

# 1,3,5-Tristyrylbenzene dendrimers: a novel model system to explore oxygen quenching in a highly organized environment

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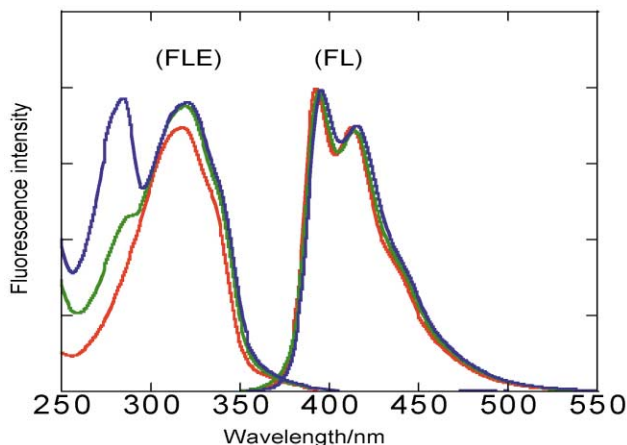
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**Control of the efficiency of photoisomerization by oxygen was demonstrated for 1,3,5-tristyrylbenzene dendrimers 1–3; the large dendrons do not significantly affect the photochemistry itself due to volume-conserving isomerization mechanisms but may affect the mobility of the molecules.**

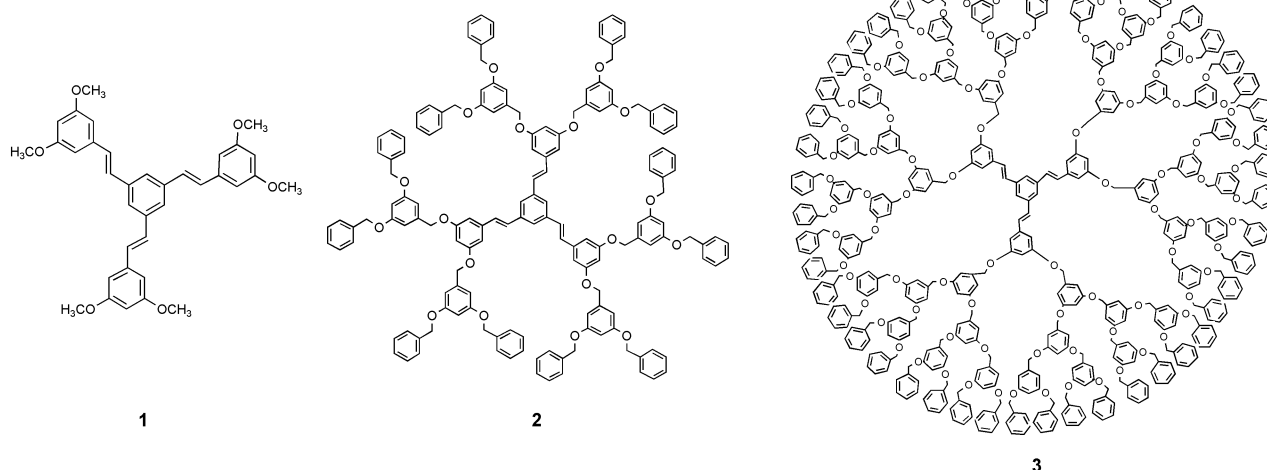
Previously we reported on the synthesis and photochemical properties of stilbene dendrimers.<sup>1</sup> The photoisomerization of the dendrimers may proceed not by a one-bond rotation of 180° but by a volume-conserving process. Water-soluble stilbene dendrimers<sup>2</sup> were also synthesized and showed unusual one-way *trans*-to-*cis* photoisomerization. We are currently interested in a model system to understand the dynamic process of quenching by oxygen in dendrimers. Incidentally, oxygen quenching of pyrene in SDS micelles with polymers has been investigated by van Stam *et al.*<sup>3</sup> As appropriate molecules for this study, we chose the photoresponsive 1,3,5-tristyrylbenzene dendrimers. Dendrimers are attracting increasing attention due to their three-dimensional, well-defined structure and ready availability through iterative synthesis.<sup>4–9</sup> The advantage of using dendrimers for this study is that the production of singlet oxygen and the dynamic quenching process by oxygen can be revealed as the quenching rate of the singlet state is measured with each generation of dendrimer. 1,3,5-Tristyrylbenzene was chosen as the dendrimer core due to its long-lived excited singlet state and so as to be able to observe the triplet state after quenching the singlet state by oxygen. Herein we report the synthesis and photochemistry of novel 1,3,5-tristyrylbenzene dendrimers. We have found that oxygen accelerates the efficiency of *E*-to-*Z* isomerization and the quenching rate constant of the excited state of the tristyrylbenzene core by oxygen decreases with increasing generation.

