Synthetic Methods

Short Synthesis of [5]- and [7]Phenacenes with Silyl Groups at the Axis Positions

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Abstract: [5]Phenacene with trimethylsilyl groups at the axis positions was synthesized by the ruthenium-catalyzed direct C–H arylation of a 1-formyl-7-phenanthrene-derived aldimine, followed by sequential Wittig olefination and bismuth-catalyzed cyclization of the resulting vinyl ethers. By using the same synthetic building blocks and sequential Wittig olefination and photocyclization, the number of fused benzene rings was readily increased to seven to afford 3,12-disi-

Introduction

The synthesis of fused polycyclic aromatic hydrocarbons for optoelectronic applications has received considerable attention, owing to their potential utility in organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and organic field-effect transistors (OFETs).^[1] Among many promising small molecules, pentacene and rubrene are known to be key components of high-performance OFETs.^[2] Such OFETs are lighter, more flexible, and more-easily shaped than transistors based on silicon or other inorganic materials, and they have attracted interest owing to their potential use in flexible displays, electronic paper, and large-area chemical sensors. Although these acene-type organic semiconductors show excellent performance,^[2] their major drawback is instability in air, owing to their high HOMO energy levels. Therefore, the development of new molecules with superior device performance, better stability, and solubility remains a challenge. Recently, [n]phenacenes that contains fused benzene rings in a "W-shape" have attracted interest as a new and promising class of organic OFETs.^[3,4] Because of their low HOMO energies, these compounds exhibit improved chemical stability under ambient conditions compared with their isostructural analogues, [n]acenes. Further-

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lyl[7]phenacene. The introduction of silyl groups endowed the [*n*]phenacene frameworks with good solubility, as well as enabling further functionalization. The electronic structure of these new [*n*]phenacenes was determined by photophysical measurements and by density functional theory calculations, which clearly implied effective conjugation throughout the entire π framework.

more, [5]phenacene (picene) is the first hydrocarbon to show unique superconductivity through intercalation with an alkali metal.^[5] The importance of [*n*]phenacenes means that an efficient route is required for the direct synthesis of suitably functionalized [*n*]phenacenes from simple building blocks in fewer steps. However, although numerous studies have investigated the transition-metal-catalyzed synthesis of fused polyaromatic hydrocarbons,^[6] their application to the short and efficient synthesis of functionalized [*n*]phenacenes has so far been limited.^[7]

To further develop the unique properties of [*n*]phenacenes, we investigated short transition-metal-catalyzed syntheses of [*n*]phenacenes that contained appropriate functional groups at the axis positions. This design was inspired by a recent mobility study of 3,10-di(tetradecyl)[5]phenacene (**1a**) by Kubozono and co-workers (Scheme 1).^[4e] The hole mobility of compound **1a** reached 20 cm²V⁻¹s⁻¹ (average value: 14 cm²V⁻¹s⁻¹), the second-highest among *p*-channel organic thin-film FETs. In view of the fact that the mobility of picene without any substituents was less than 5 cm²V⁻¹s⁻¹, it was concluded that the



Scheme 1. Structures and average hole mobilities of high-performance thinfilm OFETs.

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effect of alkyl side-chains is important for the development of high-performance organic FET devices.^[4a-d] This hypothesis is likely to be true, because [1]benzothieno[3,2-b][1]benzothiophene (1 b), which contains two octyl groups at the axis positions, has been reported to possess the highest mobility value $(43 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1})$ reported to date.^[8c] In addition, thiophenefused polycyclic aromatic compounds with linear alkyl chains at the axis positions, such as 2,7-dioctyl[1]benzothieno[3,2-b] [1]benzothiophene (1c) and 2-tridecyldinaphtho[2,3-d:2',3'd']benzo[1,2-b:4,5-b']dithiophene (1 d), have been found to be good candidates for application in organic transistors.[8b,d] These side-chains are considered essential to high-performance organic thin-film transistors because they result in the formation of well-defined layered crystal structures.^[4e,8] Based on these results, we chose [n]phenacenes with two trimethylsilyl groups as targets for this study, because the trimethylsilyl groups can be easily transformed into various functional groups, including halogen, hydroxy, and aryl groups, by oxidative halogenation, Tamao oxidation, and Hiyama cross-coupling reactions (Scheme 2).^[9–11]

