Review

Exploring and Exploiting the Symmetry-Breaking Effect of Cyclodextrins in Mechanomolecules

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Abstract: Cyclodextrins (CDs) are cone-shaped molecular rings that have been widely employed in supramolecular/host–guest chemistry because of their low cost, high biocompatibility, stability, wide availability in multiple sizes, and their promiscuity for binding a range of molecular guests in water. Consequently, CD-based host–guest complexes are often employed as templates for the synthesis of mechanically bonded molecules (mechanomolecules) such as catenanes, rotaxanes, and polyrotaxanes in particular. The conical shape and cyclodirectionality of the CD "bead" gives rise to a symmetry-breaking effect when it is threaded onto a molecular "string"; even symmetrical guests are rendered asymmetric by the presence of an encircling CD host. This review focuses on the stereochemical implications of this symmetry-breaking effect in mechanomolecules, including orientational isomerism, mechanically planar chirality, and topological chirality, as well as how they support applications in regioselective and stereoselective chemical synthesis, the design of molecular machine prototypes, and the development of advanced materials.

Keywords: catenane; rotaxane; machanomolecule; stereochemistry; mechanostereochemistry; chirality; isomerism; molecular machine; cyclodectrin

1. Introduction

Cyclodextrins (CDs) [1] are a class of macrocyclic natural products that were first isolated in 1891 from cultures of starch-fermenting bacteria by Villiers [2]. Structurally, all CDs are oligomeric loops of glucose; different sized rings [3] are denoted by Greek prefixes, beginning with α-CD (6-mer) and continuing up to at least the 26-mer, u-CD [4]. The first three CDs—α-CD, β-CD, and γ-CD (6–8 glucose subunits; Figure 1)—are by far the most common and most widely available. After more than half a century of historically important investigations by Schardinger [5], French [5], Freudenberg [6], Cramer [6], and Pringsheim [7] on the structure and properties of CDs, it was Cramer [8,9] who pioneered the study of cyclodextrin nclusion complexes beginning in the early 1950s—long before the Nobel-recognized work of Pedersen [10], Cram [11], and Lehn [12] of a similar nature. The three main CDs possess a conical shape; the wider "2,3-rim" (secondary face) is reinforced by hydrogen bonds between the secondary alcohol groups at the 2 and 3 positions of the glucose subunits, while the narrower "6-rim" (primary face) displays all of the primary alcohol groups at the 6 position. The hydrophobic cavities of α-CD, β-CD, and γ-CD are approximately 5, 7, and 9 Å in diameter, respectively, and ~8 Å in depth, allowing them to ensconce thousands of appropriately sized lipophilic guests in water [13,14]. While CDs continue to serve as a cornerstone of supramolecular/host–guest chemistry, they are also important compounds in organocatalytic chemistry [15–17], analytical chemistry [18], separations [19], medicine [20,21], food science [22], and other industrial applications [23].
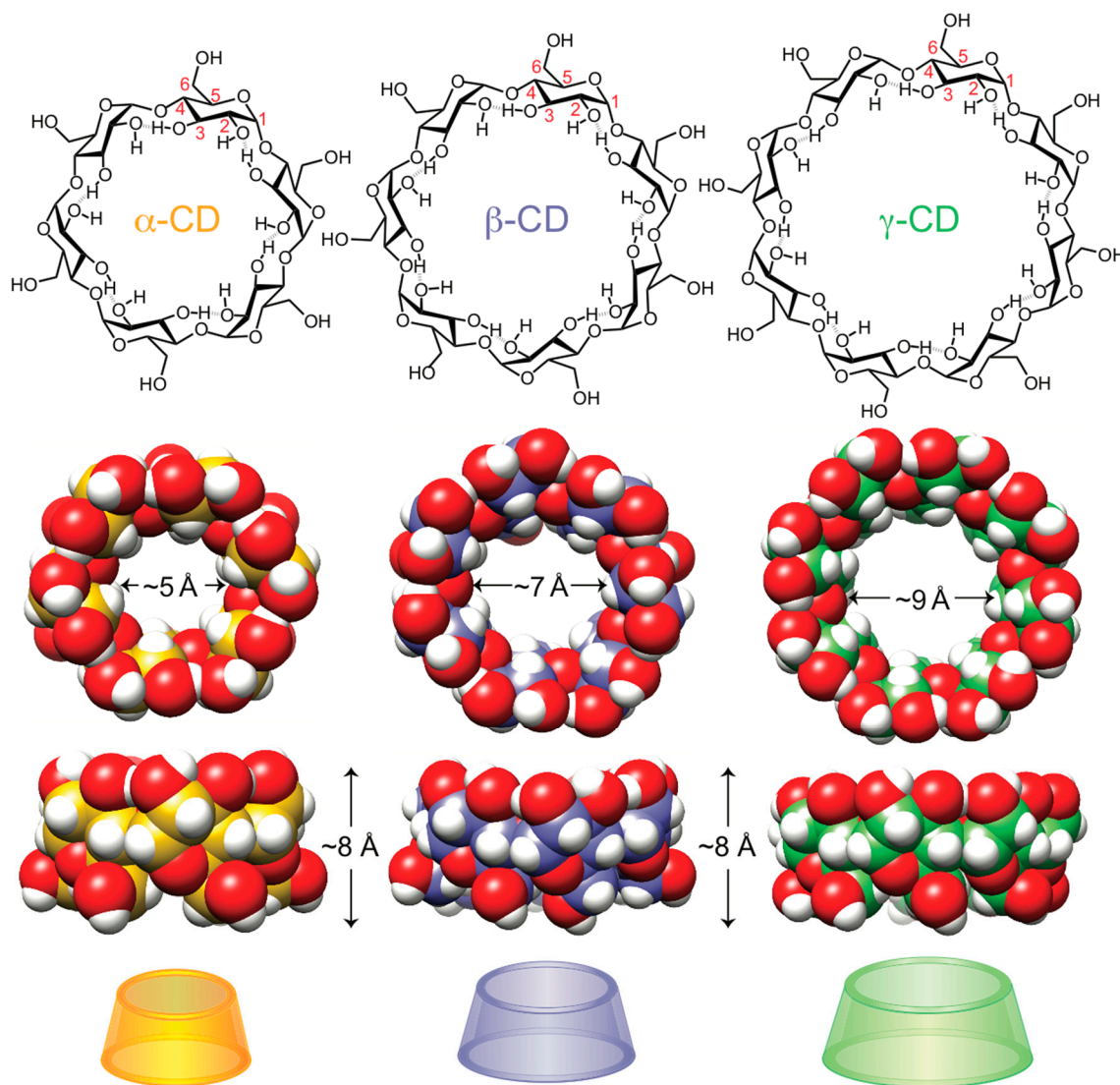
Figure 1. Structural, space-filling, and graphical representations of the three main cyclodextrin (CD) molecules: α-CD (yellow), β-CD (blue), and γ-CD (green).

