

- Supporting Information -

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

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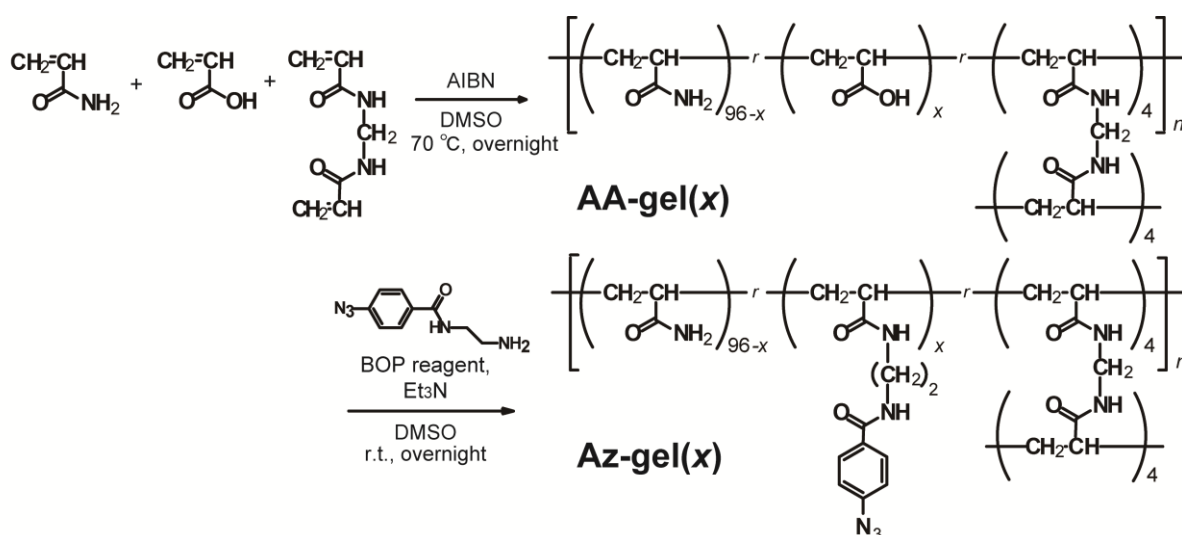
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1. Preparation of Az-gel(x)

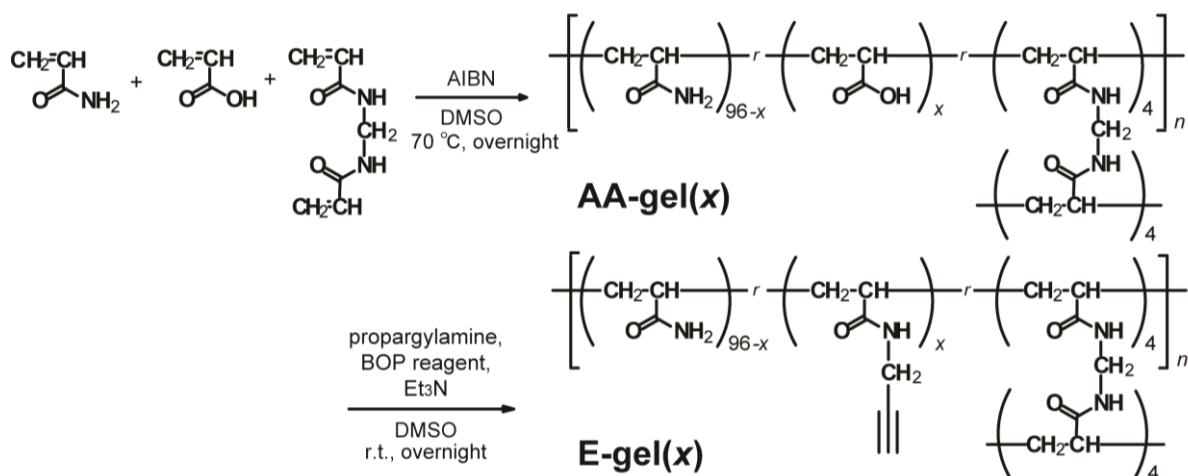
Typical procedure for Az-gel(10). AAm (188 mg, 2.6 mmol), AA (20.6 μ L, 0.30 mmol), MBAAm (19 mg, 0.12 mmol) and AIBN (2.5 mg, 0.015 mmol) were dissolved in DMSO (1.5 mL). The solution was purged with argon gas for 1 hour and was then heated at 70 °C overnight to form a gel. The gel was soaked in 4 mL DMSO solution containing *N*-(2-aminoethyl)-4-azidobenzamide (185 mg, 0.90 mmol), BOP reagent (400 mg, 0.90 mmol) and Et₃N (124 μ L, 0.90 mmol) and shaken for 48 hours at 25 °C. After the reaction, the gel was washed repeatedly with DMSO, followed by water. The gel was soaked in water and used as hydrogels.