Results and Discussion

We recently reported a short synthesis of [6]phenacenes (fulminenes) that contained two long alkyl chains at the axis positions.^[7d] This synthesis consisted of ruthenium-catalyzed direct C–H arylation,^[12] followed by sequential Wittig olefination and bismuth-catalyzed cyclization of the resulting vinyl ethers (Scheme 3).^[13] Based on this success, we initially attempted the synthesis of 3,10-disilyl[5]phenacene (**2**) and 3,12-disilyl[7]phenacene (**3**) through a similar three-step synthesis strategy. However, in the first reaction that we attempted, the ruthenium-catalyzed direct C–H arylations of aldimines that were derived from 3-silylbenzaldehyde with 1,4-dibromobenzene (Scheme 4a) or 1,8-diformylphenanthrene with bromo-4-silyl-



Scheme 2. Structures of the target [5]- and [7]phenacenes with silyl groups at the axis positions.



Scheme 3. Short transition-metal-catalyzed synthesis of 3,11-dialkyl[6]phenacenes.

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benzene (Scheme 4b) did not proceed efficiently. Only a small amount of the desired coupling products (**4** and **5**) were formed and the corresponding monoarylated compounds (2formylbiaryl, Scheme 4a, and 2-arylphenanthrene, Scheme 4b, respectively) were obtained in low yields. These monoarylated compounds were obtained as mixtures of the corresponding debrominated compounds and these mixtures were inseparable. In view of these results, we decided to change the synthetic route, as shown in Scheme 5. This new design has the advantage of allowing the synthesis of both [5]- and [7]phenacenes from a common synthetic intermediate, 1-formyl-7phenanthrene (**9**), without the requirement for a two-fold direct C–H arylation reaction.

First, building block **9** was synthesized by direct C–H bond arylation, Wittig reaction, and cyclization of the resulting vinyl ether (Scheme 6). Ruthenium-catalyzed direct arylation of the C–H bond of an aldimine derived from 2-tolualdehyde gave 2biarylcarbaldehyde **6** in 72% yield.^[12] Next, the formyl group of compound **6** was converted into a methoxyethenyl group by Wittig reaction with chloromethoxymethyltriphenylphosphine and potassium *tert*-butoxide. Treatment of the resulting regioisomeric mixture of methyl vinyl ether **7** (E/Z=81:19) with a catalytic amount of [Bi(OTf)₃] furnished the corresponding 1methyl-7-silylphenanthrene (**8**) in 92% yield.^[13] Subsequent bromination, which led to dibromomethylphenanthrene, followed by hydrolysis, provided the key synthetic building block 1-formyl-7-trimethylsilylphenanthrene (**9**) in 90% yield.

Aldehyde 5 was submitted to the same pattern of reactions again to increase the number of benzene rings in [3]phenacene 9 (Scheme 7). The ruthenium-catalyzed direct C–H bond arylation of aldimine 9' was slightly less efficient than that in the synthesis of compound 6, although the subsequent Wittig reaction afforded vinyl ether 11 in moderate yield with similar stereoselectivity, which was observed in the formation of compound 7. Finally, bismuth-catalyzed cyclization afforded the de-

> sired 3,10-di(trimethylsilyl)[5]phenacene (**2**) in 77% yield.^[9]

The number of benzene rings could also be increased to seven in three steps by using compound 8 as a synthetic building block (Scheme 8). First, phenanthrene 8 was brominated by using N-bromosuccinimide (NBS) to yield the corresponding benzyl bromide, which was used in the subsequent Wittig reaction directly without purification. After heating at reflux in CH₂Cl₂ with triphenylphosphine, the resulting phosphonium salts were treated with aldehyde 9 and K₂CO₃ to furnish diphenanthryl ethylene 12 as a mixture of E and Z stereoisomers. Photocyclization under irradiation by a UV lamp in the presence of ACES

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Scheme 4. Attempted synthesis of [5]- and [7] phenacenes with silyl groups at the axis positions.



