DOI: 10.1002/asia.200900754

Synthesis of 1,2,3,4,8,9,10,11-Octasubstituted Pentacenequinone Derivatives and their Conversion into Substituted Pentacenes

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Abstract: A series of 1,2,3,4,8,9,10,11-octasubstituted pentacenequinone derivatives were prepared by the oxidation of 1,2,3,4,8,9,10,11-octasubstituted pentacenes, which were synthesized by the double homologation method. Oxidation of the pentacenes was carried out with H_5IO_6 or air and DDQ. These octasubstituted pentacenequinones were converted into 1,2,3,4,6,8,9,10,11,13-decasubstituted or 2,3,6,9,10,13-hexasubstituted pentacene derivatives by the introduction of aryl or alkynyl groups at the carbonyl carbons. The photophysical properties of these new pentacenes have been measured in solution, and the substituent effects are discussed.

Keywords: NMR spectroscopy · oxidation · pentacenes · polycycles · quinones

Introduction

Since pentacene film has shown high performance as an organic semiconductor,[1] substituted soluble pentacene derivatives have gained importance because they can be used for wet process.[2a] Since then we have developed several methods for the formation of substituted pentacene derivatives, such as homologation method (Figure 1, [Eq. (1)]),[2a,3] double homologation method (Figure 1, [Eq. (2)]),[4] coupling method,[5] and others. After our first report in 2000, several groups also reported the formation and performance of the substituted pentacenes.[6,7]

One general and simple introduction of substituents at 6,13-positions is the reaction of pentacenequinone with organo Grignard or lithium reagents (Figure 1, [Eq. (3)]). This promoted us to combine our double homologation method and this pentacenequinone method. Here, we would like to report the combination of the double homologation

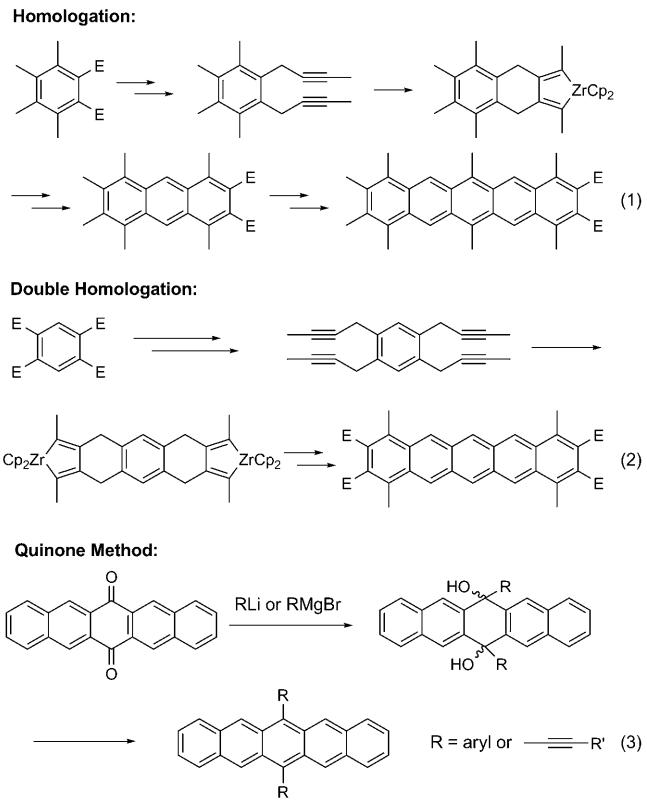

Figure 1. The concept of homologation and double homologation, quinone method.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/asia.200900754.

and pentacenequinone methods for the formation of multisubstituted pentacene derivatives. Octasubstituted pentacenes prepared by the double homologation method were oxidized by H_5IO_6 or air and DDQ to give the corresponding pentacenequinones. The organic substituents were introduced at the 6,13-positions for the formation of decasubstituted or hexasubstituted pentacenes with tetra ester groups (Figure 2).

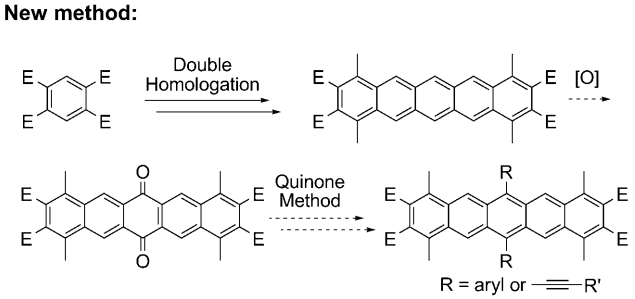


Figure 2. New strategy for synthesis of substituted pentacene.

