Profile of Vivian W.-W. Yam

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Primary school children do not typically handle droplets of the toxic element mercury with bare hands. However, for a young Vivian Yam, an early experience with a broken thermometer sparked a career synthesizing metal complexes for use in light-harvesting and light-emitting materials. Yam, a recently elected foreign associate of the National Academy of Sciences and a chemistry professor at the University of Hong Kong, says, “I was amazed by mercury’s ability to flow and coalesce—unlike most metals we’re exposed to.” Over the past three decades, through a combination of molecular design and physical inorganic chemistry, Yam has helped create new classes of metal-containing chromophores and luminophores—molecules that absorb or radiate light and some of which may help mitigate the growing global demand for energy. Yam’s Inaugural Article (1) explores how a platinum(II)-containing compound assembles and forms varied 3D structures with individual spectroscopic properties.

Chemist from Hong Kong

Born in Hong Kong when the region was under British rule, Yam attended an Anglican grammar school. Her mother was a homemaker, and her father, a civil engineer. “I really admired him and still remember him using the slide rule back in the days when you didn’t have a calculator,” she says. However, Yam’s parents did not urge her to enter professional schools or study medicine. She says her curiosity with the natural world and an analytical disposition prompted her to pursue science. In her secondary school biology teacher, Yam found another inspiration. “She embodied the Chinese commitment to one’s field—that whatever you do, you should respect your work, enjoy it, and be very much devoted to it. Even when she was pregnant, she taught until the last moment!”

Yam majored in chemistry at one of Hong Kong’s two universities of the time, the University of Hong Kong. She also competed on the university’s badminton team, playing several times a week. Yam conducted research with inorganic chemist Chi-Ming Che while at the University of Hong Kong, and he remains influential in her career.

Che worked on metal-mediated and metal-catalyzed oxidation chemistry with the elements ruthenium and osmium. These metals can exist in a high valence or high oxidation state, reflecting the number of free electrons in the elements that are capable of forming bonds.

In the 1980s, a decade before Hong Kong formed its Research Grants Council to fund science, the University of Hong Kong lacked resources for purposes unrelated to teaching. Instead, the institution relied on the ingenuity of professors such as Che who had been trained by prominent chemists from around the world; Che studied with Caltech chemist Harry Gray. Yam recalls that “many of the chemicals we ordered were not allowed to be transported by plane, and so they arrived months later by ship from the United States or Europe.” As a result, the Chinese chemists had to carefully schedule experiments. “Occasionally, you’d order a chemical and then by the time it arrived half a year later you wouldn’t remember what it was for,” Yam adds with a laugh.

Oxidation and Life

Despite the challenges, Yam remained at the University of Hong Kong for her doctorate, studying with Che. She met her husband Patrick Shing-Tat in Che’s laboratory. Together, the couple worked on high-valent metal and oxidation chemistry, the study of which, Yam notes, is inspired by a fundamental biological reaction.

“Interest in this type of chemistry originates from our understanding of the enzyme cytochrome P450—a form of it exists in nearly every species and even in some viruses.” Cytochromes use a metal ion, often iron, to help metabolize chemical bonds and harness their energy. “The enzyme’s ability to oxidize unactivated carbon–hydrogen bonds in particular is a very difficult task, but cytochromes do so under the typically mild conditions in the body. Life may not exist as we know it without these enzymes and their reactions,” says Yam.

Oxidation chemistry is also of crucial importance to the conversion of sunlight into solar fuels or for splitting water, a process similar to a key reaction in photosynthesis. The metals ruthenium and osmium emerged

Vivian W.-W. Yam. Image courtesy of the University of Hong Kong.

as suitable models because they belong to the same group as iron and have similar chemical properties. Being less reactive than iron, however, ruthenium and osmium are more amenable to experimentation and studies of reaction mechanisms.

In Che’s laboratory, Yam crystallized a ruthenium precursor and demonstrated that the compound can be used in the synthesis of a ruthenium(V)–oxygen multiple-bond complex (2) (the number in parentheses refers to the valence of the metal). “We were the first to obtain this species back in the late 1980s,” she says. “It had important implications in proton-coupled electron transfer, which is at the heart of reduction and oxidation reactions, like water oxidation for example.”

