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Photochemical and photophysical properties of a poly(propylene amine) dendrimer functionalised with *E*-stilbene units†

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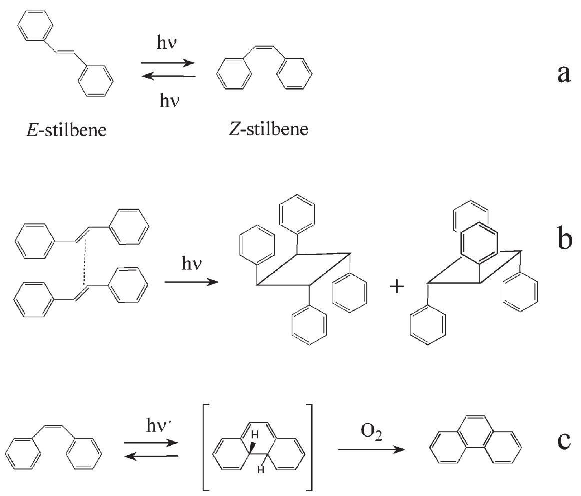
A second generation poly(propylene amine) dendrimer (**2**) functionalised at the periphery with eight *E*-stilbene and eight 4-*tert*-butylbenzenesulfonyl units has been prepared. The absorption spectrum, fluorescence spectrum and decay, $E \leftrightarrows Z$ photoisomerization, and photocyclization of the *Z*-isomer of the stilbene units have been investigated in air equilibrated acetonitrile solutions. For comparison purposes, a reference compound of the peripheral dendrimer units, namely 4-*tert*-butyl-*N*-propyl-*N*-(4-styryl-benzyl)-benzenesulfonamide (**1**), has also been studied. The quantum yield of the $E \rightarrow Z$ photoisomerization reaction (0.30) and the fluorescence quantum yield of the *E* isomer (0.014) are substantially smaller for the units appended to the dendrimer compared to those of the reference compound **1** (0.50 and 0.046, respectively). The presence of a red tail and the biexponential decay of the emission band of the dendrimer indicate formation of excimers between the stilbene units appended at the poly(propylene amine) dendritic structure. Under the experimental conditions used ($\lambda_{exc} = 313$ nm), a *Z*/*E* photostationary state (around 9 : 1 for both reference compound **1** and dendrimer **2**) is reached in the time scale of minutes. On continuing irradiation, other photoreactions take place in the time scale of hours: the stilbene moiety of compound **1** undergoes photocyclization to phenanthrene (quantum yield 0.015), whereas in dendrimer **2** photocyclization to phenanthrene is accompanied by other processes, including a photoreaction involving the internal amine groups.

Introduction

Stilbene, which can exist as an *E* (lower energy) and *Z* (higher energy) isomers (a, Scheme 1), is one of the most interesting molecules from a photochemical and photophysical viewpoint.[1] As early as 1931, Olson[2] discussed the mechanism of the *Z*/*E* (at that time, called *cis*/*trans*) photoisomerization and in 1968 Wald[3] discussed the molecular basis of visual excitation demonstrating the involvement of geometrical isomerization. A vast amount of experimental results has since been gathered concerning the photochemical and photophysical behavior of stilbene and stilbene-like molecules under a variety of experimental conditions.[1] Among the other points of interest of stilbene photochemistry, it should be recalled that it provides a classic example of the fact that light excitation can allow the selective conversion of a lower energy (*E*) to a higher energy (*Z*) isomer.

The photophysical and photochemical events that can take place upon light excitation of stilbene can be summarized as follows. In solution at ambient temperature *E*-stilbene and some of its derivatives show a relatively strong fluorescence in the range 340–400 nm, whereas the fluorescence of the *Z* isomer is extremely weak.[1d,f] The singlet excited state of *E*-stilbene can interact with amines to give exciplexes.[4] Formation of exciplexes causes a quenching of the *E*-stilbene fluorescence and the appearance of a broad emission in the 400–500 nm region.[4a] Excimers are also formed as precursors of the photocyclodimerization of *E*-stilbene and excimer emission has also been reported.[5]

Besides photochemical $E \leftrightarrows Z$ photoisomerization (a, Scheme 1), other photochemical reactions can be obtained upon irradiation of stilbene. *E*-stilbene can undergo photodimerization (b, Scheme 1), a reaction first observed by Ciamician and Silber.[6] This photoreaction, which originates from the singlet excited state, requires very high concentration of *E*-stilbene, but in water, where stilbene molecules are partly associated, photodimerization can be observed also in diluted solution (1 μM).[7] The extent of dimerization is considerably high when the reaction takes place in the cavity of γ-cyclodextrin[8] and cucurbit[8]uril,[9] or when two stilbene-like units are self-assembled in pseudorotaxane-type structures[10] or in hydrogen-bonded tape architectures.[11] *Z*-stilbene undergoes either photoisomerization to the *E*-isomer (a, Scheme 1) or photocyclization to dihydrophenanthrene[12] which can revert to the *Z*-isomer but, in the presence of oxygen, is irreversibly transformed into phenanthrene[13] (c, Scheme 1). Photocyclization of *Z*-stilbenes is indeed a valuable synthetic route for generation of phenanthrenes.



