Chapter 26
Interplay of Photoisomerization and Phase Transition Events Provide a Working Supramolecular Motor

Yoshiyuki Kageyama

Abstract Autonomous molecular-based microrobots have not been created despite progress in our understanding of the chemistry of molecular motors and machines. In the field of chemistry, the design and synthesis of molecular structures remain an ongoing and diverse challenge. The creation of a system in which molecular structures interact represents an additional challenge. In order to functionalize a molecule for a motor, it must be exposed to a specific reaction field. Synchronization of the molecules involved is also required. In this chapter, we discuss our research results on self-oscillatory flipping motions of azobenzene-containing assemblies. Briefly, reversible photoisomerization of an azobenzene derivative occurs under steady light irradiation. In coordination with phase transition events, a cycle modulated by the components involved leads to repetitive structural changes. When this azobenzene-based assembly is placed in water, the assembly exhibits autonomous swimming. This macroscopic light-powered motion is the result of the self-organization of a large number of nanometer-scale molecules and it provides an example of the potential for mechanical work to be performed by molecular assemblies. We subsequently describe the driving concept of far-from-equilibrium dynamics, namely a dissipative structure by which a spatial pattern maintains dynamic behavior to drive the mechanical motion observed.

Keywords Molecular motor · Self-organized motion · Hierarchical structure · Azobenzene photoisomerization · Collective dynamics · Active matter · Limit-cycle dissipative structure

Y. Kageyama (✉)
Faculty of Science, Hokkaido University, Sapporo, Hokkaido 060-0810, Japan
e-mail: y.kageyama@sci.hokudai.ac.jp

26.1 Introduction

26.1.1 *Achieving Mechanical Work with Molecular Motors*

The creation of active matter and active transporters is currently an exciting area of research. For chemists, the synthesis of molecules which continuously and mechanically perform work is a fundamental task in the preparation of such active molecular devices. From this viewpoint, synthetic molecular motors have been proposed to date [1–3]. Similar to the enzymatic molecular motors in biological systems, molecular motors generally involve a molecular-based catalyst which spontaneously repeats a cyclic structural change while converting a source of energy (e.g., a chemical substrate, electric power, or light) into mechanical energy. The mechanical energy generated by these molecular motors is the sum of kinetic energy and potential energy. In this chapter, the definition of "molecular motor" extends beyond the traditional focus on salient and repetitive structural changes in molecules (Fig. 26.1). For example, if a molecule achieves even a small structural change that converts energy to mechanical potential energy, it is considered a molecular motor in this chapter. Conversely, a molecule that does not attain an energy conversion to mechanical energy will not be considered a molecular motor in the near future, even if chemists traditionally recognize it as a molecular motor. The latter is based on the observation that molecular motors have traditionally been defined based on structural equations of molecules, and not necessarily on actual and realized functions.

In addition to light-powered molecular motors (or rotators) described by Feringa [4–9], several light-powered [10, 11], redox-activated [12–14], and chemical-fueled [15–17] molecular motors have also been proposed. Chemical-fueled molecular motors provide work with a small supply of energy, and thus, the development of
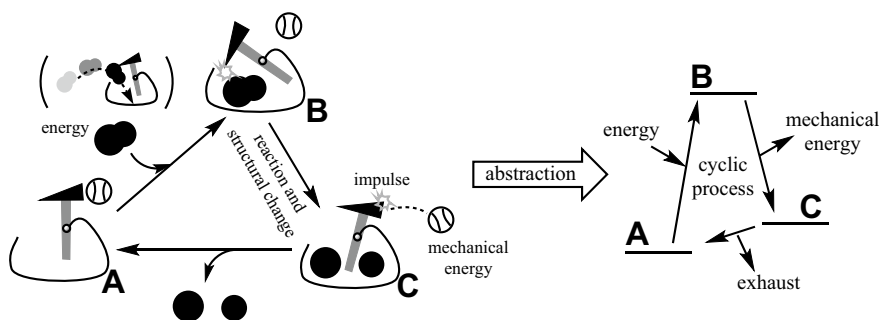

Fig. 26.1 Basic concept of the molecular motor model discussed in this chapter. Left: An illustration of an object which accomplishes a mechanical task by consuming a substrate. A, B, and C indicate the states (structures) of the molecule or super-molecule which constitutes the motor. In this chapter, we also describe molecules which do not produce mechanical work or exhaust as a type of molecular motor

such motors is of great interest. To achieve spatially unidirectional motion of a molecular motor, molecular-level chirality is key. However, it is not sufficient due to the principle of microscopic reversibility. To realize an effective and powerful molecular motor that performs work, a nonlinear process is required in the motor system to control the reverse process [18–20]. Recently, time-delayed chemical processes, such as that employed in a "molecular information ratchet" [16, 21–24], have been considered a good choice for generating molecular motors [25–28]. To date, light-powered motors have been developed more rapidly than chemical-fueled motors. This is partly because microscopic reversibility is not a concern for light-powered molecular motors [25, 29–31].

However, even if excellent molecular motors are identified, the task remains to have these motors act on another object to produce work. It is a straightforward concept that the mechanical energy of a molecular motor in a monodispersed solution is converted immediately to thermal energy, without mentioning the physical principle of Onsager's reciprocal relation [25, 32]. Given the importance of friction for actual work, it is important that the spatial and temporal scales of a working system be considered. A relative size difference between a motor and an object is required in a mesoscale system. The concept represents a challenge in the field of molecular motor research. One promising approach is to place a molecular motor on a large substrate and construct an anisotropic reaction field [33]. A pioneering example is light-powered electron transportation through a vesicular membrane to generate a proton-motive force [34, 35] or electromotive force [36]. In this model, the molecular motor (generally referred to as the "sensitizer") cyclically changes its shape as a result of changes in structure to achieve an excited state, followed by the generation of a radical/ion state. These cyclic changes are represented with triangle, square, and circle symbols, respectively, in Fig. 26.2a. Another well-known example involves the long-term rotation of small rods on cholesteric liquid crystals with light-powered molecular motor dopants [37–40]. To achieve a continuous motion with relative size difference, synchronization of molecular motion is required (Fig. 26.2b). If molecular-level motions are not synchronized, the system falls into a static steady-state and no further mechanical motion is expected (Fig. 26.2c). Thus, it is necessary to keep a system far-from-equilibrium state via a nonlinear process [41].

