

**STUDY OF SOME SUPRAMOLECULAR AGGREGATES PORPHYRINS-
PHTHALOCYANINES**

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Abstract

Macroheterocyclic compounds, such as metal porphyrins and phthalocyanines, 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, EA and AFM analysis.

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.

Key words: porphyrins, phthalocyanine, thermal analysis

1. INTRODUCTION

Porphyrins (P) and phthalocyanine (Pc), 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. One of the most important properties of the porphyrin and phthalocyanine molecules is their ability to coordinate to metal ions, yielding stable intercomplex salts. Stable complexes of porphyrins or metalloporphyrins and complexes of phthalocyanines or metal phthalocyanines results from formation of four equivalent σ bonds $N \rightarrow M$. Both of them have a planar macrocycle with an 18 π -electron system and large applications due to their unique optical, electronic, catalytic and structural properties. (B. I. Kharisov 2000; V. N. Nemykin 2000; R.M. Ion 2005)

Moreover, numerous studies on π - π complexes of the porphyrins and the metalloporphyrins with aromatic molecules show that these complexes are formed due to donor-acceptor interactions.(O. A. Chamaeva 1990; G. P. Fulton 1976; E. V. Antina 1995; N. Sh. Lebedeva 2003; N. Sh. Lebedeva 1999).

Thermal decomposition of alkylsubstituted porphyrins starts with elimination of alkyl groups. Comparison of the weight loss in the second step with the contribution of alkyl groups to the molecular weight of meso-tetramethyltetrabenzoporphyrin complexes showed that oxidation of

peripheral substituents in complexes meso-tetramethyltetrabenzoporphyrin is not a separate step. (R.M.Ion 1999; S.A.Girtas 1999; D.Wrobel 1998; D.Wrobel 1998).

The aim of the present work is to study the physical- chemical characteristics (composition, temperature of decomposition) of zinc porphyrins and zinc phthalocyanine, π - π complexes with some aromatic molecules having different nature, number and mutual arrangement of substituents.

2. EXPERIMENTAL

2.1. Materials and methods

To estimate the effects of the symmetry and nature of peripheral functional substituents on the thermal oxidation, we choose to study the following nano-complexes: zinc(II) meso-tetramethyltetrabenzoporphyrin (ZnTBTMP), zinc(II) hematoporphyrin (ZnHP), zinc(II) protoporphyrin (ZnPP) and zinc(II) phthalocyanine (ZnPc) Fig. 1-4.

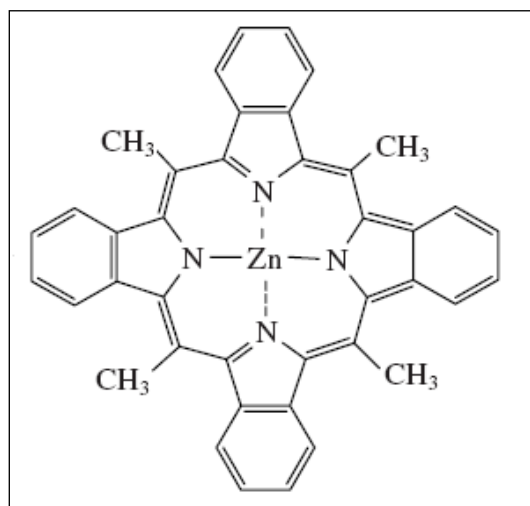


Figure 1. The structure of the zinc (II) meso-tetramethyltetrabenzoporphyrin zinc (ZnTBTMP)

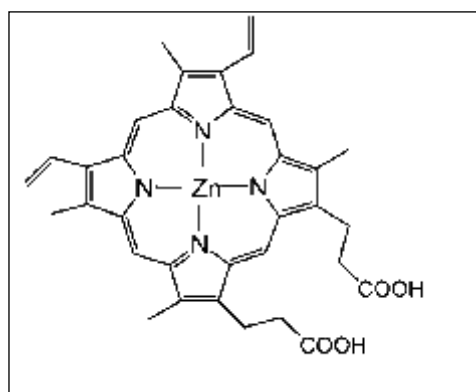


Figure 2. The structure of the zinc (II) hematoporphyrin (ZnHP)