Scheme 1 (a) Photoisomerization of *E*- and *Z*-stilbene; (b) photocyclodimerization of *E*-stilbene; (c) photocyclization of *Z*-stilbene to dihydrophenanthrene followed by oxidation to phenanthrene.

Because of their very interesting photochemical and photophysical properties, stilbenoid compounds have found several applications in material science,[1d] *e.g.*, for optical brighteners,[14] light-emitting diodes,[15] functionalization of surfaces,[16] photopolymerizable materials,[17] nonlinear optics,[18] and photoresponsive hybrid materials.[19] Recently, stilbene has also been used in the field of molecular machines[20] and to investigate antibody-based photochemical sensors for diagnostic and clinical applications.[21]

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† Dedicated to Jean-Pierre Sauvage on the occasion of his 60th birthday.

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Table 1 Spectroscopic, photophysical and photochemical data (acetonitrile solution, 298 K)

	Absorption		Emission[a]			Photoreaction[b]	
	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	Φ	τ	$\Phi_{E\rightarrow Z}$	%Z[c]
E-stilbene	294, 306	27100, 26200	352	0.031	<200 ps[d]	0.51	92
E-**1**	298, 310	31400, 31900	353	0.046	<200 ps	0.50	90
E-**2**	300, 312	202400, 198100	361, 410[e]	0.014	<200ps, 3.5 ns	0.30	90

[a] λ_{ex}= 291 nm. [b] λ_{irr}= 313 nm. [c] At the pseudo-photostationary state. [d] 70 ps in *n*-pentane or hexane.[35] [e] See text and Fig. 2.

In the last few years, great attention has been devoted to dendrimers, tree-like macromolecules with a well defined composition, a high degree of order, and the possibility to contain selected chemical units at predetermined sites of their structure.[22] Particularly interesting dendrimers are those containing photoactive units.[23] A great number of photoluminescent dendrimers have been investigated, in an attempt to construct antenna systems that might be useful for solar energy conversion as well as for other purposes, such as signal amplification in luminescence sensors,[24–26] and spectral energy concentrator ('molecular lens').[27] Less attention has been devoted to photoreactive dendrimers, with the exception of species containing photoisomerizable azobenzene unit(s) in the core,[28] branches,[29] or appended at the periphery.[30] Since stilbene is at the same time a luminescent and photoreactive unit, its incorporation in dendrimer structures should result in interesting functional compounds. Recently, several dendrimers with a stilbene core have been investigated[31] and a few other studies on stilbene containing dendrimers have appeared.[32–34]

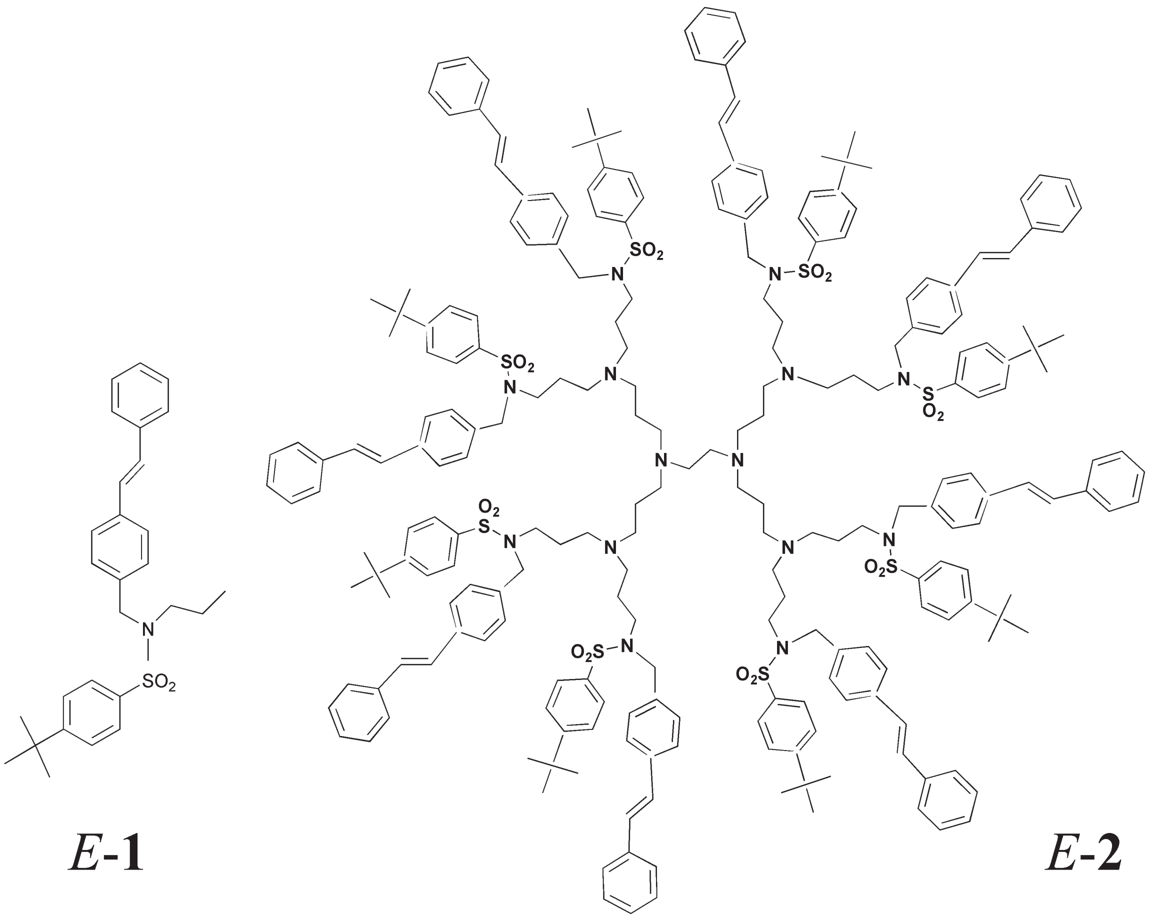
In this paper we have investigated the properties of a second generation poly(propylene amine) dendrimer (POPAM) functionalized at the periphery with eight *E*-stilbene units (**2**, Scheme 2). For comparison purposes, a model compound of the peripheral dendrimer units, namely 4-*tert*-butyl-*N*-propyl-*N*-(4-styryl-benzyl)benzenesulfonamide (**1**, Scheme 2), has also been studied.

