Supplmentary Information

Solid State Structures and Photophysical Properties of (Trimethylsilyl)methyl-substituted Anthracenes and Pyrenes

Masaki Shimizu,* Hironori Tatsumi, Kenji Mochida and Tamejiro Hiyama

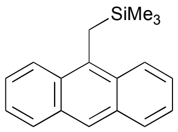
Department of Material Chemistry, Graduate School of Engineering, Kyoto University,
Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

E-mail: shimizu@npc05.kuic.kyoto-u.ac.jp

General Information

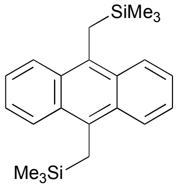
Melting points were determined using Seiko Instrument Inc. DSC6200. ^{1}H NMR spectra measured on a Varian Mercury 300 (300 MHz) and 400 (400 MHz) spectrometers. The chemical shifts of ^{1}H NMR are expressed in parts per million downfield relative to the internal chloroform (δ = 7.26 ppm). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet, q, quartet; m, multiplet. ^{13}C NMR spectra were measured on a Varian Mercury 300 (75 MHz) and 400 (100 MHz) spectrometers with chloroform (δ = 77.0 ppm). ^{29}Si NMR spectra were measured on a Varian Mercury 400 (80 MHz) spectrometer with tetramethylsilane as an internal standard (δ = 0 ppm). Chemical shift values are given in parts per million downfield relative to the internal standard. Infrared spectra (IR) were recorded on a Shimadzu FTIR-8400 spectrometer. UV and fluorescence spectra were measured with Shimadzu UV-2100PC and RF-5300PC spectrometers, respectively. Thin films spin-coated on quartz were prepared with MIKASA SPINCOATER MS-A100. GC-MS analyses were performed with a JEOL JMS-700 spectrometer by electron ionization at 70 eV. FAB-MS analyses were performed with a JEOL-HX110A spectrometer. Elemental analyses were carried out with a YANAKO MT2 CHN CORDER machine at Elemental Analysis Center of Kyoto University. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} and column chromatography was carried out using Merck Kieselgel 60 (230-400 mesh). Preparative HPLC was carried out with a Japan Analytical Industry Co., Ltd, LC-908 chromatograph using a JAIGEL-1H and -2H GPC columns. 9-Bromoanthracene, 9,10-dibromoanthracene, and 1-bromopyrene were purchased from Aldrich and used as received. Et_2O and THF were distilled from benzophenone ketyl before use. All reactions were carried out under an argon atmosphere.

Preparation of 9-(trimethylsilyl)methylanthracene (1a)



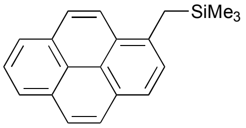
To a Schlenk tube (80 mL) equipped with a magnetic stirring bar were added 9-bromoanthracene (1.90 g, 7.5 mmol), and $NiCl_2(PEt_3)_2$ (82 mg, 0.23 mmol). The tube was then capped with a rubber septum, evacuated, and purged with argon. The evacuation–purge operation was repeated three times. Diethyl ether (23 mL) was added to the tube at 0 °C. To the solution was added 1 M solution of (trimethylsilyl)methylmagnesium chloride in Et_2O (9.0 mL, 9.0 mmol) dropwise at 0 °C over a period of 10 min. Then, the solution was refluxed for 70 h. After the resulting solution was cooled to room temperature, 5% aq. HCl (10 mL) was added to the solution at 0 °C. The aqueous layer was extracted with Et_2O (10 mL x 3). The combined organic layer was washed with sat. aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane) followed by recrystallization (hexane/EtOH 1:1) to give **1a** (1.89 g, 95% yield, CAS NO. 88920-42-7) as a colorless solid. Mp: 65.4 °C. TLC: R_f 0.30 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.00 (s, 9H), 3.18 (s, 2H), 7.42–7.48 (m, 4H), 7.95–8.00 (m, 2H), 8.14-8.19 (m, 2H), 8.23 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ –0.2, 19.1, 123.5, 124.4, 124.6, 125.3, 128.8, 129.0, 131.5, 134.1. ^{29}Si NMR (80 MHz, $CDCl_3$): δ 4.31 (s). IR (KBr): ν = 3045, 2950, 1620, 1340, 1244, 1148, 885, 862, 839, 731 cm^{-1}. MS (EI) *m/z*: 265 (2, [M^+] + 2), 264 (10, [M^+] + 1), 264 (38, [M^+]), 191 (30), 73 (100). Anal. Calcd for $C_{18}H_{20}Si$: C, 81.76; H, 7.62. Found: C, 81.56; H, 7.62.

