configurational dependence of scalar quantities, such as formation enthalpies, bandgaps, bulk moduli, Curie temperatures and so on. On page 455 of this issue, Axel van de Walle presents a profound extension of this method[11]. The extension allows prediction of anisotropic properties, that is, tensor properties such as elasticity, optoelectronic coupling and piezoelectricity.

The cluster expansion approach is particularly effective when the structural question is one of 'configuration' rather than location (see Fig. 1). For example, in nickel-based superalloys the atomic sites essentially constitute a body-centered-cubic lattice. The arrangement, or ordering, of nickel, aluminium, or impurity atoms, or even vacancies, on those b.c.c. sites profoundly influences the performance of the alloy, and the best energetic preferences can be accurately predicted via cluster expansion.

The cluster expansion method can be used to calculate, essentially instantly and with first-principles accuracy, the target property for any atomic configuration. Because computing the target quantity is so efficient, the cluster expansion can be used in thermodynamic simulations or kinetic Monte Carlo modelling. With van de Walle's extension to the method it can now be applied to a much broader range of target properties. The significance goes beyond a mere algorithmic advance — it's likely to make a real difference in computational-based materials design. The cluster expansion has so far been used to predict maximum bandgaps, maximum critical temperatures in magnetic semiconductors, and so on. But finding an atomic configuration that optimizes a target quantity is a far cry from actually making such a material. One cannot simply 'build' a compound with an arbitrary arrangement of atoms on a given lattice — nature dictates that free-energy minimization ultimately determines the atomic configuration. But van de Walle's approach will be useful in epitaxial systems in which materials scientists can make metastable structures, where some control over the atomic configuration is possible.

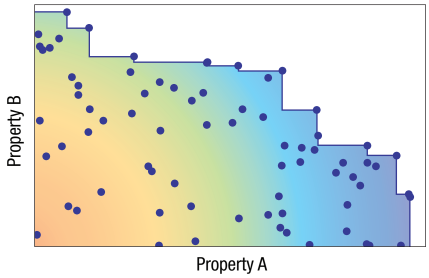

Figure 2 Illustration of how the tensorial cluster expansion can be used in practical materials design problems. After calculating the values of property A and B for all possible atomic configurations, one constructs the 'Pareto front'. Knowing the Pareto front, a materials engineer can select nature's best solution to maximizing competing requirements for a particular application.

Van de Walle's tensorial cluster expansion will be useful in epitaxial systems because many of the target properties of interest are anisoptropic and cannot be treated with a standard scalar cluster expansion. The most exciting aspect of this new method is that one can immediately see how it could be used in a practical materials design problem. Imagine a material with two properties A and B that one wishes to maximize but which are competing — maximizing one decreases the other and *vice versa*. Such 'trade off' problems are inevitable in materials applications. Using the tensorial cluster expansion one could determine the best possible compromise (Fig. 2). After calculating property A and B for every experimentally realizable configuration, one simply constructs the Pareto front to find the best possible trade-offs between A and B irrespective of any application-limited requirements on either property.

The authors' findings are exciting because of the potential to bring together first-principles modelling with practical materials design. The extension of a well-established computational method to a new class of properties is sure to open unanticipated avenues of exploration.

References

1. Fischer, C. C., Tibbetts, K. J., Morgan, D. & Ceder, G. *Nature Mater.* **5**, 641–646 (2006).
2. Curtarolo, S., Morgan, D. & Ceder, G. *Calphad* **29**, 163 (2005).
3. Abraham, N. L. & Probert, M. I. J. *Phys. Rev. B* **73**, 224104 (2006).
4. Oganov, A. R. & Glass, C. W. *J. Phys. Condens. Matter* **20**, 064210 (2008).
5. Wolverton, C. & Zunger, A. *Phys. Rev. Lett.* **81**, 606–609 (1998).
6. Sanchez, J. M., Ducastelle, F. & Gratias, D. *Physica A* **128**, 334–350 (1984).
7. de Fontaine, D. *Solid State Phys.* **47**, 33–176 (1994).
8. Muller, S. *J. Phys. Condens. Matter* **15**, R1429–R1500 (2003).
9. Hart, G. L. W., Blum, V., Walorski, M. & Zunger, A. *Nature Mater.* **4**, 391–394 (2005).
10. Zunger, A. in *Statics and Dynamics of Alloy Phase Transitions* (eds Turchi, P. E. A. & Gonis, A.) 361–419 (NATO ASI Series, Ser. B, Plenum Press, New York, 1994).
11. van de Walle, A. *Nature Mater.* **7**, 455–458 (2008).
12. Hart, G. L. W & Forcade, R. W. *Phys. Rev. B* (in the press); preprint at <http://arXiv.org/abs/0804.3544v1> (2008).

