthacenes (Type VII). As for substituted naphthacene derivatives, many examples have been reported in the literature.[6,17,18] 5,6,11,12-Tetraphenylnaphthacene is com-

(16) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.

SCHEME 6



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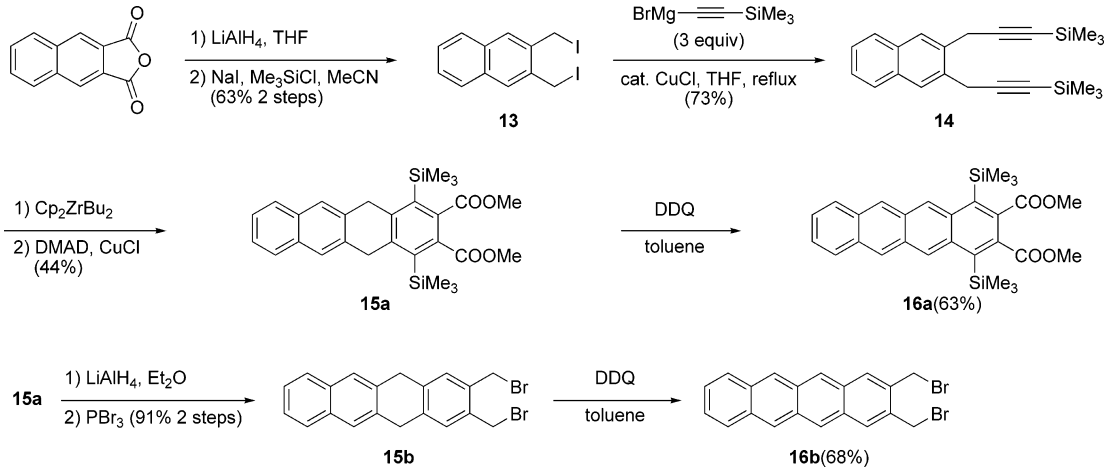

mercially available, well-known as rubrene, and very attractive as an organic material.[19−21] Its derivatives have been prepared.[18]

In our homologation method, we have already reported the formation of hexasubstituted naphthacene derivatives (Type V).[6] Naphthacenes of Types VI and VII were prepared from 2,3-naphthalenedicarboxylic anhydride, which was used as the commercially available starting material. Reduction, iodination, and alkynylation of 2,3-naphthalenedicarboxylic anhydride afforded **14** via **13**, as shown in Scheme 7. Cyclization of **14** with Cp_2ZrBu_2 gave **15a**, which could be aromatized with DDQ to give naphthacene **16a**. Reduction and bromination of **15a** afforded **15b**. Aromatization of **15b** gave **16b**.

Effect of the Substituents on the Packing System of 1,2,3,4,6,8,9,10,11,13-Decasubstituted Pentacenes. Structures of **9a** and **9b** were determined by X-ray analysis. Those structures are shown in Figure 1. It is well-known that nonsubstituted pentacene has the herringbone structure[22] which has an important role for its physical properties, such as FET mobility. According to the theoretical study, the parallel stacking of pentacenes can have better properties.[23] However, it is not

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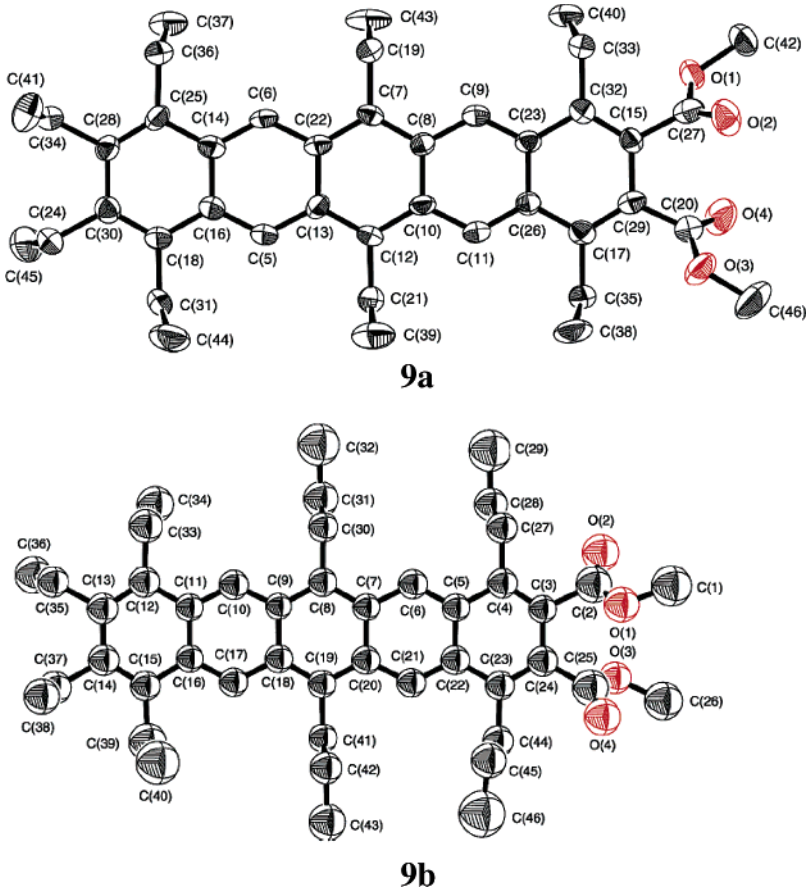

FIGURE 1. Perspective views of pentacenes **9a** and **9b**.

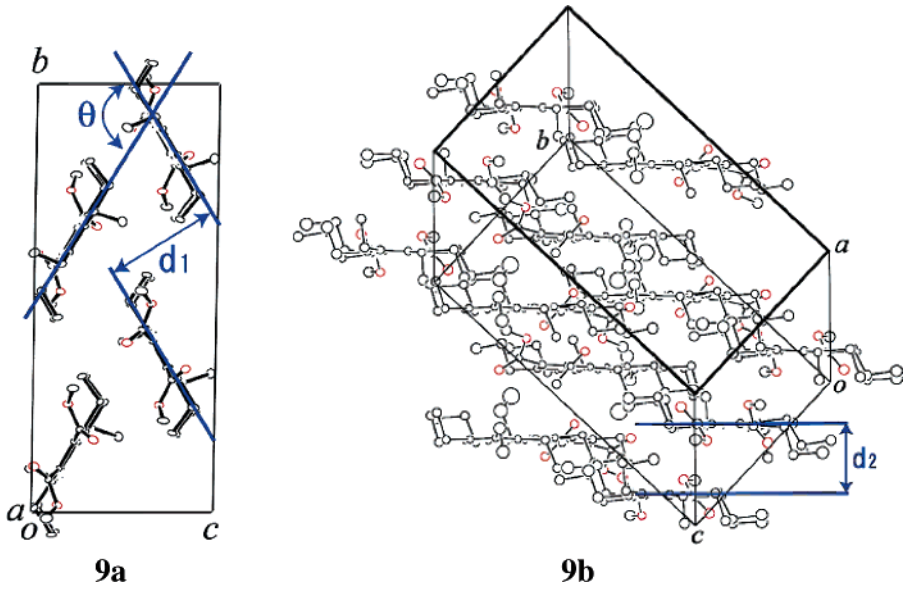

FIGURE 2. Packing systems of **9a** and **9b**.

clear which factors control the packing system of substituted pentacenes. Most of the substituted pentacenes have the herringbone structures. Only alkynyl-substituted or phenyl-substituted pentacenes have the parallel stacking system.[7,11b] There has been no information how to control the stacking system.

