JOC The Journal of Organic Chemistry

Article

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Dehydro Side Coupling of Substituted Pentacene Derivatives

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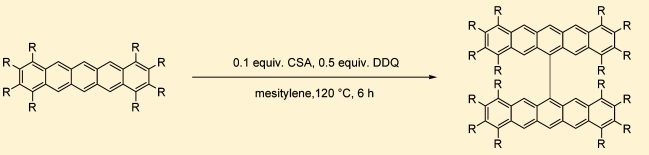
Supporting Information

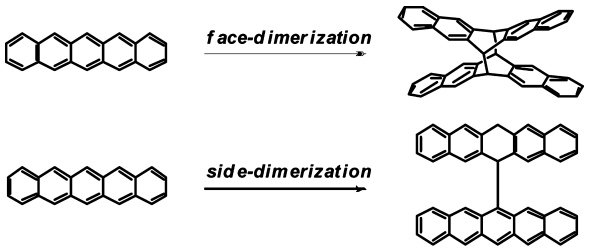
ABSTRACT: 1,2,3,4,8,9,10,11-Octaalkylpentacenes were synthesized in high yields from tetrahydropentacenes by the pentacene−DDQ adduct method in the presence of amine. Dehydro side-coupling reactions of pentacene derivatives proceeded to give the corresponding 6,6′-dipentacenyl derivatives in high yields in the presence of a catalytic amount of CSA and 0.5 equiv of DDQ. The structures of dehydro side-coupling products of substituted pentacenes were determined by NMR and X-ray analysis. The combination of acid and DDQ was necessary for the dehydro side coupling of substituted pentacenes.



INTRODUCTION

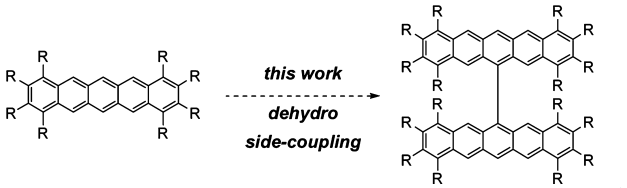
Substituted pentacenes have attracted much attention, since pentacene has been found to be useful in organic electronic materials such as semiconductors.[1,2] In the dimerization reactions of pentacenes, there are formally two modes, face dimerization and side dimerization, as shown in Scheme 1.

Scheme 1. Two Modes of Pentacene Dimerization: Face Dimerization and Side Dimerization



Several examples of face dimerization of pentacene derivatives have been reported, and the face dimers were fully characterized.[3] In contrast, side-dimer products have not been isolated, to the best of our knowledge.[4] In this paper, we report the synthesis of 1,2,3,4,8,9,10,11-octaalkylpentacenes and their dehydro side-coupling reactions (Scheme 2).

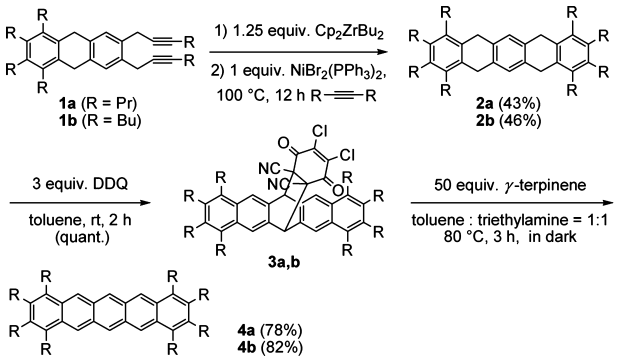
Scheme 2. Dehydro Side Coupling of Substituted Pentacene Derivatives



RESULTS AND DISCUSSION

We have developed a systematic preparative method of substituted pentacene derivatives.[5] 1,2,3,4,8,9,10,11-Octaalkylpentacenes **4** were successfully synthesized from diynes **1** by our homologation method (Scheme 3). The zirconium-mediated cyclization of diynes **1a**,**b** with 4-octyne or 5-decyne proceeded in the presence of $NiBr_2(PPh_3)_2$ to give tetrahydropentacene derivatives **2a**,**b** in 43% and 46% yields, respectively.[6] Tetrahydropentacenes **2a**,**b** reacted with an excess of DDQ (2,3-dichloro-5,6-dicyanobenzoquinone, 3 equiv) at room temperature to give their Diels−Alder adducts **3a**,**b** in quantitative yields. To remove DDQ from **3a**,**b**, the reaction mixture was treated with 50 equiv of γ-terpinene and then heated to 80 °C in the presence of triethylamine to induce the retro-Diels−Alder reaction.[7] Finally, pentacenes **4a**,**b** were obtained as stable purple solids under nitrogen in 78% and 82% yields, respectively. They were soluble in organic solvents such as toluene and chloroform.

