

1 **Supporting Information:**

2 **SI.1 Calculations to determine the analytical values of k_H of dimers in Table 1**

3 The scenario considered here (Table 1) is a dimer consisting of two monomers,
4 where only the adsorbing monomer(s) has a favourable interaction (χ_{2s}) with the surface.
5 The number of monomers belonging to chains (i.e., the adsorbed amount) present in the
6 first layer at a specific bulk volume fraction ϕ can be calculated as follows.

7 There are two possible conformations of a dimer that would result in its monomers
8 being present in layer 1 (i.e., to be in contact with the surface). One is the dimer lying
9 “parallel” to the surface, thus contributing two monomers to the first layer. The relative
10 probability of dimers taking this conformation (relative to its confirmations in the bulk) is
11 $2\left(\frac{4}{6}\exp(-2\chi_{2s})\right)$. Here $\exp(-2\chi_{2s})$ is the Boltzmann factor associated with the two
12 monomers of the dimmer, each with a surface interaction strength of χ_{2s} , $\frac{4}{6}$ is the lattice
13 parameter λ (here for the chosen cubic lattice) indicating the 4 out of 6 orientations where
14 the two monomers both reside in the same layer, with the term being multiplied by 2
15 because the two monomers are interchangeable in terms of their position. The second
16 conformation is the dimer adsorbing “perpendicular” to the surface, hence contributing
17 only one monomer to layer 1 adjacent to the surface, with the other monomer residing in
18 layer 2 and not in contact with the surface. The relative probability in this case is
19 $2\left(\frac{1}{6}\exp(-\chi_{2s})\right)$, where similarly $\exp(-\chi_{2s})$ is the Boltzmann factor for one monomer
20 interacting with the surface, $\frac{1}{6}$ is the lattice parameter λ indicating the possibility of
21 monomers being in the adjacent layers, and once again the entire term is multiplied by 2
22 due to the interchangeability of the monomers with regards to their positions. Adding the

23 two possibilities together, and considering the bulk volume fraction ϕ and number of
24 monomers per polymer chain, N , then the adsorption (Γ) in layer 1 can be expressed as

$$\Gamma = 2 \frac{\phi}{N} \left(\frac{4}{6} \exp(-2\chi_{2s}) + \frac{1}{6} \exp(-\chi_{2s}) \right)$$

25 For a dimer, the degree of polymerisation N is equal to 2 and so the equation becomes

$$\Gamma = \left(\frac{4}{6} \exp(-2\chi_{2s}) + \frac{1}{6} \exp(-\chi_{2s}) \right) \cdot \phi$$

26 Identifying the above equation with $\Gamma = k_H \phi$, we have

$$k_H = \frac{4}{6} \exp(-2\chi_{2s}) + \frac{1}{6} \exp(-\chi_{2s})$$

27 The dimer described in Table 1a has two adsorbing monomers. When the magnitude
28 of the interaction potentials χ_{2s} are sufficiently large (and favourable, i.e., χ_{2s} is very
29 negative), most of such adsorbed dimers should lie flat on the surface, with both
30 monomers in layer 1. This means the “parallel” adsorbed conformation dominates, and
31 the other “perpendicular” configuration can be ignored to a first approximation. In other
32 words, in such a case $k_H \approx \frac{4}{6} \exp(-2\chi_{2s})$. On the contrary, for the dimer consisting of an
33 adsorbing monomer and a non-adsorbing one (Table 1b), the “perpendicular”
34 conformation would dominate, and the contribution from the “parallel” configuration
35 becomes negligible. In this case, $k_H \approx \frac{1}{6} \exp(-\chi_{2s})$.

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37 **SI.2 Outline for implementing the SCF Sheutjens-Fleer theory**

38 A detailed account of the Self-Consistent-Field (SCF) theory can be found in many
39 books and excellent reviews [1-5]. In particular, in relation to the problem of adsorption of

40 polymers at interfaces and the Scheutjens-Fleer scheme adopted by us here, we point the
41 readers to [6-8]. We shall confine ourselves to only providing a preliminary overview.