As shown in Figure 2, **9a** has clearly the same herringbone system as that of nonsubstituted pentacene and most of substituted pentacenes. Surprisingly, when only the substituent was changed from Et to Pr at 1,4,6,13-positions from **9a** to **9b**, the molecular order could be changed from the herringbone to

(23) Deng, W.-Q.; Goddard, W. A., III. *J. Phys. Chem. B* **2004**, *108*, 8614.

face parallel stacking, as shown in Figure 2, although the neighbor long axes of pentacene **9b** are not parallel in the crystal.

In the herringbone packing system of **9a**, the distance between the two least-squares planes of neighboring pentacenes (d_1) is 5.4 Å, and the dihedral angle (Θ) is 115.6°. The distance is considerably longer than those for nonsubstituted pentacene (2.1 and 2.6 Å).[23] It seems that the ethyl groups cause the strong intermolecular steric hindrance in the packing system. The dihedral angle of the two least-squares planes of neighboring nonsubstituted pentacene is 128.0°. On the other hand, **9b** has the parallel stacking system (d_2 = 3.6 Å).

Conclusion

In conclusion, we developed a homologation method for the preparation of substituted pentacene and naphthacene derivatives starting from substituted phthalic acid ester compounds and naphthalenedicarboxylic anhydride, respectively. Introduction and elimination of trimethylsilyl groups could control the position of substituents on pentacenes and naphthacenes. Multi-substituted alkylpentacenes were obtained as stable compounds with electron-withdrawing groups, such as methoxycarbonyl groups under N_2. Structures of the alkyl-substituted pentacenes were determined. Slight change of the alkyl groups from the Et group to the Pr group of some substituents caused the change of packing system from herringbone to parallel in the crystal.

Experimental Section

Preparation of 1,2-Bis(iodomethyl)benzene (2c). A mixture of 1,2-bis(bromomethyl)benzene (25.0 g, 95 mmol), NaI (85 g, 0.57 mol), and acetone (500 mL) was refluxed for 12 h. After cooling to room temperature, the solvent was removed in vacuo. To the resulting solid was added water (500 mL), and the mixture was stirred for 30 min. The resulting precipitate was filtered and washed with 10% aqueous $Na_2S_2O_3$ solution, water, and MeOH. The solid was dried in vacuo to afford the title compound as pale-yellow powder (31 g, 91% yield). All spectral data were identical to the reported ones.[24]

Preparation of 1,2-Bis(2-hexynyl)-3,4,5,6-tetraethylbenzene (3b) from 2a. To a solution of 1-pentyne (0.79 mL, 8.0 mmol) in 10 mL of THF was added *n*-BuLi (1.58 M hexane solution, 5.1 mL, 8.0 mmol) at −78 °C, and the mixture was warmed to room temperature. After stirring for 1 h, the solution was re-cooled to −78 °C, and DMPU (0.96 mL, 8.0 mmol) and 1,2-bis(bromomethyl)-3,4,5,6-tetraethylbenzene (**2a**, 752 mg, 2.0 mmol) were added to the mixture. The resulting mixture was warmed to room temperature by removal of the cooling bath and stirred for 3 h. The mixture was quenched with saturated NH_4Cl solution and extracted with $CHCl_3$. The combined organic phase was washed with water, saturated aqueous $NaHCO_3$ solution, and brine. The solution was dried over anhydrous $MgSO_4$. The solvent was evaporated, and the resulting yellow oil was purified by a flash chromatography (silica gel, hexane to hexane:ethyl acetate = 50:1 as eluent) to afford the title compound **3b** as a pale-yellow oil (647 mg, 92% yield).

3b: ^{1}H NMR ($CDCl_3$, δ) 0.93 (t, J = 7 Hz, 6 H), 1.18 (t, J = 8 Hz, 6 H), 1.22 (t, J = 8 Hz, 6 H), 1.48 (tq, J = 7, 7 Hz, 4 H), 2.08 (tt, J = 7, 2 Hz, 4 H), 2.65 (q, J = 8 Hz, 4 H), 2.74 (q, J = 8 Hz, 4 H), 3.61 (t, J = 2 Hz, 4 H); ^{13}C NMR ($CDCl_3$, δ) 13.6, 15.4, 15.7, 19.2, 21.0, 22.3, 22.4, 22.7, 78.4, 80.4, 132.9, 138.3, 138.9. HRMS calcd for $C_{26}H_{38}$: 350.2973. Found: 350.2966.

(24) Inaba, S.; Wehmeyer, R. M.; Forkner, M. W.; Rieke, R. D. *J. Org. Chem.* **1988**, *53*, 339.

Preparation of 1,4-Dipropyl-2,3-bis(methoxycarbonyl)-5,6,7,8-tetraethyl-9,10-dihydroanthracene (4b) from 3b. To a solution of Cp_2ZrCl_2 (436 mg, 1.49 mmol) in 5 mL of THF was added *n*-BuLi (1.58 M hexane solution, 1.9 mL, 3.0 mmol) at −78 °C, and the solution was stirred for 1 h. To the solution was added 1,2-bis(2-hexynyl)-3,4,5,6-tetraethylbenzene (**3b**, 435 mg, 1.24 mmol), and the mixture was warmed to room temperature by removal of the cooling bath. After stirring for 3 h, CuCl (246 mg, 2.48 mmol) and DMAD (0.46 mL, 3.7 mmol) were added to the mixture, and the mixture was stirred for 3 h at room temperature. The mixture was quenched with aqueous 3 N HCl and extracted with ethyl acetate. The combined organic phase was washed with water, saturated aqueous $NaHCO_3$ solution, and brine. The solution was dried over anhydrous Na_2SO_4. The solvent was evaporated, and the resulting brown viscous oil was purified by a flash chromatography (silica gel, hexane:ethyl acetate = 5:1 as eluent) to afford the title compound **4b** as colorless crystals (412 mg, 67% yield).