Scheme 3. Synthesis of Pentacene Derivatives 4



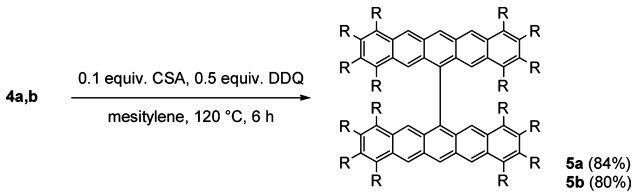
Received: August 21, 2011
Published: October 28, 2011

dx.doi.org/10.1021/jo201659q | J. Org. Chem. 2011, 76, 9983–9987

The ^{1}H NMR of pentacene **4a** recorded in $CDCl_3$ clearly showed two characteristic singlet signals at 8.76 and 8.94 ppm assignable to four protons of the second aromatic rings from both ends and two protons of the central aromatic ring in the pentacene skeleton, respectively. In its ^{13}C NMR spectrum, six sp^2 carbons of the pentacene ring were observed in the range 122.6−136.1 ppm.

Interestingly, the dehydro side coupling of pentacene derivatives **4** occurred by heating **4** with DDQ (0.5 equiv) and a catalytic amount of acid to give the corresponding 6,6′-dipentacenyl derivatives **5** in high yields (Scheme 4).

Scheme 4. Synthesis of Side-Coupling Products 5 from 4

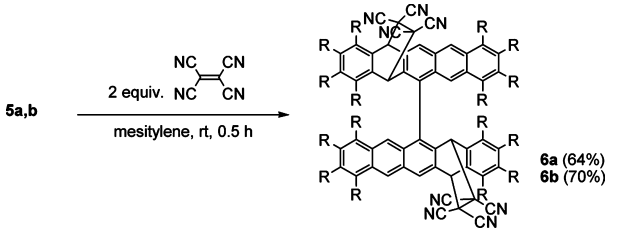


Pentacenes **4a,b** were heated with 0.1 equiv of (±)-10-camphorsulfonic acid (CSA) and 0.5 equiv of DDQ in mesitylene at 120 °C for around 6 h. Monitoring the mixture by ^{1}H NMR revealed that **4a,b** gradually disappeared and side-coupling products **5a,b** were formed, increasing to 84% and 80% yields, respectively. The compounds **5** were stable blue solids under nitrogen and have much lower solubility than the corresponding pentacene derivatives **4** in toluene and chloroform.[8]

The ^{1}H NMR spectrum of **5a** recorded in DMSO-d_6 at 150 °C showed three characteristic singlet signals at 7.92, 9.03, and 9.43 ppm assignable to protons attached to C3, C21, C25, and C43, protons attached to C10, C14, C32, and C36, and protons attached to C12 and C34 of pentacene rings in **5a**, respectively. Also, 12 sp^2 carbons appeared from 120.9 to 135.3 ppm in the ^{13}C NMR spectrum of **5a**.[8]

Compounds **5a,b** reacted with 2 equiv of tetracyanoethylene (TCNE) at room temperature to give the corresponding Diels−Alder adducts **6a,b** with high selectivity in 64% and 70% yields, respectively (Scheme 5). The X-ray crystal structure of

Scheme 5. Synthesis of TCNE Adducts 6



6a showed a σ bond connecting the central rings of two pentacene units. The tetracyanoethylenes were attached on the second ring of pentacene units of the 6,6′-dipentacenyl type dimer from different ends but the same side (Figure 1).

The side-coupling products **5** also could be directly synthesized from tetrahydropentacenes **2** in high yields (Scheme 6). Tetrahydropentacenes **2a,b** were treated with 2.5 equiv of DDQ in mesitylene at 120 °C. After around 6 h, the side-coupling products **5a,b** were obtained as single products in 82% and 76% yields instead of pentacenes **4a,b**, respectively. This result indicated that the hydroquinone derivative DDQ-H_2, which was formed in situ from DDQ, played the same role as the acid in the dehydro side-coupling reaction of pentacenes **4**.

