

Post-polymerization of preorganized assemblies for creating shape-controlled functional materials

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Received 25th September 2006

First published as an Advance Article on the web 18th December 2006

DOI: 10.1039/b603555h

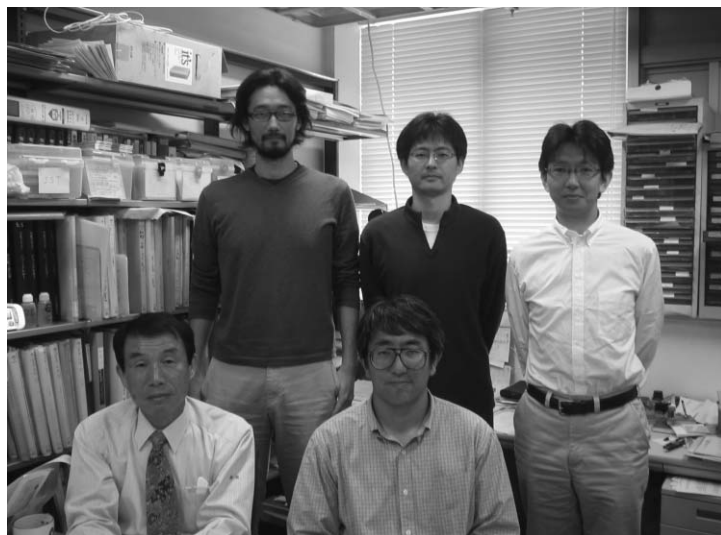
Combination of supramolecular chemistry with molecular recognition has been successfully applied to creating large superstructures with a wide variety of morphologies. Control of shapes and patterns of ordered molecular assemblies in nano and micro scales has attracted considerable interest as promising bottom-up technology. It is known, however, that these molecular assembling superstructures are fragile, reflecting the characteristic of the non-covalent interaction, a driving force operating in these molecular systems. In fact, they easily collapse or change by small perturbation in the environmental conditions. Thus, over the last decade, researchers have been seeking possible methods for the immobilization these superstructures. This *critical review* focuses on recent advances in *in situ* post-modification under the influence of the molecular assemblies as templates and polymerization of ordered molecular assemblies such as organogel fibers and crystals to preserve their original superstructures and intensify their mechanical strength.

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Introduction

Shapes and patterns, many examples of which come from nature, have greatly influenced areas such as art and architecture. Scientists too have long been interested in the origin of shapes and structures found in nature. In the last two decades, organic chemistry and supramolecular chemistry have



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been approaching a successful stage in creating large superstructures of tremendous morphology as arts of atoms and molecules utilizing both covalent and non-covalent bonds.^{1–3} In general, supramolecular chemistry utilizing non-covalent bonds can provide a wide variety of superstructures having different morphologies but which are rather fragile and easily collapse or change by small perturbation in the environmental conditions. In contrast, polymer chemistry utilizing covalent bonds can provide robust materials, but the morphological variety is rather limited. Therefore, researchers in various fields of chemistry have been studying novel methods through which the shapes and patterns of the organic superstructures can be precisely fixed at the micro- or nanoscopic level.

A method that has been proven very successfully to preserve the organic superstructures is polymerization of monomers in the preorganized assemblies that define shapes or patterns. They include the following two approaches. One is *in situ* polymerization of the monomers in the anisotropic condensed phases that have specific shapes and patterns such as micelles, lipid bilayers, liquid crystals, organic crystals and inclusion complexes.^{4,5} The monomers have both the polymerizable groups that provide the polymers by various stimuli and the supramolecular building blocks that provide the superstructures through molecular assembling. The different polymerizabilities in the isotropic solution state have often been discussed in relation to the controlled polymerization in the condensed phase.⁴ A typical example is the topochemical polymerization of acetylene groups in the crystalline state and in the organogel fibers. The other is post-polymerization of the monomers that are polymerized on the surfaces of the templating superstructures.⁶ The polymerizable groups are separated from the supramolecular building blocks, and the controlled molecular assembly of the monomers along the templates plays a key role for the post-polymerization. For examples, many groups including our own, have explored the surface post-polymerization to transcribe a variety of organic superstructures into inorganic materials by a sol–gel reaction of metal alkoxides (‘templating sol–gel reaction’),⁶ by which one can finely tune the morphology of inorganic compounds. This method has resulted in the generation of a larger variety of structured inorganic materials that are currently unattainable through any other methods. This review focuses on recent advances in post-modification by organic molecules under the influence of the molecular assemblies as templates and polymerization of ordered molecular assemblies such as nano- or micrometer sized fibers in the organogels and micro- or millimeter sized crystals to preserve the original superstructures. Post-modification of the superstructures by inorganic materials is excluded here, since it has been covered in many

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preceding reviews.⁶ In particular, this review covers our research achievements in the following four aspects; (1) oxidative polymerization in the presence of organic templates that yield conjugated polymers with controlled shapes, (2) soluble helical polymers as a new template for inclusion polymerization, (3) polymerization of fibrous aggregates in organogels, (4) new monomers and their steric requirements for crystalline-state polymerization.

1. Oxidative polymerization in the presence of organic templates

Recently, oriented polymers and polymer nanostructures have attracted wide attention. Especially, such structures that consist of conjugated polymers have been of particular attention because of their potential application to electrochemical switches, electric devices, sensors and so forth.^{7–9} Poly(ethylenedioxythiophene) (PEDOT), poly(pyrrole) (PP) and poly(aniline) (PANI) are typical examples of such conjugated polymers easily obtained by chemical or electrochemical oxidative polymerization of the corresponding monomers. In addition to supramolecular assembly schemes, several attempts have been made to construct oriented polymers and polymeric nanostructures: for example, they were prepared in the oriented environments such as LB membranes,¹⁰ surfactant aggregates,^{11,12} liquid crystals¹³ and so forth.^{14,15} It is known, however, that in these systems the prediction of the resultant superstructures and the control of the morphologies of polymer assemblies are very difficult. It occurred to us that the morphology of the aggregates constructed by assembling these conjugated polymers would be controllable, applying the templating concept: that is, as oxidative polymerization of the corresponding monomers produces cationic intermediates, the stable anionic assemblies should act as a potential template due to the mutual electrostatic attractive force (Fig. 1). In this section it is demonstrated that conjugated polymers assemble into novel superstructures when they are prepared by chemical or electrochemical oxidation of EDOT, pyrrole, or aniline in the presence of supramolecular ‘anionic’ templates. In fact, we found that when single-walled carbon nanotubes (SWNTs) dispersed into aqueous solution by sodium dodecylsulfate are

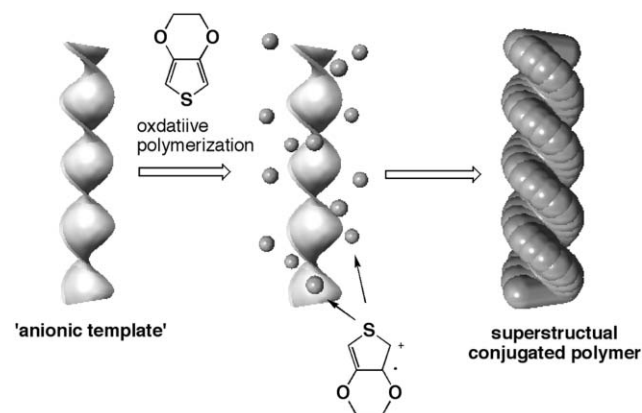


Fig. 1 Schematic illustration of a template-programmed oxidative polymerization using an anionic template.

used as a template, the conjugated polymers are yielded by electrochemical polymerization on the ITO electrode.^{16,17} The scanning electron microscope (SEM) observation established that the resulting conjugated polymers assemble into the fibrous superstructure similar to that of the original template. This implies that the structure of the SWNTs is transcribed into the polymeric assembly structure. These findings motivated us to apply the concept to a variety of anionic templates with unique superstructures. The ‘anionic’ templates used are anionic porphyrin J-aggregate, anionic synthetic lipids, DNAs and DNA/single-walled carbon nanotube complex. Thus, one can create dots, fibers, helical tapes, circles and so forth from the assemblies of these conjugated polymers.

1.1. A fibrillar structure using a porphyrin J-aggregate as a template

PANI, PP and EDOT are well-known conductive polymers easily obtained by electrochemical polymerization of the corresponding monomers. In spite of the convenient method of preparation and cheapness of the monomers, the application has been rather limited.^{18–20} One reason for this is the serious disadvantage related to the difficulty in controlling the morphology in the polymerization process. Thus, there has been increased interest in controlling the morphology of conductive polymers, for example, into a fiber or a sheet. In order to synthesize PANI, for example, it is known that the presence of certain polymers,²¹ camphorsulfonic acid,²² or amphiphile,¹² which are considered to be effective as templates in the polymerization process, is indispensable. However, there was no preceding report, in which the organic superstructure acting as the template was strictly compared with that of the resultant polymeric assembly to clarify whether or not the fine transcription is really achieved. As aniline is protonated under the acidic conditions the same as other oxidized monomers, the anionic assemblies should act as the appropriate template because of the mutual electrostatic interaction.

We here used the assembly of an anionic porphyrin (TPPS: 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin) as a template, because this porphyrin tends to aggregate in a one-dimensional fashion and the J-aggregate structure is well characterized by microscopic methods (Fig. 2).^{23,24} We found that TPPS acts as a template for electropolymerization of aniline, EDOT and pyrrole on the ITO electrode.^{25,26} Examinations using cyclic voltammetry (CV) and UV-VIS spectroscopy established that the J-aggregated TPPS²⁻ molecules are entrapped in the resultant conjugated polymers. SEM observation established that the corresponding monomers grow up to a nanosized rod-like structure (30–50 nm in diameter and several hundred nanometers in length), reflecting the aggregation mode of TPPS (Fig. 3).

Very interestingly, the J-aggregation mode of TPPS in the PANI/TPPS composite dissolves when the pH of the medium is shifted from acidic to basic, but it is regenerated when the pH is shifted from basic to acidic. This interconversion could be visually recognized by changes in the colour and the fluorescence intensity.²⁶ This behaviour, which may be regarded as a sort of the memory effect, implies that when shifted from basic to acidic, the protonation of PANI

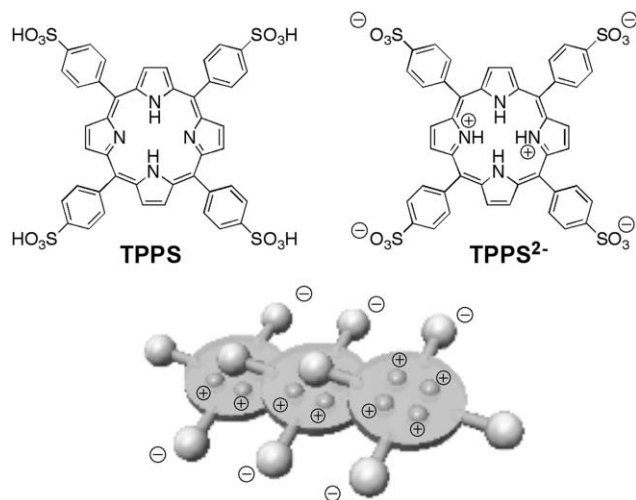


Fig. 2 Chemical structures of TPPS and TPPS²⁻ and the proposed J-aggregation mode of TPPS²⁻.

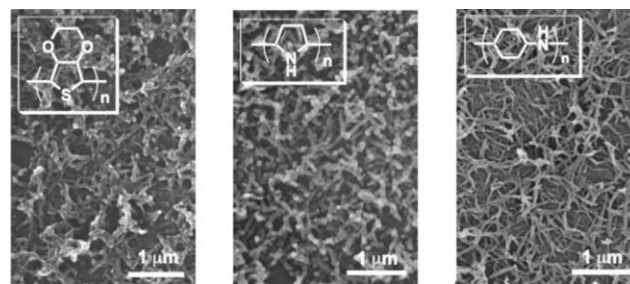


Fig. 3 SEM images of PEDOT, PP and PANI films produced on ITO in the presence of J-aggregates of TPPS.

occurs in the sites energetically favourable to the J-aggregate construction.

