Molecular dynamic simulations of self-assembly of amphiphilic comb-like anionic polybenzoxazines

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The iBnXz concentrations ~~have~~ systematically varied from ~~the~~ 8.3 mM to 149.4 mM for all of 3BnXz, 4BnXz, 6BnXz, 8BnXz and 10BnXz, as shown in figure (S1). More specifically, we have performed simulations A, B, D, E and C for the same size systems (10 nm^3) with different number of molecules that is described in figure (S1):

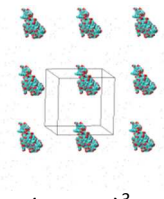
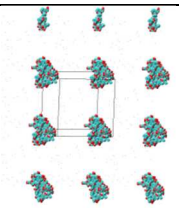
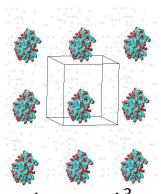
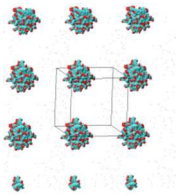
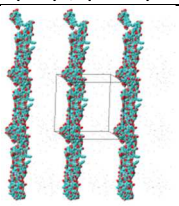
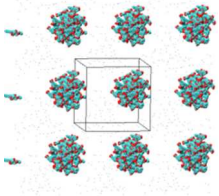
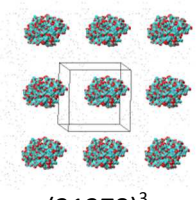
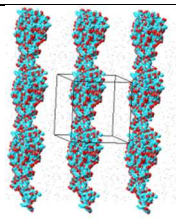
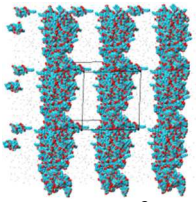
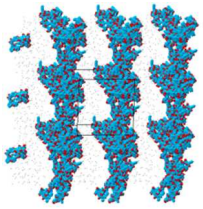
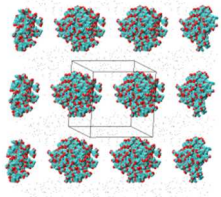
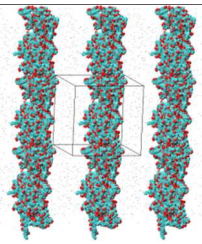
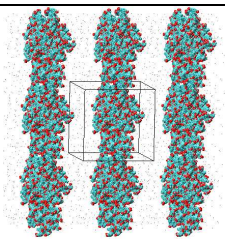
System	3BnxZ	4BnXz	6BnXz	8BnXz	10BnXz
A $(8.3)^1$ $(5)^2$	----------	----------	----------	 $(32595)^3$ $(40)^4$, $(1.80)^5$	 $(32425)^3$ $(50)^4$, $(2.28)^5$
B $(16.6)^1$ $(10)^2$	----------	----------	 $(32291)^3$ $(60)^4$, $(2.63)^5$	 $(31923)^3$ $(80)^4$, $(3.60)^5$	 $(31616)^3$ $(100)^4$, $(4.56)^5$
C $(49.8)^1$ $(30)^2$	 $(31921)^3$ $(90)^4$, $(4.13)^5$	 $(31378)^3$ $(120)^4$, $(5.86)^5$	 $(30255)^3$ $(186)^4$, $(7.91)^5$	 $(29079)^3$ $(248)^4$, $(8.92)^5$	 $(28943)^3$ $(260)^4$, $(11.70)^5$
D $(99.6)^1$ $(60)^2$	 $(30601)^3$ $(180)^4$, $(8.27)^5$	 $(29493)^3$ $(240)^4$, $(11.72)^5$	----------	----------	----------
E $(149.4)^1$ $(90)^2$	 $(29324)^3$ $(270)^4$, $(12.40)^5$	----------	----------	----------	----------

Figure S1: Overview of simulations performed: The snapshots at t= 20 ns represent the effect of both the molecule size and the molecules concentration on the micellization morphology. The

letters in the first row define the systems. The numbers between the brackets represent the following: 1- milli-molarity (mM), 2- iBnXz molecules, 3- water molecules, 4- Na ions, 5- wt% of amphiphile. The micelles in the center of the cell represented as van der Waals spheres; Red spots represent the oxygen atoms, cyan color represents the carbon and hydrogen atoms, and the nitrogen atoms are blue.