Scheme S1. Preparation of the Az-gel(x).

2. Preparation of E-gel(x)

Typical procedure for E-gel(10). AAm (188 mg, 2.6 mmol), AA (20.6 μ L, 0.30 mmol), MBAAm (19 mg, 0.12 mmol) and AIBN (2.5 mg, 0.015 mmol) were dissolved in DMSO (1.5 mL). The solution was purged with argon gas for 1 hour and was then heated at 70 $^{\circ}$ C overnight to form a gel. The gel was soaked in 4 mL DMSO solution containing propargylamine (34 μ L, 0.90 mmol), BOP reagent (400 mg, 0.90 mmol) and Et₃N (124 μ L, 0.90 mmol) and shaken for 48 hours at 25 $^{\circ}$ C. After the reaction, the gel was washed repeatedly with DMSO, followed by water, respectively. The gel was soaked in water and used as hydrogels.



Scheme S2. Preparation of the E-gel(x).

Table S1. Preparation of the AA-gel(x) varying the mol% of the AA unit.

AA-gel(x)	AA		AAm		MBAAm	AIBN
	/ mmol	/mol%	/ mmol	/mol%	/ mmol	/ mmol
AA-gel(2)	0.06	2	2.9	96	0.06	0.015
AA-gel(5)	0.15	5	2.8	93	0.06	0.015
AA-gel(7)	0.21	7	2.7	91	0.06	0.015
AA-gel(10)	0.30	10	2.6	88	0.06	0.015
AA-gel(12)	0.36	12	2.6	86	0.06	0.015

