

Supporting Information

Influence of Ionic Strength on the Deposition of Metal–Phenolic Networks

Junling Guo,^{†,‡,⊥} Joseph J. Richardson,^{†,‡,§,⊥} Quinn A. Besford,^{†,‡} Andrew J.

Christofferson,[‡] Yunlu Dai,^{†,‡} Chien W. Ong,[‡] Blaise L. Tardy,[‡] Kang Liang,^{§,#} Gwan H.

Choi,[∇] Jiwei Cui,^{†,‡} Pil J. Yoo,[∇] Irene Yarovsky,[‡] and Frank Caruso^{,†,‡}*

[†]ARC Centre of Excellence in Convergent Bio-Nano Science and Technology, The
University of Melbourne, Parkville, Victoria 3010, Australia

[‡]Department of Chemical Engineering, The University of Melbourne, Parkville,
Victoria 3010, Australia

[§]CSIRO Manufacturing Flagship, CSIRO, Clayton South, Victoria 3169, Australia

[‡]School of Engineering, RMIT University, GPO Box 2476, Melbourne, Victoria 3001,
Australia

[#]School of Chemical Engineering and Graduate School of Biomedical Engineering,
The University of New South Wales, Sydney, NSW 2052, Australia

[∇]School of Chemical Engineering and SKKU Advanced Institute of Nanotechnology
(SAINT), Sungkyunkwan University (SKKU), Suwon 16419, Republic of Korea

[⊥]These authors contributed equally to this work

*Corresponding author. E-mail: fcaruso@unimelb.edu.au

Instruments and Softwares

Differential interference contrast images were captured on an inverted Olympus IX71 microscope. Transmission electron microscopy (TEM) images were obtained using a FEI Tecnai TF20 microscope at an operating voltage of 200 kV. UV-Visible spectroscopy measurements were conducted on an Infinite M200 PRO microplate reader (Tecan Group, Switzerland).

Atomic Force Microscope (AFM) Measurements

For the AFM experiments, capsule suspensions (2.0 μL) were allowed to air-dry on Piranha cleaned silicon wafers (*Caution! Piranha solution is highly oxidizing and corrosive! Extreme care should be taken during preparation and use*). The AFM experiments were carried out with a JPK NanoWizard II BioAFM. Typical scans were recorded in intermittent contact mode with MikroMasch silicon cantilevers (NSC/CSC). The film thickness of the capsules was analyzed using JPK SPM image processing software (version V.3.3.32).

Small-Angle X-Ray Scattering (SAXS) Analysis

Synchrotron SAXS data were collected at the SAXS beamline of the Australian Synchrotron facility. Capillaries were loaded with aqueous samples. The samples were investigated using the SAXS/WAXS beamline (16 keV, 900 mm camera length using Pilatus 1M and 200k detectors, transmission mode). Scatterbrain software was used for analysis.

Optical Waveguide Light-Mode Spectroscopy (OWLS)

OWLS measurements were performed on an OWLS 210 instrument equipped with a syringe pump (MicroVacuum, Budapest, Hungary) and a Biosense 2.6 software. Measurements were performed on silica-coated sensor chips (cleaned with Piranha solution), immersed in the required NaCl aqueous solution. The system was allowed to equilibrate until the signal stabilized (i.e. $dm/dt < 10^{-8}$, where m and t denote mass and time, respectively). TA was dissolved in an Eppendorf tube at the desired salt concentration, and FeCl_3 was subsequently added. The tube was rapidly vortexed before injection of the suspension into the OWLS instrument at a flow rate of 20 $\mu\text{L min}^{-1}$. The injected suspension concentrations corresponded to $[\text{TA}] = [\text{FeCl}_3] = 0.23$ mM. The complexes were flowed across the sensor chip to generate the film. Excess complex was washed off under a constant flow of solvent. Measurements progressed until the final adsorbed mass signal stabilized. This mass was used for subsequent analysis. The sensor chips were then checked for “clean” film formation via AFM experiments, which revealed little excess complex on the films.

