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Journal Name

ARTICLE

Direct Covalent Bond Formation between Materials Using Copper(I)-Catalyzed Azide Alkyne Cycloaddition Reactions

Tomoko Sekine, Yoshinori Takashima and Akira Harada*

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) reactions have been used to prepare organic molecules and polymeric materials, however direct adhesion between polymeric materials and between polymeric and inorganic materials via irreversible reactions has not been reported, except for reversible adhesion using some reversible reactions. Herein we realize direct adhesion of materials using the CuAAC reaction in which a poly(acrylamide) gel (pAAM gel) modified with a pendent terminal ethynyl group (E-gel) selectively adheres to the pAAM gel with a pendent azide group (Az-gel). The E-gel selectively bonds to a glass substrate whose surface is modified with the azide groups, but the adhesion strength depends on the ratio of the functional groups. These results indicate that direct adhesion using the CuAAC reaction should be applicable to various environments regardless of the materials' quality.

Introduction

Studies on adhesion between materials are important not only to improve the adhesive strength but also to analyze the molecular states at the interface.¹⁻³ Typically a glue is applied to bond two materials. In this case, the two materials do not adhere directly to each other via bond formation, but adhere through the glue. Several effect between adhesives and adherend, such as adsorption, wetting, diffusion electrostatic interactions, mechanical interlocking chemical bonding and weak boundary layers, comprehensively perform to bring adhesive functions.⁴ Utilizing the chemical interaction between the surface of an adherend and adhesives or between adherends, we realize a stable adhesion system without glue.

Recently, direct bonding between materials has attracted much attention for the applications as self-healing materials that form non-covalent bonds.⁵⁻¹⁰ Adhesion via non-covalent bonds does not require a third component because these types of bonds (e.g., hydrogen bonds,¹¹ π - π stacking interactions,¹²⁻¹⁴ Cation- π interaction,^{15,16} metal-ligand coordination bonds,¹⁷ ionic interactions,¹⁸ and hydrophobic interactions¹⁹⁻²⁰) act as glue on the molecular level, exhibiting selective and reversible properties. However, the adhesion strength could be improved. Although formation of covalent bonds at the material interface is considered as one of the methods to improve adhesion strength, studies on direct-covalent bond formation between materials are relatively rare²¹

because choice of basic material properties (hardness, hydrophobicity, and hydrophilicity) and suitable bond-formation reactions is difficult. Although reversible dynamic covalent bonds²² and a Diels-Alder reaction²³ have attracted much attention to realize self-healing materials, the dissimilar materials joining between organic and inorganic materials by covalent bond formation has yet be reported, except some cases²¹. We have focused on the dissimilar materials joining through non-covalent interaction²⁴ and covalent bond formations²⁵.

Previously, we reported direct covalent bond formation between polymeric materials and between polymeric and inorganic materials using Suzuki-Miyaura cross-coupling reactions.²⁵ To realize a high reactivity, a high environmental adaptability, and quick bond formation, herein we chose the copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) reaction²⁶ to prepare a material system with direct adhesion. An azide (Az) group or an ethynyl (E) group, which acts as a nucleophile or an electrophile, respectively, is modified on a scaffolding material (poly(acrylamide) gel or a glass substrate). Bonding between hydrogel materials or between a hydrogel and a glass substrate is investigated using the CuAAC reaction at the interface.

Experimental

Materials. Acrylamide (AAM), dimethyl sulfoxide (DMSO), and D₂O were purchased from Wako Pure Chemical Industries. Acrylic acid (AA), acryloyl chloride, 2,2'-azobis(isobutyronitrile) (AIBN), copper(II) sulfate pentahydrate (CuSO₄•5H₂O), dichloromethane (DCM), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), *N,N*-dimethylformamide (DMF), 3-glycidyloxypropyltrimethoxysilane (GOPTS), *N*-hydroxysuccinimide (NHS), sodium *L*-ascorbate, triethylamine (Et₃N), potassium carbonate, and *N,N'*-methylenebis(acrylamide) (MBAAM) were obtained from Nacalai Tesque.

Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan.

E-mail: harada@chem.sci.osaka-u.ac.jp; Fax: +81 6 6850 5445;

Tel: +81 6 6850 5445

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Aminopropyltriethoxysilane (APTES), 4-azidobenzoic acid, propargylamine, 1H-benzotriazol-1-yloxytris (dimethylamino) phosphonium hexafluorophosphate (BOP reagent), and ethylenediamine were purchased from Tokyo Chemical Industry.