The time evolution of the radius of gyration (Rg), figure (S2) describes the aggregation structure, and shows the molecule size dependence of Rg for the different iBnXz molecules in the spherical region. Assuming that the clusters are on average spherically shaped, the physical radius of the micelle (R_s) can be estimated from the gyration radius (Rg), in order to compare it with the experimental data, using[1]:

$$R_s = \left(5/3\right)^{1/2} \times R_g$$

For the last 5 ns of the simulation, the average radii of gyrations for the spherical micelles were determined and the micelles radius was calculated. The experimental[2] Rs of the 9BnXz is 1.364 nm, the relationship between the theoretical Rs and molecule size is linear. So, the theoretical Rs of 9BnXz is 1.356 nm, consistent with experimental Rs.

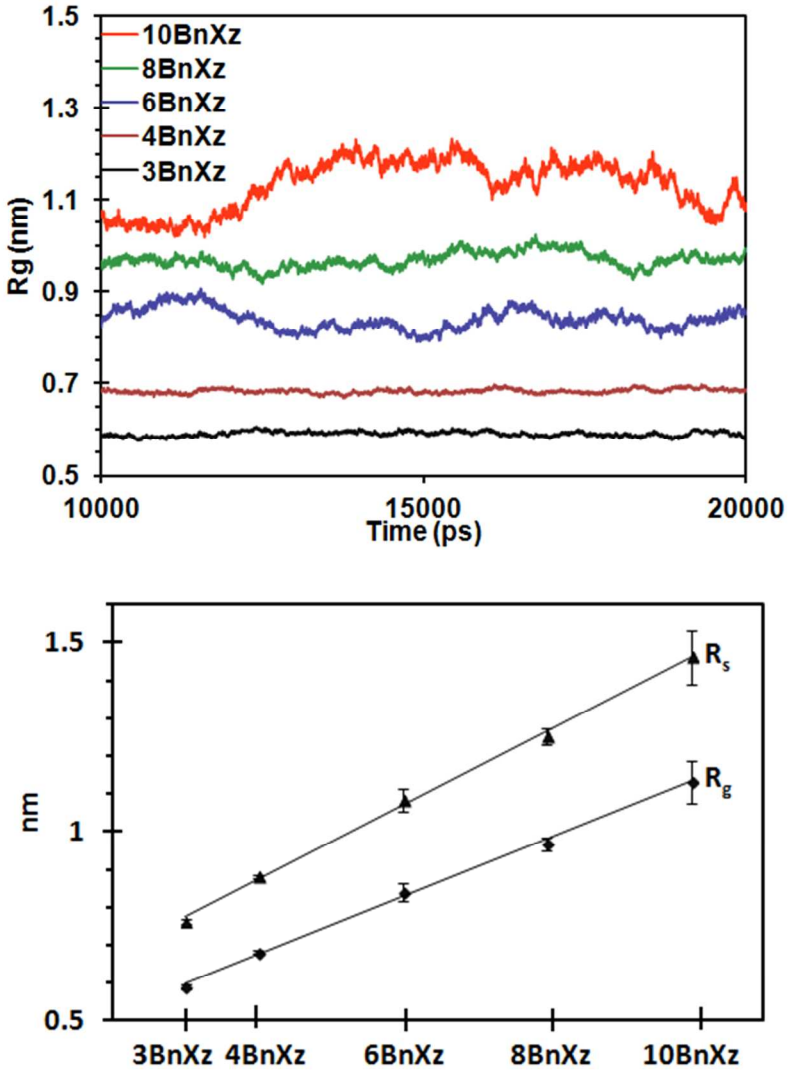


Figure S2: The radius of gyration of the spherical micelles for the last 10 ns of the simulation (upper). The average radii of gyrations (Rg) and the micelles radius (R_s) of the spherical micelles for the last 10 ns of the simulation (lower).

The intramolecular interactions, ~~introduced based on the interactions~~ between atoms separated by three bonds, account for the one to four interactions (the so-called 1-4 interactions) in which electrostatic and van der Waals parts are reduced by 50%, both scalings are identical to the OPLS-AA force field for consistency. The intramolecular interactions of the iBnXz molecules were examined by utilizing the intramolecular potential in computing the forces between two atoms of the same molecule, the results are given in figure S3.a and figure S3.b. It is seen from these figures that the interaction energy of the larger molecules is much larger than that of the smaller molecules in both electrostatic and vdW terms, which attributed to the larger molecules' experience of larger London forces than smaller molecules, represented by the London dispersion terms.