1.2. A helical superstructure of conjugated polymers using synthetic lipid assemblies as a template

As mentioned above, the morphology of conjugated polymers (PEDOT, PP and PANI) is controllable by applying the concept of the templating method to the oxidative polymerization. As the corresponding monomers produce cationic intermediates in their oxidative polymerization processes, the anionic assemblies can act as potential templates due to the mutual electrostatic attractive force (Fig. 1). We found that when the oxidative polymerization of EDOT, pyrrole and aniline is carried out in the presence of a helical superstructure of synthetic chiral lipid assemblies of lipid–CO₂Na and lipid–SO₃Na as templates, electro- or chemical-oxidative polymerization results in the novel polymeric aggregates such as a helical tape structure and an intertwined helical structure; these morphologies are very similar to those of the original templates. Furthermore, both the right-handed (in the presence of lipid–CO₂Na) and left-handed helical structures (in the presence of lipid–SO₃Na) of conjugated polymers can be created by a change in the hydrophilic head groups (Fig. 4).²⁷ This is the first example that the helical superstructures composed of conjugated polymers are designed

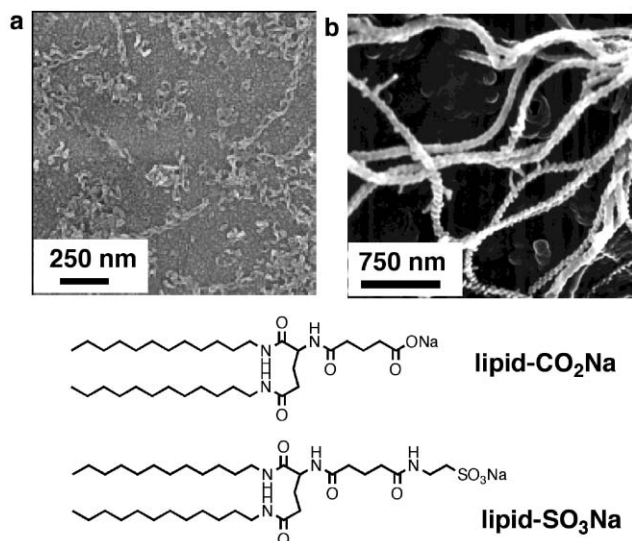


Fig. 4 SEM images of PP with a right- (a) and a left-handed helical motif (b) created by the oxidative electropolymerization in the presence of lipid-CO₂Na and lipid-SO₃Na, respectively.

utilizing a convenient templating method. As these lipid/conjugated polymer composites tend to grow into one-dimensional architectures, they can bridge the interdigitated electrodes separated on the micrometer scale. This has enabled us to estimate the electroconductivity of these helical conjugated polymers. It was found that they show moderate electroconductivity when the EDOT units in PEDOT are partially oxidized.²⁸

1.3 DNAs as templates for oxidative polymerization

To design and create functional materials in a nanometer-sized level is a major research target in the field of nanotechnology. When we apply such functional materials to practical materials, immobilization by a fabrication technique based on a template method seems to be most convenient and promising. Here, we noticed that a polymeric template, which is not yet used in this system but would be the most suitable for the functional materials, is a “polynucleotide”. Among these biological molecules, DNAs exhibit various unique higher-order structures, so that they should act as fascinating templates to create novel PP-based superstructures.²⁸ However, DNAs are highly water-soluble and biochemically unstable; these properties have been making it difficult to utilize them as functional materials and devices. We thus employed a few DNAs as templates and carried out oxidative polymerization of pyrrole by chemical and electrochemical methods.²⁹

It was found that DNAs can act as attractive templates for oxidative polymerization of pyrrole and result in novel higher-order superstructures composed of the DNA and conjugated polymers;²⁹ the resultant DNA-PP composites were deposited on an ITO electrode. The TEM and SEM observations have shown that when plasmid DNA is used as a template, nanosized rod-like, circular, or supercoiled structures of PP were created, depending on the higher-order conformations of DNA used as templates. From several lines of evidence, it became clear that the used DNA is included in these polymeric superstructures. Furthermore, we found that salmon testes DNA is deposited on an ITO electrode as a stable composite with a PP film. The deposition of the DNA onto the electrode was evidenced by (1) ATR IR absorption bands assignable to the DNA, (2) XPS binding energy of the phosphate group assignable to the DNA and (3) binding of ethidium bromide (EB) as detected by UV-VIS spectroscopy and confocal laser scanning microscope (CLSM). Interestingly, the electrode modified by the DNA-PP composite showed the CV responsiveness to DNA intercalators, indicating a potential to apply this system to a new amperometric DNA-based chemosensor (Fig. 5). To the best of our knowledge, this is the first example where a variety of higher-order DNA conformers have been successfully transcribed into conjugated polymers and shown to be useful as novel functional materials.

1.4 SWNTs-DNAs composites as templates for oxidative polymerization of EDOT

Recently, Nakashima *et al.* demonstrated that double stranded DNA is capable of wrapping SWNTs to dissolve them into aqueous media.³⁰ Because of the rigid and anionic nature of the composite, it should be suitable for the template of the present system and for the estimation of the transcription reality. We found that SWNTs solubilized into water by complexation with DNA (salmon testes) can be readily obtained on the ITO electrode by electrochemical oxidative polymerization of EDOT.³¹ The driving force for this novel deposition is also expected to be electrostatic interaction between the anionic charges of wrapping DNA and the PEDOT or EDOT cation radicals formed in the oxidative polymerization process. The presence of PEDOT, SWNTs and DNA in the composite was confirmed by measurements of UV-VIS, IR, Resonance Raman spectra, CV and CLSM. The composite absorbed DNA intercalators (for example, EB) very efficiently, which is regarded to be further evidence for inclusion of DNA. The surface morphology, characterized by CLSM, SEM and AFM, featured the network structure consisting of 0.5 ~ *ca.* 10 nm nanorods. Very interestingly,

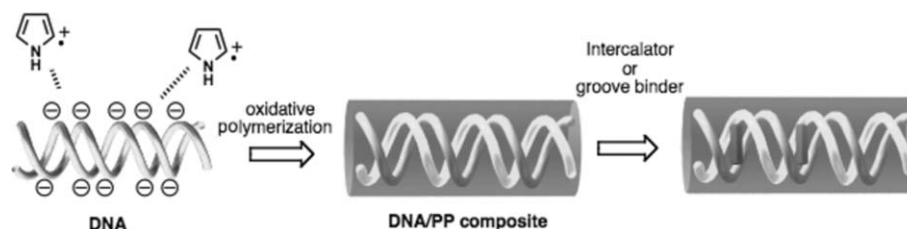


Fig. 5 Schematic illustration of the formation of the DNA-PP composite.

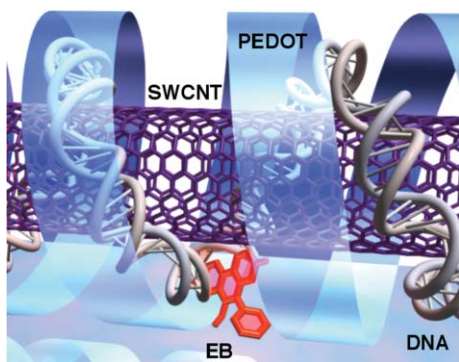


Fig. 6 Schematic representation of photocurrent generation of the SWCNT–DNA–PEDOT–EB composite occurring in a cascade of DNA-bound EB → SWCNT → conductive polymer → ITO electrode.

we found that photoexcitation of EB bound to the DNA generates a photocurrent, indicating that the electron produced from the excited energy of EB is injected into SWNTs, whereas the cationic hole on EB is collected by the electroconductive PEDOT film on the ITO electrode (Fig. 6). We believe, therefore, that the present system is a very convenient method to assemble multi-component systems into organized matrices and to explore new materials related to redox and photochemical functions, retaining the basic characters of DNAs. Furthermore, we expect that these polymeric assemblies would show novel functions inherent to their unique superstructures.

1.5. Summary for templated oxidative polymerization

The concept presented here is that the oxidative polymerization of EDOT, pyrrole and aniline proceeds along the anionic template, owing to the efficient electrostatic force operating

between the conjugated polymers and the templates. The templates we have shown are supramolecular aggregates, amphiphile aggregates and DNAs. We further expect that proteins, nanoparticles and block copolymers would also be effective as templates as long as they offer the ‘anionic’ surface. The results presented herein have three important lines of significance: namely, (1) the morphology control of conjugated polymers has become readily possible by applying appropriate anionic templates, (2) this process is useful as a new fabrication or immobilization method for labile, temporarily associated assemblies and (3) the produced composites show new redox and photochemical properties. We believe, therefore, that this concept would provide very general interest not only from a structural viewpoint but also from a functional viewpoint.

2. Soluble helical polymers as template for inclusion polymerization

Schizophyllan (SPG) is a natural polysaccharide produced by fungus *Schizophyllum commune* and its repeating unit consists of three β -(1–3) glucoses and one β -(1–6) glucose side chain linked at every third main-chain glucose (Fig. 7a and 7b).³² SPG adopts a triple helix (t-SPG) in nature, which can be dissociated into a single chain (s-SPG) by dissolving in dimethyl sulfoxide (DMSO).³³ The s-SPG chain can retrieve the original triple helix by exchanging DMSO for water.³⁴ Recently, we found that it has a novel solution property that when this renaturing process is carried out in the presence of certain polynucleotides, the resultant triple helix consists of two s-SPG chains and one nucleotide chain.^{35,36} These preceding findings suggest that SPG may show a unique function to form stable complexes with one-dimensionally extended compounds.

It is known that the 2nd hydroxy groups and the surrounding structure along the β -1,3-glucan main-chain form

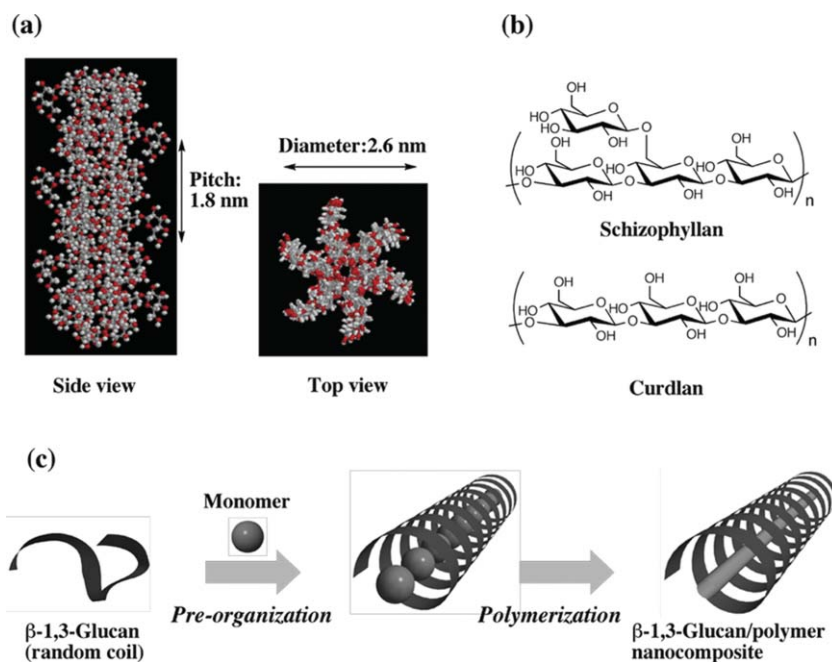


Fig. 7 (a) Repeating unit of schizophyllan and curdlan, (b) a representative model of schizophyllan triple helix and (c) schematic illustration of our concept for inclusion polymerization utilizing β -1,3-glucan as a one-dimensional vessel.

a more hydrophobic site in comparison to that of primary hydroxy groups or β -1,6-glucoside appendages.³⁷ This hydrophobic site, therefore, forms a hydrophobic cavity within the helical superstructure of SPG when s-SPG retrieves its original triple-stranded helical structure in aqueous media. This unique amphiphilic core-shell structure resembles that of cyclodextrins and, therefore, SPG can be considered as a cylindrical, or one dimensional analogue of cyclodextrins that are well-established hosts and mainly bind small spherical compounds.³⁸ This idea encouraged us to pursue a possibility that SPG could act as a novel one-dimensional host, in which various guests are accommodated to provide the corresponding linear assemblies. In the series of our research, we have found several successful examples that SPG-based one-dimensional hosts can accommodate various guest molecules including not only polymeric guests but also small compounds as well as nanoparticles to produce unique fibrous assemblies of these entities.³⁹

Our research efforts are particularly focused on low molecular-weight compounds as guests. Especially, it is of great significance to establish SPG-templated polymerization of various monomers in the one-dimensional cavity to construct the corresponding polymers with fibrous morphologies, where SPG is expected to act not only as a one-dimensional host for monomers but also as one-dimensional vessel for stereoselective polymerization reaction (Fig. 7c). Herein, we show several successful examples where SPG can accommodate various reactive monomers, including 1,4-diphenylbutadiyne derivatives, EDOT and alkoxy silane, within the one-dimensional cavity and can produce unique water-soluble nanofibers through their *in situ* polymerization reactions.

