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

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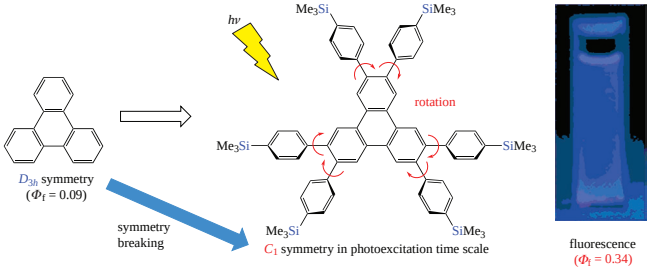
The fluorescence quantum yield of triphenylene is low because the transition moment between the HOMOs and the LUMOs is negligibly small. To improve the fluorescence quantum yield, break of the symmetrical structure of triphenylene is necessary. We found that the rotational effect of the 4-(trimethylsilyl)phenyl groups of 2,3,6,7,10,11-hexakis[4-(trimethylsilyl)phenyl]triphenylene is effective to break the symmetry in spite of the symmetrical structure, leading to improvement of the fluorescence quantum yield.



Keywords: fluorescence, fluorescence quantum yield, rotation, transition moment, 4-(trimethylsilyl)phenyl group, triphenylene, Suzuki–Miyaura coupling, organosilicon compounds.

Studies on organic light-emitting diodes (OLEDs) are a rapidly developing research area.[1–3] OLED devices usually consist of an electron transport layer, a hole transport layer and an emitting layer. In the emitting layer, the energy transfer from the excited state of a host material to a guest compound occurs to generate the excited state of the guest compound, which emits light. Until now, red and green light-emitting compounds with satisfactory performances have been developed. However, studies on blue light-emitting compounds are still required to improve quantum yields of light emission and deterioration time.[4]

Triphenylene, a versatile optoelectronic material, is used as a mesogen of discotic liquid crystals[5–7] which show efficient photoconductivities[8,9] and are used as light-emitting diodes[10–13] or optical compensation films.[14,15] Triphenylene has been known to emit blue fluorescence,[16] but its quantum yield is low (Φ_f = 0.09).[17] We reported that trimethylsilyl groups improve the fluorescence quantum yield of triphenylene (Φ_f = 0.14),[18] but further improvement is necessary.

The low fluorescence quantum yield of triphenylene is ascribed to the negligibly small transition moment between the HOMOs and the LUMOs. Triphenylene has the doubly degenerate HOMOs and the doubly degenerate LUMOs (Figure 1). The TD-DFT calculation shows that the π–π* transition is generated by interactions between two HOMO–LUMO transitions (Figure 2). In the lowest energy π–π* transition (**A** and **C**), the transition moments (μ) of the two transitions compensate each other completely due to the symmetrical structure (D_{3h}). As a result, the transition moments become zero. In fact, the molecular extinction coefficient of the lowest energy π–π* transition (^1L_b band) of triphenylene has been reported to be quite small (ε = 300 dm^3 mol^{-1} cm^{-1}).[16,18]

We report herein that the rotating 4-$Me_3SiC_6H_4$ groups of 2,3,6,7,10,11-hexakis[4-(trimethylsilyl)phenyl]triphenylene **1**

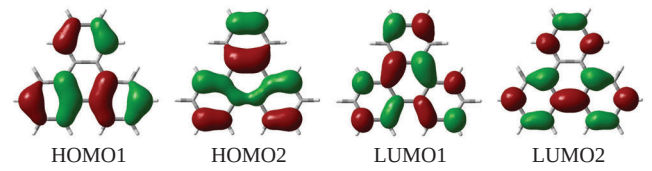


Figure 1 Doubly degenerate HOMOs and doubly degenerate LUMOs of triphenylene calculated at the B3LYP/6-31G(d) level. Isovalues are 0.03.