Results and discussion

We have investigated the absorption and emission spectra, and photochemical reactivity of *E*-stilbene (Scheme 1), *E*-**1** reference compound, and *E*-**2** dendrimer (Scheme 2) in acetonitrile solution at 298 K. The results are illustrated and discussed in the following sections. The most important data have been gathered in Table 1.

Absorption and emission spectra

The UV absorption spectrum of *E*-stilbene in *n*-pentane is known to exhibit two absorption bands, one with maximum near 230 nm, and the other one with two peaks at 292 and 306 nm.[1f] The absorption spectra of *E*-stilbene, *E*-**1** reference compound, and dendrimer *E*-**2** in acetonitrile solution are shown in Fig. 1. As one can see, the spectra of *E*-**1** and *E*-**2** are slightly red-shifted compared to *E*-stilbene, presumably because of the presence of a substituent in the *para* position.[1b] Compared with the spectrum of eight *E*-**1** units, *E*-**2** shows somewhat smaller ε values, a result that could be attributed to incomplete functionalization. The spectrum of *E*-**2**, however, differs from that of *E*-**1** also because of the presence of a weak tail at low energy, suggesting that the observed spectral differences can be due to the fact that in *E*-**2** the stilbene units 'feel' a different environment since they can interact with other components of the dendritic structure.



E-**1**

E-**2**

Scheme 2 Structure formulas of the *E*-form of 4-*tert*-butyl-*N*-propyl-*N*-(4-stiryl-benzyl)-benzenesulfonamide (*E*-**1**), and of the second generation poly(propylene amine) dendrimer functionalized at the periphery with eight *E*-stilbene and eight 4-*tert*-butylbenzenesulfonyl units (*E*-**2**).

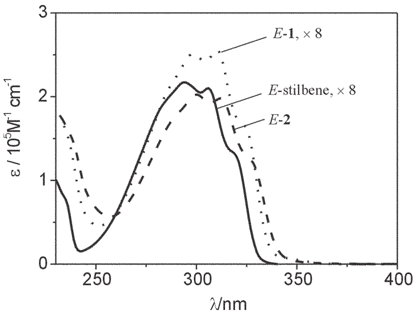


Fig. 1 Absorption spectra of *E*-stilbene (solid line), *E*-**1** reference compound (dotted line) and *E*-**2** dendrimer (dashed line) in acetonitrile solutions at 298 K.

E-stilbene is known to exhibit a fluorescence band with $\lambda_{max} = 352$ nm, $\Phi = 0.035$, and $\tau = 70$ ps in *n*-pentane or hexane.[35] The emission spectra in acetonitrile solution of the examined compounds are shown in Fig. 2 and some relevant data are gathered in Table 1. *E*-stilbene shows an emission band with maximum at 352 nm, $\Phi = 0.031$, and lifetime too short (<200 ps) to be measured with our equipment. The fluorescence band of the *E*-**1** reference compound ($\lambda_{max} = 353$ nm) is similar to that of *E*-stilbene, but somewhat more intense ($\Phi = 0.046$); the excited state lifetime is again too short (<200 ps) to be measured. The emission spectrum of dendrimer *E*-**2** is slightly red-shifted ($\lambda_{max} = 361$ nm), much less intense ($\Phi = 0.014$), and exhibits a long tail at low energy. Subtraction of the spectrum of *E*-**1** from that of *E*-**2** (after normalization at 353 nm) yields a broad and weak band with λ_{max} around 410 nm (Fig. 2, inset) that can be assigned to the emission of stilbene units perturbed by intradendritic interactions. The relatively long emission decay (3.5 ns) that can be observed in the case of *E*-**2** is indeed consistent with the presence of another emitting species besides unperturbed stilbene units, whose lifetime is shorter than 200 ps. It has been reported that interaction of stilbene with amines gives rise to a broad and weak emission band in the 450–550 nm region with lifetime in the nanosecond time scale.[4a] Since several amine groups are present in the *E*-**2** dendritic structure, the broad and weak band observed at 410 nm might thus be due to exciplexes or ground state charge-transfer complexes involving amines. An alternative assignment could involve excimers or stilbene dimers. As we have seen above, the lower intensity of the absorption band around 300 nm and the slight red shift for *E*-**2** compared with *E*-**1** is indeed consistent with the presence of ground state interactions. Excitation spectrum of *E*-**2**, collected at 500 nm, matches its absorption spectrum, thus ruling out the presence of impurity quenching of the stilbene emission and definitively assigning the long emission decay to intradendritic interactions of peripheral stilbene units.

