Supporting Information

Synthesis and characterization of a new class of cationic protein polymers for multivalent display and biomaterial applications

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Bacterial Expression of Protein Polymers. Protein polymer growth rate was determined from a single colony inoculation into 5 ml of Difco Terrific Broth supplemented with ampicillin (200 g/ml) and tetracycline (12.5 g/ml). Culture optical density at 600 nm was determined approximately every hour (Figure S1). No decrease in optical density was observed before or after protein induction with 0.5 mM isopropyl thiogalactoside (IPTG).

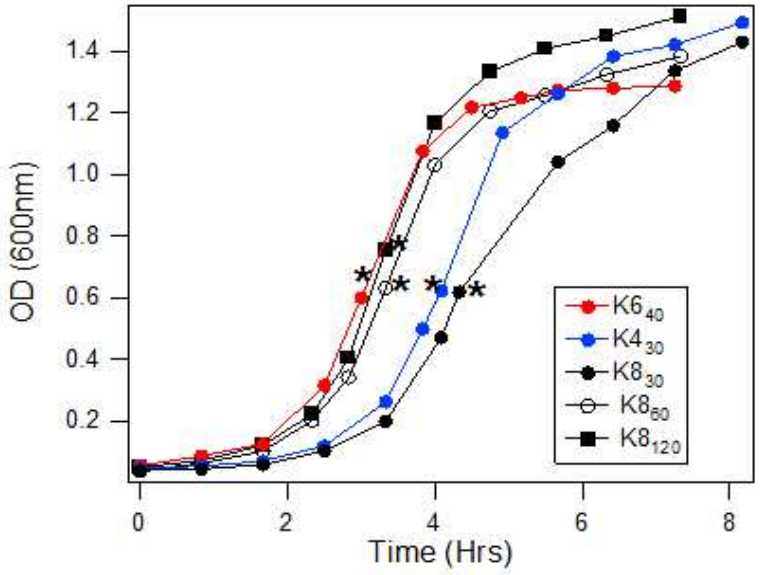


Figure S1: Growth curve for protein polymers from inoculation to harvest. Induction with IPTG is denoted by astericks.

Molar Mass Analysis of Protein Polymers. Protein polymer molar mass was analyzed with matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS) (Perspective Biosystems Voyager Pro DE) using sinipinic acid matrix (Figure S2).

