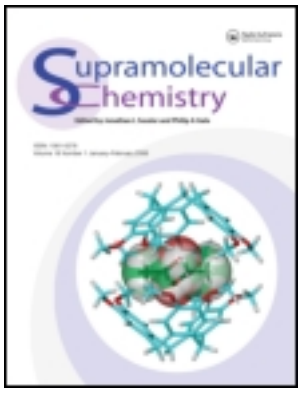

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Dynamic supramolecular systems at interfaces

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Nanotechnology from a bottom-up approach relies heavily on supramolecular chemistry that can potentially provide nano- and microstructures with molecular level precision of internal configurations through low-energy spontaneous processes. Moreover, supramolecular assemblies at the two-dimensional interface have great potential to be integrated into artificial devices. Studies on supramolecular chemistry at interfaces are, therefore, highly relevant for the development of nanotechnology. Another distinct aspect of supermolecules exists in their advanced dynamic properties that are anticipated to provide various stimuli-responsive systems. Here, we summarise the recent literature describing the dynamic behaviours of supermolecules at interfaces and supramolecular chemistry at dynamic interfaces categorised into three classes: (i) dynamic behaviour at solid surfaces, (ii) supermolecules at dynamic interfaces in liquid media and (iii) supermolecules at the air–water interface.

Keywords: dynamic function; interface; molecular assembly; molecular recognition; supramolecular material

Introduction

Although supermolecules have been regarded as an attractive scientific topic for a long time, any significant attention has only recently been paid to their practical applications (*1–14*). Reasons for the increasing concentration of research effort on supermolecules are based on requirements for breakthrough concepts and technological advancement of nanotechnology. Many advances in nanotechnology can be mostly attributed to the development of top-down microfabrication techniques, which are, however, likely to encounter manufacturing limitations in the near future. Therefore, complementary approaches, including the so-called bottom-up processes, have become of great interest in recent years. Bottom-up approaches rely heavily on supramolecular chemistry, especially self-assembly aspects, because they can potentially provide nano- and microstructures with molecular level precision of internal configurations through low energy and costless spontaneous processes. Although various works on self-assembled materials have been reported to date (*15–20*), assembled structures in three-dimensional (3D) media such as solutions or solids are not well connected to current device-oriented nanotechnology. However, supramolecular chemistry at 2D interfaces has great potential for the assembly of artificial devices such as field-effect transistors, electrodes and even integrated circuits. Therefore, studies on supramolecular chemistry at interfaces are highly relevant to the development of nanotechnology.

Another distinct aspect of supermolecules, as compared with inorganic metallic and semiconductive nanomaterials, exists in their advanced dynamic properties (*21–27*). Because supermolecules are assembled through non-covalent soft interactions, their structures have dynamic properties. This aspect is strongly anticipated to provide various stimuli-responsive systems that cannot be obtained using hard and inflexible inorganic materials. Here, we summarise the recent literatures regarding dynamic behaviours of supermolecules at interfaces and supramolecular chemistry at dynamic interfaces categorised into three classes: (i) dynamic behaviour at solid surfaces, (ii) supermolecules at dynamic interfaces in liquid media and (iii) supermolecules at the air–water interface.

Dynamic behaviour at solid surfaces

At a confined 2D interface, programmed molecules tend to assemble according to limitations in their orientation, interaction modes and directions, which are quite different from those contained in 3D systems, which have greater flexibility in their motion. Hence, supramolecular complex formation and supramolecular assemblies at interfaces have become attractive research topics.

Advanced microscopic methods such as atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) are frequently used for the observation and analysis of molecular assemblies on well-defined solid surfaces which enable direct observation of assembly behaviour with molecular-level precision on a 2D solid interface. Zimmt

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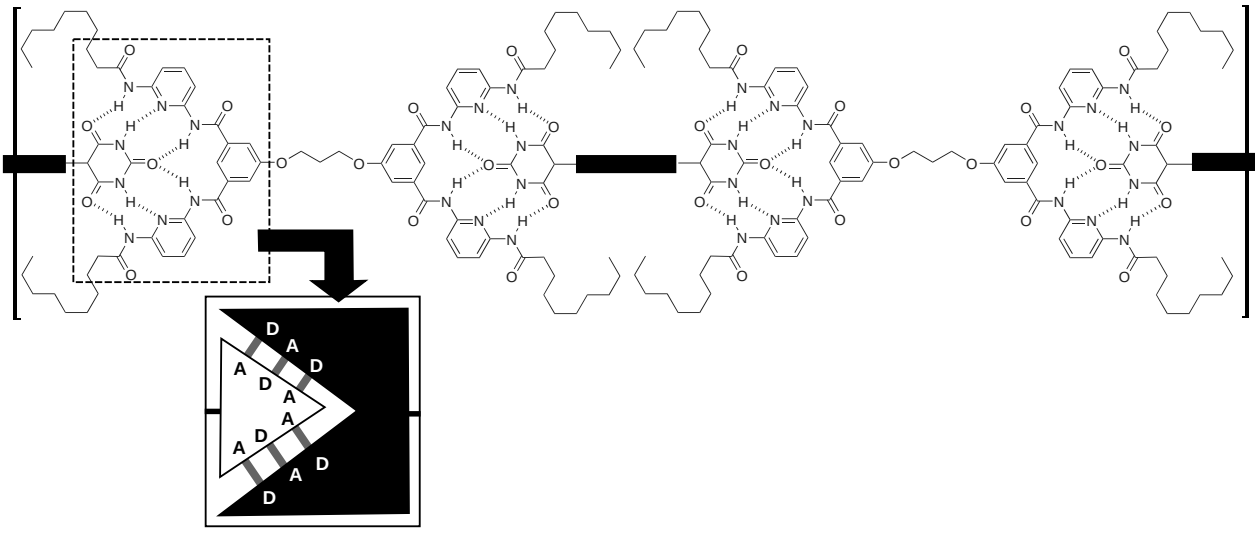