Preparation of 9,10-bis[(trimethylsilyl)methyl]anthracene (1b)



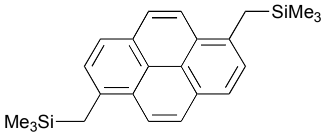
To a Schlenk tube (20 mL) equipped with a magnetic stirring bar were added 9,10-dibromoanthracene (0.34 g, 1.0 mmol) and $NiCl_2(PPh_3)_2$ (33 mg, 0.05 mmol). The tube was then capped with a rubber septum, evacuated, and purged with argon. The evacuation–purge operation was repeated three times. Diethyl ether (10 mL) was added to the mixture at 0 °C. To the solution was added a 1 M solution of (trimethylsilyl)methylmagnesium chloride in Et_2O (3.0 mL, 3.0 mmol) at 0 °C. The solution was refluxed for 18 h. After the resulting solution was cooled to room temperature, 5% aq. HCl (4 mL) was added to the tube at 0 °C. The aqueous layer was extracted with CH_2Cl_2 (5 mL x 3). The combined organic layer was washed with sat. aq. NaCl (15 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by recrystallization from the EtOH solution to give **1b** (0.21 g, 61% yield, CAS NO. 69020-25-3) as a colorless solid. Mp: 143.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ –0.02 (s, 18H), 3.15 (s, 4H), 7.42–7.46 (m, 4H), 8.17–8.21 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ –0.2, 18.7, 123.8, 126.0, 128.8, 130.2. ^{29}Si NMR (80 MHz, $CDCl_3$): δ 3.95. IR (KBr): ν = 2951, 1364, 1250, 1151, 1026, 876, 837, 748, 689 cm^{-1}. MS (EI) *m/z*: 352 (8, [M$^+$] + 2), 351 (21, [M$^+$] + 1), 350 (60, [M$^+$]), 277 (25), 73 (100).

Preparation of 1-(trimethylsilyl)methylpyrene (2a)



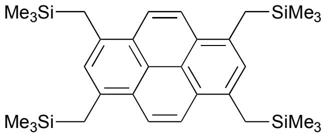
To a Schlenk tube (20 mL) equipped with a magnetic stirring bar were added 1-bromopyrene (84 mg, 0.3 mmol), $NiCl_2$ (1.9 mg, 15 μmol), and tri(2-furyl)phosphine (8.4 mg, 36 μmol). The tube was then capped with a rubber septum, evacuated, and purged with argon. The evacuation–purge operation was repeated three times. THF (2 mL) was added to the mixture at room temperature. To the solution was added 1 M solution of (trimethylsilyl)methylmagnesium chloride Et_2O (0.45 mL, 0.45 mmol) at room temperature. The resulting solution was refluxed for 12 h. The solution was allowed to cool to room temperature before adding sat. aq. NH_4Cl (2 mL) at 0 °C. The aqueous layer was extracted with Et_2O (4 mL x 3). The combined organic layer was washed with sat. aq. NaCl (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (hexane/EtOAc 100:1) followed by recrystallization (hexane/EtOH 1:1) to give **2a** (79 mg, 91% yield) as a colorless solid. Mp: 79.7 °C. TLC: R_f0.18 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.05 (s, 9H), 2.87 (s, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.94–8.07 (m, 5H), 8.12–8.18 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ –1.0, 24.6, 124.1, 124.3, 124.4, 124.6, 125.0, 125.1, 125.6, 125.7, 126.2, 127.0, 127.5, 127.6, 128.3, 131.0, 131.5, 135.7. ^{29}Si NMR (80 MHz, $CDCl_3$): δ 3.17. IR (KBr): ν = 3042, 2953, 2893, 1601, 1506, 1246, 1182, 1151, 843, 760 cm^{-1}. MS (FAB) *m/z*: 290 (18, [M$^+$] + 2), 289 (50, [M$^+$] + 1), 288 (100, [M$^+$]), 215 (20), 73 (25). Anal. Calcd for $C_{20}H_{20}Si$: C, 83.28; H, 6.99. Found: C, 83.44; H, 7.06.