DMSO- d_6 was obtained from Merck & Co. No. S1126 glass, which was made from Inorganic Glass (B270) of SCHOTT AG, Plant Grünplan, was purchased from Matsunami Glass Ind. Water, which was purified with a Millipore Elix 5 system, was used to prepare the aqueous solutions. Other reagents were used as received.

Measurements. The ^1H NMR spectra were recorded at 500 MHz with a JEOL JNM-ECA 500 NMR spectrometer. The FGMAS NMR spectra were recorded at 400 MHz with a JEOL JNM-ECA 400WB NMR spectrometer. The sample spinning rate was 7 kHz. In all NMR measurements, chemical shifts were referenced to the solvent values ($\delta = 2.49$ ppm and 4.79 ppm for DMSO- d_6 and D_2O , respectively). The glass substrates were cleaned with O_3/UV cleaner (UV253S, Filgen, Inc.). The contact angles were measured by a Dynamic Contact Angle Analyzer (DCA-700, Kyowa Interface Science). The IR spectra of the gels were measured using a JASCO FT/IR-410 spectrometer with a KBr disc, while those of the substrates were measured using a JASCO FT/IR-6000 spectrometer via the attenuated total reflection method (ATR). The mechanical properties of the gels were measured by a mechanical tension testing system (Rheoner, RE-33005, Yamaden), and X-ray photoelectron spectroscopy (XPS) data were collected with an AXIS 165 (KRATOS ANALYTICAL) using a monochromatic Al-K α X-ray source.

Results and discussion

Preparation of Az-gel and E-gel

The Az-group and the E-group functionalize the base materials (the poly(acrylamide) gel and the glass substrate), allowing them to adhere via the CuAAC reaction (Fig. 1a). Figure 1b depicts the chemical structures of a hydrogel with the E-group (E-gel(x)) and that with the Az-group (Az-gel(x)), where x denotes the mol% of the functional groups. Poly(acrylamide) gel does not interact with the functional groups. As a chemical crosslinker, 4 mol% of the N,N' -methylenebisacrylamide (MBAAm) units is introduced into each gel (Table S1).

To prepare the E-gel(x) and the Az-gel(x), a scaffold gel (AA-gel: poly(acrylic acid)- r -poly(acrylamide) gel) was initially prepared by homogeneous radical copolymerization of acrylamide (AAM), MBAAm, and acrylic acid (AA) monomers in dimethyl sulfoxide (DMSO) using 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator. The condensation reaction of N -(2-aminoethyl)-4-azidobenzamide with the AA-gel gave the Az-gel(x) (Scheme S1). The E-gel(x) was prepared by a condensation reaction of propargylamine with the AA-gel (Scheme S2). The AAm-gel with 4 mol% of MBAAm without functional groups was prepared as a control. Each gel was purified by washing with DMSO to remove the unreacted compounds and then with water to give a hydrogel.

The ^1H solid state field gradient magic angle spinning (FGMAS) nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FT-IR) spectroscopy characterized the

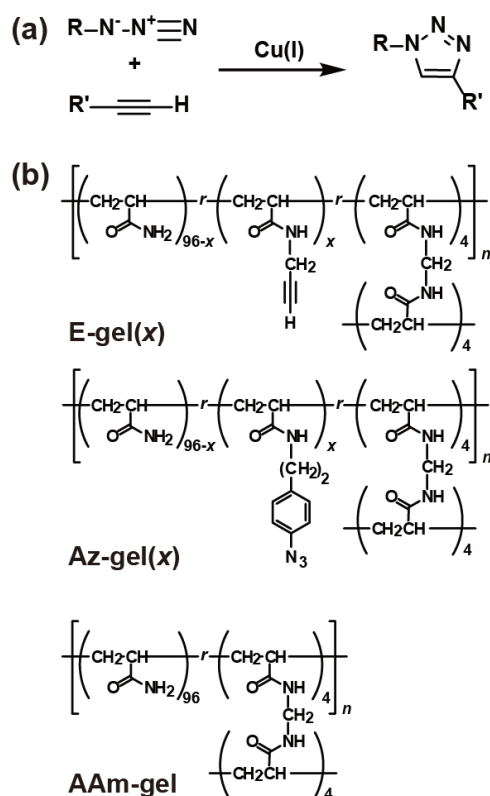


Figure 1. (a) The copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) reaction. (b) Chemical structures of the E-gel(x), the Az-gel(x), and the AAm-gel. x denotes the mol% of the functional groups (E group or Az group). N,N' -methylenebisacrylamide (MBAAm) unit is standardized at 2

Az-gel(x) and the E-gel(x) (Supplementary Figs. S1-S2). The ^1H FGMAS NMR results of the Az-gel(5) and the E-gel(5) show that 4.4 mol% of the Az-group and 3.2 mol% of the E-group are introduced into each gel, which are consistent with the feed ratio.