Figure 1. One-dimensional hydrogen-bonded arrays from Janus-type barbituric wedge (ADA–ADA array) and DAD–DAD counterpart unit.

and co-workers (*28*) showed co-crystallisation of 1,5-side chain-substituted anthracene derivatives at the liquid–highly oriented pyrolytic graphite interface. The target compounds were designed based on dipole interactions and chain length discrimination during 2D assembly. Lehn and co-workers (*29*) showed STM visualisation of 1D supramolecular polymers assembled at the liquid–solid interface. As illustrated in Figure 1, 1D hydrogen-bonded arrays were formed using a Janus-type cyanuric wedge or barbituric wedge (ADA–ADA array; A and D represent hydrogen bond acceptor and donor, respectively) and a corresponding counterpart unit (DAD–DAD array). Use of these two molecules having different spacer moieties can result in geometric control of the linear supramolecular polymers. They also proposed that introduction of cross-linking components may produce extended supramolecular assemblies spreading into two dimensions.

Deposition of molecules from the gas phase onto well-defined solid surfaces also provides appropriate opportunities to observe supramolecular assemblies with molecular level precision (*30*–*33*). For example, Champness and co-workers (*34*) observed formation of 2D supramolecular structures of perylene tetracarboxylic diimide derivatives on a graphene monolayer by means of STM under ultra-high vacuum (UHV) conditions. They demonstrated that a moiré-like superstructure can lead to the stabilisation of the extended 1D supramolecular assemblies with the help of intermolecular hydrogen bonds between imide groups and neighbouring molecules.

Hill and co-workers (*35*) investigated 2D supramolecular arrays of phenol-substituted porphyrin derivatives, as well as quinonoidal oxocyclohexadienylidene porphyrinogen derivatives, and revealed interesting phenomena such as conformational adaptation at the phase boundary and a hydrogen-bonded 2D network array, Kagomé lattice (*36*). They also demonstrated dynamic behaviours of a 2D supramolecular array at the solid interface (*37*, *38*). STM images of the porphyrin derivatives adsorbed at a Cu(111) surface under UHV are shown in Figure 2. The hexagonal packing of the porphyrin derivatives was observed at a lower temperature. This packing motif was formed through a hexagonal arrangement of the disc-like porphyrin derivatives with planar conformation because of the intermolecular van der Waals contacts. Hence,

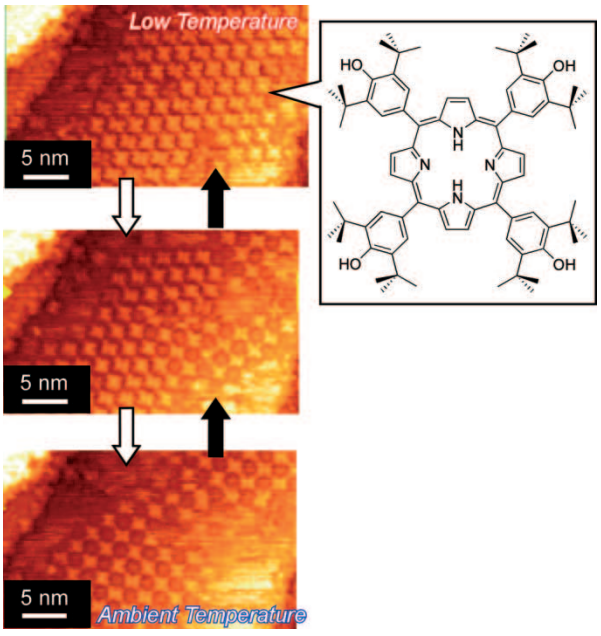

Figure 2. STM images of porphyrin derivatives deposited onto a Cu(111) surface under UHV showing phase transition between hexagonal and square arrangements.

an increasing coplanarity between porphyrin macrocycles and *meso*-substituents contributes to the stabilisation of the structure in the presence of electron-donating hydroxyl groups at the periphery. Interestingly, heating to ambient temperature induced dynamic transition of the packing from lattice to square packing. The latter packing pattern is associated with the molecular conformation having a large dihedral angle between the porphyrin macrocyclic plane and the phenyl substituent. From their research, the square packing is found to be preferable with regard to the conformational energy of an individual molecule, although van der Waals contacts among neighbouring molecules and those between molecules and surface are reduced. Basically, the stability of the hexagonal packing originates from their enhanced intermolecular and surface molecule contacts. Therefore, the coexistence of the hexagonal and square domains and facile transition between these domains indicate that both phases are metastable and the energy barrier between these domains is relatively small. That is, the transition from a hexagonal to a square phase is highly dynamic and cooperative.

Supramolecular films prepared on solid surfaces such as electrodes and various devices often show dynamic interaction with external molecules, which is useful for the design and construction of molecular sensing systems. At present, various dynamic organic thin films can be formed through appropriate methods such as the self-assembled monolayer (SAM) method (*39–42*), Langmuir–Blodgett techniques (*43–46*) and layer-by-layer assembly (*47–55*), providing various sensing systems such as glucose sensing by enzyme-modified thin films (*56–58*) and calcium sensing by phospholipid analogues (*59*). Such supramolecular thin films have great potential to be used for control of permeation of small analytes, resulting in selective sensing. To date, many studies have been devoted to the realisation of highly sensitive devices using such concepts.