4b: ^{1}H NMR ($CDCl_3$, δ) 1.05 (t, J = 7 Hz, 6 H), 1.19 (t, J = 7 Hz, 6 H), 1.24 (t, J = 7 Hz, 6 Hz), 1.64 (tq, J = 8, 8 Hz, 4 H), 2.69 (q, J = 8 Hz, 4 H), 2.73−2.87 (m, 8 H), 3.84 (s, 6 H), 3.92 (s, 4 H); ^{13}C NMR ($CDCl_3$, δ) 14.6, 15.3, 15.9, 22.28, 22.31, 24.4, 29.5, 32.6, 52.2, 130.0, 132.4, 135.2, 136.4, 137.9, 139.3, 169.6. HRMS calcd for $C_{32}H_{44}O_4$: 492.3240. Found: 492.3242.

Preparation of 1,4-Dipropyl-2,3-bis(methoxycarbonyl)-5,6,7,8-tetraethylanthracene (5b) from 4b. 9,10-Dihydroanthracene **4b** (475 mg, 0.96 mmol) and DDQ (240 mg, 1.06 mmol) were dissolved in 5 mL of toluene, and the mixture was heated to 100 °C for 3 h. A colorless precipitate of 2,3-dichloro-5,6-dicyanohydroquinone was observed. After cooling to room temperature, 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 MeOH. The mixture was stirred for 10 min to produce a pale-yellow precipitate of the title compound **5b**, which was collected by filtration (161 mg). The filtrate was concentrated in vacuo and was purified by silica gel column chromatography ($CHCl_3$) to afford the additional product (163 mg). The total isolated yield was 69%.

5b: ^{1}H NMR ($CDCl_3$, δ) 1.22 (t, J = 7 Hz, 6 H), 1.30 (t, J = 7 Hz, 6 H), 1.42 (t, J = 7 Hz, 6 H), 1.78−1.95 (m, 4 H), 2.91 (q, J = 7 Hz, 4 H), 3.18−3.33 (m, 8 H), 3.93 (s, 6 H), 8.86 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 14.7, 15.4, 15.8, 20.0, 23.0, 24.7, 32.5, 52.3, 121.4, 126.5, 128.9, 130.3, 135.1, 137.6, 138.8, 169.8. HRMS calcd for $C_{32}H_{42}O_4$: 490.3083. Found: 490.3087.

Preparation of 1,4-Dipropyl-2,3-bis(bromomethyl)-5,6,7,8-tetraethylanthracene (6b) from 5b. $LiAlH_4$ (46 mg, 1.2 mmol) was added to 5 mL of THF and cooled to 0 °C. To the suspension was added a solution of 2,3-bis(methoxycarbonyl)-1,4-dipropyl-5,6,7,8-tetraethylanthracene (**5b**, 294 mg, 0.60 mmol) in 7 mL of THF dropwise for 15 min. The mixture was warmed to room temperature and stirred for 1 h. After cooling to 0 °C, to the mixture was slowly added aqueous 3 N HCl. It was extracted with $CHCl_3$. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent in vacuo gave the corresponding diol as a pale-yellow solid in almost quantitative yield. The solid was dissolved in 10 mL of 1,2-dichloroethane and treated with phosphorus tribromide (53 μL, 0.56 mmol) and stirred at room temperature for 1 h. The mixture was quenched with water and extracted with $CHCl_3$. The combined organic phase was washed with brine and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was dissolved in 2 mL of $CHCl_3$, and it was put into 20 mL of MeOH. The resulting yellow precipitate was collected by filtration and dried in vacuo to afford the pure title compound **6b** (233 mg, 69% yield).

6b: ^{1}H NMR ($CDCl_3$, δ) 1.23 (t, J = 7 Hz, 6 H), 1.32 (t, J = 7 Hz, 6 H), 1.41 (t, J = 8 Hz, 6 H), 1.72−2.00 (m, 4 H), 2.90 (q, J = 8 Hz, 4 H), 3.18−3.36 (m, 8 H), 5.00 (s, 4 H), 8.77 (s, 2 H); ^{13}C

NMR ($CDCl_3$, δ) 14.9, 15.4, 15.8, 22.0, 23.0, 24.4, 30.0, 31.5, 120.7, 129.1, 129.2, 129.9, 135.0, 138.3, 138.7. HRMS calcd for $C_{30}H_{40}Br_2$: 558.1497. Found: 558.1493.

Preparation of 1,4-Dipropyl-2,3-bis(2-hexynyl)-5,6,7,8-tetraethylanthracene (7b) from 6b. *n*-BuLi (1.56 M hexane solution, 0.90 mL, 1.40 mmol) was added dropwise to a solution of 1-pentyne (0.14 mL, 1.42 mmol) in 5 mL of THF at −78 °C. The mixture was warmed to room temperature and stirred for 1 h. The mixture was cooled to −78 °C, and to the mixture was added 2,3-bis(bromomethyl)-1,4-dipropyl-5,6,7,8-tetraethylanthracene (**6b**, 203 mg, 0.36 mmol). The mixture was warmed to room temperature and heated to 50 °C for 3 h. After cooling to room temperature, the mixture was quenched with aqueous 3 N HCl and extracted with $CHCl_3$. The combined organic phase was washed with water, saturated $NaHCO_3$ solution, and brine and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was dissolved in 1 mL of $CHCl_3$, and it was put into 10 mL of MeOH. The resulting yellow precipitate was collected by filtration and dried in vacuo to afford the pure title compound **7b** (144 mg, 75% yield).

7b: ^{1}H NMR ($CDCl_3$, δ) 0.93 (t, J = 7 Hz, 6 H), 1.20 (t, J = 7 Hz, 6 H), 1.29 (t, J = 7 Hz, 6 H), 1.37−1.55 (m, 10 H), 1.75−1.92 (m, 4 H), 2.05−2.18 (m, 4 H), 2.89 (q, J = 7 Hz, 4 H), 3.19−3.33 (m, 8 H), 3.87 (s, 4 H), 8.73 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 13.5, 14.9, 15.3, 15.9, 20.1, 20.9, 22.0, 22.4, 23.0, 24.1, 31.7, 78.5, 81.0, 119.7, 129.0, 129.2, 131.1, 134.6, 134.8, 137.0. HRMS calcd for $C_{40}H_{54}$: 534.4226. Found: 534.4226.

Preparation of 1,4,6,13-Tetrapropyl-2,3-bis(methoxycarbonyl)-8,9,10,11-tetraethyl-5,14-dihydropentacene (8b) from 7b. Cp_2ZrCl_2 (1.27 g, 4.34 mmol) was dissolved in 40 mL of THF. The solution was cooled to −78 °C. *n*-BuLi (1.58 M hexane solution, 5.5 mL, 8.7 mmol) was added dropwise to the solution and stirred for 1 h. To the mixture was added 1,4-dipropyl-2,3-bis(2-hexynyl)-5,6,7,8-tetraethylanthracene (**7b**, 2.30 g, 4.30 mmol), and it was warmed to room temperature. After stirring for 3 h, CuCl (0.87 g, 8.8 mmol) and DMAD (1.61 mL, 13.1 mmol) were added to the mixture at 0 °C, and it was stirred at room temperature for 12 h. The mixture was quenched with aqueous 3 N HCl and extracted with hexane three times. The combined organic phase was washed with water, saturated $NaHCO_3$ solution, and brine and dried over $MgSO_4$. After removal of the solvent, the residue was purified by silica gel chromatography (hexane:ethyl acetate = 10:1) to afford the title compound **8b** as a colorless powder (1.76 g, 60% yield).

