Supporting Information

(J. Mat Chem. C Manuscript ID TC-ART-04-2013-030766)

Polymer-peptide templates for controlling electronic interactions of organic chromophores

Nandita Bhagwat, Kristi L. Kiick

Department of Materials Science and Engineering, University of Delaware, Newark DE 19716

Electrospray ionization (ESI) mass spectra

ESI-MS measurements were performed on peptide solutions (~0.1 mg/ml) in methanol.

1. Peptides before PEGylation
2. Peptides after PEGylation
3. PEGylated peptides after Oxa-PPV coupling

1. Peptides before PEGylation

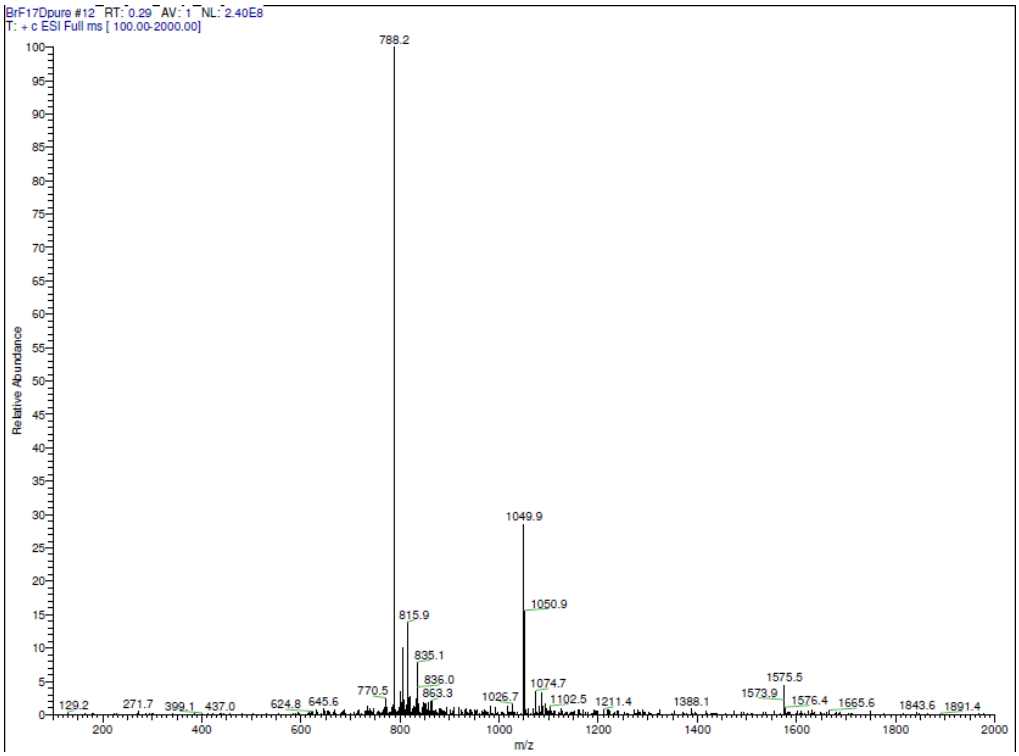

Figure S1. Full scan mass spectrum for BrF17D

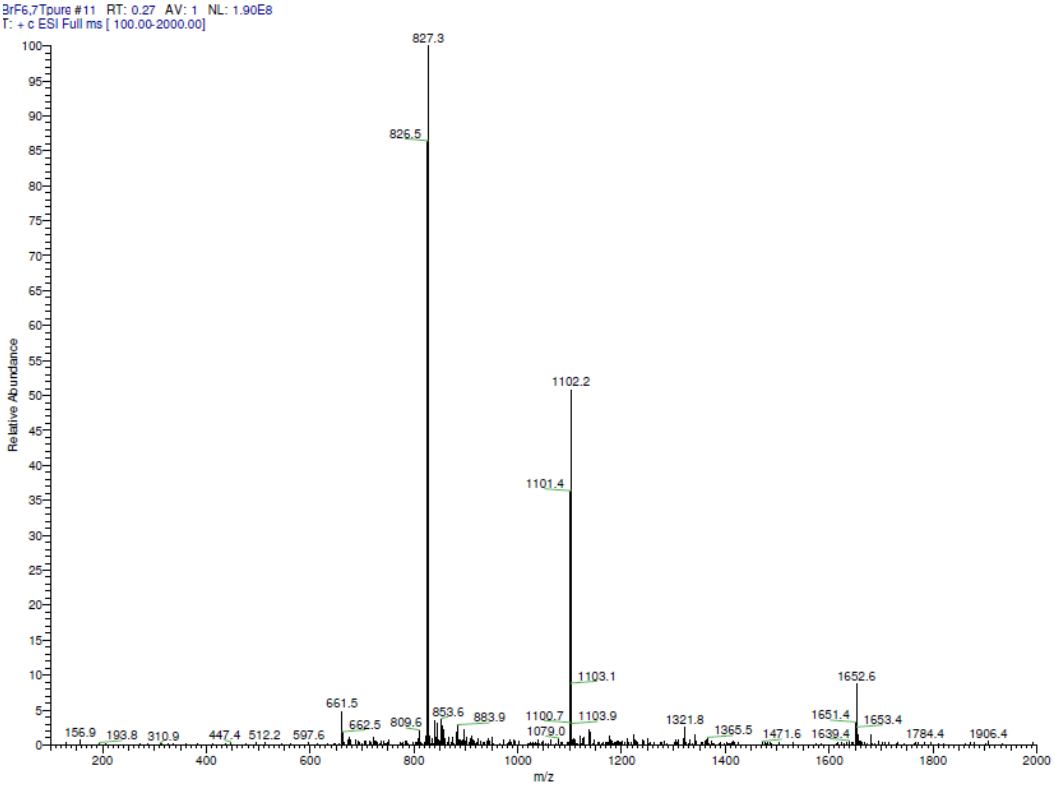

Figure S2. Mass spectrum for BrF6,7T

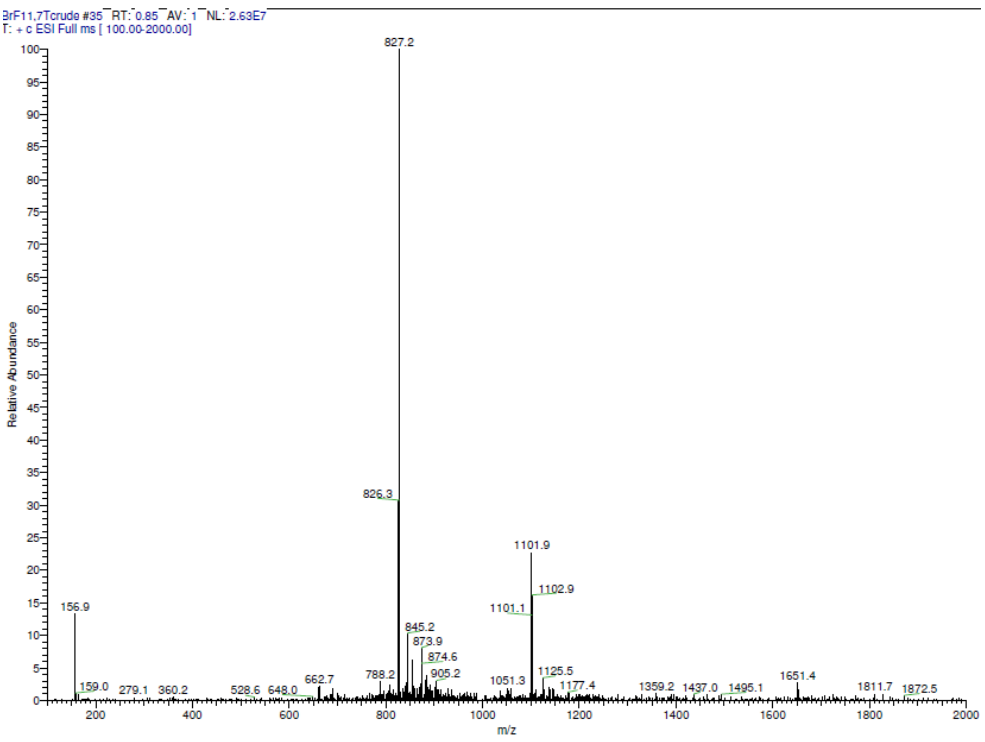