Department Building

Unlike many academic scientists, Yam did not begin a postdoctoral fellowship after receiving her graduate degree. Instead, in 1988, she accepted a junior faculty position at the then-new Department of Applied Science at

This is a Profile of a recently elected member of the National Academy of Sciences to accompany the member’s Inaugural Article on page 7986.

the City Polytechnic of Hong Kong (now the City University of Hong Kong). The department, an ambitious attempt to bridge several physical and life sciences, had little precedent in an institution that lacked chemistry, biology, and physics departments.

Yam recalls, “A colleague and I literally started from scratch. In the library, there wasn’t a single book on chemistry. We split the chemical catalog and ordered material for both teaching and research purposes: The very first beaker, the first kilograms of sodium chloride, the first gas chromatograph, and on and on. We built the infrastructure and facilities by hand.” Although it was a daunting process, she says that the effort is among her fondest memories as a young scientist.

For the next two years at the City Polytechnic of Hong Kong, Yam taught undergraduates, and in her limited free time, endured long commutes to conduct research using the facilities in her former advisor Che’s laboratory. Her work also took a new direction as she began studying the luminescence of complexes with metal–metal interactions.

“This research originated from Che’s association with Harry Gray at Caltech,” Yam notes. Che and Gray had been investigating a system called platinum pop, a chemical complex with two closely interacting platinum(II) centers. The complex is held together by covalent bonds and noncovalent, metal–metal bonding interactions, which have strengths similar to those of hydrogen bonds. The interactions between the platinum centers create an “excited” or elevated energy state that produces a strong luminescence in the visible region. Yam pursued gold(I), which also luminesces due to metal–metal interactions.

In 1990, she returned to the University of Hong Kong to join the faculty and continue working on luminescence. She has since remained at the university and now holds both the chair professorship of chemistry and the Philip Wong Wilson Wong professorship of chemistry and energy. Along the way, in 2001, she became the youngest member elected to the Chinese Academy of Sciences, breaking the record held by her mentor Che. “Working in Hong Kong,” Yam says, “you sometimes feel isolated from mainland China and the rest of the scientific community. So the honor from the Chinese government along with my membership in the National Academy of Sciences and in 2011 the L’Oréal-UNESCO for Women in Science Award were recognitions I’d never dreamed of.” Yam cherishes her role as a mentor for female scientists. Yam says her advice to young

women interested in science has been: “Pursue your dreams, and do not be burdened by social or familial prejudices.”

Illuminating Chemistry

Like her mentor Che, Yam traveled widely to amass skills to further her research. She paid a short visit to Caltech in the late 1980s to perform spectroscopic measurements in Harry Gray’s laboratory and spent the summer of 1990 studying photochemical properties in microenvironments like spherical micelles with David Whitten, then at the University of Rochester in New York. Yam spent the summers of 1991 and 1992 in England, learning from another distinguished chemist, Nobel laureate Geoffrey Wilkinson of Imperial College, London. “I wanted to study organometallic synthesis because not a lot of people were working with excited states in these compounds,” Yam explains. Notoriously difficult to create because they involve air- and moisture-sensitive chemicals, organometallics, such as the now-banned gasoline additive tetraethyllead, consist of metal centers bound to carbon-containing ligands; their study bridges organic and inorganic chemistry.

The visits with Wilkinson helped launch Yam’s career in organometallic luminophores and metal alkynyl chemistry. Alkynyls are complexes that contain a carbon–carbon triple bond; the linear geometry of the bond gives the complexes defined structures and allows them to dissolve in common solvents. Organometallic materials that contain strong electron-donating alkynyl groups often have characteristic spectroscopic properties. The luminescence originates from the valence of the metals as well as the interactions between the metal centers and the carbon atoms.

Upon returning to Hong Kong, Yam and colleagues began developing new classes of organometallic luminophores. Many of the compounds showed long-lived luminescence and produced excited states with lifetimes in the microsecond range—orders of magnitude longer than that of green fluorescent protein (GFP) and other fluorescent materials (3). “We found that, by varying the number and type of metal centers, gold(I) versus the iso-electronic copper(I) for example, we could affect not only the excited state reduction–oxidation properties but could also tune luminescence colors and behavior,” she adds. In a gold(I)···gold(I) compound, the binding of potassium ions instigates conformational changes that produce low-energy red and near infrared emissions (4). By swapping the atom that bridged the gold(I) centers, the researchers further tweaked the color of the luminescence (5).

