論文 / 著書情報
Article / Book Information

Title	Liquid-crystalline [2]rotaxanes and their phase transition behavior
Authors	Gosuke Washino, Suzushi Nishimura, Atsushi Shishido
Citation	Proc. SPIE
Pub. date	2025, 9
DOI	https://doi.org/10.1117/12.3063438
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Liquid-crystalline [2]rotaxanes and their phase transition behavior

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ABSTRACT

Supramolecular liquid crystals (LCs), which integrate non-covalent molecular interactions with long-range structural order, represent a promising platform for the development of advanced functional materials. Rotaxanes and pseudorotaxanes, characteristic molecular architectures in which axle-shaped molecules are threaded through ring components, are notable for their dynamic behavior and molecular recognition capabilities. However, liquid-crystalline materials based on rotaxane architectures remain largely unexplored, likely due to the difficulty of incorporating liquid-crystalline features into rotaxane architectures, as suggested by the limited number of reported molecular design strategies. In this study, we propose a new molecular design concept for liquid-crystalline [2]rotaxanes: integrating an axle molecule as mesogen core with a ring molecule as flexible tail via a threaded structure. We successfully synthesized a representative [2]rotaxane based on this concept. Although neither the axle nor the ring component exhibited liquid crystallinity on its own, the resulting [2]rotaxane exhibited thermotropic liquid crystallinity. Furthermore, we extended this concept to a pseudorotaxane system capable of reversible assembly and disassembly, and successfully synthesized a liquid-crystalline [2]pseudorotaxane. These findings demonstrate a novel design strategy for constructing supramolecular liquid crystals based on rotaxane architectures.

Keywords: Supramolecular liquid crystal, Rotaxane, Pseudorotaxane

1. INTRODUCTION

Liquid crystals (LCs) are typically designed by incorporating a rigid mesogenic core and flexible tails within a single molecule. Beyond covalent designs, supramolecular LCs can be constructed through non-covalent interactions such as hydrogen bonding. Supramolecular LCs can couple the dynamic nature of non-covalent interactions with the structural ordering, enabling high material functions. Among supramolecules, rotaxanes and pseudorotaxanes have attracted considerable attention due to their unique molecular architecture, in which an axle-shaped molecule is threaded through a ring molecule. The threaded structures exhibit distinctive dynamic features: pseudorotaxanes undergo reversible association and dissociation and show molecular recognition based on size complementarity, while rotaxanes allow for directional motion of the ring along the axle. These dynamic characteristics have inspired the development of unique functional materials, including macroscopic self-assembly gels[1], molecular elevators[2], and slide-ring gels[3].

Incorporating liquid crystallinity into rotaxane systems introduces higher structural ordering to directional molecular motion, offering a promising route to advanced functional materials. However, only a few liquid-crystalline rotaxanes[4, 5] have been reported to date. One major reason is the difficulty of incorporating liquid-crystalline features into rotaxane architecture. In previous studies, both the mesogen core and the flexible tail were placed on the axle with bulky stoppers. This limited design imposes a synthetic burden and has become a bottleneck for further development in this field. Moreover, because this design relies on stoppers, it cannot be applied to pseudorotaxane systems.

In this study, to overcome this limitation, we propose a new molecular design: assigning the mesogen core to the axle and the flexible tail to the ring, separately (Figure 1). By integrating the axle as mesogen core and the ring as flexible tail via a threaded structure, the resulting rotaxanes can now exhibit liquid crystallinity. Based on this concept, we synthesized and characterized a liquid-crystalline [2]rotaxane[6]. Furthermore, we adopted the design concept to a pseudorotaxane system and investigated its phase transition behavior.

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Liquid Crystals XXIX, edited by Iam-Choon Khoo, Proc. of SPIE
Vol. 13587, 1358705 · 2025 Published by SPIE
0277-786X · doi: 10.1117/12.3063438

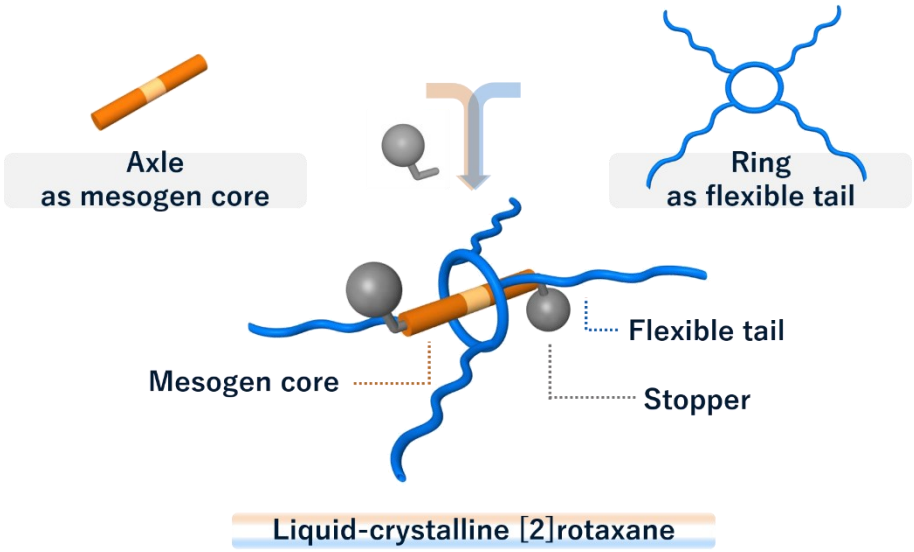

Figure 1. Molecular design concept of liquid-crystalline [2]rotaxane.