26.1.2   Motion of Macroscopic Objects

In this chapter, we focus on the synchronization of molecular motors in regard to a "photosynergetic" aspect. As mentioned above, one of the advantages of chemical-fueled molecular motors is their energy efficiency. In cooperation with thermal fluctuations, the energy efficiency of structural transitions can potentially reach up to 100% [42]. However, it is rather difficult to accommodate the injection and elimination of chemical substrates when constructing an artificial motorization system in a solid phase. To date, most studies of self-organized motion using chemical processes have
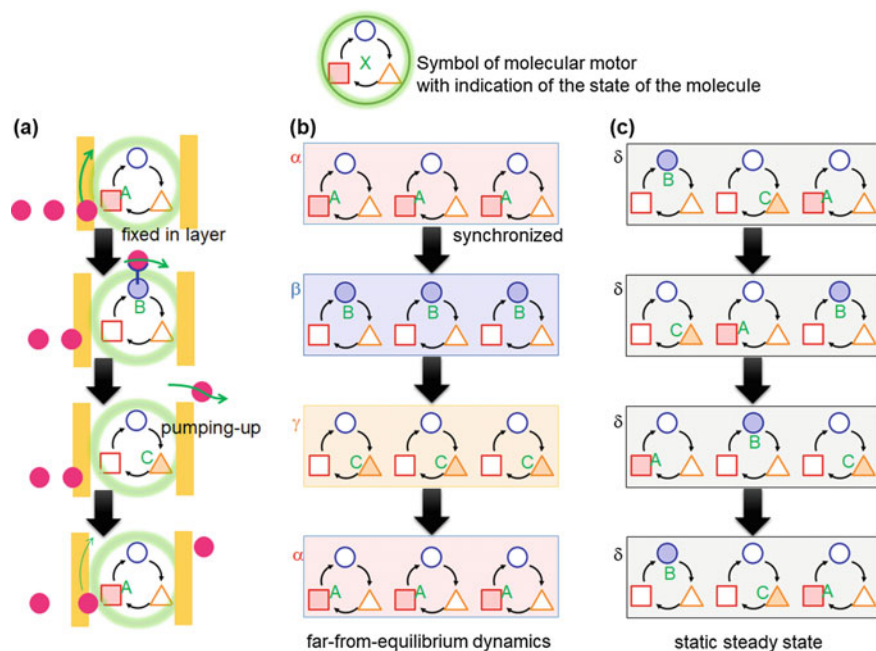
Fig. 26.2 Strategies for achieving mechanical work by a molecular motor. **a** Molecular motors can work individually by being placed in an anisotropic reaction field. This concept is realized in transport systems that exist across biological membranes. **b** Mesoscale materials can assemble into molecular motors. By synchronizing a molecular motor to create a cyclic process, a mesoscopic supramolecular motor is expected to be realized. **c** If a system does not achieve synchronization, the material will not produce a work function

used systems constructed in a liquid phase, or systems which employ diffusion and a surface-based reaction [43]. In contrast, a light-powered molecular motor has its fuel supplied in a bulk phase without contact or discharge being an issue. To achieve work by a molecular motor, synchronizing of motor function is a fundamental issue. Therefore, the use of light-powered molecular motors is preferred given the current chemistry available, despite the low energy efficiency of these motors.

To date, macroscopic, continuous dynamics of synchronized light-powered molecular motors have mainly been realized by using polymer films [44–51]. In these studies, a self-shading mechanism where light triggers a morphological change in a polymer causes auto-switching of light-absorption efficiency. An overview of the periodic cycle for this model is summarized in Fig. 26.3. The relative location of the light source, the polarization state of the light, and/or the anisotropic structure of the polymers involved provoking the structural change which occurs. It is important to note that it is a shape change that affects the light-receiving property to modulate the region for photoreaction and its reaction velocity. As a result, repetitive dynamics are observed. In a system exhibiting periodic motion, a time delay, existing in relation to the change in polymer shape which occurs after isomerization
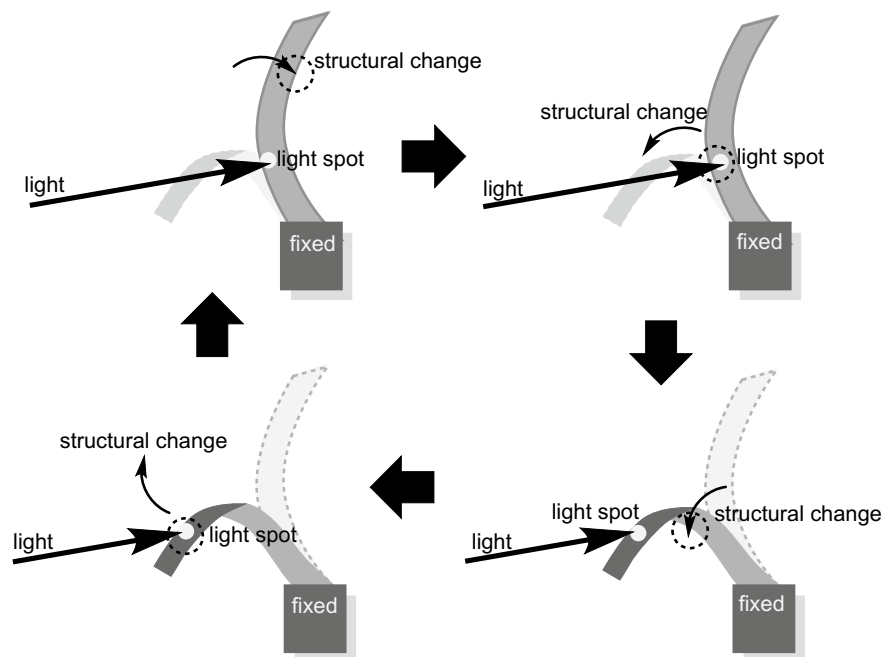
Fig. 26.3 Schematic illustration of a cycle which provides self-continuous flipping motion of light-responsive polymers fixed on a solid stage. The motion is powered by directional light. Structural changes occur after photoisomerization, and this automatically induces a change in the irradiated face (position)

