5-(4-PYRIDYL)DIPYRROMETHANEE-SILICA SOL SYNTHESIS AND LUMINESCENT PROPERTIES

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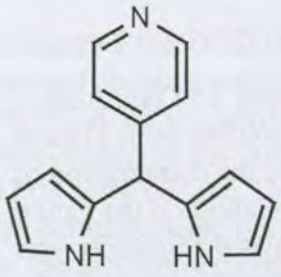
ABSTRACT

Methodologies for the immobilization and characterization of *5*(4-pyridyl)dipyrromethane into silica gel are described. The corresponding spectroscopic, thermal, and photochemical properties are used for their characterization and study.

INTRODUCTION

Nano-and micro-materials, based on pyrrole derivatives received great attention because of their optoelectronic properties, with extended applications from photosensing materials, catalysts, sensors for heavy metals [1], and biochemical agents [2] detection and recovery and gas sensors. In order to obtain new nanomaterials, various synthesis route of sol-gel methods are performed to improve dimension of pores, using different silica precursors mixtures, but also different types of organic compounds are used to be embeded in these hybrids. Based on our previously reported results [3, 4] Due to the great importance of sustainable chemistry in EU countryes, studies concerning the toxicity of these materials were also developed [5]. The aims of the initial study were to obtain hybrid porphyrin - materials with tailored dimension pores [6] and exhibiting intense red-absorption in Uv-vis and emmision spectra. The present experiment takes into consideration the use of an dipyrro compound for synthesis of porphyrins, namely *5*(4-pyridyl)dipyrromethane (PPM), to see the fluorescence properties it introduced. *5*(4-pyridyl)dipyrromethane, represent a valuable intermediate for the synthesis of asymmetrical trans A_2B_2 porphyrins, bearing pyridyl functional rings. The structure of *5*(4-pyridyl)dipyrromethane is represented on figure from the left.



MATERIALS and METHODS

Methyltriethoxysilane (MeTEOS) ≥ 98% from Fluka, Tetraetoxysilane (TEOS) ≥ 99% from Merk, Tetrametoxysilane (TMOS) 99% from Acros Organics, Tetrahydrofuran (THF) 99,8% and Sodium Fluoride 99% from Scharlau, Clorhidric Acid 37% from Silal Tradings. ***Apparatus*** *^{1}H-NMR* spectra were registered on a 400 MHz Bruker spectrometer, in DMSO. The chemical shifts are expressed in δ (ppm). A Bruker esquire HCT series mass spectrometer with Atmospheric Pressure Interface-ElectroSpray Ionization was used for registering MS. *Thermal analysis* experiments were carried on a Mettler-Toledo Intrument. Samples were heated from 25 to 800 °C in a 10 °Cmin^{-1} rate under air atmosphere. *IR spectra* (4000–400 cm^{-1}) were collected on a JASCO 430 FT-IR spectrophotometer using pellets with samples dispersed in KBr. *The photoemission and photoexcitation spectra* were recorded with a Perkin Elmer LS55 luminescence spectrometer, by using a special holder for powdered solid samples. The luminescence spectra were recorded with constant slit widths, for excitation (2,5 nm) and for emission (5 nm). Excitation spectra were recorded by monitoring the red emission wavelength 656 nm, corresponding to maxima intensities. Emission spectra were obtained using 420 nm excitation wavelength corresponding to maximum emission intensity

for each samples. In order to eliminate harmonic or scattering peaks a 505 nm cut-off filter to. ***Method for synthesis of 5(4-pyridyl)dipyrromethane*** named also as 4-(di-pyrrol-2-yl-methyl) pyridine was synthesized after previously reported literature data [7] by stirring for 12 h around 85°C a mixture of 4-pyridinecarboxaldehyde (1.9 mL, 20 mmol) and pyrrole (30 mL, 420 mmol). The product was evaporated to dryness, separated by column chromatography on alumina gel using hexane:ethyl acetate, 1:1. The yield was 42%. ***5(4-pyridyl)dipyrromethane***: ^{1}H-NMR (400 MHz, DMSO), δ (ppm): 10.58 (s, 2H, *NH*-pyrrole); 8.26 (m, 2H, 2,6-Pyridyl); 7.10(m, 2H, 3-5-Pyridyl); 6.60 (m, 2H, pyrrole); 5.93 (m, 2H, pyrrole); 5.68 (m, 2H, pyrrole); 5.29 (s, 1H); MS (ESI$^+$): m/z=223.11 M]$^{+\cdot}$ $(C_{14}H_{13}N_3]^{+\cdot}$ molecular ion. ***Method for sol-gel synthesis*** Two step acid catalysed hydrolysis of different type of precursors (TEOS, TMOS or MeTEOS in different molar ratios with TEOS), water, ethanol (EtOH) and 37% hydrochloric acid (HCl) with a silica precursor:H_2O:EtOH:HCl of 1.0:3.7:2.9:1.2 × 10^{-4} mole ratios, were employed to prepare acid catalyzed silica precursors solution. After one hour of hydrolysis of the silca sprecursors, a solution consisting in PPM dissolved in THF, corresponding to 3.48 * 10^{-5} mole of PPM/ 1 mole silica precursors was added. Finally, for the second step of catalysis, 1.5 mmol of natrium fluoride was added The synthesis parameters and gelation time of samples are presented in table 1.