3. Characterization of gels (Solid-state ^1H FGMAS NMR, FT-IR spectra)

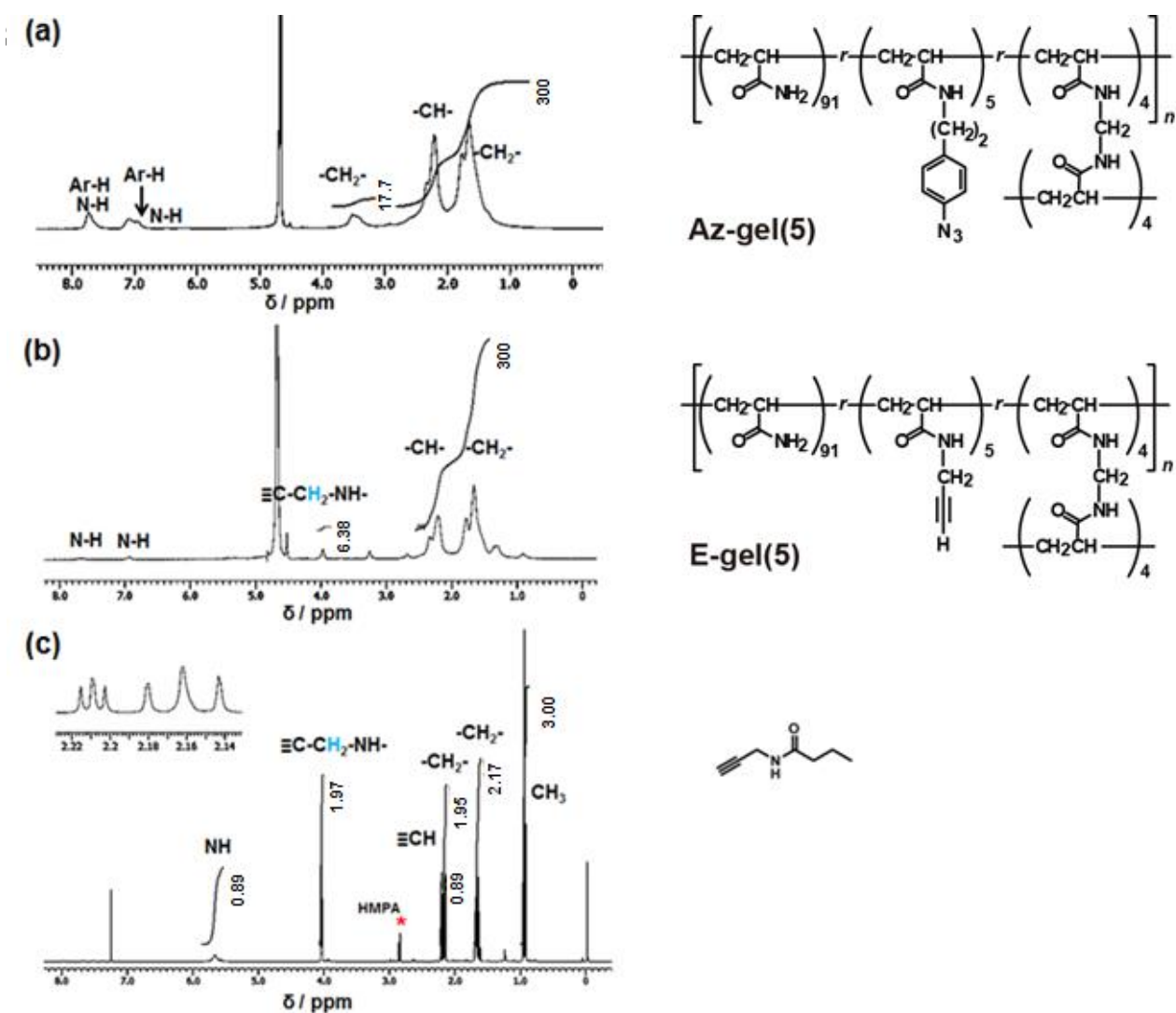


Figure S1. ^1H solid state field gradient magic angle spinning nuclear magnetic resonance (^1H FGMAS NMR) spectra of (a) Az-gel(5), (b) E-gel(5), and ^1H NMR spectra of (c) N -(prop-2-yn-1-yl)butyramide. Az-gel(5) and E-gel(5) : immersed in D_2O , 400 MHz, 30 °C, rotation frequency = 7 kHz. N -(prop-2-yn-1-yl)butyramide : solved in CDCl_3 , 400 MHz, 30 °C.

