The interplay of soft-hard substituents in photochromic diarylethenes

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ABSTRACT

A series of diarylethenes with substituents of different size and chemical nature was synthesised showing that beside some intermolecular interactions involving the central diarylethene core, lateral groups clearly play a key role in the crystal packing arrangements. These structural features were further analyzed in relation to the thermal data obtained by differential scanning calorimetry (DSC) and monitored using FT-IR spectroscopy, thus providing a rationalization of the observed thermal transitions processes. The role of van der Waals interactions is crucial in driving crystal packing formation towards loosely packed arrangements characterized by large hydrophobic contact areas. Interestingly, some functional substituents favour an amorphous state after thermal treatment, a peculiar feature that can be exploited to design uniform photochromic layers.

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1. Introduction

Progress in the development of photochromic switches requires a detailed characterization of the behaviour of photoactive compounds in the solid state. Indeed, for some applications, completely amorphous thin films are needed, whereas for others, fully crystalline materials are required, possibly in the form of single crystals. For example, photochromic materials showing remarkable optical contrast [1,2] in specific spectral regions are attractive as active layers in photolithography, both in the form of molecules dispersed within a polymer matrix [3,4] and pure as a thin amorphous evaporated layer [5]. In the latter, the quality of the optical layer is the key to the success of the lithography process, as aggregation and crystalline domains can cause light scattering. For application of photochromic switches where crystalline materials are preferred, the long-range molecular packing order in the crystalline phase and the limited free volume for the photoconversion process may inhibit photochromic reactions. Interestingly, Irie and co-workers successfully developed thermally irreversible and fatigue-resistant photochromic crystals of furylfulgide [6] and diarylethenes [7–9].

As a result of the relative orientation of the molecules in the lattice, photochromic crystals may show specific anisotropic physical properties such as, for instance, dichroism [10,11]. Moreover, the cooperative structural changes of diarylethenes molecules that are regularly packed in a crystal may determine macroscopic mechanical modifications of the single crystal upon irradiation. In selected photochromic crystals, a change in surface morphology [12] or a dramatic shape change occur upon light irradiation [7,13–15]. Based on this morphological behaviour, a photodriven nano-scale actuator, consisting in a rod-like crystal that bends towards the direction of the incident light, has been developed [16].

Beside twisted and bent crystals that are known to be present in nature [17], crystals that can be morphologically modified using light have been obtained [18] by exploiting the chiral properties of photoactive molecules [19–22]. These light-induced changes are caused by the shrinkage of the irradiated portion of the crystal [23] and show crystal thickness dependence [24]. This behaviour is determined by a photoisomerization gradient inside the crystal; in fact, the light-induced conversion of the photochromic layer in the solid state is not uniform throughout the sample, and depends on both the thickness of the material and the illumination source [25]. Photochromic co-crystals [26–28] have also been studied for the development of hybridized structures of novel photonic devices. However, not only are multi-component crystals difficult to obtain, but whenever they form, energy transfer from one component to the other may prevent cyclization.

Despite the wealth of solid state diarylethene optical and photomechanical switches described to date, a large scale rational

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approach to the design of diarylethene molecules that takes into account the intermolecular forces governing the molecular packing in the lattice is still missing. Indeed, the effect of intermolecular interactions on the crystal packing has been stimulating an interesting and still on-going debate in the field of photochromic switches [29–35].

Here we show how the subtle interplay of substituents of different size and chemical nature affects the packing, the morphology and the aggregation of active diarylethenes in the solid state. Specifically, we have designed a series of molecules that share the same 1,2-bis-(2-methyl-5-phenyl-3-thienyl)perfluoro-cyclopentene central unit, but with their phenyls differently substituted in the *para*-position (Fig. 1). We show that, beside some intermolecular interactions involving the central part of the diarylethenes, lateral groups play a key role in guiding and stabilizing the crystal packing arrangements. We relate the nature and the extent of the observed intermolecular interactions within each crystal to the Differential Scanning Calorimetry (DSC) profile of the corresponding molecule, thus providing a rationalization of the progression of the thermal transitions in the studied materials. Overall, extended Van der Waals interactions guide nucleation and crystal growth both from solution and from the melt, as shown by the evolution of IR spectra with time.

2. Materials and methods

All the photochromic compounds **DTE-1** to **DTE-7** were synthesized according to the procedures reported in the Supplementary material.

Crystals obtained from solution: crystals of **DTE-1** to **DTE-7** were obtained by slow solvent evaporation or by vapour diffusion, as described in detail in the Supplementary material.

