Supporting Information

Tannic acid-inspired star polymers for functional metal-phenolic networks with tunable pore sizes

Bohan Cheng, Sifan Lu, Wenting Liao, Chenyu Wang, Joseph J. Richardson and Hirotaka Ejima*

Department of Materials Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

*Corresponding author

E-mail: ejima@material.t.u-tokyo.ac.jp
Table of Contents

1. Experimental procedures .......................................................................................................................3
   1.1 Materials ..............................................................................................................................................3
   1.2 Synthesis of initiator ............................................................................................................................3
      1.2.1 Synthesis of 1,2,3,4,6-penta-O-isobutyryl bromide-α-D-glucose (Glu-Br$_5$) ................................3
      1.2.2 Synthesis of 1,2,3,4,6-Penta-O-(2,2,6,6-tetramethylpiperidinyloxy) isobutyrate-α-D-glucose (Glu-TEMPO$_5$) .......................................................................................................................................4
   1.3 Synthesis of monomers ........................................................................................................................4
      1.3.1 Synthesis of catechol monomer 3,4-di(methoxymethoxy)styrene (DMMS)................................4
      1.3.2 Synthesis of gallol monomer 3,4,5-tri(methoxymethoxy)styrene (TMMS).................................5
   1.4 Synthesis of polymers ..........................................................................................................................6
      1.4.1 Typical polymerization process of TIPs .......................................................................................6
      1.4.2 Typical polymerization process of reference linear polymers......................................................6
      1.4.3 Deprotection of polymers .............................................................................................................6
      1.4.4 Synthesis of polystyrene (PS) particles.........................................................................................6
   1.5 Preparation of polymer-based metal-phenolic networks capsules .......................................................7
   1.6 Characterizations..................................................................................................................................7
      1.6.1 Nuclear magnetic resonance (NMR) ..........................................................7
      1.6.2 High resolution mass spectrometry (HRMS) ........................................................................8
      1.6.3 Gel permeation chromatography (GPC) ..................................................................................8
      1.6.4 Quartz crystal microbalance (QCM) .....................................................................................8
      1.6.5 Atomic force microscope (AFM) ..........................................................................................8
      1.6.6 Scanning electron microscope (SEM) ................................................................................9
      1.6.7 Dynamic light scattering (DLS) ............................................................................................9
      1.6.8 Ultraviolet-visible (UV-Vis) spectrophotometry .................................................................9
      1.6.9 Conformation and permeability of capsules ........................................................................9
      1.6.10 Cytotoxicity assay .............................................................................................................9
2. Supplementary figures .........................................................................................................................11
3. Supplementary tables ...........................................................................................................................26
4. Supplementary references ....................................................................................................................28
1. Experimental procedures

1.1 Materials

N, N-diisopropylethylamine (DIEA), methyl gallate, 3,4-dihydroxybenzaldehyde, and chloromethyl methyl ether (MOM-Cl) were purchased from Tokyo Chemical Industry. Styrene (used after removing stabilizer by basic alumina column purification), tannic acid, 2-methoxyethanol (EGME), iron(III) chloride hexahydrate, ethanol (99.5%), 3-(N-morpholino)propanesulfonic acid (MOPS), 2-bromoisobutyryl bromide (BiBB), hydrochloric acid in diethyl ether, activated manganese dioxide (MnO₂), and Polyvinylpyrrolidone (PVP, Mw ~ 4,000) were purchased from Sigma-Aldrich. Methyltriphenyl phosphonium bromide ((Ph)₃PCH₃Br), lithium aluminum hydride (LiAlH₄), potassium tert-butoxide (t-BuOK), 2,2'-azobis(2-methylpropionitrile) (AIBN), D(+)-glucose, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), anhydrous MgSO₄, copper (I) bromide (CuBr), copper (0) (Cu), N, N', N'', N''-Pentamethyldiethylenetriamine (PMDETA), anhydrous tetrahydrofuran (THF), anhydrous dichloromethane (DCM), anhydrous pyridine, and other organic solvents or reagents were purchased from Wako Pure Chemical Industry. 3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-2H-tetrazolium bromide (MTT) from Dojindo Laboratories Co., Ltd. MTT solution was prepared by dissolving 100 mg MTT powder in 20 mL PBS, filter-sterilized with a 0.22 μm filter, and stored in the dark at −20 °C.