42 In SCF theory the interactions between different molecules are represented by a
43 spatially varying effective field, acting on molecules at each point in the system. In
44 common with all mean-field type theories, the essential approximation made in SCF theory
45 is that this field is equal to the average value of the interactions felt by the molecule, but
46 otherwise any temporal fluctuations in its value are small and are ignored. Within the
47 framework of this approximation, a multi-body interacting problem is thus replaced with a
48 more tractable one of a single polymer chain placed in an external field. The value of the
49 field at each point will depend on the local concentrations (volume fractions) of solvent
50 and polymer surrounding the point. The value of the field will depend on the type of
51 interactions one wishes to include. However, adopting the usual Flory-Huggins parameters
52 for specifying the interactions, this is given by equation (5), as discussed in section 2.1.
53 With the aid of equation (5) the field is easily calculated, but only if one knows a priori the
54 density profile variation of various molecules in the solution. This of course is not available
55 in advance and must be determined itself. To overcome this problem, SCF calculations
56 adopt an iterative type procedure. One starts with a rough, but sensible initial guess to the
57 field. All possible conformations available to a chain are then considered. That is to say
58 that each configuration w is included and is weighted according to its appropriate
59 Boltzmann factor ($\sim \exp(-E_w/k_B T)$), where E_w is the energy of that conformation under the
60 influence of the field. This allows the determination of the density profile variation of each
61 molecular specie in the solution using a set of segment density functions, as is described
62 further below.

63 As with any numeric computational scheme, it is necessary to first discretize the
64 part of the solution under investigation. In the Fler-Scheutjens formulation of SCF [9, 10],
65 this space is taken as the gap between two (often solid) flat planes. The gap is divided into
66 layers running parallel to the surfaces. Each layer is then subdivided further into a set of
67 lattice grids. It is possible to use many different lattice grids, but the one chosen in our
68 work was the cubic lattice. As often is the case, the thickness of the layers (and hence also
69 the size of each grid point) can be decided as a compromise between accuracy and the
70 computational speed or resources. In S-F scheme it is customary to take the lattice size,
71 denoted as a_o , to be the nominal size of the monomers comprising the chains. In this way
72 the computation scheme can be given a useful physical interpretation and mapped on to a
73 Flory-Huggins type lattice model for polymers. The layers are numbered $i=1$ to L , running
74 from one surface to the next, hence making the distance between the two surfaces a_oL . For
75 an incompressible solution, all lattice grids must either be occupied by a monomer or a
76 solvent molecule. This requirement leads to the equation (4) in section 2.1.

77 For homogenous surfaces, any variation in the average value of the polymer and
78 solvent volume fractions will only be in a perpendicular direction to the surface, along the
79 gap from one side to the other. That is to say that all lattice points in the same layer will
80 have the same average segment densities, value of fields, etc. To obtain the polymer
81 density for each layer, a set of segment density functions $G(s,i)$ is defined. The function
82 $G(s,i)$ represents the probability that the first s segment of a polymer chain are in a
83 conformation where the s^{th} monomer resides in layer i . Where the polymer chains are not
84 symmetrical in composition, it becomes necessary to define two such sets of functions,
85 $G^{\text{f}}(s,i)$ and $G^{\text{b}}(s,i)$, counting the first s monomers from different terminus ends of the chain.

86 It is also useful to define a function $t(s)$ that evaluate to a number, indicating what type of
87 monomer the s^{th} residue of the chain happens to be. For example, 1 for hydrophilic and 2
88 for hydrophobic, as is the case in our study involving amphiphilic copolymers with two
89 types of monomers. The segment density functions can be readily calculated using a
90 recurrence relation reflecting the fact that if s^{th} monomer is in layer i , then $(s-1)^{\text{th}}$ monomer
91 must have either been in the same layer or one of the adjacent layers $i-1$ or $i+1$. The
92 recurrence relations read

$$93 \quad G^b(s, i) = [\lambda_{-1}G^b(s-1, i-1) + \lambda_{+1}G^b(s-1, i+1) \\ 94 \quad + \lambda_0G^b(s-1, i)] \exp(-\psi_{t(N-s+1)}(i))$$