Figure S3. Mass spectrum for BrF11,7T

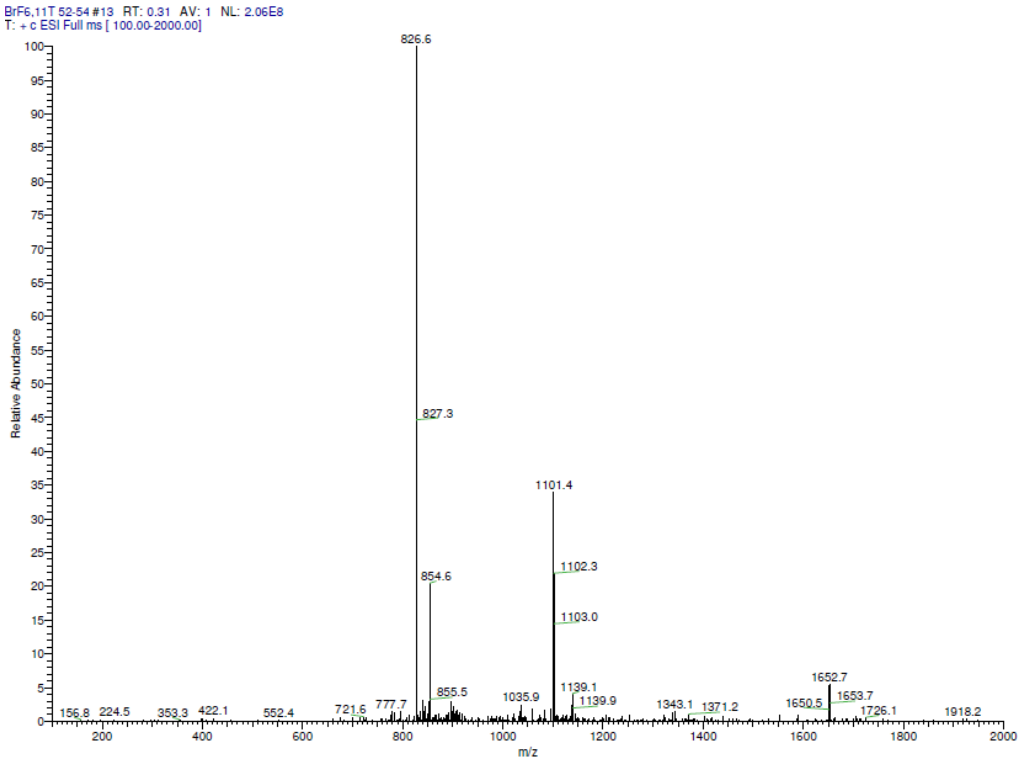

Figure S4. Mass spectrum for BrF6,11T

2. Peptides after PEGylation

The mass for the PEGylated peptides is calculated based on the M_n value of the PEG used to cap the helical peptides.

M_n for PEG = 1000 Da

For example: Calculated molecular weight for the BrF17D PEG: 3148.4 (M_n of BrF17D) + 1000 (M_n of PEG) – 42 (acetylation) – 18 (water) = 4088.4 Da

The mass spectrum of PEG 1K is shown in Fig. S5; under these experimental conditions, gives rise to ions in the +1 and +2 charged states. The mass spectrum can be deconvoluted to a distribution of oligomers for each charge state.

Such similar distribution is observed for all PEGylated peptides, before and after modification with the Oxa-PPV oligomer.