Yitzchaik and co-workers (*60*) prepared a dilute assembly of acetylcholine esterase on a floating gate-derived field effect transistor towards a highly sensitive device for the detection of acetylcholine. The enhanced sensitivities were explained by the combined response of the device to the local pH changes and the molecular dipole variations through the enzyme–substrate recognition event. McDermott and co-workers (*61*) prepared an array of disaccharide epitopes on thin gold films for the effective sensing of the corresponding antibody using surface plasmon resonance (SPR) imaging. Fort and co-workers (*62*) used electrochemical SPR (E-SPR) for the detection of carbohydrate-binding proteins. In their approach, electrochemically polymerised films of oligosaccharide derivatives functionalised with pyrrole groups were used for the detection of lectins, *Arachis hypogaea* and *Maackia amurensis*. Liu and co-workers (*63*) immobilised a thiol-mixed monolayer comprising conjugates of 3-aminophenylboronic acid with 11-mercaptoundecanoic acid and 11-mercapto-1-undecanol on a gold surface. These electrodes were designed as a reusable amperometric immunosensor for detection of the reversible boronic acid–sugar interaction by means of voltammetric and electrochemical impedance spectroscopy and SPR. Krozer and co-workers (*64*) prepared spin-coated films of molecularly imprinted nanoparticles on flat transducer surfaces for specific molecular sensing. In this paper, the quartz crystal microbalance with dissipation (QCM-D) technique was used to show a moderate chiral selectivity. Dalcanale and co-workers (*65*) investigated molecular recognition properties of third-generation tetraphosphonate cavitand receptors for the detection of alcohols and water by means of combined analyses of electrospray ionisation mass spectrometry, X-ray crystallography and QCM. They also demonstrated detection of halogen-tagged aromatic volatile compounds by a quinoxaline cavitand-decorated Si surface (*66*). Boyen and co-workers (*67*) investigated chemical interactions between organic components and metals at the solid interface towards detection of small molecules in solution by monitoring the tunnelling resistance between two metal electrodes. For this purpose, a SAM structure of 4-aminothiophenol was prepared on top of an Au(111) crystal, followed by a metalisation by a nearly closed Pd overlayer of monoatomic height. According to the analyses with photoelectron spectroscopy and density functional theory, strong chemical interactions between the metal atoms and the amino groups of the organic molecules result in a drastically reduced density of states at the Fermi level for the metal overlayer, a quantity of importance for the charge transport across the metal–molecule interface.

Apart from the typical flat film systems, various types of solid interfaces have been proposed for the investigation and application of dynamic functions. Urban and co-workers (*68*) synthesised poly(methyl methacrylate/*n*-butyl acrylate) colloidal particles stabilised by a phospholipid towards an artificial mimic of potential lipid–protein interactions and investigated formation of surface-localised ionic clusters. Azzaroni et al. (*69*) assembled ferrocene-labelled streptavidin molecules as electroactive bioinorganic building blocks onto a metal electrode which was covered with biotin-terminated thiol. This was achieved by strong ligand–receptor biological interactions and was used to fabricate electroactive multilayered structures using multivalent macromolecular ligands. These redox-active molecular platforms were used as molecular rectifiers with tunable and amplifiable electronic readout. Hashimoto and co-workers (*70*) reported a new type of ordered monolayer for the surface modification of organic semiconductors where fullerene derivatives with fluorocarbon chains spontaneously segregated on the surface of a [6,6]-phenyl-C_{61}-butyric acid methyl ester film during a spin-coating process. The surface-segregated monolayer provides a potentially excellent way to modify the surface of

organic semiconductors that could be applicable in various organic optoelectronic devices. In other examples, several integrated surface structures such as pore surfaces of mesoporous materials have been used for dynamic supramolecular functions (*71–75*). Such systems are among the promising candidate functional materials for applications such as efficient separation, sensing and drug delivery due to their large surface areas.

Supermolecules at dynamic interfaces in liquid media

Dynamic properties and functions can be commonly constructed when interfaces themselves are dynamic. Interfaces formed in fluidic media are essentially dynamic in nature and are often supported by molecular assemblies such as micelles and lipid bilayer membranes (vesicles and liposomes). In this section, recent research on supramolecular chemistry at dynamic interfaces in liquid media will be briefly introduced.

One of the simplest interfaces is the micelle interface, but its dynamic nature creates various interesting properties, which has prompted researchers to establish various fundamental micelle sciences. Correa and co-workers (*76*) studied interactions between different non-aqueous polar solvents including ethylene glycol, propylene glycol, glycerol, dimethylformamide and dimethylacetamide, and polar heads of sodium 1,4-bis-2-ethylhexylsulphosuccinate in reverse micelles. Detailed investigation by FT-IR provided insights into the unique reverse-micelle microenvironment created upon encapsulation of these polar solvents. This is important scientifically because these media might be used for the creation of nanoreactors for heterogeneous chemistry, as templates for nanoparticles or as models for membranes. Menger and Shi (*77*) studied micelle formation of low levels of non-aggregating anionic additives, bearing one to six negative charges, with excess of the cationic amphiphile, dodecyltrimethylammonium bromide. They pointed out that the sharp inflection observed in a surface tension vs. concentration of the surfactant plot, which is routinely measured for the evaluation of the critical micelle concentration value, does not always assign micelle formation. Suades and co-workers (*78*) synthesised platinum(II) metallosurfactants as a new family of linear surfactant phosphines. They studied the aggregation properties by dynamic light scattering and cryo-TEM and showed the formation of spherically dispersed medium-sized vesicles.

As discovered by Kunitake and co-workers (*79*) in their pioneering work, molecular recognition through hydrogen bonding and electrostatic interaction at the surface of micelles and lipid bilayer membranes is much enhanced as compared with that observed in aqueous solutions, although the binding efficiencies at micelle and bilayer interfaces are much less than those at the air–water interface as described in 'Supermolecules at air–water interface' section. Supramolecular chemistry including molecular recognition and subsequent events between bilayer vesicles has also been attractive targets (*80–82*).