In order to elucidate the factors which control the side coupling of pentacenes, the following reactions were carried out.[9] Without addition of a catalytic amount of CSA, pentacene derivative **4a** was treated with 0.5 equiv of DDQ in mesitylene at 120 °C for 6 h. Only its DDQ adduct **3a** was formed in 49% yield along with the recovery of unreacted **4a** in 51% yield. Side-coupling product **5a** was not observed. Without the presence of DDQ (0.5 equiv), pentacene derivative **4a** was heated with 0.1 equiv of CSA under the same conditions. The side-coupling product **5a** was also not obtained, but further reaction products were detected.[10]

EXPERIMENTAL SECTION

General Experimental Methods. All reactions including air- and moisture-sensitive materials were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and toluene were distilled from sodium benzophenone ketyl under nitrogen. 6,7-Di-2-hexynyl-1,2,3,4-tetrapropyl-9,10-dihydroanthracene (**1a**) and 6,7-dihex-2-ynyl-1,2,3,4-tetrabutyl-9,10-dihydroanthracene (**1b**) were prepared according to the literature procedure.[5b] All other reagents were commercially available and were used as received.

Preparation of 1,2,3,4,8,9,10,11-Octapropyl-5,7,12,14-tetrahydropentacene (2a) from 1a. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in 10 mL of toluene was added *n*-BuLi (1.56 M hexane solution, 1.60 mL, 2.50 mmol) at −78 °C, and the mixture was stirred for 1 h. Diyne **1a** (508 mg, 1.0 mmol) was added to the solution, and the mixture was warmed to room temperature by removal of the cooling bath. After the mixture was stirred for 3 h, $NiBr_2(PPh_3)_2$ (743 mg, 1.0 mmol) and 4-octyne (0.29 mL, 2.0 mmol) were added to it. After it was stirred for 12 h at 100 °C, the mixture was quenched with 3 M HCl at 0 °C and extracted with ethyl acetate. The combined organic phase was washed with water and saturated aqueous $NaHCO_3$ solution. The organic phase was added to a 30% aqueous solution of H_2O_2 and stirred for about 1 h to oxidize PPh_3. The organic phase was separated, washed with brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the resulting brown viscous oil was purified by flash chromatography (silica gel, hexane:toluene 50:1 as eluent) to afford the title compound (266 mg, 43% isolated yield) as a colorless solid. **2a**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.04 (t, J = 7.2 Hz, 12 H), 1.10 (t, J = 7.2 Hz, 12 H), 1.43−1.61 (m, 16 H), 2.52−2.56 (m, 8 H), 2.66−2.70 (m, 8 H), 3.85 (s, 8 H), 7.23 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.9, 15.1, 24.3, 25.1, 32.0, 32.3, 33.0, 125.3, 133.5, 135.3, 135.5, 136.4; HRMS (EI; m/z) calcd for $C_{46}H_{66}$ 618.5164, found 618.5158.

Preparation of 1,2,3,4,8,9,10,11-Octapropylpentacene (4a) from 2a via the Pentacene−DDQ Adduct 3a. In a 20 mL Schlenk tube, tetrahydropentacene **2a** (62 mg, 0.10 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (69 mg, 0.30 mmol) were dissolved in degassed toluene (3 mL). Under a nitrogen atmosphere, the mixture was stirred for 2 h at room temperature. The pentacene−DDQ adduct **3a** was formed in quantitative yield and could be isolated by silica gel flash chromatography (silica gel, hexane:ethyl acetate 10:1 as eluent) to afford the adduct **3a** (79 mg, 94% isolated yield) as a red solid. Without isolation of pentacene−DDQ adduct **3a**, γ-terpinene (0.80 mL, 5.0 mmol) was first added into the reaction solution. Next, triethylamine (3 mL) was added to consume the formed hydroquinone. After the formed precipitate was removed, the clean filtrate was degassed by three freeze−pump−thaw cycles and heated at 80 °C for about 3 h in the dark. After the mixture was cooled to room temperature, the solvent was removed in vacuo. Degassed MeOH (10 mL) was added to the resulting residue. The mixture was stirred for 10 min to produce a purple-blue precipitate of pentacene derivative **4a** (48 mg, 78% isolated yield), which was collected by filtration. **3a**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.08 (t, J = 7.2 Hz, 6 H), 1.11 (t, J = 7.2 Hz,