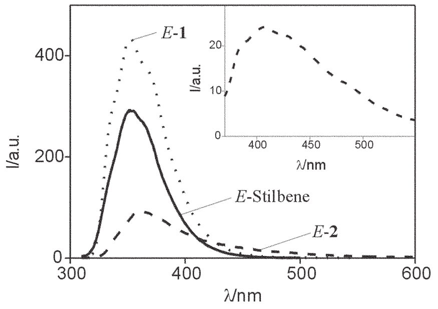


Fig. 2 Emission spectra (λ_{exc}=291 nm) of *E*-stilbene (solid line), *E*-**1** reference compound (dotted line), and *E*-**2** dendrimer (dashed line) in acetonitrile solutions at 298 K. The inset shows the spectrum obtained after subtraction of the normalized spectrum of *E*-**1** from that of *E*-**2**.

In previous investigations we have found that dendrimers containing propylene amine[36] or cyclam[37] units functionalized at the periphery with naphthalene show three different types of emission bands, namely 'monomer' emission, charge transfer/exciplex emission deriving from interaction of the naphthalene units with the internal amine groups, and dimer/excimer emission due to the interaction between naphthalene units. In such compounds we also found that, by addition of trifluoroacetic acid, protonation of the amine groups caused, as expected, the disappearance of the charge transfer/exciplex emission and a strong increase in the monomer emission.[36,37] In the case of *E*-**2**, which contains 6 amine units, we have found that addition of an excess (30 equivalents per dendrimer) of trifluoroacetic acid has no effect on the emission spectrum. Therefore, we conclude that the broad and weak band with maximum around 410 nm (Fig. 2, inset) is not related to the presence of charge-transfer/exciplex species involving amines and can therefore be assigned to dimer/excimer stilbene-based species. We can also conclude that the protonation of the amine groups of the dendrimer does not cause structural rearrangements capable of affecting the interactions between stilbene units.

Photoisomerization reactions

As mentioned in the introduction, stilbene and stilbenoid compounds undergo a variety of photochemical processes. We have investigated the photochemical behavior of stilbene, reference compound *E*-**1**, and dendrimer *E*-**2** in acetonitrile solution at 298 K. Some relevant data are gathered in Table 1.

It is well known[1] that *E*-stilbene undergoes an *E*→*Z* photoisomerization upon excitation with UV light. The spectral changes observed on irradiating with 313 nm light in acetonitrile solutions of *E*-stilbene, reference compound *E*-**1**, and dendrimer *E*-**2** are shown in Fig. 3. Clearly, the *E*→*Z* photoisomerization reaction is a clean process for each one of the three compounds until a pseudo-photostationary state is reached (see also below). From the known spectrum of *Z*-stilbene (Fig. 3a), it can be calculated that in the case of stilbene such a pseudo-photostationary state is reached when 92% of the *E*-isomer has been converted into the *Z* one. Since the pure forms of *Z*-**1**, and *Z*-**2** were not available, we have used the spectrum of *Z*-stilbene to estimate the composition of the pseudo-photostationary state for compounds **1** and **2**, obtaining a *Z*/*E* ratio about 9 : 1 in both cases. For each compound, the quantum yield of the *E*→*Z* photoisomerization reaction was measured at very low conversion ratios (see Experimental). The value obtained for the reference compound *E*-**1** (0.50) is substantially the same as that obtained for *E*-stilbene (0.51), whereas that of dendrimer *E*-**2** (0.30) is considerably smaller. The lower quantum yield of isomerization found for dendrimer *E*-**2** could be due to steric crowding, but it seems more likely related to the occurence of excited state deactivation *via* excimer formation, as shown by the fluorescence results. In stilbene-containing monolayers and vesicles[5a] and DNA stilbene systems[5b] it has been found that excimer formation is accompanied by [2 + 2] dimerization (Scheme 1b). However no evidence for such a reaction has been found for *E*-**2**. Apparently, in our dendrimer, the excimer concentration is very low and/or the excimer cannot reach a structure useful for dimerization.

Photocyclization reaction of the *Z*-isomers

As we have seen above, irradiation with 313 nm light of *E*-stilbene, *E*-**1**, and *E*-**2** led, in less than 10 minutes, to a pseudo-photostationary state in which the two isomers are present in a 9 : 1 *Z*/*E* ratio (Table 1). On a much longer time scale, however, continuous irradiation with 313 nm light caused other spectral changes, as illustrated in Fig. 4.

