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Mechanochemical Tuning of Binaphthyl Conformation at the Air–Water Interface

Daisuke Ishikawa, Taizo Mori, Yusuke Yonamine, Waka Nakanishi*, David Cheung*, Jonathan P. Hill, and Katsuhiko Ariga*

Abstract: Gradual and reversible tuning of the torsion angle of an amphiphilic chiral binaphthyl, from -90° to -80° , was achieved by application of a mechanical force to its molecular monolayer at the air–water interface. This 2D interface was an ideal location for mechanochemistry for molecular tuning and its experimental and theoretical analysis, since this lowered dimension enables high orientation of molecules and large variation in the area. A small mechanical energy (<1 kcal/mol) was applied to the monolayer, causing a large variation ($>50\%$) in the area of the monolayer and modification of binaphthyl conformation. Single molecular simulations revealed that mechanical energy was converted proportionally to torsional energy. Molecular dynamics simulations of the monolayer indicated that the global average torsion angle of a monolayer was gradually shifted.

Mechanochemistry^[1] is a growing field that involves the use of mechanical forces for operation and control of molecular structures and their resulting properties, instead of the more usually applied stimuli of heat, light or electric potential.^[2–3] Recent advances have been partly derived from a shift towards the use of soft materials (e.g., polymers and liquid crystals) rather than hard materials (e.g., crystals).^[4] Although mechanical forces can be applied to oriented molecules in the crystal state^[5–6] only minor structural (or conformational) changes involving only an up to 1% change in volume are possible, in most cases, prior to loss of crystal integrity (Figure 1a).^[7] In contrast, polymers,^[8–12] and liquid crystals^[13–14] are flexible permitting dynamic variation of their structures and those of their constituent molecules (Figure 1b). Although the flexible nature of soft materials makes their structures capable of undergoing deformation, a molecular level understanding of these processes under an applied force is lacking. Because these systems are not highly ordered (*cf.* crystalline materials), control of the effects of an applied force is less effective, due to the wide range of different conformations and orientations of the molecules.

Although the difficulty of transformation from macroscopic forces to molecular force remains in polymer mechanochemistry, recent work on force-affected reactions with theoretical considerations help quantitative understanding of molecular force.^[15] On the other hand, measurement of the applied force or energy as a cause of mechanochemical phenomena is mainly limited to single-molecule investigations using atomic force microscopy (AFM).^[16–19] We have investigated dynamic molecular structures and their assemblies by applying a force (mechanical energy) to such a structure at the 2D air–water interface (Figure 1c). At the air–water interface, amphiphilic molecules can assemble to form molecularly-oriented films, known as Langmuir-monolayers. The area of the film interface can be varied dynamically at the macroscopic level by applying an external force, although the film thickness is maintained at a nanoscopic molecular level. Application of an external force to the film causes changes in the local minima in the potential energy and can be used quantitatively to tune the molecular structures and hence their properties.^[20] Recently, we have reported that molecular properties can be tuned by applying a mechanical force to a monolayer at the air–water interface.^[21–23] However, although variation of properties should originate from changes at the molecular level, at that time these could be only inferred.

