Photoinduced movement: how photoirradiation induced the movements of matter

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ABSTRACT

Pioneered by the success on active transport of ions across membranes in 1980 using the regulation of the binding properties of crown ethers with covalently linked photoisomerizable units, extensive studies on the movements by using varied interactions between moving objects and environments have been reported. Photoinduced movements of various objects ranging from molecules, polymers to microscopic particles were discussed from the aspects of the driving for the movements, materials design to achieve the movements and systems design to see and to utilize the movements are summarized in this review.

1. Introduction

Photoirradiation induces many movements in nature in different size scales. In geosphere, ocean currents originate from the differences in sun light irradiation, which is stronger at the equator and weaker at the polar regions. In biosphere, phototaxis, which is an ability of organisms to move toward or away from light, is seen in different size scales, ranging from bacteria and protists to invertebrates such as insects and jelly fish [1,2]. In a smaller world, photosynthesis is a photoinduced phenomenon, in which chemical reactions and movement of reactant and product molecules occur simultaneously under sun light [3]. Many more macroscopic phenomena in biological and geological systems are initiated by photochemical, photothermal and photobiochemical events at the molecular level [4].
As the above mentioned phenomena are induced by the molecular reactions, chemical systems that show movements of matter have been called as smart materials (photoresponsive materials) [5,6]. One of the key developments in the photoinduced movement in artificial systems had been reported by Shinkai et al. in the 1980s, who demonstrated the regulation of the binding properties of crown ethers by covalently linked photoisomerizable azobenzene units to drive active transport of ions across liquid membranes and membrane mimetic systems by photoirradiation [7]. Since then, set-up to follow the movement, molecules to act as receptor, and the moving objects have been designed from various expertise extensively. The range of the objects that can be moved by irradiation has been extended from molecule/ion to macroscopic bodies, which is followed directly using an optical microscope and naked eyes. As an extension, photoinduced motion of macromolecules in micrometer scale has been used to create grating (surface relief grating) for optical application. In some systems, Marangoni flow, which was induced by photochemical and photothermal reaction, was thought to play the movement of objects; it can be regarded as 'nano' ocean current! In this review article, molecular design, supramolecular design and system design to show photoinduced movements of various objects from nano- to micro-meter scales will be introduced. Photochromic molecules [8] have been used to convert light to mechanical energy using photoinduced changes (photoinduced molecular structure changes, photocatalytic reactions, photoinduced hydrophilicity and photothermal effects).

2. Photochromic units used in the studies introduced in this review

As photochromic molecules [8] have been used to convert light to mechanical energy, photochromic molecules introduced in the present review articles are introduced here. There are several photochromic species and, among them, azobenzene (abbreviated as AZ), stilbene (abbreviated as SB), diarylethene (abbreviated as DAE), spiropyran (abbreviated as SP) and spirooxazine (abbreviated as SO) have commonly been used to design photoresponsive systems. The changes in the molecular geometry and molecular polarity are shown in Scheme 1. AZ shows photoisomerization from trans- to cis-isomers by UV irradiation as shown in Scheme 1(a). Metastable cis-isomer returns to thermodynamically stable trans-isomer by visible light irradiation or heat. The molecular structure change of AZ accompanied change in dipole moment (trans-isomer: 0.52 D and cis-isomer: 3.08 D) [9,10]. trans-SB also shows trans-cis isomerization as shown in Scheme 1(b). The cis-isomer of SB shows both the isomerization to the trans-isomer and a ring closing reaction. The dipole moments of the trans- and cis-isomers were reported as 0.4–0.9 D and 2.8 D, respectively [11]. SB shows [2 + 2] photodimerization following Woodward-Hoffmann rules when two SB molecules are close each other. The substitution of the ethylene moiety of cis-SB suppressed the trans-cis isomerization and the dimerization of SB, where the substituted derivatives are called diarylethene (DAE). DAE shows reversible ring-closing and ring-opening reactions by UV and visible light irradiation, respectively, as shown in Scheme 1(c) [14]. The isomerization does not occur by heat because both of the isomers are thermodynamically stable, so that one can expect real photochromic systems. The dipole moments of the two isomers of DAE were almost same, while the difference was controllable by the substituents up to 3 D [12]. SP transforms to zwitterionic form called as mercocyanine (MC) or photomerocyanine by UV irradiation as shown in Scheme 1(d). The electronically neutralized SP has smaller dipole moment (5 D) than that (20 D) of the zwitterionic MC [13]. SP is the stable isomer in non-polar conditions.

Scheme 1. Photochromism of (a) azobenzene (AZ), (b) stilbene (SB), (c) diarylethene (DAE) and (d) spiropyran (SP), where values in brackets are dipole moments of the photochromic compounds [9–13].
environment to show photochromism. On the other hand, MC is stabilized in polar environment to show negative photochromism [15,16], which is the opposite reaction of conventional photochromism from colorless SP to colored MC. In order to control the photochromic reactions from the aspects of reaction yield, kinetics, selectivity, color variation and stability, molecular design of those photochromic molecules has been done extensively [17–19]. Host-guest systems and supramolecular systems containing photochromic moieties have been designed for possible smart materials (photoresponsive materials) [20–22].

3. Photoinduced adsorption/desorption on/from solids

Photoswitching of gas adsorption has been achieved by combining photoresponsive molecular units and nanospace materials, such as mesoporous silicas (MPs) [23–25], metal-organic frameworks (MOF) and clay minerals [26,27]. Optical illumination, change in local temperature, void volume, polarity in pore, and pore structure, as well as open/close the pore entrances, were used as physical mechanisms of the photoswitching. In this section, photocontrol of gas adsorption on MOFs and layered materials such as clay minerals will be discussed.

3.1. Photoinduced adsorption/desorption onto metal-organic framework

Metal-organic framework (MOF) or porous coordination polymer (PCP) is a porous crystalline material consisting of metal ions or metal oxide clusters (node) and organic ligands (linkers) [28–31]. The porous structure of MOF has been used for gas storage [28] and molecular separation [32,33], in addition, photochromism of organic photochromic molecules in MOFs have been reported [34–37]. The photoresponsive MOFs are categorized into three types: MOFs with photoresponsive moieties (Type A) as the side chain of backbone, (Type B) in the framework backbone and (Type C) as the guest (Figure 1) [31]. Covalently attached photoresponsive units (Type A and B) have been more conveniently used to achieve photoinduced movements and there are few examples of photoresponses for Type C structure. The release of nitrogen (N$_2$) gas from an azide incorporated in a MOF by the photodecomposition of the azide groups was reported [38]. Photochromism of azobenzene (unsubstituted AZ) adsorbed in MOF was used to switch the N$_2$ adsorption capacity [39].

3.1.1. Type A, MOFs including photochromic moiety in the side chain of linker

As the photochromic moieties were in the pore and on the external surface as shown in Figure 1, the photochromism of MOFs with photochromic side chains (Type A) does not accompany significant crystal lattice change. The polarity change in the pore by the photochromism caused the change in the host-guest interactions, and local heating by the light irradiation may also affect the response [40,41]. Photoswitching of the adsorption/desorption of N$_2$ [39], methane [42], CO$_2$ [40,41,43–47,47] and Ar [45,47] for Type A photofunctional MOFs has been reported.

As shown in Figure 2, the adsorption of CO$_2$ on a MOF containing zirconium o xo cluster as the node (Azo-MOF, Zr$_6$O$_4$(OH)$_4$L$_4$: L$^2$- = 2′-phenyldiazenyl-1,1′:4′,1′′-terphenyl-4,4′-dicarboxylate) largely depended on the cis-/trans-isomer ratio, while the adsorption of Ar was not affected by the cis-/trans-isomer ratio [45]. The effect of the polarity of gasses on the diffusion in Azo-MOF was examined from Equation (1) [48]. It was hypothesized that the diffusion of gasses in Azo-MOF occurs through two types; diffusion through triangular windows and in polyhedral pores with diffusion constants $k_{td}$ and $k_{bd}$ respectively.

\[
M_t/M_e = A_1 \left[1 - \exp\left(-W k_{td}\right) + A_2 \left[1 - \exp\left(-P k_{bd}\right)\right]\right]
\]

$M_t$ and $M_e$ represent the amounts of gas molecules adsorbed at time $t$ and at equilibrium, respectively, whereas $A_1$ and $A_2$ denote relative contributions of the triangular window and polyhedral pores. The $W k_{td}$ and $P k_{bd}$ values for Ar were almost same at high (15%) and low (1%) cis-/trans-AZ ratio. On the other hand, the $W k_{td}$ (0.04 s$^{-1}$) for CO$_2$ at the lower cis-/trans-AZ ratio was larger than that at the higher cis-
trans-ratio (0 s⁻¹), although $k_d$ values were same irrespective of the ratio. Taking the sizes of CO₂ and Ar into account, the polar cis-AZ disturbed the diffusion through the trihedral window of the MOF by the dipole-dipole interactions.

A SP functionalized MOF-808 ([Zr₆O₁₄(OH)]₄(btc)₂ (HCOO)_5.95(P)₀.₀₂(SP-MeCOOH)₀.₀₂], where btc: 1,3,5-benzenetricarboxylate, P: 1-(carboxymethyl)-2,3,3-trimethyl-3H-indol-ium iodide (precursor of SP), SP-MeCOOH: 2-(3',3'-dimethyl-6-nitrospiro[chromene-2,2'-indolin]-1'-yl)acetic acid), was synthesized by post-synthetic grafting and showed the photoswitching of adsorption of Ar and CO₂ gasses [47]. The adsorbed amount of Ar decreased by UV irradiation, while that of CO₂ increased. The generation of polar MC was thought to contribute the increase in the adsorbed amount of CO₂.