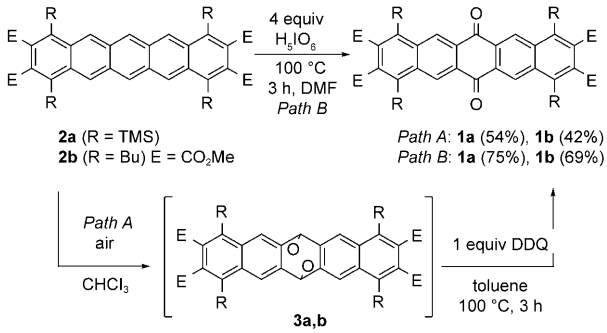
Results and Discussion

Preparation of Octasubstituted Pentacenequinones by Oxidation

Octasubstituted 6,13-pentacenequinones **1** were prepared by the oxidation of the corresponding pentacenes **2**, which were prepared by a zirconium-mediated double homologation method as reported previously (Scheme 1).[4] The blue chloroform solution of pentacenes **2** was stirred in air under sunlight. The solvent was evaporated in vacuo after the blue color had disappeared completely. The resulting yellow residue that mainly contained pentacene endoperoxides **3** was treated with 1 equiv of DDQ in toluene at 100 °C for 3 h to afford pentacenequinones **1a,b** as yellow solids in 54 and 42 % yields, respectively (Path A). The yields of pentacenequinones **1** obtained by the oxidation of pentacenes **2** with 4 equiv of H_5IO_6 in DMF at 100 °C were higher. The blue colour of **2** had disappeared completely within 3 h. The usual workup and silica gel chromatography gave pentacenequinones **1a,b** in 75 and 69 % yields, respectively (Path B).

Abstract in Japanese:

ダブルホモロゲーションにより合成した1,2,3,4,8,9,10,11-八置換ペンタセンの酸化反応により、対応するペンタセンキノンを合成した。酸化剤には、過ヨウ素酸、もしくは空気およびDDQを用いた。得られたペンタセンキノン誘導体は、カルボニル部位へアリール、またはアルキニル基を導入することによって、対応する十置換ペンタセンへと変換することができた。このようにして得られた新規ペンタセン誘導体の溶液中での光物理的性質や、それに及ぼす置換基効果を考察した。

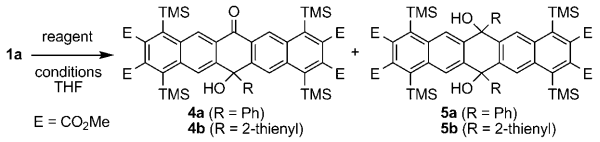


Scheme 1. Synthesis of pentacenequinones **1** from pentacenes **2** by oxidation.

6,13-Diarylpentacenes from Pentacenequinones

The formation of 6,13-diarylpentacene derivatives **6** from pentacenequinone **1a** is described below. The conditions of the reaction of phenyllithium with pentacenequinone **1a** were optimized as shown in Table 1. Pentacenequinone **1a**

Table 1. Reaction of pentacenequinone **1a** with arylmetals.



Entry	Reagent	Equiv	T [°C]	t [h]	Yield of **4** [%][a]	Yield of **5** [%][a]
1	PhLi	2	RT	6	75	–
2	PhLi	2	50	12	62	trace
3	PhLi	2	reflux	12	11	43
4	PhLi	3	reflux	6	–	58
5[b]	PhLi	6	reflux	6	–	12
6	PhMgBr	3	reflux	6	–	56
7	2-thienylLi	3	reflux	6	–	45

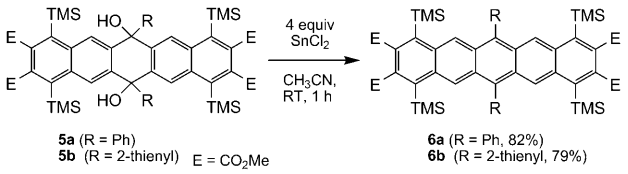
[a] NMR yield. [b] Unidentified polar compounds were formed.

was reacted with 2 equiv of phenyllithium in THF at room temperature. After 6 h, the corresponding keto alcohol **4a** was formed in 75 % NMR yield (entry 1). When the reaction proceeded at 50 °C, only trace amounts of diol **5a** was formed after 12 h (entry 2). In refluxing THF for 12 h, diol **5a** was formed as a major product with keto alcohol **4a** by using 2 equiv of phenyllithium (entry 3). The optimized condition for the reaction is 3 equiv of phenyllithium in refluxing THF for 6 h. Diol **5a** was obtained in 58 % yield from **1a** (entry 4). On increasing the amount of phenyllithium to 6 equiv, the desired diol **5a** was formed in a very low yield because unidentified polar compounds were formed which could be detected by TLC (entry 5). The reaction of pentacenequinone **1a** with phenyl Grignard reagent gave a similar yield of diol **5a** under the same conditions (entry 6). Similarly, diol **5b** was also prepared from **1a** by its reaction with 2-thienyllithium (entry 7).

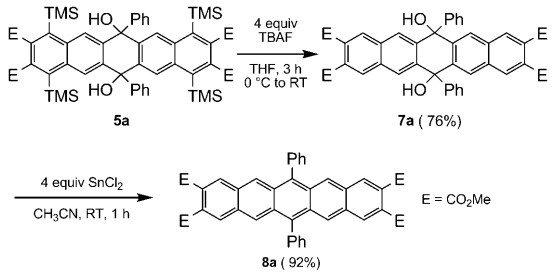
Diols **5a,b** were purified by silica gel column chromatography and then treated with 4 equiv of tin(II) chloride in

acetonitrile. The desired 6,13-diarylpentacene derivatives **6a,b** were formed as blue solids in 82 and 79% yields, respectively (Scheme 2).

Upon treatment with TBAF, trimethylsilyl groups were efficiently removed as shown in Scheme 3. Diol **5a** with four



Scheme 2. Synthesis of 6,13-diarylpentacene derivatives **6** from diols **5**.