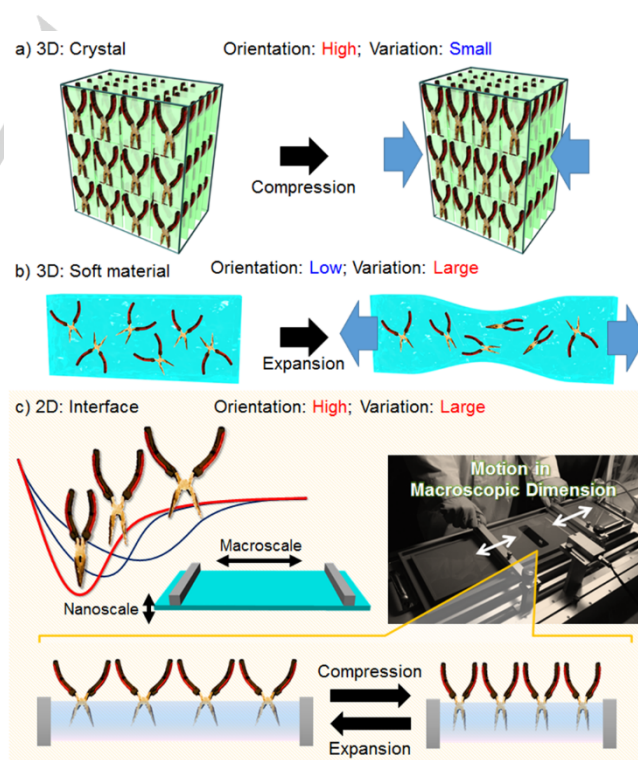


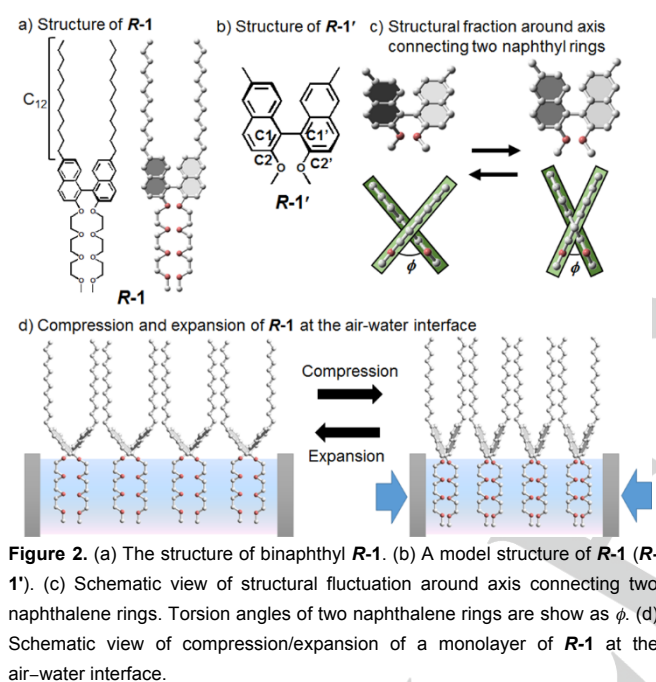
Figure 1. Mechanochemical control of molecular structures. (a) Molecules contained in a 3D crystal: minimal dynamic variation is allowed. (b) Molecules contained in a 3D soft material: relatively wide dynamic range is possible, but molecules are randomly oriented and any applied force is dispersed. (c)

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Supporting information for this article is given via a link at the end of the document.

Molecules at a 2D interface. Molecules are oriented and dynamic conformational variation is allowed: external force is transferred efficiently to individual molecules.

In this work, we have designed and synthesized an amphiphilic chiral binaphthyl^[24] molecule (Figure 2a) whose circular dichroic (CD) activity is directly related to the torsion angle subtended between the planes of its two naphthyl moieties (Figure 2b,c).^[25-26] This feature enabled us to monitor precisely structural changes due to any force applied to its monolayer films prepared at an air–water interface. Ultimately, we demonstrate that the structures of molecules contained in such a monolayer can be precisely controlled by applying only a small mechanical energy (~ 1 kcal mol⁻¹) (Figure 2d).