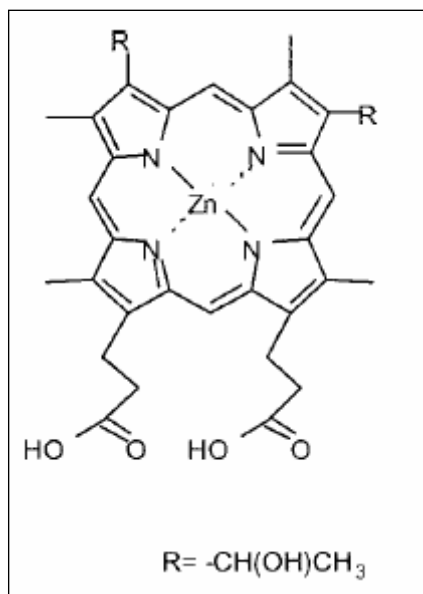


Figure 3. The structure of the zinc(II) protoporphyrin (ZnPP)

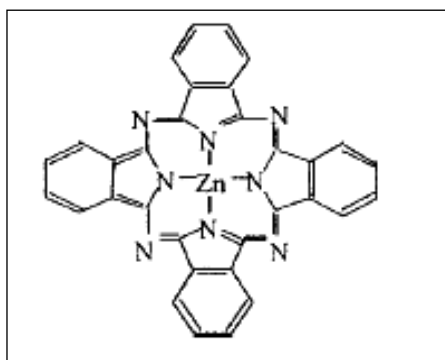


Figure 4. The structure of the zinc(II) phthalocyanine (ZnPc)

ZnPc has been prepared in the lab after a literature method.(A.Siejak, 2000). All the others compounds have been purchased by Aldrich company and have been used without subsequent purification.

The thermal oxidative decomposition of crystalline samples of macro heterocyclic compound was studied in air, in Al_2O_3 crucibles at a heating rate of 5 K/min. We used a Mettler Toledo sistem TGA/SDTA 851°.

3. RESULTS AND DISCUSSION

The analyzed compounds have different structures, with different meso- substituents, responsible for their thermal decomposition step.

It is noted in the literature (Berezin 1988), that the thermal oxidation of the porphyrins and phthalocyanines occurs in several steps involving the oxidation of peripheral substituents, accompanied by some macrocycle breaks, and metals oxidation to higher oxides.

The obtained data indicated that the metal complexes of the macroheterocyclic substances under study are rather stable against thermal oxidative decomposition. They start to decompose at temperatures exceeding 500 K, and the decomposition process is complicated, as demonstrated by the presence of several, sometimes not resolved, maxima and minima in the DTG curves.

The processes under study include several stages accompanied by exo effects in the DTG curve. In the case of ZnTBTMP four main steps are seen, in the case of ZnHP three main steps are clearly seen, whereas two steps take place for ZnPP and only one for ZnPc (Tab. 1).

Table 1. Temperature ranges (K) of steps I-III of thermal oxidative decomposition of metal complexes of macroheterocyclic compounds

Compound	I	II	III	IV
ZnHP	500-650	650-720	720-800	
ZnPP	600-700	700-815		
ZnPc			700-850	
ZnTBTMP	295-398	443-653	699-762	781-905

Heating of complex ZnPc 393-423 K leads to a small loss in weight due to elimination of adsorbed and crystallization water.

Further rise in temperature induces decarboxylation and linking of molecules to oligomeric structures; the subsequent gradual decarboxylation is accompanied by partial decomposition of the complex, which eventually gives the corresponding metal oxide.

Metal complexes derived from phthalocyanine are fairly stable to thermal and oxidative decomposition, and parameters of that process depend on the number and position of the carboxy groups, as well as on the presence of other substituents.