FT-IR spectra

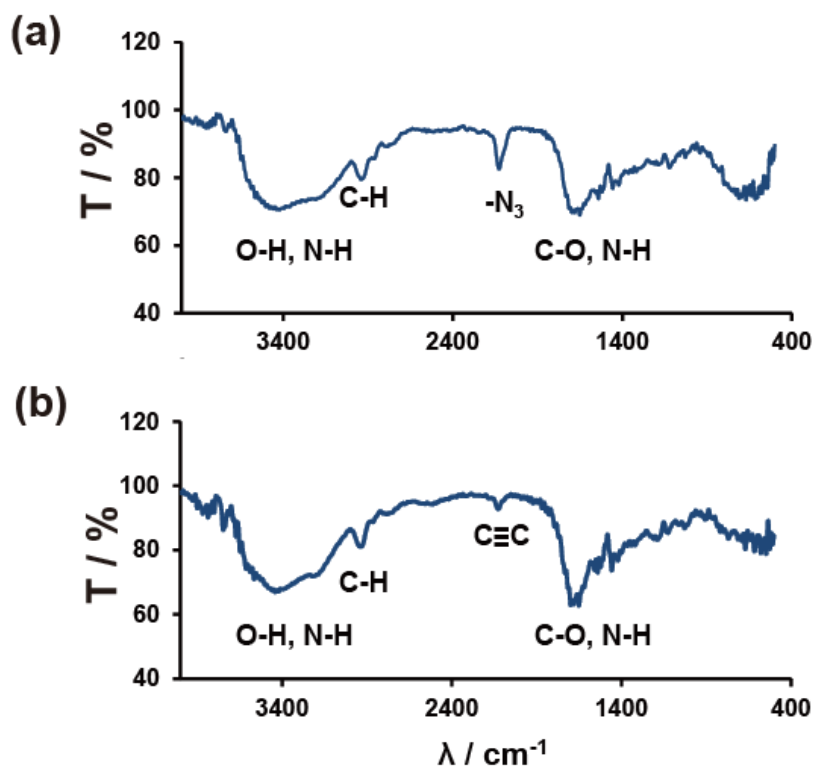


Figure S2. FT-IR spectra of (a) Az-gel(10) and (b) E-gel(10). %T represents transmittance percentage. (KBr disc, r.t.)

Az-gel(10): 3436, 3185 cm^{-1} (O-H stretching vibration, N-H asymmetric stretching vibration, and N-H symmetric stretching vibration), 2933, 2857 cm^{-1} (methylene C-H stretching vibration), 2121 cm^{-1} ($-\text{N}_3$ asymmetric stretching vibration), and 1697 cm^{-1} (C=O stretching vibration, N-H bending vibration).

E-gel(10): 3430, 3208 cm^{-1} (O-H stretching vibration, N-H asymmetric stretching vibration, and N-H symmetric stretching vibration), 2927, 2861 cm^{-1} (methylene C-H stretching vibration), 2119 cm^{-1} ($\text{C}\equiv\text{C}$ stretching vibration), 1698 cm^{-1} (C=O stretching vibration, N-H bending vibration).

