Final Report: Infinite Coordination Polymer Particles from Polymeric Coordinating Precursors

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Major Goals: Infinite coordination polymers (ICPs) represent a highly tailorable class of inorganic materials that can be reversibly assembled and disassembled in response to specific chemical or physical stimuli. ICP particles are typically synthesized via a modular approach, for which multidentate organic ligands are linked through cationic metal nodes to form extended polymeric structures. The highly modular synthesis and stimuli-responsive nature of ICPs enable their chemical composition and physical morphology to be tailored for a wide range of applications including those of interest to the ARO, such as small molecule detection, catalysis, drug delivery, gas storage, and chemical separations. Many such applications depend on the ability to predictably tune the size and shape of ICP particles and, as a result, control their physical properties such as surface area and porosity. The major goals of this project were to develop new approaches for the controlled synthesis of ICPs. In particular, we aimed to access ICP particles further along the particle condensation pathway via the assembly of soluble and stimuli-responsive polymer precursors. Broadly, the work discussed herein allowed us to explore and develop novel polymers that undergo predictable conformational and/or chemical changes in response to specific external stimuli, while targeting applications in nanoparticle technology.

The major goals of this project were as follows:

   Our initial work focused on developing strategies to synthesize and modify stimuli-responsive polymeric precursors that could be exploited as nucleation seeds for ICP particles. In this work, we planned to utilize individual polymeric chains as the sole constituent of the ICP particle. The targets were heterobimetallic coordination polymers, which possess two types of metal centers—a stimuli-responsive metal center with multiple coordination modes that is responsible for controlling the polymer backbone rigidity and a structural metal center that is used as a stable linkage for coordination-based polymerization. We expected that properties of the precursor polymer, such as its dispersity, would affect the size distribution and overall morphology of the resulting ICP particles. The use of polymer chains with coordinating units that display high specificity for particular metal cations allowed us to focus on dramatically improving the physical properties of ICP particles, as well as enabling novel capabilities and broadening their applicability.

2. Synthesis of Homopolymeric Precursors
   To synthesize and modify polymeric precursors that are chemically responsive and could be exploited as monodisperse ICP seeds, we aimed to develop synthetic strategies for creating such building blocks from commercial sources and to discover the optimal conditions for controlling ICP particle size and morphology. Achieving this goal required gaining a fundamental understanding of intra-polymer interactions and polymer
functionalization methodologies. We also sought to investigate the effects these novel building-blocks had on the
growth and morphology of ICP particles, for example, by altering the degree of substitution, association/dissociation
kinetics, and molecular rigidity. Ligands for hard metal ions were of interest as well, namely catechols and
terpyridines, which could be accessed via established synthetic methods and form exceptionally strong
coordination complexes with iron. Furthermore, chain length, degree of ligand substitution, coordination
stoichiometry, and the addition of monodentate coordinating ligands were synthetic variables that allowed us to
identify the optimal conditions for constructing ICP particles with controlled dispersity whose morphologies could be
affected via external stimuli.

3. Synthesis of ICP Particles from Homopolymeric Ligands
After the polymers were synthesized and characterized, we sought to examine their chemical behavior in the
presence of coordinating metal ions. Ultimately, we sought to determine the optimal degree of substitution and
precursor molecular weight to give the best control over the size and shape of the resulting particles. Variables that
we sought to study, upon the introduction of metal cations to polymer precursor solutions, included precursor
dispersity, stoichiometry, concentration, temperature, solvent type, and mixing rates. In addition, the precursor’s
metal-ligand binding strengths could be tuned to control the kinetic stability of the resultant ICPs, a common
strategy for the formation of supramolecular metal-ligand assemblies under thermodynamic control. Conversely,
the assembly could be performed in the presence of weakly coordinating metal cations, such as zinc (II), to vary the
kinetics of complexation of the more stable iron, palladium, or platinum ions. Finally, the condensed polymer
particles could be used as seeds for further ICP growth upon subsequent addition of chelating ligands in the
monomeric state.

