

## MATERIALS BASED ON URANYL ION AND THEIR POTENTIAL FOR SOLAR ENERGY CONVERSION CELLS.

**Maria Claudia F.C. Felinto<sup>1</sup>, Luiz Felipe M. Maceta<sup>1</sup>, José Eduardo M. Sá Luiz<sup>1</sup>,  
Hermi F. Brito<sup>2</sup>, Ercules E. S. Teotonio<sup>2</sup>, Duclerc. F. Parra<sup>1</sup>**

<sup>1</sup> Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)  
Av. Professor Lineu Prestes 2242  
05508-000 São Paulo, SP  
mfelinto@ipen.br

<sup>2</sup> Instituto de Química da Universidade de São Paulo (IQ/ USP - SP)  
Av. Professor Lineu Prestes 748  
05508-000 São Paulo, SP  
hefbrito@iq.usp.br

### ABSTRACT

In this work it is described synthesis, characterization and spectroscopic study of the supermolecules of  $\text{UO}_2^{2+}$  and octaacetatecalix[8]arene. The compounds obtained were characterized by complexation analyses for determine  $\text{U}^{6+}$  concentration, infrared spectra and luminescence spectra. The results agree with the following composition  $\text{UO}_2(\text{MS})_2 \subset \text{octaacetatecalix[8]arene}$  and  $\text{UO}_2(\text{TCA})_2 \subset \text{octaacetatecalix[8]arene}$  (where MS is methanesulfonate and TCA is trichloroacetate). The IR analyses show coordination of counter ion and the inclusion on the calixarene cavity. The life time behavior as a first order exponential decay for  $\text{UO}_2(\text{TCA})_2 \cdot (\text{H}_2\text{O}) \subset \text{octaacetatecalix[8]arene}$  and  $\text{UO}_2(\text{MS})_2 \cdot (\text{H}_2\text{O}) \subset \text{octaacetatecalix[8]arene}$

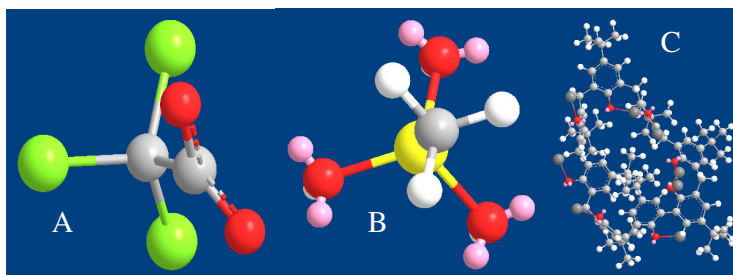
### 1. INTRODUCTION

The search for renewable sources of energy has led to an increasing interest in photochemical cells because of their possible role as transducers of solar to electrical energy. The photoeffects in electrochemical systems were first observed by Becquerel<sup>[1]</sup> in his investigation on the solar illumination on metal electrodes in 1839. Later it was observed by Moser<sup>[2]</sup> and Rigollot<sup>[3]</sup> that the sensitivity of silver/silver halide and copper/copper oxide electrode could be increased by coating them with a dye stuff. Thompson<sup>[4]</sup> and Stora<sup>[5]</sup> reported that pure metal electrodes were also sensitive to light when coated with a dye or immersed in a dye solution. The result of the first 100 years had been reviewed by Copeland and co-workers<sup>[6]</sup>. A summary of the properties of photoelectrochemical (PEC) cells described in the literature up to 1965 was compiled by Kuwana<sup>[7]</sup> and later work has been reviewed by Archer<sup>[8]</sup>.

The uranyl ion possesses some properties which makes it a potential component for a solar energy conversion system. It absorbs light in the shorter wavelength range of the solar spectrum, producing a relatively long lived excited state. The excited state has fluorescence peaking at 520 nm, a property that makes it relatively convenient to investigate its reaction. The redox potential of the excited uranyl ion makes a powerful oxidizing agent. This may be of potential use in the photogeneration of oxygen, which is of great importance for the photocleavage of water<sup>[9,10]</sup>.

