higher if they are buried in the protein. This means that the rate of electron transfer from those sites will depend on the reduction potential of P450-I and the distance from those residues.

Green and co-workers estimate that this trade-off between redox potential and a very basic pKₐ allows the cysteine thiolate-ligated CYP158 to produce an oxidant that is wired for C–H bond cleavage, taking advantage of the basic ferryl species while suppressing long-range electron transfer rates — by as much as 10,000-fold compared with neutral histidine ligation that is typical of electron-transfer haem proteins such as peroxidases. Insights like this are important to understand the range of subtle strategies the enzyme has exploited to accomplish these very difficult C–H oxidations and to apply those strategies to the development of new catalysts.

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GRAPHENE SYNTHESIS

Nanoribbons from the bottom-up

The organic synthesis of graphene nanostructures requires exceptionally efficient chemistry and is made more challenging by difficulties in characterization and processing. Now, solution-dispersible graphene nanoribbons have been synthesized on the gram scale.

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Graphene has been the focus of intense research effort since it was first isolated and characterized in 2004, principally because of its potential in next-generation electronics. Substructures of graphene represent attractive targets for new materials, with properties intimately tied to their sizes and the arrangement of the six-membered rings along their edges (for example, so-called zigzag or armchair patterns). Fundamentally, graphene fragments can be constructed in two different ways. ‘Top-down’ approaches typically begin with exfoliation of graphite through physical or chemical means, and the resulting separated graphene sheets can be patterned by methods such as lithography. An alternative approach is to construct graphene structures from the ‘bottom-up’, either through epitaxial growth of graphene sheets (by using techniques such as chemical vapour deposition) or by applying the principles and procedures of synthetic organic chemistry.

Ideally, stepwise organic chemistry strategies would enable graphene-based materials to be produced in a massively parallel fashion with very high structural precision, and offer a complementary approach to other methods. Although the synthesis of nanometre-scale polycyclic aromatic hydrocarbons predates the current interest in graphene by decades (for example, the synthesis of hexa-para-benzocoronene in 1958), our capabilities on this front remain fairly limited. Key challenges include (i) the development of sufficiently efficient chemistry for the creation of large numbers of C–C bonds in a single step, (ii) the management of the low solubility typical of large aromatics, which limits the processability of the resulting materials, and (iii) the characterization of nanometre-scale graphenes, for which even small numbers of undetected structural defects could have significant effects on their properties.

Now, writing in Nature Chemistry, Müllen, Feng and co-workers describe the design, synthesis and characterization of soluble graphene nanoribbons (GNRs). Because the confinement of graphene to the nanometre scale in one dimension opens up a width-dependent bandgap — which is critically important in electronics applications — GNRs represent a privileged class of graphene-based structures. They can be made using various top-down routes, including the lithographic patterning of larger graphene sheets or the ‘unzipping’ of carbon nanotubes. Although effective, these methods offer limited control over edge structures and ribbon widths. Bottom-up approaches have also been reported, including examples of surface-mediated planarizations of polyphenylene precursors to give GNRs with incredible structural precision. The drawback of this method, however, is that only limited quantities of surface-bound products are produced.

An attractive route to GNRs would be to prepare them by analogy with more ‘traditional’ conjugated polymers — such as polythiophenes or poly(p-phenylene)s — beginning with small-molecule monomers and carrying out a bulk solution-phase synthesis. Indeed, some examples of this approach towards GNRs have been reported previously, but the resulting nanoribbons are relatively short (<50 nm), and the generally low solubility of the products has limited both their characterization and ultimate usefulness. In the present work, Müllen, Feng and colleagues began with a bifunctional alkyne-cyclopentadienone monomer (Fig. 1a). On heating, this monomer condenses to give high-molecular-weight polythiophenes (up to ~640 kg mol⁻¹) through a Diels–Alder polymerization process. These precursor polymers are obtained as complex mixtures of regiosomers, but planarize effectively — on gram scales — to give structurally well-defined GNRs when treated with FeCl₃, typical conditions for the Scholl reaction. Based on the molecular weights of the polyphenylene precursors, the longest of the synthesized GNRs should approach 500 nm in length.

Characterization of such GNRs is a challenge, but critically important given that exceptional fidelity in the planarization chemistry is required if one is to obtain products with low levels of structural defects. The materials were
characterized by infrared, Raman and solid-state 1H NMR spectroscopies, relying both on the predicted properties for GNRs of this size and comparisons to small oligomeric analogues that could themselves be characterized unambiguously by MALDI mass spectrometry. Remarkably, the GNRs produced in this work could be readily dispersed in common organic solvents such as tetrahydrofuran. Although certainly still aggregated, this dispersibility enabled characterization by techniques common for typical conjugated polymers, such as UV–visible spectroscopy. The dispersibility of the GNRs was enhanced further through the replacement of the dodecyl side-chains with more-solubilizing branched alkyl groups.

Although no single technique constitutes complete characterization of the synthesized GNRs, their improved solubility enabled visualization by scanning probe microscopy techniques, providing strong evidence for their structures. Scanning tunnelling microscopy of the GNRs with unbranched (dodecyl) solubilizing groups revealed (Fig. 1b) a well-organized self-assembled monolayer with elongated, parallel features spaced by roughly half their predicted width, consistent with a partially stacked structure. For these less-soluble GNRs, nanoribbons up to 60 nm long were observed. This length is considerably below that predicted from the molecular weight of the precursors, but the discrepancy can be rationalized by preferential leaching of the shorter GNRs into solution during deposition. The use of branched side-chains (improving the solubility) allowed GNRs >200 nm in length to be observed directly by atomic force microscopy.

Interestingly, the improved solution dispersibility of the GNRs reported in this study allowed their carrier mobilities to be characterized by time-resolved terahertz spectroscopy. Compared with ‘conventional’ conjugated polymers such as polythiophenes and poly(phenylene vinylene)s, the GNRs exhibit exceptionally low defect densities and a highly planar geometry, as would be expected. Their overall carrier mobility was estimated to be between 150 and 15,000 cm2 V−1 s−1, well below that of graphene itself (~200,000 cm2 V−1 s−1), but consistent with laterally confined graphene nanoribbons.

The chemistry developed for making these materials can, in principle, be adapted to prepare nanoribbons in bulk quantities with a range of structural modifications, including varying widths, edge structures and appended functionalities. This work lays the foundation for new challenges: for example, the rather high polydispersity of the polyphenylene precursors obtained by the Diels–Alder polymerization means that the resulting GNR products have a wide range of lengths, and this is one area that could be improved on in future work. Furthermore, despite many decades of use, the effectiveness of the Scholl reaction remains highly substrate-dependent and many substrates give rise to rearranged products7. Thus, although the polyphenylene precursors used by Müllen and co-workers seem to planarize very well, more work is required before this strategy can be effectively adapted to make GNRs with a wide variety of core structures. Nevertheless, this report represents a milestone in the organic synthesis of graphene-based nanostructures, and a nice complement to related materials such as graphene quantum dots8. The demonstration that such GNRs can be made solution-processable is a significant achievement that should encourage further developments in this area and, ultimately, the challenge of incorporating such synthesized materials into functional devices.

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