of the molecule, prevents the system from reaching equilibrium [52]. However, if the polymer's structural change occurs within the same time span as the photochemical process involved, the system will not achieve self-continuous dynamics. Indeed, the experimental results described by White and coworkers indicate that a decrease in incident light intensity slows down the photochemical process and the amplitude from the so-called equilibrium position becomes closer [45]. Very recently, when a polymer film was affixed to a solid frame, locomotive objects working on a solid surface [51] or a water surface were realized. In these systems, the direction of motion was determined according to the direction of the incident light.

As shown above, "reversible molecular transformation", "spatial anisotropy", and "time-delayed switching of reaction efficiency" are a set of conditions that are required to achieve a system with self-continuous macroscopic dynamics. By applying this set of requirements to an object, autonomous work independent from direction by external anisotropy is expected. Unfortunately, there have been very few examples of successful systems. However, our group previously reported a self-oscillatory flipping motion by azobenzene assemblies under steady light irradiation [53]. Thus, a discussion of our ongoing research and results for the latter light-powered motion system is subsequently provided.

26.2 Realization of Self-Oscillatory Flipping Motion of Azobenzene Assemblies

The theory of self-organization in continuous dynamics was established based on a series of studies of dissipative structures [54]. This type of structure is dynamic, yet it maintains an ordered configuration, in the presence of an energy source. In regard to photochemical self-oscillation, Nitzan and Ross first proposed that a reversible photochemical process which involves immediate thermal relaxation and a time-delayed reversible thermal process may form a dissipative structure (Fig. 26.4a) [55]. According to their theory, temporal patterns form as follows. A photo-process-induced fluctuation in temperature causes a shift in the equilibrium of a thermal process. The behavior of this system then modulates the velocity of the photo-process. However, under regular experimental conditions, keeping the system from achieving "equilibrium" (namely, achieving an attractive state in the presence of energy supply) is difficult without involving additional processes due to the required steep change in temperature. Experimentally, oscillations in fluorescence have been observed in solutions containing 10^{-3} mol/L solutes [56]. Further studies concluded that convection of light-irradiated solutions in optical cuvettes mediates the fluctuation in fluorescence observed (Fig. 26.4b) [57, 58].

Alternatively, we focused on shifts in reaction rates as a result of phase transitions. Since the reaction rate of a photochemical process depends on the conditions of the molecule involved, a phase shift represents an opportunity to alternate the reaction kinetics of a photochemical process. Correspondingly, a photoisomerization-triggered molecular realignment of an assembly was recognized as a good target for generating a system characterized by self-continuous dynamics.

Azobenzene is a well-known photochromic compound that undergoes a *trans*-to-*cis* and *cis*-to-*trans* photoisomerization event via n-π* excitation. This event generally occurs at a wavelength of 450 nm. We first designed a system composed of an azobenzene derivative and a fatty acid, since the shape of a molecular assembly of fatty acids has been shown to depend on the activity of protons surrounding the assembly [59]. By changing the molecular association externally, a shift in proton
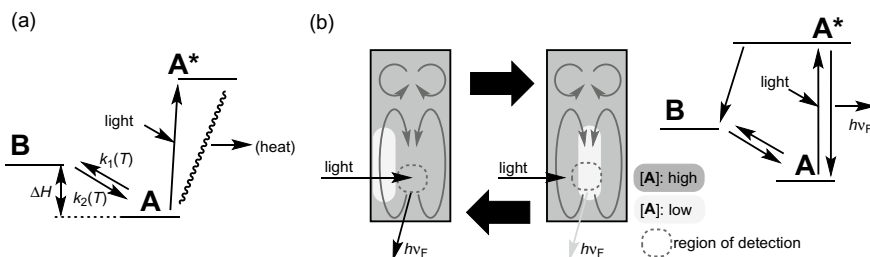

