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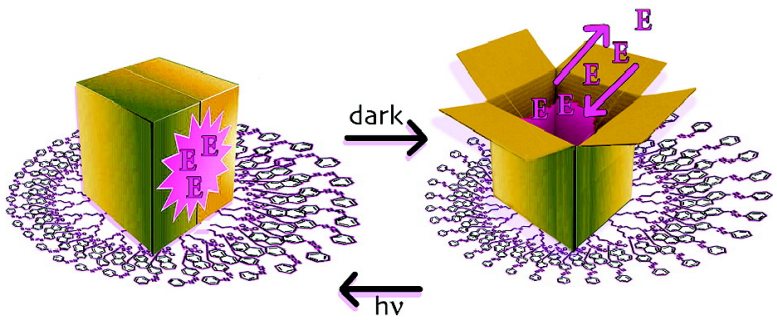

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Photoswitchable Dendritic Hosts: A Dendrimer with Peripheral Azobenzene Groups

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Abstract: We have studied the adducts formed by eosin (**E**) with a fourth generation dendrimer (**D**) that comprises 30 tertiary amine units in the interior and 32 naphthyl and 32 trans azobenzene units in the periphery. We have found that: (i) the all trans dendrimer **D**(32t) can be converted by irradiation with 365 nm light (Φ=0.12) into species containing, as an average, 4 trans and 28 cis azobenzene units, **D**(4t28c), that at 313 K undergoes a **D**(4t28c) → **D**(32t) thermal back reaction ($k = 7.0 \times 10^{-5}$ s^{-1}); (ii) **D**(32t) and **D**(4t28c) extract 8 and, respectively, 6 eosin molecules from water at pH 7, yielding the species **D**(32t)⊃8**E** and **D**(4t28c)⊃6**E**; (iii) eosin uptake is significantly faster for **D**(32t) than for **D**(4t28c); (iv) irradiation at 365 nm of the **D**(32t)⊃8**E** species at 298 K leads to the release of two eosin molecules with formation of a photostable **D**(15t17c)⊃6**E** species (Φ = 0.15) that is also obtained from the back thermal reaction of **D**(4t28c)⊃6**E** at 313 K ($k = 2.7 \times 10^{-5}$ s^{-1}); (v) thermal release of **E** from **D**(32t)⊃6**E** is much faster than from **D**(4t28c)⊃6**E**; and (vi) excitation of **E** in the adducts sensitizes the cis → trans (but not the trans → cis) isomerization. The results obtained show that the isomerization of the 32 peripheral azobenzene units controls to some extent the hosting capacity of the dendrimer and, viceversa, eosin molecules hosted in the dendrimer affect the isomerization process of its azobenzene units.

Introduction

Dendrimers[1,2] are complex, but well defined, chemical compounds that can contain selected functions in predetermined sites of their structure. They usually consist of a core upon which radially branched layers are covalently attached. Because of their tree-like multi-branched structure, dendrimers can form internal dynamic niches in which small molecules or ions can be hosted.[3,4] Molecular recognition properties of a dendrimer ("dendritic box") may also be changed upon structural or chemical variation in the peripheral groups.[5] Dendrimers are currently attracting increasing attention for a wide range of potential applications in such different fields as medicine, biology, chemistry, physics, and engineering.[2]

Dendrimers containing photoactive components[6,7] are particularly interesting because (i) luminescence signals offer a handle to better understand the dendritic structures and superstructures, (ii) cooperation among the photoactive components can allow the dendrimer to perform useful functions such as light harvesting, (iii) changes in the photophysical properties can be exploited for sensing purposes with signal amplification,

