

Photochromism of dihydroazulene-based polymeric thin films



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ABSTRACT

We report on the preparation of polymeric thin films doped with six dihydroazulene derivatives whose photochromic properties were previously screened in organic solution studies. Spectroscopic investigations into the photochromic behavior of the polymeric matrices have given important insights on the stability and the photophysical properties of the photoswitches impregnated into polymers.

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1. Introduction

The field of light-responsive photochromic materials has been widely investigated in the past few decades for the design of advanced materials with a broad variety of applications, from the well-known ophthalmic lenses or photochromic eye-glasses, to cosmetics or novelty products, which all take advantage of the color change induced by light exposure [1]. Indeed, the most used photochromes are colorless/pale yellow in their stable form and turn intensely colored upon light irradiation. In some cases (such as for T-type switches), a thermally driven back reaction (TBR) reverts the colored species to the colorless low energy parent molecule; in others (P-type), the original form is recovered only by irradiation with light at a different wavelength. Among the different classes of

molecular switches, dithienylethenes, spiropyrans and azobenzenes are considered the most promising for organic photochromic materials, and the properties and applications achieved in the past decades have been reviewed several times [2].

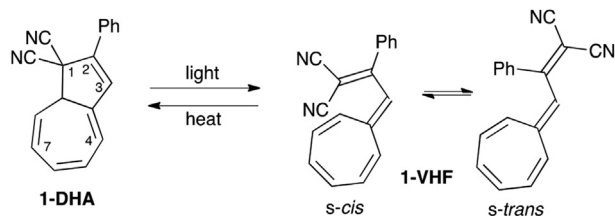
In the context of T-type molecular switches, the dihydroazulene/vinylheptafulvene (DHA/VHF) pair, discovered by J. Daub in 1984 [3], is a less explored class of photo/thermochromes (Scheme 1). The effect on the photophysical properties of the system by functionalization at positions 2, 3, 4 and 7 of the DHA scaffold has been broadly investigated in Nielsen's group since 2007, in solution studies [4].

Single-molecule break-junction studies involving these DHA derivatives have been performed [5] and, more recently, photo-responsive liquid crystalline materials based on neat photoactive DHA derivatives and in a nematic host have been reported for the first time [6]. Given the energy conversion involved during the forward and back isomerizations, the photochromism of this class of molecules has been lately probed for energy storage applications [7]. One challenge in this regard is to achieve both sufficiently high energy storage capacity and control of the energy-releasing back reaction. By various functionalizations, we have so far found that the energy storage capacity (in MJ kg⁻¹) can be increased up to

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Scheme 1. The DHA/VHF T-type photoswitch with the numbering of the core structure.

fourfold relative to the **1-DHA/1-VHF** couple, but these improvements were unfortunately accompanied by undesirable sigma-tropic rearrangements and degradation upon irradiation [7].

Detailed studies on the photochromic behavior of this class of molecules in solid matrices, more suitable for real applications, are still lacking. It was thus decided to investigate the photochemical properties of some carefully selected DHA molecules embedded into polymers. This study provides useful insights for the design of new DHA derivatives valid for incorporation into optically switchable materials. Indeed, in the development of fast responsive materials, fast switching may be desirable for some applications, while for other applications (i.e. solar energy storage) slow switching is preferred. In relation to the latter challenge, recently we reported a series of singly substituted monocyano-dihydroazulenes, prepared in one-step from the parent dihydroazulene (DHA) **1** or the 2,3-diphenyldihydroazulene **2** (Fig. 1), showing that substitution of one nitrile at C-1 of the original scaffold with another group has dramatic consequences on the photochemical properties of the molecules in solution, expanding the lifetimes of the VHF form from milliseconds to days [8]. Conveniently, this change also resulted in a doubling of the energy storage capacity (value of ca. 0.2 MJ kg^{-1}) relative to **1-DHA/1-VHF** (ca. 0.1 MJ kg^{-1}), but reversible “slow” switching without degradation is still a necessary issue to be overcome for such structural modifications. In any case, the energy storage capacities of these simple derivatives are similar to those of *cis/trans* azobenzenes [9], but one particular advantage of the DHA/VHF system is the T-type photochromism, which in azobenzenes is not always observed since the back isomerization can be photoinduced as well. On the other hand, a photoswitch with high potential for energy storage is the norbornadiene/quadracyclane couple, which in fact has had the storage calculated at ca. 0.7 MJ kg^{-1} . While the quantum yield of photoisomerization of **1-DHA** is 55% [10], it is, however, only 9% for norbornadiene (characterized by undesirable, poor overlap with the solar

spectrum) [11].