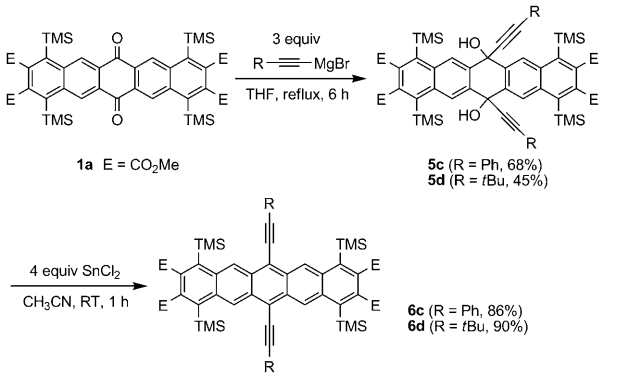


Scheme 3. Synthesis of hexasubstituted pentacene **8a**.

trimethylsilyl groups was treated with 4 equiv of TBAF in THF. After 3 h at room temperature, the silyl groups were removed to afford diol **7a** in 76% yield. Finally, the hexasubstituted pentacene **8a** was prepared by treatment with $SnCl_2$ under the same conditions as mentioned above.

6,13-Dialkynylpentacenes from Pentacenequinones

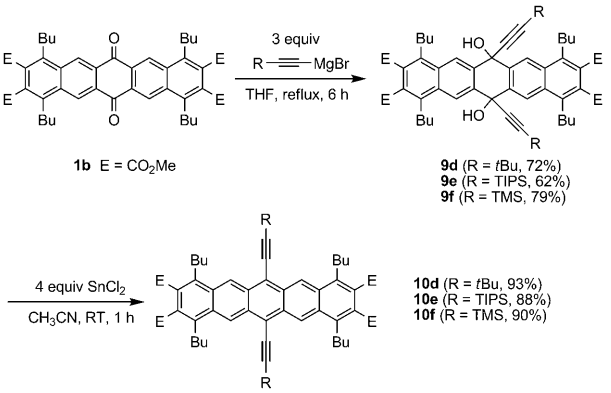
The synthesis of 6,13-dialkynylpentacenes **6c,d** was achieved by using the corresponding pentacenequinone **1a** (Scheme 4). The reaction of pentacenequinone **1a** with 1-alkynylmagnesium bromide gave the desired diols **5c,d**. When the corresponding alkynyllithium reagents, however, were



Scheme 4. Synthesis of 6,13-dialkynylpentacenes **6c**,**d**.

used instead of alkynylmagnesium bromides, the yield of the diols **5c,d** were significantly decreased. The reduction of the diols **5c,d** with $SnCl_2$ in acetonitrile produced the corresponding 6,13-dialkynylpentacenes **6c,d** in 86 and 90% yields, respectively.

Alkynyl groups with various bulky substituents such as *t*Bu, TMS, and TIPS could be introduced into the pentacene skeleton by using pentacenequinone **1b** (Scheme 5). Diols



Scheme 5. 6,13-Dialkynylpentacene formation from pentacenequinone **1b**.

9d–f were obtained in reasonable yields by the reaction of pentacenequinone **1b** and the corresponding alkynyl Grignard reagents in refluxing THF. The 6,13-dialkynylpentacenes were afforded in excellent yields by the same aromatization method mentioned above.

The structure of pentacene **10f** was determined by X-ray analysis as shown in Figure 3. Pentacene **10f** exhibited a nearly planar π-conjugated framework, and the angles between the two adjacent six-membered rings were within 3.30–4.04°. The dihedral angles between the carbonyl planes and the pentacene plane were within the range of 48.9–

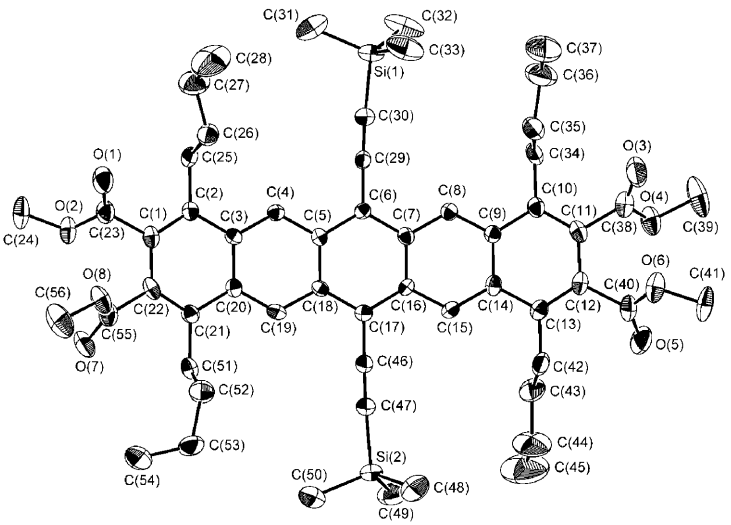


Figure 3. Structure of 6,13-bis(trimethylsilylethynyl)pentacene **10f.**

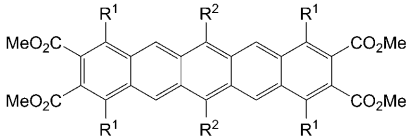
59.2°, which suggested that the four ester groups did not strongly alter the electronic properties of the pentacene skeleton.

The stability of all the obtained pentacenes **6a–d, 8a, 10d–f** were similar to the other derivatives reported thus far. Our pentacenes were also thermally stable both in solution and in solid state under nitrogen atmosphere, but gradually oxidized upon exposure to light and air.

