



Vibrational spectroscopic characterization of cyclic and acyclic molecular rotors with 1,4-diethynylphenylene- d_4 rotators

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ARTICLE INFO

Article history:

Received 5 September 2017

Received in revised form 21 November 2017

Accepted 24 November 2017

Available online 26 November 2017

Keywords:

Molecular rotors

Vibrational spectroscopy

Temperature measurements

ABSTRACT

The synthesis and characterization of acyclic and cyclic molecular rotors with 1,4-diethynylphenylene- d_4 rotators are described. The ATR-FTIR and Raman spectra of acyclic rotor **3** and cyclic rotor **5E** were measured and interpreted. A feature of ATR-FTIR spectrum of rotor **5E** is a strong two-component band around 1730 cm^{-1} attributed to symmetric and asymmetric stretching vibration of the carbonyl group, while this is not observed in rotor **3**. Raman investigation in the wide temperature range of 350 - 10 K was carried out. The splitting of Raman bands in the region of stretching vibration of CC double and triple bonds at 170 and 260 K for rotor **5E** is observed. The splitting of bands is due to changes in molecular structure.

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1. Introduction

In recent years the subject of molecular machines has frequently been discussed by nanotechnologists resulting in a wide spectrum of different structures capable of performing controlled work in their environment being synthesized [1,2]. Some of those imitate a behavior of proteins that are responsible for all kinds of movement in biological cells [3]. A good example of this approach is an inorganic nanodevice, powered by a molecular motor, that can act as a nanopropeller [4]. Other machines are created in the image of macroscopic systems. Even creating a light-driven nanocar is a possibility [5]. Among those artificial machines, a group of molecular gyroscopes is especially promising. Molecular gyroscopes, analogous to their macroscopic counterparts known from mechanical systems, consist of a rotating element called rotator, an axle around which the rotator turns, and a stator, whose role is to act as a rigid frame and shield the rotator from a contact with adjacent molecules. That kind of structure makes molecular gyroscopes ideal candidates to produce ‘amphidynamic crystals’ – ordered solids that combine rigid lattice constraints and highly mobile components inside the lattice [6]. As a result, molecular gyroscopes can provide various functional materials that can find application in different fields of industry and science. One can envisage to create a new type of device to store rotational energy inside an amphidynamic crystal structure and

later release it. Similar structures that use molecular motors connected to long polymers were depicted by Weysser et al. [7]. Those rotors could store not only energy but also information [8]. Rotors that contain electric dipoles may provide amphidynamic crystals that can be used as tunable dielectrics [2,9]. Molecular rotors could also find applications as different kinds of sensors: photosensors in optoelectronics [10], thermosensors in metrology and microviscosity sensors [11] in medicine.

Numerous kinds of molecular gyroscopes have been synthesized until now and, in most of them, the 1,4-diethynylphenylene group acts as a rotator and an axis of rotation [8,12–14]. Stators are attached on either side of the 1,4-diethynylphenylene group and can be linked by additional bridging chains. As the main function of a stator is shielding the rotator its massiveness is one of its main requirements. By this, organic molecules are frequently employed and one of the approaches has been to use steroidal derivatives for the synthesis of molecular gyroscopes [8]. Such molecular rotors derived from 12-oxosapogenins has shown the capability of reaching rotary frequencies between the kilohertz and megahertz interval [12].

In this paper, we present the synthesis and vibrational spectroscopy characterization that can provide information on molecular dynamics and differences between the molecular structure of acyclic (rotor **3**) and cyclic (rotor **5E**) rotors. As the subject of the examination, we used newly synthesized molecular rotors with the 1,4-diethynylphenylene- d_4 group acting as a rotator and steroidal stators. In the cyclic molecular rotor, steroidal molecules of the stators were

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