JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 12, No. 9, September 2010, p. 1976 - 1980

Thermal stability – singlet oxygen quantum yields relationship of some metallophtalocyanine sensitizers for photodynamic tests

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Metallophthalocyanines (MPcs) have potential applications in many areas such as in medicine and material science [1]. Owing to their strong and long-wavelength absorption and efficient reactive oxygen specie generation (ROS) phthalocyanines have emerged as a promising class of second-generation photosensitizers for photodynamic therapy (PDT) [2]. Over the last decade, a substantial number of phthalocyanine-based photosensitizers have been prepared and evaluated for their photodynamic activity. In this work, the stability of metallophtalocyanine has been studied through thermogravimetry analysis, elemental analysis, quantum yields of singlet oxygen photogeneration and FT-IR analysis. Quantum yields of singlet oxygen photogeneration were determined in air (no oxygen bubbled) using the relative method with DPBF as chemical quencher for singlet oxygen [3].

(Received August 6, 2010; accepted September 15, 2010)

Keywords: Phthalocyanine, Photodynamic activity, Thermal analysis, Singlet oxygen

1. Introduction

Metallophthalocyanines (MPcs) have potential applications in many areas such as in medicine and material science. [1] Owing to their strong and long-wavelength absorption and efficient reactive oxygen specie generation (ROS) phthalocyanines have emerged as a promising class of second-generation photosensitizers for photodynamic therapy (PDT) [2].

Metallophthalocyanines (MPc) are paid much attention in molecular electronics, non-linear optics, liquid crystals, gas sensors, catalysts, semiconductive materials, photovoltaic cells and electrochromic displays over the last few decades. [5]

In addition, metalloporphyrins are investigated extensively because they play an important role in biology due to their crucial function in many biological processes like photosynthesis, biological red-ox reactions, and transport of oxygen. In recent years, metalloporphyrins are widely used as catalysts because of their extremely high selectivity in catalytic reactions [4].

In particular, cobalt phthalocyanine (CoPc) is often utilized in the fields of gas and radiation sensors, optoelectronics, in medical applications. Nowadays, CoPc is considered as a material for development of low dimensional molecular magnets [5]. Especially, the cobalt(II) phthalocyanine (CoPc) and its derivatives are shown to catalyze reactions like the reduction of oxygen, carbon dioxide, formic acid, formaldehyde, trichloro acetic acid, and cysteine-containing proteins [4].

The composition of these metalic compounds were determined from the TGA curves and confirmed by carbon, nitrogen, sulphur and hydrogen micro-analytical determinations.

2. Experimental

2.1. Materials and methods

Phtalocyanines are azaporphyrins consisting of four benzoindole nuclei connected by nitrogen bridges in a 16-membered ring of alternating carbon and nitrogen atoms arround a central metal atoms which form stable chelates with metal cations (dia or paramagnetic ion). The molecule consists of the central metal atom (Co, Cu, Zn or Ni), which is surrounded by four nitrogen atoms—pyrrole; four other nitrogen atoms—bridging aza; 32 carbon atoms—the pyrrole and the benzene ones. (Fig. 1) [5].

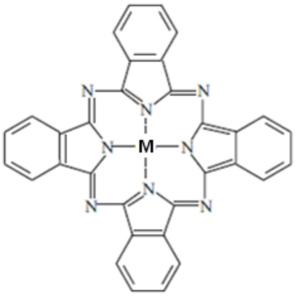

Fig. 1. Chemical structures of metallophthalocyanines.

In general, phthalocyanines have UV-Vis absorption spectra with intense p-p* transitions, usually referred to as Q bands in the range 660-700 nm with higher energy vibration associated components in the range 600-660 nm. Also phthalocyanines have Soret B band in the range 420-

320 nm, N band around 330-285 nm and an L-band at 270-230 nm. [6]

Infrared spectra were measured using an Perkin-Elmer FT-IR spectrometer coupled to a PC with analysis software. The samples were done in KBr pellet placed in the holder directly in the IR laser beam.

The TG curves of the CoPc, CuPc, ZnPc and NiPc were performed on a thermogravimetric analyzer Mettler Toledo 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 10^0 C /min and the flow rate of nitrogen was 80 mL /min. The TG equipment was calibrated by indium and aluminium pills.

3. Results and discussion

Quantum yields of singlet oxygen photogeneration were determined in air (no oxygen bubbled) using the relative method with DPBF as chemical quencher for singlet oxygen. [3]

Singlet oxygen quantum yields were studied in toluene using a chemical method (1,3-diphenylisobenzofuran, DPBF). The Φ_Δ values for the studied phthalocyanines were Φ_Δ =0.58 for CoPc, Φ_Δ =0.55 for NiPc, Φ_Δ = 0.52 for ZnPc, and Φ_Δ =0.05 for CuPc in toluene.