8b: ^{1}H NMR ($CDCl_3$, δ) 1.11 (t, J = 7 Hz, 6 H), 1.22 (t, J = 7 Hz, 6 H), 1.29 (t, J = 7 Hz, 6 H), 1.43 (t, J = 7 Hz, 6 H), 1.61−1.93 (m, 8 H), 2.78−2.97 (m, 8 H), 3.20−3.42 (m, 8 H), 3.85 (s, 6 H), 4.14 (s, 4 H), 8.76 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 14.7, 14.9, 15.3, 15.9, 22.0, 23.0, 24.3, 24.6, 30.4, 31.1, 32.9, 52.2, 119.6, 128.8, 128.9, 130.2, 131.2, 131.7, 134.7, 135.1, 137.1, 139.8, 169.5. HRMS calcd for $C_{46}H_{60}O_4$: 676.4492. Found: 676.4497.

Preparation of 1,4,6,13-Tetrapropyl-2,3-bis(methoxycarbonyl)-8,9,10,11-tetraethylpentacene (9b) from 8b. 1,4,6,13-Tetrapropyl-2,3-bis(methoxycarbonyl)-8,9,10,11-tetraethyl-5,14-dihydropentacene (**8b**, 600 mg, 0.89 mmol) and DDQ (221 mg, 0.97 mmol) were dissolved in 12 mL of toluene. Under nitrogen atmosphere, the solution was heated to reflux for 24 h. After cooling to room temperature, the solvent was removed in vacuo. The residue was put into 120 mL of degassed MeOH. The resulting blue precipitate was collected by filtration under nitrogen. The precipitate was dissolved in 20 mL of $CHCl_3$ and purified by chromatography of silica gel (deactivated with 10 wt % of water). After removal of the solvent, the residue was crystallized from hexane to afford the title compound **9b** as blue fluffy solid (207 mg, 35% yield).

9b: ^{1}H NMR ($CDCl_3$, δ) 1.20 (t, J = 7 Hz, 6 H), 1.28 (t, J = 7 Hz, 6 H), 1.32 (t, J = 8 Hz, 6 H), 1.50 (t, J = 8 Hz, 6 H), 1.87−2.14 (m, 8 H), 2.90 (q, J = 7 Hz, 4 H), 3.15−3.41 (m, 8 H), 3.85−4.05 (m, 4 H), 3.94 (s, 6 H), 9.13 (s, 2 H), 9.19 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 14.9, 15.1, 15.2, 15.8, 22.1, 23.1, 24.6, 25.1, 31.1, 32.7, 52.3, 120.1, 122.8, 126.2, 127.6, 127.9, 128.4, 129.7, 133.9, 134.6, 137.6, 138.2, 169.7. HRMS calcd for $C_{46}H_{58}O_4$: 674.4335. Found: 674.4343.

Preparation of 1,2-Bis(3-trimethylsilyl-2-propynyl)benzene (3e) from 2c. To a solution of trimethylsilylacetylene (13.6 mL, 96 mmol) in 100 mL of THF was added ethylmagnesium bromide (0.96 M THF solution, 100 mL, 96.0 mmol) slowly, and the mixture was heated to 40 °C for 1 h. To the resulting solution were added CuCl (1.19 g, 12 mmol) and 1,2-bis(iodomethyl)benzene (**2c**, 8.59 g, 24 mmol), and the mixture was heated to reflux for 3 h. After cooling to room temperature, the mixture was quenched with aqueous saturated NH_4Cl and extracted with hexane. The combined organic phase was washed with water and brine and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by silica gel chromatography (hexane:ethyl acetate = 50:1) to afford the title compound **3e** (5.59 g, 78% yield) as a colorless oil.

3e: ^{1}H NMR ($CDCl_3$, δ) 0.19 (s, 18 H), 3.65 (s, 4 H), 7.25−7.28 (m, 2 H), 7.45−7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 0.1, 23.9, 87.4, 103.4, 127.2, 128.6, 134.2. Anal. Calcd for $C_{18}H_{26}Si_2$: C, 72.41; H, 8.78. Found: C, 72.32; H, 8.84.

1,4-Bis(trimethylsilyl)-2,3-bis(methoxycarbonyl)-9,10-dihydroanthracene (4e) from 3e. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in 5 mL of THF was added *n*-BuLi (1.56 M hexane solution, 1.60 mL, 2.50 mmol) at −78 °C, and the mixture was stirred for 10 min. The solution was warmed to −40 °C for 30 min and then re-cooled to −78 °C. After 10 min, diyne **3e** (298 mg, 1.0 mmol) was added to the solution, and it was warmed to room temperature by removal of the cooling bath. After stirring for 3 h, CuCl (297 mg, 3.0 mmol) and DMAD (0.48 mL, 3.9 mmol) were added to the mixture, and it was stirred for 6 h at room temperature. The mixture was quenched with 3 N HCl and extracted with ethyl acetate. The combined organic phase was washed with water, saturated aqueous $NaHCO_3$ solution, and brine. The solution was dried over anhydrous Na_2SO_4. The solvent was evaporated, and the resulting brown viscous oil was purified by a flash chromatography (silica gel, hexane:ethyl acetate = 5:1 as eluent) to afford the title compound **4e** as colorless crystals (171 mg, 39% yield).

4e: ^{1}H NMR ($CDCl_3$, δ) 0.46 (s, 18 H), 3.85 (s, 6 H), 4.04 (s, 4 H), 7.23−7.27 (m, 2 H), 7.32−7.35 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 1.7, 38.4, 52.3, 126.2, 126.4, 135.6, 135.9, 137.2, 145.9, 170.5. HRMS calcd for $C_{24}H_{32}O_4Si_2$: 440.1839. Found: 440.1845.

Preparation of 2,3-Bis(bromomethyl)-9,10-dihydroanthracene (4f) from 4e. 1,4-Bis(trimethylsilyl)-9,10-dihydroanthracene-2,3-dicarboxylic acid dimethyl ester (**4e**, 440 mg, 1.0 mmol) was added to $LiAlH_4$ (83.6 mg, 2.2 mmol) in 10 mL of diethyl ether at 0 °C. After stirring for 3 h at room temperature, hydrolysis with water was performed carefully. The mixture was treated with aqueous 2 N H_2SO_4 and extracted with diethyl ether. The extract was washed with brine and dried over Na_2SO_4, and then the solvent was removed. Phosphorus tribromide (0.28 mL, 3.0 mmol) was added dropwise to the residue in 10 mL of $CHCl_3$ at 0 °C. After stirring for 1 h at room temperature, the mixture was treated with water at 0 °C and extracted with $CHCl_3$. The extract was washed with brine and dried over Na_2SO_4. Chromatography on silica gel (hexane:ethyl acetate = 20:1 as eluent) gave 328 mg of the title compound **4f** as pale-yellow crystals in 90% isolated yield.

