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Double Homologation Method for Substituted Soluble Pentacenes and Dimerization Behaviours of Pentacenes

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Abstract: A double homologation method for the formation of substituted soluble pentacenes was developed by a zirconium-mediated cyclization of tetrayne derivatives. Thermal dimerization of tetra- and octasubstituted pentacenes was observed. The dimerization behavior was observed to be strongly related to the substituent groups affixed to the pentacenes.

Keywords: alkynes · cyclization · dimerization · double homologation · zirconium

Introduction

It was reported in 1997 that a pentacene film showed a comparable or higher field-effect transistor (FET) mobility compared with amorphous silicon.[1] Pentacene is acknowledged as possessing the highest FET mobility among organic thin films. Pentacene is insoluble in organic solvents at ambient conditions. Therefore, we proposed that soluble pentacenes with organic substituents are attractive and important.[2a]

We have reported two methods for the construction of a linear pentacyclic system of substituted pentacene derivatives using zirconacyclopentadienes. One is homologation[2] and the other is coupling.[3] The homologation method introduces organic substituents into naphthacenes and pentacenes by diyne cyclization. This method can extend the aromatic ring system in one direction as shown in Figure 1.[2] As a more efficient method for symmetrical pentacene formation, we reported a double homologation method to extend the aromatic ring system in both directions by tetrayne cyclization to prepare pentacene derivatives also shown in Figure 1.[4a] More recently, Stone et al. also reported the same reaction using the double homologation reactions with zirconacycleopentadienes.[4b]

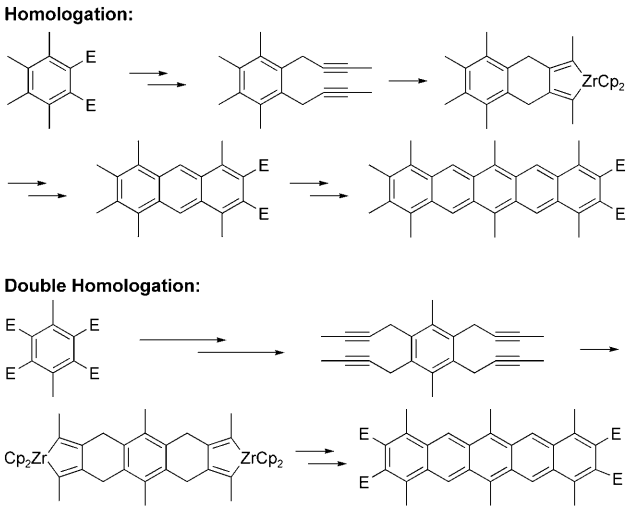

Figure 1. The concept of homologation and double homologation.

Four substituted patterns of pentacenes could be prepared by the double homologation reaction as shown in Figure 2. Compared with the homologation method, double homologation reduces the number of synthesis steps. For example, the homologation method requires 2 steps each for alkynylation, zirconacyclopentadiene formation, and aromatic ring formation. However, the double homologation method requires only one step each. Therefore, for symmetrical pentacene formation, the double homologation method has the advantage over the homologation method.

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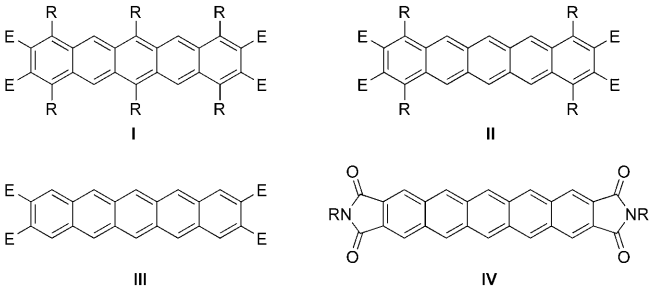


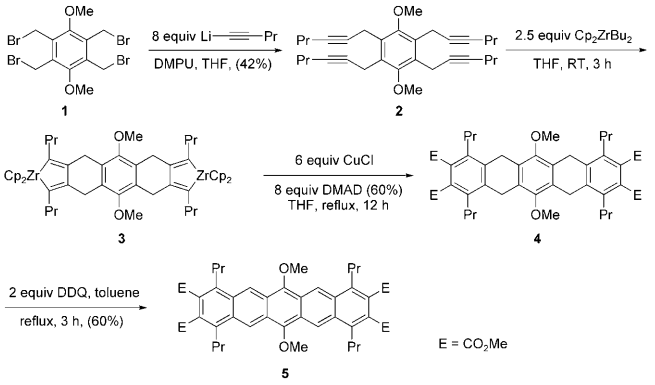
Figure 2. Substituted patterns of pentacenes prepared by double homologation.

In this paper, we report in full detail the double homologation method which we have developed.

Results and Discussion

Preparation of Symmetrically Octa- and Deca-Substituted Pentacenes by Double Homologation

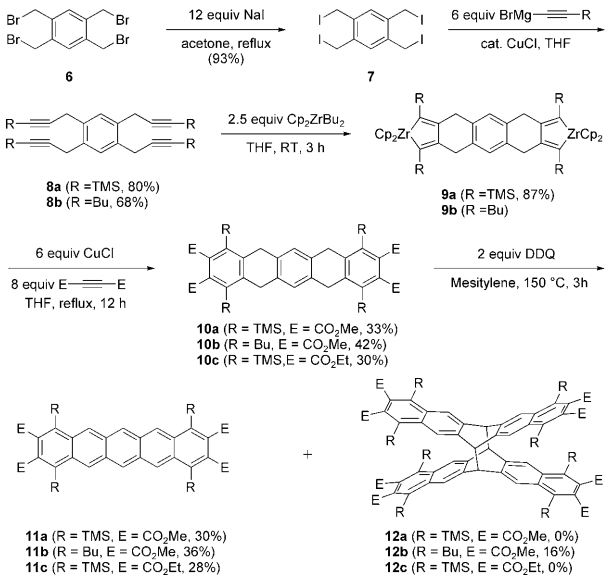
We have preliminarily reported the preparation method for the 1,2,3,4,6,8,9,10,11,13-decasubstituted pentacene **5**.[4a] It was successfully prepared by zirconium-mediated double-ring extension as shown in Scheme 1. The reaction of



Scheme 1. Synthesis of pentacene **5**.

1,2,4,5-tetrakis(bromomethyl)-3,6-dimethoxybenzene **1** with 1-pentynyllithium in THF and DMPU led to the clean formation of the corresponding tetrayne **2** in 42% yield. Tetrayne **2** was then treated with 2.5 equiv of Cp_2ZrBu_2 to give bis(zirconacyclopentadiene) **3** followed by coupling with dimethyl acetylenedicarboxylate (DMAD) in the presence of CuCl to form the first and fifth rings of the pentacene skeleton. The tetrahydropentacene derivative **4** was obtained in 60% yield. Tetrahydropentacene **4** was aromatized with 2 equiv of DDQ in toluene at 100°C for 3 h. The corresponding symmetrically decasubstituted pentacene **5** was obtained as a blue solid in 60% yield (Scheme 1).

