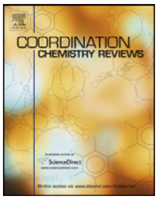
Coordination Chemistry Reviews 257 (2013) 369–380

Contents lists available at SciVerse ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Electronic spectra of porphyrins in the solid state: Newly observed transitions, collective and structural effects, and protein-mimicking environments

Ronald L. Musselman[a,b,*], Randy W. Larsen[a], Brian M. Hoffman[c]

[a] University of South Florida, Tampa, FL, United States
[b] Franklin and Marshall College, Lancaster, PA, United States
[c] Northwestern University, Evanston, IL, United States

Contents

ARTICLE INFO

Article history:
Received 31 July 2012
Received in revised form 16 August 2012
Accepted 17 August 2012
Available online 10 September 2012

Keywords:
Specular reflectance
Solid-state
Porphyrins
Phthalocyanines
Electronic spectra
Ruffling induced red-shift
Solid network encapsulation
One-dimensional conductivity

ABSTRACT

Solid-state porphyrins allow detailed electronic spectroscopy, evaluation of structural effects, and new catalytic environments not possible in solution. A difficulty with studying porphyrins and other highly absorbing species with UV–vis spectroscopy in the solid state is the opacity of the samples. Fortunately, this is in fact a major plus with specular reflectance spectroscopy. This paper reviews several solid-state porphyrin systems having notable delocalized electrons, structural effects on spectra and environments that allow heterogeneous catalysis and protein-mimicking environments, all studied with polarized specular reflectance spectroscopy. The porphyrins include free-base and metalloporphyrins with simple (octaethyl) through complex (tetraaza-tetrabenzo) substituents and ring insertions. Applications include new electronic transition assignments, determination of ring vs. metal conductivity, correlation of ring puckering to red-shifting of Q and Soret transitions, and identifying the presence of and environmental effects on porphyrins in network solids.

1. Introduction

1.1. Metalloporphyrins in general

Metalloporphyrins are of interest because of their broad biological presence [1,2], including light-gathering processes [3], metal-catalyzed reductions [4–7], and semiconductive properties

---

* Corresponding author at: University of South Florida, Tampa, FL, United States. Tel.: +1 941 330 7079.
E-mail addresses: rmusselm@fandm.edu, rmusselm@usf.edu (R.L. Musselman).

0010-8545/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.ccr.2012.08.015

[8–10]. The biological applications have been well documented in numerous reviews [11–14]. We have been recently looking at heme models and other metalloporphyrins encapsulated in network solids [15,16] that have the potential of mimicking the protein environment of porphyrins in a variety of active biological systems. In addition to biological functions, some porphyrins are useful in industrial applications. Tetraazatetrabenzoporphyrins, also known as phthalocyanines or pcs, for example, are highly absorbent in the visible part of the EM spectrum and are stable, thus making them excellent textile dyes and paint pigments. When phthalocyanines are partially oxidized with, for instance, I_2, the planes stack cleanly and closely along their normal vector and exhibit collective interactions along the stacking direction, commonly called, "one-dimensional conductivity" [9,10,17–23]. Other pcs coupled with C_{60} are used in photovoltaic applications [24–29].

This review looks at the spectroscopic study of solid-state porphyrins using polarized specular reflectance spectroscopy, a technique especially well-suited for solid-state work. After a review of this technique, we'll look at increasing aggregation of porphyrin units, beginning with monomers in network solids and concluding with tightly stacked planes exhibiting one-dimensional conductivity.

1.2. *Specular reflectance*

Solid materials with intense absorbers typically are too opaque to study with transmission spectroscopy. Alternate methods are specular reflectance [30,31] and diffuse reflectance [32–35]. Specular, or mirror-like, reflectance [36–38] which is a re-emittance process where the absorbed light is reflected from the surface, is used for single crystals with reflective surfaces and for reflective films [16,39]. Diffuse reflectance, which is essentially an absorption process where the unabsorbed light is scattered back to the observer, is widely used for powder samples and is a true absorbance phenomenon. There is a report of its having been used for single crystals: zeolites containing mobile small molecules of interest [40]. The principal advantages of specular reflectance are that (1) polarizations may be obtained from samples ordered appropriately, (2) absolute absorptivities may be obtained (3) electrical conductivities may be obtained from specular reflectance data [41] processed with standard Kramers–Kronig transformations [30] and (4) thin films [42–45] may be studied. Most of the spectroscopic data reported in this review are from specular reflectance.