CD-based host–guest complexes are convenient templates for the synthesis of molecules with mechanical bonds [24–29], also known [30] as mechanomolecules. A mechanical bond is defined [30] as "an entanglement in space between two or more molecular entities (component parts) such that they cannot be separated without breaking or distorting chemical bonds between atoms". The archetypal mechanomolecules are (i) [*n*]catenanes, in which *n* ring-shaped component parts are interlocked, and (ii) [*n*]rotaxanes, in which the *n* component parts comprise one or more rings encircling one or more acyclic "dumbbells", which possess endgroups or "stoppers" that prevent the ring(s) from dissociating. Since complexation is driven by a hydrophobic effect, a simple and convenient template for making mechanomolecules is a hydrocarbon⊂CD pseudo-[2]rotaxane (the prefix pseudo- denotes an unstoppered threaded assembly). In general, CDs exhibit increased affinity for oligomethylenes as chain length increases, assuming the guests are water soluble [31,32]. Indeed, the first successful template-directed synthesis of a [2]rotaxane was carried out by Ogino [33] (Scheme 1) using an amine-terminated dodecane (C_{12}) guest with α-CD or β-CD hosts. Ogino used *cis*-dichlorobis(ethylenediamine)cobalt(III) chloride [$CoCl_2(en)_2$]Cl to stopper CD-threaded $H_2NC_{12}H_{24}NH_2$ chains in Me_2SO at 75 °C, generating either **α-R1^{4+}** (19% yield) or **β-R1^{4+}** (7% yield) upon isolation by size-exclusion chromatography. The higher yield for **α-R1^{4+}** compared to **β-R1^{4+}** reflects the alkanes' higher affinity for α-CD. Note that while the cobalt-capped hydrocarbon chain has

a high symmetry ($D_{\infty h}$) by itself, the overall symmetry of the corresponding rotaxanes are reduced (C_n) to that of the encircling cyclodextrin, where each end of the dumbbells become differentiated by their proximity to a different rim of the CD ring.
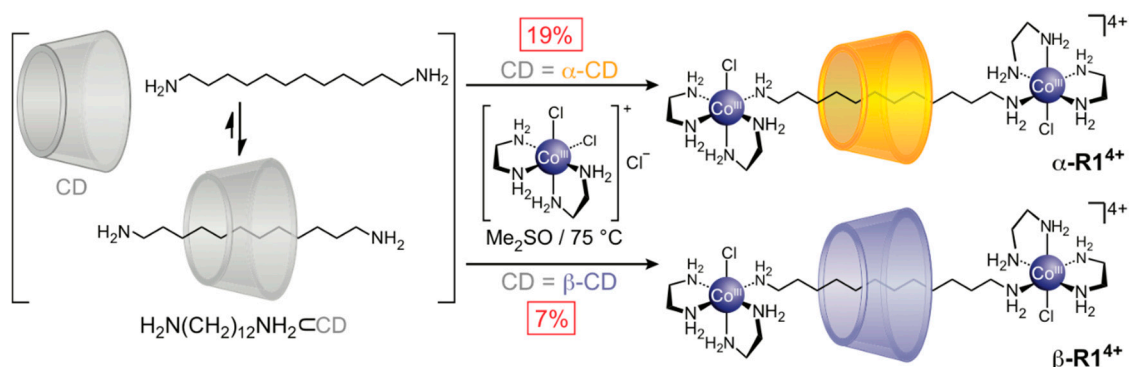
Scheme 1. Ogino's seminal template-directed synthesis of [2]rotaxanes **α-R1⁴⁺** and **β-R1⁴⁺** from diaminododecane and α-CD or β-CD, respectively.

This mini-review describes how the symmetry-breaking effect of cyclodextrin can be leveraged to generate mechanomolecules with unique stereochemical and dynamic properties, which may be useful in the generation of novel syntheses, molecular machines, and advanced materials.

2. The Stereochemistry of CD-Based Mechanomolecules

Since stereochemistry [34] is the branch of chemistry that deals with the three-dimensional arrangements of atoms in space, mechanostereochemistry is simply defined [35] as the stereochemistry of molecules with mechanical bonds. Mechanical bonding gives rise to completely new types of molecular isomerism and dynamics that are not observed in other types of compounds. As stereoisomers are molecules that have identical constitutions but different arrangements of atoms in space, mechanostereoisomers [30] are mechanomolecules that have identical co-constitutions, but differences in the arrangement of their component parts in space. The symmetry-breaking effect of CDs—in particular their lack of any mirror planes—can give rise to orientational mechanostereoisomers (see Section 2.1), as well as emergent types of chirality (objects having non-superimposable mirror images), namely, mechanically planar (see Section 2.2) and topological (see Section 2.3) chirality.

2.1. Orientational Mechanostereoisomers

As the name suggests, orientational mechanostereoisomers arise from having different possible ring orientations in mechanomolecules. If a ring lacks mirror symmetry across the plane of its cavity, its rims may be differentiated into a "head" and a "tail", and it can therefore be threaded onto a string either head-first or tail-first. In the case of cyclodextrins, we refer to the wider 2,3-rim as the "head" and narrower 6-rim as the "tail". If a second component part is mechanically bonded to a CD, orientational isomerism can arise if it too lacks mirror symmetry across the plane of the CD's cavity. Orientational mechanostereoisomerism arising from CDs may be observed in [2]rotaxanes (see Section 2.1.1), [3]rotaxanes (see Section 2.1.2), and polyrotaxanes (see Section 2.1.3), as well as [3]catenanes (see Section 2.1.4) and larger [*n*]catenanes (see Section 2.1.5) in principle. In the case of [2]catenanes, the conditions for achieving orientational isomerism are also sufficient for topological chirality, so these compounds are discussed in Section 2.3.

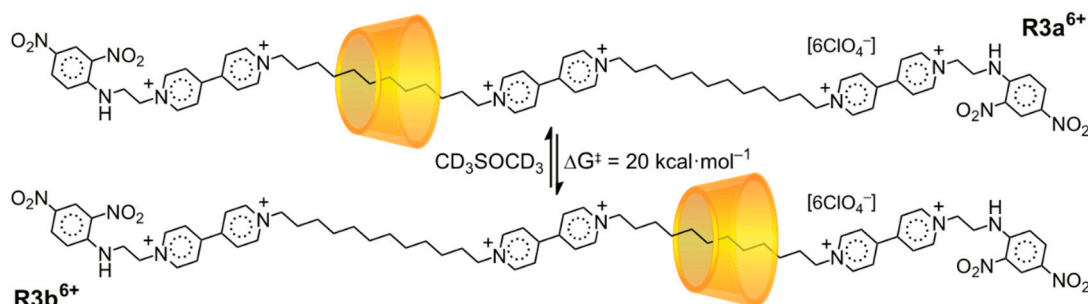### 2.1.1. [2]Rotaxane Orientational Isomers

The earliest rotaxanes to exhibit orientational mechanostereoisomerism were based on α-CD. In 1991, Kaifer [36,37] coupled a carboxylic acid-terminated half-dumbbell with a sulfonated aminonaphthalene stopper in the presence of α-CD to generate (Scheme 2) a mixture of orientational

mechanostereoisomers **R2a** and **R2b**. In this case, the CD rings had no orientational bias; both isomers were obtained in equal proportion. When the isomers were separated by thin-layer chromatography and isolated as pure compounds, they showed a surprising behavior: the CD ring slowly escaped from the dumbbell in **R2a**, but not in **R2b**. This kind of face-selective motion presents a promising opportunity for the design of molecular machine prototypes (see Section 3.2).
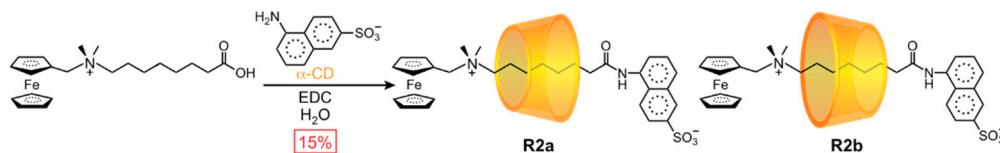
Scheme 2. Kaifer's seminal synthesis of a mixture of [2]rotaxane orientational isomers.