### 3.1.2. Type B, MOFs with photochromic framework backbone

For Type B MOF, pore structure of MOFs transforms by the photochromism. Because of the rigidity of the framework, some MOFs did not accept the structural change to be photochemically silent [35,49–54]. The photoinduced change in the pore structure led to the controlled adsorption of gasses and the change in the crystal shape [14,55]. Photoinduced adsorption/desorption of gasses by the Type B photofunctional MOFs was reported using AZ [56–61], DAE [62] and SB [63] as photoresponsive units.

Because the crystal structure did not accept the drastic change of the molecular structure of AZ [35], some reports concluded that local molecular conformation change [61] and heat generated by light absorption [60] affected the adsorbed amount more than the pore structure change. By UV irradiation, adsorbed amount of CO₂ on a MOF, JUC-62 (Cu₂(ABTC)(H₂O)₂·(DMF)₂(H₂O); ABTC; 3,3',5,5'-azobenzenetetracarboxylate anion) changed from 102 cm³/g to 52 cm³/g at standard pressure and temperature (STP) (Figure 3) [61,64]. UV-vis absorption spectrum of JUC-62 changed slightly before and after the UV irradiation while IR spectrum changed by the UV irradiation, suggesting that small conformation change of ABTC in JUC-62 affected the adsorption of CO₂. In order to use the change of the molecular structure of AZ for the change in the crystal structure of MOFs, DUT-49 [65] was functionalized with AZ linkers [66]. The MOF showed effective photochromism and contraction of the crystal structure with 0.1–0.15 mm sample thickness by the UV irradiation, although photoswitching of the adsorbed amount of H₂ was not observed. DUT-49 was known to be softened to accept disorienting of the crystal structure by functionalizing with 4,4'-diamino-SB [67,68].
3.1.3. Type C, MOFs with photochromic guests

Photochromic compounds were incorporated in MOFs to give Type C structure [69–72]. Photoinduced adsorption/desorption of N₂ by a MOF, [Zn₂(terephthalate)₂(triethylendiamine)]ₙ, loaded with azobenzene (unsubstituted AZ) was reported [39]. Azobenzene was incorporated into the 2D pore (7.5 Å ×7.5 Å) of the MOF by soaking the MOF in molten azobenzene at 120°C. By UV irradiation, the adsorbed amount of N₂ on the azobenzene loaded MOF increased from ca. 5 to 45 mL g⁻¹ by the photoisomerization of the incorporated azobenzene. The difference in the adsorbed amount of N₂ caused by the UV irradiation was explained by the structural change of the MOF, which was shown by powder X-ray diffraction patterns (XRD). After the subsequent heating at 120°C, the structure of the MOF returned to the original one as the incorporated azobenzene returned to trans-isomer, which was not achieved by light irradiation. After the heating, the MOF adsorbed the same amount of N₂ as the MOF adsorbed before the UV irradiation.

Photoinduced adsorption/desorption of gasses by MOFs in Type A [46] and Type B [59] has been used for gas separation. Selectivity coefficients $s_{i,2}$ were derived as follows [73],

$$s_{i,2} = \frac{x_i/y_i}{x_2/y_2} = \frac{P_i^0}{P_2^0}$$

(2)

Where, $x_i$ and $y_i$ ($i = 1$ and $2$) are mole fractions of component $i$ in adsorbed and gas phases, respectively, and $P_i^0$ is equilibrium pressure of pure component $i$. The $s_{i,2}$ values for CO₂ against CH₄ and N₂ before and after UV irradiation were different in a Zn based MOF with an AZ side chain ligand (2-(phenyldiazenyl)terephthalate) [43] adsorbed tetrahydropyrimidine [46]. The $s_{i,2}$ values for CO₂ against CH₄ and N₂ before the UV irradiation was 456 and 334 at 273 K and 0.1 bar, which became 92 and 137 after the UV irradiation. It was thought that the intercalated tetrahydropyrimidine acted as an adsorption site for CO₂ and the polar cis-AZ ligand interacted with the tetrahydropyrimidine to disturb the adsorption of CO₂. Adsorbed amount of CO₂ was larger than those of CH₄ and N₂ and the differences of the adsorption of

As the photochromism of DAE accompanies relatively small change in molecular structure, the photochromism was acceptable in MOFs. As shown in Figure 4, the change of the crystal structure of a DAE-substituted MOF ([Zn₄(bdc)₄(DAE)₂·4DMF·H₂O]ₙ, bdc; 1,4-benzenedicarboxylate anion) induced switching of adsorption/desorption of CO₂ by UV irradiation [62]. Before the UV irradiation, the adsorbed amount of CO₂ was 136 cm³/g (STP), which was 96 cm³/g (STP) after the UV irradiation.

Figure 3. (a) Crystal structure of JUC-62, (b) molecular structure of AZ linker for JUC-62 (ABTC) and (c) CO₂ adsorption of JUC-62 in static and dynamic condition at 273 K. (Reproduced from the reference [61] with permission.)
CH$_4$ and N$_2$ before and after the irradiation were smaller than that of CO$_2$, suggesting possible photoinduced gas separation. Furthermore, the photocontrolled gas adsorption by the MOFs is expected to be applied as a light harvesting system by using the heat generation by the light irradiation [74] and for the decomposition of the adsorbed gasses by the hybridized photocatalyst [75].

### 3.2. Photoinduced structural change of layered materials incorporating photochromic compounds

Layered materials provides large surface area so that they have been used as adsorbent for noble species and pollutants from environments [76,77]. The controlled release of drugs and pesticide/herbicide has also been well documented [78]. Smectite group of clay minerals, which is composed of negatively charged silicate layer and interlayer exchangeable cations [79–81], is well-investigated layered materials for a wide variety of application. In addition to smectites, there are several ion exchangeable layered solids used for the photoresponsive materials [82]. Cationic photochromic molecules have been intercalated [78,83,84] to show unique photochromic phenomena such as improvement of reversibility of photochromic reaction of DAE [85–87], controlled selectivity of dimerization/isomerization of cinnamic acids in layered double hydroxides (LDHs) [88–91] and SB in smectites [89,91–93], and photoresponsive magnetic layered materials including layered cobalt oxides [94–101].

As the first example of photoinduced structural change of the intercalation compounds, ionically neutral p-aminoazobenzene was incorporated into the interlayer space of a smectite after the organophilic modification [102]. Later on, cationic AZs were synthesized and were intercalated into the interlayer spaces of various layered silicates including smectites. The basal spacing increased by 0.06 nm in AZ$^-$-1-magadiite (the change is shown in Figure 5(a)) [105,106]. The basal spacing of an AZ$^+$-1 intercalated montmorillonite with the cation exchange capacity (CEC) of 119 meq/100 g did not change by the photoisomerization [107] while that of AZ$^-$-1-magadiite (CEC: 159 meq/100 g) changed [108,109]. The basal spacings of p-aminoazobenzene- and 4,4′-diaminoazobenzene-montmorillonite (CEC: 143 meq/100 g) were examined by molecular dynamics simulation in order to discuss the mechanism of the changes in the basal spacings.

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**Figure 4.** (a) Molecular structure of DAE ligand and photograph for color change of the MOF, (b) adsorption isotherms for CO$_2$ of the DAE-functionalized MOF before and after UV irradiation at 195 K and (c) crystal structure the MOF (left) as prepared, (middle) guest free and (right) after the UV irradiation. (Reproduced from the reference [62] with permission.)
observed by the experiments [110]. The basal spacings decreased from 2.0 nm (for the trans-p-aminoazobenzene-montmorillonite) and 2.1 nm (for the trans-4,4′-diaminoazobenzene-montmorillonite) to 1.8 nm for the both cis-products, which was not consistent with the experimental results showing the increase of the basal spacing from 3.0 nm to 3.1 nm [102]. This suggested that the change in basal spacing observed in the experiments was caused by adsorption/desorption of molecular species (such as water) to/from the products from/to the environments. As shown in Figure 5(b), the basal spacing of AZ⁺-1-magadiite increased by UV irradiation under the humidity of 95%, while it did not change under the humidity of 5%, indicating that photoinduced adsorption of water in air was important for the changes in the basal spacing [103].

Photoisomerization of azobenzene (unsubstituted AZ) in organophilic clays led to a decrease in the basal spacing [102]. The change was observed in fluorotetrasilicic mica intercalated with azobenzene and trimethylalklyammonium with varied alkyl chain length (C₁₂, C₁₄, C₁₆ and C₁₈) and the exchange ratio
(ammonium surfactant/CEC, varied from 0.25 to 2.0) [111,112]. Trimethyloctadeylammonium surfactant (C_{18}) formed bimolecular paraffin-type aggregate in fluor-tetrasilic mica. The basal spacing of C_{18}-fluor-

tetrasilic mica did not change by photoisomerization of incorporated azobenzene [112,113], while the basal spacing became smaller when trimethyldecelyun-

monium surfactant (C_{12}), which formed pseudo-

trimolecular layer in the interlayer space, was used [113,114]. Azobenzene was intercalated from vapor into trimethylalkylammonium-beidellite with varied alkyl chains (12, 14 and 16) and the changes in the basal spacing upon irradiation were larger when shorter alkyl chain was used [115].