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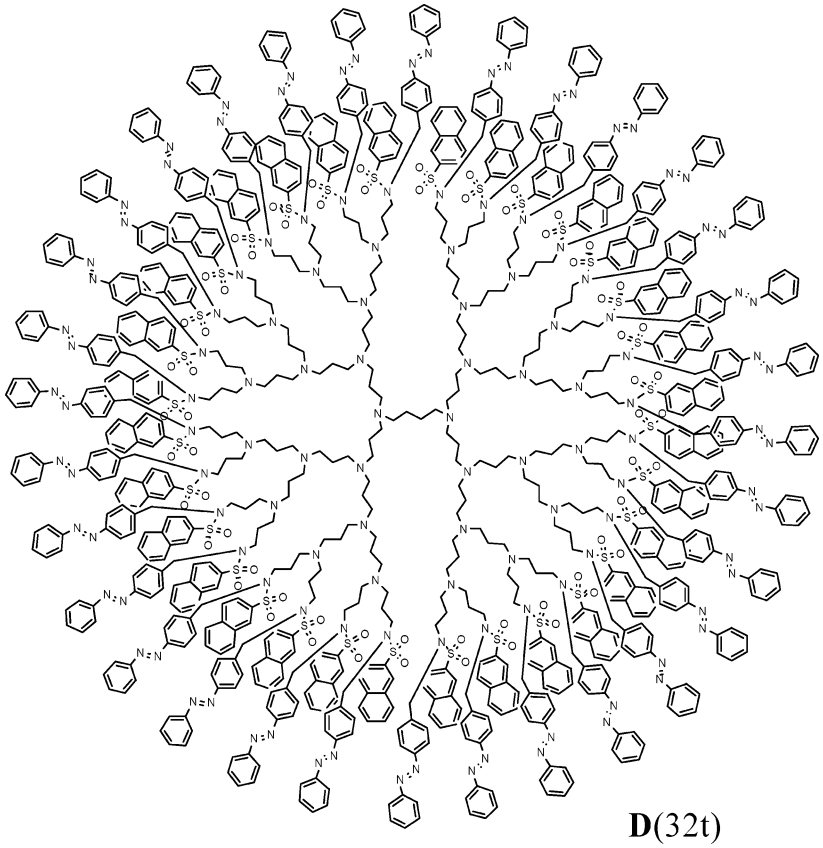
Scheme 1. Structure Formulas of Dendrimer **D** in its All-Trans Form **D**(32t) and Eosin, **E**



and (iv) photochemical reactions can change the structure and other properties of dendrimers.

Continuing our studies in the field of photoactive dendrimers,[4a,6e,f,8] we have investigated the adducts formed by eosin Y (2′,4′,5′,7′-tetrabromofluorescein dianion, hereafter simply called eosin and indicated by **E**) with a fourth generation dendrimer (**D**) of the poly(propylene amine) family functionalized with naphthyl and trans azobenzene units. The investigated dendrimer (Scheme 1) comprises 30 tertiary amine units in the interior and 32 naphthyl and 32 trans azobenzene units in the periphery.

It is well-known that azobenzene-type compounds undergo an efficient and fully reversible photoisomerization reaction.[9] For this reason, they have been extensively used to construct photoswitchable devices.[10] It is also known that they are reversibly switched from the trans to the cis form by UV light and can then be converted back to the trans form by heating.[8] Isomerization of azobenzene units involves a large structural

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rearrangement (Scheme 1), because in going from the trans to the cis isomer the distance between the *para* carbon atoms of azobenzene decrease from 9 to 5.5 Å and the dipole moment increases from zero (because the trans form is planar and symmetric) to 3.0 D.[8] Dendrimers containing azobenzene groups[11] in the core, branching points, or periphery can modify their structure and flexibility according to the isomerization state of the azobenzene units. In particular, structural changes in the peripheral units of a dendrimer can modify the surface properties and cause rearrangements in the internal cavities. For all these reasons, dendrimers bearing azobenzene groups in the periphery could play the role of photoswitchable hosts, a result that would be of interest in the field of controlled drug delivery.[12] The dendrimer studied in this paper differs from a previously examined compound[13] because of a different bridging unit to the poly(propylene amine) (POPAM) dendrimer and, especially, the presence at the periphery of 32 naphthyl units that are expected to increase steric crowding and therefore to amplify the difference caused by the trans → cis photoisomerization of the azobenzene units on the permeation through the dendrimer surface.