Zeroth, second and fourth generations of *E,E,E*-tristyrylbenzene dendrimers 1–3 were synthesized for this study (Scheme 1). † Zeroth generation dendrimer 1, which serves as a

basic unit for comparison with other dendrimers, was prepared from reaction of the Wittig–Horner reagent<sup>10</sup> with 3,5-dimethoxybenzaldehyde. A coupling reaction of 1,3,5-tris(3,5-dihydroxystyryl)benzene with second and fourth generations of aryl ether dendric bromides<sup>11,12</sup> (**G2-Br** and **G4-Br**) gave dendrimers 2 and 3, respectively. After purification by column chromatography or GPC, dendrimers 1–3 were characterized by <sup>1</sup>H NMR, MALDI-TOF MS, and UV absorption spectroscopy. Fluorescence and fluorescence excitation spectra of 1–3 are shown in Fig. 1. Fluorescence spectra of 1–3 were almost the same whilst the fluorescence excitation spectra were different, especially in the shorter wavelength region. The difference is due to singlet energy transfer from the dendron group to the core.



**Fig. 1** Fluorescence (FL) and fluorescence excitation (FLE) spectra of 1 (red), 2 (green), and 3 (blue) in THF. The spectra were measured with the absorption maximum set to be < 0.1 and were normalized.



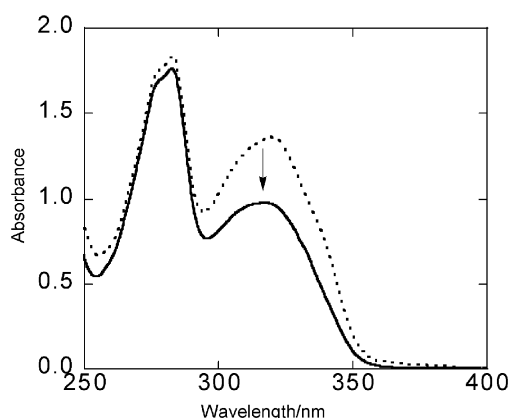
**Scheme 1** Structures of tristyrylbenzene dendrimers 1–3.

**Table 1** Quantum yields, fluorescence lifetimes, rate constants for quenching, fluorescence emission, intersystem crossing, and quantum yield of intersystem crossing of tristyrylbenzene dendrimers 1–3

	$\Phi_{E \rightarrow Z}(\text{Ar})$	$\Phi_{E \rightarrow Z}(\text{O}_2)$	$\frac{\Phi_{E \rightarrow Z}(\text{O}_2)}{\Phi_{E \rightarrow Z}(\text{Ar})}$	$\Phi_f$	$\tau_s(\text{Ar})$ /ns	$\tau_s(\text{air})$ /ns	$\tau_s(\text{O}_2)$ /ns	$k_q/10^{10}$ $\text{M}^{-1} \text{s}^{-1}$	$k_f/10^7$ $\text{M}^{-1} \text{s}^{-1}$	$k_{\text{isc}}(\text{Ar})$ $/10^6 \text{M}^{-1} \text{s}^{-1}$	$k_{\text{isc}}(\text{O}_2)$ $/10^8 \text{M}^{-1} \text{s}^{-1}$	$\frac{k_{\text{isc}}(\text{Ar}) + k_{\text{isc}}(\text{O}_2)}{10^8 \text{M}^{-1} \text{s}^{-1}}$	$\Phi_{\text{isc}}$
1	0.08	0.58	7.3	0.68	20.3	13.2	4.6	1.71	3.3	7.9	1.68	1.76	0.81
2	0.08	0.50	6.3	0.64	18.6	14.0	5.8	1.21	3.4	8.6	1.17	1.26	0.73
3	0.07	0.23	3.3	0.61	17.5	13.9	8.0	0.67	3.5	8.0	0.68	0.76	0.61