Preparation of 1,6-bis[(trimethylsilyl)methyl]pyrene (2b)



To a Schlenk tube (20 mL) equipped with a magnetic stirring bar were added 1,6-dibromopyrene (110 mg, 0.3 mmol), $NiCl_2$ (1.9 mg, 15 μmol), and tri(2-furyl)phosphine (8.4 mg, 36 μmol). The tube was then capped with a rubber septum, evacuated and purged with argon. The evacuation–purge operation was repeated three times. THF (2 mL) was added to the mixture at room temperature. To the solution was added 1 M solution of (trimethylsilyl)methylmagnesium chloride in Et_2O (0.90 mL, 0.90 mmol) at room temperature. The resulting solution was refluxed for 12 h. Then, the mixture was allowed to cool to room temperature before adding sat. aq. NH_4Cl (2 mL) at 0 °C. The aqueous layer was extracted with Et_2O (4 mL x 3). The combined organic layer was washed with sat. aq. NaCl (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was dissolved in CH_2Cl_2 and filtered through a pad of Florisil. The filtrate was concentrated by rotary evaporator and the residue was purified by GPC ($CHCl_3$) followed by recrystallization (hexane/EtOH 1:1) gave **2b** (80 mg, 71% yield) as a colorless solid. Mp: 144.1 °C. TLC: R_f0.19 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.07 (s, 18H), 2.86 (s, 4H), 7.68 (d, $J = 7.8$ Hz, 2H), 8.00 (d, $J = 9.4$ Hz, 2H), 8.02 (d, $J = 7.8$ Hz, 2H), 8.07 (d, $J = 9.4$ Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ –1.0, 24.7, 122.7, 123.9, 125.5, 126.4, 126.9, 128.1, 128.3, 135.0. ^{29}Si NMR (80 MHz, $CDCl_3$): δ 3.11. IR (KBr): ν = 2953, 2893, 1603, 1495, 1418, 1246, 845, 692 cm^{-1}. MS (EI) *m/z*: 376 (4, [M^+] + 2), 375 (13, [M^+] + 1), 374 (30, [M^+]), 301 (20), 73(100). Anal. Calcd for $C_{24}H_{30}Si_2$: C, 76.94; H, 8.07. Found: C, 76.81; H, 8.08.

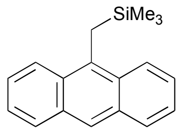
Preparation of 1,3,6,8-tetrakis[(trimethylsilyl)methyl]pyrene (2c)

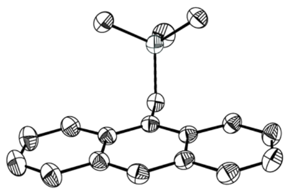


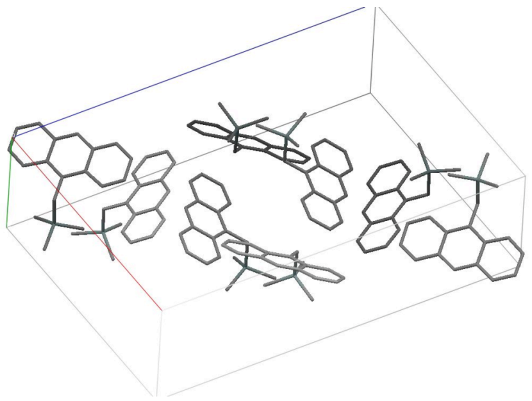
To a Schlenk tube (20 mL) equipped with a magnetic stirring bar were added 1,3,6,8-tetrabromopyrene (100 mg, 0.20 mmol), $NiCl_2$ (1.3 mg, 10 μmol), and dppp (4.9 mg, 12 μmol). The tube was then capped with a rubber septum, evacuated, and purged with argon. The evacuation–purge operation was repeated three times. THF (2 mL) was added to the mixture at room temperature. To the solution was added 1 M solution of (trimethylsilyl)methylmagnesium chloride in Et_2O (1.2 mL, 1.2 mmol) at room temperature. The resulting solution was refluxed for 5 days. The solution was allowed to cool to room temperature before adding sat. aq. NH_4Cl (2 mL) at 0 °C. The aqueous layer was extracted with Et_2O (5 mL x 3). The combined organic layer was washed with sat. aq. NaCl (10 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo. The crude product was dissolved in CH_2Cl_2 and filtered through a pad of Florisil. The filtrate was concentrated by rotary evaporator and the residue was purified by GPC ($CHCl_3$) and then recrystallization (hexane) to give **2c** (24 mg, 21% yield) as a colorless solid. Mp: 197.1 °C. TLC: R_f 0.39 (hexane/EtOAc 10:1). ^1H NMR (400 MHz, $CDCl_3$): δ 0.05 (s, 36H), 2.76 (s, 8H), 7.35 (s, 2H), 7.94 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ –0.8, 24.5, 121.8, 125.5, 126.5, 128.0, 133.6. ^{29}Si NMR (80 MHz, $CDCl_3$): δ 3.12. IR (KBr): ν = 2952, 2891, 1605, 1504, 1248, 1155, 895, 837, 692 cm^{-1}. MS (EI) *m/z*: 548 (10, $[M^+]$ + 2), 547 (28, $[M^+]$ + 1), 546 (100, $[M^+]$), 473 (30), 73 (40). Anal. Calcd for $C_{32}H_{50}Si_4$: C, 70.25; H, 9.21. Found: C, 70.17; H, 9.26.

