Behind platinum's sparkle

As a rare and precious metal that is also resistant to wear and tarnish, platinum is known to be particularly well-suited to jewellery. **Vivian Yam** reflects on how, beyond its prestigious image, platinum has also found its way into a variety of fields ranging from the petrochemical to the pharmaceutical industry.

Platinum was in fact named after another element — its name derives from the Spanish word 'platina' meaning 'little silver', because of its colour. It usually occurs in nature as elemental platinum, or is alloyed with small quantities of other metals, especially iridium.

The most widespread role of platinum is as a catalyst, in particular in the automobile industry, where it is used in catalytic converters to catalyse the complete combustion of low concentrations of unburned hydrocarbon from the exhaust into carbon dioxide and water vapour, and in the petrochemical industry to cleave large hydrocarbon chains. It also finds its place with the advent of renewable energy, as platinum nanoparticles are used in fuel cells for the clean production of hydrogen.

Another important area is in the development of platinum drugs, and more recently prodrugs — compounds first introduced in the body in an inactive form, which are later converted into their active form. Since the first report by Rosenberg in 1969 on the antitumour properties of the platinum complex cisplatin[1], there has been an enormous interest in understanding its action mechanism. This has led to the development of second- and third-generation platinum(II) anticancer drugs (carboplatin and oxaliplatin), and platinum(IV) prodrugs — for example satraplatin, currently under consideration for approval of the US Food and Drugs Administration. Although the mechanisms are still unclear, it is now known that square-planar platinum(II) drugs crosslink to DNA, and a number of other platinum(II) complexes with planar auxiliary ligands act as DNA metallointercalators.

Recently, photo-sensitive moieties have also been incorporated to platinum complexes for the development of photo-activated cancer chemotherapy or (pro) drug delivery. Platinum(II) porphyrins,

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chlorins and derivatives can also serve as photosensitizers for singlet oxygen production for photodynamic therapy (PDT) — their heavy atom effect would facilitate intersystem crossing and improves the quantum yield of singlet oxygen ($^1O_2$), which is key to the success of PDT.

Parallel to these developments, platinum(II) porphyrins have been found to be phosphorescent compounds with long-lived triplet excited states. As such, they are highly susceptible to luminescence quenching by oxygen, and thus promising for oxygen optical sensing applications — of interest for the development of pressure-sensitive paints in pressure sensing. A number of other platinum(II) complexes, for example polypyridine compounds, also show rich phosphorescent properties combined with a rich polymorphism that gives rise to a variety of intense colours. An early example of a highly coloured platinum(II) species comes from the one-dimensional compound Magnus's green salt[2] ($[Pt(NH_3)_4][PtCl_4]$).

Square-planar platinum(II) compounds are well known for their strong propensity towards metal–metal interactions, which lead to interesting spectroscopic features — both in the UV–visible range and in emission spectroscopy. In general, a red shift in absorption and emission wavelengths would be observed in the presence of metal–metal interactions, which sometimes translates into visual colour or emission colour changes[3]. The rich phosphorescent properties of platinum(II) compounds have also led to their use for white organic light-emitting diodes, vapochromic and vapoluminescence sensors for various volatile organic compounds, chemosensors, bio-probes, labels and imaging agents.

The flat planar structure and charge-transport properties of platinum(II) compounds also leads to interesting field-effect charge mobility. The charge-transfer properties of a number of platinum(II) compounds and polymers have been exploited for photosensitizing and organic photovoltaic applications. The unique non-covalent metal–metal interactions in platinum(II) compounds — which have a comparable energy to that of hydrogen bonds — offer novel strategies for building supramolecular assemblies, organogels, polymers and nanostructures.

The characteristic colour and emission changes in these assemblies can be exploited to detect sol–gel transitions and stimuli-responsive microenvironment variation. Molecular wires and multimetallic self-assembled coordination architectures have also been constructed[4] based on platinum(II) compounds; some of which stabilize unusual guest molecules whereas others serve as site-selective nanoreactors.

Platinum has proved to be a versatile element with fascinating reactivity. It has become of great importance in very diverse areas, and there is little doubt that platinum chemistry will continue to attract increasing attention in the forthcoming decades. ❐

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