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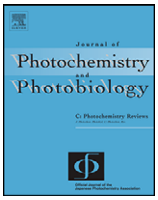

Review

Stimuli-responsive dendritic structures: The case of light-driven azobenzene-containing dendrimers and dendrons

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ABSTRACT

Azobenzene derivatives are very attractive for light-driven experiments, due to their easy *trans*/*cis* isomerization, which is one of the cleanest photochemical processes known to date. Azobenzenes have been linked in various places to the structure of dendrimers and dendrons. The azobenzene groups can constitute the terminal functions of the dendrimers (or dendrons); a single azobenzene can be located at the core of a dendron or a dendrimer; finally, several azobenzene groups can be incorporated at one or several layers of dendrimers or dendrons. The first part of this review is an exhaustive compilation of all these types of azobenzene-containing dendritic structures.

Most dendritic macromolecules possessing azobenzenes in their structure were synthesized with the aim of studying their photo-responsive properties. The influence of the placement of azobenzene groups on the isomerization properties was determined in solution: generally, burying the azobenzene inside the structure induces reluctance to isomerization, especially when the generation increases, but has a larger influence on the size modification. Several dendritic azobenzenes were also studied as thin films, in particular monolayer Langmuir and Langmuir–Blodgett films. Photo-induced alignment was observed for thin films obtained by spin-coating, others were used for holographic experiments. Self-arrangements of photo-responsive dendrimers have resulted in liquid crystalline organizations, vesicles, nano-fibers, and organogels. In addition to these particular properties, some more practical uses were reported such as for molecular imprinting, to trap/release guest molecules, or for drug delivery by cleavage of the N=N bond.

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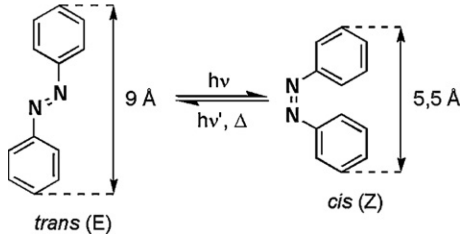
Rodolphe Deloncle received his PhD from Université Paul Sabatier of Toulouse under the direction of Dr Anne-Marie Caminade in 2007. After his thesis concerning the synthesis of azobenzene-containing phosphorus dendrimers for photo-adaptive nanomaterials, he has obtained two successive postdoctoral fellowships to work on nanostructured materials for optical devices. His research interest is focused on nanoparticles, functionalized colloids and hybrids materials mainly elaborated by wet chemical processes.

Anne-Marie Caminade is First Class Director of Researches at the CNRS since 2004 and head of the research group “Dendrimers and Heterochemistry” in Toulouse. After two Ph.D.s (1984 and 1988 in Toulouse), and two Post-docs (Institut Français du Pétrole in Paris and as an A. Von Humboldt fellow in M. Veith’s group, Saarbrücken, Germany), she entered the CNRs in the group of J.-P. Majoral in 1985. Her research interest is on Main group elements. She developed several aspects of the chemistry of phosphorus, including low coordinated compounds, coordination of transition metals, and synthesis of macrocycles. Her current research interest is on the synthesis, reactivity, and study of properties and applications of dendrimers and dendritic molecules, in particular in the fields of catalysis, nanomaterials and biology. She is the co-author of 300 publications (including 215 about dendrimers) and 26 patents, and received in 2006 the Organic Chemistry Prize of the French Chemical Society.

1. Introduction

Dendrimers [1–4] constitute one of the most flourishing and attractive field of research in chemistry, with about 17 000 papers published to date. Indeed, these macromolecules constituted of branched monomers associated around a central core by an iterative process can be customized at will at each level of their structure (core, branches, surface), resulting in well defined and highly functionalized three-dimensional architectures. Their size (a few nanometers) is determined by the number of generations (each iterative cycle creates a new generation). Depending on the type of functional groups of dendrimers, numerous properties developed for potential applications have already been proposed concerning in particular catalysis, materials, and biology. Among these properties, those concerning the controlled response to light have large potential of applications. Indeed, the noncontact manipulation inducing small changes at the molecular level can cause important modifications at the macroscopic level. Several types of dendrimers were synthesized with the aim of investigating the influence of a highly organized or congested environment on the properties of the stimuli-responsive group(s). Several reviews have gathered the first examples of photo-responsive dendrimers [5–7], including several examples of azobenzene-containing dendrimers. Another review concerned exclusively azobenzene dendrimers [8], but it was focused on the work of a single research group. Furthermore, numerous papers have appeared since the publication of all these reviews. In this new review, we will give an exhaustive view of the literature about azobenzene-containing dendrimers and dendrons up to early 2009 (dendrons are dendritic wedges having one functional group at the level of the core, generally different from the terminal groups). Polymers, including hyperbranched polymers and dendronized polymers, having azobenzene in their structure were previously reviewed [9,10] and will not be considered.