Results and Discussion

Dendrimer **D**(32t) (Scheme 1) is a fluorescent and photoreactive compound. The fluorescence of the naphthalene units is partially quenched by the tertiary amines (via electron transfer) as well as by the trans and cis azobenzene units (via energy transfer).[14] In dichloromethane solution at 298 K upon irradiation with 365 nm light, the all-trans dendrimer **D**(32t) is converted into species containing, as an average, 4 trans and 28 cis azobenzene units, **D**(4t28c).[15] Figure 1 shows that the photoreaction proceeds maintaining isosbestic points up to the photostationary state. The quantum yield of the trans → cis photoisomerization reaction, extrapolated at zero time, i.e., when all the incident light is absorbed by the trans form, is 0.12 (Figure 1, inset a, Table 1). In dichloromethane solution at 313 K, the rate constant of the **D**(4t28c) → **D**(32t) back reaction is 7.0×10^{-5} s^{-1} (Figure 1, inset b, Table 1).[14]

Eosin Extraction. It is well-known[5,16,17] that poly(propylene amine) dendrimers in dichloromethane solution can extract **E** from aqueous solution. The number of **E** extracted is strongly dependent on the generation number and pH of the aqueous phase, but less sensitive to the nature of the units appended in the periphery. In the present case, dichloromethane solutions of dendrimer **D** were mixed and shaken with aqueous solutions of the disodium eosin salt at pH 7.0 (phosphate buffer). This pH value has been chosen because eosin is present only as its $\mathbf{E}^{2-}$ form and extraction is efficient. Indeed, according to previous studies,[16c] extraction efficiency is maximum between pH 5 and 7 and is practically negligible at pH 12. The extraction procedure, based on mixing and shaking the two solutions, is described in the experimental section. No extraction occurs when the dendrimers are not present in the dichloromethane phase. The number of eosin molecules extracted can be easily measured from the changes in absorbance of the water phase at 540 nm, where **E** exhibits an intense absorption band.

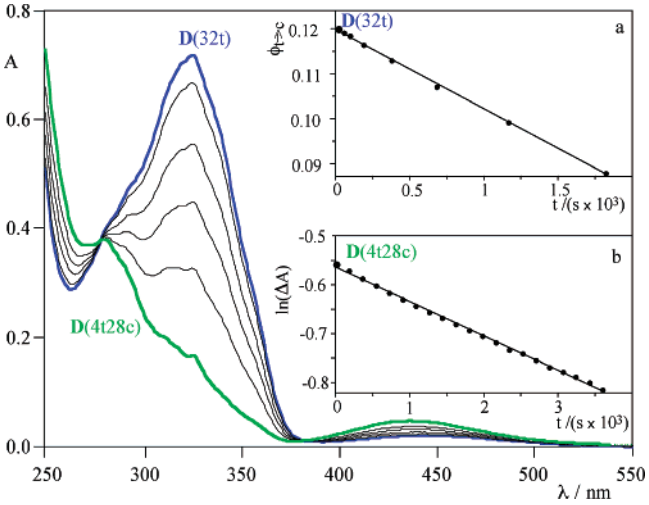

Figure 1. Spectral changes observed in dichloromethane solution at 298 K upon irradiation of the all trans dendrimer **D**(32t) (blue line) with 365 nm light. The product obtained at the photostationary state (green line) corresponds to the species **D**(4t28c).[15] (Inset a) Extrapolation of the apparent quantum yield values versus time to obtain the real quantum yield of the **D**(32t) → **D**(4t28c) photoisomerization. (Inset b) Absorption changes at 325 nm observed during the **D**(4t28c) → **D**(32t) back reaction at 313 K.

Table 1. Isomerization Quantum Yields and Kinetic Constants of Thermal Cis → Trans Isomerization ($k_{c\to t}$) and of Eosin Release (k_r) in Dichloromethane Solution

	$\phi_{t\to c}$ (365 nm, 298K)	$\phi_{c\to t}$ (540 nm, 298K)	$k_{c\to t}/10^{-5}$ s^{-1} (313K)	$k_r/10^{-6}$ s^{-1} (313K)
D(32t)	0.12			
D(4t28c)[a]			7.0	
D(32t)⊃8**E**	0.15			-
D(32t)⊃6**E**	-			10, 13[b]
D(4t28c)⊃6**E**		0.11, (0.31)[c]	2.7	< 0.001, 3.1[b]

[a] Species obtained at the photostationary state. [b] Data obtained using 2.5 mL of solution in the presence of an aqueous phase (0.5 mL, pH 10) at 298 K. [c] Deaerated solution.