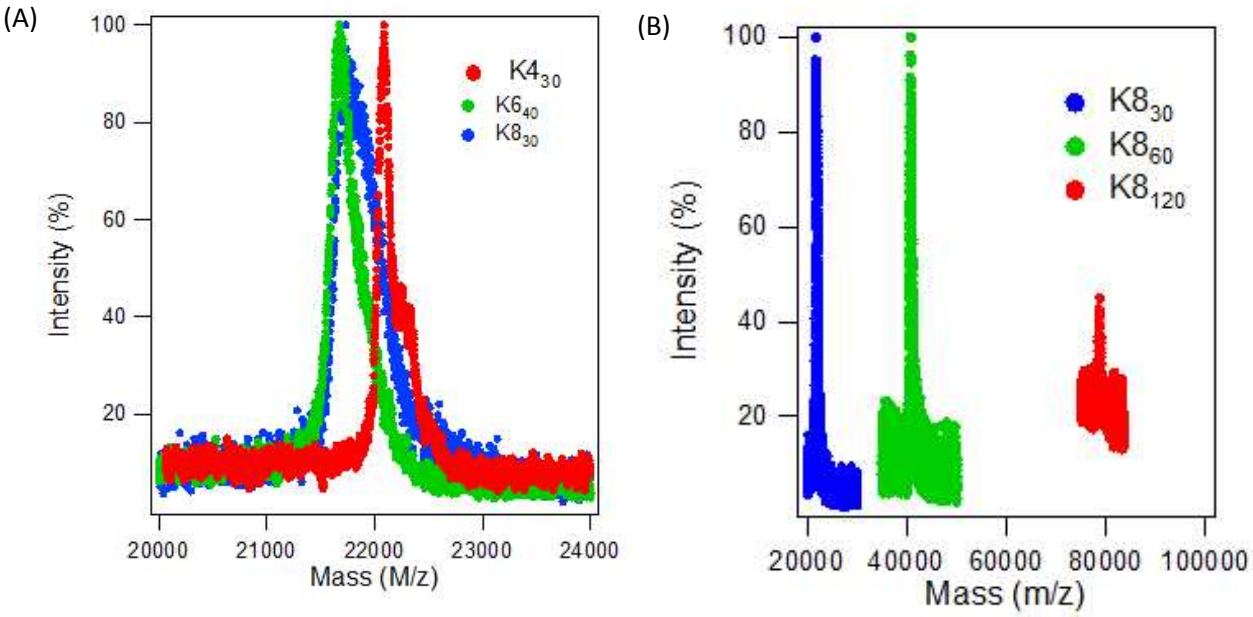


Figure S2: MALDI-TOF spectra of protein polymers as a function of (A) amino acid sequence and (B) length.

Turbidity of Protein Polymers in Solution. Protein solubility was determined by UV absorbance at 500nm on a Varian Cary 500 UV-Vis-NIR spectrophotometer (Palo Alto, CA) with Peltier temperature control. The proteins were dissolved at 1 mg/ml in ddH_2O and absorbance was measured as the temperature was ramped at 1°C/min from 5°C to 80°C and then back down to 5°C (Figure S3).

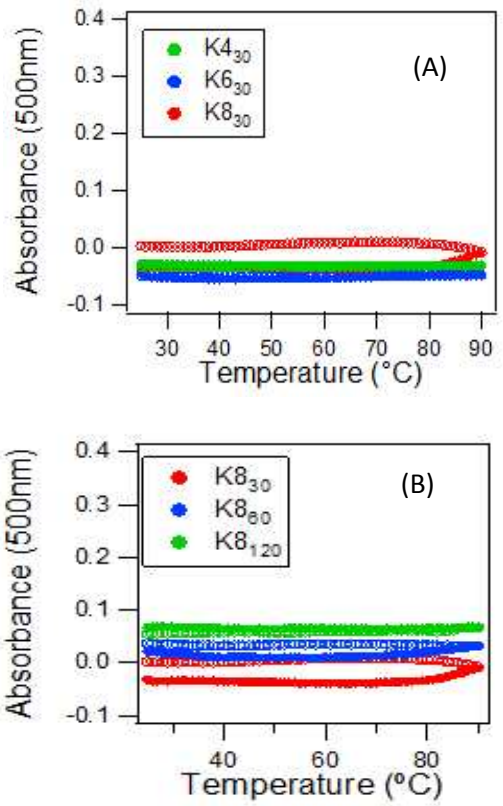
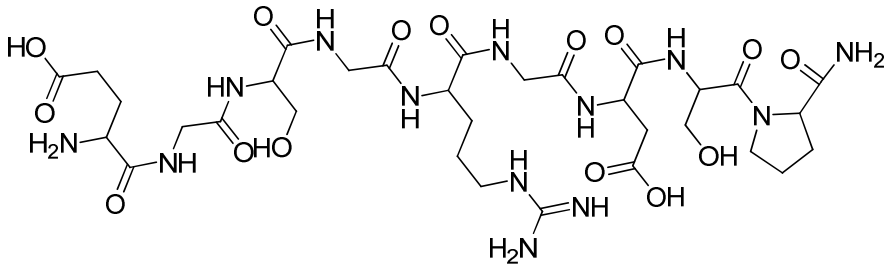


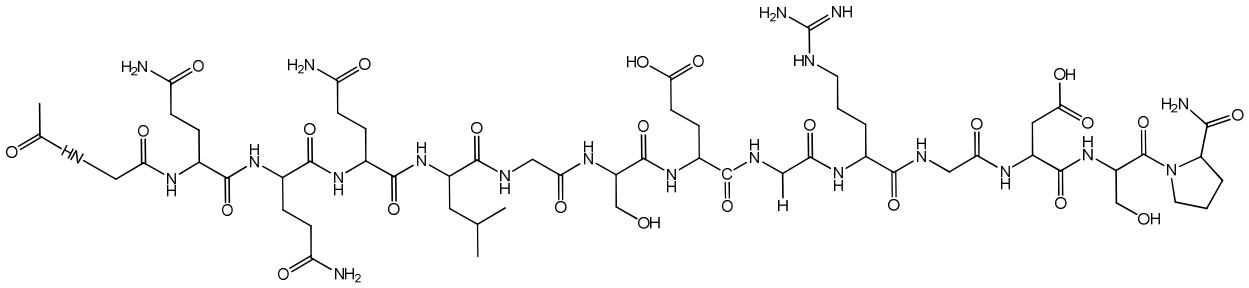
Figure S3: Protein polymer absorbance at 500nm as a function of amino acid sequence (A) and protein polymer length (B). Protein solution absorbances during heating and cooling are indicated by closed and open symbols, respectively.

