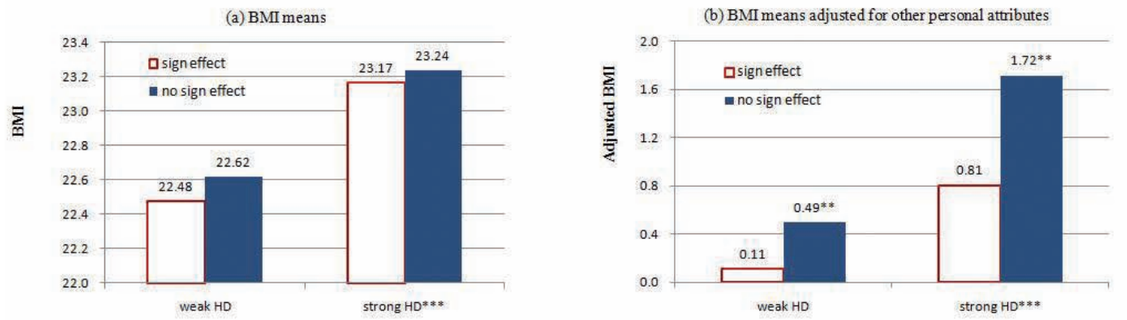

Fig.2 BMI under weak and strong hyperbolic discounting (HD) and with/without the sign effect. *, **, *** Statistical significance at the 10%, 5%, and 1% levels, respectively.

Figure 1 depicts the means of BMI and attribute-adjusted BMI in the quintiles stratified by the degree of impatience. In either case, the BMI means are shown to be positively correlated with impatience.

By sorting the sample by whether predilection toward hyperbolic discounting (HD) is strong or weak, and whether the sign effect is displayed or not, Figures 2(a) and 2(b) compare the BMI means and those means adjusted for other personal attributes. In either figure, BMI is associated positively with the degree of hyperbolic discounting, and negatively with the sign effect.

Based on regressions, Figure 3 estimates the impacts (or marginal effects) of increases in the time discounting variables on BMI and on the probabilities of being obese, severely obese, and underweight. As is shown, a higher degree of impatience is associated with higher probabilities of being obese and of being severely obese, and with a lower probability of being underweight. For example, an increase in impatience by one unit of the standard deviation is associated with an increase in BMI by 1.09% of the BMI mean, a 2.28 percentage-point increase in the probability of being obese, and a 0.83 percentage-point decrease in the probability of being underweight. A one-unit increase in the degree of hyperbolic discounting is associated with a 2.81 percentage-point increase in the probability of being obese and a 0.92 percentage-point decrease in the probability of being underweight. Respondents exhibiting the sign effect show a smaller BMI by 2.17% of the BMI mean, a 1.06 percentage-point smaller probability of being severely obese, and a 4.02 percentage-point higher probability of being underweight than those without the sign effect. These marginal effects are substantial compared with the prevalence rates of the corresponding body status (e.g., 18.92% for obesity and 6.97% for underweight).

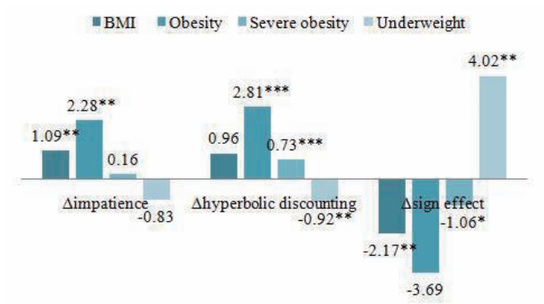

Fig.3 The impacts of an increase in time discounting variables on BMI and the probabilities of being obese, severely obese, and underweight are listed in percentage points. "Δimpatience" represents the impacts of an increase in the discount rate by one unit of sample S.D. of the average discount rate. "Δhyperbolic discounting" shows the impacts of a one-point increase in the degree of procrastination. The row "Δsign effect" summarizes the effect of the presence of the sign effect, compared with the case without the effect. *, **, *** Statistical significance at the 10%, 5%, and 1% levels, respectively. The estimated results are from Tables 9 and 13 of Ikeda et al. (2010).

Conclusions and policy implications

Analysis of an original nationwide survey of Japanese adults confirms that their body weight is expectedly related to their time discounting via impatience, hyperbolic discounting, and the sign effect. The impacts of these preferences on the probabilities of being obese and underweight are not that small, especially compared with the corresponding prevalence rates. Caloric intake and the resultant body mass formation could thus be taken as determined by interetemporal decision-making with behavioral decision bias toward immediacy and/or toward aversion of future losses.