1.2 Synthesis of initiator

1.2.1 Synthesis of 1,2,3,4,6-penta-O-isobutyryl bromide-α-D-glucose (Glu-Br₅)

Glu-Br₅ was synthesized according to the previous reports.¹² Briefly, 38.60 g (0.17 mol) of BiBB was added to a solution of 5.00 g (0.028 mol) D (+)-glucose in a mixture of 30 mL anhydrous pyridine and 50 mL anhydrous chloroform by a slow addition. The mixture was stirred at 55 °C for 72 h. Then, the solution was subsequently diluted in diethyl ether and washed with ice water, 0.1 M NaOH solution and water, prior to drying over anhydrous MgSO₄. The crude product was recrystallized from methanol and used in the next step without further purification (yield ~50%). ¹H-NMR (400 MHz, CDCl₃, Fig. S1): (δ, ppm) 6.36 (d, 1H, J= 3.66), 5.64 (t, 1H, J= 9.62), 5.33 (dd, 1H, J= 10.07, J' = 10.07), 5.23 (dd, 1H, J= 10.07, J' = 3.66), 4.40 (m, br, 3H), 1.80 (m, br, 30H). ¹³C-NMR (125 MHz, CDCl₃, Fig. S2) 163.9 to 171.5 (5C), 89.8 (1C), 68.1 to 73.0 (4C), 62.5 (1C), 54.4 to 53.3 (5C), 30.07 to 30.73 (10C).
1.2.2 Synthesis of 1,2,3,4,6-Penta-O-(2,2,6,6-tetramethylpiperidinyloxy) isobutyrate-α-D-glucose (Glu-TEMPO$_5$)

Initiator Glu-TEMPO$_5$ for nitroxide-mediated polymerization (NMP) was prepared via the reactions between ATRP initiators Glu-Br$_5$ and TEMPO radicals referring to the previous paper.$^3$ 1.10 g TEMPO (7 mmol), 0.70 g Glu-Br$_5$ (0.5 mmol), 0.49 g Cu (7.7 mmol), 1.10 g CuBr (4.9 mmol), and 30 mL chloroform were added into a two-neck round flask. The flask was sealed with a rubber septum and degassed with freeze-pump-thaw cycling for 3 times. Then, 3.2 mL of PMDETA was added into flask using dry medical syringes. The mixture was stirred at room temperature for 72 h. After reaction, the resulting solution was diluted with 50 mL of diethyl ether and washed with brine, EDTA, ascorbic acid and HCl, subsequently, to remove catalyst and excess TEMPO. Then dried over anhydrous MgSO$_4$, filtered, and concentrated. The alkoxyamine was then purified by silica gel chromatography (hexane: ethyl acetate = 8:2) to obtain white solid (yield ~50%). $^1$H-NMR (400 MHz, CDCl$_3$, Fig. S3): (δ, ppm) 6.27 (d, 1H, $J$ = 3.66), 5.58 (t, 1H, $J$ = 9.62), 5.33 (dd, 1H, $J$ = 10.07, $J'$ = 10.07), 5.23 (dd, 1H, $J$ = 10.07, $J'$ = 3.66), 4.40 (m, br, 3H), 0.8 to 1.7 (m, br, 120 H).

$^{13}$C-NMR (125 MHz, CDCl$_3$, Fig. S4) 173.0 to 176.0 (5C), 89.8 (1C), 68.5 to 71.0 (4C), 62.1 (1C), 59.5 (10C), 40.5 (10C), 34.0 (10C), 25.0 (10C), 20.5 (10C), 17.5 (5C). HRMS (ESI): calculated [M+H$^+$] 1306.9356 measured [M+H$^+$] 1306.9228.

1.3 Synthesis of monomers

Two kinds of monomers were synthesized respectively referring to the synthetic routes established in our laboratory,$^4$ to mimic gallol and catechol groups in tannic acid.