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(15) The absorption spectra indicate the overall number of trans and cis azobenzene moieties present in the experimental condition used.
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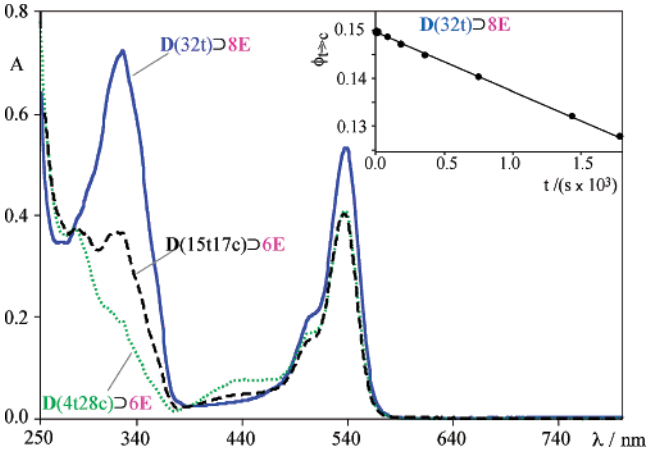
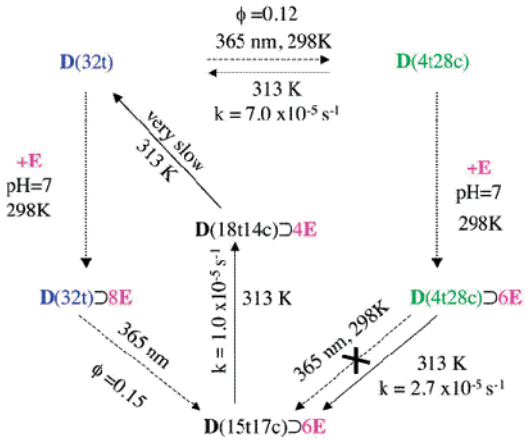


Figure 2. Absorption spectra of the species **D**(32t)⊃8**E** (full blue line), **D**(4t28c)⊃6**E** (dotted green line), and **D**(15t17c)⊃6**E** (dashed black line). (Inset) Extrapolation of the apparent quantum yield values versus time to obtain the real quantum yield of the **D**(32t)⊃8**E** → **D**(15t17c)⊃6**E** photoisomerization (dichloromethane solution, 298 K, 365 nm light). For more details, see text and Scheme 2.

Scheme 2. Photochemical (Dashed Arrow) and Thermal (Solid Arrow) Processes Taking Place Starting from **D**(32t) in Dichloromethane Solution and Extraction of **E** from a Water Solution (Dotted Arrows)



As shown in Scheme 2 and Figure 2, **D**(32t) and **D**(4t28c) extract 8 and 6 eosin molecules, respectively, from water at pH 7 yielding the species **D**(32t)⊃8**E** and **D**(4t28c)⊃6**E**. Because the number of **E** extracted is only slightly sensitive to the nature of the units appended in the periphery, we believe that the main driving force for extraction is the interaction between **E** and the tertiary amine units in the interior of the dendrimer.[16c] When **E** is encapsulated in the dendrimers, its fluorescence quantum yield (0.65 in dichloromethane) is strongly quenched (0.027 for **D**(32t)⊃8**E** and 0.011 for **D**(4t28c)⊃6**E**). A similar quenching effect had previously been reported for encapsulation of **E** inside the dansylated POPAM dendrimers ($\Phi = 0.020$)[16c,d] and it was attributed to photoinduced electron transfer between the amine units and **E**. The different degree of quenching observed for **D**(32t)⊃8**E** and **D**(4t28c)⊃6**E** can be related to a different location of **E** inside each dendrimer. The fluorescence quantum yield of **E** encapsulated into the dendrimer is not sensitive to dioxygen, as expected because of the short lifetime (a few ns) of the lowest singlet excited-state of **E**. The results obtained show that the hosting abilities of **D**(32t) and **D**(4t28c) are somewhat different presumably because the isomerization state of the azobenzene peripheral units affects the dendrimer cavities.

