Electronic Supplementary Information (ESI) for

Synthesis and Properties of the Metallo-Supramolecular Polymer Hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃: Ag⁺/Cu²⁺ Ion Exchange and Effective Antibacterial Activity

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Part S1. Detailed experimental methods

Powder-XRD (powder X-ray diffraction) measurements: Powder-XRD of PVM/MA and polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃-vacuum dried powder were measured on a Bruker D8 Powder X-Ray Diffractometer .

PVE/MA molecular weight confirmation

For polymer molecular weight determination, polymer solutions (2 mg mL⁻¹) were prepared using HPLC grade Tetrahydrofuran. Samples were briefly sonicated and then filtered through a 0.45 μ m PTFE filter prior to injection to ensure full solubility. GPC was performed with HPLC grade Tetrahydrofuran at an elution rate of at 1.0 mL min⁻¹ through PLgel Mixed-C columns. The particle size in the columns was 5 μ m and the columns were maintained at room temperature. The GPC system consisted of a Agilent 1200 series Separation Module and Agilent 1515 Tunable Absorption Detector. The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear polystyrene standards using Chemstation software. The system was calibrated using polystyrene standards and, therefore, all molecular weight values quoted are relative to these standards. Agilent EasiCal calibrants were used to obtain a 10-point calibration from only 2 injections.

PVE/MA	Mn (g/mol)	Mw (g/mol)	PDI
Aldrich Value	311,000	1080,000	3.47
Experimental Result	313,000	783,000	2.50

Cryo SEM:

Low temperature experiments were carried out using a Quorum PP2000T cryo-transfer system (Qurorum Technologies, Newhaven, UK) that was fitted to an FEI Quanta 3DFEG SEM with a field emission electron source. To do cryo-SEM on the polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃, a small amount of sample was mounted in a 1.5-mm in diameter machined-hole on an aluminum stub that was secured on the specimen holder. The sample holder, attached to a transfer rod, was then rapidly plunged into liquid nitrogen slush and under vacuum transferred into the PP2000T preparation chamber, pre-cooled to -185°C and allowed to equilibrate for 2 minutes. The sample temperature was raised to -90°C for 2 min to sublime residual ice contamination on the surface of sample that happened during transfer to preparation chamber. The temperature was then lowered to -150°C and the surface of frozen gel was sputter-coated with 5 nm thick platinum in an argon atmosphere. The fractured surface of hydrogel was obtained by hitting the top of frozen gel kept at -150°C with a knife cooled at -185°C. The sample was then transferred to the SEM cryo-stage which was held at -130°C and the revealed fractured plane of frozen hydrogel was imaged. In order to remove the water from the fractured plane and reveal further surface details, samples were sublimed inside the SEM chamber at -90°C for up to 37 min and SEM images from the same areas were captured during the sublimation process. To avoid charging problems, the sample was transferred back to the preparation chamber and sputter-coated with 3 nm thick platinum in an argon atmosphere at -150°C. The sample was then transferred back to the SEM cryo-stage, which was held at -130°C and high quality SEM

images were captured. In all cases, the imaging was performed using an accelerating voltage of 3-5 kV and a working distance of 7-10 mm.

Antibacterial Activity Assay: The Kirby-Bauer Zone of Inhibition test method was used to examine the antibacterial activity against the three bacterial strains: *E.coli* (CGSC 5240), *S. epidermidis* (ATCC 12228), and *P. aeruginosa* (ATCC 14885). Details of the antibacterial tests were as follows.

LB agar broth was prepared by mixing of LB Broth (Lennox, 45 g), DifcoTM Agar Granulated (5.4 g) and deionized water (360 mL) and sterilized at 121°C for 20 minutes. The sterilized LB agar broth was cooled to 60°C and poured into aseptic Petri dishes to solidify. Then, 100 μ L of the freshly grown bacteria (about 1 × 10⁸ cfu/mL (cfu, colony-forming unit)) were dropped on the surface of the solidified LB broth and spread evenly on the surface. Small holes (inner diameter 2mm) were made on the surface of the solidified LB broth. The intact polymer hydrogel poly[methyl vinyl ether-*alt*-monosodium maleate]·AgNO₃ (Ag(I) content was 1.1% by weight, 5 μ L, and 10 μ L), Aqueous solution of poly (methyl vinyl ether-*alt*-maleic anhydride) (20 mg/mL, 5 μ L) and ampicillin (5 μ g/ml, 5 μ l) were injected carefully into the small holes. The plates were incubated at 37°C for 24 hours. Colonies were visualized and digital images were captured.

