**pH and concentration effect on the optical absorption properties of Sn(V) tetrakis (4-pirydyl) porphyrin functionalized graphene oxide.**

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**Abstract.** The graphene oxide functionalized Sn(V) tetrakis (4-pirydyl) porphyrin [SnTPyP²⁺] nanostructure, was prepared by simple method with multiple GO concentrations and different acidity levels. The vibrational properties were investigated by means of Raman scattering and FT- Infrared spectroscopies, and showed that electronic interactions take place at the interface. At a structural level the X-Ray Diffraction [XRD] analysis revealed the effect of the SnTPyP²⁺ on the GO sheets interSpacing. The optical absorption was studied for many pH values and GO concentrations, and led to confirming the existence of strong interaction between both components of the composite GO-SnTPyP²⁺. The resulting GO-SnTPyP²⁺ was proved to be pH-sensitive in the absorption of photons, and hence lead to choose the best composite for efficient electron/energy transfer between GO and the porphyrin, and affords improved optical nonlinearities compared to those of the GO and the pristine porphyrin.

**1. Introduction**

Graphene, a single atomic layer of sp²-bonded carbon atoms arranged in a honeycomb lattice [1], exhibits remarkable electronic, thermal and mechanical properties [2]. A variety of applications have been demonstrated for graphene materials, such as structural nanocomposites [3-5], catalyst supports, electronic devices, and energy storage in batteries and supercapacitors [6]. One of the most promising methods for large scale production of graphene is by chemical oxidation exfoliation of graphite leading to graphene oxide (GO)[7], which can subsequently be reduced to graphene. GO has generated significant interest due to its ability to form stable colloids in water and other solvents as well as in different matrices due to the presence of carboxylic and hydroxyl groups[8, 9]. Furthermore, graphene’s strong interactions with photons and electrons, and chemical functionalization ability could add more functions to photoactive composites[10, 11].
Porphyrids have features that allow molecular and π-conjugated surfaces to gather in the form of the tetrapyrrole macrocycles. Porphyrids are very attractive molecules in many aspects. The first reason is related to their unique spectroscopic properties both in absorption and emission. Porphyrids and related tetrapyroles have been extensively studied because of their importance in biological processes and they are often used in the development of artificial light-harvesting, energy conversion[12, 13]. They are also interesting from a fundamental point of view, as systems to study the nature and dynamics of excited states in molecular assemblies of reduced dimensionality, as well as models for understanding the photophysics of natural light-harvesting complexes. The extraordinary optical properties of these molecular aggregates are to a large extent governed by exciton delocalization, transport, and relaxation phenomena[14]. To develop these properties, composites based on those structures show their potentials for optical and optoelectronic applications by the association of porphyrin properties to carbon nanotubes, polymers and other molecular materials [15-17].

Another interesting aspect is the functionalization of few layers of GO with Sn(IV) tetrakis(4-pyridyl) porphyrin dichloride (SnTPyP2+), by van der Waals and/or electrostatic forces. Previous reports have demonstrated that GO has the excellent and tunable hydrophilicity. However, few reports have focused in detail on the influences of particle size and pH value on the hydrophilicity of GO. Herein, we investigate the impacts of pH value on the GO- SnTPyP2+ composites.

In this paper, we studied the vibrational and structural variations that affect the composite, and also the effect of pH on the absorption properties of graphene oxide (GO) when incorporated into SnTPyP2+. X-ray diffraction, FTIR, Raman spectroscopy and optical absorption were used in order to investigate the structural and electronic properties of this system for optoelectronic applications.

2. Materials setup

Using Hummer's method we succeeded to obtain Graphene oxide from graphite [18]. The GO solution was prepared using (K\text{MnO}_2H_2\text{SO}_4), and then the precipitate was washed many times with deionized water. After obtaining a grey solution of GO, we prepared many pH concentrations of the solution, starting from an acidic level of 2 rising up to 10, and then added to already prepared SnTPyP2+ solutions. For optical characterization we prepared also different concentrations of the GO sample. The final GO solutions were diluted and sonicated for a major exfoliation of the oxidized sheets. The solutions were then submitted to a dropcasting and drying process to obtain homogeneous films.

