Two Dimensional Structures from Cobaltocenium-containing Block Copolymers by Crystallization-Driven Self-Assembly

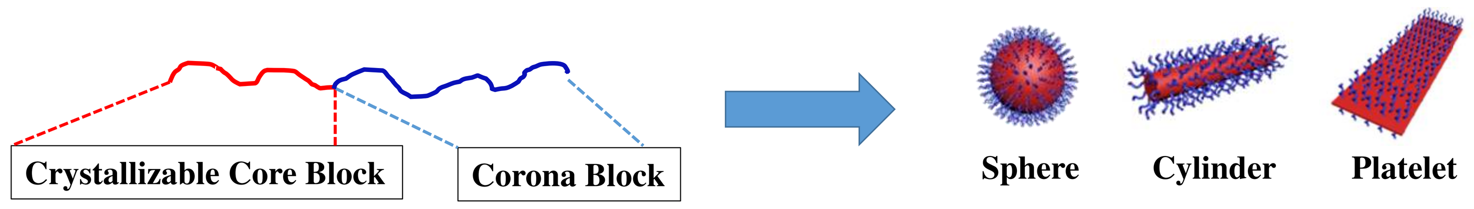
TANG POLYMER GROUP
Next-generation Polymer Innovations

UNIVERSITY OF SOUTH CAROLINA

Yujin Cha, Charles Jarrett-Wilkins, Tianyu Zhu, Ian Manners, Chuanbing Tang*
Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208

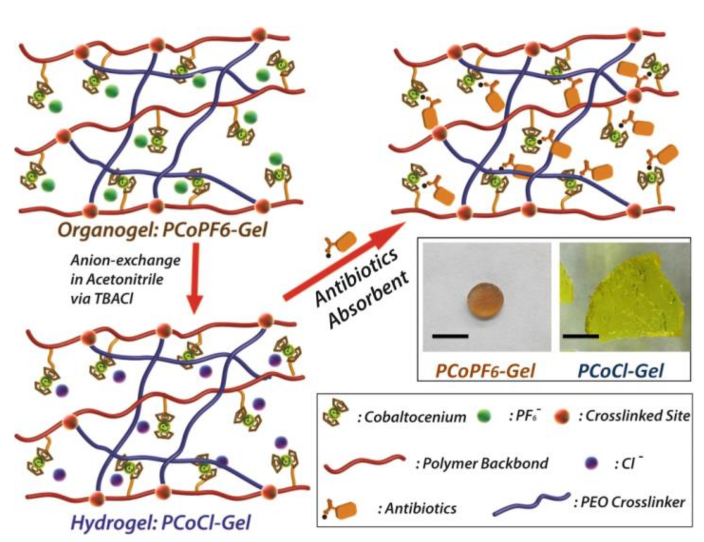
Introduction

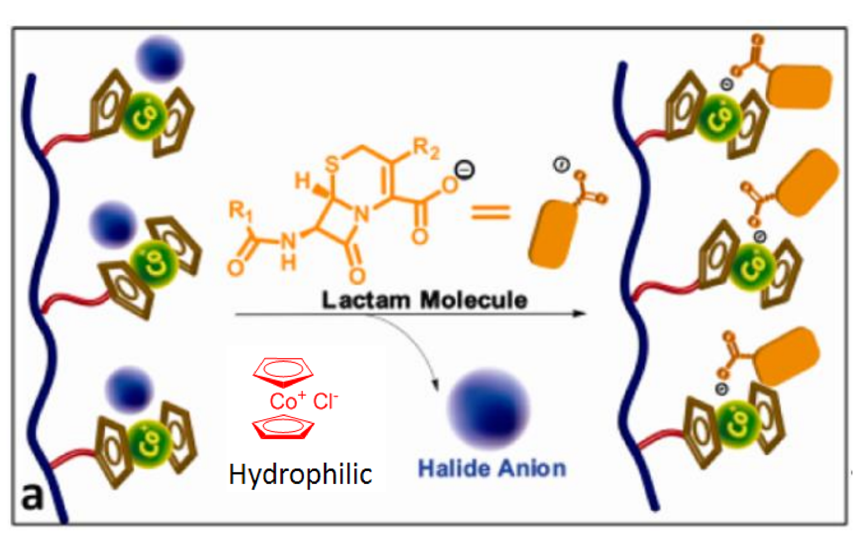
Self-assembly of amphiphilic block copolymers is one of the most fascinating approaches to the creation of nanoscale particles. Block copolymers with a crystallizable core-forming block self-assemble into the various forms of micelles, such as spheres, cylinders, and platelets.