2.1. Diacetylene photo-polymerization^{40,41}

The first example of this system was observed for poly(diacetylene) formation through photo-polymerization of 1,4-diphenylbutadiyne (DPB) (Fig. 8a). Poly(diacetylene)s are a family of the most interesting research targets among the π -conjugated polymers, since they are readily produced through photo-irradiation (UV or γ -ray) without any initiators.⁴² Instead, closely-packed pre-organization of the corresponding monomers is indispensable for their photo-mediated polymerization (topochemical polymerization).⁵ Poly(diacetylene)s can be, therefore, usually prepared from molecular assemblies (crystals, micelles, Langmuir-Blodgett films, *etc.*) of the corresponding monomers, in which the monomers are aligned in a parallel but slightly slipped packing mode suitable for the topochemical polymerization. In the present system, pre-organization of the diacetylene monomer can be easily achieved by incorporation of monomers into the one-dimensional SPG cavity.^{40,41}

As a general procedure, we mixed a DMSO solution containing s-SPG ($M_w = 150$ kDa) with DPB DMSO solution and diluted it with water to regenerate a t-SPG helical structure. Although DPB was scarcely soluble by itself in water, the resultant slightly turbid solution showed a clear circular dichroism (CD) spectrum, in which a negative CD exciton-coupling (260 ~ 600 nm) assignable to an absorption band of DPB was observed. Furthermore, as reference experiments, when other polysaccharides and carbohydrate-appended detergent (amylose, pullulan, dextran and dodecyl- β -D-glucopyranoside) were used instead of s-SPG, no or a negligibly weak CD signal was observed (Fig. 8b). Together

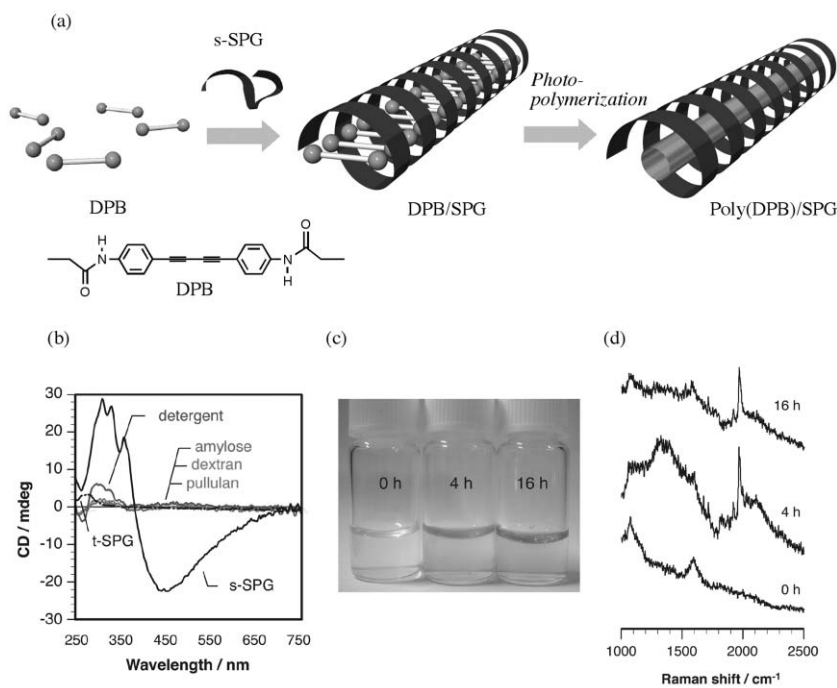


Fig. 8 (a) Schematic illustration of the creation of poly(diacetylene) nanofiber utilizing β -1,3-glucan as a one-dimensional vessel, (b) CD spectra of DPB in the presence of s-SPG, amylose, dextran, pullulan, t-SPG and the detergent: $d = 1.0$ cm, 20 °C, $[\text{H}_2\text{O}] = 70$ v/v%, $[\text{DPB}] = 25$ $\mu\text{g ml}^{-1}$, $[\text{polysaccharide}]$ or $[\text{detergent}] = 25$ $\mu\text{g ml}^{-1}$, (c) photo image of the reaction mixture and (d) Raman spectra of DPB in the presence of s-SPG after 0, 4 and 16 h.

with the fact that SPG or DPB itself gave no CD signal at this wavelength region, the observed negative CD exciton-coupling is indicative of twisted-conformations or π -packings of DPB arising from the strong helix-forming capability of SPG. These results support the view that DPBs are pre-organized only in the presence of s-SPG to form one-dimensional supramolecular assembly, which is favourable to polymerization reaction under UV-irradiation.

UV-irradiation using a high pressure Hg lamp induced a gradual colour change of the solution containing DPB–SPG complex from colourless to pale blue (Fig. 8c). The UV-VIS spectrum of the resultant solution shows an absorption band at around 720 nm which is characteristic of poly-(diacetylene)s with extremely long π -conjugated length and/or tight inter-stranded packing.⁴³ UV-mediated polymerization of DPB was also confirmed by Raman spectra (Fig. 8d), in which DPB–SPG complex shows a clear peak at 2000 cm^{-1} assignable to poly(diacetylene)s ($-\text{CH}=\text{CH}-$ stretching vibration) after 16 h UV-irradiation. On the contrary, no such Raman peak appeared without SPG. Together with the fact that UV-mediated polymerization of diacetylenes proceeds in a topochemical manner, these data suggest that SPG accommodates DPB to align them in a packing suitable for such topochemical polymerization. It should be noted that *p*-amido-functionalities of DPB are essential for the UV-mediated polymerization. We assume that the *p*-amido-functionalities should form hydrogen-bonds with SPG and/or neighbouring monomers to orientate the monomers in the suitable packing for the polymerization. The results presented here will open a way to construct poly(diacetylene)-nanofibers with uniform diameters from various DPB-derivatives.

2.2. Sol–gel polycondensation reaction⁴⁴

To create supramolecular inorganic materials in the nanoscale has been a challenging research target in recent years.^{45,46} In particular, inorganic nanofibers which have well-regulated shape and high water-solubility are desired for potential applications to biosensors, switches, memories and circuits. So far, silica nanofibers have been created using the templating method that anionic silica particles are deposited on a cationic fibrous template. However, the difficulties in surface modification, by which one may dissolve the organic/inorganic composite into the solvent, still remain unsolved because the solvophobic inorganic layer always exists outside the solvophilic organic template. It thus occurred to us that when hydrophobic metal alkoxides can also be entrapped in the one-dimensional SPG cavity, sol–gel polycondensation takes place inside the cavity to afford a silica nanofiber which shows the water-solubility as well as the biocompatibility arising from surface-covering SPG, making their biological applications possible. Here, we carried out the sol–gel polycondensation reaction in the presence of s-SPG using TMPS (trimethoxypropylsilane) as monomer.

TMPS was dissolved in DMSO and the solution was mixed with s-SPG or s-curdlan during the renaturation process. After leaving the mixed solution for 20 days at room temperature, the resultant water–DMSO mixed solvent was

subjected to dialysis. The IR spectrum showed the appearance of a strong new vibration band assignable to the Si–O–Si bond at around 1000–1200 cm^{-1} region. Interestingly, the obtained silica did not form any precipitate even after dialysis against water, indicating that the created silica is successfully wrapped by hydrophilic SPG or curdlan.

The aqueous silica suspension obtained from the TMPS–SPG system was cast on a grid with carbon mesh and the morphologies of the obtained silica were observed by TEM. As expected, the fine silica nanofiber structure with a uniform 15 nm diameter was observed (Fig. 9a–9c), whereas no such fibrous structure was found from the sample prepared in the absence of SPG. From these TEM images, one can propose that sol–gel polycondensation of TMPS predominantly proceeds in the one-dimensional SPG cavity to afford silica nanofibers soluble in water. Furthermore, the diameter of the obtained silica nanofiber became larger (*ca.* 25 nm) with increase in the feed TMPS concentration up to 3.0 eq. TMPS per s-SPG repeating unit (Fig. 9d). However, when more than 3.0 eq. TMPS per s-SPG repeating unit was used, the silica nanofiber structure was no longer created and instead the amorphous silica mass was formed. The results support the view that under such a condition where TMPS exists in great excess, s-SPG cannot cover the original one-dimensional assembly structure of TMPS during the renaturing process, so that it can no longer act as the host effectively. This view is also supported by the fact that sol–gel polycondensation in the presence of t-SPG instead of s-SPG did not give any fibrous structure as seen in Fig. 9: that is, the renaturing process from s-SPG to t-SPG is indispensable for inclusion of TMPS followed by the creation of the silica nanofiber structure.

It is well-known that a catalytic amount of benzylamine or HCl accelerates the sol–gel polycondensation. However, in the present system, we could not find any fibrous structure from such reaction conditions. The result indicates that the very slow condensation reaction is favourable for one-dimensional growth of silica nanofibers. In fact, it took more than two weeks to create the complete nanofiber structures. Thus, to elucidate the reaction mechanism of the polycondensation reaction, we stopped the sol–gel reaction only after 5 days and observed the morphologies of the obtained silica by TEM. Very interestingly, the morphology of the obtained silica is not a fiber but a one-dimensional array of silica nanoparticles of 10–15 nm (Fig. 9e and 9f). Here, one can propose a possible growth mechanism as following; that is, SPG acts as a one-dimensional host for TMPS or its oligomers and the polycondensation occurs inside the cavity to give rod-like oligomeric silica after 5 days. This rod-like oligomeric silica is easily destroyed and finally converted into particles during the dialysis process due to the hydrophobic interaction among propyl groups. These results strongly support the view that SPG and curdlan have a potential ability to act not only as a one-dimensional host for TMPS but also as a vessel for sol–gel polycondensation reactions. We believe that the present system would be readily applicable to the creation of novel organic/inorganic hybrid nanomaterials and their functionalized derivatives.

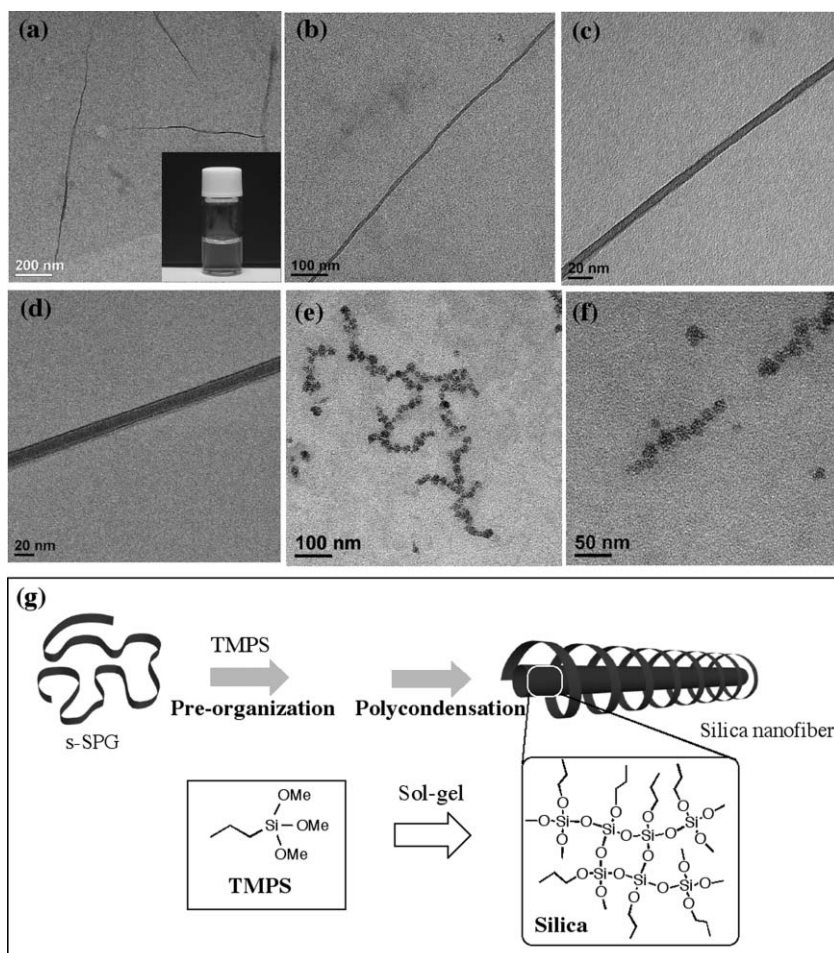


Fig. 9 (a) TEM image of silica nanofibers (inset: photo image of aqueous solution of silica nanofibers) (1.0 eq. TMPS per s-SPG repeating unit), (b) (c) its magnified images, (d) TEM image of silica nanofiber (3.0 eq. TMPS per s-SPG repeating unit), (e) TEM image of silica nanoparticle one-dimensional arrays, (f) its magnified image and (g) schematic illustration of our concept to utilize SPG as a vessel for sol-gel polycondensation reaction.

