Supporting Information

Self-Healing Hybrids via Dual Noncovalent Networks Using Urethane/Imidazole–Zinc Functionalized Silsesquioxane Nanoparticles

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Experimental section

Materials and measurements

2-Mercapt-1-methylimidazole (>98.0%), phenyl isocyanate (>98.0%), hexamethylene diisocyanate (>98.0%), methylenediphenyl 4,4'-diisocyanate (>97.0%), LiOH (>98.0%), and 4-dimethylaminopyridine (99.0%) were purchased from Tokyo Kasei. $ZnCl_2$ (Wako, 98.0%) and triethylamine (99%) were used as received without further purification. (3-Glycidyloxypropyl)triethoxysilane (Shin-Etsu Chemical, 100%), NH_4F (Kanto Chemical, 97%) were also used as received. The synthesis of the epoxy-functionalized SQNP, (Gly-SQNP, corresponding to $(R\text{-}SiO_{1.5})_n$, R = glycidyloxypropyl group) was conducted by a base-catalyzed condensation of (3-glycidyloxypropyl)triethoxysilane according to a method reported previously [30].

Product structures were characterized by ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) using a JEOL JNM-ECX400 spectrometer and Fourier-transform infrared (FT–IR) spectroscopy on a JASCO FT-IR 210 spectrometer. Thermal properties of the products were evaluated via thermogravimetric analysis (TGA) using a Seiko TGA6200 analyzer and differential scanning calorimetry (DSC) on a Seiko EXSTER DSC 6200 instrument at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Samples for TGA measurements were pre-treated at 100 °C for 20 min under a nitrogen atmosphere, in order to remove a small amount of solvent residue. Transmission electron microscopy (TEM) images were obtained using a JEOL TEM-2100 F field-emission electron microscope at an accelerating voltage of 200 kV. A TEM sample was prepared by dropping a diluted dispersion on a carbon-coated Cu grid followed by air drying at room temperature. X-ray diffraction (XRD) was performed on a SmartLab diffractometer (Rigaku Denki Co., Ltd), as reported previously [30,31]. Atomic force microscopy (AFM) was performed on an Agilent Technologies 5500 scanning probe microscope (TOYO corporation). AFM samples were prepared by spin-coating a drop of the DMF dispersion of the epoxy-functionalized SQNP and $CHCl_3$ solution of the imidazole/urethane-functionalized SQNPs (concentration: 1.0 mg/L) onto a freshly cleaved mica surface. The dilute solutions were used to evaluate isolated nanoparticles. Height images were acquired in a tapping mode under ambient conditions at room temperature. Scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS) was evaluated using scanning electron microscopy (SEM), Hitachi SU8000, EDS: HORIBA X-Max.

Mechanical and self-healing tests. Mechanical flexural stress–strain experiment was performed by using an ZTA-50N machine (IMDA Co., Ltd) under the three-point flexural mode with span of 20 mm. Rectangular films (25 mm length – 7.0 mm width – 2.0 mm height) were prepared using a Teflon mold either by solution casting from DMF (conc. 40 wt.%), or by hot-press at 120 °C for 1 min. Each test was repeated at least three times. Dynamic mechanical analysis (DMA) was conducted using an MCR 702(Anton Paar) rheometer with circular samples (height = 1-2 mm). Temperature-dependent measurements were conducted in the temperature range from 35°C to 100°C at a temperature increase rate of 10°C/min, strain of 0.02%, and frequency of 1.0 Hz. Strain-dependent measurements were conducted over a strain range of 0.01–100.

For the self-healing test, the film was cut into two pieces and then put together and healed for different durations. To evaluate the self-healing properties of the fabricated specimens, a 0.1 mm-thick Teflon sheet (15 mm × 15 mm) with a hole in its center (diameter: 2 mm) was sandwiched between two 1.2-mm-thick discs (diameter: 2 mm) prepared from the complexed sample at 120 °C using a Teflon mold. The assembled test pieces were set on a stage and pressed with a jig followed by heat treatment at approximately 50 °C using a dryer. The upper and lower discs were connected inside the Teflon sheet hole and integrated. After cooling the resulting specimen to a specified temperature, the stage and jig were separated at a rate of 10 mm/min. After a brittle fracture, the fracture surfaces were brought into contact again and compressed at various temperatures and a constant stress of 1.0 MPa. The healed films were then tested following the same procedure to obtain the stress–strain curves. Self-healing efficacy was calculated as follows [30].

Healing efficacy(%) = (*Max.strength Healed/ Max.strength Pristine)* × 100

Synthesis and characterization

Methylimidazole/phenylurethane (MI/PU)-SQNP

A representative synthetic procedure of MI/PU-SQNP is as follows. To a round bottom flask, MI/OH-SQNP (2.59 g, 10 mmol hydroxyl groups), triethyl amine (1.4 mL, 10 mmol), and chloroform (50 mL) were added under a nitrogen atmosphere, and then cooled with ice. To this mixture, one spatula of 4-dimethylaminopyridine was added, followed by the slow dropwise addition of phenyl isocyanate (1.09 mL,10 mmol). The mixture was stirred at 50 °C for 20 h. Subsequently, it was diluted with methylene chloride (20 mL) and extracted twice with saturated NaCl solution. After the mixture was dried over anhydrous magnesium sulfate and filtered, the solvent from the organic phase was removed under reduced pressure. The residue was dissolved in a small volume of methylene chloride and precipitated into 500 mL of hexane. Following decantation, any remaining product adhering to the container surface was redissolved in methylene chloride, and the solvent was again evaporated. Finally, the product was dried under vacuum at 60 °C for 5 h to give a buff solid (81%, 3.45 g). ^{1}H NMR ($CDCl_3$): δ = 0.59 (br, 2H, –SiC$\boldsymbol{H_2}$$CH_2$–), 1.62 (br, 2H, –Si$CH_2C\boldsymbol{H_2}$$CH_2$–), 3.08–3.59 (br, 9H, –Si$CH_2$$CH_2C\boldsymbol{H_2}$O–, –OC$\boldsymbol{H_2}CHCH_2$S–, –O$CH_2CHC\boldsymbol{H_2}$S–, –NC$\boldsymbol{H_3}$), 4.03 (br, 1H, –O$CH_2$C***H***OCONH–), 6.72 (br, 2H, –C***H***– in imidazole unit), 7.12-7.67 ppm (br, 5H, –C***H***–Ar). ^{13}C NMR ($CDCl_3$): δ = 9.6 (–Si***C***$H_2$$CH_2$–), 23.0 (–Si$CH_2$***C***$H_2$$CH_2$–), 33.6 (–***C***$H_2$S–), 35.2 (–***C***$H_3$), 70.4 (–Si$CH_2$$CH_2$***C***$H_2$O–), 73.5 (–O***C***$H_2CHCH_2$S–, –O$CH_2$***C***H$CH_2$S–), 120.5, 129.2, 136.8 (–***C***H–, –N–***C***=N– in imidazole unit), 115.2, 118.2, 124.9, 136.8 (–***C***H–, –Ar), 161.4 (–O***C***ONH–).

