Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 87-90

Improvement of the fluorescence quantum yield of triphenylene by the rotational effect of 4-(trimethylsilyl)phenyl groups

Soichiro Kyushin, Hidetoshi Fujii, Keisuke Negishi and Hideyuki Matsumoto

Contents

1. Experimental details

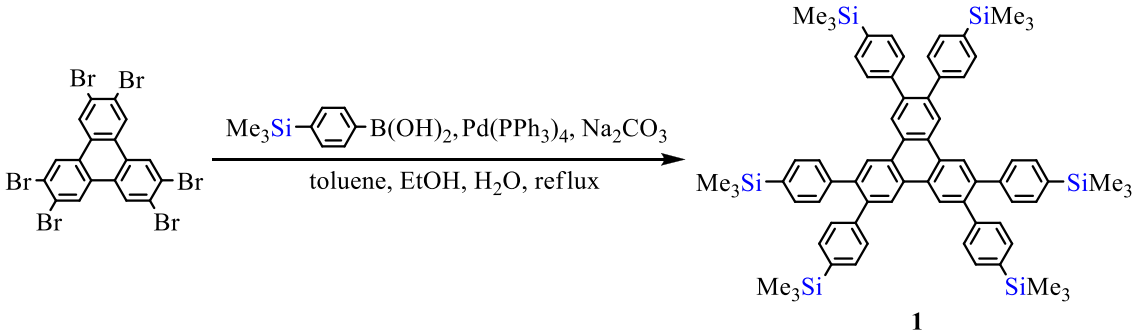
Reaction

All experiments were performed under an argon atmosphere. Toluene, ethanol, hexane and dichloromethane were distilled. 4-(Trimethylsilyl)phenylboronic acid (Aldrich) was purchased and used without further purification. Tetrakis(triphenylphosphine)palladium(0) was supplied by Chisso Petrochemical Corp. 2,3,6,7,10,11-Hexabromotriphenylene was prepared according to the reported procedure.[S1,S2] 2-Bromotriphenylene and 3,6-dibromotriphenylene were prepared by bromination of triphenylene according to the reported procedure.[S3]

Measurements

^{1}H (500 MHz), ^{13}C (126 MHz), and ^{29}Si (99 MHz) NMR spectra were measured with a JEOL JNM-LA500 spectrometer. IR spectra were recorded on a Shimadzu FTIR-8700 spectrophotometer. Mass spectra were recorded on a JEOL JMS-SX102 mass spectrometer (EI) and an Applied Biosystems API 2000 LC/MS/MS System (ESI). Elemental analyses were performed in the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University, Japan. UV spectra were recorded on a JASCO V-570 spectrophotometer. Fluorescence spectra were obtained on a Hitachi F-4500 spectrofluorometer. Fluorescence quantum yields were determined by using a Hamamatsu Photonics C9920-02 absolute PL quantum yield measurement system. Fluorescence lifetimes were measured by using an Edinburgh Analytical Instruments FL900CDT time-correlated single photon counting fluorometer.

Synthesis of 2,3,6,7,10,11-hexakis[4-(trimethylsilyl)phenyl]triphenylene (1)



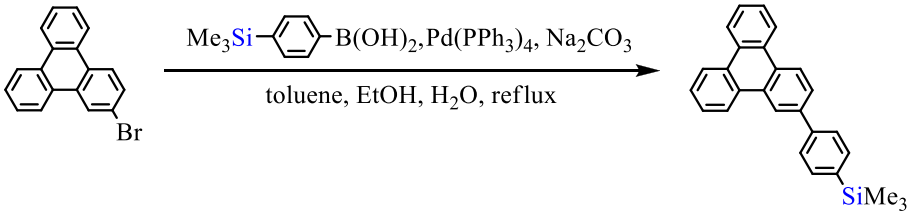
1

Argon was bubbled through a mixture of 2,3,6,7,10,11-hexabromotriphenylene (201 mg, 0.286 mmol), 4-(trimethylsilyl)phenylboronic acid (366 mg, 1.89 mmol), sodium carbonate (455 mg, 4.29 mmol), toluene (50 mL), ethanol (50 mL) and deionized water (20 mL) for 30 min. Tetrakis(triphenylphosphine)palladium(0) (30.8 mg, 26.7 μmol) was added, and the mixture was refluxed for 17 h. The solvents were evaporated, and the residue was dissolved in dichloromethane (20 mL). The organic layer was washed with saturated aqueous sodium chloride. The aqueous layer

was extracted with dichloromethane, and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was separated by column chromatography over silica gel (eluent: hexane–dichloromethane (8:2)). The crude product was recrystallized from ethanol–dichloromethane–hexane to give **1** (182 mg, 57%) as colorless crystals.

1. Mp: > 300 °C. ^{1}H NMR (500 MHz, C_6D_6): δ 0.15 (s, 54H), 7.35 (d, 12H, J = 8.0 Hz), 7.50 (d, 12H, J = 8.0 Hz), 9.03 (s, 6H). ^{13}C NMR (126 MHz, C_6D_6): δ –1.2, 126.7, 129.8, 129.9, 133.8, 138.7, 140.8, 142.6. ^{29}Si NMR (99 MHz, C_6D_6): δ –4.4. IR (KBr): 3060, 3020, 2950, 2900, 1600, 1480, 1410, 1380, 1250, 1110, 1060, 850, 820, 750, 730, 620, 600 cm^{-1}. UV (dichloromethane): λ_{max} (ε) 301 nm (160000 mol^{-1} L cm^{-1}). MS (ESI): m/z 1140.5 (M^+(^{28}Si$_5$^{29}Si)+Na, 100), 1117.5 (M^+(^{28}Si$_5$^{29}Si), 83).

Synthesis of 2-[4-(trimethylsilyl)phenyl]triphenylene (2)



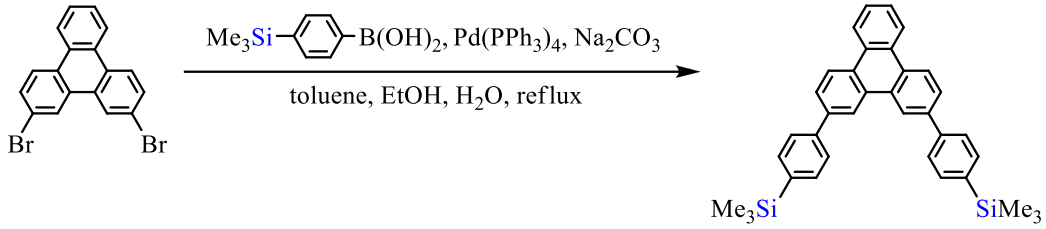
2

Argon was bubbled through a mixture of 2-bromotriphenylene (511 mg, 1.66 mmol), 4-(trimethylsilyl)phenylboronic acid (352 mg, 1.81 mmol), sodium carbonate (2.57 g, 24.2 mmol), toluene (50 mL), ethanol (50 mL) and deionized water (20 mL) for 30 min. Tetrakis(triphenylphosphine)palladium(0) (20.1 mg, 17.4 μmol) was added, and the mixture was refluxed for 9 h. The solvents were evaporated, and the residue was dissolved in dichloromethane (20 mL). The organic layer was washed with saturated aqueous sodium chloride. The aqueous layer was extracted with dichloromethane, and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was separated by column chromatography over silica gel (eluent: hexane–dichloromethane (9:1)). The crude product was recrystallized from ethanol–dichloromethane to give **2** (418 mg, 67%) as colorless crystals.

2. Mp: 130–131 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.33 (s, 9H), 7.65–7.69 (m, 6H), 7.79 (d, 2H, J = 7.3 Hz), 7.90 (dd, 1H, J = 8.5, 1.8 Hz), 8.65–8.67 (m, 3H), 8.70–8.74 (m, 2H), 8.85 (d, 1H, J = 1.5 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ –1.1, 121.8, 123.29, 123.34, 123.4, 123.9, 126.3, 126.7 (two overlapped signals), 127.2, 127.27, 127.30, 127.34, 128.1, 128.9, 129.6, 129.76, 129.78, 130.0, 134.0 (two overlapped signals), 139.8, 141.5. ^{29}Si NMR (99 MHz, $CDCl_3$): δ –0.8. IR (KBr): 3060, 3020, 2950, 2890, 1490, 1440, 1390, 1250, 1110, 1000, 950, 850, 830, 810, 750, 720, 620, 520 cm^{-1}. UV (dichloromethane): λ_{max} (ε) 273 (79000 mol^{-1} L cm^{-1}), 305 nm (28000). MS (EI, 70 eV): m/z 376 (M^+, 100), 361 (91), 304 (12), 181 (28). Anal. Found: C, 85.88; H, 6.33. Calcd for $C_{27}H_{24}Si$: C, 86.12;

H, 6.42.

Synthesis of 3,6-bis[4-(trimethylsilyl)phenyl]triphenylene (3)



3

Argon was bubbled through a mixture of 3,6-dibromotriphenylene (49.2 mg, 0.127 mmol), 4-(trimethylsilyl)phenylboronic acid (56.8 mg, 0.293 mmol), sodium carbonate (0.217 g, 2.05 mmol), toluene (50 mL), ethanol (50 mL) and deionized water (20 mL) for 30 min. Tetrakis(triphenylphosphine)palladium(0) (10.4 mg, 9.00 μmol) was added, and the mixture was refluxed for 16 h. The solvents were evaporated, and the residue was dissolved in dichloromethane (20 mL). The organic layer was washed with saturated aqueous sodium chloride. The aqueous layer was extracted with dichloromethane, and the combined organic layer was dried over anhydrous magnesium sulfate. The solvent was evaporated, and the residue was separated by column chromatography over silica gel (eluent: hexane–dichloromethane (9:1)). The crude product was recrystallized from ethanol–dichloromethane to give **3** (48.7 mg, 73%) as colorless crystals.

3. Mp: sublimed at ca. 200 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.33 (s, 18H), 7.68–7.70 (m, 6H), 7.80 (d, 4H, J = 8.5 Hz), 7.91 (dd, 2H, J = 8.5, 1.0 Hz), 8.71–8.75 (m, 4H), 8.85 (d, 2H, J = 1.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$): δ –1.1, 121.8, 123.4, 123.9, 126.4, 126.7, 127.4, 128.7, 130.01, 130.03, 134.0, 139.6, 139.8, 141.5. ^{29}Si NMR (99 MHz, $CDCl_3$): δ –3.9. IR (KBr): 3060, 3020, 2950, 2900, 1600, 1490, 1440, 1390, 1250, 1110, 850, 830, 810, 760, 660, 620, 520 cm^{-1}. UV (dichloromethane): λ_{max} (ε) 281 (80000 mol^{-1} L cm^{-1}), 325 nm (46000). MS (ESI): m/z 524.2 (M^+, 100). Anal. Found: C, 82.09; H, 7.09. Calcd for $C_{36}H_{36}Si_2$: C, 82.38; H, 6.91.