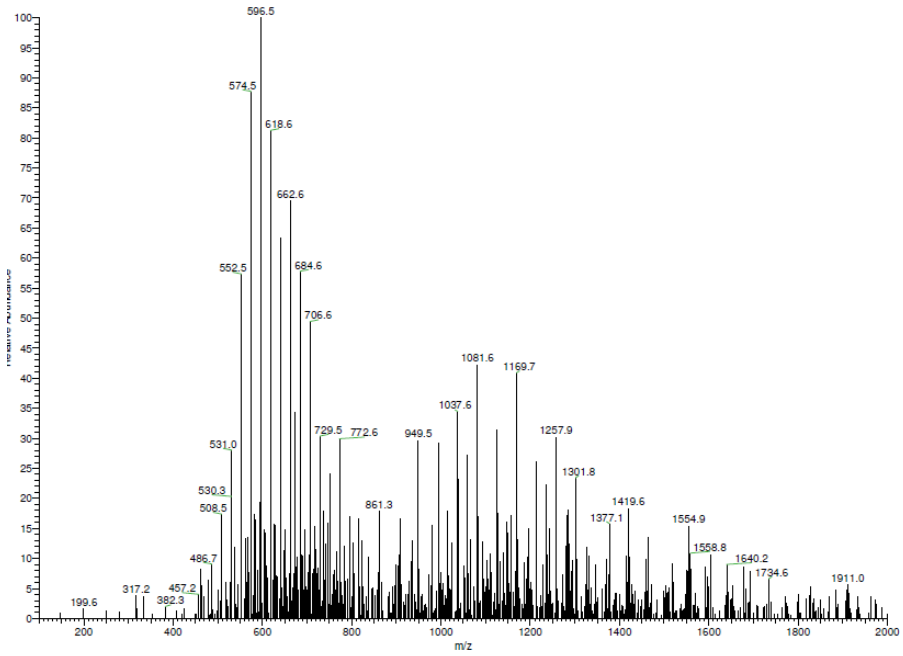

Figure S5. Mass spectrum for PEG

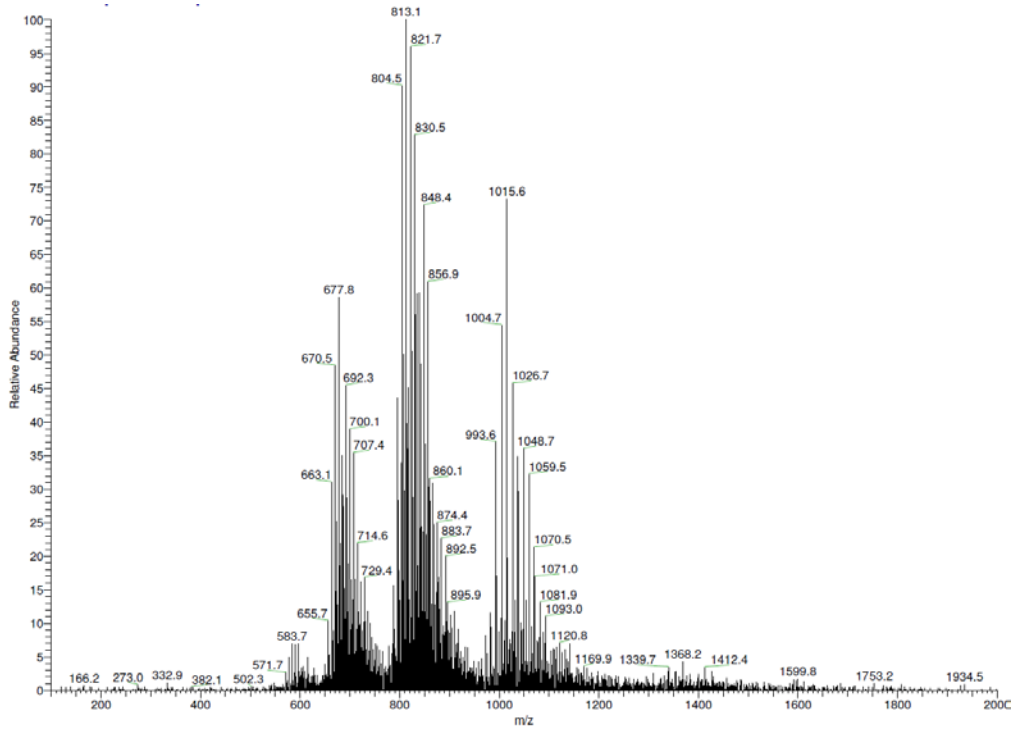

Figure S6. Mass spectrum for BrF17D PEG

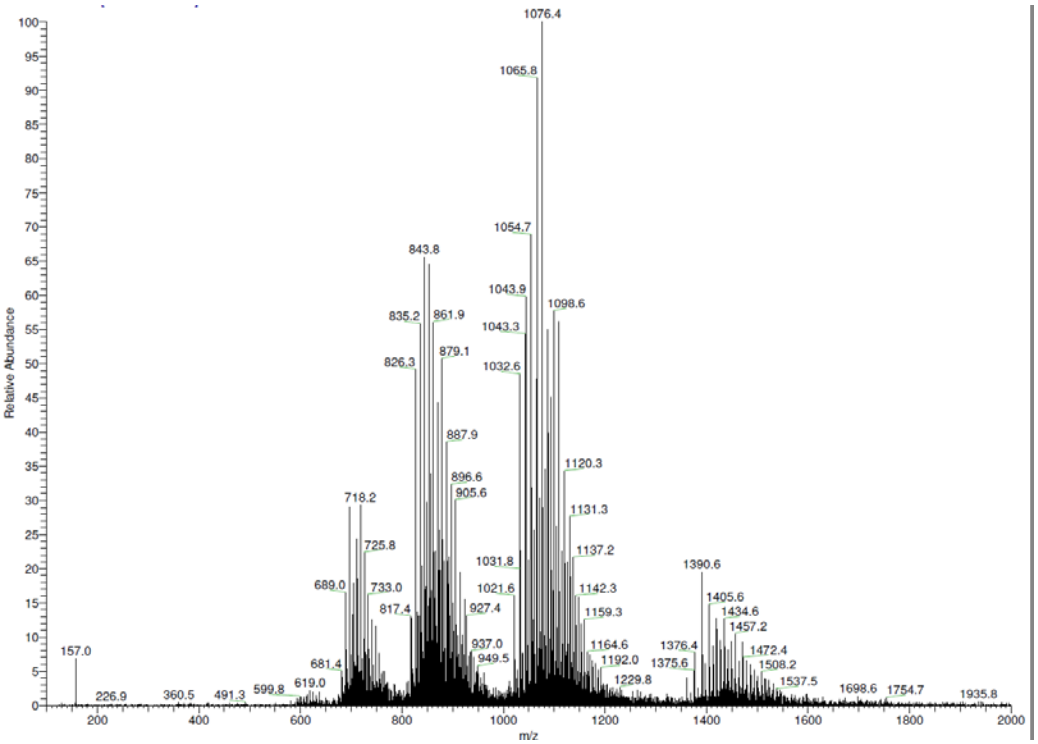

Figure S7. Mass spectrum for BrF6,7T PEG

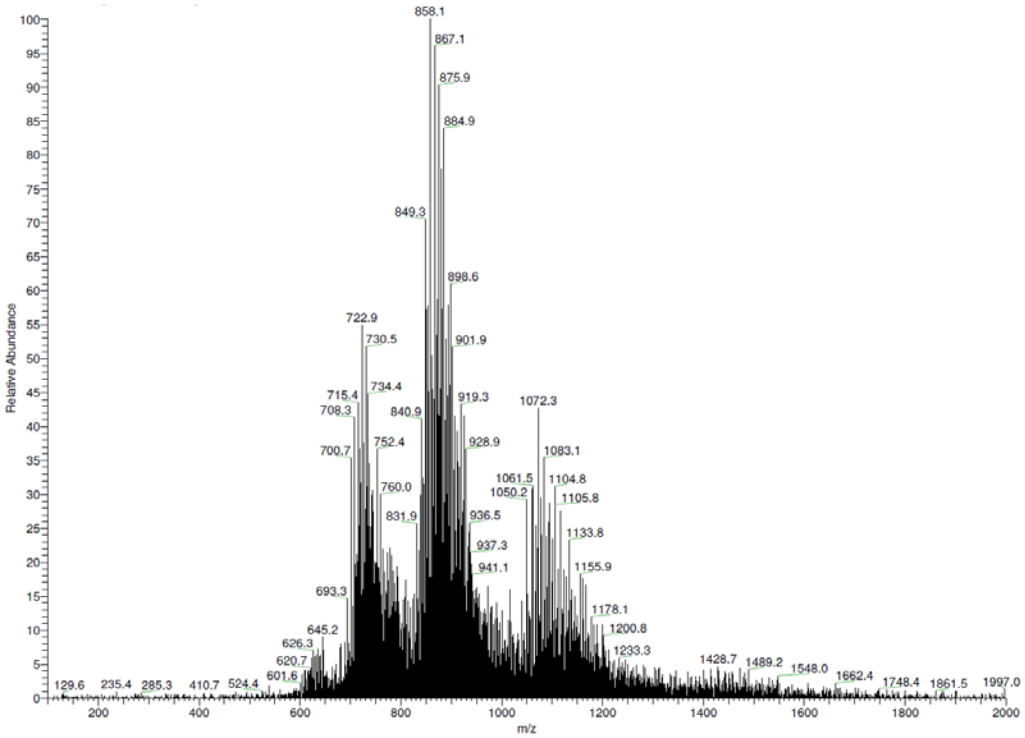

Figure S8. Mass spectrum for BrF11,7T PEG