To investigate oxygen quenching of the excited core of these dendrimers, fluorescence lifetimes were measured at room temperature in THF. Dendrimers 1–3 had fluorescence lifetimes of 17–18 ns under argon. Under oxygen, these were 4.6, 5.8 and 8.0 ns for 1, 2 and 3, *i.e.* less than half of the corresponding value under argon. Although the fluorescence lifetime under argon was almost the same for each generation, those under oxygen were different. Thus, the quenching rate constant decreased from  $1.71 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$  for 1 to  $1.21 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$  for 2 to  $0.67 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$  for 3 (Table 1). This result, in which higher generations underwent oxygen quenching less effectively than lower generations, suggests two simple effects of macromolecules on the interaction of oxygen with the excited core moiety. One is the so-called eggshell effect, which derives from the presumption that higher generation dendrimers have harder outer layers (or higher density) thereby inhibiting interaction between the core moiety and oxygen. Another is the effect of the molecular size which reduces the mobility of higher generation dendrimers resulting in lower reaction rates.

On irradiation with 330 nm light in THF under argon, dendrimers 1–3 exhibited a decrease in their absorption spectra in the region 300–350 nm. The absorption change for irradiation of 3 is shown in Fig. 2. Changes in the spectral profile among 1–3 are almost the same. Therefore, 1–3 should undergo the same reaction on photoirradiation. The photochemical reaction of 1 was followed by  $^1\text{H-NMR}$  spectroscopy and revealed that the isomerization of 1 took place only between *E,E,E* and *Z,E,E* isomers. Since the spectral changes upon photoirradiation of 2 and 3 are almost the same, we can surmise that 2 and 3 also undergo isomerization only between *E,E,E* and *Z,E,E* isomers. The quantum yields of photoisomerization were 0.07–0.08. The efficiency of the isomerization is almost the same among all generations in spite of huge differences in volume between 1 and 3.



**Fig. 2** Change of the absorption spectrum of 3 on irradiation with 330 nm light in THF under argon: before (dotted line) and after irradiation (solid line).

Usually, *E*-olefins deactivate from the excited singlet state by three processes: intersystem crossing to the triplet state, fluorescence emission and *E*–*Z* isomerization.<sup>13,14</sup> Of these deactivation processes, only *E*–*Z* isomerization is expected to be affected by temperature. In all cases, however, changing the

temperature did not affect the efficiency of the photoisomerization which must therefore occur in the excited triplet state. The photoisomerization was dramatically accelerated under oxygen and the quantum yield of *E*-to-*Z* isomerization enhanced from 0.08 to 0.58, 0.08 to 0.50, and 0.07 to 0.23, respectively for 1, 2, and 3 (Table 1). This result shows that the oxygen effect decreased with increasing generation and is in good agreement with the observed quenching rate constant by oxygen.