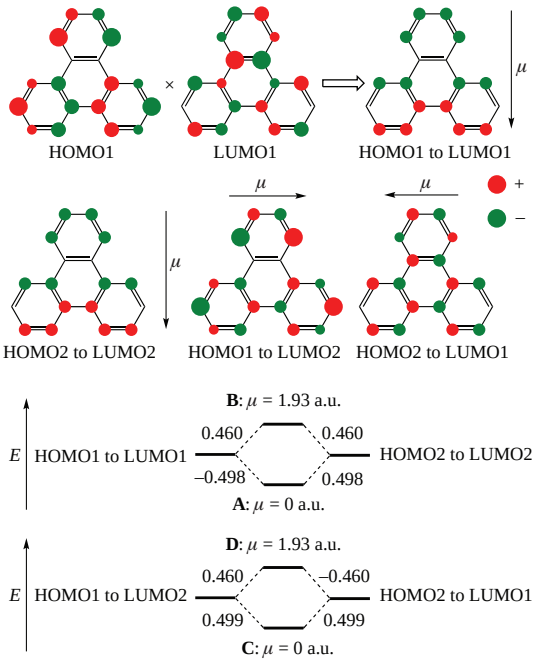


Figure 2 Transition moments and configuration interactions of the π–π* transitions of triphenylene calculated at the TD-DFT B3LYP/6-31+G(2d,p) level.

are effective substituents to break the D_{3h} symmetry and to improve the fluorescence quantum yield in spite of the symmetrical structure. As the 4-$Me_3SiC_6H_4$ groups rotate freely in the NMR time scale, compound **1** has the D_{3h} structure in solution. In the ^{1}H NMR spectrum, one signal of $SiMe_3$ protons at 0.15 ppm, two signals of substituent benzene protons at 7.35 and 7.50 ppm and one signal of triphenylene protons at 9.03 ppm are observed (see Online Supplementary Materials, Figure S1). Similarly, the ^{13}C and ^{29}Si NMR spectra show the D_{3h} structure (Figures S2 and S3). However, on photoexcitation, the symmetry of **1** is broken (Figure 3). All six 4-$Me_3SiC_6H_4$ groups rotate freely, although two of them on the same benzene ring of triphenylene may rotate according to the gear effect.[19–22] During the rotation, molecule **1** has the C_1 symmetry at almost every moment. The Franck–Condon principle states that electron transition takes place much more rapidly than molecular vibration and rotation.[23,24] Therefore, the D_{3h} symmetry of **1** is broken down into C_1 on photoexcitation, and the transition moment is expected to increase compared with that of the D_{3h} geometry.

In order to examine this consideration, compound **1** was synthesized by the Suzuki–Miyaura coupling[25,26] of 2,3,6,7,10,11-hexabromotriphenylene with 6.6 equiv. of 4-(trimethylsilyl)phenylboronic acid in the presence of the $Pd(PPh_3)_4$ catalyst (Scheme 1). Related compounds **2** and **3** were also prepared similarly from 2-bromotriphenylene and 3,6-dibromotriphenylene, respectively. These compounds were obtained as air-stable colorless solids.

The UV spectra of **1** and 2,3,6,7,10,11-hexaphenyltriphenylene **4** are shown in Figure 4. Compounds **1** and **4** show intense absorption bands at 301 nm (ε = 160 000 dm^3 mol^{-1} cm^{-1}) and 295 nm (ε = 150 000 dm^3 mol^{-1} cm^{-1}) with shoulders at *ca.* 325 and 320 nm, respectively. The absorption band shifts bathochromically in the order triphenylene [λ_{max} = 257 nm (ε = 148 000 dm^3 mol^{-1} cm^{-1}) in hexane][18] ≪ **4** < **1**. These intense absorption bands are due to the interaction of two HOMO–LUMO transitions **B** and **D** in Figure 2 according to TD-DFT calculations (Table S2). The lowest energy π–π* absorption bands corresponding to **A** and **C** in Figure 2 are expected to be detected at 349 and 361 nm (**1**) and 343 and 356 nm (**4**) (Table S2). Although these absorption bands are observed as the tailing curves in the UV spectra, the molecular extinction coefficients of **1** (ε = 3600 dm^3 mol^{-1} cm^{-1} at 355 nm) and **4** (ε = 2000 dm^3 mol^{-1} cm^{-1} at 350 nm) are larger than that of triphenylene (ε = 300 dm^3 mol^{-1} cm^{-1} at 335 nm).[16,18] The growth of the molecular extinction coefficient corresponds to the growth of the transition moment by the rotational effect of the six aryl groups. The additional increase in the molecular extinction coefficient of **1** shows electronic effects of the trimethylsilyl groups (*vide infra*).