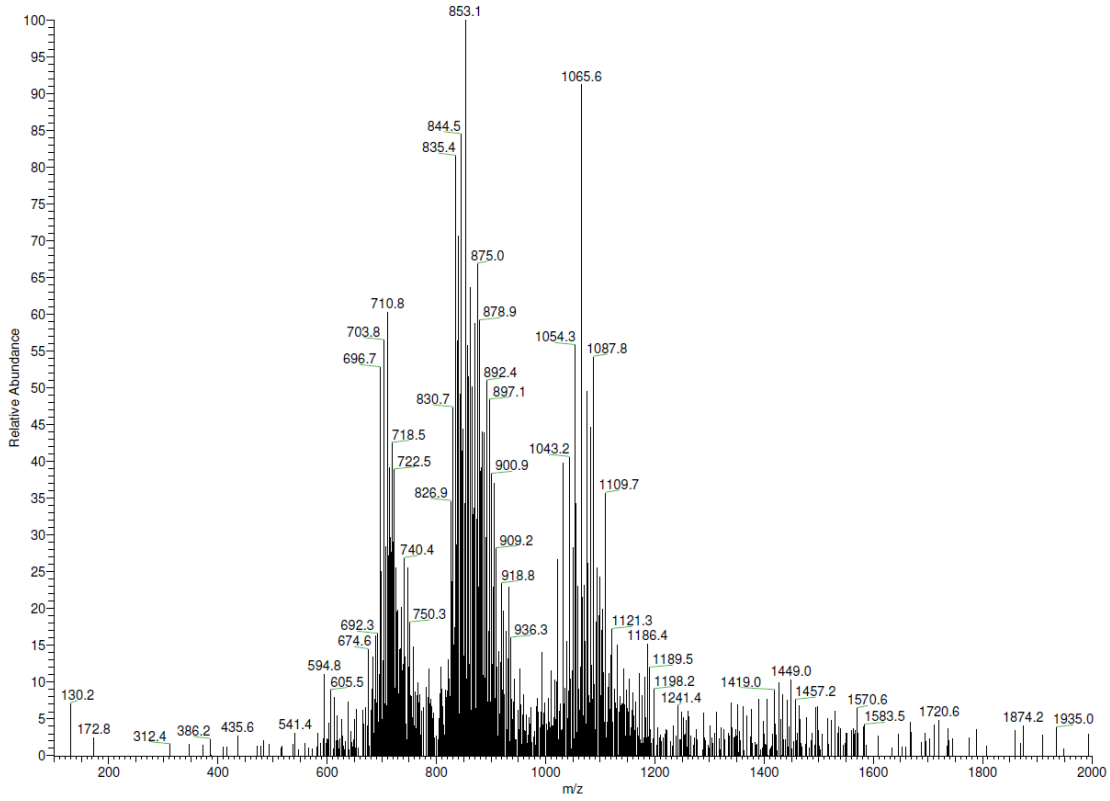

Figure S9. Mass spectrum for BrF6,11T PEG

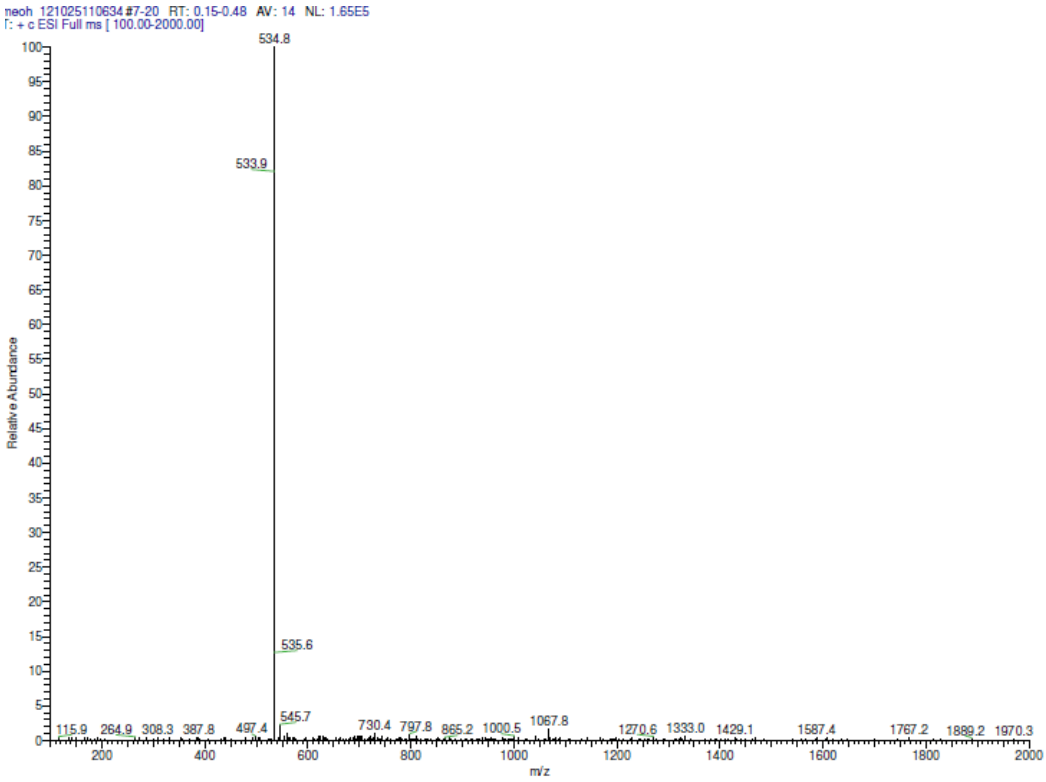

Figure S10. Mass spectrum for BrF control peptide

3. PEGylated peptides after Oxa-PPV conjugation

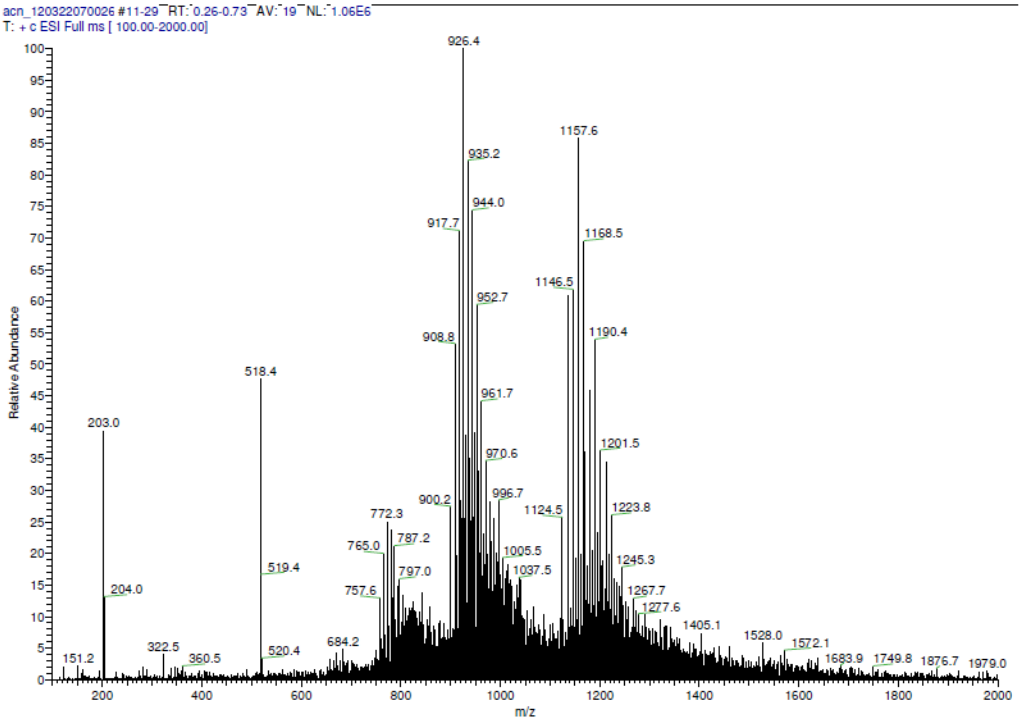

Figure S11. Mass spectrum for Oxa17D PEG

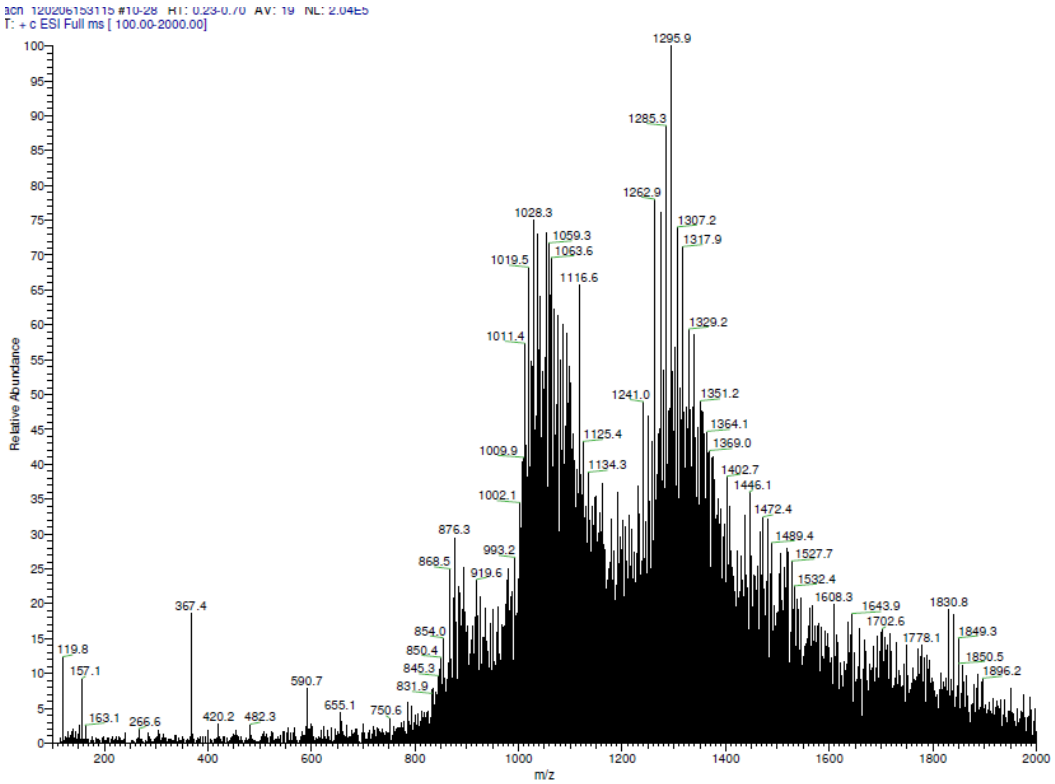