Chiral amphiphilic binaphthyl **R-1** (Figure 2a) was synthesized from commercially available (*R*)-1,1'-bi-2-naphthol (see the Supporting Information). A monolayer of **R-1** on a water surface was prepared and it was mechanically compressed in situ thus decreasing the area per molecule. A plot of surface pressure vs. molecular area (π - A) of **R-1** on pure water (Figure 3a) indicates a well-condensed phase with a collapse pressure of 42 mN m⁻¹ at a molecular area of 0.68 nm². This area is smaller than the molecular area estimated for **R-1** (0.9 nm² with the optimized structure), which is attributed to its structural variation and partial overlapping of molecules. Molecular area of **R-1** in the monolayer varied in the range 1.4 to 0.68 nm², which corresponds to a 50 % compression of area. Integration of the π - A curve leads to quite precise estimation of the energy of compression (Figure S8, Table S1 in the Supporting Information). The monolayer gradually increased in energy: 0.179 ± 0.002 , 0.526 ± 0.003 , and 0.937 ± 0.009 kcal mol⁻¹ at 10, 20, and 30 mN m⁻¹, respectively.

A surface pressure-dependent increase in the intensity of the CD signal was observed for monolayers transferred to a quartz substrate (Figure 3b). The intensities of CD signals were normalized according to occupied molecular area at the corresponding surface pressure taking into account the effect of the increasing lateral density of the monolayer at higher surface pressures. From the normalized CD spectra of **R-1**, the absolute intensity of the negative peak around 242 nm increased gradually up to 1.3 during compression of the monolayer from 1 to 30 mN m⁻¹. CD activity of binaphthyls is known to be dependent on the torsion angle between the naphthalene planes.^[27-28] Binaphthyls can occupy either cisoid or transoid configurations where torsion angles are respectively less than $|\theta| < 90^\circ$ or greater than $|\theta| > 90^\circ$. The shape of the CD spectra obtained from the transferred monolayers corresponds to a cisoid form, similar to that observed in solution phase. The enantiomer of **R-1** (**S-1**) showed a mirror image of CD spectra upon compression (Figure S7 in the Supporting Information).

Energies necessary for structural variations were estimated by using DFT calculations (Figure 3c) and single point energies estimated using spin-component-scaled (SCS)-MP2^[29] calculations (Table S2 in the Supporting Information). Considering that thermal energy is estimated to be $kT = 0.6$ kcal mol⁻¹ at 20°C, **R-1** fluctuates with a torsion angle in the range -110° to -70° .^[30]

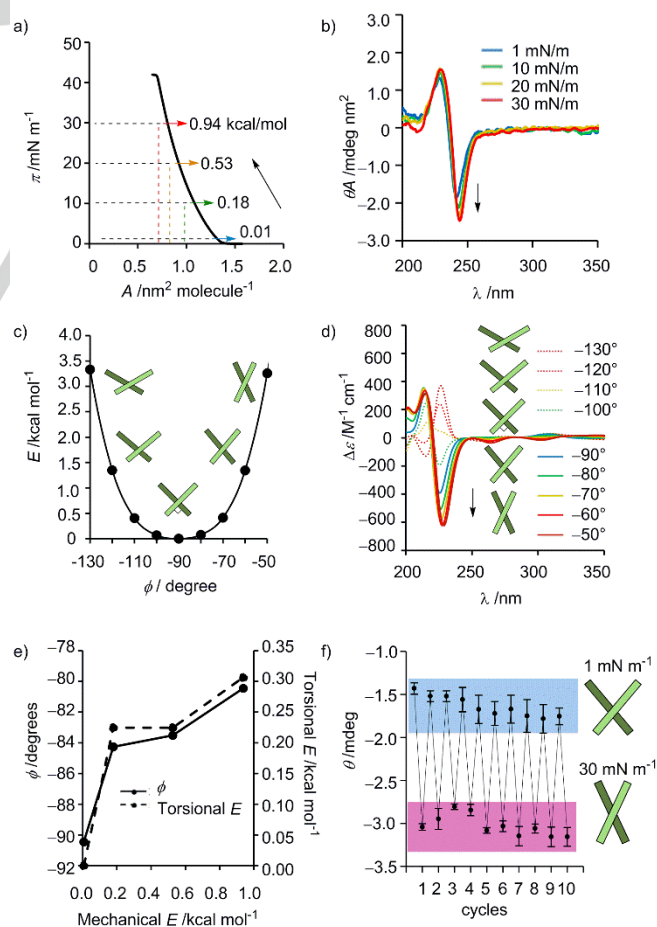
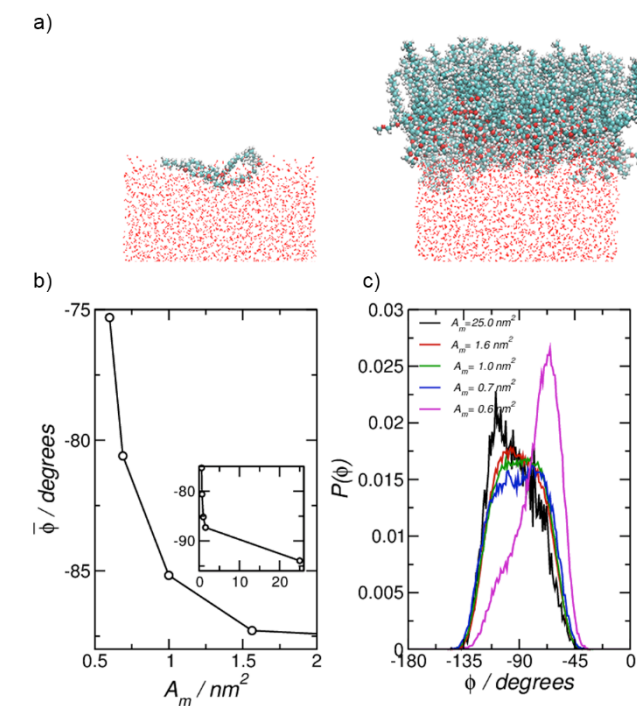