In the case of stilbene, the absorption (Fig. 4a) and emission spectra (Fig. 4a, inset) obtained after 10 hours of irradiation showed the characteristic bands of phenanthrene. This result indicates the occurrence of the well known photocyclization of the *Z*-isomer to dihydrophenanthrene,[12] followed by spontaneous oxidation to phenanthrene (Scheme 1c).[13] The photocyclization reaction is very clean and takes place with a low quantum yield (0.015). The absorbance values indicate that under the experimental conditions used around 90% of stilbene was converted to phenanthrene; complete photocyclization would probably occur on a much longer time scale because of the very low quantum yield.

Fig. 4b shows that, under the experimental conditions used, a clean photocyclization reaction occurs also in the case of reference

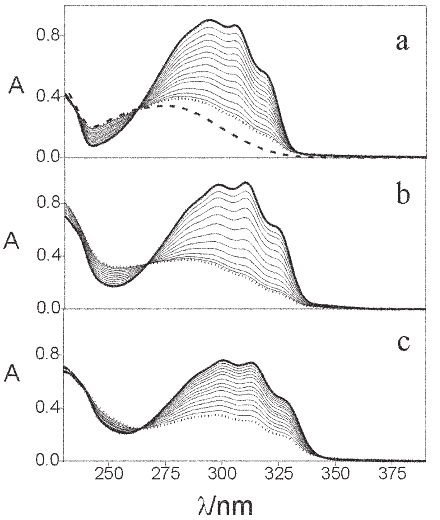


Fig. 3 Spectral changes observed on a short time scale (min) upon irradiation of acetonitrile solutions of *E*-stilbene (a), *E*-**1** (b) and *E*-**2** (c) with 313 nm light. The concentration of stilbene units was the same in all cases (3.05×10^{-5} M). The solid and dotted curves represent the spectra of the solutions before and after (photostationary state) irradiation, respectively. The dashed line in (a) represents the absorption spectrum of pure *Z*-stilbene.

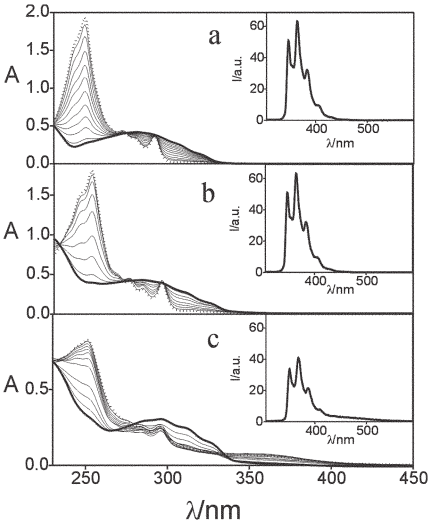


Fig. 4 Spectral changes observed on a long time scale (10 h) upon irradiation of acetonitrile solutions of *E*-stilbene (a), *E*-**1** (b) and *E*-**2** (c) with 313 nm light. The solid and dotted curves represent the initial (photostationary state of the *E*→*Z* isomerization) and final (end of irradiation) spectra, respectively. The insets show the emission spectra of the solutions at the end of irradiation.

compound **1**, with the same quantum yield as for stilbene. The behaviour of dendrimer **2**, however, is substantially different (Fig. 4c). Photocyclization to phenanthrene does take place, as shown by the increase in absorption at 250 nm and by the appearance of the characteristic phenanthrene emission band (Fig. 4c, inset), but the lack of isosbestic points shows that other processes take place besides photocyclization. In order to understand whether the dendrimer amine groups play some role in determining the observed spectral changes, we have protonated *E*-**2** by addition of 30 eqs of trifluoroacetic acid before irradiation. Under such conditions, the formation of the absorption tail above 330 nm was no longer observed upon prolonged irradiation, showing that, in the unprotonated form, there is indeed a reaction involving the amine groups. It is not clear, however, whether such a reaction takes place from a *Z*-stilbene or a phenanthrene excited state. The complexity of the reactions taking place upon prolonged irradiation of **2** is also shown by the lack of isosbestic points even in the cases of the acidified solutions, and the presence of a red tail around 450 nm in the emission spectrum of the photoproducts (Fig. 4c, inset).

Conclusions

We have investigated the spectroscopic, photophysical, and photochemical properties of stilbene, reference compound **1**, and dendrimer **2** in acetonitrile solution at ambient temperature. The results obtained show that **1** behaves like stilbene, whereas the behaviour of the stilbene units of dendrimer **2** substantially differs from that of their model compound **1**. Such a 'dendrimer effect'[38] shows up as follows: (i) small differences in the absorption spectrum of the *E*-stilbene units, caused by interactions among contiguous units in the dendritic structure; (ii) strong decrease in the fluorescence quantum yield of the *E*-stilbene units and appearance of a broad and weak emission at lower energies, assigned to the formation of *E*-stilbene excimers; (iii) strong decrease in the quantum yield of the *E*→*Z* photoisomerization reaction, presumably because of excited state deactivation *via* excimer formation; (iv) lower quantum yield of the photocyclization process of the *Z*-isomer to phenanthrene; (v) occurrence of secondary reactions, one of which involves the internal amine groups of the dendrimer, during the slow photocyclization process. Finally, there is no evidence that the dendritic architecture favors a [2 + 2] dimerization between *E*-stilbene units.