2. Spectral data

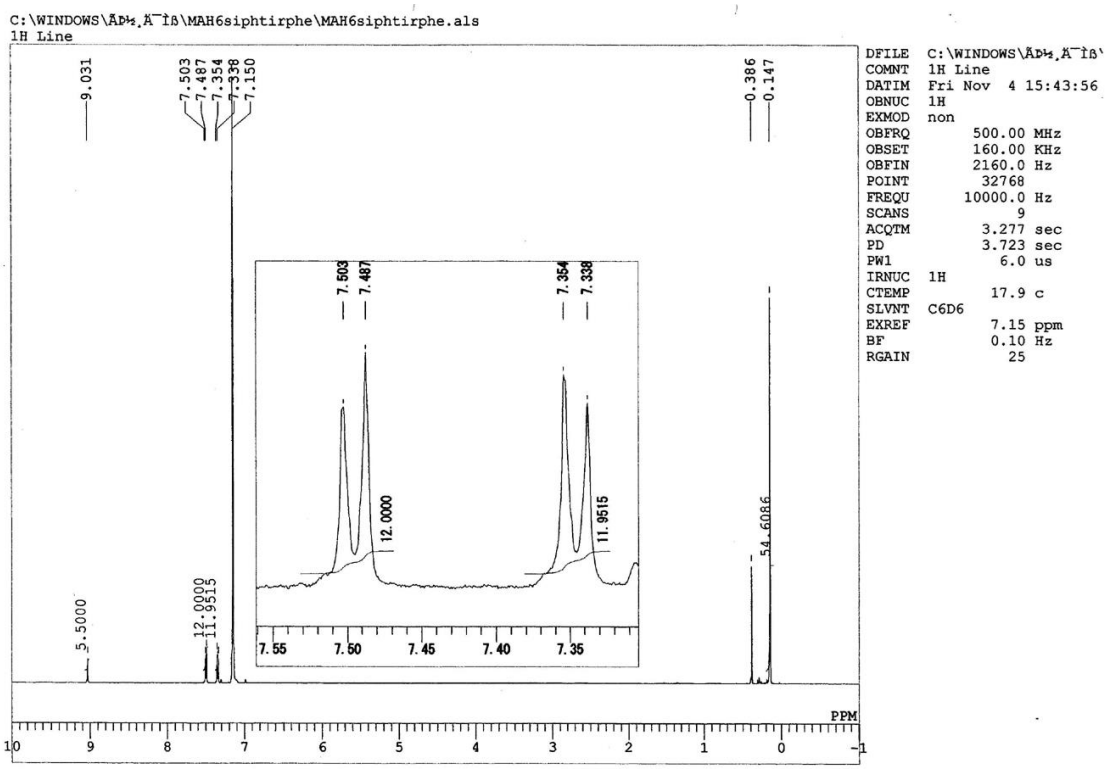


Figure S1 ^{1}H NMR spectrum of **1** in C_6D_6 at room temperature.

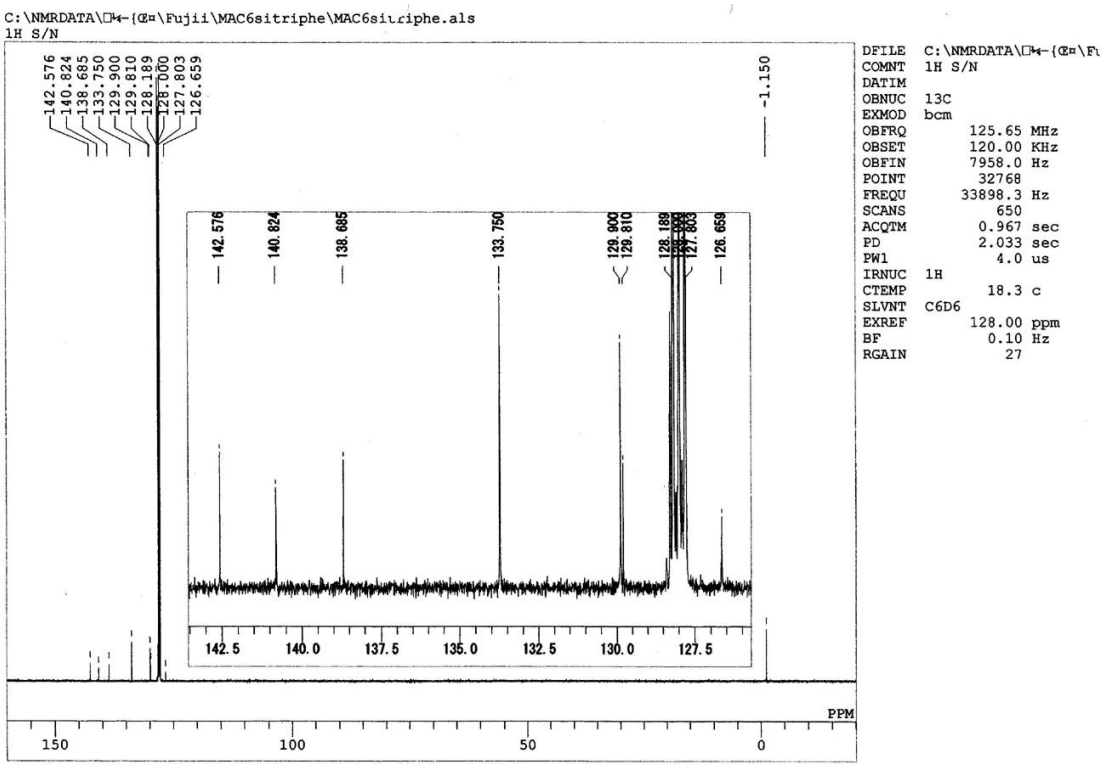


Figure S2 ^{13}C NMR spectrum of **1** in C_6D_6 at room temperature.

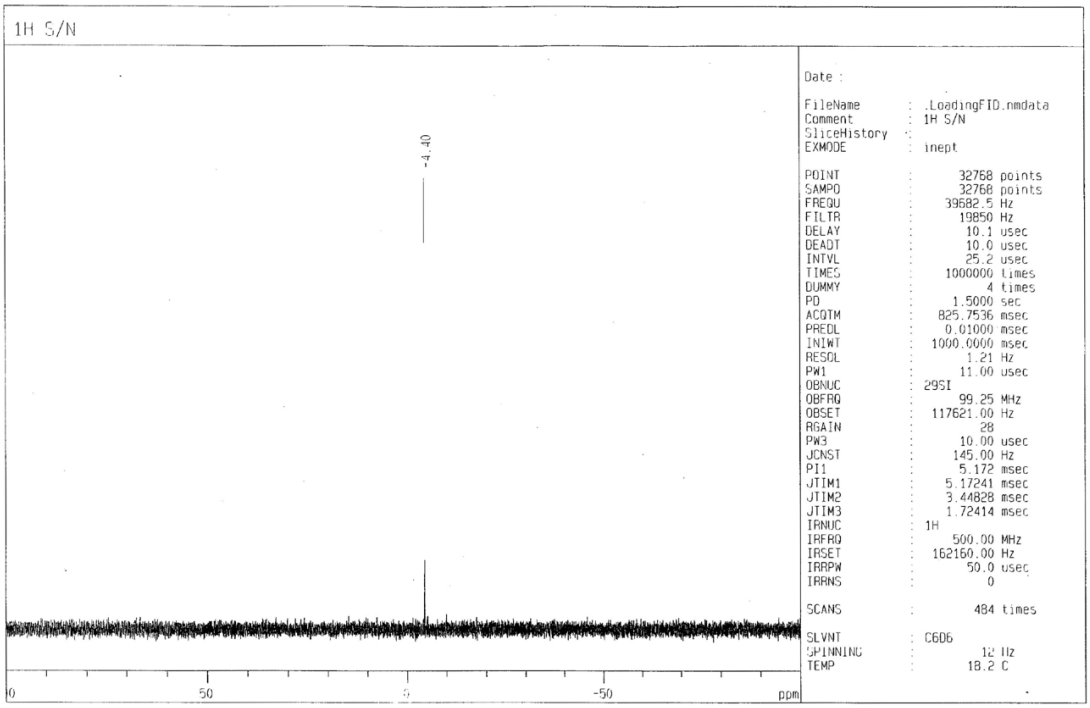


Figure S3 ^{29}Si NMR spectrum of **1** in C_6D_6 at room temperature.

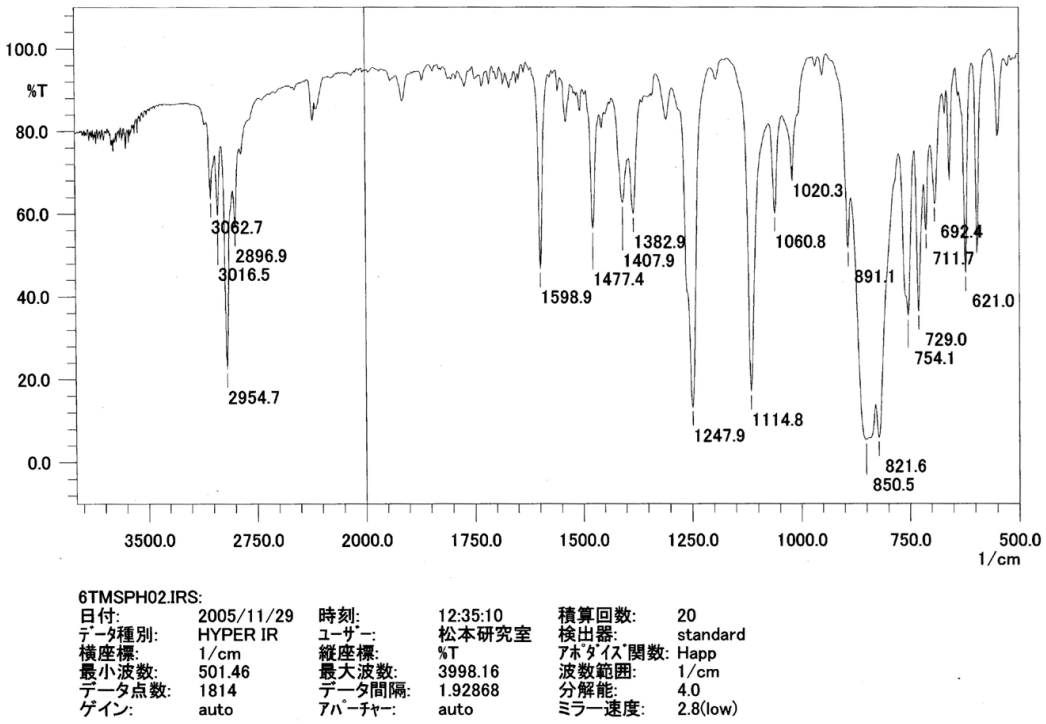


Figure S4 IR spectrum of **1** (KBr).

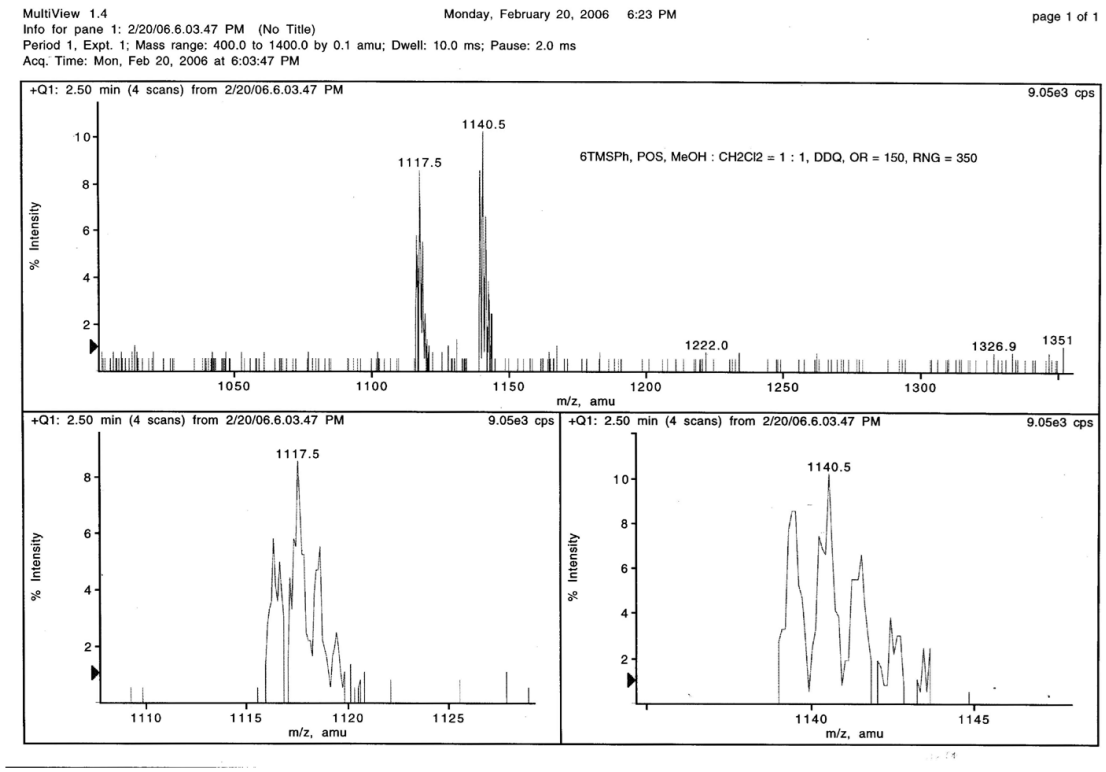


Figure S5 Mass spectrum of **1** (ESI).