1.3.1 Synthesis of catechol monomer 3,4-di(methoxymethoxy)styrene (DMMS)

Under a nitrogen atmosphere at 0 °C, 32.50 g chloromethyl methyl ether (400 mmol) was added to a solution of 13.80 g 3,4-dihydroxybenzaldehyde (100 mmol) and 26.20 g DIEA (200 mmol) in 100 mL of THF. After reacting for 24 h at 40 °C, the reaction mass was filtered, concentrated under vacuum, and extracted with 50 mL of ether three times. The organic layer was washed with 50 mL of brine three times, dried over MgSO$_4$, filtered, and evaporated to yield colorless oil 3,4-di(methoxymethoxy)benzaldehyde (DMMB) without further purification.
Under a nitrogen atmosphere at 0 °C, 13.40 g t-BuOK (120 mmol) was added to a suspension of 42.80 g (Ph)3PCH3Br (120 mmol) in 200 mL of THF. After the reaction mixture was warmed to room temperature, 22.60 g DMMB (100 mmol) was added. The resulting solution was stirred overnight and then poured into 100 mL of deionized water, extracted with diethyl ether, dried over MgSO4, filtered, evaporated, and purified by column chromatography (hexane: ethyl acetate = 9:1) to yield a colorless oil DMMS. The total yield was 90%.

1H-NMR (400 MHz, DMSO-d6, Fig. S5): (δ, ppm) 7.17 (d, 1H, J=1.0 Hz), 7.02 (d, 1H, J=1.8 Hz), 7.01 (dd, 1H, J=1.8 Hz, J'=1.0 Hz), 6.63 (dd, 1H, J=18.3 Hz, J'=10.99 Hz), 5.63 (dd, 1H, J=18.3 Hz, J'=0.6 Hz) 5.26 (s, 2H), 5.24 (s, 2H), 5.17 (dd, 1H, J=10.99 Hz, J'=0.6 Hz), 3.53 (s, 3H), 3.51 (s, 3H).

1.3.2 Synthesis of gallol monomer 3,4,5-tri(methoxymethoxy)styrene (TMMS)

25.20 g (126 mmol) of methyl gallate, 62.40 g (756 mmol) of MOM-Cl and 50 mL of THF was first added to a flask under nitrogen atmosphere at 0 °C. After stirring for 5 min, 65.50 g DIEA (504 mmol) in 50 mL THF solution was added dropwise. The mixture was then stirred at 45 °C for 24 h and then concentrated under vacuum. The resulting reaction mass was extracted twice with 50 mL of diethyl ether and washed with brine, dried over anhydrous MgSO4, filtered, and evaporated to yield a colorless oil 3,4,5-tris(methoxymethoxy)benzoate (MTMB). The crude product was then directly moved to the next step without further purification.

At 0 °C, MTMB obtained from the last step was added dropwise to a suspension of 7.74 g LiAlH4 (200 mmol) in 100 mL anhydrous THF. After reacting 24 h at room temperature, the reaction was quenched with 8 mL water, 8 mL 15% NaOH, and 24 mL water. Then anhydrous MgSO4 was added to the mixture, and the mixture was stirred for 30 min. The reaction mass was filtered, washed with THF, and evaporated to yield white crystals 3,4,5-tris(methoxymethoxy)benzyl alcohol (TMBA).

Activated MnO2 6.09 g (70.0 mmol) was added into a solution of the TMBA 2.88 g (10.0 mmol) in DCM (150 mL). The reaction mixture was stirred overnight at room temperature. The solids were removed via filtration, and the filtrate was concentrated. The resulting material was purified by silica gel chromatography (hexane: ethyl acetate = 9:1) to obtain white solid 3,4,5-tris(methoxymethoxy)benzaldehyde (TMMB).