Fig. 26.4 A solution-phase dissipative structure formed by a photochemical process. **a** This model was proposed by Nitzan and Ross in 1973. **b** The model was confirmed experimentally with observations of fluorescence fluctuation

activity and reassembling of molecules are predicted. Correspondingly, our system was designed so that photoisomerization of the azobenzene derivative would trigger realignment of the fatty acid molecules to modulate the kinetics of the photoisomerization events. A helical assembly of oleic acid (**1**) and an amphiphilic azobenzene (**2**) never showed repetitive motion under steady light irradiation [60]. Rather, a multi-step recoiling motion was observed involving acid-dissociation behavior of a carboxyl group [61]. Vesicular, tubular, and block-like assemblies also did not exhibit repetitive dynamics [60]. However, we eventually observed that plate-like assemblies of **1** and **2** exhibited repetitive flips under steady blue-light irradiation (Fig. 26.5) [53].
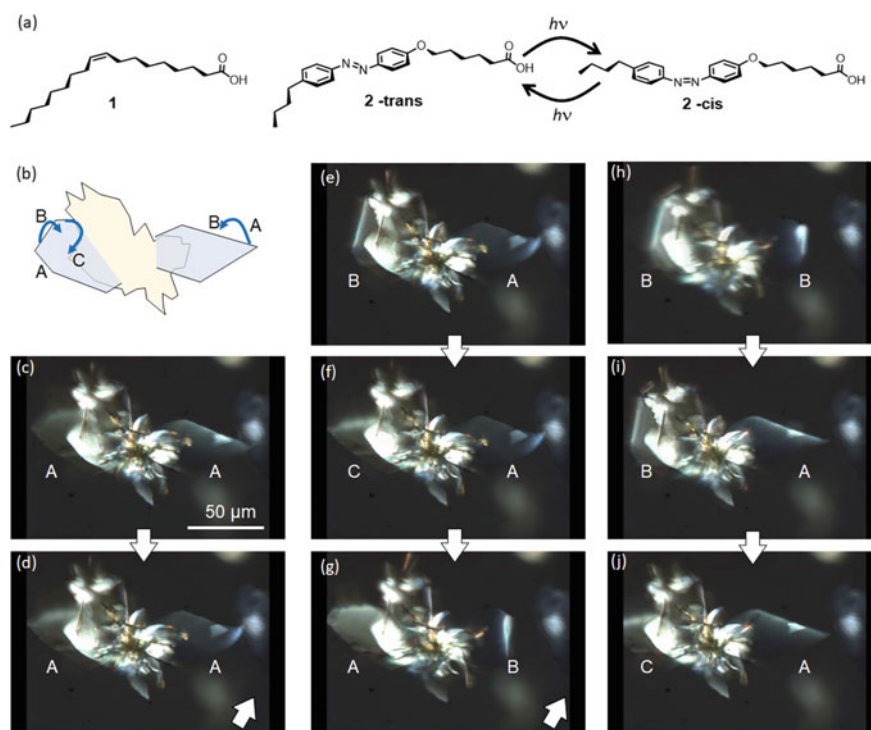

Fig. 26.5 Self-continuous flipping motion observed for a co-assembly of oleic acid (**1**) and an azobenzene derivative (**2**) by Ikegami in 2016 [53]. **a** The chemical structures of **1** and **2** are shown along with the photochromism step of **2**. **b** A generalized illustration of the flipping motion of azobenzene with states A-C and A and B indicated. **c**–**j** Video imaging of the flipping motion of a **1** crystal detected with a differential interference contrast microscope equipped with a mercury lamp unit ($\lambda_{irr} = 435$ nm). The left side of the crystal exhibited alternating flips (cyclically around A, B, and C), while the right side of the crystal exhibited singular flips between the A and B states. A video is available from the website listed in Ref. [53]

26.3 Mechanism for Self-Continuous Flipping Motion

A co-assembly of molecules **1** and **2** leads to two types of self-oscillatory flipping motion under blue-light irradiation [53]. One type involves a single flipping event, while the second type involves a multi-step flipping event. The mechanistic study described in this section targets the singular flipping motion, while the multi-step motion is described below in Sect. 26.4, and in further detail in [62]. When a dispersion of the co-assembly was analyzed in situ with X-ray diffraction (XRD), the small-angle profile showed one-peak and two-peaks in the dark versus under blue-light irradiation, respectively (Fig. 26.6a). These results indicate that a new phase co-exists with the original phase under light irradiation. Figure 26.6b shows the time-course behavior of the self-oscillatory motion detected under various intensities of steady 435-nm light. Figure 26.6c shows the time-course behavior of another assembly under 435 and 470-nm light, while Fig. 26.6d shows the time-course of thermal behavior of the co-assembly after light irradiation. Taken together, these results indicate that one-cycle of the flipping motion of the co-assembly consists of four steps. Step 1 is a *trans*-to-*cis* photoisomerization event, while step 3 is a *cis*-to-*trans* photoisomerization event. Meanwhile, reversal of the isomerization events occurs due to phase transitions that occur in steps 2 and 4. These transitions are caused by shifts in the kinetic properties of **2**. Slope values for the logarithmic relationship between incident light power and the duration times of steps 1 and 3 are 1 (Fig. 26.6b), indicating that these steps are photon number-determined processes. In other words, to shift from the photo-process events (e.g., steps 1 and 3) to the phase transition-processes (e.g., steps 2 and 4), the isomer ratio of the assembly must achieve a particular threshold. This means that the self-oscillation property of this system is not chaotic, but rather represents a type of limit-cycle (Fig. 26.7). Therefore, the assembly charges internal energy (the sum of the mechanical stress and the enthalpy of molecular formation) up to its threshold by accepting light in step 1. The assembly then discharges part of the energy with morphological changes in steps 2 and 4. Overall, these events demonstrate that this assembly has the ability to apply mechanical work to other objects periodically. For example, when the co-assembly is placed in water, it applies impulses to the water which manifests as a swimming motion [53]. Details regarding this system are reported elsewhere [63, 64].