Heating of ZnPP to 494 K yield to some conformational changes, with a small exo effect accompanied by no weight loss is detected at this temperature in the DTA curve, whereas no second-kind transitions were found for ZnHP. In ZnHP molecule, there are four oxygen containing substituents, in contrast to the other natural zinc(II) porphyrins represented by dimethyl esters. It is possible that the absence of conformation changes in the case of ZnHP to be caused by the macrocycle stabilization due to formation of hydrogen bonds between the neighboring ZnHP molecules, as a hydrogen-bond assembly process. It is generally known that the natural porphyrins have lower decomposition temperatures than synthetic macroheterocycles; also, the asymmetry of the peripheral substitution negatively affects the macrocycle thermal stability. The temperatures of the onset of the thermal oxidative decomposition of zinc(II) porphyrins and the activation energies of the processes increase in the following order: ZnHP < ZnPP.

Let us consider step-by-step the thermal oxidation of ZnHP. The weight loss of the sample under study in the first and second steps is 24.56% and 16.15%, which agrees with the percent content of

peripheral substituents in positions 6,7 (24.22%) and 2,4 (16.43%) of the macroring. (Fig. 5). It was logical to expect that the thermal oxidative decomposition of ZnPP would also start with the oxidation of peripheral oxygen-containing substituents. (Fig. 6). However, the weight percentage of two $(\text{CH}_2)\text{COOCH}_3$ groups in ZnPP (26.60%) disagrees with the weight loss determined from the TG curve. The weight loss in step II of the ZnPP pyrolysis is 19.77%. The natural metal porphyrins shows that its peripheral substituents not only significantly affect the macrocycle stability, but also determine the thermal oxidation mechanism. Metal complex ZnPc is fairly stable to thermal and oxidative decomposition, and depend on the absence of the carboxy groups, as well as on the absence of other substituents. (Fig. 7).

