Networked calix[4]arene polymers with unusual mechanical properties

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Polymeric networks built from calix[4]arenes that form a three dimensional folded structure have been predicted to exhibit negative Poisson's ratios (auxetic), an unusual property which makes them superior to conventional materials in many practical applications.

Unlike most conventional materials, auxetics (i.e. materials with a negative Poisson's ratio, see methods section, eqn. (2)†) exhibit the unexpected property of becoming wider when stretched and thinner when compressed.[1,2] This property is responsible for several beneficial effects,[1–3] such as increased shear stiffness, increased plane strain fracture toughness, increased indentation resistance and have a natural ability to form dome-shaped surfaces. Although this is not a common feature in most everyday materials, several auxetics have now been predicted, discovered or manufactured (e.g. foams,[3] microporous polymers,[4] silicates[5] and zeolites[6–8]).

Alongside this research, considerable attention has been focused towards designing and synthesising molecular-level auxetics.[2,8–10] Auxetic behaviour at the molecular level is also likely to offer additional enhanced characteristics, such as the ability to act as tuneable molecular sieves.[7] Man-made molecular auxetics would offer the advantage over naturally occurring counterparts that they can be tailor-made to have a pre-defined set of mechanical properties.

In this communication we present two examples of a new type of molecular-level auxetic that have been predicted to exhibit negative Poisson's ratios. These novel polymeric systems have been designed so as to mimic the behaviour of a folded macrostructure illustrated schematically in Fig. 1a. The macrostructure is composed of alternate facing 'four-legged claws' arranged on a square grid. When the structure is loaded in tension, the connectivity of the 'claws' forces them to open in all directions like an umbrella, hence producing a negative Poisson's ratio in the plane of the structure. This is accompanied by a large positive Poisson's ratio in the out-of-plane direction, a very useful property in its own accord. An example of this structure is manufactured commercially from steel wire for use as an egg rack (see Fig. 1b). This 'egg rack' structure has been mechanically tested and measured to have a Poisson's ratio in the plane of the structure of $v_{23} = v_{32} = -1.02 \pm 0.04$.[8]

A simple geometry based model of the egg container macrostructure has shown that the auxetic behaviour is independent of the scale of the structure (predicted Poisson's ratios of $v_{23} = v_{32} = -1$).[8] This means that in theory, it should be possible to implement this effect at the molecular level, by using molecular sub-units with similar geometric features as the 'claws' in the structure. An example of such a structure is the calix[4]arene sub-units in the 'cone' conformation.

The simplest such system may be constructed by connecting calix[4]arenes directly together with para–para biphenyl-like linkage as illustrated in Fig. 2a (R = none). The bowl shaped geometry of the calix[4]arene sub-units and the connectivity of the network force this system to assume a three dimensional configuration with the same type of folding as illustrated in Fig. 1a. Variations on this network may be produced by introducing additional groups between the adjacent calix[4]arene such as an additional phenyl ring as illustrated in Fig. 2b (R = phenyl). Since there is no simple nomenclature for these systems, we shall henceforth refer to them collectively as 'double calixes'. We note that although the synthesis of these 'double calix' polymeric systems has not been attempted as yet, a

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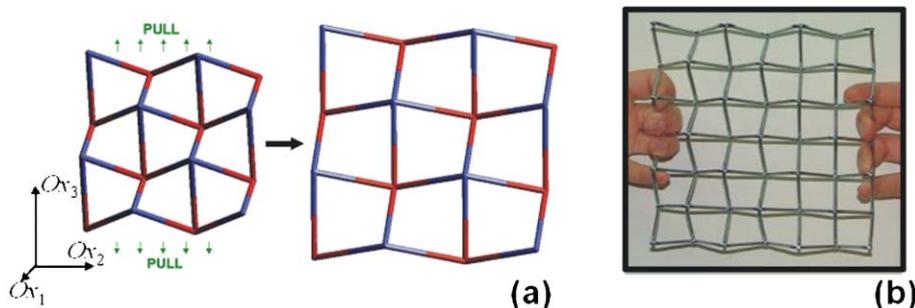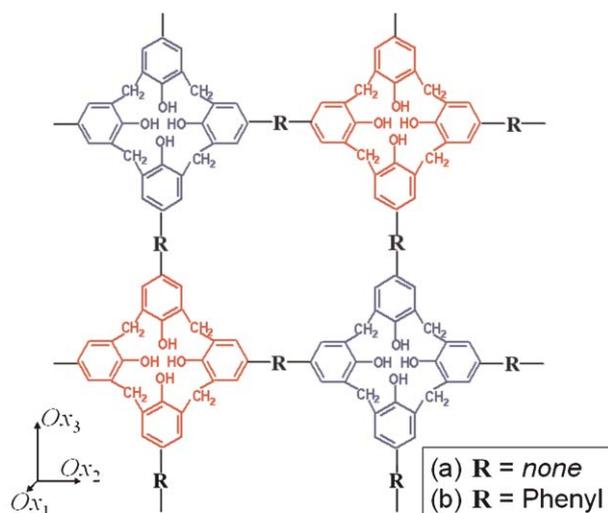Tel: 0044 1392 217965