Compounds of this series feature an extremely high stability, a large closed system of π electrons, and the possibility of attaining record-breaking degrees of purification for organic products (using vacuum sublimation). Among other organic dyes, specifically dyes of the tetrapyrrole series are characterized by the highest ecological safety [3]. Also noteworthy is the relatively simple synthesis, hence, availability of metal-phthalocyanines themselves and their derivatives.

In particular, IR spectra Fig. 2 - Fig. 5 should somewhat reflect changes in the configuration of phthalocyanine macrocycles due to the introduction or substitution of a template metal.

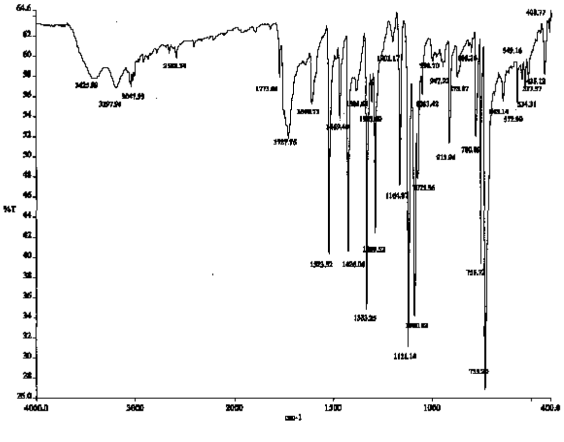

Fig. 2. IR spectra of CoPc.

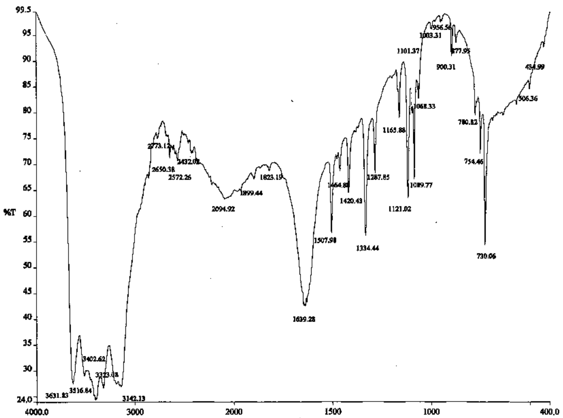

Fig. 3. IR spectra of CuPc.

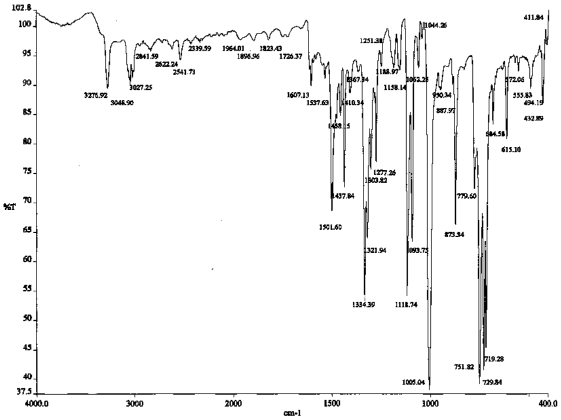

Fig. 4. IR spectra of ZnPc.

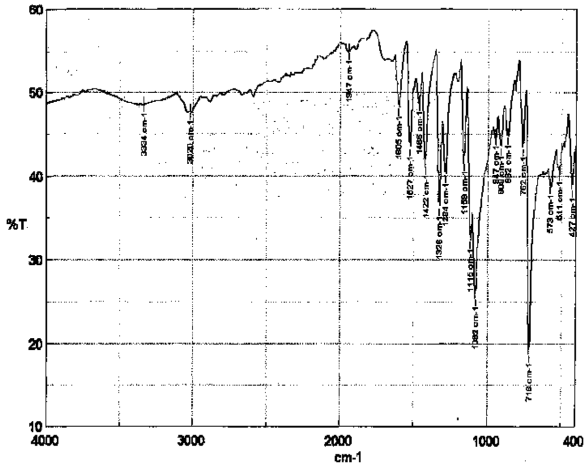

Fig. 5. IR spectra of NiPc.

Table 1. Vibration frequencies (cm $^{-1}$) in IR spectra of MPc.