4f: ^{1}H NMR ($CDCl_3$, δ) 3.93 (s, 4 H), 4.68 (s, 4 H), 7.19−7.31 (m, 6 H); ^{13}C NMR ($CDCl_3$, δ) 30.3, 35.7, 126.3, 127.4, 130.1, 134.3, 135.7, 138.3. HRMS calcd for $C_{16}H_{14}Br_2$ 363.9461. Found: 363.9464.

Preparation of 2,3-Bis(bromomethyl)anthracene (6e) from 4f. DDQ (1.16 g, 5.11 mmol) was added to 2,3-bis(bromomethyl)-9,10-dihydroanthracene (**4f**, 1.7 g, 4.6 mmol) in toluene, and the mixture was stirred at 90 °C for 3 h. After filtration, the filtrate was evaporated to dryness and washed with MeOH, and the pale-yellow powder product **6e** was obtained in 78% yield.

6e: ^{1}H NMR ($CDCl_3$, δ) 4.94 (s, 4 H), 7.50 (dd, J = 6.0, 3.0 Hz, 2 H), 8.00 (dd, J = 6.0, 3.0 Hz, 2 H), 8.04 (s, 2 H), 8.38 (s, 2

H); ^{13}C NMR ($CDCl_3$, δ) 31.6, 126.1, 126.6, 128.3, 131.0, 131.2, 132.5, 133.1. HRMS calcd for $C_{16}H_{12}Br_2$: 361.9305. Found: 361.9318.

Preparation of 2,3-Bis(2-heptynyl)anthracene (7e) from 6e. 2,3-Bis(bromomethyl)anthracene (**6e**, 1.24 g, 3.41 mmol) was added to 17.1 mmol 1-hexynyllithium solution, which was prepared from 1-hexyne and butyllithium in THF/toluene (1/1) solution. The resulting mixture was stirred at 50 °C for 3 h and hydrolyzed with 3 N HCl (aq). The reaction mixture was extracted with ethyl ether, washed with $NaHCO_3$ (aq) and brine and dried over $MgSO_4$. Column chromatography (silica gel, hexane/ethyl ether = 10/1 as eluent) gave 1.01 g of the title compound **7e** as yellow−green powder in 81% isolated yield.

7e: ^{1}H NMR ($CDCl_3$, δ) 0.95 (t, J = 6.6 Hz, 6 H), 1.52 (m, 8 H), 2.29 (t, J = 7.2 Hz, 4 H), 3.76 (s, 4 H), 7.42 (dd, J = 6.0, 3.0 Hz, 2 H), 7.98 (dd, J = 6.0, 3.0 Hz, 2 H), 8.06 (s, 2 H), 8.36 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 13.7, 18.6, 22.0, 23.3, 31.1, 76.8, 83.9, 125.1, 125.5, 126.9, 128.1, 131.0, 131.7, 133.6. HRMS calcd for $C_{28}H_{30}$: 366.2348. Found: 366.2349.

Preparation of 1,4-Dibutyl-2,3-bis(methoxycarbonyl)pentacene (9e) from 8e. DDQ (13.6 mg, 0.06 mmol) in 2 mL of toluene was dropwise added to **8e** (30.5 mg, 0.06 mmol) in 1 mL of toluene at 100 °C over 12 h. Then the mixture was filtered through Celite, and the filtrate was kept at −30 °C overnight to afford the title compound **9e** as violet−blue crystals (15 mg, 49% yield).

9e: ^{1}H NMR ($CDCl_3$, δ) 1.04 (t, J = 7.2 Hz, 6 H), 1.60 (m, 4 H), 1.85 (m, 4 H), 3.23 (t, J = 8.1 Hz, 4 H), 3.93 (s, 6 H), 7.35 (dd, J = 6.6, 3.3 Hz, 2 H), 7.94 (dd, J = 6.6, 3.3 Hz, 2 H), 8.65 (s, 2 H), 8.88 (s, 2 H), 8.95 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 14.0, 23.3, 30.1, 33.3, 52.3, 125.5, 125.7, 126.5, 127.0, 128.4, 129.0, 129.6, 129.9, 130.6, 131.9, 138.0, 169.6. HRMS calcd for $C_{34}H_{34}O_4$: 506.2457. Found: 506.2465.

Preparation of 2,3-Bis(hydroxymethyl)-9,10-dihydroanthracene (4g) from 3e Using a Rhodium Catalyst. K_2CO_3 (13.3 g, 96 mmol) was added to 1,2-bis(3-trimethylsilyl-2-propynyl)benzene **3e** (7.17 g, 24 mmol) in 300 mL of degassed MeOH/ethyl ether (1/1) solvent. The reaction mixture was vigorously stirred for 3 h at room temperature. Then 50 mL of water was introduced and kept stirring for another 10 min. Then the reaction mixture was extracted by ether. The organic phase was washed with water and brine and dried over Na_2SO_4. The solvent was removed by evaporation below 40 °C to afford a yellow liquid of the desilylated diyne. The residue was added with BHT (ca. 10 mg). In another flask, 2-butyne-1,4-diol (8.26 g, 95.9 mmol) and $RhCl(PPh_3)_3$ (444 mg, 0.48 mmol) were dissolved into 250 mL of degassed ethanol and slowly heated to reflux. To the solution was added the desilylated diyne dropwise within 5 h. Then the reaction mixture was refluxed for 1 h. After removal of the solvent, 50 mL of cold ether was added to it. The mixture was filtered, and the resulting solid was washed with 200 mL of water to afford deep colored powder of the crude product **4g** (2.27 g, 44% yield).

4g: HRMS calcd for $C_{16}H_{16}O_2$: 240.1150. Found: 240.1145.

Preparation of 2,3-Bis(iodomethyl)-9,10-dihydroanthracene (4h) from 4g. 2,3-Bis(hydroxymethyl)-9,10-dihydroanthracene (**4g**, 2.27 g, 9.45 mmol) was put in 160 mL of anhydrous acetonitrile. Then NaI (8.45 g, 56.4 mmol) and chlorotrimethylsilane (7.12 mL, 56.1 mmol) were introduced.[16] After usual workup, the title compound **4h** was obtained (3.04 g, 70% yield).

Preparation of 2,3-Bis(iodomethyl)-9,10-dihydroanthracene (4h) from 4f. Dihydroanthracene **4f** (364 mg, 1.0 mmol) in 25 mL of acetone was refluxed with NaI (900 mg, 6.0 mmol) for 3 h. After removing the solvent, the reaction mixture was treated with $Na_2S_2O_3$ and extracted with $CHCl_3$. The extract was washed with brine and then dried over Na_2SO_4. After evaporation of the solvent, 414 mg of title compound **4h** was obtained as yellow crystals in 90% isolated yield.