The frontier orbitals of **1**, **4** and triphenylene calculated theoretically are shown in Figure 5. The optimized structure of triphenylene has the D_{3h} symmetry, whereas those of **1** and **4** have the D_3 symmetry. The dihedral angles between the triphenylene plane and substituent benzene planes are 48.5 and

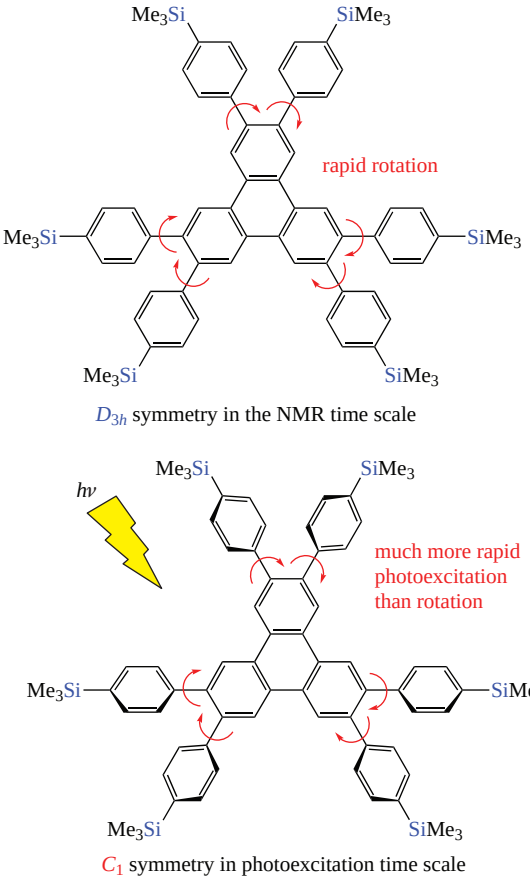
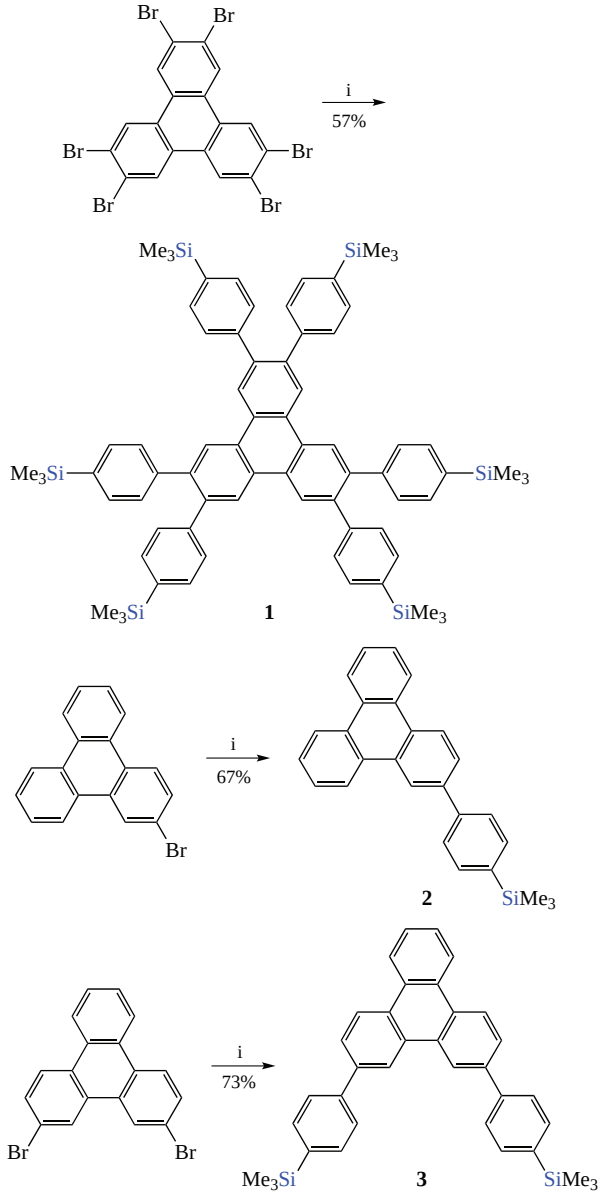


Figure 3 Difference of the symmetry of **1** in the NMR and photoexcitation time scales.