dx.doi.org/10.1021/jo201659q | J. Org. Chem. 2011, 76, 9983−9987

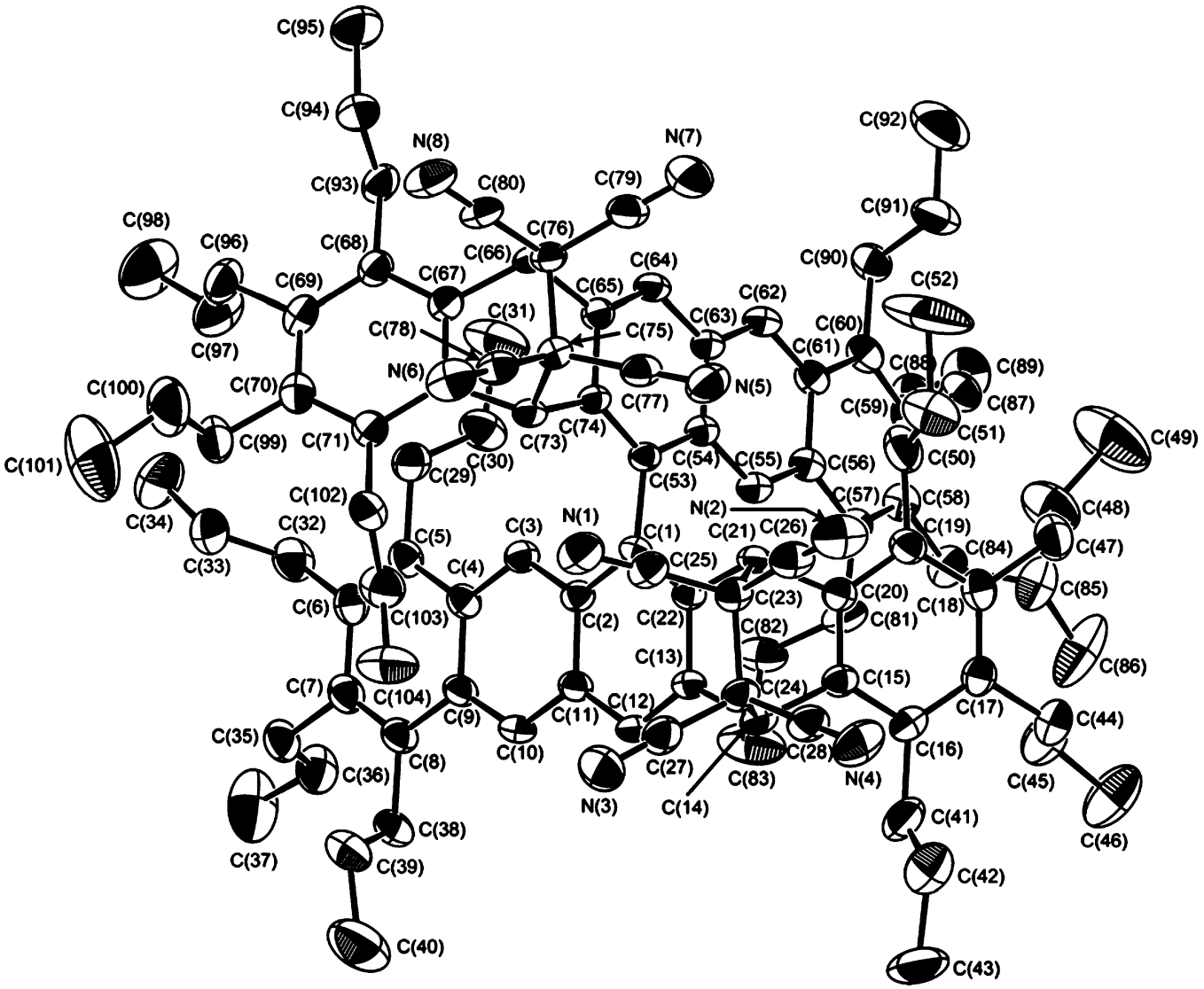
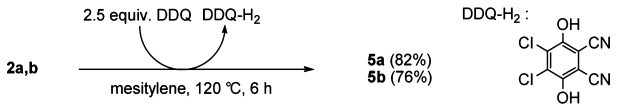


Figure 1. Crystal structure of **6a**.

Scheme 6. Synthesis of Side-Coupling Products 5 from 2



6 H), 1.13 (t, J = 7.2 Hz, 6 H), 1.17 (t, J = 7.2 Hz, 6 H), 1.47−1.80 (m, 16 H), 2.68−2.77 (m, 8 H), 2.88−2.99 (m, 4 H), 3.01−3.12 (m, 4 H), 5.25 (s, 2 H), 7.87 (s, 2 H), 8.24 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.8, 14.9, 15.0, 15.1, 24.6, 24.7, 24.8 (2 C), 31.2, 31.5, 32.6, 32.7, 56.7, 57.8, 114.6, 122.3, 122.7, 129.4, 130.7, 130.8, 131.2, 134.66, 134.69, 138.6, 139.2, 142.7, 179.8; HRMS (ESI; m/z) calcd for $C_{54}H_{62}Cl_2N_2O_2Na$ (M + Na^+): 863.4086, found 863.4107. **4a**: mp 172−173 °C dec; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.13 (t, J = 7.2 Hz, 12 H), 1.23 (t, J = 7.2 Hz, 12 H), 1.62−1.66 (m, 8 H), 1.82−1.86 (m, 8 H), 2.74−2.77 (m, 8 H), 3.15−3.17 (m, 8 H), 8.76 (s, 4 H), 8.94 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 15.1 (2 C), 24.3, 24.8, 31.6, 32.8, 122.6, 125.8, 129.6, 130.3, 133.2, 136.1; HRMS (EI; m/z) calcd for $C_{46}H_{62}$ 614.4852, found 614.4851. Anal. Calcd for $C_{46}H_{62}$: C, 89.84; H, 10.16. Found: C, 89.96; H, 10.10.

