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ROTAXANES

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In the paper rotaxanes containing an electron accepting ring are described, they are followed by those having electron donating ring. Syntheses, properties and possible applications of considered species are presented.

Key words: rotaxanes, molecular connector, isomers.

Rotaxanes belong to supramolecular chemistry species; they are a topic of a great number of reports due to their interesting properties and possible applications [1–3]. Rotaxanes of a quaternary azaaromatic character are a special class of interlocked assemblies, since they combine properties of rotaxanes and of quaternary azaaromatics [7–8].

The present review is continuation of our former papers on supramolecular species of quaternary azaaromatic character [9] as well as those concerning quaternary azaaromatics [10]. Supramolecular species are promising for application in nanotechnology; it should be pointed out that studies concerning molecular devices and machines [11] are developing rapidly, and numerous works concerning catenanes knotanes and cryptands have been published. Moreover interesting examples of rotaxanes containing cyclodextrin calixarene and cucurbituril units are known. Recently many reports on synthesis of rotaxanes using “click chemistry” appeared. A considerable attention is paid now to quaternary azaaromatics, due to their promising application possibilities; here ionic liquids, cyanine dyes, DNA binders and polymers [12] should be mentioned.

The first part of the present review deals with rotaxanes containing an electron accepting ring, and then rotaxanes having an electron donating ring are described. Since the number of rotaxanes of a quaternary azaaromatic character is enormous, only selected examples of these species are presented. In the paper mainly reports appeared since 2006 are discussed; the citations are given starting from 2005.

Rotaxanes containing electron accepting ring are predominantly those with the tetracationic cyclophane A. This compound is widely used as a strong electron acceptor interacting with the thread containing electron donor stations. The ring A is at the LUMO, whereas the thread at the HOMO energy level [13].

The synthesis of [2] rotaxane 1 consisting of the tetracationic cyclophane ring A and the thread containing 3,3'-difluorobenzidine has been performed. The rotaxane 1 is blue, this color results from the charge transfer absorption band between the LUMO of

the ring and the HOMO of the thread. Since the absorption wavelength depends on the energy gap between the LUMO of the ring and the HOMO of the thread, the different colors can be generated by altering the HOMO energy level of the thread.

The behavior of [2] rotaxane 1 is related to that of the tristable [2] catenane consisting of the ring A and three stations – tetrathiafulvalene (TTF), 1,5-dioxynaphthalene (DNP) and 3,3-difluorobenzidine. This system shows green, red and blue colors, respectively, depending on the position of A which is controlled by oxidation of each station.

It was established that in the highly constrained [2] rotaxane 2 the ring A is restricted to reside on pyrrolo TTF unit F due to the close proximity of two stoppers [14]. The large di-*t*-butylbenzyl stopper and the smaller one, consisting of thioethyl and diethyleneglycol groups are attached to both ends of the F unit. In the case of deslipping, the ring A moves in the direction of the smaller stopper.

Upon oxidation of the F unit the system is destabilized, and the barrier of deslipping of A is lowered. The design of 2 enables the determination of the deslipping free energy barrier for the ring A in all three redox states of the rotaxane, *i.e.* when F is neutral, as well as singly or doubly oxidized. The above results are promising for the construction of molecular machines.

In the study of rotaxanes the redox potential of the highly constrained bistable rotaxane 3 has been measured [15]. In bistable rotaxanes, consisting of an electron accepting ring A and of a thread incorporating two π donor units, F and DNP, the ring prefers to encircle the stronger π donor, *i.e.* F; this is the ground state co-conformation GS. Upon an oxidation-reduction cycle of the F unit, the switching resulting in the movement of the ring A to the DNP occurs, generating a meta-stable co-conformation MS.