Adhesion between the E-gel and the Az-gel

Figure 2a shows the experimental procedure for adhesion of the Az-gel(x) and the E-gel(x) with the CuAAC reaction at the contact interface. Cuboids of Az-gel(10) and E-gel(10) (size: $5 \times 4 \times 3$ mm 3) were stacked vertically and subsequently immersed in an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3 mL, 0.02 M) and sodium L -ascorbate (0.03 M) (3 mL, depth: 2 mm). After standing for 5 hours, the Az-gel(10) and the E-gel(10) strongly adhere to each other, and the assembly can be easily picked up (Fig. 2b). On the other hand, the Az-gel(10) and the E-gel(10) do not adhere upon immersing the stacked gels into a solution without $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ or sodium L -ascorbate (Fig. 2c). In addition, the control experiments between the AAm-gel and the E-gel(10) or between the AAm-gel and the Az-gel(10) do not result in adhesion, even in the presence of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Figs. 2d-e). These results indicate that $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a catalyst and the functional groups play important roles in adhesion between the Az-gel and the E-gel. A wedged-shaped strain compression test was performed to determine the adhesion strength between the Az-gel(x) and the E-gel(x). The rupture of the wedge-shaped plunger ($\theta = 45^\circ$) at the contact interface of the adhered A -

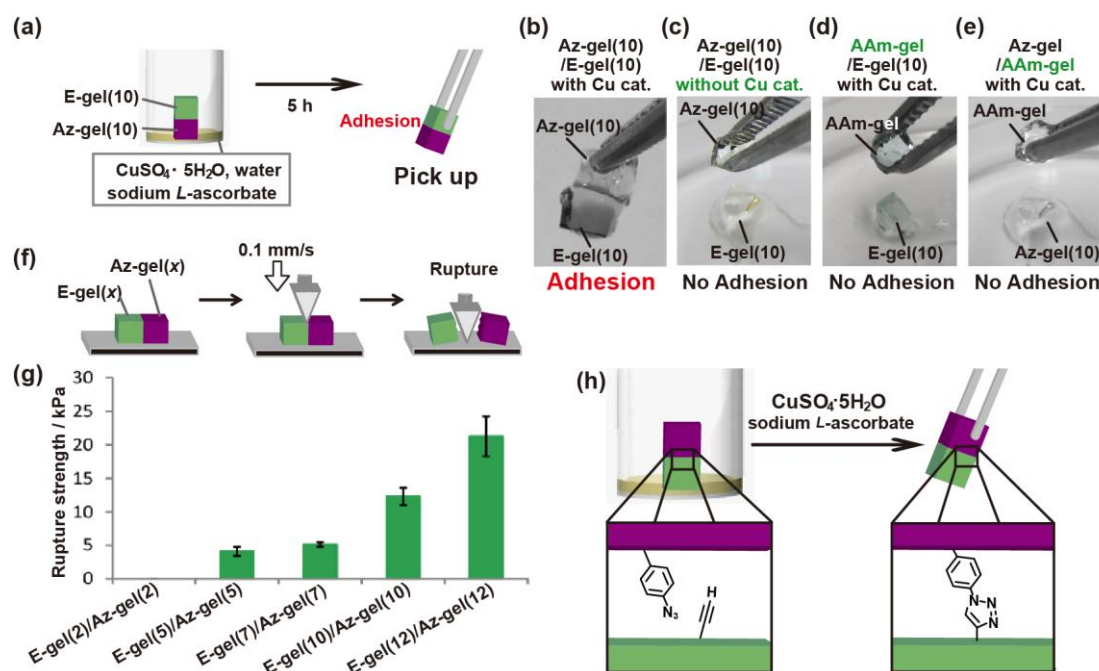


Figure 2. CuAAC reaction on the contact interface between the gels using a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ catalyst. (a) Adhesion experimental procedure of the E-gel with the Az-gel. Cuboid-shaped E-gel(10) (size: $5 \times 4 \times 3 \text{ mm}^3$) and Az-gel(10) immersed in an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3 mL, 0.02 M) and sodium L-ascorbate (0.03 M). Results of adhesion experiments between (b) E-gel(10)/Az-gel(10) with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, (c) E-gel(10)/Az-gel(10) without the Cu catalyst, (d) AAm-gel/E-gel(10) with the Cu catalyst, and (e) AAm-gel/Az-gel(10) with the Cu catalyst. (f) Experimental procedure of the wedged-shaped strain compression test. (g) Stress values between E-gel(x)/Az-gel(x) where the error bars denote the standard deviation of three samples. (h) Proposed mechanism of covalent bond formation at the gel–gel interface.

gel(x) and the E-gel(x) (Az-gel(x)/E-gel(x)) was measured at a creeping speed of 0.1 mm/s (Fig. 2f). The rupture strength of Az-gel(x)/E-gel(x) increases as the molar contents of the functional groups (Az-group and E-group) increase (Fig. 2g). At a lower molar content (<2 mol%) of the functional groups, the Az-gel(2) and the E-gel(2) do not adhere, and the rupture strength is minimal.

We also investigated the time-dependence of the rupture strength in E-gel(10)/Az-gel(10) (Fig. S3); the rupture strength increases with reaction time, but becomes saturated within 9 hours.