Synthesis of 1,2,3,4,8,9,10,11-octasubstituted pentacenes **11** proceeded from commercially available 1,2,4,5-tetrakis-(bromomethyl)benzene **6** (Scheme 2). However, the reaction



Scheme 2. Synthesis of pentacene **11**.

of tetrakis(bromomethyl)benzene **6** with 1-alkynyllithium or magnesium halide did not lead to a clean formation of the desired tetraynes **8**. Therefore, tetrabromide **6** was converted to tetraiodide **7**.[5] **7** cleanly reacted with 1-alkynylmagnesium bromide in the presence of CuCl to give the desired tetraynes **8** in moderate yields.[6] Similarly, the zirconium-mediated double cyclization of tetraynes **8** with dialkyl acetylenedicarboxylate proceeded in the presence of CuCl in refluxing THF. Tetrahydropentacenes **10** were obtained via bis(zirconacyclopentadiene) complexes **9**.

Aromatization of octa-substituted tetrahydropentacenes **10** with 2 equiv of DDQ at 150°C gave the corresponding pentacenes **11** (Scheme 2). The trimethylsilyl-substituted pentacene **11a,c** were obtained as single products in 30% and 28% yield, respectively, from the corresponding tetrahydropentacenes **10a,c** by using 2 equiv of DDQ at 150°C. However, aromatization of tetrahydropentacene **10b** under the same conditions led to the corresponding pentacene **11b** and its dimer **12b** formed in 36% and 16% yield, respectively. The structure of pentacene dimer **12b** was determined by X-ray analysis as shown in Figure 3.

The yields of desired pentacenes **11** could be improved by the pentacene–DDQ adduct method which we have reported recently (Scheme 3).[3] Tetrahydropentacene **10** reacted with an excess of DDQ (3 equiv) at 50°C to give Diels–Alder adducts **13** in quantitative yields.[7] Once formed pentacene with 2 equiv of DDQ was converted into **13** with the third DDQ. To remove DDQ from **13**, the pentacene–DDQ adducts **13** were treated with 50 equiv of γ-terpinene at 100°C in toluene to induce the retro-Diels–Alder reaction.[3] The silyl-substituted pentacenes **11a,c** were obtained as single products in good yields. For tetrahydropentacene **10b**, the dimer **12b** was also formed under the conditions used here, but the yield of pentacene **11b** was improved. Pentacenes **11a–c** were deep blue powders with a good solubility in a variety of organic solvents.

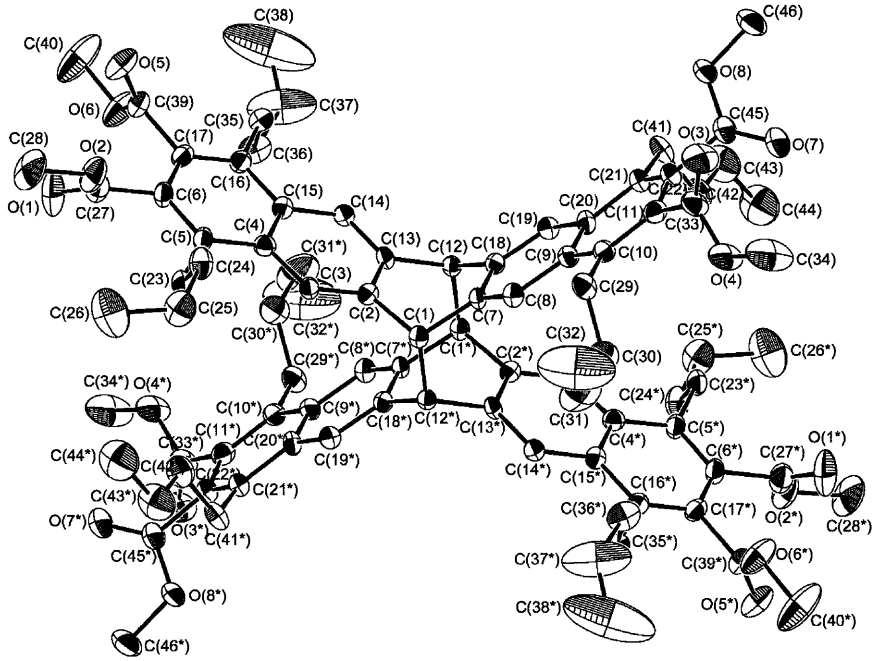
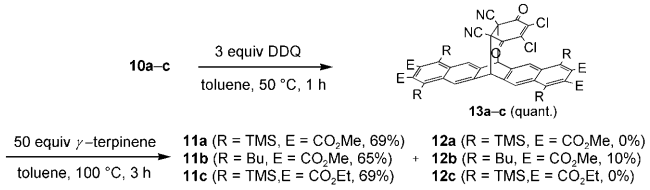


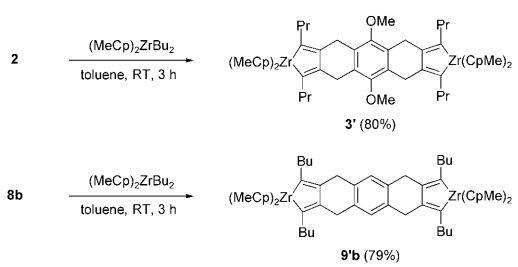
Figure 3. Structure of pentacene dimer **12b**.



Scheme 3. Pentacene formation by pentacene-DDQ adduct method.

Formation of Bis(zirconacyclopentadiene)s as Key Intermediates

The key intermediates, bis(zirconacyclopentadiene)s **3′**, **9a**, and **9′b**, were successfully observed and characterized by NMR (Scheme 4). The tetrayne **8a** was treated with 2.5 equiv of Cp_2ZrBu_2 (Negishi's reagent), generated in situ from zirconocene dichloride and *n*-butyllithium in THF at −78 °C for 1 h. The reaction proceeded at room temperature for 3 h. ^{1}H NMR analysis showed **9a** was formed in 94% NMR yield. Upon changing the reaction solvent from THF to toluene, the precipitated LiCl was removed by filtration.



Scheme 4. Formation of bis(zirconacycle)s **3′** and **9′b**.