4. Synthesis of Block Copolymer Precursors
A fundamental advantage arising from synthesizing ICP particles from polymeric precursors is the ability to
introduce different coordinating units within a single polymer chain and thus rationally control the composition of the
ensuing particles. The introduction of different coordinating groups and metal centers within a single ICP particle
using monomeric precursors in a controllable or programmable manner has so far not been possible due to the
dynamic nature of the particle formation process. This becomes particularly synthetically demanding when the
desired mixed-composition particles are built with metal complexes of different solubility. Thus, it is highly desirable
to create block copolymers with multiple ligands that undergo orthogonal coordination chemistry and act as ICP
precursors. We hypothesized that this would allow for the selective collapsing of a given segment of the polymer
via sequential or parallel addition of metal cation, providing access to highly advanced, mixed-composition ICP
particles. In the case of ICP cores composed of multiple polymeric seeds, sequential assembly would provide a
venue towards segregated or core-shell structures, whereas ICP particles comprised of a single polymer chain
would give way to Janus particles. We were interested in studying the selective formation of complex ICP particle
structures by adding hard and soft metal cations that display different affinities for different polymer blocks in order
to understand the stimuli-responsive behavior of mixed-composition ICPs.

5. Synthesis of ICP Nanoparticles from Block Copolymer Ligands
With a range of chelating diblock copolymers in hand, we aimed to study the morphologies that can be accessed
using these novel ICP particle precursors. We sought to focus on varying the manner of addition of the coordinating
cations to affect the mode in which the polymer precursors collapse into particles (i.e. sequential versus concerted
addition of two different metal cations). The approach proposed instead allowed for the partial disassembly of the
ICP particle while preserving the overall integrity of the construct. In addition, the ability to disassemble a portion of
the particle while simultaneously condensing another portion allowed us to chemically toggle the surface chemistry
of ICPs in a reversible fashion. This capability is particularly beneficial in tuning particle porosity, enabling
applications in energy storage and catalysis.

Accomplishments: Major Activities. Our efforts towards the project goals focused on developing coordination
compounds that can act as precursors for the assembly of novel ICPs. Specifically, we developed stimuli-
responsive coordination compounds for incorporation into ICP particles. Being part of the polymer backbone allow
these structures to be regulated at the molecular level, thereby enabling the overall properties of the material to be
impacted via application of external stimuli. Along with developing novel coordination compound precursors, we
focused on using chemical and physical means to control the size (from nanometer to micron scale) and uniformity
of ICP particles, both of which play important roles in influencing the properties and applications of ICP particles.
Lastly, we developed a generalizable approach to controllably functionalize ICP particles with a chemically
programmable ligand, such as DNA. These surface-functionalized ICP particles were then utilized for constructing
hybrid materials with control over the stoichiometry, shape, and composition of the resulting assembly.
Significant Results. We developed a new class of architectures that have yet to be explored in the context of ICP particles; these particles are made from Weak-Link Approach (WLA) building blocks. WLA complexes are supramolecular coordination compounds that are assembled from transition metal precursors (typically, d8 metal centers) and hemilabile ligands. They are defined by open (flexible) and closed (rigid) structural states that can be interconverted through the introduction or removal of chemical effectors (Fig. 1). Although they have not been studied in the context of polymeric systems and ICPs, they could be valuable modalities for modulating the chemical and physical properties of such structures post-synthetically.

Synthesize stimuli-responsive ICP particle precursors.
We synthesized a novel tritopic ligand with three coordinating moieties in series: a terpyridine (Terpy) moiety covalently attached to a thioether followed by a diphenyl phosphine, referred to as “P,S-Terpy” (Fig. 1A). When one equivalent of PtII was added to two equivalents of P,S-Terpy, a rigid square planar complex was formed with the PtII bound to two thioether and two phosphine ligands, leaving two pendant terpyridine units for subsequent polymerization (referred to as 2-Pt-Closed, Fig. 2A). We demonstrated the stimuli-responsive properties of these ICP particle precursors by adding coordinating chloride ions to displace the chelating thioether ligands and generate a flexible and roughly linear bis(terpyridine) ligand (referred to as 2-Pt-Open).