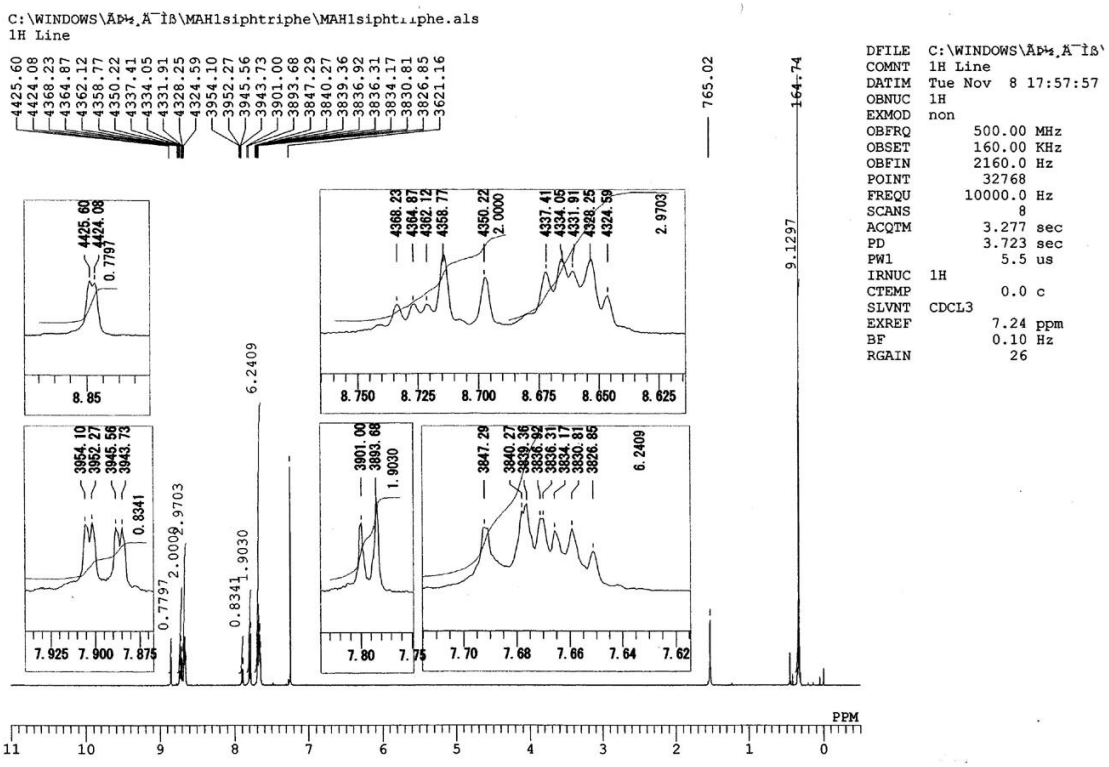


Figure S6 ^{1}H NMR spectrum of **2** in $CDCl_3$ at room temperature.

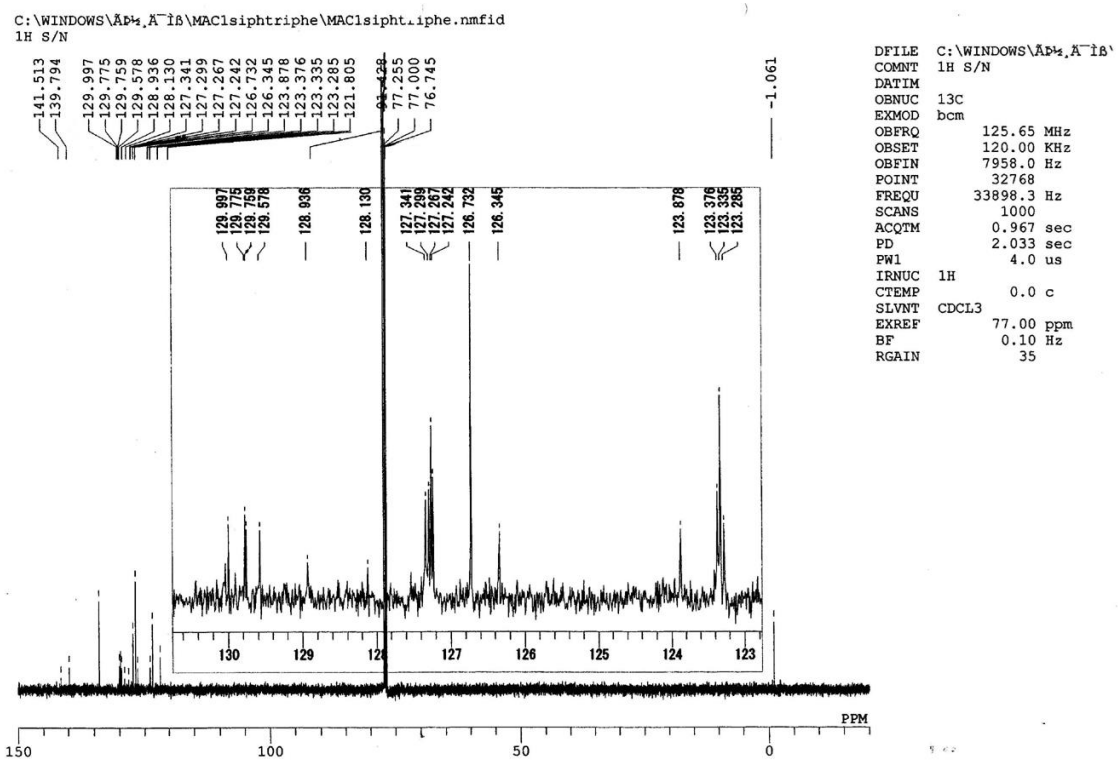


Figure S7 ^{13}C NMR spectrum of **2** in $CDCl_3$ at room temperature.

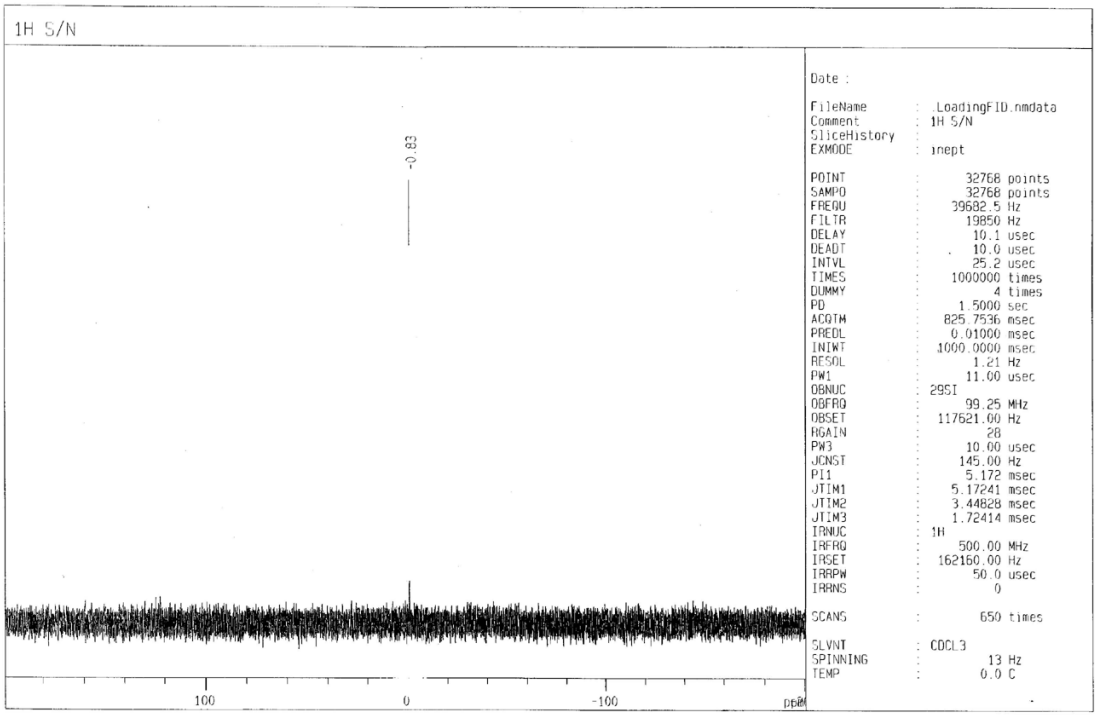


Figure S8 ^{29}Si NMR spectrum of **2** in $CDCl_3$ at room temperature.

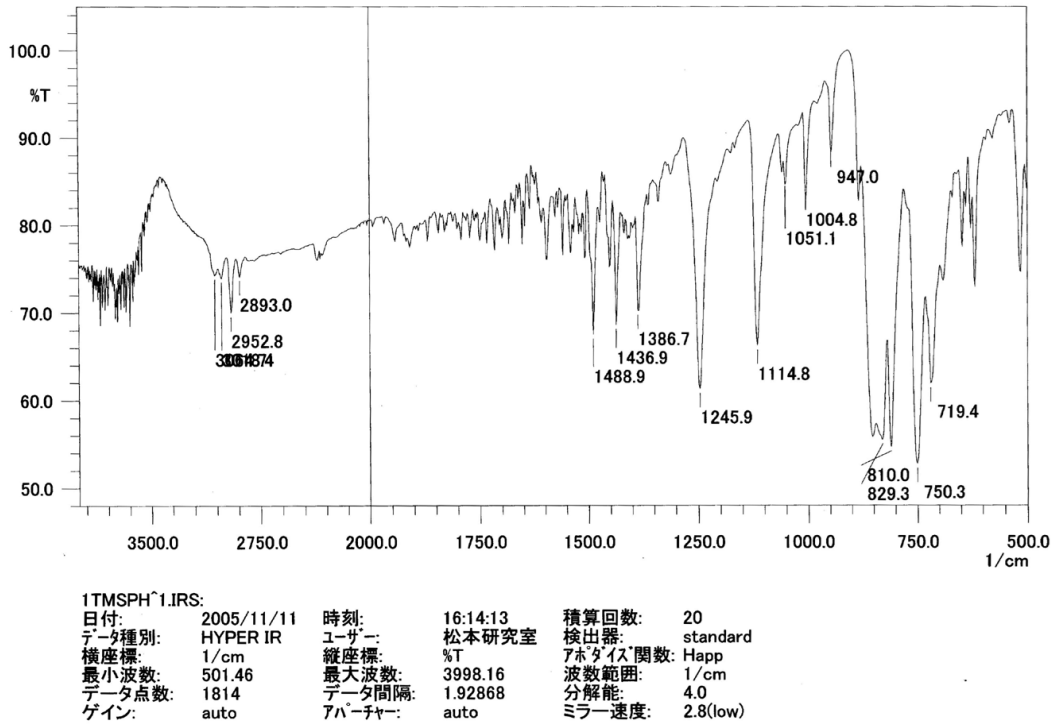


Figure S9 IR spectrum of **2** (KBr).