26.4 Analogues also Exhibiting a Self-Oscillatory Flipping Motion

The simple mechanism described above may also be observed in other assemblies composed of photochromic compounds. However, until now, we have not investigated photochromic compounds other than azobenzene derivatives. To date, we have successfully generated several self-oscillatory motions in co-assemblies of several
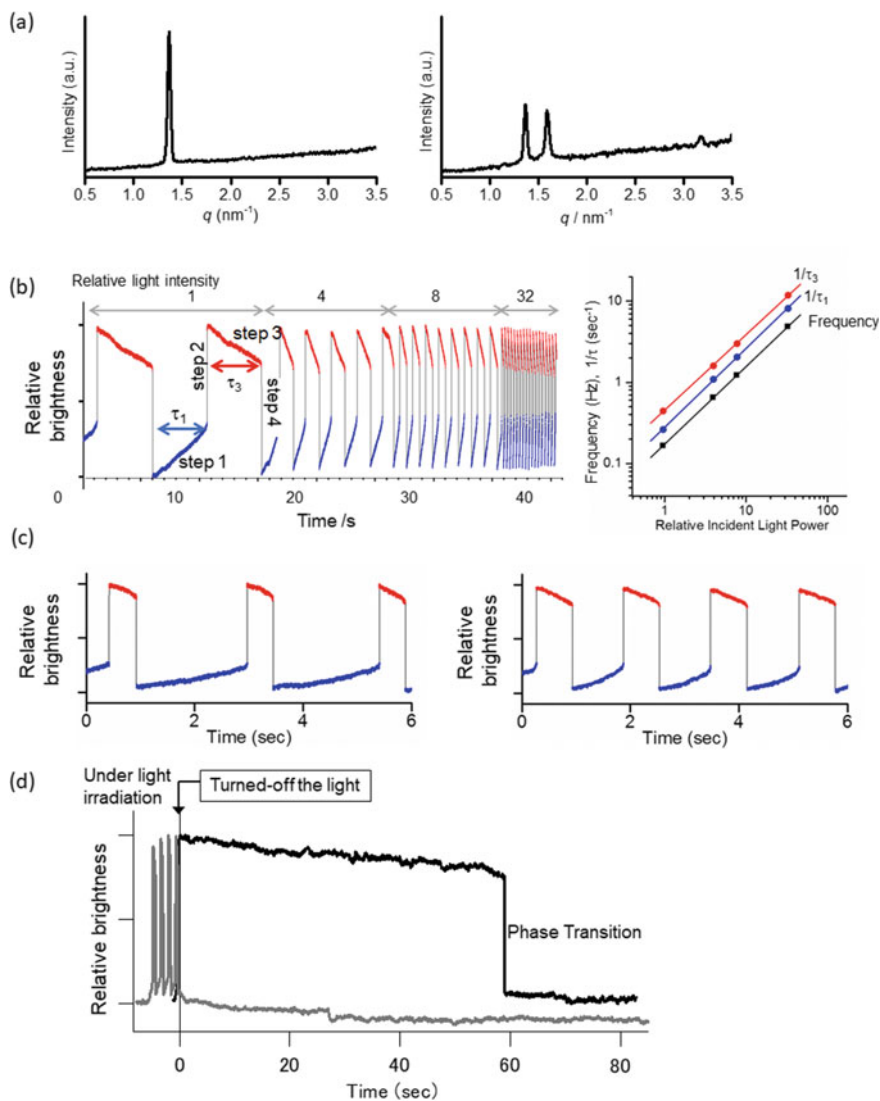
Fig. 26.6 Characteristics of the light-powered periodic flips of an azobenzene-containing co-assembly. **a** The *in situ* small-angle XRD profiles of the co-assembly under dark conditions (left) and under blue-light irradiation (right). **b** Time profile of the periodic motion of the co-assembly under irradiation with various intensities of steady 435-nm light (left). Light power dependencies of duration time (τ_1, and τ_3) and frequency (right) are shown. **c** Time profiles of the periodic motion of the co-assembly under irradiation with 470-nm light (left) versus 435-nm light (right). **d** Behavior of the co-assembly after removing the light source. When the co-assembly was in its bent-shape phase and the light source was removed, thermal relaxation via a phase transition was observed. All figures were produced from the original data [53]

Fig. 26.7 Schematic of the
energy cycle employed for
the limit-cycle
self-oscillation of an
azobenzene-based assembly
which undergoes a
photochemical process under
steady light irradiation
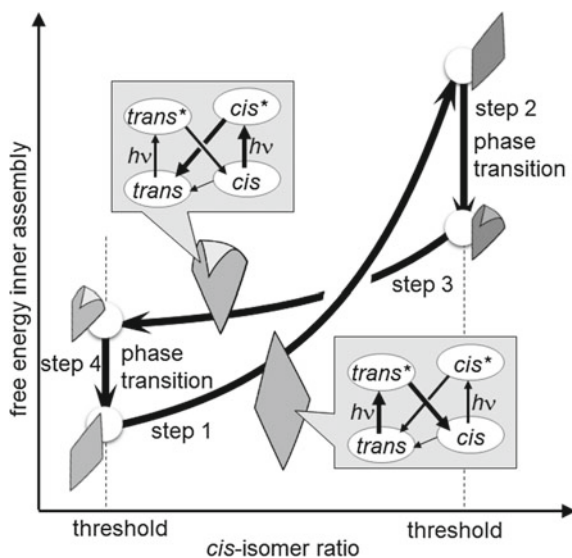
fatty acids and azobenzene derivatives, examples of which are shown in Fig. 26.8
[65]. A waved, ribbon-like assembly of stearic acid, **1**, and **2** exhibits a multi-step
frog-kick motion [53]. A plate-like assembly of the same compounds was observed
when they were maintained at 80-Hz for more than 5 min [66]. Many of the hexag-
onal or parallelogram plate-like assemblies of fatty acids and azobenzene derivatives
exhibit self-oscillatory flipping motions, while ribbon-shape assemblies exhibit a
wavy motion [65, 66]. Many varieties of motions have been observed, and there
appears to be some trends in the relationship between molecular structure and the
spatial pattern of the motion observed. The details of these trends are currently being
investigated [65].