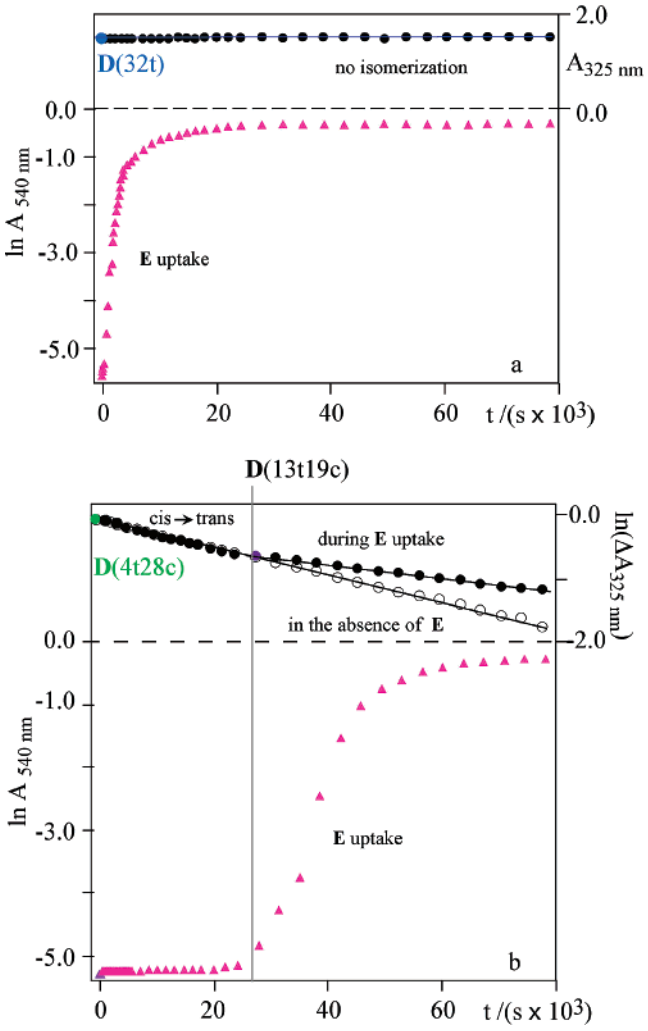


Figure 3. Kinetics of eosin uptake (▲, A_{540} nm) and cis → trans isomerization (●, A_{325nm}) for a dichloromethane solution of (a) **D**(32t) and (b) **D**(4t28c) in contact with a water solution of **E** at pH 10 at 298 K. For comparison purposes, cis → trans isomerization (○, panel b, A_{325nm}) for a dichloromethane solution of **D**(4t28c) not in contact with the water phase is reported. For more details, see the experimental section.

To investigate the kinetics of eosin extraction as a function of azobenzene isomerization state, dichloromethane solutions of **D**(32t) and **D**(4t28c) were brought into contact with a water solution of **E** at pH 10 (for more details, see experimental section), at variance with previously described experiments in which vigorous shaking was employed to accelerate the extraction process. The water solution was buffered at pH 10 and not 7, as in the previous experiments, to slow down the extraction rate constant and make easier the detection. As reported in Figure 3, substantial differences can be observed: in the case of **D**(32t), eosin uptake (pink triangles in Figure 3a) starts as soon as the two solutions are in contact, whereas for **D**(4t28c) a delay is observed (pink triangles in Figure 3b) and no eosin extraction takes place until a significant fraction of azobenzene units is converted from cis to trans, i.e., when the **D**(13t19c) species is formed. Furthermore, eosin extraction is faster in the first case. The rate constant for the thermal cis → trans isomerization, monitored by absorbance changes at 325 nm, is the same, starting with a dichloromethane solution of **D**(4t28c) alone (empty circles in Figure 3b) or in contact with a water solution of **E** (full circles in Figure 3b) until no extraction of **E**