Multiple hydrogen bond formation between melamine derivatives and cyanuric acid (or barbituric acid) derivatives has been well investigated in various media such as at vesicle surfaces and the air–water interface (*83–85*). Recently, Bong and co-workers (*86*) synthesised phospholipids bearing cyanuric acid and melamine as part of a head group (Figure 3) and investigated their selective heterovesicular apposition, fusion and adhesion between electrostatically identical vesicular membranes in suspension and on a solid support, in order to evaluate the pure contribution of hydrogen bonding without electrostatic interaction. This research group also developed a minimal recognition cluster in which three cyanuric acid or melamine groups were forced into proximity by covalent attachment to the phospholipid (*87*). They demonstrated that their minimal design imparts robust molecular recognition and selective membrane fusion, because the trivalent lipid–lipid binding could induce membrane apposition. Moreover, the addition of a membrane-disrupting peptide as a third component was required for lipid mixing with high efficiency. Paleos and co-workers (*88*) investigated structural features of complementary liposomes and factors favouring formation of multicompartment systems using liposomal pairs consisting of guanidinium moieties which were located at the distal end of polyethylene glycol chains and phosphate moieties. The guanidinium group recognised the phosphate group of unilamellar liposomes effectively, initiating adhesion and fusion processes of vesicles, followed by the formation of multicompartment systems, where enrichment of polyethylene glycol chains at an appropriate interaction ratio promoted fusion processes.

An interesting dynamic phenomenon, the 'breathing vesicle', was reported by Eisenberg and co-workers (*89*). They demonstrated the highly reversible volume change of a vesicle by a factor of *ca.* 7, accompanied by diffusion of species into and out of the vesicle with a relaxation time of *ca.* 1 min. The vesicles have a wall structure with three layers prepared from a triblock copolymer, poly(ethylene oxide)$_{45}$-*block*-polystyrene$_{130}$-*block*-poly(2-diethylaminoethyl methacrylate)$_{120}$. The vesicle breathing not only dramatically increased the wall permeability to water but also greatly enhanced the rate of proton diffusion from practically zero to extremely high.

Dynamic changes of polymer conformation in molecular assemblies and their interfaces are also attractive targets for dynamic functions. Thermochromism, solvatochromism and alkalinochromism of a poly-10,12-pentacosadiynoic acid vesicle solution were studied through electronic absorption spectroscopy by Sukwattanasinitt and co-workers (*90*). In the thermochromic transition, gradual conformational alteration of the methylene chains

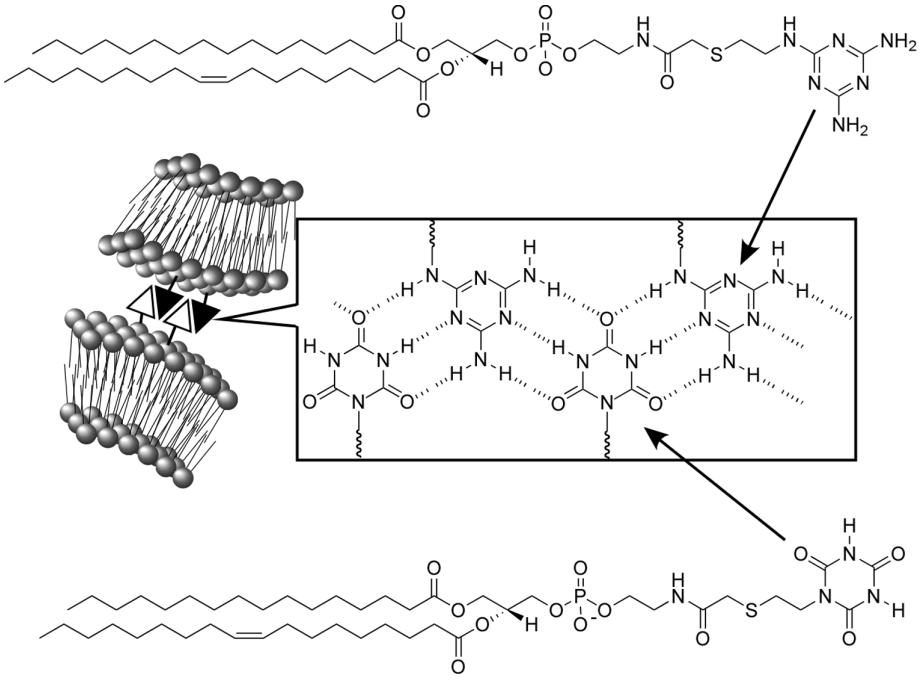

Figure 3. Molecular recognition at the surfaces of cyanuric acid-functionalised vesicle and melamine-functionalised vesicle.

converted the blue vesicles into the thermally unstable purple form reversibly, due to the breaking of hydrogen bonding at the carboxylic head group by excess heating. In contrast, the solvatochromic and alkalinochromic transitions were initiated by the vesicle interface interaction with the solvent molecules or hydroxide ions, resulting directly in the disruption of hydrogen bonding and the irreversible formation of red vesicles.

Vesicles with dynamic properties are among the most promising candidates for the application of drug delivery systems. Xu et al. (*91*) prepared temperature-responsive nano-sized polymersomes capable of triggered drug release. They synthesised triblock copolymers, poly(ethylene oxide)-*block*-poly(acrylic acid)-*block*-poly(*N*-isopropylacrylamide), in one pot by sequential reversible addition–fragmentation chain-transfer polymerisation. The triblock copolymers were quickly self-assembled into nano-sized vesicles when the solution temperature was raised to 37°C. The vesicles formed could be readily cross-linked at the interface using cysteamine as a reaction site via carbodiimide chemistry, yielding cross-linked robust polymersomes. High loading and rapid release efficiencies of fluorescein isothiocyanate-dextran, used as a model protein, into and out of the cross-linked polymersomes were achieved by the dissociation process triggered by the addition of dithiothreitol. This system is very promising for triggered intracellular delivery of biopharmaceutics such as DNA, siRNA, peptides and proteins.