Scheme 1 *Reagents and conditions*: i, 4-$Me_3SiC_6H_4B(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, toluene, EtOH, H_2O, reflux.

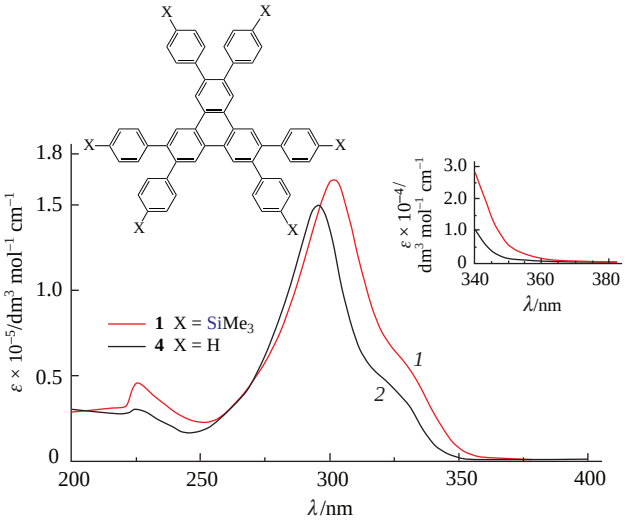


Figure 4 UV spectra of (*1*) **1** and (*2*) **4** in CH_2Cl_2 at room temperature.

49.4° for **1** and **4**, respectively. The HOMO and the LUMO of **4** consist of the π and π* orbitals of the triphenylene core and substituted benzene rings, showing extension of π conjugation (Figure S21). The π conjugation makes the energy levels of the HOMOs high and those of the LUMOs low, leading to the bathochromic shift of the π–π* absorption bands. In addition, the HOMOs of **1** show the σ–π conjugation between σ(Si–C) orbitals and π orbitals of the benzene rings (Figure S22).[27–31] The σ*–π* conjugation between σ*(Si–C) orbitals and π* orbitals of the benzene rings contributes to the LUMO of **1** (Figure S22).[18,27,29–33]

The fluorescence spectra in Figure 6 show that compounds **1** and **4** exhibit blue fluorescence with maxima at 393 and 389 nm, respectively. The fluorescence maximum of **1** is shifted slightly to the longer wavelength region compared with that of **4**, which is in accord with the results of the UV spectra. The fluorescence quantum yield increases in the order triphenylene (Φ_f = 0.09)[17] < **4** (Φ_f = 0.24) < **1** (Φ_f = 0.34). The results support the effects of the rotating aryl groups: (1) the symmetry breaking from D_{3h} to C_1, (2) extension of the π conjugation between the triphenylene core and substituent benzene rings and the σ–π and σ*–π* conjugations of the trimethylsilyl groups. These rotational and electronic effects increase the transition moment of the lowest energy π–π* transition and the fluorescence quantum yield.

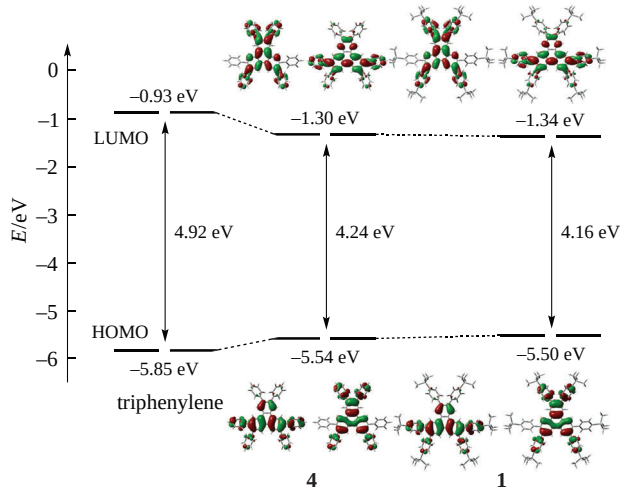


Figure 5 Frontier orbitals and their energy levels of **1**, **4** and triphenylene calculated at the B3LYP/6-31G(d) level. Isovalues are 0.02. The HOMOs and the LUMOs of triphenylene are shown in Figure 1.