2.3. Chemical polymerization of 3,4-ethylenedioxythiophene (EDOT)⁴⁷

Poly(3,4-ethylenedioxythiophene) (PEDOT) has been widely investigated during the past decade owing to its low band gap, high conductivity, good environmental stability, and excellent transparency in its oxidized state.^{19,48} More recently, the preparation and characterization of PEDOT nanostructures have become a topic of increasing interest due to their potential applications to electrical, optical and sensor devices.⁴⁹ Herein, we carried out the polymerization reaction of EDOT in the presence of s-SPG initiated by the oxidant ammonium persulfate (APS), expecting PEDOT nanofibers to be created in the SPG cavity.⁴⁷ After polymerization (48 h at 35 °C), homogeneous and stable aqueous dispersions with dark blue colour were obtained. The aggregated structure of the PEDOT-SPG composites was examined by TEM (Fig. 10a and 10b). Unexpectedly, it is clearly seen from the TEM images that the resultant composite does not construct PEDOT nanofibers but PEDOT nanoparticles of uniform size and regular shape. Furthermore, when the concentration of SPG used increased, the diameter of the nanoparticles

decreased from 160 nm ($[s\text{-SPG}] = 0.5 \text{ mg ml}^{-1}$) to 70 nm ($[s\text{-SPG}] = 3.0 \text{ mg ml}^{-1}$), indicating that SPG acts as a template for the polymerization reaction. Further reliable evidence that s-SPG really acts as the template for the particle formation was obtained from the energy dispersive X-ray (EDX) analysis; that is, the O/S elements ratio in the nanoparticle clearly shows that PEDOT and SPG coexist in the created nanoparticles.

To elucidate the growth mechanism of PEDOT-SPG nanostructures, CD spectra of the resultant solution were recorded. The CD spectra revealed that PEDOT-SPG nanoparticles were CD-silent and no significant interaction occurred between SPG and PEDOT. This fact leads us to the conclusion that at the initial stage, the polymerization of EDOT proceeds mainly in the bulk phase due to the good solubility of EDOT in water-DMSO mixed solvent. On the other hand, PEDOT is hydrophobic and insoluble in water-DMSO mixed solvent. Therefore, once PEDOT is formed, the polymer chains intend to aggregate through intermolecular π -stacking; that is, after nucleation and growth, the more hydrophobic EDOT oligomer or polymeric PEDOT may interact with s-SPG to form PEDOT-SPG complex through

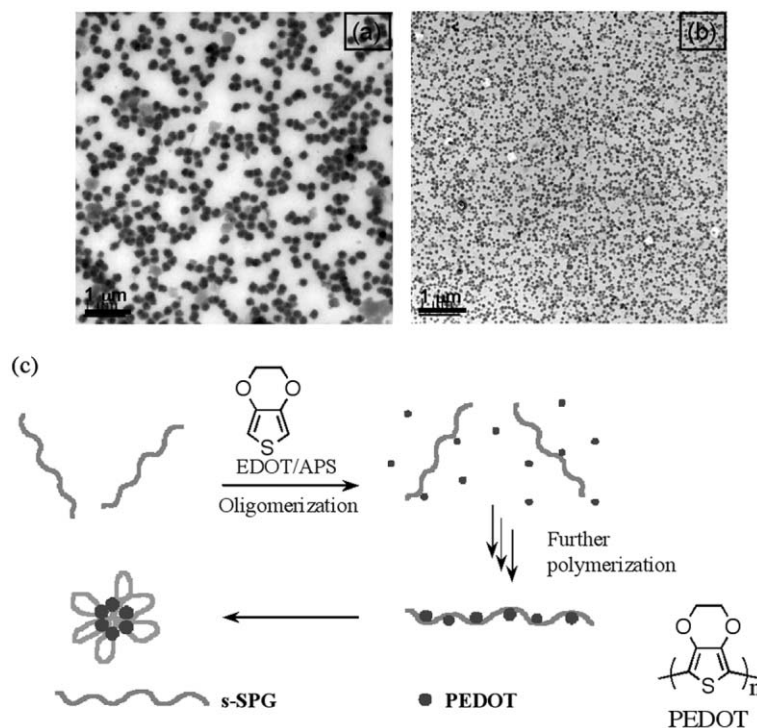


Fig. 10 TEM images of PEDOT–SPG nanoparticles prepared by APS oxidant in the presence of s-SPG ([EDOT] = 9.4 mM, [APS] = 94 mM) : (a) [SPG] = 0.5 mg ml⁻¹, (b) [SPG] = 3.0 mg ml⁻¹ and (c) schematic illustration of the possible growth mechanism of water-soluble PEDOT/SPG nanocomposites. (Reproduced with permission from ref. 47. Copyright 1996 The Chemical Society of Japan.)

hydrophobic interactions. We can say, therefore, that the PEDOT–SPG composite acts as a sort of amphiphilic block copolymer, which can self-aggregate into nanoparticles under the experimental conditions. We believe that this system would provide novel methodologies to create water-soluble PEDOT nanoarchitectures.

2.4. Summary for inclusion polymerization utilizing natural polysaccharide

We have demonstrated that the creation of water-soluble nanostructures with regular morphologies are possible by utilizing the one-dimensional SPG cavity. The findings clearly show that SPG has a potential ability to act not only as a one-dimensional host for polymers but also as a one-dimensional vessel for inclusion polymerization reactions, leading to water-soluble nanofibers with uniform diameters. Moreover, when the created polymers have strong tendency to form inter-polymer aggregates through π – π stacking in addition to hydrophobic interactions, the resultant polymer–SPG composite would act as amphiphilic polymers, which has potential to produce numerous phase-separated nanostructures. As the side-chain glucose of SPG or 6-OH groups of curdlan can be chemically modified, the obtained nanostructures including nanofibers and nanoparticles can be easily functionalized by a supramolecular strategy, making further organization of the composites possible. We believe that the present systems can provide the novel concept for inclusion polymerization reaction and the novel strategy for the creation of functional nanomaterials, including nanofibers, nanoparticles, and further organized nanoarchitectures.

3. Polymerization in self-assembled superstructures in low molecular-weight gels

Low molecular-weight gel (LMWG) is a sort of soft material prepared from low molecular-weight compounds with fluid media.^{50–58} It has gathered broad interest from wide area of practical applications such as modifiers for paints, inks, cleaning agents, cosmetics, polymers, drugs and so on. Oil fixation is a well-known utilization. More recently, researchers have been interested in their application to nanomaterials such as sensors, molecular electronics, catalysts, *etc.* However, the challenge of understanding structure–property relationships of the LMWGs is still ongoing. Accordingly, in the early days of the history of LMWG, the examples were found by chance in solvent evaporation or recrystallization processes. Since this morning twilight, chemists have molecularly designed many gelators and have tried to understand the mechanism underlying the gelation processes. As a result of these investigations, one can understand that LMWGs are sustained by elongated fibrous nanostructures constructed through highly programmed self-assembly by multiple non-covalent interactions such as hydrogen bonds, van der Waals interactions, π – π stacking and so on. LMWGs, however, commonly suffer from the micro- and macroscopic weakness upon mechanical stimuli or spontaneous crystallization leading to a phase separation into precipitate and solvent. To transform the noncovalent interactions in the gel fibers into covalent bonds to obtain robust gels having a certain mechanical stability has been a target. This step seems to be indispensable to design ‘functional materials’ from LMWGs. In this section, the successful methods which have been applied for

post-modification of the gel fibers by covalent bond formation are highlighted.

3.1. Polymerization of vinyl groups

As one can anticipate, the gel phase is not a favourable situation for organic reactions because of its low fluidity. At the first stage in this field, researchers designed photoinitiated polymerizable groups directly attached to low molecular-weight gelators. Kellogg and Feringa *et al.* reported a (1*R*,2*R*)-*trans*-1,2-bis(ureido)cyclohexane-based gelator having methacrylate units at the ends of alkyl chains (**1**; Fig. 11).⁵⁹ Molecular modeling studies of *trans*-1,2-bis(3-methylureido)cyclohexane which is an analogous compound of **1**, revealed that cyclohexane rings are self-assembled one-dimensionally by hydrogen bonding interactions between amide groups. Thus, the polymerizable units would contact each other along these fibrous superstructures. FT-IR measurements of the **1** gel prepared from common organic solvents also support hydrogen bonding interactions from the shifts of the NH and amide I and II bands. Upon photoirradiation of the gel with a high-pressure Hg lamp in the presence of 5 mol% of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone, successful

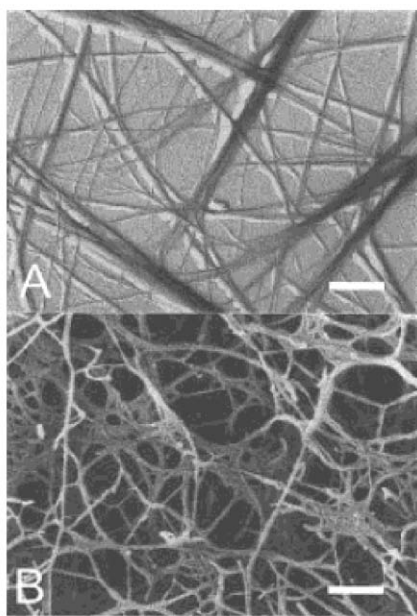
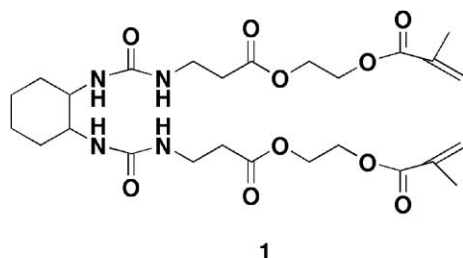


Fig. 11 (Top) Molecular structure of methacrylate-functionalized low molecular-weight gelator and (bottom A and B) TEM (bar = 1 μm) and SEM (bar = 400 nm) images of **1** gels (5 mg mL^{-1}) before and after polymerization. (Reproduce with permission from ref. 59. Copyright 1997 the American Chemical Society.)

photopolymerization was achieved, which was confirmed by the disappearance of the methacrylate CH vibration peaks.

As a result, the sol-to-gel transition temperature (T_{gel}) dramatically increases by more than 100 $^{\circ}\text{C}$ up to at least 135 $^{\circ}\text{C}$. The key in this system is that compound **1** contains two polymerizable units which can react within the fibers and give the highly cross-linked structure after polymerization (Fig. 11).

Bisurea-based polymerizable gelators were reported by Hamilton *et al.*⁶⁰ In this system, methacrylate groups are also utilized and they undergo photopolymerization upon UV irradiation in the gel phase. Similar to the previous example, T_{gel} significantly increases after photopolymerization, keeping the morphologies of the fibers. Polymerization along the gel fibers resulted in the improvement of the T_{gel} values of the polymeric gels.

3.2. Reaction of appended functional groups

Stabilization of the gel by an added cross-linker is also possible. Glucosamine-based gelator (**2**; Fig. 12) is an excellent gelator for many organic solvents.⁶¹ The gels can be stabilized by intermolecular hydrogen bonds between sugar OH groups and amide groups as well as van der Waals interactions between alkyl groups. The OH groups can act as interacting groups as well as active cross-linking points with diisocyanates.

Upon addition of toluene-2,4-diisocyanate (TDI; 10 molar equivalent to **2**) as a cross-link reagent, T_{gel} of the cross-linked benzene gel prepared from **2** increased from 40 $^{\circ}\text{C}$ to 70 $^{\circ}\text{C}$. Interestingly, when a molar equivalent of TDI is added to the xylene gel of **2**, the T_{gel} is increased from 58 $^{\circ}\text{C}$ up to 118 $^{\circ}\text{C}$. The IR spectrum of the resultant gel confirmed complete loss of unreacted TDI. This system is classified as a sort of hybrid gel which can be prepared with a pre-formed gel state and a reactive cross-linker to give a robust polymeric organogel.