While it may seem initially that [2]rotaxane orientational isomers cannot interconvert without the ring either turning inside-out or executing an escape–rotate–rethreading sequence, Kawaguchi and Harada [38] demonstrated an interesting case (Scheme 3) of orientational isomers that exchange by a ring-shuttling mechanism. As the α-CD ring of the [2]rotaxane oscillates between two ends of a symmetrical dumbbell, it alternately exposes its head (**R3a^{6+}**) and tail (**R3b^{6+}**) to the bipyridinium barrier at the center of the dumbbell. Rotating **R3b^{6+}** 180° such that its stoppers exchange sites can help one see that it is the orientational isomer of **R3a^{6+}**, owing to the mirror symmetry of the dumbbell.


Scheme 3. A molecular shuttle in which the oscillation of a ring between two sites leads to interconversion between two orientational isomers.

While CD (pseudo)-[2]rotaxanes with desymmetrized dumbbells are often obtained as a mixture of orientational isomers [39–46], it is also common to obtain one orientational isomer selectively (see Section 2.2).

2.1.2. [3]Rotaxane Orientational Isomers

When two or more desymmetrized rings are threaded onto a string, they can access different orientations with respect to one another, so a symmetry-breaking dumbbell is no longer required for orientational isomerism to occur. Such a scenario is exemplified in Scheme 4.
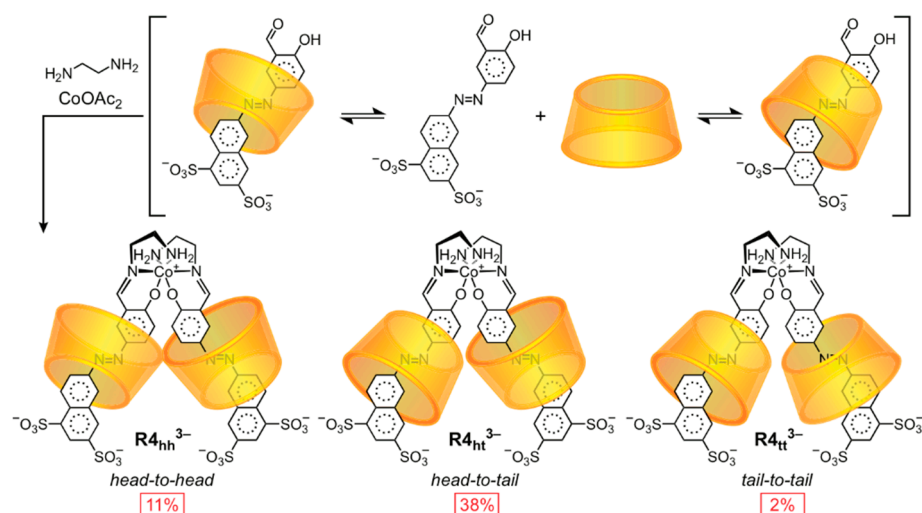
Scheme 4. A mixture of three [3]rotaxane orientational isomers is obtained upon dimerization of salicylaldehyde-terminated α-CD pseudo-[2]rotaxanes around a Co^{III} metal center [47].

A team led by Anderson [47] isolated, by anion exchange chromatography, all three orientational isomers—head-to-head $\mathbf{R4_{hh}}^{3-}$ (11%), head-to-tail $\mathbf{R4_{ht}}^{3-}$ (38%), and tail-to-tail $\mathbf{R4_{tt}}^{3-}$ (2%)—of [3]rotaxane upon conjoining a pair of salicylaldehyde-functionalized pseudorotaxanes around a Co^{3+} ion to create a symmetrical dumbbell in the presence of α-CD. The unequal distribution of products indicates a bias, but not complete selectivity, for the head-to-tail orientation. Later, the team prepared [48] a head-to-tail orientational isomer with high selectively on an oligophenylene(ethynylene) dumbbell on porous glass solid supports. Selective syntheses of tail-to-tail [49,50] and head-to-head [51–54] [3]rotaxanes have also been reported (see Section 3.1.2). A [3]rotaxane based on oligothiophene-threaded β-CD rings has also been synthesized [55] as a mixture of orientational isomers.

2.1.3. [*n*]Rotaxane Orientational Isomers

There are a few examples of discrete [*n*>3]rotaxanes [56–59] based on CD templates, but the ring orientations are not well characterized. In 1992, Harada [60] reported the first synthesis of a CD polyrotaxane, comprising polyethylene glycol (PEG) threaded by many α-CD rings. It is believed [60,61] that α-CD/PEG poly(pseudo)rotaxanes self-assemble with high mechanostereoselectivity into an arrangement with a repeating sequence of head-to-head/tail-to-tail orientations.

2.1.4. [3]Catenane Orientational Isomers

Although the synthesis of CD-based catenanes was attempted [62] as early as 1958, Stoddart [63] first reported the synthesis (Scheme 5) of catenated cyclodextrins in 1993.
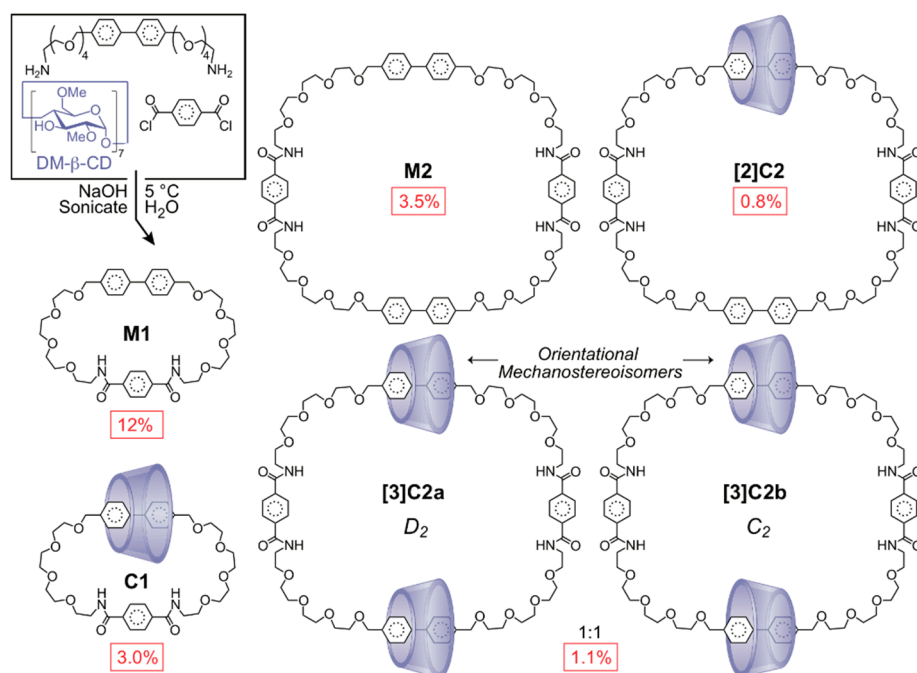
Scheme 5. The synthesis of catenated cyclodextrins [63].