Preparation of 1,2,3,4,8,9,10,11,1′,2′,3′,4′,8′,9′,10′,11′-Hexadecapropyl[6,6′]bipentacenyl (5a) from 4a. In a 20 mL Schlenk tube, pentacene derivative **4a** (62 mg, 0.10 mmol), 2,3-dichloro-5,6-dicyanobenzoquinone (11.4 mg, 0.05 mmol), and CSA (2.3 mg, 0.01 mmol) were dissolved in degassed mesitylene (5 mL). Under a nitrogen atmosphere, the mixture was stirred for 6 h at 120 °C. After the mixture was cooled to room temperature, the solvent was removed in vacuo. Degassed MeOH (10 mL) was added to the resulting residue. The mixture was stirred for 10 min to produce a blue precipitate of the side-coupling product **5a** (52 mg, 84% isolated yield), which was collected by filtration. **5a**: mp 196−197 °C dec; ^{1}H NMR (DMSO-d_6, Me_4Si, 423 K) δ −0.11 (t, J = 7.2 Hz, 12 H), 0.53−0.65 (m, 8 H), 0.88 (t, J = 7.2 Hz, 12 H), 1.04 (t, J = 7.2 Hz, 12 H), 1.24 (t, J = 7.2 Hz, 12 H), 1.29−1.40 (m, 8 H), 1.48−1.60 (m, 8 H), 1.83−1.93 (m, 8 H), 2.09−2.17 (m, 8 H), 2.50−2.54 (m, 8 H), 2.71−2.80 (m, 8 H), 3.21−3.30 (m, 8 H), 7.92 (s, 4 H), 9.03 (s, 4 H), 9.43 (s, 2 H); ^{13}C NMR (DMSO-d_6, Me_4Si, 423 K) δ 12.1, 13.0, 13.2, 13.4, 21.9, 23.0, 23.2, 23.3, 29.8, 30.0, 31.0, 31.2, 120.9, 122.1, 126.0, 128.5, 128.8, 129.3, 129.4, 131.6, 132.1, 132.2, 135.1, 135.3; HRMS (FAB; m/z) calcd for $C_{92}H_{122}$ 1226.9546, found 1226.9552. Anal. Calcd for $C_{92}H_{122}$: C, 89.99; H, 10.01. Found: C, 89.89; H, 10.09.

Preparation of 1,2,3,4,8,9,10,11,1′,2′,3′,4′,8′,9′,10′,11′-Hexadecapropyl[6,6′]bipentacenyl (5a) from 2a. In a 20 mL Schlenk tube, tetrahydropentacene **2a** (62 mg, 0.10 mmol) and 2,3-dichloro-5,6-dicyanobenzoquinone (57 mg, 0.25 mmol) were dissolved in mesitylene (3 mL) and degassed by three freeze−pump−thaw cycles. Under a nitrogen atmosphere, the mixture was stirred for 6 h at 120 °C. After the mixture was cooled to room temperature, the

dx.doi.org/10.1021/jo201659q | J. Org. Chem. 2011, 76, 9983−9987

solvent was removed in vacuo. Degassed MeOH (10 mL) was added to the resulting residue. The mixture was stirred for 10 min to produce a blue precipitate of the title compound (50 mg, 82% isolated yield), which was collected by filtration.