95 and

$$96 \quad G^f(s, i) = [\lambda_{-1}G^f(s-1, i-1) + \lambda_{+1}G^f(s-1, i+1) \\ + \lambda_0G^f(s-1, i)] \exp(-\psi_{t(s)}(i))$$

97 for backward and forward segment density functions, as was mentioned above. The
98 constants λ_{+1} , λ_{-1} and λ_0 reflect the number of neighbours that a grid point has in its own or
99 adjacent layers. For the cubic lattice used by us, the values are 1/6, 1/6 and 4/6, respectively.
100 The initial condition for starting the recurrence above is $G^f(1, i) = \exp[-\psi_{t(1)}(i)]$ and
101 $G^b(1, i) = \exp[-\psi_{t(N)}(i)]$, where N is the degree of polymerisation of the chains, and
102 $\psi_{\alpha}(i)$ the value of the field acting on monomers of type α in layer i (expressed in units of
103 $k_B T$ here). Note that a similar field $\psi_0(i)$ also acts for solvent molecules (taken as type 0).
104 These are treated on the same footing as the polymers, accept that they have $N=1$. With the
105 set of segment density functions at hand, the all-important polymer density functions in
106 each layer can be obtained using the compositional law:

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$$\phi^\alpha(i) = \frac{\Phi}{N} \sum_s \frac{G^f(s, i) G^b(N - s + 1, i) \delta_{\alpha, t(s)}}{\exp[-\psi_{t(s)}(i)]}$$

108 where $\delta_{\alpha, t(s)}$ represents Kronecker delta function, equal to 1 if $t(s)=\alpha$ and 0 otherwise, and
 109 the volume fraction of the polymer in bulk solution is denoted as Φ . The newly calculated
 110 density profiles can now be substituted back in equation (5) to provide an “improved” set
 111 of fields. These fields are then used to obtain $\phi^\alpha(i)$ as described above. The process is
 112 repeated until a “self-consistent” solution is obtained. That is to say that the resulting set
 113 of fields $\{\psi_\alpha(i)\}$, obtained from a set of density profiles $\{\phi^\alpha(i)\}$, leads to the same density
 114 profiles.

115 In practice, the algorithm we implemented for the above purpose used equation (5) and the
 116 fact that hard core part of the potential $\psi_h(i)$, ensuring the incompressibility of the solution,
 117 acts equally on all monomers within the same layer, irrespective of their type. In other
 118 words

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$$\psi_\alpha(i) - \left(\sum_\beta \chi_{\alpha\beta} \langle \sum_i \phi_i^\beta(r) \rangle \right) + \chi_{\alpha s} [(\delta_{i,1} + \delta_{i,L})]$$

120
$$= \psi_0(i) - \left(\sum_\beta \chi_{0\beta} \langle \sum_i \phi_i^\beta(r) \rangle \right) + \chi_{0s} [(\delta_{i,1} + \delta_{i,L})]$$

121 with $\alpha = 1$ or 2 for hydrophobic and hydrophilic monomers, respectively and the continuous
 122 variable r replaced with the discretised layer number i . The above equations are solved in
 123 conjunction with the condition (4), to obtain $\{\psi_\alpha(i)\}$ and hence also $\{\phi^\alpha(i)\}$. We deployed
 124 the publicly available subroutine MINPAK for solving a system of none-linear
 125 simultaneous equation, for this part of the calculations. As in this work we were mainly

