target a particular cell type (for example, ligand patches that target a particular cancerous cell type). The particles produced by Christian *et al.* have the potential to be truly multifunctional as the vesicles can still contain a payload, still have the mechanical properties associated with polymer membranes, and can show different chemistries in a defined pattern on the surface owing to the trigger of ligand-type binding to the corona chains.

I look forward to the complexity of future designs by the researchers whereby they take advantage of triggered pattern formation on particles consisting of blends of block copolymers to produce complexity and functionality not possible without their designs. The ligand-induced pattern formation could allow one to design particles for the human body with no surface pattern, but that transform to patchy particles only on finding the correct chemical environment. For example, vesicles with an encapsulated drug payload would form patterns and interact with surrounding human cells in a desired manner only on experiencing a high ligand concentration present on and around particular cells. Thus the ligand-induced pattern formation would encourage a targeting mechanism for the particles to interact exclusively with specific cells, an important idea for areas such as chemotherapy to treat only cancerous cells and not healthy cells. Pattern formation on assembled soft-matter particles make smarter materials a possibility that scientists and engineers should exploit. ❐

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MATERIAL WITNESS

OLDER AND MADDER

PHILIP BALL

When painters before the late nineteenth century wanted a deep, rich red, they generally reached for their red lake. These pigments were made from organic dyes adsorbed onto colourless carrier particles, and were typically more crimson than the orangey hues of inorganic materials such as vermilion and red lead. The dyes had diverse sources, ranging geographically from India to Mexico.

So the composition of red lakes may disclose trade practices in the pre-industrial world. But deducing their ingredients is hard. Their very terminology indicates a confusion about sources in former times: the generic term lake comes from 'lac', the resin secreted by a south-east Asian insect, whereas the colour terms carmine and crimson both derive from a different red dye, called kermes in medieval Latin, and extracted from a Mediterranean insect. Crimson lake could, however, equally be made from the root of the madder plant or cochineal extracted from insects in eastern Europe or, after the Spanish conquests, the New World. The berry-like appearance of kermes encrustations led to the misleading name 'grain' in the Middle Ages — the root of the word 'ingrained', because the dye was relatively long-lasting.

This confusion extends to the chemical nature of the colourants: they are all anthroquinones, quinone derivatives of anthracene. Madder is a mixture of two very similar compounds, alizarin and purpurin, whereas lac, kermes and cochineal contain somewhat larger derivatives, mostly carminic and laccaic acid. In principle, the structures and proportions of these components can reveal the origin of the dye, but that's challenging to discern in practice. High-performance liquid chromatography can separate the organics but requires large samples, which are rarely available for paintings. Raman spectroscopy is rendered useless by the dyes' fluorescence, which obscures the signal.

This problem can be avoided with surface-enhanced Raman scattering (SERS), in which the amplitude is boosted by adsorbing the molecules on metal nanoparticles, where they interact with surface plasmons. Yet SERS still typically requires a prohibitive amount of material, particularly when the intense red colourants are highly diluted in the paint, and has so far been successfully applied only to the analysis of textile dyes. Marco Leona of the Metropolitan Museum of Art in New York has now shown that a variant in which the scattering is enhanced by a resonance with the plasmon frequency (called SERRS) offers more sensitivity (*Proc. Natl Acad. Sci. USA* doi:10.1073/pnas.0906995106; 2009).

Leona has already used the technique to draw some significant conclusions about ancient art-materials use. He has detected madder lake in a painted leather quiver from Egypt dated at 2124–1981 BC — about 700 years older than the previous earliest recorded use. As its preparation requires some clever chemistry to precipitate the white carrier particles, this deepens our appreciation of the technological sophistication of the Egyptians. And a wooden sculpture of the Virgin and Child from Auvergne, made in AD 1150–1200, turns out to be painted with a lac glaze. Lac is known to have been imported to Europe from the early thirteenth century, but this pushes the date of trading back into the previous century. ❐

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