The selection of dihydroazulenes **1–6**, whose syntheses have been already reported elsewhere [8,12–15], was made on the basis of structural features. Compounds **1–2** are considered reference compounds, that is, parent systems on which the scaffold is based, and compound **3** is the first derivative containing two DHA units which influence the photoactivity of one another (exhibiting stepwise ring openings in solution) [14]. Compounds **4–6** were selected for the short half-lives exhibited by the corresponding VHFs in solution, which was achieved either by locking the VHF in its reactive *s-cis* conformation by an ethylene bridge (**4**) [15] or by replacement of one cyano group with a primary amide (**5**) [8] or with a benzothiazole ring (**6**) [8].

We report herein a) the preparation of photoresponsive polymeric films through the doping of DHA derivatives into the matrix, and b) the photophysical characterization of the obtained materials. PMMA was selected as matrix because it is a readily available, cheap and inert polymer in which organic photochromes (e.g. spiropyrans, chromenes, etc.) have shown good solubility and maintain photochromic properties, despite a drastic reduction in the inter-conversion rate [16]. Polycarbonate (PC) was also tested as matrix, since it is a standard polymeric material used in photochrome-based applications such as ophthalmics [2].

2. Materials and methods

2.1. Materials

Poly(methylmethacrylate) (PMMA, molecular weight of $120,000 \text{ g/mol}$, $T_g = 105^\circ\text{C}$ [17]), poly(bisphenol A carbonate) (PC, $T_g = 146^\circ\text{C}$ [18]) were purchased from Sigma-Aldrich. The syntheses of the DHA dyes were described elsewhere [8,12–15]. The solvents (CH_2Cl_2 and CHCl_3) for the film preparation were provided by Scharlab and were used as received.

2.2. Methods

2.2.1. Preparation of the photochromic polymer films

To prevent photodegradation of the photochromes, the film preparations were carried out in the dark. 115–120 mg of PMMA (or PC) and 0.5–5 mg (specified in the text) of DHA (0.4–4 wt%) photochromic dye were dissolved in 5 mL of degassed CHCl_3 or CH_2Cl_2 . The solution was stirred until all PMMA was completely dissolved. Once a homogeneous solution was obtained, the liquid was transferred on a glass Petri plate (6 cm in diameter) and the solvent was evaporated in the dark at room temperature over 12 h,

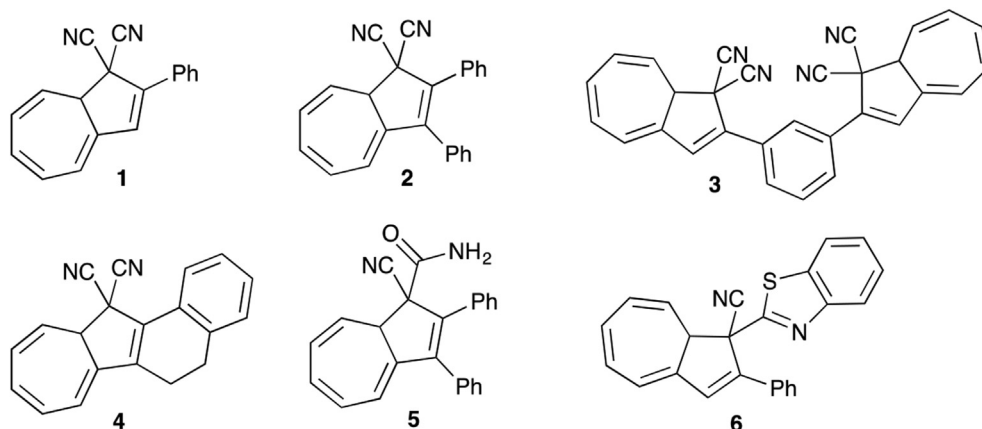


Fig. 1. The DHAs **1–6** investigated in PMMA.

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