4. Dependency of rupture strength of the E-gel(10)/Az-gel(10) on reaction time

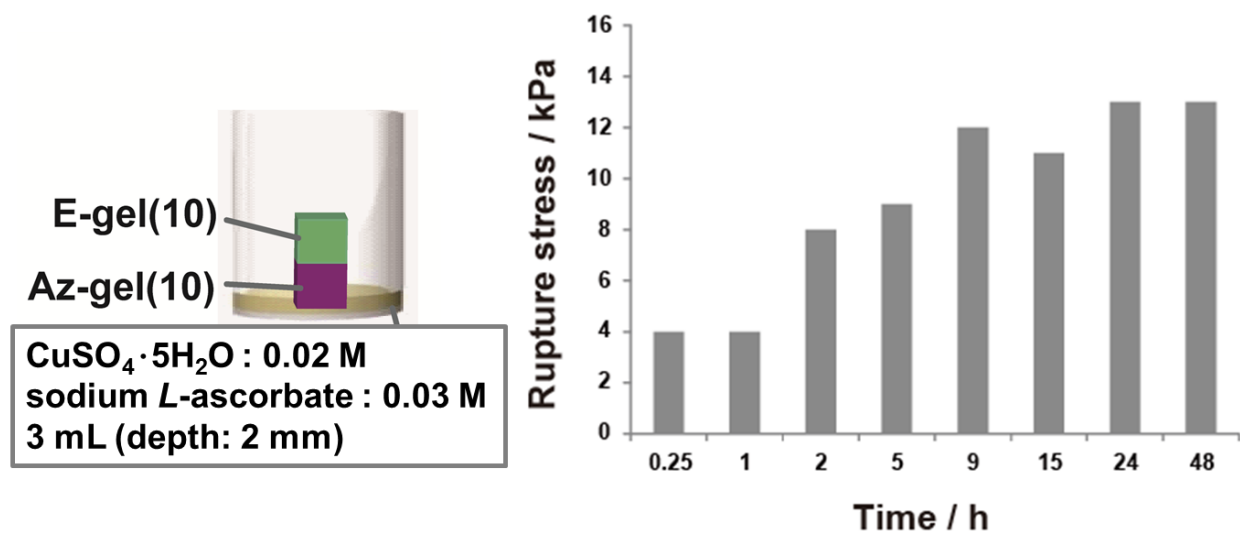


Figure S3. Dependency of rupture stress values of E-gel(10)/Az-gel(10) on reaction time of the CuAAC reaction. See the main text for reaction conditions.

5. Rupture strength of E-gel(x) and Az-gel(x)

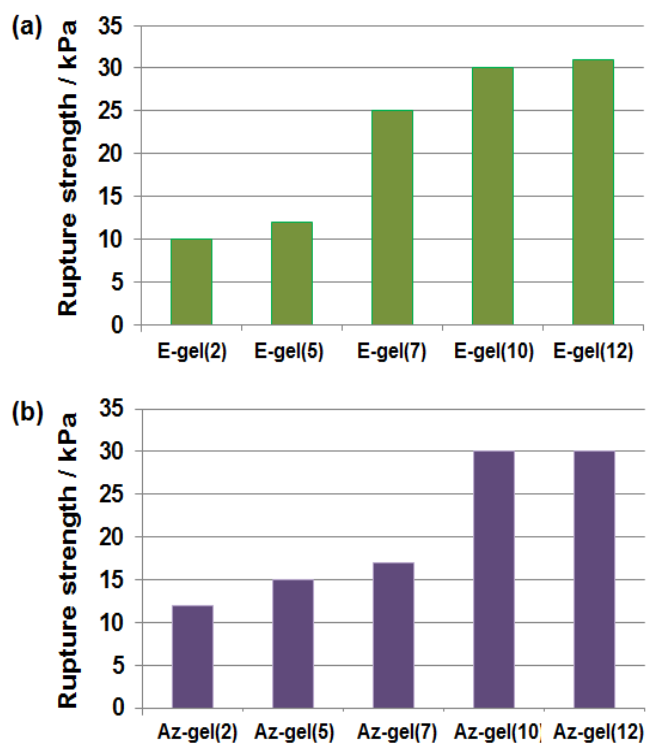
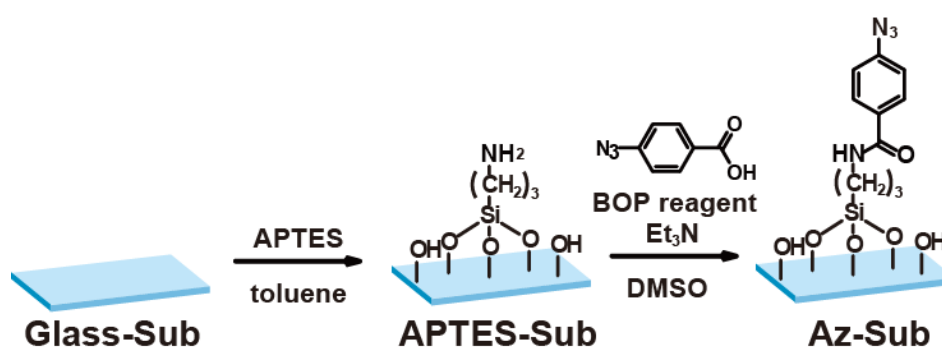


Figure S4. Rupture strength of E-gel(x) (a) and Az-gel(x) (b). x denotes the mol% of the functional groups (E group or Az group).