These results indicate that covalent bonds form at the interface between the Az-gel and the E-gel via the CuAAC reaction (Fig. 2h). Consequently, the molar contents of the functional groups and the reaction time can control the adhesion strength of E-gel(x)/Az-gel(x).

Adhesion between hydrogels and glass substrates

One of the most important characteristics through direct covalent bond formation between materials is adhesion between heterogeneous materials with different qualities. Adhesion between heterogeneous materials is difficult due to different chemical properties and swelling-shrinking ratios. Here we chose a glass substrate as an inorganic hard material. To immobilize the Az-group and the E-group on hard materials, glass plates were treated with 3-aminopropyltriethoxysilane (APTES-Sub) and 3-glycidyloxypropyltrimethoxysilane (GOPTS-Sub), respectively.

The Az-Sub was prepared from the APTES-Sub, while the E-Sub was prepared from the GOPTS-Sub (Schemes S3 and S4).

The Az-Sub and the E-Sub (Figure 3a) were characterized by contact angle measurements, attenuated total reflection (ATR) Fourier transform infrared (FT-IR) spectroscopy, and X-ray photoelectron spectroscopy (XPS). The contact angle measurements confirm the wettability of the modified surfaces (Fig. S5). After treatment with O_3/UV , the contact angle of the unmodified glass substrate changes from 36° to 3.4° due to the increased hydrophilic property of the glass substrate. The contact angle of the Az-Sub is slightly altered due to the modification of the Az-group to the APTES-Sub (84° and 82° , respectively), indicating that both the APTES-Sub and the Az-Sub have highly hydrophobic surfaces. The E-Sub shows a 76° contact angle, which differs from GOPTS-Sub (49°) through the condensation reactions with propargylamine. These results show that the functional groups on the glass substrates are modified.

ATR-FT-IR spectra of the Az-Sub show a unique band at 2121 cm^{-1} (Fig. S6a), which is derived from the azide group. The E-Sub has a significantly weak band at 2122 cm^{-1} (Fig. S6b). These spectra indicate that the Az-group and the E-group are successfully attached to each surface.

The XPS spectra of the APTES-Sub demonstrate the corresponding peaks of nitrogen (N 1s at 398 eV) and silicon (Si 2p at 99 eV, and 2s at 151 eV), indicating that the APTES groups are immobilized on the surfaces. The Az-Sub shows a new peak at 399 eV.

eV, corresponding to nitrogen (N 1s) of the azide group (Figs. S7a, b). The XPS spectra of the E-Sub (Figs. S7c, d) show a new peak of nitrogen (N 1s), indicating that new compounds with nitrogen atoms are attached to the surface. These measurements demonstrate that the Az-group and the E-group are successfully introduced on the surface of the Az-Sub and the E-Sub.