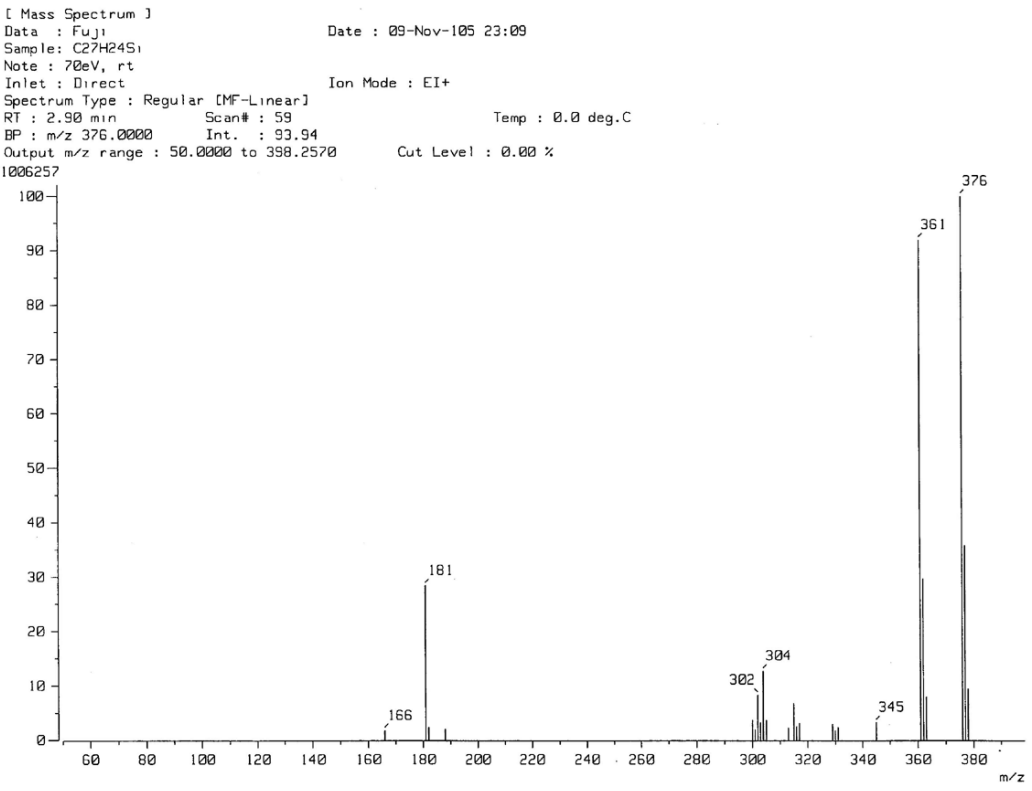


Figure S10 Mass spectrum of **2** (EI, 70 eV).

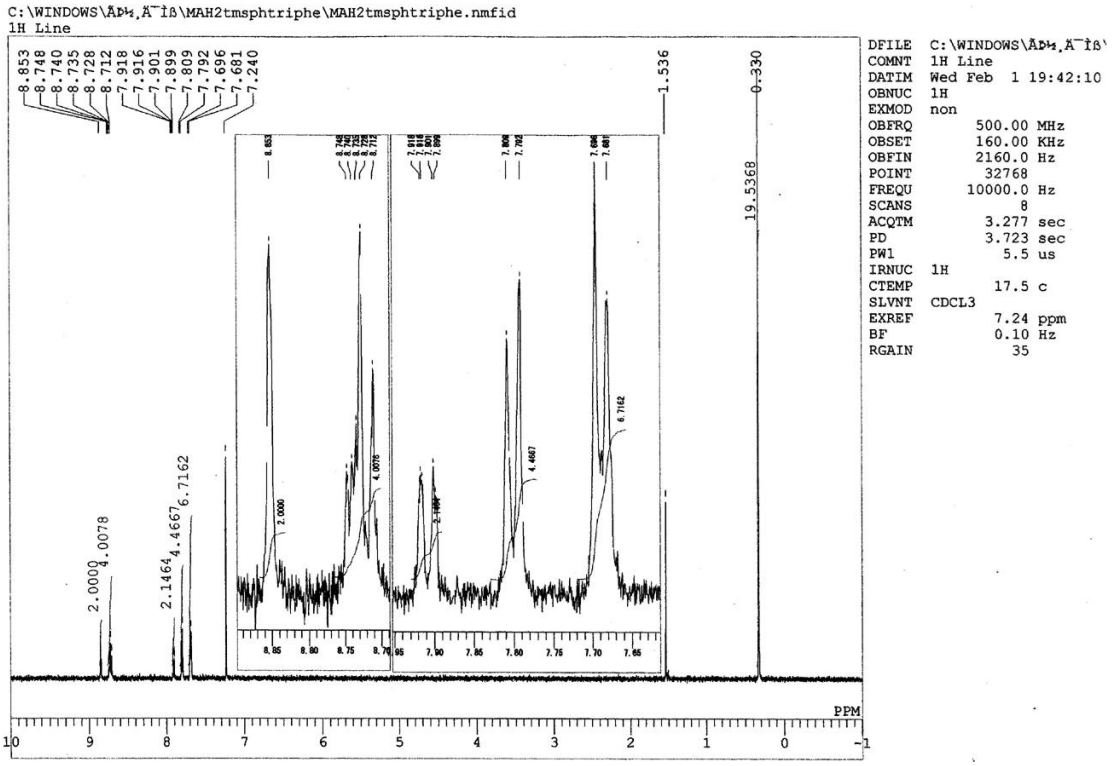


Figure S11 ^{1}H NMR spectrum of **3** in $CDCl_3$ at room temperature.

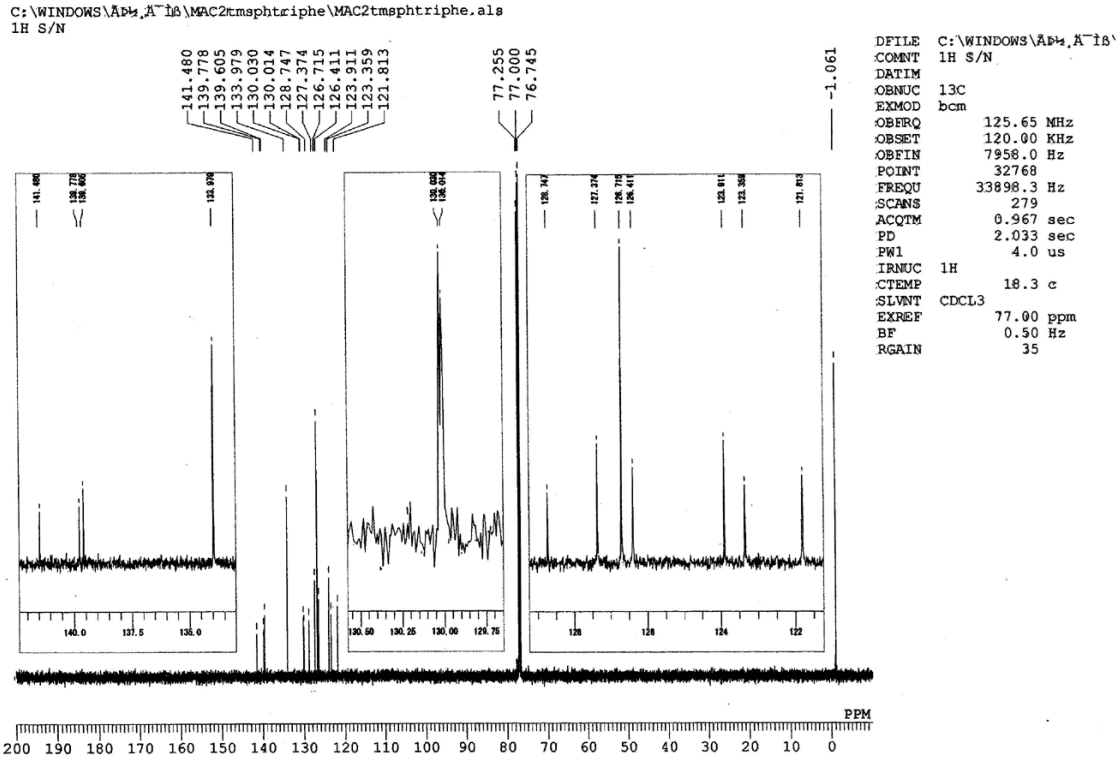


Figure S12 ^{13}C NMR spectrum of **3** in $CDCl_3$ at room temperature.

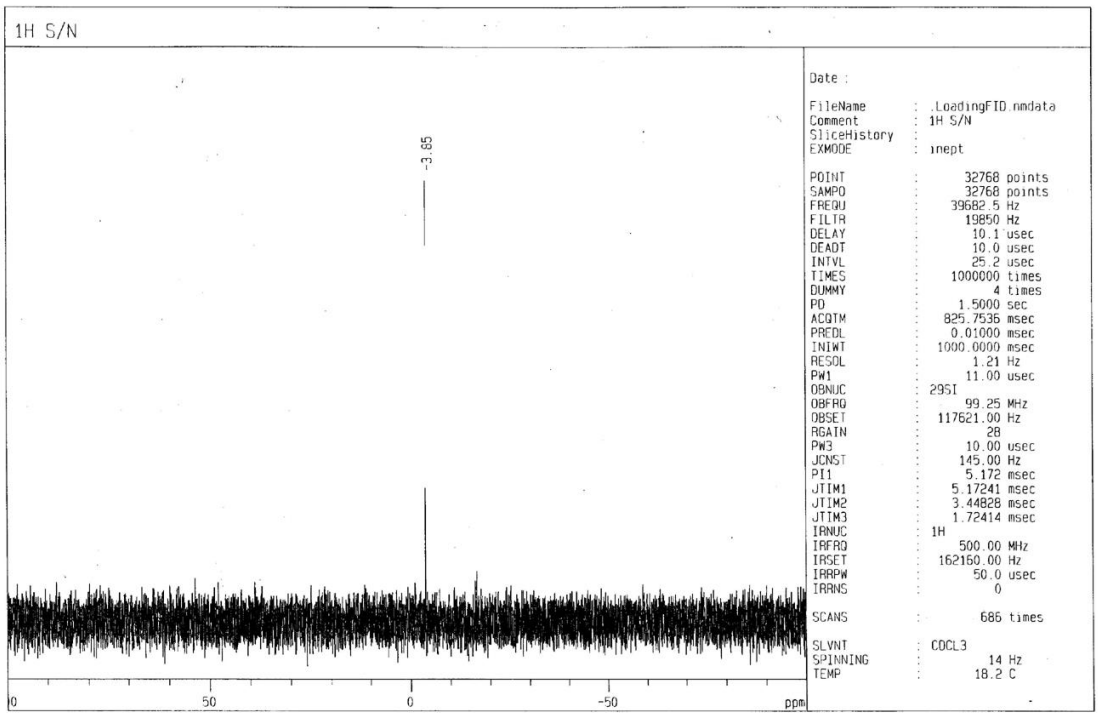


Figure S13 ^{29}Si NMR spectrum of **3** in $CDCl_3$ at room temperature.

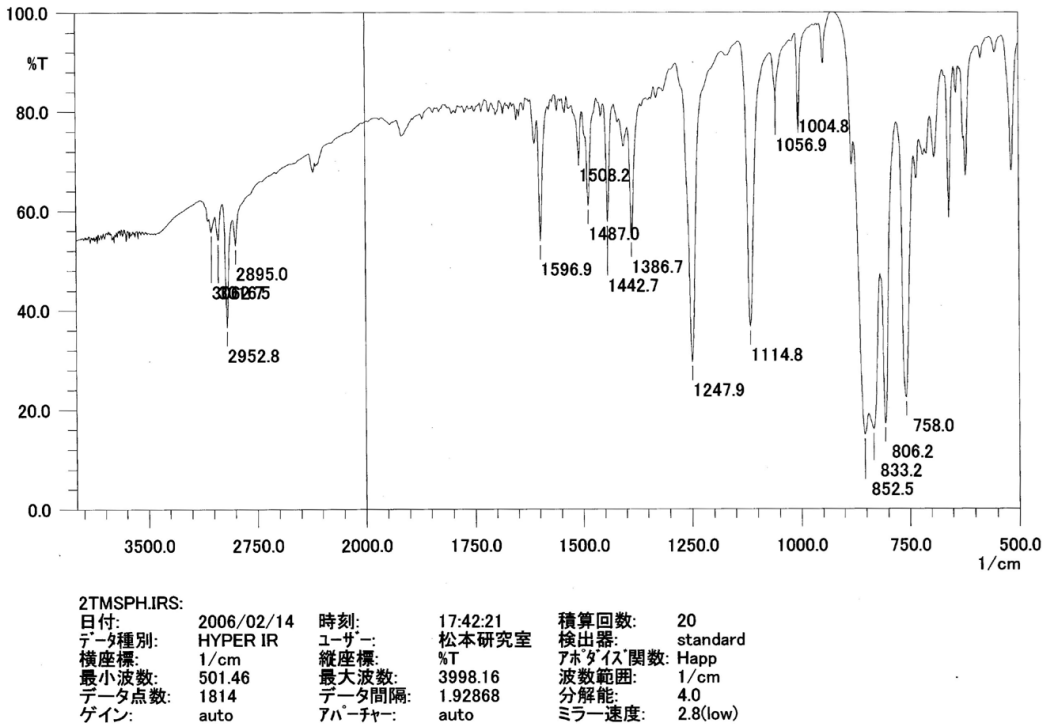


Figure S14 IR spectrum of **3** (KBr).