Control the size, dispersity and morphology of ICP particles.
With stimuli-responsive ICP particle precursors in hand, we assembled these soluble precursors into extended polymeric structures (Fig. 3). When Fell cations were added to 2-Pt-Open, a high molecular weight coordination polymer seed formed, whereas the addition of Fell cations to 2-Pt-Closed resulted in the formation of small macrocyclic seeds. Additionally, all experiments were performed with PdII instead of PtII which gave similar results in the open state. ICPs were then prepared under different conditions by the slow diffusion of diethyl ether into the ICP precursor solution, and their sizes and morphologies were characterized by Scanning Transmission Electron Microscopy (Fig. 3). Moreover, a simple strategy was developed to control the ICP particle size and dispersity, with less concentrated precursor solutions giving smaller, more uniform ICP particles (Fig. 4).

Synthesize stimuli-responsive ICP crystalline networks containing WLA subunits.
To incorporate stimuli-responsive building blocks into 3D ICP networks, we developed linear-actuating WLA motifs that can be utilized as pillar ligands, in hopes that the networks would undergo 1D expansion and contraction when the WLA-pillar ligands are toggled between the open and closed states (Fig. 5). A linear-actuating model system was developed with bis(NHC)PdII (NHC = N-heterocyclic carbene) complexes tethered with thioaryl groups (Fig. 6). The two NHC ligands in the bis(NHC)PdII complexes adopt a trans conformation to minimize steric hindrance; therefore, we hypothesized that the dynamically addressable binding of the thioaryl moieties to the metal center would result in an one-dimensional change in geometry when the complexes are switched between the open and closed states. Based on the solid-state structures of these complexes, a 9 Å change in length measured upon switching between the two states (Fig. 6b and c). Therefore, this group of complexes was utilized for the synthesis of WLA-pillar ligands with pyridyl moieties (Fig. 7), which could potentially function as stimuli-responsive building blocks to generate ICP materials that would dynamically respond to external stimuli.

Devis strategies for functionalizing ICP particles with oligonucleotides for multi-component assembly.
We developed a general strategy to synthesize uniform, colloidal stable ICP particles and functionalize them with oligonucleotides (Fig. 8). Using terminal phosphate-modified oligonucleotides, we chemically addressed the coordinatively unsaturated metal sites on the ICP particle surface. Solid-state nuclear magnetic resonance spectroscopy and powder X-ray diffraction confirmed that the DNA-functionalization occurs by metal–phosphate coordination and that the structure and porosity of the ICP particles are preserved post-modification (Fig. 9). This approach was extended to ICPs featuring different metal nodes (Zr, Fe, Cr, Al) and organic linkers, illustrating the generality of this strategy. By taking advantage of the specific base-pair interactions of DNA, distinct ICP particle–inorganic particle clusters were synthesized with precise control over stoichiometry, shape and composition (Fig. 10), providing a route towards programmable, multi-component ICP particles with novel physical and chemical properties.
Key Outcomes. We identified three major outcomes of this work: 1) A new family of responsive ICP particles was synthesized by the assembly of WLA-based building blocks. Chloride ions were used to interconvert these building blocks between rigid closed and flexible semi-open states. The changes in molecular geometry manifested as morphological changes in the ICP particles, which may have utility in chemical sensing applications.

2) The study on the linear-actuating model system provided insights into the design of the WLA-pillar ligands. Metal binding pyridyl moieties were incorporated into the WLA structures, and the closed and open states were successfully accessed. The development of these linear-actuating WLA-pillar ligands laid the foundation for the development of sophisticated, stimuli-responsive networks capable of undergoing crystalline transitions via addition or abstraction of small molecule stimuli.

3) A general approach to the synthesis of DNA-modified ICPs, independent of the choice of organic linkers and applicable to a variety of metal clusters, was developed. The functionalized ICP particles are colloidally stable and can be assembled with complementary DNA-modified nanoparticles, providing a route to multi-component nanoparticle assembly with tunable properties that may be useful in biology, catalysis, optics, and beyond.