Next, we investigated the adhesion between the functional gels and the functional glass substrates with the CuAAC reaction. The Az-Sub was put on the cuboid E-gel(10) (size : $5 \times 4 \times 3 \text{ mm}^3$) and an aqueous solution of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3 mL, 0.02 M) and sodium L-ascorbate (0.03 M) (3 mL, depth: 2 mm) was added. After a reaction time of 24 hours, the E-gel(10) and the Az-Sub strongly adhere to each other (Fig. 3b). Similarly, the Az-gel(10) adheres the E-Sub under the same reaction conditions (Fig. 3c), whereas the gels and the functional glass substrates do not adhere in the absence of the Cu catalyst (Fig. 3d). The unmodified glass substrate or AAm-gel, which lacks the Az-group and E-group, do not adhere the functional gels or the functional glass substrates, respectively (Figs. 3e, f). These results confirm that both the existence of the Cu catalyst and a suitable combination between the Az-group and the E-group are

important for adhesion via the CuAAC reaction.

The friction test determined the adhesive strength of the E-gel(x) with Az-Sub (E-gel(x)/Az-Sub) quantitatively. The following procedures were used to evaluate the initial friction loads. (1) The E-gel(x) ($5 \times 5 \times 5 \text{ mm}^3$) was put on the Az-Sub ($26 \times 26 \times 1 \text{ mm}^3$) (Fig. 4a). (2) The aqueous solutions of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (3 mL, 0.02 M) and sodium L-ascorbate (0.03 M) (3 mL, depth: 2 mm) were added to the E-gel(x). (3) After 24 hours, the friction test evaluated the initial friction load of the E-gel with the Az-Sub, which was fixed on the sample stage using a Teflon plunger (Sliding rate: 1 mm s^{-1} , vertical load : 8 mN) (Fig. 4a). Additionally, the initial friction load of the Az-gel(x) with the E-Sub (Az-gel(x)/E-Sub) was evaluated by the same method. Figures 4b and 4c show the initial friction load of E-gel(x)/Az-Sub and Az-gel(x)/E-Sub, respectively, as functions of the molar ratio of the Az-group or the E-group in the hydrogel. The initial friction loads of E-gel(x)/Az-Sub and Az-gel(x)/E-Sub increase with the feed ratio of the functional groups (E-group and Az-group) in the gels, suggesting that the adhesion strength is closely related to the concentration of the E-group and the Az-group of the gels. Covalent bonds form between the proper functional groups on their surfaces via the CuAAC reaction, realizing direct adhesion between the gel and glass substrate.

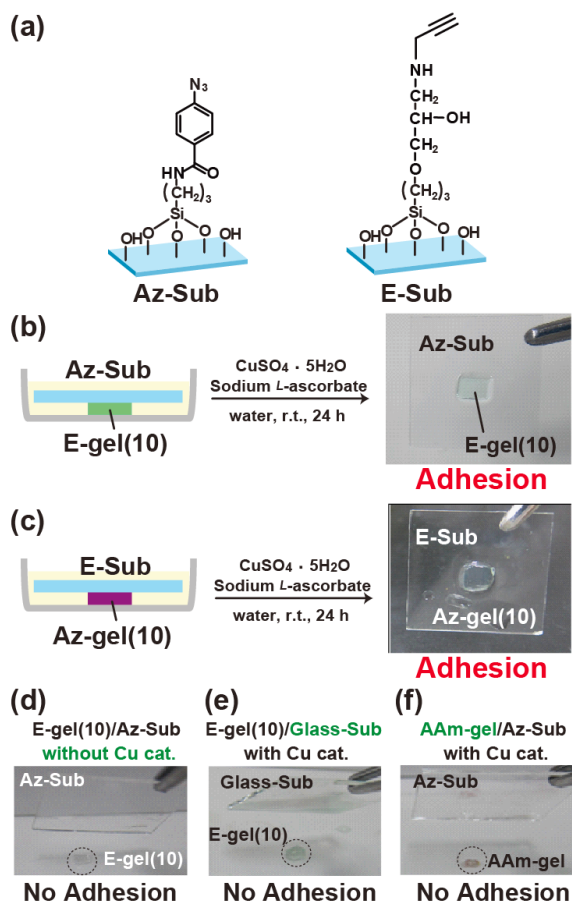


Figure 3. (a) Chemical structure of Az-Sub and E-Sub. (b) CuAAC reaction between the E-gel(10) and the Az-Sub (E-gel(10)/Az-Sub), and (c) between the Az-gel(10) and the E-Sub (Az-gel(10)/E-Sub). Reference experiments of (d) E-gel(10)/Az-Sub without $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, (e) E-gel(10)/unmodified glass substrate with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and (f) AAm-gel/Az-Sub with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

