

Malachite Green/Polyphosphate Gel Hybrid Materials: Synthesis and Optical Properties

J. Del Nero¹, J.A.P. Silva², S.B.C. Silva², A. Galembeck^{2*}

¹Departamento de Física, ²Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50670-901 Recife, Pernambuco, Brazil

Abstract

In this work we describe the synthesis of a new supramolecular hybrid material based on the incorporation of the dye malachite green in an aluminum polyphosphate gel network and theoretical calculations on the optical properties of the organic guest molecule based in semi-empirical (PM3, PM5 and INDO/S-CI) methods. The dye is incorporated in its unprotonated form within the host matrix, leading to greenish-blue transparent free-standing films. The optical properties of the entrapped dye are sensitive to chemical changes within the matrix caused either by gel aging or an external stimulus such as exposition to ammonia vapors that can percolate through the gel.

Keywords: Sol-gel methods, Hybrid materials, Semi-empirical models and model calculations, UV-Vis-NIR absorption.

1. Introduction

The association of inorganic and organic compounds to develop new hybrid materials is an important and expanding area in materials research. Silica-based networks are most widely used as the inorganic fraction, either as a host structure or covalently bonded to organic polymers.

Also interesting are polyphosphate-based materials, which can be synthesized in a broad range of morphologies and compositions with synthesis/processing features that make them attractive as hosts to new hybrid materials [1].

Polyphosphate gels, for example, are supramolecular ionic swollen networks formed by polyphosphate polyanions and Al³⁺ cations association. Hence, the system cohesion is due to electrostatic interactions rather than the covalent bonding that results from alkoxide hydrolysis/condensation reactions.

In this work, we report the incorporation of the dye malachite green (MG) in an aluminum polyphosphate (APP) gel network leading to MG/APP hybrid materials. We also performed semi-empirical calculations on the electronic structure and spectroscopic properties of MG.

2. Methodology

The MG/APP hybrid composites were prepared in a similar way we described for the incorporation of terbium cryptate within the polyphosphate gel, starting from sodium polyphosphate (NaPP) and aluminum nitrate aqueous solutions [2]. A MG chloride salt aqueous solution (0,5%) was added to the polyphosphate solution.

Transparent greenish-blue samples form after 1 to 3 days. Free-standing films were prepared spreading the gel samples on a flat surface and letting them dry at room temperature in a moisture-controlled environment (50% relative humidity) for one week. The samples were characterized by absorption spectra (UV-vis-NIR Perkin-Elmer LAMBDA 6 spectrophotometer) within the 200–800 nm range.

Theoretical calculations were performed for MG⁺ (basic form) and MG_H²⁺ (acidic form). The geometries were optimized using the Parametric Methods 3 and 5 (PM3, PM5), which were carried out with the MOPAC and CaChe programs, respectively. The absorption spectrum of each molecule was calculated using the INDO/S-CI, with parameters chosen to give the best description of the UV-visible optical transitions [3–5]. Approximately 150 to 200 configurations were investigated for each molecule, including singlet and doublet states. We have taken into account from the first 9-UMOs (Unoccupied Molecular Orbitals) to the last 9-OMOs (Occupied Molecular Orbitals).

3. Results and Discussion

The MG/APP samples are transparent. The greenish-blue color resembles to unprotonated MG aqueous solutions. The dye incorporation within the polyphosphate matrix was confirmed by absorption spectra, presented in Fig. 1b. The spectrum of the APP gel, which is colorless and highly transparent, is also shown for comparison.

* Corresponding author: andre@npd.ufpe.br Fax: 55-81-3271 8442

Fig. 1b also presents a comparison between a MG/APP film and a MG/NaPP aqueous solution. The dye absorption band centered at 619 nm in the solution shifted to 642 nm upon incorporation within the gel. This effect may arise from the host-guest interactions between MG^+ and PP polyanions.

