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Semiconductor Quantum Dots for Synthetic Photoredox Catalysis and Method Development for Cross Electrophile Coupling

by
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1. Quantum Dots and Photoredox Catalysis

"Scientific writing" as it appears in journal articles and other peer-reviewed publications exists primarily to communicate research between members of the scientific community, with emphasis on conciseness, formality, and precision of language. Too often, this writing style renders primary scientific literature unintelligible to the general public, whose tax dollars are often the ultimate funding source for the science being done. This chapter of my dissertation was written to communicate my research with my friends, family, and the general public, with the hope that anyone who wants to read it can better understand the significance of the research they've supported me through in grad school. I'd like to thank the Wisconsin Initiative for Scientific Literacy (WISL) at UW – Madison for supporting the writing of this chapter, especially Emeritus Professor Bassam Shakhashiri and WISL editor Elizabeth Reynolds for their help and guidance.

Light and Power

Interactions between light and matter are, and have always been, central to the human experience. Differences in how matter interacts with photons, the individual energetic particles which make up light, determine how we perceive matter visually, and help us tell one material from another. Over eons, our eyes have evolved to discern between photons carrying different amounts of energy, which we perceive as the phenomenon of color. The color, texture, and every other visibly discernable property of any matter arise as our human interpretation of which photons reach our eyes after interacting with that matter. Some substances allow most visible light to pass through them, appearing transparent, while others reflect only certain wavelengths of light to our eyes while absorbing others, giving them the appearance of color (Figure 1.1).

no light absorbed: transparent object

all light absorbed: dark object

all light reflected: light object

some light reflected: colorful object

Figure 1.1 Different interactions of matter with light lead to visible traits.

Beyond forming the basis of our most information-rich sense, light-matter interactions are a major component of our energy economy on Earth. When unimpeded by matter, photons travel infinitely in straight lines without losing energy or speed, and are thus idealized long-range carriers of energy and information as they flow throughout our universe. Events which release energy to their surroundings can emit some of that energy as photons, which can travel indefinitely before colliding with a substance. The energy of the absorbed photons is then converted into other forms, as in the sunlight-driven fixation of carbon dioxide and water into sugar molecules by some organisms, allowing energy from the sun to be stored and used on demand. In pursuit of the same goal, the invention of technologies which effectively interconvert light energy with other energy forms has been a centerpiece of modern human development. These inventions, from the first electric lightbulb to modern solar panels, computers, and digital displays have all capitalized on immensely useful fundamental properties of various materials, bringing energetic fluidity to power our innovations.

Differences in the ways materials interact with light predispose them toward individual applications. For example, pigments used in paints and inks are comprised of minerals or dye molecules which absorb specific wavelengths of light, giving them characteristic colors for which they are known: cadmium sulfide and selenide minerals provide vibrant fiery hues, while iron cyanide complexes form the basis for rich Prussian blue. By discovering multitudes of substances each with their own optical properties, we have populated our lives with color and light.

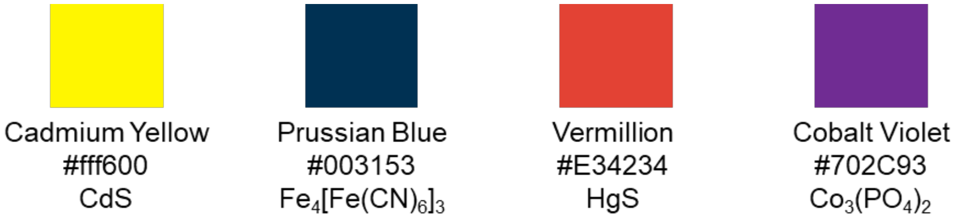

Figure 1.2 Colored materials that have been used as pigments for various applications.

Quantum Dots

Under ordinary circumstances, the color of an object does not depend on its size. The ways in which substances interact with light are normally examples of intensive properties – properties which are independent of the quantity of material under consideration, such as temperature, density, or melting point. At the atomic level, this is because materials absorb photon energy through the temporary displacement of electrons from their most stable resting positions within the material, much like it requires the input of a specific amount of energy to separate a magnet with some given strength from a magnetic surface. This mechanism of absorbing photons functions identically whether an object made from the material is the size of a planet or a grain of sand, so the coloration remains consistent at these scales. Consequently, different materials are ordinarily used to make things absorb or emit different colors of light, as observed in the wide assortment of different pigments used to make sets of oil paints or colored pencils of different colors.