Training Opportunities: As a direct result of the support provided by this grant, extensive and significant training, professional development, and mentoring opportunities have been given to a diverse set of emerging scientists in the Mirkin group. All researchers involved in this project meet with Prof. Mirkin on a regular basis to discuss research progress, results, and future directions both inside and beyond the laboratory. Students involved in the project all received training in advanced concepts in supramolecular chemistry, including coordination chemistry and organometallic chemistry, as well as training in advanced characterization techniques such as multinuclear NMR spectroscopy, mass spectroscopy, x-ray crystallography, electron microscopy, and infrared spectroscopy. All postdoctoral researchers, graduate students, and undergraduate researchers presented their progress regularly in subgroup and group meetings, and thus received feedback from fellow researchers. Additionally, young researchers have participated in preparing manuscripts for publication based on the work supported by this grant, thus this grant supported another important aspect for the training and development of future scientists. Student activities also included presentation of this project in venues such as conferences, seminars, and workshops. This provides invaluable opportunities for young researchers to practice communicating their results to a wider scope of audience.
Results Dissemination: The research made possible by this grant will greatly impact a broad range of fields of scientific and chemical research, including catalysis, energy, and bioinorganic chemistry. These stimuli-responsive systems have great potential for sensing chemical analytes and, subsequently, transmitting or reporting a readily measurable signal. Therefore, we expect powerful repercussions across different scientific disciplines. The knowledge gained has enabled us to make great strides towards our goals. The results of this research were disseminated through publications and presentations, both nationally and internationally. For the purpose of enhancing public understanding and increasing interest in learning and careers in science and technology, Mirkin group researchers actively participated in various outreach programs. The students funded by this grant participated in the following programs:

1. Jugando con la Ciencia (JCLC — translates to “Playing with Science”): JCLC is a program geared towards teaching science to Latino and minority students who speak Spanish. Mirkin students helped develop science lessons to inspire the next generation of STEM leaders, and organize and implement community outreach events geared towards young students with a goal to inspire them as scientists.

2. Northwestern’s Helix Magazine (produced by Science in Society and NU): Northwestern’s Helix magazine is an online magazine that works to bridge the gap between the community and university. Mirkin students wrote about their research as well as other recent developments in the scientific community at a level appropriate for general interest.

3. Northwestern’s Science in the Classroom (SITC): SITC is the flagship service program for Northwestern Chemistry’s Phi Lambda Upsilon (PLU). NU SITC teamed with eight 3rd and 4th grade classes at Chicago’s Stephen K. Hayt School to provide monthly hands-on science experiences. Mirkin students taught basic concepts in chemistry to these students.

4. National Society for Advancement of Hispanics/Chicanos and Native Americans in Science is a society of scientists dedicated to fostering the success of Hispanic/Chicano and Native American scientists—from college students to professionals—to attain advanced degrees, careers, and positions of leadership in science. Mirkin students helped organize outreach events geared towards promoting minorities in science.

5. Science Club and Junior Science Club, Science in Society, Northwestern: These are afterschool programs held in Chicago public schools that aim to promote interest in science and serve underprivileged youth in Chicago. Mirkin students taught lessons, designed fun scientific experiments, and mentored youth.

6. Mentorship Opportunities for Research Engagement: Mirkin students helped guide high school students through a science project.

Prof. Chad Mirkin, Invited talks:

23. The University of Austin Department of Chemistry, Austin, TX, “Combinatorial Nanoscience: Expanding the Materials Genome” (2018).

Student Presentations

Honors and Awards: Chad A. Mirkin
2018 Ralph N. Adams Award in Bioanalytical Chemistry
2018 Harrison Howe Award
2018 Remsen Award, Johns Hopkins and Maryland Section of the American Chemical Society
2017 Elected Foreign Member of the Chinese Academy of Sciences

Andrea D’Aquino
2018 P.E.O. Scholar Award
2017 McBride Award

Yuan Liu
2017 Ryan fellowship, International Institute of Nanotechnology

Shunzhi Wang
2017 PPG 4th Year fellowship

Protocol Activity Status:

PARTICIPANTS:

