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Toroid formation by the co-assembly of charged triblock copolymers with divalent organic counterions HONGGANG CUI, KELLY HALES, DARRIN POCHAN, Department of Materials Science and Engineering and Delaware Biotechnology Institute, University of Delaware, Newark, DE 19716, ZHIYUN CHEN, QI KAI, KAREN WOOLEY, Center for Materials Innovation and Department of Chemistry, Washington University in Saint Louis, Saint Louis, MO 63130 — The toroid, or ring, micelle morphology, which is theoretically predicted but rarely observed, has been produced by the self assembly of PAA-b-PMA-b-PS triblock copolymer in combination with an organic counterion and mixed THF/H2O solvent. The toroids consist of a PS core, a sheath of PMA, and the PAA corona. The interaction of positively-charged, multivalent organic salts with the negatively-charged PAA corona plays a decisive role in the formation of rings. The ring formation cannot be explained exclusively by traditional theories that focus on the fusion of high-energy end caps of cylindrical micelles at the expense of a higher micelle curvature penalty. It was also found that final assembled morphologies, including discs, rings, spheres, could be targeted by choosing the correct organic, multivalent counterion characteristic, such as hydrocarbon or polyether chain length between amine groups, the number of amine groups and the molar ratio of amine group to acid group in PAA. Ring morphology is observed in situ with cryoTEM experiments or can be kinetically trapped by either ridding the system of organic solvent or chemically crosslinking the PAA corona.

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