2.40 g t-BuOK (23.1 mmol) and 8.25 g methyltriphenyl phosphonium bromide (23.1 mmol) were stirred in 100 mL THF for 30 min under nitrogen atmosphere at 0 °C. Then, the reaction solution was brought to r.t.,
4.05 g (14.2 mmol) of TMMB was added, and the mixture was stirred overnight at 45 °C. Pure water (10 mL) was added, extracted with diethyl ether, dried over anhydrous MgSO₄, concentrated, and purified by silica gel column chromatography (hexane: ethyl acetate = 9:1) to obtain white solid TMMS. The yield was 60%. ¹H-NMR (400 MHz, CDCl₃, Fig. S6): (δ, ppm) 6.89 (s, 2H), 6.60 (dd, 1H, J = 17.40 Hz, J’ = 10.99 Hz), 5.71 (dd, 1H, J = 17.40 Hz, J’ = 0.92 Hz), 5.21 (dd, 1H, J = 10.99 Hz, J’ = 0.92 Hz), 5.20 (s, 4H), 5.04 (s, 2H), 3.50 (s, 3H), 3.40 (s, 6H).

1.4 Synthesis of polymers

1.4.1 Typical polymerization process of TIPs

TA-inspired star polymers were synthesized through nitroxide-mediated polymerization in different feed ratios. Typically, 426 mg TMMS (1.5 mmol), 336 mg DMMS (1.5 mmol), 1.31 mg Glu-(TEMPO)₅ (0.001 mmol), and 2 mL anisole were charged into test tube and purged with nitrogen for 15 min. The polymerization was carried out at 130 °C for 72 h. After polymerization, the reaction mixture was cooled to room temperature and precipitated in hexane.

1.4.2 Typical polymerization process of reference linear polymers

Linear phenolic polymers were synthesized through conventional free radical polymerization in different feed ratios. Typically, 426 mg TMMS (1.5 mmol), 336 mg DMMS (1.5 mmol), 1.68 mg of AIBN (0.01 mmol), and 2 mL anisole were charged into a test tube and purged with nitrogen for 15 min. The polymerization was carried out at 65 °C for 24 h. After polymerization, the reaction mixture was cooled to room temperature and precipitated in hexane.

1.4.3 Deprotection of polymers

Precipitate obtained in 1.4.1 and 1.4.2 was dissolved in 10 mL methanol and THF solution (v/v = 1:1) under nitrogen atmosphere, followed by dropwise addition of 1 mL of 1 M HCl in diethyl ether. After stirring at room temperature for 24 h, the mixture was evaporated and dried under vacuum. (Fig. S8 and S9)

1.4.4 Synthesis of polystyrene (PS) particles

Uniform polystyrene beads were synthesized through dispersion polymerization of styrene which modified from the previous reports.⁵,⁶ In brief, 0.20 g of AIBN, 0.90 g of PVP and 5.00 g of styrene were fed into a
round bottom flask with 25 mL EtOH, 25 mL EGME and 2mL MQ water as mixed solvent. After purging with nitrogen for 30 min, the flask was sealed. Polymerization was performed at 70°C for 24 h with 200 rpm rotating rate. After completion of the polymerization, obtained particles were washed with ethanol and distilled water by serial replacement for at least 5 times, to remove unreacted monomer and dispersion medium components. Resulting polystyrene particles (D = 3.0 ± 0.3 μm, Fig. S18) were freeze-dried and stored as solid powder.

1.5 Preparation of polymer-based metal-phenolic networks capsules

Capsules were prepared based on the modification of the previous method. Briefly, 5 μL of polymer solution (40 mg/mL, in ethanol) and 5 μL of FeCl₃·6H₂O (6 mg/mL, in MQ water) were added to 490 μL of polystyrene particles solution (10 mg/mL, dispersed in MQ water and sonicated). Then 500 μL of MOPS buffer (20 mM, pH 7.4) were added into suspension to raise the pH. The suspension was mixed vigorously by vertexing for 20 s immediately after the individual additions. Then 10 min incubation at room temperature was done to stabilize the coating layers. Coated particles were washed with MQ water three times to remove excess complexes by centrifugation (2000 g, 60 s). Aforementioned coating process was repeated three times to achieve layer-by-layer coatings on particles. Afterwards, polystyrene templates were removed by washing with THF three times by centrifugation (3000 g, 60 s) so as to obtain (Fe³⁺/TIP)₃ capsules.