Scheme 5. Modified synthetic route to [5]- and [7]phenacenes 2 and 3 from [3]phenacene.



Scheme 6. Preparation of the synthetic building blocks of [5]- and [7] phenacenes ($Si = SiMe_3$).

iodine yielded 3,12-di(trimethylsilyl)[7]phenacene (**3**) in 46% yield. This is a rare example of the synthesis of functionalized [n]phenacenes (n > 6).^[7,d, 14]

The photophysical properties of 3,10-disilyl[5]phenacene (2) and 3,12-disilyl[7]phenacene (3) were investigated by UV/Vis absorption spectroscopy to obtain insight into their electronic

structures (Figure 1). [5]Phenacene **2** showed a maximum peak at 297 nm, along with two shoulder peaks at 308 and 330 nm. The absorption peaks of [7]phenacene **3** shifted bathochromically by 14–16 nm with respect to those of compound **2**, thereby reflecting the effective expansion of π conjugation through the phenacene backbone. These values are summarized in Table 1, along with the HOMO–LUMO gaps (E_g^{opt}) that were calculated from the onset of absorption. A clear shift in emissions (11 nm) was also observed for [5]phenacene **2** and [7]phenacene **3**.

To obtain further insight into the effects of the silyl substituents and the number of fused benzene rings on the conjugated π system, the molecular orbitals and energy levels of the frontier orbitals were calculated by using density functional theory (DFT) at the B3LYP/6-31G(d) level of theory (Figure 2). The calculated band-gaps were higher than those obtained from the UV/Vis absorption onset study (see E_g^{opt} in Table 1) by about 1.0 eV. Although the distribution of the LUMO orbital of [5]phenacene looked different to that of compound **2**, the



Scheme 7. Synthesis of 3,10-disilyl[5]phenacene (2).

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Scheme 8. Synthesis of 3,12-disilyl[7]phenacene (3).



Figure 1. UV/Vis absorption (solid lines) and emission spectra (dashed lines) of 3,10-disilyl[5]phenacene (**2**) and 3,12-disilyl[7]phenacene (**3**) in CH_2CI_2 at 25 °C.

Table 1. Optical data for [n]phenacenes.							
Compound	λ_{\max}^{abs}	$\varepsilon [M^{-1} cm^{-1}]$	λ_{\max}^{abs} [nm] ^[a]	E_g^{opt} [eV] ^[b]	λ _{max} em [nm] ^[c]		
[5]phenancene ^[d]	285	94 300	384	3.23	378		
2	292	60800	388	3.20	383		
[6]phenacene ^[e]	293	-	389	3.19	385		
3	308	47 300	412	3.01	394		
[a] In CH_2CI_2 (1×10 ⁻⁵ M); [b] Determined from the onset wavelength							

 (λ_{onset}) in the absorption spectrum $(E_g^{\text{opt}}=1240/\lambda_{\text{onset}})$; [c] Maximum fluorescence emission in CH_2Cl_2 (5×10⁻⁶ M); [d] Ref. [7a]; [e] Ref. [7c]; the molar absorption coefficient could not be determined, owing to the low solubility of [6]phenacene.

energy levels of these compounds were almost identical. This similarity was because the LUMO coefficient of picene in the 3-position was relatively small and, therefore, the electronic effect of functional groups at this position was not significant. In contrast, the optical band-gap became slightly narrower as the number of fused benzene rings increased (2 versus 3), thus implying that there was effective conjugation over the whole π framework of compound 3.