Preparation of TCNE Adduct 6a from 5a. In a 20 mL Schlenk tube, tetracyanoethylene (26 mg, 0.20 mmol) was added to a degassed toluene solution (3 mL) of compound **5a** (62 mg, 0.10 mmol) under a nitrogen atmosphere. The mixture was stirred at room temperature. The blue color disappeared gradually after around $^1/_2$ h. Then the reaction mixture was purified by flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the title compound as a yellow solid (56 mg, 64% isolated yield, 86% NMR yield). **6a**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.27 to −0.18 (m, 2 H), −0.11 (t, J = 7.2 Hz, 6 H), 0.33 (t, J = 7.2 Hz, 6 H), 3.31−0.36 (m, 4 H), 0.48−0.56 (m, 2 H), 0.65 (t, J = 7.2 Hz, 6 H), 0.81−0.90 (m, 4 H), 0.96 (t, J = 7.2 Hz, 6 H), 1.05 (t, J = 7.2 Hz, 6 H), 1.06 (t, J = 7.2 Hz, 6 H), 1.16 (t, J = 7.2 Hz, 6 H), 1.19−1.37 (m, 10 H), 1.27 (t, J = 7.2 Hz, 6 H), 1.44−1.54 (m, 8 H), 1.65−1.78 (m, 8 H), 1.87−1.92 (m, 2 H), 2.05−2.10 (m, 2 H), 2.14−2.19 (m, 2 H), 2.33−2.38 (m, 4 H), 2.50−2.56 (m, 4 H), 2.57−2.62 (m, 2 H), 2.65−2.70 (m, 2 H), 2.82−2.87 (m, 2 H), 2.90−2.95 (m, 2 H), 3.06−3.11 (m, 2 H), 3.14−3.19 (m, 2 H), 5.54 (s, 2 H), 5.91 (s, 2 H), 6.71 (s, 2 H), 8.43 (s, 2 H), 8.62 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9, 14.2, 14.67, 14.74, 14.87, 14.91, 14.94, 15.0, 23.1, 23.3, 24.2, 24.3, 24.4, 24.7, 24.9, 25.6, 30.4, 30.7, 31.0, 31.4, 31.8, 31.9, 32.65, 32.68, 45.8, 47.1, 47.2, 49.8, 110.3, 110.9, 112.1, 114.0, 122.6, 123.8, 127.9, 128.0, 129.1, 129.2, 129.7, 130.78, 130.82, 130.9, 131.8, 131.9, 133.3, 133.5, 135.9, 137.2, 137.3, 137.9, 140.5, 141.4; HRMS (FAB; m/z) calcd for $C_{104}H_{122}N_8$ 1482.9792, found 1482.9807.

Preparation of 1,2,3,4,8,9,10,11-Octabutyl-5,7,12,14-tetrahydropentacene (2b) from 1b. The title compound (336 mg) was prepared in the same way as described for **2a** in 46% yield from **1b** (592 mg, 1.0 mmol). **2b**: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.98 (t, J = 7.2 Hz, 12 H), 1.02 (t, J = 7.2 Hz, 12 H), 1.46−1.58 (m, 32 H), 2.53−2.57 (m, 8 H), 2.68−2.71 (m, 8 H), 3.86 (s, 8 H), 7.22 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9, 14.0, 23.4, 23.5, 29.3, 29.4, 32.9, 33.1, 33.9, 125.3, 133.3, 135.3, 135.5, 136.4; HRMS (FAB; m/z) calcd for $C_{54}H_{82}Na$ (M + Na^+) 753.6314, found 753.6313.

Preparation of 1,2,3,4,8,9,10,11-Octabutylpentacene (4b) from 2b via the Pentacene−DDQ Adduct 3b. The title compound (595 mg) was prepared in the same way as described for **4a** in 82% yield from **2b** (730 mg, 1.0 mmol). **3b**: yellow solid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.01 (t, J = 7.2 Hz, 6 H), 1.03 (t, J = 7.2 Hz, 6 H), 1.05 (t, J = 7.2 Hz, 6 H), 1.05 (t, J = 7.2 Hz, 6 H), 1.46−1.75 (m, 32 H), 2.68−2.78 (m, 8 H), 2.93−2.99 (m, 4 H), 3.04−3.14 (m, 4 H), 5.26 (s, 2 H), 7.88 (s, 2 H), 8.25 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 13.9 (2 C), 14.07, 14.09, 23.4, 23.51 (2 C), 23.54, 28.7, 28.9, 29.97, 30.01, 33.49, 33.53 (2 C), 33.73, 56.70, 57.74, 114.5, 122.2, 122.6, 129.4, 130.7, 130.8, 131.2, 134.71, 137.73, 138.5, 139.1, 143.7, 179.8; HRMS (ESI; m/z) calcd for $C_{62}H_{78}Cl_2N_2O_2Na$ (M + Na^+) 975.5338, found 975.5331. **4b**: blue solid; mp 168−169 °C dec; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.05 (t, J = 7.2 Hz, 12 H), 1.11 (t, J = 7.2 Hz, 12 H), 1.53−1.82 (m, 32 H), 2.76−2.79 (m, 8 H), 3.17−3.20 (m, 8 H), 8.77 (s, 4 H), 8.94 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 14.0, 14.2, 23.6, 23.7, 29.0, 30.1, 33.1, 33.6, 122.5, 125.7, 129.6, 130.3, 133.2, 136.1; HRMS (EI; m/z) calcd for $C_{54}H_{78}$ 726.6104, found 726.6099. Anal. Calcd for $C_{54}H_{78}$: C, 89.19; H, 10.81. Found: C, 89.24; H, 10.66.