Macrocyclizing terephthaloyl chloride with a biphenylene unit bis-functionalized with flexible amine-terminated tetraethylene glycol linkers in the presence of heptakis (2,6-di-*O*-methyl)-β-cyclodextrin (DM-β-CD) afforded a mixture of [1+1] products (macrocycle **M1**, [2]catenane **C1**) and [2+2] products (macrocycle **M2**, [2]catenane **[2]C2**, and [3]catenanes **[3]C2a-b**). The pair of [3]catenanes, **[3]C2a** and **[3]C2b**, were isolated [64] as a 1:1 mixture of head-to-head/tail-to-tail and head-to-tail orientational isomers, respectively, which may be distinguished by their different time-averaged (D_2 and C_2) symmetries. A group led by Otto [65] has also observed [3]catenane orientational isomers within a dynamic combinatorial library of catenated cyclodextrins.

2.1.5. [*n*]Catenane Orientational Isomers

Radial-type [*n*]catenanes possess a structure in which multiple small rings interlock a single large ring. With the exception of their probable formation [66] as a side-product in the photopolymerization of anthracene-stoppered poly [*n*]rotaxanes, this type of topology was not realized using CDs until very recently. Higashi et al. reported [67] a one-pot approach to making radial [*n*]catenanes with many (>10) β-CD rings encircling a polymer macrocycle. While the ring orientations were not characterized (to do so would be very challenging), it is likely that a multitude of different orientations occur, although polydispersity in chain length and ring-threading ratios preclude the presence of true isomers. The number of possible isomers —both orientational and topological—increases exponentially as more and more oriented or cyclodirectional rings are added to either [*n*]rotaxanes or [*n*]catenanes.

2.2. Mechanically Planar Chirality

Whereas orientational mechanostereoisomers require rings that are desymmetrized across the plane of their cavity, mechanically planar enantiomers require rings that lack mirror symmetry across any plane orthogonal to the ring's cavity. Such rings are said to be "cyclodirectional", denoting a polarity in the sequence of atoms constituting the macrocycle. It is noteworthy that chirality and cyclodirectionality are not equivalent. Although CDs are chiral, an achiral yet cyclodirectional ring may combine with an appropriate achiral yet sufficiently desymmetrized dumbbell to produce this emergent type of chirality.

The mirror-image enantiomers of cartoonized mechanically planar chiral [2]rotaxanes with achiral yet directional component parts are illustrated in Figure 2. Employing vocabulary inspired by Prelog [68], rotaxanes expressing this type of asymmetry have been described [69–74] as "cyclochiral", or having "cycloenantiomers" and "cyclodiastereomers". This language can be misleading because cycloenantiomers are macrocycles [75], not rotaxanes. After Takata [76] described it as a form of planar chirality, Goldup [77] proposed the term "mechanically planar" to differentiate this kind of rotaxane-specific chirality from more classical forms of planar chirality. Left-handed and right-handed co-configurations of mechanically planar rotaxanes are written as (R_{mp}) and (S_{mp}), respectively, where the subscript "mp" denotes mechanically planar. The assignment of absolute co-configuration relies on Cahn–Ingold–Prelog [78] rules to define the directionality of each component part.
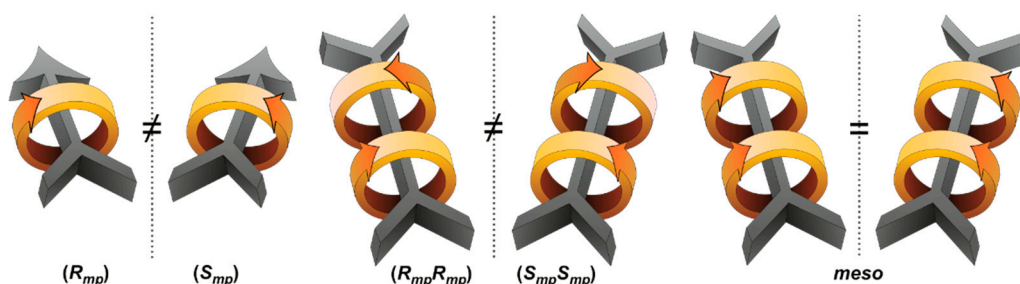

Figure 2. Illustration of enantiomeric mechanostereoisomers possessing mechanically planar chirality. A [2]rotaxane requires an oriented dumbbell, while a [3]rotaxane does not.

CD cyclodirectionality is attributable to the polarity of the glycosidic bonds linking glucose subunits. This cyclodirectionality means that any CD-based [2]rotaxane capable of orientational isomerism necessarily possesses mechanically planar chirality. A collection of [2]rotaxanes from Anderson [48,79] (**R5³⁻**, **R11**), Zhao [80–82] (**R546a-c²⁻**), Tian [83–85] (**R7³⁻**, **R8²⁻**, **R9³⁻**, **R10²⁻**), Park [86] (**R12⁺**), and Mezzina and Lucarini [87] (**R13**) are shown in Figure 3 as examples of [2]rotaxanes that were isolated as pure orientational isomers (and therefore also as single mechanically planar enantiomers).
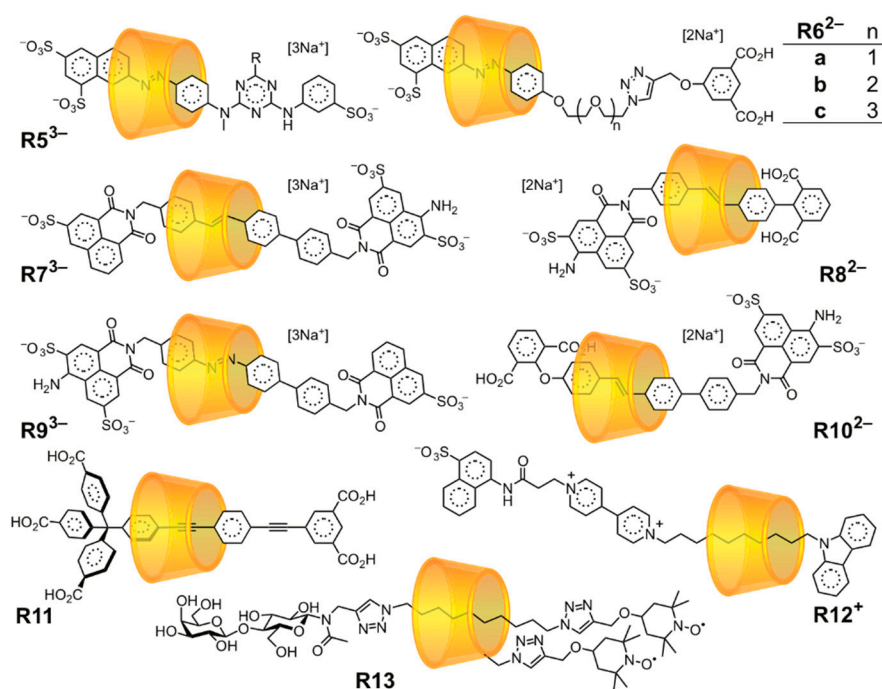

Figure 3. Examples of mechanically planar chiral [2]rotaxanes based on α-CD, all isolated as single orientational isomers [48,79–87].

Although flipping the orientation of the CD ring in these rotaxanes would change the mechanically planar chirality from R_{mp} to S_{mp} or vice versa, the two orientational isomers are not enantiomers (they are diastereomers). CD rotaxanes are never obtained as mixtures of mechanically planar enantiomers because cyclodextrins are homochiral; the mirror-image cyclodextrin of opposite chirality (and opposite cyclodirectionality) does not exist.

