CHAPTER 19

LINEAR AND NONLINEAR OPTICAL PROPERTIES
OF SELECTED ROTAXANES AND CATENANES

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Abstract: Linear and nonlinear optical properties of catenanes and rotaxanes in thin films and in solution are reviewed and discussed. The compounds represent a new class of molecules, with mobile subparts. It offers a new kind of applications, particularly for optical switching. The rotational mobility of the subparts of these molecules was studied by the electro-optic Kerr effect. Both catenanes and rotaxanes can be processed into partly ordered thin films by vacuum sublimation. The degree of order may be controlled by an adequate chemical modification of the molecules, as it was observed in a series of substituted rotaxanes. Methods for controlling the motion of the components using light and electric fields are presented. The linear optical properties were studied by UV-Vis spectrometry and m-lines technique. The nonlinear optical properties were studied in solution and/or in thin films by the optical second and third harmonic generation techniques and by the quadratic electro-optic Kerr effect. The knowledge on the rotaxanes and the catenanes linear and nonlinear optical properties obtained by these studies is important for the future construction of synthetic molecular machines and optical switching elements.

Keywords: catenanes, rotaxanes, molecular switching, electro-optic effect, Kerr effect, photoisomerization, second harmonic generation, third harmonic generation, refractive index dispersion, absorption, molecular motors

1. INTRODUCTION

Catenanes and rotaxanes (for a review see [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]), belong to a new class of supramolecules composed from, mechanically bond, constituent smaller molecules, able to move independently. Due to this unique property these new class of organic molecules represent a great interest for potential applications in photonics, particularly in all optical and electro-optic switching [14, 15, 16, 17, 18].

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The name of catenanes originates from Latin *catena* which means a chain. Indeed these supramolecules are fundamentally made from interlocked macrocycles (Figure 1(a)) with, as already mentioned, ability of a relative movement of one macrocycle with respect to the other one(s) (piroetting). The number of macrocycle is included in the used notation: [n] catenanes denote n interlocked chains. Up to now supramolecules of up to 4 macrocycles were synthesized. Large catenanes (M_w = 10^5) are present in nature in DNA as intermediates during the replication, transcription, and recombination process. Since the first two-ring catenane was obtained in early sixties, smaller synthetic catenanes (M_w = 10^3) have attracted the interest of chemists and physicists.

The name of rotaxanes takes its origin in Latin too. *Rota* and *axis* mean, respectively wheel and axle. In the case of rotaxanes the macrocycle (or more of them) is locked onto a linear thread terminated on both sides with bulky stoppers (cf. Figure 1(b)). Rotaxanes exhibit more degrees of freedom than catenanes. The macrocycle can not only rotate along the thread (piroetting as in the case of catenanes, cf. Fig. 2a) but can also move along it (shuttling, Fig. 2b). The shuttling movement of macrocycle is limited by stoppers located at the both ends of thread (two phenyl rings in the case of nitrone [2] rotaxane, cf. Figure 1(b)). Another degree of freedom consists on a “bending” movement of rotaxane thread which may lead to clipping. This could be realized by an appropriate design of thread (e.g. a photo isomerising one). It may be leading to a reversible (or irreversible) transformation of a [2] rotaxane into [2] catenane under an external stimulus (e.g. light), as shown in Figure 2c. This could be possible with threads containing alternate e.g. photoisomerizable –C = C– or –N = N– segments [19, 20, 21, 22]. Because of these different degrees of freedom in these molecules they represent a particular interest for the fabrication of the nanoscale (nano motors) devices [6, 9, 14, 16, 23, 24, 25, 26, 27, 28, 29].

The interest in the development of these supramolecules is triggered not only by the possible applications in photonics, but also in medicine, biology and everyday life. Indeed many phenomena of biological interest originate directly from the light induced and/or controlled mechanical motions at the molecular level. One of the very well known exemple is our vision which exploits the trans-cis isomerisation of

![Diagram of catenanes and rotaxanes](image)

*Figure 1. Schematic representation of a [2] catenane (a) and a [2] rotaxane (b)*