

Electronic Supplementary Information (ESI) for:

Composition and Property Tunable Ternary Coacervate: Branched Polyethylenimine and a Binary Mixture of a Strong and Weak Polyelectrolyte

*Mengmeng Zhao,^a Xuhui Xia,^a Jingyi Mao,^a Chao Wang,^a Mahesh B. Dawadi,^b David A. Modarelli^b and Nicole S. Zacharia^{*a}*

^a *Department of Polymer Engineering, University of Akron, 250 S. Forge St, Akron, OH 44325, USA*

^b *Department of Chemistry, University of Akron, Akron, Ohio 44325, USA*

**** To whom correspondence should be addressed: nzacharia@uakron.edu***

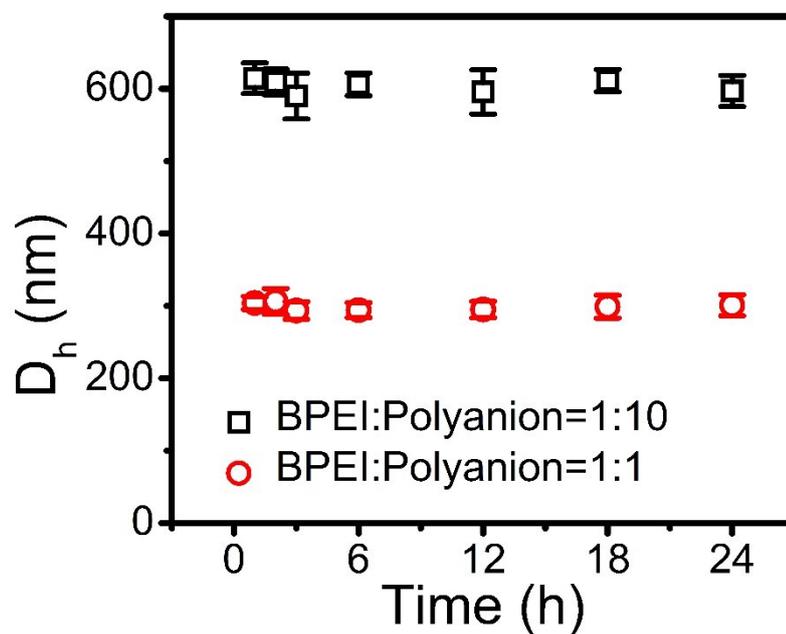


Figure S1. Hydrodynamic diameter of BPEI-(PAA/SPS) coacervate prepared using BPEI to polyanion ratio of 1:1 and 1:10, respectively, as a function of stirring time. Polycation solution used is 40 mM BPEI and the polyanion solution was overall 40 mM in functional groups with a PAA to SPS ratio = 1:1.