On the other hand, coordination chemistry of the simplest of calix[4]arene, is now relatively well developed as highlighted by a number of recent reviews<sup>[11]</sup>. The vast majority of these metalocalix[4]arene derivatives exist as either mono or binuclear complexes, retaining a cone-like conformation for the parent ligand. By contrast, metal compounds containing larger ring systems ( $n > 5$ ) are still quite rare despite the conformational variations offered by the increased flexibility of a large number of polyphenolic rings. An additional attractive feature of the latter is their ability to simultaneously coordinate more than one metal centre.

The uranyl compounds ( $\text{UO}_2^{2+}$ ) presents a great potential as luminescent materials, for instance, applied in technology laser, luminescent probes, cells for conversion of energy, etc. In this work it was studied two compounds of  $\text{UO}_2^{2+}$  based on calixarenes to be used as efficient Light Conversion Molecular Devices (LCMD) and/or in solar cells for energy conversion. In figure 1, it is showed molecular structure of ligands and octaacetatecalix[8]arene used in this work.



**Figure 1. Structures of the ligands trifluoroacetate, methanesulphonate and octaacetatecalix[8]arene.**

## 2. EXPERIMENTAL SECTION

The supermolecules were synthesized using precipitation method. Solutions of uranyl salts and ligand, octaacetatecalix[8]arene, in toluene and chloroform, were added one to another under constant stir for about 24 hours. This step was followed by evaporation of solvents and crystallization. The crystalline powders obtained were washed with acetone three times for purification. These compounds were characterized using the following techniques described below.

The carbon and hydrogen contents were determined by the usual microanalytical procedures using an elemental analyzer model CHN 2400 (Perkin-Elmer, USA) while the  $\text{UO}_2^{2+}$  content was obtained by spectrophotometric analyses using arsenazo III as chromophore; the infrared spectra of the samples were used to provide information about the nature of the coordination of MS and TCA ligands to  $\text{UO}_2^{2+}$  ion. These spectra were recorded in the range from 4000 to 400  $\text{cm}^{-1}$  in nujol emulsion by using a Bomem model MB102 FTIR spectrophotometer; thermogravimetric (TG) curves were performed with a SDTA-822 thermobalance (Mettler Toledo), using samples with approximately 10 mg in sapphire crucibles, under dynamic

nitrogen atmosphere ( $50\text{mL}\times\text{min}^{-1}$ ), at heating rate of  $10\text{ }^{\circ}\text{C}\times\text{min}^{-1}$ ; the excitation spectra of the complexes in the solid state were obtained in the spectral range of 250-450 nm by monitoring the intensity of the  ${}^3\Pi_u \rightarrow {}^1\Sigma_g+$  transitions at 514.5 and 542.4 nm for MS and TCA respectively, while the emission spectra were obtained in the range of 420 to 720 nm with excitation monitored at  ${}^3\Pi_u \rightarrow {}^1\Sigma_g+$  at 400 and 255 nm; the luminescence decay curve of the  ${}^3\Pi_u$  emitting level was measured using a phosphorimeter SPEX 1934D accessory coupled with the spectrofluorometer. These luminescence instruments were fully controlled by a DM3000F spectroscopic program and computer, and the spectral intensities were automatically corrected for the photomultiplier response.

### 3. RESULTS AND DISCUSSION

Percentage of uranium in the supermolecules was determined by spectrophotometric analyses using Arsenazo III (bis-2,7-[2-arsenobenzol-1-azo] as chromophore agent<sup>[12]</sup>. The carbon and hydrogen contents were determined by microanalytic procedures. The C, H and U percentages found/calculated for the supermolecules with the ligands are MS (C 61.73/ 61.18; H 6.55/ 6.71 and  $\text{U}^{6+}$  11.54/ 11.32) and TCA (C 59.86/ 58.36 H 6.5 /6.7 and  $\text{U}^{6+}$ 10.98/ 10.73). These data agree with the stoichiometries expected.