Mechanically planar chirality can arise in [3]rotaxanes even if the dumbbell is not oriented, depending on the relative orientation of the rings (see Figure 2). If both rings are oriented in the same direction, an achiral meso structure is obtained, but two rings with opposing cyclodirectionality will give either of two topological enantiomers. Head-to-head and tail-to-tail orientational isomers of [3]rotaxanes therefore possess a mechanically planar chiral architecture, regardless of the dumbbell's constitution.

2.3. Topological Chirality

In catenanes, the conceptual equivalent of mechanically planar chirality is topological chirality. A groundbreaking 1961 paper by Frisch and Wasserman [88] marked the birth of a new subfield called "chemical topology", which applies mathematical topology to molecular structure. Topology characterizes the attributes of an object that remain invariant throughout continuous deformation, which allows bonds to compress, stretch, or bend without breaking, intersecting, or crossing, whereas conventional stereochemistry typically deals only with Euclidean geometry. A number of reviews [69,88–99] are available on topological stereochemistry.

In mathematics, the topology of a catenane is called a link. A link can be either conditionally or unconditionally chiral. Conditionally chiral links do not have inherently chiral topologies, as unconditionally chiral links do. The simplest [2]catenane (known in mathematics as a Hopf link) is not a chiral topology. In order for a Hopf link to have conditional chirality, therefore, its rings must be directionally oriented. Interlocking a cyclodirectional CD with a second cyclodirectional ring will therefore lead to conditional topological chirality.

Most examples [63,64,100–102] of CD [2]catenanes do not possess a second cyclodirectional ring. However, Kuhnert and Tang [103] have created diastereomeric [2]catenanes (**RRRRRR**)-**C3** and (**SSSSSS**)-**C3** (Figure 4) by [3+3] cyclocondensation of *trans*-1,2-diaminocyclohexane and terephthalaldehyde in the presence of β-CD to form the hexaimine macrocycle known [104] as trianglimine. The corresponding trianglamine catenanes were also obtained and characterized by reduction of the imine bonds. By using pure (*RR*)- or (*SS*)-diaminocyclohexane during cyclocondensation, it is possible to capture either the *all-R* or *all-S* enantiomer, respectively, of the trianglimine in β-CD. Since β-CD is also a chiral macrocycle, these two catenanes are diastereomers rather than enantiomers. Although the authors did not comment on the presence of orientational isomers or their distribution, the cyclodirectionality of the trianglimines should lead to two possible orientational isomers for each of these catenanes. Since both rings are cyclodirectional, these orientational isomers are also topological isomers.
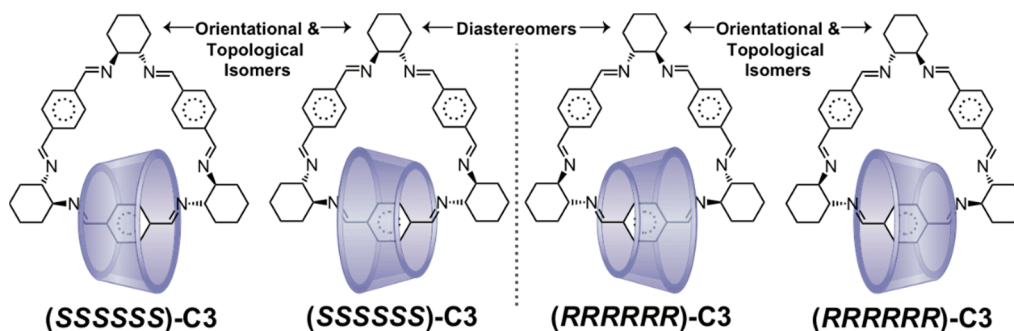

Figure 4. Each diastereomer of the trianglimine/β-CD [2]catenane **C3** may also exist as a pair of orientational and topological isomers arising from the cyclodirectionality of both interlocked macrocycles.

While linear [3]catenane also represents an achiral topology, [3]catenanes can also display conditional topological isomerism if at least two rings are oriented [105]. Thus, the seminal CD [3]catenanes [63,64] (see Section 2.1.4) provide another example of conditional topological isomers. Compounds **[3]C2a** and **[3]C2b** are not only orientational mechanostereoisomers, but also conditional topological isomers, since their peripheral CD rings are oriented by the polarities of their glycosidic bonds.

It is worth noting that the Solomon link [106] is a doubly interlocked [2]catenane with an intrinsically chiral topology. Although Solomon links can be prepared from rings that encapsulate two guests, and γ-CD is known [107,108] to bind two guests, a CD-based Solomon link has not yet been reported.

3. Applications of CD Symmetry Breaking in Mechanomolecules

It is clear that the symmetry-breaking effect of the cyclodextrins has interesting (mechano)stereochemical implications. Here we briefly discuss applications that take advantage of this effect in stereoselective synthesis (see Section 3.1) and the biased directional motion important for molecular machine prototypes (see Section 3.2) and advanced materials (see Section 3.3).

3.1. Stereoselectivc Synthesis

A reaction is said to be stereoselective [34] if one stereoisomer is preferentially formed over another. The symmetry-breaking effect of the cyclodextrins often leads to stereoselective reactions, especially regioselectivity (see Section 3.1.1) in the modification of the CD ring, and orientational selectivity (see Section 3.1.2) with respect to the ring direction.

3.1.1. Regioselectivity

Reactions for the selective modification of cyclodextrins almost always occur via the hydroxyl groups. Regioselective reactions around the cyclodextrin ring are challenging to achieve because the hydroxyl groups at the 2, 3, and 6 positions of the glucopyranose rings may have similar reactivities. Nevertheless, researchers have managed to find ways [109] to achieve mono-, di-, tri-, or per-substitution selectively at either the primary or the secondary face of CDs. These regioselective modifications have afforded an opportunity to create novel covalently bridged rotaxane architectures and exercise even greater control over their structures.