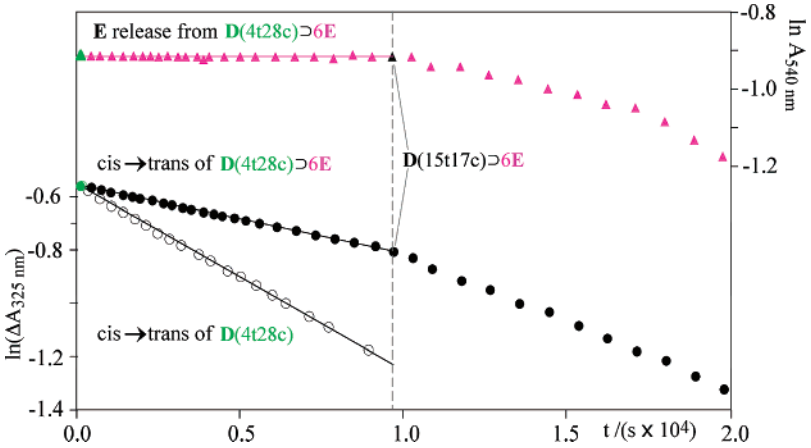


Figure 4. Kinetics of eosin release (▲, A_{540} nm) and cis → trans isomerization (●, A_{325nm}) for a 1×10^{-6} M solution of **D**(4t28c)⊃6**E** in dichloromethane solution at 313 K. For comparison purposes, the kinetics of the cis → trans isomerization for **D**(4t28c) is also shown (○, A_{325} nm).

takes place, whereas it is significantly slowed down as soon as eosin molecules are encapsulated in the dendrimers. Such a decrease of the cis → trans thermal isomerization rate is likely related to steric effects and suggests that the presence of the guest molecules modifies the dendrimer structure (*vide infra*).

Eosin Release. After extraction, the dichloromethane phase containing **D**(32t)⊃8**E** or **D**(4t28c)⊃6**E** was separated from the aqueous phase and experiments were performed on the dichloromethane phase. Upon irradiation at 298 K with 365 nm light, **D**(32t)⊃8**E** is converted to a photostable species, **D**(15t17c)⊃6**E** (Scheme 2, dashed black line in Figure 2). This process requires photoisomerization of about half of the trans azobenzene units as well as the release of 2 eosin molecules that precipitate. The initial quantum yield of the photoisomerization reaction (Φ = 0.15, Figure 2 inset, Table) is not much different, considering the experimental errors, from that found for **D**(32t). The photostationary state reached for **D**(32t) and **D**(32t)⊃8**E** upon irradiation at 365 nm is substantially different (Scheme 2), and this is likely due to steric hindrance imposed by the hosted eosin molecules that hamper the trans → cis isomerization. Note that such a different behavior cannot be due to the light absorbed by **E**, which is negligible at 365 nm, as shown by the fact that no spectral change has been observed upon irradiation of **D**(4t28c)⊃6**E** under the same experimental conditions.

The dichloromethane solution of **D**(4t28c)⊃6**E** was heated at 313 K and the absorbance changes at 325 nm, measuring the relative concentration of trans and cis azobenzene units (black circles in Figure 4), and 540 nm, measuring the hosted eosin molecules (pink triangles in Figure 4), were monitored. The cis → trans isomerization within the **D**(4t28c)⊃6**E** species occurs at the beginning (up to about 1×10^4 s) by a first-order process ($k = 2.7 \times 10^{-5}$ s^{-1}) without any loss of **E**, leading to the same **D**(15t17c)⊃6**E** species obtained from light irradiation of **D**(32t)⊃8**E**. Apparently, eosin release is substantially prevented until about half of the peripheral azobenzene units remain in the cis form. Note also that, as evident from Figure 4 (open vs full circles), the rate constant for the isomerization process is much smaller than that found for **D**(4t28c), 7.0×10^{-5} s^{-1} (Table). In a successive step, **E** begins to be released from **D**(15t17c)⊃6**E** with a concurrent increase in the rate of the cis → trans isomerization process (Figure 4). After about 2×10^4 s, the average composition corresponds to **D**(18t14c)⊃4**E** and