According to IR spectroscopy (figure not showed), the bands at  $\sim 3396\text{ cm}^{-1}$  confirms that precursor salts and supermolecules were isolated in the hydrated form. The dioxouranium compounds studied at this work exhibits  $\nu_{\text{as}}(\text{O}=\text{U}=\text{O})$  and  $\nu_{\text{s}}(\text{O}=\text{U}=\text{O})$  stretching vibrational modes at around  $\nu_{\text{as}}$  942 and  $872\text{ cm}^{-1}$  and  $\nu_{\text{s}}$  at  $784$  and  $817\text{ cm}^{-1}$  for MS supermolecule and  $\nu_{\text{as}}$   $931\text{ cm}^{-1}$  and  $\nu_{\text{s}}$  at  $848\text{ cm}^{-1}$  for TCA supermolecule, that commonly appear at  $\nu_{\text{as}}(\text{O}=\text{U}=\text{O}) = 870\text{-}950\text{ cm}^{-1}$  and  $\nu_{\text{s}}(\text{O}=\text{U}=\text{O}) = 780\text{-}885\text{ cm}^{-1}$  region<sup>[13]</sup>. It is not observed displacement of C=O stretching mode from  $\sim 1760\text{ cm}^{-1}$  in free octaacetatecalix[8]arene to the compounds, which is an evidence that no metal ion is coordinated through these oxygen atoms<sup>[14]</sup> and the missing of bands at  $751$ ,  $719$  and  $682\text{ cm}^{-1}$ , in the region of fingerprint of calixarenes, indicating that the interaction is via a very low intensity and attributed to a inclusion of the uranyl. The stretching vibrations of S=O group were found at  $\nu(\text{S}=\text{O}_{\text{ass}})$  ( $-1168\text{ cm}^{-1}$ ) and  $\nu(\text{S}=\text{O}_{\text{sim}})$  ( $-1043\text{ cm}^{-1}$ ) and the stretching vibration of TCA groups are  $\nu(\text{COO})$  ( $-1355\text{ cm}^{-1}$ )  $\delta(\text{OCO})$  ( $723$ ) and  $\nu(\text{C}=\text{O})$  ( $-1749\text{ cm}^{-1}$ ). In both spectra of MS, salt and supermolecule, stretching at  $\sim 3500\text{ cm}^{-1}$  and bending at  $1620\text{ cm}^{-1}$  are observed. This behaviors differ from that found for TCA compounds.

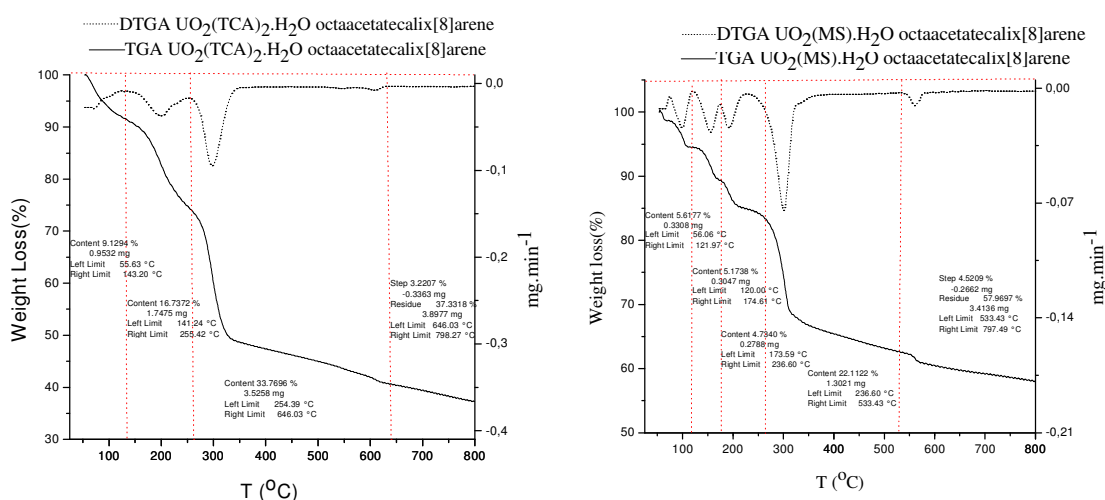
TGA curve in Fig 2 from TCA supermolecule showed one first event in the range of  $\sim 55$  to  $\sim 143\text{ }^{\circ}\text{C}$  with mass loss of 9.1 % corresponding to water molecules in the compound. In the range of  $\sim 143$  to  $\sim 255\text{ }^{\circ}\text{C}$  occurs water crystallization loss (16.7 %). A third event was observed in the interval of  $\sim 255\text{-}646\text{ }^{\circ}\text{C}$  (33.8%) and was attributed to decomposition of supermolecule phases and ligand formed in the precipitation reaction. Another event is observed in the range of  $\sim 646\text{-}798\text{ }^{\circ}\text{C}$  with mass loss of 37.3% attributed to crystalline reorganization.

