The Scientific Bulletin of VALAHIA University – MATERIALS and MECHANICS – Nr. 8 (year 11) 2013

COMPLEX INVESTIGATIONS OF SUPRAMOLECULAR PORPHYRINS NANOMATERIALS

Simona-Florentina Pop[1] and Rodica-Mariana Ion[1,2]
[1] National Research & Development Institute for Chemistry and Petrochemistry – ICECHIM, Spl. Independentei, 202, sect. 6, Bucharest, Romania
[2] Valahia University, 2 Carol I Bd, Targoviste, Romania
E-mail: popsimfc@yahoo.com

Abstract. Macroheterocyclic compounds, such as metal porphyrins have unique physical and chemical properties. New possibilities of the functional use of porphyrin and phthalocyanine compounds have been revealed recently, their capability for self-organization (self-assembly) can form a basis for nanotechnologies.

Some supramolecular aggregates has been investigated in this paper using TGA/DTG. Thermogravimetry (TG) have been used to examin the thermochemistry, to study the thermal stability and thermal decomposition of a wide set of complexes of porphyrins and phthalocyanines. The composition of these compounds were determined from the TGA curves and confirmed by carbon, nitrogen, sulphur and hydrogen micro-analytical determinations.

The current study focuses on characterizing the new nanomaterial system using dynamic light scattering (DLS). Observations of material-specific surface properties were also recorded. Additionally, a stock solution of nanomaterials was analyzed for changes in agglomeration and zeta potential of the material over time. In summary, our results demonstrate that the nanomaterials agglomerate in solution and that depending upon the solution particle agglomeration is either agitated or mitigated. It was also observed that sonication slightly reduces agglomeration and has minimal effect on particle surface charge. Finally, the stock solution experienced significant changes in particle agglomeration and surface charge over time.

Keywords: porphyrins, phthalocyanine, thermal analysis, dynamic light scattering, nanomaterials, characterization.

1. INTRODUCTION

Porphyrins (P) either as free bases or metallocomplexes have been intensively studied during last few years because of their electrical and optical properties as well as their chemical and thermal stability [1]. One of the most important properties of the porphyrin molecules is their ability to coordinate to metal ions, yielding stable intercomplex salts. Stable complexes of metallo-porphyrins results from formation of four equivalent σ bonds N→ M [2]. Metallo-porphyrins have a planar macrocycle with an 18 π-electron system and large aplications due to their unique optical, electronic, catalytic and structural properties [3].

The main application of the metalloporphyrins are related to π-electron conjugated system, thermal and chemical stability allied to the self-organization capability. Metalloporphyrins are fairly stable to some thermal and oxidative processes, and parameters of that process depend on the number, position of the substituents. However, the synthesis of tungsten and titanium porphyrins are difficult. In the W porphyrin system, the effect of peripheral functional groups or spacer ligands on the thermal stability has not been fully investigated [4-6].

The rarity of these metalloporphyrins is explained by their reduced photostability [7-10].

It is known that the enhanced stability and the efficiency of the metalloporphyrins are due to their stereochemical features and to the electron-withdrawing halogen substituents. The metallo-porphyrins are very susceptible to photodegradation due to the instability of their excited states.

In this work, the stability of metallo-porphyrins (MTPP) has been studied through thermogravimetry analysis TGA/DTG and Dynamic Light Scattering (DLS).

2. EXPERIMENTAL

2.1. Materials and methods

Porphyrins are tetrapyrrolic pigments, Fig. 1, with four pyrrole subunits joined together by four methine bridges to give a cyclic molecule. With a highly conjugated skeleton, porphyrins have a characteristic ultra-violet visible (UV-VIS) spectrum. The spectrum typically consists of an intense, narrow absorption band at around 400 nm, known as the Soret or B band, followed by four longer wavelength (450–700 nm), weaker absorptions (free-base porphyrins) referred to as the Q bands.

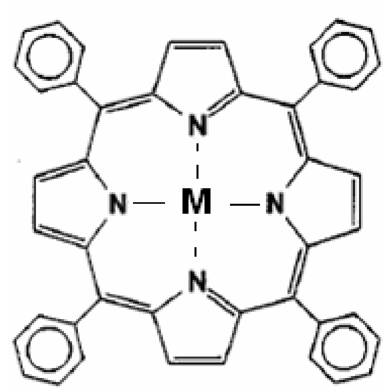

Fig. 1 Chemical structures of metallo-tetraphenylporphyrin MTPP

The TG curves of the samples were performed on a thermogravimetric analyzer Mettler Tolledo sistem TGA/SDTA 851^{e} under nitrogen atmosphere (99.999%) from 25 to 900 ^{0} C, in Al_2O_3 crucibles (70 μL). The heating rate was 20^{0} C /min and the flow rate of nitrogen was 80 mL /min. The TG equipment was calibrated by indium and aluminium pills.
Determinations about particle size measurements by Dynamic Light Scattering (DLS) will establish the nano dimensions of these porphyrins and phthalocyanines.