3. Characterization

Raman spectra were obtained using a Bruker spectrometer SENTERRA Raman Stokes and spectral range of 90-3200 cm\(^{-1}\) with an excitation wavelength \(\lambda = 514\) nm and for our samples the laser power is adjusted to a low power 10 mW. FTIR spectra were recorded at room temperature in the transmittance mode using a Vertex 70 spectrophotometer, with a resolution of 4 cm\(^{-1}\) over a wavenumber range of 400-4000 cm\(^{-1}\). UV–Vis spectra were measured on a PerkinElmer LAMBDA950/1050 UV/VIS/NIR; spectrophotometers are dual-beam; dual-monochromator instruments equipped with an optional 150 mm integrating sphere accessory.

Time-resolved photoluminescence (TR-PL) experiments were acquired with a regenerative amplified femtosecond Ti: Sapphire laser system (Spectra Physics Hurricane X). This setup generates 100 fs pulses at 800 nm with a repetitive rate of 1 kHz and a power of 1 W. The laser line is frequency-doubled (tripled) with thin BBO crystals to obtain an excitation line \(\lambda_{exc}= 400\) nm (3.1 eV). The pump energy pulse is controlled to ensure that the excitation density in the sample did not exceed 10 17cm\(^3\), to avoid bimolecular annihilation process and sample photodegradation. The emission is temporally resolved with a high dynamic range Hamamatsu C7700 streak camera coupled to an imaging
spectrograph with a temporal resolution to be estimated 20 ps and processed using the HPDTA Hamamatsu software.

4. Results & discussion

4.1 Raman measurement

Raman spectroscopy is a non-destructive technique that is widely used to obtain structural information of nanocarbons. In Figure 1 the Raman spectrum of GO presents a D-band at 1352 cm\(^{-1}\) associated to defects and disorders in carbon nanostructure. The G-band appearing at 1588 cm\(^{-1}\) arises from the E\(_{2g}\) phonon modes of graphite in the \(\Gamma\)-point and it is originating from the stretching of the C-C bond in graphitic materials, and is common to all sp\(^2\) carbon systems [19, 20]. Meanwhile, the D peak which is also present due to the breathing mode of aromatic rings, which comes from the structural imperfections created by the attachment of oxygenated groups on the carbon basal plane. Therefore, the D-peak intensity is often used as a measure for the degree of disorder [21-23].

![Raman spectra of GO, SnTPyP\(^{2+}\) and GO–SnTPyP\(^{2+}\)](image_url)

**Figure 1.** Raman spectra of GO, SnTPyP\(^{2+}\) and GO–SnTPyP\(^{2+}\). The functionalized GO with various porphyrins results in small changes in the D, G and 2D peaks. When the Raman spectra of GO–SnTPyP\(^{2+}\) are compared with that of GO, subtle rather than drastic changes were observed. The G-band up shifted from 1588 to 1595 cm\(^{-1}\), which might be caused by the increasing number of layers in their solid states. As porphyrins are covalently linked to GO, they can absorb on both sides of the graphene sheets. Moreover the 2D band intensity decreases when compared with that of GO. Generally, the integrated intensity ratio of the D and G-bands (ID/IG) indicates the oxidation degree and the size of sp\(^2\) ring clusters in a sp3/sp2 hybrid network of carbon.
Moreover, the intensity ratio of D/G bands increased from 0.91 for GO to 0.96 for GO-SnTPyP²⁺. These changes indicate the presence of π-π interaction between the GO and SnTPyP²⁺.

4.2 FT Infrared measurements

FT-IR spectroscopy is recognized as an important tool to study different types of functional groups. In Figure 2, the FT-IR spectra of GO, SnTPyP²⁺ and GO-SnTPyP²⁺ composite are exhibited. In the GO spectrum, we note firstly, the peak at 1408 cm⁻¹ is assigned to the C=O vibrational mode. Secondly, the band centered at 1616 cm⁻¹ is attributed to aromatic C=C bonds. Another peak at 1715 cm⁻¹ corresponds to the vibrational mode of the ketone groups C=O. Finally, the peak at 3200 cm⁻¹ denotes C‒OH stretching [25, 26].