Chemical Structures of Pendant Molecules and Crosslinkers

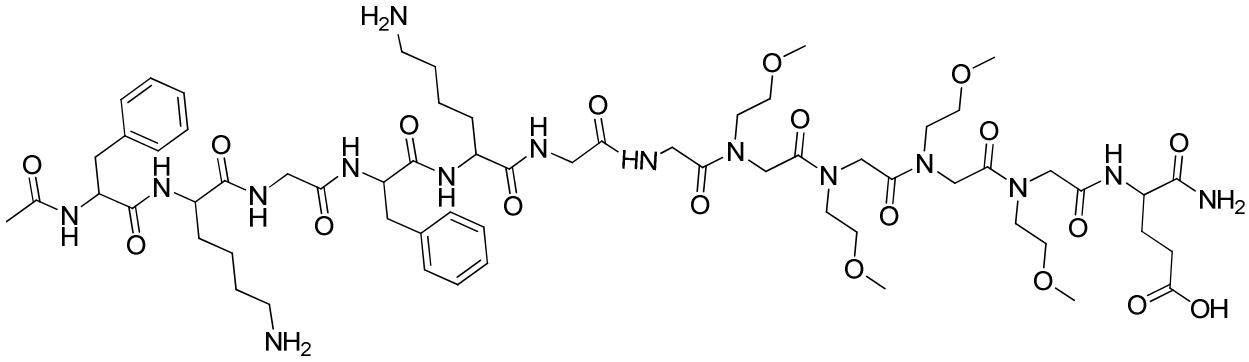
Figure S4 shows the chemical structures of peptides, polymer, fluorophore and the peptoid-peptide hybrid used to illustrate grafting onto $K8_{30}$.



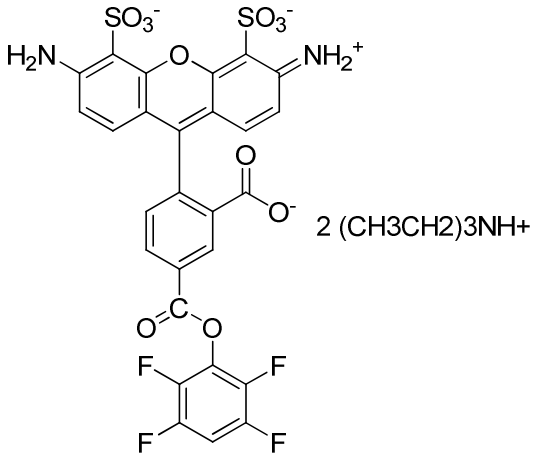
Peptide (1): Ac-EGSGRGDSP-NH_2 expected mass 859.38 Da



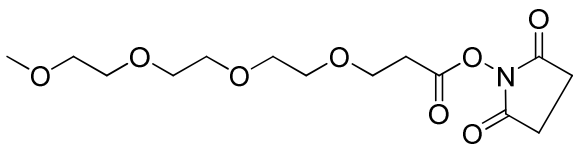
Peptide (2): Ac-GQQQLGSEGRGDSP-NH_2 expected mass 1455.67 Da



Peptoid-peptide hybrid (3): Ac-$(FKG)_2$-$(NMEG)_4$-E-NH_2 expected mass 1370.55 Da