4h: ^{1}H NMR ($CDCl_3$, δ) 3.87 (s, 4 H), 4.58 (s, 4 H), 7.18−7.28 (m, 6 H); ^{13}C NMR ($CDCl_3$, δ) 2.2, 35.7, 126.3, 127.4, 129.7, 135.1, 135.9, 137.9. HRMS calcd for $C_{16}H_{14}I_2$: 459.9185. Found: 459.9182.

Alternative Method for the Preparation of 2,3-Bis(iodomethyl)-9,10-dihydroanthracene (4h) from 4e. To a suspension of $LiAlH_4$ (1.52 g, 40.0 mmol) in diethyl ether (150 mL) at 0 °C was added 1,4-bis(trimethylsilyl)-2,3-bis(methoxycarbonyl)-9,10-dihydroanthracene (**4e**, 8.82 g, 20.0 mmol). The mixture was warmed to room temperature and stirred for 1 h. After cooling to 0 °C, the mixture was slowly added with aqueous 3 N HCl and extracted with $CHCl_3$. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent in vacuo afforded the corresponding diol as a colorless solid in a quantitative yield. NaI (12.1 g, 80.7 mmol) was added to the mixture, and it was dissolved in 100 mL of acetonitrile. To the mixture was added chlorotrimethylsilane (10.2 mL, 80.4 mmol), and it was stirred at room temperature for 1 h.[16] The mixture was quenched with water and extracted with $CHCl_3$. The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was dissolved in 16 mL of $CHCl_3$, and it was put into 160 mL of MeOH. The resulting pale-yellow precipitate was collected by filtration and dried in vacuo to afford the pure title compound **4h** (6.14 g, 67% yield for two steps).

Preparation of 2,3-Bis(3-trimethylsilylprop-2-ynyl)-9,10-dihydroanthracene (10) from 4h. To a solution of trimethylsilylacetylene (12.9 mL, 91.3 mmol) in 100 mL of THF was added ethylmagnesium bromide (0.91 M THF solution, 100 mL, 91 mmol). The mixture was heated to 40 °C for 1 h. CuCl (1.13 g, 11.4 mmol) and diiodide **4h** (13.99 g, 30.4 mmol) were added to the mixture, and it was heated to reflux overnight. After cooling to room temperature, the mixture was quenched with aqueous saturated NH_4Cl and extracted with hexane. The combined organic phase was washed with water. After addition of 1 mg of BHT, the solution was washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel chromatography (hexane:ethyl acetate:triethylamine = 50:1:1 as eluent) to afford a colorless viscous oil, which was further purified by recrystallization from hexane. After drying in vacuo, the title compound **10** was obtained as a colorless solid (8.48 g, 70% yield).

10: ^{1}H NMR ($CDCl_3$, δ) 0.24 (s, 18 H), 3.65 (s, 4 H), 3.92 (s, 4 H), 7.17−7.24 (m, 2 H), 7.26−7.31 (m, 2 H), 7.36 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 0.1, 23.6, 35.6, 87.1, 103.9, 126.0, 127.4, 127.9, 131.8, 135.3, 136.4. HRMS calcd for $C_{26}H_{32}Si_2$: 400.2043. Found: 400.2037.

Preparation of 2,3-Bis(bromomethyl)-5,7,12,14-tetrahydropentacene (12c) from 11a. Diester **11a** (542 mg, 1.0 mmol) was added to 10 mL of a diethyl ether solution of $LiAlH_4$ (83.6 mg, 2.2 mmol) at 0 °C. After stirring for 3 h at room temperature, hydrolysis with water and 2 N H_2SO_4 was performed carefully. The mixture was extracted with diethyl ether. The extract was washed with brine and dried over Na_2SO_4, and then the solvent was removed. Phosphorus tribromide (0.28 mL, 3.0 mmol) was added dropwise to the residue in 10 mL of $CHCl_3$ at 0 °C. After stirring for 1 h at room temperature, the mixture was treated with water at 0 °C then extracted with $CHCl_3$. The extract was washed with brine and dried over Na_2SO_4. After chromatography on silica gel (hexane:ethyl acetate = 20:1 as eluent), 429 mg of title compound **12c** was obtained as yellow crystals in 92% isolated yield.

12c: ^{1}H NMR ($CDCl_3$, δ) 3.79 (s, 4 H), 3.81 (s, 4 H), 4.56 (s, 4 H), 7.04−7.21 (m, 8 H); ^{13}C NMR ($CDCl_3$, δ) 30.3, 35.3, 35.8, 126.0, 126.4, 127.4, 130.1, 133.5, 134.2, 134.8, 136.7, 138.5. HRMS calcd for $C_{24}H_{20}Br_2$: 465.9931. Found: 465.9934.

Preparation of 4,15-Bis(trimethylsilyl)-1,3,5,7,12,14-hexahydro-2-oxacyclopenta[b]pentacene (12d) from 11a. $LiAlH_4$ (114 mg, 3.0 mmol) was mixed with $AlCl_3$ (1.20 g, 9.0 mmol) at 0 °C for 0.5 h. Diester **11a** (542 mg, 1.0 mmol) was added to the mixture. After stirring for 3 h at room temperature, hydrolysis with water and 2 N H_2SO_4 was performed carefully at 0 °C. The mixture was extracted with ethyl acetate. The extract was washed with $NaHCO_3$ and brine then dried over Na_2SO_4. After column chromatography

on silica gel (AcOEt:hexane = 1:10 as eluent), 332 mg of title compound **12d** was obtained as colorless crystals in 71% isolated yield.

12d: ^{1}H NMR ($CDCl_3$, δ) 0.45 (s, 18 H), 3.92 (s, 4 H), 3.97 (s, 4 H), 5.09 (s, 4 H), 7.19−7.27 (m, 6 H); ^{13}C NMR ($CDCl_3$, δ) 2.1, 35.9, 37.8, 74.4, 125.2, 126.0, 127.3, 130.9, 134.5, 136.0, 136.8, 141.5, 143.3. HRMS calcd for $C_{30}H_{36}OSi_2$: 468.2305. Found: 468.2304.

Preparation of 1,3,5,7,12,14-Hexahydro-2-oxacyclopenta[b]-pentacene (12e) from 12d. Ether (**12d**, 468 mg, 1.0 mmol) was reacted with trifluoroacetic acid (0.37 mL, 5.0 mmol) in $CHCl_3$ (5 mL) at 50 °C for 3 h. After evaporation of the solvent, 262 mg of the title compound **12e** was obtained as colorless crystals in 81% isolated yield.

12e: ^{1}H NMR ($CDCl_3$, δ) 3.94 (s, 8 H), 5.10 (s, 4 H), 7.17−7.30 (m, 8 H); ^{13}C NMR ($CDCl_3$, δ) 35.8, 36.1, 73.4, 119.8, 126.0, 126.2, 127.4, 134.45, 134.51, 136.3, 136.8, 137.0. HRMS calcd for $C_{24}H_{20}O$: 324.1514. Found: 324.1513.