Minimum Inhibitory Concentration (MIC) Testing: The MIC values of the polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃, AgNO₃ and poly (methyl vinyl ether-*alt*-maleic anhydride) (PVM/MA) (CAS: 9011-16-9, 416320) were measured using a broth dilution method. First, solutions with various concentration gradients of the polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium

maleate]·AgNO₃, AgNO₃ and PVM/MA were prepared with LB broth in the 15 mL of cultivation tubes. Then, 5 μ L of the microorganism culture (about 1 × 10⁶ cfu/mL) was added into each of the cultivation tube. The optical density values of microorganism cultures were measured after 72 h of incubation at 37°C. The concentration at which no growth of microorganism was observed with the naked eyes and microplate reader (Tecan Infinite M200) was recorded as MIC. The tests were repeated three times. For PVM/MA, solutions of 9,500 μ g/mL, 6,500 μ g/mL, 4,000 μ g/mL, 3,500 μ g/mL, 3,000 μ g/mL and 2,500 μ g/mL polymer LB broth were prepared and tested. For polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃, solutions of 55 μ g/mL, 28 μ g/mL, 11 μ g/mL, 5.5 μ g/mL, 5.0 μ g/mL, 4.5 μ g/mL, 4.0 μ g/mL, 3.5 μ g/mL, 3.0 μ g/mL and 2.5 μ g/mL LB broth were prepared and tested.

For AgNO₃, solutions of 10.0 μ g/mL, 9.0 μ g/mL, 8.0 μ g/mL, 7.0 μ g/mL, 6.0 μ g/mL, 5.5 μ g/mL, 5.0 μ g/mL, 4.5 μ g/mL, 4.0 μ g/mL, 3.5 μ g/mL and 3.0 μ g/mL LB broth were prepared and tested.

Silver Release: The silver release experiments were carried out in PBS solution. Briefly, 12.5 grams of polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃ (Ag(I) content was 1.1% by weight) were immersed in 200 mL PBS. The solution samples were taken out at different time, filtered and diluted 1,000 times before analysis. The concentration of silver was determined by Inductively Coupled Plasma (ICP) spectrophotometer (ICP-MS Elan DRC II) with the condition of Nebulizer gas flow: 0.92 L/min, Auxiliary gas flow: 1.2 L/min, Plasma gas flow: 15 L/min, ICP RF Power: 1300 watts and Lens Voltage: 7.5 volts.

Part S2. Additional experimental data

1. NMR Test of starting material and intermediate

¹HNMR and ¹³CNMR of poly(methyl vinyl ether-*alt*-maleic anhydride) (PVM/MA) [CAS: 9011-16-9] (Mw: 1,080,000, $M_n \sim 311,000$) were measured and the images were shown in Figure S1 and S2.

¹H NMR of PVM/MA (D₂O, 700 M):

δ 1.95 (s, 2H), 2.83~2.92 (m, 1H), 3.08 (s, 1H), 3.25~3.31 (m, 3H), 3.54~3.65 (m, 1H).

Figure S1¹H NMR of PVM/MA



¹³C NMR of PVM/MA (D₂O, 175 M): 31.33, 32.21, 40.72, 41.34, 42.17, 48.80, 49.15, 49.89, 50.86, 51.48, 56.52, 57.23, 57.48, 58.54, 76.44, 76.72, 77.71, 128.46, 175.37, 176.26, 177.50, 178.26.

Figure S2 ¹³C NMR of PVM/MA



Figure S3 ¹H NMR of PVM/Na-MA



Figure S4 ¹³C NMR of PVM/Na-MA



2. Different amount of AgNO₃ were used to make polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃

The PVM/Na-MA stock solution (10.0 g, containing 2.5 mmol of sodium carboxylate groups) was added into a 20 mL of vial. Different amount of Silver nitrate aqueous solution (0.64 mol/L) was added into the vial and stirred. Hydrogel formation conditions were listed in TS1.