Preparation of 1,2,3,4,8,9,10,11,1′,2′,3′,4′,8′,9′,10′,11′-Hexadecabutyl[6,6′]bipentacenyl (5b) from 4b. The title compound (158 mg) was prepared in the same way as described for **5a** in 80% yield from **4b** (200 mg, 0.27 mmol). The title product **5b** could also be synthesized from **2b** in 76% yield in the same way as desired for **5a** from **2a**. **5b**: mp 176−177 °C dec; ^{1}H NMR (C_6D_6, Me_4Si, 352 K) δ 0.17 (t, J = 5.2 Hz, 12 H), 0.55−0.59 (m, 8 H), 0.80 (t, J = 5.2 Hz, 12 H), 0.92−0.99 (m, 8 H), 0.97 (t, J = 5.2 Hz, 12 H), 1.14 (t, J = 5.2 Hz, 12 H), 1.26−1.29 (m, 8 H), 1.35−1.41 (m, 8 H), 1.46−1.50 (m, 8 H), 1.56−1.64 (m, 8 H), 1.72−1.78 (m, 8 H), 2.02−2.04 (m, 8 H), 2.34−2.37 (m, 8 H), 2.58−2.60 (m, 8 H), 2.83−2.85 (m, 8 H), 3.39−3.42 (m, 8 H), 8.52 (s, 4 H), 9.20 (s, 4 H), 9.38 (s, 2 H); ^{13}C NMR (DMSO-d_6, Me_4Si, 423 K) δ 11.7, 12.4, 12.5, 12.8, 21.1, 21.6, 21.7, 21.9, 27.3, 27.6, 28.5, 28.6, 31.3, 32, 1, 32.2, 32.4, 120.7, 122.0, 125.9, 128.5, 128.8, 129.31, 129.34, 131.8, 132.2, 132.4, 135.1, 135.2; HRMS (ESI) calcd for $C_{108}H_{154}$ 1451.2051, found 1451.2029. Anal. Calcd for $C_{108}H_{154}$: C, 89.31; H, 10.69. Found: C, 89.23; H, 10.57.

Preparation of TCNE Adduct 6b from 5b. The title compound (120 mg) was prepared in the same way as described for **6a** in 70% yield from **5b** (145 mg, 0.1 mmol). **6b**: yellow solid; ^{1}H NMR ($CDCl_3$, Me_4Si) δ −0.27 to −0.17 (m, 2 H), −0.03 to −0.10 (m, 2 H), 0.01 (t, J = 7.2 Hz, 6 H), 0.28−0.46 (m, 8 H), 0.42 (t, J = 7.2 Hz, 6 H), 0.59−0.69 (m, 2 H), 0.65 (t, J = 7.2 Hz, 6 H), 0.74−1.17 (m, 14 H), 0.90 (t, J = 7.2 Hz, 6 H), 0.95 (t, J = 7.2 Hz, 6 H), 0.99 (t, J = 7.2 Hz, 6 H), 1.04 (t, J = 7.2 Hz, 6 H), 1.16 (t, J = 7.2 Hz, 6 H), 1.26−1.50 (m, 24 H), 1.54−1.61 (m, 8 H), 1.62−1.75 (m, 10 H), 1.93−2.01 (m, 2 H), 2.07−2.19 (m, 4 H), 2.34−2.43 (m, 4 H), 2.51−2.62 (m, 6 H), 2.64−2.70 (m, 2 H), 2.84−2.94 (m, 4 H), 3.05−3.15 (m, 4 H), 5.52 (s, 2 H), 5.90 (s, 2 H), 6.71 (s, 2 H), 8.42 (s, 2 H), 8.60 (s, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.8, 13.3, 13.6, 13.7, 13.8, 13.9, 14.1, 14.2, 22.9, 23.0, 23.3, 23.4 (2 C), 23.5 (2 C), 23.6, 28.1, 28.2, 28.6, 28.8, 29.1, 29.3, 30.02, 30.05, 31.4, 32.3, 32.6, 33.39 (2 C), 33.44, 33.5, 34.6, 45.7, 47.1, 47.2, 49.8, 110.3, 110.9, 112.1, 114.0, 122.6, 124.0, 127.8, 128.1, 129.1, 129.2, 129.6, 130.87, 130.91 (2C), 131.8, 132.1, 133.3, 133.5, 135.8, 137.2, 137.5, 137.9, 140.4, 141.4; HRMS (FAB; m/z) calcd for $C_{120}H_{154}N_8$ 1707.2296, found 1707.2302.