2. METHODOLOGY

The synthesis of [2]rotaxane was carried out using non-liquid-crystalline molecular components (
Figure 2). The axle, serving as the mesogenic unit, was an organic cation containing a 1,2-bis(dipyridyl)ethane core. To lower the phase-transition temperature, bis(trifluoromethanesulfonyl)imide (Tf_2N^-) was selected as the counter anion. The ring molecule **R12**, acting as a flexible tail, was designed based on dibenzo-24-crown-8 ether functionalized with four dodecyl (C12) alkyl chains. The axle and ring molecules were mixed in a solvent ($CH_3NO_2/CHCl_3$, 1:1, v/v) to form a pseudorotaxane, after which 4-*tert*-butylphenyl groups were added to modify both ends of the axle with bulky stoppers. Following purification by column chromatography, the [2]rotaxane, **Rtx**, was isolated. The synthesized **Rtx** was characterized using various analytical techniques, including ^{1}H NMR spectroscopy. The phase transition behavior of **Rtx** was evaluated by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD). To investigate the mechanism underlying the emergence of liquid-crystalline behavior in **Rtx**, we also examined the phase transition behavior of three control samples: the axle molecule with terminal stoppers, the ring molecule, and their 1:1 mixture.

To extend this design to pseudorotaxanes, we prepared an axle molecule modified with linear alkyl chains at both ends instead of bulky stoppers. The axle and equimolar **R12** were mixed in a solvent ($CH_3CN/CHCl_3$, 1:1, v/v), followed by solvent evaporation to yield a solid-state [2]pseudorotaxane. The phase transition behavior of the resulting [2]pseudorotaxane was evaluated using POM and XRD.

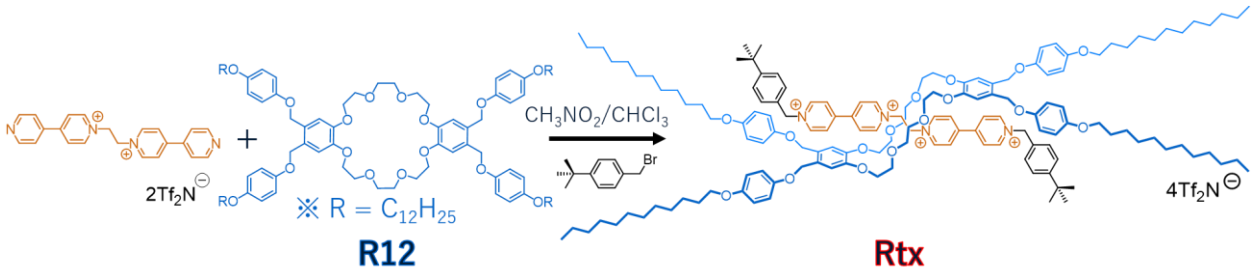

Figure 2. Reaction scheme and chemical structure of [2]rotaxane, **Rtx**.

3. RESULTS

The synthesized [2]rotaxane, **Rtx**, was characterized by ^{1}H NMR spectroscopy (Figure 3), which showed all expected signals with appropriate integration ratios, confirming the successful synthesis and isolation of the compound. DSC measurement revealed that **Rtx** exhibits a mesophase between 140 and 170 °C during heating and between 155 and 130 °C during cooling. In the mesophase, POM observations displayed a fluid Batonnets texture (Figure 4), while XRD exhibited diffraction peaks characteristic of a smectic phase. These observations indicate that **Rtx** is a thermotropic liquid crystal exhibiting a smectic A phase. The axle with terminal stoppers and the ring, which are molecular components of **Rtx**, transitioned directly from the isotropic phase to glassy and crystalline phases, respectively (Figure 4). When mixed, these components could not form a threaded structure due to the steric hindrance from the bulky stoppers. This control sample, possessing the same chemical composition as **Rtx** but lacking the threaded architecture, did not exhibit any liquid-crystalline phases. These results demonstrate that the threaded structure is essential for the emergence of liquid crystallinity. Moreover, the synthesized solid-state [2]pseudorotaxane also exhibited a smectic A phase, as confirmed by POM and XRD analyses. These results validated the effectiveness and versatility of our LC molecular design concept based on the threaded architecture.