Finally, the resulting [n]phenacenes underwent further transformations to demonstrate their synthetic utility (Scheme 9).



Figure 2. Molecular orbital plots and energy diagram of the frontier orbitals (HOMO and LUMO) of picene, compound **2**, and compound **3**, as estimated by using density functional theory at the B3LYP/6-31G(d) level of theory. The values between each level are the energy gaps of the each frontier orbitals.

For example, treatment of [5]phenacene **2** with *N*-bromosuccinimide afforded 3-bromo-10-trimethylsilyl[5]phenacene (**13**) in 93% yield. The reaction occurred selectively at one of the trimethylsilyl groups without producing 3,10-dibromo[5]phenacene.

Conclusion

We have demonstrated a short synthesis of [n]phenacenes with silyl groups at the axis positions that proceeded through sequential ruthenium-catalyzed direct C-H arylation/Wittig olefination/bismuth-catalyzed cyclization, and photocyclization reactions. UV/Vis absorption and fluorescence studies of the resulting 3,10-disilyl[5]- and 3,12-dislyl[7]phenacenes indicated that the silyl groups did not affect the energy levels of the frontier orbitals. However, effective conjugation over the whole π framework was observed for both [*n*]phenacenes. Therefore, the incorporation of trimethylsilyl groups is an effective way of endowing these polycyclic aromatic hydrocarbons with solubility without affecting their photophysical properties. The silyl groups could be transformed into bromide groups, which suggests that further tuning of the electronic properties of these compounds is possible. These results exemplify that such [n] phenacenes are π -conjugated systems with potential applications as optoelectronic devices.

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Scheme 9. Bromination of 3,11-disilyl[5]phenacene (2).

Experimental Section

General Methods

All of the reactions were performed in dry solvent under an argon atmosphere. Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Water was degassed with argon for 20 min before use. 1,2-Dichloroethane was purchased from Wako Pure Chemical Industries and dried by using the usual methods, distilled, and degassed with argon for 20 min before use. [{RuCl₂(p-cymene)}₂] was purchased from Kanto Chemical Co., Inc. [Bi(OTf)₃] was purchased from Sigma-Aldrich. 4-Trimethylsilyl-1-bromobenzene was prepared according to a literature procedure.^[15] Column chromatography was performed on neutral silica gel 60 N (40-50 µm) that was purchased from Kanto Chemical Co., Inc. ¹H NMR (400 and 600 MHz) and ¹³C NMR spectra (100 and 150 MHz) were recorded on Varian 400 and 600 MR spectrometers, respectively. ¹H chemical shifts are reported in ppm, relative to the solvent resonance resulting from incomplete deuteration (CDCl_{3r} δ = 7.26 ppm) as an internal standard. ¹³C NMR spectra were recorded with complete proton decoupling and the chemical shifts are reported relative to CDCl_3 ($\delta =$ 77.0 ppm). The following abbreviations are used: s = singlet, d =doublet, t = triplet, m = multiplet. High-resolution mass spectroscopy (HRMS) was performed on a JEOL JMS-700 MStation FAB-MS. Melting points were recorded on a Yanako MP-J3 melting-point apparatus and are uncorrected.

2-(4-Trimethylsilylphenyl)-6-tolualdehyde (6)