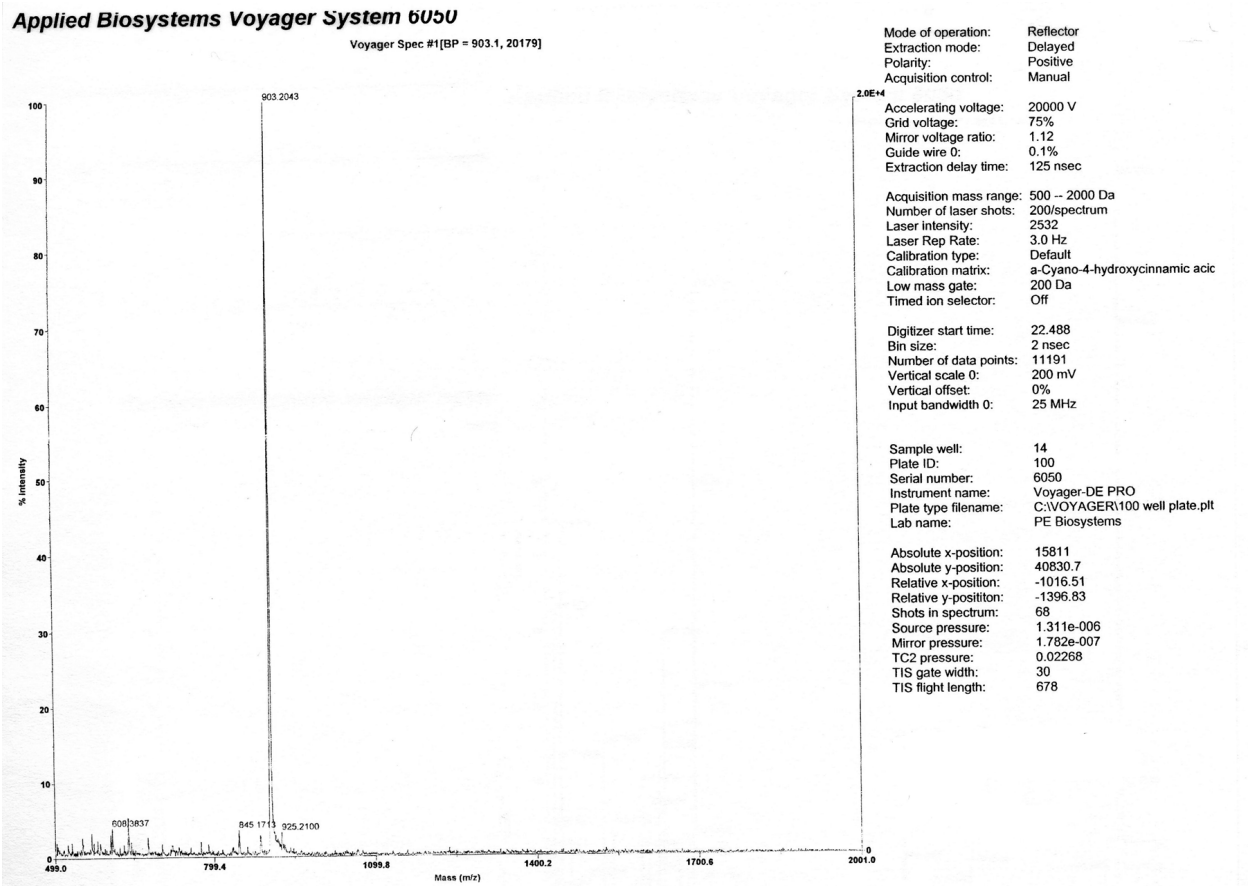
Alexa Fluor® 488 5-TFP, molar mass 884.91