Photophysical Properties of 6,13-Disubstituted Pentacene-2,3,9,10-tetraester Derivatives

The photophysical properties of pentacene-2,3,9,10-tetraester derivatives were investigated in chloroform as shown in Table 2. Compared with the wavelength of the absorption maximum of 6,13-nonsubstituted pentacene **2a**, those of 6,13-diphenyl- and di-(2-thienyl)pentacene, **6a** and **6b**, were red-shifted by 20 nm. Only small differences were observed between **6a** and **6b**, although these have different aryl groups at 6,13-positions. This can be ascribed to their preferred conformation perpendicular to the pentacene plane, and the effect of π-conjugation between the pentacene skeleton and the aryl groups is small. Compared with the absorption maximum of 6,13-diphenylpentacene ($\lambda_{max}=595$ nm in CH_2Cl_2),[6k] that of **8a** ($\lambda_{max}=616$ nm) was red-shifted by 21 nm. This is a consequence of extending the π-system through four ester groups on the terminal aromatic rings of pentacene. Substitution of trimethylsilyl groups at 1,4,8,11-positions causes a slight red-shift as can be seen in the comparison of **6a** and **8a**. In contrast to 6,13-diarylpentacenes **6a,b**, 6,13-dialkynylsubstituted **6c,d** and **10d–f** exhibited the absorption and emission maxima at much longer wavelength regions. This illustrates that alkynyl groups effectively extend the π-conjugation system of the pentacene moiety in contrast to aryl groups. Stokes shifts of 6,13-dialkynylpentacenes, **6c,d**, **10d–f** (196–270 cm^{-1}), were smaller than for the diaryl ones, **6a,b**, and **8a** (386–452 cm^{-1}).

Table 2. Photophysical properties of 6,13-disubstituted pentacene derivatives.[a]



compound	R^1	R^2	λ_{max}(abs) [nm]	λ_{max}(em) [nm]	Stokes shift [cm^{-1}]	$E_{g,optical}$ [eV][c]
2a[b]	TMS	H	602	625	611	1.98
6a	TMS	Ph	622	638	403	1.91
6b	TMS	2-thienyl	622	640	425	1.91
8a	H	Ph	616	631	386	1.93
6c	TMS	PhCC-	673	682	196	1.77
6d	TMS	*t*BuCC-	660	672	270	1.80
10d	Bu	*t*BuCC-	648	658	235	1.85
10e	Bu	TIPSCC-	655	666	252	1.83
10f	Bu	TMSCC-	652	661	209	1.84

[a] Measured in $CHCl_3$ at room temperature. [b] Ref. [4c]. [c] Optical HOMO–LUMO gaps determined from the onset of lowest-energy visible absorption band. The onset is defined as the intersection between the baseline and a tangent line that touches the point of inflection.

Comparison of HOMO–LUMO energy differences ($E_{g,optical}$) of **6a–d** to that of **1a** showed that substitution of diaryl groups at the 6,13-positions reduced the gap by 0.07 eV. This effect is much smaller than that for the dialkynyl substitution in **6c,d** (0.18–0.21 eV), which indicates small effects of the conjugation between the aryl groups and the pentacene backbone. When the gap values of **6a–c**, **8a**, and **10e,f** were compared with the reported data of 6,13-diphenylpentacene (1.94 eV),[6t] 6,13-bis(2-thienyl)pentacene (1.97 eV),[6x] 6,13-bis(triisopropylsilylethynyl)pentacene (1.81 eV),[6t] 6,13-bis(phenylethynyl)pentacene (1.88 eV),[6u] and 6,13-bis(trimethylsilylethynyl)pentacene (1.93 eV),[6u] it was found that the effects of the introduction of four methoxycarbonyl groups at the 2,3,9,10-positions were small. The differences were within only 0.03–0.11 eV. The results would reflect the conformation of these ester groups in the solid state as mentioned in the structure of **10f**. The substituents at 6,13-positions of the pentacene derivatives also provided insight into the prevention of dimerization.[4b]

Conclusions

A new method for the synthesis of substituted pentacenes was developed by the combination of the quinone method and double homologation method. 6,13-Nonsubstituted pentacenes prepared by the double homologation method were converted to the corresponding pentacenequinones by oxidation with H_5IO_6 or air and DDQ. Aryl and alkynyl groups were introduced by the reaction of the pentacenequinones with aryllithiums or alkynyl Grignard reagents, and the resulting diols were aromatized by tin(II) chloride to afford 6,13-diaryl- or dialkynylpentacenes having four ester groups. The UV absorption spectra illustrated that the alkynyl groups efficiently extended the π-conjugation system of the pentacene moiety in contrast to aryl groups.

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 the reagents were commercially available and used as received unless otherwise mentioned. Compounds **2a,b** were prepared according to the

literature.[4b] ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ (containing 0.03% TMS) solutions.

Syntheses

1,4,8,11-Tetrakis(trimethylsilyl)-6,13-pentacenequinone-2,3,9,10-tetracarboxylic acid tetramethyl ester (1a): Path A: The blue chloroform solution of pentacene **2a** (800 mg, 1.0 mmol) was kept in air under sunlight. After several hours, the blue color disappeared completely. The solvent was evaporated in vacuo, and the resulting yellow residue was treated with DDQ (227 mg. 1.0 mmol) in toluene (15 mL) at 100 °C for 3 h. Then the reaction mixture was cooled to room temperature and purified by flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the title compound as a yellow solid (447 mg, 54% yield).