Another approach to stabilize the superstructure was reported. It is well-known that sol-gel reactions occur smoothly under mild conditions—a favourable situation for fabrication of labile molecular assemblies. The group of Shinkai and Fujita previously reported porphyrin-based gelators having four urea units in the alkyl tethers.^{62–64} In the absence or the presence of Cu(II) ion in the porphyrin core, the gelators adopt J or H aggregation modes under the appropriate conditions.

To fix the J and H aggregated porphyrin superstructures, trimethoxysilyl groups are attached to the ends of each tether in the gelator molecules (**3a** and **3b** in Fig. 13). The silylated analogues tend to possess the same aggregation modes in the gel phase as those of the non-silylated compounds, which can

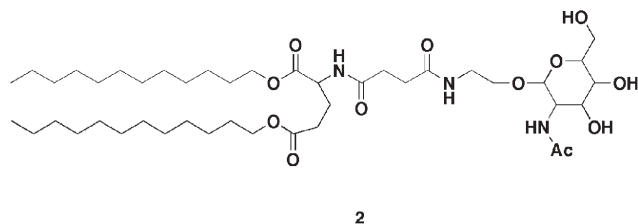


Fig. 12 Molecular structure of glucosamine-based gelator.

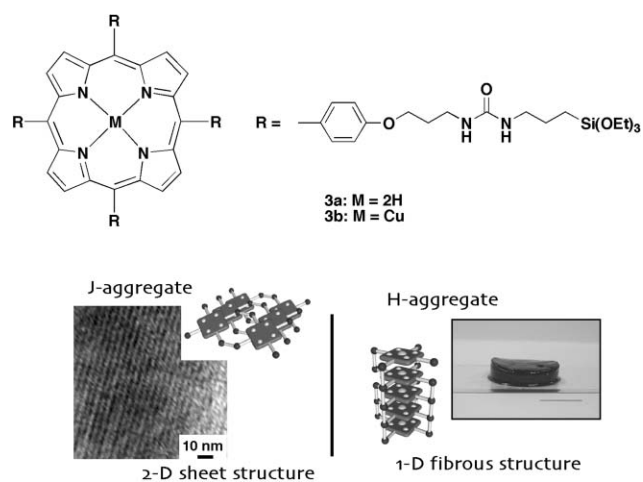


Fig. 13 (Top) Molecular structures of **3a** and **3b**. (Bottom) Illustrations and images of those superstructures in the gel phase.

be confirmed by a shift of the Soret band at around 400 ~ 420 nm. The J aggregated porphyrin gel prepared from **3a** gives a sheet-like superstructure as seen in the SEM image. After *in situ* sol-gel reaction in the gel phase of **3a**, the superstructure has been stabilized by the inorganic Si-O-Si networks. Thus, the strip width comparable with a single porphyrin molecule included in the porphyrin J aggregates can be directly observed by TEM (Fig. 13 bottom, left). On the other hand, a porphyrin gelator which has H aggregation tendency also shows the successful gelation property after being attached with trialkoxysilyl groups at the ends of the tethers, maintaining its fiber-like superstructural morphology. Surprisingly, the T_{gel} values for **3b** are enhanced up to 160 °C after *in situ* sol-gel reaction. In addition, the gelatinous mass thus obtained showed the sufficient elasticity (Fig. 13 bottom, right). These findings establish that by applying *in situ* sol-gel reaction, the J and H aggregates in porphyrin-based organogels have been immobilized and can acquire sufficient mechanical stability.

In a challenging extension of *in situ* polymerization in the gel phase, researchers have focused on the fabrication of conductive polymers using the highly anisotropic morphology in the gel state. Shinkai *et al.* reported a cyclohexanediamide-based gelator containing two diacetylene groups as polymerization sites (**4**).⁶⁵ It is an excellent gelator which can gel various organic solvents from non-polar to polar ones and also gives a fibrous structure in the gel phase as confirmed by SEM observations. The colourless gels thus obtained turned to blue by irradiation of UV light with a 500 W high-pressure Hg lamp at 25 °C. After photoirradiation, characteristic absorption bands assignable to polydiacetylene appear at around 540 nm and 500 nm. The product analyses revealed that the polymerization did occur along the gel fibers partially but a certain amount of the diacetylene was left unreacted. It is clearly seen from the SEM image that they show very similar morphology before and after photoirradiation, retaining those one-dimensional networks even after polymerization.

Masuda *et al.* reported bolaform (1-aldosamide)s containing a diacetylene unit in the central position.^{66,67} Typical fibrous morphology can be found in the gel prepared from

1-glucosamide (**5**) as shown in Fig. 14. On the other hand, the 1-galactosamide homologue (**6**: an epimer of **5**) gives amorphous solid instead of the gel, probably because the unfavourable molecular structure prohibits the fibrous structure formation. Upon exposure to UV light (254 nm) or γ -ray, **5** gel changed colour from colourless to red with absorption maxima at 506 nm and 546 nm, supporting the polymerization of the diacetylene moieties. Gel permeation chromatography revealed that the product of the photopolymerization of **5** in the gel phase consists of a mixture from dimer to 37 mer. Further irradiation resulted in a colour change to orange. As a consequence, the monomers were almost consumed and the molecular-weight distribution shifted to high molecular-weight region.

Another example of bolaform gelator having butadiyne and cholesteryl moieties was reported by Tamaoki *et al.*⁶⁸ Compound **7** (Fig. 14) gelled nonpolar solvents and it forms a fibrous structure ~ 10 nm in width. Upon UV light irradiation, the gels changed colour from colourless to dark blue, retaining those gel state and fibrous morphologies. The absorption spectrum of the photoirradiated sample shows absorption maxima at 630 nm and 582 nm. They appear at relatively longer wavelength than those of precedent examples observed in the polymerized diacetylene products in the gel phase. The molecular weight of the product covalently-linked by photo-reaction and the planarity of the polydiacetylene which is called effective conjugation length was estimated by the absorption maxima (at around 500 ~ 600 nm). According to this information, Tamaoki *et al.* concluded that intermolecular hydrogen bonding between the urethane groups works efficiently to prepare the stable gel and provides the favourable situation for the 1,4-addition reaction. As another example, a series of simple molecular structures containing polymerizable diacetylene units were reported, which have two long alkyl chains and one amide or ester group.⁶⁹

Recently, the group of Shinkai and Fujita reported a porphyrin-based organogelator containing four diacetylene units at the periphery (**8**: Fig. 15).⁷⁰ Molecular design of this gelator comes from H aggregated porphyrin-based gelator, for which π - π stacking interaction between porphyrins and hydrogen-bonding interactions between amide groups can be expected.⁷¹ Although a free base porphyrin analogue (**8a**) does not show any gelation property, Cu porphyrin analogue (**8b**) shows successful gelation properties in cyclohexane and Decalin.

TEM and AFM observations of the **8b** gel revealed that the gel fibers are consistent with unimolecular width of **8b** and a several 10000 porphyrin stacks in length (Fig. 16e, f and h). Surprisingly, the unimolecular stacks behave stably even on highly oriented pyrolytic graphite. Upon photoirradiation with a 500 W high-pressure Hg lamp, the diacetylene monomer smoothly polymerizes along the gel fibers. The rinsing experiment before and after photopolymerization with a good solvent confirmed that photopolymerization successfully proceeds and one cannot find any defect in the fiber (Fig. 16f-h). Additionally, the porphyrin-based gel prepared from **8b** with Decalin has an interesting physical property called 'thixotropy'. When the mechanical stimuli are applied, the gel is readily converted to the sol as shown in Fig. 16c.

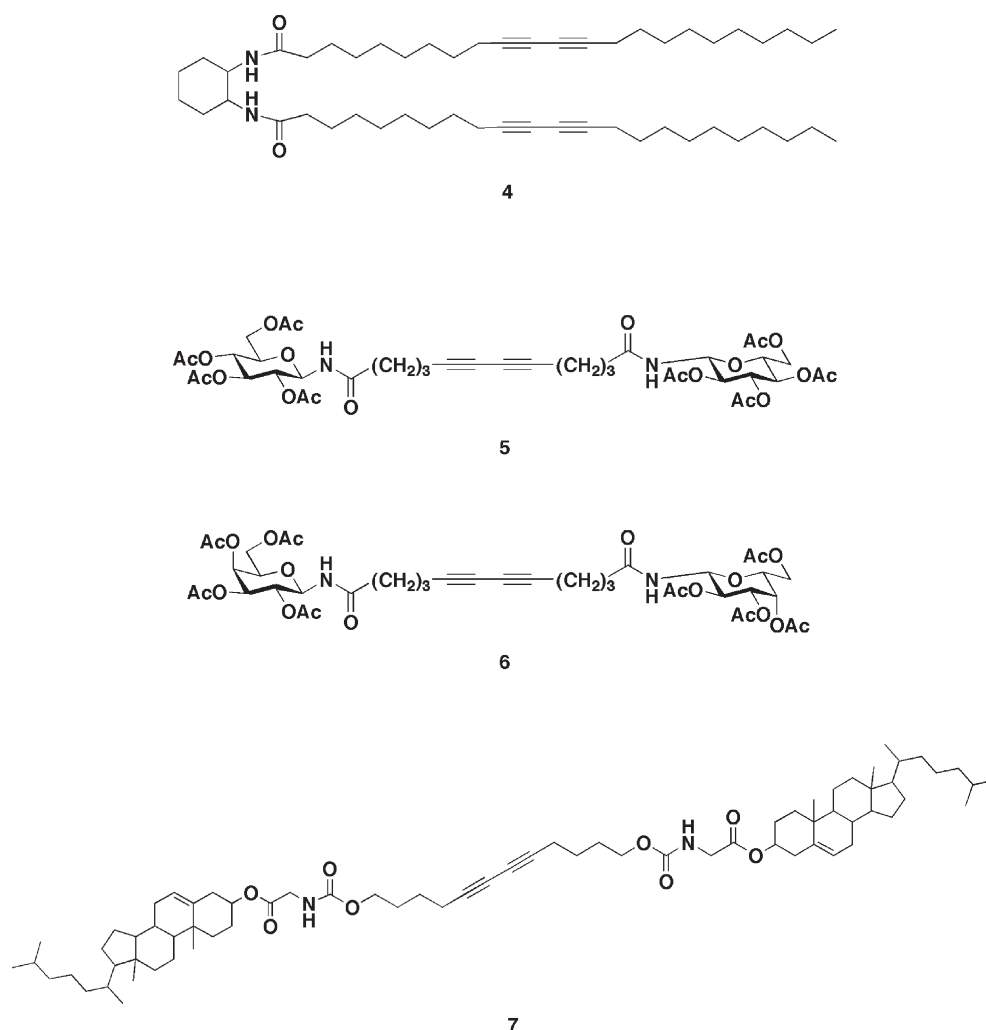


Fig. 14 Molecular structures of low molecular-weight gelators containing diacetylene units in those cores.^{65–68}

After leaving the fluid sol for a few seconds, it attains the gel state again (Fig 16d). It is known that thixotropy is an important property for ink printing technologies. Ink should have certain a viscosity before drawing, whereas on the surface of the printed materials it should be solid to suppress its spread. It is possible that when this special ‘thixotropic ink’ is applied to the nanocircuit technology, one may created very narrow-width nanowires.

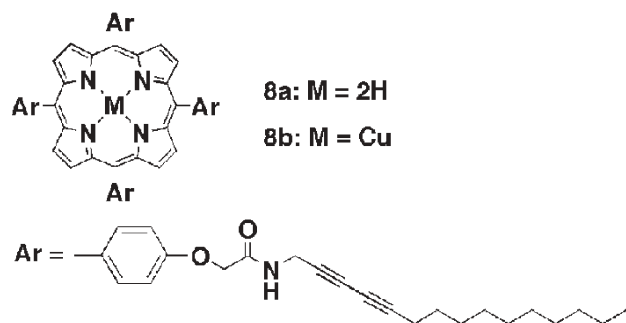


Fig. 15 Molecular structures of porphyrin-based gelators (8a and 8b) containing diacetylene units.