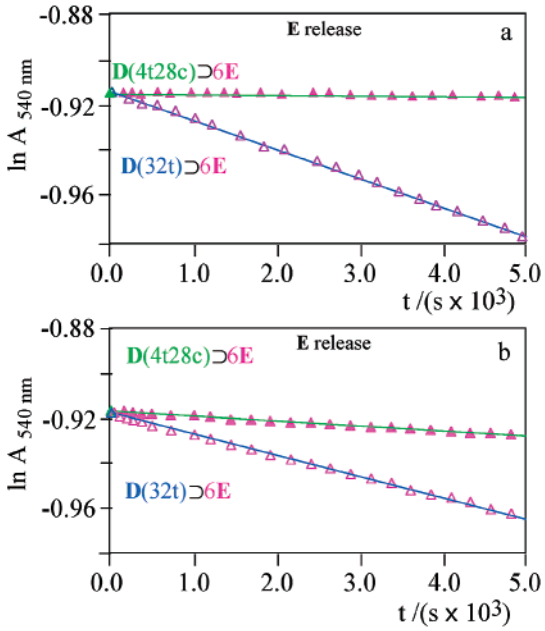
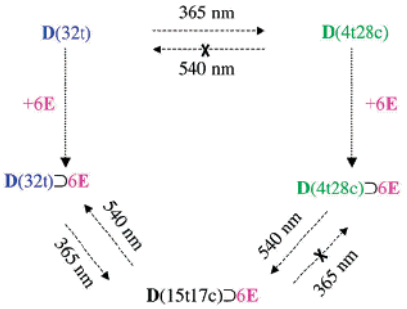


Figure 5. Kinetics of eosin release: (a) in dichloromethane solution at 313 K, from **D**(4t28c)⊃6**E** (▲) and **D**(32t)⊃6**E** (○); (b) in dichloromethane solution in contact with water at 298 K, from **D**(32t)⊃6**E** (△) and **D**(4t28c)⊃6**E** (△). Eosin release is measured in both cases from the decrease of absorbance at 540 nm in dichloromethane.

on a very long time scale eosin release and cis → trans isomerization become strongly entangled and **D**(32t) can be recovered.

In order to understand whether the isomeric form of the azobenzene units is related to the release of the guest, we have also compared the rate of eosin release in dichloromethane solution at 298 K from a **D**(32t)⊃6**E** species (open circles in Figure 5a) and a **D**(4t28c)⊃6**E** (full circles in Figure 5a), both of them prepared by extraction of **E** from an aqueous solution at pH 7 (see experimental section). We have found that **E** is released from the beginning following a first-order process with rate constant 1×10^{-5} s^{-1}. In an additional experiment, we have compared the rate of eosin release at 298 K from dichloromethane solutions of **D**(32t)⊃6**E** and **D**(4t28c)⊃6**E** in contact with an aqueous phase (see experimental section) at pH 10. As shown in Figure 5b, eosin release occurs by a first-order process that is about four times faster in the case of **D**(32t)⊃6**E** ($k = 1.33 \times 10^{-5}$ s^{-1} vs 3.09×10^{-6} s^{-1}). The results shown

Scheme 3. Photochemical (Dashed Arrow) Interconversion Processes upon Excitation of the Dendrimer Host (365 nm) or the Eosin Guest (540 nm) and Thermal (Solid Arrow) Processes



in Figure 5 demonstrate that the presence of cis azobenzene units in the periphery of the dendrimer does reduce the rate of eosin release, as expected because of the larger steric hindrance caused by the cis compared with the trans isomer. Such a result is relevant to the problem of photocontrolled drug delivery.

Photochemical Interconversion Processes. As shown in Figure 2, **E** exhibits an intense absorption band with λ_{max} = 540 nm, well separated from the dendrimer absorption bands. We have found that excitation of **E** at 540 nm sensitizes the cis → trans but not the trans → cis isomerization.[18] Indeed, irradiation of **D**(4t28c)⊃6**E** in dichloromethane solution with 540 nm light leads to **D**(32t)⊃6**E** (Scheme 3). The sensitized cis → trans isomerization quantum yield is strongly dependent on dioxygen concentration (Table 1), indicating that the sensitized mechanism involves triplet excited states, as previously observed for other acceptors.[19]

As illustrated in Scheme 3, light excitation at 365 nm in the absence of **E** leads to a photostationary state rich in the cis isomer, whereas in the presence of **E** irradiation with 540 nm light leads to the all trans form. It follows that, in principle, this photocontrollable dendritic system may be used to carry **E** molecules from a water solution to another one, across a dichloromethane phase.