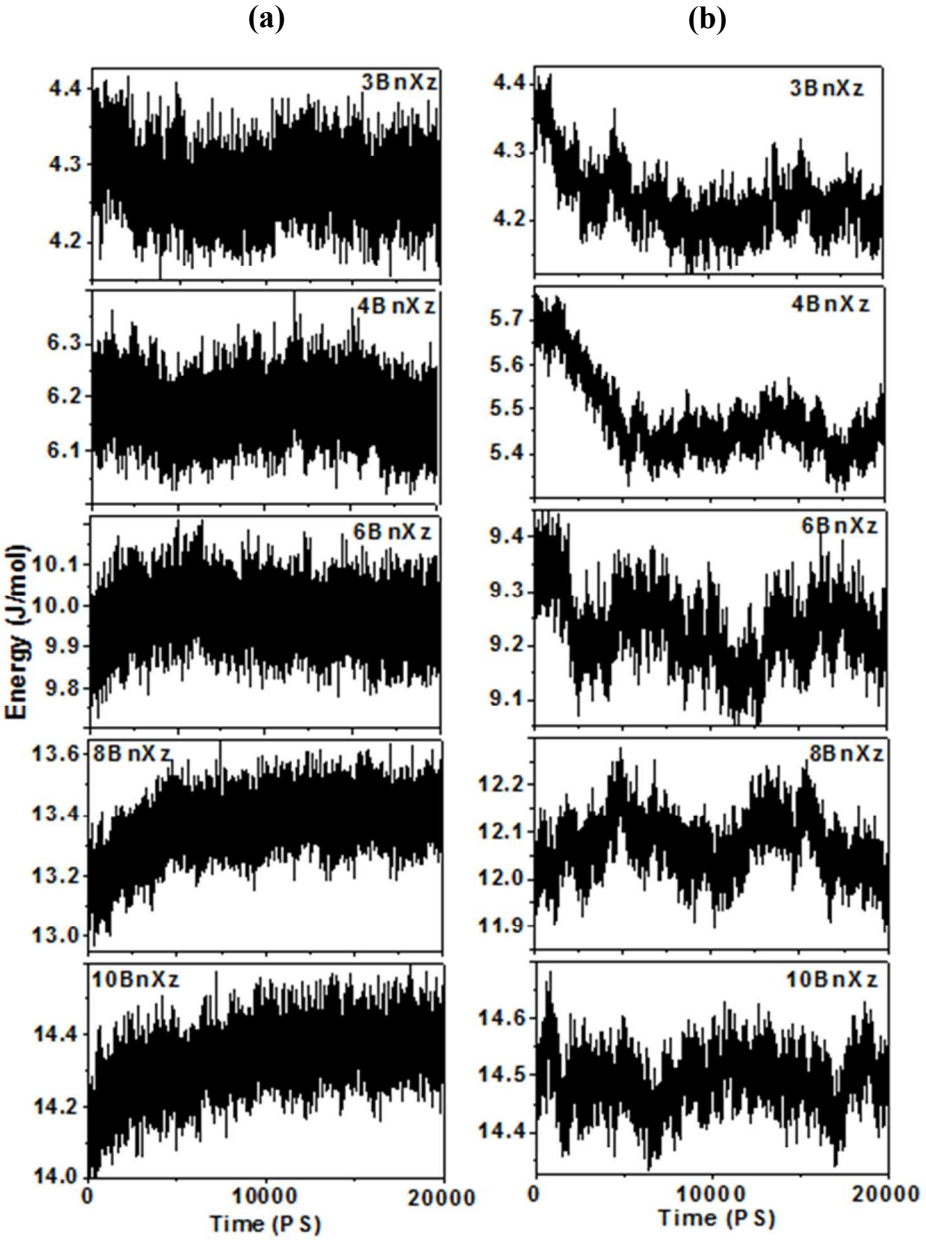


Figure S3: Atom_Atom 1-4 interactions (a) van der Waals (LJ-14), (b) electrostatic (Coul-14).

References:

1. Theodorakis, P.E.; Hsu, H.-P.; Paul, W.; Binder, K. Computer simulation of bottle-brush polymers with flexible backbone: Good solvent versus theta solvent conditions, *J. Chem. Phys*. **2011**, 135, 164903.
2. Mahfud, R.; Agag, T.; Ishida, H.; Shaikh, S.; Qutubuddin, S. Synthesis and evaluation of novel anionic polymeric surfactants based on polybenzoxazines. *J. Colloid Interf. Sci*. **2013**, *407*, 339–347.