Data of X-ray crystallographic analysis:

Compound **1a:** The detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the number CCDC-662226.



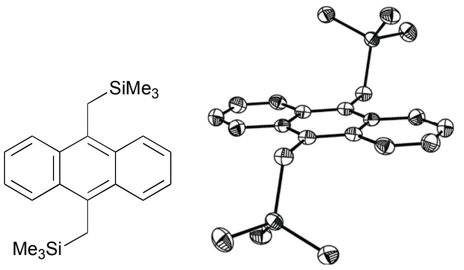


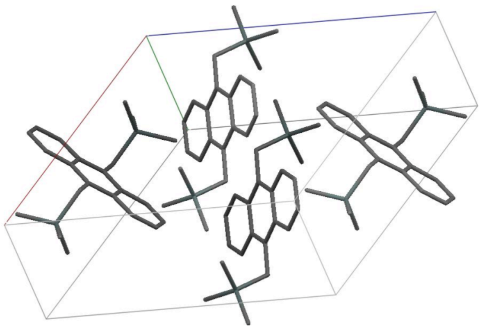


Crystal data and structure refinement for **1a**.

Empirical formula	C18 H20 Si	
Formula weight	264.43	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 17.266(4) Å	α = 90°.
	b = 7.1904(17) Å	β = 90°.
	c = 25.133(6) Å	γ = 90°.
Volume	3120.2(13) Å^3	
Z	8	
Density (calculated)	1.126 Mg/m^3	
Absorption coefficient	0.136 mm^{-1}	
F(000)	1136	
Crystal size	0.50 x 0.40 x 0.40 mm^3	
Theta range for data collection	1.62 to 27.05°.	
Index ranges	-20<=h<=22, -9<=k<=7, -32<=l<=31	
Reflections collected	17759	
Independent reflections	3411 [R(int) = 0.0272]	
Completeness to theta = 27.05°	99.6 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9477 and 0.9352	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3411 / 0 / 175	
Goodness-of-fit on F2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1288	
R indices (all data)	R1 = 0.0669, wR2 = 0.1415	
Largest diff. peak and hole	0.343 and –0.168 e. Å^{-3}	

Compound **1b**: The detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the number CCDC-662227.

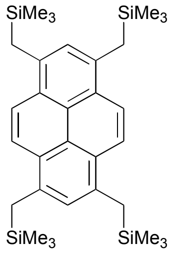


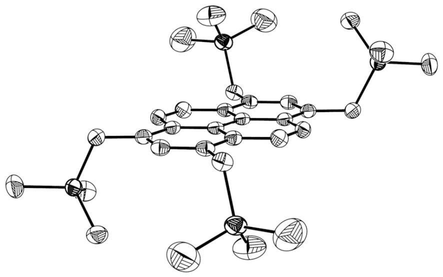


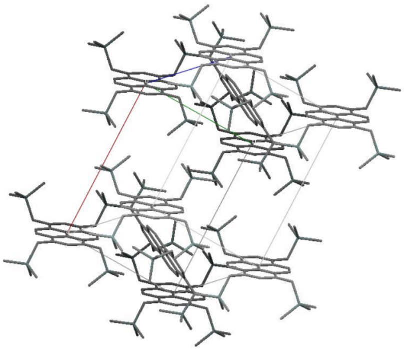
Crystal data and structure refinement for **1b**.

Empirical formula	C22 H30 Si2	
Formula weight	350.64	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 12.4707(9) Å	α = 90°.
	b = 6.2382(5) Å	β = 111.4620(10)°.
	c = 14.2962(11) Å	γ = 90°.
Volume	1035.05(14) $Å^3$	
Z	2	
Density (calculated)	1.125 Mg/m^3	
Absorption coefficient	0.172 mm^{-1}	
F(000)	380	
Crystal size	0.50 x 0.50 x 0.40 mm^3	
Theta range for data collection	1.75 to 26.99°.	
Index ranges	-15<=h<=15, -7<=k<=7, -11<=l<=18	
Reflections collected	5986	
Independent reflections	2232 [R(int) = 0.0186]	
Completeness to theta = 26.99°	99.2 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9343 and 0.9188	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2232 / 0 / 113	
Goodness-of-fit on F^2	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.1007	
R indices (all data)	R1 = 0.0406, wR2 = 0.1042	
Extinction coefficient	0.046(5)	
Largest diff. peak and hole	0.253 and –0.263 e. $Å^{-3}$	

Compound **2c**: The detailed crystallographic data have been deposited at the Cambridge Crystallographic Data Centre and allocated the number CCDC-662228.