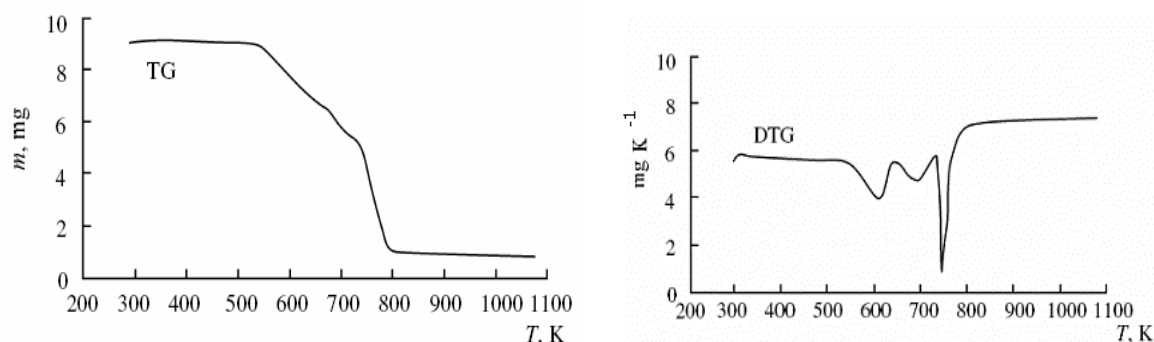


Figure 5. TGA and DTG of ZnHP

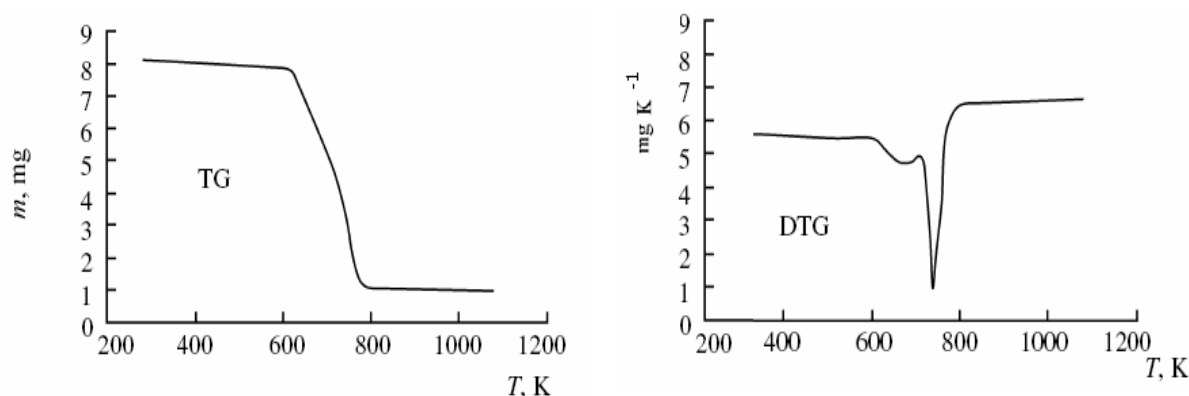


Figure 6. TGA and DTG of ZnPP

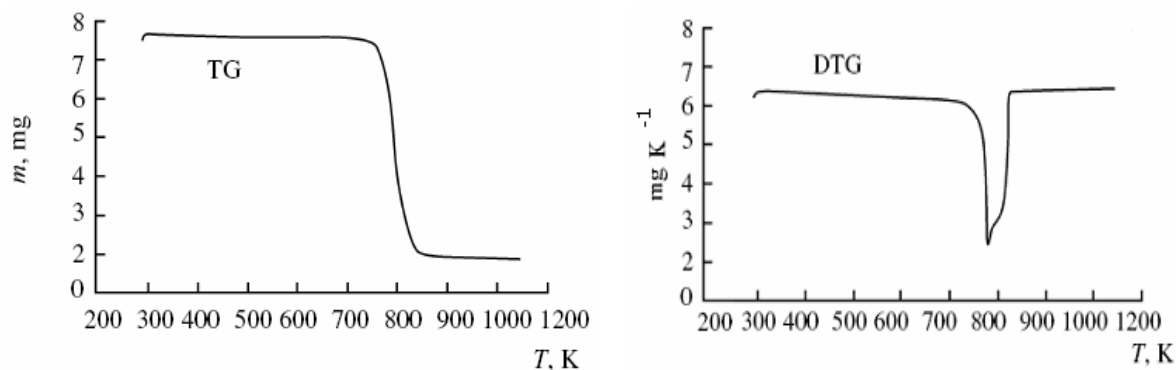


Figure 7. TGA and DTG of ZnPc

Compound ZnTBTMP is a green substance that is characterized by different solubility in organic solvents.

The structure of zinc complexes of macroheterocycles was confirmed by elemental analysis. (Tab. 2)

Table 2. Elemental analysis of zinc complexes of macroheterocycles

Complex	Found, %			Formula	Calculated, %		
	C	H	N		C	H	N
ZnHP	62.62	7.18	6.86	$\text{ZnC}_{34}\text{H}_{36}\text{N}_{40}\text{O}_6$	61.82	5.45	8.48
ZnPP	65.13	4.85	8.97	$\text{ZnC}_{34}\text{H}_{32}\text{N}_4\text{O}_4$	65.38	5.13	8.97
ZnPc	67.52	2.80	19.11	$\text{ZnC}_{32}\text{H}_{16}\text{N}_8$	66.66	2.77	19.44
ZnTBTMP	75.28	4.55	8.24	$\text{ZnC}_{40}\text{H}_{28}\text{N}_4$	76.43	4.46	8.91

Methyl groups in the meso positions insignificantly affect the geometric structure of the macrocycle.

The thermal decomposition of ZnTBTMP is a multi-step process from the presence of several peaks on the DTG curve. The decomposition patterns of ZnTBTMP complex are fairly similar (Fig. 8).