Participant Type: PD/PI
Participant: Chad Mirkin
Person Months Worked: 1.00
Funding Support:
Project Contribution: 
International Collaboration: 
International Travel: 
National Academy Member: Y
Other Collaborators: 

Participant Type: Graduate Student (research assistant)
Participant: Andrea D’Aquino
Person Months Worked: 8.00
Funding Support:
Project Contribution: 
International Collaboration: 
International Travel: 
National Academy Member: N
Other Collaborators: 

Participant Type: Graduate Student (research assistant)
Participant: Ho Fung Cheng
Person Months Worked: 4.00
Funding Support:
Project Contribution: 
International Collaboration: 
International Travel: 
National Academy Member: N
Other Collaborators: 

Participant Type: Graduate Student (research assistant)
Participant: Yuan Liu
Person Months Worked: 9.00
Funding Support:
Project Contribution: 
International Collaboration: 
International Travel: 
National Academy Member: N
Other Collaborators: 

Participant Type: Graduate Student (research assistant)
Participant: Shunzhi Wang
Person Months Worked: 6.00
Funding Support:
Project Contribution: 
International Collaboration: 
International Travel: 
National Academy Member: N
Other Collaborators: 

Other Collaborators:
## CONFERENCE PAPERS:

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<td><strong>Conference Name:</strong> Emerson Center Lectureship Award Symposium</td>
<td><strong>Authors:</strong> Chad Mirkin</td>
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<td>Date Received: 30-Aug-2016 Conference Date: 05-Oct-2015 Date Published: 30-Aug-2016</td>
<td>Acknowledged Federal Support: Y</td>
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<td><strong>Conference Location:</strong> Atlanta, GA <strong>Paper Title:</strong> Nanotechnology: Revolutionary Force behind Today’s Advances in Biology and Medicine</td>
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<td><strong>Conference Name:</strong> Dan David Nanotechnology: The Magic of Small Things Symposium</td>
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<td>Date Received: 30-Aug-2016 Conference Date: 23-May-2016 Date Published: 23-May-2016</td>
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<td><strong>Conference Location:</strong> Tel Aviv University, Israel <strong>Paper Title:</strong> SNAs: Unlocking the Source Code for Programmable Materials</td>
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<td><strong>Conference Location:</strong> Brunswick, ME <strong>Paper Title:</strong> Nanotechnology: A Small World with Big Potential</td>
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<td><strong>Conference Name:</strong> Illumina Scientific Advisory Board Meeting</td>
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<td><strong>Conference Location:</strong> San Diego, CA <strong>Paper Title:</strong> The Convergence of Nanoscience with Biology and Medicine</td>
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<td><strong>Conference Location:</strong> San Diego, CA <strong>Paper Title:</strong> Pluripotent nanoparticles with programmable and responsive DNA bonds</td>
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<td><strong>Conference Location:</strong> Dallas, TX <strong>Paper Title:</strong> Realizing the Promise of Nanomedicine</td>
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Conference Name: Young Investigator Network Lecture Series, Karlsruhe Institute of Technology  
Date Received: 30-Aug-2016  
Conference Location: Karlsruhe, Germany  
Paper Title: The Convergence of Nanoscience and Nanomedicine: New Approaches for Studying, Tracking, and Treating Disease  
Authors: Chad Mirkin  
Acknowledged Federal Support: Y

Publication Type: Conference Paper or Presentation  
Conference Name: Gordon Research Conference – Bioinspired materials  
Date Received: 30-Aug-2016  
Conference Location: Les Diablerets, Switzerland  
Paper Title: i. Surface-Specific Functionalization of Metal-Organic Framework Nanoparticles  
Authors: Shunzhi Wang  
Acknowledged Federal Support: Y

Publication Type: Conference Paper or Presentation  
Conference Name: National Science Foundation Mathematical and Physical Sciences Directorate Poster Session  
Date Received: 30-Aug-2016  
Conference Location: Evanston, IL  
Paper Title: ii. Stimuli-Responsive Supramolecular Assemblies via the Weak-Link Approach  
Authors: Andrea d’Aquino  
Acknowledged Federal Support: Y

