

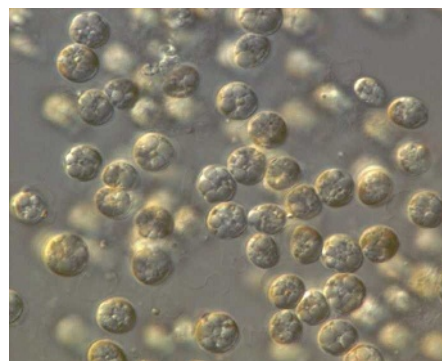
they have attracted interest from industry. Indeed, one company, SupraPolix, produces supramolecular polymers with the ability to self-heal, although temperatures of 140 °C must be used.

Now, however, Cordier *et al.* have applied supramolecular chemistry to create a material that can heal at room temperature. Other chemists will soon be searching for, and designing and studying, a variety of small molecules to obtain specific mechanical properties in new self-healing materials. Cordier and colleagues' starting ingredients are fatty acids from vegetable oils, which offer a vast amount of variety for fine-tuning their material. Even now that material can withstand multiple fractures,

needs no catalysts and is otherwise straightforward to produce (see Fig. 2 of the paper¹ on page 978). A final blessing is that it can be broken down with heat and easily recycled — so it is environmentally friendly, too. ■

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1. Cordier, P., Tournilhac, F., Soulié-Ziakovic, C. & Leibler, L. *Nature* **451**, 977–980 (2008).
2. White, S. R. *et al.* *Nature* **409**, 794–797 (2001).
3. Toohey, K. S. *et al.* *Nature Mater.* **6**, 581–585 (2007).
4. Chen, X. *et al.* *Science* **295**, 1698–1702 (2002).
5. Bosman, A. W., Sijbesma, R. P. & Meijer E. W. *Mater. Today* **7** (7), 34–39 (2004).



P. J. KEELING

Figure 1 | Evolutionary illumination in the round. These unassuming little brown balls, which are 5–7 micrometres in diameter, are cells of the marine alga newly described by Moore *et al.*¹. In providing a connection between the apicomplexan parasites and their algal ancestors, the organism becomes a prime candidate for the complete genome analysis that should help lift more of the veil from ancient evolution.

EVOLUTIONARY BIOLOGY

Bridge over troublesome plastids

Patrick J. Keeling

Identification of a direct link between apicomplexan parasites and their algal ancestors is a development full of promise. It illuminates a dark corner in the evolution of photosynthesis, and further insights are to come.

One of the parallels between archaeology and evolutionary biology is that the most ordinary-looking objects can sometimes be the most revealing. An ancient ornament of unrivalled artistry might reveal little about the lives of the people who made it. But a monochrome pattern on a modest potsherd can, in the right context, furnish evidence that connects events contributing to an upheaval in human history.

On page 959 of this issue, Moore *et al.*¹ describe an analogous situation bearing on a problem in evolutionary biology. They describe a tiny marine alga that is superficially undistinguished: a 'little brown ball', like many other unexceptional marine microbes. But this little brown ball proves to be different, because it connects two pieces in one of the bigger puzzles of early evolution.

This puzzle is the interconnected histories of photosynthesis and of endosymbiosis, the process by which one organism engulfs another to mutual benefit, and which is a recurring theme in evolutionary history. The two pieces are apicomplexan parasites and dinoflagellate algae. Apicomplexa are exclusively intracellular parasites that cause many diseases, notably malaria. Therefore, it came as a surprise when they were discovered to contain plastids, the organelles derived from cyanobacteria that are responsible for photosynthesis in plants and algae^{2,3}. The discovery of these 'apicoplasts' immediately sparked debate about their origins, because the closest relatives of apicomplexa, the dinoflagellates, also possess plastids. Dinoflagellate plastids are derived from the engulfment and retention of the plastid of a red

alga. One side of the debate argues that apicoplasts evolved from this same red endosymbiont, which may have given rise to plastids in many other lineages as well^{4–6}. The other side contends that apicoplasts are derived from an independent event, perhaps involving a green algal endosymbiont^{7,8}.

To distinguish between such disparate possibilities, one would normally compare the apicomplexan and dinoflagellate plastids and their genomes for clues to how they are related. But these plastids have proved curiously difficult to compare. The apicoplast could be forgiven for being a bit odd — it is, after all, found in non-photosynthetic, intracellular parasites — and not surprisingly all of its genes relating to photosynthesis have been lost³. The dinoflagellate plastid has no such excuses, yet it is arguably even stranger than the apicoplast: dinoflagellate plastid genes have undergone a mass migration to the nucleus, leaving only a handful of highly derived, mainly photosynthetic genes, and the genome itself has broken down into many miniature single-gene chromosomes⁹.