The electronic transitions of primary interest in porphyrins are intense, with some absorptivities greater than 200,000 M^{-1} cm^{-1}. (For comparison, visible transitions in highly colored transition metal salts are typically less than 1000 M^{-1} cm^{-1}.) The intense transitions are symmetry-allowed, where the transition moment integral,

$$Q = \int \Psi_e |\mathbf{r}| \Psi_g \, d\tau, \qquad (1)$$

is formally non-zero. This means that the combined symmetry of the ground state, perturbing operator, and excited state is the totally symmetric member of the point group of the system at hand. For example, in a D_{4h} system, the integrand would need to have a direct product of A_{1g}.[1] This typically results in an absorbance coefficient, epsilon, of between 1000 and 200,000 M^{-1} cm^{-1}. If one were using absorbance spectroscopy to study solids with an epsilon of up to 200,000 M^{-1} cm^{-1} the path length would need to be about 2×10^{-3} mm. Since this would be difficult to achieve experimentally, it is easier to use natural crystals and take advantage of the fact that high absorbers are also high reflectors. Conveniently, materials with smooth crystalline surfaces and absorbances of 1000 M^{-1} cm^{-1} or greater reflect at least 0.5% of the incident light which is readily measurable with the proper apparatus [41].

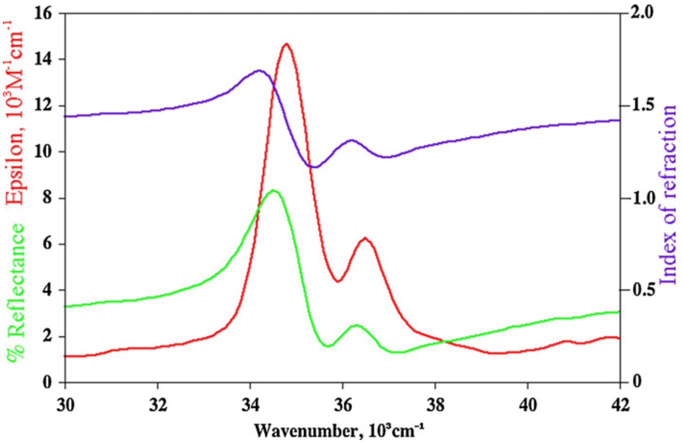


Fig. 1. Correlation of reflectance (green), index of refraction (purple), and absorptivity or epsilon (red).
From Ref. [31].

The factors determining the allowedness of a transition also determine which spatial orientation of the incident electric vector will effect a transition. Based upon the total electronic symmetry (from all partially or fully filled orbitals) of both the ground and excited states, the effective perturbation vector (the **r** in Eq. (1)) will be oriented along the *x*, *y*, or *z* axes of the chromophore. In some cases, a transition is forbidden under all orientations. For the transitions that are allowed, the allowedness direction narrows down the possible orbital transitions comprising a spectroscopic peak and thus aids in the assignment of a transition. Polarized spectroscopy also allows one to see minor components in one polarization that may have been hidden by a larger peak allowed in another direction [46].

Specular reflectance data, while interesting and somewhat informative in themselves, are most useful in the context here upon transformation into absorbance data via a Kramers–Kronig transformation [30,47]. For Kramers–Kronig analysis which formally includes integration over an infinite range of photon energies, reflectivities beyond our experimental region are estimated in the infrared region and below to be equal to the lowest-energy experimental measurements and are approximated in the vacuum ultraviolet and beyond so as to produce baselines approaching zero absorbance in regions having no absorbance in solution spectra. Examples of such "effective transitions" are discussed in a recent paper [48]. The resultant index of refraction, "n," and absorption coefficients, "eps," are shown compared to reflectance in Fig. 1.

Our current polarized specular reflectance spectrophotometer is described in a recent review [31].

2. Solution vs. solid

While most UV–vis spectroscopy is performed on solutions, this environment can cause problems for accurate spectroscopic determination and does not provide the total information available. Porphyrins in solution are known to exhibit solvent effects [49–53] and specifically, their spectra are dependent on the solvent polarizability [54]. While in solids there are some and, indeed in extreme cases, tremendous, solid-state effects, these can be identified because of the known structure in the solid state. Another

---

[1] In the case of degenerate components, several irreducible representations would result upon reducing the direct product, but only one of them needs to transform as A_{1g}.