1.6 Characterizations

1.6.1 Nuclear magnetic resonance (NMR)

The polymer compositions were determined by ¹H-NMR (400 MHz) and ¹³C-NMR (125 MHz) analysis using JEOL-400/500 spectrometer in MeOD, CDCl₃ or DMSO-d₆ (Fig. S1–S16).
1.6.2 High resolution mass spectrometry (HRMS)
Newly synthesized initiator was characterized by ESI-TOF MS (micrOTOF-II, BRUKER, USA) with methanol as eluent.

1.6.3 Gel permeation chromatography (GPC)
Number-averaged molecular weight ($M_n$) and PDI of polymers were measured by GPC (SHIMAZU Prominence-i GPC System) using THF as the eluent. The calibration curve was prepared using polystyrene as a standard.

1.6.4 Quartz crystal microbalance (QCM)
QCM sensors with Au-based, SiO$_2$-based, Carbon-based and Steel-based (SUS316L) surfaces (9 MHz, Seiko EG&G) were dipped into a TIP polymer solution (40 mg/mL in ethanol) or an aqueous solution of tannic acid (40 mg/mL) and incubated for 20 s, followed by drying in a N$_2$ stream. Then, the surfaces were dipped into Fe$^{3+}$ solution (6 mg/mL) and incubated for 20 s, followed by drying in a N$_2$ stream. After that, coated surfaces were dipped into polymer solution or TA solution again and incubated for 20 s, rinsed with ethanol and water, and dried by a N$_2$ stream. The quantities of MPN adsorbed on the surface were determined according to the frequency shift recorded by the quartz crystal microbalance (QCM-992A, SEIKO EG&G) (Fig. S17).

1.6.5 Atomic force microscope (AFM)
AFM experiments were conducted using a JPK NanoWizard II BioAFM instrument. Capsule thickness and roughness were measured from 5 different areas on each sample, and the data are reported as the mean value ± standard deviation.

1.6.6 Scanning electron microscope (SEM)
SEM images were obtained by a benchtop SEM (JCM-7000 NeoScope, JEOL, Japan) operated at an accelerating voltage of 15 kV with elemental analysis.
1.6.7 Dynamic light scattering (DLS)
Size measurements of polymers in buffer before and after coordinating with Fe$^{3+}$ were performed using a Zetasizer Nano ZS instrument (Malvern Instrument, UK).

1.6.8 Ultraviolet-visible (UV-Vis) spectrophotometry
Light absorbance of the solutions of Fe$^{3+}$/TIP capsules were characterized in various pH buffer solution by a UV-Vis Spectrophotometer (NanoDrop OneC, Thermo Scientific, USA). Briefly, 3 mL of capsule suspensions (~$1.0\times10^7$ capsules/mL) in 20 mM KCl-HCl buffer (pH 1.0 and 2.0), citrate buffer (pH 3.0), acetate buffer (pH 4.0), phosphate buffer (pH 5.0 and 6.0), MOPS buffer (pH 7.4), and tris-HCl buffer (pH 8.5) were prepared in quartz cuvettes.

1.6.9 Conformation and permeability of capsules
Conformation of capsules were confirmed by an optical microscope (Eclipse TE2000, Nikon). Different types of (Fe$^{3+}$/TIP)$_3$ capsules derived from various kinds of polymers were applied to examine permeability. Typically, (Fe$^{3+}$/TIP)$_3$ capsules (~$2.0\times10^7$ capsules/mL) were mixed with an equal volume of FITC-dextran solution (1 mg/mL). Fluorescent images of the capsules were taken with a confocal laser scanning microscope (CLSM, FV-1200, Olympus) within 10 min after incubation of the capsules with FITC-dextran solutions for 15 min in the dark. Capsules with interiors of similar fluorescence intensity as the outer environment were considered to be permeable, whereas dark interiors were considered to be impermeable. At least 500 capsules were counted.

1.6.10 Cytotoxicity assay
Cytotoxicity assay was conducted on mouse fibroblast cells in vitro. L929 cells were cultured in DMEM containing 1% (v/v) penicillin-streptomycin and 10% (v/v) of fetal bovine serum, and incubated in a humidified atmosphere containing 5% CO$_2$ at 37 °C. The cells were seeded at a density of $0.05\times10^6$ cells/mL in 24-well plates coated with Fe$^{3+}$/TIP films, in 2 mL culture media for 48 h. Control groups were untreated plates, and plates coated with Fe$^{3+}$/TA films.