Table S1 . Investigation of hydrogel formation condition of PVM/Na-MA solution (10.0
g) with different amount of AgNO ₃ aq. solution (0.64 mol/L)

No	AgNO ₃ Amount	OCH ₃ 	Hydrogel Formation	Hydrogel Formation Conditions
1	1.0 mL	3.9 : 1	No	Colorless solution but no hydrogel formed.
2	1.5 mL	2.6 : 1	Yes	Colorless hydrogel formed in 2 hours and changed into dark brown color in 1 month
3	2.0 mL	2.0 : 1	Yes Colorless hydrogel formed within 5 minute changed into dark brown color in 1 more	
4	3.0 mL	1.3 : 1	Yes Colorless hydrogel formed within 5 minute changed into dark brown color in 1 mor	
5	3.5 mL	1.1 : 1	No	Something like hydrogel formed but it was not real hydrogel. The items could not stand at the bottom of the vial while the vial was put up-side-down.
6	3.9 mL	1:1	No	Some cloudy items but not hydrogel formed.

3. PVM/Na-MA of different concentrations were used to make polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃

Table S2. Investigation of hydrogel formation condition of PVM/Na-MA* (10.0 g) of different concentration with AgNO₃ aq. solution (2 mL, 0.64 mol/L, 1.28 mmol)

No.	Polymer Concentration (g/L)	Hydrogel Formation Condition	
1	20	White solution but no hydrogel formed.	
2	40	Colorless hydrogel formed within 10 minutes.	
3	80	The solution was too viscous and AgNO ₃ appeared as precipitate. Hydrogel did form but some solution still remained.	
4	120	The solution was too viscous and AgNO ₃ appeared as precipitate. Hydrogel did form but some solution still remained.	

* PVM/Na-MA stock solution was prepared by the method described in the paper. For each of the stock solutions, one equivalent of sodium hydroxide was used to open the cyclo anhydride in the polymer chain.

4. PVM/2Na-MA stock solution was used to make polymer hydrogel poly[methyl vinyl ether-*alt*-disodium maleate]·AgNO₃

Table S3. Investigation of hydrogel formation condition of PVM/2Na-MA stock solution (10.0 g) with different amount of AgNO₃ aq. solution (0.64 mol/L)

No	AgNO ₃ Amount	OCH ₃ 0 0 0 : Ag (I)	Hydrogel Formation	Hydrogel Formation Conditions
1	2.0 mL	2.0 : 1	Yes	Only 10% of the total solution formed hydrogel 12 hours later. Solution remained.
2	3.0 mL	1.3 : 1	Yes	Only 20% of the total solution formed hydrogel 12 hours later. Solution remained.
3	4.0 mL	1:1	Yes	Hydrogel formed after 2 hours. The color changed into dark yellow and black within 1 week.
4	5.0 mL	1:1.3	No	Something like hydrogel formed but it was not real hydrogel. The items could not stand at the bottom of the vial while the vial was put up-side-down.

5. Different alkali metal bases were used to make polymer hydrogel

Table S4. Investigation of hydrogel formation condition of "polymer-alkali metal base stock solution*" (10.0 g) with $AgNO_3$ aq. solution (2 mL, 0.64 mol/L, 1.28 mmol)

No.	Alkali metal base	Hydrogel Formation	Hydrogel Formation Conditions	
1	LiOH	Yes	Colorless hydrogel formed within 5 minutes and changed into dark brown color in 1 month.	
2	КОН	Yes	Colorless hydrogel formed within 5 minutes and change into dark brown color in 1 month.	
3	RuOH	Yes	Colorless hydrogel formed within 5 minutes and change into dark brown color in 1 month.	
4	CsOH	Yes	Colorless hydrogel formed within 5 minutes and changed into dark brown color in 1 month.	

Figure S5. Hi-resolution SEM image of CO₂ Critical Point Drier dried power of polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃.



Figure S6. Hi-resolution SEM image of polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃ -vacuum dried powder.