Methylimidazole/hexamethyleneurethane (MI/HMU)-SQNP

Urethane formation of MI/OH-SQNP (5.18 g, 20 mmol hydroxyl groups) with hexamethylene diisocyanates (1.6 mL, 10 mmol), according to the procedure described above (protocol for MI/PU-SQNP), gave the product as an off-white solid (44%, 6.8 g).

^{1}H NMR (CDCl$_3$): δ = 0.57 (br, 2H, –SiC***H***$_2$CH$_2$–), 1.18 (br, 2H, –SiCH$_2$C***H***$_2$CH$_2$–), 1.44 (br, 2H, –NHCH$_2$CH$_2$C***H***$_2$–), 1.65 (br, 2H, –NHCH$_2$C***H***$_2$CH$_2$–), 3.05–3.40 (br, 11H, –SiCH$_2$CH$_2$C***H***$_2$O–, –OC***H***$_2$CHCH$_2$S–, –OCH$_2$CHC***H***$_2$S–, –NHC***H***$_2$CH$_2$CH$_2$–, –NC***H***$_3$), 3.99 (br, 1H, –OCH$_2$C***H***OCONH–), 6.65, 7.55 (br, 2H, –C***H***– in imidazole unit). ^{13}C NMR (CDCl$_3$): δ = 17.8 (–Si***C***H$_2$CH$_2$–), 26.2 (–SiCH$_2$***C***H$_2$CH$_2$–), 26.6 (–SiCH$_2$CH$_2$***C***H$_2$–), 29.1 (–SiCH$_2$***C***H$_2$CH$_2$–), 33.6 (–***C***H$_2$S–), 35.1 (–Si***C***H$_2$CH$_2$CH$_2$–), 37.2 (–***C***H$_3$), 73.5 (–SiCH$_2$CH$_2$***C***H$_2$O–, –O***C***H$_2$CHCH$_2$S–, –OCH$_2$***C***HCH$_2$S–), 115.2, 117.8, 149.8 (–***C***H–, –N–***C***=N– in imidazole unit), 161.2 (–O***C***ONH–).

Methylimidazole/methylenediphenyl urethane (MI/MDU)-SQNP

Urethane formation of MI/OH-SQNP (0.50 g, 20 mmol hydroxyl groups) with methylenediphenyl 4,4'-diisocyanates (2.50 g, 10 mmol), according to the procedure described above (protocol for MI/PU-SQNP), gave the product as a white solid (41%, 7.0 g).

^{1}H NMR (CDCl$_3$): δ = 0.59 (br, 2H, –SiC***H***$_2$CH$_2$–), 1.25 (br, 2H, –SiCH$_2$C***H***$_2$CH$_2$–), 1.62 (br, 2H, –SiCH$_2$CH$_2$C***H***$_2$–), 3.03–3.59 (br, 7H, –OC***H***$_2$CHCH$_2$S–, –OCH$_2$CHC***H***$_2$S–, –NC***H***$_3$), 3.85 (–Ar–C***H***$_2$–Ar–), 4.15 (br, 1H, –OCH$_2$C***H***OCONH–), 6.71 (br, 2H, –C***H***– in imidazole unit), 7-.05-7.66 (br, 8H, –C***H***–Ar). ^{13}C NMR (CDCl$_3$): δ = 14.6 (–Si***C***H$_2$CH$_2$–, –SiCH$_2$***C***H$_2$CH$_2$–), 33.6 (–***C***H$_2$S–), 35.2 (–***C***H$_3$), 40.9 (–Ar–***C***H$_2$–Ar–), 61.2 (–SiCH$_2$CH$_2$***C***H$_2$–), 73.3 (–O***C***H$_2$CHCH$_2$S–, –OCH$_2$***C***HCH$_2$S–), 115.2, 118.1, 134.9, 137.7 (–***C***H–, Ar), 120.7, 129.5 , 147.0 (–***C***H–, –N–***C***=N– in imidazole unit), 161.4 (–O***C***ONH–).

Metal complexation with $ZnCl_2$. A representative synthesis was carried out as follows. MI/PU-SQNP (3.02 g, corresponding to 8 mmol of imidazole units) and $ZnCl_2$ (0.54 g, 4 mmol) were placed in a two-necked round-bottom flask. Dimethylformamide (DMF, 10 mL) was added under a nitrogen atmosphere, and the mixture was stirred at 80 °C overnight. After completion of the reaction, the solution was poured into an excess of methanol to induce precipitation. The resulting solid was collected by filtration, allowing the removal of unreacted $ZnCl_2$. Finally, the product was dried in a vacuum oven at 60 °C to afford a yellow solid (2.30 g).