Table 1. Synthesis parameters of samples and gelation time

Sample	Precursors	Gelation time (min)
1	TEOS	Instant
2	TMOS	Instant
3	MeTEOS/TEOS 1:3	2
4	MeTEOS/TEOS 1:2	5
5	MeTEOS/TEOS 1:1	7

RESULTS

The fluorescence emission spectra of all samples, present a maximum around 656 nm. Also, it can be observed a weak maximum, peaking around 720 nm. As can be noticed from Figures 1, the shape and positions of emission bands remain unchanged regardless the composition of sols. Instead, it could be observed changes in the emission intensities depending on the nature of silica precursors or mole ratio of precursors mixture. The highest emission intensity was obtained in the case of sample obtained from methyltriethoxysilane, as silica precursor. In the case of precursors mixture the better result was observed in the case of sample 5, synthesized from MeTEOS/TEOS in the 1:1 mole ratio.

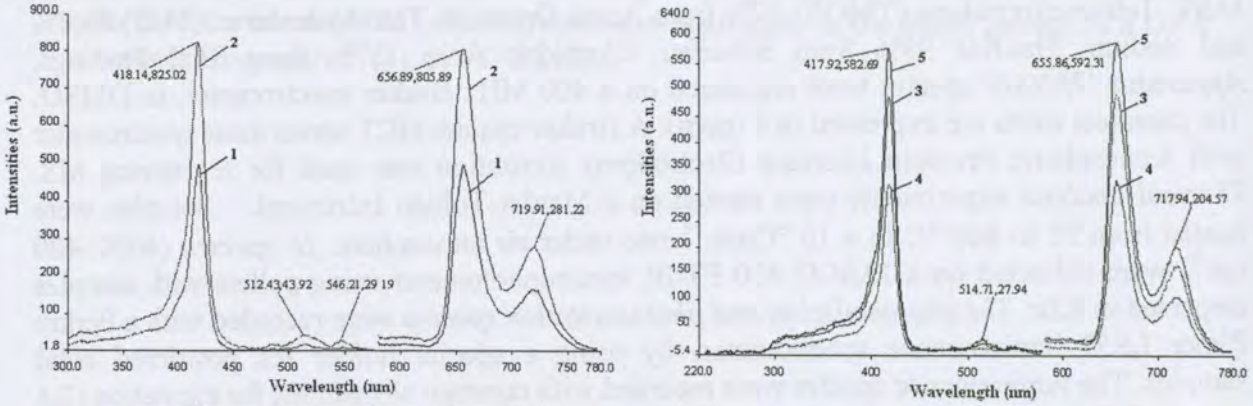


Figure 1. Overlapped emission spectra of synthesized sol samples

Figure 2 shows the IR spectra of samples 1 and 5 after drying at 105 °C. The peak at 460cm^{-1} is due to the deformation of Si–O–Si, bending modes of silicon dioxide. The signal centered at 800cm^{-1} is the typical peak of Si–O–Si vibrational mode and the 960cm^{-1} comes from the Si–OH stretching. Sample 5 shows a relatively weaker peak at 960cm^{-1} than sample 1, suggesting less hydroxylated silica existing in sample 5. The band at 1090–1200cm^{-1} was attributed to Si–O–Si skeletal vibration. The peak at 1630cm^{-1} should correspond to the vibration of water, where peak intensity of sample 1 is stronger than that of sample 5, showing the hydrophobic feature of sample 5. A broad band is observed at 3400–3500cm^{-1} due to the absorbed molecular water, where the difference in peak intensity for samples 1 and 5 is another indication of the more hydrophobic feature of sample 5 [8]. In conclusion the introduction of the methyl groups on the silica network offers a more hydrophobic profile to the silica xerogels.