NiPc	**ZnPc**	**CoPc**	**CuPc**	**Identification**
1.24	1.34	1.25	1.28	Atomic radius of metal, Å
3020	3049	3056	3047	$\upsilon_{C\text{-}H}$ (arom.)
1605	1607	1610	1612	υ (C=C)
1527	1538	1523	1507	υ (-N=)
1466	1460	1470	1480	υ (isoindole)
1422	1437	1426	1421	υ (isoindole)
1326	1334	1332	1333	υ (pyrrole)
1284	1277	1289	1287	$\delta_{C\text{-}H}$ (in-plane)
1159	1158	1164	1165	$\delta_{C\text{-}H}$ (in-plane + isoindole)
1115	1118	1120	1119	Isoindole totally symm.
1082	1093	1096	1091	$\delta_{C\text{-}H}$ (in-plane)
947	950	946	947	Benzene totally symm.
862	873	874	870	δ (isoindole + nitrogen mesoatoms)
770	780	781	770	$\delta_{C\text{-}H}$ (out-of-plane)
762	752	756	754	δ (Pc rings)
716	730	731	725	$\delta_{C\text{-}H}$ (out-of-plane)

The IR spectra of aromatic condensed benzene rings of metal phthalocyanines include the most extensive set of stretching and bending vibration bands: stretching vibrations of C–H bonds (3046–3060 cm $^{-1}$) of relatively low intensity and skeletal C–C vibrations (1580– 1610 cm $^{-1}$) with intensities varying from moderate to very low. In this case, the frequency of 1580 cm $^{-1}$ caused by stretching vibrations of the C–C bond condensed with the pyrrole cycle sometimes does not manifest itself at all. Intense vibrations in the region of 947 cm $^{-1}$ are totally symmetric stretching vibrations of C–C bonds of the aromatic ring. Plane bending vibrations of C ar –H are in the ranges of 1283–1289, 1158–1167, 1091–1096, and 1033–1060 cm $^{-1}$; their intensity, as a rule, varies from moderate to low. Out-of-plane bending vibrations of C–H bonds of metal phthalocyanines appear in the range of 720–780 cm $^{-1}$.

A high-intensity band at 1500–1530 cm $^{-1}$ corresponds to vibrations of nitrogen bridging atoms (mesoatoms –N=). Stretching vibrations of isoindole fragments (including vibrations of the pyrrole and benzene residues) manifest themselves in the range of 1420–1480 cm $^{-1}$; the band intensity varies from low to very high. Vibrations of the –C=C–N= group (pyrrole fragment and nitrogen mesoatoms) appear as a lowintensity band at 1396–1407 cm $^{-1}$ and a very strong (characteristic of all phthalocyanines) band at 1320– 1365 cm $^{-1}$. Strong totally symmetric vibrations of isoindole fragments are in the range of 1112–1120 cm $^{-1}$. The vibration frequencies corresponding to the stretching vibrations of benzene fragments of phthalocyanines, as well as frequencies of stretching and out-of- plane bending vibrations, are almost independent of the atomic radius of the complexing metal.

The electronic absorption spectra of all the examined complexes (Table 2) contain a strong long-wave *Q* band originating from π-π-electron transition in the main conjugation system of the phthalocyanine macroring. The position of the *Q* band and the shape of spectral curve are determined by the nature of the metal, substituents in the benzene rings, solvent, concentration, and other factors. The spectra recorded from solutions in organic solvents (DMF) exhibit strong absorption in the region λ 647-705 nm (Table 2).

Table 2. Position of the first absorption band (λ max, nm) in the electronic spectra of phthalocyanine metal complexes in DMF.

Complex	**λ max, nm**
CoPc	660
NiPc	667
CuPc	668
ZnPc	647

The samples were analyzed by elemental analysis (Perkin-Elmer 2400 analyzer) at 975 ° C in He atmosphere; the results are shown in Table 3.

Table 3. Elemental analysis data for metal complexes.

Complex	**Found, %**			
	C	**H**	**N**	**M**
ZnPc	67.52	2.80	19.11	10.56
CuPc	66.09	1.98	18.85	13.08
CoPc	66.78	2.01	19.15	12.05
NiPc	66.63	2.00	19.12	12.15
Formula	**Calculated, %**			
	C	**H**	**N**	**M**
$ZnC_{32}H_{16}N_8$	66.55	2.77	19.41	11.26
$CuC_{32}H_{16}N_8$	66.67	2.78	19.44	11.11
$CoC_{32}H_{16}N_8$	67.25	2.80	19.61	10.33
$NiC_{32}H_{16}N_8$	67.37	2.81	19.65	10.17

One of the most important properties of the phthalocyanine 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 [7].

The thermal oxidation of the phthalocyanines occurs in several steps involving the oxidation of peripheral substituents, accompanied by some macrocycle breaks, and metals oxidation to higher oxides.