Figure S12. Mass spectrum for Oxa6,7T PEG

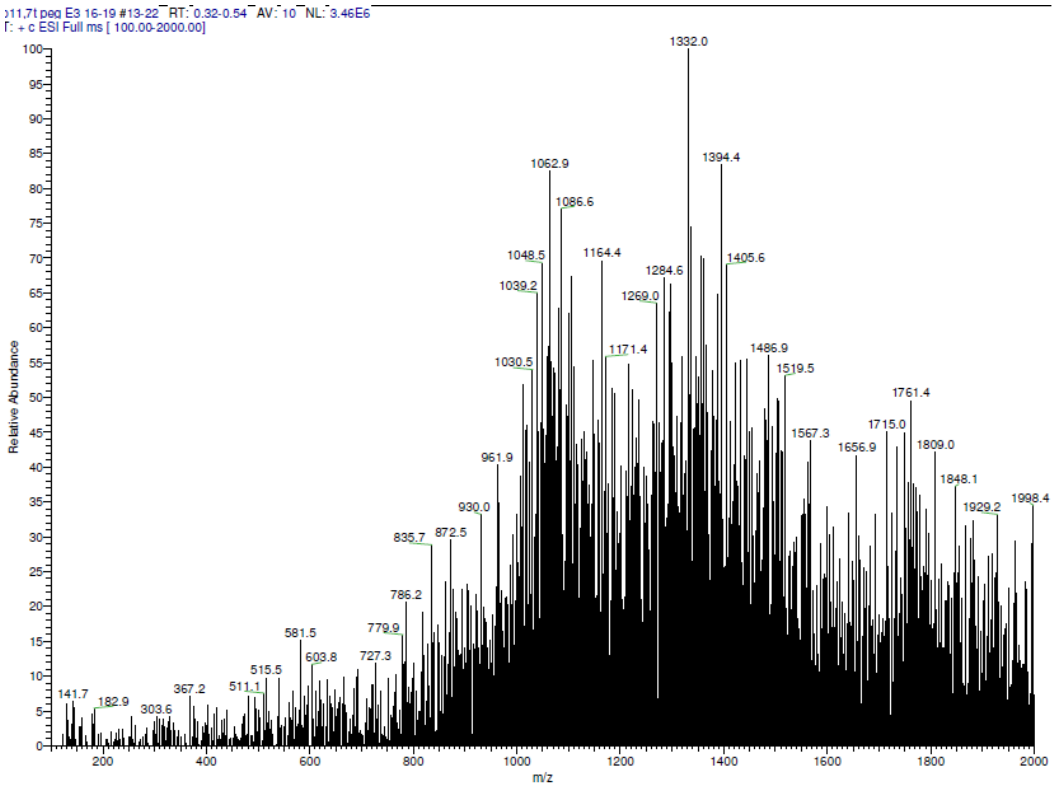

Figure S13. Mass spectrum for Oxa11,7T PEG

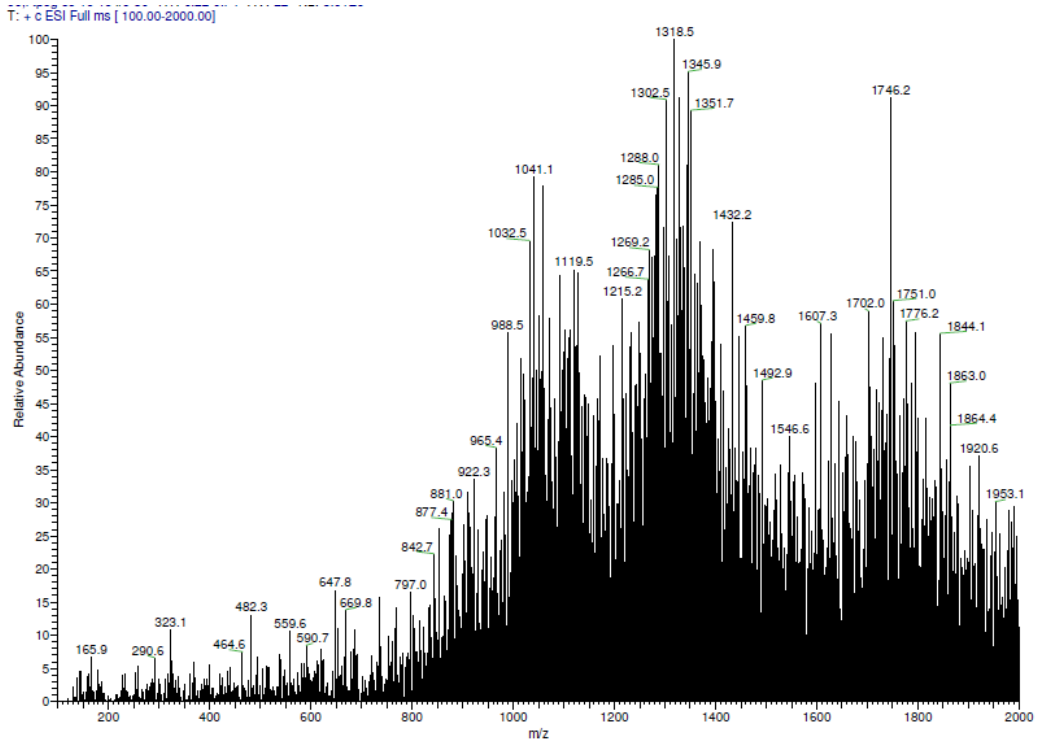

Figure S14. Mass spectrum for Oxa6,11T PEG

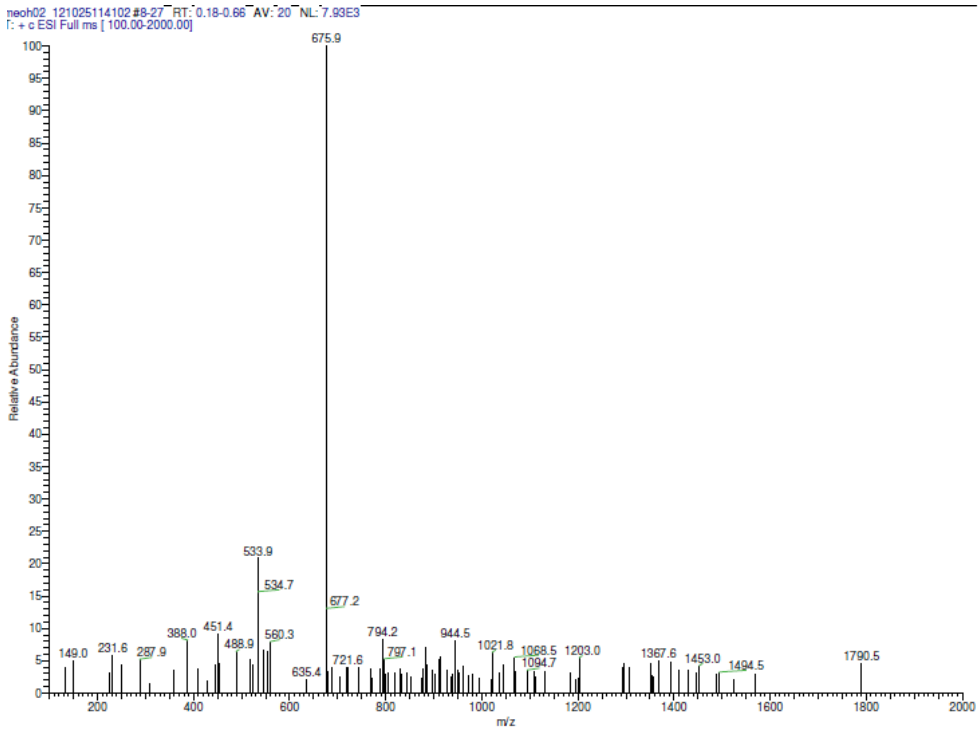

Figure S15. Mass spectrum for the Oxa control peptide

Circular Dichroic (CD) Spectroscopy