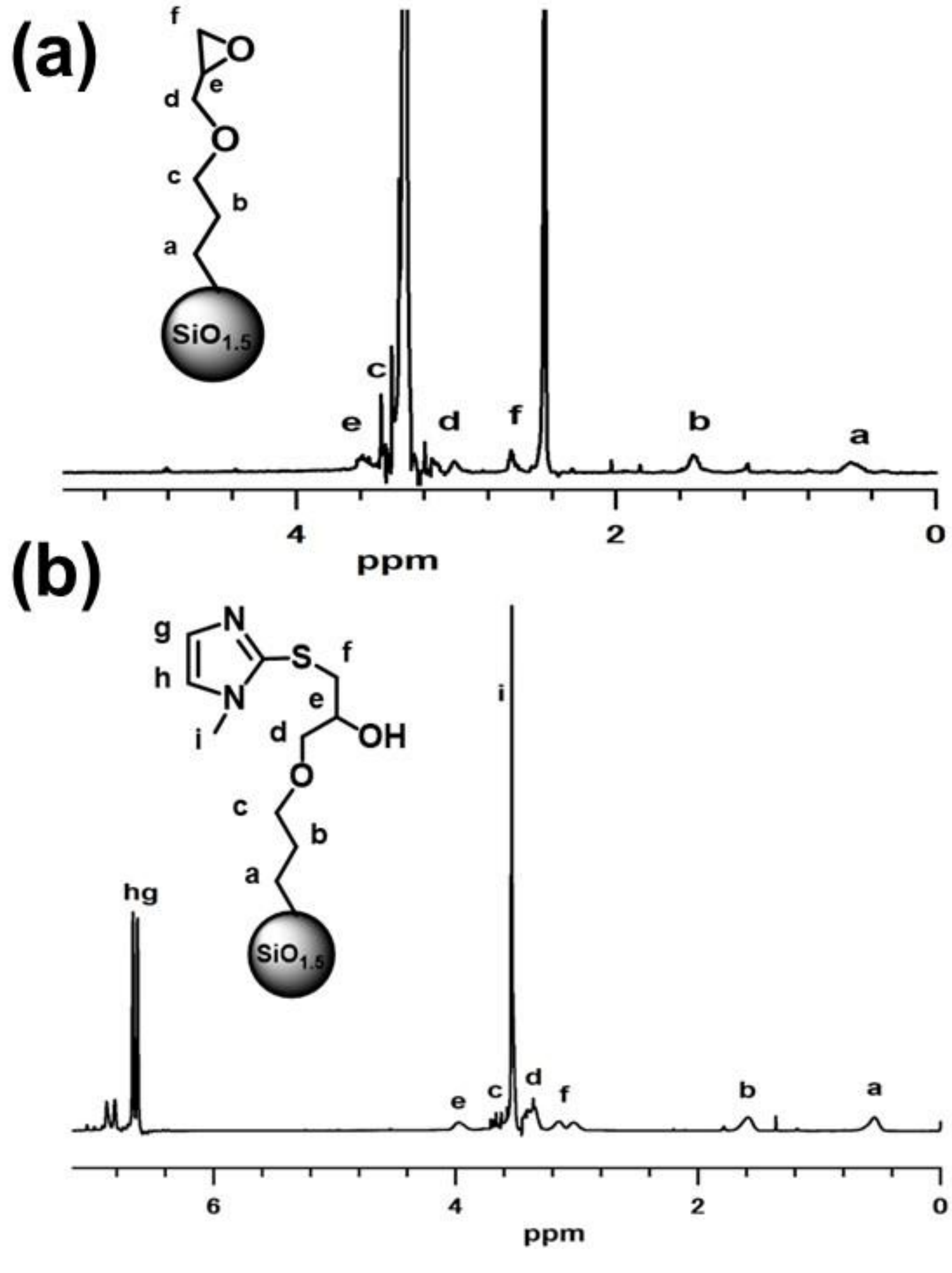

Figure S1. [1]H NMR spectra of (a) epoxy-functionalized SQNP (DMSO-d_6) and (b) MI/OH-SQNP ($CDCl_3$).

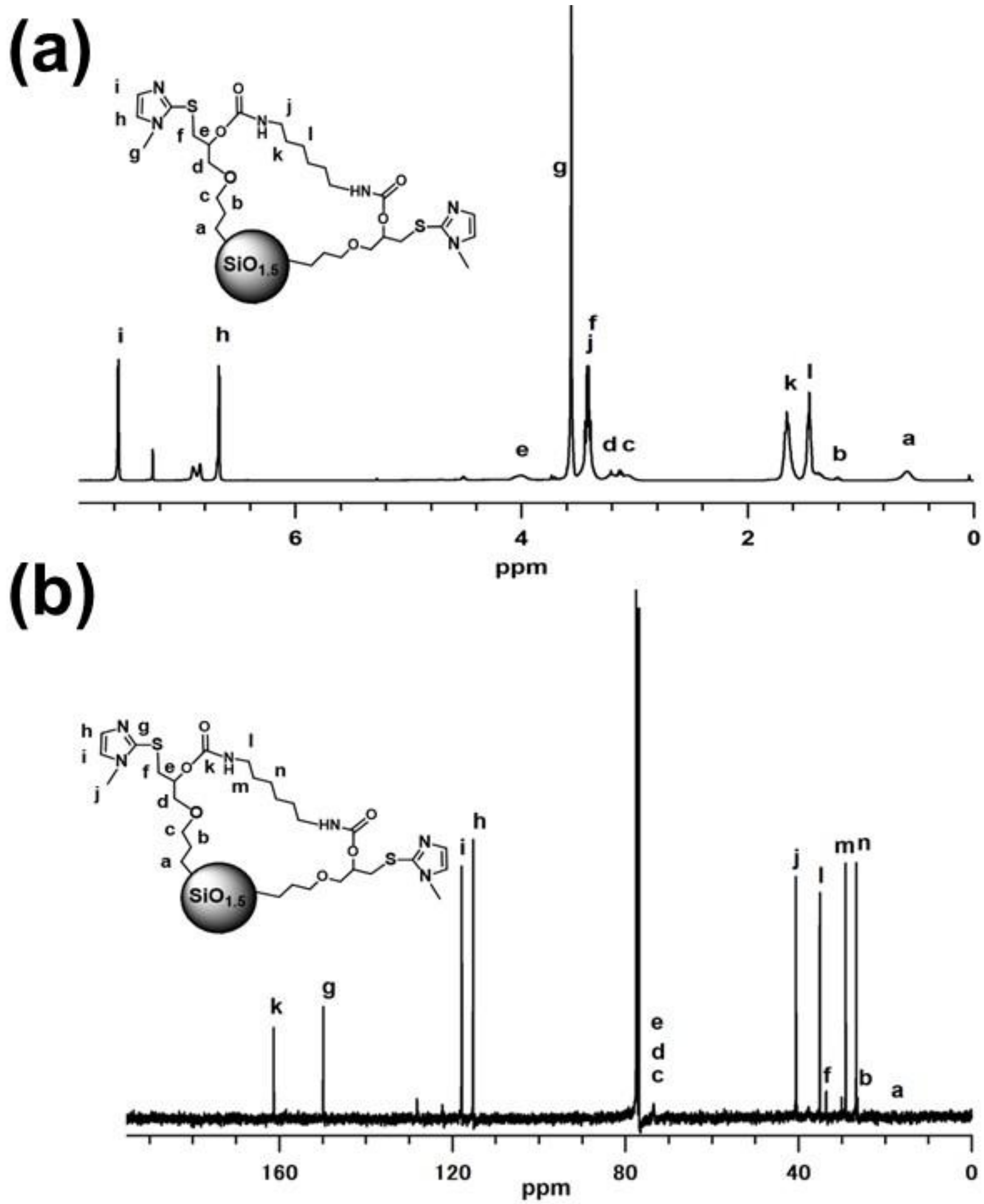

Figure S2. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of MI/HMU- SQNP ($CDCl_3$).