Figure 3. Analysis of the monolayer of **R-1**. (a) Surface pressure-molecular area (π - A) curve of the monolayer. Applied total energies of compression were estimated by integration of π - A curve. (b) CD spectra of monolayers of **R-1** at different surface pressures multiplied by molecular area. (c) Estimated energies (DFT) required for changing the torsion angle (ϕ) of binaphthyls **R-1**'. (d) TD DFT based CD spectral simulations of a model structure **R-1'** as a function of ϕ . (e) Estimated ϕ and obtained torsional energies are shown as a function of applied mechanical force. Torsional energy was estimated from the torsional energy of **R-1'** (single point SCS-MP2). (f) CD intensity during cycles of compression (30 mN m⁻¹) and expansion (1 mN m⁻¹) of **R-1** at the air-water interface. Each point is shown as an average with standard deviations ($n = 3$).

The relationship between structure and CD spectrum based on the torsion angle of the naphthalene planes was investigated using theoretical calculations (Figure 3d). The experimental spectrum of **R-1** in solution matches that simulated based on an optimized structure (Figure S9 in the Supporting Information) obtained using time-dependent density functional theory (TD DFT) calculations using B3LYP/6-31G(d,p). Simulation of CD spectra as a function of the torsion angle was performed for the model compound **R-1** (= **R-1'**, Figure 2b). A comparison of simulated (Figure 3d) and experimental (Figure 3b) CD spectra indicates that an increase in the absolute intensity for **R-1** originates from a structural change in the cisoid direction. It suggests that the torsion angle $|\phi|$ gradually decreases and that the torsional energy gradually accumulates with applied mechanical energy (Figure 3e). The torsion angles ϕ gradually increased from -90° to -80° upon compression (Figure S10 in the Supporting Information for details). Variation in intensity of the CD signals was reversible upon compression and expansion of **R-1** in monolayer (Figure 3f), indicating that the tuning of molecular structure is also reversible at the dynamic air-water



interface.