The dilemma in comparing apicomplexan and dinoflagellate plastid genomes is therefore not simply that they are unusual, but that they are unusual in different ways. Most importantly, the absence in the apicoplast of genes that encode the photosynthetic machinery, and the corresponding removal of just about every other kind of gene from the dinoflagellate plastid genome, means there is virtually no overlap in plastid gene content: it is almost impossible to compare these genomes directly, and so their evolutionary

relationship has remained stubbornly elusive.

This is where Moore and colleagues' alga comes in. While surveying coral symbionts, they found a little brown ball (Fig. 1). The sea is full of little brown and green balls, and they are often overlooked in favour of more interesting things. But further investigation of this particular little ball showed that it is special because, although it is a fully photosynthetic alga, it is also specifically related to the apicomplexan parasites. 'Missing links' do not really exist in the living world, but this is the next best thing because it has retained many ancestral features that were lost in apicomplexa and/or dinoflagellates.

Specifically, the new data provide a bridge between the non-overlapping gene content of the apicomplexan and dinoflagellate plastids, and so provide a definitive case that these plastids had a single endosymbiotic origin. Moore *et al.* show that housekeeping genes from the plastid of the new algal species are most closely related to apicomplexan homologues, while at the same time the photosynthetic proteins encoded in the plastid are most closely related to dinoflagellate homologues. At a stroke, this solves two outstanding puzzles: the apicoplast was derived from a red (as opposed to a green) alga in the same endosymbiotic event (as opposed to independent events) that gave rise to the dinoflagellate plastid.

This in itself is a fair day's work. But it is just the beginning. The unusual characteristics of apicomplexan and dinoflagellate plastids extend beyond their genomes to their membranes, pigments and protein-importing apparatus¹⁰. A similar situation is also true of their mitochondria, the organelles responsible for energy generation, where massive gene loss has accompanied the evolution of RNA editing and changes to the architecture of both the genome and the genes it contains¹¹. In each case, further research on the new species could help reveal how such major transformations occur.

Indeed, its very existence also has implications for tackling much broader questions about how intracellular parasites evolved from algae, and whether the single origin of these plastids can be pushed even farther back in time to explain the origin of an even greater diversity of complex algae with red algal plastids, as proposed by the 'chromalveolate hypothesis'^{5,6}.

The discovery of an organism that falls at such an interesting junction in the tree of life happens only rarely, and this little brown ball will surely become the subject of a complete genome analysis soon after the ink of this commentary has dried. When it does, its genome will be a source of clues to many events that defined ancient evolutionary history. ■

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1. Moore, R. B. *et al. Nature* **451**, 959-963 (2008).
2. McFadden, G. I., Reith, M., Munholland, J. & Lang-Unnasch, N. *Nature* **381**, 482 (1996).
3. Wilson, R. J. M. I. *et al. J. Mol. Biol.* **261**, 155-172 (1996).
4. Williamson, D. H. *et al. Mol. Gen. Genet.* **243**, 249-252 (1994).
5. Cavalier-Smith, T. *J. Eukaryot. Microbiol.* **46**, 347-366 (1999).
6. Fast, N. M. *et al. Mol. Biol. Evol.* **18**, 418-426 (2001).
7. Köhler, S. *et al. Science* **275**, 1485-1489 (1997).
8. Funes, S. *et al. Science* **298**, 2155 (2002).
9. Green, B. R. *Protist* **155**, 23-31 (2004).
10. Hackett, J. D., Anderson, D. M., Erdner, D. L. & Bhattacharya, D. *Am. J. Bot.* **91**, 1523-1534 (2004).
11. Slamovits, C. H., Saldarriaga, J. F., Laroque, A. & Keeling, P. J. *J. Mol. Biol.* **372**, 356-368 (2007).

phase, it is extremely difficult for the atoms to move and generate a newly coupled product with the release of carbon monoxide.

Kuzmanich *et al.*³ set out to turn this wisdom on its head by designing a crystalline ketone that would ensure one bond breakage and in doing so make a second unavoidable. Their starting point is diphenylcyclopropenone, a ketone whose central carbonyl forms one corner of a triangular cyclopropene ring with three carbon atoms. The other two corners are connected to two identical phenyl (C₆H₅) rings (Fig. 1a-c).

The authors hypothesized that an initial bond breakage, caused by incident ultraviolet radiation, would release the large strain energy stored in the three-membered cyclopropene ring. Once unleashed, this energy would prevent the molecule from returning to the ground state, stopping the covalent bond from reforming. The energy released would at the same time promote the breaking of the second bond, casting the carbonyl group adrift as carbon monoxide. As a result, single crystals of diphenylcyclopropenone would react to produce solid diphenylacetylene (Fig. 1d).