Challenges and Motivation

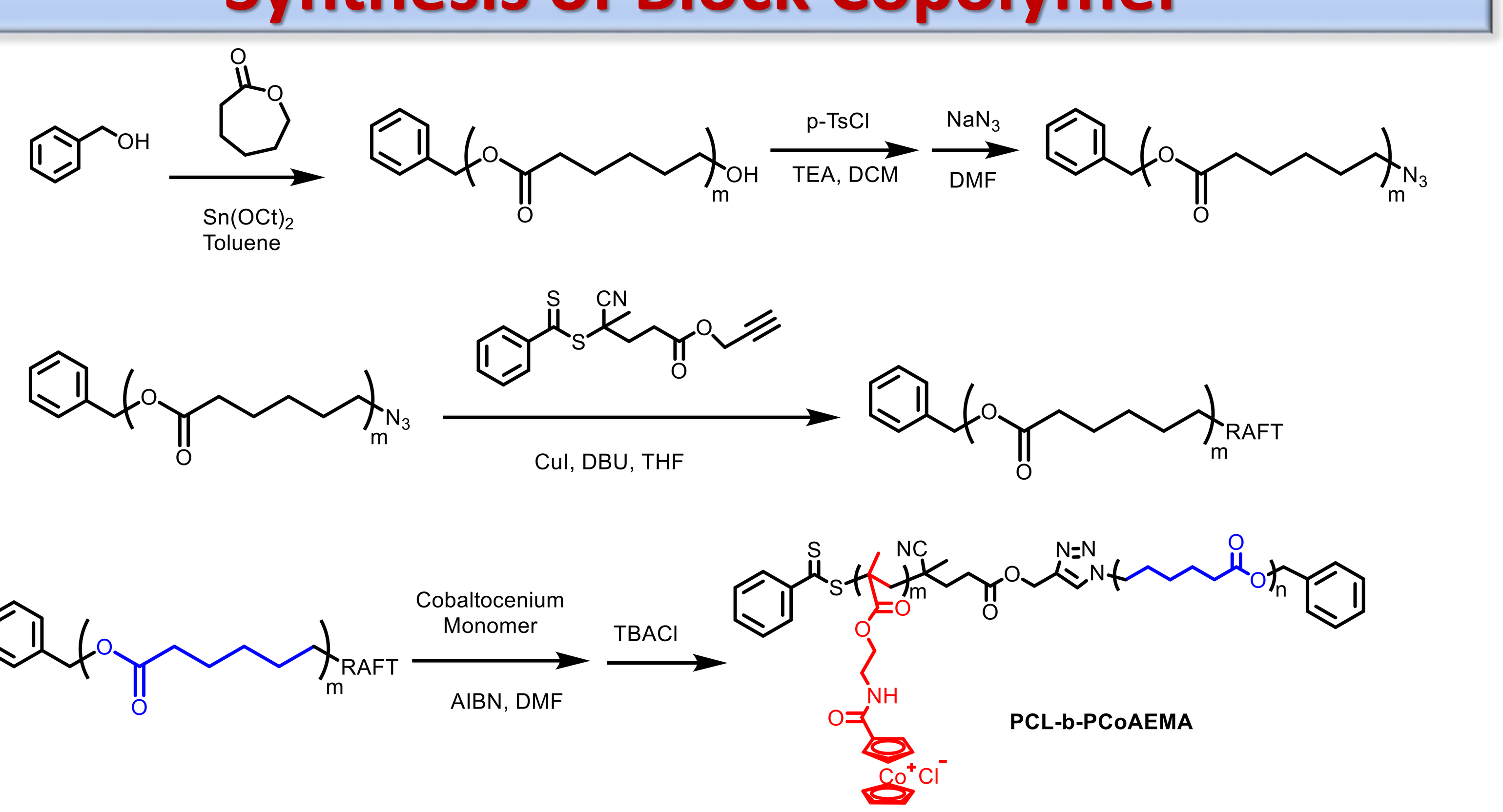
As a corona-forming block, cationic cobaltocenium moieties have been utilized for solution self-assembly. Moreover, cobaltocenium-based polyelectrolytes can be used for antimicrobial applications. Combining crystallization behavior of polycaprolactone and cationic characteristics of cobaltocenium, Crystallization-Driven Self-Assembly opens the door to making nanostructures toward biomedical applications.