Path B: To a degassed solution of pentacene **2a** (160 mg, 0.2 mmol) in DMF (10 mL) was added H_5IO_6 (182 mg, 0.8 mmol). On heating to 100 °C, the blue color disappeared completely. After the mixture was heated at 100 °C for 3 h, it was cooled to room temperature. The solvent was evaporated in vacuo, and the resulting yellow residue was purified by flash chromatography (silica gel, $CHCl_3$ as eluent) to afford the title compound as a yellow solid (124 mg, 75% yield).

1a: M.p.: >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 0.57$ (s, 36H; $Si(CH_3)_3$), 3.92 (s, 12H; CO_2CH_3), 9.39 ppm (s, 4H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta = 2.0$, 52.8, 129.7, 131.2, 138.8, 139.1, 141.8, 169.8, 182.3 ppm; HRMS (FAB): *m/z* (%) calcd for $C_{42}H_{53}O_{10}Si_4$: 829.2716 $[M+H]^+$; found: 829.2719; elemental analysis: calcd (%) for $C_{42}H_{52}O_{10}Si_4$: C 60.84, H 6.32; found: C 60.69, H 6.35.

6,13-Dihydroxy-6,13-diphenyl-1,4,8,11-tetrakis(trimethylsilyl)-6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (5a): To an oven dried 50 mL flask cooled under N_2 was added pentacenequinone **1a** (415 mg, 0.5 mmol) and dry THF (15 mL). Then phenyllithium (0.98 M in cyclohexane-diethyl ether, 1.53 mL, 1.50 mmol) was added dropwise at 0 °C and the mixture was refluxed for 6 h. The mixture was quenched with aqueous saturated NH_4Cl 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 black viscous oil was purified by flash chromatography (silica gel, hexane/ethyl acetate = 3:1 as eluent) to afford the title compound as a yellow solid (285 mg, 58% yield).

5a: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 0.13$ (s, 36H, $Si(CH_3)_3$), 3.80 (s, 12 CO_2CH_3), 7.39–7.49 (m, 6H, Ph), 7.57–7.64 (m, 4H, Ph), 8.06 ppm (s, 4H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta = 1.6$, 52.4, 77.2, 127.7, 128.3, 128.4, 130.4, 135.8, 136.3, 138.8, 140.3, 143.5, 170.4 ppm; HRMS *m/z* (FAB) calcd for $C_{54}H_{54}O_{10}Si_4Na$: 1007.3474 $[M+Na^+]$; found: 1007.3477.

6,13-Diphenyl-1,4,8,11-tetrakis(trimethylsilyl)pentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (6a): Diol **5a** (99 mg, 0.1 mmol) was dissolved in degassed CH_3CN (5 mL) and anhydrous $SnCl_2$ (76 mg, 0.40 mmol) was then added. The mixture was stirred at room temperature under N_2. After 2 h, the blue precipitate was collected by filtration, and dissolved in degassed CH_2Cl_2, and filtered again to remove the inorganic tin residue. The filtrate was concentrated in vacuo to yield the title compound as a blue solid, which was further purified by re-precipitation from dichloromethane and hexane (78 mg, 82% yield).

6a: M.p.: >300 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 0.17$ (s, 36H, $Si(CH_3)_3$), 3.84 (s, 12H, CO_2CH_3), 7.60–7.77 (m, 10H, Ph), 8.73 ppm (s, 4H, aromatic CH). ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta =$ 1.4, 52.4, 128.1, 128.2, 128.9, 129.4, 131.5, 132.3, 135.6, 137.2, 138.8, 139.7, 170.5 ppm; HRMS *m/z* (ESI) calcd $C_{54}H_{62}O_8Si_4$: 950.3522 $[M]^+$; found: 950.3516; elemental analysis: calcd (%) for $C_{54}H_{62}O_8Si_4$: C 68.17, H 6.57; found: C 68.10, H 6.65.

6,13-Dihydroxy-6,13-bis(2-thienyl)-1,4,8,11-tetrakis(trimethylsilyl)-6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (5b): The title compound (45 mg) was prepared by the same way as described for **5a** in 45% yield from **1a** (83 mg, 0.10 mmol).

5b: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 0.51$ (s, 36H, $Si(CH_3)_3$), 3.90 (s, 12H, CO_2CH_3), 6.08 (dd, $J = 3.6$ Hz, 1.8 Hz, 2H, thienyl), 6.46 (dd, $J =$ 5.1 Hz, 3.6 Hz, 2H, thienyl), 7.02 (dd, $J = 5.1$ Hz, 1.8 Hz,, 2H, thienyl), 9.02 ppm (s, 4H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta =$ 2.0, 52.6, 73.3, 126.3, 126.6, 127.3, 127.5, 136.2, 136.5, 138.4, 139.0, 148.3, 170.5 ppm. HRMS *m/z* (FAB) calcd for $C_{50}H_{60}O_{10}Si_4S_2Na$: 1019.2603 $[M+Na^+]$; found: 1019.2598.

6,13-Bis(2-thienyl)-1,4,8,11-tetrakis(trimethylsilyl)pentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (6b): The title compound (76 mg) was prepared as a purple–blue solid by the same way as described for **6a** in 79% yield from **5b** (100 mg, 0.10 mmol).