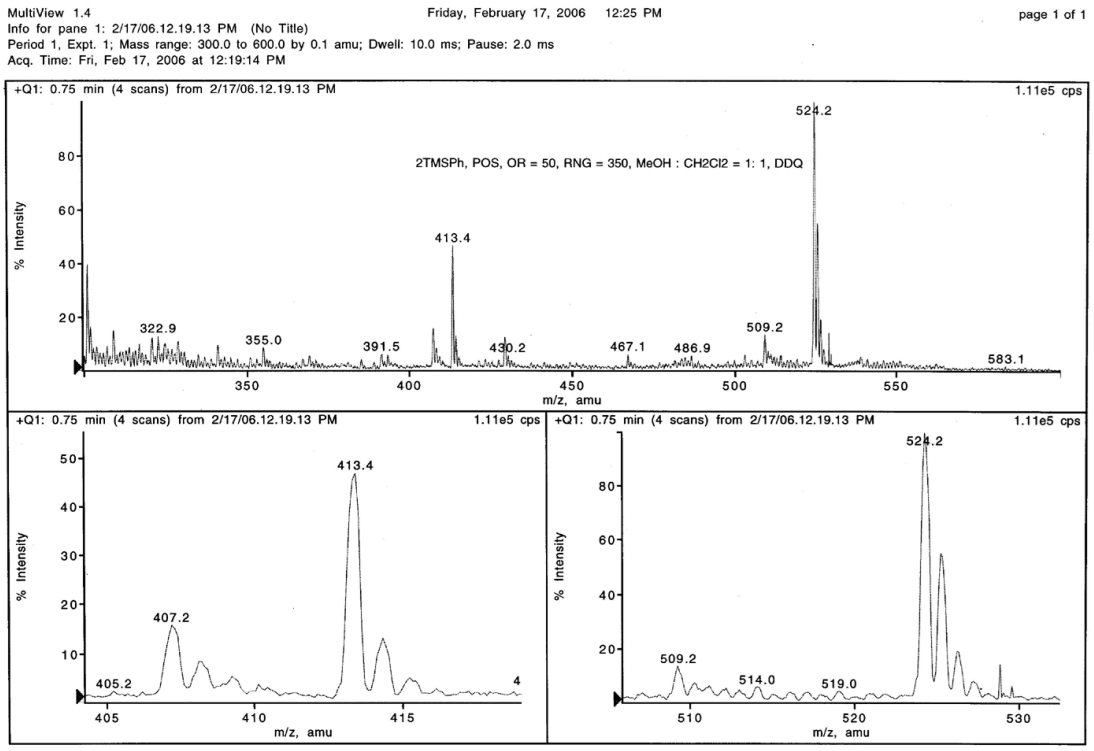


Figure S15 Mass spectrum of **3** (ESI).

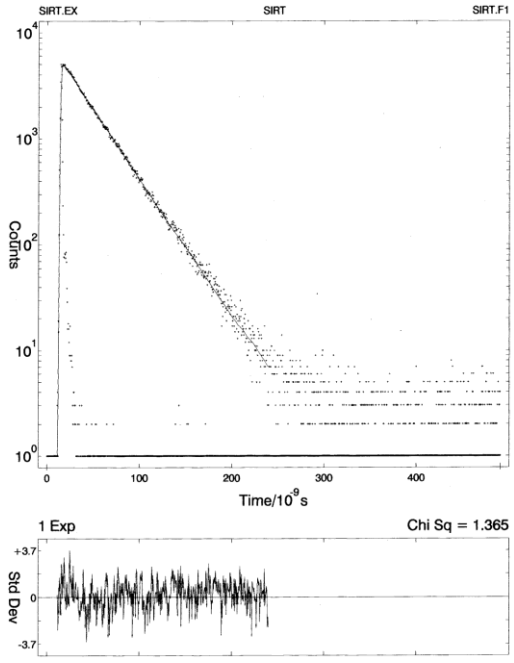


Figure S16 Fluorescence decay of **1** in 3-methylpentane at room temperature. The excitation wavelength is 300 nm.

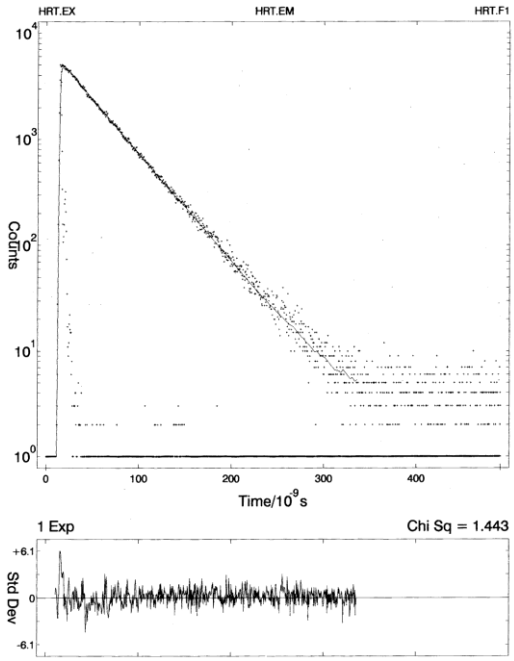


Figure S17 Fluorescence decay of **4** in 3-methylpentane at room temperature. The excitation wavelength is 290 nm.

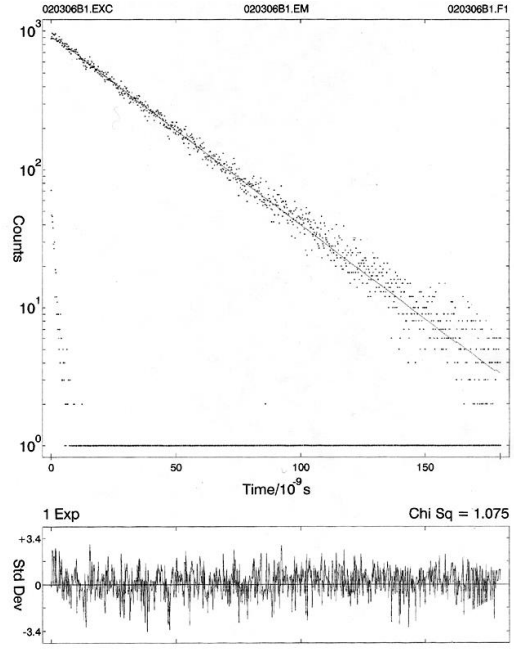


Figure S18 Fluorescence decay of triphenylene in 3-methylpentane at room temperature. The excitation wavelength is 305 nm.

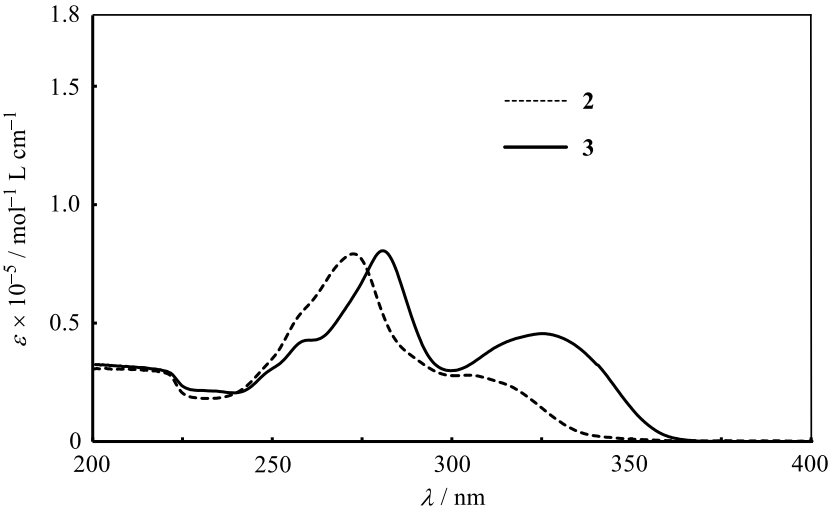


Figure S19 UV spectra of **2** and **3** in dichloromethane at room temperature.

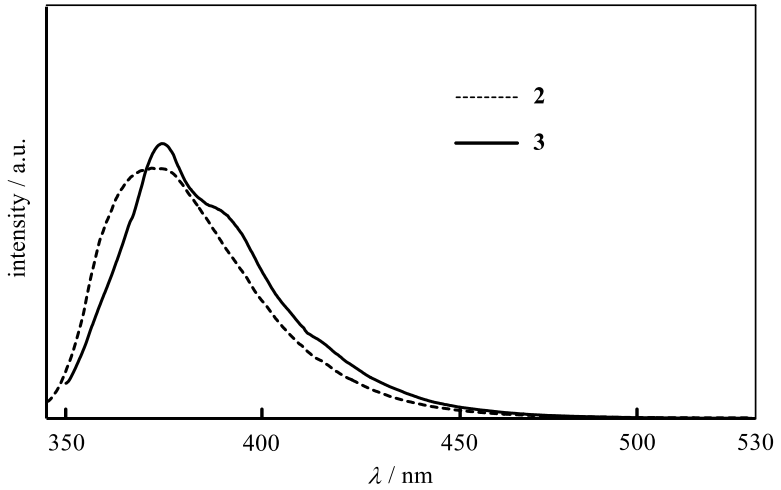
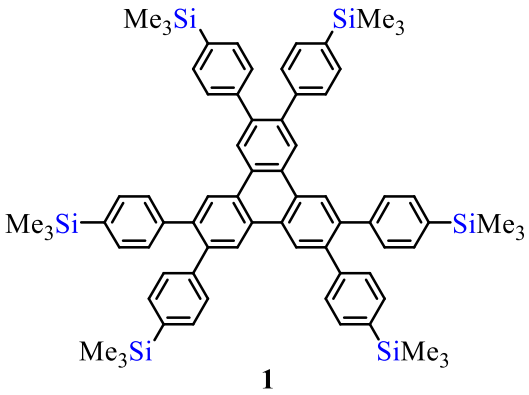


Figure S20 Fluorescence spectra of **2** and **3** in 3-methylpentane at room temperature.

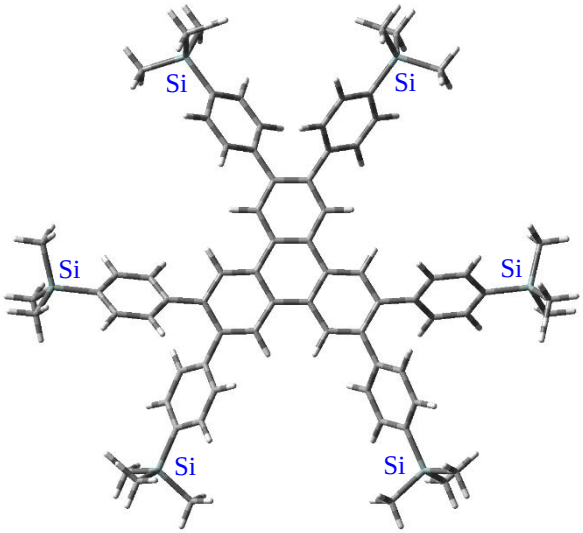
3. Theoretical calculations

All theoretical calculations were performed using Gaussian 09[S4] on a Fujitsu PRIMERGY RX300 system of the Research Center for Computational Science, Japan. The structures were optimized at the B3LYP/6-31G(d) level, and the optimization was confirmed by frequency calculations. The results are summarized in Table S1. TD-DFT calculations were performed at the B3LYP/6-31+G(2d,p) level using the optimized structures. The results are summarized in Table S2.