Tang, C. et al. *Sci. Rep.*, **2015**, *5*, 11914. Tang, C. et al. *J. Am. Chem. Soc.* **2014**, *136*, 4873.

Synthesis of Block Copolymer

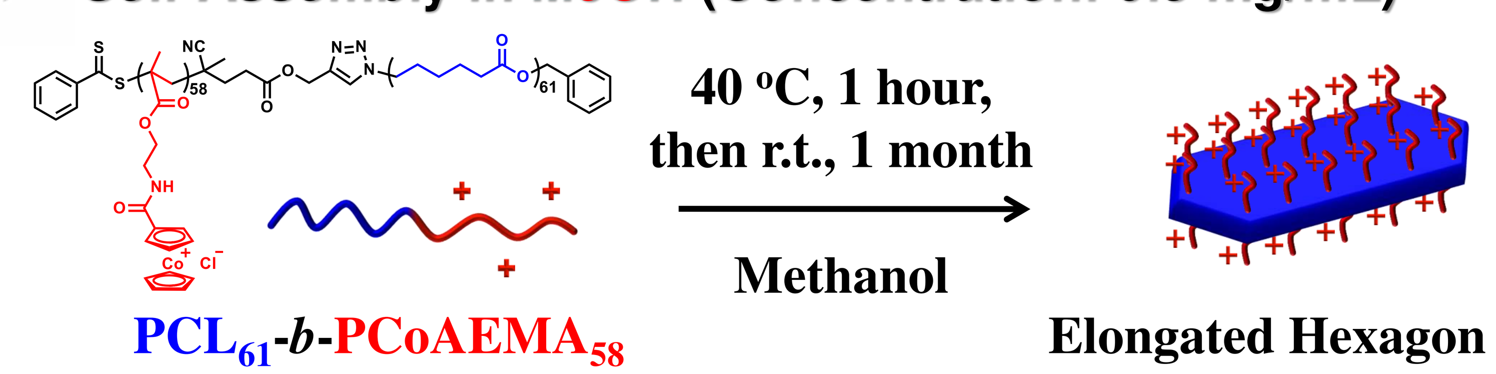


✓ The cobaltocenium-containing block copolymer was synthesized via sequential ring-opening polymerization (ROP) and reversible addition–fragmentation chain transfer (RAFT) polymerization.

