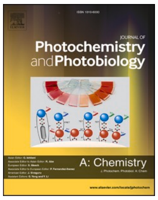
Journal of Photochemistry & Photobiology, A: Chemistry 407 (2021) 113033

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology, A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Stereoregular hybrid azobenzene-cyclosiloxanes with photoinduced reversible solid to liquid transition properties

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ARTICLE INFO

Keywords:
Azobenzene
Stereoregular
Cyclosiloxane
Photoliquefaction
Trans-cis isomerization

ABSTRACT

A new type of stereoregular hybrid azobenzene-organocyclosiloxane discrete molecular structures with photoactive azobenzene groups unidirectionally connected to rigid cyclosiloxane frames through alkyl spacers of different lengths were developed for the first time.

The kinetics and thermodynamics of nondegradative reversible trans-cis photoisomerization processes of the synthesized azobenzene-cyclosiloxane conjugates investigated using UV/Vis spectroscopy, DSC and XRD methods showed dependency on their molecular structures.

It has been observed that room temperature UV (365 nm) irradiation of the synthesized hybrids leads to photoliquefaction effect consisting of a photoinduced phase transition of crystal solids into liquids. The photoliquefaction process was observed and confirmed with DSC, XRD and POM methods. Backward solidification process was generated with visible light and by heating.

The tetra-azobenzene substituted cyclosiloxane single molecule compounds described in this work can be regarded as promising candidates for the development of new hybrid smart materials with many potential high-tech applications.

1. Introduction

Photoresponsive compounds with azobenzene units capable of reversible trans–cis photoisomerization transitions leading to changes in molecular configurations have been a subject of increased interest for a long time because of potential applications of such substances in a vast array of high-tech applications, such as optical and electronic switching, information storage, and use in construction of non-linear optical and photoactuator devices [1].

Some azobenzene-containing compounds are known to have unique transition properties from solid to liquid state when trans-cis photoisomerization occurs. Though the phenomenon of athermal photoliquefaction has known for quite some time, it has been somewhat neglected for several decades [2] until recently, when an interest towards new azobenzene developed materials capable of photoinduced reversible solid-to-liquid phase transitions due to their many potential high-tech applications has grown significantly and a number of investigations dedicated to azobenzene based healable coatings, photocontrolled switchable adhesives, lithography photoresists [2], solar thermal fuels [3] have been published.

The photoliquefaction effect was observed both for azobenzene polymers and for single molecule azo-compounds. It was estimated that for polymers with side-chain azobenzene moieties reversible solid to liquid phase transformations [4] proceed due to changes in polymers glass transition temperatures when their azo- groups undergo trans-cis photoisomerization transition. At the same timefor highly ordered crystalline solid single molecule azo-compounds the photoliquefaction process is based on the crystal-to-melt first order phase transition but due to the insufficient molecular free volume bulk photoisomerization in this type of compoundsis often suppressed and therefore that only a limited number of azo-functionalized single molecule structures have been reported to be capable of undergoing a photoliquefaction process under certain conditions [5,6].

One example of the room temperature single molecule photoliquefaction effect was observed for multi-azobenzene functionalized sugar alcohol scaffolds [5]. While the photoliquefaction effect was

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https://doi.org/10.1016/j.jphotochem.2020.113033
Received 13 August 2020; Received in revised form 10 October 2020; Accepted 5 November 2020