Preparation of 1,3-Dihydro-2-oxacyclopenta[b]pentacene (9i) from 12e. A mixture of mesitylene (2 mL) solution of ether **12e** (324 mg, 1.0 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (454 mg, 2.0 mmol) was heated for 3 h at 120 °C. After addition of degassed MeOH (40 mL), a precipitate was formed. After filtration, 304 mg of the title compound **9i** was obtained as blue crystals in 95% isolated yield.

9i: ^{1}H NMR (nitrobenzene-d_5, 423 K, δ) 5.15 (s, 4H), 7.30−7.33 (m, 2H), 7.71 (s, 2H), 7.91−7.94 (m, 2H), 8.60 (s, 2H), 8.62 (s, 2H), 8.92 (s, 2H). HRMS calcd for $C_{24}H_{16}O$: 320.1201. Found: 320.1199.

Preparation of 2,3-Bis(methoxycarbonyl)-5,7,12,14-tetrahydropentacene (12a) from 11a. 1,4-Bis(trimethylsilyl)-5,7,12,14-tetrahydropentacene-2,3-dicarboxylic acid dimethyl ester (**11a**, 542 mg, 1.0 mmol) was mixed with NaI (600 mg, 4.0 mmol) and chlorotrimethylsilane (0.51 mL, 4.0 mmol) in acetonitrile at room temperature. After 0.5 h, water (72 μL, 4.0 mmol) was added, and then the mixture was heated to 70 °C for 0.5 h. The reaction was quenched by aqueous $Na_2S_2O_3$ at 0 °C and extracted with $CHCl_3$ (15 mL, three times). The combined extract was washed with brine and then dried over Na_2SO_4. Column chromatography on silica gel (AcOEt:hexane = 1:5 as eluent) afforded 247 mg of the title compound **12a** as colorless crystals in 62% isolated yield.

12a: ^{1}H NMR ($CDCl_3$, δ) 3.93 (s, 4 H), 3.94 (s, 4 H), 3.96 (s, 6 H), 7.19 (s, 2 H), 7.22−7.25 (m, 2 H), 7.28−7.35 (m, 2 H), 7.66 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 35.3, 35.7, 52.5, 126.0, 126.3, 127.3, 128.0, 129.7, 132.7, 134.9, 136.6, 140.3, 168.1. HRMS calcd for $C_{26}H_{22}O_4$: 398.1518. Found: 398.1518.

Preparation of 2,3-Bis(ethoxycarbonyl)-5,7,12,14-tetrahydropentacene (12b) from 11b. The compound **12b** was prepared in 76% isolated yield from **11b** by the same way as described for dimethyl ester **12a**.

12b: ^{1}H NMR ($CDCl_3$, δ) 1.44 (t, J = 7.2 Hz, 6 H), 3.85 (s, 4 H), 3.91 (s, 4 H), 4.45 (q, J = 14.1, 7.2 Hz, 4 H), 7.11 (s, 2 H), 7.22−7.25 (m, 2 H), 7.31−7.34 (m, 2 H), 7.65 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 14.0, 35.2, 35.6, 61.4, 125.9, 126.2, 127.2, 127.8, 129.9, 132.6, 134.6, 136.5, 140.1, 167.7. HRMS calcd for $C_{28}H_{26}O_4$: 426.1831. Found: 426.1834.

Preparation of 2,3-Bis(methoxycarbonyl)pentacene (9f) from 12a. A mixture of mesitylene (2 mL) solution of tetrahydropentacene dimethyl ester **12a** (398 mg, 1.0 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (454 mg, 2.0 mmol) was heated for 3 h at 150 °C. After addition of degassed MeOH (40 mL), a blue precipitate was observed. After filtration under nitrogen, 342 mg of the title compound **9f** was obtained as blue crystals. Isolated yield was 87%.

9f: ^{1}H NMR (DMSO-d_6, 373 K, δ) 3.92 (s, 6 H), 7.42−7.45 (m, 2 H), 8.05−8.08 (m, 2 H), 8.47 (s, 2 H), 8.90 (s, 2 H), 9.04 (s, 2 H), 9.21 (s, 2 H). HRMS calcd for $C_{26}H_{18}O_4$: 394.1206. Found: 394.1205. Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.82; H, 4.65.

Preparation of 2,3-Bis(ethoxycarbonyl)pentacene (9g) from 12b. A mixture of a mesitylene (2 mL) solution of tetrahydropentacene diethyl ester **12b** (426 mg, 1.0 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (454 mg, 2.0 mmol) was heated for 3 h at 150 °C. After addition of degassed MeOH (40 mL), a blue precipitate was observed. Filtration under nitrogen gave 338 mg of the title compound **9g** as blue crystals. Isolated yield was 80%.

9g: ^{1}H NMR ($CDCl_3$, 323 K, δ) 1.43 (t, J = 7.2 Hz, 6 H), 4.43 (q, J = 7.2 Hz, 4 H), 7.35−7.38 (m, 2 H), 7.94−7.98 (m, 2 H), 8.36 (s, 2 H), 8.70 (s, 2 H), 8.74 (s, 2 H), 9.00 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 14.3, 61.5, 125.7, 126.6, 127.4, 127.9, 128.5, 128.8, 130.0, 130.78, 130.80, 131.9, 132.2, 167.6. HRMS calcd for $C_{28}H_{22}O_4$: 422.1518. Found: 422.1514. Anal. Calcd for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.97; H, 4.96.

Preparation of 2,3-Bis(bromomethyl)pentacene (9h) from 12c. A degassed mesitylene solution (2 mL) of 2,3-bis(bromomethyl)-5,7,12,14-tetrahydropentacene (466 mg, 1.0 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (454 mg, 2.0 mmol) was heated at 120 °C for 3 h. After addition of degassed MeOH (40 mL), a formed precipitate was collected by filtration under nitrogen followed by drying in vacuo to afford the title compound as blue powder (407 mg, isolated yield 88%).

9h: ^{1}H NMR (*o*-dichlorobenzene-d_4, 393 K, δ) 5.02 (s, 4H), 7.97 (s, 2H), 7.97−8.02 (m, 2H), 8.59 (s, 2H), 8.70 (s, 2H), 8.98 (s, 2H); a multiplet (2H) was overlapped with the solvent peaks. Thermal stability of the compound was relatively low, and decomposition was observed during the measurement of ^{1}H NMR spectrum at 393 K. HRMS calcd for $C_{24}H_{16}Br_2$: 461.9618. Found: 461.9623. Anal. Calcd for $C_{24}H_{16}Br_2$: C, 62.10; H, 3.47. Found: C, 62.42; H, 3.59.

