Supporting Information

Amino Acid-Derived Cu(II)-Coordinated Supramolecular Hydrogel with Tunable Mechanics, Self-Healing, and Underwater Adhesion

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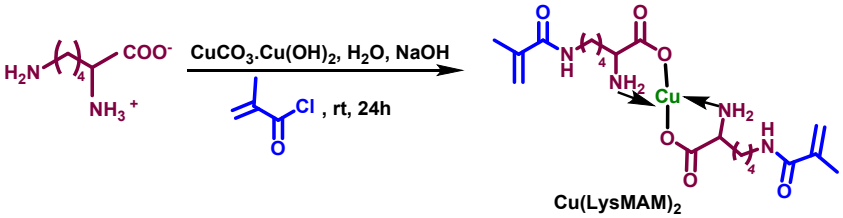
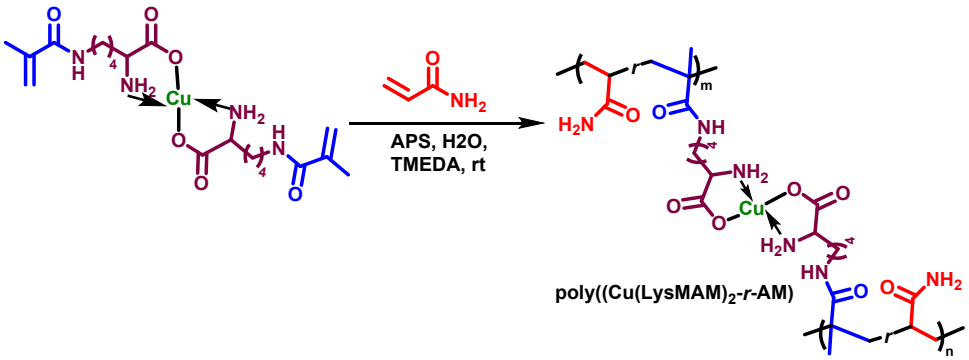
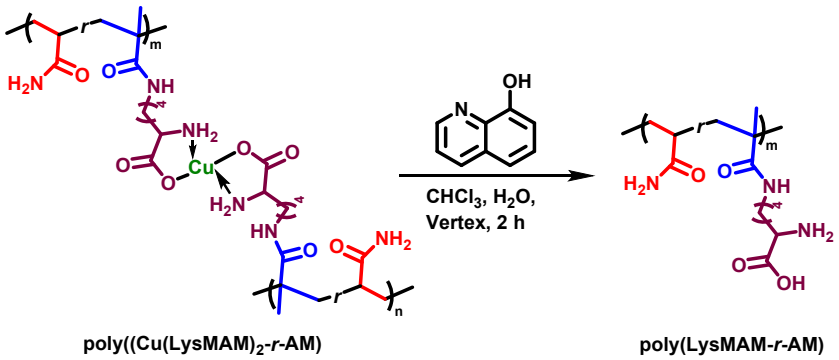
B. Supporting Tables, Schemes, and Figures



Scheme S1. Synthesis of Cu(LysMAM)$_2$ crosslinker**.**



Scheme S2. Synthesis of poly(Cu(LysMAM)$_2$-*r*-AM) hydrogel**.**



Scheme S3. Deprotection of poly(Cu(LysMAM)$_2$-*r*-AM) to poly(LysMAM-*r*-AM).