3.3. Summary for post-modification of gel systems

It is clear from the foregoing examples that various *in situ* reactions are useful not only to immobilize the architectures constructed from gel fibers by covalent bonds but also to reinforce the gel stability. The fascinating process, in which the thermodynamically metastable architectures constructed by non-covalent bonds can be immobilized by simple treatments should provide new chemical and physical properties that cannot be attained with the simple solution-polymerized polymeric products.

4. New trends for crystalline-state polymerization

In order to transcribe supramolecular architectures as templates into polymeric materials, the monomers that undergo topochemical polymerization have attracted much attention.^{72–76} They should have the abilities to aggregate to form well-ordered one-dimensional arrays and to polymerize under restricted movement of the monomers in the relatively small space. The former ability can be controlled by various supramolecular building blocks, but the latter is not so easy in comparison with solution polymerization, and a limited

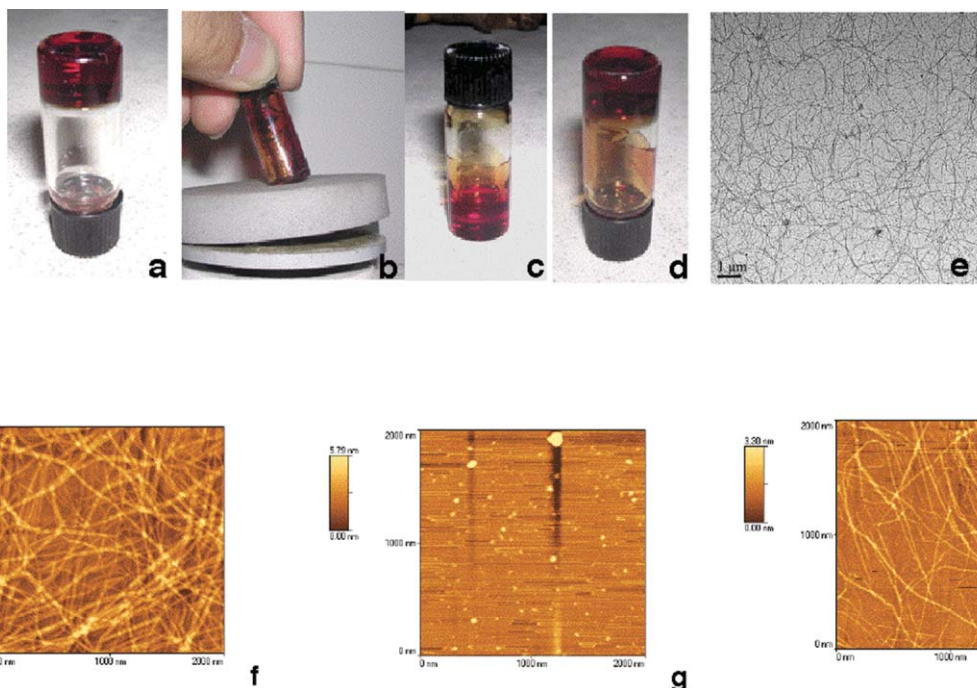


Fig. 16 (a)–(d) Photographs showing the thixotropic behaviour of the Decalin gel of **8b** and (e) its TEM image. AFM images of the Decalin gel of (f) **8b**, and (g) after chloroform rinsing and (h) after UV irradiation followed by chloroform rinsing. (Reproduced with permission from ref. 70. Copyright 2005 the American Chemical Society.)

number of monomers has been developed so far. Indeed, in the template polymerizations, diacetylene moieties have been used most frequently, because they are classical examples of the topochemically polymerizable monomers and the conjugated polymer structures of the resultant poly(diacetylene)s provide unique electronic and photochemical properties.⁷⁷ Thus, it is of importance to design the monomers for topochemical polymerization in the crystalline state. They access to controlled polymerizations in the various anisotropic media and in the presence of various templates.

Concept of topochemical polymerization was proposed in 1960s by Wegner in his research on the anisotropic polymerization of diacetylene monomers in the crystalline state as shown in Fig. 17a.⁷⁸ The [2+2] photodimerization polymerization of 2,5-distyrylpyrazine (DSP) crystals is another example investigated by Hasegawa *et al.* as shown in Fig. 17b.⁷⁵ Definition of the topochemical polymerizations is crystalline

state polymerization without movement of the centre of gravity of the monomers in the crystal lattice.^{72–76} The minimum movement of the monomers is allowed only near the polymerizable groups, and the rest of the monomers remains static. The crystallinity maintains during the polymerizations as shown in Fig. 18. In some cases, the change in the molecular geometries during the polymerizations can be monitored by X-ray crystallography in the atomic resolution.⁷⁹ Investigations of the polymerizabilities and crystal structures of the related compounds reveal that the reactivities are controlled by arrangement of the monomers, especially orientations of the polymerizable groups in the crystalline state. If the monomer crystals satisfy specific steric requirement of the polymerizable groups, they can undergo the topochemical polymerizations. As the result, they have the following two characteristic properties as compared with the polymerizations in the solution state. One is high specificity

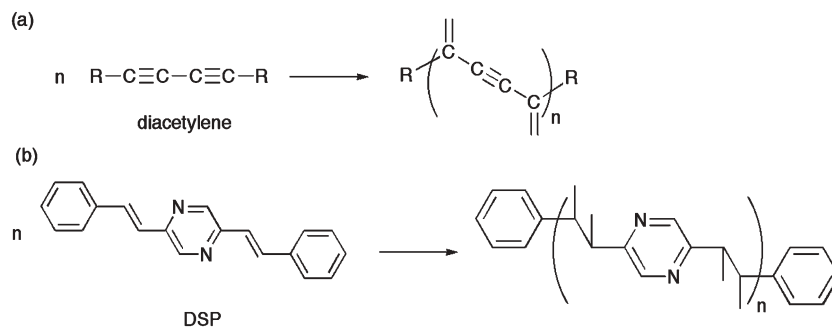


Fig. 17 Classical examples of topochemical polymerizations; (a) diacetylene and (b) DSP (distyrylpyrazine).

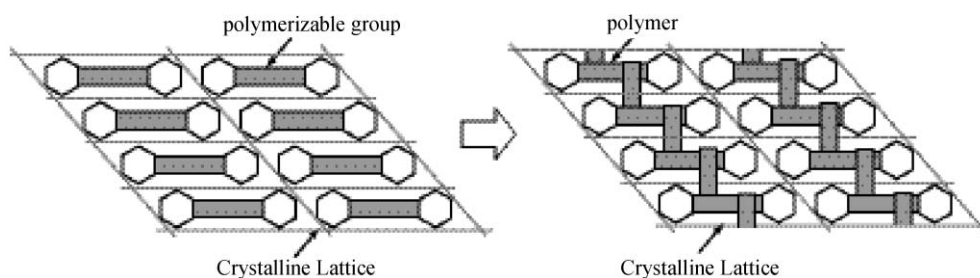


Fig. 18 Schematic representation of topochemical polymerization in the crystalline state.

of the regio- and stereo-selectivities by highly ordered arrangement of the monomers in the crystalline state. The other is limitation of the monomers, because they have to form crystalline materials and the proper arrangements of the monomers for the topochemical polymerizations. Thus, the polymerizabilities are quite unpredictable, and affected drastically by perturbation of the molecular structures far from the polymerizable groups due to the changes of orientation. This is in contrast to the versatile polymerizations of various monomers in the isotropic solution state. Therefore, most of the topochemical polymerizations have been found accidentally or by trial and error.^{72–76}

To develop new topochemical polymerization systems, we have to take two factors into consideration: one is how to design the steric requirement of the polymerizable groups in the crystalline state, and the other is how to arrange the monomers for the suitable orientations. They should be designed by the accumulated data of the polymerizabilities and the crystal structures. For the former problem, since the topochemical polymerizations occur without motion and movement of the monomers during the polymerization, the packing of the polymerizable groups should be preorganized to be similar to that of the resultant polymers. This similarity in the crystalline state is the first principle to develop topochemical polymerizable monomers. For the latter, the remarkable advances of crystal engineering and supramolecular chemistry by using hydrogen bonds, metal coordination and π - π /CH- π interactions have partially enabled us to control the arrangements of the molecules in the crystalline state. In this section, we reviewed recent advances of rational design and new monomers of the topochemical polymerizations in the crystalline state.

4.1 Crystalline-state polymerization of diacetylene derivatives

Diacetylenes are a classical and most popular class of monomer for topochemical polymerization. Structure–function relationship for the topochemical polymerization has been already well-known^{73,74} and used in various supramolecular assemblies as described in the former sections. The steric requirement for the topochemical polymerization is one-dimensional stacking of the diacetylene groups in translational positions around 4.9 Å and the inclination angles of the diacetylene axes to the packing axis are about 45°, as shown in Fig. 19. In the structure, the rod-like diacetylene groups are packed closely, and the intermolecular closest contact of the nearest diacetylene carbon atoms are just 3.5–4.0 Å. The translational distance of the diacetylene monomers is similar to the lengths of the repeating units in the poly(diacetylene)s. The orientation and packing of the substituents both in the monomer state and in the polymer state are very close to each other. Thus, the minimum movement of the reactive carbon atoms and no movement of the non-polymerizable part provide efficient polymerization even in the crystalline state.

Studies on the topochemical polymerizations of diacetylenes have been shifted from the combinatorial screening of new monomers to rational design by using various intermolecular interactions and host–guest chemistry. Recently, Lauher and Fowler reported various diacetylene polymerization systems by using reliable robust supramolecular building blocks such as urea and oxalamide groups as shown in Fig. 20.⁸⁰ Their design depends on the following two ideas. One is similarity between the steric requirement for the topochemical polymerizations and the repeating distance (*ca.* 4.5–5.0 Å) along the one-dimensional hydrogen-bond network of urea and

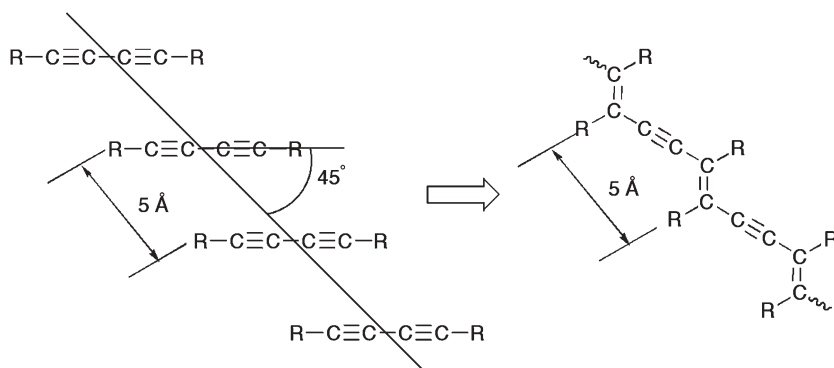


Fig. 19 Steric requirement of diacetylene polymerization.