The rate constant for fluorescence emission,  $k_f$ , estimated from the fluorescence quantum yield and the fluorescence lifetime was almost constant at *ca.*  $(3.4 \pm 0.1) \times 10^7 \text{s}^{-1}$  (Table 1). The quantum yield of intersystem crossing,  $\Phi_{\text{isc}}$ , was estimated from the quantum yield of isomerization and the fluorescence lifetime, assuming that the isomerization takes place in the excited triplet state after intersystem crossing to the triplet state as suggested from the lack of a temperature effect as described above.  $k_{\text{isc}}$  is also almost constant at *ca.*  $(8.3 \pm 0.4) \times 10^6 \text{s}^{-1}$  (Table 1). These results indicate a very interesting finding, *viz.* that the intrinsic photochemical behaviour was scarcely affected by the presence of a large dendron group. As described above, the increase of the quantum yield of *E*-to-*Z* isomerization should be a consequence of acceleration of the intersystem crossing to the triplet state by oxygen. Therefore, one can estimate the rate constant of the intersystem crossing from the singlet excited state to the triplet excited state accelerated by oxygen,  $k_{\text{isc}}(\text{O}_2)$ , from the fluorescence lifetime as shown in Table 1. The  $k_{\text{isc}}(\text{O}_2)$  values are  $1.68 \times 10^8$ ,  $1.17 \times 10^8$ , and  $0.68 \times 10^8 \text{s}^{-1}$ , respectively for 1–3. In addition, we could assume that most of the oxygen quenching results in the production of singlet oxygen and the triplet excited state of stilbene dendrimers.

In conclusion, control of the efficiency of photoisomerization by oxygen was demonstrated for aryl ether type dendrimers containing photoresponsive 1,3,5-tristyrylbenzene. The large dendrons do not affect the photochemistry itself, due to volume-conserving isomerization mechanisms, but do affect the mobility of the molecules. In addition, the results provide essential information for understanding the behavior of photoresponsive large dendritic macromolecules. The present finding that oxygen can interact with photoexcited states in large congested molecules—and be monitored by the quenching rate constant and the reaction efficiency of the excited state molecule—should be important in the construction of artificial biomolecular systems and may open a new approach to reveal dynamic quenching of excited states by oxygen in highly organized and congested biological environments. Further investigation into practical applications and the synthesis of corresponding higher generation dendrimers is underway.

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## Notes and references

† [3,5-Bis(diethoxyphosphorylmethyl)benzyl]phosphonic acid diethyl ester: A mixture of 1,3,5-tris-bromomethylbenzene (2.2 g, 5.7 mmol) and triethylphosphite (3.1 g, 18.6 mmol) was heated under nitrogen at 160 °C for 4 h. The mixture was dried under reduced pressure to give [3,5-bis(diethoxyphosphorylmethyl)benzyl]phosphonic acid diethyl ester (yellow oil, yield 2.96 g, 98.6%), which was used in the next reaction without further purification.  $\delta_{\text{H}}$  (200 MHz,  $\text{CDCl}_3$ ) 1.26 (18H, t,  $J = 7.0$  Hz,  $-\text{OCH}_2\text{CH}_3$ ), 3.06 (3H, s,  $\text{Ph}-\text{CH}_2\text{PO}-$ ), 3.17 (3H, s,  $\text{Ph}-\text{CH}_2\text{PO}-$ ), 3.95–4.14 (12H, q,  $J = 7.0$  Hz,  $-\text{OCH}_2\text{CH}_3$ ), 7.14–7.15 (3H, m,  $\text{C}_6\text{H}_3$ ).

1: A solution of potassium *tert*-butoxide (2.08 g, 18.6 mmol) in THF (15 ml) was added to the solution of [3,5-bis(diethoxyphosphorylmethyl)benzyl]phosphonic acid diethyl ester (2.96 g, 5.6 mmol) in THF (15 ml) under nitrogen at 0 °C and the mixture was stirred for 1 h. 3,5-Dimethoxybenzaldehyde (3.08 g, 18.5 mmol) in THF (15 ml) was added and stirred for 1 h at room temperature. The reaction mixture was poured into water and extracted with ether. The organic layer was dried over  $\text{MgSO}_4$  and concentrated *in vacuo*. The residue was purified by silica-gel column chromatography (eluent: hexane/ethyl acetate = 5/1) to give 0.68 g (22%) of 1,3,5-tri(3,5-dimethoxystyryl)benzene **1** as white needles; mp 182–183 °C;  $\delta_{\text{H}}$  (200 MHz,  $\text{CDCl}_3$ ) 3.86, (12H, s,  $\text{OCH}_3$ ), 6.43 (3H, t,  $J = 2.2$  Hz, Ar–H), 6.72 (6H, d,  $J = 2.2$  Hz, Ar–H), 7.14 (6H, s,  $-\text{CH}=\text{CH}-$ ), 7.56 (3H, s, Ar–H);  $\delta_{\text{C}}$  (50 MHz,  $\text{CDCl}_3$ ) 55.34, 100.17, 104.69, 129.27, 139.62, 161.10.