Fig. 1   (a) A schematic diagram of the model macrostructure, and (b) a photograph of the commercially manufactured 'egg rack' structure with the same geometry.

Fig. 2 The structural formulae of the repeat units for the molecular 'double calix' structures discussed here.

double-calixarene system with *para–para* biphenyl-like linkage, which constitutes 'half' of the 'repeat unit' of these networks has already been synthesised.[11]

In an attempt to simulate the mechanical properties of these "double calix" systems, the networks in Fig. 2a and b (*i.e.* R = none, phenyl) were modelled through force-field based simulations using *Cerius*^{2} V3.0 (Molecular Simulations Inc., San Diego, USA). Parallel infinite layers of the double calix networks (*i.e.* as in graphite) were aligned parallel to the to Ox_2–Ox_3 plane and allowed to stack freely inside one another in the third dimension (*i.e.* down the Ox_1 axis). This was achieved by having calix[4]arene cones from adjacent layers lying inside one another as illustrated in Fig. 3. Modelling simulations confirmed that this three dimensional stacking arrangement (where the calixes stack inside one another like egg racks) was the lowest energy (most stable) arrangement compared to other possible stacking arrangements such as for example where the calixes are "back to back".[12] In the egg rack formation, the different layers stack in the third
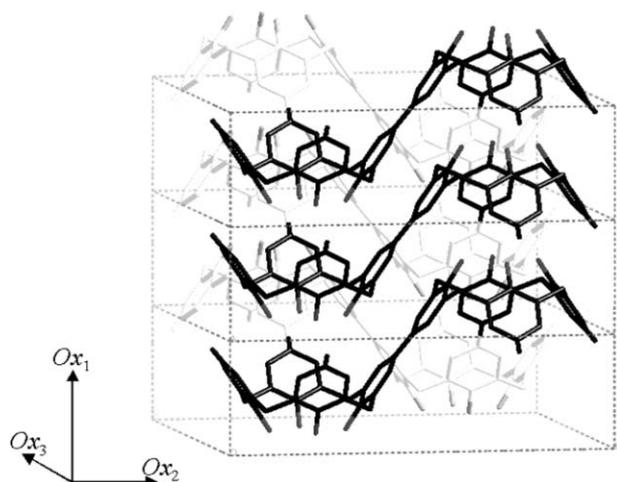
Fig. 3 The minimum energy configuration of the molecular 'double calix' structure illustrated in Fig. 2a.

dimension in such a way so as to optimise the π–π interactions between phenyl rings in the adjacent layers. In fact, the distance between parallel layers of calixarenes was found to be 3.38 Å for the simplest calixarene network which is comparable to the distance between layers of graphite (3.35 Å).[13]

The simulations also predict that in analogy with the behaviour of the model macrostructure, both systems in Fig. 2 exhibit negative Poisson's ratios (auxetic) in the Ox_2–Ox_3 plane (*i.e.* negative v_{23} and v_{32}) and positive Poisson's ratios in the other directions (*i.e.* v_{12}, v_{21}, v_{13} and v_{31}) as illustrated in Table 1. It was also observed that the larger system in Fig. 2b mimics the behaviour of the model 'egg rack' macrostructure more effectively than the system in Fig. 2a where the calix[4]arenes are connected directly with the result that the auxetic effect is more pronounced in the system in Fig. 2b. This result is due to the fact that at the molecular level, there are non-bonding interactions which do not allow the calixes to act as simple 'mechanical systems' and the effects of these non-bonding interactions are more pronounced in the denser structure shown in Fig. 2a (non-bonding interactions between two atoms become weaker as the separation between the atoms increases). It can also be seen that a much higher Young's modulus is obtained for the denser system shown in Fig. 2a than that in Fig. 2b as illustrated in Table 1. Furthermore, one should note that the geometry of the system in Fig. 2b is closer to that of the model macrostructure than the geometry of the system in Fig. 2a.