The solvent was evaporated, and the resulting solid was washed with hexane to afford bis(zirconacycle) **9a** as a yellow solid in 87% yield. ^{1}H NMR spectrum of **9a** in C_6D_6 showed four singlet signals at 0.26, 3.44, 5.82, and 7.05 ppm assigned to 36 protons of four TMS groups, eight protons of four CH_2, 20 protons of four Cp ligands, and two protons of the central aromatic ring, respectively. ^{13}C NMR showed the characteristic carbon of Cp ligand at 110.7 ppm. The sp^2 carbons of zirconacycle appeared at 140.8 and 197.6 ppm, respectively.[8]

When the trimethylsilyl group in **9a** was changed to a butyl group, bis(zirconacycle) **9b** was not soluble in toluene. Therefore, the LiCl salt could not be completely removed. In order to increase the solubility of **9b**, the methylcyclopentadienyl ligand was introduced instead of cyclopentadienyl ligand as shown in Scheme 4. Compared with **9b**, the solubility of bis(methylcyclopentadienyl)zirconacycle **9′b** is improved. Bis(zirconacycle) **9′b** was easily isolated by the same procedure in 79% yield. Similarly, the methylcyclopentadienyl ligand was introduced to **3**. The complex bis(methylcyclopentadienyl)zirconacycle **3′** prepared from tetrayne **2** showed similar characteristic ^{13}C NMR data as that of **9′b** in C_6D_6 at room temperature. Three Cp carbons appeared at 105.1, 111.9, and 123.6 ppm and the characteristic sp^2 carbon attached to zirconium metal appeared at 186.8 ppm.[8] These spectra clearly show that these bis(zirconacycle)s **3′**, **9a**, and **9′b** are stable under N_2 at room temperature.

Preparation and Functionalization of Pentacene–2,3,9,10-Tetraesters

Formation of 2,3,9,10-tetrasubstituted pentacene **11d** was shown in Scheme 5. Desilylation of **10a** with 4 equiv of Bu_4NF in THF at 0 °C gave desilylated tetrahydropentacene **14** in 75% yield. Tetrahydropentacene **14** was aromatized with 2 equiv of DDQ at 150 °C to give a mixture of desired pentacene **11d** and its dimer **12d** in 40% and 10% yield, respectively. However, when tetrahydropentacene **14** was aromatized by the pentacene–DDQ adduct method at 100 °C, pentacene **11d** was formed as a single product in 72% yield. The desilylated pentacene **11d** still has good solubility in organic solvents. The ^{1}H NMR of **11d** recorded in $CDCl_3$ clearly show three singlet signals at 8.36, 8.72, and 8.98 ppm in the aromatic region assignable to ten protons of the pentacene skeleton.

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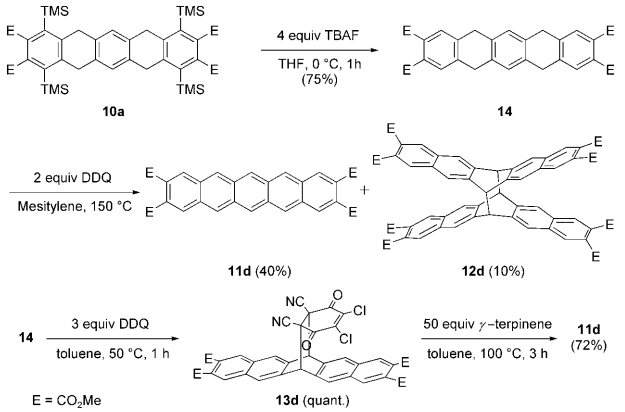
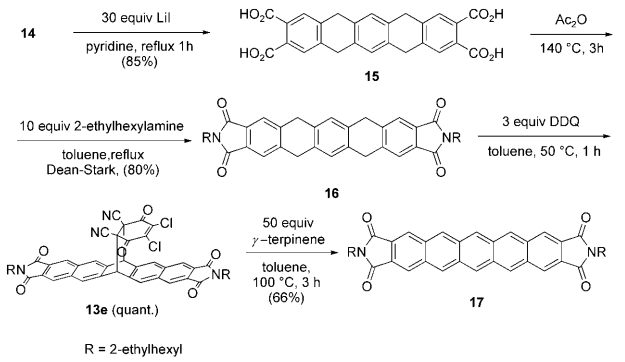


Scheme 5. Synthesis of pentacene **11d**.

Pentacene diimide **17** also could be prepared by functionalization and aromatization of **14** (Scheme 6). Tetraesters **14** reacted with lithium iodide in refluxing pyridine to afford

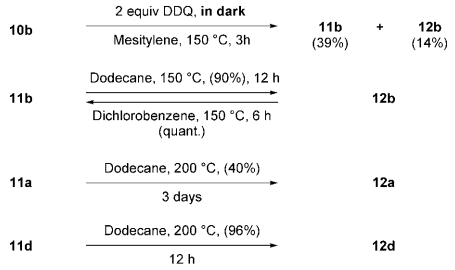


Scheme 6. Synthesis of pentacene imide **17**.

the corresponding tetracarboxylic acid **15**.[9] **15** could be converted to dianhydride in high yield by treatment with acetic anhydride at 140 °C. The anhydride reacted with 2-ethylhexylamine in refluxing toluene. The corresponding diimide **16** was formed in 80 % yield. The tetrahydropentacene **16** was aromatized by the pentacene–DDQ adduct method at 100 °C in degassed toluene to afford the corresponding pentacene diimide **17** in 66 % yield. The pentacene **17** could be isolated as a stable blue solid by methanol precipitation.

Dimerization of Symmetrically Substituted Pentacenes

When tetrahydropentacene **10b** was aromatized with 2 equiv of DDQ in the dark, the corresponding dimer **12b** was still formed (Scheme 7).[10] Interestingly, a reversible conversion between pentacene monomer **11b** and its dimer **12b** was observed by changing the solvent. For example, when pentacene **11b** was heated in degassed dodecane solution at 150 °C, the monomer **11b** was converted to its dimer **12b** as a white precipitate owing to the low solubility of **12b** in dodecane. The dimer **12b** could also be quantitatively



Scheme 7. Dimerization of symmetrically substituted pentacenes.

converted to monomer **11b** in dichlorobenzene at 150 °C (Scheme 7). Pentacene **11a** did not dimerize when it was prepared in mesitylene as described above, owing to the bulky trimethylsilyl groups. However, it also was converted to its dimer **12a** in dodecane, although a longer reaction time and higher temperatures were needed (200 °C for 3 days, yield: 40 % of dimer **12a**). The less substituted pentacene **11d** dimerized under the same conditions in 96 % yield, with high temperatures required to improve its solubility in dodecane.

Compared with pentacene **11**, no dimerization was observed for decasubstituted pentacene **5** and 2,3-disubstituted pentacene.[2b] For pentacene **5**, the lack of dimerization arises from the steric repulsion between methoxy groups in the pentacene pair.[10]

Conclusions

Double homologation was successfully developed by a zirconium mediated double ring extension of 1,2,4,5-tetrakis(propargyl)benzene derivatives. Dimerization of tetra- and octa-substituted pentacenes was observed. Reversible conversion between monomeric pentacene and its dimer was observed for tetra- and octa-substituted pentacenes.

Experimental Section

General

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) and toluene were distilled over sodium and benzophenone under a nitrogen atmosphere. All of the reagents were commercially available and used as received unless stated. 1,2,4,5-Tetrakis(bromomethyl)-3,6-dimethoxybenzene (**1**) was prepared according to the literature.[11] ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ (containing 0.03 % TMS) solutions.