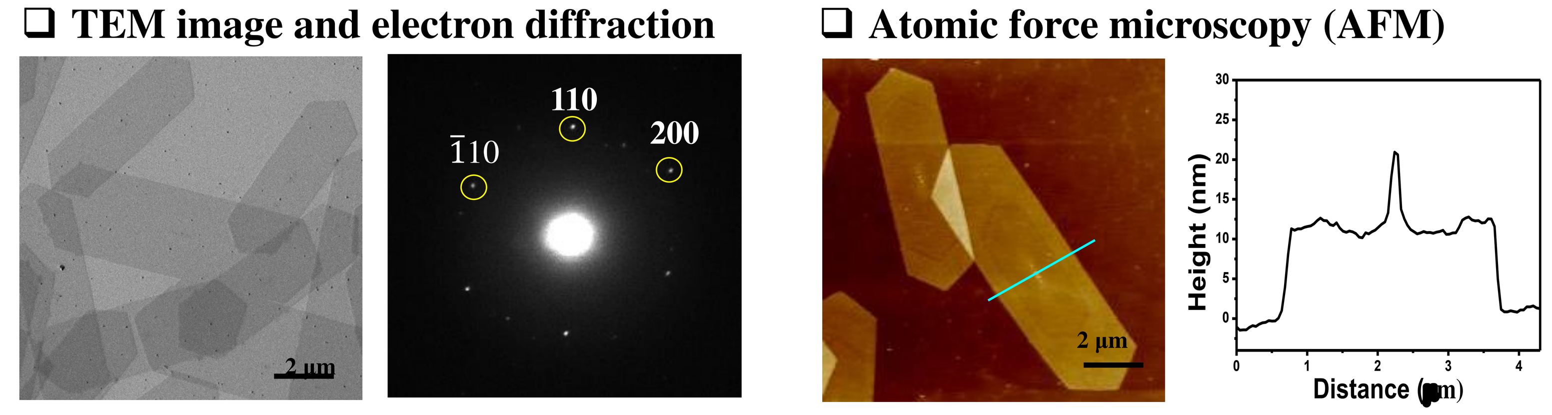
Cha, Manners, Tang *et. al. ACS Macro Lett.* **2019**, *8*, 835