Photoinduced adsorption and release [116] of non-

ionic organic molecules [104,117,118] were reported for cationic AZ intercalated smectites. As shown in Figure 5(c), the basal spacings of AZ⁺-1- and AZ⁺-2-montmorillonites increased by the adsorption of phenol form water [104]. The adsorbed amount of phenol increased by UV irradiation, which was suggested by the increase of the basal spacing, and returned to the initial values by subsequent visible light irradiation. Imidazolium cation substituted AZs (AZ-Em-In⁺ and AZ-Bu-Im⁺), the molecular structures are shown in Figure 6(a) were intercalated in a montmorillonite from water/ethanol (=5/3) mixture and subsequently a model drug, p-aminobenzoic acid, was intercalated to the hybrids [116]. The p-aminobenzoic acid loaded AZ/ montmorillonite hybrids were placed in a phosphate buffer (pH 5.8) at 34 ± 1°C in the dark and release ratios of the model drug by UV irradiation was examined. As shown in Figure 6(b), the released ratios in the dark in 12 h were 30% for AZ-Em-In⁺ and 33% for AZ-Bu-Im⁺, while those under the UV irradiation were 71% for AZ-Em-In⁺ and 80% for AZ-Bu-Im⁺, respectively. It was thought that increase of the basal spacing was origi-
nated by the photoisomerization of AZ-Em-In⁺ (0.06 nm) and AZ-Bu-Im⁺ (0.10 nm) in the interlayer space, which resulted in the efficient release of the model drug by the irradiation.

The particle shape is expected to change by the photoisomerization of the intercalated AZ in the layered materials, and as examples, sliding of niobate nanosheet in μm scale [119–122] and bending motion of a layered siloxane film in mm scale [123] have been reported. These morphological changes may involve associating changes such as volume, lubricant, rheology, etc. so it is worth investigating further from different aspects also.

4. Ion and molecular transport through liquid-liquid interface

Extraction of solute from solution by using immiscible solvents combination is a common way of separation and purification. Photoinduced migration of a molecule between two immiscible solvents through liquid-liquid interface has been reported as a smart separation triggered by light. The systems can be categorized into two; photoresponsive materials are 1) dissolved and move with the target species through the interface and 2) fixed on the membrane to act as valves.

![Figure 6](image_url)

**Figure 6.** (a) Molecular structure of imidazolium cation substituted AZs and (b) in vitro release profiles of p-aminobenzoic acid from the AZ-Em-In⁺ and AZ-Bu-Im⁺ intercalated montmorillonites in the dark and under UV radiation at 34 ± 1°C in phosphate buffer solution. (Reproduced from the reference [116] with permission).
4.1. Molecular migration through liquid-liquid interface

Donor-acceptor Stenhouse adduct (DASA) [124] changes its electronic state by light irradiation to give zwitter ionic colorless state and it shows negative photochromism in non-polar environment thanks to the long π-conjugated system as the thermodynamically stable colored state (Figure 7(a)) [125, 126]. The change in the electronic state led photoinduced migration of DASA between water (for colorless) and toluene (for colored), which is shown in Figure 7(b).

4.2. Ion transport through liquid membrane by photoresponsive molecules

The photoresponsive molecules were not fixed at liquid-liquid interface and acted as vehicles for ion transport through the membrane. The ion transport was triggered by photochromism [127] of such as AZ [7, 128–130] and SP [131–133], photoinduced charge separation of porphyrin [134–138] and photodecomposition of ligand in a metal complex [139]. The first example of the photoinduced cation transport through liquid-liquid interface was reported by Shinkai et al [7]. Photosomerization of AZ-crown-1 (shown in Figure 8(a)) enabled photoswitching of its metal cation capturing [128–149]. By the change of the affinity between AZ-crown-1 and the metal cations, alkali metal cations were transported through a liquid membrane by irradiation [7, 128–130]. Cation binding ability of both the trans- and cis-isomers of AZ-crown-1 was estimated by the solvent extraction of metal salts of methyl orange from water to o-dichlorobenzene induced by irradiation. The binding ability for cis-AZ-crown-1 for K⁺ (55.2%) was 42.5 times higher than that (1.3%) of trans-AZ-crown-1 [7]. The photoinduced transport of the metal cations was also examined in a U-shaped tube as shown in Figure 8(b). Two aqueous solutions were separated by the liquid membrane of o-dichlorobenzene containing AZ-crown-1. An aqueous solution (left side in Figure 8(b) noted ‘IN’) contained metal cations and an indicator (2-nitrodiphenylamine-4-sulfonic acid) and the other solution (right side in Figure 8(b) noted ‘OUT’) did not contain metal ions. Absorbance due to the indicator in the right side solution was measured to quantify the cation transport to show that the transport of K⁺ by AZ-crown-1 under high pressure Hg lamp (0.34 μmol/h) was 17 times higher than that (0.02 μmol/h) in the dark.

By using this concept, anion transport was also achieved using AZ-urea (the molecular structure is shown in Figure 8(a)) [150–152]. AZ-urea had two urea substituents and the cis-isomer interacted with Cl⁻ effectively. An association constant of cis-AZ-urea for Cl⁻ (8400 M⁻¹) was 15 times larger than that of trans-AZ-urea (570 M⁻¹) [150]. Fluorescence intensity in Fischer rat thyroid epithelial cells including halide sensitive fluorescent proteins (YFP) was used to quantify the halide in a cell separated by a plasma membrane. The concentration of Cl⁻ decreased to 90% of the initial concentration by UV irradiation for 2 h while the concentration did not change in the dark.

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Figure 7. (a) Photochromism of DASA and (b) photoinduced migration from toluene (upper) to water (bottom) by visible light irradiation. (Reproduced from the reference [124] with permission.)
These observations indicated that AZ-urea accommodated Cl\(^-\) to transport across the plasma membrane. A cyanide ion sensor was proposed by using the different interactions between the substituents of the two phenyl rings of AZ and cyanide ion \([153]\). In addition, photoinduced adsorption/desorption of metal cations on polymer beads crosslinked with AZ-crown-1 \([154]\), and photoinduced extraction of metal cations from water to organic solvent \([155–159]\) and transport between two liquid phases through a liquid membrane \([131–133]\) with crown ether functionalized SP were reported. Proton transport by utilizing protonated MC which released proton by light irradiation (Scheme 1(d)) was reported to make electric voltage (up to 210 mV) \([133]\).

Inspired by the light-driven cation pumps in biological systems seen in bacteriorhodopsin \([160,161]\) and photosynthesis, cation transport through lipid bilayer membranes of liposome was designed \([134–137]\). As shown in Figure 9, a photocatalytic cycle of cation transport was achieved in the liposome incorporating 2,5-diphenylbenzoquinone (Q\(_s\)) and molecular triad (C-P-Q) composed of tetraerythrophyrin (P), naphthoquinone with norbornene and carboxylic acid (Q) and carotenoid (C) \([134]\). The photocatalytic cycle progressed as 1) photoexcitation of P induced electron transfer from C to Q in order to form a charge separated state (C\(^+\)-P-Q\(^-\)), 2) Q\(_s\) accepted the electron from the radical anion (Q\(^-\)) and converted to a radical anion Q\(_s\)\(^-\), 3) Q\(_s\)\(^-\) reacted with H\(^+\) in water outside of the liposome, 4) the protonated radical Q\(_s\)H\(^+\) moved into the lipid layer and 5) oxidation of Q\(_s\)H\(^-\) by the radical cation C\(^+\) in the triad to regenerate the initial state of the triad (C-P-Q) with emitting H\(^+\) to inside of the liposome. Each intermediate was characterized by transient absorption spectroscopy. The local pH value in the liposome was estimated by the pH dependent emission of 8-hydroxyxpyrene-1,3,6-trisulfonic acid (HPTS) at 510 nm \([134]\). ATP was synthesized by the photoinduced H\(^+\) transfer with the molecular triad in the liposome with F\(_o\)F\(_i\)-ATP synthase \([135]\). When hydroquinone derivative (1-(2,5-dihydroxypyphenyl)hexadecan-1-one) was used instead of Q\(_s\), transport of Ca\(^{2+}\) was reported \([137]\).

Anion (Cl\(^-\)) transport was also achieved by photo-decomposition of N-phenyl-1H-indole-2-carboxamides named as 'procarrier'. The schematic representation of the transport is shown in Figure 10 \([139]\). The procarrier (shown in Figure 10(b)) decomposed by UV irradiation to give 'carrier' which formed a complex with Cl\(^-\). The complex transported Cl\(^-\) into vesicle of egg-yolk phosphatidylcholine (EYPC) following the concentration gradient. After the UV
Irradiation, fluorescence from HPTS in the vesicle at 510 nm increased. The fluorescence of HPTS at 510 nm was attributed to the protonated HPTS, and the protonation occurred at lower pH probably caused by Cl\(^{-}\) in the present system. Thus, the change in the fluorescence of HPTS at 510 nm was used to show the transportation of Cl\(^{-}\). The Cl\(^{-}\) amount increased by the light irradiation while no change was seen without the irradiation.

4.3. Ion transfer using photoresponsive membrane

The development of an artificial ion pump driven with sun light is expected to provide a novel light harvesting system [133,162,163]. Materials mimicking the ion channels on 1) the modification of channel proteins and 2) the preparation of artificial ion channels in lipid bilayer have been examined in addition to 3) design fully artificial ion channel.