*Preparation of 1,2,4,5-Tetrahex-2-ynyl-3,6-dimethoxybenzene (**2**) from **1***

To a solution of 1-pentyne (0.79 mL, 8.0 mmol) in THF (25 mL) was added *n*BuLi (1.56 M hexane solution, 5.13 mL, 8.0 mmol) and DMPU (1,3-dimethyl-tetrahydro-pyrimidin-2-one, 0.96 mL, 8.0 mmol). The mixture was stirred at room temperature (RT) for 1 h. Tetrabromide **1** (510 mg, 1.0 mmol) was added to the mixture and it was stirred at RT for 12 h. The reaction mixture was quenched with saturated aqueous NH_4Cl at 0 °C and extracted with ethyl acetate. The combined extract was washed with water. After addition of BHT (3 mg), 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 **2** as a colorless solid (188 mg, 42% yield).

2: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.93$ (t, $J = 7.2$ Hz, 12H), 1.44–1.51 (m, 8H), 2.06–2.11 (m, 8H), 3.73 (t, $J = 2.4$ Hz, 8H), 3.91 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta =$ 13.5, 15.9, 20.8, 22.3, 62.4, 78.0, 80.3, 130.1, 152.3 ppm; HRMS (EI) calcd for $C_{32}H_{42}O_2$: 458.3185. Found: 458.3196.

*Preparation of Bis[bis(methylcyclopentadienyl)zirconacyclopentadiene] (**3′**) from **2***

To a solution of bis(methylcyclopentadienyl)zirconium dichloride (160 mg, 0.5 mmol) in 15 mL of toluene was added *n*BuLi (1.56 M hexane solution, 0.64 mL, 1.0 mmol) at −78 °C, and the mixture was stirred at −78 °C. After 1 h, tetrayne **2** (92 mg, 0.2 mmol) was added to the solution, and it was warmed to RT by removal of the cooling bath. After stirring for 3 h, ^{1}H NMR measurements showed **3′** was formed in 92% yield. The precipitated LiCl was removed by filtration. The solvent was evaporated, and the resulting solid was washed with hexane (20 mL) to afford **3′** as a yellow solid (153 mg, 80% yield).

3′: ^{1}H NMR (C_6D_6, Me_4Si): $\delta = 1.10$ (t, $J = 7.2$ Hz, 12H), 1.38–1.52 (m, 8H), 1.80 (s, 12H), 2.47–2.51 (m, 8H), 3.61 (s, 8H), 3.74 (s, 6H), 5.44–5.45 (t, $J = 2.8$ Hz, 8H), 5.92–5.94 ppm (t, $J = 2.8$ Hz, 8H); ^{13}C NMR (C_6D_6, Me_4Si): $\delta = 15.3$, 15.5, 24.4, 27.2, 40.7, 61.5, 105.1, 111.9, 123.6, 127.3, 129.9, 149.4, 186.8 ppm; HRMS (FAB) calcd for $C_{56}H_{70}O_2Zr_2$: 954.3470. Found: 954.3484.

*Preparation of 6,13-Dimethoxy-1,4,8,11-tetrapropyl-5,7,12,14-tetrahydro-2,3,9,10-tetrakis(methoxycarbonyl)pentacene (**4**) from **2***

To a solution of Cp_2ZrCl_2 (730 mg, 2.5 mmol) in 15 mL of THF was added *n*BuLi (1.56 M hexane solution, 3.2 mL, 5.0 mmol) at −78 °C with constant stirring. After 1 h, tetrayne **2** (459 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 (594 mg, 6.0 mmol), DMAD (dimethyl acetylenedicarboxylate, 0.96 mL, 8.0 mmol), and DMPU (0.97 mL, 8.0 mmol) were added to the mixture, and it was stirred for 12 h under refluxing. The mixture was quenched with 3 N HCl at 0 °C 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 flash chromatography (silica gel, hexane/ethyl acetate = 5:1 as eluent) to afford **4** as colorless crystals (445 mg, 60% yield).

4: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 1.05$ (t, $J = 7.4$ Hz, 12H), 1.60–1.74 (m, 8H), 2.77–2.81 (m, 8H), 3.85 (s, 12H), 3.87 (s, 8H), 3.98 ppm (s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 14.5$, 24.2, 26.4, 32.7, 52.3, 61.4, 128.0, 130.4, 135.8, 138.1, 150.0, 169.5 ppm; HRMS (FAB) calcd for $C_{44}H_{54}O_{10}$: 742.3717. Found: 742.3708.

*Preparation of 6,13-Dimethoxy-1,4,8,11-tetrapropyl-2,3,9,10-tetrakis(methoxycarbonyl)pentacene (**5**) from **4***

A mixture of tetrahydropentacene **4** (60 mg, 0.08 mmol) and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone, 37 mg, 0.16 mmol) was refluxed for 3 h in degassed toluene (5 mL). After cooling to RT, the solvent was removed in vacuo. The remaining mixture was put into 10 mL of degassed MeOH and stirred for 10 min to dissolve the hydroquinone. The blue precipitate was collected by filtration. The blue solid was reprecipitated in degassed $CHCl_3$ (1 mL) and hexane (10 mL). **5** was afforded as a blue solid (35 mg) in 60% yield of isolated product.

5: M.p.: 241–243 °C (dec); ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 1.19$ (t, $J =$ 7.2 Hz, 12H), 1.90–2.10 (m, 8H), 3.20–3.35 (m, 8H), 3.95 (s, 12H), 4.36 (s, 6H), 9.25 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 14.7$, 24.6, 32.5, 52.4, 63.9, 120.5, 123.6, 127.3, 129.8, 138.1, 149.0, 169.4 ppm; HRMS (FAB) calcd for $C_{44}H_{50}O_{10}$: 738.3404. Found: 738.3405. elemental analysis: calcd (%) for $C_{44}H_{50}O_{10}$: C 71.52, H 6.82; found: C 71.22, H 6.74.

*Preparation of 1,2,4,5-Tetrakis(iodomethyl)benzene (**7**) from **6***

1,2,4,5-Tetrakis(bromomethyl)benzene (449 mg, 1.0 mmol) in 25 mL of acetone was refluxed with sodium iodide (1.8 g, 12.0 mmol) for 8 h. After removal of the solvent, the reaction mixture was extracted with $CHCl_3$ and treated with saturated aqueous $Na_2S_2O_3$. The extract was washed with water and brine. After evaporation of the solvent, the title compound was obtained as a pale-yellow solid (592 mg, 93% yield).

7: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 4.50$ (s, 8H), 7.28 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 0.2$, 132.9, 138.0 ppm; HRMS (EI) calcd for $C_{10}H_{10}I_4$: 637.6961. Found: 637.6962.

*Preparation of 1,2,4,5-Tetrakis(3-trimethylsilyl-2-propynyl)benzene (**8a**) from **7***

To a solution of 1-trimethylsilylacetylene (0.85 mL, 6.0 mmol) in 15 mL THF was added ethylmagnesium bromide (0.97 M THF solution, 6.18 mL, 6.0 mmol) at 0 °C. The mixture was heated to 40 °C for 1 h. Copper chloride (99 mg, 1.0 mmol) and tetraiodide **7** (637 mg, 1.0 mmol) were added to the mixture and it was heated to reflux for 6 h. After cooling to 0 °C, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined extract was washed with water. After addition of BHT (3 mg), 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 = 100:1:3 as eluent) to afford **8a** as colorless solid (414 mg, 80% yield).