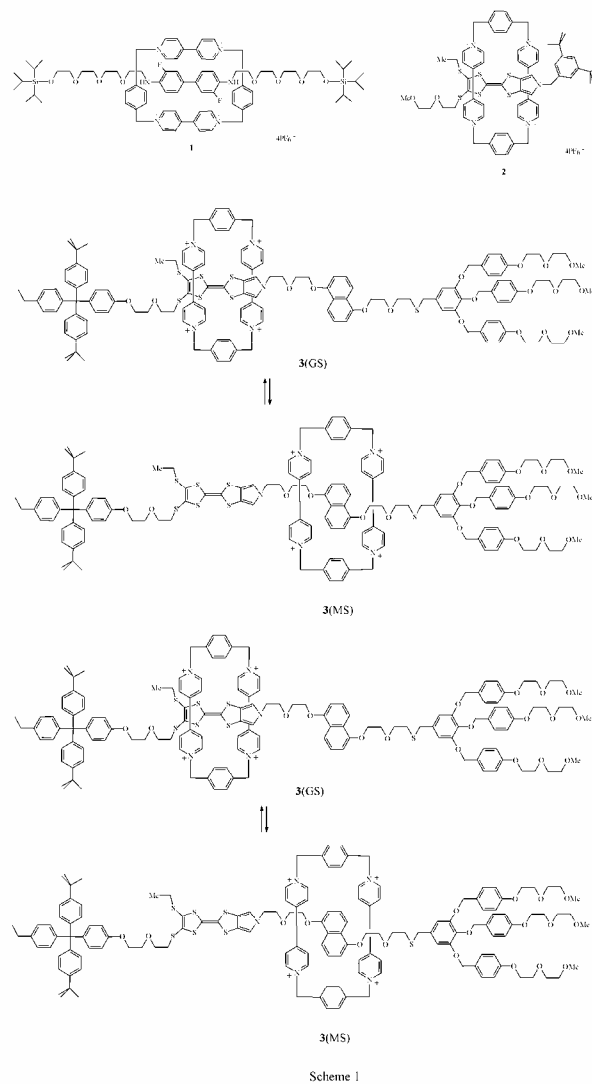
It was observed that the oxidation potential of F shifts anodically between ground and meta-stable states; it should be noted that such a shift plays an important role in switching of conductivity existing in the memory devices. In memory devices the change in conductivity across the rotaxane is dependent on the change in energy gap (ΔE) between HOMO and LUMO. In bistable rotaxanes LUMO is localized on the ring A and HOMO on the F unit. These localizations are irrespective of the position of the ring A, *i.e.* for both GS and MS co-conformations.

In GS (OFF state of the memory device, *i.e.* when ring A encircles the F unit), the energy gap (ΔE) is larger than in MS (ON state, *i.e.* when the ring A encircles the DNP unit). The stabilization of HOMO in GS results mainly from the electrostatic interaction of the ring A with the unit F.

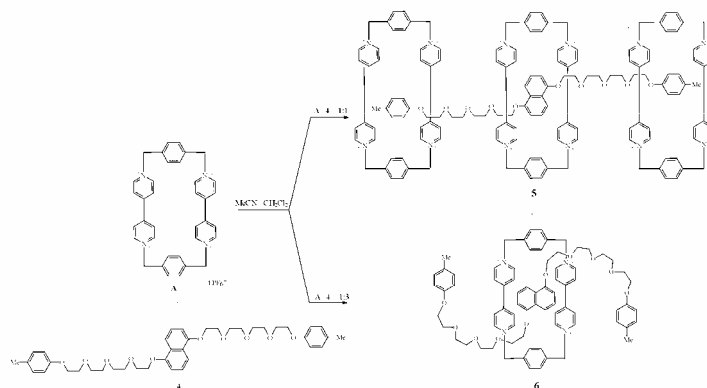
The mixing of A with 4 in MeCN/CH₂Cl₂ affords two products, depending on ratio of starting compounds. In the case of 1:1 ratio, the [2] pseudorotaxane (not shown) is formed in solution; on crystallization it yields [4] pseudorotaxane 5 [16]. The formation of 5 results from additional noncovalent interactions which do not exist in solution, but are present in the crystal. They interactions involve the PF₆⁻ anions in the form of short [F...H] contacts between the anions and hydrogen bond donors on both the ring A and the polyether chains of E. Besides many C-H...F contacts, the stabilizing noncovalent [π ... π] and [C - H... π] interactions between the ring A and terminal aromatic units of the thread exist.

In order to obtain crystals of 6 the vapor diffusion of methyl *t*-butyl ether into a MeCN/CH₂Cl₂ solution of A and the thread 4 in the 1:3 ratio was performed. In crystal

of 6 the thread wraps itself around the ring A in such a way that the terminal aromatic groups of 4 are $\pi \dots \pi$ stacked along bipyridinium units.



Stabilities and dynamics of Langmuir monolayers consisting of amphiphilic bistable [2] rotaxanes 7 and 8 have been investigated using light scattering microscopy, atomic force microscopy and surface pressure- area isotherms [17]. In 7 and 8 being constitutional isomers, the ring A is situated predominantly at the TTF moiety.



Scheme 2

The unusual two-dimensional (2D) to three-dimensional (3D) transition was found, in which superstructures resembling localized mobile solitons are formed during the compression of monolayers below their collapse pressures. Solitons move in a linear trajectory across the film, perpendicular to the compression direction. It should be pointed out that solitons are not formed from dumbbells of 7 and 8.

In investigation of rotaxanes [18–20], the bistable [2] rotaxane (F/NP) 9 and degenerate [2] rotaxane (NP/NP) 10 have been synthesized and characterized in solution [21] (NP=naphthalene). The threads of 9 and 10 contain rigid arylolethynyl and butadiynyl spacers, respectively.