Table S1 Atomic coordinates of the optimized structures of **1**, **4** and triphenylene.



1



Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.7091240	1.2553090	0.0023790
C	-0.7091240	1.2553090	-0.0023790
C	-1.3702730	2.4985520	-0.0265030
C	-0.7113140	3.7251070	-0.0242030
C	0.7113140	3.7251070	0.0242030
C	1.3702730	2.4985520	0.0265030
H	-2.4513080	2.5253020	-0.0906740
H	2.4513080	2.5253020	0.0906740
C	-1.4416910	-0.0135350	0.0023790
C	-2.8489460	-0.0625850	0.0265030
C	-0.7325670	-1.2417730	-0.0023790
C	-3.5816940	-1.2465380	0.0242030
H	-3.4126300	0.8602440	0.0906740
C	-1.4786730	-2.4359670	-0.0265030

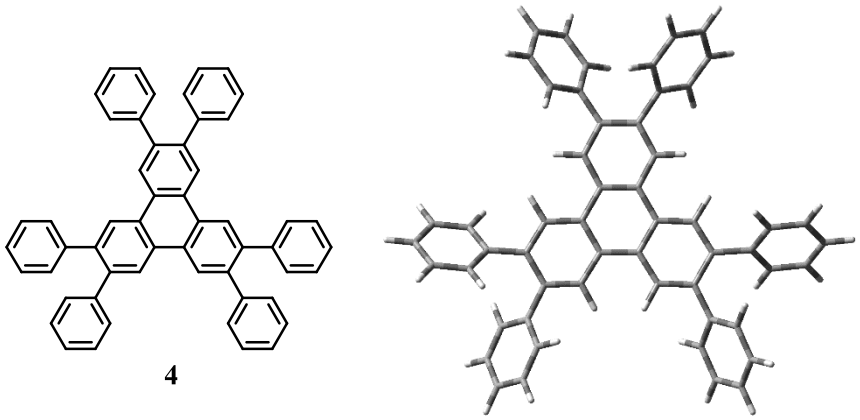
C	-2.8703800	-2.4785690	-0.0242030
H	-0.9613220	-3.3855460	-0.0906740
C	1.4416910	-0.0135350	-0.0023790
C	2.8489460	-0.0625850	-0.0265030
C	0.7325670	-1.2417730	0.0023790
C	3.5816940	-1.2465380	-0.0242030
H	3.4126300	0.8602440	-0.0906740
C	1.4786730	-2.4359670	0.0265030
C	2.8703800	-2.4785690	0.0242030
H	0.9613220	-3.3855460	0.0906740
C	1.5365430	4.9624730	0.1185870
C	2.6515010	5.1380830	-0.7180370
C	1.2708230	5.9556300	1.0737090
C	3.4622890	6.2655070	-0.6034830
H	2.8715990	4.3892630	-1.4749780
C	2.0892640	7.0787120	1.1833470
H	0.4221090	5.8422820	1.7414250
C	3.2056010	7.2688390	0.3492340
H	4.3114450	6.3604350	-1.2785260
H	1.8483090	7.8191950	1.9424960
C	-1.5365430	4.9624730	-0.1185870
C	-1.2708230	5.9556300	-1.0737090
C	-2.6515010	5.1380830	0.7180370
C	-2.0892640	7.0787120	-1.1833470
H	-0.4221090	5.8422820	-1.7414250
C	-3.4622890	6.2655070	0.6034830
H	-2.8715990	4.3892630	1.4749780
C	-3.2056010	7.2688390	-0.3492340
H	-1.8483090	7.8191950	-1.9424960
H	-4.3114450	6.3604350	1.2785260
C	-5.0658990	-1.1505510	0.1185870
C	-5.7931380	-1.8772500	1.0737090
C	-5.7754610	-0.2727750	-0.7180370
C	-7.1749760	-1.7300010	1.1833470
H	-5.2706190	-2.5555840	1.7414250
C	-7.1572330	-0.1343230	-0.6034830
H	-5.2370130	0.2922460	-1.4749780
C	-7.8977990	-0.8582880	0.3492340
H	-7.6957760	-2.3089150	1.9424960
H	-7.6640210	0.5536030	-1.2785260
C	-3.5293560	-3.8119220	-0.1185870
C	-3.1239600	-4.8653090	0.7180370
C	-4.5223150	-4.0783800	-1.0737090

C	-3.6949440	-6.1311840	0.6034830
H	-2.3654140	-4.6815100	1.4749780
C	-5.0857130	-5.3487120	-1.1833470
H	-4.8485100	-3.2866980	-1.7414250
C	-4.6921990	-6.4105510	-0.3492340
H	-3.3525760	-6.9140380	1.2785260
H	-5.8474670	-5.5102800	-1.9424960
C	3.5293560	-3.8119220	0.1185870
C	3.1239600	-4.8653090	-0.7180370
C	4.5223150	-4.0783800	1.0737090
C	3.6949440	-6.1311840	-0.6034830
H	2.3654140	-4.6815100	-1.4749780
C	5.0857130	-5.3487120	1.1833470
H	4.8485100	-3.2866980	1.7414250
C	4.6921990	-6.4105510	0.3492340
H	3.3525760	-6.9140380	-1.2785260
H	5.8474670	-5.5102800	1.9424960
C	5.0658990	-1.1505510	-0.1185870
C	5.7931380	-1.8772500	-1.0737090
C	5.7754610	-0.2727750	0.7180370
C	7.1749760	-1.7300010	-1.1833470
H	5.2706190	-2.5555840	-1.7414250
C	7.1572330	-0.1343230	0.6034830
H	5.2370130	0.2922460	1.4749780
C	7.8977990	-0.8582880	-0.3492340
H	7.6957760	-2.3089150	-1.9424960
H	7.6640210	0.5536030	1.2785260
Si	4.3243290	8.7920290	0.4743850
Si	-4.3243290	8.7920290	-0.4743850
Si	-9.7762850	-0.6510360	0.4743850
Si	-5.4519560	-8.1409930	-0.4743850
Si	5.4519560	-8.1409930	0.4743850
Si	9.7762850	-0.6510360	-0.4743850
C	3.7195250	9.9265000	1.8641350
H	2.6958970	10.2782300	1.6891220
H	3.7388680	9.4252640	2.8391140
H	4.3617730	10.8125650	1.9389210
C	4.2876740	9.7330470	-1.1707170
H	4.9511530	10.6063660	-1.1419470
H	4.6121690	9.0994850	-2.0048670
H	3.2768990	10.0893240	-1.4018520
C	6.1001440	8.2382640	0.8378780
H	6.1632410	7.7135930	1.7984460

H	6.4771410	7.5572240	0.0654920
H	6.7808590	9.0975520	0.8809200
C	-3.7195250	9.9265000	-1.8641350
H	-2.6958970	10.2782300	-1.6891220
H	-3.7388680	9.4252640	-2.8391140
H	-4.3617730	10.8125650	-1.9389210
C	-4.2876740	9.7330470	1.1707170
H	-4.9511530	10.6063660	1.1419470
H	-4.6121690	9.0994850	2.0048670
H	-3.2768990	10.0893240	1.4018520
C	-6.1001440	8.2382640	-0.8378780
H	-6.1632410	7.7135930	-1.7984460
H	-6.4771410	7.5572240	-0.0654920
H	-6.7808590	9.0975520	-0.8809200
C	-10.4563640	-1.7420470	1.8641350
H	-10.2491570	-2.8044000	1.6891220
H	-10.0319520	-1.4746780	2.8391140
H	-11.5448420	-1.6288760	1.9389210
C	-10.5729020	-1.1532890	-1.1707170
H	-11.6609590	-1.0153580	-1.1419470
H	-10.1864690	-0.5554870	-2.0048670
H	-10.3760610	-2.2067840	-1.4018520
C	-10.1846170	1.1637480	0.8378780
H	-9.7617870	1.4807270	1.7984460
H	-9.7833190	1.8307560	0.0654920
H	-11.2691410	1.3236200	0.8809200
C	-6.7368390	-8.1844530	-1.8641350
H	-7.5532600	-7.4738300	-1.6891220
H	-6.2930840	-7.9505870	-2.8391140
H	-7.1830690	-9.1836890	-1.9389210
C	-6.2852290	-8.5797580	1.1707170
H	-6.7098060	-9.5910070	1.1419470
H	-5.5743010	-8.5439970	2.0048670
H	-7.0991610	-7.8825400	1.4018520
C	-4.0844740	-9.4020110	-0.8378780
H	-3.5985470	-9.1943190	-1.7984460
H	-3.3061780	-9.3879810	-0.0654920
H	-4.4882820	-10.4211720	-0.8809200
C	6.7368390	-8.1844530	1.8641350
H	7.5532600	-7.4738300	1.6891220
H	6.2930840	-7.9505870	2.8391140
H	7.1830690	-9.1836890	1.9389210
C	6.2852290	-8.5797580	-1.1707170

H	6.7098060	-9.5910070	-1.1419470
H	5.5743010	-8.5439970	-2.0048670
H	7.0991610	-7.8825400	-1.4018520
C	4.0844740	-9.4020110	0.8378780
H	3.5985470	-9.1943190	1.7984460
H	3.3061780	-9.3879810	0.0654920
H	4.4882820	-10.4211720	0.8809200
C	10.4563640	-1.7420470	-1.8641350
H	10.2491570	-2.8044000	-1.6891220
H	10.0319520	-1.4746780	-2.8391140
H	11.5448420	-1.6288760	-1.9389210
C	10.5729020	-1.1532890	1.1707170
H	11.6609590	-1.0153580	1.1419470
H	10.1864690	-0.5554870	2.0048670
H	10.3760610	-2.2067840	1.4018520
C	10.1846170	1.1637480	-0.8378780
H	9.7617870	1.4807270	-1.7984460
H	9.7833190	1.8307560	-0.0654920
H	11.2691410	1.3236200	-0.8809200

Framework group D_3, energy: -4531.56524043 a.u.



4

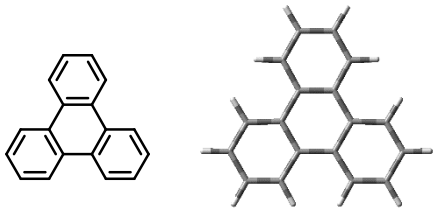
Atomic	Coordinates (Angstroms)		
Type	X	Y	Z

C	-0.7091050	1.2553390	-0.0020490
C	0.7091050	1.2553390	0.0020490
C	1.3703300	2.4986290	0.0245360
C	0.7111950	3.7249500	0.0224520
C	-0.7111950	3.7249500	-0.0224520
C	-1.3703300	2.4986290	-0.0245360
H	2.4515360	2.5257290	0.0862190

H	-2.4515360	2.5257290	-0.0862190
C	1.4417080	-0.0135660	-0.0020490
C	2.8490410	-0.0625730	-0.0245360
C	0.7326030	-1.2417720	0.0020490
C	3.5814990	-1.2465620	-0.0224520
H	3.4131140	0.8602280	-0.0862190
C	1.4787110	-2.4360550	0.0245360
C	2.8703040	-2.4783880	0.0224520
H	0.9615780	-3.3859570	0.0862190
C	-1.4417080	-0.0135660	0.0020490
C	-2.8490410	-0.0625730	0.0245360
C	-0.7326030	-1.2417720	-0.0020490
C	-3.5814990	-1.2465620	0.0224520
H	-3.4131140	0.8602280	0.0862190
C	-1.4787110	-2.4360550	-0.0245360
C	-2.8703040	-2.4783880	-0.0224520
H	-0.9615780	-3.3859570	-0.0862190
C	-1.5362270	4.9638750	-0.1119450
C	-2.6379830	5.1429770	0.7409240
C	-1.2768420	5.9490120	-1.0793410
C	-3.4525600	6.2707700	0.6340390
H	-2.8455180	4.3969110	1.5036560
C	-2.0925510	7.0736660	-1.1888130
H	-0.4357750	5.8257280	-1.7544660
C	-3.1830460	7.2406500	-0.3321800
H	-4.2955040	6.3916900	1.3095320
H	-1.8777490	7.8201570	-1.9490390
H	-3.8164320	8.1196070	-0.4174810
C	1.5362270	4.9638750	0.1119450
C	1.2768420	5.9490120	1.0793410
C	2.6379830	5.1429770	-0.7409240
C	2.0925510	7.0736660	1.1888130
H	0.4357750	5.8257280	1.7544660
C	3.4525600	6.2707700	-0.6340390
H	2.8455180	4.3969110	-1.5036560
C	3.1830460	7.2406500	0.3321800
H	1.8777490	7.8201570	1.9490390
H	4.2955040	6.3916900	-1.3095320
H	3.8164320	8.1196070	0.4174810
C	5.0669550	-1.1515250	-0.1119450
C	5.7904160	-1.8687280	-1.0793410
C	5.7729400	-0.2869280	0.7409240
C	7.1722500	-1.7246310	-1.1888130