Table S1. Average values, standard deviations (SDs), and 95% confidence intervals (CIs) for the simulation results of Fe^{III}-TA₃ monomer systems in pure water and 2 M NaCl

	Pure water	SD	95% CI	2 M NaCl	SD	95% CI
SASA (Å ²)	3967	275	5	3942	238	5
R_g (Å)	13.1	1.4	0.01	13.2	1.2	0.01
End-to-end distance (Å)	46.5	5.5	0.1	47.2	4.1	0.1
Fe ^{III} -TA ₃ intramolecular H-bonds (%)	10	3	0.1	10	3	0.06
Fe ^{III} -TA ₃ ···water H-bonds (%)	125	7	0.1	110	8	0.2
Aromatic ring contacts	15	3	0.20	15	3	0.17
RMSF (Å)	18.3	5	0.16	15.2	4	0.12
Water contacts (4 Å radius)	281	20	0.39	276	18	0.35
Sodium contacts (4 Å radius)	n/a	n/a	n/a	12	3	0.05
Chloride contacts (4 Å radius)	n/a	n/a	n/a	3	2	0.03

SASA, solvent-accessible surface area; R_g , radius of gyration; RMSF, root mean square fluctuation; n/a, not applicable.

Table S2. Average values, standard deviations (SDs), and 95% confidence intervals (CIs) for the simulation results of Fe^{III}-TA₃ dimer systems in pure water and 2 M NaCl

	Pure water	SD	95% CI	2 M NaCl	SD	95% CI
SASA (Å ²)	6771	454	7	6917	324	5
Contact area (Å ²)	850	208	3	767	245	4
R_g (Å)	16.4	1.8	0.01	17.3	1.9	0.02
End-to-end distance (Å)	58.0	6.6	0.1	62.6	9.3	0.15
Fe ^{III} -TA ₃ intermolecular H-bonds (%)	9	2	0.04	8	2	0.03
Fe ^{III} -TA ₃ ···water H-bonds (%)	116	6	0.1	105	5	0.1
Aromatic ring contacts	9	3	0.17	8	3	0.15
RMSF (Å)	16.4	5	0.09	14.9	4	0.07
Water contacts (4 Å radius)	486	32	0.52	486	24	0.38
Sodium contacts (4 Å radius)	n/a	n/a	n/a	22	3	0.06
Chloride contacts (4 Å radius)	n/a	n/a	n/a	6	2	0.04

SASA, solvent-accessible surface area; R_g , radius of gyration; RMSF, root mean square fluctuation; n/a, not applicable.

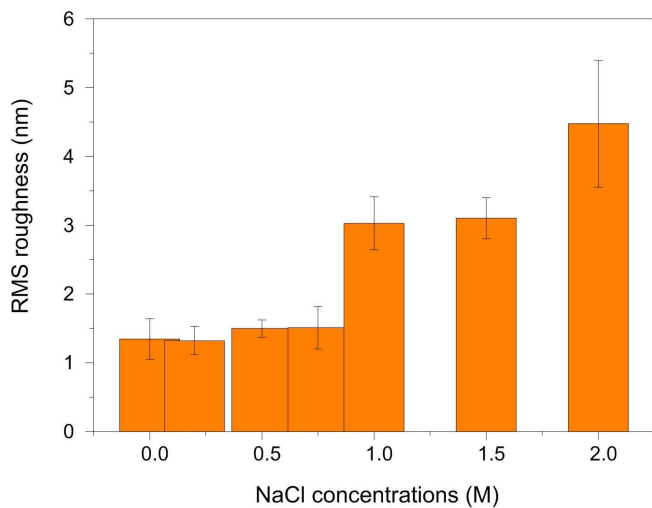


Figure S1. Root mean square (RMS) roughness of the Fe^{III} -TA film thickness prepared at different NaCl concentrations. When the NaCl concentration was less than 1.0 M, the RMS roughness values were ~ 1.5 nm, which was indicative of molecularly smooth Fe^{III} -TA films. The RMS roughness of the Fe^{III} -TA film increased when the [NaCl] increased from 1.0 to 2.0 M, suggesting an increase in film roughness and inhomogeneity.