It should be noted that π - π interactions are not the only interactions determining the distribution of translational isomers; also weak interactions such as [C-H $\cdots\pi$] and hydrogen bonding exist. All these interactions influence the position of the ring A on the dumbbell, *i.e.* determine the distribution of translational isomers.

The use of poly(ethyleneglycols) (PEGs) as flexible spacers in the dumbbell would introduce additional weak noncovalent interactions between them and the ring A. Moreover, in the case of PEG the backfolding is possible, *i.e.* the ring encircles a station, and dumbbell folds back allowing interaction of the ring with the second, unoccupied station. To overcome the above behavior which would not allow the precise examination of the structure of rotaxanes, the rigid spacer has been built into their threads.

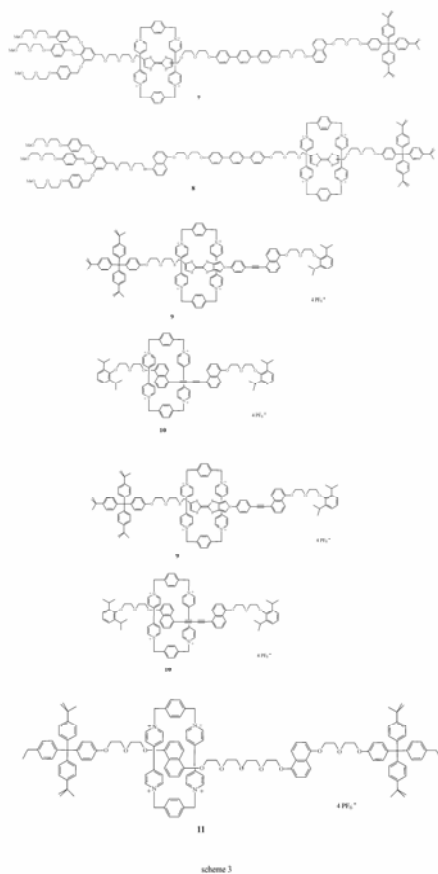
The ^1H NMR analysis has shown that the rotaxane 9 exists preferentially as a single translational isomer in which A predominantly encircles the F unit; this result is rather unexpected, since [2] rotaxanes containing flexible PEG linkers usually have been isolated as two possible translational isomers.

For the work of 9 as a molecular switch, the ring A is moved from its ground state position around the F unit to the NP station by using an appropriate chemical or electrochemical stimulus. Chemical switching of 9 may be achieved by oxidizing the F unit with tris (*p*-bromophenyl)ammonium hexafluoroantimonate to F^{2+} and then reducing

F^{2+} back to its neutral state with zinc powder. In the switched state (upon oxidation of F) the ring A encircles the NP station, and the switched state returns to the stable ground state (upon reduction of F^{2+}) when A encircles F.

Considering 10 as compared with analogous degenerate [2] rotaxane containing flexible PEG linkers between two NP stations, 11 (not shown), it was found that in 10 the interaction between A and NP units is weaker than in 11 due to the absence of oxygen atoms in 10. The results of dynamic 1H NMR spectroscopy indicate that the barrier to the movement of A from one NP station to another in 10 is much lower than in 11. The shuttling process in 10 is faster than in 11, therefore it may be concluded that the shuttling rate in [2] rotaxanes can be tuned by use of appropriate linkers between both recognition sites.

The above experiments show that the introduction of rigid linker allows to construct molecular switches displaying strong ON-OFF ratios that are temperature-independent as well as to design simple motor molecules.



The large number of reports on rotaxanes of a quaternary azaaromatic character appearing today shows the rapid development of this chemistry area. Among supramolecular species, the novel molecular plug-socket connectors as well as interlocked compounds deserve an attention.

In the study of rotaxanes new synthetic methods are used, as an example may serve the "threading-followed-by-stoppering" approach to rotaxanes and catenanes, proceeding efficiently under mild conditions of "click chemistry" which is now widely applied in various chemistry fields [22]. The above review, albeit not exhaustive shows to some extent the importance of rotaxanes bearing quaternary azaaromatic moieties in view of their properties and various application possibilities.

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У статті описано ротаксани, які містять електронні приймальне та передавальне кільця. Представлено особливості синтезу, властивості та можливості застосування цих різновидів.

Ключові слова: ротаксани, молекулярне з'єднання, ізомери.

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В статье описано ротаксаны, которые содержат электронные приемное и передаточное кольца. Представлены особенности синтеза, свойства и возможности применения этих разновидностей.

Ключевые слова: ротаксаны, молекулярное соединение, изомеры.

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