A mixture of 2-tolualdehyde (4.6 mL, 40 mmol) and toluidine (4.3 g, 40 mmol) was stirred at 25 °C for 1 h before 4-bromo(trimethylsilyl)benzene (13.8 g, 60 mmol), potassium carbonate (16.6 g, 120 mmol), triphenylphosphine (2.1 g, 8.0 mmol), potassium acetate (1.6 g, 16 mmol), dichloro(p-cymene)ruthenium dimer (2.45 g, 4.0 mmol), and water (80 mL) were added. The resulting mixture was stirred at 130 °C for 36 h, and then a concentrated aqueous solution of HCl (20 mL) was added dropwise at 0°C. After stirring at 25 °C for 4 h, the mixture was quenched with brine and extracted three times with EtOAc (3×100 mL). The combined organic layer was dried over MgSO4 and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (n-hexane) to give 2-(4-trimethylsilylphenyl)-6-tolualdehyde (6) as a yellow oil (72% yield, 7.7 g, 29 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C): $\delta = 9.97$ (s, 1 H), 7.60 (d, J = 7.6 Hz, 2 H), 7.46 (t, J=7.2 Hz, 1 H), 7.34 (d, J=7.8 Hz, 2 H), 7.27 (d, J= 7.8 Hz, 2 H), 2.66 (s, 3 H), 0.32 ppm (s, 9 H); $^{13}{\rm C}~{\rm NMR}$ (100 MHz, $CDCl_{3}$, 25 °C): $\delta = 194.5$, 147.1, 140.2, 139.9, 139.2, 133.3, 132.6, 132.1, 131.1, 129.4, 128.5, 21.5, -1.1 ppm; HRMS (FAB⁺): m/z calcd for C₁₇H₂₀OSi: 268.1283 [M]⁺; found: 268.1288.

3-(4-Trimethylsilylphenyl)-2-(methoxyethenyl)toluene (7)

A solution of potassium *tert*-butoxide (4.5 g, 40 mmol) in THF (50 mL) was added to a stirring solution of (methoxymethyl)triphenylphosphonium chloride (13.1 g, 40 mmol) in THF (120 mL) at 0 °C. The resulting mixture was warmed to 25 °C and stirred for 1 h. A solution of 2-(4-trimethylsilylphenyl)-6-tolualdehyde (6; 7.7 g, 29 mmol) in THF (30 mL) was added dropwise at 0°C and the resulting mixture was stirred at 25 °C for an additional 15 h. The mixture was quenched with NH₄Cl and extracted three times with EtOAc (3×100 mL). The combined organic layer was dried over MgSO₄ and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (n-hexane) to give (E)-3-(4-trimethylsilylphenyl)-2-(methoxyethenyl)toluene (7) as a yellow oil (77% yield, 6.5 g, 22 mmol). Another fraction contained a mixture of two stereoisomers, (E)-7 and (Z)-7, as a yellow oil (17% yield, 1.5 g, 4.9 mmol). (E)-7: ¹H NMR (400 MHz, CDCl₃, 25 °C): $\delta \!=\! 7.56$ (d, $J \!=\! 8.4$ Hz, 2H), 7.37 (d, $J \!=\!$ 8.4 Hz, 2 H), 7.24–7.15 (m, 3 H), 6.22 (d, J=13.2 Hz, 1 H), 5.64 (d, J= 13.2 Hz, 1 H), 3.51 (s, 3 H), 2.44 (s, 3 H), 0.34 ppm (s, 9 H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 151.7, 143.0, 141.4, 138.1, 136.5, 133.1, 132.8, 129.4, 129.2, 128.0, 125.8, 56.1, 21.5, -1.1 ppm; HRMS (FAB⁺): *m/z* calcd for C₁₉H₂₄OSi: 296.1596[*M*]⁺; found: 296.1585.

1-Methyl-7-(trimethylsilyl)phenanthrene (8)

