

Photo-induced charge transfer in molecular materials based on Prussian blue analogs: A photoacoustic study

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Abstract. Photoacoustic spectra of molecular materials based on the assembling of the $[\text{Fe}(\text{CN})_6]$ molecular block were recorded and evaluated. An intense absorption band around 600 nm was observed for compounds where the valence of the involved metals allows charge transfer through the CN ligand (inner photo-induced redox reactions). In the absence of this transition, only the signal corresponding to d-d transitions within the metal was observed, which falls below 450 nm. This suggests that photoacoustic spectroscopy provides a fast and reliable method to explore the existence of tunable photo-induced charge transfer in molecular materials.

1. INTRODUCTION

The absorption of a photon by a molecule is usually related to an electronic transfer within a given atom, between neighboring metals, from metal to ligand and vice versa, and also from ligand to ligand. When the charge transfer induces the appearance of unpaired spins and their coupling, a magnetic order can be observed, whose stability usually depends on temperature. In these cases, below certain critical temperature T_c a long-term meta-stable state is obtained. The photo-induced magnetization has been observed in pentacyanometallates (nitroprussides), hexacyanometallates and in octacyanometallates. The phenomenon has generated a high expectation in connection with its potential applications in molecular electronics, molecular communications and development of functional molecular devices [1-3]. For instance, cobalt(III) iron(II) cyanide is a diamagnetic compound, which on light absorption adopts a magnetic order.

This paper illustrates the application and scope of Photoacoustic Spectroscopy (PAS) as an appropriate technique to explore the existence of photo-induced charge transfer processes in molecular materials. The studied materials were 3D arrays of the molecular block $[\text{Fe}(\text{CN})_6]$ assembled through covalent ions of transition metals (Mn, Co, Ni, Cu, Zn, Cd). The application of PAS to the study of this family of materials remains poorly documented [4].

2. MATERIALS AND EXPERIMENTAL METHODS

As a source of the molecular blocks $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Fe}(\text{CN})_6]^{4-}$, an alkali ferrocyanide or ferricyanide, or the corresponding acids were used. In some cases, from the required charge balance, an alkali (exchangeable) cation remained in their composition. Molecular assembling takes place when solutions of the complex anion and of the involved metal are mixed. The obtained precipitate was isolated by filtration and washed several times with distilled water until a filtrate free of soluble ions was obtained.

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