3. RESULTS AND DISCUSSION

Metal complexes derived from porphyrins are fairly stable to thermal and oxidative decomposition, and parameters of that process depend on the number, position, and on the presence of other substituents.
The effect of peripheral functional groups or spacer ligands on the thermal stability has not been fully investigated.
One of the most important properties of the pophyrins molecules is their ability to coordinate to metal ions, yielding stable intercomplex salts. It is well known that phthalocyanine unit is resistant to thermal oxidation.
The thermal oxidation of the porphyrins occurs in several steps involving the oxidation of peripheral substituents, accompanied by some macrocycle breaks, and metals oxidation to higher oxides [8].
Metal complexes derived from pophyrins are fairly stable to thermal and oxidative decomposition, and parameters of that process depend on the number, position, and on the presence of other substituents [11-14]. The decomposition consists of two stages for $TPPTiCl_2$ and $TPPWCl_4$ (Table 1).

Table 1. Thermal decomposition data

Compounds	Temp. range (^{0} C)	Mass loss calculated (%)	Mass loss found (%)	Tentative assignment
$TPPWCl_4$	25-380 380-900	7,1 43,6	7,3 40,7	 TPP ring
$TPPTiCl_2$	25-350 350-900	15 39,1	15,9 32,3	 TPP ring

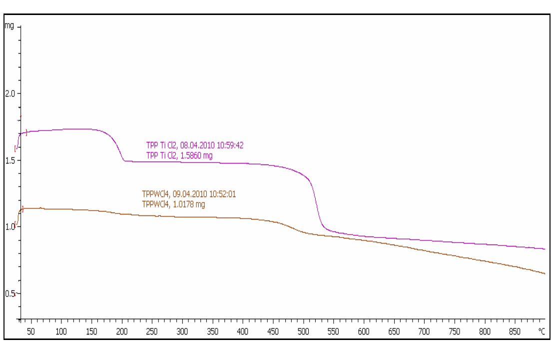

Fig. 2 TGA curves of ($TPPTiCl_2$, $TPPWCl_4$)

All the samples exhibit high thermal stability however $TPPTiCl_2$ temperature suggests that this complex has higher stability than $TPPWCl_4$ (Fig. 2).
DLS measures Brownian motion and correlates with particle size. This is achieved by illuminating the particles with a laser and analyzing the intensity fluctuations of scattered light. The particles suspended in liquid are constantly moving due to Brownian motion. Brownian motion is the random movement of particles due to collisions with the molecules of the liquid surrounding the particle. An important feature for DLS Brownian motion is that small particles move faster and larger ones more slowly. Zetasizer Nano device measures the scattered light intensity fluctuations and uses them to calculate the particle size of the sample. If large particles are measured, the intensity of scattered light will vary slowly. If small particles are measured scattered light intensity will fluctuate quickly.
$TPPTiCl_2$ is the most stable and nano-aggregates appeared in solution $TPPWCl_4$.