A solution of a mixture of (*E*)- and (*Z*)-3-(4-trimethylsilylphenyl)-2-(methoxyethenyl)toluene (**7**; 6.4 g, 22 mmol) in 1,2-dichloroethane (130 mL) was treated with [Bi(OTf)₃] (709 mg, 1.1 mmol) and the mixture was stirred at 25 °C for 1 h. The solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel (*n*-hexane) to afford 1-methyl-7-(trimethylsilyl)phenanthrene (**8**) as a white solid (92% yield, 5.3 g, 20 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ =8.70 (d, *J*=8.4 Hz, 1H), 8.62 (d, *J*= 8.4 Hz, 1H), 8.09 (s, 1H), 7.99 (d, *J*=8.8 Hz, 1H), 7.83 (d, *J*=8.4 Hz, 1H), 7.82 (dd, *J*=1.2, 8.4 Hz, 1H), 7.58 (t, *J*=8.8 Hz, 1H), 7.48 (d, *J*=7.6 Hz, 1H), 2.79 (s, 3H), 0.43 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ =138.1, 134.5, 133.8, 130.7 (overlapped), 130.6, 130.0, 127.5, 126.5, 125.8, 122.5, 121.7, 120.6, 19.6, -1.1 ppm. HRMS (FAB⁺): *m/z* calcd for C₁₈H₂₀Si: 264.1334 [*M*]⁺; found: 264.1335.

1-Formyl-7-(trimethylsilyl)phenanthrene (9)

N-bromosuccinimide (1.78 g, 10 mmol) and benzoyl peroxide (20 mg) were added to a stirring solution of 1-methyl-7-(trimethylsilyl)phenanthrene (8; 1.32 g, 5.0 mmol) in CCl₄ (20 mL). The resulting mixture was heated at reflux for 16 h. The mixture was washed with brine and extracted three times with EtOAc (3×40 mL). The combined organic layer was dried over MgSO₄ and the organic solvent was removed under reduced pressure. To the resulting mixture dissolved in DMSO (40 mL) was added NaHCO₃ (840 mg, 10 mmol), and the solution was heated at 90 °C for 3 h. The mixture was quenched with brine and extracted three times with EtOAc (3×40 mL). The combined organic layer was dried over MgSO₄ and the organic solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (n-hexane/EtOAc, 25:1 v/v) to give 1-formyl-7-(trimethylsilyl)phenanthrene (9) as a yellow solid (90% yield, 1.3 g, 4.5 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C): $\delta = 10.5$ (s, 1 H), 9.14 (d, J = 8.8 Hz, 1 H), 8.97 (d, J=8.8 Hz, 1 H), 8.65 (d, J=7.6 Hz, 1 H), 8.10 (s, 1 H), 8.08 (dd, J=1.2, 8.0 Hz, 1 H), 7.97 (d, J=8.8 Hz, 1 H), 7.84 (dd, J= 1.2, 9.6 Hz, 1 H), 7.79 (t, J=8.0 Hz, 1 H), 0.41 ppm (s, 9 H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 193.2, 139.4, 134.9, 133.9, 131.2, 131.2, 130.7, 130.5, 130.2, 130.1, 129.7, 128.7, 125.3, 121.8, 121.5, -1.4 ppm; HRMS (FAB⁺): *m/z* calcd for C₁₈H₁₈OSi: 278.1127 [*M*]⁺; found: 278.1137.

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1-Formyl-2-(4-(trimethylsilyl)phenyl)-7-(trimethylsilyl)phenanthrene (10)

According to a similar procedure for the synthesis of biphenyl **6**, the reaction of an aldimine derived from compound **9** (268 mg, 0.96 mmol) afforded 1-formyl-2-(4-(trimethylsilyl)phenyl)-7-(trimethylsilyl)phenanthrene (**10**) as a yellow solid (49% yield, 201 mg, 0.47 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C) : δ = 10.2 (s, 1H), 9.13 (d, *J* = 10.0 Hz, 1H), 8.92 (d, *J* = 8.8 Hz, 1H), 8.65 (d, *J* = 8.8 Hz, 1H), 8.12 (s, 1H), 7.97 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 0.42 (s, 9H), 0.38 ppm (s, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 195.0, 146.9, 140.7, 139.5, 138.8, 134.1, 133.3, 131.4, 131.0, 130.3, 129.9, 129.88, 129.85, 129.83, 129.6, 128.5, 127.6, 123.2, 121.7, -1.1, -1.0 ppm; HRMS (FAB⁺): *m/z* calcd for C₂₇H₃₀OSi₂: 426.1835 [*M*]⁺; found: 426.1855.