Metal complexes derived from phthalocyanine 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 initial decomposition temperature decreased in the order: Co, Cu, Ni, and Zn phthalocyanines showed better thermal stability under working conditions. The decomposition consists of two stages for all phthalocyanines. The first step in the decomposition started at ca. 45–330 ^{O}C for CuPc, ca. 45–270 ^{O}C for CoPc, ca. 45–298 ^{O}C for NiPc and ca. 45–450 ^{O}C for ZnPc. Then, the second step in the decomposition (the main decomposition) occurred at 690 ^{O}C for CuPc, 390 ^{O}C for CoPc, 380 ^{O}C for NiPc and 680 ^{O}C for ZnPc (Fig. 6).

These correspond to the loss and fragmentation of one unit of the peripheral environment of the phthalocyanine molecule. For instance, for CuPc, a group at peripheral part corresponding to one fourth of the ionized organic group left with an estimated mass loss of 33.41% (calcd. mass loss 33.59%); for CoPc, similarly, an estimated mass loss of 29.9% (calcd. mass loss 30.2%); in case of NiPc, the leaving group with observed mass loss of 38.1% could not be identified; for ZnPc, was an estimated mass loss of 43.3% (calcd. mass loss 43.2%).

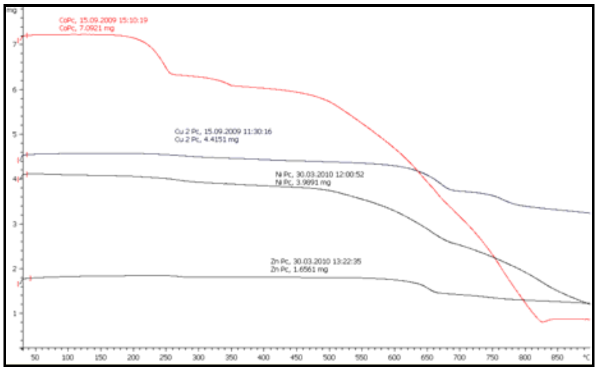

Fig. 6. TGA curves of metallophthalocyanines Co Pc, CuPc, NiPc and ZnPc.

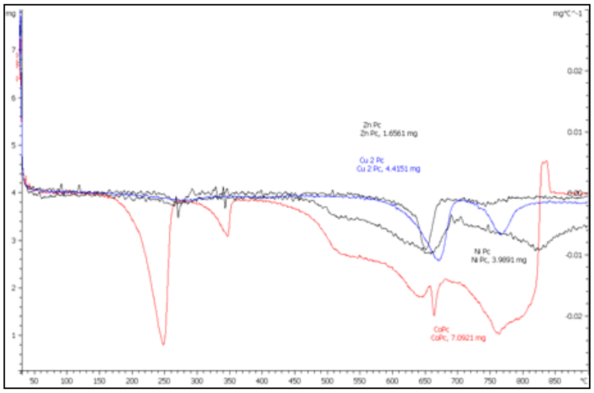

Fig. 7. DTG curves of metallophthalocyanines Co Pc, CuPc, NiPc and ZnPc .

Zn Pc macrocycle was stable up to 450 ^{0} C, Cu Pc up to 330^{0} C, Ni Pc up to 298^{0} C and Co Pc to 270^{0} C. All the metallophthalocyanines exhibit high thermal stability as described in literature, however ZnPc onset temperature suggests that zinc complex has higher stability. Nevertheless, DTG peak temperature (Fig. 7) has not shown significant differences between the four phthalocyanine complexes. The onset temperature suggests that the stability follows the order: Zn Pc > Cu Pc > Ni Pc > Co Pc.

4. Conclusions

In this work, the stability of metallophtalocyanine has been studied through thermogravimetry analysis, elemental analysis, quantum yields of singlet oxygen photogeneration and FT-IR analysis. Thermal properties of the metallophthalocyanines were investigated by TGA/DTG methods, trying to appreciate the thermal stability of these compounds. DTG curves exhibited exothermic changes for the studied compounds in the region investigated; it means that there was no melting point for any of the phthalocyanines. The singlet oxygen quantum yields for the studied phthalocyaninesx: Φ_{Δ} =0.58 for CoPc, Φ_{Δ} =0.55 for NiPc, Φ_{Δ} = 0.52 for ZnPc, and Φ_{Δ} =0.05 for CuPc in toluene, direct proportional correlated with the above decomposition temperature.

Acknowledgments

Results were obtained in a project co-financed from European Social Fund through the Sectoral Operational Program Human Resources Development 2007-2013 - "Invest in people!".

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