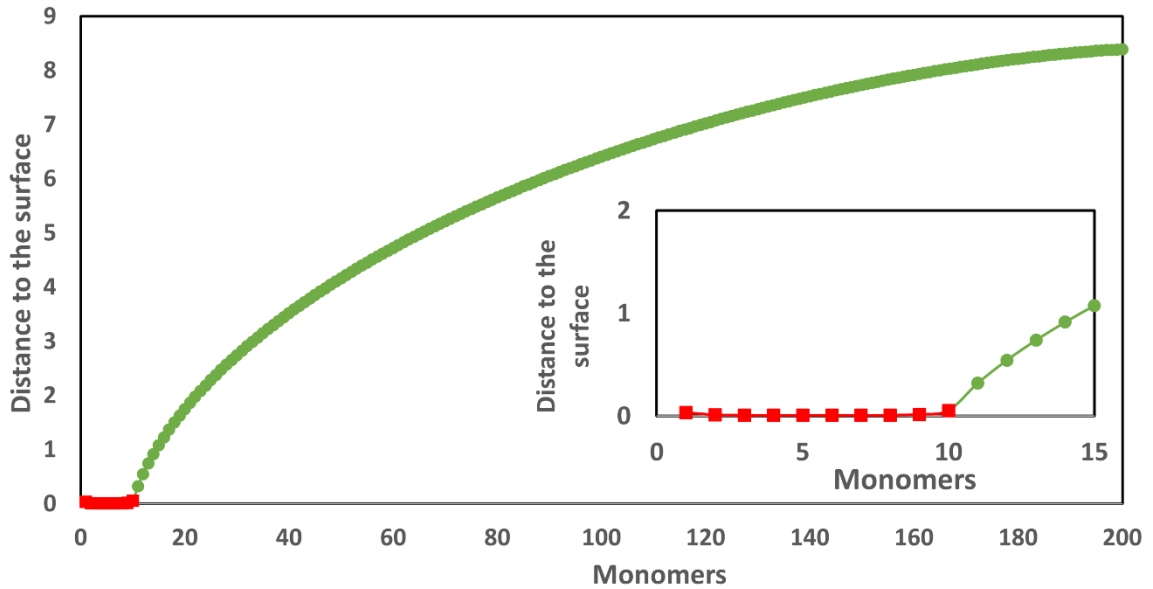
126 interested in the adsorption behaviour occurring on a single interface, we made the gap size
127 between the two surfaces quite larger. As such, the presence of one surface does not
128 influence the adsorption on the other surface. This was checked by increasing the
129 separation distance even further and ensuring that none of the quantities of interest altered
130 (by less than 1 part in 10 million) as a result.

131 Finally, with the density profiles at hand, the adsorbed amounts were calculated viz.
132 equation (8). For simplicity, we kept the above discussions to linear chains only. However,
133 the extension to branched and dendritic chains can also be found in suitable references [8,
134 11, 12].

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137 **SI.3 Graph exemplifying hydrophobic monomers adsorbed onto the surface and**
138 **hydrophilic ones extending away from it, for a linear polymer structure**



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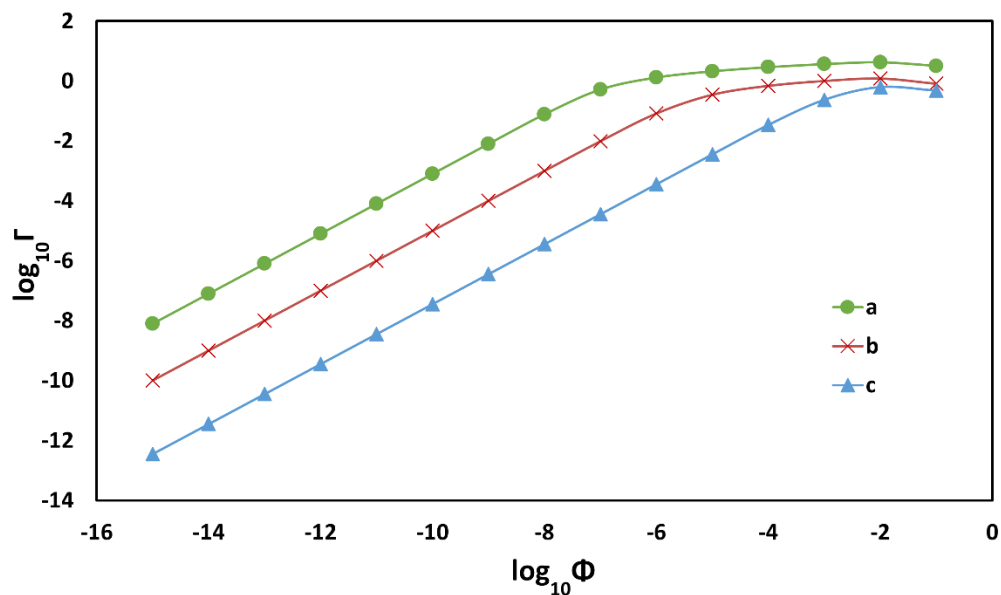
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SI.3 The average distance of each monomer in a linear chain away from the surface. The linear chain shown was an example taken from Section 3.2. It has 10 hydrophobic monomers (labelled as red squares) and 190 hydrophilic monomers (labelled as green circles). The inset shows the results in more detail for the first 15 monomers. It confirms that the hydrophobic segment of the chain does indeed lie flat on the surface.