6. Preparation of Az-Sub and E-Sub.

Preparation of Az-Sub.

Glass plates (MATSUNAMI No. S1126, 76 mm×26 mm×1.0 mm) were cut into 26 mm×26 mm×1.0 mm pieces. 8 plates of the glass were ultrasonicated in acetone, and methanol for 15 min, respectively, and subsequently dried. The substrates were cleaned with a O₃/UV cleaner (Filgen UV253S) for 12 hours to create a hydrophilic surface. The cleaned substrates were immersed in a toluene solution (70 mL) of 3-aminopropyltriethoxysilane (APTES) (1.6 mL, 6.8 mmol) at 70 °C and shaken for 3 hours. These substrates were washed 4 times with toluene, and immersed in a DMSO solution (70 mL) with 4-azidobenzoic acid (570 mg, 3.5 mmol), BOP reagent (1.86 g, 4.2 mmol) and Et₃N (0.6 mL, 4.3 mmol) at 45 °C for two days. Each substrate was washed with DMSO and water repeatedly.

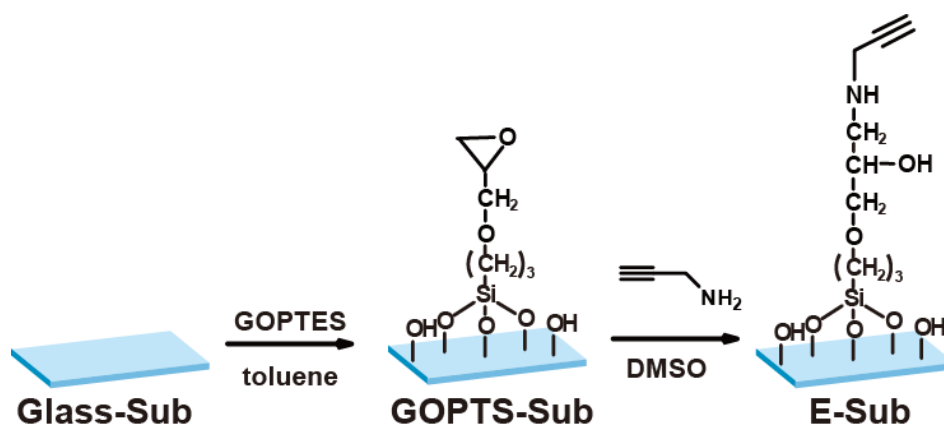


Scheme S3. Preparation of the Az-Sub.

Preparation of E-Sub.

Glass plates were cut into 26 mm×26 mm×1.0 mm pieces. 8 plates of the glass were ultrasonicated in acetone, and methanol for 15 min, respectively, and subsequently dried. The substrates were cleaned with a O₃/UV cleaner for 12 hours to create a hydrophilic surface. The cleaned substrates were immersed in a toluene solution (70 mL) of 3-

glycidyoxypropyltrimethoxysilane (GOPTS) (1.6 mL, 6.8 mmol) at 70 °C and shaken for 3 hours. These substrates were washed 4 times with toluene, and immersed in a DMSO solution (70 mL) with propargyl amine (223 μ L, 3.5 mmol) for two days at room temperature. Each substrate was washed with DMSO and water repeatedly.



Scheme S4. Preparation of the E-Sub.

7. Characterization of Az-Sub and E-Sub (Contact angles, ATR-FT-IR, X-ray photoelectron spectroscopy)

Contact angles.