6b: purple–blue solid; m.p.: >300 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 0.28$ (s, 36H, $Si(CH_3)_3$), 3.86 (s, 12H, CO_2CH_3), 7.40–7.41 (m, 2H, thienyl), 7.43–7.46 (m, 2H, thienyl), 7.75 (dd, $J = 5.0$ Hz, 1.2 Hz, 2H, thienyl), 8.91 ppm (s, 4H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta = 1.6$, 52.5, 127.4, 127.5, 129.1, 129.6, 130.3, 130.4, 132.8, 136.0, 138.3, 139.8, 170.4 ppm. HRMS *m/z* (EI) calcd for $C_{50}H_{58}O_8Si_4S_2$: 962.2650 $[M]^+$; found: 962.2619. elemental analysis: calcd (%) for $C_{50}H_{58}O_8Si_4S_2$: C 62.33, H 6.07; found: C 62.42, H 5.95.

6,13-Dihydroxy-6,13-diphenyl-6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (7a): To an oven dried 50 mL flask cooled under N_2 was added diol **5a** (197 mg, 0.20 mmol) and dry THF (5 mL). Tetrabutylammonium fluoride (1.0 M in THF, 0.8 mL, 0.8 mmol) was added dropwise at 0 °C and the mixture was stirred at room temperature for 3 h. The mixture was 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 black viscous oil was purified by flash chromatography (silica gel, hexane/ethyl acetate = 3:1 as eluent) to afford the title compound as yellow oil (105 mg, 76% yield).

7a: ^{1}H NMR (400 MHz, [D_6]DMSO, Me_4Si): $\delta = 3.90$ (s, 12H; CO_2CH_3), 6.50–6.52 (m, 4H; Ph), 6.63–6.65 (m, 4H; Ph), 6.77–6.79 (m, 2H; Ph), 6.93 (s, 2H; OH), 8.56 (s, 4H; aromatic CH), 8.80 ppm (s, 4H; aromatic CH); ^{13}C NMR (400 MHz, [D_6]DMSO, Me_4Si) $\delta = 52.7$, 74.9, 126.18, 126.23, 126.9, 127.4, 128.3, 130.0, 132.0, 142.9, 143.0, 167.5 ppm; HRMS *m/z* (EI) calcd for $C_{42}H_{32}O_{10}$: 696.1996 $[M]^+$; found: 696.2010.

6,13-Diphenylpentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (8a): The title compound (61 mg) was prepared as a blue solid by the same way as described for **6a** in 92% yield from **7a** (70 mg, 0.10 mmol).

8a: Blue solid; m.p. >300 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 3.92$ (s, 12H; CO_2CH_3), 7.58–7.61 (m, 4H; Ph), 7.68–7.76 (m, 6H; Ph), 8.22 (s, 4H; aromatic CH), 8.46 ppm (s, 4H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta = 52.6$, 127.6, 128.40, 128.44, 128.9, 129.6, 129.8, 131.5, 132.2, 138.2, 138.9, 167.8 ppm; HRMS *m/z* (EI) calcd for $C_{42}H_{30}O_8$: 662.1941 $[M]^+$; found: 662.1944; elemental analysis: calcd (%) for $C_{42}H_{30}O_8$: C 76.12, H 4.56; found: C 76.10, H 4.61.

6,13-Dihydroxy-6,13-bis(phenylethynyl)-1,4,8,11-tetrakis(trimethylsilyl)-6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (5c): To an oven dried 50 mL flask cooled under N_2 was added phenylacetylene (0.55 mL, 5.0 mmol), and dry THF (15 mL). EtMgBr (0.96 M in THF, 3.15 mL, 3.0 mmol) was added dropwise at 0 °C and the mixture was stirred at 40 °C for 1 h. Pentacenequinone **1a** (829 mg, 1.0 mmol) was added and the mixture was refluxed for 6 h. The mixture was quenched with aqueous saturated NH_4Cl 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 yellow viscous oil was purified by flash chromatography (silica gel, hexane/ethyl acetate = 3:1 as eluent) afford the title compound as a yellow solid (352 mg, 68% yield).

5c: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): $\delta = 0.41$ (s, 36H, $Si(CH_3)_3$), 3.86 (s, 12H, CO_2CH_3), 7.43–7.49 (m, 6H, Ph), 7.69–7.72 (m, 4H, Ph), 9.22 ppm (s, 4H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): $\delta =$ 1.8, 52.6, 72.5, 87.6, 91.3, 121.5, 128.5, 129.3, 129.5, 132.1, 135.7, 136.5, 136.9, 139.3, 170.4 ppm; HRMS *m/z* (FAB) calcd for $C_{58}H_{64}O_{10}Si_4Na$: 1055.3474 $[M+Na]^+$; found: 1055.3459.

6,13-Bis(phenylethynyl)-1,4,8,11-tetrakis(trimethylsilyl)pentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (6c): The title compound

(43 mg) was prepared as a dark green solid by the same way as described for **6a** in 86% yield from **5c** (52 mg, 0.05 mmol).

6c: Dark green solid; m.p.: >300°C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.62 (s, 36H, $Si(CH_3)_3$), 3.91 (s, 12H, CO_2CH_3), 7.47–7.55 (m, 6H, Ph), 7.82–7.86 (m, 4H, Ph), 9.81 ppm (s, 4H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 2.1, 52.4, 87.5, 104.7, 118.5, 123.0, 128.7, 129.1, 129.6, 130.2, 131.8, 134.0, 136.7, 140.0, 170.3 ppm; HRMS *m/z* (FAB) calcd for $C_{58}H_{63}O_8Si_4$: 999.3600 $[M+H]^+$; found: 999.3580; elemental analysis: calcd (%) for $C_{58}H_{62}O_8Si_4$: C 69.70, H 6.25; found: C 69.55, H 6.17.