In an analogous fashion, liquid–liquid interfaces provide media with appropriate dynamic functions. Sarles and Leo (*92*) proposed a novel method for regulated reconstitution of lipid bilayers at the oil–water interface. They used a mechanical force to controllably open and close an aperture of a flexible substrate that separated two aqueous volumes by a lipid bilayer, permitting large changes in the size of the bilayer. Phospholipids incorporated as vesicles in the aqueous phase were self-assembled at the oil–water interface to form lipid monolayers that encapsulated each aqueous volume. Their technique can yield highly precise microfluidic networks which offer a highly modular and customisable platform capable of constructing biomolecular networks. Cooke and co-workers (*93*) developed a simple and mild way to fabricate stable colloidal microcapsules that were compatible with host–guest systems. In their strategy, orthogonally functionalised FePt nanoparticles were self-assembled at the oil–water interface and cross-linked via dithiocarbamate chemistry (Figure 4). They studied the host–guest interaction between a flavin polymer encapsulated in the microcapsules and an external diaminopyridine amphiphile at the liquid–liquid interface. Sanyal and co-workers (*94*) fabricated stimuli-responsive colloidal microcapsules consisting of β-cyclodextrin and adamantane functionalised gold nanoparticles at the oil–water interface using host–guest molecular interactions. This non-covalent approach results in the reversible and dynamic nature of the systems for structural manipulation, especially for tuning the size of the microcapsules. Amemiya and co-workers (*95*) reported electrochemically controlled molecular recognition of a structurally well-defined Arixtra, a synthetic heparin mimetic, at the nitrobenzene–water microinterface. Quaternary ammonium ionophores, octadecylammonium and octadecylguanidinium, were used

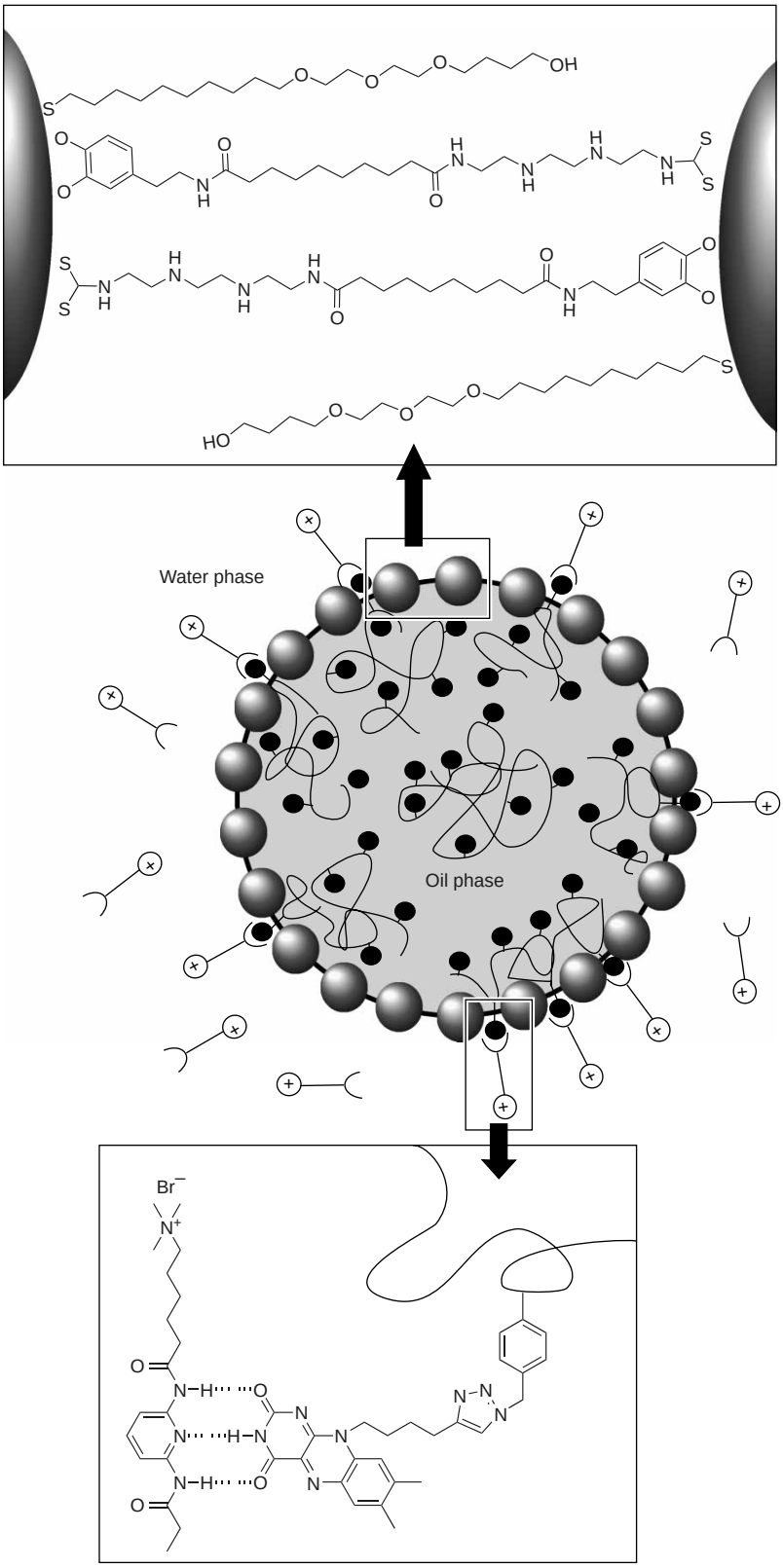

Figure 4. FePt nanoparticles assemble at the oil–water interface with host–guest interaction between entrapped flavin polymer and external diaminopyridine amphiphile.

as model recognition sites of heparin-binding proteins and their molecular recognition was investigated by cyclic voltammetry and chronoamperometry at the tip of a glass micropipette electrode. Watarai and Oyama (*96*) investigated interfacial aggregation of the complex of copper (II) ions with 5-(octadecyloxy)-2-(2-thiazolylazo)phenol at the heptane–water interface by means of centrifugal liquid membrane spectrometry and direct liquid–liquid interfacial mass spectrometry. This analysis is useful for the evaluation of the interfacial aggregation stoichiometrically, as well as the disaggregation by nucleic acid bases.