CDSA of Block Copolymers

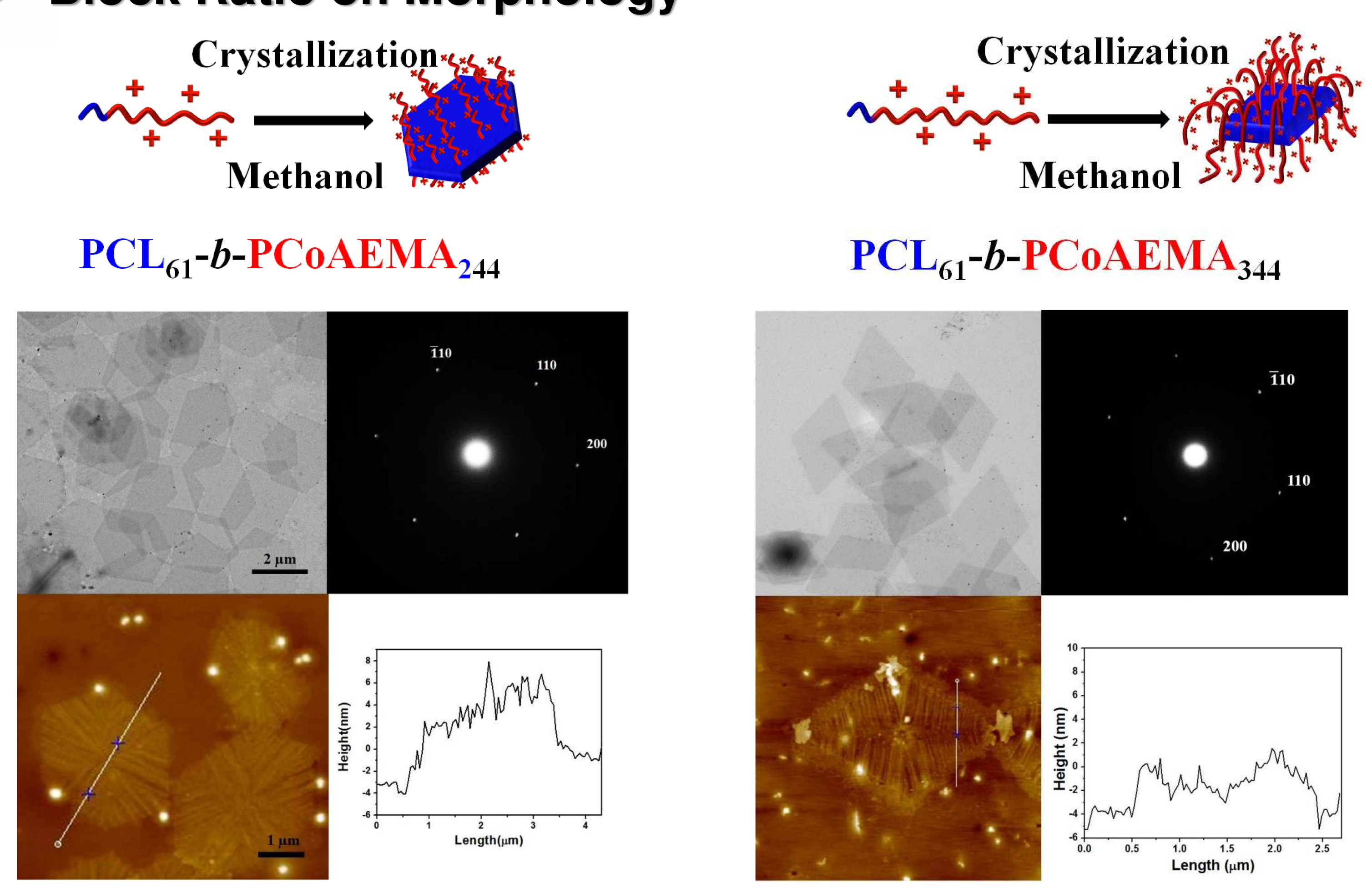
➢ **Self-Assembly in MeOH (Concentration: 0.5 mg/mL)**