Experimental

Synthesis of *N*-propyl-(4-*tert*-butylbenzenesulfonyl)amide

To the mixture of 1-propylamine (400 mg, 6.8 mmol) and triethylamine (830 mg, 8.2 mmol) in chloroform 4-*tert*-butylbenzenesulfonyl chloride (1.6 g, 6.8 mmol) in chloroform was added dropwise. After stirring for 24 h at RT the mixture was washed with water, aq. $NaHCO_3$ and again with water. The organic phase was dried with Na_2SO_4 and the solvent was removed *in vacuo*. Further purification was achieved by column chromatography (SiO_2, 40–60 nm, dichloromethane/methanol: 40/1) yielding 1.5 g (87%) of a colourless solid. ^{1}H NMR: (400 MHz, $CDCl_3$, 25 °C), δ [ppm] = 0.87 (t, 3H, $^3J_{HH}$ = 7.45 Hz, $\mathrm{CH_2CH_2C}\mathit{H}_3$), 1.34 (s, 9H, $\mathrm{C(C}\mathit{H}_3)_3$), 1.50 (sext, 2H, $^3J_{HH}$ = 7.33 Hz, $^3J_{HH}$ = 7.20 Hz, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_3}$), 2.91(q, 2H, $^3J_{HH}$ = 7.07 Hz, $^3J_{HH}$ 6.32 Hz, $\mathrm{NHC}\mathit{H}_2\mathrm{CH_2CH_3}$), 4.59 (t, 1H, $^3J_{HH}$ = 6.19 Hz, $\mathrm{N}\mathit{H}\mathrm{CH_2}$), 7.51 (AA′BB′, 2H, $^3J_{HH}$ = 8.72 Hz), 7.79 (AA′BB′, 2H, $^3J_{HH}$ = 8.84 Hz). ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25 °C), δ [ppm] = 11.10 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_3}$), 23.00 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_3}$), 31.10 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 35.13 ($\mathit{C}\mathrm{(CH_3)_3}$), 44.99 ($\mathit{C}\mathrm{H_2CH_2CH_3}$), 126.04, 126.92 ($C_{Ar}$), 137.03, 156.31 ($C_{qAr}$). EI-MS: *m*/*z* (%): 255.1 ($M + H^{\oplus}$, 20). $C_{13}H_{21}NO_2S$: (255.38).

Synthesis of the *E* form of 4-*tert*-Butyl-*N*-propyl-*N*-(4-styrylbenzyl)benzenesulfonamide (*E*-1)