Supermolecules at air–water interface

Unlike interfaces dispersed in the solution phase, monolayers at the air–water interface can provide an easily controllable dynamic system. It is also known that this interface provides a highly effective molecular recognition media (*97*, *98*). For example, Kunitake and co-workers (*99*) found that the binding constants of guanidinium–phosphate pairs at the air–water interface were 10^6–$10^7\,M^{-1}$ under ambient conditions. As mentioned before, these values were significantly larger than those in molecularly dispersed states ($1.4\,M^{-1}$) and at the solution-dispersed interface (10^2–$10^4\,M^{-1}$). Sakurai and co-workers (*100–102*) considered theoretical aspects of molecular recognition at the air–water interface using a quantum chemical approach including reaction field calculations combined with AM1 molecular orbital methods. The calculated binding energies depend significantly on the position of the binding site relative to the two-phase boundary. Even when positioned in the water phase, the hydrogen bonding site is affected electronically by the low dielectric lipid layer, which strengthens intermolecular hydrogen bonding and electrostatic interactions. As a result, the binding constant increases significantly at the border between lipid and aqueous phases. Therefore, the air–water interface is a very promising medium for investigating molecular recognition of aqueous biomolecules. In recent examples, Kalinina and co-workers. (*103*) reported recognition of uracil and adenine nucleobases by the Langmuir monolayer of zinc-complexed amphiphilic cyclen derivatives. Ijiro and co-workers (*104*) achieved molecular control of an amphiphilic azobenzene having an adenine moiety by use of specific base paring with an oligonucleotide template at the air–water interface.

Another interesting feature of molecular recognition may exist in dynamic construction of sophisticated recognition sites derived from rather simple components (*105–108*). As shown in Figure 5, a mixing of a benzoic acid amphiphile with a peptide amphiphile enhanced the binding constant of a dipeptide guest (*109*, *110*). Because the benzoic acid moiety can interact with both C-terminal COOH and N-terminal NH_2 of the guest peptide, efficient binding to the mixed monolayer was achieved for both (a) GlyLeu and (b) LeuGly. On the other hand, introduction of a guanidinium amphiphile as the second component resulted in selective insertion of the guest dipeptide due to the strong interaction between guanidinium and C-terminal carboxylate (*111*). The binding efficiency was governed by the position of hydrophobic side chains of the guest dipeptide and the steric hindrance between host and guest side chains (c). Apart from these examples, various types of multicomponent recognition systems have been reported.

Specific molecular recognition at the air–water interface can also be used for the formation of artificial arrangements within a 2D plane. This methodology is called 2D molecular patterning (*112–114*). The general strategy of 2D molecular patterning is to use aqueous template molecules capable of binding selectively to amphiphiles at the air–water interface. For example, packing and crystallinity of amphiphilic guanidinium-functionalised molecules in a single-component monolayer were controlled by dicarboxylates as aqueous template molecules through multi-point binding and extended complex formation (*115*). A sequence-controlled array of amphiphiles at the air–water interface was also achieved by binding of an aqueous template guest with the heterogeneous recognition sites of amphiphiles. Flavin adenine dinucleotide (FAD), an aqueous template molecule having multiple binding sites, can recognise guanidinium and orotate amphiphiles at fixed stoichiometry (*116*, *117*). The AFM images of the complex monolayer on a mica surface showed a periodic wave-like structure composed almost entirely of two kinds of peaks with different heights. Competing recognition of two kinds of amphiphiles with the FAD template molecule enables control of the 2D molecular patterning with height difference. Oishi and co-workers (*118*) reported formation of a nanoscopic domain structure in a mixed monolayer consisting of hydrocarbon guanidinium and fluorocarbon carboxylic acid (Figure 6). Their approach is based on combination of ionic and/or hydrogen bonding interactions between the two polar head groups and surface-free energy difference between the hydrophobic parts of hydrocarbon and fluorocarbon. Control of the domain size from nanometre to micrometre in a phase-separated monolayer can be achieved by varying the pH and/or the ionic strength of the subphase.

Formation of controlled nanostructures is not limited to 2D objects. For instance, Gokel and co-workers (*119*) reported formation of cogged hydrogen-bonded nanotube structures from a pyrogallol[4]arene having a branched side chain in the solid state and at the air–water interface. Swager and co-workers (*120*, *121*) investigated dynamic behaviours of polymer chains at the air–water interfaces as exemplified by conjugated polymers. Lin and co-workers