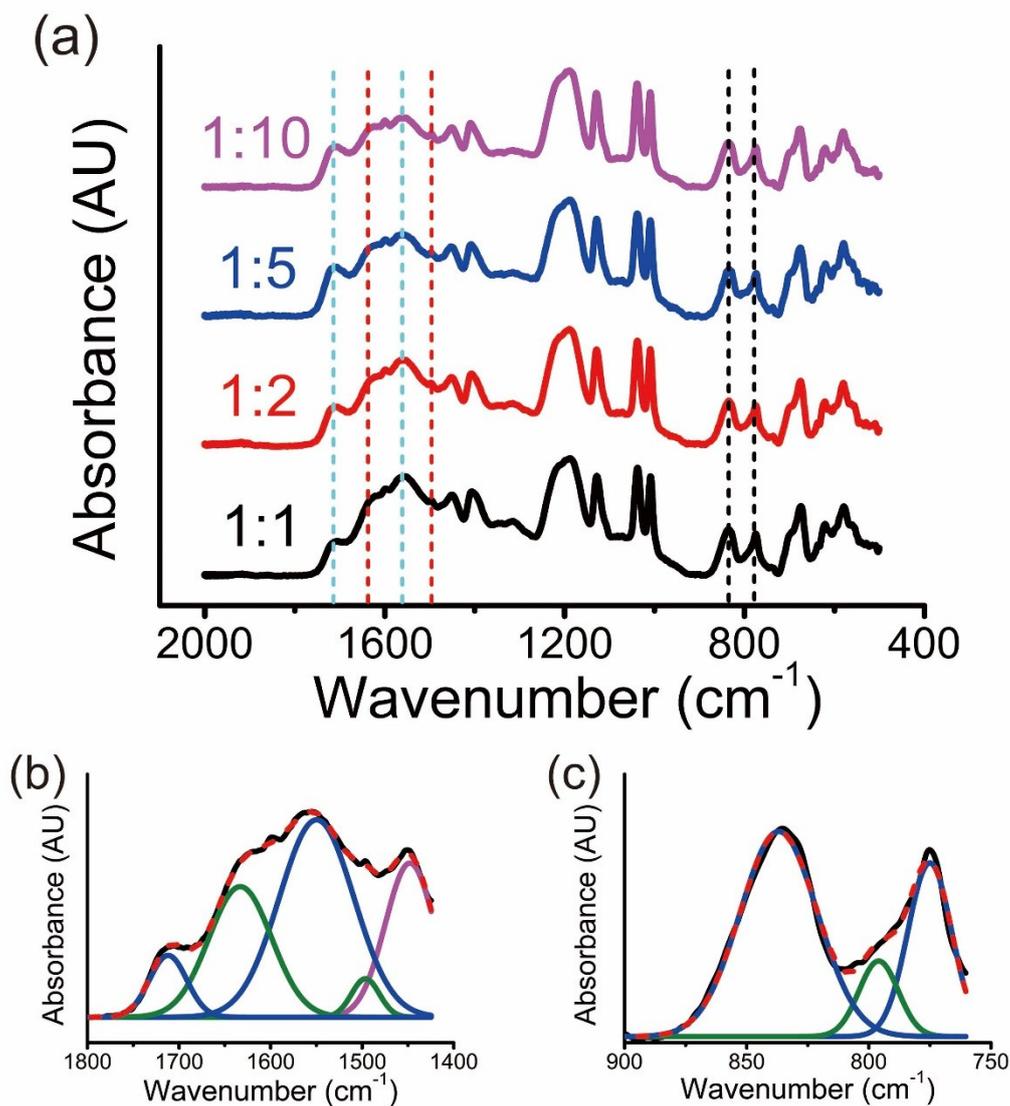


Figure S2. (a) FTIR of BPEI-(PAA/SPS) coacervate prepared using different BPEI to polyanion ratio. Polycation solution used is 40 mM BPEI and the polyanion solution was overall 40 mM in functional groups with a PAA to SPS ratio = 1:1. Deconvolution of FTIR peaks at (b) 1400 – 1800 cm^{-1} and (c) 750 – 900 cm^{-1} regions using Gaussian distributions.