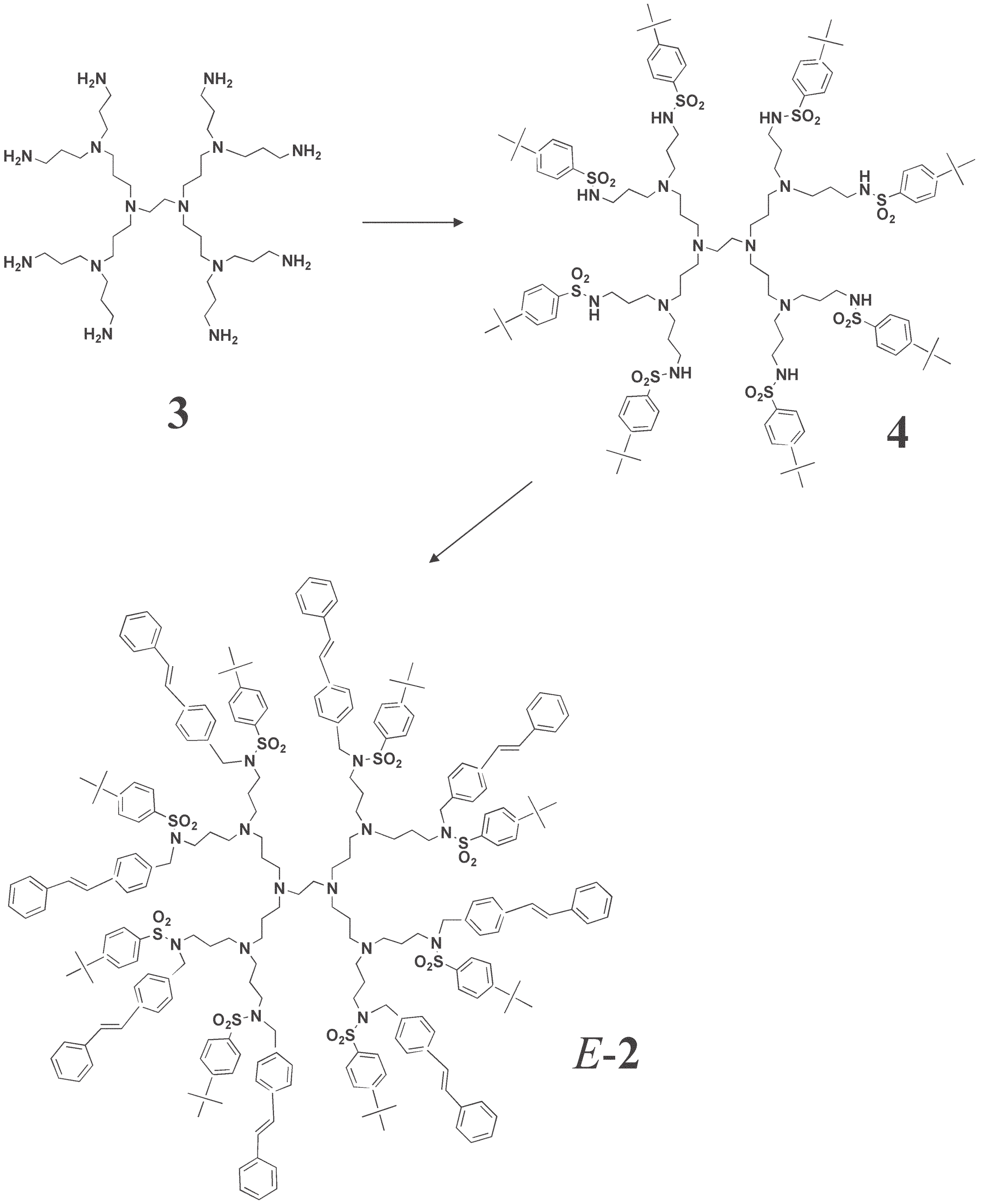
N-Propyl-(4-*tert*-butylbenzenesulfonyl)amide (200 mg, 0.78 mmol) and potassium carbonate (330 mg, 2.34 mmol) was dissolved in 100 ml acetonitrile. Under reflux 4-bromomethyl-stilbene (260 mg, 0.94 mmol) was added dropwise and the mixture was stirred for 3 d. After filtering the undissolved potassium carbonate, the solvent was removed *in vacuo* and the residue was collected in chloroform. After washing with water, aq. $NaHCO_3$ and again with water the organic phase was dried with Na_2SO_4 and the solvent was removed again *in vacuo*. Further purification was achieved by column chromatography (SiO_2, 40–60 nm, dichloromethane/n-hexane: 2/1, 1% Et_3N) yielding 300 mg (86%) of a colourless solid. ^{1}H NMR: (400 MHz, $CDCl_3$, 25 °C), δ [ppm] = 0.74 (t, 3H, $^3J_{HH}$ = 7.33 Hz, $\mathrm{CH_2CH_2C}\mathit{H}_3$), 1.36 (s, 9H, $\mathrm{C(C}\mathit{H}_3)_3$), 1.39 (sext, 2H, $^3J_{HH}$ = 7.33 Hz, $^3J_{HH}$ = 7.58 Hz, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_3}$), 3.09(t, 2H, $^3J_{HH}$ = 7.58 Hz, $\mathrm{NHC}\mathit{H}_2\mathrm{CH_2CH_3}$), 4.34 (s, 2H, Ar–$\mathrm{C}\mathit{H}_2\mathrm{N}$), 7.09 (s, 2H, $\mathrm{C}\mathit{H}{=}\mathrm{C}\mathit{H}$), 7.24–7.27 (m, 4H, Ar–*H*), 7.36 (t, 2H, $^3J_{HH}$ = 7.71 Hz, Ar–*H*), 7.44 (d, 2H, $^3J_{HH}$ = 8.31 Hz, Ar–*H*), 7.50–7.54 (m, 4H, Ar–*H*), 7.77 (AA′BB′, 2H, $^3J_{HH}$ = 8.71 Hz). ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25 °C), δ [ppm] = 11.16 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_3}$), 21.61 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_3}$), 31.14 ($\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 35.14 ($\mathit{C}\mathrm{(CH_3)_3}$), 50.09 ($\mathit{C}\mathrm{H_2CH_2CH_3}$), 51.80 (Ar–$\mathit{C}\mathrm{H_2N}$), 126.03, 126.53, 126.61, 127.03, 127.70, 128.19 ($\mathit{C}\mathrm{H}{=}\mathit{C}\mathrm{H}$), 128.63, 128.71, 128.92 ($\mathit{C}\mathrm{H}{=}\mathit{C}\mathrm{H}$), 136.14, 136.84, 137.17, 137.28, 156.17 (C_{Ar}). FAB-MS: *m*/*z* (%): 447.2 ($M + H^{\oplus}$, 30). GC-MS: R_t = 20.99 min; *m*/*z* (%) = 447 ($M^{\oplus}$). $C_{28}H_{33}NO_2S$: (447.63).