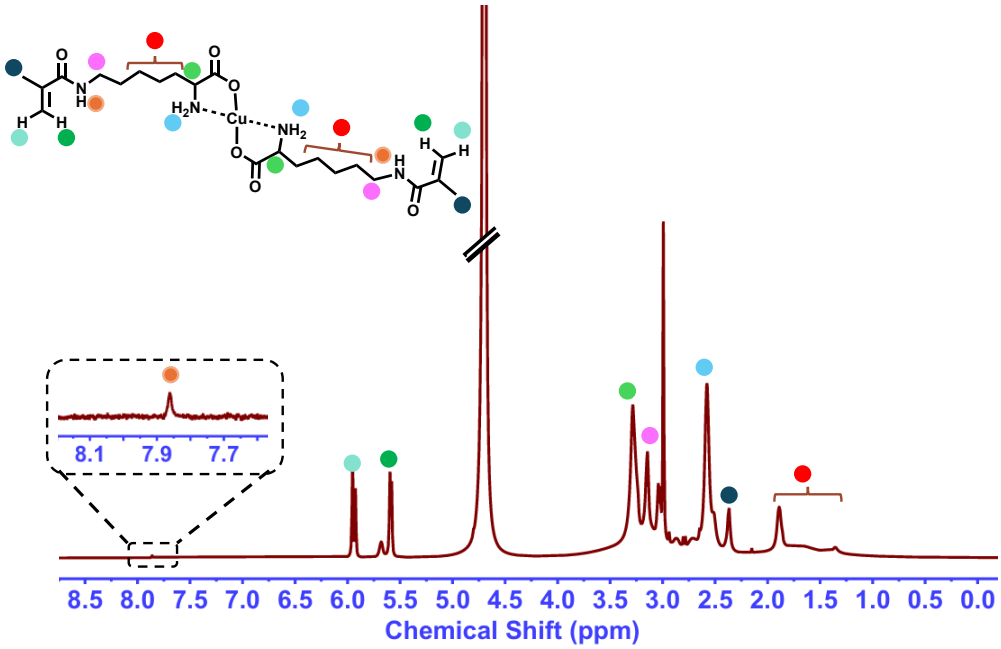


Figure S1. ^{1}H NMR spectrum of Cu(LysMAM)$_2$ crosslinker in D_2O.

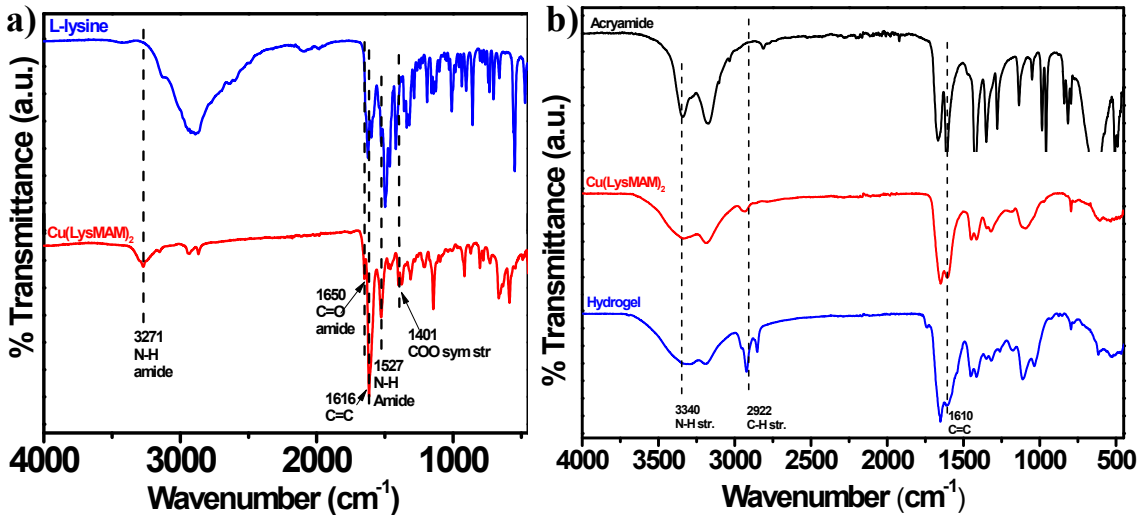


Figure S2. ATR-IR spectra of (a) L-lysine and Cu(LysMAM)$_2$. (b) poly(Cu(LysMAM)$_2$-*r*-AM) hydrogel, Cu(LysMAM)$_2$ and AM.

ATR-IR spectroscopy (Figure S2(a)) shows the characteristic stretching of N-H of amide at 3271 cm^{-1}, C=O of amide at 1650 cm^{-1}, N-H sym stretching at 1527 cm^{-1}, 1640 cm^{-1} corresponds to C=C of Cu(LysMAM)$_2$. (Figure S2(b)) shows the ATR-IR spectroscopy of poly(Cu(LysMAM)$_2$-*r*-AM) hydrogel at 3400−3000, νN−H (amine, amide); 2925, νC−H (vinyl); 1530, absence of 1610, νC=C; confirms the successful polymerization of AM and Cu(LysMAM)$_2$.