4.3.1. Modification of ion channel

Activation of channel proteins was controlled by the modification with photochromic moiety [164–167] and with an inhibitor containing a photochromic unit [168]. A channel protein, large conductance mechanosensitive channel (M\(_{SC}\)L), acts as a stretch-activated osmotic release valve in the inner membrane of \(E.\) coli [169]. A glycine residue at 22nd amino acid in M\(_{SC}\)L was replaced with cysteine in order to incorporate a SP derivative as shown in Figure 11(a). The SP functionalized M\(_{SC}\)L opened by UV irradiation thanks
to the hydrophilic MC and the release of calcine from a liposome containing the M5cL functionalized with SP was observed as shown in Figure 11(b) [164, 165]. Two cysteine residues of SecY, which are parts of a gate in a protein-translocating channel (SecYEG) [170], were crosslinked with bis(bromomethyl)azo-benezene. Translocation of a protein, proOmpA, was stopped by the UV irradiation, which indicated that the gate was closed by the shorter distance between two cysteine residues with the cis-isomer than that with the trans-isomer.

GroEL, which is a tubular assembly of 14 identical protein subunits [171], incorporates denatured proteins and assists the refolding of the proteins in presence of adenosine triphosphate (ATP). ATP has a role in opening the cavity of GroEL to release the refolded protein. A cysteine at 231st in GroEL was functionalized with 4-carboxyl-AZ to control the release of incorporated proteins from GroEL [166,167]. Green fluorescence protein (GFP) was incorporated in the AZ functionalized GroEL in a tris(hydroxymethyl)aminomethane hydrochloride (Tris-HCl) buffer. The release of GFP was monitored by fluorescence. The release of GFP from the AZ functionalized GroEL was initiated by the addition of ATP. The cis-AZ functionalized GroEL showed three times more efficient release of GFP than that from the trans-AZ functionalized GroEL, although unfunctionalized GroEL did not refold GFP. The difference in the accessibility of ATP to the trans- and cis-AZ functionalized GroELs was shown to affect the release of GFP.

An ion channel called calcium-release activated calcium (CRAC) channel is activated at low $\text{Ca}^{2+}$ concentration to increase $\text{Ca}^{2+}$ concentration in plasma membrane [172]. The activation of CRAC was inhibited by a channel blocker named GSK-5498A (Figure 11(a)) with a half maximal inhibitory concentration ($\text{IC}_{50}$) of 3.10 $\mu$M [173]. Inspired by GSK-5498A, an AZ derivative (AZ-inhibitor, the molecular structure shown in Figure 11(b)) was designed to have the similar molecular structures with GSK-5498A [168]. The trans-AZ-inhibitor acted as a channel blocker for CRAC with $\text{IC}_{50}$ of 73.2 $\mu$M, which was larger than that of GSK-5498A. On the other hand, cis-AZ-inhibitor, whose molecular structure was different from GSK-5498A, showed a lower $\text{IC}_{50}$ value (0.5 $\mu$M) than trans-AZ-inhibitor and GSK-5498A. It was proposed that the structural difference between trans- and cis-AZ-inhibitor caused the change in CRAC.

### 4.3.2. Artificial ion channel

Artificial ion channels have been prepared in lipid bilayers [174–177] and photoinduced transmembrane molecular transport was achieved [178–182]. As shown in Figure 12, naphthalene diimide octamer (NDO, the structure is shown in Figure 12) formed a rod-like structure in a lipid bilayer of EYPC. NDO (Figure 12) generated a charge separated state by 635 nm irradiation to oxidize ethylenediaminetetraacetic acid (EDTA) and to reduce 1,4-naphthoquinone (Q), which caused pH difference [178]. Intercalation of 3-((5-butoxynaphthalen-1-yl)oxy)propyl hydrogen...
sulfate (BNS, the molecular structure is shown in Figure 12) induced transformation of the rod-like structure to ion channel with 0.48 nm pore. The ion channel transported OH\(^-\) to neutralize the pH difference between both sides of the lipid bilayer.

Scheme 2 shows examples of the crown ethers connected with some photoresponsive units. Channel-1 and Channel-2, AZ-crown-2 and Crown-motor formed ion channels in the lipid bilayers of EYPC and Channel-3 did in diphytanoylphosphatidylcholine. The ion channels composed of Channel-1 and Channel-2 were decomposed by light irradiation to deactivate the ion transport. Reversible on/off switching of the ion transport was reported by using isomerization of AZ-crown-2, Channel-3 and Crown-motor (Scheme 2) [180–182]. Vesicles of EYPC incorporating with AZ-crown-2 were prepared with encapsulating 8-hydroxy-1,3,6-pyrene-trisulfonate (HPTS) in an inner water phase [181]. The vesicle was irradiated UV light in an aqueous KCl solution, then, the increase of fluorescence at 425 nm ascribable to the emission from deprotonated HPTS was observed. The fluorescence at 425 nm was used as an indicator (probe) of the local environment of HPTS molecule. Deprotonation of HPTS was thought to occur by the transportation of K\(^+\) from the outer aqueous solution of the vesicle to the inside of the vesicle through the ion channel of AZ-crown-2 with simultaneous transportation of OH\(^-\) [183]. After the UV irradiation for 150 s, the fluorescence intensity became higher than that in the dark, suggesting the efficient transportation of K\(^+\) with cis-AZ-crown-2 compared to trans-AZ-crown-2, even though the channel size (0.58 nm) in trans-AZ-crown-2 was larger than that (0.28 nm) in cis-AZ-crown-2. The reason for the efficient transport through cis-AZ-crown-2 was proposed to be the hydrophilicity for cis-AZ-crown-2 in the channel.

Figure 11. (a) Molecular structure of SP derivative to control M_{50L}, GSC-5498A and AZ-inhibitor and (b) photoinduced release of calcein from liposome with SP functionalized M_{50L}. (Reproduced from the reference [164] with permission).

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The photoswitching of fluorescence intensity caused by cation transport was also observed with Crown-motor (the molecular structure is shown in Scheme 2). The preferential cation transport at the order of Rb\(^+\) > K\(^+\) > Na\(^+\) was reported for Channel-3 and Crown-motor systems [180,182]. The sequence was attributed to the selectivity of alkali metal ions binding by the photosensitive molecules shown in Scheme 2.

Fully artificial ion channel has been prepared with conical shaped pores and photocontrol of impedance of the pores [184–187]. Fully photodriven ion pumps are scarcely reported [162]. As shown in Figure 13, a conical shaped pore was prepared in a polyimide membrane (thickness: 12\,\mu m, pore size: 500/10–15 nm) and subsequently AZ moieties were incorporated by a reaction with surface COOH which was generated during the pore formation [162]. The charged molecules such as sulforhodamine B and rhodamine 6 G did not transport through the pore due to the hydrophobic pore surface given by the AZ moieties while cyclodextrins (CDs) transported by the UV irradiation, suggesting the higher affinity of CDs with trans-AZ than cis-AZ [188,189].

Ion transport through membrane was also achieved by photothermal effect [190]. Photoinduced charge separation between cationic and anionic polyacetylenes [191] and p/n heterojunction of TiO\(_2\)/graphitic carbon nitride (g-C\(_2\)N\(_4\)) [163] was also used to trigger the ion transport. As shown in Figure 14(a), a porous anodic alumina (AAO) membrane with the cylindrical pore with the diameter of 100 nm was coated with TiO\(_2\) and g-C\(_2\)N\(_4\) sequentially with the 10 nm thickness for each to prepare p/n heterojunction [163]. Light irradiation to the semiconductor induced charge separation and, as the result, localized negative charges were generated on the surface in the pore with the gradient to the light. The gradient of the negative charge induced cation transport to the light. On the other hand, the coating with reverse sequence (g-C\(_2\)N\(_4\) => TiO\(_2\) as shown in Figure 14(b)) generated surface positive charges by the light irradiation and anion transport to the light was seen.

5. Photoinduced molecular migration in solid and on solid surface

Microscopic patterning such as gratings and dots is useful for lithography, holographic imaging, metamaterials and superhydrophobic surfaces. Mass transfer of polymer in film induced by light irradiation has been used to make images such as lithography and holography [192]. The light irradiation through

Figure 12. Photocatalytic electron transfer by naphthalene diimide octamer (NDO) and transformation by BNS to neutralize pH gradient. (Reproduced from the reference [178] with permission).
a photomask or interfering laser to the polymer film induced the periodic surface texture (pattern), which is called as surface relief gratings (SRGs) \[193\]. The patterns were generated by molecular migration from irradiated to non-irradiated regions in the polymer films \[194–197\]. In this chapter, the strategy for the generation of SRG caused by photochemical reaction such as photodecomposition, polymerization and photoisomerization will be discussed. The surface tension change by the photochemical reaction leads to the motion of macroscopic objects.

5.1. Surface relief grating modified by photodecomposition and photopolymerization

In order to accelerate the SRG formation, photodecomposition \[198,199\] and photopolymerization \[200–211\] have been utilized. The doping of photosensitizer has also been examined to obtain SRG by longer and weaker light irradiation \[212\]. SRG formed in a cast film of mixture of polystyrene (PS) and poly (\textit{tert}-butoxy styrene-\textit{ran}-styrene) containing a photoacid, triphenylsulfonium nonaflate, by light (200–800 nm) irradiation for 1 min with a photomask and subsequent annealing at 120°C for 30 min \[199\]. \textit{tert}-Butoxy groups in the copolymer were decomposed to hydroxyl groups by the photoacid to generate surface tension difference in the irradiated and the non-irradiated regions, leading to Marangoni flow, which is material flow caused by the difference in surface tension, of PS from the non-irradiated region to the irradiated region during the annealing.

Photopolymerization of diene \[201\], acrylates \[200,204,205,209–211\], epoxy \[208\], benzoic acid \[203\] and anthracene \[202\] has been used for the SRG formation. Because monomer was mobile during the light irradiation and photopolymer stabilized the
**Figure 13.** (a) The light-driven proton-pumping system of bacteriorhodopsin, (b) photochromism of a retinal Schiff base in bacteriorhodopsin, (c) bio-inspired light-driven CD-transportation system by (d) photoisomerization of AZ. (Reproduced from the reference [162] with permission).