The work of Yam and others on organometallic luminophores has contributed to the development of organic light emitting diodes (OLEDs). Similar to standard light emitting diodes, such as those found in car headlamps and traffic signals, OLEDs convert energy into light efficiently and require little power to achieve the same level of brightness as incandescent lamps. OLEDs can also be incorporated into flexible sheets of glass and plastic; thin, lightweight layers produce sufficient luminosity for smartphones, portable tablet computers, and even large flat-screen televisions. Yam has helped develop gold(III) phosphorescent materials as well as solution-processable gold(III) phosphors for OLED applications (6). Solution processing allows materials to be easily deposited onto glass, plastic, and other surfaces.

The novelty of these compounds, Yam emphasizes, pales in comparison with their potential applications. “Energy consumption is perhaps the most pressing issue we face today. Nineteen percent of the total power used on the earth annually, almost 3 terawatts, is due to lighting. These organometallics have the potential to reduce that significantly and help meet our ever-increasing demands.” She explains that the internal quantum efficiency of these metal-containing materials can reach 100% in theory. “That’s what aroused our and other’s interest,” she says.

She adds: “[Researchers] have to start using cheaper, more abundant, and robust materials if we want this work to drive change globally, reduce energy consumption, and repair the environment. We’ve got to be innovative, and work across disciplines—chemistry, physics, biology, engineering, etc.—to solve the problems that we are facing on our planet.”

Sensing Changes

Yam has also been studying another use of luminescent metal complexes—as biological or environmental sensors. Her group at the University of Hong Kong developed a platinum(II) alkynyl-containing compound with square-planar geometry. The organometallic self-aggregated in solution, and its spectroscopic properties differed depending on the way it assembled; it displayed colors from red to emerald green and blue (7).

“Water-soluble derivatives of this and similar complexes could function like GFP, which is now widely used to detect mRNA expression or protein levels,” she explains. “Our compounds are much smaller, less susceptible to background interference, and have increased emission lifetimes.” Yam used her platinum(II) alkynyl derivative as an

indicator to bind short sequences of DNA (8) and also to detect the enzyme lysozyme as it bound to a specific nucleotide sequence (9). “The simple act of binding produced a rearrangement of the platinum compound in solution and a different luminescence,” she adds. “So we can easily see the results.”

Materials of the Future

In more recent work, Yam exploited metal-metal interactions in the organometallic compounds to create luminescent materials in nontraditional forms. Her group made metallogels (10, 11) and created spherical vesicles and cylindrical rod nanostructures that could interconvert—each with different colors and luminescent properties (12). “I’m a synthetic chemist, and what we like to do is to create new molecules,” she notes. “However, it’s equally important to understand how these molecules interact with each other and understand the factors that govern their interactions. This way, we can provide guiding principles on how to control their assembly.”

Yam has also been designing molecular materials that react to visible light in atypical ways. She began by examining classes of photochromic compounds including diarylethenes, which reversibly change from one structural form to another. Unlike alkynyls, these molecules contain a carbon-carbon double bond that bridges two separate aromatic groups. “Think of a bicycle where the wheels are rings of carbon atoms or occasionally nitrogen and sulfur and the frame in between is a carbon-carbon double bond—that’s similar to a diarylethene,” Yam explains.

To these carbon compounds, her group attached metal-containing chromophores—small clusters of molecules that absorb light. The chromophore’s excited state sensitized the resulting material. When the researchers shined different wavelengths of light, the metal-diarylethene complex shifted conformation, reversibly changing between structurally different forms. Yam says that this kind of photochromism, as the phenomenon is called, “is ideal for any system that relies on binary on- and off-states like digital memory” (13). In her Inaugural Article, she examines the noncovalent, metal-metal interactions that stabilize the 3D structures of a platinum(II)-containing compound. Modula-

tion of the compound’s self-assembly, her group discovered, can lead to folding and unfolding events, which emerge as spectroscopic changes.

Yam believes that understanding and manipulating 3D molecular structures holds a key to harnessing synthetic materials. To support that notion, she takes a cue from the natural world: “In proteins, whatever the amino acid sequence, they would not function without the correct secondary, tertiary, and quaternary conformations. We need to better control structure in the rational design of new materials so that they end up with the desired functions and performance.”

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