NEW PHTHALOCYANINE COMPOUND POTENTIALLY USED AS PHOTOSENSITIZER DYE IN GRATZEL-TYPE SOLAR CELLS

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The paper present the synthesis and characterization of a novel phthalocyanine compound, obtained by binding two units of Zn phthalocyanin tetracarboxylic acid via a spacer with pentaerythritol structure. The synthesized compound was analyzed in terms of its photophysical properties, and of the interaction with the TiO_2 substrate. Experimental data show a significant increase of light absorption in the visible range and an improved fit on TiO_2, the compound being a good candidate for use in Gratzel type solar cells.

Keywords: phthalocyanine, Gratzel-type solar cells, TiO_2, pentaerythritol

1. Introduction

Photosensitizers dye cells are devices based on organic compounds that use molecules in order to absorb solar radiation photons separating the two functions, harvesting light energy and charge transfer, respectively [1]. The working principle of such a cell is similar with the photosynthesis process in green plants. The advantage of these solar cells is that they are compatible with a large variety of support materials and that they can be produced in normal conditions, which leads to a low cost. This type of solar cells appeared in 1991 when O'Regan and Grätzel reported devices with yields between 7-8%, based on ruthenium complexes and nanoporous titania films [2].

Until now, researches aimed the obtaining of new types of photosensitizing dyes in order to increase the efficiency of the device, yields of

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about 11% being reported so far, and up to 2015 yields of 13% are to be expected [3].

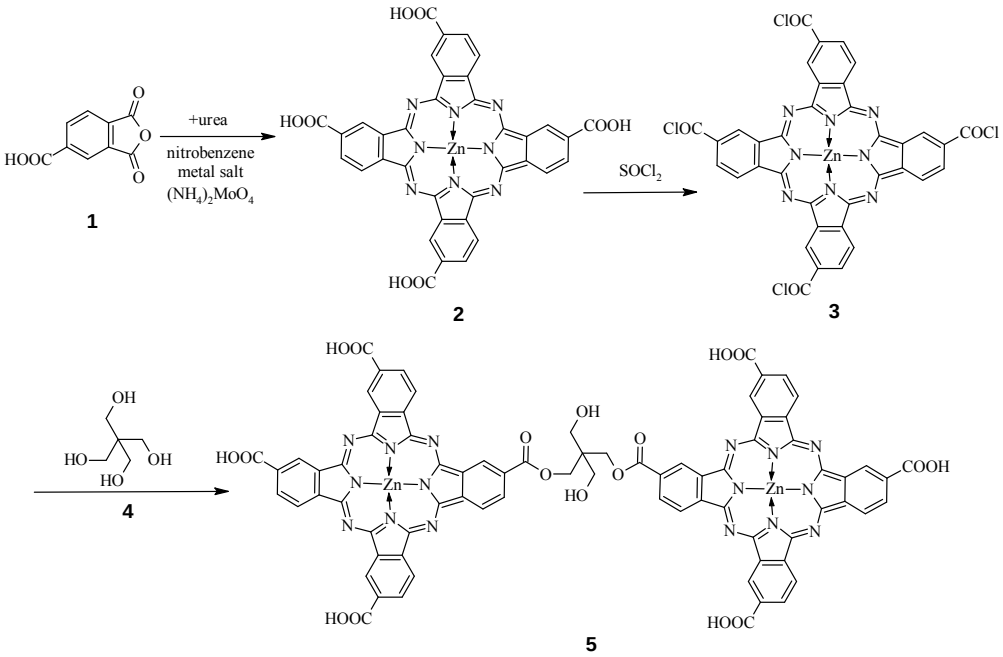
The chromophore structures raised great interest and thus a great number of studies were performed upon them. These structures are especially the ones that absorb in the wavelength range of 550-700 nm and have high resistance at light, chemical agents and temperatures, namely porphyrinic and phtalocyanine structures [4]. Another challenge is represented by the improvement of the way of transfer of the electric charge towards the transport system, the sensitized film and then towards the electrolyte, respectively. For this a good bond through complexation or other interactions between the TiO_2 layer and the light absorbing cromophore system is needed [5]. The molecular structure of the dye plays an important role in the DSSC type cells. The performance of a solar cell of this type depends on the ability to harvest light radiation provided by the chromophore system and on the relative energy levels of the dye and the charge transfer kinetics at the existing interfaces. In order to obtain efficient solar cells it is necessary to use some synthesized organic pigments with high physico-chemical properties [6,7].

The aim of the paper was to obtain new chromogens, of own design, which are able to assure a good light absorption (phthalocyanine structures- Zn complexes which absorb in the range of 650-750 nm) and to have o good binding with TiO_2 by increasing the number of anchors with the possibility of forming 3D aggregates similar with chlorophyllian pigments and to test them in order to obtain Gratzel type solar cells.

The synthesis steps included:

- synthesis and characterization of zinc phthalocyanine tetracarboxylic acid;
- the connection of two phtalocyanine chromophore units by means of a spacer according to scheme 1.

The proposed structures considered above are part of the research area which aims since 1991 to replace the ruthenium based complexes with chromophore systems which have at least similar performance and are easily obtained. If some researches regarding the obtaining of some coupled phtalocyanine dyes have been made before [8], the novelty in this paper consists in the use as spacer between the two molecules of a residue of pentaerythritol, which, due to hydroxyl groups offers the possibility of obtaining complex three-dimensional aggregates with potential beneficial effects on the ability to absorb light and to generate electric charges.



Scheme 1. The synthesis of new chromophores with potential use in obtaining Gratzel type solar cells

2. Experimental part

2.1. Materials

All reagents and solvents were of reagent grade quality and were purchased from Aldrich, Germany. All solvents were dried and purified.