CONJUGATED POLYMERS

What makes a chromophore?

The spectral complexity shown by conjugated polymers has been explained by interactions between chromophores in tangled chains, but experiments on model oligomers reveal that it may arise from the chromophores themselves.

Benjamin J. Schwartz
is at the Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, USA.
e-mail: schwartz@chem.ucla.edu

Conjugated polymers, such as poly(phenylene vinylene) derivatives (Fig. 1a), are remarkable materials: they combine the electrical properties of semiconductors with the mechanical properties of plastics. These materials can be processed inexpensively by techniques such as spin-coating and ink-jet printing, and they are already finding application in optoelectronic devices such as plastic light-emitting diodes (LEDs[1]) and photovoltaic cells[2]. Yet, despite their enormous practical potential and years of study, it has not been clear how best to think about the electronic properties of conjugated polymers. The typical picture of their electronic structure has been that electronic excitations on each chain are confined to separate, rigid chromophores that act largely independently, and that most of the electronic complexity is a consequence of interactions between chromophores, or interchain effects. This picture, however, has been challenged recently by Becker *et al.*, who report in the *Journal of Physical Chemistry B* that much of the spectral complexity associated with conjugated polymers may arise from the chromophores themselves[3]. This has direct consequences for devices such as LEDs and solar cells: optimizing their stability and performance will require control over the conformation of individual chromophores, rather than the arrangement of the chromophores or the form of the polymer chain.

Becker and colleagues have elegantly revisited the single-molecule spectroscopy of conjugated oligomers of phenylene–vinylene[3]. Their findings cast serious doubts on the basic 'particle in a 1D box' picture of conjugated polymer chromophores: the colour of the emission from a conjugated polymer chromophore does not seem to correlate simply with the extent of backbone planarity, the extent of depolarization does not seem to be always the result of energy transfer between chromophores, and evidence of interchromophore interactions — supposedly caused by chromophores being brought close together by polymer chains — can appear when studying single oligomers.

Conjugated polymer chains are quasi-one-dimensional, so the most straightforward picture of their electronic properties comes from thinking of an excitation of one of the polymer's π-electrons as analogous to that of a particle in a box, in which the ground-to-excited-state energy gap scales inversely with the square of the box size. Quantum-mechanical considerations, however, limit the extent to which an excited electron can delocalize along the polymer backbone. Indeed, studies using oligomers with a well-defined number of repeat units show that the absorption and emission spectra redshift as the number of monomers is increased, and become indistinguishable from that of the polymer when the number of repeat units reaches around six to ten.

Of course, the chains in real conjugated polymer films do not have an idealized planar structure (Fig. 1a); instead, bulk conjugated polymer samples consist of twisted and bent chains in a spaghetti-like mass. In such a morass, how should one think about the electronic excitations? The standard picture has been that delocalization of the π-electrons occurs only when the polymer repeat units are co-planar: twists in the backbone have been assumed to 'break' the conjugation (Fig. 1b). In this picture, complexity in electronic structure arises primarily from two sources. First, segments with different numbers of coplanar repeat units behave independently and can be excited at different energies. Once created, excitations can transfer from shorter, high-energy segments to those with a longer conjugation length and a lower energy. Second, if two conjugated segments are properly oriented (Fig. 1c), an excitation might be shared between them. This has been associated with a redshift and broadening of the polymer's emission spectrum[4].