**Figure 14.** Schematic drawing of the fabrication of p/n heterojunction of TiO$_2$/C$_3$N$_4$ (a) and (b), photoinduced charge separation in the heterojunctions (c) and (d) and ion transport under light irradiation (e) and (f). (Reproduced from the reference [163] with permission).
SRG structure, effective formation and high thermal and photostability of SRG were achieved. However, the SRG was not rewritable as the polymerization is not reversible. In order to form rewritable SRG, a film of an anthracene derivative (Anth-1, the molecular structure is shown in Figure 15) with the thickness of 0.1 μm was prepared by spin coating [202]. SRG formation was seen by UV irradiation with a photomask (365 nm, 0.12 mW cm⁻²) at 333 K for 10 min. The AFM image of the SRG is shown in Figure 15(b). The SRG was stable at around 360 K and the structure was maintained at 390 K by the subsequent UV irradiation thanks to the dimerization of Anth-1. The effect of the back reaction to monomer was not reported, which is worth investigating to introduce rewritable property.

### 5.2. Surface relief grating by photochromism

Micrometer sized SRG formed in the systems containing photochromic units such as AZ [196,197,213–285], SP [286–289], SO [290], DAE [291], imidazole dimer [292], SB [293], phenylacetylene carboxylic acid [294], cinnamic acid [295–297], benzilidenaniline [298] and fluorene [299]. The importance of Marangoni flow was pointed out in the SRG formation in the systems containing AZ [300–323].

Extensive studies on the SRG formation suggested the importance of Marangoni flow induced by interactions among polymers and light [224,248,255,267,269,285,313]. As an example, the contact angle of 95° for a water droplet on the surface of trans-form of poly(4-(acryloyloxyhexyloxy)-4′-pentylazobenzene) was higher than that (73°) seen on the cis-form, suggesting that the surface tension in the cis-form was larger than that in the trans-form [269]. As shown in Figure 16, UV irradiation to a film with the trans-form induced mass flow from the non-irradiated (low surface tension) to the irradiated (high surface tension) areas. In contrast, visible light irradiation to a cis-rich film induced mass flow from the irradiated (low surface tension) to the non-irradiated (high surface tension) area. These facts suggested that the Marangoni flow played an important role on the SRG formation in the AZ polymers.

In order to clarify the effect of the surface tension on the SRG formation, SRG of a photoinactive polymer (PCPBz, the structure is given in Figure 17, (b)) film coated with AZ polymer (PAz, the structure is given in Figure 17, (b)) was studied [314]. Although the PCPBz film (the thickness of 200 nm) without the PAz coating did not give SRG by UV irradiation with a photomask as shown in Figure 17, (Ca), the PCPBz films with the PAz coating prepared by Langmuir-Schaefer (LS)

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**Figure 15.** (a) Molecular structure of Anth-1 and (b) the AFM image of the resulting SRG formed in Anth-1 film by the UV irradiation (365 nm, 0.12 mW cm⁻²) for 10 min at 333 K under N₂ atmosphere using photomask. (Reproduced from the reference [202] with permission).
method gave the SRG. Moreover, the formation of SRG of the PAz films was disturbed by poly(octadecyl methacrylate) (PC18, the structure is given in Figure 17, (b)) coating, suggesting that change of the surface tension was suppressed by the photoinactive PC18 coating (Figure 17, (d)). It was concluded that Marangoni flow was major driving force for the SRG formation in AZ polymers and further studies to establish a unified model which explains all SRG systems are expected. Based on the conclusion, studies on SRG of photoinactive polymers ionically interacted with AZ molecules were reported to show beneficial aspects of photoinduced surface tension difference with keeping high mobility of the components [237,278,315,324].

5.3. Structure variation of SRG

Interfering laser and photomasks have been used to form grating structures, while several structures such as holes, needles, wells, spiral reliefs and lattice structures formed by controlling optical polarity [281], optical vortex [248,255] and shaping of irradiated area [212,269,281]. As shown in Figure 16(c), micrometer sized structures such as a truncated cone with the diameter of ca. 60 μm and a well with the diameter of 81 μm were obtained by the controlled light irradiation. Nanometer scale SRG whose size was same as the wavelength of visible light enabled to prepare holographic images [203,274,325–331]. By combining real time holography whose response time was within 200 ms [332–338], holography with a clearer image and quicker response time was suggested. Furthermore, inkjet printing technique led arbitrary shaped surface morphology by the SRG as shown in Figure 18 [313]. A block copolymer consisting of PAz (see Figure 17) and polybutyl methacrylate was printed on a PAz substrate (thickness: ca. 350 nm) by the inkjet printing with a sub-femtoliter droplet and was subsequently irradiated by UV light to form SRG with the shapes of Nazka Desert humming bird (Figure 18(b), upper) and a spiral circle (Figure 18(b), lower).

5.4. Movement of macroscopic objects

Not only for molecular species and colloidal particles, the movements of macroscopic objects are worth investigating even though the larger energy is required for the movement as the kinetic energy is expressed as a function of the weight of the object [339–342]. Surface tension difference [343–353] and resulting

Figure 16. Schematic drawing of the SRG formation by irradiating to induce (a) trans-rich and (b) cis-rich polymer and (c) resulting surface structures. (Reproduced from the reference [269] with permission).
Marangoni flow [354,355] have been used to induce the movement of μm to cm sized objects such as liquid droplet, glass particles and molecular crystal [345,349–353]. In this section, photoinduced movement of the macroscopic size objects modified with photoresponsive surface tension control units is discussed.

A rod-shaped glass particle (ca. 5 μm diameter × 24 μm length) functionalized with AZ moved to the light on a nematic liquid crystal film of 4-cyano-4′-pentylbiphenyl (5CB) as illustrated in Figure 19(a) [343]. Before the irradiation, the trans-AZ groups aligned along the surrounding 5CB molecules, while by the irradiation, photogenerated cis-isomers caused the disordered alignment of 5CB and a phase transition to an isotropic phase. The phase transition was thought to induce the difference in the surface tension between the irradiated and the non-irradiated regions, being the driving force for the movements of the particle.

DMAB crystals (the molecular structure is given in Figure 19, (Ba)) moved by simultaneous UV and
The crystals became longer along the light irradiation during the movement to the visible light, suggesting the driving force for the movement was melting of the crystals by the UV irradiation to generate the cis-isomer and simultaneous recrystallization by the visible light irradiation [344,348]. The crystal moved by the difference in wettability in the melted and the crystalline regions.

As shown in Figure 19, (Ca), a droplet of 1-hexadecyloxybenzaldehyde in an aqueous solution of hexadecyltrimethylammonium bromide (CTAB) and CnAzo (the molecular structure is given in Figure 19, (Cb)) moved away from the UV light [355]. Before the UV irradiation, CTAB and trans-CnAzo being surrounded the oil droplet. The cis-isomer became the major isomer in the irradiated area and caused the change of surface tension and simultaneous Marangoni flow in the droplet (Figure 19, (Cb)). At the photostationary state, the migration was stopped as a result of the homogeneous surface tension.

An aqueous solution of an AZ surfactant moved to the light in the glass tube with the inner diameter of...
2.5 mm as shown in Figure 19, (D) [347]. The surface tension of the irradiated region of the solution changed by the photogenerated cis-isomer to be a driving force for the movement [356].

5.5. Movement of macroscopic objects on photoresponsive surface

Micrometer sized glass rods and flakes rotated on the surface of chiral nematic liquid crystals, which are also known as cholesteric liquid crystals (ChLCs) [357–369]. ChLCs are prepared by adding chiral molecules to nematic liquid crystals and have a twisted alignment. On a glass substrate, ChLCs show characteristic fingerprint textures reflecting the twisted alignment as shown in Figure 20, (Aa) and (C). The pitch length was controlled by photoresponsive chiral dopants such as AZ [370] and DAE [371]. The photoinduced change in the pitch length caused the change in the surface energy (Figure 20, (Ab)) of ChLC, enabling the rotation of micrometer sized (30 μm) glass rods (Figure 20, (c)). A glass rod (average length: 25 μm, diameter: 5 μm) rotated almost 3 cycles (1150°) on a nematic liquid crystal E7 doped with a naphthopyran, which was functionalized with helicene (1 wt%, Figure 20, (Ba)) by the UV irradiation for 5 min [369]. Subsequently the glass rod retuned 206° in the dark. A nematic liquid crystal E44 containing AZ-dopant-1 (Figure 20, (Bb)) rotated a glass rod (length: ca. 30 μm, diameter: 7 μm) ca. 1200° by UV light irradiation [372]. By using the phase transition from a fingerprint texture to a focal conic state by the light irradiation, unidirectional rotation of a glass flake (size: several tens of μm) was achieved [360]. The fingerprint texture of AZ-dopant-2 (Figure 20, (Bc)) added 5CB (1.7 wt%) changed to the focal conic state by the UV irradiation without rotating the glass flake and the subsequent visible light irradiation led the focal conic state to the initial fingerprint texture with rotating the glass flake.