1,4,8,11-Tetrakis(trimethylsilyl)-6,13-dihydroxy-6,13-bis(3,3-dimethyl-but-1-ynyl)-6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (5d): The title compound (45 mg) was prepared by the same way as described for **5c** in 45% yield from **1a** (83 mg, 0.10 mmol).

5d: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.55 (s, 36H, $Si(CH_3)_3$), 1.29 (s, 18H, *t*Bu), 3.88 (s, 12H, CO_2CH_3), 9.02 ppm (s, 4H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 2.1, 27.7, 30.9, 52.5, 69.1, 80.0, 98.0, 128.0, 136.3, 136.4, 136.6, 139.1, 170.4 ppm; HRMS *m/z* (FAB) calcd for $C_{54}H_{72}O_{10}Si_4Na$: 1015.4100 $[M+Na^+]$; found: 1015.4117.

1,4,8,11-tetrakis(trimethylsilyl)-6,13-bis(3,3-dimethyl-but-1-ynyl)pentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (6d): The title compound (86 mg) was prepared as a purple–blue solid by the same way as described for **6a** in 90% yield from **5d** (99 mg, 0.10 mmol).

6d: Purple–blue solid; m.p.: >300°C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.64 (s, 36H, $Si(CH_3)_3$), 1.63 (s, 18H, *t*Bu), 3.92 (s, 12H, CO_2CH_3), 9.64 ppm (s, 4H, aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 2.3, 29.3, 31.8, 52.5, 77.5, 113.7, 118.6, 129.5, 130.1, 133.5, 136.2, 139.9, 170.5 ppm; HRMS *m/z* (EI) calcd for $C_{54}H_{70}O_8Si_4$: 958.4148 $[M]^+$; found: 958.4129; elemental analysis: calcd (%) for $C_{54}H_{70}O_8Si_4$: C 67.60, H 7.35; found: C 67.41, H 7.34.

1,4,8,11-Tetrabutyl-6,13-pentacenequinone-2,3,9,10-tetracarboxylic acid tetramethyl ester (1b): The title compound (528 mg) was prepared as a yellow solid by the same way as described for **1a** in 69% yield from **2b** (path B, 740 mg, 1.0 mmol).

1b: Yellow solid; m.p.: >300°C; ^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): δ = 1.03 (t, $^3J_{H,H}$ = 7.2 Hz, 12H, $-CH_2CH_2CH_2CH_3$), 1.50–1.62 (m, 8H, $-CH_2CH_2CH_2CH_3$), 1.73–1.85 (m, 8H, $-CH_2CH_2CH_2CH_3$), 3.21–3.26 (m, 8H, $-CH_2CH_2CH_2CH_3$), 3.96 (s, 12H, CO_2CH_3), 9.22 ppm (s, 4H, aromatic CH);. ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 13.9, 23.1, 30.1, 34.0, 52.7, 127.3, 130.9, 131.6, 134.9, 139.3, 168.7, 182.4 ppm; HRMS *m/z* (EI) calcd for $C_{46}H_{52}O_{10}$: 764.3560 $[M]^+$; found: 764.3568; elemental analysis: calcd (%) for $C_{46}H_{52}O_{10}$: C 72.23, H 6.85; found: C 72.03, H 6.85.

1,4,8,11-Tetrabutyl-6,13-dihydroxy-6,13-bis(3,3-dimethyl-but-1-ynyl)-6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (9d): The title compound (67 mg) was prepared by the same way as described for **5c** in 72% yield from **1b** (76 mg, 0.10 mmol).

9d: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.97 (t, $^3J_{H,H}$ = 7.2 Hz, 12H; $-CH_2CH_2CH_2CH_3$), 1.29 (s, 18H; *t*-Bu), 1.46–1.52 (m, 8H; $-CH_2CH_2CH_2CH_3$), 1.70–1.80 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.07–3.19 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.83 (s, 2H; CO_2CH_3), 8.89 ppm (s, 4H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 13.9, 23.1, 27.7, 29.9, 30.7, 33.6, 52.4, 69.2, 80.6, 98.1, 123.5, 128.9, 132.3, 137.3, 138.0, 169.4 ppm; HRMS *m/z* (FAB) calcd for $C_{58}H_{72}O_{10}Na$: 951.5023 ($[M+Na]^+$); found: 951.5009.

1,4,8,11-Tetrabutyl-6,13-bis(3,3-dimethyl-but-1-ynyl)pentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (10d): The title compound (33 mg) was prepared as a blue solid by the same way as described for **6a** in 93% yield from **9d** (46 mg, 0.05 mmol).

10d: Blue solid; m.p.: 220–221°C (dec); ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.02 (t, $^3J_{H,H}$ = 7.2 Hz, 12H; $-CH_2CH_2CH_2CH_3$), 1.55 (s, 18H; *t*-Bu), 1.65–1.72 (m, 8H; $-CH_2CH_2CH_2CH_3$), 2.07–2.12 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.50 (t, $^3J_{H,H}$ = 7.2 Hz, 8H; $-CH_2CH_2CH_2CH_3$), 3.66 (s, 12H; CO_2CH_3), 9.76 ppm (s, 4H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 14.1, 23.5, 29.2, 30.4, 31.3, 33.5, 52.3, 114.6, 119.1, 125.4 (2C), 127.4, 130.5, 130.6, 138.2, 169.4 ppm; HRMS *m/z* (EI) calcd for $C_{59}H_{74}O_8$: 910.5384 $[M]^+$; found: 910.5388; elemental analysis: calcd (%) for $C_{59}H_{74}O_8$: C 77.77, H 8.19; found: C 77.76, H 8.16.