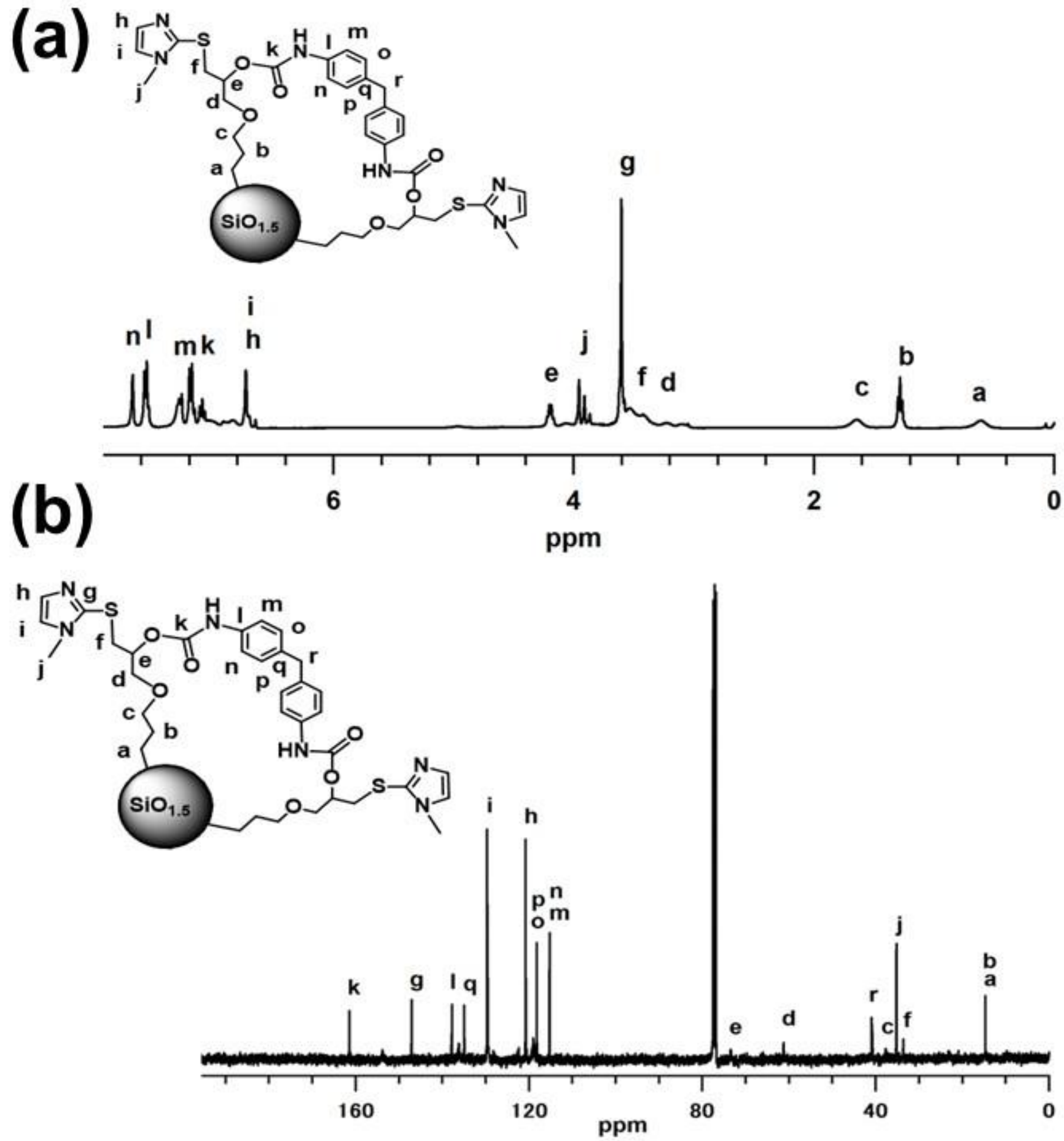

Figure S3. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of MI/MDU- SQNP ($CDCl_3$).