To prepare Fe$^{3+}$/TIP and Fe$^{3+}$/TA films on culture plates, 10 μL of TIP (gallol/catechol=1:2, $M_n$ ~4 kDa) or TA solution (40 mg/mL, in ethanol, filter-sterilized) and 10 μL FeCl$_3$·6H$_2$O solution (10 mg/mL, in MQ water, filter-sterilized) were added into a 24-well plate containing 1 mL MQ water in each well. Then 500 μL of MOPS buffer (20 mM, pH 7.4, filter-sterilized) was added into suspension to raise the pH. The suspension was
mixed vigorously by patting for 1 min immediately after the individual additions. Then 10 min incubation at room temperature was done to stabilize the coating layers. Culture plates were washed with MQ water three times to remove excess complexes. The coating process was repeated three times.

Cell viability was determined by trypan blue dye exclusion test and an MTT assay. For the trypan blue dye exclusion test, cells were trypsinized by Trypsin-EDTA (0.25%), collected by centrifugation at 1000 rpm for 3 min and resuspended in 4 mL culture media. 50 μL of cell suspension was mixed with the same volume of trypan blue solution (0.4%). After that, an aliquot of the trypan blue/cell mixture was placed into a hemocytometer, and the number of viable cells (unstained) and dead cells (stained) were manually counted under an optical microscope. The cell viability was calculated by the ratio of the number of viable cells to the total numbers of cells (Fig. S21a).

For the MTT assay, cells were incubated in a 1 mL MTT solution (5 mg/mL in PBS) at 37 °C in a CO₂ incubator for 4 h. After incubation, the solutions were discarded. 2 mL of DMSO was added to each well and stirred gently until all the formazan crystals were dissolved. The absorbance of each sample was read at 540 nm by a UV-vis spectrophotometer. The cell viability was calculated by the ratio of the absorbance at 540 nm of each sample to a blank control (Fig. S21b).
2. Supplementary figures

Figure S1. $^1$H-NMR spectrum of Glu-Br$_5$. (CDCl$_3$).

Figure S2. $^{13}$C-NMR spectrum of Glu-Br$_5$. (CDCl$_3$).

Figure S3. $^1$H-NMR spectrum of Glu-TEMPO$_5$. (CDCl$_3$).
Figure S4. $^{13}$C-NMR spectrum of Glu-TEMPO$_3$ (CDCl$_3$).

Figure S5. $^1$H-NMR spectrum of DMMS (DMSO).

Figure S6. $^1$H-NMR spectrum of TMMS (CDCl$_3$).
Figure S7. $^1$H-NMR spectrum and $^{13}$C-NMR spectrum of TIP (Catechol: gallol=2:1, 6.8 kDa) before deprotection (CDCl$_3$).
Figure S8. $^1$H-NMR and $^{13}$C-NMR spectrum of TIP (Catechol: gallol=1:1, 6.0 kDa) before deprotection (CDCl$_3$).
Figure S9. $^1$H-NMR and $^{13}$C-NMR spectrum of TIP (Catechol: gallol=1:2, 7.0 kDa) before deprotection (CDCl$_3$).
Figure S10. $^1$H-NMR and $^{13}$C-NMR spectrum of TIP (Catechol: gallol=1:0, 3.0 kDa) before deprotection (CDCl$_3$).
Figure S11. $^1$H-NMR and $^{13}$C-NMR spectrum of TIP (Catechol: gallol=0:1, 7.0 kDa) before deprotection (CDCl$_3$).
Figure S9. $^{13}$C-NMR spectrum of TIP after deprotection (Catechol: Gallol=1:1, 6.5 kDa) (500 MHz, MeOD).