Functionalization of substrate surface with AZ was done to impart switching function; the surface tension caused by the photoisomerization induced the movements of liquid droplet [373–379], PS sphere [380,381] and silica particles [382]. An olive oil droplet on a surface of a silica plate functionalized with CRACM (Figure 21, (Aa)) moved by light irradiation [373]. As shown in Figure 21, (Ab), the UV light was irradiated to the silica plate to prepare a cis-rich surface (a) and subsequent blue light irradiation made trans-rich (low surface energy) and cis-rich (high surface energy) regions. Consequently, the droplet transferred from the trans-rich (left) to the cis-rich regions (right) (b). Blue light irradiation to the substrate reset the surface state so that the droplet transferred opposite direction by the same protocol (d). Droplet with a molecular shuttle moved by the light irradiation, where the droplet climbed up 12° inclination [385].

Photodecomposition of surface components induced change in the wettability, which induced the movement of water droplets on the surfaces [383,386,387]. TiO₂ particles on the surface of a poly (methyl methacrylate) (PMMA) film generated oxygen vacancies by UV irradiation, and the vacancies

![Figure 20](image-url)

Figure 20. (A) Twisted alignment of ChLC (a), periodic surface energy of ChLC (b) and surface structure of ChLC (c), (B) molecular structures of photochromic chiral dopant discussed in this section and (C) rotation of a glass rod by photochromism of the naphthopyran (in Ba) in E7. (Reproduced from the references [357,360] and [369] with permission).
Figure 21. (A) Molecular structure of calixarene functionalized with AZ moieties (CRA-CM) (a) and lateral photographs of light-driven motion of an olive oil droplet on a silica plate modified with CRA-CM (b), (B) photoresponsive bifunctional alkynes and multifunctional thiols used for the preparation of thiol–yne networks with multigradient surface properties (a) and schematic representation of the photoinduced formation of a Laplace pressure gradient and a wettability gradient on thiol–yne photopolymer surfaces (b) and (C) exchange reaction of diselenide bonds on the surface of a capillary by (EG₄Se)₂ (a) and liquid motion was achieved by altering surface wettability inside the diselenide bond modified capillary tube (b). (Reproduced from the references [373,383] and [384] with permission).

were used for the adsorption of water in air to form a hydrophilic surface [386]. The water contact angle decreased from 73° to 28° by the UV irradiation for 90 min. The difference in the surface wettability in the irradiated and the non-irradiated regions led the movement of the droplet to the irradiated region (more hydrophilic). A polymer shown in Figure 21, (Ba) synthesized from alkynes and thiol crosslinkers by visible light irradiation decomposed by subsequent UV irradiation. The photodecomposition of the polymer gave polar products such as carboxylates (Figure 21, (Bb) from middle to right) [383,387]. The asymmetric irradiation with a photomask resulted in a pattern, which led the water droplet to move to the irradiated area as a result of the hydrophilicity shown by the contact angle from 139° to 10° (Figure 21, (Bb) right).

Movement of liquid in tubes coated with diselenide bonds and AZ polymers was reported [384,388,389]. Diselenide bonds showed hemolytic bond cleavage by visible light irradiation or heat and recombined to the initial diselenide bonds, so that hetero dimers were obtained from homo dimers in the presence of some diselenide compounds [390–392]. The surface of a capillary (inner diameter of 0.5 mm) was functionalized with 3-aminopropyltriethoxysilane and subsequent di(valeric acid) diselenide [384]. The capillary was put into an aqueous solution of (EG₄Se)₂ (Figure 21, (Ca)) and was irradiated by the visible light. The height of the solution in the capillary rose probably caused by the changing of surface wettability by the substitution of the surface selenide bonds with hydrophilic ethylene glycol units in (EG₄Se)₂ (Figure 21(C)). Such liquids as isopropanol, silicon oil and water moved away from the light in ethylene-vinyl acetate tube (inner diameter: 0.4 mm) coated with the AZ polymer by the irradiation shorter than 470 nm [388,389]. The difference in Laplace pressure in the irradiated and the non-irradiated regions was thought to be a driving force of the movement.

6. Photoinduced adsorption/desorption between liquid-solid

Adsorption/desorption on solids from solutions is important phenomenon connecting to the application for concentration, separation and purification especially for/from aqueous solutions. The desorption is a key for the slow or controlled release for agricultural and medical applications. Accordingly, photoresponsive adsorption/desorption is expected as advanced separation and controlled release systems.
6.1. Photoinduced adsorption/desorption of photochromic compounds

Photochromic reactions accompany changes in the polarity, which has been used as a trigger for several photoinduced phenomena as introduced previously. It was reported that AZ derivatives such as methyl red induced change in the orientation of liquid crystals by UV irradiation [393–395]. The mechanism of the phenomena was explained as photoinduced adsorption of polar cis-isomers onto the substrates [396–398]. The non-polar trans-isomers followed the molecular orientation of the host nematic liquid crystals on the substrate, on the other hand, the polar cis-isomers were adsorbed on the substrate and caused the change in the molecular orientation as shown in Figure 22(a). The molecular structure of AZ derivatives affected the orientation of the liquid crystals [399–401]. As shown in Figure 22(b), a 4,4′-substituted AZ derivative was shown to induce the change in the orientation of a nematic liquid crystal, DON-103 (LODIC), from planar (parallel to the substrate) to homeotropic orientation (perpendicular to the substrate) by light irradiation [399]. It was explained that the substituents oriented perpendicular to the substrate. In contrast, the nematic liquid crystal changed its orientation from random planar (parallel to the substrate without preferred direction of the alignment) to uniform planar one (parallel to the substrate with one direction of the alignment) by photoisomerization of a 3,3′-substituted AZ derivative. The AZ derivative was adsorbed on the substrate with the molecular long axis parallel to the substrate and acted as a director of the alignment. The photoinduced adsorption of AZ derivatives caused the changes in the orientation of nematic liquid crystals from planar to homeotropic orientation [402–404], the rotation of the direction of cholesteric liquid crystal (ChLC) in planar orientation [405] and the phase transition from nematic to twisted nematic phases [402,406,407].

The changes of the surface tension and the refractive index caused by the photoinduced adsorption of AZ derivatives were used for making SRG [408–411] and holography [412]. A methyl red doped nematic liquid crystal, E7 (Merck), formed surface reliefs with 380 μm distance gratings by the interference fringes of He-Ne laser [408–411], which is regarded as a kind of SRG. By utilizing the refractive index change with the SRG formation, a holographic image was obtained as shown in Figure 23(a) [413,416]. Developments of display [414,417–419] and Fresnel lens [415,420,421] by photoinduced adsorption of methyl red were reported. As shown in Figure 23(b) left top, gray colored letters of ‘NCKU’ were written by 532 nm laser irradiation to E7 doped with methyl red [414]. The letters were written by the phase transition to twisted nematic phase. The letter of ‘K’ was erased by subsequent circularly polarized laser irradiation (right top). A square shaped mark was written instead of ‘K’ by the laser irradiation (bottom), where the bright and the dark parts were opposite due to a quarter-wave plate. By 532 nm irradiation to E7 doped with methyl red through a Fresnel zone plate mask (Figure 23(c)), Fresnel lens based on liquid crystal was prepared [415,420,421] with the first order diffraction efficiency.

![Figure 22](image_url)

Figure 22. Schematic drawing of (a) photoinduced adsorption of AZ derivative with changing molecular orientation of liquid crystal and (b) adsorption of 4,4′-substituted and 3,3′-substituted AZ derivatives. (Reproduced from the reference [399] with permission).
up to 35% in the presence of addition of operating voltage at 3.6 V [421].

SP changed from colorless to blue by UV irradiation in toluene, while SP turned to red in the presence of mesoporous silicas (MPSs) as shown in Figure 24 [422]. The difference in color with/without the MPSs was thought to be due to the adsorption of the photo-generated MC. Adsorption kinetics were estimated by UV–vis absorption spectra depending on the irradiation time [423,424]. The changes of the concentration of SP followed pseudo-first or pseudo-second order kinetics and a MPS with larger pore (SBA-15 with 9.5 nm diameter) gave a larger pseudo-second adsorption rate constant \(9.55 \times 10^{-5} \text{ g(mg min)}^{-1}\) than that with the smaller pore (MCM-41 with 2.2 nm diameter, \(8.91 \times 10^{-3} \text{ g(mg min)}^{-1}\)), suggesting that the diffusion of MC in the pore played an important role for the adsorption. The same phenomenon, photoinduced adsorption of MC, was reported in the presence of a clay mineral (a synthetic hectorite) [425,426]. Electrostatic interactions of MC with a negatively charged silicate layer and/or ion-dipole interactions with the interlayer cation were thought to be the driving forces. The effect of the interlayer cation on the photoinduced adsorption was examined by using Na\(^+\) and H\(^+\) intercalated hectorites [426]. The adsorption of MC onto the hectorites had two pseudo-first order constants attributed to the adsorption of MC and the protonated MC. The rate constant of the slower component for the Na\(^+\)-hectorite (0.186 min\(^{-1}\)) was larger than that (0.054 min\(^{-1}\)) for H\(^+\)-hectorite, suggesting that the importance of the interlayer cations on the photoinduced adsorption rate. The adsorbed amount of MC on H\(^+\)-hectorite (8.75 mg/g) was larger than that (7.33 mg/g) on Na\(^+\)-hectorite. Generation of the thermodynamically stable protonated MC instead of MC was thought to be a reason for the larger adsorbed amount seen for H\(^+\)-hectorite [427].

6.2. Photoinduced uptake and release by photoresponsive vehicles

Adsorbent which shows controlled release is expected as vehicles to deliver the guest drugs into a target tissue in our body, which is known as drug delivery system (DDS). The light induces contactless release of the guest molecules only in the irradiated region.