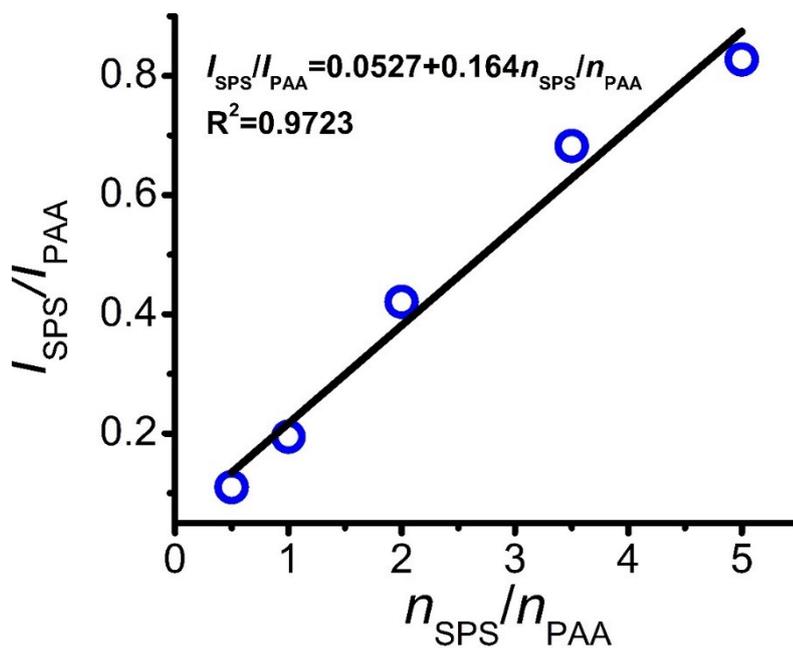


Figure S3. Calibration curve plotted using SPS/PAA repeat unit ratio versus SPS/PAA peak intensity ratio, using the peak intensity at 836 cm^{-1} for SPS and the sum of peak intensity at 1710 cm^{-1} and 1560 cm^{-1} for PAA.

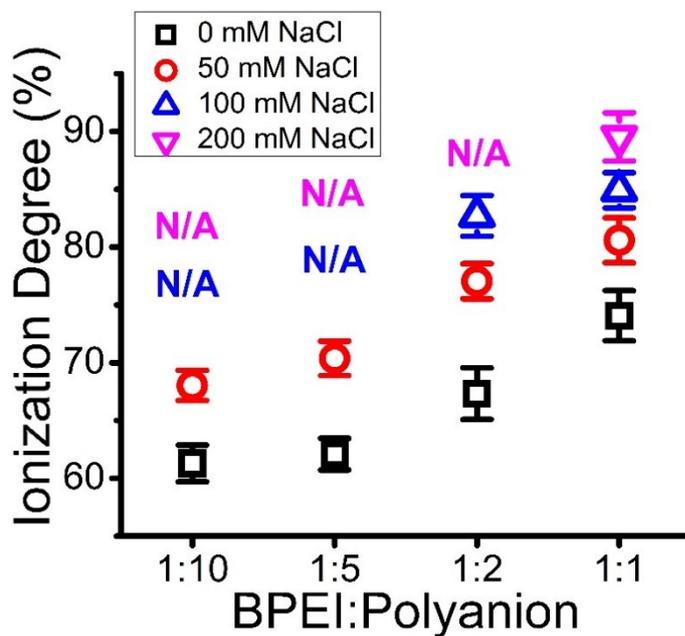


Figure S4. Ionization degree of PAA in ternary coacervate formed at different BPEI to polyanion stoichiometry and ionic strength.

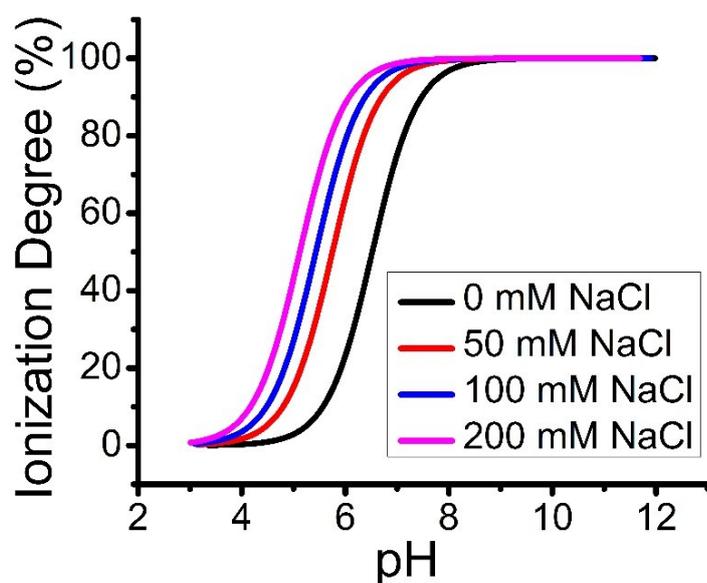


Figure S5. Variation of PAA ionization degree in aqueous solution with different ionic strength.