8a: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.17$ (s, 36H), 3.65 (s, 8H), 7.40 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 0.1$, 23.7, 87.0, 103.6, 129.9, 133.3 ppm; HRMS (EI) calcd for $C_{30}H_{46}Si_4$: 518.2677. Found: 518.2673.

*Preparation of Bis(dicyclopentadienylzirconacyclopentadiene) (**9a**) from **8a***

9a (167 mg) was prepared in 87% yield of isolated product (94% NMR yield) from **8a** (1.0 mmol) by the same method as described for **3′**.

9a: ^{1}H NMR (C_6D_6, Me_4Si): $\delta = 0.26$ (s, 36H), 3.44 (s, 8H), 5.82 (s, 20H), 7.05 ppm (s, 2H); ^{13}C NMR (C_6D_6, Me_4Si): $\delta = 2.8$, 43.7, 110.7, 123.6, 136.1, 140.8, 197.6 ppm; HRMS (FAB) calcd for $C_{50}H_{66}Si_4Zr_2$: 958.2336. Found: 958.2332.

*Preparation of 1,4,8,11-Tetrakis(trimethylsilyl)-5,7,12,14-tetrahydropentacene-2,3,9,10-tetracarboxylic Acid Tetramethyl Ester (**10a**) from **8a***

10a (268 mg) was prepared in 33% yield of isolated product from **8a** (1.0 mmol) by the same method as described for **4**.

10a: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.41$ (s, 36H), 3.80 (s, 12H), 3.97 (s, 8H), 7.18 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 1.8$, 38.1, 52.3, 124.1, 135.48, 135.52, 135.8, 145.9, 170.5 ppm; HRMS (FAB) calcd for $C_{42}H_{58}O_8Si_4Na$ $[M+Na]^+$: 825.3106. Found: 825.3130.

*Preparation of DDQ Adduct of 1,4,8,11-Tetrakis(trimethylsilyl)-5,7,12,14-tetrahydropentacene-2,3,9,10-tetracarboxylic Acid Tetramethyl Ester (**13a**) from **10a***

2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (227 mg, 1.0 mmol) was added to a toluene solution (5 mL) of tetrahydropentacene **10a** (268 mg, 0.33 mmol). The mixture was stirred at 50 °C under N_2. After 2 h, the reaction mixture was purified by a flash chromatography (silica gel, $CHCl_3$ as eluent) to afford **13a** as a yellow solid (309 mg) in 90% yield of isolated product (100% NMR yield).

13a: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.43$ (s, 18H), 0.52 (s, 18H). 3.85 (s, 6H), 3.88 (s, 6H), 5.32 (s, 2H), 8.19 (s, 2H), 8.54 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 2.0$, 2.1, 52.6, 52.7, 55.9, 56.8, 114.1, 127.5, 127.7, 130.9, 131.9, 136.4, 136.7, 137.4, 137.5, 139.1, 139.4, 145.0, 169.9, 170.1, 178.8 ppm; HRMS (ESI) calcd for $C_{50}H_{54}Cl_2N_2NaO_{10}Si_4$ $[M+Na]^+$: 1047.2130. Found: 1047.2145.

*Preparation of 1,4,8,11-Tetrakis(trimethylsilyl)pentacene-2,3,9,10-tetracarboxylic Acid Tetramethyl Ester (**11a**) from **13a***

DDQ adduct **13a** (277 mg, 0.27 mmol) and γ-terpinene (2.2 mL, 13.5 mmol) were stirred in toluene (3 mL) at 100 °C under N_2. After 3 h, the reaction mixture was cooled to RT and purified by flash chromatography (silica gel, degassed $CHCl_3$ as eluent) under N_2 to afford **11a** as a blue solid (148 mg, 69 % yield, 82 % NMR yield).

11a: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.60$ (s, 36H), 3.91 (s, 12H), 8.92 (s, 2H), 9.08 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 2.2$, 52.5, 126.7, 129.5, 129.9, 133.0, 135.9, 139.7, 170.5 ppm; HRMS (FAB) calcd for $C_{42}H_{54}O_8Si_4$: 798.2896. Found: 798.2905.

*Preparation of 1,2,4,5-Tetra-hept-2-ynyl-benzene (**8b**) from **7***

8b (308 mg) was prepared in 68 % yield of isolated product from **7** (1.0 mmol) by the same method as described for **8a**.

8b: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.91$ (t, $J = 7.2$ Hz, 12H), 1.37–1.55 (m, 16H), 2.17–2.23 (m, 8H), 3.56 (t, $J = 2.4$ Hz, 8H), 7.47 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 13.6$, 18.6, 22.0, 22.5, 31.1, 77.0, 82.7, 129.2, 133.8 ppm; HRMS (EI) calcd for $C_{34}H_{46}$: 454.3599. Found: 454.3611.

*Preparation of Biszirconacycle (**9′b**) from **8b***

9′b (150 mg) was prepared in 79 % yield of isolated product (85 % NMR yield) from **8b** (1.0 mmol) by the same method as described for **3′**.

9′b: ^{1}H NMR (C_6D_6, Me_4Si): $\delta = 1.07$ (t, $J = 7.2$ Hz, 12H), 1.36–1.54 (m, 16H), 1.80 (s, 12H), 2.41–2.46 (m, 8H), 3.48 (s, 8H), 5.44–5.45 (t, $J = 2.8$ Hz, 8H), 5.92–5.94 (t, $J = 2.8$ Hz, 8H), 7.07 ppm (s, 2H); ^{13}C NMR (C_6D_6, Me_4Si): $\delta = 14.6$, 15.3, 24.2, 33.3, 34.0, 37.7, 105.2, 111.8, 123.6, 124.3, 128.3, 136.8, 186.1 ppm; HRMS (FAB) calcd for $C_{58}H_{74}Zr_2$: 950.3885. Found: 950.3877.

*Preparation of 1,4,8,11-Tetrabutyl-2,3,9,10-tetrakis(methoxycarbonyl)-5,7,12,14-tetrahydropentacene (**10b**) from **8b***

10b (310 mg) was prepared in 42 % isolated yield from **8b** (1.0 mmol) by the same method as described for **4**.

10b: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.98$ (t, $J = 7.2$ Hz, 12H), 1.41–1.58 (m, 16H), 2.74–2.80 (m, 8H), 3.84 (s, 12H), 3.92 (s, 8H), 7.27 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 13.9$, 23.0, 30.3, 32.6, 32.9, 52.2, 125.6, 130.2, 134.4, 135.6, 138.5, 169.5 ppm; HRMS (EI) calcd for $C_{46}H_{58}O_8$: 738.4132. Found: 738.4131.