Conclusions

A fourth generation dendrimer (**D**) of the poly(propylene amine) family functionalized with 32 naphthyl and 32 azobenzene units can host eosin molecules in dichloromethane solution as a function of the isomerization state of the peripheral azobenzene units. **D**(32t) can be converted to **D**(4t28c) upon irradiation with 365 nm light. The hosting capacity of the two isomeric forms of the dendrimer is not much different: **D**(32t)⊃8**E** and **D**(4t28c)⊃6**E** species are formed. Trans → cis isomerization quantum yield is not significantly affected by eosin encapsulation, but cis → trans thermal reaction is noticeably slowed down by the presence of **E** in the dendritic structure and the kinetics of eosin uptake or release is much faster in the case of the all trans dendrimer. Therefore, the isomerization state of the peripheral azobenzene units controls, to some degree, the *permeability* of the dendrimer cavities to **E** and, viceversa, eosin molecules hosted in the dendrimer cavities affect the velocity of thermal isomerization process of its peripheral azobenzene units. The results obtained suggest that a more extensive study of dendrimers with isomerizable azobenezene units in the periphery may lead to photocontrollable membranes and drug delivery systems.

Experimental Section

Extraction Experiments. To check the maximum hosting ability of the dendrimer, 5 mL of the dichloromethane solution of dendrimer **D** (1×10^{-6} M) and 1 mL of **E** (5×10^{-4} M) in water buffered (pH = 7 or 10) solution are mixed together and shaken vigorously. To prepare species with lower eosin content, e.g., **D**(32t)⊃6**E**, 5 mL of **D** (1×10^{-6} M) and 5 mL of **E** (6×10^{-6} M) in water buffered solution were mixed and shaken.

Kinetic experiments on eosin encapsulation has been performed in a quartz cell of 1.0 cm path length containing 2.5 mL of dendrimer (1×10^{-6} M) and 0.5 mL of **E** (5×10^{-4} M) in water at pH = 10. Kinetic experiments on eosin release has been performed in a quartz cell of 1.0 cm path length containing 2.5 mL of dendrimer (1×10^{-6} M) in the presence or absence of 0.5 mL of water at pH = 10.

Photophysical Experiments. The experiments were carried out in air-equilibrated dichloromethane or water solution at 298 K. UV−vis absorption spectra were recorded with a Perkin-Elmer λ40 spectrophotometer, using quartz cells with path length of 1.0 cm. Fluorescence spectra were obtained with a Perkin-Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube. The estimated experimental errors are: 2 nm on the band maximum, 5% on the molar absorption coefficient, 10% on the fluorescence quantum yield.

Photochemical Experiments. Photochemical experiments were performed by a medium-pressure mercury lamp. An interference filter (Oriel) was used to select a narrow spectral range with λ_{max} = 313 nm. The irradiated solution (2.5 mL, 1×10^{-6} M) was contained in a spectrophotometric cell. The intensity of the incident light was measured by the ferrioxalate,[20] or Aberchrome 540 actinometer.[21] The photoisomerisation quantum yield ($\Phi_{c\to t}$ or $\Phi_{t\to c}$) was calculated by extrapolation to zero time of the apparent quantum yield values obtained for short irradiation periods. The relative amounts of cis and trans isomers during photochemical experiments has been calculated on the basis of the previously reported results.[14]

The rate of thermal cis → trans reaction has been calculated by plotting changes of absorbance, namely $\Delta A = A_\infty - A_t$ (where A_∞ is the absorbance at the end of the reaction, i.e., for the all trans species), versus time and by determining the slope of the corresponding straight line.

The estimated experimental errors are: 10% on the photoreaction quantum yield, 5% on the composition of the photostationary state.

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(18) In a prevoious paper,[13a] a different solvent was employed and direct absorbance of azobenzene at 540 nm was not negligible, at variance with the present case, because of the very low number of **E** encapsulated into the dendrimer.

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