

# The New Photocrystallography

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heterometallic complexes · magnetic properties ·  
photocrystallography · structure elucidation ·  
X-ray diffraction

Although the term photocrystallography was only coined in 1997, light-induced reactions in solids have been observed since the turn of the 20th century. As recalled by Schmidt in a review of photodimerization in the solid state,<sup>[1]</sup> the field of light-induced reactions in solids went through a “heroic” era, in which physical methods for characterizing the internal structure of crystals were completely non-existent. It was only with the development of methods for the determination of more complex molecular structures by X-ray diffraction that significant progress could be made. A strong concerted effort to exploit the new crystallography to gain insight into chemical reactivity in the solid state was made by Schmidt and co-workers, starting in the 1960s.<sup>[2]</sup> In a series of articles, they reported on the validity of topochemical principles governing the occurrence and nature of the products formed in [2+2] solid-state dimerization reactions of cinnamic acids and related compounds, a concept that had already been suggested in 1923 and referred to in 1943<sup>[3]</sup> but which was impossible to prove at that time. This seminal work stimulated many subsequent studies. Topochemical principles proved similarly applicable to the reactivity and product type in the “four-center” polymerization of diolefins.<sup>[4]</sup>

While in the early work the crystal structures would generally not survive the reaction unless simple ring closures were involved, more gentle methods made the observation of topotactic single-crystal-to-single-crystal reactions much more common. For example, irradiation in the tail of an absorption band could be used. Similarly, the advent of multicomponent supramolecular crystals was especially important, as photoactive molecules could be embedded in the cavities or channels formed by the host component. An early example is the study of the photochemistry of aliphatic ketones embedded in the channels formed by deoxycholic acid and apocholic acid.<sup>[5]</sup> The subsequent pronounced revival of photocrystallography during the past decade is due to the great increase in the complexity of crystal structures that can now be readily solved, to the advent of variable-temperature techniques, and to a large extent to the availability of highly intense tunable laser sources. The progress of photochemical reactions can be monitored as a function of time, molecular motions can be followed as the reaction proceeds,<sup>[6]</sup> reactions

can be engineered to be stereospecific,<sup>[7]</sup> and activation energies and standard enthalpies of activation can be measured by analysis of the temperature dependence of the reactions.<sup>[8]</sup>

The availability of pulsed synchrotron X-ray sources that can be synchronized with pulsed lasers now make it possible to perform time-resolved photocrystallographic studies of species with microsecond<sup>[9]</sup> or even lower lifetimes. In such pump–probe experiments, the laser pulse precedes the interrogating X-ray pulse or pulses, which measure the induced change with a time resolution limited only by the width of the probe pulse, which is typically 70–100 ps at current sources. In addition to molecular changes, light is capable of introducing phase changes in crystals. Important examples are the neutral-to-ionic and reverse phase transitions of the molecular crystal tetrathiafulvalene-chloranil, in which cation–anion pairs are formed on transition to the ionic phase.<sup>[10,11]</sup>

The recent work by Iversen and co-workers represents a new direction in the field.<sup>[12]</sup> The process studied is not a time-resolved one, as at temperatures below 50 K the light-induced phase has a lifetime of several hours,<sup>[13]</sup> but it is important because the reaction is accompanied by a pronounced change in physical properties of the crystal, in this case a large increase in the magnetic susceptibility of the solid.<sup>[13]</sup> Such changes can now be monitored at the atomic level. Photo-induced magnetic changes occur in spin-crossover transitions (e.g. from high spin to low spin), in which a change in spin state is typically confined to one metal center (see, for example, Ref. [14]). In the neodymium–iron heterobimetallic complex reported by Iversen and co-workers,<sup>[12]</sup> a striking change occurs in the metal-to-metal bridging bonds, which shorten by a total of 0.10 Å (Figure 1). The change is accompanied by a concomitant significant decrease in all iron–ligand distances. The latter observation rules out an increase in electron density on the Fe<sup>III</sup> atom through ligand-to-metal charge transfer (LMCT), as proposed on the basis of the UV and IR spectra,<sup>[13]</sup> as well as a change in spin state of the Fe atom, which would lead to the population of

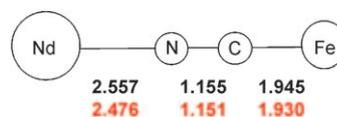


Figure 1. Schematic depiction of the change in distances in the Fe–Nd linkage (in Å); black: ground state; red: photoinduced state.

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antibonding orbitals and would contradict the observed lack of change in the Mössbauer isomer shift.<sup>[13]</sup> It follows that the change in susceptibility is more likely due to a change in the 3d–4f magnetic coupling between the two metal centers related to the shortening of the bonds linking Nd and Fe. Complementary theoretical calculations are desirable to further shed light on this intriguing change.

Photomagnetic switching has drawn considerable attention as it may be implemented in memory devices and has potential signaling applications. It is noteworthy that the photomagnetic effect can be enhanced by formation of polymer-coated nanorods.<sup>[15]</sup> The photomagnetism in other cyano-bridged bimetallic complexes has been interpreted as arising from electron transfer between the metal centers, as in trinuclear  $\{\text{Mo}(\text{CN})_8\text{Cu}_2\}$  molecules and coordination networks.<sup>[16]</sup> The current results point in a different direction and call for photocrystallographic studies of additional complexes in this class.

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