148 **SI.4 Full adsorption isotherms for selected star-like polymers, providing a**
149 **prospective on the linear Henry's regime.**



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SI.4 The full adsorption isotherm obtained from SCF, for 5-arm star-like polymers in Section 3.3.1, with hydrophobic monomers located at (a) concentrated on one arm only, at one free end, (b) evenly distributed among all arms, at the centre close to the cross-link point, and (c) evenly distributed among the arms, situated on all the free ends.

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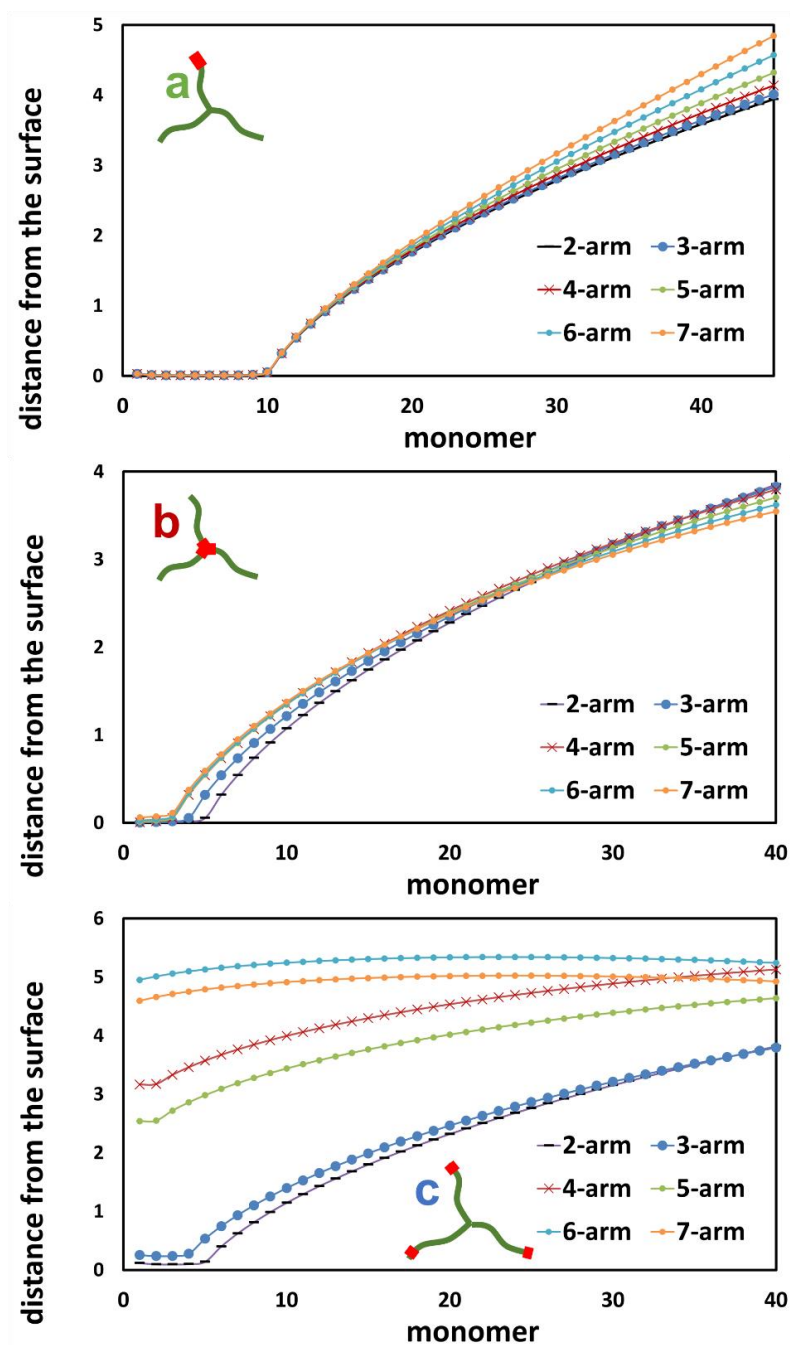
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163 SI.5 The average distance of monomers belonging to star-like polymers of Section
164 3.3.1, away from the surface.