Reaction of Pentacene Derivative 4a with (±)-10-Camphorsulfonic Acid. In a 20 mL Schlenk tube, pentacene derivative **4a** (62 mg, 0.10 mmol) and (±)-10-camphorsulfonic acid (CSA; 2.3 mg, 0.01 mmol) was dissolved in degassed mesitylene (3 mL). Under a nitrogen atmosphere, the mixture was stirred for 6 h at 120 °C in the dark. The color of the reaction mixture changed from purple to blue. After it was cooled to room temperature, the reaction mixture was purified by silica gel chromatography under nitrogen (hexane:toluene 50:1 as eluent). The blue solution was collected and evaporated to produce a blue solid, which was purified by GPC under nitrogen again to afford the trimeric species **7** (32 mg, 53% isolated yield) as a blue solid. **7**: ^{1}H NMR (C_6D_6, Me_4Si) δ 0.17 (t, J = 7.2 Hz, 6 H), 0.35−0.40 (m, 8 H), 0.36 (t, J = 7.2 Hz, 6 H), 0.55−0.73 (m, 12 H), 0.62 (t, J = 7.2 Hz, 3 H), 0.80−1.18 (m, 24 H), 0.81 (t, J = 7.2 Hz, 6 H), 0.87 (t, J = 7.2 Hz, 12 H), 0.88 (t, J = 7.2 Hz, 6 H), 0.94 (t, J = 7.2 Hz, 3 H), 0.96 (t, J = 7.2 Hz, 3 H), 0.98 (t, J = 7.2 Hz, 3 H), 1.04 (t, J = 7.2 Hz, 6 H), 1.07 (t, J = 7.2 Hz, 3 H), 1.17 (t, J = 7.2 Hz, 6 H), 1.23 (t, J = 7.2 Hz, 3 H), 1.28−1.45 (m, 18 H), 1.34 (t, J = 7.2 Hz, 6 H), 1.48−1.53 (m, 2 H), 1.57−1.72 (m, 8 H), 1.83−1.96 (m, 8 H), 2.10−2.13 (m, 4 H), 2.19−2.26 (m, 8 H), 2.31−2.39 (m, 8 H), 2.40−2.59 (m, 20 H), 2.65−2.68 (m, 2 H), 2.73−2.85 (m, 12 H), 3.12−3.19 (m, 2 H), 3.24−3.39 (m, 6 H), 3.48−3.54 (m, 2 H), 4.57 (d, J = 17.4 Hz, 1 H), 5.10 (d, J = 17.4 Hz, 1 H), 5.14 (d, J = 11.4 Hz, 1 H), 5.50 (d, J = 11.4 Hz, 1 H), 7.45 (s, 2 H), 7.50 (s, 2 H), 7.75 (s, 2 H), 8.31 (s, 2 H), 8.57 (s, 1 H), 8.79 (s, 1 H, sp^3 CH, determined by C−H COSY), 9.13 (s, 1 H), 9.14 (s, 1 H), 9.25 (s, 1 H), 10.28 (s, 1 H); ^{13}C NMR (C_6D_6, Me_4Si) δ 14.2, 14.87, 14.89, 14.98, 15.00, 15.03, 15.1, 15.2, 15.27, 15.32, 15.34, 15.6, 23.5, 23.7, 23.8, 24.4, 24.5, 24.7, 24.9, 25.0, 25.1, 25.2, 25.3, 25.4, 31.2, 31.28, 31.31, 31.8, 31.9, 32.0, 32.1, 32.5, 32.7, 32.8, 32.9, 33.2, 37.6, 44.5, 54.3, 55.1, 118.0, 122.5, 123.8, 124.4, 125.3, 126.2, 126.3, 126.6, 129.9, 130.3, 130.4, 130.6,130.66, 130.73, 131.0, 131.3, 132.1, 132.2, 132.3, 133.4, 133.6, 133.96, 134.04, 134.4, 134.7, 134.9, 135.6, 135.77, 135.84, 136.3, 136.9, 137.8.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

A CIF file and ORTEP diagram of compound **6a** and figures and tables giving ^{1}H and ^{13}C NMR spectra of compounds **2a**−**6a**, **2b**−**6b**, and **7**, UV absorption and fluorescence spectra of compounds **4a**, **5a**, **4b**, **5b**, and **7**, GPC separation chart, mass spectra, and a C−H COSY NMR spectrum of **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) The preliminary X-ray structure of **5a** is shown in the Supporting Information.

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(10) A side-trimer species **7** was isolated. HRMS (ESI; *m*/*z*): calcd for $C_{138}H_{186}$ 1843.4555, found 1843.4546. The structure of this compound was not fully characterized.