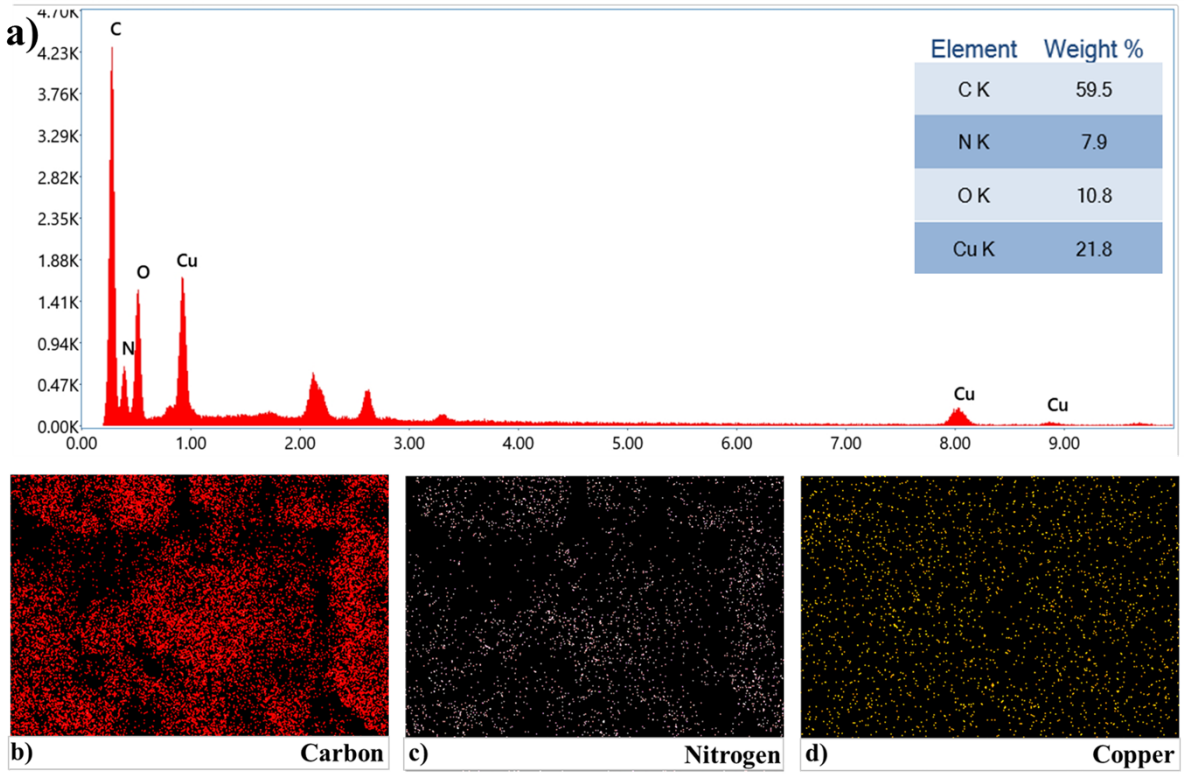


Figure S3. EDS mapping of $Cu(LysMAM)_2$.

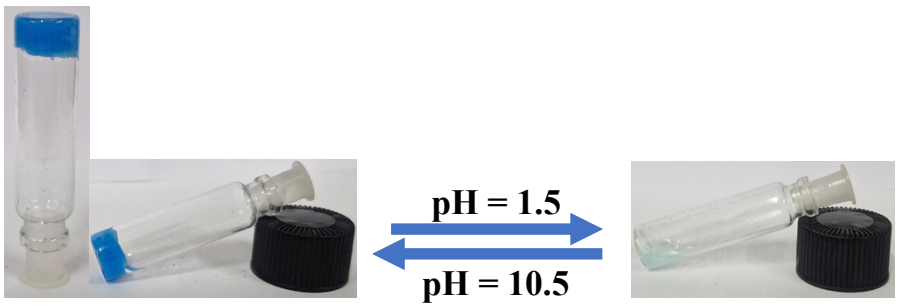


Figure S4. Represents the reversibility of poly($Cu(LysMAM)_2$-*r*-AM) hydrogel. Adding NaOH binds the polymer with metal ions to form a hydrogel material, which can be reversed by adding HCl to the hydrogel.

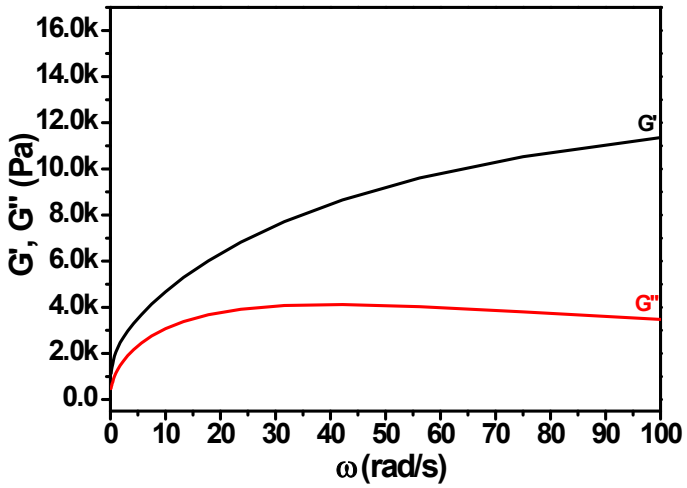


Figure S5. Rheology of the metallo-supramolecular hydrogel poly(Cu(LysMAM)$_2$-*r*-AM).