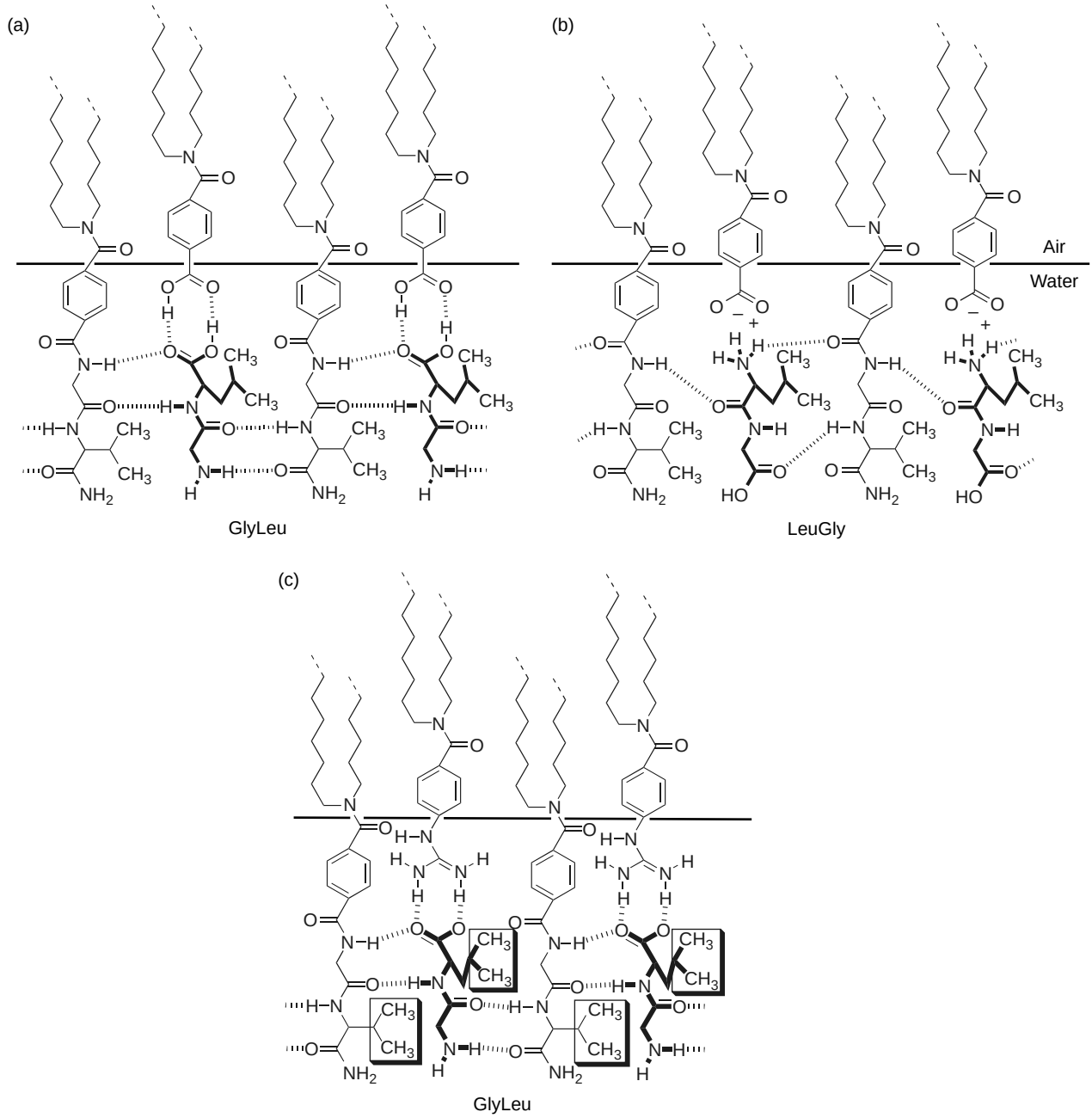

Figure 5. Molecular recognition of aqueous dipeptides by mixed monolayers: (a) binding of GlyLeu to mixed monolayer of benzoic acid amphiphile and peptide amphiphile, (b) binding of LeuGly to mixed monolayer of benzoic acid amphiphile and peptide amphiphile and (c) binding of GlyLeu to mixed monolayer of guanidinium amphiphile and peptide amphiphile.

(*122*) reported interfacial behaviour of bottlebrush-like block copolymers at the air–water interface.

Obviously, Langmuir monolayers at the air–water interface can be macroscopically compressed and expanded in lateral directions. However, drastic nanoscopic and/or molecular level changes can occur in perpendicular directions against the film plane, stimulated by macroscopic deformation and displacement of the Langmuir monolayers in lateral directions. This principle allows us to construct a dynamic interface for the control of nano/molecular systems through macroscopic mechanical motions. For example, we have previously demonstrated capture and release of a molecule at the air–water interface by using macroscopic motions. As shown in Figure 7(a), a steroid cyclophane molecule with a cyclic core consisting of a 1,6,20,25-tetraaza[6.1.6.1]paracyclophane connected to four steroid moieties (cholic acid) through a flexible L-lysine spacer was used as a monolayer component (*123–127*). This molecule worked like a molecular machine to catch a guest molecule in the water

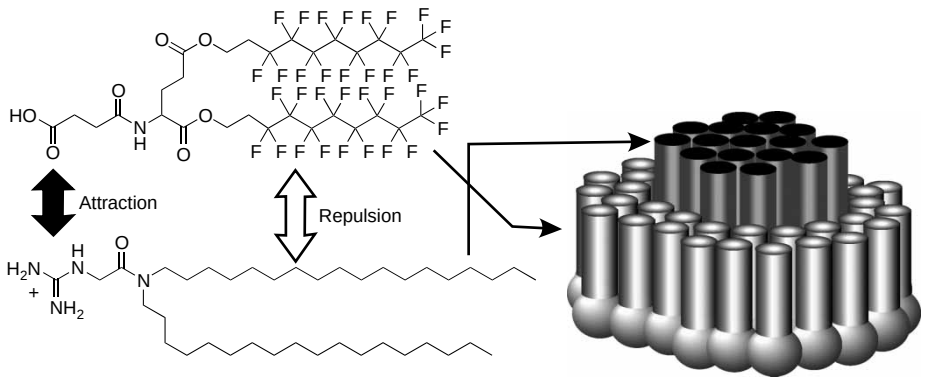

Figure 6. Nanometre-sized surface morphology constructed in a mixed monolayer by a combination of the ionic and/or hydrogen bonding interaction between the two polar head groups and the surface-free energy difference between the hydrophobic parts of the hydrocarbon and fluorocarbon.