*Preparation of DDQ Adduct of 1,4,8,11-Tetrabutylpentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (**13b**) from **10b***

13b (298 mg) was prepared in 93 % yield of isolated product (100 % NMR yield) from **10b** (1.0 mmol) by the same method as described for **13a**.

13b: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.99$ (t, $J = 4.8$ Hz, 6H), 1.00 (t, $J = 4.8$ Hz, 6H), 1.45–1.67 (m, 12H), 1.70–1.79 (m, 4H), 2.96–3.06 (m, 4H), 3.10–3.20 (m, 4H), 3.90 (s, 6H), 3.91 (s, 6H), 5.38 (s, 2H), 8.05 (s, 2H), 8.43 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 13.9$ (Two peaks were overlapped.), 23.1, 23.2, 30.0, 30.2, 33.6, 33.7, 52.5, 52.7, 56.0, 57.2, 114.0, 123.68, 123.72, 129.9, 130.3, 132.2, 132.3, 132.7, 133.2, 137.2, 137.3, 144.4, 168.9, 168.1, 179.0 ppm; HRMS (ESI) calcd for $C_{54}H_{55}Cl_2N_2O_{10}$ [M+H]: 961.3234. Found: 961.3256.

*Preparation of 1,4,8,11-Tetrabutyl-2,3,9,10-tetrakis(methoxycarbonyl)pentacene (**11b**) from **10b***

A mixture of tetrahydropentacene **10b** (148 mg, 0.2 mmol) and DDQ (2,3-dichloro-5,6- dicyanobenzoquinone, 91 mg, 0.4 mmol) was heated in degassed mesitylene (2 mL) for 3 h at 150 °C. After cooling to room temperature, the reaction mixture was purified by silica gel chromatography under N_2 (degassed $CHCl_3$ as eluent) to afford **11b** as a blue solid (52 mg) in 36 % yield of isolated product.

11b: M.p.: 232–235 °C (dec); ^{1}H NMR (1,2-[D_4]dichlorobenzene, Me_4Si): $\delta = 1.20$ (t, $J = 7.2$ Hz, 12H), 1.74–1.82 (m, 8H), 2.03–2.16 (m, 8H), 3.47–3.57 (m, 8H), 4.05 (s, 12H), 9.16 (s, 4H), 9.17 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 13.0$, 22.3, 29.2, 32.3, 51.3, 124.8, 125.9, 126.8, 129.0, 129.4, 136.9, 168.4 ppm; HRMS (ESI) calcd for $C_{46}H_{54}O_8Na$ [M+Na]$^+$: 757.3716. Found: 757.3731. elemental analysis: calcd (%) for $C_{46}H_{54}O_8$: C 75.18, H 7.41; found: C 75.04, H 7.66.

*Preparation of Pentacene Dimer (**12b**) from **10b***

12b (117 mg, 0.08 mmol) was prepared in 16 % yield of isolated product from **10b** (1.0 mmol) by the same method as described for **11b**.

12b: M.p.: 260–262 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 1.02$ (t, $J = 7.2$ Hz, 24H), 1.46–1.64 (m, 32H), 2.81–3.00 (m, 16H), 3.82 (s, 24H), 5.36 (s, 4H), 7.77 ppm (s, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 13.9$, 23.2, 29.9, 33.3, 52.1, 54.2, 123.5, 128.2, 131.2, 136.2, 141.2, 169.4 ppm; HRMS (ESI) calcd for $C_{92}H_{108}O_{16}Na$ [M+Na]$^+$: 1491.7535. Found: 1491.7540; elemental analysis: calcd (%) for $C_{92}H_{108}O_{16}$: C 75.18, H 7.41; found: C 74.94, H 7.13.

*Conversion of 1,4,8,11-Tetrabutyl-2,3,9,10-tetrakis(methoxycarbonyl)pentacene (**11b**) to Its Dimer (**12b**)*

A degassed dodecane (2 mL) solution of pentacene **11b** (73 mg, 0.1 mmol) was heated for 12 h at 150 °C. A white precipitate was observed during heating. After about 12 h, the blue color had disappeared completely. The reaction mixture was cooled to RT and purified by silica gel chromatography ($CHCl_3$ as eluent) to afford compound **12b** (65 mg) as a colorless solid in 90 % yield of isolated product.

*Conversion of 1,4,8,11-Tetrabutyl-2,3,9,10-tetrakis(methoxycarbonyl)pentacene Dimer (**12b**) to Its Monomer (**11b**)*

A degassed 1,2-[D_4]dichlorobenzene (0.5 mL) solution of pentacene dimer **12b** (5 mg) was heated for 6 h at 150 °C in the dark. The colour of the reaction mixture changed from colorless to blue. Pentacene monomer **11b** was formed in quantitative NMR yield.

*Preparation of Pentacene Dimer (**12a**) from **11a***

A degassed dodecane (2 mL) solution of pentacene **11a** (798 mg, 1.0 mmol) was heated for 3 d at 200 °C. Although formation of a white precipitate was observed, the blue color of **11a** remained. The reaction mixture was cooled to RT and purified by silica gel chromatography ($CHCl_3$ as eluent) to afford compound **12a** (320 mg) as a colorless solid in 40 % yield of isolated product.

12a: M.p.: > 300 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.35$ (s, 72H), 3.78 (s, 24H), 5.28 (s, 4H), 7.92 ppm (s, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 2.5$, 52.3, 54.2, 127.8, 135.4, 136.1, 138.1, 140.1, 170.5 ppm; HRMS (FAB) calcd for $C_{84}H_{108}O_{16}Si_8Na$ [M+Na]$^+$: 1619.5689. Found: 1619.5682; elemental analysis: calcd (%) for $C_{84}H_{108}O_{16}Si_8$: C 63.12, H 6.81; found: C 63.10, H 6.86.

*Preparation of 1,4,8,11-Tetrakis(trimethylsilyl)-5,7,12,14-tetrahydropentacene-2,3,9,10-tetracarboxylic Acid Tetraethyl Ester (**10c**) from **8a***

The compound **10c** (250 mg) was prepared by the same method as described for **4** in 30 % yield from **8a** (518 mg, 1.0 mmol).

10c: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.42$ (s, 36H), 1.33 (t, $J = 7.2$ Hz, 12H), 3.96 (s, 8H), 4.24 (q, $J = 7.2$ Hz, 8H), 7.17 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 1.9$, 13.8, 38.2, 61.5, 124.1, 135.5, 135.6, 135.8, 145.8, 170.1 ppm; HRMS (ESI) calcd for $C_{46}H_{66}O_8Si_4Na$ [M+Na]$^+$: 881.3732. Found: 881.3705.

*Preparation of 1,4,8,11-Tetrakis(trimethylsilyl)pentacene-2,3,9,10-tetracarboxylic Acid Tetraethyl Ester (**11c**) from **10c***

Tetrahydropentacene **10c** (858 mg, 1.00 mmol) was treated with DDQ by the same way as described for **13a** to afford the corresponding DDQ adduct **13c** (1.00 g) in 93 % yield of isolated product.

