Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Aggregation of Cyclic Polypeptoids bearing Zwitterionic End-groups with Attractive Dipole-Dipole and Solvophobic Interactions: A Study by Small-Angle Neutron Scattering and Molecular Dynamics Simulation

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Partial charges

The partial charges obtained from the CHELPG electronic structure method using the B3LYP functional and the 6-31G basis set are tabulated below. Note that the terminal charges were not calculated using this method but were directly assigned values of +1 and -1.

Type	Charge (e)	Type	charge
Methanol O	-0.72	Backbone N	-0.22
Methanol H	0.44	Backbone C	-0.02
Methanol CH_3	0.28	Side chain C	-0.26
Amide C	0.5	terminal N(of NH_3^+)	1.0
Amide O	-0.5	terminal O^-	-1.0
Hydrogen	0.1	chloride ion	-1.0

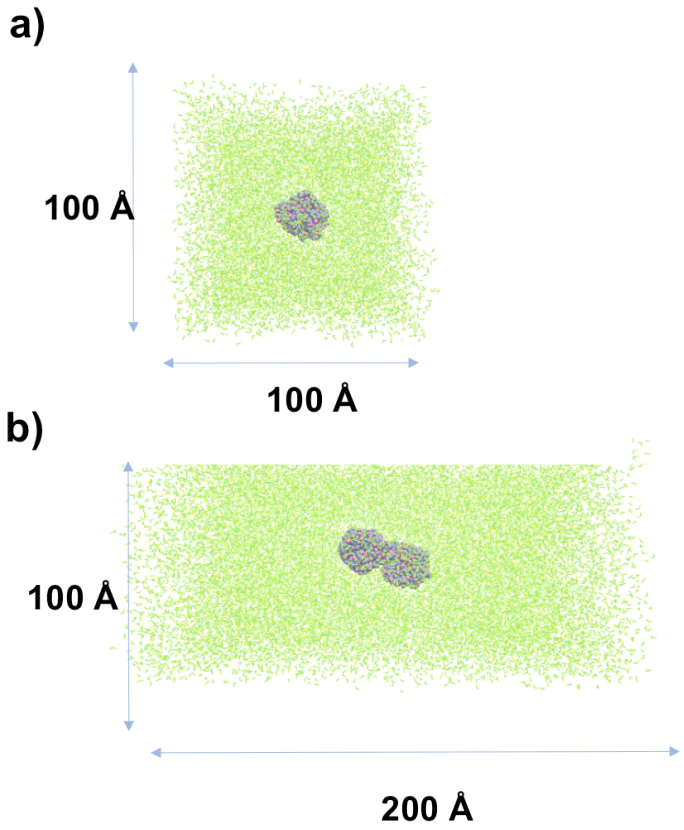

Figure S1: Representative snapshot of the simulation box with a) just one cyclic polypeptoid (*c*-$PNMG_{100}$) in a box of methanol solvent b) two *c*-$PNMG_{100}$ in methanol. The methanol solvent is shown in green.

Free Energy profile using a second collective variable

Method. For the cyclic polypeptoid case, the collective variable was defined as the distance between the center of mass of the groups forming the dipole on one polypeptoid chain to the corresponding center of mass on the other polypeptoid chain. Using the same simulation box setup as in the case of the first collective variable umbrella sampling simulations were carried out using A total of twenty umbrella sampling windows ranging from an inter-polymer distance of 48 Å to 8 Å were carried out, each with a 10 ns equilibration run followed by a 30 ns production run. A harmonic force constant of 3.0 kcal/mol was used for the 8 and 16 Å windows and 2.0 kcal/mol for the remaining windows.

In the case of the linear polypeptoid, the second collective variable was the distance between the charged end group on one polypeptoid chain and the uncharged end group of the other chain. Once again using the same setup as the first collective variable for the linear case, umbrella sampling simulations were carried out with a total of fourteen umbrella sampling windows ranging from an inter-polymer distance of 48 Å to 22 Å, each with a 10 ns equilibration run followed by a 30 ns production run. A harmonic force constant of 3.0 kcal/mol was used for the 22 and 23 Å windows and 2.0 kcal/mol for the remaining windows.

Results and Discussion. Figure S2 clearly shows that the linear case has a potential of mean force that increases monotonically with decreasing distance, suggesting that at best aggregation can take place only transiently. However the free energy profile of the cyclic polypeptoid (Figure S3) does suggest that the dimer is a stable configuration. These results are consistent with the results obtained using the first set of collective variables described in the main article and Figure 8.