❑ TEM image and electron diffraction ❑ Atomic force microscopy (AFM)

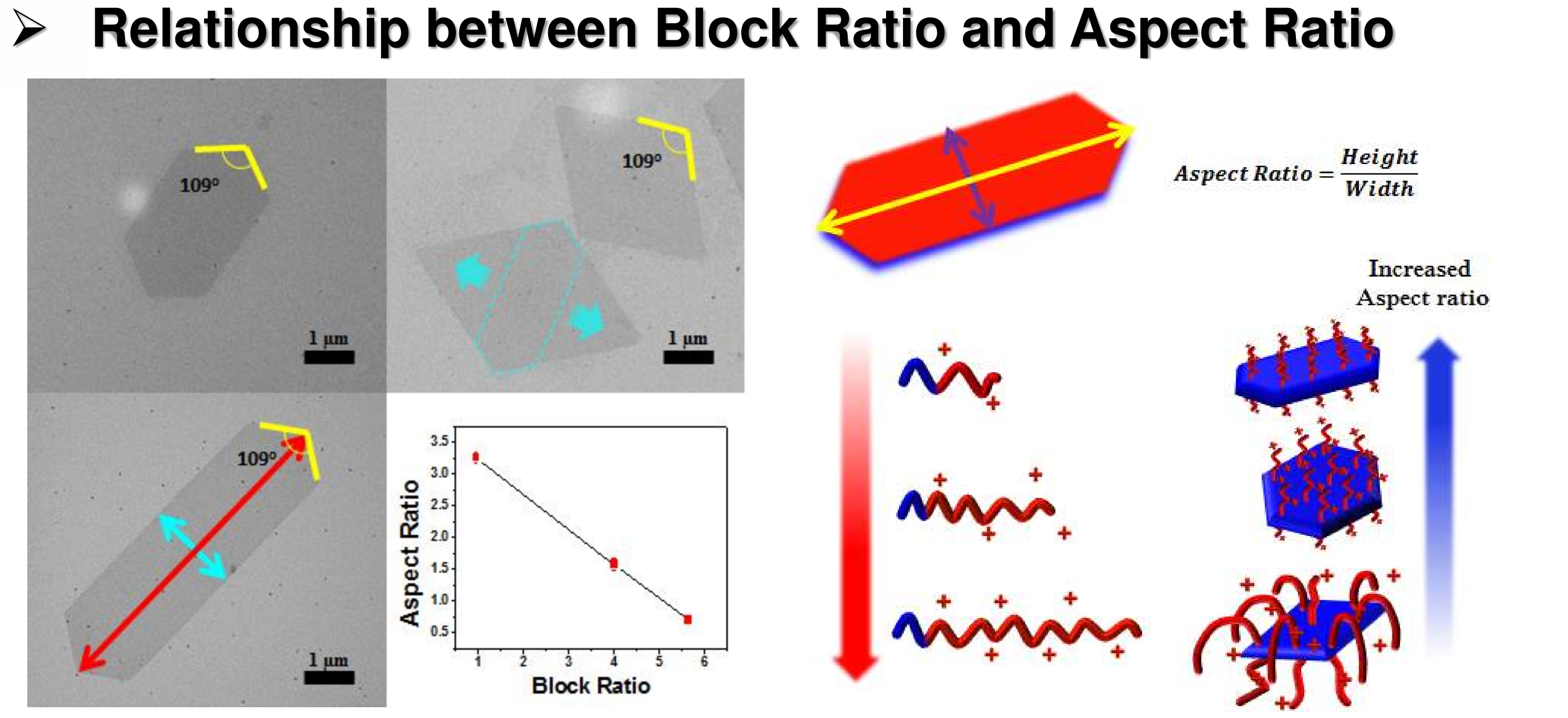


➢ **Block Ratio on Morphology**



✓ Increased corona length induces more folding, reducing the thickness.

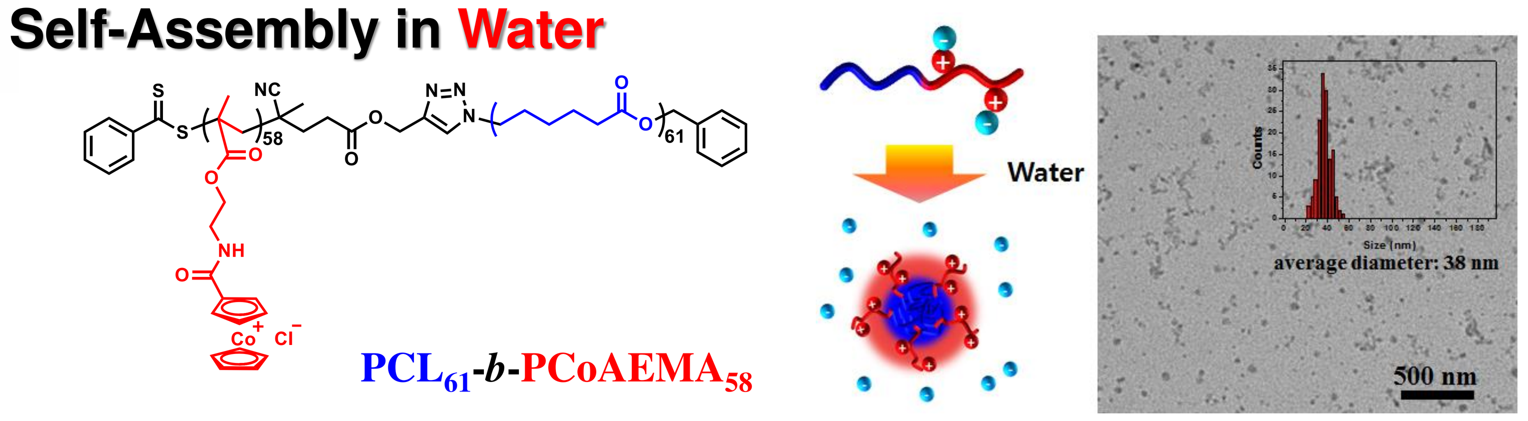
➢ **Relationship between Block Ratio and Aspect Ratio**