Three policy implications follow. First, policies that raise the immediate costs of caloric intake (e.g., greasy food tax) are likely to be effective at reducing the prevalence of obesity. Second, policies that ease self-control problems (e.g., school education, counteracting advertisements that stimulate consumers' impulsiveness) are also effective. Third, "nudging" policies that change defaults of eaters' choices would also be effective.

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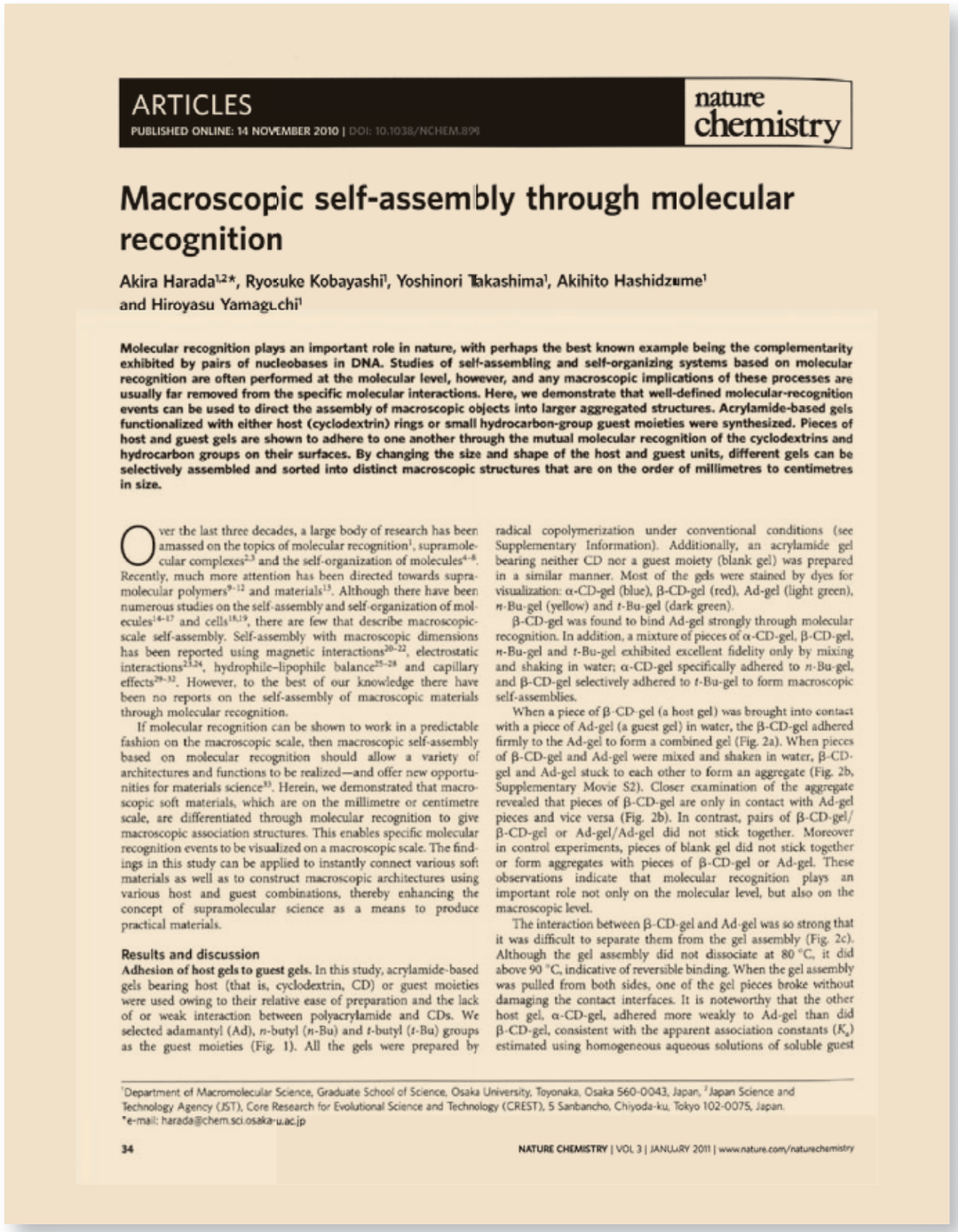
Macroscopic Self-Assembly through Molecular Recognition

Paper in journals: this is the first page of a paper published in ***Nature Chemistry***.
[*Nature Chemistry*] 3, 34-37(2011)



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Macroscopic self-assembly through molecular recognition