We have been particularly interested in one of the polymorphs of a single-
component crystal of **2**, which showed repetitive winding dynamics during exposure
to blue-light irradiation [62]. The crystal has a symmetry-broken space-group (P_1)
with six independent molecules in each unit-cell [67]. Additional characteristics of
this crystal include a spare-and-dense layered structure, as well as an anisotropic
structure related to a directive flipping motion under non-directional light irradi-
ation. Based on the fact that the average isomer ratio in its steady-state was less
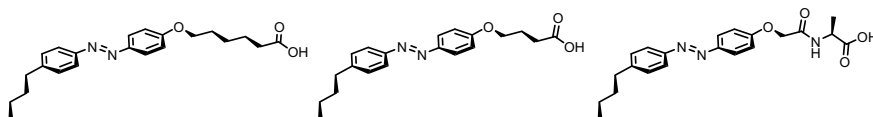than 8%, we have assumed that a particular molecule undergoes isomerization to

Fig. 26.8 Structures of the azobenzene molecules which generate light-powered self-oscillation
motions when they assemble with fatty acids

trigger a phase transition of the crystal, and then it accepts feedback in the manner described above. Meanwhile, the other molecules serve as building blocks to prevent the assembly from breaking down. Our most recent results further indicate that the latter molecules also play a role in selecting the path for the periodic cycle of this system. As a result, periodic changes in shape are varied according to the externally defined light-polarity.

26.5 Conclusion and Remarks Regarding Self-Organized Molecular Motors

The inventions of the water mill and windmill have proved very important for advances in agriculture. Meanwhile, the invention of the steam engine has allowed humans to move objects as small as electrons to objects as large as ships. The key to all of these inventions is that the objects involved are connected to motors. There is no exception. Thus, when we create a self-moving microrobot, we must have a suitable motor.

To date, organic chemists have synthesized molecules that undergo salient changes in their structures. If a cyclic change occurs when steady energy supply is available, this has been considered a molecular motor according to traditional definition. On the other hand, if the change in structure requires alterations in the conditions of the molecule to achieve the change in structure, this has been considered a molecular machine. In parallel, material scientists have worked on generating microrobots which move under the direction of remote control. In these microrobots, molecular machine has been employed rather than molecular motors [68, 69], because an unsynchronized molecular motor is never worked. However, to attain an autonomous function in microrobot, a suitable molecular motor system is needed.

To date, our ability to obtain work from a molecular motor remains insufficient. One reason may be that we need to better understand molecular self-organization. A series of theoretical studies related to dissipative structures have clearly indicated how autonomous energy conversion can occur in a mesoscale molecular system. A dissipative structure involves a dynamic whereby multiple nonlinear processes are coupled in a feedback manner. As a result, they form a spatial and temporal system which exhibits self-continuous dynamics compared with the original process shown in Figs. 26.2 and 26.7. The importance of dissipative structures is their far-from-equilibrium behavior: the distance from so-called equilibrium (not thermal equilibrium) is related to the capability of the mechanical function which a system can accomplish. Moreover, this distance from equilibrium is required to be maintained despite the generation of external disturbances as the system acts on external objects. Therefore, the limit-cycle-type self-oscillation system described in this chapter appears to be the best system for developing a motorization system [70].

Thus, while strategies for creating such dynamics at the molecular level have not been successful to date, recent efforts to construct a multi-molecular motor system appear to be a promising approach for attaining a working molecular system in the near feature.

References

1. Kay ER, Leigh DA, Zerbetto F (2007) Synthetic molecular motors and mechanical machines. Angew Chem Int Ed 46:72–191
2. von Delius M, Leigh DA (2011) Walking molecules. Chem Soc Rev 40:3656–3676
3. Kassem S, van Leeuwen T, Lubbe AS, Wilson MR, Feringa BL, Leigh DA (2017) Artificial molecular motors. Chem Soc Rev 46:2592–2621
4. Koumura N, Zijlstra RWJ, van Delden RA, Harada N, Feringa BL (1999) Light-driven monodirectional molecular rotor. Nature 401:152–155
5. Feringa BL (2001) In control of motion: from molecular switches to molecular motors. Acc Chem Res 34:504–513
6. ter Wiel MKJ, van Delden RA, Meetsma A, Feringa BL (2003) Increased speed of rotation for the smallest light-driven molecular motor. J Am Chem Soc 125:15076–15086
7. van Delden RA, Koumura N, Schoevaars A, Meetsma A, Feringa BL (2003) A donor–acceptor substituted molecular motor: unidirectional rotation driven by visible light. Org Biomol Chem 1:33–35
8. Vicario J, Walko M, Meetsma A, Feringa BL (2006) Fine tuning of the rotary motion by structural modification in light-driven unidirectional molecular motors. J Am Chem Soc 128:5127–5135
9. Wezenberg SJ, Feringa BL (2018) Supramolecularly directed rotary motion in a photoresponsive receptor. Nat Commun 9:1984
10. Ragazzon G, Baroncini M, Silvi S, Venturi M, Credi A (2014) Light-powered autonomous and directional molecular motion of a dissipative self-assembling system. Nat Nanotechnol 10:70–75
11. Yu J-J, Zhao L-Y, Shi Z-T, Zhang Q, London G, Liang W-J, Gao C, Li M-M, Cao X-M, Tian H, Feringa BL, Qu D-H (2019) Pumping a ring-sliding molecular motion by a light-powered molecular motor. J Org Chem 84:5790–5802
12. Pezzato C, Nguyen MT, Kim DJ, Anamimoghadam O, Mosca L, Stoddart JF (2018) Controlling dual molecular pumps electrochemically. Angew Chem Int Ed 57:9325–9329
13. Cheng C, McGonigal PR, Schneebeli ST, Li H, Vermeulen NA, Ke C, Stoddart JF (2015) An artificial molecular pump. Nat Nanotechnol 10:547–553
14. Kudernac T, Ruangsupapichat N, Parschau M, Maciá B, Katsonis N, Harutyunyan SR, Ernst K-H, Feringa BL (2011) Electrically driven directional motion of a four-wheeled molecule on a metal surface. Nature 479:208–211
15. Collins BSL, Kistemaker JCM, Otten E, Feringa BL (2016) A chemically powered unidirectional rotary molecular motor based on a palladium redox cycle. Nat Chem 8:860–866
16. Wilson MR, Solà J, Carlone A, Goldup SM, Lebrasseur N, Leigh DA (2016) An autonomous chemically fuelled small-molecule motor. Nature 534:235–240
17. Fletcher SP, Dumur F, Pollard MM, Feringa BL (2005) A reversible, unidirectional molecular rotary motor driven by chemical energy. Science 310:80–82