3-(4-(Trimethylsilyl)phenyl)-4-methoxyethenyl-8-(trimethylsilyl)phenanthrene (11)

According to a similar procedure for the synthesis of methyl vinyl ether **7**, the reaction of 1-formyl-2-(4-(trimethylsilyl)phenyl)-7-(trimethylsilyl)phenanthrene (**10**; 200 mg, 0.47 mmol) afforded 1-(methoxyethenyl)-2-(4-(trimethylsilyl)phenyl)-7-(trimethylsilyl)phenanthrene (**11**) as a yellow solid (71% yield, 147 mg, 0.33 mmol). ¹H NMR (400 MHz, CDCl₃, 25 °C): δ = 8.69 (d, *J* = 8.4 Hz, 1 H), 8.66 (d, *J* = 8.8 Hz, 1 H), 8.26 (d, *J* = 8.8 Hz, 1 H), 8.07 (s, 1 H), 7.81 (d, *J* = 7.6 Hz, 1 H), 7.79 (d, *J* = 8.8 Hz, 1 H), 7.60 (d, *J* = 7.6 Hz, 1 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 6.41 (d, *J* = 12.8 Hz, 1 H), 6.02 (d, *J* = 12.8 Hz, 1 H), 3.64, (s, 3 H), 0.41 (s, 9 H), 0.35 ppm (s, 9 H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 152.8, 142.9, 139.5, 138.6, 138.4, 134.0, 133.0, 131.6, 131.2, 131.0, 130.9, 130.7, 129.8, 129.5, 128.5, 126.9, 124.6, 122.0, 121.1, 101.1, 56.4, -1.0 ppm; HRMS (FAB⁺): *m/z* calcd for C₂₉H₃₄OSi₂: 454.2148 [*M*]⁺; found: 454.2161.

3,10-Di(trimethylsilyl)[5]phenacene (2)

According to a similar procedure for the synthesis of phenanthrene **8**, the reaction of 3-(4-(trimethylsilyl)phenyl)-4-methoxyethenyl-8-(trimethylsilyl)phenanthrene (**11**; 105 mg, 0.23 mmol) afforded 3,10-di(trimethylsilyl)[5]phenacene (**2**) as a white solid (77% yield, 75 mg, 0.18 mmol). M.p. > 300 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C): δ =8.95 (s, 2 H), 8.82 (d, *J*=8.8 Hz, 2 H), 8.78 (d, *J*=8.8 Hz, 2 H), 8.16 (s, 2 H), 8.04 (d, *J*=8.8 Hz, 2 H), 7.87 (d, *J*=9.6 Hz, 2 H), 0.41 ppm (s, 18H); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ =138.7, 134.2, 131.2, 131.1, 130.7, 128.9, 128.8, 128.7, 127.6, 122.2, 121.6, -1.0 ppm; HRMS (FAB⁺): *m/z* calcd for C₂₈H₃₁Si₂: 422.1886 [*M*]⁺; found: 422.1893.

1,2-(8-Trimethylsilyl-4-phenanthryl)ethene (12)

N-bromosuccinimide (170 mg, 0.96 mmol) and benzoyl peroxide (5.0 mg) were added to a mixture of phenanthrene **8** (396 mg, 0.87 mmol) in CCl₄ (3 mL) and the resulting mixture was heated at reflux for 16 h. The mixture was washed with brine and extracted three times with EtOAc (3×10 mL). The combined organic layer was dried over MgSO₄ and the organic solvent was removed under reduced pressure. The mixture was dissolved in CH₂Cl₂ (10 mL), triphenylphosphine (228 mg, 0.87 mmol) and potassium carbonate (240 mg, 1.7 mmol) were added, and the resulting mixture was heated at reflux for 24 h. A solution of 1-formylphenanthrene **9** (242 mg, 0.87 mmol) in CH₂Cl₂ (10 mL) was added and the mixture was stirred for 10 min at 25°C. The white