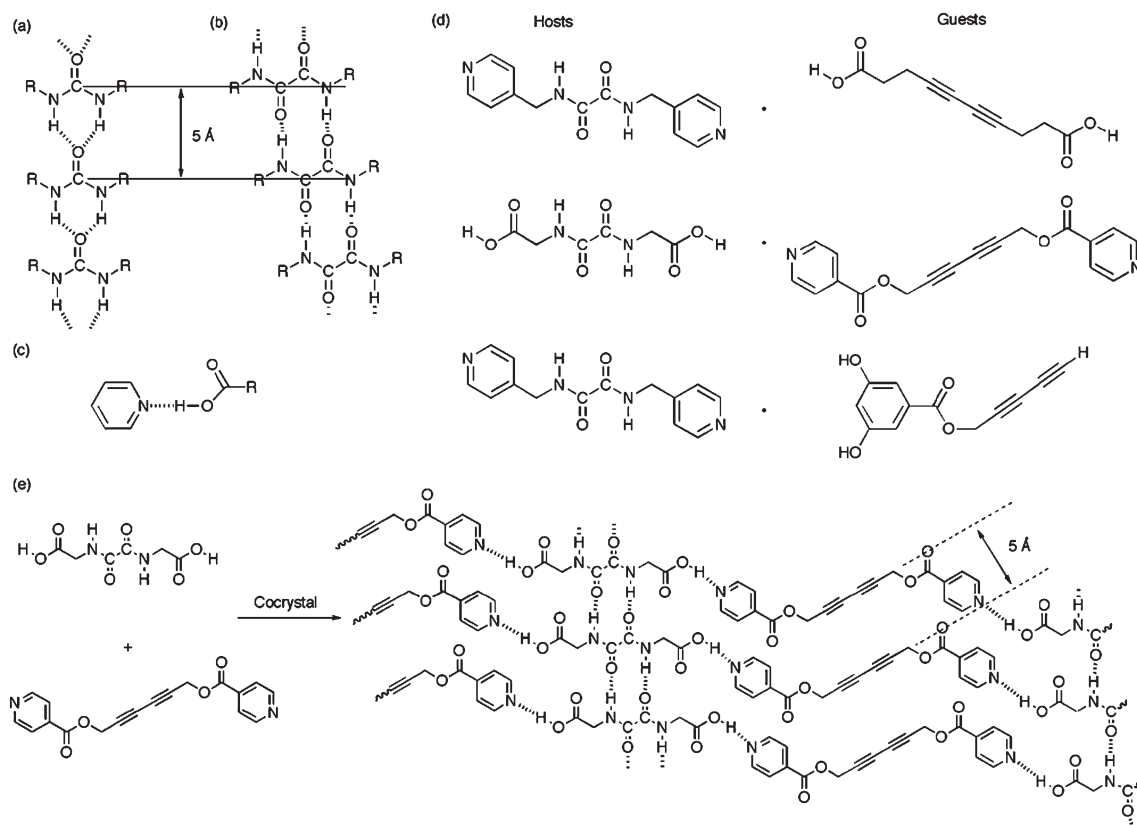


Fig. 20 Designed topochemical polymerization by host-guest co-crystal approach, (a) a one-dimensional hydrogen-bond network of ureas, (b) a one-dimensional hydrogen-bond network of oxalamides, (c) Intermolecular interaction between pyridine and carboxylic acid, (d) various combinations of the topochemical polymerizable host-guest co-crystals that proceeds topochemical polymerization of diacetylene and (e) molecular arrangement of topochemical polymerizable co-crystals.

oxalamide groups as hosts. The other is formation of 1 : 1 host-guest co-crystals between carboxylic acid and pyridine as a reliable interaction for arrangement of the monomers as guests along the one-dimensional arrays of the hosts. With the aid of the co-crystals, the polymerizable groups can be separated from the supramolecular building blocks that construct the three-dimensional designed crystal structures. This approach has an advantage for combinatorial screening and easy synthetic works for candidates of topochemical polymerizations in contrast to the covalently linked ones. As the result, they can employ various diacetylene monomers in sophisticated designs. Thus, the steric requirement of the diacetylene monomers can be generated by rational crystal design. They expanded the acetylene monomers and presented the utility of the host-guest co-crystals. They open the door for rationally designed topochemical polymerization systems that have ever only been found accidentally or by trial-and-errors approaches. By using this approach, Goroff and Lauher successfully prepared unique poly(diacetylene) that consists of only iodine atoms and carbon atoms.⁸¹

4.2 Crystalline-state polymerization of diene derivatives

Compared to the extensive investigations of the diacetylenes, the topochemical polymerization of diene had been quite limited.⁸² However, in 1994, Matsumoto reported the topochemical polymerization of muconate esters,⁸³ which was

followed by the extensive X-ray crystallographic studies of various related diene esters and salts as shown in Fig. 21. They revealed that the steric requirement is face-to-face stacking of the diene groups to form a one-dimensional array, that the translational distance between the two monomer is around 5 Å and that the inclination angles of the diacetylene axes to the packing axis are about 30–60°, as shown in Fig. 22.^{76,84} In this orientation, the intermolecular closest distance between the diene carbon atoms is just 3.5 Å. Compared to the diacetylene monomers, the diene groups have restricted steric requirement. In the former, isotropic nature along the C–C triple bond would provide many stacking possibilities. However, in the latter, the face-to-face arrangement of the C–C double bond is requisite. This difference and no colour development of the diene groups during the polymerization should avoid us investigating the topochemical polymerization of the diene groups. Moreover, the stereo regularity of the resultant polymer can be controlled by *cis* or *trans* isomers of the starting diene monomers and the translational or alternate packing.⁸⁵ This control is caused by the reliable and robust crystal structures of the 1-naphthylmethylammonium salts of muconates and sorbetes, regardless of the geometry of the diene group. Moreover, they provide us to robust organic layered materials both in the monomer state and the polymer state.^{86,87} The latter polymeric materials exhibit intercalation phenomena of the layered polymer crystals.⁸⁸ Formation of the layered structure is caused by ion-pairs and hydrogen

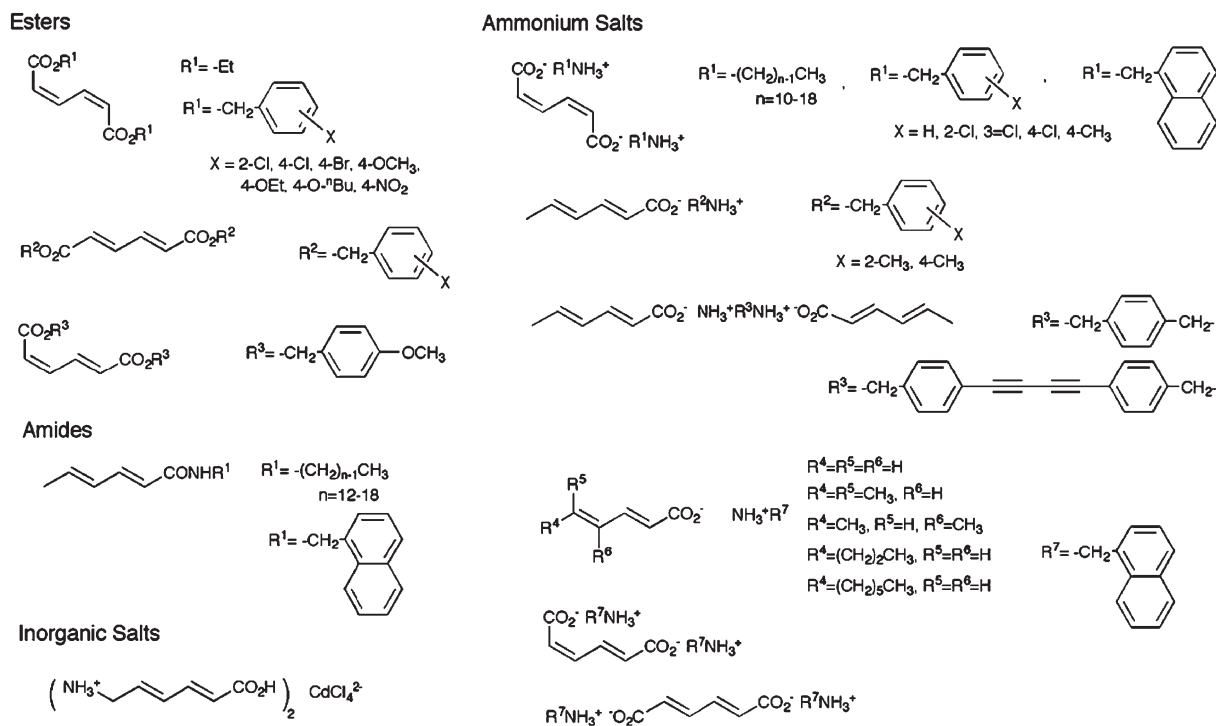


Fig. 21 Topochemical polymerizable diene monomers.

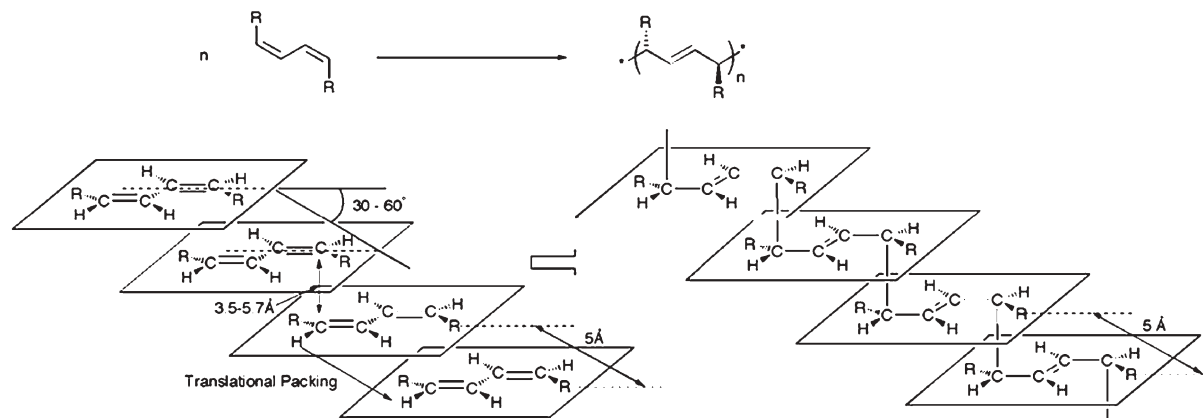


Fig. 22 Steric requirement of diene polymerization.

bonds between the carboxylate anions and 1-naphthylmethylammonium cations, π - π stacking of the naphthalene rings and alkyl chain interactions of the alkyl groups. More recently, we demonstrated the successful topochemical polymerizations of the diacetylene acids by salt formation with 1-naphthylmethylamine.⁸⁹ The steric requirement for diene monomers is more strict than that for diacetylene monomers. As a result, this system is one of the rationally designed systems for topochemical polymerization.

4.3 Crystalline-state polymerization of oligoene and oligoyne derivatives including *p*-quinodimethanes

Topochemical polymerizations developed by Matsumoto and co-workers ignited exploration of new topochemical polymerization systems. Itoh and ourselves investigated the solid

state polymerization of the *p*-quinodimethane monomers (QM), that undergo isomerization polymerization to form xylene as shown in Fig. 23.⁹⁰ X-ray crystallographic studies of 10 QM esters including polymorphic forms reveal that the stacking of the QM plays an important role for the polymerizability of QM in the crystalline state. The reactive monomers have face-to-face stacking with slight offset along the longer molecular axis. The translational stacking distance is around 7.0 Å and the inclination angles of the QM axes to the packing axis are about 30° as shown Fig. 23. Otherwise, the crystals exhibit no or low polymerizabilities induced by photo, heat and γ -ray irradiation. The crystals are longer than those of dienes and diacetylenes, and this is attributed to the longer repeating units distances of the polymer structures between the two xylene groups in the polymer of QM. In conclusions, the preorganized molecular assembly of the monomers in the

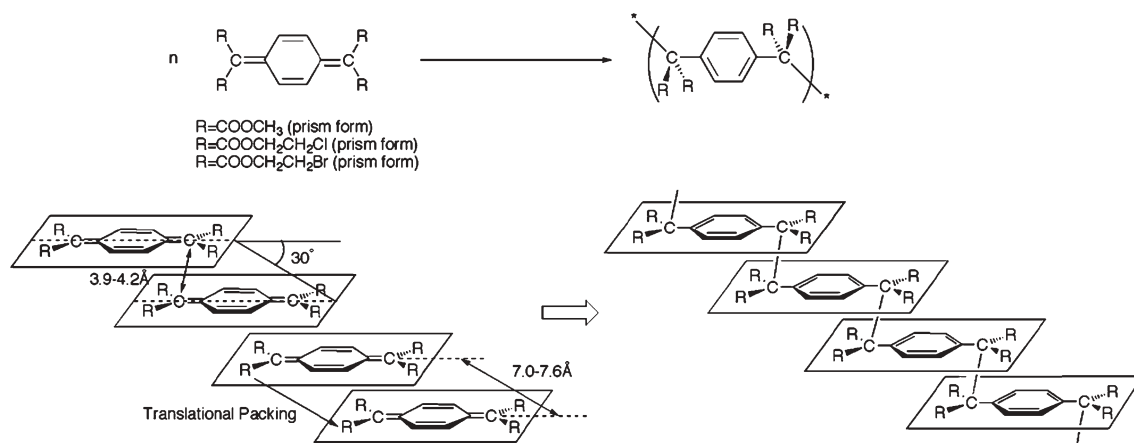


Fig. 23 Steric requirement of QM polymerization.

crystalline state enables them to undergo efficient topochemical polymerization.