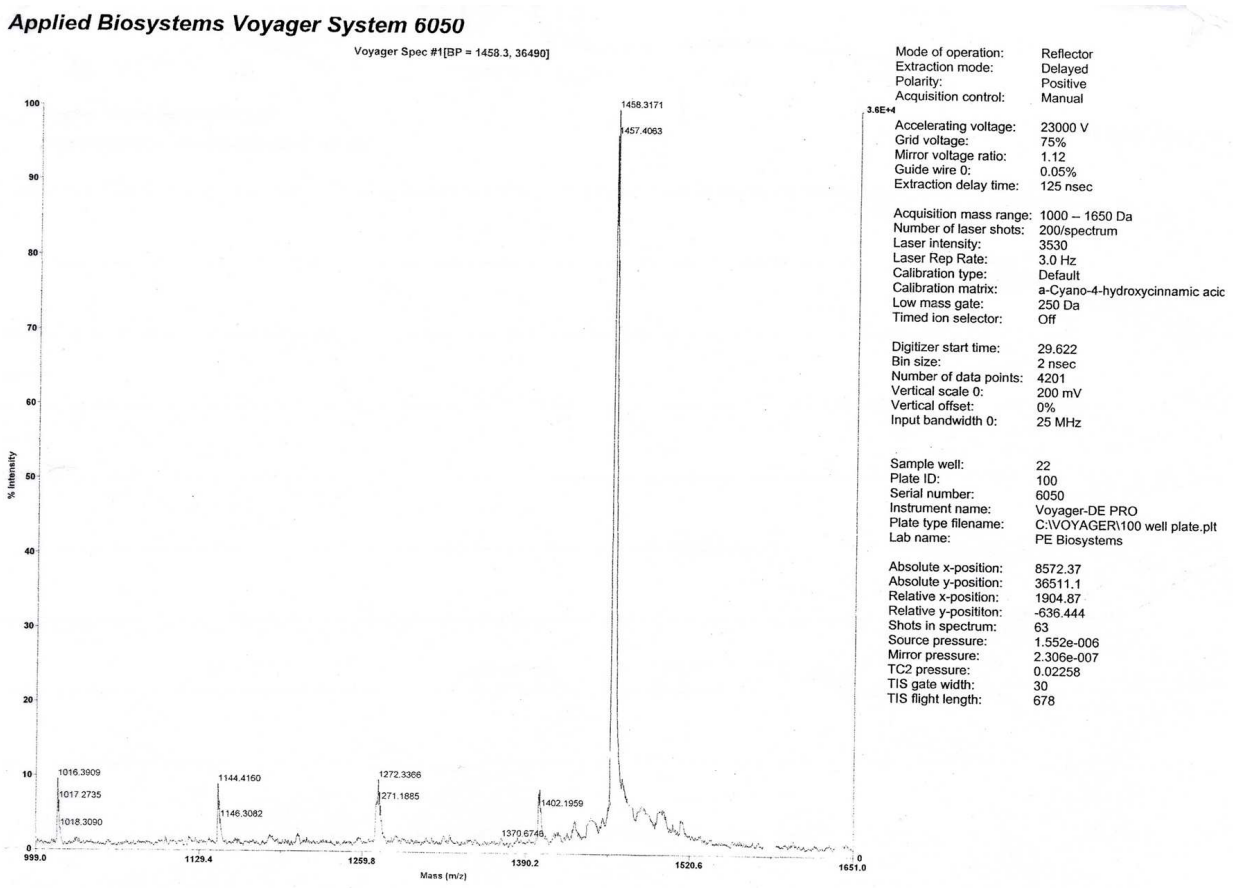
NHS-mPEG™: expected mass 333.33

Figure S4: Chemical structures of molecules grafted onto the protein polymer.