H	5.2631160	-2.5354710	-1.7544660
C	7.1569270	-0.1453810	0.6340390
H	5.2305950	0.2658350	1.5036560
C	7.8621100	-0.8637260	-0.3321800
H	7.7113290	-2.2839000	-1.9490390
H	7.6831180	0.5241700	1.3095320
H	8.9400010	-0.7546770	-0.4174810
C	3.5307280	-3.8123490	0.1119450
C	3.1349570	-4.8560480	-0.7409240
C	4.5135740	-4.0802840	1.0793410
C	3.7043660	-6.1253900	-0.6340390
H	2.3850780	-4.6627460	-1.5036560
C	5.0796990	-5.3490350	1.1888130
H	4.8273410	-3.2902560	1.7544660
C	4.6790640	-6.3769230	0.3321800
H	3.3876140	-6.9158610	-1.3095320
H	5.8335800	-5.5362560	1.9490390
H	5.1235700	-7.3649300	0.4174810
C	-3.5307280	-3.8123490	-0.1119450
C	-3.1349570	-4.8560480	0.7409240
C	-4.5135740	-4.0802840	-1.0793410
C	-3.7043660	-6.1253900	0.6340390
H	-2.3850780	-4.6627460	1.5036560
C	-5.0796990	-5.3490350	-1.1888130
H	-4.8273410	-3.2902560	-1.7544660
C	-4.6790640	-6.3769230	-0.3321800
H	-3.3876140	-6.9158610	1.3095320
H	-5.8335800	-5.5362560	-1.9490390
H	-5.1235700	-7.3649300	-0.4174810
C	-5.0669550	-1.1515250	0.1119450
C	-5.7904160	-1.8687280	1.0793410
C	-5.7729400	-0.2869280	-0.7409240
C	-7.1722500	-1.7246310	1.1888130
H	-5.2631160	-2.5354710	1.7544660
C	-7.1569270	-0.1453810	-0.6340390
H	-5.2305950	0.2658350	-1.5036560
C	-7.8621100	-0.8637260	0.3321800
H	-7.7113290	-2.2839000	1.9490390
H	-7.6831180	0.5241700	-1.3095320
H	-8.9400010	-0.7546770	0.4174810

Framework group D_3, energy: -2079.50837835 a.u.



Atomic Type	Coordinates (Angstroms) X	Y	Z
C	0.7003710	3.7028420	0.0000000
C	-0.7003710	3.7028420	0.0000000
C	-1.3837450	2.5000890	0.0000000
C	-0.7109050	1.2573880	0.0000000
C	0.7109050	1.2573880	0.0000000
C	1.3837450	2.5000890	0.0000000
H	1.2512580	4.6393750	0.0000000
H	-1.2512580	4.6393750	0.0000000
H	-2.4667990	2.5284330	0.0000000
H	2.4667990	2.5284330	0.0000000
C	-1.4443820	-0.0130320	0.0000000
C	-0.7334770	-1.2443560	0.0000000
C	-2.8570130	-0.0516860	0.0000000
C	-1.4732680	-2.4484030	0.0000000
C	-3.5569410	-1.2448820	0.0000000
H	-3.4230870	0.8720940	0.0000000
C	-2.8565700	-2.4579600	0.0000000
H	-0.9562870	-3.4005270	0.0000000
H	-4.6434450	-1.2360660	0.0000000
H	-3.3921870	-3.4033090	0.0000000
C	1.4443820	-0.0130320	0.0000000
C	2.8570130	-0.0516860	0.0000000
C	0.7334770	-1.2443560	0.0000000
C	3.5569410	-1.2448820	0.0000000
H	3.4230870	0.8720940	0.0000000
C	1.4732680	-2.4484030	0.0000000
C	2.8565700	-2.4579600	0.0000000
H	4.6434450	-1.2360660	0.0000000
H	0.9562870	-3.4005270	0.0000000
H	3.3921870	-3.4033090	0.0000000

Framework group D_{3h}, energy: -693.18107666 a.u.

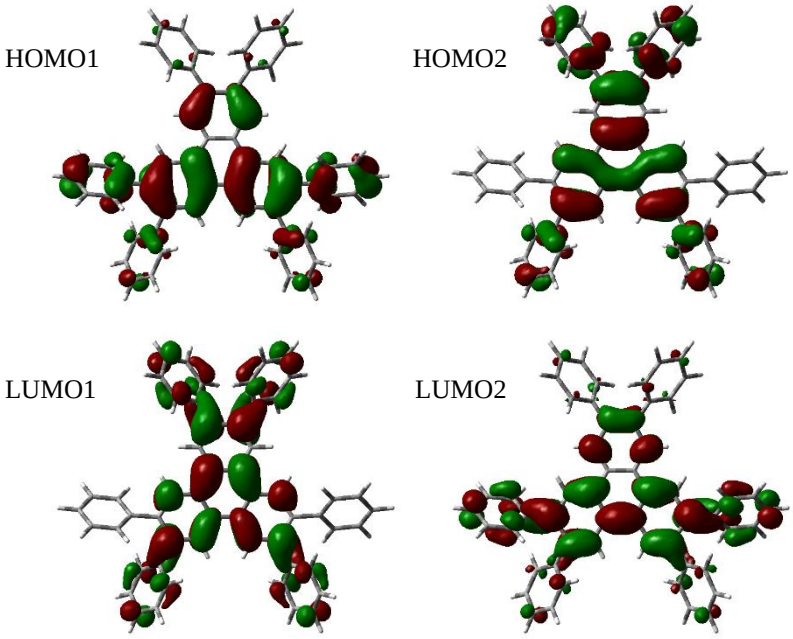


Figure S21 The HOMOs (top two) and the LUMOs (bottom two) of **4** calculated at the B3LYP/6-31(d) level. Isovalues are 0.02.

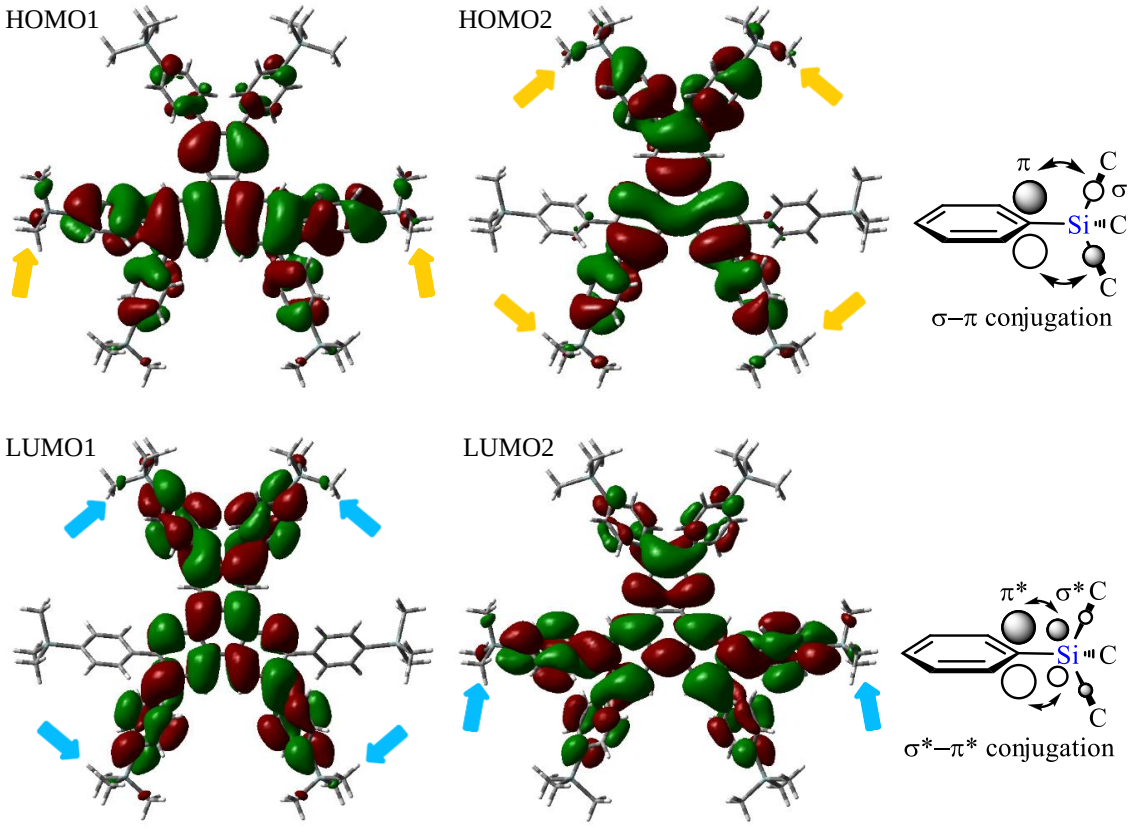


Figure S22 The HOMOs (top two) and the LUMOs (bottom two) of **1** calculated at the B3LYP/6-31G(d) level. Isovalues are 0.01 to show the σ–π and σ*–π* conjugations.

Table S2 Transition energies, wavelengths, and oscillator strengths of the transitions of **1**, **4** and triphenylene.

Compound 1[a]

Excited State	1:	Singlet-A	3.4306 eV	361.40 nm	f=0.0000	<S**2>=0.000
299 -> 302		0.48948				
300 -> 301		0.48957				
Excited State	2:	Singlet-B	3.5519 eV	349.07 nm	f=0.0023	<S**2>=0.000
299 -> 301		-0.49623				
300 -> 302		0.49631				
Excited State	3:	Singlet-A	3.7600 eV	329.75 nm	f=0.2062	<S**2>=0.000
298 -> 302		0.21411				
300 -> 303		0.65439				
Excited State	4:	Singlet-B	3.7601 eV	329.74 nm	f=0.2104	<S**2>=0.000
298 -> 301		-0.21401				
299 -> 303		0.65406				
Excited State	5:	Singlet-A	3.7982 eV	326.43 nm	f=1.3038	<S**2>=0.000
299 -> 302		0.49006				
300 -> 301		-0.48999				
Excited State	6:	Singlet-B	3.7983 eV	326.42 nm	f=1.2995	<S**2>=0.000
299 -> 301		0.48982				
300 -> 302		0.48974				
Excited State	7:	Singlet-B	4.1713 eV	297.24 nm	f=0.5921	<S**2>=0.000
297 -> 302		0.25216				
298 -> 301		0.60578				
299 -> 303		0.22900				
Excited State	8:	Singlet-A	4.1713 eV	297.23 nm	f=0.5921	<S**2>=0.000
297 -> 301		-0.25234				
298 -> 302		0.60576				
300 -> 303		-0.22889				
Excited State	9:	Singlet-B	4.2338 eV	292.84 nm	f=0.0800	<S**2>=0.000
297 -> 302		0.61488				
298 -> 301		-0.23592				
300 -> 304		-0.16820				

Excited State 10: Singlet-A 4.2338 eV 292.84 nm f=0.0800 <S**2>=0.000
297 -> 301 0.61481
298 -> 302 0.23612
299 -> 304 0.16813

Excited State 11: Singlet-B 4.3633 eV 284.15 nm f=0.0004 <S**2>=0.000
295 -> 302 0.10865
296 -> 301 -0.10894
297 -> 302 0.18876
300 -> 304 0.64646