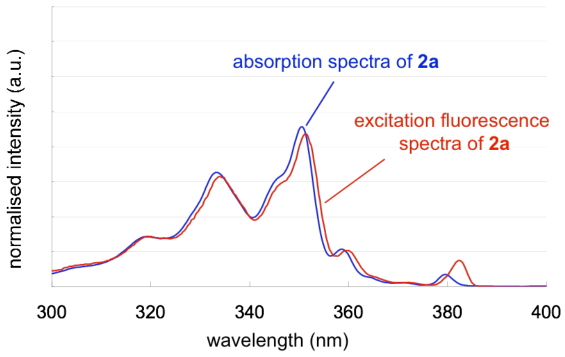




Crystal data and structure refinement for **2c**.

Empirical formula	C32 H50 Si4	
Formula weight	547.08	
Temperature	300(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 13.524(3) Å	α = 90°.
	b = 10.663(3) Å	β = 109.495(4)°.
	c = 12.834(3) Å	γ = 90°.
Volume	1744.7(8) Å^3	
Z	2	
Density (calculated)	1.041 Mg/m^3	
Absorption coefficient	0.188 mm^{-1}	
F(000)	596	
Crystal size	0.50 x 0.50 x 0.50 mm^3	
Theta range for data collection	2.49 to 25.50°.	
Index ranges	-14<=h<=16, -12<=k<=10, -15<=l<=14	
Reflections collected	9289	
Independent reflections	3243 [R(int) = 0.0196]	
Completeness to theta = 25.50°	99.8 %	
Absorption correction	Empirical	
Max. and min. transmission	0.9119 and 0.9119	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3243 / 0 / 170	
Goodness-of-fit on F^2	1.084	
Final R indices [I>2sigma(I)]	R1 = 0.0552, wR2 = 0.1695	
R indices (all data)	R1 = 0.0614, wR2 = 0.1771	
Largest diff. peak and hole	0.522 and –0.249 e. Å^{-3}	

Comparison of absorption and excitation spectra of **2a** and **2b**.



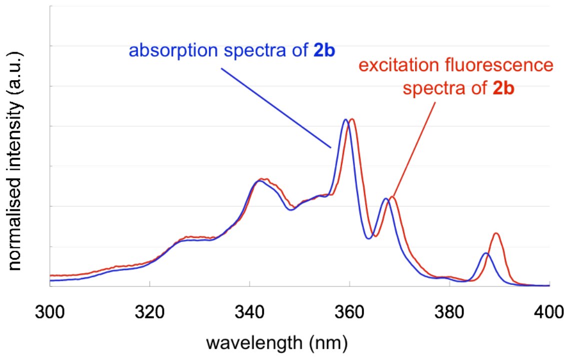
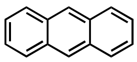
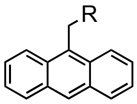
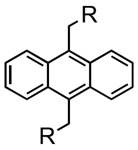


Chart S1

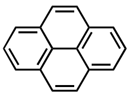
Comparison of HOMO and LUMO Energy Levels by the DFT Method at the B3LYP/6-31G(d)//B3LYP/6-31G(d) Level

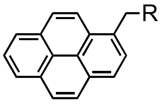


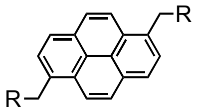


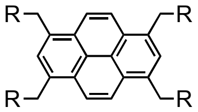


R		H	SiH$_3$	H	SiH$_3$
LUMO/eV	–1.63	–1.60	–1.67	–1.59	–1.73
HOMO/eV	–5.23	–5.11	–5.13	–5.01	–5.05
LUMO-HOMO/eV	3.60	3.51	3.46	3.42	3.32









R		H	SiH$_3$	H	SiH$_3$	H	SiH$_3$
LUMO/eV	–1.48	–1.46	–1.49	–1.45	–1.51	–1.42	–1.54
HOMO/eV	–5.33	–5.22	–5.23	–5.12	–5.13	–4.94	–4.99
LUMO-HOMO/eV	3.85	3.76	3.74	3.67	3.62	3.52	3.45