The supermolecule base on methanesulphonate of uranyl ion, TG curves showed five events. First event presents loss of weight (5.6%) between  $\sim 56$  to  $\sim 121\text{ }^{\circ}\text{C}$  and was attributed to water molecules, the second one is between  $\sim 122\text{-}174\text{ }^{\circ}\text{C}$  and was also from crystallized water, the event in the range of  $\sim 175\text{-}236\text{ }^{\circ}\text{C}$  was due to a second type of crystallization water

and parts of ligand. On the other hand it was verified that at 650 °C the residual solid (57.97%) was produced and above this temperature there is no mass loss [15].

Excitation spectra showed the same spectral profile for supramolecule and uranyl salts with maximum in the range of 300 and 350 nm, except for methanesulphonate supermolecule (Fig 3).

The emission spectra showed characteristic fluorescence bands of uranyl ion, attributed to the  ${}^3\Pi_u \rightarrow {}^1\Sigma_g+$  transition of the matrix [16]. For the supermolecule with MS<sup>-</sup>, the spectra obtained in  $\lambda_{exc} = 400.0$  nm showed a group of six narrow bands than that recorded at 255 nm (not showed). Spectra obtained for this supermolecule showed sharp bands, see Fig 4B.



**Figure 2.** TGA/DTGA curves for  $UO_2(MS)_2 \cdot nH_2O$  octaacetatecalix[8]arene. and  $UO_2(TCA)_2 \cdot nH_2O$  octaacetatecalix[8]arene.

Besides uranyl trichloroacetate supermolecule shows identical profile for the spectra in the two-excitation energies. When precursor salt and supermolecule spectra are compared, shifting bands for the blue region are observed.

The qualitative comparison of emission intensities suggests that TCA supramolecule shows higher luminescent intensity than the salt precursor. In contrast, the emission intensity of supermolecule of methanesulphonate is lower than the salt precursor. The intensity ratio of supermolecule and its salts is about 51% indicating a luminescence quenching from the molecule with TCA.

As the spectral intensity is related to the area under curve, it was calculated and found quantitative ratios of growth or reduction of luminescence for these supermolecules. For MS supermolecule this relation is at about -51%, that is, a quenching of luminescence is observed

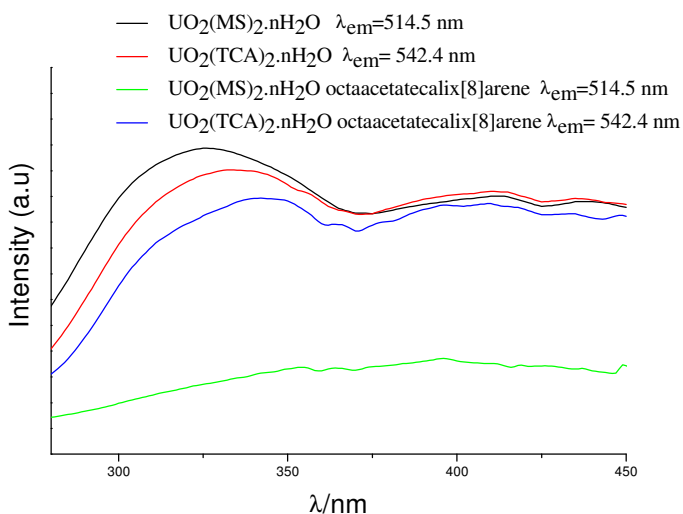
with the formation of the supermolecule. Since for the supermolecule with TCA this intensity ratio among the emission of the supermolecule and of precursor salt is at about 214%.