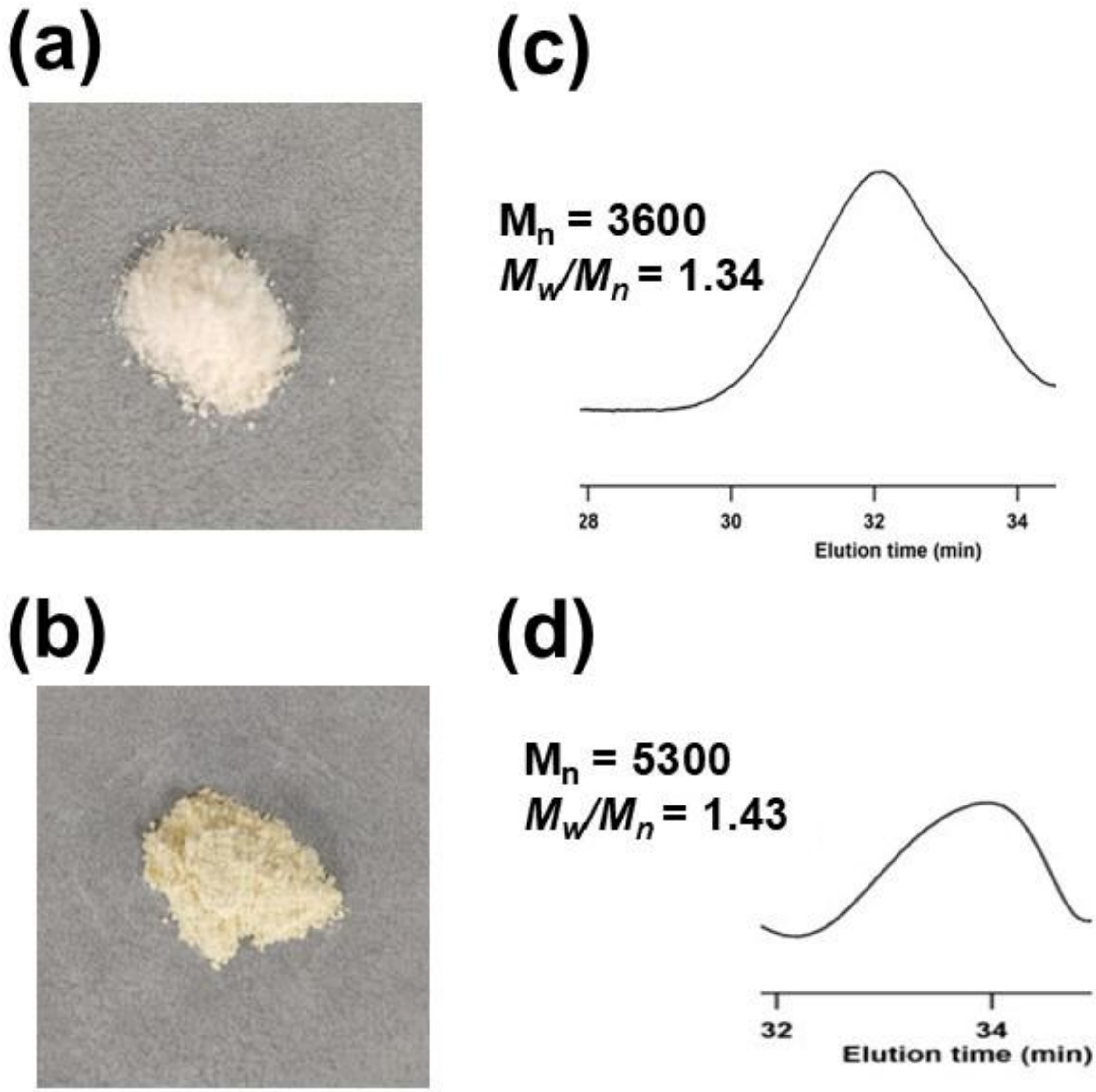

Figure S4. (a,b) Photographs of MI/HMU-SQNP-Zn and MI/MDU-SQNP-Zn, and (c,d) SEC curves of MI/HMU-SQNP and MI/MDU-SQNP.

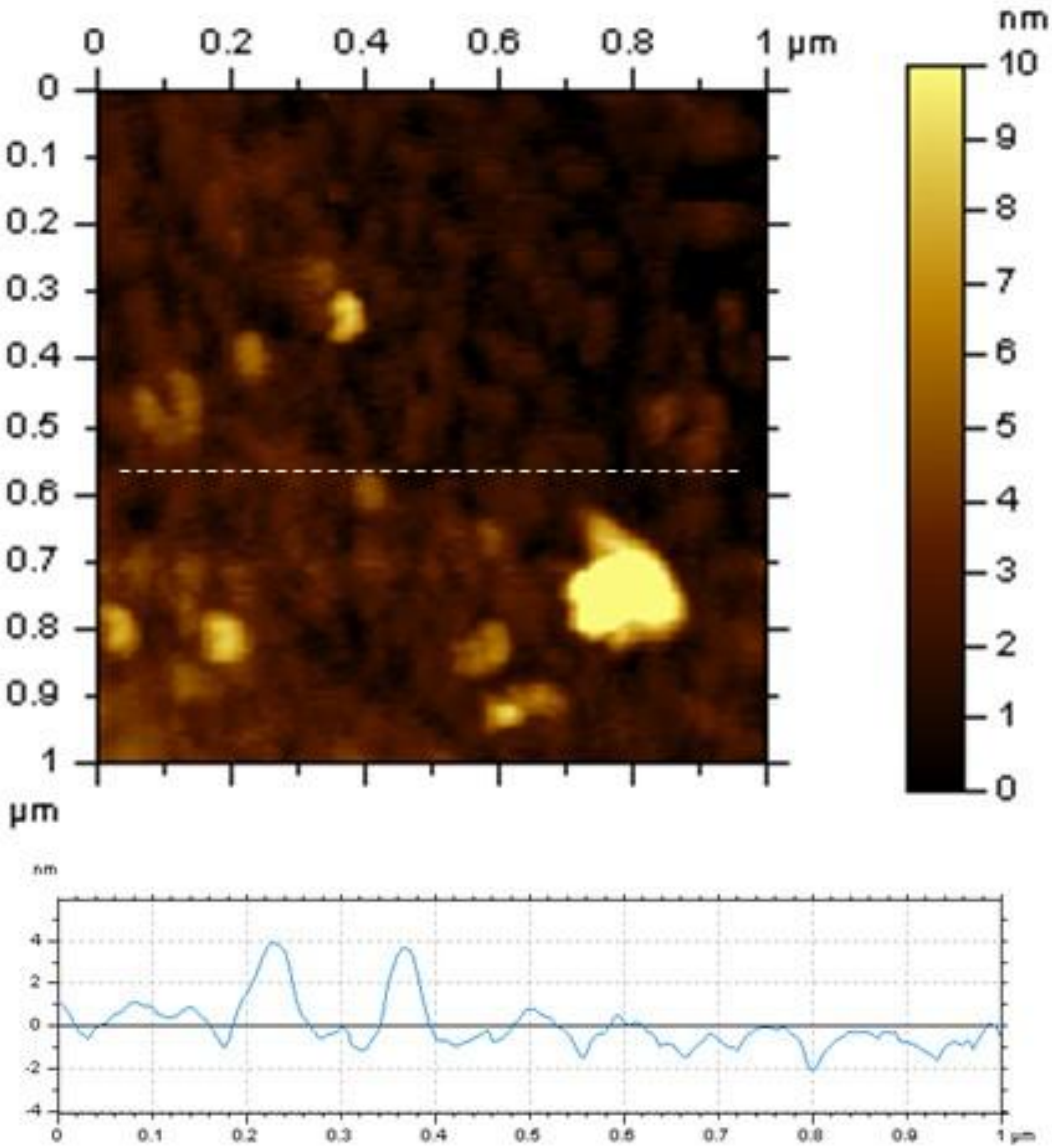

Figure S5 AFM height image of epoxy-functionalized SQNP (Gly-SQNP) prepared by spin-coating from a DMF solution (25 mg/L).