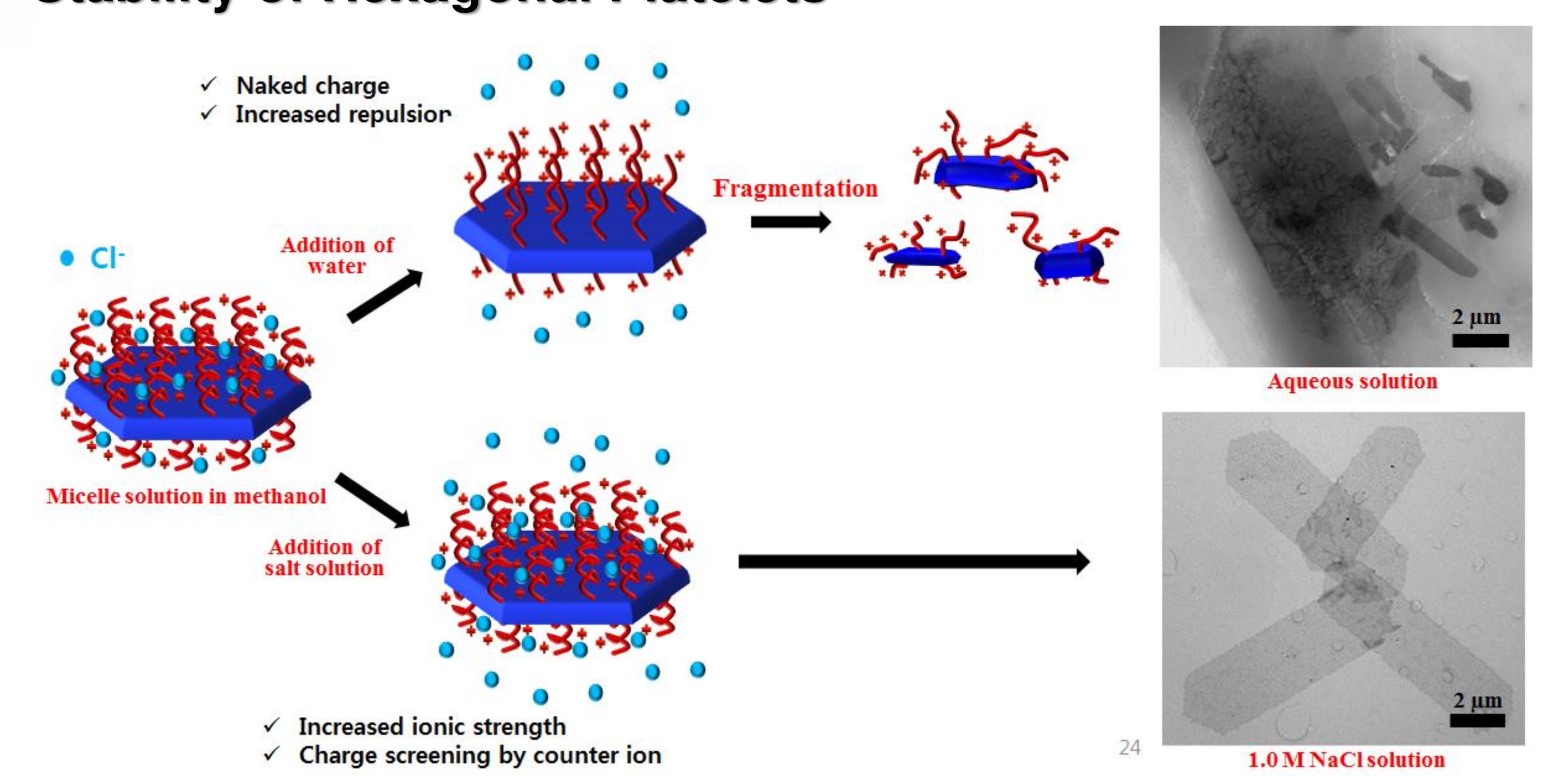
✓ 2D structures show an overlapped corner at an angle of ca. 109°.
✓ Increased corona length shows a linear relationship between block ratio and aspect ratio.