18. Astumian RD (2007) Design principles for Brownian molecular machines: how to swim in molasses and walk in a hurricane. Phys Chem Chem Phys 9:5067–5083
19. Pezzato C, Cheng C, Stoddart JF, Astumian RD (2017) Mastering the non-equilibrium assembly and operation of molecular machines. Chem Soc Rev 46:5491–5507
20. Astumian RD (2017) How molecular motors work – insights from the molecular machinist's toolbox: the Nobel prize in chemistry 2016. Chem Sci 8:840–845
21. Serreli V, Lee C-F, Kay ER, Leigh DA (2007) A molecular information ratchet. Nature 445:523–527
22. Alvarez-Pérez M, Goldup SM, Leigh DA, Slawin AMZ (2008) A chemically-driven molecular information ratchet. J Am Chem Soc 130:1836–1838
23. Carlone A, Goldup SM, Lebrasseur N, Leigh DA, Wilson A (2012) A three-compartment chemically-driven molecular information ratchet. J Am Chem Soc 134:8321–8323
24. Martin CJ, Lee ATL, Adams RW, Leigh DA (2017) Enzyme-mediated directional transport of a small-molecule walker with chemically identical feet. J Am Chem Soc 139:11998–12002
25. Astumian RD (2018) Trajectory and cycle-based thermodynamics and kinetics of molecular machines: the importance of microscopic reversibility. Acc Chem Res 51:2653–2661
26. Astumian RD (2019) Kinetic asymmetry allows macromolecular catalysts to drive an information ratchet. Nat Commun 10:3837
27. Rex A (2017) Maxwell's demon—a historical review. Entropy (Basel, Switzerland) 19:240
28. Zhang L, Marcos V, Leigh DA (2018) Molecular machines with bio-inspired mechanisms. Proc Nat'l Acad Sci 115:9397–9404
29. Credi A, Venturi M, Balzani V (2010) Light on molecular machines. ChemPhysChem 11:3398–3403
30. Silvi S, Venturi M, Credi A (2011) Light operated molecular machines. Chem Commun 47:2483–2489
31. Kathan M, Hecht S (2017) Photoswitchable molecules as key ingredients to drive systems away from the global thermodynamic minimum. Chem Soc Rev 46:5536–5550
32. Onsager L (1931) Reciprocal relations in irreversible processes. I Phys Rev 37:405–426
33. Watson MA, Cockroft SL (2016) Man-made molecular machines: membrane bound. Chem Soc Rev 45:6118–6129
34. Steinberg-Yfrach G, Liddell PA, Hung S-C, Moore AL, Gust D, Moore TA (1997) Conversion of light energy to proton potential in liposomes by artificial photosynthetic reaction centres. Nature 385:239–241
35. Steinberg-Yfrach G, Rigaud J-L, Durantini EN, Moore AL, Gust D, Moore TA (1998) Light-driven production of ATP catalysed by F_0F_1-ATP synthase in an artificial photosynthetic membrane. Nature 392:479–482
36. Mizushima T, Yoshida A, Harada A, Yoneda Y, Minatani T, Murata S (2006) Pyrene-sensitized electron transport across vesicle bilayers: dependence of transport efficiency on pyrene substituents. Org Biomol Chem 4:4336–4344
37. Eelkema R, Pollard MM, Vicario J, Katsonis N, Ramon BS, Bastiaansen CWM, Broer DJ, Feringa BL (2006) Nanomotor rotates microscale objects. Nature 440:163
38. Bosco A, Jongejan MGM, Eelkema R, Katsonis N, Lacaze E, Ferrarini A, Feringa BL (2008) Photoinduced reorganization of motor-doped chiral liquid crystals: bridging molecular isomerization and texture rotation. J Am Chem Soc 130:14615–14624
39. Thomas R, Yoshida Y, Akasaka T, Tamaoki N (2012) Influence of a change in helical twisting power of photoresponsive chiral dopants on rotational manipulation of micro-objects on the surface of chiral nematic liquid crystalline films. Chem Eur J 18:12337–12348
40. Kim Y, Tamaoki N (2019) Photoresponsive chiral dopants: light-driven helicity manipulation in cholesteric liquid crystals for optical and mechanical functions. ChemPhotoChem 3:284–303
41. As an example of non-photochemical motion, a catalyst-pendent-macrocycle sliding on a polymer chain has been reported: Hashidzume A, Kuse A, Oshikiri T, Adachi S, Okumura M, Yamaguchi H, Harada A (2018) Toward a translational molecular ratchet: face-selective translation coincident with deuteration in a pseudo-rotaxane. Sci Rep 8:8950