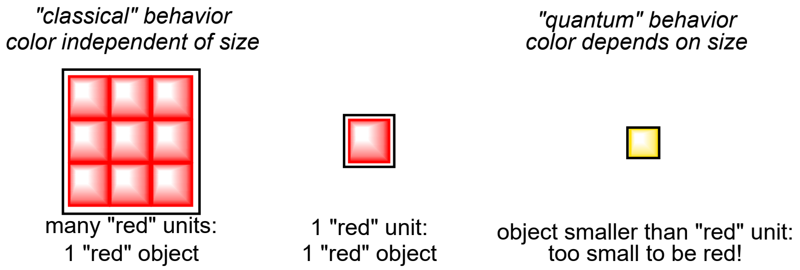

Figure 1.3 Conceptual representation of quantum confinement. Here, a "unit" is equivalent to the amount of space used within a material to store the energy from an absorbed photon. When an object gets smaller than this size, everything starts to change.

In contrast to this "classical" behavior, for some materials known as semiconductors, individual particles of the material which are smaller than a critical size interact differently with light than larger pieces of the same substance (Figure 1.3). Such particles, known as semiconductor quantum dots, exist only at the nanometer-scale, exhibiting size-dependent “quantum” optical properties not displayed by the material at larger size regimes. Due to the way that semiconductors absorb energy from photons, confining the space available for a particle to accommodate the absorbed photon energy increases the energy of photons which may be absorbed, changing the apparent color of the particle. This phenomenon, known as quantum confinement, allows sufficiently small particles made from a single material to absorb and emit different colors of light based upon the particle size. This behavior can be observed in many different semiconducting materials, including pure elements like carbon and silicon, as well as compounds of elements like zinc oxide (an active component in some sunscreens), however ordinary forms of these materials lack the small particle sizes required for quantum-confinement effects.

The useful optical qualities of quantum dots have rendered them excellent materials for a plethora of applications. Quantum dots can be found as the light-emitting components of digital displays in televisions and computers, and as light-harvesting materials for solar energy capture. The size dependent optical properties of quantum dots allow them to absorb and emit photons across the entire visible spectrum simply by producing different sizes of dots from the same material, which in many cases has allowed quantum dots made from inexpensive materials to replace other, more costly materials. The ability to control how matter absorbs and emits light by tuning the physical size of its particles has truly created a new design strategy to create complex photoreactive materials, which we are only just beginning to apply to real-world challenges.

Organic Chemistry

Organic molecules, consisting primarily of frameworks of carbon atoms, form the physical building blocks of our bodies and almost everything we interact with. The countless ongoing tasks within every living organism are all governed by the creation, interaction, and destruction of organic molecules. By uncovering the molecules responsible for regulating processes within our bodies, scientists have developed molecular agents to impact how we function at every level, and how we interact with our environment. Many of these molecules come directly from natural sources, including humans and other organisms, and can be repurposed to have effects different from their natural function. Alternatively, by creating new molecules which imitate or improve upon the properties of natural molecules, we can arrive at substances with new and potentially useful effects on organisms. Over the years, we have obtained unimaginably many substances, either harvested from nature or created in labs, to help, harm, or otherwise affect ourselves and our environment. From lifesaving antibiotics obtained from fungi, to crop-protection agents like herbicides and pesticides, to hallucinogens which distort our basic perceptions of self and reality, our capacity for molecular innovation is only limited by our creativity and our available tools to synthesize new molecules.

Since organic chemistry emerged as a field of study in the mid nineteenth century, organic chemists have sought to understand the innate reactivity of different types of molecules with one another, and in doing so discovered thousands of useful chemical reactions which can be harnessed to produce valuable substances. With modern technology and tools to help chemists perform reactions, understand their inner workings, and purify the products of chemical reactions, the field of organic chemistry has progressed to a point of maturity. Notwithstanding the time and resources required, virtually any conceivable stable molecule could be produced by some series of known reactions, as long as the target molecule is worth the endeavor. Modern research in organic synthesis then, largely seeks to improve the ways in which chemists approach making desirable molecules, in pursuit of reactions which generate less waste, save time, employ safer chemical reagents (specialized chemicals used for certain reactions), and consume less energy.