This parameter gives a quantitative displacement to blue region of spectra. The values of  $\beta$  calculated for the supermolecules MS e TCA were 0.964 e 1.038, respectively.

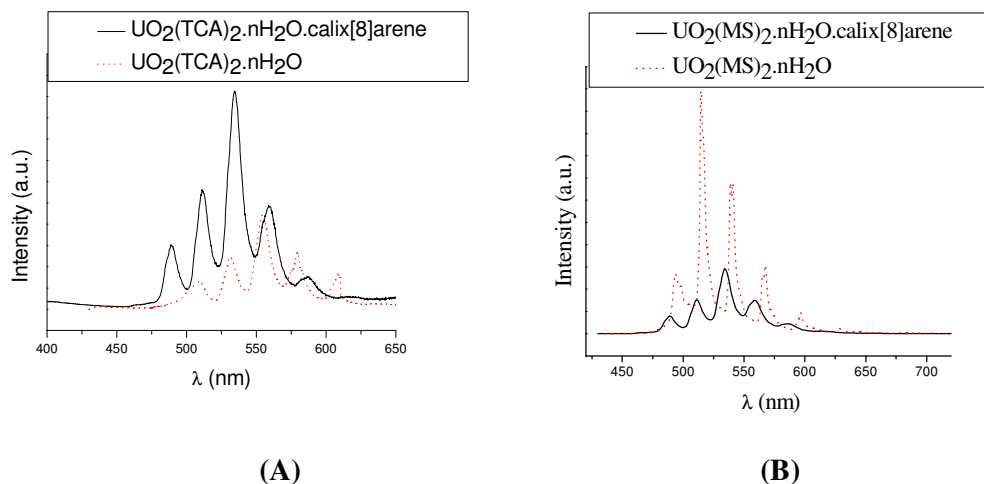
The nephelauxetic parameter  $\beta$  was determined by the following equation:

$$\beta = \frac{E \text{ baricenter of supermolecule}}{E \text{ baricenter of hydrated salt}} \quad (1)$$

The lifetime behaviors shows order exponential decays for  $\text{UO}_2(\text{TCA})_2 \cdot \text{octaacetatecalix}[8]\text{arene}$  ( $\tau_1 = 168.4 \pm 0.19 \mu\text{s}$ ) and  $\text{UO}_2(\text{MS})_2 \cdot \text{octaacetatecalix}[8]\text{arene}$  ( $\tau_1 = 413.1 \pm 0.19 \mu\text{s}$ ).



**Figure 3. Excitation spectra of  $\text{UO}_2(\text{MS})_2 \cdot \text{nH}_2\text{O} \cdot \text{octaacetatecalix}[8]\text{arene}$  and  $\text{UO}_2(\text{TCA})_2 \cdot \text{nH}_2\text{O} \cdot \text{octaacetatecalix}[8]\text{arene}$ .**



(A) (B)  
**Figure 4. Emission Spectra of  $\text{UO}_2(\text{TCA})_2 \cdot n\text{H}_2\text{O}$ ,  $\text{UO}_2(\text{TCA})_2 \cdot n\text{H}_2\text{O} \subset$  octaacetatecalix[8]arene,  $\text{UO}_2(\text{MS})_2 \cdot n\text{H}_2\text{O}$  and  $\text{UO}_2(\text{MS})_2 \cdot n\text{H}_2\text{O} \subset$  octaacetatecalix[8]arene.**

**Table 1. Life time for uranyl salts and their supermolecules**

COMPOUNDS	T (K)	$\tau$ ( $\mu\text{s}$ )	${}^3\Pi_u$
		$\tau_1$	$\tau_2$
$\text{UO}_2(\text{MS})_2 \cdot 6\text{H}_2\text{O}$	298	$429.06 \pm 14$	$766.00 \pm 37,98$
$\text{UO}_2(\text{MS})_2 \cdot 6\text{H}_2\text{O} \subset$ octaacetatecalix[8]arene	298	$413.11 \pm 1.91$	-
$\text{UO}_2(\text{TCA})_2 \cdot 6\text{H}_2\text{O}$	298	$268.45 \pm 1.09$	-
$\text{UO}_2(\text{TCA})_2 \cdot 6\text{H}_2\text{O} \subset$ octaacetatecalix[8]arene	298	$168.46 \pm 0.19$	-