CD scans as a function of increasing temperature (5°C to 80°C) in methanol were conducted on all the peptides. (15 - 140 μM)

1. Peptides before PEGylation

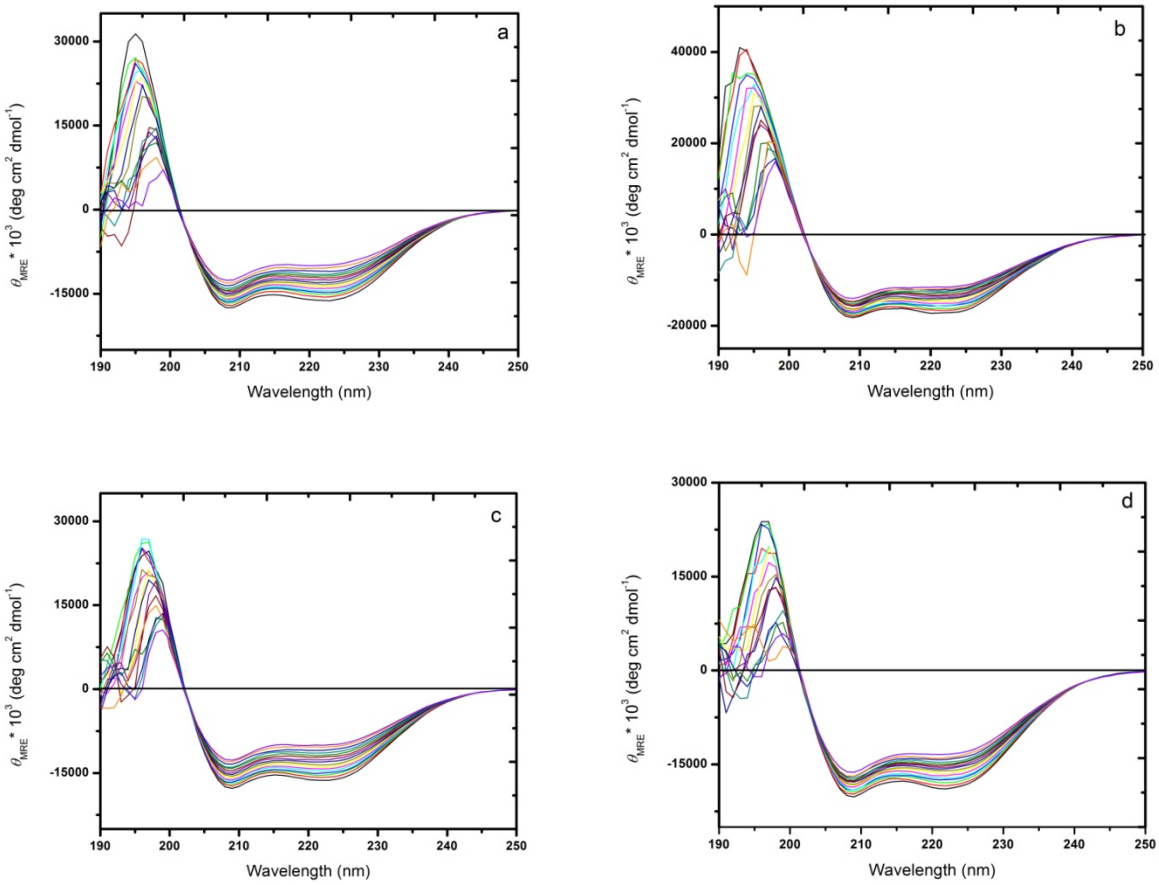

Figure S16. CD scans as a function of increasing temperature for non-PEGylated peptides a) BrF17D b) BrF6,7T c) BrF11,7T d) BrF6,11T