13c: ^{1}H NMR ($CDCl_3$, Me_4Si): $\delta = 0.44$ (s, 18H), 0.53 (s, 18H), 1.36 (t, $J = 7.2$ Hz, 6H), 1.38 (t, $J = 7.2$ Hz, 6H), 4.26–4.34 (m, 8H), 5.29 (s, 2H), 8.19 (s, 2H), 8.53 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): $\delta = 2.1$, 2.2, 13.72, 13.76, 55.9, 56.9, 61.9, 62.1, 114.3, 127.4, 127.6, 130.9, 131.9, 136.3, 136.6, 137.6, 137.7, 138.8, 139.0, 144.7, 169.5, 169.7, 179.0 ppm.

DDQ adduct **13c** (1.08 g, 1.0 mmol) was treated with γ-terpinene by the same method as described for **11a** to afford pentacene **11c** (589 mg) in 69% yield of isolated product.

11c: M.p.: >300 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.62 (s, 36H), 1.43 (t, J = 7.2 Hz, 12H), 4.35 (t, J = 7.2 Hz, 8H), 8.92 (s, 2H), 9.08 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 2.3, 13.9, 61.8, 126.6, 129.5, 129.8, 133.0, 136.2, 139.3, 170.1 ppm; HRMS (EI) calcd for $C_{46}H_{62}O_8Si_4$: 854.3522. Found: 854.3510; elemental analysis: calcd (%) for $C_{46}H_{62}O_8Si_4$: C 64.59, H 7.31; found: C 64.73, H 7.20.

*Preparation of 5,7,12,14-Tetrahydropentacene-2,3,9,10-tetracarboxylic Acid Tetramethyl Ester (**14**) from **10a***

To a solution of 1,4,8,11-tetrakis(trimethylsilyl)-5,7,12,14-tetrahydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester **10a** (802 mg, 1.0 mmol) in 15 mL of THF was added tetrabutylammonium fluoride (1.0 M THF solution, 4.0 mL, 4.0 mmol) at 0 °C, and the mixture was stirred for 1 h. The mixture was then quenched with 3 M HCl at 0 °C 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 flash chromatography (silica gel, $CHCl_3$ as eluent) to afford **14.** **14** was obtained as a pale-yellow solid (386 mg, 75% yield) by washing with methanol (3 mL).

14: ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 3.90 (s, 12H), 3.97 (s, 8H), 7.22 (s, 2H), 7.65 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 35.5, 52.6, 126.5, 128.1, 129.8, 133.4, 140.2, 168.2 ppm; HRMS (EI) calcd for $C_{30}H_{26}O_8$: 514.1627. Found: 514.1613.

*Preparation of DDQ Adduct of 2,3,9,10-Tetracarboxylic Acid Tetramethyl Ester Pentacene (**13d**) from **14***

The compound **13d** (555 mg) was prepared by the same method as described for **13a** in 90% yield (100% NMR yield) from **14** (514 mg, 1.0 mmol).

13d: ^{1}H NMR ($CDCl_3$, 323 K, Me_4Si): δ = 3.94 (s, 6H), 3.96 (s, 6H), 5.32 (s, 2H), 7.85 (s, 2H), 8.19 (s, 4H), 8.30 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, 323 K, Me_4Si): δ = 52.81, 52.89, 55.4, 56.9, 113.9, 126.66, 126.74, 129.9, 130.3, 130.4, 130.8, 133.1, 133.4, 133.7, 134.5, 144.9, 167.2, 167.5, 178.5 ppm; HRMS (ESI) calcd for $C_{38}H_{22}Cl_2N_2NaO_{10}$ $[M+Na]^+$: 759.0549. Found: 759.0574.

*Preparation of 2,3,9,10-Tetracarboxylic Acid Tetramethyl Ester Pentacene (**11d**) from **13d***

The compound **11d** (367 mg) was prepared by the same method as described for **11a** in 72% yield from **13d** (736 mg, 1.0 mmol).

11d: M.p.: >300 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 3.99 (s, 12H), 8.36 (s, 4H), 8.72 (s, 4H), 8.98 ppm (s, 2H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 52.7, 127.7, 128.2, 129.0, 130.2, 131.0, 132.0, 167.9 ppm; HRMS (EI) calcd for $C_{30}H_{22}O_8$: 510.1315. Found: 510.1328; elemental analysis: calcd (%) for $C_{30}H_{22}O_8$: C 70.58, H 4.34; found: C 70.53, H 4.04.

*Preparation of Pentacene Dimer (**12d**) from **11d***

12d (490 mg) was prepared in 96% yield of isolated product from **11d** (510 mg, 1.0 mmol) by the same method as described for **12a**.

12d: M.p.: >300 °C; ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 3.87 (s, 24H), 5.21 (s, 4H), 7.52 (s, 8H), 7.94 ppm (s, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 52.6, 53.5, 126.6, 128.4, 129.5, 132.1, 142.1, 168.0 ppm; HRMS (FAB) calcd for $C_{60}H_{44}O_{16}Na$ $[M+Na]^+$: 1043.2527. Found: 1043.2521; elemental analysis: calcd (%) for $C_{60}H_{44}O_{16}$: C 70.58, H 4.34; found: C 70.53, H 4.48.

*Preparation of 5,7,12,14-Tetrahydropentacene-2,3,9,10-tetracarboxylic Acid (**15**) from **14***

2,3,9,10-Tetrakis(methoxycarbonyl)-5,7,12,14-tetrahydropentacene **14** (514 mg, 1.0 mmol) and lithium iodide (4.0 g, 30.0 mmol) were added to 40 mL 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 M HCl and extracted with $CHCl_3$. After removal of the solvent, the residue was dissolved in 3 mL of $CHCl_3$ and added to 10 mL of MeOH. The resulting precipitate was collected by filtration, and dried in vacuo to afford **15** as a pale-yellow solid (389 mg, 85% yield).

15: ^{1}H NMR ([D_6]DMSO, Me_4Si): δ = 3.97 (s, 8H), 7.26 (s, 2H), 7.63 ppm (s, 4H); ^{13}C NMR ([D_6]DMSO, Me_4Si): δ = 34.6, 126.2, 127.3, 130.7, 133.5, 139.8, 168.7 ppm; HRMS (FAB, negative) calcd for $C_{26}H_{17}O_8$ $[M-H]$: 457.0923. Found: 457.0917.

*Preparation of 5,7,12,14-Tetrahydropentacene Diimide (**16**) from **15***

Tetraacid **15** (457 mg, 1.0 mmol) was heated in acetic anhydride (10 mL) at 140 °C for 3 h. After cooling to RT, the solvent was removed in vacuo. The corresponding dianhydride (450 mg) was obtained in quantitative yield. In a 50 mL flask fitted with a water separator and a refluxing condenser were placed anhydride, 2-ethylhexylamine (1.62 mL, 10.0 mmol) and toluene (20 mL). The flask was heated to maintain a vigorous reflux for 6 h. After cooling to RT, the mixture was washed with aqueous 3 M HCl, saturated aqueous $NaHCO_3$ solution, and brine, then dried over Na_2SO_4. After evaporation of the solvent, the resulting residue was purified by flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the **16** as a pale-yellow solid (515 mg, 80% yield).