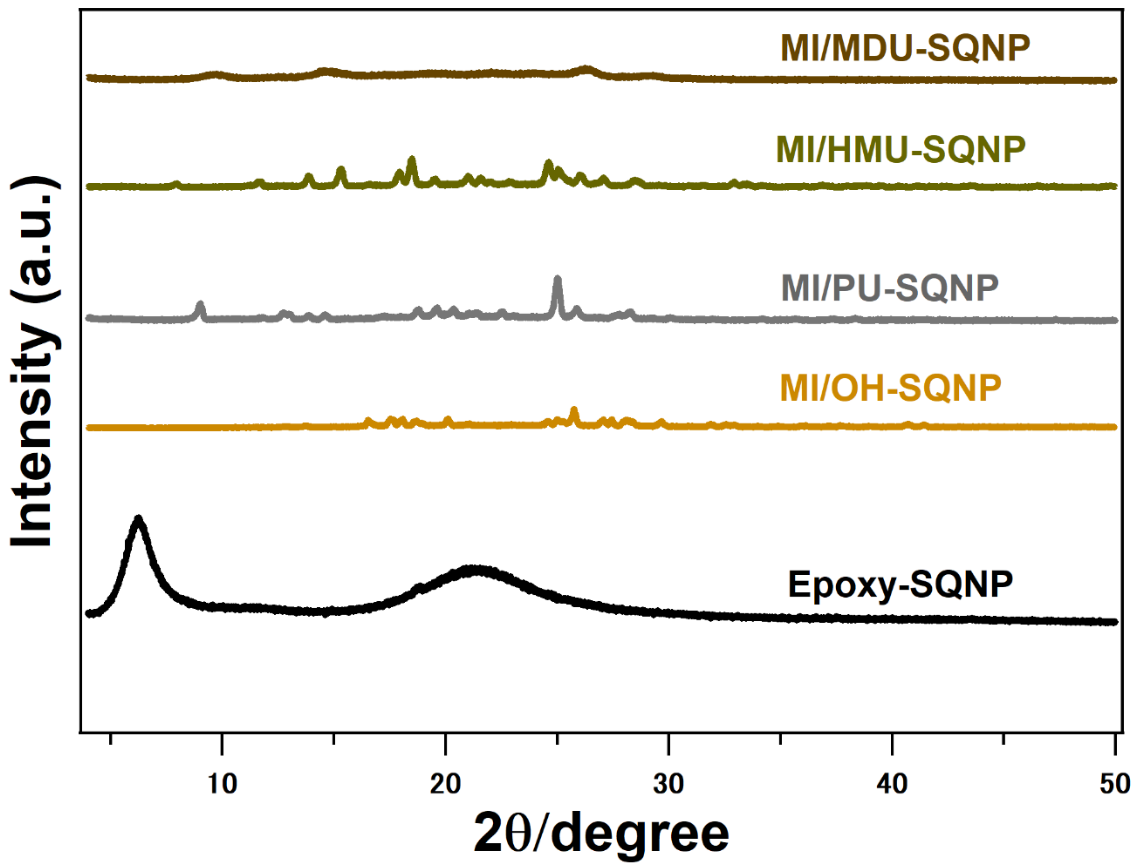

Figure S6. XRD traces of epoxy-functionalized SQNP, MI/OH-SQNP, MI/PU-SQNP, MI/HMU-SQNP, and MI/MDU-SQNP.

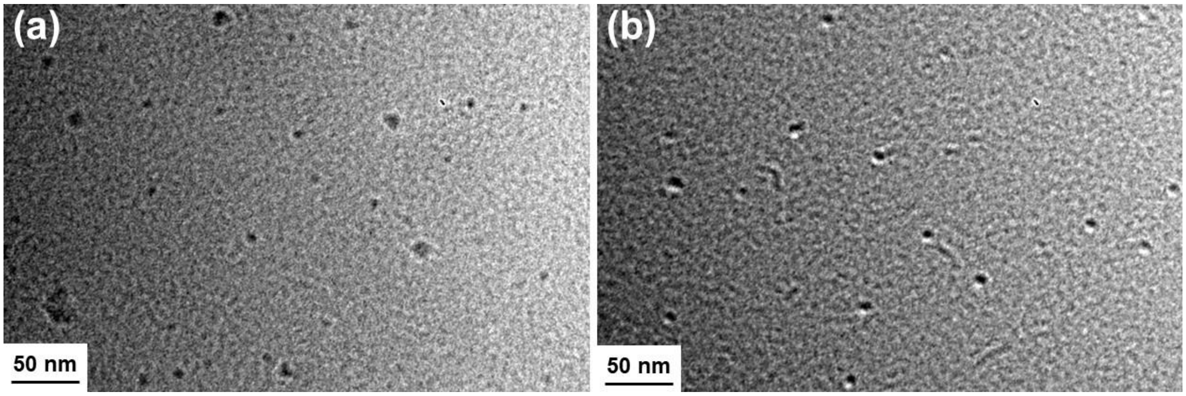

Figure S7. TEM images of (a) epoxy-functionalized SQNP (Gly-SQNP), and (b) methylimidazole/phenylurethane-functionalized SQNP, $(MI/PU\text{-}SiO_{1.5})_n$. Samples (a,b) were prepared by mounting a drop of the dispersion, conc. = 1.0 mg/ml in $CHCl_3$, on carbon-coated Cu grids.

Table S1. Solubility of dual-functionalized silsesquioxane nanoparticles (SQNPs) [a)]

	H_2O	MeOH	DMSO	DMF	Acetone	THF	$CHCl_3$	Et_2O	Hex
Gly-SQNP	—	—	+	—	—	—	—	—	—
MI/OH-SQNP	—	—	+	+	+	+	+	—	—
MI/PU-SQNP	—	+	+	+	+	+	+	—	—
MI/HMU-SQNP	—	—	+	+	—	—	+	—	—
MI/MDU-SQNP	—	—	+	+	—	—	+	—	—

[a)] + = soluble at r.t. (1 mg/ml), — = insoluble at r.t., time = 1 day

Table S2. Transparency of MI/PU-SQNP-Zn hybrids.

