— to break disulfide bonds, thus reverting to a system that is significantly easier to comprehend from a chemical point of view, but, as it turns out, poses a new question. In the same fashion as before, the polypeptide is expanded in basic solution (Fig. 1). Analysis of the response to different forces reveals two different regimes of reactivity. Up to forces of about 500 pN the rate of disulfide cleavage grows quickly. At higher tensile forces, however, a significantly slower growth of the reaction rate is observed. The authors correctly emphasize the difficulty in directly deriving an explanation from experiment only. Nevertheless, as a very plausible mechanism they propose a planarization of the reactive disulfide under higher tensile load. The carbon–sulfur–sulfur–carbon dihedral angle, which initially is about 90 degrees, changes to 180 degrees, bringing these four atoms into a plane. This leads to an elongation of the chain and causes the sulfur atoms to be more exposed to the basic solution. The resulting

energetics are in good agreement with data from static calculations. The overall process may be interpreted as switching at the molecular level. Such mechanical switching alters the chemical reactivity.

The challenge now is to perform reactive molecular dynamics simulations of the experimental situation at different tensile loads and to see if two different regimes of reactivity are found. This would ultimately prove the mechanism — or demonstrate that an alternative mechanism applies. Such theoretical investigations serve to give qualitative information about the chemical dynamics, such as the reaction path and reaction mechanism. In combination with the data gained from experiment, a very clear moving picture of a reaction can be developed. The remarkably well-defined results of the AFM study represent a wonderful motivation for performing such simulations.

Manipulating single molecules with an atomic force microscope is still far from easy, and requires an elaborate experimental

set-up. Nevertheless, it is obvious that experiments like those presented here can, in principle, be performed for a large variety of tailor-made systems. The goal of controlling and monitoring complex chemical reactions of single molecules is about to be realized. □

Irmgard Frank and Florian Hofbauer are at the Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Callinstrasse 3A, 30167 Hannover, Germany. e-mail: Irmgard.Frank@theochem.uni-hannover.de

References

1. Xie, X. S. *Acc. Chem. Res.* **29**, 598–606 (1996).
2. Grandbois, M., Beyer, M., Rief, M., Clausen-Schaumann, H. & Gaub, H. E. *Science* **283**, 1727–1730 (1999).
3. Rief, M. & Grubmüller, H. *ChemPhysChem* **3**, 255–261 (2002).
4. Garcia-Manes, S., Liang, J., Szoszkiewicz, R. Kuo, T.-L. & Fernández, J. M. *Nature Chem.* **1**, 236–242 (2009).
5. Ainaurapu, S. R. K., Wiita, A. P., Huang, H. H. & Fernandez J. M. *J. Am. Chem. Soc.* **130**, 436–437 (2008).
6. Wiita, A. P. et al. *Nature* **450**, 124–127 (2007).

PUBLISHED ONLINE 10 May 2009

FULLERENE ANALOGUES

Elusive icosahedral symmetry

Fullerenes have many potential isomers and the most stable ones do not have adjacent pentagons. For C_{80} , the icosahedral form is the least energetically favoured isomer, and although it has not yet been isolated, it has been indirectly observed as a host structure. Fullerene-like inorganic structures have also recently been built around guest molecules, but these have so far remained incomplete shells.

Using a carborane as a template, Manfred Scheer at the University of Regensburg and colleagues have now prepared an 80-atom icosahedral inorganic structure that resembles the unstable C_{80} cage (pictured; *Angew. Chem. Int. Ed.* doi:10.1002/anie.200900342; 2009). The fullerene pentagons are defined by the phosphorus atoms (purple) in a pentaphosphorus ligand, which forms half of a ferrocene-like structure ($Cp^+FeP_5^-$). These phosphorus atoms take four of the positions in the fullerene hexagons, with the other two positions occupied by copper atoms (blue).

With the chloride ions (light green), iron centres (dark green) and cyclopentadienyl ligands (grey) surrounding this icosahedral core (orange), the complete molecule is about twice as large as a C_{80} fullerene.

ANNE PICHON