The regioselective mono-functionalization of CDs has facilitated the synthesis of [1]rotaxanes, wherein axles are covalently bonded to the encircling rings. Kaneda [110] and Easton [111] independently first exploited the regioselective alkylation of α-CD to make [1]rotaxanes in 2003. Tian [112] has also prepared a *β-CD*[1]rotaxane. Terao [27,113–122] has developed an extensive family (Figure 5) of oligo- and poly[1]rotaxanes **R14-R26** with fully π-conjugated phenylene–ethynylene backbones. Polyrotaxanes possessing π-conjugated (semiconducting) backbones are known [123] as insulated molecular wires (IMWs). An advantageous outcome of using CDs to make [1]rotaxane monomers is that their regioselective functionalization leads to the formation of mechanostereochemically pure orientational isomers. Fixing the rings to the backbone allows one to exercise perfect control over the location and orientation of the insulating CD beads that protect the inner molecular wire. Note that all of these compounds also exhibit mechanically planar chirality (see Section 2.2).
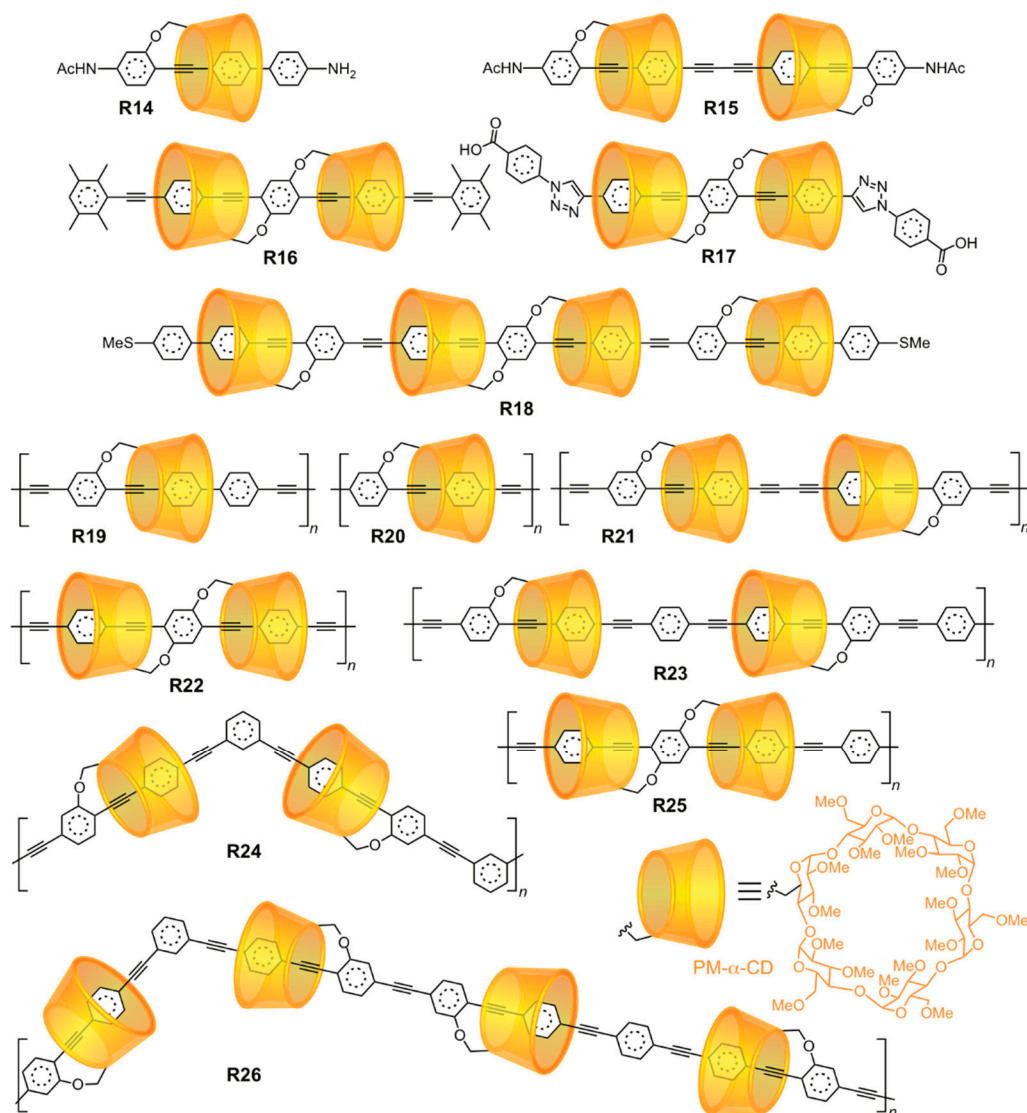
Figure 5. The regioselective functionalization of α-CD enables the development of [1]rotaxanes that engender a high degree of control over the orientation and location of the rings surrounding phenylene–ethynylene insulated molecular wires (IMWs).

Another group of mechanomolecules enabled by the regioselective functionalization of CD with CD-binding moieties are known [124,125] as daisy chains (Figure 6), in which two or more self-complementary ring-axle dyads are cross-threaded into cyclic (denoted [*cn*]daisy chain) or acyclic ([*an*]daisy chain) structures. Kaneda [126] and Harada [127] independently and almost simultaneously introduced the first α-CD daisy chains (**Na₄R27** and **R28**) as cyclic dimers and trimers, respectively. Harada [128] also obtained the [*an*]daisy chain oligomer **R29** from 2-cinnamoyl-α-CD monomers, possessing up to 10 repeating units. A number of other CD-based daisy chains with these architectures have followed these seminal works [129–133]. Daisy chains are important compounds in the field of molecular machines (see Section 3.3).
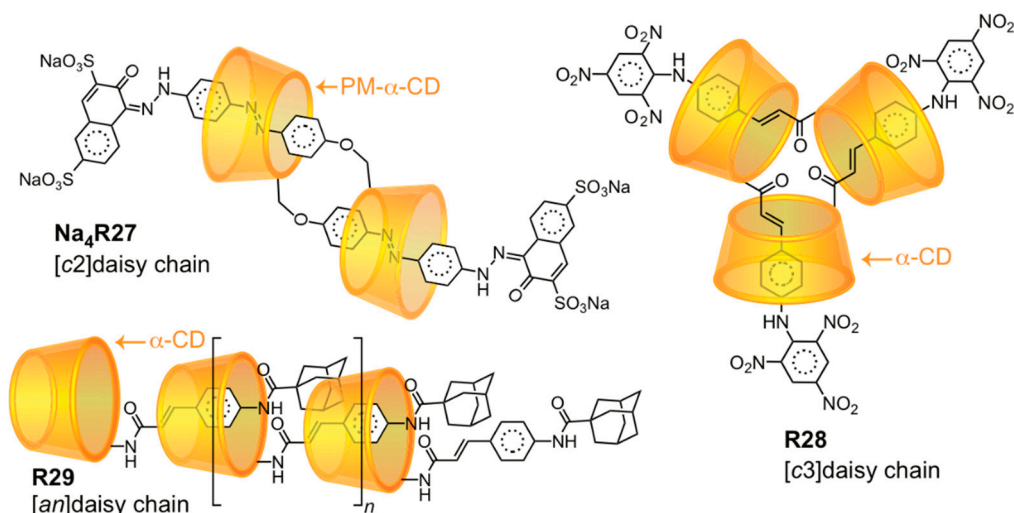
Figure 6. Daisy chain architectures enabled by the regioselective modification of α-CD with CD-binding axles.

3.1.2. Orientational Selectivity

Another kind of stereoselectivity is possible in the synthesis of mechanomolecules capable of displaying orientational isomerism (see Section 2.1). In many cases, the syntheses of CD-based rotaxanes yield predominantly only one orientational isomer. Note that all of the [2]rotaxanes featured in Figure 3 were obtained with high orientational stereoselectivity.