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Molecular recognition plays an important role in nature, with perhaps the best known example being the complementarity exhibited by pairs of nucleobases in DNA. Studies of self-assembling and self-organizing systems based on molecular recognition are often performed at the molecular level, however, and any macroscopic implications of these processes are usually far removed from the specific molecular interactions. Here, we demonstrate that well-defined molecular-recognition events can be used to direct the assembly of macroscopic objects into larger aggregated structures. Acrylamide-based gels functionalized with either host (cyclodextrin) rings or small hydrocarbon-group guest moieties were synthesized. Pieces of host and guest gels are shown to adhere to one another through the mutual molecular recognition of the cyclodextrins and hydrocarbon groups on their surfaces. By changing the size and shape of the host and guest units, different gels can be selectively assembled and sorted into distinct macroscopic structures that are on the order of millimetres to centimetres in size.

Over the last three decades, a large body of research has been amassed on the topics of molecular recognition[1], supramolecular complexes[2,3] and the self-organization of molecules[4–8]. Recently, much more attention has been directed towards supramolecular polymers[9–12] and materials[13]. Although there have been numerous studies on the self-assembly and self-organization of molecules[14–17] and cells[18,19], there are few that describe macroscopic-scale self-assembly. Self-assembly with macroscopic dimensions has been reported using magnetic interactions[20–22], electrostatic interactions[23,24], hydrophile–lipophile balance[25–28] and capillary effects[29–32]. However, to the best of our knowledge there have been no reports on the self-assembly of macroscopic materials through molecular recognition.

If molecular recognition can be shown to work in a predictable fashion on the macroscopic scale, then macroscopic self-assembly based on molecular recognition should allow a variety of architectures and functions to be realized—and offer new opportunities for materials science[33]. Herein, we demonstrated that macroscopic soft materials, which are on the millimetre or centimetre scale, are differentiated through molecular recognition to give macroscopic association structures. This enables specific molecular recognition events to be visualized on a macroscopic scale. The findings in this study can be applied to instantly connect various soft materials as well as to construct macroscopic architectures using various host and guest combinations, thereby enhancing the concept of supramolecular science as a means to produce practical materials.

Results and discussion

Adhesion of host gels to guest gels. In this study, acrylamide-based gels bearing host (that is, cyclodextrin, CD) or guest moieties were used owing to their relative ease of preparation and the lack of or weak interaction between polyacrylamide and CDs. We selected adamantyl (Ad), *n*-butyl (*n*-Bu) and *t*-butyl (*t*-Bu) groups as the guest moieties (Fig. 1). All the gels were prepared by radical copolymerization under conventional conditions (see Supplementary Information). Additionally, an acrylamide gel bearing neither CD nor a guest moiety (blank gel) was prepared in a similar manner. Most of the gels were stained by dyes for visualization: α-CD-gel (blue), β-CD-gel (red), Ad-gel (light green), *n*-Bu-gel (yellow) and *t*-Bu-gel (dark green).

β-CD-gel was found to bind Ad-gel strongly through molecular recognition. In addition, a mixture of pieces of α-CD-gel, β-CD-gel, *n*-Bu-gel and *t*-Bu-gel exhibited excellent fidelity only by mixing and shaking in water; α-CD-gel specifically adhered to *n*-Bu-gel, and β-CD-gel selectively adhered to *t*-Bu-gel to form macroscopic self-assemblies.

When a piece of β-CD-gel (a host gel) was brought into contact with a piece of Ad-gel (a guest gel) in water, the β-CD-gel adhered firmly to the Ad-gel to form a combined gel (Fig. 2a). When pieces of β-CD-gel and Ad-gel were mixed and shaken in water, β-CD-gel and Ad-gel stuck to each other to form an aggregate (Fig. 2b, Supplementary Movie S2). Closer examination of the aggregate revealed that pieces of β-CD-gel are only in contact with Ad-gel pieces and vice versa (Fig. 2b). In contrast, pairs of β-CD-gel/β-CD-gel or Ad-gel/Ad-gel did not stick together. Moreover in control experiments, pieces of blank gel did not stick together or form aggregates with pieces of β-CD-gel or Ad-gel. These observations indicate that molecular recognition plays an important role not only on the molecular level, but also on the macroscopic level.

The interaction between β-CD-gel and Ad-gel was so strong that it was difficult to separate them from the gel assembly (Fig. 2c). Although the gel assembly did not dissociate at 80 °C, it did above 90 °C, indicative of reversible binding. When the gel assembly was pulled from both sides, one of the gel pieces broke without damaging the contact interfaces. It is noteworthy that the other host gel, α-CD-gel, adhered more weakly to Ad-gel than did β-CD-gel, consistent with the apparent association constants (K_a) estimated using homogeneous aqueous solutions of soluble guest

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The following is a comment on the published paper shown on the preceding page.