Preparation of 2,3-Bis(iodomethyl)naphthalene (13). To a suspension of $LiAlH_4$ (1.52 g, 40.0 mmol) in THF (40 mL) was added naphthalene 2,3-dicarboxylic anhydride (3.96 g, 20.0 mmol) at 0 °C and stirred at room temperature for 1 h. The mixture was carefully quenched with water and 3 N HCl solution and extracted with $CHCl_3$. The organic phase was washed with water, saturated $NaHCO_3$ solution, and brine and dried over Na_2SO_4. Removal of the solvent in vacuo provided the corresponding diol as a colorless solid (3.45 g, 92% yield). The solid was added with NaI (11.0 g, 73.4 mmol) and dissolved in 200 mL of acetonitrile. The mixture was added with chlorotrimethylsilane (9.3 mL, 73 mmol) and stirred at 70 °C for 1 h. After cooling to room temperature, the mixture was quenched with water and extracted with $CHCl_3$ three times. The combined organic phase was washed with brine and dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was washed with 100 mL of MeOH and dried in vacuo to afford the pure title compound **13** (5.27 g, 70% yield). The spectral data were identical to the literature ones.[25]

Preparation of 1,4-Bis(trimethylsilyl)-2,3-bis(methoxycarbonyl)-5,12-dihydronaphthacene (15a) from 14. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in 5 mL of THF was added *n*-BuLi (1.56 M hexane solution, 1.60 mL, 2.50 mmol) at −78 °C, and the mixture was stirred for 10 min. The solution was warmed to −40 °C for 30 min and then re-cooled to −78 °C. After 10 min, to the solution was added diyne **14** (348 mg, 1.0 mmol), and it warmed to room temperature by removal of the cooling bath. After stirring for 3 h, CuCl (297 mg, 3.0 mmol) and DMAD (0.48 mL, 3.9 mmol) were added to the mixture at 0 °C. After stirring for 6 h at room temperature, the mixture was hydrolyzed with 3 N HCl and extracted with ethyl acetate. The extract was washed with $NaHCO_3$ and brine and dried over Na_2SO_4. Column chromatography (silica gel, hexane:ethyl acetate = 10:1 as eluent) gave 215 mg of the title compound **15a** as colorless crystals in 44% isolated yield.

15a: ^{1}H NMR ($CDCl_3$, δ) 0.45 (s, 18 H), 3.81 (s, 6 H), 4.18 (s, 4 H), 7.42−7.45 (m, 2 H), 7.73 (s, 2 H), 7.79−7.82 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 1.8, 38.6, 52.3, 124.3, 125.5, 127.3, 132.5, 135.5,

(25) Taillemite, S.; Fichou, D. *Eur. J. Org. Chem.* **2004**, 4981.

135.7, 136.0, 145.7, 170.5. HRMS calcd for $C_{28}H_{34}O_4Si_2$: 490.1996. Found: 490.1989.

Preparation of 1,4-Bis(trimethylsilyl)-2,3-bis(methoxycarbonyl)naphthacene (16a) from 15a. 2,3-Dichloro-5,6-dicyanobenzoquinone (250 mg, 1.1 mmol) was added to a toluene solution of **15a** (490 mg, 1.0 mmol), and then the mixture was refluxed for 3 h. After filtration, the mixture was evaporated in vacuo. Crystallization from $CHCl_3$/MeOH afforded 307 mg of the title compound **16a** as orange crystals. NMR yield was 97%. Isolated yield was 63%.

16a: ^{1}H NMR ($CDCl_3$, δ) 0.59 (s, 18 H), 3.91 (s, 6 H), 7.43−7.46 (m, 2 H), 8.01−8.04 (m, 2 H), 8.66 (s, 2 H), 9.05 (s, 2 H); ^{13}C NMR ($CDCl_3$, δ) 2.2, 52.5, 125.7, 126.4, 128.3, 129.3, 129.6, 132.1, 132.7, 135.6, 139.4, 170.6. HRMS calcd for $C_{28}H_{32}O_4Si_2$: 488.1839. Found: 488.1845.

Preparation of 2,3-Bis(bromomethyl)-5,12-dihydronaphthacene (15b) from 15a. Diester **15a** (490 mg, 1.0 mmol) was added to an anhydrous Et_2O solution (10 mL) of $LiAlH_4$ (83.6 mg, 2.2 mmol) at 0 °C. After stirring for 3 h at room temperature, hydrolysis with water and 2 N H_2SO_4 was performed carefully. The mixture was extracted with diethyl ether. The extract was washed with brine and dried over Na_2SO_4, and then the solvent was removed. Phosphorus tribromide (0.28 mL, 3.0 mmol) was added dropwise to the residue in 10 mL of $CHCl_3$. After stirring for 1 h, the mixture was treated with water and extracted with $CHCl_3$. The extract was washed with brine and dried over Na_2SO_4. Chromatography on silica gel (hexane:ethyl acetate = 20:1 as eluent) gave 375 mg of the title compound **15b** as yellow crystals in 90% isolated yield.

15b: ^{1}H NMR ($CDCl_3$, δ) 4.07 (s, 4 H), 4.68 (s, 4 H), 7.35 (s, 2 H), 7.41−7.44 (m, 2 H), 7.75 (s, 2 H), 7.77−7.80 (m, 2 H); ^{13}C NMR ($CDCl_3$, δ) 30.2, 36.4, 125.4, 125.5, 127.2, 130.0, 132.3, 134.4, 134.6, 138.7. HRMS calcd for $C_{20}H_{16}Br_2$: 413.9618. Found: 413.9627.

Preparation of 2,3-Bis(bromomethyl)naphthacene (16b) from 15b. A mixture of a toluene solution (10 mL) of 2,3-dichloro-5,6-dicyanobenzoquinone (250 mg, 1.1 mmol) and 2,3-bis(bromomethyl)-5,12-dihydronaphthacene (**15b**, 414 mg, 0.99 mmol) was refluxed for 3 h. After filtration, the solvent was evaporated in vacuo. Then degassed MeOH was added, and 280 mg of the title compound **16b** precipitated as orange crystals in yield 68%.

16b: ^{1}H NMR ($CDCl_3$, 323 K, δ) 4.94 (s, 4 H), 7.41−7.44 (m, 2 H), 7.99−8.02 (m, 2 H), 8.04 (s, 2 H), 8.62 (s, 2 H), 8.66 (s, 2 H); ^{13}C NMR ($CDCl_3$, 323 K, δ) 31.7, 125.7, 126.7, 127.0, 128.4, 130.8, 130.9, 131.5, 132.2, 133.0. HRMS calcd for $C_{20}H_{14}Br_2$: 411.9461. Found: 411.9463.

Supporting Information Available: Spectral data of compounds **3c**, **4c**,**d**, **5a**,**c**−**e**, **6a**,**c**,**d**, **7a**,**c**,**d**, **8a**,**c**−**e**, **9a**,**c**,**d**, **11a**,**b**, and **14**. NMR charts for all new compounds. UV−vis absorption spectra of pentacenes **9a**−**d**,**g** (in solution) and **9f**,**h**,**i** (in solid). Crystallographic data for **9a** and **9b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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