16: ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 0.87 (t, J = 7.2 Hz, 6H), 0.90 (t, J = 7.2 Hz, 6H), 1.21–1.38 (m, 16H), 1.80–1.86 (m, 2H), 3.54 (d, J = 7.2 Hz, 4H), 4.05 (s, 8H), 7.28 (s, 2H), 7.73 ppm (s, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 10.4, 14.0, 22.9, 23.8, 28.5, 30.5, 36.5, 38.2, 41.9, 122.2, 126.3, 130.4, 133.6, 143.6, 168.8 ppm; HRMS (FAB) calcd for $C_{42}H_{49}O_4N_2$ $[M+H]$: 645.3692. Found: 645.3681.

*Preparation of DDQ Adduct of Pentacene Diimide (**13e**) from **16***

The compound **13e** (780 mg) was prepared by the same method as described for **13a** (90% yield, 100% NMR yield) from **16** (644 mg, 1.0 mmol).

13e: ^{1}H NMR ($CDCl_3$, 323 K, Me_4Si): δ = 0.87 (t, J = 7.2 Hz, 3H), 0.88 (t, J = 7.2 Hz, 3H), 0.93 (t, J = 7.2 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H), 1.19–1.62 (m, 16H), 1.51–1.62 (m, 1H), 1.84–1.94 (m, 1H), 3.64 (d, J = 7.2 Hz, 2H), 3.67 (d, J = 7.2 Hz, 2H), 5.41 (s, 2H), 8.01 (s, 2H), 8.29 (s, 2H), 8.36 (s, 2H), 8.41 ppm (s, 2H). ^{13}C NMR ($CDCl_3$, 323 K, Me_4Si): δ = 10.4, 10.5, 13.9 (2 C), 23.0 (2 C), 24.07, 24.15, 28.58, 28.61, 30.7, 30.8, 38.4, 38.5, 42.57, 42.59, 55.2, 56.8, 113.8, 124.2, 124.6, 128.1, 128.2, 129.8, 130.2, 134.2, 134.9, 135.4, 135.7, 145.0, 167.4, 167.7, 178.2 ppm; HRMS (ESI) calcd for $C_{50}H_{45}Cl_2N_4O_6$ $[M+H]$: 867.2716. Found: 867.2732.

*Preparation of Pentacene Diimide(**17**) from **13e***

The compound **17** (422 mg) was prepared by the same method as described for **11a** (66% yield) from **13e** (866 mg, 1.0 mmol).

17: M.p.: >300 °C; ^{1}H NMR (1,1,2,2-[D_2]tetrachloroethane, 419 K, Me_4Si): δ = 0.99 (t, J = 6.8 Hz, 6H), 1.06 (t, J = 7.2 Hz, 6H), 1.33–1.58 (m, 16H), 1.99–2.10 (m, 2H), 3.77 (d, J = 7.2 Hz, 4H), 8.50 (s, 4H), 8.94 (s, 4H), 9.11 ppm (s, 2H); ^{13}C NMR (1,1,2,2-[D_2]tetrachloroethane, 419 K, Me_4Si): δ = 10.6, 13.6, 22.8, 24.7, 28.8, 31.3, 38.8, 42.9, 125.9, 127.4, 128.5, 131.1, 131.5, 132.1, 167.3 ppm; HRMS (FAB) calcd for $C_{42}H_{45}N_2O_4$ $[M+H]$: 641.3379. Found: 641.3364; elemental analysis: calcd (%) for $C_{42}H_{44}N_2O_4$: C 78.72, H 6.92, N 4.37; found: C 78.61, H 7.04, N 4.28.

[1] a) D. J. Gundlach, Y.-Y. Lin, T. N. Jackson, S. F. Nelson, D. G. Schlom, *IEEE Electron Device Lett.* **1997**, *18*, 87; b) Y.-Y. Lin, D. J. Gundlach, S. F. Nelson, T. N. Jackson, *IEEE Electron Device Lett.* **1997**, *18*, 606; c) Y.-Y. Lin, D. J. Gundlach, S. F. Nelson, T. N. Jackson, *IEEE Trans. Electron Devices* **1997**, *44*, 1325; d) S. F. Nelson, Y.-Y. Lin, D. J. Gundlach, T. N. Jackson, *Appl. Phys. Lett.* **1998**, *72*, 1854.

[2] a) T. Takahashi, M. Kitamura, B. Shen, K. Nakajima, *J. Am. Chem. Soc.* **2000**, *122*, 12876; b) T. Takahashi, S. Li, W. Huang, F. Kong, K. Nakajima, B. Shen, T. Ohe, K. Kanno, *J. Org. Chem.* **2006**, *71*, 7967; c) S, Li, L. Zhou, Z. Song, F. Bao, K. Kanno, T. Takahashi, *Heterocycles* **2007**, *73*, 519; d) T. Takahashi, Y. Li, J. Hu, F. Kong, K. Nakajima, L. Zhou, K. Kanno, *Tetrahedron Lett.* **2007**, *48*, 6726.

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[3] T. Takahashi, K. Kashima, S. Li, K. Nakajima, K. Kanno, *J. Am. Chem. Soc.* **2007**, *129*, 15752.
[4] a) T. Takahashi, Z.-P. Li, *Jpn. Kokai Tokkyo Koho* **2004**, JP2004-331534. Experimental detail in English is also available through SciFinder. See Patent & Utility Model Gazette Data Base of National Center for Industrial Property Information and Training, Japan (website: http://www.inpit.go.jp/english/index.html); b) M. T. Stone, H. L. Anderson, *J. Org. Chem.* **2007**, *72*, 9776.
[5] S. Inaba, R. M. Wehmeyer, M. W. Forkner, R. D. Rieke, *J. Org. Chem.* **1988**, *53*, 339.
[6] V. Gopalsamuthiram, W. D. Wulff, *J. Am. Chem. Soc.* **2004**, *126*, 13936.
[7] X. Zhou, M. Kitamura, B. Shen, K. Nakajima, T. Takahashi, *Chem. Lett.* **2004**, *33*, 410.
[8] F. Mohamadi, M. M. Spees, *Organometallics* **1992**, *11*, 1398.
[9] F. Elsinger, J. Schreiber, A. Eschenmoser, *Helv. Chim. Acta.* **1960**, *43*, 113.
[10] a) S. H. Chan, H. K. Lee, Y. M. Wang, N. Y. Fu, X. M. Chen, Z. W. Cai, H. N. C. Wong, *Chem. Commun.* **2005**, 66; b) C. P. Benard, Z. Geng, M. A. Heuft, K. Vancrey, A. G. Fallis, *J. Org. Chem.* **2007**, *72*, 7229.
[11] A. D. Thomas, L. L. Miller, *J. Org. Chem.* **1986**, *51*, 4160.

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