Extension of the longer monomers from diacetylenes to triacetylenes was not so easy.⁹¹ In 2000, Lauher and Fowler successfully demonstrated the elegant design of the 1,6-polymerization of a triacetylene by using it as a host molecule.⁹² The designed compounds are shown in Fig. 24. The guest has a triacetylene moiety and two pyridine moieties at both ends for host-guest interactions. The host has a vinylogous amide group that arranges the guest molecules in the translational 7.3 Å distance by the one-dimensional

hydrogen-bond network, and COOH for interaction site for the guest. The crystal structure of the 2 : 1 co-crystal of the host and the guest is shown in Fig. 24c. The translational distance is just *ca.* 7.1 Å and tilt angle is about 30° with respect to the translational direction. This arrangement guarantees the full packing of the triacetylene groups by van der Waals interaction. The γ -ray irradiation yields the poly(triacetylene) by selective 1,6-polymerizations.

Moreover, they demonstrated the 1,6-polymerization of triene monomer.⁹³ In this, there is no host-guest interaction nor design to arrange them in a stacking arrangement with a

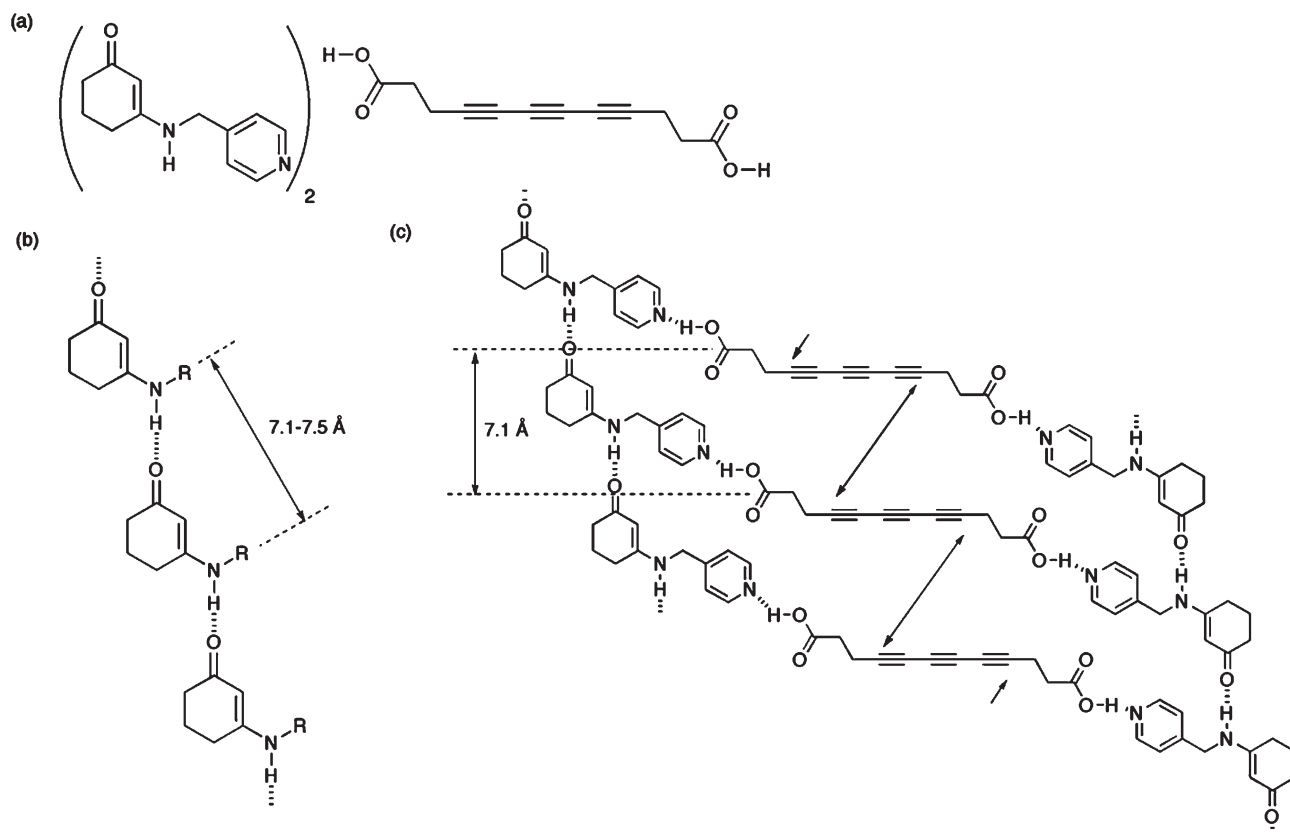


Fig. 24 (a) A triacetylene monomer for topochemical polymerization, (b) designed hydrogen-bond network of vinylogous amide, and (c) crystal packing model of triacetylene monomer. Arrows indicate formation of C-C bonds by topochemical polymerization.

translational distance of 7.4 Å. However, they spontaneously form the desirable arrangement in the crystalline state accidentally by π - π stacking of the pyridine moieties without host molecules, and yield the selective 1,6-polymerization of triene monomers. The crystal structure is shown in Fig. 25. The steric requirement is close to that of the triacetylene monomers. The translational distance is 7.2 Å and tilt angle is 34° and orientational angle is 68°. The face-to-face stacking of the triene moieties precedes the polymerization in the crystalline state. This example is the only one for the successful 1,6-polymerization of triene monomer. Thus, the longer 7.2 Å is essential for topochemical polymerization of trienes and triacetylenes.

4.4 Crystalline-state polymerization of other polymerizable groups

Other monomers such as vinyl and acetylene groups have been not so investigated with respect to crystalline state polymerization. In the vinyl and acetylene monomers, the translation distances are much shorter (*ca.* 2.8 Å). Thus, the very close packing of vinyl and acetylene monomers has been not frequently observed. However, Foxmann *et al.* reported the crystalline-state controlled polymerization of a substituted phenylacetylene with high reactivity.⁹⁴ In the crystalline state, the molecular packing of the acetylene groups is in parallel arrangement, and the orientation is suitable for the resultant poly(acetylene) structures. However, the distance between the monomers is longer than that of the expected repeating distances. As another example of the crystalline state

polymerization, some bifunctional diol compounds treated with strong acid in the solid state induced the formation of poly(ether)s.⁹⁵ High efficiency of polymerization compared with the concentrated solution state should be caused by the preorganized crystal structures and the high concentration of the monomers in the absence of solvents. This is the crystalline lattice controlled process. Since many solid state organic reactions have been found by Toda *et al.*,⁹⁶ they should access for various lattice-controlled solid state polymerizations. Finally, with respect to electronic properties of the resultant polymers, crystalline-state polymerization of EDOT⁹⁷ and high-pressure topochemical polymerizations of C₇₀ have been demonstrated.⁹⁸

4.5 Summary for crystalline-state polymerization

In summary, the new trend of topochemical polymerization depends on the utility of co-crystals such as host-guest crystals or salts. This strategy has an advantage over screening of functional crystalline materials due to combinatorial approaches and easy preparations of the related molecules. They provide a relative wide range of monomers that have similar packing in the crystalline state and perturbation for the host part, which governs the host frameworks directly, and controls reactivities in the crystalline state by adjusting the intermolecular distances. This should access to reveal both the structure-function relationship and the crystal engineering.

With respect to understanding of topochemical polymerization abilities, the steric requirements of the several new monomers have been demonstrated. In all the systems, the

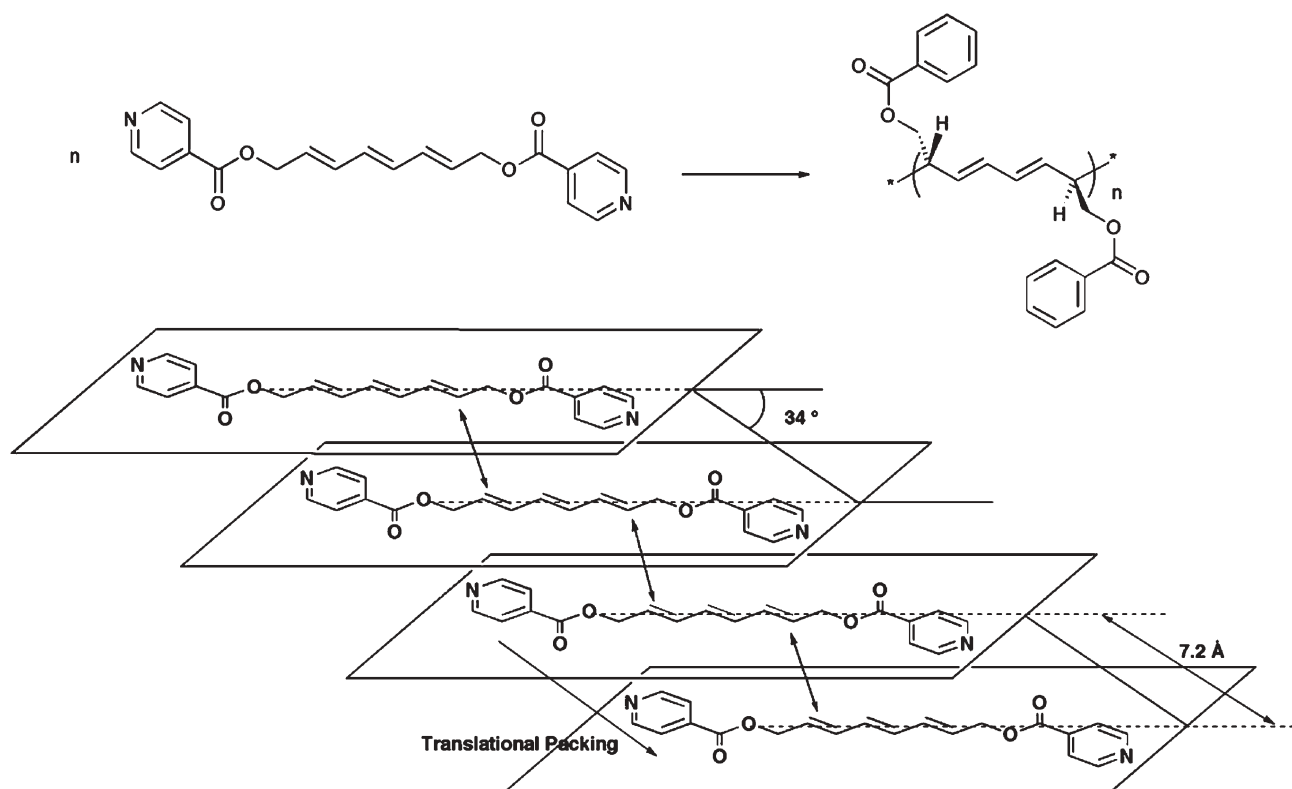


Fig. 25 A triene monomer for topochemical polymerization and steric requirement of the triene monomer. Arrows indicate formation of C-C bonds by topochemical polymerization.

packings of the monomers in the crystalline state are quite similar to the expected packing of the resultant polymers. This similarity induces the minimum movement of the atoms during the polymerization, and plays a key role for design of topochemical systems. Especially, the difference of the repeating distances of the polymers provides the difference of the steric requirements of the monomer arrangement. The topochemical polymerizations of other monomers including vinyl compounds should be explored by design of the steric requirement that is expected from the geometry of the resultant polymers. Further, variation of the steric requirement will enable us to use them for various polymerizations in anisotropic media and along the templates.

Conclusion

Supramolecular chemistry was essentially brought to us by discovery of the 1 : 1 molecular complex between a metal cation and a macrocyclic ligand in the late 1960s and early 1970s. This was followed by creation of host–guest chemistry in solution and molecular recognition that provided the selective “host–guest” complexes in particular, in which a host molecule recognizes and selectively binds a certain guest by steric and electronic complementarity between the host and the guest. Then, explosive advances in the molecular design of “host–guest” complexes provided fruitful results contributing enormously to an understanding of non-covalent bonds and architectures of the three-dimensional structures composed of molecules and ions. Nowadays, more intelligent and sophisticated “host–guest” complexes have been developed by accumulation of various molecular functions and molecular recognition toward functional molecular devices and molecular machines. Besides this progress, interest in supramolecular chemistry is gradually shifting from simple 1 : 1 complexes to more complicated multi-molecular complexes. These include self-assembled architectures such as micelles, lipid bilayers, liquid crystals and organic crystals and macromolecular complexes such as protein–protein recognition, dendrimers and phase-separated structures of block copolymers. In supramolecular architectures comprising many components, the functions and structures are in general not the sum of each component but can provide quite different, novel functional materials. Moreover, since the sizes of supramolecular complexes are becoming larger and larger, and the complexities are ever increasing, it is undoubted that supramolecular chemistry plays a key role for bottom-up approaches to nanotechnology. The precise control of shape and size of molecules and supramolecular assemblies will continue as main subjects in chemistry and the material sciences in the 21st century.

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