This is wizardry, albeit of a more conventional chemical type. But a sign of something rather extraordinary was provided by the observation that the crystals took just minutes to crumble: a mark of a very efficient process. To quantify this observation, the authors determined the quantum yield of the reaction — the number of molecules that reacted per photon of incident light.

This is a notoriously difficult measurement owing to the differential scattering of light on

ORGANIC CHEMISTRY

Solid awakening

Leonard R. MacGillivray

Once dismissed as chemical graveyards, organic solids can in fact be manipulated to surprising effect: one example is a crystal designed to embark on a remarkable domino-rally of reactions when bathed in light.

A crystal, the chemistry Nobel laureate Leopold Ruzicka is reported to have said¹, is a chemical cemetery. Molecules in the solid state occupy the most restrictive of quarters: lying just ångströms apart, the lively spontaneity of processes such as conformational change, enjoyed by molecules in solution, is largely forbidden to them. But although some effects of close packing might make molecules in solids relatively inert, this packing does determine important physical properties, such as a crystal's conductivity and reactivity. That fact has animated the field of crystal engineering², which in recent years has made great strides in controlling the properties of organic solids. As a case in point, Kuzmanich *et al.*³, writing in the *Journal of the American Chemical Society*, describe how they have designed an organic solid that has truly remarkable 'chain reactivity'.

Reactions involving molecules are typically unimolecular (with just one player at the starting-gun) or bimolecular (with two). Both types of reaction occur less often in solids than in liquids, but they do occur. Kuzmanich and his colleagues focus on a unimolecular reaction: the photodecarbonylation of a ketone. A ketone is a molecule characterized by a carbonyl (C=O) group, the carbon atom of which forms a covalent bond to a carbon atom in each of two additional organic groups. When light excites such a molecule, the two carbon-carbon single bonds can break, generating reactive fragments known as radicals. If the conditions are right, the radicals combine, releasing the elements of the carbonyl group as carbon monoxide gas.

The breaking of the carbon-carbon bonds is

reversible. In the solid state, this is an essential point: because the atoms of a crystal are locked in position by the lattice, the covalent bonds can easily re-form when the molecule returns to the ground state after the initial excitation⁴. Compared with the situation in the liquid

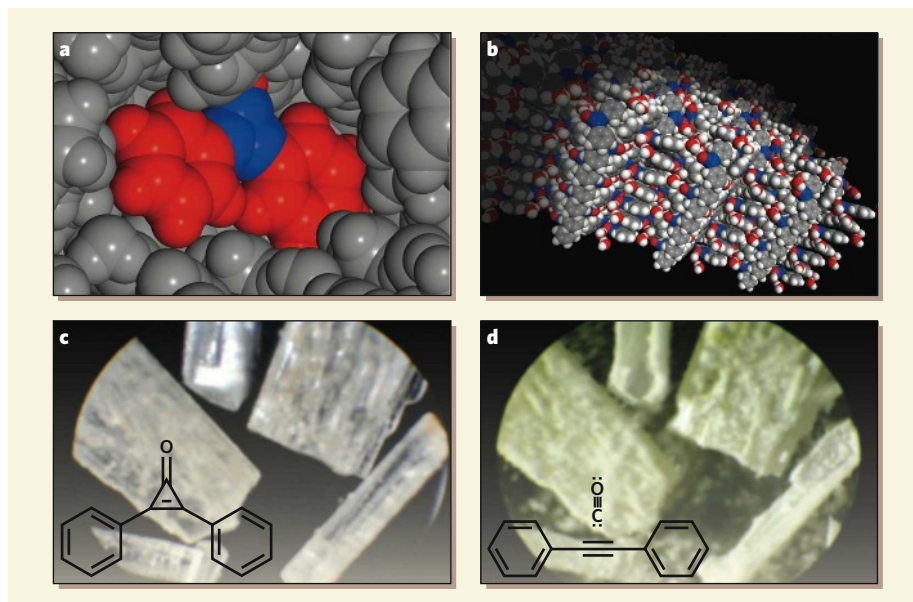


Figure 1 | Excited by light. a, b, These models, derived from X-ray data, show diphenylcyclopropenone monohydrate in close-up (a; blue, cyclopropenone ring; red, phenyl and oxygen; remaining atoms, grey) and in their long-range structure (b; blue, cyclopropenone ring; grey, carbon; red, oxygen; white hydrogen). Nearest-neighbour diphenylcyclopropenones are 4–5 ångströms from each other. c, d, The before and after of Kuzmanich and colleagues' quantum chain reaction¹: photoexcitation breaks a bond in the cyclopropenone ring (central triangle of structure), unleashing the strain energy pent up there. A second bond breaks, releasing carbon monoxide and leaving behind a powder of diphenylacetylene, C₆H₅C≡CC₆H₅.