Publication Type: Conference Paper or Presentation  
Conference Name: ACS Spring Conference  
Date Received: 30-Aug-2016  
Conference Location: New Orleans, LA  
Paper Title: General and Direct Method for Preparing Oligonucleotide-Functionalized Metal-Organic Framework Nanoparticles  
Authors: Shunzhi Wang, Chad Mirkin  
Acknowledged Federal Support: Y

Publication Type: Conference Paper or Presentation  
Conference Name: American Chemical Society Spring Meeting  
Date Received: 30-Aug-2016  
Conference Location: New Orleans, LA  
Paper Title: Allosteric regulation of a four-state WFA macrocycle  
Authors: 38. Andrea d’Aquino, Ho Cheng, Joaquin Barroso, Zachary Kean, Jose E Mendez, C. Michael McGuirk  
Acknowledged Federal Support: Y

Publication Type: Conference Paper or Presentation  
Conference Name: Gordon research conference: Multifunctional materials and structures,  
Date Received: 30-Aug-2016  
Conference Location: Ventura, CA  
Paper Title: General and Direct Method for Preparing Oligonucleotide-Functionalized Metal-Organic Framework Nanoparticles  
Authors: Shunzhi Wang, Chad Mirkin  
Acknowledged Federal Support: Y
Figure 1. WLA complexes (counterions omitted for clarity) containing hemilabile coordinating motifs can be toggled between an open (A) and a closed state (B). Coordination-based assembly of these subunits results in extended structures (C & D).
Figure 2. (A) Building blocks used in the synthesis of ICP particles bearing WLA subunits. (B) X-ray crystal structure of complex 2-Pt-Closed, drawn with 50% thermal ellipsoid probability. Hydrogens, solvent molecules, and anions were omitted for clarity (black, platinum; orange, sulfur; purple, phosphorous; grey, carbon; blue, nitrogen).
Figure 3. Proposed repeating unit (top) and STEM micrographs (bottom) of ICPs bearing (A) open and (B) closed platinum-based WLA subunits, and (C) open and (D) closed palladium-based WLA subunits. ICP particles were prepared at different precursor concentrations.
Figure 4. (A) STEM images of ICP particles prepared at different precursor concentrations. (B) Plot of the diameter of the ICP particles with the concentration of the precursor solution (n = 3). (C) Percentage standard deviation of particle diameters of samples prepared from different precursor solutions (n = 3).

Figure 5. Design of stimuli-responsive ICP crystalline networks bearing WLA subunits. The ICP networks are expected to undergo one-dimensional expansion and contraction as the WLA-pillar ligands are toggled between an open and a closed state.
Figure 6. (A) Linear-actuating WLA complexes as a model system. Crystal structures of the (B) open and (C) closed complexes drawn with 50% thermal ellipsoid probability. Hydrogen atoms, solvent molecules and counterions were omitted for clarity.

Figure 7. (A) Linear-actuating WLA-pillar ligands and their reversible interconversion. (B) Crystal structures of the open-state WLA pillar ligand drawn with 50% thermal ellipsoid probability. Hydrogen atoms and solvent molecules were omitted for clarity.
Figure 8. (A) Schematic representation of the solvothermal synthesis of UiO-66 ICP particles. Inset: Zr₅O₄(OH)₆ secondary building units (SBU). (B) DNA modification of the ICP particles using terminal phosphate-modified DNA, and subsequent sequence-specific assembly of hybrid ICP-NP architectures.
Figure 9. (A) TEM image and (B) PXRD showing the structural integrity of ICP particles before and after surface functionalization with DNA. (C) $^{31}\text{P}(\text{H})$ MAS solid state NMR confirms that surface functionalization of ICP particles is driven by a metal-phosphate coordination bond.
Figure 10. (a) Representative HADDF image of DNA interconnected ICP particle -metal nanoparticle assemblies. TEM images showing the ability of programmable DNA ligands on ICP particles surface to provide control over (b) stoichiometry and size, and (c) shape of ICP particle-metal nanoparticle assemblies. (d) EDX mapping shows control over the composition of ICP particle-metal nanoparticle assemblies. Scale bars: 100 nm, except for panel a, which is 1 μm.