precipitate was filtered and dried under reduced pressure to yield 1,2-(8-trimethylsilyl-4-phenanthryl)ethene (**12**) as a mixture of two stereoisomers (71% yield, 0.62 mmol, 332 mg). (*E*)-**12**: m.p.> 300 °C; ¹H NMR (600 MHz, CDCl₃, 60 °C): δ = 8.74 (d, *J* = 8.4 Hz, 2 H), 8.71 (d, *J* = 8.4 Hz, 2 H), 8.22 (d, *J* = 9.0 Hz, 2 H), 8.07 (s, 2 H), 8.00 (d, *J* = 7.2 Hz, 2 H), 7.99 (s, 2 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 7.81 (d, *J* = 9.0 Hz, 2 H), 7.72 (t, *J* = 7.2 Hz, 2 H), 0.40 ppm (s, 18 H); ¹³C NMR (150 MHz, CDCl₃, 60 °C): δ = 139.0, 136.1, 134.2, 131.3, 131.2, 131.0, 130.8, 130.2, 130.0, 127.4, 126.3, 125.1, 122.7, 122.6, 122.1, -1.0 ppm; HRMS (FAB⁺): *m/z* calcd for C₃₆H₃₆Si₂: 524.2356 [*M*]⁺; found: 524.2337.

3,12-Di(trimethylsilyl)[7]phenacene (3)

lodine (17 mg, 0.067 mmol) and THF (91 µL, 1.1 mmol) were added to a solution of diphenanthryl ethylene **12** (30 mg, 0.056 mmol) in toluene (43 mL) and the solution was irradiated with a UV lamp (125 W) at 25 °C for 24 h. The resulting precipitate was filtered and dried under reduced pressure to give 3,12-di(trimethylsilyl)[7]phenacene (3) as a white solid (46% yield, 14 mg, 0.026 mmol). M.p. > 300 °C; ¹H NMR (600 MHz, CDCl₃, 60 °C): δ = 9.10 (d, *J* = 9.0 Hz, 2H), 9.05 (s, 2H), 9.02 (d, *J* = 9.0 Hz, 2H), 8.88 (d, *J* = 9.6 Hz, 2H), 8.86 (d, *J* = 9.6 Hz, 2H), 8.19 (s, 2H), 8.09 (d, *J* = 9.6 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 0.44 ppm (s, 18H); ¹³C NMR spectra were not recorded, owing to the low solubility of the product; HRMS (FAB⁺): *m/z* calcd for C₃₆H₃₄Si₂: 522.2199 [*M*]⁺; found: 522.2203.

3-Bromo-10-trimethylsilyl[5]phenacene (13)

N-bromosuccinimide (6.4 mg, 0.036 mmol) was added to a solution of 3,10-di(trimethylsilyl)[5]phenacene (**2**; 12.5 mg, 0.030 mmol) in MeCN (1.0 mL) and the mixture was heated at reflux for 24 h. DMF (5 mL) was added and the mixture was washed three times with brine (3×10 mL). The organic solvent was removed under reduced pressure to afford 3-bromo-10-trimethylsilyl[5]phenacene (**13**) as a white solid (93% yield, 12 mg, 0.028 mmol). M.p. > 300 °C; ¹H NMR (600 MHz, CDCl₃, 60 °C): δ = 8.97 (d, *J* = 9.0 Hz, 1H), 8.87 (d, *J* = 9.6 Hz, 1H), 8.82–8.72 (m, 3 H), 8.70 (d, *J* = 9.0 Hz, 1H), 8.16 (s, 1H), 8.15 (s, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 0.43 ppm (s, 9H); ¹³C NMR spectra were not recorded, owing to the low solubility of the product; HRMS (FAB⁺): *m/z* calcd for C₂₅H₂₁BrSi: 428.0596 [*M*]⁺; found: 428.0568.

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