A number of [3]rotaxanes (Figure 7) have also been obtained with high orientational selectivity. Anderson [49] achieved the first mechanostereoselective synthesis of the [3]rotaxane **R30** as the tail-to-tail orientational isomer. Tian [50] has also observed high orientoselectivity in the synthesis of tail-to-tail α-CD [3]rotaxane **Na₃R31**. In contrast, Anderson's oligophenylene(ethynylene)/α-CD [3]rotaxane was obtained [48] solely as the head-to-tail orientational isomer **R32** by solid-phase synthesis. Finally, the head-to-head isomer of **R33**, as reported by the group of Takata, [51] has been characterized in the solid state (Figure 7e) by X-ray crystallography.
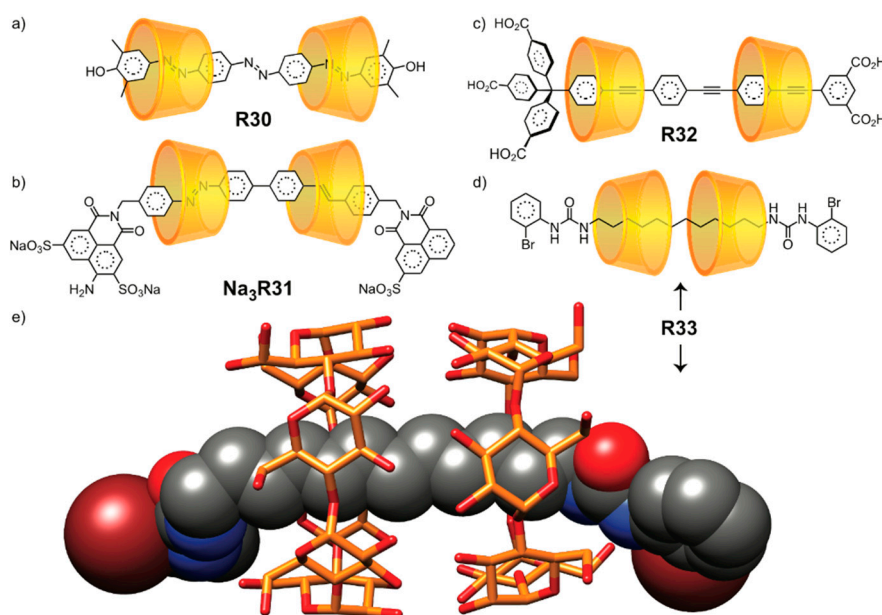

Figure 7. Examples of [3]rotaxanes obtained as single orientational isomers with high selectivity in tail-to-tail (**a**,**b**), head-to-tail (**c**), and head-to-head (**d**,**e**) arrangements.

3.2. Mechanostereoselectivity—Biased Directional Motion

Mechanostereoselectivity is a term introduced by Stoddart [30,134,135] to describe the biased directional motion of component parts in mechanomolecules. An intramolecular motion in a catenane or rotaxane is mechanostereoselective if it happens faster along one pathway than another. The term "unidirectional" is problematic when describing the kind of biased Brownian motion undergone by molecular machines, because a net displacement does not imply a linear path. Indeed, the component parts of a mechanomolecule move incessantly and randomly in many directions at all times. The minimum requirements for biased Brownian/mechanostereoselective motion are non-equilibrium conditions and a source of broken symmetry. Thus, the symmetry-breaking effect of cyclodextrin may lead to mechanostereoselective motion in mechanomolecules if they are made to be stimulus-responsive for the design of artificial molecular machines.

The mechanostereoselective translation of an α-CD ring along the dumbbell of a [2]rotaxane was first observed (Scheme 6) by Anderson [136]. The α-CD ring travels only head-first along the symmetrical isophthalate-stoppered stilbene dumbbell of **(E)-R34^{4-}** upon photoisomerization to **(Z)-R34^{4-}**.
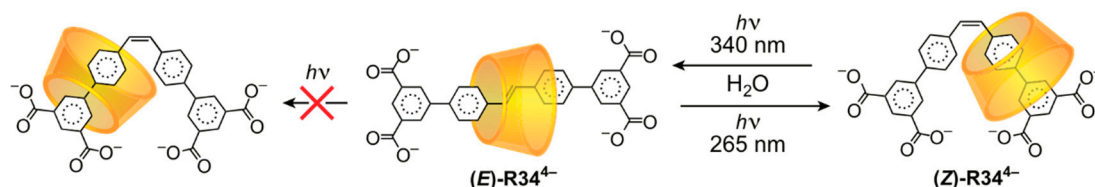
Scheme 6. The mechanostereoselective translation of α-CD in a head-first direction upon photoisomerization of a *trans*-stilbene unit in the dumbbell.

When stimulus-responsive features are incorporated into a daisy chain, the mechanostereoselective motion of each component part can lead to a net contraction or extension in molecular length, serving as the basis for rotaxane-based artificial molecular muscles [137]. Several examples of daisy chain molecular muscles based on α-CD are illustrated in Figure 8.
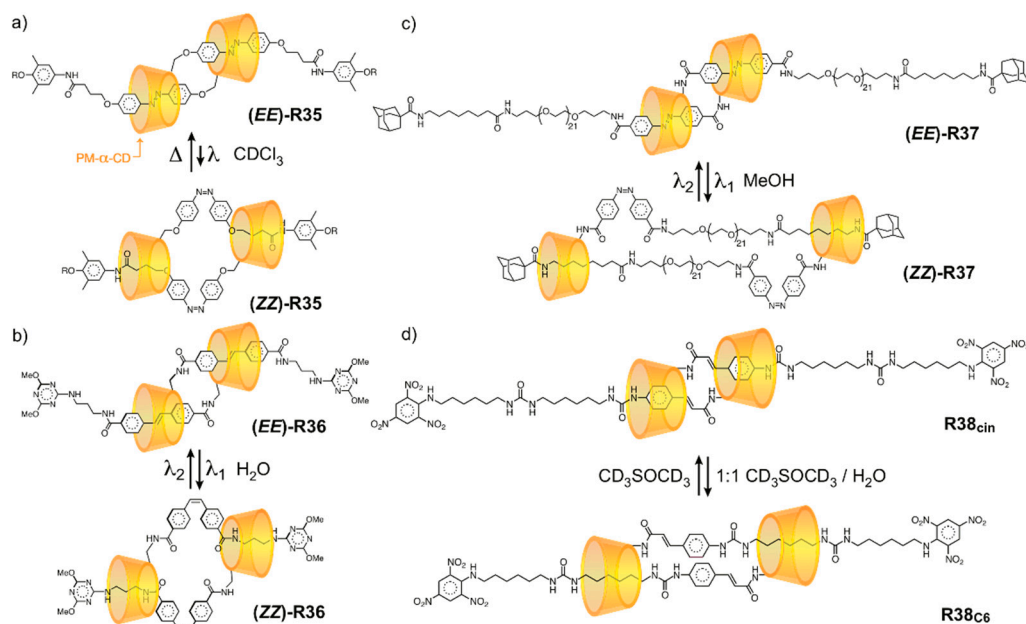

Figure 8. Switchable [*c*2]daisy chain "molecular muscles" undergo contractions in molecular length on account of the antiparallel face-selective translation of each α-CD ring.

In Kaneda's daisy chain **(EE)-R35** [131], the self-complementary monomers comprise permethylated a-CD (PM-a-CD) rings linked directly to *trans*-azobenzene units. The **(EZ)-R35** and **(ZZ)-R35** isomers emerge (Figure 8a) in 20% and 5% yields, respectively, upon irradiation at 366 nm, owing to the E→Z photoisomerization of one or two azobenzenes. Easton's daisy chain **(EE)-R36** operates [130] analogously (Figure 8b), but the more stable nature of the photoactive stilbene unit allows **(EE)**, **(EZ)**, and **(ZZ)** isomers to be isolated and characterized as pure compounds. The hydrodynamic radius (R_H) in water is shortened from 4.4 nm in Harada's **(EE)-R37** to 3.6 nm in **(ZZ)-R37**, which is populated (Figure 8c) with up to 85% efficiency in the photostationary state in MeOH [133]. Harada [132] also made a solvent-switchable daisy chain **R38** in which the α-CD rings encircle cinnamamide units in CD_3SOCD_3, but migrate to a peripheral hexamethylene chain upon addition of water, affording a net contraction (Figure 8d) driven by the hydrophobic effect.