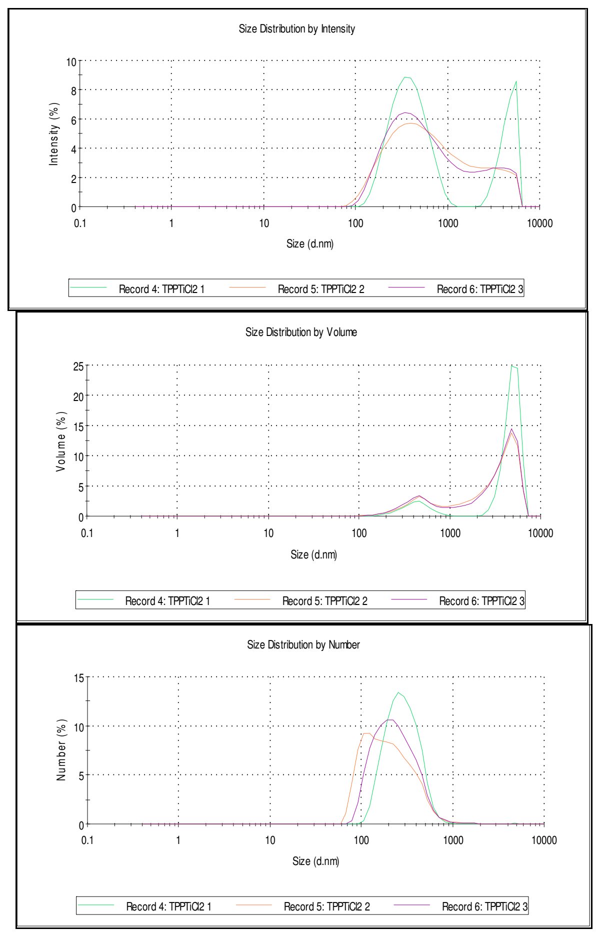

Fig. 3 DLS analysis of $TPPTiCl_2$

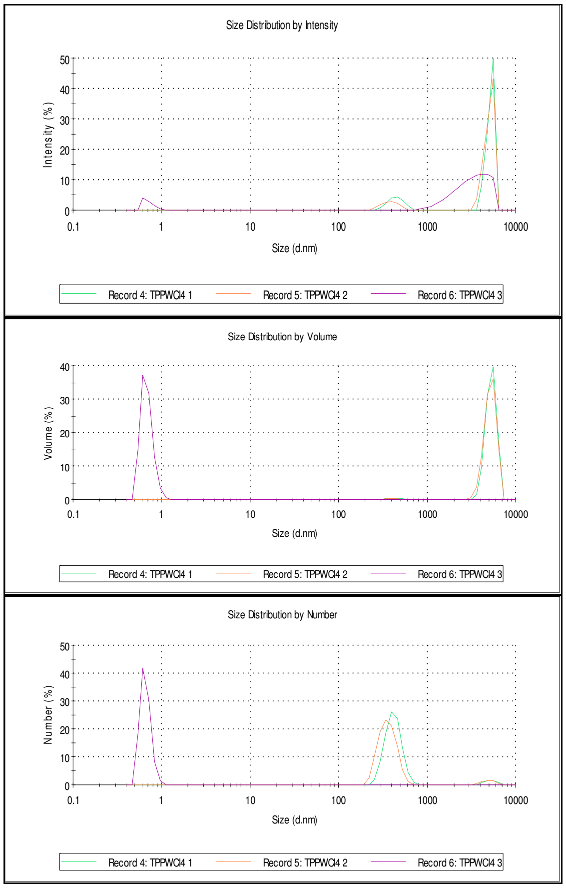

Fig. 4 DLS analysis of $TPPWCl_4$

4. CONCLUSIONS

In this work, the stability the metalloporphyrins $TPPTiCl_2$ and $TPPWCl_4$ has been studied through thermogravimetry analysis and DLS analysis. Thermal properties of the metalloporphyrins were investigated by TGA/DTG methods, trying to appreciate the thermal stability of these compounds.

REFERENCES

1. RM Ion, Nnaocristaline materials, FMR Ed., Bucharest, 2003
2. Collman, J.P., Garner, J.M., Woo, L.K. The chemistry of rhenium and tungsten porphyrin complexes in low oxidation states. Synthesis and characterization of rhenium and tungsten porphyrin dimers containing metal-metal multiple bonds (1989) Journal of the American Chemical Society, 111 (21), pp. 8141-8148.
3. S.-F. Pop, R.-M. Ion, Multifunctional supramolecular materials, Ed. Victor, Bucharest 2012.
4. S.-F. Pop, R.-M. Ion Study of some supramolecular aggregates porphyrins- phthalocyanines, J.Int.Res.Pub., Issue Materials, Methods & Technologies 2010, 4(2) pp. 112-120.
5. Collman, J.P., Garner, J.M., Hembre, R.T., Ha, Y.Relative strength of 4d vs 5d δ-bonds: Rotational barriers of isostructural molybdenum and tungsten porphyrin dimers (1992) Journal of the American Chemical Society, 114 (4), pp. 1292-1301.
6. Collman, J.P., Harford, S.T., Franzen, S., Eberspacher, T.A., Shoemaker, R.K., Woodruff, W.H. Spectroscopic comparisons of $MoW(porphyrin)_2$ heterodimers with homologous Mo_2 and W_2 quadruple bonds: A dynamic NMR and resonance raman study (1998) Journal of the American Chemical Society, 120 (7), pp. 1456-1465.
7. S.-F. Pop, R.-M.Ion Thermal stability – singlet oxygen quantum yields relationship of some metallophtalocyanine sensitizers for photodynamic tests The Journal of Optoelectronics and Advanced Materials, Vol. 12, 9, 1976 – 1980 (2010).
8. RM Ion, Synthesis, photophysical properties and photocatalytic activity of tungsten porphyrin (TPPWCl4) (2013) Journal of Porphyrins and Phthalocyanines, 17 (6-7), pp. 460-472.
9. Cotton, F.A.Discovering and understanding multiple metal-to-metal bonds (1978) Accounts of Chemical Research, 11 (6), pp. 225-232.
10. Kim, J.C., Goedken, V.L., Lee, B.M. Synthesis and rotational barrier of tungsten(II) porphyrin dimer, $[W(TPP)]_2$ (TPP = tetraphenylporphyrin) (1996) Polyhedron, 15 (1), pp. 57-62.
11. Srivastava, T.S., Fleischer, E.B. New oxomolybdenum (V) compounds of tetraphenylporphine (1970) Journal of the American Chemical Society, 92 (18), pp. 5518-5519.
12. Newton, C.M., Davis, D.G. ESR and electrochemical studies of some transition metal porphyrins (1975) Journal of Magnetic Resonance (1969), 20 (3), pp. 446-457.
13. Motorina, E.V., Lomova, T.N. Hydroxyoxo (5,10,15,20-tetraphenylporphinato tungsten (V) as a receptor for foodstuff and drug components. Thermodynamics of supramolecular complexation (2010) Russian Journal of Inorganic Chemistry, 55 (5), pp. 727-733.
14. Yang, C.-H., Dzugan, S.J., Goedken, V.L. Structure and reactivity of an unusual tungsten(VI) porphyrin complex having cis oxo and peroxo groups (1985) Journal of the Chemical Society, Chemical Communications, (20), pp. 1425-1426.