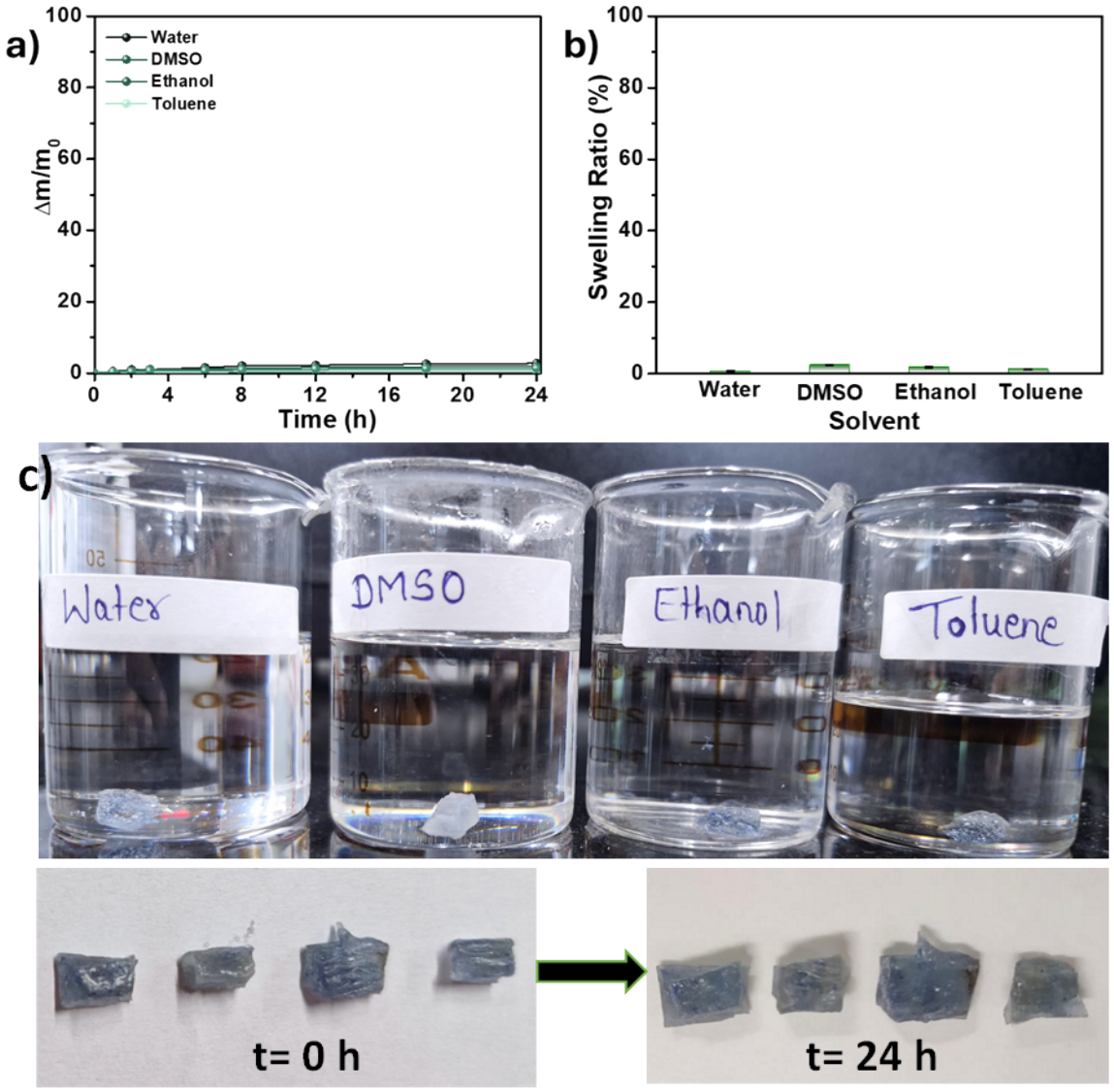


Figure S6. Swelling study of the hydrogel in different solvents, i.e. deionized water, DMSO, ethanol, and toluene; (a) time-dependent swelling behavior ($\Delta m/m_0$) of poly(Cu(LysMAM)$_2$-*r*-AM) gels, (b) corresponding equilibrium swelling ratios (%), (c) Images of hydrogels illustrating their swelling in various solvents, along with a comparison of their appearance before and after swelling.