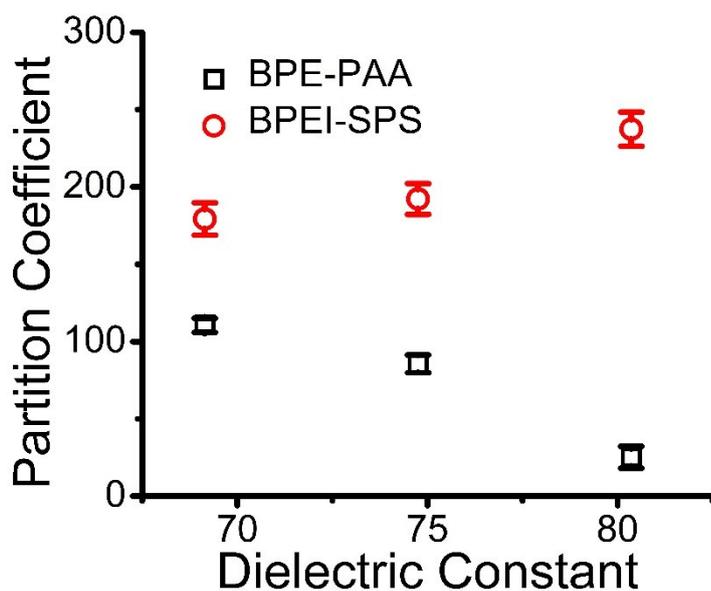


Figure S6. Partition coefficient of MB into BPEI-PAA or BPEI-SPS coacervate as a function of dielectric constant of solvent. The solvent dielectric constant was adjusted by using ethanol-water mixture with volume percentage of ethanol at 0%, 10% and 20%.

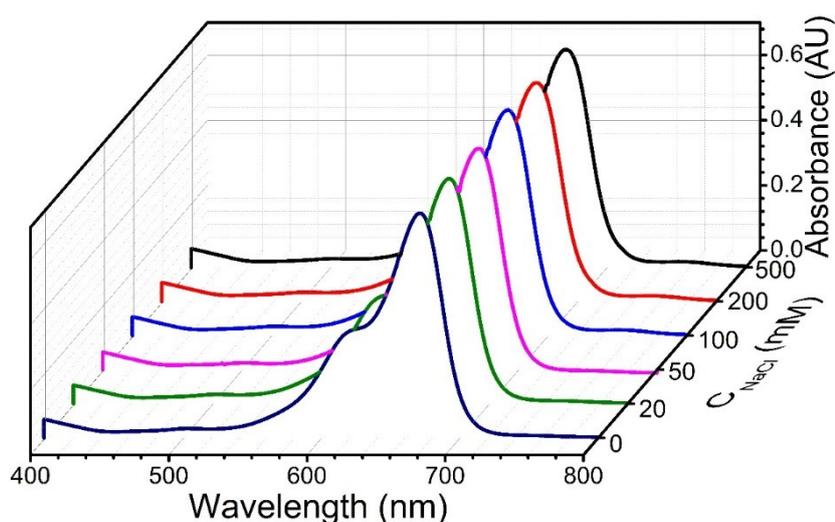


Figure S7. UV-vis spectra of 0.01 mM MB in aqueous solution with presence of 20 mM SPS and NaCl ranging from 0 to 500 mM. Maximum absorbance wavelength of MB is fixed at 671 nm at various NaCl concentration, indicating that ionic strength has little influence on the π - π interaction between MB and SPS.

