

A Novel Kind of Dye

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Light is difficult to understand because of its “dualistic nature” and we need to know just a little bit about light to develop a conceptual understanding of dyes. A “photon” is the smallest amount of light. In a way, a photon is to a light beam what a rain drop is to rain and sometimes photons actually behave just like tiny particles. On the other hand, a photon also behaves like a “wave” and this behavior is much harder to explain; there simply are no good analogies. Fortunately, all we need to know right now about the wave nature of light, is that the color of the light is related to the frequency of the waves (don’t worry about *what* is vibrating). Let’s get some idea about the magnitude of the frequency by looking at the rainbow spectrum. Photons of violet light, for example, have a frequency of 750 TeraHertz. One TeraHertz means 10^{12} Hertz, that is, whatever it is that vibrates in the photon, “it” vibrates up and down on the order of 100,000,000,000,000 times per second, that is, one hundred trillion times per second. At the low-energy side of the rainbow spectrum, red light has a lower frequency of 375 THz. The higher the frequency of the light, the higher is its energy. Violet light is on the high-energy side of the visible spectrum. The energy of ultraviolet light, just outside the visible range on the high-energy side, is responsible for sun burns. Infrared “light” cannot be seen, instead IR light can be felt as heat and infrared light has frequencies below 375 THz and IR photons contain less energy than photons of visible light.

One kind of interaction between light and a molecule consists in absorption. The photon is absorbed and its energy is used to promote the molecule into a higher energy state. Such an “excited” molecule can return to its ground state by the reverse process, that is, the molecule falls back into its lower energy state while emitting a photon of light (fluorescence & phosphorescence). Normal dyes are materials that allow for such absorption-emission sequences with photons of visible light. If a dye absorbs one color, then it reflects light of all other colors and it is of the color

that is complementary to the absorbed light. This may sound complicated, but it is very simple to understand based on the three basic colors red, green, and blue. The dye of a blue dress absorbs orange (red and green); a red tie absorbs blue-green, and green lawn absorbs purple light (red and blue). Many of the big chemical companies started out in the “age of the dyestuffs,” the period between 1865 and 1900, which includes the discovery of the azo dyes and of indigo. Dye discovery, development, and fabrication remain one of the pillars of the modern chemical industry and the art and science of dye making is very mature. Organic chemists have been able to design complex organic molecules that are intensely colored and the dye molecules can be fine-tuned to absorb or emit light of *any* desired color of the rainbow spectrum.

In my research group, we are interested in a different and novel kind of “dye” we are making “nonlinear dyes.” We create materials that interact with light of one color and emit light of a different color—and best of all—they emit light of a color that is higher (!) in energy than the source light. And the emitted light is not just a little bit more energetic; we create materials that emit light with twice the energy of the source light. Shining infrared laser light (very intense heatwaves) on such a so-called “second-order nonlinear optical material” leads to emission of visible light with twice the frequency of the infrared light. The design of such “nonlinear dyes” is still in its pioneering stages and fundamental problems remain. Nonlinear dyes are at the heart of photonics applications. In photonics technology light is used as the primary carrier of information and photonics is thought to replace much of today’s electronics in communications and computing applications in the near future.

Normal and nonlinear dye molecules share a few features in that they often are rod-like and have large electrical dipole moments along the long molecular axis. For the novel kind of dye the *relative orientation of the individual dye molecules becomes a key issue and this is very different from normal dyes*. A blue material will be blue no matter what the orientations of the neighboring molecules happen to be. The color of all the dye molecules simply adds up for normal dyes. For the novel kind of dyes, however, the optical effects add up only if the nonlinear dye molecules are

oriented in the same direction and they cancel otherwise! And this is where the problem lies. Most dye molecules have large electrical dipole moments and nature prefers to arrange polar molecules such that neighboring molecules are oriented in opposite directions. This orientation problem is indeed fundamental. It has long been considered impossible to have polar molecules form crystals in which all the molecules in the crystal are oriented in the same direction. Trying to make such highly dipole parallel-aligned organic materials seemed like a worthwhile goal to pursue in academia. To tackle this problem, we employ a multidisciplinary approach that includes mathematical modeling of crystals of dipolar molecules, theoretical and computational studies to arrive at and to test rational design concepts, and, most importantly, the experimental realization of prototypes. In the mid-90s, we convinced ourselves that it is not impossible to realize such dipole-parallel aligned molecular crystals. In 1995, we made the first near-perfectly dipole parallel-aligned organic molecular crystal of a nonlinear dye. The second and third prototypes were realized in 1997 and 2000. An improved design resulted in prototypes four and five in 2000.

Aside from a novel idea, truly innovative academic research takes time, good faith, patience, a supportive environment and bright and talented students. Several enthusiastic graduate students worked with me on this project and they are Grace Chen (PhD Chemistry 1996, Humboldt post-doctoral fellow in Zürich, Switzerland, and Heidelberg, Germany), Don Steiger (PhD Mathematics 1999, University of Illinois, Urbana-Champaign, and UC San Diego post-docs), Michael Lewis (PhD Chemistry 2001, Harvard post-doc), Zhengyu Wu, and Nathan Knotts. Two undergraduate students also contributed significantly to this effort and they are Jason Wilbur (BS, Chemistry 1995, now in Medical School) and Mitchell Anthamatten (BS, Chem. Eng. 1996, PhD Chem. Eng. 2001, MIT). We patented these materials and the patent is being issued this month. We are only beginning to understand, and the best is yet to come.

Biography: Rainer Glaser was born in Freudenstadt, Germany, studied chemistry and physics at the University of Tübingen, obtained MS and PhD degrees in chemistry from the University of

California-Berkeley, and was a post-doctoral fellow at Yale University before joining the MU Department of Chemistry in 1989. Dr. Glaser's research is characterized by an interplay of theory, computation and experimentation, focuses on materials research and studies of DNA deamination, and has resulted in over 95 research publications. Dr. Glaser has a strong interest in teaching and he has published on Chemical Education as well. Dr. Glaser's home pages on the world wide web are located at <http://www.missouri.edu/~chemrg>.