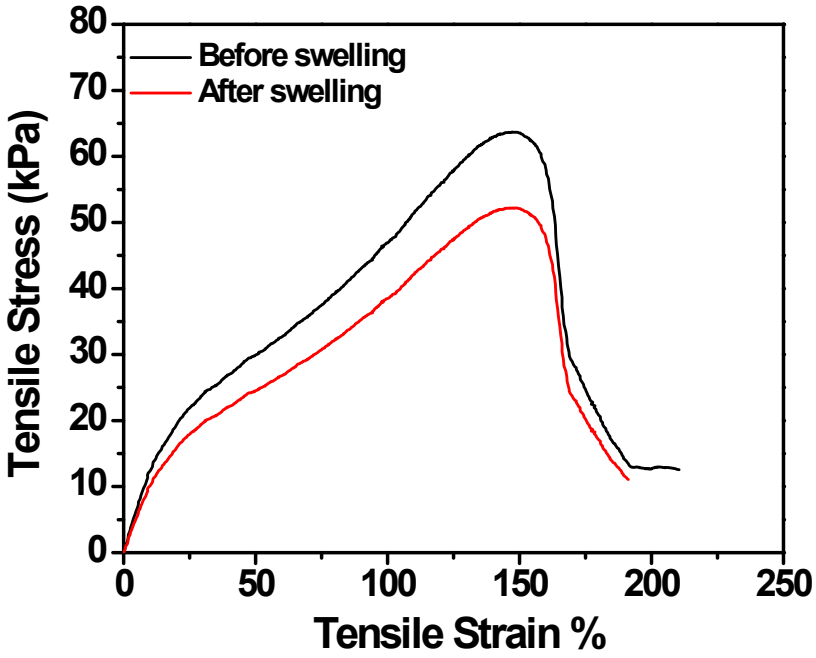


Figure S7. Lap-shear test data of poly(Cu(LysMAM)$_2$-*r*-AM) hydrogel adhesive on glass surfaces before and after swelling in water for 24 h.

Table S1. Correlations and participants' information on flat foot detection

Gender	No. of participants	Average age	Average Shoe size	Average body weight
Female	22	22-28	38	48 kg
Male	25	22-28	42	65 kg