![FTIR spectra of GO, SnTPyP²⁺, and GO-SnTPyP²⁺](image)

**Figure 2:** FTIR spectra of GO, SnTPyP²⁺, and GO-SnTPyP²⁺

For SnTPyP²⁺ we note the presence of a broad intense band centered at 3400 cm⁻¹ which is attributed to the N-H bond stretching, and the band situated at 2914 cm⁻¹ is related to stretching vibration of aromatic C-H bonds. In addition, a band was observed at around 1629 cm⁻¹ corresponding to the stretching bond in the phenyl nuclei. Moreover, the band at 1540 cm⁻¹ is attributed to Cβ-Cβ' stretching which may be due to symmetrical deformation of the pyrrole rings and the bending strain Cα-N-Cα'. The band at 1415 cm⁻¹ is attributed to the symmetric stretching Cα-N-Cα' and the Cβ-Cβ' bond stretching in pyrrole nuclei, there is also a band which appears at 1318 cm⁻¹ corresponding to the asymmetric HN-Cα-Cβ stretching bond. The bands at 1261 cm⁻¹ and 1298 cm⁻¹ are assigned to the asymmetric Cα-N-Cα' stretching [27, 28]. In GO-SnTPyP²⁺ we find that the intensities of these bands change significantly. Moreover, the vanishing of the band at 1408 cm⁻¹ indicates a strong interaction between GO and SnTPyP²⁺ which can be explained by covalent functionalization in GO-SnTPyP²⁺[29].
4.3 X-ray diffraction

Figure 3 shows the XRD patterns of GO, SnTPyP$^{2+}$, and GO-SnTPyP$^{2+}$. GO spectrum exhibits an intense and strong peak at $2\theta = 11.10^\circ$ which is attributed to the (001) lattice spacing of 0.78 nm due to the interlamellar water trapped between the hydrophilic graphene oxide layers [30-33]. For SnTPyP$^{2+}$ the XRD patterns shows a peak at $2\theta = 8.8^\circ$ attributed to the (001) diffraction plan and another peak at $2\theta = 43.75^\circ$ attributed to the (701) [34, 35]. The GO-SnTPyP$^{2+}$ composite pattern shows the characteristic peak (001) of the GO shifted to $2\theta = 10.60^\circ$ ($d$-spacing = 0.881 nm). In addition, the intensity of all diffraction peaks corresponding GO decreased after the interaction with the SnTPyP$^{2+}$, this behavior can be explained by the increase of the inter-planar distance (001) due to the effect of SnTPyP$^{2+}$ trapped by GO sheets.

![Figure 3. XRD of GO, SnTPyP$^{2+}$, and GO-SnTPyP$^{2+}$](image)

4.4 UV-Visible Absorption

UV-Vis absorption spectra of the different samples are shown in Figure 4. The absorption of GO, Figure 4(b), exhibit two peaks centered at 230 and 300 nm are observed for the GO dispersion, corresponding to the $\pi$-$\pi^*$ transition of aromatic C=C bonds and the n-$\pi^*$ transition of the C=O bond, respectively [8, 36]. we note a widening of the band characteristic of GO situated at 230 nm and broad band at 308 nm when going from concentration 0.1% to 1% and 2% and also we can observe an increasing in the intensity. This intensity changing and widening of the bands associated with the increase in concentration can be understood in terms of the increase in the size of the graphene layer. In figure 4(a), we show the variations occurring at the absorption spectrum when changing the pH values of GO. The nature of the carboxylic, hydroxyl and epoxy group of GO also changes, causing a different degree of passivation of the GO surface. For pH$\leq$4, the GO is fully protonated, and at pH$>$4, the anchored–COOH groups become deprotonated such that the intensity decreases significantly
The broad peak absorbance situated at 304 nm decreased with increasing pH explained the effect of solvent and the NaOH or HCl concentration.

**Figure 4.** Optical absorption of GO, and GO- SnTPyP²⁺; (a) and (c): pH effect; (b) and (d): concentration effect

The UV-Visible absorption spectrum of SnTPyP²⁺, Figure 4(c), consists of two distinct regions. In the violet region, an extremely intense absorption known as the Soret or B band situated at 416 nm in the visible region, a number of absorptions known as the Q bands are present, two major absorption bands situated at 554 nm and 591 nm attributed Q(0.0) and Q(1.0) respectively. The lower energy band, Q(0,0), is attributed to excitation to the first excited state. The higher energy band, Q(1,0), is a result
of vibrational transitions interacting with the electronic transitions of the porphyrin, and has been
to as a vibronic overtone of the Q(0,0) band. The Soret band is attributed to excitation to the
second excited state, and in well resolved spectra a vibronic overtone, B(1,0). Both of these transitions
are π−π* transitions that involve electron redistribution within the conjugated π systems of the
porphyrin rings.[41]