Stability of 2D Structures in Water

➢ **Self-Assembly in Water**



➢ **Stability of Hexagonal Platelets**



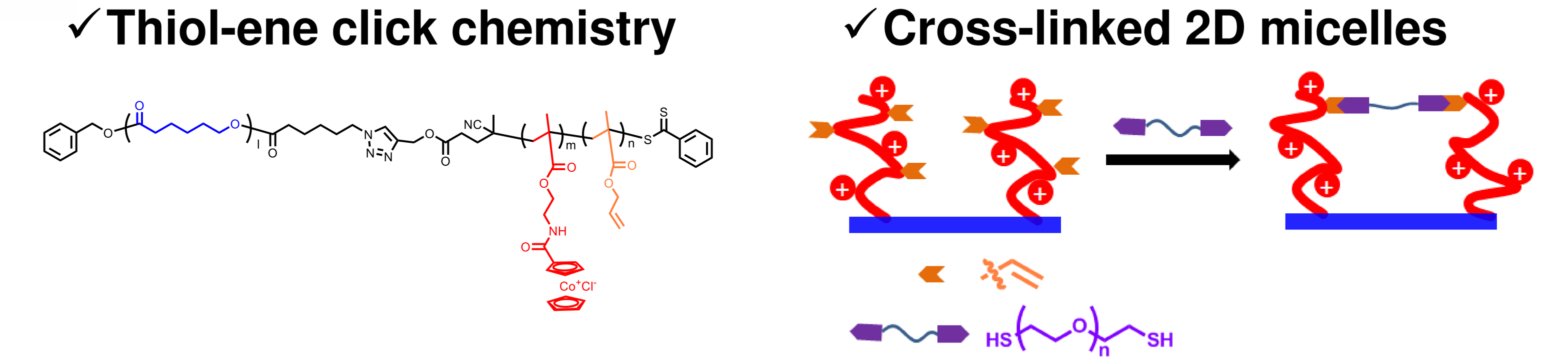
Conclusions

Cobaltocenium-containing metallo-polyelectrolyte block copolymers show unique crystallization-driven self-assembly behaviors in protic solvents. The block ratios have a large impact on the morphology transformation from the elongated hexagon to diamond. The resulting hexagonal structures showed enhanced stability when ionic strength in the aqueous solution increased.

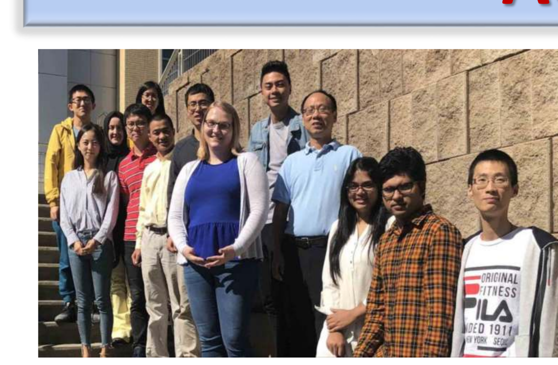
Outlook

➢ **Stabilization of micelles in water by cross-linking of corona**

✓Thiol-ene click chemistry ✓Cross-linked 2D micelles



Acknowledgements



Prof. Chuanbing Tang
Tang Polymer Group

Prof. Ian Manners
University of Victoria

NIH

UNIVERSITY OF SOUTH CAROLINA