1,4,8,11-Tetrabutyl-6,13-dihydroxy-6,13-bis(triisopropylsilylethynyl)-6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (9e): The title compound (70 mg) was prepared by the same way as described for **5c** in 62% yield from **1b** (76 mg, 0.1 mmol).

9e: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.94 (t, $^3J_{H,H}$ = 7.2 Hz, 12H; $-CH_2CH_2CH_2CH_3$), 1.05 (brs, 6H; $-CH(CH_3)_2$), 1.06 (brs, 36H; $-CH(CH_3)_2$), 1.41–1.47 (m, 8H; $-CH_2CH_2CH_2CH_3$), 1.68–1.77 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.17 (t, $^3J_{H,H}$ = 7.2 Hz, 8H; $-CH_2CH_2CH_2CH_3$), 3.43 (s, 2H; OH), 3.88 (s, 12H; CO_2CH_3), 8.96 ppm (s, 4H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 11.2, 14.0, 18.6, 23.0, 29.6, 33.7, 52.4, 69.4, 90.3, 108.8, 124.0, 129.0, 132.5, 137.3, 137.4, 169.5 ppm; HRMS *m/z* (FAB) calcd for $C_{68}H_{96}O_{10}Si_2Na$: 1151.6440 $[M+Na]^+$; found: 1151.6455.

1,4,8,11-Tetrabutyl-6,13-bis(triisopropylsilylethynyl)pentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (10e): The title compound (48 mg) was prepared as a blue solid by the same way as described for **6a** in 88% yield from **9e** (57 mg, 0.05 mmol).

10e: Blue solid; m.p.: >300°C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.90 (t, $^3J_{H,H}$ = 7.2 Hz, 12H; $-CH_2CH_2CH_2CH_3$), 1.32 (brs, 6H; $-CH(CH_3)_2$), 1.33 (brs, 36H; $-CH(CH_3)_2$), 1.38–1.50 (m, 8H; $-CH_2CH_2CH_2CH_3$), 1.78–1.86 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.37 (t, $^3J_{H,H}$ = 7.2 Hz, 8H; $-CH_2CH_2CH_2CH_3$), 3.94 (s, 12H; CO_2CH_3), 9.64 ppm (s, 4H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 11.7, 14.2, 19.0, 23.1, 29.7, 33.6, 52.4, 103.9, 108.6, 119.4, 125.5, 127.9, 130.9, 131.2, 138.1, 169.5 ppm; HRMS *m/z* (EI) calcd for $C_{68}H_{94}O_8Si_2$: 1094.6487 $[M]^+$; found: 1094.6504; elemental analysis: calcd (%) for $C_{68}H_{94}O_8Si_2$: C 74.54, H 8.65; found: C 74.39, H 8.66.

1,4,8,11-Tetrabutyl-6,13-dihydroxy-6,13-bis(trimethylsilylethynyl)-6,13-dihydropentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (9f): The title compound (380 mg) was prepared by the same way as described for **5c** in 79% yield from **1b** (382 mg, 0.50 mmol).

9f: ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.22 (s, 18H; $Si(CH_3)_3$), 0.97 (t, $^3J_{H,H}$ = 7.2 Hz, 12H; $-CH_2CH_2CH_2CH_3$), 1.45–1.52 (m, 8H; $-CH_2CH_2CH_2CH_3$), 1.70–1.80 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.06–3.16 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.82 (s, 12H; CO_2CH_3), 8.92 ppm (s, 4H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 0.3, 14.0, 23.1, 29.8, 33.6, 52.4, 69.5, 94.0, 106.2, 123.8, 129.1, 132.4, 137.2, 137.3, 169.4 ppm; HRMS *m/z* (EI) calcd for $C_{56}H_{72}O_{10}Si_2$: 960.4664 $[M]^+$; found: 960.4675.

1,4,8,11-Tetrabutyl-6,13-bis(trimethylsilylethynyl)pentacene-2,3,9,10-tetracarboxylic acid tetramethyl ester (10f): The title compound (41 mg) was prepared as a blue solid by the same way as described for **6a** in 90% yield from **9f** (48 mg, 0.05 mmol).

10f: Blue solid; m.p.: 208–210°C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si): δ = 0.52 (s, 18H; $Si(CH_3)_3$), 1.02 (t, $^3J_{H,H}$ = 7.2 Hz, 12H; $-CH_2CH_2CH_2CH_3$), 1.57–1.64 (m, 8H; $-CH_2CH_2CH_2CH_3$), 1.88–1.93 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.32–3.35 (m, 8H; $-CH_2CH_2CH_2CH_3$), 3.95 (s, 12H; CO_2CH_3), 9.58 ppm (s, 4H; aromatic CH); ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 0.2, 14.1, 23.5, 30.3, 33.5, 52.4, 102.0, 111.6, 119.2, 125.5, 127.8, 130.86, 130.92, 138.2, 169.4 ppm; HRMS *m/z* (FAB) calcd for $C_{56}H_{70}O_8Si_2$: 926.4609 $[M]^+$; found: 926.4619; elemental analysis: calcd (%) for $C_{56}H_{70}O_8Si_2$: C 72.53, H 7.61; found: C 72.78, H 7.62.

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Received: December 25, 2009
Published online: May 7, 2010