Macroscopic Self-Assembly through Molecular Recognition

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Introduction

Over the past 30 years, much attention has been focused on molecular recognition, host-guest chemistry, and supramolecular science [1]. Simple cyclic molecules, crown ethers, cyclophanes, and cyclodextrins were found to be able to recognize small ions and simple molecules [2], [3]. However, in biological systems, such as enzyme-substrates, antibodies-antigens, and DNA, macromolecular recognition, recognition of macromolecules by macromolecules plays an important role in maintaining their lives. While we were investigating macromolecular recognition, we have a simple question whether we can see molecular recognition by our own eyes. Here, we demonstrate that well-defined molecular recognition events can be used to direct the assembly of macroscopic objects into larger aggregated structures [4], [5]. Acrylamide-based gels functionalized with either host

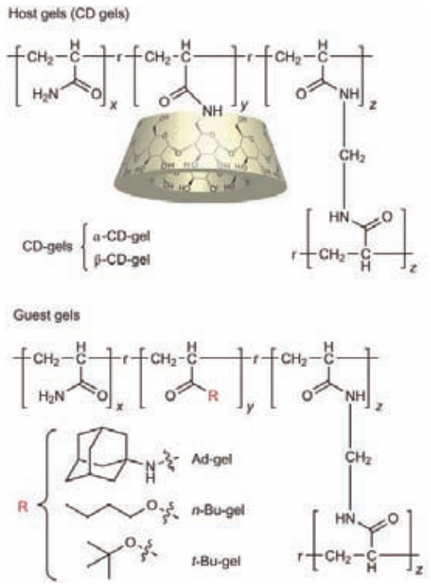

Fig.1 Chemical structures of host and guest gels.

cyclodextrin(CD) rings or small hydrocarbon guest moieties were synthesized. Pieces of host and guest gels are shown to adhere to one another through the mutual molecular recognition of the CDs and hydrocarbon groups on their surfaces. By changing the size and shape of the host and guest units, different gels can be selectively assembled and sorted into distinct macroscopic structures that are on the order of millimeters to centimeters in size

Adhesion of Host Gels to Guest Gels

We chose polyacrylamide gels as a scaffold for the macroscopic self assembly studies, because they have no interactions with proteins, DNA, and polysaccharides. We have prepared gels containing CDs (host gels) and gels containing guest groups (guest gels) by copolymerization with host (or guest) monomers, acrylamide, and bisacrylamide.

When a piece of β-CD gel (host gel) was brought into contact with a piece of Adamantane-gel (Ad-gel, a guest gel), the β-CD gel and Ad-gel stuck to each other to form an aggregate (Fig.2b). Closer examination of the aggregate revealed that pieces of β-CD gel are only in contact with Ad-gel pieces and vice versa. The interaction between β-CD-gel and Ad-gel was so strong that it was difficult to separate them from the gel assembly (Fig. 2c). When the gel assembly was pulled from both sides, one of the gel pieces broke without damaging the contact interfaces.

It is noteworthy that the other host gel, α-CD gel, adhered more weakly to Ad-gel than did β-CD-gel, consistent with the apparent association constants (*Ka*) estimated using