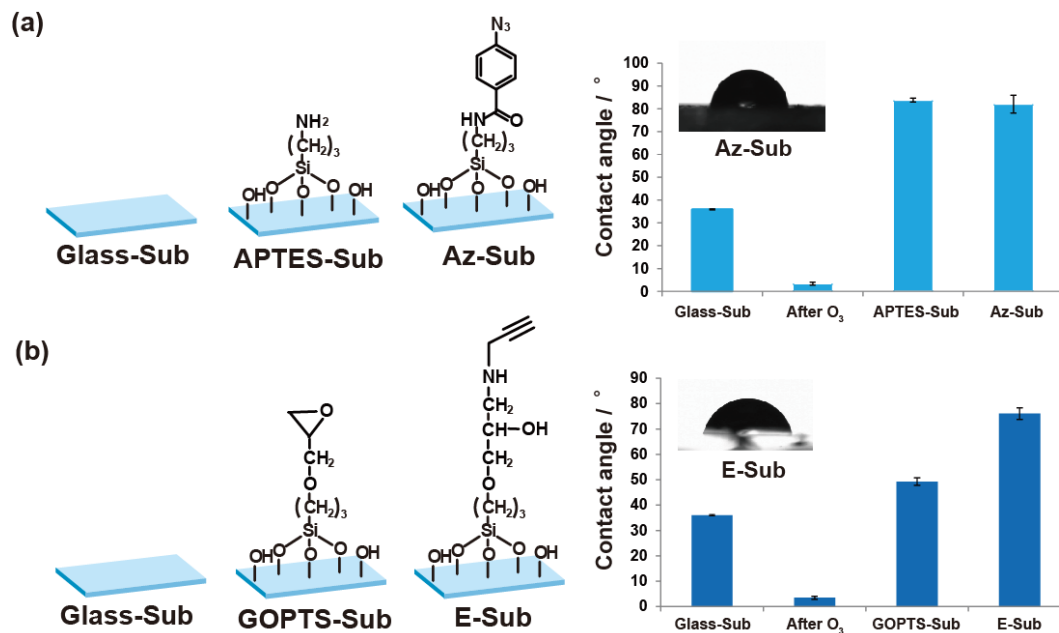


Figure S5. The values of contact angle. (a) Glass-Sub, Glass-Sub after treating with O₃/UV, APTES-Sub and Az-Sub. (b) Glass-Sub, Glass-Sub after treating with O₃/UV, GOPTS-Sub and E-Sub. The error bars were standard deviations of three samples.