Figure S7. Powder-XRD (powder X-ray diffraction) analysis results of polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃-vacuum dried powder, PVM/MA, NaOH, AgNO₃ and NaNO₃.



Figure S8. N₂ adsorption desorption isotherm of polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃-vacuum dried powder. No substantial gas absorption was observed.



Figure S9. N₂ adsorption desorption isotherm of polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃-CPD powder



Table S5. Results of intact polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃ exchanged by Cu(NO₃)₂ aq. solution

Entry	Amount of Cu ²⁺ /Ag ⁺	Exchange time	Cu/Ag after exchange
1	1 eq.	24 h	1:0.2
2	5 eq.	24 h	1:0
3	10 eq.	24 h	1:0
4	5 eq.	8 h	1:0.1
5	5 eq.	16 h	1:0
6	5 eq.	24 h	1:0

Figure S10. Image of intact polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃ before and after exchanged by Al(III)



Figure S11. EDX of dried powder of intact polymer hydrogel poly[methyl vinyl ether*alt*-mono-sodium maleate]·AgNO₃ after exchanged by Al (III)



T 1	TTZ-0/	A 40 /
Element	W1%	AI%
СК	50.71	60.32
ОК	37.73	33.70
NaK	00.00	00.00
AlK	11.20	05.93
AgL	00.36	00.05
Matrix	Correction	ZAF

Figure S12. EDX of dried powder of intact polymer hydrogel poly[methyl vinyl ether*alt*-mono-sodium maleate]·AgNO₃ after exchanged by Cu (II)



Element	Wt%	At%
СК	43.99	58.65
ОК	36.00	36.04
NaK	00.69	00.48
AgL	00.44	00.07
CuK	18.88	04.76
Matrix	Correction	ZAF

Figure S13. EDX of dried powder of intact polymer hydrogel poly[methyl vinyl ether*alt*-mono-rubidium maleate]·AgNO₃ after exchanged by Al (III)



Element	Wt%	At%
СК	54.59	64.19
ОК	34.32	30.30
AlK	10.35	05.42
AgL	00.68	00.09
RbK	00.05	00.01
Matrix	Correction	ZAF

Figure S14. EDX of dried powder of intact polymer hydrogel poly[methyl vinyl ether*alt*-mono-rubidium maleate]·AgNO₃ after exchanged by Cu (II)



Element	Wt%	At%
СК	44.65	56.08
ОК	43.70	41.20
AgL	00.41	00.06
CuK	11.17	02.65
RbK	00.07	00.01
Matrix	Correction	ZAF

Figure S15. EDX of dried powder of intact polymer hydrogel poly[methyl vinyl ether*alt*-mono-cesium maleate]·AgNO₃ after exchanged by Al(III)



Element	Wt%	At%
СК	49.41	58.63
ОК	40.92	36.45
AIK	09.19	04.85
AgL	00.40	00.05
CsL	00.08	00.01
Matrix	Correction	ZAF

Figure S16. EDX of dried powder of intact polymer hydrogel poly[methyl vinyl ether*alt*-mono-sodium maleate]·AgNO₃ after exchanged by Cu(II)



Element	Wt%	At%
CK	45.97	56.50
ОК	44.88	41.41
AgL	00.21	00.03
CsL	00.14	00.02
CuK	08.79	02.04
Matrix	Correction	ZAF

Figure S17. Image of polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃-vacuum dried powder before and after exchanged by Cu(II)



Figure S18. Antibacterial activity of ampicillin 5 μ g/ml (I), polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃ [10 μ g/ml (II), 5 μ g/ml (III)] and Aqueous solution of poly (methyl vinyl ether-*alt*-maleic anhydride) (IV) against (a) *E. coli*, (b) *S. epidermidis*, and (c) *P. aeruginosa* (three replicates for each) The photographs were taken after incubation at 37°C overnight.



Figure S19. Amount of silver released from the intact polymer hydrogel poly[methyl vinyl ether-*alt*-mono-sodium maleate]·AgNO₃ in PBS solution as a function of immersion time



Figure S20. DTGA plot. Peak temperatures were used in the paper.