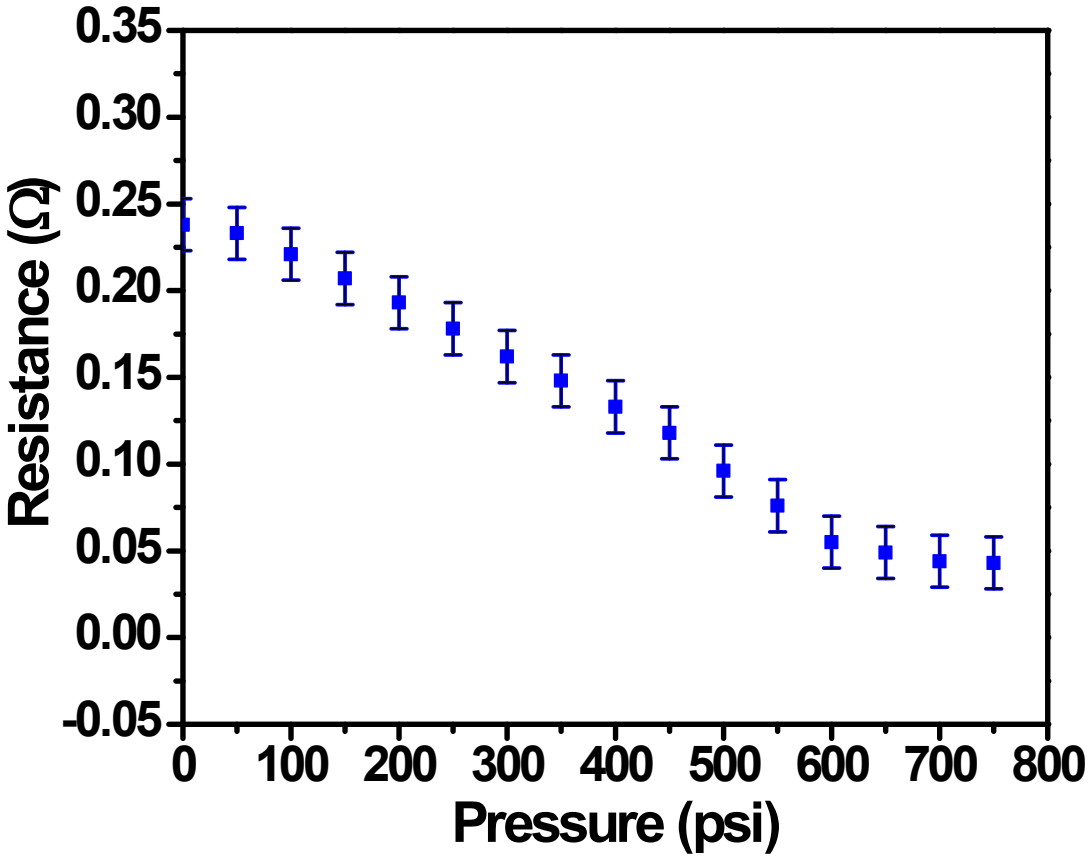


Figure S8. Represents the effect of pressure on the resistance of poly(Cu(LysMAM)$_2$-*r*-AM) hydrogel.

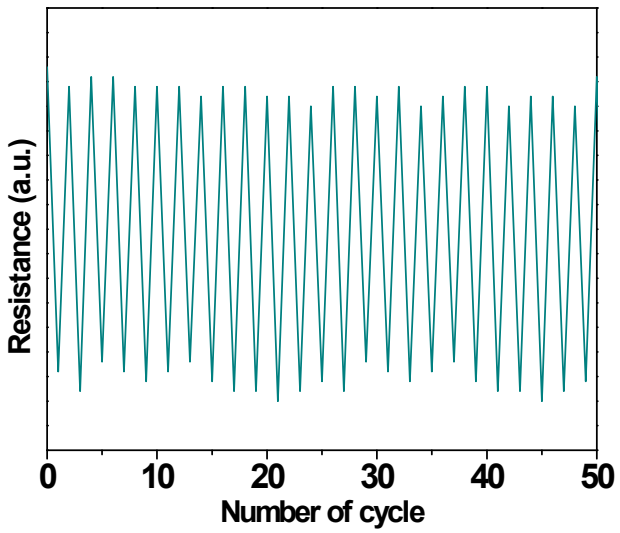


Figure S9. Represents the reversibility of poly(Cu(LysMAM)$_2$-*r*-AM) hydrogel in flat foot setup.

Table S2. Comparison with other reported metal-ion and supramolecular hydrogels.

Hydrogel System	Tensile Strength	Self-Healing Efficiency	Adhesion	Reference
This Work (poly(Cu(LysMAM)$_2$-*r*-AM))	140 kPa	~92% in 1 h	Good underwater adhesion	This Work
Zn(II) Salphen metallogel complexes	~100 Pa	No Self-healing	No adhesion	[1]
peptide/Zn^{2+} hydrogel	~80 Pa	No Self-healing	No adhesion	[2]
TA@CNC/PVA/gel hydrogels	25.54 kPa	93 % in 1 h	The strong adhesion to wood, paper, copper sheets, glass, and surface.	[3]
Cu(II)−Inosine Supramolecular Gel	10 kPa	3 h	No adhesion	[4]
DCMC/CS/PAA Polysaccharide-Composite Hydrogel	90 kPa	93% in 24 h	Self-adhesion	[5]
CNF–Al^{3+}–Xylan Nanocomposite	31.1 kPa	95% in 2 h	Yes	[6]
Chitosan–HA–Al^{3+} Hydrogel	379.5 kPa	~87%	Not specified	[7]
P(AM-HisMA)-Fe^{3+}– Hydrogel	89 kPa	>84% in 5 min	Porcine skin	[8]
3D-printed PVC/DBA Hydrogel	26.4 kPa	Not reported	Not reported	[9]

Ru(II)-metallogel	1.4 kPa	No Self-healing	No adhesion	[10]
Ag^{+} and Fe^{3+}-metallogels	10 kPa	No Self-healing	No adhesion	[11]
Fe^{3+}–P(AAm-*co*-AAc) Hydrogel	7 kPa	Yes	Not reported	[12]

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