subphase. The steroid cyclophane was spread onto the water surface to form a Langmuir monolayer in which the isotherm of the surface pressure as a function of molecular area (π-A isotherm) showed a phase transition from an expanded phase to a condensed phase with a limiting area of *ca.* 2 nm^2. The latter value corresponds to the cross-sectional area of the steroid cyclophane with cavity conformation, indicating the dynamic change from a 2D flat conformation to a 3D cavity one. Capture of a guest molecule dissolved in the water subphase was investigated using a fluorescent dye, 6-(*p*-toluidino)naphthalene-2-sulphonate (TNS). Because the fluorescence of the TNS molecule is largely quenched in a highly polar aqueous medium but exhibits strong emission when trapped in a non-aqueous cavity, the fluorescence at the air–water interface was monitored in order to estimate the molecular capture by the steroid cyclophane. As expected, an abrupt increase in the TNS fluorescence intensity was observed when the monolayer of steroid cyclophane was compressed to the condensed phase, indicating that the cavity conformation induces capture of the guest TNS molecule. This molecular capture is caused by bulk motion over several tens of square centimetres. Consequently, the capture of the guest molecule from an aqueous phase by bulk mechanical motions is realised.

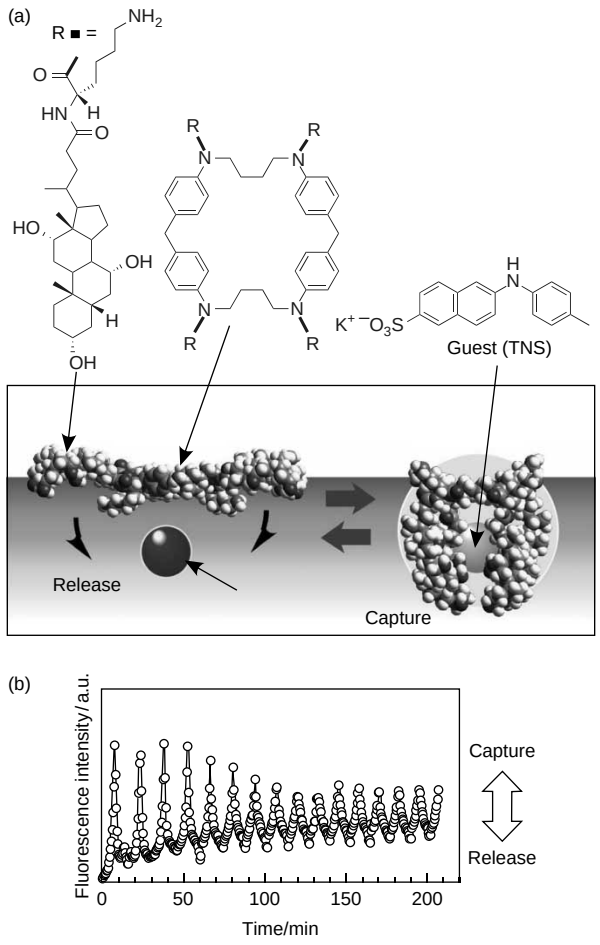

Figure 7. (a) Molecular capture and release of the guest molecule at the air–water interface by steroid cyclophane molecules by mechanical compression and expansion. (b) Changes of fluorescence intensity upon repeated capture and release of the TNS guest molecules.

Furthermore, reversibility of the molecular capture and release was examined by the repeated mechanical motions between high pressure (but below the collapse pressure of the monolayer) and zero pressure. Continuous monitoring of the fluorescence intensity emitted from the monolayer surface clearly revealed repeated increase and decrease in the fluorescence intensity (Figure 7(b)). The observed fluorescence changes were synchronous with the bulk monolayer motions. Compression of the monolayer resulted in an increase in fluorescence of TNS, while expansion of the monolayer led to a decrease. Some decay in the fluorescence intensity was observed during the first few runs, but subsequently became constant. Therefore, the capture and release of the guest molecule could be repeated by compression and expansion of the monolayer. This is a

clear demonstration of molecular capture and release by the application of bulk mechanical forces.

In another example, inversion of enantioselectivity in molecular recognition was controlled by macroscopic lateral pressure applied to the monolayer of a cholesteryl-substituted cyclen complex as a host molecule at the air–water interface (*128*, *129*). In practice, these systems are realised using a machine, the film balance apparatus, but in principle could also be done by hand. Therefore, these examples can be regarded as nanotechnology operation by hand motion (macroscopic motion). This can be conceptually called hand-operating (hand-operated) nanotechnology (*130*).

Future perspectives

Undoubtedly, the role of supramolecular chemistry is becoming more and more important in nanoscience and nanotechnology. The soft and dynamic nature of supramolecular materials is highly desirable for stimuli-responsive processes. Constructed devices and materials can be regarded as good mimics of highly sophisticated biological mechanisms. Although huge numbers of supramolecular systems have been proposed using bulk solutions and materials, these systems might not be particularly compatible with artificial nanodevices prepared through top-down fabrication approaches. The application of supramolecular materials and structures to appropriate interfaces is crucial to the control and utilisation of their dynamic properties and functions as illustrated by the examples contained in this short review. Connection between nano/molecular-sized structures and conventional bulk-sized stimuli such as mechanical deformation will become more and more important in developing nanodevices useful in our everyday lives. Dynamic interfaces can also provide media appropriate for this purpose as demonstrated in the final example, hand-operating (hand-operated) nanotechnology.

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