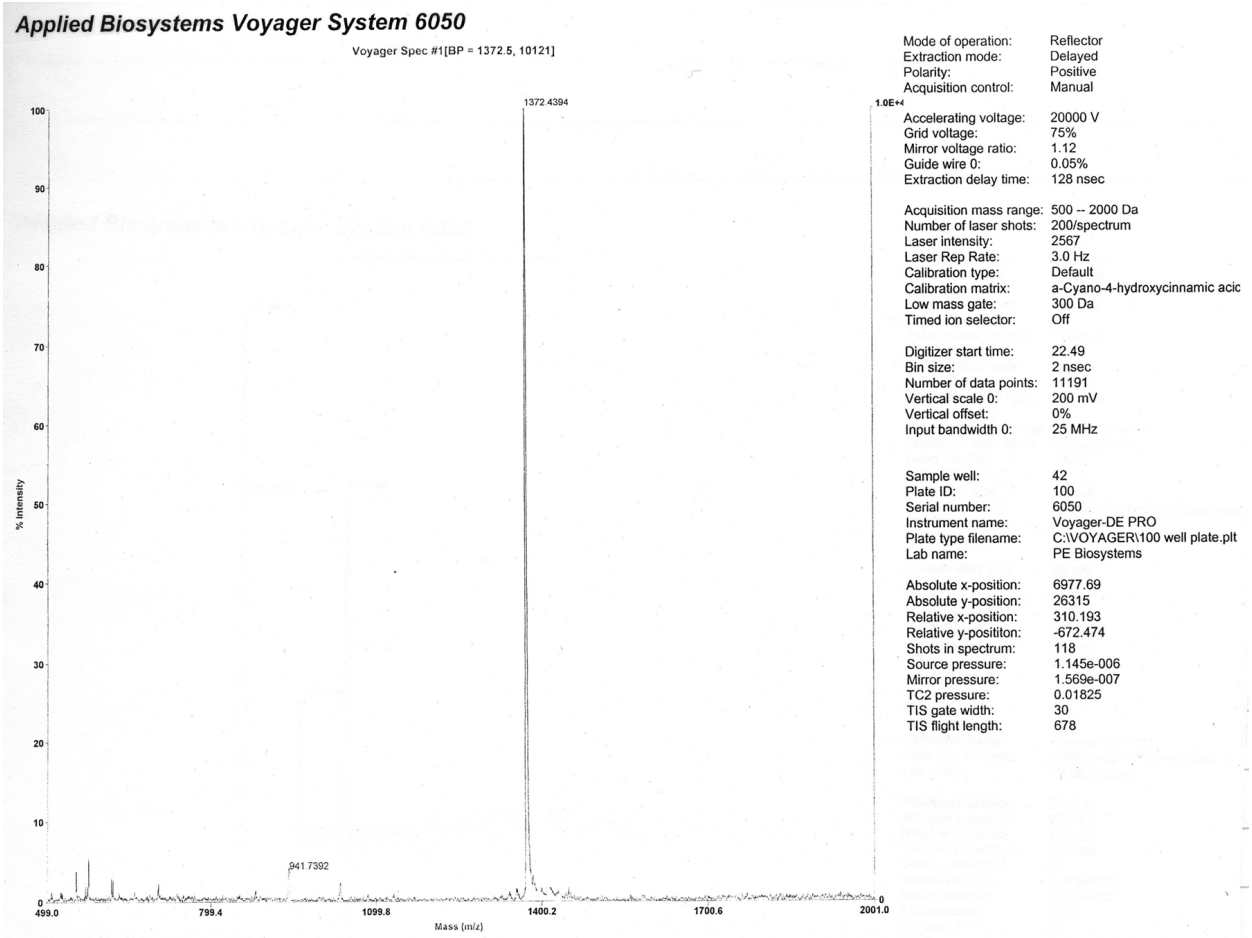
The molar masses of (1), (2), and (3) were verified by MALDI-TOF (Figure S5).



Peptide (1): Ac-EGSGRGDSP-NH_2 expected mass 859.38 Da



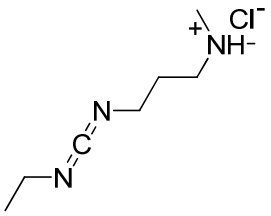
Peptide (2): Ac-GQQQLGSEGRGDSP-NH_2 expected mass 1455.67 Da



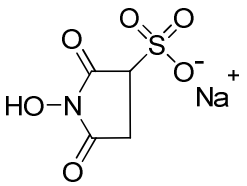
Peptoid peptide hybrid (3): Ac-$(FKG)_2$-$(NMEG)_4$-E-NH_2 expected mass 1370.55 Da

Figure S5: MALDI-TOF spectra of the peptides and the peptoid-peptide hybrid.

Amine-reactive crosslinkers used for conjugating peptides (1) and (3) and the fluorophore are shown in Figure S6.



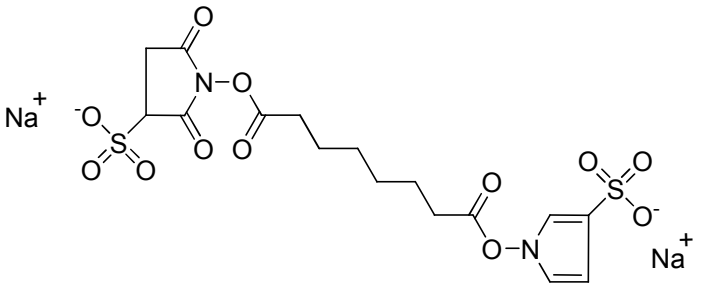
EDC



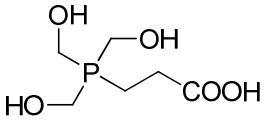
Sulfo-NHS

Figure S6: Chemical structures of chemical crosslinkers used for conjugation of pendant molecules onto the protein polymer scaffold.

Figure S7 illustrates the amine-reactive bi- and tri-functional crosslinkers used to create and crosslink protein polymer hydrogels.



BS^3



THPP

Figure S7: Chemical structures of crosslinkers used for protein polymer gelation.