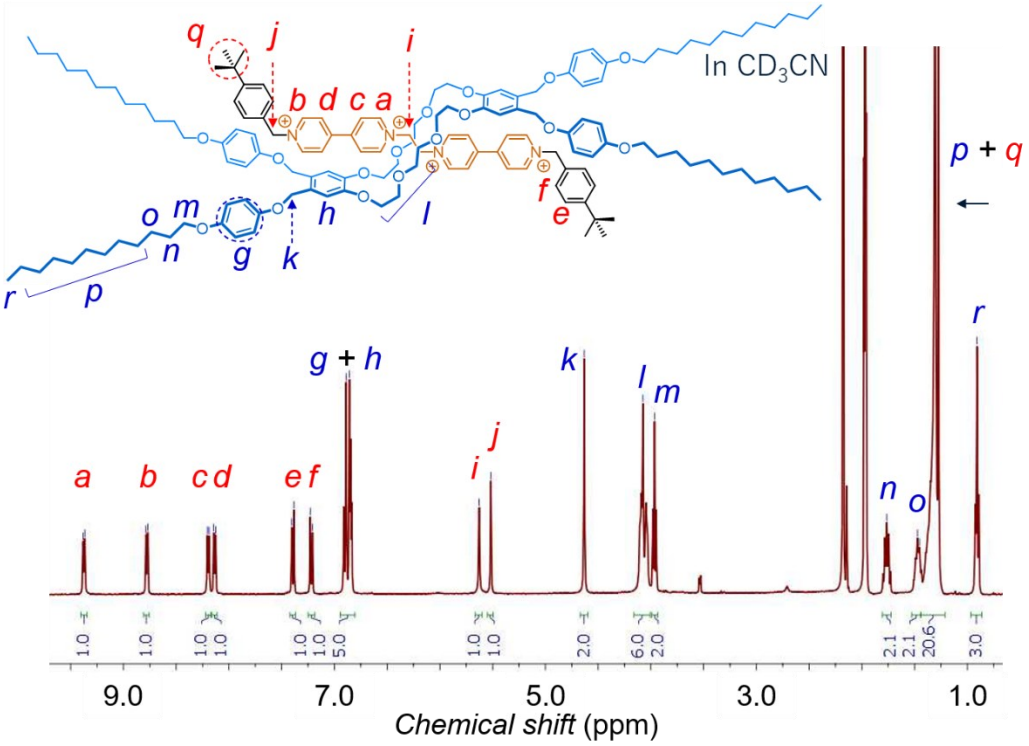

Figure 3. ^{1}H NMR spectrum of **Rtx**.

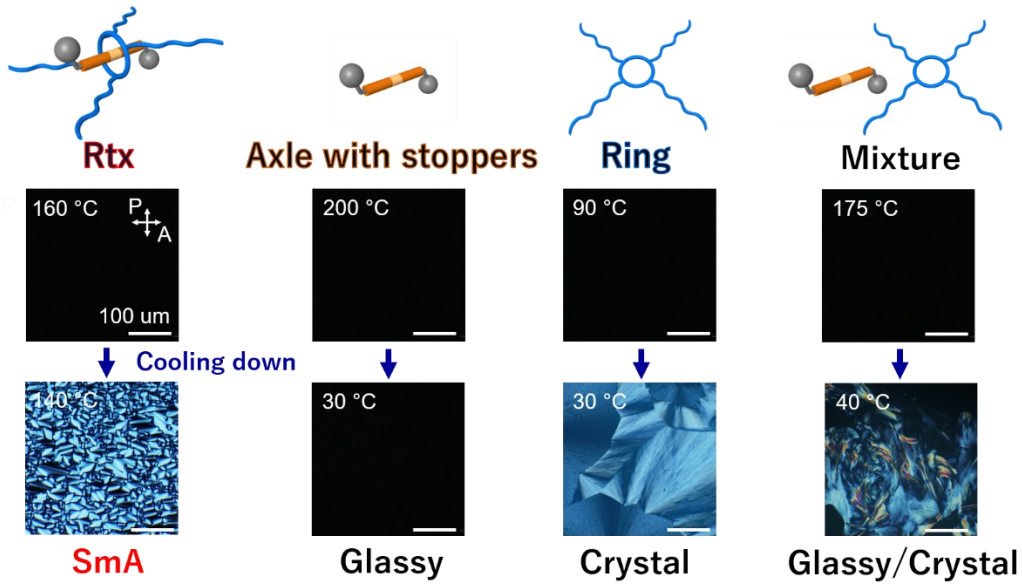

Figure 4. POM images of **Rtx** and its control samples upon cooling from the isotropic phase.

4. CONCLUSIONS

We established a novel molecular design strategy for liquid-crystalline rotaxanes and pseudorotaxanes by integrating an axle as mesogen core and a ring as flexible tail via a threaded structure. This concept was validated through the synthesis and characterization of a [2]rotaxane exhibiting smectic A mesophase. Furthermore, the design was successfully extended to a unique example of a liquid-crystalline [2]pseudorotaxane. These findings offer a new and straightforward approach to advanced materials that integrate liquid crystallinity with rotaxane architectures.

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