Azobenzenes are very attractive to study light-driven experiments, since their photo-isomerization (*trans* (E) → *cis* (Z)) is one of the cleanest photochemical processes known to date. This process is fully reversible, thus azobenzenes can undergo innumerable reaction cycles [11]. The *trans* form is generally the most stable ($\Delta E \approx 50$ kJ/mol). Azobenzenes have an intense π–π^* band in the UV region, and a weak n–π^* band in the visible region. Isomerization induces changes in the intensity of these bands, and can be monitored by UV–visible spectroscopy. Furthermore, this process induces very large structural changes in conformation and size, and the dipole moment increases from 0 for *trans*-azobenzene to 3.0 D in *cis*-azobenzene [12] (Scheme 1). These particular properties can be useful to probe conformational dynamics of macromolecules, as well as for designing dendrimers responsive to external stimuli.



Scheme 1. Structural changes induced by isomerization of azobenzene.

Fig. 1 displays the various types of location of azobenzene groups in dendrimers and dendrons. The azobenzene groups can constitute the terminal functions of the dendrimers (or dendrons); this is the first example ever described [13], and the most frequent case. A single azobenzene can be located at the core of a dendron or a dendrimer; the greatest geometrical effects are expected for the isomerization of such dendrimers. Finally, several azobenzene groups can be incorporated at one or several layers of dendrimers or dendrons. An exhaustive compilation of all these types of dendritic structures will be given in the first part of this review. The photoisomerization properties of most of these compounds were studied, and in several cases some uses in the fields of materials and biology were proposed. These properties and uses will be emphasized in several paragraphs in the second part of this review.

2. The various types of dendritic macromolecules incorporating azobenzene derivatives in their structure

In this part of the review, the various types of dendrimers and dendrons incorporating azobenzene groups in their structure will be ordered depending on their location. Linking azobenzenes to dendrimers necessitates first to have chemically functionalized azobenzenes; if they are used as terminal groups of dendrimers, or as core of dendrons, a single reactive function is needed; if they are used as core of dendrimers, azobenzenes must have two identical functional groups; finally, if they are used as branches of dendrimers or dendrons, azobenzenes must have two different functional groups, allowing the growing of the structure.

2.1. Azobenzenes as terminal groups of dendrimers and dendrons

The very first example of dendrimers functionalized by azobenzene groups was described by Vögtle and co-workers [13]. It is a sophisticated compound of type **A** in Fig. 1; only half of the terminal groups are azobenzenes, very precisely linked to each terminal branching point (Fig. 2). The interior of compound **1** is composed of aryl amines, but most of the examples following this first one were obtained from poly(propyleneimine) (PPI) dendrimers built from either ethylenediamine [14] or 1,4-diaminobutane [15,16] as core.

Contrarily to the first example, all the terminal groups are generally constituted of azobenzenes (compounds of type **B** in Fig. 1). They can be linked to the dendrimer via an amide linkage through a para (**2a-G$_1$**–**2a-G$_4$**) or meta (**2b-G$_1$**–**2b-G$_4$**) position of one aryl group [17], or through a sulfonate linkage (**3c-G$_1$**–**3c-G$_5$**) [18], or through an amide linked to a long alkyl chain and ended by another alkyl group (**3d-G$_1$**–**3d-G$_5$**) [19] or a cyano group (**3e-G$_3$**) [20] (Fig. 3). In these later cases, random substitutions (type **D** compounds in Fig. 1) were also carried out either with palmitoyl- and azobenzene-containing alkyl chains in a 1:1 ratio (statistically 32