ATR-FT-IR

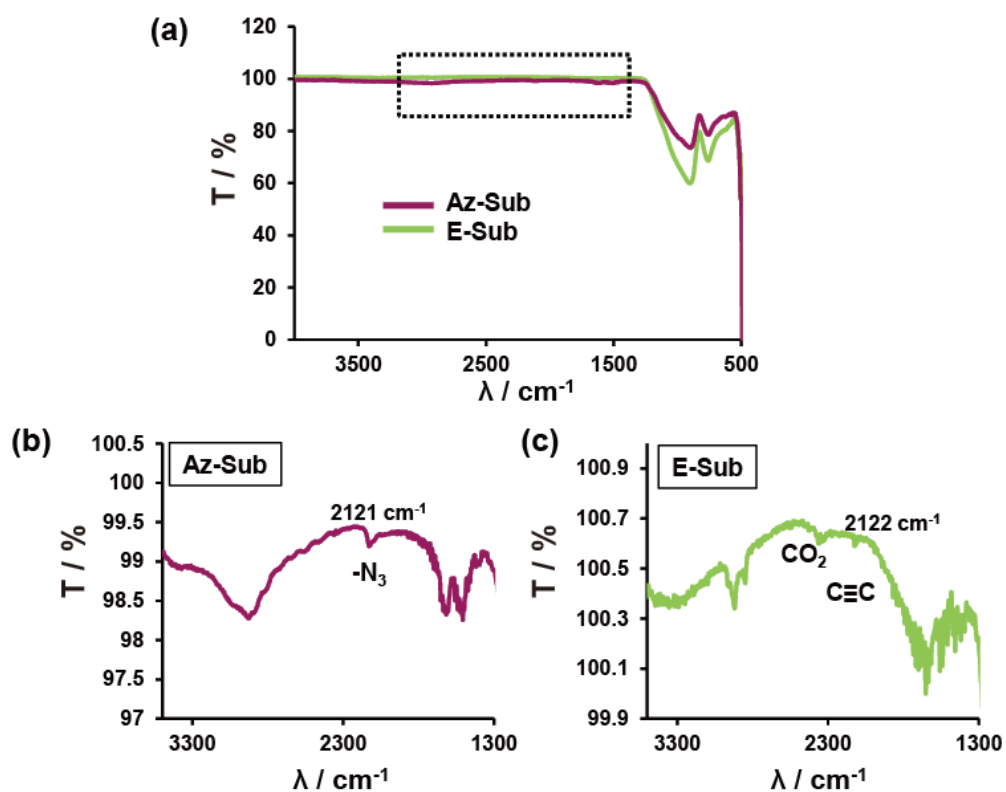


Figure S6. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR) of (a) the Az-Sub (purple) and the E-Sub (green). (b) and (c) show the high-resolution spectra around 3500 – 1300 cm^{-1} of the Az-Sub (b) and the E-Sub (c).

X-ray photoelectron spectroscopy (XPS)

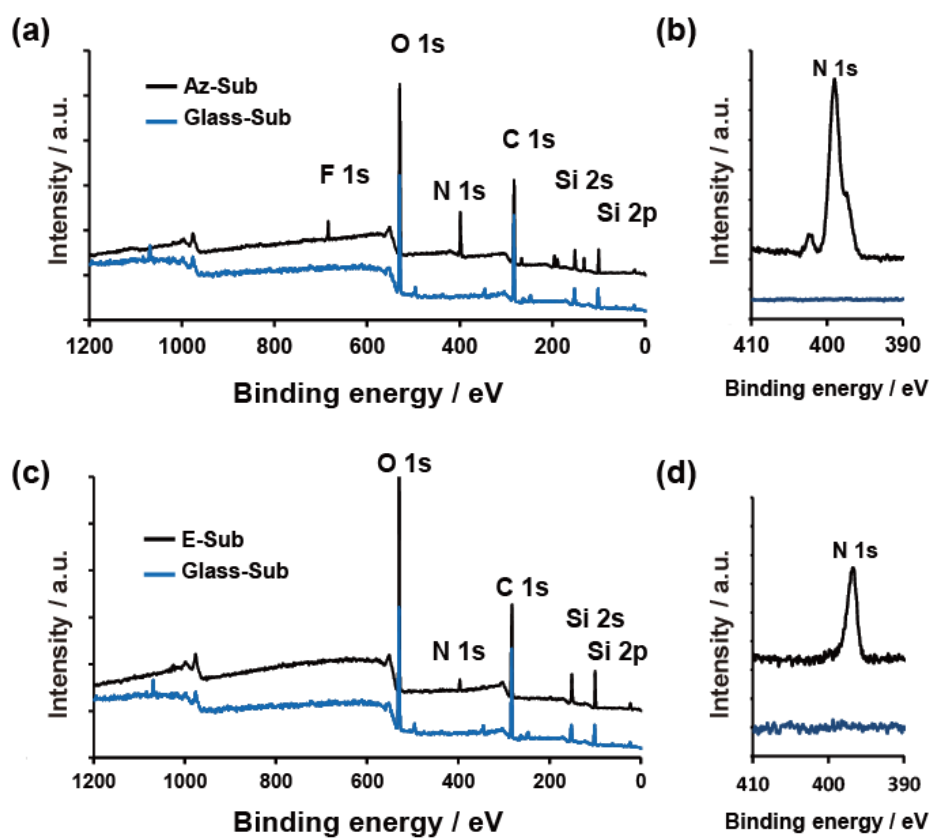


Figure S7. X-ray photoelectron spectroscopy (XPS) spectra of the Az-Sub ((a), (b)) and the E-Sub ((c), (d)). (a) and (c) show the wide range spectra of the Az-Sub and the E-Sub, respectively. (b) and (d) show the high-resolution spectra around 390 - 410 eV.