Figure 23. (a) Optical system to make holographic images and (inset) the resulting image, (b) example of display image of letters written by photoinduced adsorption (left top), subsequently erasing the latter of “K” (right top) and rewriting of a square shaped mark (bottom) and (c) a set up to prepare fresnel lens. (Reproduced from the references [413,414] and [415] with permission).

Figure 24. Photochromism of SP in toluene (blue square) and toluene with MPS (red square).
6.2.1. Release by photoinduced molecular vibration

Dyes such as fluorescein [428], rhodamine 6 G [429] and B [430], and propidium iodide [430] and drugs such as camptothecin [430] and doxorubicin [431] were released by photoinduced molecular vibration of AZ attached on MPSs with Type B functionalization shown in Figure 25. Near infrared (NIR) light triggered release of doxorubicin was reported by using an upconverting core-shell particle consisting of the core of NaYF₄ containing 0.5 mol% Tm³⁺ and 20 mol% Yb³⁺ and the inner and external shells (inner shell: NaYF₄ and external shell: Type B MPS functionalized with AZ moieties) as shown in Figure 26(a) [431]. Doxorubicin was released up to 80% from the MPS shell by 980 nm irradiation with 8.9 W/cm² for 17 h, although the release was less than 5% in the dark. The efficient release by the irradiation was thought to be due to the molecular motion of AZ excited by 350 nm light upconverted in the core (Figure 26(b)). The light irradiation contributed to the release of the guest molecules through the induced molecular vibration.

6.2.2. Release by photodecomposition

Nitrogen oxide [432], dyes such as AZ [433], Nile red [434] and anisaldehyde [435] and drugs such as 5-fluorouracil [436,437], camptothecin [438], doxorubicin [439–441] and bromoisophosphoramide [442] were released by the photodecomposition of polymers, MPS, Au nanoparticle and graphene oxide. As summarized in Figure 27, several strategies have been used for the photodecomposition via (a) ring-opening reaction of coumarin unit, (b) switching of host-guest interaction of AZ and cyclodextrin, and bond cleavage by (c) photocid and activated oxygen, and of (d) o-nitrobenzil groups and diselenide bonds (Figure 21(C)). By using ring opening reaction of coumarins (Figure 27(a)), 5-fluorouracil was released from a block copolymer, poly(ethylene oxide) methyl ether and poly(n-butyl methacrylate), functionalized with coumarins [436]. Agglomerate of polyamidoamine (PAMAM) dendrimers was decomposed by the ring opening reaction of coumarin linkers with releasing of contained 5-fluorouracil and DNA [437]. By utilizing photoswitching of interactions of AZ with cyclodextrin as shown in Figure 27(b), a hydrogel of poly(ethylene glycol) functionalized β-cyclodextrin released AZ-peptide (molecular structure is in Figure 27(b)) by UV irradiation [433]. Anisaldehyde was released from poly (4-vinyl phenol) substituted with anisaldehyde through acetal by decomposition of the acetal by photoacid (SP) (Figure 27(c)) [435,443]. The bond cleavage of o-nitrobenzyl groups shown in Figure 27(d) [444] induced the release of camptothecin from self-assembled DNA particle [438], doxorubicin from DNA [440] and chitosan particle [439]. A semiconducting polymer consisted of cyclopenta[2,1-b:3,4-b’]dithiophene and benzo[c] [1,2,5]thiadiazole generated activated oxygen by light irradiation and the activated oxygen decomposed 2-nitroimidazole side chain of the polymer to release bromoisophosphoramide [442]. A polyphosphoester substituted with doxorubicin through thioketal and amide groups released doxorubicin by 660 nm irradiation [441]. Oxygen was activated by photoexcitation of the thioketal side chain and the activated oxygen decomposed the amide group to release doxorubicin [441].

Photodecomposition of hydrogels [445,446] and vesicle [447–450] resulted in the photoinduced release of the drugs such as doxorubicin and mitoxantrone, DNA and a protein (GFP). Two dextrans with β-cyclodextrin and AZ side chains connected each other by using host-guest interaction of β-cyclodextrin and AZ (Figure 27(b)) to form a hydrogel. The hydrogel showed gel-sol transition by UV irradiation with releasing encapsulated GFP [445]. Photosomerization of AZ incorporated in vesicles of liposome [447], sodium dodecylbenzene sulfonate (SDBS) [448], sodium dodecyl sulfate (SDS) [448] and pillar [6]arene [449] induced change in critical aggregation concentrations of the vesicles by UV irradiation [450]. Liposome incorporating a cholesterol functionalized AZ released encapsulated calcein by UV irradiation and the release was stopped by subsequent visible light irradiation [447].

Figure 25. Schematic drawing for organic functionalization of MPSs (Type A) as framework backbone and grafted (Type B) in pores and (Type C) at orifices.
6.2.3. Release by photoinduced structure change of host vehicles

Isomerization of photochromic compounds such as AZ and SP induced structural changes of the hosts such as polymers, MPS and MOF, which accompanied the changes in the polarity [451–461], pore size [462–466] and switching of open/close of orifice of the vehicles [467–482]. The polarity change in polymers by the photochromism of AZ and SP was used to release butanediol [455], dyes such as fluorescein [456], methylene blue [457], Nile red [458] and coumarin [460], drugs such as 2′-deoxy-5-fluorouracil [459], dextran [459] and doxorubicin [460] and proteins such as lysozyme [452,454], chymotripsinogen [454] and chymotripsin [454]. Vesicles composed of PEO-b-PSPA and SP units (molecular structure is shown in Figure 28, (A)) were used as vehicles, which release 2′-deoxy-5-fluorouracil and dextran by UV irradiation [459]. Before the irradiation, the hydrophobic SP blocked the release of the hydrophilic guests in the vesicle, while the photogenerated hydrophilic MC allowed the release of the guests from the vesicle. The release was terminated in the dark due to the back reaction of MC to SP. An opposite phenomenon, photoinduced adsorption, was also achieved by the vesicle of PEO-b-PSPA with SP. Cysteine grafted Au nano particles was adsorbed to the vesicle by the UV irradiation. A Type A MOF substituted with AZ shown in Figure 28, (Ba) (and the category is in Figure 1) with the chemical composition of Cu₂(DCam)₃(AzoBiPyB) where DCam: D-camphoric acid and AzoBiPyB: (E)-2-(phenyldiazenyl)-1,4-bis (4-pyridyl)benzene) showed preferential adsorption of (S)-phenyl ethanol compared to (R)-phenyl ethanol in the presence of trans-AzoBiPyB (Figure 28, (Bb)) [453]. As the adsorbed amount of (S)- and that of (R)-phenyl ethanol with cis-AzoBiPyB was almost same as shown in Figure 28, (Bc), possible photoinduced chiral separation was proposed.

Pore size of MPS and MOF has been controlled by photochromism of AZ and coumarin, which enabled photoinduced release of propidium [463], butanediol [464,465], U(VI) [466] and Au nanoparticles [462]. A Type A MPS (category is shown in Figure 25) was synthesized from tetraethoxysilane (TEOS) and AZ-silanol (shown in Figure 29) in the presence of cetyltrimethylammonium bromide (CTAB), and was used for the collection of Au nanoparticles [462]. The efficiency shown by the removal of Au nanoparticles with the diameter less than 2.6 nm was different before (83%) and after the UV irradiation (64%). Change in the XRD pattern shown in Figure 29 suggested the
pore size difference in the trans-rich and the cis-rich conditions achieved by the UV irradiation.

Reversible opening and closing of orifices of MPSs [483] and MOFs [484] by light irradiation were used for the controlled release of butanediol [471], dyes such as pyrene [473], phenanthrene [468], methylene blue [481], methyl orange [474], brilliant blue [481], fluorescein [469,480,482] and rhodamine B [472], drugs such as cholestane [467], cholesterol [475], doxorubicin [470,476,479] and curcumin [478], and DNA [477]. Type B MPSs (category is shown in Figure 25) were prepared by substitution with photochromic units such as AZ [477–481], SP [469,470,482], coumarin [467,468,475,476] and SB [474]. The first example of this concept was reported in a MPS (MCM-41) functionalized with coumarin [467]. The orifice of Type B MPSs grafted with AZ was opened by photo-switching of interactions with cyclodextrins [478–480] and DNA [477] which acted as cap of the orifices. The orifice of Type B MPSs reversibly opened and closed by photoswitching of the polarity caused by the photochromism of the SP at the orifice [469,470,482]. Hydrophilic (polar) guests were not able to pass the orifice substituted with hydrophobic SP, while hydrophilic MC which was formed by UV irradiation allowed them to be released. Phenanthrene [468], cholestane [467] and cholesterol [475] were released by the ring opening reaction of coumarin dimers by 250 nm irradiation. As shown in Figure 20(a), an external surface of a hollow MPS particle synthesized with polystyrene (PS) latex template was grafted with octadecyltrimethoxysilane and subsequently coated with HAMAFAB·DDACMM incorporating coumarin unit [476]. The polymer, HAMAFAB·DDACMM, showed two photon absorption at 800 nm by the coumarin units, which caused the hydrolysis of the ester moieties. The decomposition induced the release of the polymer from the MPS and opened the pore of the MPS to release the loaded doxorubicin.

