Evolvability of Designs and Computation with Porphyrins-based Nano-tiles

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Self-assembly research and practice (regardless of the scale at which it operates) often encounters three key problems (a) the *forward problem*, (b) the *backward problem* (also known as the *designability problem*) and (c) the *yield problem* [1]. The forward problem is concerned with trying to predict what the final product of the self-assembly process would be, given a set of objects, environmental conditions and the natural laws (physical, chemical, biological) that are prevalent at a given specific scale. Usually the forward problem is addressed through the use of simulations and mathematical models. The backward problem, the most difficult of the three, addresses the issue of how the objects and the environment that contains them can be designed in such a way that the final outcome of the self-assembling process is a specific pre-ordained one. As surveyed in [1], this problem is usually addressed through very sophisticated heuristics methods as, in lieu of the NP-hardness (in some cases even undecidability) of the most relevant backward problems, exact analytical solutions are very rarely achievable. The third problem, that of the yield of a self-assembly process is related to the estimation and control of how many of the intended target self-assembled objects one can expect from a particular self-assembling system (this problem is ubiquitous in the chemical sciences). The observation that *"Self-assembly and computation are linked by the study of mathematical tiling"*[2] has produced a step change in the way the forward, yield and, more significantly, the backward problems in molecular self-assembly are dealt with.

More specifically, Winfree and co-workers[3,4,5,6] have shown that universal computation can be carried out by self-assembling discrete *DNA tiles* in a 2D plane and, by utilizing *the power of universal computation*, complex DNA-based patterns have been implemented in the lab through a clever (but laborious) programming of the DNA tiles. Indeed, linking self-assembly and computation provides a powerful new approach to addressing profound questions about the controllability of complex physico-chemical nanosystems. We could ask, for example [5,7,8,9] *what are the least complex molecular tiling 'motifs' which may be exploited in the programming of self-assembly 2D lattices with specific geometries?*. It was shown in [7,8] that answering this question might, in some cases, be a computationally undecidable query while in other cases it might give rise to NP-hard problems, thus it is strongly suspected that exact polynomial time deterministic algorithms do not exist for these problems. It is important to remark that the idea is not necessarily to use self-assembly for computational purposes (as in DNA computing) but, rather, the other way around: to use computation in such a way as to *program* nano tiles so they self-assemble, with exquisite detail, specific patterns. That is, computation embedded in the tiles' design allows for an enhanced control of the self-assembling entities; this remarkable formal connection between self-assembly and computation is the subject of our work.

We have recently demonstrated that a combination of experiments, modelling and evolutionary computation can automatically program idealized models of discrete self-assembly tiling systems [10,11] and also self-organising gold nanoparticle assemblies [12] in such a way that they achieve

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specific self-assembled conformations. In one of our studies we concentrated on a system that consisted of so called Wang tiles. Wang tiles "live" in a 2-dimensional world and can freely move in this 2D space. When two tiles collide, the glue type of the colliding sides is used to decide whether the tiles should stick to each other or bounce back. Given a set of glue types with their characteristic strengths and a given temperature, we were able to solve the backward problem and provide answers to the question of *What is the (optimal) family of tiles that will self-assemble into a specific spatio-temporal pattern?* We have also shown [12,10,13,14] that it is possible to evolve the parameters of a cellular automata-based Monte Carlo model to coerce a specific spatio-temporal pattern closely matching observed nanoscience experiments imaged with an atomic force microscope while substantially speeding-up the process of nanoscaning[15]. In addition to our computational capabilities for the automated design of self-assembling systems, our collaborators have also developed sophisticated techniques to tune the self-assembly of molecular arrays[16] and they have advanced scanning probe microscope (SPM) technology that facilitates the *molecule-by-molecule* construction, manipulation, and probing of two dimensional assemblies [17]. In this paper we describe our approach to significantly extend the recent advances outlined above and achieve a step change in pattern programmability by *evolving* "nano-tiles". In contrast to work mentioned previously, we focus on *abiotic*, i.e. non DNA-based, assemblies on suitably processed solid substrates. Indeed, outside of DNA-based systems (e.g. [5,9,18,19]), analogues of *programmable* molecular tiling of complex self-assembling patterns have yet to be systematically studied. Our work presents a unique combination of advanced evolutionary algorithms, supramolecular chemistry of porphyrins, and scanning probe microscopy (SPM), that combined help identify and synthesise a family of molecular units whose interactions may be evolved *in silico* to produce specific emergent self-assembled patterns *in materio*.

Acknowledgements: EPSRC project EP/H010432/1.

References:

[1] J.A. Pelesko, *Self Assembly, The Science of Things that Put Themselves Together*, Chapman & Hall/CRC, 2007
[2] P. W. K. Rothemund, *Proc. Nat. Acad. Sci.*, 97:984-989, 2000
[3] E. Winfree, in *DNA Based Computers*, volume 27 of DIMACS, pp 199-221, American Mathematical Society, 1996
[4] E. Winfree, et al., *Nature* 394, 6:539-544, 1998
[5] D. Soloveichick and E. Winfree , *Proceedings of DNA Computing 10*, LNCS, Springer, 2005
[6] C. Mao et al. *Nature*, 407 493-496, 2000
[7] L. Adleman et al., *Proc. of STOC*, 2002
[8] L. M. Adleman et al., *ACM Symposium on Theory of Computing*, pp. 740–748, 2000
[9] P. W. K. Rothemund and E. Winfree, *ACM Symposium on Theory of Computing*, pp. 459–468, 2000
[10] G. Terrazas et al, *Proceedings of the 2005 IEEE Congress on Evolutionary Computation*, v2, pp1808-1814, IEEE, 2005
[11] G. Terrazas et al., *Proceedings of the 2007 IEEE Congress on Evolutionary Computation*, 2007 pp2001-2008
[12] P. Siepmann et al., *Nano Letters*, 7(7):1985-1990, 2007
[13] P. Siepman et al., *7th International Conference of Adaptive Computing in Design and Manufacture*, pp199-208, 2006
[14] G. Terrazas et al., *Journal of Cellular Automata*, 2(1):77-102, 2007
[15] R.A.J. Woolley, J. Stirling, A. Radocea, N. Krasnogor, and P. Moriarty. Automated probe microscopy via evolutionary optimization at the atomic scale. *Applied Physics Letters*,

98(25):253104, 2011
[16] J.A. Theobald et al., *Nature*, 424, 1029-1031, 2003
[17] P. Moriarty et al., *Surf. Sci.* 407 27, 1998
[18] E. Winfree and R. Bekbolatov, in Chen and Reif [30] , pp126-144, 2004
[19] J. Chen and J. Reif , editors, *DNA Computing 9*, LNCS 2943, Springer-Verlag 2004.