Figure S12. $^1$H-NMR (DMSO-$d_6$) and $^{13}$C-NMR spectrum (MeOD) of TIP (Catechol: gallol=2:1, 6.8 kDa) after deprotection.
Figure S13. $^1$H-NMR (DMSO-$d_6$) and $^{13}$C-NMR spectrum (MeOD) of TIP (Catechol: gallol=1:1, 6.0 kDa) after deprotection.
Figure S14. $^1$H-NMR (DMSO-$d_6$) and $^{13}$C-NMR spectrum (MeOD) of TIP (Catechol: gallol=1:2, 7.0 kDa) after deprotection.
Figure S15. $^1$H-NMR (DMSO-d$_6$) and $^{13}$C-NMR spectrum (MeOD) of TIP (Catechol: gallol=1:0, 3.0 kDa) after deprotection.
Figure S16. $^{1}$H-NMR (DMSO-$d_6$) and $^{13}$C-NMR spectrum (MeOD) of TIP (Catechol: gallol=0:1, 7.0 kDa) after deprotection.
Figure S17. Adsorbed amount of TIP-based and TA-based MPN coating on various QCM chip surfaces.

Figure S18. SEM picture of PS particles synthesized in this research.
Figure S19. Conformation of different (TIPs/Fe$^{3+}$)$_3$ and (LP/Fe$^{3+}$)$_3$ capsules.

Figure S20. UV-Vis spectra of capsules in different pH.
Figure S21. Cell viability tests of MPN films: (a) Trypan blue dye exclusion test (b) MTT assay.

Figure S22. Microscope images of different TIPs/Fe\textsuperscript{3+} conjugations.
### 3. Supplementary tables

**Table S1.** Polymers used in this research.

<table>
<thead>
<tr>
<th>Feed</th>
<th>Obtained</th>
<th>Feed</th>
<th>Obtained</th>
<th>Feed</th>
<th>Obtained</th>
<th>Feed</th>
<th>Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gallol (mol%)</td>
<td>Catechol (mol%)</td>
<td>Gallol: Catechol : Initiator (mmol)</td>
<td>Gallol[a] (mol%)</td>
<td>Catechol[a] (mol%)</td>
<td>$M_n$ (x10^3)</td>
<td>PDI[b]</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>3: 0: 0.01</td>
<td>100</td>
<td>0</td>
<td>3</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>33</td>
<td>2: 1: 0.01</td>
<td>63</td>
<td>37</td>
<td>3</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>1.5: 1.5: 0.01</td>
<td>48</td>
<td>52</td>
<td>3</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>67</td>
<td>1: 2: 0.01</td>
<td>35</td>
<td>65</td>
<td>3</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0: 3: 0.005</td>
<td>0</td>
<td>100</td>
<td>7</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>3: 0: 0.15</td>
<td>100</td>
<td>0</td>
<td>4</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>33</td>
<td>2: 1: 0.15</td>
<td>66</td>
<td>34</td>
<td>3</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>1.5: 1.5: 0.15</td>
<td>44</td>
<td>56</td>
<td>3</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>67</td>
<td>1: 2: 0.15</td>
<td>36</td>
<td>64</td>
<td>3</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0: 3: 0.15</td>
<td>0</td>
<td>100</td>
<td>4</td>
<td>2.3</td>
<td></td>
</tr>
</tbody>
</table>

[a] Determined by NMR  
[b] Determined by GPC

**Table S2.** Elemental compositions of Fe in capsules measured by EDS

<table>
<thead>
<tr>
<th>Type of TIP used (Catechol: Gallol)</th>
<th>Fe compositions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>1:1</td>
</tr>
<tr>
<td>Fe compositions (%)</td>
<td>2.08 ± 0.8</td>
</tr>
</tbody>
</table>

S-26
Table S3. Thicknesses of capsules measured by AFM.

<table>
<thead>
<tr>
<th>Type of TIP used (Catechol: Gallol and $M_a$)</th>
<th>2:1, 3-4 kDa</th>
<th>1:1, 3-4 kDa</th>
<th>1:2, 3-4 kDa</th>
<th>1:1, 6-8 kDa</th>
<th>1:1, 10-12 kDa</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (nm)</td>
<td>14.50 ± 0.12</td>
<td>12.44 ± 0.07</td>
<td>13.73 ± 0.10</td>
<td>14.74 ± 0.20</td>
<td>13.9 ± 0.06</td>
</tr>
</tbody>
</table>
4. Supplementary references