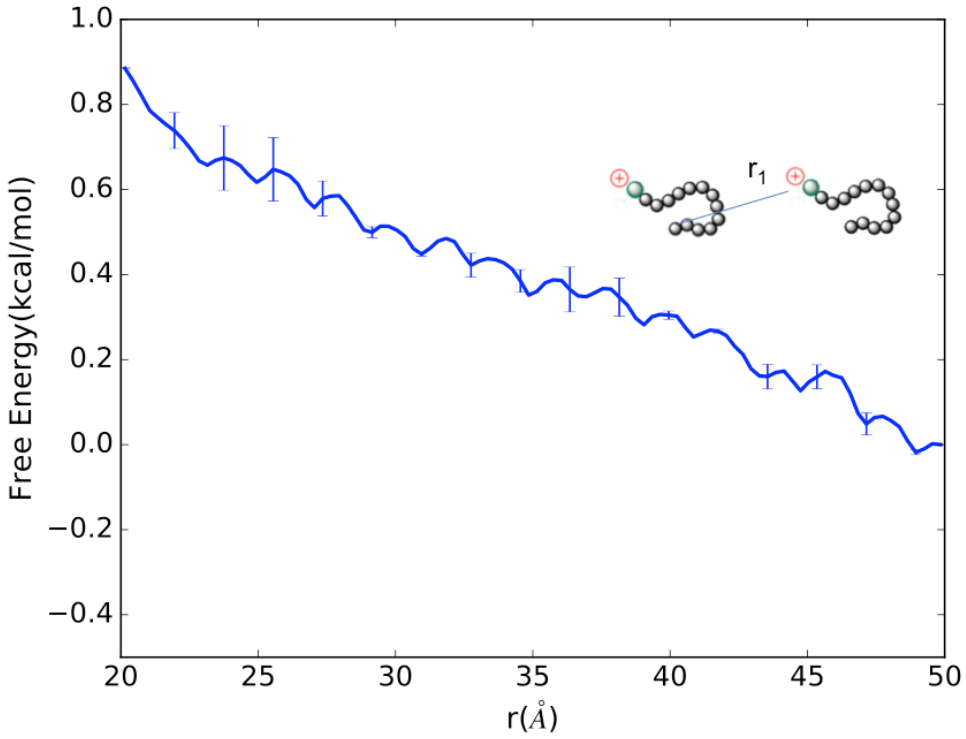

Figure S2: Free energy profile as a function of the distance between a charged end of one linear polypeptoid chain and the uncharged end of the other chain. Inset is a sketch of the collective variable.

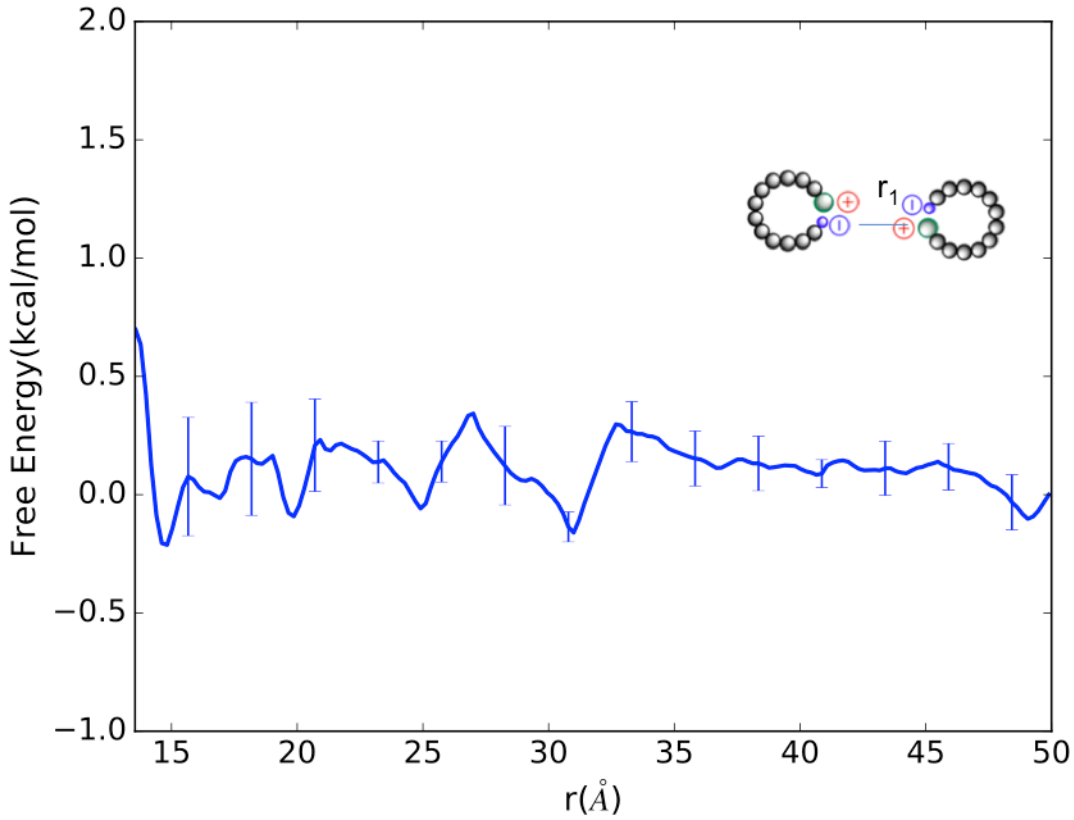

Figure S3: Free energy profile as a function of the distance between the dipoles for the cyclic polypeptoid case. Inset is a sketch of the collective variable.