Much like humans, molecules will not perform processes which they lack the energy to do. Some chemical reactions are poised to happen spontaneously and give a net release of energy, while others require the net input of energy to fully proceed. The energy to power chemical reactions which will not happen on their own must come from another source such as reactive chemicals, heat, electricity, or light. Harnessing light energy to power other types of chemical reactions which could not otherwise occur is an attractive prospect for several reasons. Sunlight is an incredibly abundant source of energy, and photosynthesis has evolved to harness and store it as chemical energy in the form of sugars and oxygen. This process would be impossible without the input of solar energy, and that same energy is what is ultimately released when organisms metabolize sugars to sustain their growth, survival, and reproduction. This utilization of solar energy is central to life on Earth, and while cellular machinery has evolved to perform photosynthesis and create complex biomolecules, chemists have long sought ways to harness light energy to power non-natural chemical transformations which would otherwise be impossible.

The use of light to power organic chemistry can be broadly classified into two categories. Pure photochemistry proceeds when a molecule absorbs light directly, temporarily entering a more energetic “excited” state, in which it has enough energy to undergo reaction with another molecule to produce a product. Unfortunately, many organic molecules do not efficiently absorb visible light on their own (appearing colorless), and require very powerful light sources or highly energetic ultraviolet light to undergo these reactions. These approaches can be successful, but ultraviolet radiation can be hazardous to work with, and can sometimes destroy the starting molecules before the desired reaction occurs. To circumvent this obstacle, scientists have developed compounds called photocatalysts, highly colored molecules which effectively act as antennae to absorb the energy of visible light, before transmitting that energy to molecules which cannot absorb the light on their own, thereby giving them the needed energy to react with one another (Figure 1.4). This general strategy, known as photocatalysis, is the subject of my own research.

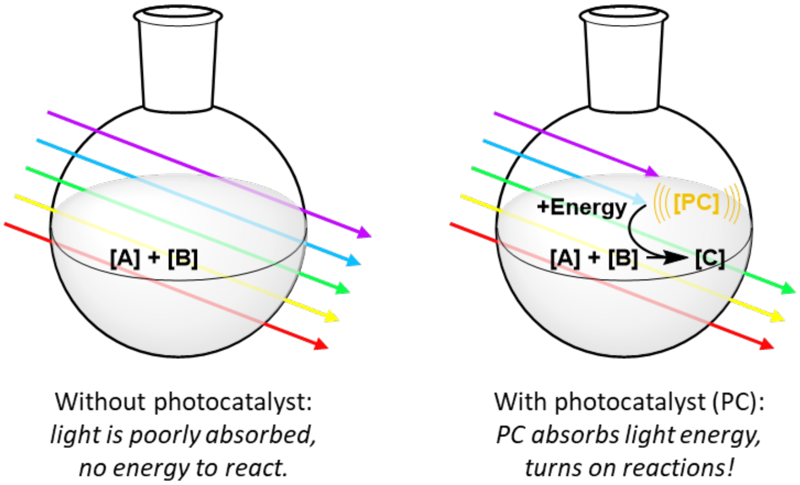

Figure 1.4 Photocatalysts absorb visible light that most molecules can't and use the energy to power chemical reactions.

Photocatalysis

Photocatalysis has reframed how organic chemists think about what reactions are possible for virtually every category of organic molecule. When a photocatalyst funnels light energy into an organic molecule, the rules governing the fundamental reactivity of the energized molecule can be completely shifted, temporarily allowing it to partake in chemical reactions that would not otherwise occur. Molecules energized by light effectively gain access to "secret passages" while energized, letting them reach new places (turn into different molecules) by alternative routes. This has effectively added a new dimension to the canonical reactivity by which organic chemists can stitch together molecules into desirable compounds. Many photocatalyzed chemical reactions have been invented that can accomplish what previously required multiple sequential reactions, resulting in faster and more efficient organic synthesis. The input of light energy also reduces or eliminates the need for other reagents as chemical energy sources which contribute to waste, much like how using solar energy to power electric cars circumvents gasoline consumption and CO_2 emission. Furthermore, many years of inventions have produced a huge variety of light sources that can be used to power photocatalysis with excellent control over the color, power, and spatial delivery of light.