Excited State 12: Singlet-A 4.3633 eV 284.15 nm f=0.0004 <S**2>=0.000
295 -> 301 0.10879
296 -> 302 0.10892
297 -> 301 -0.18875
299 -> 304 0.64643

Excited State 13: Singlet-B 4.4141 eV 280.88 nm f=0.0024 <S**2>=0.000
295 -> 302 0.38551
296 -> 301 0.38622
297 -> 304 -0.10138
298 -> 303 0.35873
299 -> 306 -0.12867
300 -> 305 -0.12958

Excited State 14: Singlet-B 4.4301 eV 279.87 nm f=0.0017 <S**2>=0.000
295 -> 302 -0.23118
296 -> 301 -0.23236
298 -> 303 0.60062

Excited State 15: Singlet-A 4.4518 eV 278.50 nm f=0.0000 <S**2>=0.000
295 -> 301 0.31333
296 -> 302 -0.31155
297 -> 303 0.39495
299 -> 305 -0.24339
300 -> 306 0.24118

Excited State 16: Singlet-B 4.4602 eV 277.98 nm f=0.0028 <S**2>=0.000
295 -> 302 0.38332
296 -> 301 -0.38121
296 -> 303 0.10066
299 -> 306 -0.28110
300 -> 304 -0.11070

300 -> 305	0.28191				
Excited State 17:	Singlet-A	4.4602 eV	277.98 nm	f=0.0028	<S**2>=0.000
295 -> 301	0.38166				
295 -> 303	0.10066				
296 -> 302	0.38305				
299 -> 304	-0.11071				
299 -> 305	-0.28114				
300 -> 306	-0.28165				
Excited State 18:	Singlet-A	4.4989 eV	275.59 nm	f=0.0000	<S**2>=0.000
295 -> 301	-0.20983				
296 -> 302	0.21160				
297 -> 303	0.56093				
299 -> 305	0.19161				
300 -> 306	-0.19152				
Excited State 19:	Singlet-B	4.5221 eV	274.17 nm	f=0.0001	<S**2>=0.000
295 -> 302	0.18478				
296 -> 301	0.18922				
299 -> 306	0.44140				
300 -> 305	0.44573				
Excited State 20:	Singlet-B	4.5466 eV	272.70 nm	f=0.0214	<S**2>=0.000
295 -> 302	0.24946				
296 -> 301	-0.24712				
299 -> 306	0.38894				
300 -> 304	-0.16602				
300 -> 305	-0.38318				

[a] The 299th and 300th orbitals are the HOMOs, and the 301st and 302nd orbitals are the LUMOs.

Compound 4[b]

Excited State 1:	Singlet-A	3.4790 eV	356.38 nm	f=0.0000	<S**2>=0.000
179 -> 182	0.49102				
180 -> 181	0.49107				
Excited State 2:	Singlet-B	3.6171 eV	342.78 nm	f=0.0015	<S**2>=0.000
179 -> 181	-0.49651				
180 -> 182	0.49655				
Excited State 3:	Singlet-A	3.8071 eV	325.67 nm	f=0.0584	<S**2>=0.000
178 -> 182	-0.22865				

180 -> 183 0.65511

Excited State 4: Singlet-B 3.8072 eV 325.66 nm f=0.0589 <S**2>=0.000
178 -> 181 0.22874
179 -> 183 0.65512

Excited State 5: Singlet-A 3.9020 eV 317.74 nm f=1.1009 <S**2>=0.000
179 -> 182 0.49242
180 -> 181 -0.49236

Excited State 6: Singlet-B 3.9021 eV 317.74 nm f=1.1004 <S**2>=0.000
179 -> 181 0.49243
180 -> 182 0.49239

Excited State 7: Singlet-B 4.2570 eV 291.25 nm f=0.5108 <S**2>=0.000
177 -> 182 -0.20908
178 -> 181 0.62063
179 -> 183 -0.23768

Excited State 8: Singlet-A 4.2571 eV 291.24 nm f=0.5108 <S**2>=0.000
177 -> 181 0.20913
178 -> 182 0.62066
180 -> 183 0.23761

Excited State 9: Singlet-A 4.3698 eV 283.73 nm f=0.0544 <S**2>=0.000
177 -> 181 0.65010
178 -> 182 -0.20346

Excited State 10: Singlet-B 4.3698 eV 283.73 nm f=0.0544 <S**2>=0.000
177 -> 182 0.65013
178 -> 181 0.20340

Excited State 11: Singlet-B 4.4805 eV 276.72 nm f=0.0000 <S**2>=0.000
178 -> 183 0.69939

Excited State 12: Singlet-B 4.5124 eV 274.76 nm f=0.0008 <S**2>=0.000
175 -> 182 -0.16791
176 -> 181 0.16850
177 -> 182 -0.10975
180 -> 184 0.62711

Excited State 13: Singlet-A 4.5124 eV 274.76 nm f=0.0008 <S**2>=0.000
175 -> 181 -0.16781

176 -> 182 -0.16804
177 -> 181 0.10979
179 -> 184 0.62726

Excited State 14: Singlet-B 4.5360 eV 273.33 nm f=0.0020 <S**2>=0.000
175 -> 182 0.43377
176 -> 181 0.43407
177 -> 184 -0.10319
179 -> 186 0.19183
180 -> 185 -0.19239

Excited State 15: Singlet-A 4.5695 eV 271.33 nm f=0.0000 <S**2>=0.000
175 -> 181 -0.25781
176 -> 182 0.25575
177 -> 183 0.51778
179 -> 185 0.17739
180 -> 186 0.17556

Excited State 16: Singlet-A 4.5757 eV 270.96 nm f=0.0078 <S**2>=0.000
175 -> 181 0.37600
175 -> 183 -0.10718
176 -> 182 0.37660
179 -> 184 0.16755
179 -> 185 -0.26074
180 -> 186 0.26068

Excited State 17: Singlet-B 4.5757 eV 270.96 nm f=0.0078 <S**2>=0.000
175 -> 182 0.37688
176 -> 181 -0.37583
176 -> 183 -0.10737
179 -> 186 0.26017
180 -> 184 0.16809
180 -> 185 0.26060

Excited State 18: Singlet-A 4.6091 eV 269.00 nm f=0.0000 <S**2>=0.000
175 -> 181 0.29249
176 -> 182 -0.29421
177 -> 183 0.45191
179 -> 185 -0.21116
180 -> 186 -0.21134

Excited State 19: Singlet-B 4.6153 eV 268.64 nm f=0.0017 <S**2>=0.000
173 -> 182 0.11015

174 -> 181 0.11032
175 -> 182 0.22849
176 -> 181 0.22969
179 -> 186 -0.38272
179 -> 188 0.13720
180 -> 185 0.38321
180 -> 189 0.13707

Excited State 20: Singlet-B 4.6421 eV 267.09 nm f=0.0000 <S**2>=0.000
172 -> 182 0.13380
173 -> 182 -0.11613
174 -> 181 0.11611
175 -> 182 0.13535
176 -> 181 -0.13534
177 -> 189 -0.10075
179 -> 186 -0.22924
179 -> 188 0.21134
180 -> 184 0.21218
180 -> 185 -0.22886
180 -> 187 0.33406
180 -> 189 -0.21025

[b] The 179th and 180th orbitals are the HOMOs, and the 181st and 182nd orbitals are the LUMOs.

Triphenylene[c]

Excited State 1: Singlet-?Sym 3.9360 eV 315.00 nm f=0.0000 <S**2>=0.000
59 -> 61 -0.49802
60 -> 62 0.49802

Excited State 2: Singlet-?Sym 4.1285 eV 300.31 nm f=0.0000 <S**2>=0.000
59 -> 62 0.49864
60 -> 61 0.49864

Excited State 3: Singlet-E' 4.2595 eV 291.07 nm f=0.0020 <S**2>=0.000
58 -> 61 0.27840
60 -> 63 0.64016

Excited State 4: Singlet-E' 4.2595 eV 291.07 nm f=0.0020 <S**2>=0.000
58 -> 62 0.27841
59 -> 63 0.64015

Excited State 5: Singlet-?Sym 4.6787 eV 265.00 nm f=0.4264 <S**2>=0.000
57 -> 63 0.10818

58 -> 61 -0.21422
59 -> 61 0.46034
60 -> 62 0.46034

Excited State 6: Singlet-?Sym 4.6787 eV 265.00 nm f=0.4263 <S**2>=0.000
56 -> 63 0.10815
58 -> 62 0.21423
59 -> 62 0.46034
60 -> 61 -0.46033

Excited State 7: Singlet-E' 4.8934 eV 253.37 nm f=0.3165 <S**2>=0.000
58 -> 61 0.59853
59 -> 61 0.14910
60 -> 62 0.14910
60 -> 63 -0.28008

Excited State 8: Singlet-E' 4.8934 eV 253.37 nm f=0.3165 <S**2>=0.000
58 -> 62 0.59852
59 -> 62 -0.14913
59 -> 63 -0.28010
60 -> 61 0.14911

Excited State 9: Singlet-A2' 4.9220 eV 251.90 nm f=0.0000 <S**2>=0.000
58 -> 63 0.69831

Excited State 10: Singlet-E" 5.5533 eV 223.26 nm f=0.0000 <S**2>=0.000
59 -> 64 0.69423

Excited State 11: Singlet-E" 5.5533 eV 223.26 nm f=0.0000 <S**2>=0.000
60 -> 64 0.69423

Excited State 12: Singlet-?Sym 5.6281 eV 220.29 nm f=0.0046 <S**2>=0.000
56 -> 61 0.32410
57 -> 62 -0.32408
59 -> 67 -0.36529
60 -> 68 0.36530

Excited State 13: Singlet-?Sym 5.6281 eV 220.29 nm f=0.0046 <S**2>=0.000
56 -> 62 0.32419
57 -> 61 0.32419
59 -> 68 0.36521
60 -> 67 0.36524

Excited State	14:	Singlet-?Sym	5.7026 eV	217.42 nm	f=0.0000	<S**2>=0.000
56 -> 61		0.34962				
57 -> 62		0.34964				
59 -> 67		0.35156				
60 -> 68		0.35155				
Excited State	15:	Singlet-?Sym	5.7192 eV	216.79 nm	f=0.0000	<S**2>=0.000
58 -> 64		0.25507				
59 -> 66		0.46348				
60 -> 65		0.46354				
Excited State	16:	Singlet-?Sym	5.7238 eV	216.61 nm	f=0.0308	<S**2>=0.000
59 -> 65		0.49647				
60 -> 66		-0.49644				
Excited State	17:	Singlet-?Sym	5.7377 eV	216.09 nm	f=0.0000	<S**2>=0.000
59 -> 66		0.49330				
60 -> 65		-0.49324				
Excited State	18:	Singlet-?Sym	5.7377 eV	216.09 nm	f=0.0000	<S**2>=0.000
59 -> 65		0.49325				
60 -> 66		0.49328				
Excited State	19:	Singlet-?Sym	5.7674 eV	214.97 nm	f=0.0000	<S**2>=0.000
56 -> 62		0.32688				
57 -> 61		-0.32686				
59 -> 68		0.37784				
60 -> 67		-0.37783				
Excited State	20:	Singlet-?Sym	5.9868 eV	207.09 nm	f=0.0914	<S**2>=0.000
55 -> 62		-0.15790				
56 -> 61		-0.29575				
57 -> 62		0.29575				
57 -> 63		-0.28974				
59 -> 67		-0.31341				
60 -> 68		0.31342				

[c] The 59th and 60th orbitals are the HOMOs, and the 61st and 62nd orbitals are the LUMOs.

4. References

S1 H. Heaney and I. T. Millar, *Org. Synth., Coll. Vol.,* 1973, **5**, 1120.

S2 R. Breslow, B. Jaun, R. Q. Kluttz and C.-Z. Xia, *Tetrahedron,* 1982, **38**, 863.

S3 H. Meier and B. Rose, *J. prakt. Chem.,* 1998, **340**, 536.

S4 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09,* Revision E.01, Gaussian, Inc., Wallingford, 2013.