

# Re-entrant DNA gels

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Thanks to the pioneering work of N. Seeman [1], DNA plays nowadays a key role in the development of new materials, based on its capability to self-assemble by design into supramolecular nanometric aggregates [2], which act as versatile building blocks. Here we present the successful design and experimental realization of an innovative material, a one-pot DNA hydrogel able to melt both on heating and on cooling, completely based on competitive interactions encoded in smartly designed DNA sequences. Specifically, we exploit a mixture of tetravalent DNA nanostars (A particles) [3] and monovalent single-stranded DNA sequences (B particles), acting as competitors, to recreate in the laboratory the theoretical model proposed in Ref. [4]. In this model, the relative strength of the AA and AB interactions determines the low temperature structure of the system: either a fluid of diffusive AB<sub>4</sub> clusters (in which four B particles saturate all the bonding sites of particle A) or a spanning tetravalent network of AA bonds, i.e. a highly viscous gel. Interestingly, such a system exhibits a Safran's like re-entrant phase behaviour [4], resulting from the competition of different bonding patterns (which creates on cooling a cross-over from fluid to gel to fluid again). We thus provide an example of the possibility to rationally design biocompatible bulk materials with unconventional phase diagrams and tunable properties. Dynamic light scattering experiments show that the gel changes its structural relaxation time by several orders of magnitude in a few temperature degrees, dissolving both at high and at low temperatures.

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[1] N. Seeman, *Nature*, 2003, **421**, 427.

[2] Y. Ke, L. Ong, W. Shih, P. T. Yin, *Science*, 2012, **338**, 1177.

[3] S. Biffi, R. Cerbino, F. Bomboi, E.M. Paraboschi, R. Asselta, F. Sciortino, T. Bellini, *PNAS*, 2013, **110**, 15633.

[4] S. Roldàn-Vargas, F. Smallenburg, W. Kob, F. Sciortino, *Sci. Rep.* (2013), **3**, 2451.

[5] T. Tlusty and S. A. Safran, *Science*, 2000, **290**, 1328.