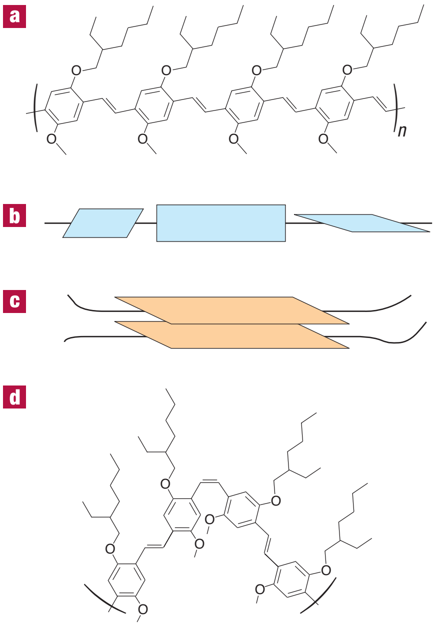

Figure 1 The semiconducting conjugated polymer, poly(2-methoxy 5-[2′-ethylhexyloxy]-*p*-phenylene vinylene) (MEH-PPV). **a**, The idealized chemical structure of MEH-PPV. **b**, Schematic showing idealized chromophores along a conjugated polymer backbone. The rectangles represent planar, conjugated chromophore segments of ~6–10 repeat units. Twists along the backbone break planarity and provide separation between chromophores. **c**, A motif for possible interchain interaction, where two chromophores meet in a face-to-face manner, facilitating the sharing of π-electrons between the two segments. **d**, The chemical structure of a portion of an MEH-PPV chain with a *cis* defect.

This picture of largely independent chromophores supplemented by interchromophore interactions has explained many experimental results. For example, the emission from conjugated polymers in solution is strongly polarized (relative to the polarization of the excitation light) but emission from conjugated polymer films is not. This is because energy can migrate from shorter to longer segments in conjugated polymer films, and each time an excitation hops between segments the direction of its emission dipole can rotate. In contrast, chromophores in solution are too far apart to undergo significant through-space energy transfer, and energy migration along the polymer backbone turns out to be slow[5].

This standard picture of conjugated polymer electronic structure becomes less clear, however, when the results of single-molecule spectroscopy are added to the fray. Emission measurements by Summers *et al.* on single oligomeric chromophores showed that most of them, but not all, gave highly polarized emission[6]: some had weakly polarized emission and a few oligomers gave depolarized emission. The fraction of the oligomers with depolarized emission correlated perfectly with the fraction that had the most *cis* defects (Fig. 1d) compared with the all-*trans* structure (Fig. 1a)[6]. This suggests that depolarized emission may not always be a signature of energy migration; instead, a single (albeit bent) conjugated chromophore can also have depolarized emission.

Now Becker and co-workers have found that oligomers, which at least in solution are all *trans*, can show a variety of levels of emission depolarization[3]. Perhaps more importantly, they found that when the emission from oligomers was highly depolarized, it was also broad and redshifted; in fact, the depolarized emission looks remarkably like that associated with interchromophore aggregation. The quantum chemistry calculations performed by Becker and colleagues suggest that highly bent, non-planar chromophores are responsible for the depolarized emission[3]. Of course, this bending is associated with shortening the conjugation length, which would be expected to give a blueshifted emission. This paradox may arise because the single oligomer chromophores are not isolated in the gas-phase but have interactions with the surrounding matrix.

One of the particular difficulties in sorting out the electronic structure of conjugated polymers is their extraordinary sensitivity to chain morphology. It is well known that processing conjugated polymer films in different ways leads to different amounts of interchain interactions and thus different electronic properties[4,7]. Now we know that changes in single-chromophore conformation and structure can also lead to a variety of electronic properties, it is critical to revisit the relationship between the single molecule and bulk film properties of these materials if we are to exploit them to their maximum potential in optoelectronic applications.

References

1. Friend, R. H. *Pure Appl. Chem.* **73,** 425–430 (2001).
2. Brabec, C. J., Sariciftci, N. S. & Hummelen, J. C. *Adv. Funct. Mater.* **11,** 15–26 (2001).
3. Becker, K. *et al. J. Phys. Chem. B* **112,** 4859–4864 (2008).
4. Schwartz, B. J. *Annu. Rev. Phys. Chem.* **54,** 141–172 (2003).
5. Nguyen, T.-Q., Wu, J., Doan, V., Schwartz, B. J. & Tolbert, S. H. *Science* **288,** 652–656 (2000).
6. Summers, M. A. *et al. J. Am. Chem. Soc.* **125,** 5199–5203 (2003).
7. Nguyen, T.-Q., Martini, I. B., Liu, J. & Schwartz, B. J. *J. Phys. Chem. B* **104,** 237–255 (2000).