The interactions between GO and SnTPyP2+ in such a system are mainly electrostatic in origin, and
energy is transferred non-radiative from the excited state of one molecule to the next by a long range
dipole-dipole coupling mechanism. The energy of the exciton state in a porphyrin is dependent on
whether the dipole interaction is attractive or repulsive, and an exciton state is only allowed if the
dipoles are in-phase. Moreover, two mechanisms for energy transfer are generally anticipated to
operate in the singlet states; Dexter and Förster. The former mechanism involves a double electron
exchange between the donor in its singlet excited state and the acceptor in its ground state (LUMO
donor* →LUMO (acceptor) and HOMO (donor*)—HOMO(acceptor)) and consequently strongly
depends on the degree of orbital overlap between the donor and acceptor.

After SnTPyP2+ was incorporated with the GO at different pH values, we note a widening of the band
characteristic of GO when going from pH2 to pH10 increasingly moving spikes to low energies. This
redshifted with the increase in pH can be understood in terms of the restored electronic conjugation
pulling the highest occupied molecular orbital and lowest unoccupied molecular orbital. Moreover,
GO-SnTPyP2+ we observe a change in the intensity in the composite when passing from PH2 to PH10 can
be explained the intramolecular donor-acceptor structure usually allows charge-transfer interaction
or the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO)
transitions to occur. Moreover, in the visible region the band around to 380 nm of SnTPyP2+
disappeared in composite GO-SnTPyP2+ and the redshift B-band when going from pH2 to pH10 can be
explained by decrease in oxygen functional groups and an increase in aromatic rings, causing electrons
to be easily excited at a lower energy.

These results prove interaction between the electron and the hole is strong and the excitons tend to be
localized almost exclusively on porphyrin. The efficiency of this energy transfer is inversely
proportional to the sixth power of the distance between donor and acceptor. So, the energy transfer
rate depends on the strengths of the electronic transitions for donor and acceptor molecules, and
requires resonance between donor fluorescence and acceptor absorption. Energy transfer between GO
and SnTPyP2+ is known as heterogeneous transfer, unlike the homogeneous transfer that occurs
between identical molecules. Direct evidence of energy transfer between different composite (GO and
SnTPyP2+) is provided by optical absorption.

4.5 Photoluminescence measurements

In this study, the excitation wavelength is 420 nm, in order to be closer to the resonance of the
porphyrin molecules. We would then see if excitation resonant with transitions of the molecule allows
the same photostability of deposit. Figure 5 shows the steady-state photoluminescence spectra of GO,
SnTPyP2+ and GO-SnTPyP2+.
These samples are obtained very simply by leaving a drop of solution to dry. We acquired a PL spectrum at regular intervals. Note after inserting GO in SnTPyP\(^{2+}\) the intensity undergoes a decrease. In addition, the acquired spectrum of GO-SnTPyP\(^{2+}\) composite has a low red shift and a slight narrowing relative to SnTPyP\(^{2+}\) spectrum. The discrepancy is probably due to the change in the electronic structure of the composite, which shows that there is an interaction between GO and SnTPyP\(^{2+}\) always gives rise to energy/charge transfer. Subsequently, the band around 590 nm characteristic of SnTPyP\(^{2+}\) becomes clearer in the GO-SnTPyP\(^{2+}\) composite. This illustrates the fact that the transfer involves quenching the luminescence of the porphyrin and the higher the luminescence of the donor is attenuated and the transfer is efficient. It is found that the extinction of the porphyrin is very important when it is in the presence of the GO. It shows a resonance at 580 nm corresponding to the S22 transition and provide evidence of a transfer of energy/charge of the molecule to the graphene oxide.

**Conclusion**

In this work we have synthesized graphene oxide-SnTPyP\(^{2+}\) composite and studied the effect of concentration and pH on different optostructural properties. We demonstrated that the pH value is strongly related to the photon absorption in the composites. Vibrational and structural studies revealed that the composites we synthesized, present strong interaction between its components attributed to \(\pi-\pi\) interaction. The GO can thus serve as efficient electron acceptors, which opens the way to construct novel complexes with optimized pH and concentrations, with various types of porphyrins-graphene derivatives and other carbon nanomaterials.
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