2. *PEGylated peptides*

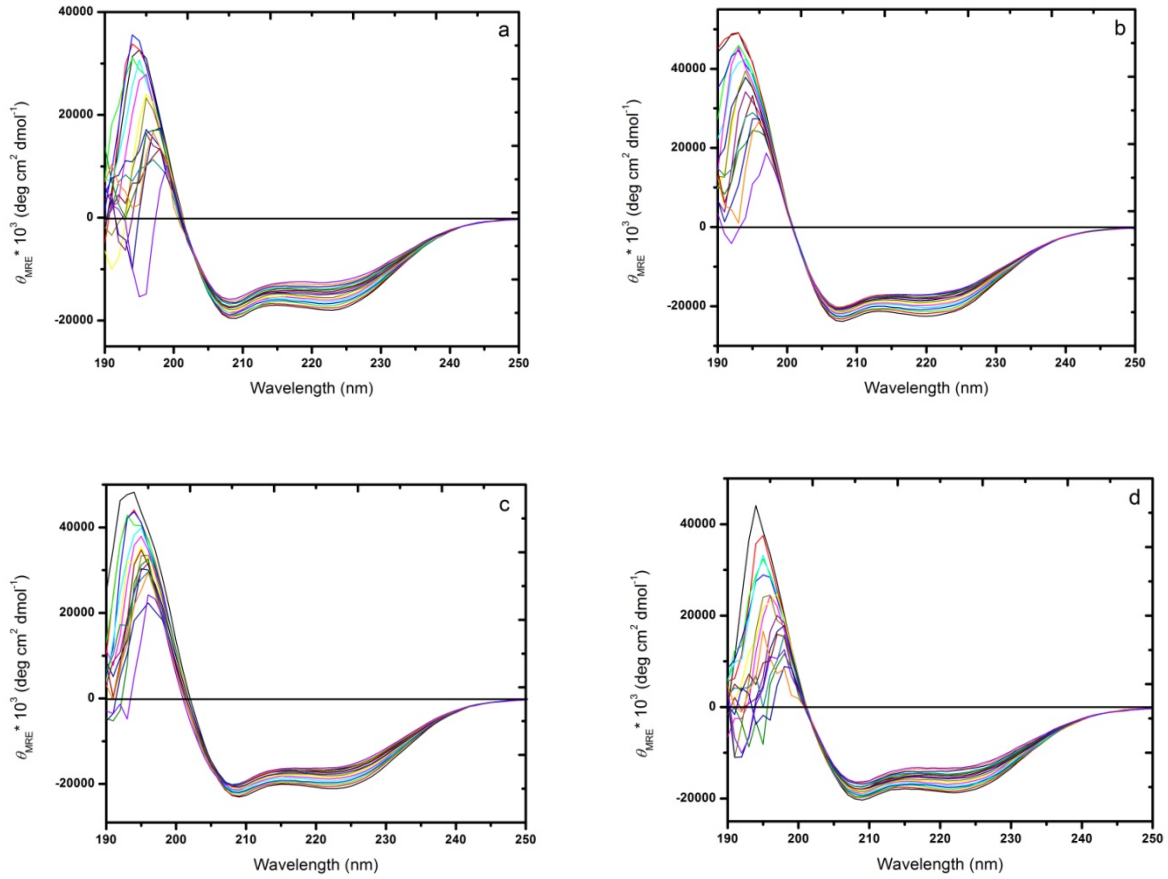

Figure S17. CD scan as a function of increasing temperature for PEGylated peptides a) BrF17D PEG b) BrF6,7T PEG c) BrF11,7T PEG d) BrF6,11T PEG

3. Oxa-PPV coupled PEGylated peptides

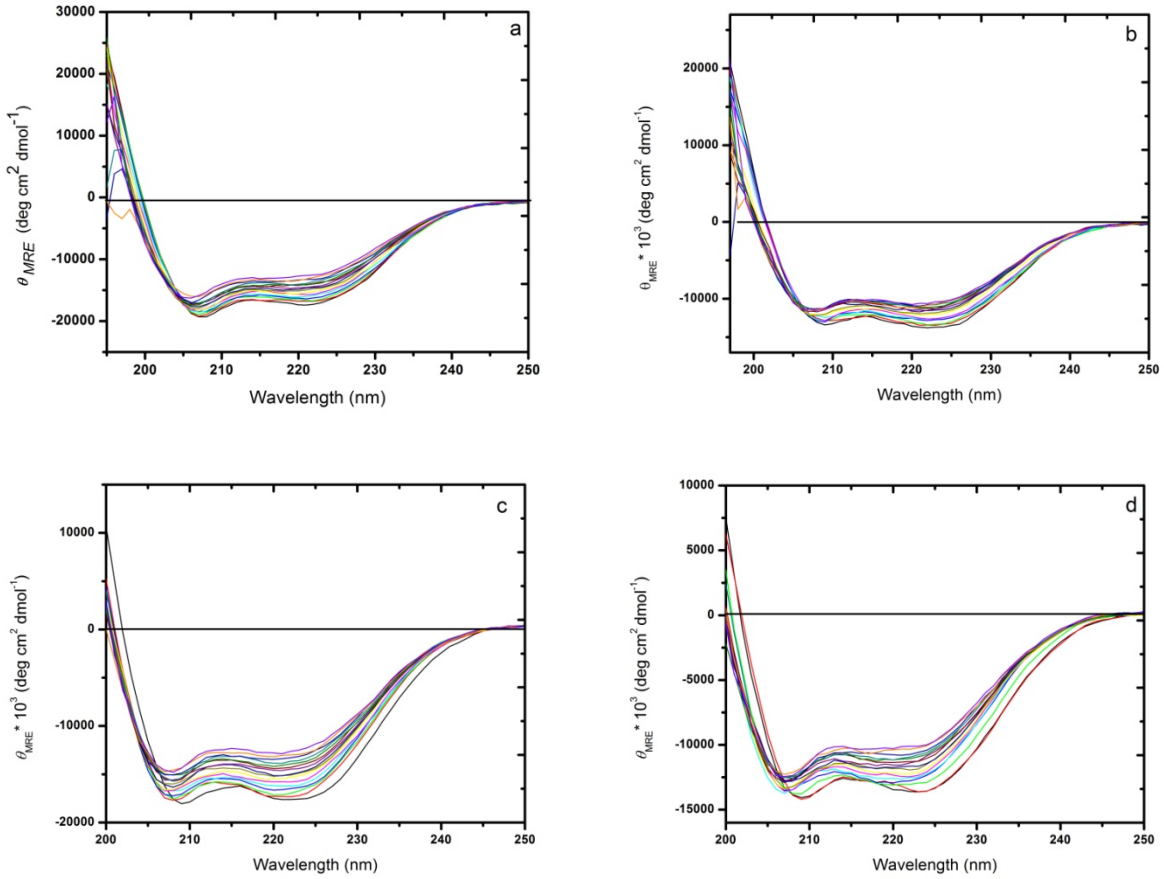

Figure S18. CD scans as a function of increasing temperature for PPV modified PEGylated peptides a) Oxa17D PEG b) Oxa6,7T PEG c) Oxa11,7T PEG d) Oxa6,11T PEG

4. Impact of PEGylation on the stability of the secondary structure of the peptide hybrids indicated in terms of fraction folded values.

