Plenary Lecture
57th Annual Convention of Chemists (ACC) - Indian Chemical Society (ICS)
Recent Trends in Chemical Sciences (RTCS 2020)

Chemical Photocatalysis: Organic Synthesis with Visible Light

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Abstract:
Sensitized photochemistry evolved over the last 20 years into an enabling technology for the synthesis of complex organic molecules due to new mechanistic concepts and advances in light sources.[1] The use of visible light and dual catalytic systems allow now challenging transformations with good selectivity under mild reaction conditions.[2] Although light is an ideal reagent for chemistry (cheap, safe, can be used in large excess) it comes with certain limitations:
1. Compared to chemical bond energies, the energy of a visible light photon is small and photocatalytic activation of stronger bonds therefore requires special strategies.[3]
2. Photoinduced electron transfer leads to radical ions or combined with proton transfer to radicals, but the majority of chemical reactions proceeds via ionic intermediates. How can we generate reactive anions by light?[4]
3. Metal complexes and organic dyes are widely used as molecular photocatalysts in synthesis, but their stability and reuse can be problematic. Organic semiconductors are a valid alternative, particular for applications at larger scale.[5]
The lecture discusses approaches from our laboratory to overcome these and other current and future challenges in chemical photocatalysis.

References and Notes:
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Burkhard König received his Ph.D. in 1991 from the University of Hamburg, Germany. He continued his scientific education as a post-doctoral fellow with Prof. M. A. Bennett, Research School of Chemistry, Australian National University, Canberra, and Prof. B. M. Trost, Stanford University. Since 1999, he is a full professor of organic chemistry at the University of Regensburg. His current research interests are the development of synthetic methods in photoredox catalysis. As one of the pioneers of chemical photocatalysis, he has develop the field of light-driven organic synthesis.

Even before the methodology attracted much attention in synthetic chemistry, he published work on flavin photocatalysis already in the year 2000. His publication on eosin photocatalysis from 2011 inspired subsequent work and the now widespread use of redox-active dyes as photocatalysts. In 2012, König and co-workers reported for the first time on a photocatalytic variant of the intermolecular Meerwein reaction, which overcomes experimental disadvantages of the classical name reaction. The methodology is easily transferable and only two years later a first review article appeared. Also in 2012, in collaboration with other researchers, the group achieved the first enantioselective heterogeneous photocatalysis with visible light. Burkhard König provided an important conceptual contribution to new mechanisms of photocatalysis with the introduction of consecutive photoinduced electron transfer, which enables chemical reactions using the excitation energy of two photons even at low radiation intensities. The new type of reaction could be realized with various photocatalysts and extends the substrate spectrum of visible light photocatalysis to compounds hitherto considered inert, such as aryl chlorides. In recent work, the group has developed carbon dioxide as a synthetic building block through dual-catalyzed photo-nickel catalysis and photocatalytic C H activation, demonstrating the great potential of heterogeneous organic semiconductor photocatalysts, such as carbonitrides, for organic synthetic chemistry and reported first examples of the photocatalytic generation of carbanions as synthesis intermediates.

In all research projects on photocatalysis, Burkhard König combines the development of synthetically useful methods with detailed mechanistic investigations, often in collaboration with spectroscopists and theoreticians. The understanding of the molecular processes and thus the conceptual development of the field of photocatalysis are central concerns of his research projects.