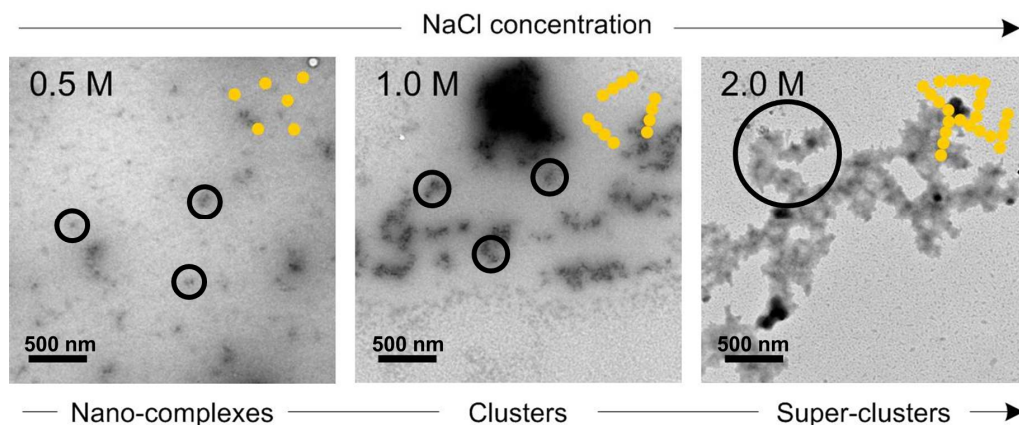


Figure S2. TEM images of the Fe^{III} -TA complexes formed at different NaCl concentrations. At lower salt concentrations, the nano-complexes were highly dispersed in solution and less than ~ 100 nm in size. When the NaCl concentration was increased, the Fe^{III} -TA complexes agglomerated and formed clusters of ~ 200 nm in size. When the NaCl concentration was increased further, the Fe^{III} -TA clusters joined together to form larger clusters (super clusters) of > 800 nm in size. Note that these observations were based on air-dried samples and so some conformation changes between the solvated complexes are expected. The yellow insets are schematic representations of the MPNs obtained at different salt concentrations. The MPNs in the samples are highlighted by the black circles.

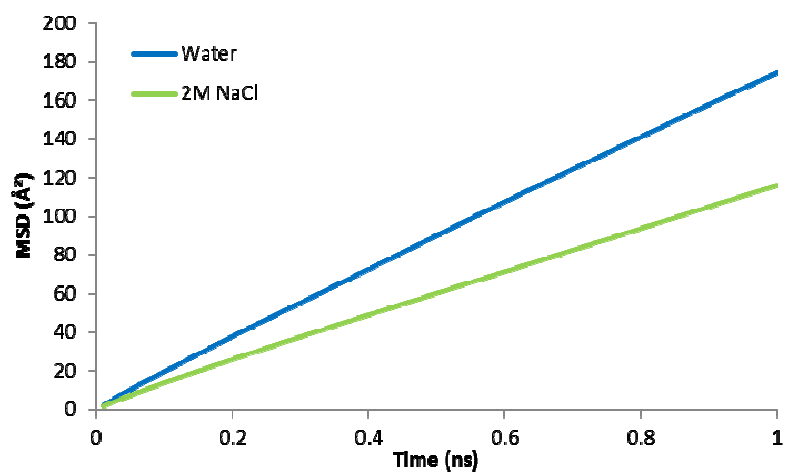


Figure S3. Mean squared displacement as a function of time of the Fe^{III}-TA₃ complex in pure water (0 M NaCl) and 2 M NaCl.