In 2005, Harada's group [44] noticed that α-CD passes head-first over a 2-methylpyridinium stopper onto a decamethylene chain much more quickly than it threads tail-first. At lower temperatures, this rim-selective difference in threading kinetics allows one to obtain only one orientational isomer of the corresponding pseudo [2]rotaxane (Scheme 7). At elevated temperatures, however, tail-first threading becomes allowable and the system gradually equilibrates to an equal mixture of orientational isomers. A similar face-selective translation has been observed in several other pseudorotaxanes with similar directionally biased barriers [138–140]. The temperature-sensitive process of a ring threading onto an axle over a size-matched barrier is known [141,142] as "slippage". The mechanostereoselective motion can be utilized for stereoselective synthesis (see Section 3.1); for example, an α-CD [3]rotaxane was obtained [143] as a pure head-to-tail orientational isomer by employing a slippage stopper that favors only a head-first threading.
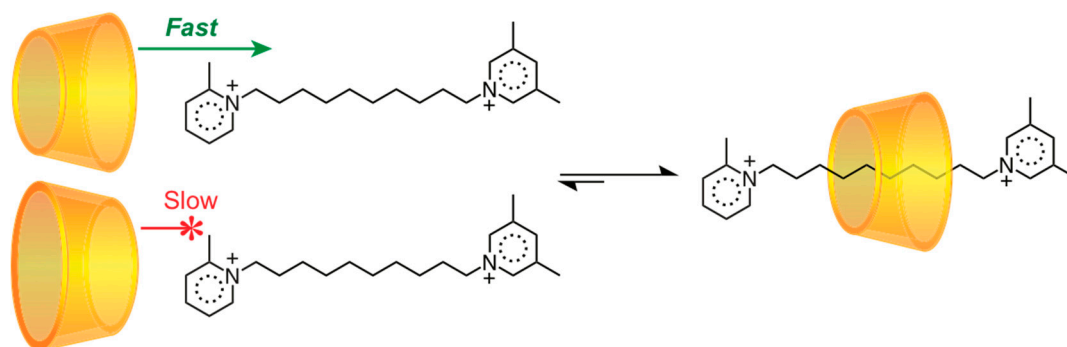
Scheme 7. Face-selective threading of an α-CD ring over a 2-methylpyridinium barrier [44].

3.3. Networked "Slide-Ring" Materials

A "slide-ring" gel [144–147] is a material comprising polyrotaxanes with crosslinked rings. Okumura and Ito [148] introduced this concept in 2001 by crosslinking the α-CD rings of a polyrotaxane with a polyethylene glycol (PEG, MW > 10,000) backbone. While slide-ring materials based on PEG/α-CD are most common [149–156], other systems based on polymers such as polyisoprene [157] and polydimethylsiloxane [158] have also been reported. Slide-ring gels exhibit [159–166] remarkable mechanical properties attributable to the so-called "pulley effect", [167–169] where the translational freedom afforded by the mechanically bonded crosslinks equalizes tension throughout the polymer network. The pulley effect makes slide-ring gels soft and stretchable, yet also tough. The original slide-ring gel [148] could be stretched to 24 times its length.

Although the symmetry-breaking effect of CDs has not been utilized significantly in slide-ring gels, there may be ample opportunity for the unusual stereochemical features and mechanostereoselective motions of CD mechanomolecules to impart these materials with new and unusual properties. One recent example from the group of Harada [170,171] involved an artificial muscle material **R39** comprising polyether networks crosslinked by photoswitchable [*c*2]daisy chains. These networks,

both in hydrogel and aerogel states, contract and bend in the direction of the light source that causes their internal sliding crosslinks to actuate (Figure 9).
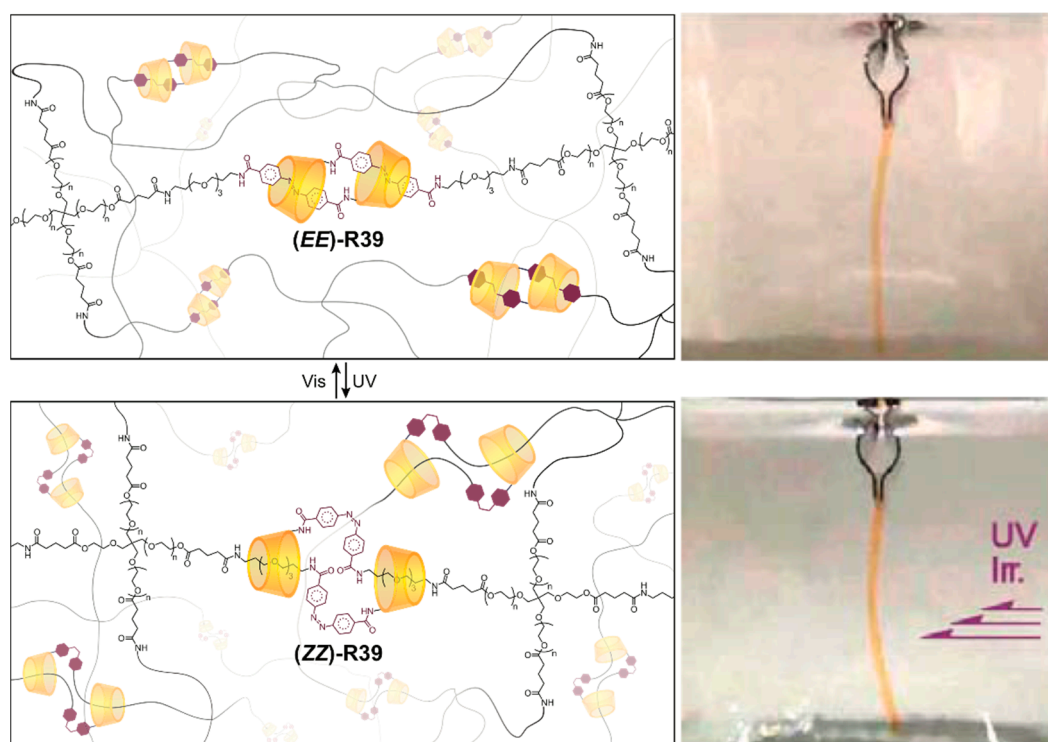

Figure 9. Graphical representation and photographs of a daisy-chain artificial muscle crosslinked polymer network before and after UV illumination, which drives the contractile motion of the crosslinks [170,171].

4. Conclusions and Outlook

It is clear that the symmetry-breaking effect of cyclodextrins, arising from their differentiated faces that lead to orientational isomerism, as well as their cyclodirectional constitutions that lead to mechanically planar and topological chirality in mechanomolecules, has dramatic implications not only on regio-, stereo-, and orientationally selective synthesis and stereochemical analysis of molecular structure, but also on molecular dynamics such as biased (mechanostereoselective) intramolecular motion.

While the cyclochirality and conical shape of cyclodextrins can be advantageous in mechanomolecular chemistry, CDs are not the only symmetry-breaking hosts available. We can consider CD mechanomolecules as a case study and test bed for investigating and leveraging the effects of symmetry-breaking in other molecular systems as well. Symmetry-breaking hosts have been developed based on motifs including calix[*n*]arene [172–182], pillar[*n*]arene [183–187], cucurbit [*n*]uril [188], and cyanostar [189] motifs, and even transmembrane proteins [190]. These materials have much to contribute to the body of knowledge on symmetry breaking in chemical systems.

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