*E,E,E*-1,3,5-Tri(3,5-dihydroxystyryl)benzene: Boron tribromide (1.7 g, 6.8 mmol) in dichloromethane (10 ml) was added to the solution of **1** (0.39 g, 0.69 mmol) in dichloromethane (40 ml) at 0 °C and was stirred at room temperature for 8 h. After the reaction completed, water was added slowly to the reaction mixture, and then extracted with ether (100 ml  $\times$  3). The combined extracts were dried over  $\text{Na}_2\text{SO}_4$  and concentrated *in vacuo*. Purification by silica-gel column chromatography (eluent hexane/ethyl acetate = 1/3) gave 150 mg (45%) of 1,3,5-tri(3,5-dihydroxystyryl)benzene.  $\delta_{\text{H}}$  (200 MHz,  $\text{CD}_3\text{OD}$ ) 4.87 (6H, s, Ph–OH), 6.22 (3H, t,  $J = 2.2$  Hz, *p*-H in outer  $\text{C}_6\text{H}_3$ ), 6.55 (6H, d,  $J = 2.2$  Hz, *o*-H in outer  $\text{C}_6\text{H}_3$ ), 7.12 (6H, s,  $-\text{CH}=\text{CH}-$ ), 7.58 (3H, s, inner  $\text{C}_6\text{H}_3$ ).

**2** (typical procedure): A mixture of **G2-Br** (0.76 g, 1.98 mmol), *E,E,E*-1,3,5-tri(3,5-dihydroxystyryl)benzene (0.13 g, 0.28 mmol), 18-crown-6-ether (0.06 g, 0.21 mmol) and  $\text{K}_2\text{CO}_3$  (0.52 g, 3.76 mmol) in 2-butanone (30 ml) were refluxed under argon for 29 h. The solvent was evaporated and the residue was dissolved in dichloromethane (50 ml). After washing with water, the aqueous layer was further extracted with another 50 ml of dichloromethane. The combined extracts were dried over  $\text{Na}_2\text{SO}_4$ , then filtered and evaporated. Purification was achieved by silica-gel column chromatography (eluent hexane/chloroform = 1/2) followed by GPC to give 226 mg of **2** (35%) as a white powder. MALDI-TOF MS found:  $m/z$  2317.4. Calc. for  $\text{C}_{156}\text{H}_{132}\text{O}_{18}\text{Na}$ :  $[\text{M} + \text{Na}]^+$ , 2317.8;  $\delta_{\text{H}}$  (200 MHz,  $\text{CDCl}_3$ ) 5.01–5.03 (36H, m,  $\text{Ph}-\text{CH}_2\text{O}-\text{Ph}$ ), 6.40–6.79 (27H, m, Ar–H), 7.08–7.17 (6H, m,  $-\text{CH}=\text{CH}-$ ), 7.28–7.38 (60H, m, Ar–H), 7.54 (3H, s, Ar–H).

**3**: MALDI-TOF MS found:  $m/z$  9962.7. Calc. for  $\text{C}_{660}\text{H}_{564}\text{O}_{90}\text{Na}$ :  $[\text{M} + \text{Na}]^+$ , 9958.7;  $\delta_{\text{H}}$  (600 MHz,  $\text{CDCl}_3$ ) 4.84–5.03 (180H, m,  $\text{Ph}-\text{CH}_2\text{O}-\text{Ph}$ ), 6.49–6.63 (135H, m, Ar–H), 7.22–7.35 (249H, m,  $-\text{CH}=\text{CH}-$  and Ar–H).

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