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The Role of Photophysics in Photochemistry

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Photochemistry is a broad subject. Figure 1 compares the number of papers in this research area written over the years with those on photophysics and photosynthesis (the circles are drawn to scale). The 284,035 papers on photochemistry cover a wide range of topics, including photodynamic therapy, the photodegradation of perovskite solar cells, the photosynthesis of hydrocarbons, the effects of airborne molecules and particles on cloud formation in the presence of solar radiation, and photocatalytic air and water purification and light sensors. Typically defined as the process occurring in living organisms to synthesize organic compounds starting from light, CO₂ and water, photosynthesis is a specific type of photochemistry and should therefore fit entirely within the field of photochemistry. However, the overlap between the two topics is surprisingly small; this implies that both topics are usually considered different fields of study and that the term 'photochemistry' is mostly used for the deliberate human activity of promoting chemical reactions with the aid of light.

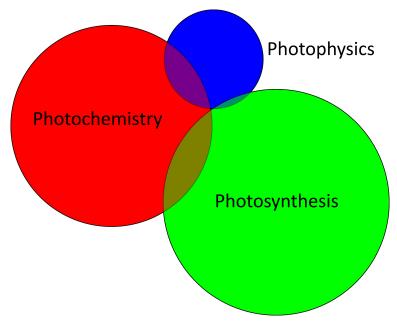


Figure 1. Comparison of the number of publications in the Web of Science up to March 2024 labeled with the following topics: photochemistry (284,035 entries), photosynthesis (359,717 entries) or photophysics (69,272 entries). The areas of the circles are proportional to the number of publications. The amount of overlap between the circles indicates the number of papers labeled with two of the topics.

Figure 1 also includes the topic of photophysics. Typical research subjects in this topic include fluorescence chemo- and bio-sensing, often using rare-earth-doped materials. There is also a lot of research activity on the topics of luminescent probes in general, metalorganic frameworks (MOFs), molecular complexes for optical applications, and, more recently, perovskite solar cells and organic light-emitting diodes (OLEDs). The overlap with



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photosynthesis is—unsurprisingly—negligible, while the overlap with photochemistry is considerable.

Why is properly classifying a research subject under a specific topic so difficult? Let us consider two examples that are close to my own research: photocatalysis and photochromism.

Photocatalysis is the phenomenon where incident light is used to initiate or promote chemical reactions in the presence of a catalyst. Most research on photocatalysis focuses on two subjects: (1) photocatalytic water splitting and subsequent hydrogen production and (2) the degradation of organic pollutants in water or air. The former—hydrogen production—holds considerable promise for green energy production, although the technology remains in its infancy, and much more research is needed to (hopefully) obtain higher efficiencies. The latter technique—the degradation of pollutants—is more mature and can be used on a small-to-medium scale to improve water and air quality by removing dyes, pesticides, drugs, etc. from waste water or by breaking down volatile organic compounds (VOCs) from ambient or exhaust air. While both processes evidently involve chemical reactions, the first step consists of a similar electronic transition: the creation of electron-hole pairs using illumination with sufficiently high photon energy to promote electrons from the valence band to the conduction band of a semiconductor by illumination. This is a purely physical process. This change in the electronic configuration is then followed by an initiation of chemical reactions. Therefore, the study of photocatalytic processes requires a multidisciplinary approach, involving the design, synthesis and possible doping of a photocatalyst; a careful choice of illumination conditions (in terms of wavelength and energy density); reactor engineering, including the optimization of flow patterns through CFD (computational fluid dynamics); and, of course, a study of the reaction kinetics, VOC reaction scheme and the identification of intermediates. Hence, any research covering the entire mechanism of photocatalysis requires the consideration of physics, materials science, chemistry and chemical engineering.

The second example, photochromism, is even more difficult to classify. The general concept of the phenomenon is a change in the optical properties (reflection, absorption, transmission, color) of a material upon illumination. In some cases, such a change is reversible, and the material returns to its original state once illumination stops. This principle is widely applied in prescription glasses that darken under bright light and decolor in dark conditions. In other cases, the transition is (quasi-)stable, with a fading time of hours to days, making the material suitable for light dosimetry. The reverse transition can then be achieved through illumination at a specific wavelength range or through heat. In the former case—the photodarkening sunglasses—the effect is pure photochemistry resulting from an oxidation–reduction reaction in organic dyes. In the latter case—the non-reversible transition—no chemical reactions take place, but the optical properties change because of electronic transitions within the dopants in the materials (typically oxides). Therefore, this should be classified as a photophysical effect. However, as photochromism can be based on different physical principles, determining a specific class for the process is, once again, not straightforward.

In both example cases, as in many others, a multidisciplinary approach is necessary to conduct research on the subject. Although this kind of collaboration between researchers with different backgrounds can lead to Babylonian confusion—each using different terminology and different approaches—at the same time, it can be highly rewarding and constructive. Ultimately, classifying research as photophysics or photochemistry is of little importance because, as William Shakespeare's fittingly remarked in Romeo and Juliet:

What's in a name? That which we call a rose by any other name would smell just as sweet.

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