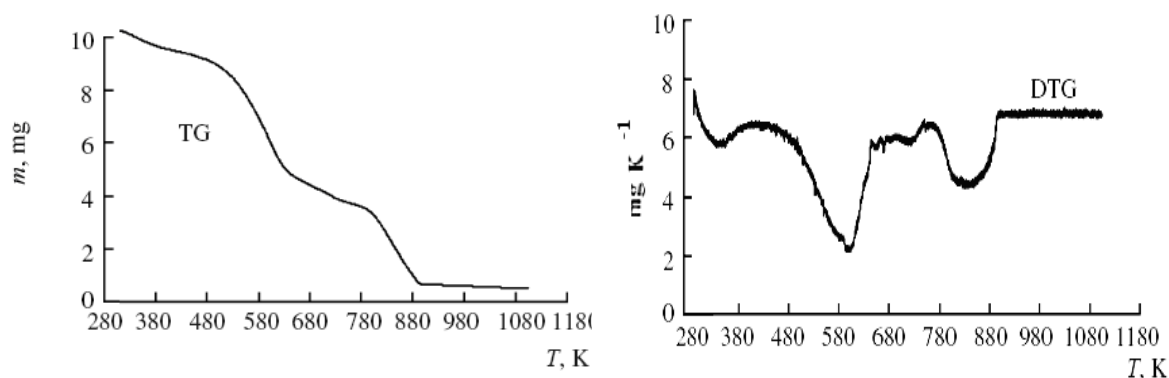


Figure 8. TGA and DTG of ZnTBTMP

The first step (Tab. 1) involves removal of solvent molecules, which is likely to be accompanied by essential reorganization of the crystal lattice. In phase-equilibrium determination, thermal methods of analysis are used to detect phase transitions. A change in phase involves structural changes in the material that are accompanied by evolution or absorption of heat. Thus, if a specimen is heated or cooled under uniform conditions, a structural change will be indicated by a temperature peak.

The thermal decomposition of meso-tetramethyltetrabenzoporphyrin zinc complex is accompanied by evolution of gaseous products (Fig. 8, DTG curve). According to (Logvinenko 1989), in such cases the thermal decomposition as a measure of thermal stability is inappropriate. Therefore, in keeping with

generally accepted view, it is better to estimate the thermal stability of a compound using the energy of activation.

It is interesting that meso-tetrametyltetrabenzoporphyrin zinc(II) (ZnTBTMP) complex are less thermally stable than unsubstituted tetrabenzoporphyrinatozinc(II) (ZnTBP) (Lebedeva 2007). Analogous relations were observed previously while studying zinc complexes of tetraphenylporphyrin, phthalocyanine, and their alkyl-substituted derivatives.

The reason is that the thermal decomposition of alkylsubstituted porphyrins starts with alkyl groups elimination. Comparison of the weight loss in the second step with the contribution of alkyl groups to the molecular weight of meso-tetrametyltetrabenzoporphyrin complex shows that the oxidation of peripheral substituents in complexes (ZnTBTMP) is not a separate step.

One of the most important properties of the porphyrin and phthalocyanine molecules is their ability to coordinate to metal ions, yielding stable intercomplex salts. The thermal oxidation of the porphyrins and 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 and position of the carboxy groups, as well as on the presence of other substituents.

An important property of supramolecular systems is their ability to be formed by anionic and cationic porphyrins structures (V. Balzan, F. Scandola, 1991). Assembly involves π cycles orientation, which are linked by strong hydrophobic intermolecular interactions and the electrostatic interactions between cations and peripheral anionic.

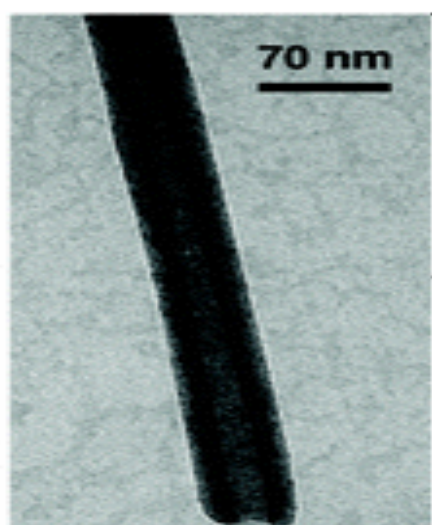
We used AFM to reveal the formation of nanotubes by self-assembly of two types of compounds with different electric charges.