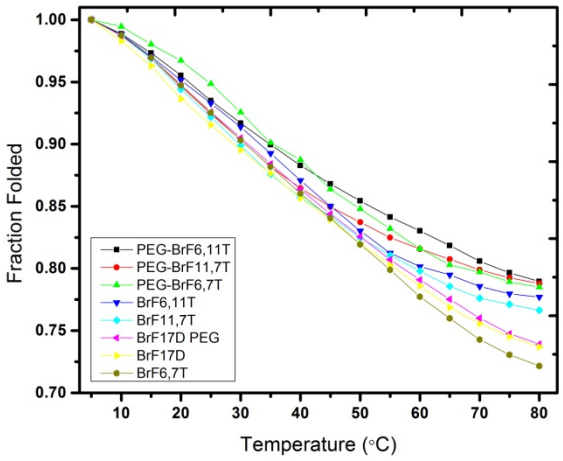

Figure S19. Thermal stability experiments for peptides **BrF17D**, **BrF6,7T**, **BrF11,7T**, **BrF6,11T**, **PEG-BrF17D**, **PEG-BrF6,7T**, **PEG-BrF11,7T** and **PEG-BrF6,11T**; the y-axis is indicated as the fraction folded to permit facile comparison between the stability of the various peptides before and after PEGylation

Energy minimization studies on Oxa control peptide

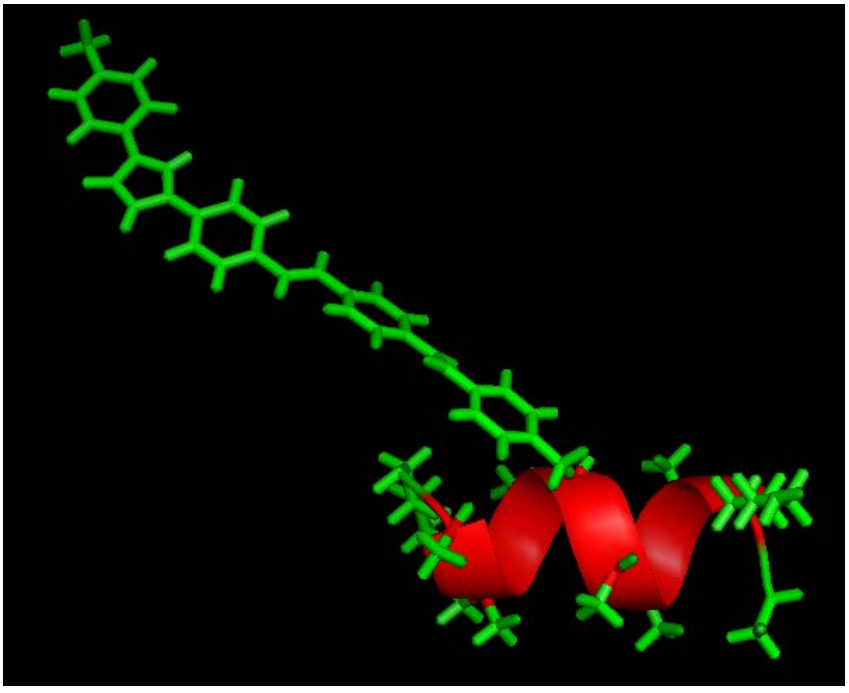

Figure S20. Energy minimization structure for Oxa control

Alternate images of energy minimized structures for tri-substituted hybrid peptides

Figure S21 shows the energy minimized molecular models of the hybrid peptides with their backbones perpendicular to the plane of the paper. The Oxa-PPV chains are marked from N terminus to the C terminus with the N terminus of the peptide facing forward. These models show that the Oxa-PPV molecules have opposite chirality for Oxa6,7T and Oxa11,7T respectively.

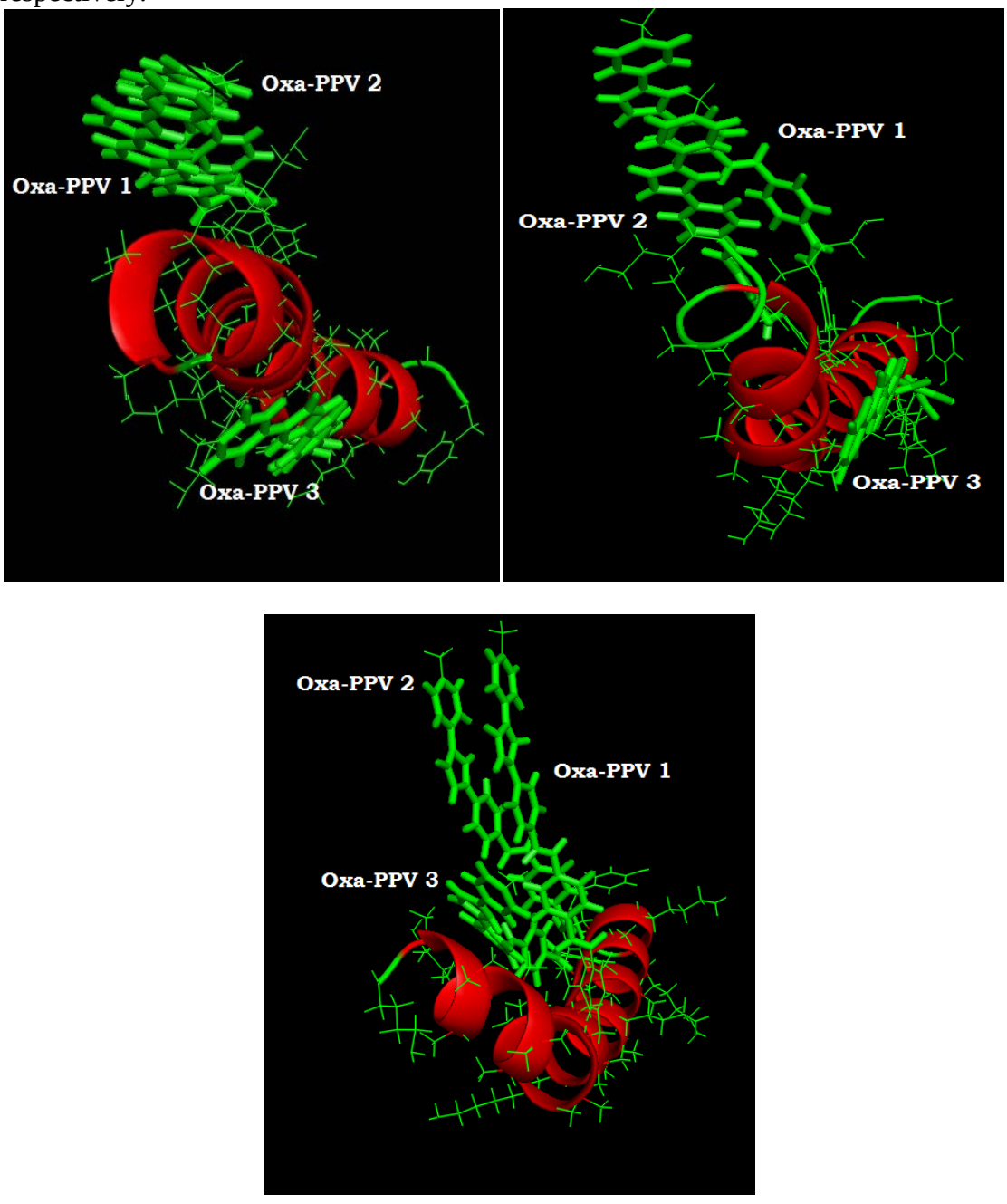

Figure S21. Molecular models of Oxa6,7T (top left), Oxa11,7T (top right) and Oxa6,11T (bottom) with their peptide backbone axis perpendicular to the page.