Conc. (wt %)	Transparency (400 nm) (%)	Thickness (μm)
1	99.56	66
10	98.70	33
20	98.66	64

The sample was prepared by drop-casting from DMF dispersion.

Table S3. Mechanical properties of MI/Urethane-SQNP-Zn hybrids using hot-press.

sample	Flexural strength (MPa)	Flexural modulus (MPa)
MI/PU-SQNP-Zn	2.79	33.1

Figure S8. Samples for bending and tensile, photographs of (a) MI/PU-SQNP-Zn, (b) MI/HMU-SQNP-Zn, and (c) MI/MDU-SQNP-Zn hybrid using drop-casting from DMF.

Figure S9. Photographs of MI/PU-SQNP-Zn hybrid used for the tensile test using hot-press.

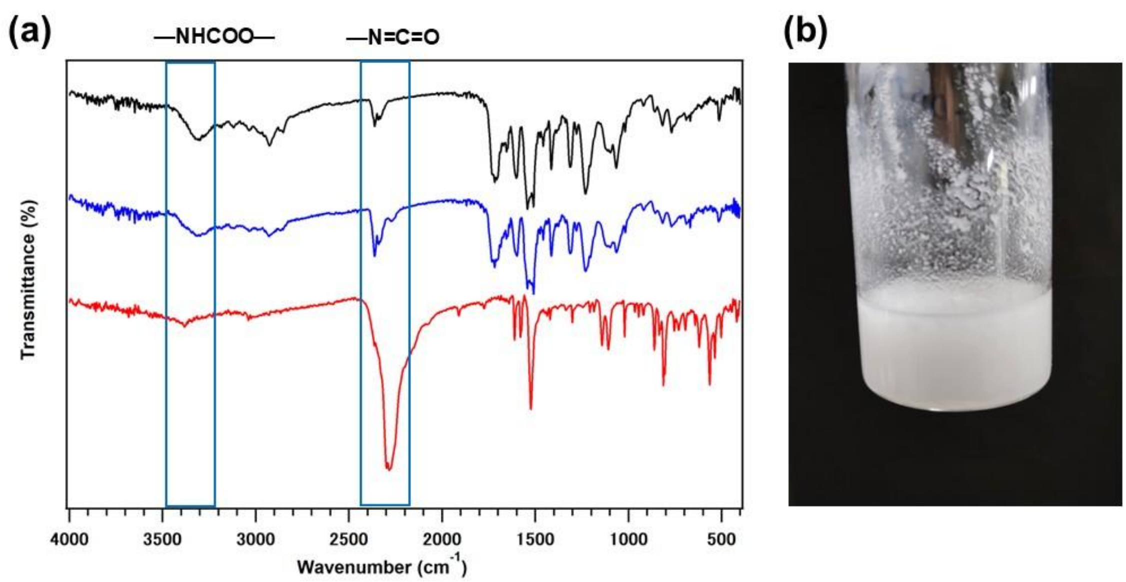

Figure S10. (a) FT–IR spectra of methylenediphenyl diisocyanate (MDI) (red line), precipitate (blue line), and filtrate (black line), and (b) photo of crude mixture obtained during equimolar reaction of crude reaction of equimolar reaction of MI/OH-SQNP and MDI (OH/ NCO = 1/1).

Table S4. The comparison between this work and prior published results.

Sample	Modulus (MPa) [a]	Ultimate tensile strength (MPa) [a]	Self-healing efficacy (%)	Ref. number
MI/PU-SQNP-$ZnCl_2$	1519	205.5	87	This work
MI/HMU-SQNP-$ZnCl_2$	1860	249.1	78.5	This work
MI/MDU-SQNP-$ZnCl_2$	4085	435.4	35	This work
MI/MT-SQ-$ZnCl_2$	2130	8.55	46	30
MI/Bu-SQ-$ZnCl_2$	1050	7.37	80	30
PU-IZ/Zn-0.50	N/D	6.68	49.6	47
CSH-PPG-Zn-1.00	5.56	4.42	100	48
ICP-4	N/D	4	100	49
B-ICP-Zn-4.5	14	3.5	100	50
IMZ-PDMS-1100 L/Z 4.5	N/D	0.06	98	51

[a] This data was estimated according to the data reported in the reference (see reference in the main text).