Synthesis of the sulfonamide-dendrimer 8-Cascade: 1,2-diaminoethane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)2:*N*-[1-thiodioxo-4-*tert*-butylbenzene] (4, Scheme 3)

The starting oligopropyleneamine(POPAM)dendrimer-$(NH_2)_8$ (**3**, Scheme 3) and 10 equivalents of triethylamine were dissolved in 50 ml of dry dichloromethane. To a refluxing mixture, a solution of 8 equivalents of 4-*tert*-butylbenzenesulfonyl chloride in 50 ml of dichloromethane was added dropwise. After stirring for four days under reflux the solvent was removed *in vacuo* and the residue was collected in dichloromethane. After washing with water, aq. Na_2CO_3 and again with water the organic phase was dried with Na_2SO_4. The solvent was removed *in vacuo* yielding a yellow solid (90%). ^{1}H NMR: (250 MHz, $CDCl_3$, 25 °C), δ [ppm] = 1.30 (s, 72 H, CH_3), 1.36 (br, 24 H, $CH_2CH_2CH_2$), 2.44 (br, 36 H, NCH_2), 2.92 (br, 16 H, SO_2NHCH_2), 7.46 (d, 16 H, $^3J_{HH}$ = 8.5 Hz, Ar–H), 7.76 (d, 16 H, $^3J_{HH}$ = 8.3 Hz, Ar–H). ^{13}C NMR: (60.9 MHz, $CDCl_3$, 25 °C), δ [ppm] = 25.9, 31.3, 35.2, 42.7, 52.6, 126.2, 127.1, 137.0, 156.1. FAB-MS: *m*/*z* (%): 2316.1 (M + H$^{\oplus}$, 20). $C_{118}H_{188}N_{14}O_{16}S_8$: (2315.3).

Synthesis of the *E* form of 8-Cascade: 1,2-diaminoethane[4-*N*,*N*,*N*′,*N*′]:(1-azabutylidene)2:*N*-(1-benzyl-2-phenylethylene)-*N*-[1-thiodioxo-4-tert-butylbenzene] (*E*-2, Scheme 3)

The monosubstituted POPAM-dendrimer (**4**) and 1.5-fold excess of potassium carbonate were dissolved in 50 ml of acetonitrile. To this suspension 4-bromomethyl-stilbene (20% excess) in 50 ml of acetonitrile was added dropwise. The mixture was stirred for three days under reflux. After filtering the undissolved potassium carbonate, the solvent was removed *in vacuo* and the residue was collected in dichloromethane. After washing with water, aq. Na_2CO_3 and again with water, the organic phase was dried with Na_2SO_4. Further purification was achieved by column chromatography (SiO_2, 40–63 µm, CH_2Cl_2/ MeOH/ Et_3N: 100/1/1) yielding a yellow solid (29%). ^{1}H NMR: (400 MHz, $CDCl_3$, 25 °C),



Scheme 3 Schematic representation of the synthesis of *E*-**2**.

δ [ppm] = 1.25 (s, 72 H, CH_3), 1.96 (s, br, 24 H, $CH_2CH_2CH_2$), 2.64 (br, 36 H, NCH_2), 3.15 (br, 16 H, SO_2NHCH_2), 4.12 (br, 16H, Ar-CH_2), 6.80–7.52 (m, 104 H, Ar–H, $CH_2{=}CH_2$), 7.70 (m, 16 H, Ar–H). ^{13}C NMR: (100.6 MHz, $CDCl_3$, 25 °C), δ [ppm] = 31.1, 35.2, 47.0, 53.1, 56.5, 62.4, 126.5, 126.7, 126.8, 127.3, 127.8, 128.8, 129.6, 127.3, 135.6, 136.6, 137.0, 156.1. MALDI-TOP-MS: *m*/*z* (%): 3294.7 ($[C_{195}H_{249}N_{14}O_{16}S_8]^{\oplus}$, 10). $C_{238}H_{284}N_{14}O_{16}S_8$: (3853.4)

Photophysical and photochemical experiments

The photophysical properties (absorption and emission spectra, emission quantum yields, and excited state lifetimes) have been investigated in acetonitrile. The equipment used was peviously described.[24] Luminescence quantum yields were measured following the method described by Demas and Crosby[39] (standard used: naphthalene in cyclohexane, $\Phi = 0.23$ [40]). The estimated experimental errors are: 2 nm on the band maximum, 5% on the molar extinction coefficient, 10% on the fluorescence quantum yield, 5% on the fluorescence lifetime.

Photochemical reactions were performed on stirred solutions, by using a Hanau Q 400 medium pressure Hg lamp (150 W). Selection of the irradiation wavelength (313 nm) was accomplished by the use of an interference filter. The number of incident photons was measured by ferrioxalate actinometry.[41] The $E{\rightarrow}Z$ photoisomerization quantum yield ($\Phi_{E\rightarrow Z}$) and the composition of the photostationary state of the isomerization reaction were determined from the change in absorbance at 310 nm, assuming that the absorption spectrum of the *Z* isomer of the stilbene units of **1** and **2** is the same as that of *Z*-stilbene. The estimated error on the quantum yield and on the composition of the photostationary state is 10%. The quantum yield of the photocyclization reaction that converts the *Z*-stilbene unit of **1** into a phenanthrene unit was estimated from the increase in absorbance at 254 nm (phenanthrene band). In both cases, the quantum yield values observed at low conversion percentages (<10%) were extrapolated to $t = 0$ in order to avoid interference from light absorption by the photoproducts.

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