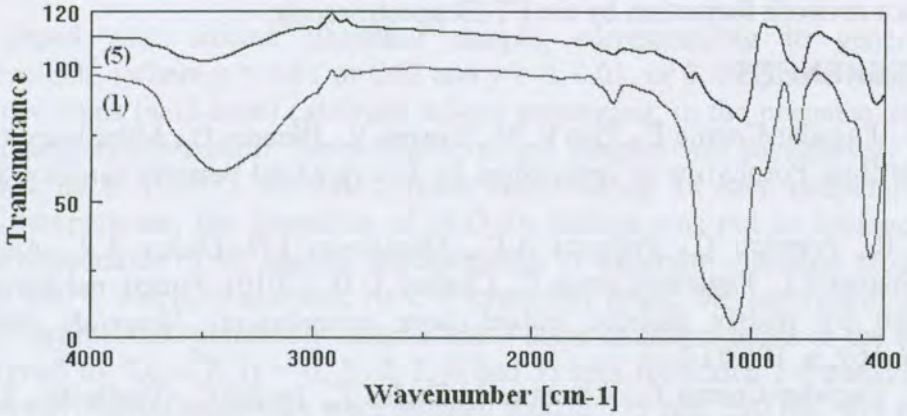


Figure 2. Comparation of the FT-IR spectra of the sample 1 and 5

In figure 3 the TG/DTG/DTA curves of the dried sample 5 are presented. The TG curve of the xerogel shows a weight loss up to 150 °C which corresponds to a broad endothermic peak in the DTA curve, attributed to the physically adsorbed water on the silica surface and the evaporation of the volatile solvents [9]. In this range of temperature the main weight loss, of 17.03 wt% occurs. The total weight loss is corresponding to 23.24 wt%. In the 150-500 °C temperature range only a small weight loss is observed without any effect on the DTA curve. In the last temperature region the weight loss is accompanied by a sharp exothermic peak in the DTA curve at the same temperature is due to the oxidation of the methyl groups responsible for the xerogel hydrophobicity [10].

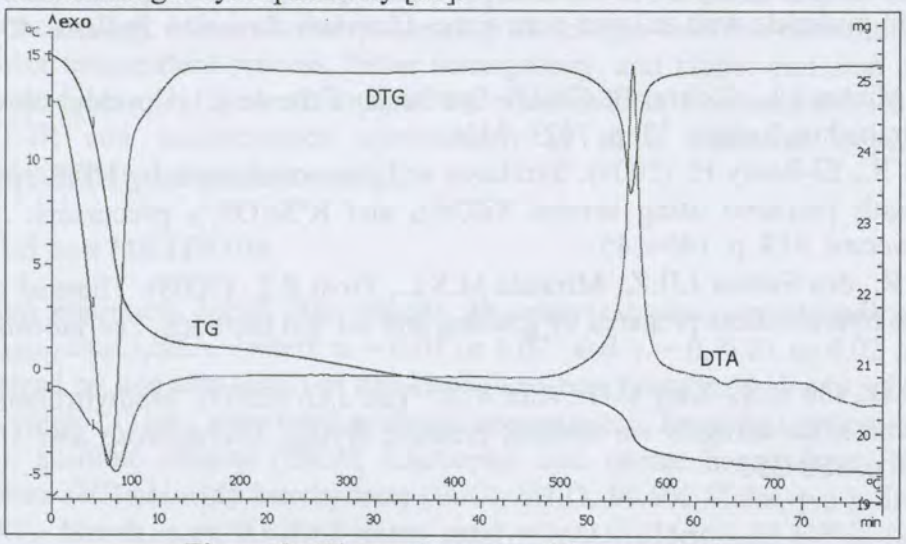


Figure 3. Thermal curves of the sample 5

CONCLUSIONS

- Novel nanocomposite with *5*(4-pyridyl)dipyrromethane embedded silica gel has been synthesized by two step catalyzed sol-gel process .
- Sol-gel immobilized PyPM nanocomposites photuluminescent properties were investigated in order to obtain high luminescent emission.
- Al synthesized samples presented luminescent emission in red domain of spectra with maxima at 656 nm and 720 nm. The highest emission intensity was obtained in the case of sample synthesized from methyltriethoxysilane, as silica precursor.
- Utilization of MeTEOS and TEOS precursor mixture better luminescent emission was observed in the case of sample prepared at MeTEOS/TEOS mole ratio of 1:1
- The thermal stability of the obtained xerogels was analyzed by thermal analysis and the silica network formation by the FT-IR spectroscopy.

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