4.CONCLUSION

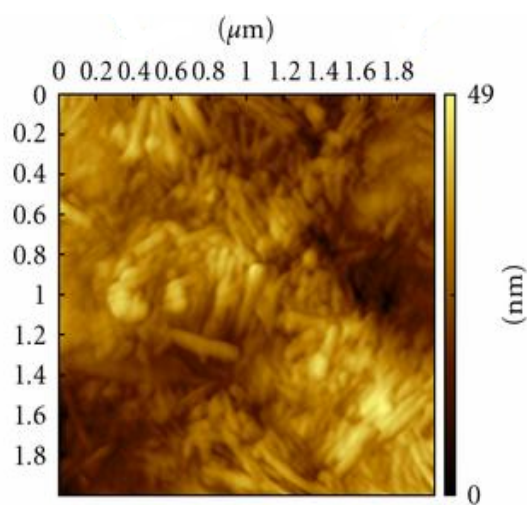
We found that the thermal stability of zinc(II) porphyrins and zinc(II) phthalocyanines obey the following series of macroheterocycles: ZnTBTMP < ZnHP < ZnPP < ZnPc.

The high aromaticity of phthalocyanine provides for its outstanding thermal stability which is much lower in the case of porphyrine and its alkyl-substituted derivatives, its volatility at low pressure, and a weak tendency to break open the conjugated system of the macroring.

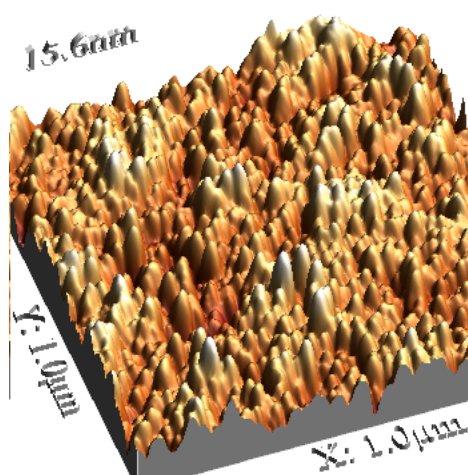
Information obtained from thermal analysis can lead us to the possibility of deposit molecules of porphyrins and phthalocyanine layers on sensor type devices.



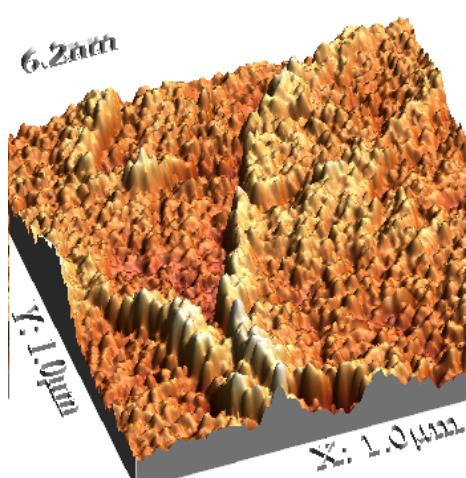
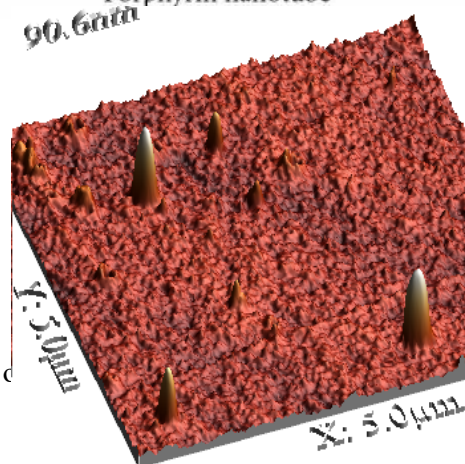
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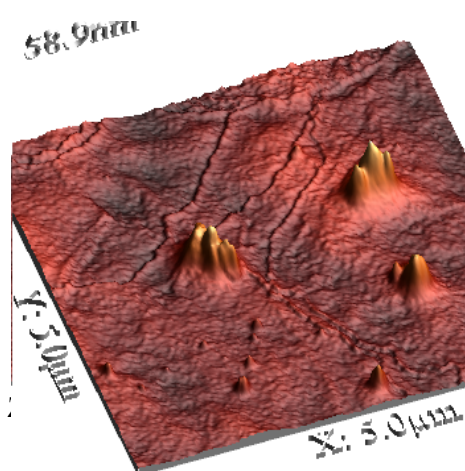
Porphyrin nanotube



M analysis c



ePyP +



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