Irrespective of these minor differences between the Poisson's ratios of the molecular 'double calix' systems and those measured in the macrostructure, the fact that negative Poisson's ratios were indeed obtained, is very important since materials with negative Poisson's ratios exhibit many enhancements in their mechanical and physical properties and are potentially superior to their conventional counterparts in many practical applications.

One novel area in which auxetics may find a use is that of 'trapping' of small molecules in an auxetic material which are then released as the trapping material expands when stretched. Single calixes have been extensively used for entrapment of small ions and molecules due to their cone shaped cavity.[14–17] We envisage that these novel calixarene networks, because of their net-like structures, are naturally disposed to trapping small molecules. Being auxetic, these networks have the advantage over single calixes that the entrapped molecules could be released as and when needed by stretching the network in a single direction. Similarly, considering the networked calixes as three dimensional polymeric structures stacked as egg racks, it is predicted that altering the

Table 1 The simulated single crystalline Poisson's ratios (v_{ij}) and Young's moduli (E_i) of the two molecular systems (Fig. 2) and those predicted for the idealised folded macrostructure (Fig. 1)

Structure	Mathematical model for macrostructure	Fig. 2a R = none	Fig. 2b R = phenyl
v_{12}	+1	0.36	0.52
v_{21}	+1	1.42	1.18
v_{13}	+1	0.36	0.52
v_{31}	+1	1.42	1.18
v_{23}	−1	−0.51	−0.87
v_{32}	−1	−0.51	−0.85
E_1	n/a	4.63	1.66
E_2	n/a	18.10	3.78
E_3	n/a	18.10	3.78

internal distance between stacked calixes through stretching or compressing would subsequently diminish or enhance diffusion between layers.

Given the many advantages of auxetics when compared to conventional materials and the recent advances in the chemistry of calix[4]arenes,[17] we hope that the predictions reported here will encourage further experimental research so as to enable the synthesis of the first purpose-built molecular auxetic material.

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Notes and references

† (A) *Simulation of the minimum energy configurations*: Molecular mechanics simulations were carried out on the two networks in Fig. 1 using the molecular modelling package *Cerius²* V3.0 (Molecular Simulations Inc., San Diego, USA). The networks were represented as crystalline systems with each unit cell containing the repeat units as illustrated in Fig. 2 (*i.e.* with four calix[4]arenes per unit cell). The energy expressions E were set up using parameters from the PCFF 300 force-field[18] as it was found that this force-field could adequately produce results for the modelling of single calixes that can be successfully compared to published data, including the ability to reproduce a C_{4v} bowl shaped geometry for the cone conformer of tetrahydroxycalix(4)arenes which is the actual geometry of calix(4)arenes in the solid state. (Other force-fields available within *Cerius²*, namely the Dreiding 2.21,[19] Universal 1.02[20] and CVFF 950[21] force-fields were found to predict the incorrect C_{2v} symmetry.[12]

Non bond terms were added using the Ewald summation technique.[22] The minimum energy configurations were derived by minimising the potential energy as a function of the atomic coordinates and unit cell parameters to the default *Cerius²* high convergence criteria (which include an atomic RMS of 0.001 kcal mol⁻¹). No constraints on the shape or size of the unit cell were applied.

(B) *Simulation of the mechanical properties*:[23] The 6×6 stiffness matrix **C** (and its inverse, the compliance matrix **S**) of the minimum energy single crystalline double calix molecular systems were calculated from the second derivative of the potential energy function since:

$$c_{ij} = \frac{1}{V}\frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j}\, i,j = 1,2,\ldots,6 \tag{1}$$

where E is the energy expression, V is the volume of the unit cell and ε_i are strain components. Other mechanical properties were then calculated from these matrices. In particular, the Poisson's ratios v_{ij} in the Ox_i–Ox_j planes ($i, j = 1, 2, 3$) for loading in the Ox_i directions are given by:

$$v_{ij} = -\frac{\text{transverse strain}}{\text{axial strain}} = -\frac{\varepsilon_j}{\varepsilon_i} = -\frac{s_{ji}}{s_{ii}} \tag{2}$$

whilst the Young's moduli E_i (a measure of the stiffness) for loading in the Ox_i ($i = 1,2,3$) directions are given by:

$$E_i = -\frac{\text{applied stress}}{\text{axial strain}} = \frac{\sigma_i}{\varepsilon_i} = -\frac{1}{s_{ii}} \tag{3}$$

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