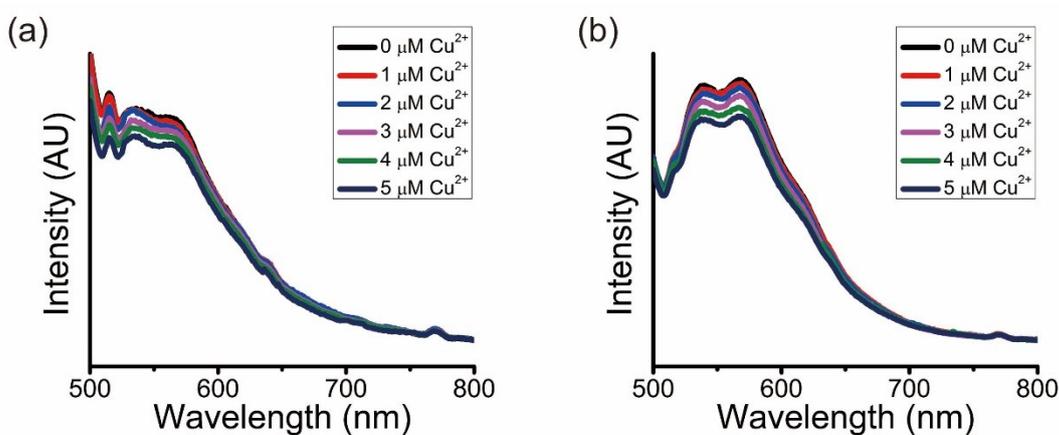


Figure S8. Fluorescence emission spectra of 5 μ M DHAQ in (a) BPEI-PAA and (b) BPEI-SPS coacervate suspension with the addition of 0 to 1 equiv. Cu^{2+} (0, 1, 2, 3, 4 and 5 μ M for the curves from up to bottom respectively).

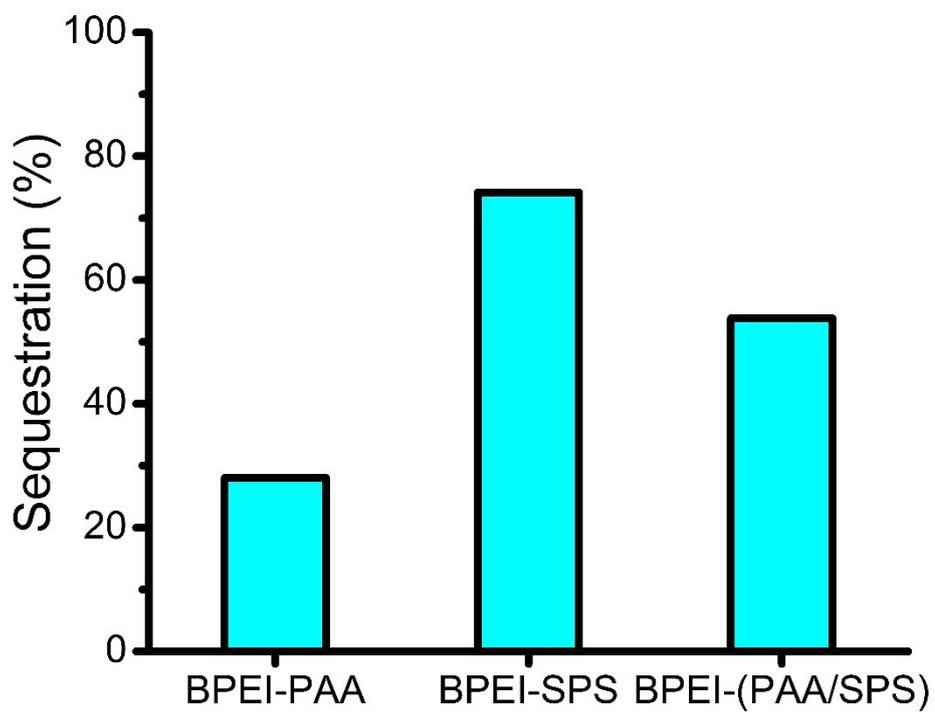


Figure S9. Sequestration of DHAQ into BPEI-PAA, BPEI-SPS and BPEI-(PAA/SPS) coacervate formed using 40 mM BPEI and 40 mM PAA, 40 mM SPS or 40 mM mixture of PAA and SPS with a PAA to SPS ratio = 1:1, at 1:1 BPEI to polyanion stoichiometry.