Orifice of MOF was opened and closed by the photochromism of the attached AZ [471,472] and SB [474]. A MOF, Cu₂(BPDC)₂(BiPy) (BPDC: biphenyl-4,4′-dicarboxylic acid, BiPy: 4,4′-bipyridine), whose external surfaces were grafted with AZ, induced a change in the pore size at the external surface by UV irradiation [471]. The change in the pore size was used as a trigger to release preloaded butanediol. Rhodamine B was loaded to a Type A MOF, which was consisted of zirconia cluster node and a terphenyl ligand substituted with trans-AZ side chain (ZrO(2′-p-terlyldiazene-1,1′,4,4′-terphenyl-4,4′-dicarboxylic acid)). In order to confine the rhodamine B, the orifice of the MOF was blocked by the complexation of β-cyclodextrin with the surface AZ side chain of the ligand of the MOF surface [471]. The loaded rhodamine B were released from the MOF by open of the orifice, which was induced by the desorption of β-cyclodextrin by the photosomerization of the AZ side chain. The external surface of a MOF, MIL-53, was grafted with SB units (styrylpyrene) as shown in

Figure 27. Photoreactions used for controlled release by (a) ring opening reaction of coumarin, (b) host-guest interaction between AZ and cyclodextrin, (c) photoacid and (d) bond cleavage of o-nitrobenzyl groups. (Reproduced from the references [188,435,436] and [443] with permission).
Figure 30(b) [474]. The comparable pore size of MIL-53 (8.5 Å) and molecular size of the SB units (7.8 Å × 18.8 Å) allowed the dimerization of the SB units in the pore by visible light irradiation. As schematically shown in Figure 30(b), methyl orange was encapsulated in the SB grafted MIL-53 and immobilized by the visible light induced dimerization of the SB units. The backward reaction of the dimer to the monomer was induced by UV irradiation, leading the release of the methyl orange.
6.3. **Movements of macroscopic objects**

Camphor boat moves on water surface by surface tension difference between the front and the back of the boat generated by the sublimation of the attached camphor, which is a known example of self-propelled objects or moving objects driven by chemical energy. The movement of a camphor boat was controlled by using molecular layer of photochromic compounds (AZ [485] and hexaarylimidazole (HABI) [486]) spread on water surface. A camphor boat moved on the water surface covered with trans-4-[[dodecyl]oxy]benz-4-yl]azo]benzoic acid and the movement was stopped by UV irradiation as a result of the surface pressure change [485]. Photoinduced movements of benzoquinone crystal (disk) [487] and 4-methoxyazo-benzene (4-OMe-AZ) crystal [488] were reported. The 4-Ome-AZ crystal moved on the water surface by the dissolution of the photogenerated cis-isomer, which has higher solubility than that of the trans-isomer [489]. The movement of benzoquinone disk on a hydroquinone aqueous solution by the dissolution of benzoquinone was stopped by UV irradiation because the UV irradiation caused photoreaction of benzoquinone around the disk to uniformize the concentration gradient of hydroquinone and benzoquinone [487].

The local heat was generated at the irradiated region owing to the thermal relaxation from the excited sate (photothermal effect). The heat caused the changes in the physicochemical properties of the irradiated region, which was used to drive a liquid flow [354,490,491]. Au coated poly(allylaminehydrochloride)/poly(styrenesulfonic acid) [492] and a MPS (MCM-41) [493] moved in water by light irradiation driven by the heat generated on the Au particle. An oil droplet coated with polyaniline moved away from the light on a water surface [494], which was explained as the heat generated in the irradiated region in polyaniline diffused on the water surface to cause Marangoni flow in the water. As shown in **Figure 31**, (A), such liquid droplets as water, glycerol and propylene glycol moved on the surface of polydimethylsiloxane (PDMS) plate embedded Fe₃O₄ nanoparticles. The heat caused by 808 nm irradiation to Fe₃O₄ induced Marangoni flow to the droplets on the PDMS surface. Consequently, the droplet moved away from the light and climbed up the hill of 10° inclination as shown in **Figure 31(Ac)** [495,497]. Photothermal effect of Au nanorods (length: 800 nm) on a glass substrate caused transformation of poly(N-isopropylacrylamide) coating, which thermotropically transformed from hydrophilic to hydrophobic at around 32°C [498]. The transformation caused the surface energy difference around the irradiated region, which induced the movement of a water droplet from hydrophobic (irradiated) to hydrophilic (non-irradiated) regions.

Movements of microscopic objects were also induced by concentration gradient generated by photocatalytic reactions [340]. A TiO₂ particle and a Janus particle of a silica particle coated with Pt moved away from the UV irradiation [499,500]. The photothermal effect and the generation of O₂ gas by the photocatalytic reaction on TiO₂ and Pt were thought to drive the movement. A Janus nano rod, which had a silicon nano rod core (ca. 10 μm length) grafted with TiO₂ nanowires and Pt nanoparticles as illustrated in **Figure 31**, (B), showed the surface charge dependent motion in water, which was induced by the photodecomposition of oxygen peroxide in the water [496]. The motion was controlled by the surface charge of the Janus rod and the external electric field caused by H⁺ and OH⁻ which were the products of the photocatalytic reactions by TiO₂ and Pt, respectively. Positive phototaxis was observed when the rod had negative or positive surfaces (a, b and d), while negative phototaxis was observed when the two parts had opposite charges (c). Movement of water in tubes by photothermal effect was reported [501–504]. A tube of poly(N-isopropylacrylamide) whose external surface was coated with graphene oxide was used to show the movement of water to the light [501]. The photothermal effect on graphene oxide induced the transformation of poly(N-isopropylacrylamide) from hydrophilic to hydrophobic, which accompanied increase of the inner diameter of the tube. The hydrophobic surface in the tube with larger diameter induced the movement of water away from the light. The photoinduced transformation of the tube surface character is expected to be used for optical actuator [505,506].

**Figure 29.** Molecular structure of AZ-silan and change in the XRD pattern (I) before and (II) after UV irradiation. (Reproduced from the reference [462] with permission).
6.4. Directional movement of macroscopic object

Both positive and negative phototaxis was observed in photoinduced transfer of nitrobenzene droplets in water, depending on surfactants surrounded the nitrobenzene droplet and photoacid/photobase in the water phase as shown in Figure 32 [489]. A nitrobenzene droplet being surrounded with 2-hexyldecanoic acid (HDA) showed negative phototaxis in an aqueous solution of a photobase, 6-methoxyquinoline (6MQ, Figure 32 (Aa)), or a photoacid, 2-naphthol-6-sulfonate (2N6S, Figure 32(Ab)). A droplet being surrounded with HDA and C_{12}-HPTS (shown in Figure 32(Ac)) showed positive phototaxis while a water/oil/water vesicle composed of didodecyldimethylammonium bromide (DDAB) and 8-hydroxyppyrene-1,3,6-trisulfonic acid (HPTS, shown in Figure 32(d)) showed negative phototaxis. In the aqueous solution of the photobase (6MQ, Figure 32(a)), 6MQ captured a proton from HDA to form deprotonated HDA (DA⁻) and non-reacted HDA diffused to the light to cause Marangoni flow away from the light. As schematically shown in Figure 32(Ab), the droplet was surrounded with DA⁻ initially. The DA⁻ accepted proton from the photoacid (2N6S), consequently the DA⁻...
diffused to the irradiated region to make Marangoni flow away from the light. Photoinduced proton transfer from $\text{C}_{12}^+\text{HPTS}$ to DA$^-\text{made}$ flow of deprotonated $\text{C}_{12}^-\text{HPTS}$ and HDA away from the light (Figure 32(Ad)), which induced the Marangoni flow to the light. In the water/oil/water vesicle shown in Figure 32(Ad), protons generated from photoacid changed the ion strength in the irradiated area in the water phase, which caused flow in the water phases to the light, as the result, the vesicle moved away from the light.

Pyroelectric effect of lithium niobate was induced by photothermal effect to provide surface charge on lithium niobate, enabling transfer of a water droplet along the electric field [507,508]. As shown in Figure 32(Ba), the glass substrate was coated with polyethyleneimine (PEI) and Prussian blue (PB) and subsequently lithium niobate, which generated surface positive charges by the photothermal effect of PB [507]. The water droplet transferred on superhydrophobic surface of silver nanoparticles to the light irradiation (Figure 32(Bb)). The photoinduced movement of the droplet by the pyroelectric effect was also reported on a superhydrophobic surface of silica nanoparticles on a lithium niobate coated polydimethylsiloxane plate doped with graphene [508]. Surface positive charges were generated on the lithium niobate coating due to the photothermal effect of the graphene. Such liquid droplets as silicon oil, ethanol, $n$-heptane, glycerol and water migrated to the surface charge generated on the surface.

7. Conclusions

Inspired by 'smart' and 'sustainable' natural photoinduced phenomena in bio and geospheres, artificial systems from nano to micrometer scales have been designed to reveal movements of various objects upon photoirradiation. Photoresponsive molecules have been built from photochromic molecules and molecular linkers allowing binding to the target. They have been attached on the surface of particle, and incorporated or dispersed in polymers. Moving objects have been extended from molecules/ions to macroscopic particles. The movement of larger objects needs more energy, which was provided by photochemical and photothermal reactions. This combination of material driving force and system analysis allowed
to create unique moving platforms; the movement direction in some of them can be controlled as an ‘artificial’ phototaxis. Driven by developments in the material design and the characterization (high-speed cameras, microscopes, positioning devices, etc.), the movements will be extended to improve the speed, direction, and response time of moving objects for applications in medical and other fields like molecular robot and actuators.

Disclosure statement

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Figure 32. (A) Migration of nitrobenzene droplets surrounded with HDA (a) in an aqueous 6MQ solution, (b) in an aqueous 2N6S solution, (c) surrounded HDA and C17-HPTS and (d) surrounded DDAB and HPTS, and (B) by pyroelectric effected of lithium niobate caused by photothermal effect by Prussian blue. (Reproduced from the references [489] and [507] with permission).
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