42. Since friction is required for generating work from a molecular motor, a value of 100% does not indicate that a particular molecular motor will be good for an assembled working system

43. Nakata S, Pimienta V, Lagzi I, Kitahata H, Suematsu JN (2019) Self-organized motion. Royal Society of Chemistry, Cambridge

44. Yamada M, Kondo M, Mamiya J, Yu Y, Kinoshita M, Barrett C, Ikeda T (2008) Photomobile polymer materials: towards light-driven plastic motors. Angew Chem Int Ed 47:4986–4988

45. Serak S, Tabiryan N, Vergara R, White TJ, Vaia RA, Bunning TJ (2010) Liquid crystalline polymer cantilever oscillators fueled by light. Soft Matter 6:779–783

46. White TJ, Tabiryan NV, Serak SV, Hrozhyk UA, Tondiglia VP, Koerner H, Vaia RA, Bunning TJ (2008) A high frequency photodriven polymer oscillator. Soft Matter 4:1796–1798

47. Vantomme G, Gelebart AH, Broer DJ, Meijer EW (2017) Preparation of liquid crystal networks for macroscopic oscillatory motion induced by light. J Vis Exp e56266

48. Vantomme G, Gelebart AH, Broer DJ, Meijer EW (2018) Self-sustained actuation from heat dissipation in liquid crystal polymer networks. J Polym Sci A: Polym Chem 56:1331–1336

49. Gelebart AH, Vantomme G, Meijer EW, Broer DJ (2017) Mastering the photothermal effect in liquid crystal networks: a general approach for self-sustained mechanical oscillators. Adv Mat 29:1606712

50. Vantomme G, Gelebart AH, Broer DJ, Meijer EW (2017) A four-blade light-driven plastic mill based on hydrazone liquid-crystal networks. Tetrahedron 73:4963–4967

51. Gelebart AH, Jan Mulder D, Varga M, Konya A, Vantomme G, Meijer EW, Selinger RLB, Broer DJ (2017) Making waves in a photoactive polymer film. Nature 546:632–636

52. Kageyama Y (2019) Light-powered self-sustainable macroscopic motion for the active locomotion of materials. ChemPhotoChem 3:327–336

53. Ikegami T, Kageyama Y, Obara K, Takeda S (2016) Dissipative and autonomous square-wave self-oscillation of a macroscopic hybrid self-assembly under continuous light irradiation. Angew Chem Int Ed 55:8239–8243

54. Nicolis G, Prigogine I (1977) Self-organization in nonequilibrium systems. John Wiley Inc, Canada

55. Nitzan A, Ross J (1973) Oscillations, multiple steady states, and instabilities in illuminated systems. J Chem Phys 59:241–250

56. Yamazaki I, Fujita M, Baba H (1976) Oscillatory behavior in photoreaction of 1,5-naphthyridine in cyclohexane solution. Photochem Photobiol 23:69–70

57. Laplante JP, Pottier RH (1982) Study of the oscillatory behavior in irradiated 9,10-dimethylanthracene/chloroform solutions. J Phys Chem 86:4759–4766

58. Bose RJ, Ross J, Wrighton MS (1977) Aperiodic and periodic oscillations in fluorescence intensity from irradiated chlorocarbon solutions of anthracene and 9,10-dimethylanthracene. J Am Chem Soc 99:6119–6120

59. Kageyama Y, Ikegami T, Hiramatsu N, Takeda S, Sugawara T (2015) Structure and growth behavior of centimeter-sized helical oleate assemblies formed with assistance of medium-length carboxylic acids. Soft Matter 11:3550–3558

60. Kageyama Y, Tanigake N, Kurokome Y, Iwaki S, Takeda S, Suzuki K, Sugawara T (2013) Macroscopic motion of supramolecular assemblies actuated by photoisomerization of azobenzene derivatives. Chem Commun 49:9386–9388

61. Kageyama Y, Ikegami T, Kurokome Y, Takeda S (2016) Mechanism of macroscopic motion of oleate helical assemblies: cooperative deprotonation of carboxyl groups triggered by photoisomerization of azobenzene derivatives. Chem Eur J 22:8669–8675

62. Kageyama Y, Ikegami T, Satonaga S, Obara K, Sato H, Takeda S (2020) Light-driven flipping of azobenzene assemblies — sparse crystal structures and responsive behavior to polarized light. Chem Eur J DOI: https://doi.org/10.1002/chem.202000701

63. Obara K, Kageyama Y, Takeda S (2019) Swimming motion of micro-sized thin crystals with autonomous and rapid flipping under blue light irradiation. In: The 99th annual meeting 2019 of chemical society of Japan, Kobe, Japan, 2I7–50

64. Obara K, Kageyama Y, Takeda S. Unpublished result

65. Kageyama Y, Ikegami T, Satonaga S, Yazaki D, Takeda S. Unpublished result

66. Ikegami T (2018) Realization of mechanical self-oscillatory motion of azobenzene-containing crystal driven by steady light. Doctoral thesis Hokkaido University
67. Crystal data is deposted in CCDC1833362
68. Zeng H, Wasylczyk P, Wiersma DS, Priimagi A (2018) Light robots: bridging the gap between microrobotics and photomechanics in soft materials. Adv Mat 30:1703554
69. Zhang X, Chen L, Lim KH, Gonuguntla S, Lim KW, Pranantyo D, Yong WP, Yam WJT, Low Z, Teo WJ, Nien HP, Loh QW, Soh S (2019) The pathway to intelligence: using stimuli-responsive materials as building blocks for constructing smart and functional systems. Adv Mat 31:1804540
70. Haken H (1978) Synergetics—an introduction (Japanese transl.). Springer, Berlin, Heidelberg