#### 4. CONCLUSIONS

New complexes presenting formulas  $\text{UO}_2(\text{TCA})_2 \cdot (\text{H}_2\text{O})$  octaacetatecalix[8]arene and  $\text{UO}_2(\text{MS})_2 \cdot (\text{H}_2\text{O})$  octaacetatecalix[8]arene, (where MS is methanesulfonate and TCA is trichloroacetate) were synthesized and characterized by elemental analysis, thermogravimetric analyses (TGA) and infrared spectroscopy. The IR analyses show coordination of counter ion and inclusion in the calixarene cavity. Photophysical properties of these compounds have also been studied. The emission spectra showed characteristic fluorescence bands of uranyl ion, attributed to transition  ${}^3\Pi_u \rightarrow {}^1\Sigma_g^+$  of matrix. For supermolecule with  $\text{MS}^-$  spectra obtained in  $\lambda_{\text{exc}} = 400,0$  nm showed narrowed bands than at 255nm. Trichloroacetate supermolecule exhibit identical profiles for the spectra in the two-excitation energies. The emission spectra of the studied supermolecules show band shiftings for the blue region as compared to precursor salts. The lifetime behaviors have a mono

exponential decay for  $\text{UO}_2(\text{TCA})_2$ .octaacetatecalix[8]arene and  $\text{UO}_2(\text{MS})_2$  octaacetatecalix[8]arene showing that it is only one channel of depopulation from emitting level.

## ACKNOWLEDGMENTS

The authors acknowledge to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) / Rede de Nanotecnologia Molecular e Interfaces (RENAMI) / Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) and the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the financial support. We also acknowledge to E. Gasparine the thermal analytic curves.

## REFERENCES

1. C. Becquerel, *C.R. Acad. Sci, Paris*, **v.9**, pp.14 (1839).
2. J. Moser, *Mh. Chem.*, **v.8**, pp.373 (1887).
3. H. Rigollot, *C.R. Acad. Sci. Paris*, **v.116**, pp.878 (1893).
4. G. E. Thompson, *Phys. Rev.*, **v.5**, pp.43 (1915).
5. C. Stora, *J. Chim. Phys.*, **v.34**, pp.536 (1937).
6. A.W. Copeland, O.D. Black and A.B. Garrett, *Chem. Rev.*, **v.31**, pp.177 (1942).
7. T. Kuwana, *Electroanal. Chem.*, **v.1**, pp.197- (1966)
8. M. D. Archer, *J. Appl. Electrochem.* **v.5**, pp.17- (1975).
9. R. Reisfeld and N. Lieblisch-Sofer, "Role of the Uranyl Ion in Conversion of Solar Energy", *Abstract of the Conference of Photochemical and Photobiology Conversion and Storage*, Weizmann Institute, Rehovot, Israel, April 3-5 (1978).
10. N. Lieblisch-Sofer, R. Reisfeld and C. K. Jørgensen, *Inorg. Chim. Acta*, **v.30**, pp.259 (1978).
11. C. Redshaw, *Coordination Chemistry Reviews*, **v.244**, pp 45-70 (2003).
12. Z. Marckenko, *Separation and spectrophotometric determination of elements*, Ellis Horwood Limited, England, Wiley & Sons (1986).
13. A. Z. El-Zonbati, *Spectroscopic Lett.*, **v.30**, pp.459- (1997).
14. D. Gutsche, *Calixarenes Revisited*, Monographs in Supramolecular Chemistry, Royal Society of Chemistry, Hertfordshire (1998).
15. P. J. Haines, *Thermal Methods as Analysis. Principles, Applications and Problems*, 1<sup>st</sup> ed. Chapman & Hall, London (1995).
16. C. K. Jørgensen and R. J. Reisfeld, *Electrochem. Soc.*, **v.130 (3)**, pp.681-684 (1983).
17. C. K. Jørgensen, *J. Lumin.*, **v.18 (9)** pp.63-68 (1979).