Melt derived crystals: **DTE-7** powder was heated up to 130 °C at a 10 °C/min rate, kept for 10 min at this temperature to ensure the complete melting of the powder, fast cooled to 65 °C and then maintained for three hours at this temperature to perform isothermal crystallization. Then, the sample was slowly cooled down to room temperature.

^{1}H NMR spectra were collected using a Bruker ARX 400. *Mass spectroscopy* was carried out using a Bruker Esquire 3000 plus.

UV–vis absorption spectra UV–vis spectra were recorded with a Varian Cary 5000 spectrophotometer from dilute hexane solution ($<10^{-5}$ M) and from thin film of the pure compound deposited onto quartz. The spectrophotometer was equipped with the integrating sphere (DRA2500) to measure the diffuse transmittance in the case of thin films. Starting from the open form, the photochromic reaction was triggered by illumination of the solution or the thin film using quasi-monochromatic UV light with wavelength corresponding to the absorption maximum of the open form, until the photostationary state (PSS) was reached.

FTIR spectra were recorded using a Nicolet NEXUS FTIR interferometer (DTGS detector). In order to monitor the melting and isothermal melt crystallization process of **DTE-7**, the compound was dissolved in diethyl ether and deposited as a thin film on a ZnSe substrate. The substrate was then set into a variable temperature cell Linkam (THMS 600) and positioned under the objective of the IR-microscope stage. Two different thermal programs were set:

i) the specimen was heated from room temperature up to 150 °C in an argon atmosphere at a 10 °C/min heating rate. IR spectra were collected (256 scans, resolution 4 cm^{-1}) at different temperatures.

ii) the specimen was heated from room temperature up to 150 °C in an argon atmosphere with a 20 °C/min heating rate. In order to monitor the isothermal crystallization process the specimen was cooled down to the desired crystallization temperature. The temperature was kept constant following the evolution of the crystallization process. IR spectra were collected every 100 s with 32 scans and 4 cm^{-1} resolution.

A baseline correction was applied to all the IR spectra. In general, the area of the bands was calculated by integrating each spectrum in the desired region (keeping the spectral boundaries constant). In order to compare the different areas of the spectra during the crystallization process, normalization to the peak area at 1600 cm^{-1} was applied. All these operations were performed using OMNIC 8.0 (Thermo Electron Corporation). The Avrami model [36–38] was used to fit the FTIR data from the isothermal crystallization process. A guess of the induction time was made from the change in the position of the CH stretching peak. The initial values of A_0 and A_{max} were determined as the mean of 10 points in the minimum and maximum of the normalized FTIR area at the beginning and at the end of the crystallization process, respectively. A_0, A_{max}, k_{app}, and n were then determined by the best fit with a least-squared method as a function of induction time, which was varied in the proximity of the guess value and used as a fixed parameter in the fitting procedure. The best induction time was then obtained as the one minimizing the fitting residuals.
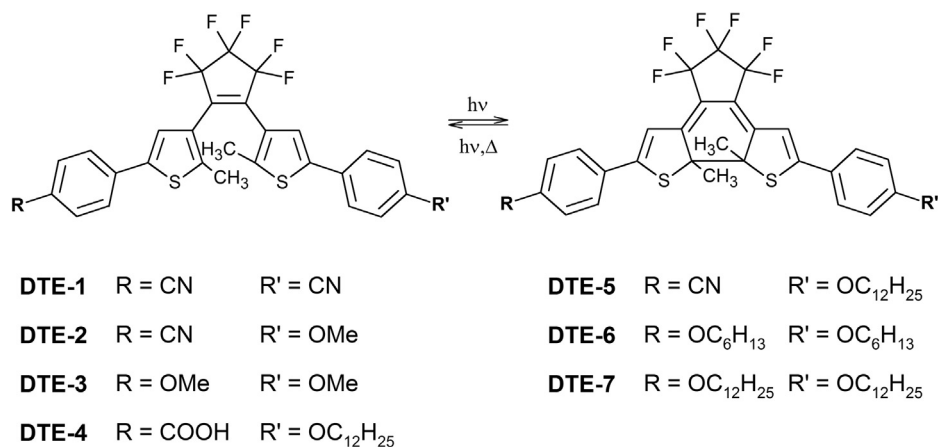

DTE-1 R = CN R' = CN
DTE-2 R = CN R' = OMe
DTE-3 R = OMe R' = OMe
DTE-4 R = COOH R' = OC$_{12}$H$_{25}$

DTE-5 R = CN R' = OC$_{12}$H$_{25}$
DTE-6 R = OC$_6$H$_{13}$ R' = OC$_6$H$_{13}$
DTE-7 R = OC$_{12}$H$_{25}$ R' = OC$_{12}$H$_{25}$

Fig. 1. Photochromic reaction in diarylethenes and chemical structure of the molecules under investigation.