Figure 4. MD calculations of **R-1** at the interface. (a) The left 3D figure corresponds to a snap shot of the simulation with a large molecular area ($A_m = 25$ nm², a single molecule in a unit box), and the right one shows that of a small molecular area ($A_m = 0.60$ nm², 84 molecules in a unit box). The simulation system is displayed with **R-1** as CPK model and water molecules as sticks. C, H, and O are shown as sky-blue, white, and red, respectively. Only half-side of the unit-box is shown. (b) Average torsion angle for monolayers of **R-1**. (c) Torsion angle distributions from molecular dynamics simulations of monolayers of **R-1**. Black, red, green, blue, and magenta lines denote molecular area $A_m = 25, 1.6, 1.0, 0.69,$ and 0.60 nm², respectively. See the Supporting Information for details.

Molecular structure of **R-1** at the air-water interface was investigated by using molecular dynamics (MD) calculations (Figure 4, see the Supporting Information for details), with compression of the monolayer being simulated by increasing the number of molecules contained in the unit box (Figure 4a). In MD simulations, individual molecules float at the interface occupying a large molecular area, but stand perpendicular to the interface in a small molecular area when contained in the monolayer, reproducing the common tendency of amphiphilic molecules.^[31] The average value of the torsion angle varied gradually (Figure 4b) from -90° to -80° going from the molecular area of 25 nm² to 0.60 nm². The values estimated by MD calculations are consistent with the values estimated from the experimentally obtained CD signals shown above. The wide ranges of angles under each set of conditions (Figure 4c) are also consistent with binaphthyls according to their broad potential energy profile.^[30]

In summary, mechanical tuning of the binaphthyl structure over a range of torsion angles between -90° and -80° was achieved, and is supported by experimental and theoretical analyses of molecular area, energies, and CD intensities. By using the 2D air-water interface where dimensionality is reduced from 3D space, structural changes within molecular assemblies were analysed as a function of surface pressure and applied mechanical energy. Although the maximum pressure that can be applied is limited until the collapse the monolayer, we have shown that a 2D air-water interface is an ideal location to perform mechanochemistry in the analysis and control of molecular structures and their assemblies under small forces where molecular conformations concerns. This is because of the unique features of molecular orientation control and dynamically variable area of the medium available using the 2D air-water interface. The former is critical for the transformation of an external force into a structural change while the latter permits dynamic tuning of molecular structure. Although the structural change described here in binaphthyl **R-1** is modest (but still larger than available in crystals), this variation in structure (10°) can lead to important effects on molecular recognition processes where only small structural changes can be significant. Small force that control conformation is important not only for chemistry but also in biology: pN level of force has reported to change the conformation and function of protein.^[33] We expect that the air-water interface as a field for mechanochemistry can open a new field for mechanochemistry that can control conformations and related functions. Apart from structural tuning, energy conversion for mechanochemically-powered molecular machines is of interest and is currently under investigation in our laboratory (see the Supporting Information).

Experimental Section

General methods, materials, synthesis, NMR spectra, monolayer measurements, computational methods, and Cartesian coordinates are shown in the Supporting Information.

Acknowledgements

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Keywords: interfaces • monolayers • lipids • chirality • biaryl

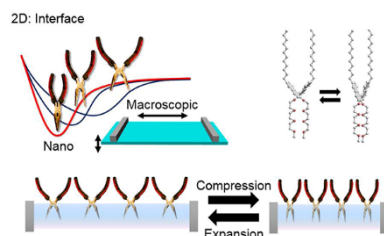
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Entry for the Table of Contents

Layout 1:

COMMUNICATION

2D interface for mechanochemistry: Mechanical force was used for tuning the torsion angle of an amphiphilic binaphthyl, molecular pliers at the air–water interface. The dynamic and repeatable control of the structure was achieved.



Daisuke Ishikawa, Taizo Mori, Yusuke Yonamine, Waka Nakanishi, David Cheung*, Jonathan P. Hill, and Katsuhiko Ariga**

Page No. – Page No.

Mechanochemical Tuning of Binaphthyl Conformation at the Air–Water Interface