Photocatalysis is still a relatively new tool in the repertoire of organic chemistry, and despite the many advantages of using photocatalysis to make valuable organic compounds, some challenges must be addressed before those advantages are fully realized at all scales of molecule production. By unfortunate coincidence, the light-absorbing photocatalysts that have so-far been the most effective in promoting photocatalyzed organic chemistry have been derived from rare metals such as ruthenium and iridium, which are among the least abundant elements on Earth. Photocatalysts employing these rare elements are extraordinarily effective at driving organic reactions, and can be used in small amounts relative to the quantity of chemicals produced. Even so, the extreme costs associated with obtaining, producing, and recovering these precious metal catalysts has largely limited their practical utility to small-scale chemistry.

Developing photocatalysts which do not rely on precious metals has been an area of great interest to make photocatalysis a more practical tool within organic synthesis. As discussed earlier, quantum dots exhibit tunable light-absorbing properties, and can be manufactured cheaply from Earth-abundant elements. Consequently, besides their utility in light-absorbing and -emitting devices, quantum dots have been studied as photocatalysts for simple chemical reactions. For example, quantum dots can harness light energy to produce hydrogen gas from water molecules, which can be collected and used for fuel or other purposes. Despite their advantageous attributes, quantum dots have only recently begun to be explored as photocatalysts for the more complex and synthetically desirable reactions that transform organic molecules. This intersection has been the focus of my research, in the hope that quantum dots can elevate photocatalyzed organic chemistry to new levels of practicality.

The biggest focus of my research has been understanding how quantum dots' inner workings can power chemical reactions. Certain types of reactions involve the net input of electrons into molecules, electrons which must come from an external source known as a "reductant". Electrons stored in reductants, including some metals and organic molecules, have differing energies and tendencies to be transferred to another species. These so-called "reductive" reactions only work if the incoming electrons have enough energy to flow from the reductant into the desired molecules, so choosing the right reductant for a reaction is crucial. Photocatalysts can be useful for reductive reactions because they can concentrate light energy into electrons to make a reaction occur using reductants that would otherwise be too "weak". Like a magnifying glass can focus sunlight to heat up tiny areas to much higher temperatures, photocatalysts can harness light to spice up electrons from a weak reductant, effectively making it stronger. This is advantageous, because weak reductants are usually cheaper, easier, and safer to use than "strong" reductants. For example, many weak organic reductants easily dissolve in solvents, reducing the need for stirring, where stronger metal reductants usually do not dissolve and must be stirred constantly.

Early in my studies, I noticed that quantum dots were able to reduce certain molecules, ultimately removing chlorine atoms and replacing them with hydrogens, a reaction which requires highly energetic electrons to proceed. Surprisingly, the reaction worked! Usually, a photocatalyzed reaction only uses energy from one absorbed photon for each run-through of a reaction, however the reaction I observed would have required more energy than one photon of the color I was using. This led me to the conclusion that the quantum dots were using the energy of two or more photons per reaction, a known but relatively uncommon scenario in photocatalysis. I then did many experiments to determine how the quantum dots were doing this, with the most likely scenario involving a process called "Auger recombination". By providing proof of concept and understanding of how, why, and which quantum dots can carry out these reactions, my studies may pave the way for quantum dots to be used for other important reductive reactions, which might not have been expected to work either.

My further work has explored quantum dots in other organic reactions. Cross-electrophile coupling is a type of reductive reaction that builds carbon-carbon bonds present in valuable organic molecules. These reactions are also powered by the input of electrons, which must come from reductants. Cross-electrophile coupling reactions have been useful in producing important molecules like drug candidates but suffer from some practical challenges. Normally, solid metal reductants like zinc and manganese metal are used, but reactions involving solid-liquid mixtures can be hard to use at large scales, (Imagine the difficulty in trying to shake up a snow globe the size of a bathtub!) and metal-derived waste can be expensive to safely dispose of. My coworkers and I have found that certain quantum dots, along with light and weaker alternative reductants, hold promise to make these reactions more practical for large-scale use. While other photocatalysts have been used for this purpose before, quantum dots maintain advantages of cheapness and stability over other photocatalysts, which are also especially important when reactions are used at bigger scales.

By demonstrating how quantum dots can replace and improve upon expensive and rare photocatalysts to promote organic chemistry, I hope that my research will set the stage for these powerful reactions to become more-widely employed, and ultimately improve the toolbox of chemical reactions used to produce the organic compounds that we depend on.