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Supporting Information

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Approaches to the design of better low-dosage gas hydrate inhibitors

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Purified Type I fish AFP from winter flounder (wfAFP) was kindly provided by A/F Protein Canada Inc. Recombinant AFP from the spruce budworm insect, *Choristoneura fumiferama*, (CfAFP) was produced as previously described (*1*). Dr. E. D. Sloan (Colorado School of Mines, USA) kindly provided the PVP (30K) sample. The wfAFP and PVP solutions were prepared with ultrapure water (18.2 mΩ·cm at 298K, produced by Milli-Q® ultrapure water purification systems, Millipore, Billerica, U.S.A.) at 25.0 μM. Samples were assessed for their ability to adsorb to SiO_2 or polystyrene (PS).

All measurements were conducted with a quartz crystal microbalance (Q-Sense D300, Q-Sense AB, Gothenburg, Sweden) with 5-MHz AT-cut crystals (Q-Sense AB). The sensor crystal was coated with SiO_2 (QSX-303) on the gold electrode on one side of the sensor. The sensor crystal was cleaned in a UV-O_3 chamber and then placed in a 250 μl measurement chamber with the coated surface facing the testing liquid and the other side facing air. Before measurements, purified water was equilibrated at 299.0 K and then introduced into the measurement cell. Once a stable baseline was achieved, 1.5 ml AFP or PVP solution was equilibrated at the same temperature and ~0.5 ml aliquots of the solution was introduced into the measurement chamber at a time, replacing the water in

the cell. Frequency shift (*f*) and dissipation factor (*D*) measurements were sampled at a rate of ~1Hz with a sensitivity of <0.5 Hz and 1×10^{-7}, respectively.

To observe the desorption of AFP/PVP from the SiO_2 surface, after the resonance frequency reached a plateau, 1.5ml MQ-water was equilibrated at the same temperature and ~0.5 ml MQ-water was introduced into the measurement cell to rinse the macromolecule-covered surface. The rinsing process was repeated for three times for each sample.

A cartoon explaining the relationship of adlayer properties and *R* values (dissipation factor) is given in Fig. 1. It can be seen that at the initial stage of adsorption, both PVP and wfAFP formed loose and porous adlayer (large *R* value). When adsorption continued and the adsorption mass increased, the *R* value (R_2 for the final adsorption stage) of wfAFP adlayer decreased significantly, revealing the formation of a firm and rigid adlayer with limited amount of water trapped. On the other hand, R_2 of PVP was still very large, revealing a final loose and porous adlayer with a large amount of trapped water.

1. V. K. Walker, M. J. Kuiper, M. G. Tyshenko, D. Doucet, S. P. Graether, Y. C. Liou, B. D. Sykes, Z. C. Jia, P. L. Davies, L. A. Graham, L.A. In: Insect Timing: Circadian Rhythmicity to Seasonality, Denlinger, D.L.; Giebultowicz, J.; Saunders, D.S. Eds; Elsevier: Amsterdam, Chapter 16, pp199-211 (2001)

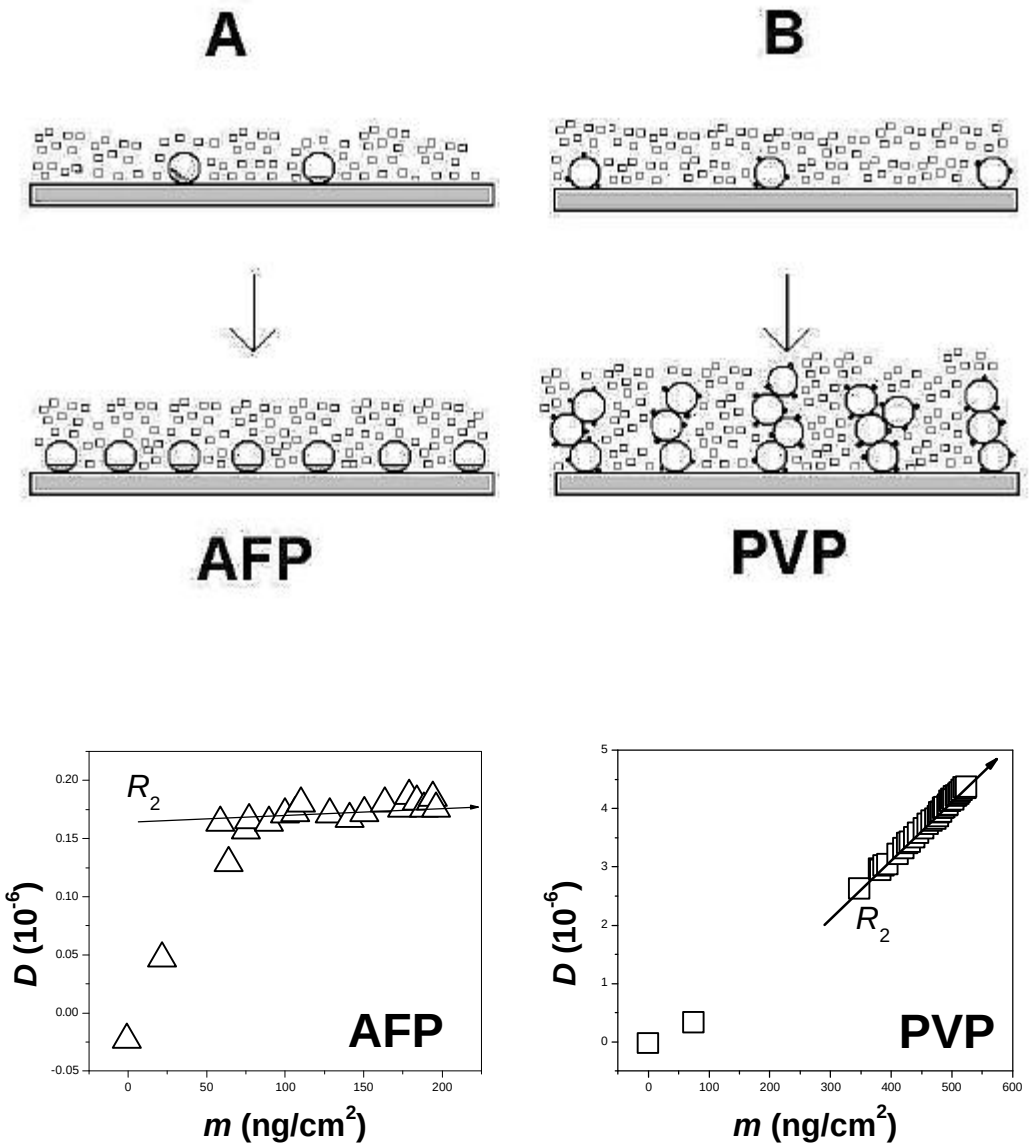

Fig.1 A cartoon explaining the relationship of the adlayer properties and corresponding *R* values. Both wfAFP and PVP were measured at 25μM on silica surface.