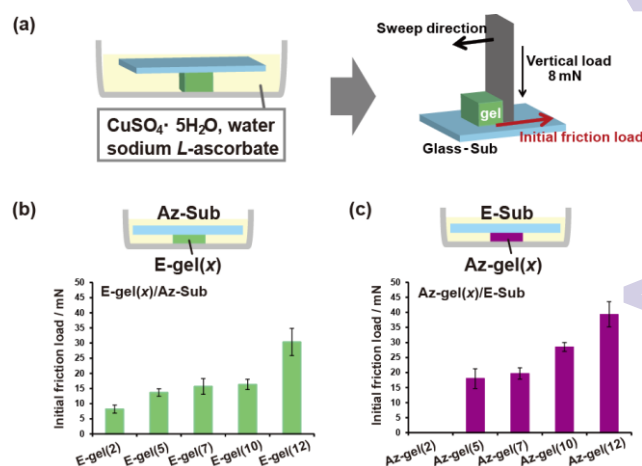


Figure 4. (a) Measurement procedure of the initial friction load between the hydrogels and functional glass substrates. Initial friction loads of (b) E-gel(x)/Az-Sub and (c) Az-gel(x)/E-Sub.

Conclusions

Covalent bonds are directly formed between macroscopic objects through the CuAAC reaction. Utilizing the mobility of the functional groups in the gels, covalent bonds are efficiently formed on the surface between gel-gel and gel-glass, achieving adhesion between heterogeneous materials like inorganic-organic materials. Although adhesion between inorganic and organic materials has been achieved by general adhesives (e.g., epoxy, cyano acrylate, and vinyl acetate adhesives), these adhesives do not form covalent bonds between the adherends and adhesives. Immersing an adhered object with a cyanoacrylate adhesive into the DMSO solvent discretely distributes the adhered object due to the adhesive dissolving in DMSO (Fig. 5b). On the contrary, the inorganic-organic adhesion

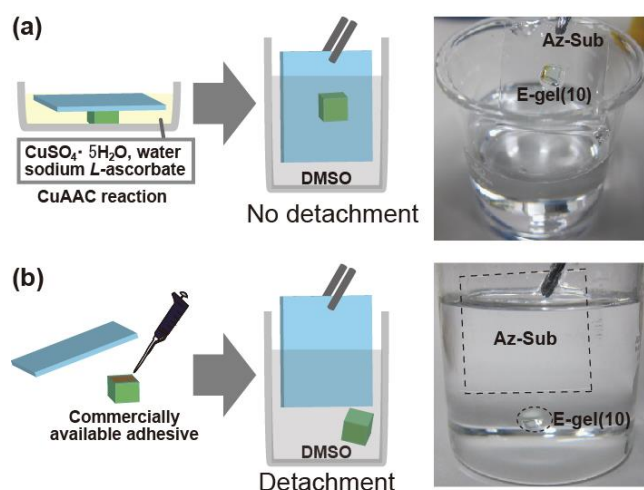


Figure 5. Adhesion between the E-gel(10) and the Az-Sub. (a) Adhered E-gel(10)/Az-Sub object using the CuAAC reaction is immersed in DMSO. E-gel(10) remains on the Az-Sub after soaking in DMSO. (b) Adhered E-gel(10)/Az-Sub object using a cyanoacrylate adhesive immersed in DMSO. E-gel(10) is dropped from the Az-Sub after soaking in DMSO.

object with direct covalent bond formation is not distribute because the triazine ring does not decompose upon immersing into organic solvents (Fig. 5a), indicating that adhesion of macroscopic objects with direct covalent bond formation is a useful, stable, and an effective approach to connect materials. In the future, we plan to investigate the formation of other covalent bonds between macroscopic objects and the adhesion between hard materials like metallic plates.

Acknowledgements

We thank the members of the Comprehensive Analysis Center, ISIR, Osaka University for X-ray photoelectron spectroscopy (XPS) measurements. This work was financially supported by the ImPACT Program of the Council for Science, Technology and Innovation (Cabinet Office, Government of Japan), Grant-in-Aid for Scientific Research on Innovative Areas of “Fusion Materials: Creative Development of Materials and Exploration of Their Function through Molecular Control” (No. 2206), and Grant-in-Aid for Scientific Research (B) (No. 26288062) from MEXT of Japan, and Research Grant Program of the Asahi Glass Foundation.

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