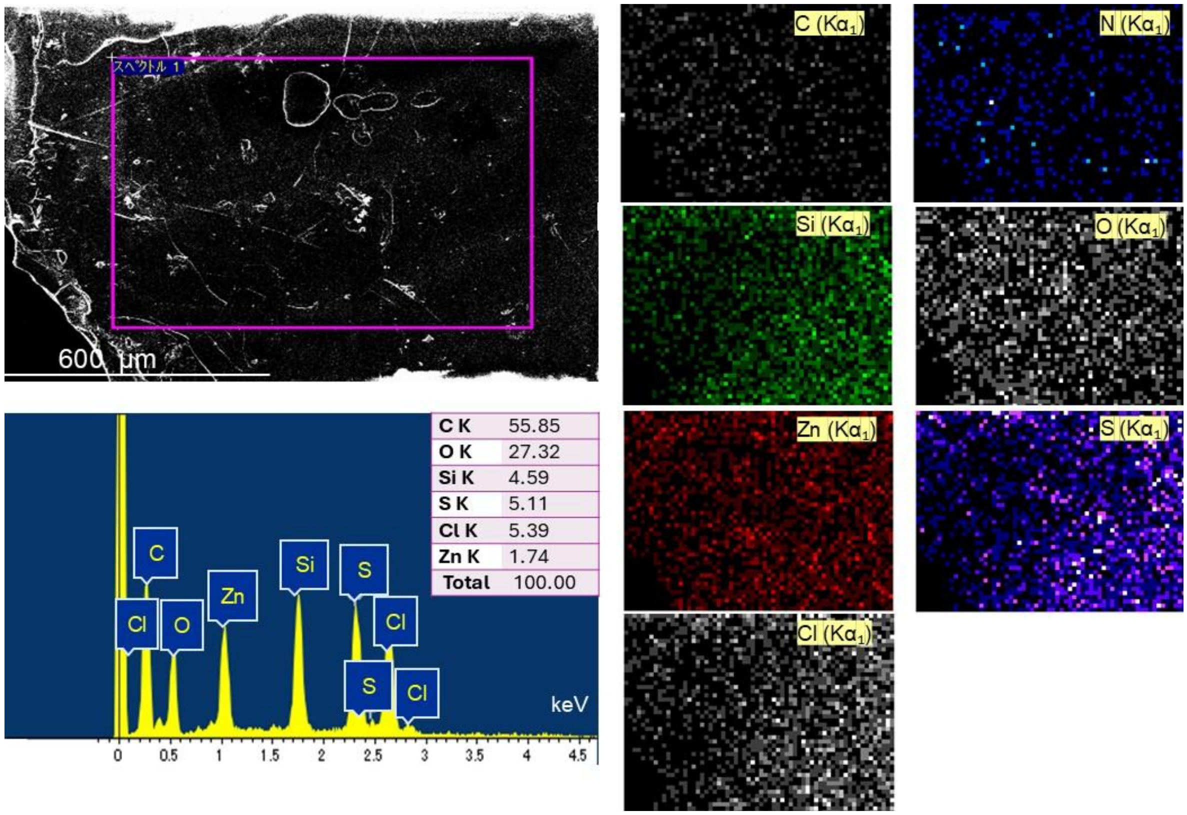

Figure S11. SEM image and corresponding EDS elemental mapping of MI/PU-SQNP-Zn.

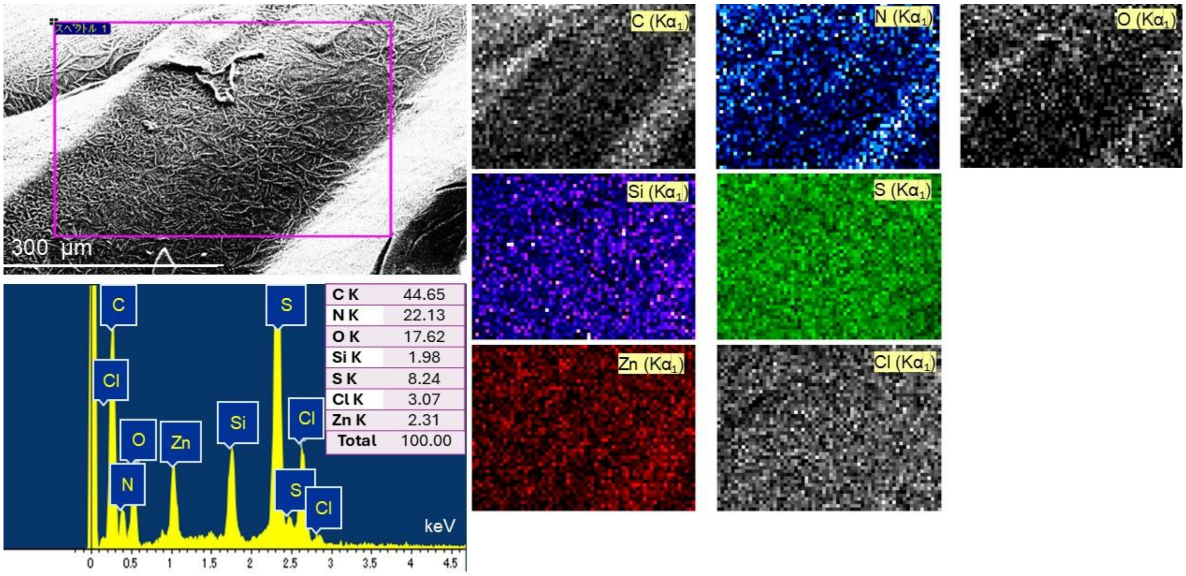

Figure S12. SEM image and corresponding EDS elemental mapping of MI/HMU-SQNP-Zn.

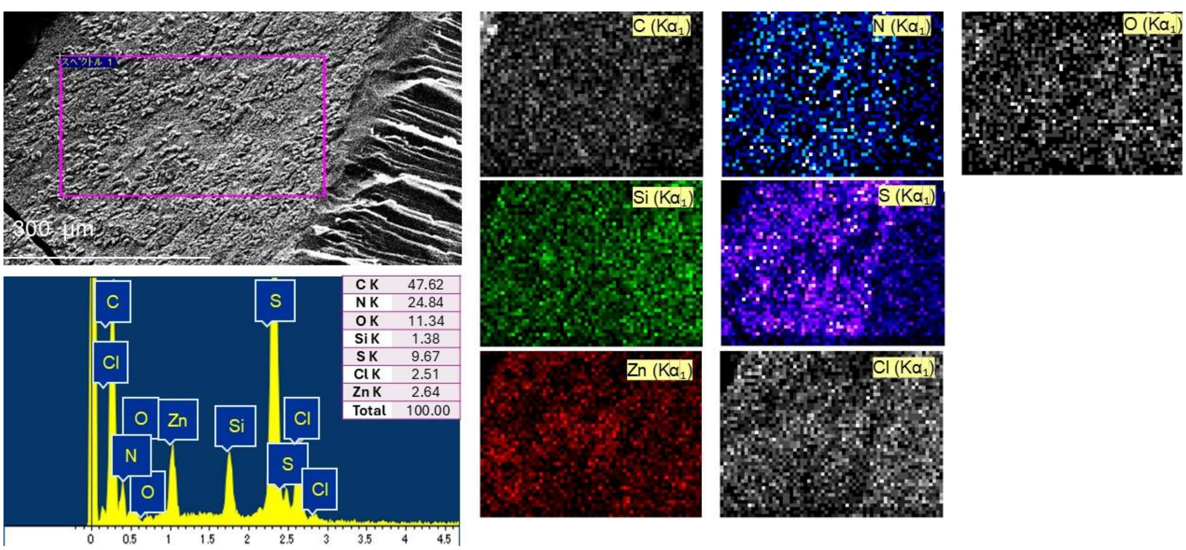

Figure S13. SEM image and corresponding EDS elemental mapping of MI/MDU-SQNP-Zn.