Online Supporting Information

## Electrostatic-Driven Self-Sorting and Nanostructure Speciation in Self-Assembling Tetrapeptides

Jugal Kishore Sahoo,<sup>1</sup> Michael A. VandenBerg,<sup>1</sup> Edgar E. Ruiz-Bello,<sup>1</sup> Calvin D. Nazareth,<sup>1</sup> Matthew J. Webber<sup>1,\*</sup>

<sup>1</sup>Department of Chemical and Biomolecular Engineering, University of Notre Dame, IN, USA, 46556

Correspondence can be addressed to:

Prof. Matthew. J. Webber

Department of Chemical and Biomolecular Engineering

University of Notre Dame

Notre Dame, IN, 46556

E-Mail: <u>mwebber@nd.edu</u>





Figure S1: <sup>1</sup>H-NMR spectrum for DWDW



**Figure S2**: Analytical HPLC trace of DWDW with 4-wavelength uv-detection monitoring absorbance at 220, 260, 280, and 350 (flat baseline)



Figure S3: Mass spectroscopy (negative mode) of DWDW. Calculated 619.2, Observed 619.1



Figure S4: <sup>1</sup>H-NMR spectrum for KWKW



**Figure S5**: Analytical HPLC trace of KWKW with 4-wavelength uv-detection monitoring absorbance at 220, 260, 280, and 350 (flat baseline)



Figure S6: Mass spectroscopy (positive mode) of KWKW. Calculated 645.4, Observed 645.3



Figure S7: pH titration curves for DWDW (left) and KWKW (right).



Figure S8: SEM images of DWDW at pH 6. and Scale bars: 500 nm



**Figure S9**: DLS data on 20 mM solutions of KWKW at pH 6, showing a complex mixture consisting of monomers or oligomers, 10-15 nm spheres, and very large aggregated structure.



**Figure S10**: Fluorescence spectra of DWDW and KWKW at 20 mM and pH 6 with excitation at 280 nm.



**Figure S11**: FTIR on 20 mM samples of pure KWKW and DWDW, as well as the various mixtures ratios studies here at pD 6 in  $D_2O$ . Highlighted peaks are stretches assigned to TFA counterions in KWKW (1673 cm<sup>-1</sup>),  $\beta$ -sheet/amide stretches in DWDW (1666 cm<sup>-1</sup> and ~1630 cm<sup>-1</sup>), and carboxylates in DWDW (1587 cm<sup>-1</sup>).



**Figure S12**: Additional TEM images of co-assembled tetrapeptide mixtures DWDW and KWKW at different stoichiometric ratio at pH 6 at 20 mM total concentration. Left panel-1:1; middle panel-3:1; right panel 5:1, Scale Bar- 100 nm.



**Figure S13:** SEM images of co-assembled tetrapeptide mixtures DWDW and KWKW at different ratios at pH 6 at 20 mM total concentration.



**Figure S14:** Near-UV circular dichroism for each peptide ratio (data) plotted alongside the arithmetic combination of the spectra for the two parent peptides (math) at each ratio.