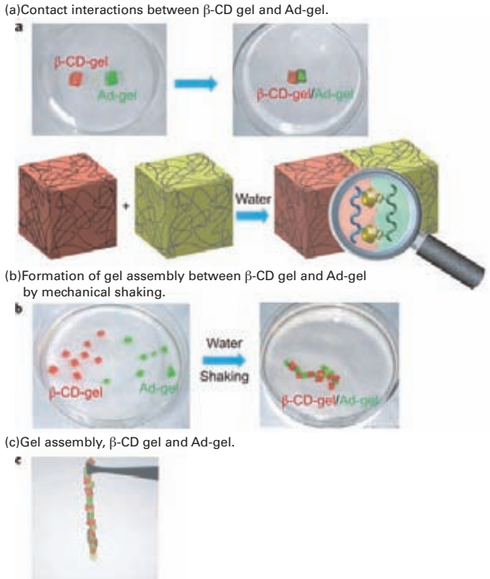

Fig.2 Macroscopic self-assembly between CD host gels and guest gels

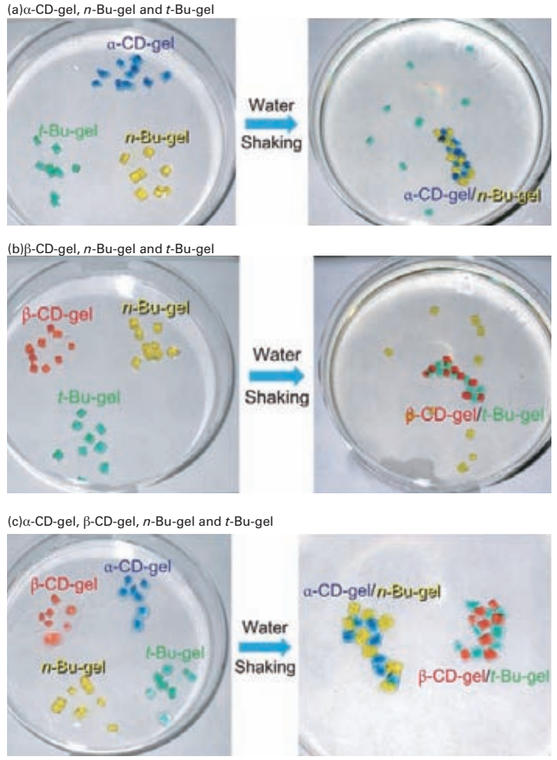

Fig.3 Visualization of specific molecular recognition events on a macroscopic scale.

homogeneous solutions of soluble guest polymers (without cross-linking) and CDs.

Competitive experiments confirmed self-assembly based on molecular recognition. Ad-gel did not form a gel assembly with β-CD gel in aqueous solution containing excess β-CD, because the added β-CD masked the Ad groups in the gel. When pieces of β-CD gel and Ad-gel were mixed and shaken in aqueous solutions of 1-adamantanmine hydrochloride, β-CD gel adhered weakly to Ad-gel.

Selective Assembly of Gels

Figure 3a shows the results following mixing and shaking pieces of α-CD-gel, *n*-Bu-gel and *t*-Bu-gel in water. Only α-CD-gel and *n*-Bu gel resulted in the formation of a gel assembly. In contrast, a mixture of pieces of β-CD-gel, *n*-Bu-gel, and *t*-Bu-gel formed a gel assembly of β-CD gel with *t*-Bu-gel (Fig.3b). These results indicate that molecular recognition through host-guest interactions works on the macroscopic scale.

When pieces of α-CD-gel, β-CD-gel, *n*-Bu-gel and *t*-Bu-gel were simultaneously mixed in water and shaken, only pieces of α-CD-gel stuck to pieces of *n*-Bu-gel, and only pieces of β-CD-gel stuck to pieces of *t*-Bu-gel, to give alternating or chequered structures (Fig. 3c). These results clearly indicate that a host gel recognizes the corresponding guest gels through

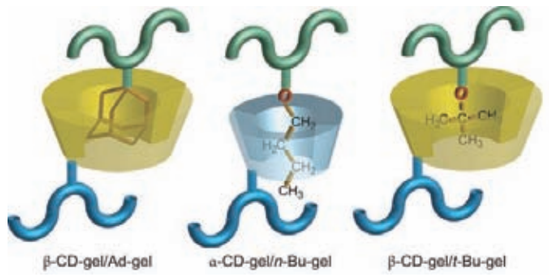

Fig.4 Proposed structures of the complexes formed between CDs and guests attached to a gel.

molecular recognition to form macroscopic structures.

α-CD-gel strongly adhered to *n*-Bu-gel, but not to *t*-Bu-gel. In contrast, β-CD-gel strongly bonded to *t*-Bu-gel, but not to *n*-Bu-gel. Figure 4 shows schematically represents the interactions between CD-gels and guest gels. The slim *n*-Bu group fits well in the α-CD cavity, and the bulky *t*-Bu group fits well in the larger β-CD cavity. Because the host gels are able to differentiate such a small difference in the guest parts, this system can be applied to differentiate macroscopic materials through molecular recognition of various guest parts.

Conclusions

We successfully constructed supramolecular architectures on a macroscopic scale. Selective molecular recognition of CDs to guest molecules led to the unique association of hydrogels. Host-guest interactions were visualized by means of the self-assembly of objects, which were on the scale of millimeters to centimeters. We expect this system to be applicable to numerous other types of gels and soft materials with components in gels and soft materials with components that have host-guest relationships [6].

Macroscopic-scale recognition by means of molecular recognition has potential use in self-assembly in the macroscopic-scale construction of new architectures by selective and reversible binding properties, and holds promise in the development of new medical applications.

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