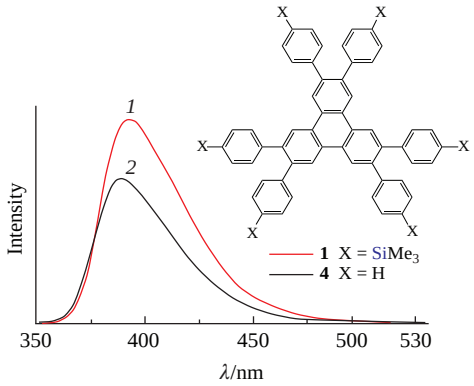


Figure 6 Fluorescence spectra of (*1*) **1** and (*2*) **4** in 3-methylpentane at room temperature.

The fluorescence lifetimes (τ_S) of **1** and **4** are listed in Table 1. From the fluorescence quantum yields and lifetimes, fluorescence radiative rate constants (k_f) and non-radiative rate constants (k_{nr}) were calculated according to the following equation.

$$\Phi_f = k_f/(k_f + k_{nr}) = k_f\tau_S$$

The k_f value increases in the order triphenylene < **4** < **1**. This order is in accord with the consideration of transition moments. The rapid fluorescence radiation contributes to the improvement of the fluorescence quantum yield.

The UV and fluorescence spectra of **2** and **3** were also measured (Figures S19 and S20). Compound **2** exhibits the absorption maxima at 273 nm (ε = 79000 dm^3 mol^{-1} cm^{-1}) and 305 nm (ε = 28000 dm^3 mol^{-1} cm^{-1}). Compound **3** shows the absorption maxima at 281 nm (ε = 80000 dm^3 mol^{-1} cm^{-1}) and 325 nm (ε = 46000 dm^3 mol^{-1} cm^{-1}). These compounds show the fluorescence maxima at 373 (**2**) and 375 nm (**3**). The fluorescence quantum yields are 0.24 (**2**) and 0.25 (**3**). These values are larger than that of triphenylene but smaller than that of **1**. These results indicate that one or two 4-$Me_3SiC_6H_4$ group(s) on triphenylene break(s) the symmetry of triphenylene, but increase of the transition moment by the extension of conjugation is not sufficient compared with the six 4-$Me_3SiC_6H_4$ groups of **1**.

In summary, compound **1** was synthesized by the Suzuki–Miyaura coupling of 2,3,6,7,10,11-hexabromotriphenylene with 4-(trimethylsilyl)phenylboronic acid. The fluorescence quantum yield of **1** was found to be significantly improved compared with those of triphenylene and **4**. This improvement is ascribed to the rotational and electronic effects of 4-$Me_3SiC_6H_4$ groups. These results give a useful methodology for improving fluorescence quantum yields of less luminescent compounds such as triphenylene.

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Table 1 Photophysical parameters of **1**, **4** and triphenylene at room temperature.[a,b]

Compound	λ_a/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_f/nm	Φ_f	τ_S/ns	k_f/s^{-1}	k_{nr}/s^{-1}
1	301 (160000)	393	0.34	4.0	8.5×10^7	1.7×10^8
4	295 (150000)	389	0.24	4.5	5.3×10^7	1.7×10^8
triphenylene[18]	257 (148000) 285 (18100) 335 (300)	356 363 372	0.09[17]	32	2.8×10^6	2.8×10^7

[a] The UV parameters were measured in CH_2Cl_2 (**1** and **4**) and hexane (triphenylene). [b] The fluorescence parameters were measured in 3-methylpentane.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.01.028.

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