Computer simulations of nanopatterning systems

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Anchoring of functionalised ink molecules to self-assembled monolayers (SAMs) is key to the development of molecular printboards for nanopatterning. One very promising system involves ink binding to immobilised β-cyclodextrin (β-CD) hosts, with molecular recognition facilitated by a hydrophobic interaction between uncharged anchor groups on the ink molecule and β-CD cavities at the surface of the printboard [1]. We use molecular dynamics free energy (MDFE) [2] simulations to describe the specificity of ink:printboard association, a crucial parameter for controlling patterning. We find good agreement with experimental thermodynamic measurements for binding enthalpy differences between three commonly-used ink anchors: benzene, toluene and tbutylbenzene (Figure 1). van der Waals interaction with the inside of the host cavity accounts for almost all of the net stabilisation of the larger phenyl guests in β-CD, while partial and full methylation of the secondary rim of β-CD decreases host rigidity and significantly impairs binding of both phenyl and larger adamantane guest molecules. The β-CD cavity is also very intolerant of guest charging, penalising the oxidised state of ferrocene by at least 7 kcal/mol. β-CD hence expresses moderate specificity towards uncharged organic guest molecules by van der Waals recognition, with a much higher specificity calculated for electrostatic recognition of organometallic guests [3].

Multivalent, or multi-site, binding strengthens the attachment of large inks to the printboard, yielding more robust patterns [4]. We performed fully-atomistic molecular dynamics (MD) simulations in bulk explicit solvent to probe the conformational space available to dendrimer and dendrite ink molecules, in both free and bound environments. We show that accurate treatment of both pH effects and binding conformations gives calculated binding modes in line with known binding multivalencies [5]. We identify and quantify the steric frustration causing small, low-generation dendrimer inks to bind to the printboard using just a subset of the available anchor groups and show that the enhanced binding energy of multi-site attachment offsets the steric strain, the feasibility of a given binding mode thus determined by the relative magnitudes of the unfavorable steric strain and favorable multi-site binding free energies (Figure 2). We use our experimentally-validated model of dendrimer binding to predict the binding mode of novel fluorophoric dendrites and find behavior consistent with confocal microscopy imaging of pattern formation at molecular printboards [6].

References:

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Figures:

Figure 1 – Thermodynamic cycle for the computation of ink binding specificity at the molecular printboard. ΔΔG quantifies the binding free energy difference between ink molecules Ink1 and Ink2.

$$\Delta\Delta G = \Delta G_1 - \Delta G_2 = \Delta G_3 - \Delta G_4$$

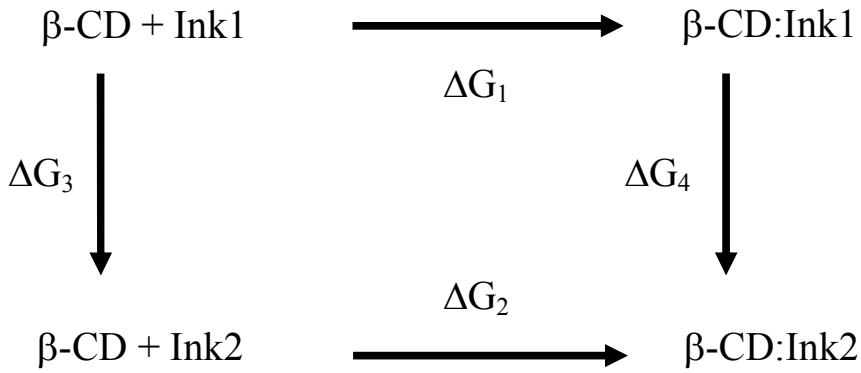

Figure 2 – Free energy balance, the sum of favourable anchor:printboard complexation and unfavourable dendrimer steric strain, predicates dendrimer binding multivalency at molecular printboards. Binding modes with a high, uncompensated, conformational energy penalty are not observed experimentally.