



Photo-induced charge transfer in Prussian blue analogues as detected by photoacoustic spectroscopy

E. Reguera^{a,b,*}, E. Marín^a, A. Calderón^a, J. Rodríguez-Hernández^b

^a Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del IPN, Legaria 694, Col. Irrigación, México, D.F. C.P. 11500, Mexico

^b Instituto de Ciencia y Tecnología de Materiales, Universidad de La Habana, Cuba

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Abstract

The photo-induced charge transfer in four series of Prussian blue (PB) analogues was studied from photoacoustic spectra. In cobaltcyanides the observed signals were assigned to a metal-to-ligand charge transfer, which appears as a shoulder below 450 nm, and to d–d transitions for Co(II), Ni(II) and Cu(II) complex salts. No evidence of metal-to-metal charge transfer was observed for this series, which is probably due to the high stability of low spin cobalt(III) in the hexacyanide complex. Photoacoustic spectra for ferricyanides are broad bands, which result particularly intense up to 750 nm. Such features were attributed to the overlapping of contributions from metal-to-ligand (<600 nm) and metal-to-metal charge transfer transitions, with probably also a minor contribution from d–d transitions in the outer metal. The spectra for the ferrocyanides series are dominated by the metal-to-ligand charge transfer band below 550 nm, approximately 100 nm above this transition in cobaltcyanides. Within the studied solids, the most intense and broad metal-to-metal charge transfer bands were found for a series of low spin Co(III) high spin Co(II) hexacyanoferrates(II,III) and with similar features also for ferric ferrocyanide (Prussian blue), assigned to Fe(II) → Co(III) and Fe(II) → Fe(III) photo-induced transition, respectively. The first of these transitions requires of more energetic photons to be observed, its maximum falls at 580 nm while for Prussian blue it is found at 670 nm. Prussian blue analogues are usually obtained as nanometric size particles and many of them have a microporous structure. The role of surface atoms on the observed charge transfer bands in the studied series of compounds is also discussed.

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1. Introduction

Prussian blue (PB) analogues or hexacyanometallates form a family of coordination compounds that has received a notable attention as prototype of molecular materials in the last decade. The CN group is a strong bridge ligand that allows a pronounced charge overlapping between the metal centers linked at its C and N ends. From this fact, PB analogues show interesting properties as molecular magnets, among them, high temperature of magnetic ordering [1,2], pole-inversion magnets [3], spin-glass behavior [4] and photo-induced magnetism [5]. This last effect is related to the photo-induced charge transfer between the metal centers changing the available population of electrons with unpaired spins and, in consequence the material magnetic properties. This is a typical metal-to-metal charge transfer (MM'CT)

but with a relatively large stability for the excited state to attain magnetic ordering below certain critical temperature (T_c). The MM'CT transitions in PB analogues have also been studied for potential applications of these compounds as electrochromic materials, e.g. smart windows and electrochromic displays [6], since the charge transfer transition leads to a color change. The MM'CT effect in hexacyanometallates is closely related to the nature of the CN ligand. It has a low energy π -antibonding orbital at the C end which overlaps with the t_{2g} orbitals of the inner metal (M'), providing a low energy route for the electron movement between the metal centers. The deep blue color of ferric ferrocyanide (Prussian blue) has been ascribed to a MM'CT transition among iron atoms [7]. The existence of that low energy π^* -orbitals also allows the occurrence of metal-to-ligand charge transfer (M'LCT) in this family of compounds. The optical absorption spectra of hexacyanometallates are mainly related to these two charge transfer mechanisms together with the possibility of d–d transitions in the involved transition metals. Such spectra are usually recorded by UV–vis spectroscopy.

* Corresponding author. Tel.: +52 57296000x67774.
E-mail address: ereguera@yahoo.com (E. Reguera).