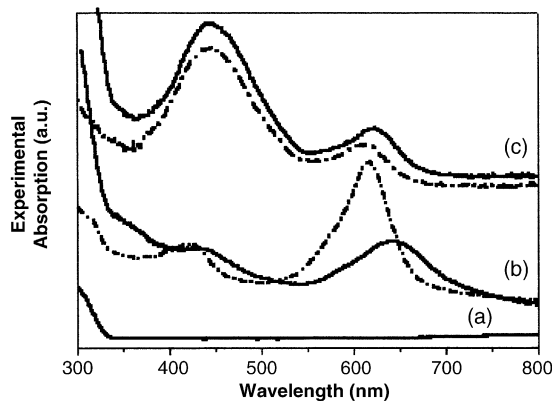


Fig. 1. Absorption spectra. (a) PP gel; (b, solid) MG/PP; (b, dashed) MG/NaPP aqueous solution; (c, solid) MG/PP gel aged for 9 days; (c, dashed) NaPP/MG aqueous acidic solution at $\text{pH} = 1,5$.

Upon gel drying, the sample turned spontaneously to green, which may arise from MG protonation in highly acidic medium. Fig. 1c presents a MG/APP sample aged for 9 days and a NaPP/MG solution to which a 3,0 M HCl solution was added.

Therefore, the dye is sensitive to the water amount in these samples. As water evaporates, the pH of the aqueous phase within the matrix decreases and the dye is protonated, leading to the observed color change.

When the aged samples were exposed to NH_3 vapors a greenish-blue color developed and the spectrum is similar to that presented in Fig 1b.

Hence, the optical response given by the guest dye may result from two reasons: (i) water evaporation and; (ii) a response to external stimuli, in this case hydrophilic vapors percolation on the sample. A similar behavior was observed for methyl orange/APP composites [6].

Theoretical calculations were performed using the INDO/S-CI approach to simulate the absorption spectrum of the MG^+ and MG_H^{2+} molecules (Fig. 2) under different conditions with fully optimized geometries. The interpretation of the main calculated transitions is presented in Table 1. The PM3 and PM5 calculations resulted in very similar values and we will present only the results for PM5. The most important optical transitions in MG_H^{2+} and MG^+ appeared at 402.3 nm and 446.6 nm, respectively. They are essentially HOMO to LUMO transitions ($|H\rangle \rightarrow |L\rangle$). The calculated spectra agreed well with the experimental data in a qualitative basis.

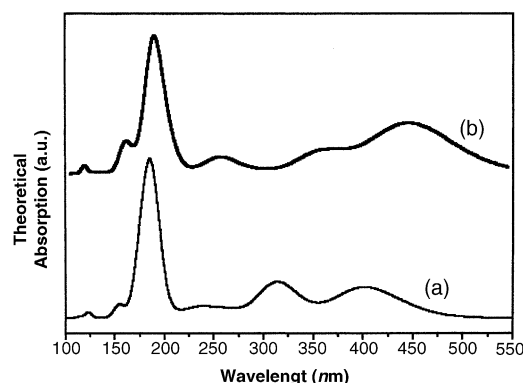


Fig. 2. Theoretical UV-vis spectra for (a) MG_H^{2+} and (b) MG^+ molecules by INDO/S-CI (absorption spectra) using the semi-empirical method calculated for optimized geometries.

Table 1. Main electronic UV-vis absorption transitions as determined from INDO/S-CI calculations based on optimized ground-state. (o.s. and nm means oscillator strength and Wavelength, respectively.)

Molecule	nm	o.s.	Absorption
MG_H^{2+}	402.3	0.67	0.67 $ H\rangle \rightarrow L\rangle$
	314.8	0.74	0.66 $ H-2\rangle \rightarrow L\rangle$
	190.3	0.67	-0.34 $ H-1\rangle \rightarrow L+5\rangle$
			-0.35 $ H-5\rangle \rightarrow L+2\rangle$
	186.0	1.07	-0.34 $ H-3\rangle \rightarrow L+2\rangle$
MG^+			0.34 $ H-5\rangle \rightarrow L+1\rangle$
	446.6	1.07	0.69 $ H\rangle \rightarrow L\rangle$
	359.7	0.48	-0.63 $ H-1\rangle \rightarrow L\rangle$
	264.6	0.14	-0.35 $ H-4\rangle \rightarrow L\rangle$
	188.4	0.86	-0.35 $ H-3\rangle \rightarrow L+2\rangle$
		0.37 $ H-2\rangle \rightarrow L+2\rangle$	

To sum up, the MG/PP gels are hybrid composites in which a disordered supramolecular ionic architecture formed by the PP gel network provides a chemical environment suitable for the incorporation of optically active species. The guest molecule could be protonated and deprotonated by changing the chemical environment provided by the gel matrix, which caused an optical response by the samples.

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