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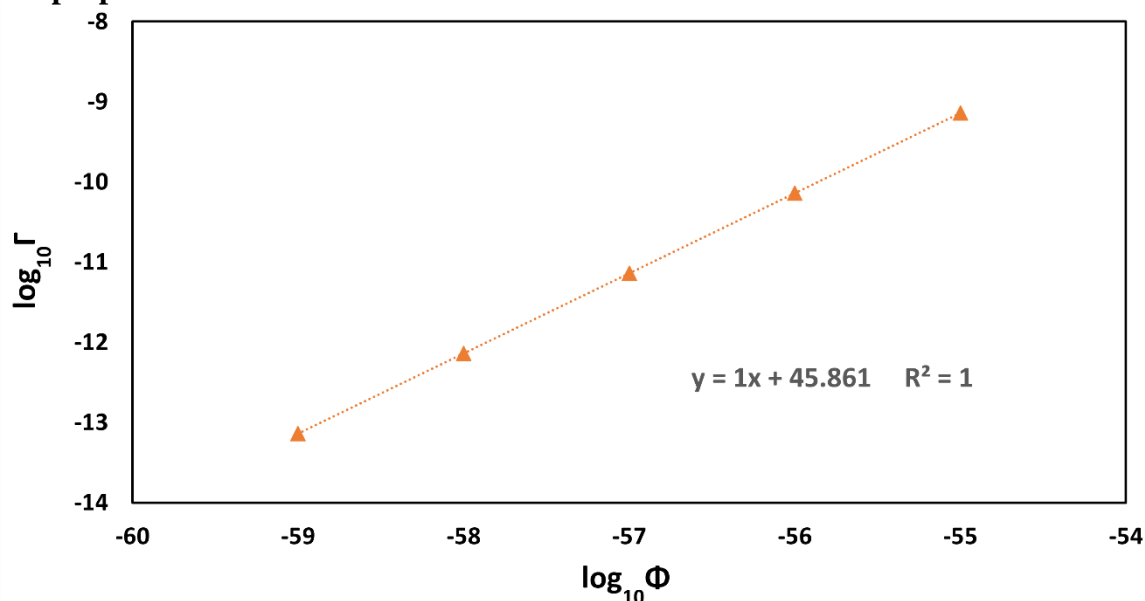
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SI.5 The average distance profiles of star-like polymers of Section 3.3.1 as
obtained from SCF calculations. As for structure (a), where all hydrophobic

168 monomers are located at the edge of one arm in a single block (labelled in red),
169 the distance profile is shown for monomers in the hydrophobe-containing arm.

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171 **SI.6 Predicting Henry's adsorption constant for a model of α_{s1} -casein protein, using**
172 **the proposed method**



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174 **SI.6** Linear part of the adsorption isotherm for α_{s1} -casein as obtained from SCF.

175 The adsorbed amount is plotted against the bulk polymer volume fraction on a
176 logarithmic scale. The equation and R^2 for the fitted linear regression are included,

177 showing a slope of 1, as would be expected. Therefore, $\log_{10}(k_H)$ has the same

178 value as the constant c of the fitted line, providing a k_H value of 7.26×10^{45} . The

179 model for protein here was based on the work of Dickinson et al. [13] for α_{s1} -

180 casein, with amino acid residues divided into 6 different groups. The results

181 demonstrate that the determination of k_H , using the method presented here, can

182 also be undertaken for more chemically complex cases that can additionally also

183 include electrically charged chains.

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185 **References for Supporting Information**

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