2.2. Equipment

The IR spectra were recorded on a FT-IR Jasco 6300 spectrophotometer equipped with ATR Specac Golden Gate (KRS5 lens) in the range 400-4000 cm^{-1}. Elemental analysis were recorded with Perkin Elmer 2400 II CHNS Analyzer. Absorption spectra in the UV-visible region were recorded with a Jasco V550 spectrophotometer. Fluorescence excitation and emission spectra were recorded on Jasco FP 6500 spectrofluorometer using 1 cm pathlength cuvettes at room temperature.

2.3. Synthesis

a. Synthesis of zinc phthalocyanine tetracarboxylic acid 2

In a 3 neck flask, with a thermometer and kept under stirring, 50 ml nitrobenzene and 15 g (0.078 mol) trimellitic anhydride are added. After their

dissolution, 44 g (0.733 mol) of urea, 0.1 g ammonium molybdate and 2.6 g (0.0195 mol) $ZnCl_2$ are added. The mixture is heated for 8 hours at 185 °C. After cooling, 100 ml of methanol is added and the mixture is stirred 1 hour at reflux, followed by filtering. Then the filtered is washed with methanol until traces of nitrobenzene are removed. The precipitate is then suspended in 40 ml KOH 20% solution and it is hydrolyzed for 24 hours at reflux. It is filtered while hot, and the filtered result is acidulated until a positive reaction on Congo Red paper takes place. The precipitated product is then filtered, washed with water and dried. For a supplementary purification the product is dissolved in 96% H_2SO_4 and is reprecipitated by pouring it into water with ice (yield of 55%).

Anal. Calc. for $C_{36}H_{16}N_8O_8Zn$ (753.97 g/mol): C, 57.35%; H, 2.14%; N, 14.86%; Found: C, 57.22%; H, 2.01%; N, 14.70%;

IR (ATR, cm^{-1}): 3300 cm^{-1}(ν_{O-H}), 3103 cm^{-1}, 3078 cm^{-1}, 3042 cm^{-1} (ν_{C-H}), 1710 cm^{-1} ($\nu_{C=O}$), 1654 cm^{-1} ($\upsilon_{C=N}$), 1590 cm^{-1} (ν_{C-C}), 1484 cm^{-1} (υ_{C-N}), 1446 cm^{-1}, 1284 cm^{-1}, 1173 cm^{-1} (δ_{C-O}), 1228 cm^{-1}, 1088 cm^{-1} (δ_{C-H}), 1004 cm^{-1}, 880 cm^{-1}, 770 cm^{-1}, 705 cm^{-1}, 570 cm^{-1}, 499 cm^{-1}, 435 cm^{-1}.

b. Synthesis of zinc phthalocyanine tetracarbonyl tetrachloride 3

In a 3 neck flask with a thermometer and under stirring 2 g (2.6 mmol) zinc phthalocyanine tetracarboxylic acid and 10 ml $SOCl_2$ are added. The mixture is heated at reflux for 12 hours. The $SOCl_2$ excess is distilled and 10 ml of benzene is added. The product is filtered and vacuum dried (yield 76%).

c. Synthesis of compound 5

In a flask 0.2 g (0.24 mmol) zinc phthalocyanine tetracarbonyl tetrachloride, 0.017 g (0.13 mmol) pentaerythritol and 25 ml DMF are added. It is heated at 100 °C for 6 hours. 25 ml water is then added and heated for 2 more hours. The mixture is then cooled, it is acidulated with acetic acid at pH = 4 and it is filtered. At the end it is washed with methanol. The product is separated by column chromatography from silicagel using as eluent a mixture of tetrahydrofuran : ethyl acetate 10:1 (v/v) (yield 20%).

Anal. Calc. for $C_{77}H_{40}N_{16}O_{18}Zn_2$ (1608.06 g/mol): C, 57.51 %; H, 2.51; N, 13.94; Found: C, 57.48; H, 2.40; N, 13.78;

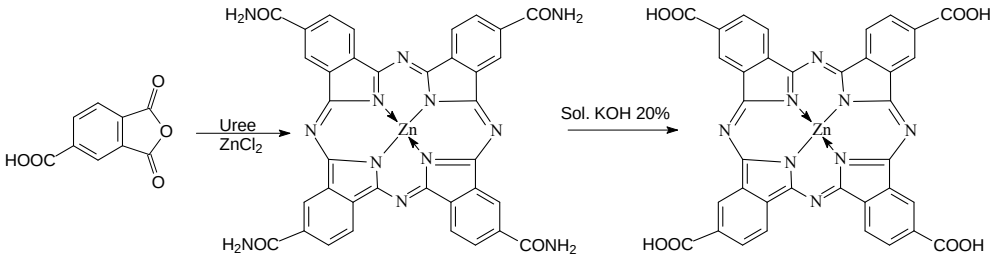
IR (ATR, cm^{-1}): 3260-3200 cm^{-1}(ν_{O-H}), 3108 cm^{-1}, 3070 cm^{-1}, 3040 cm^{-1} (ν_{C-H}), 1732 ($\nu_{C-O\ ester}$) (1705 cm^{-1} ($\nu_{C=O}$), 1650 cm^{-1}($\upsilon_{C=N}$), 1576 cm^{-1} (ν_{C-C}), 1480 cm^{-1}(υ_{C-N}), 1472cm^{-1} (υ_{C-O-C}) 1442 cm^{-1}, 1284 cm^{-1}, 1167 cm^{-1} (δ_{C-O}), 1218 cm^{-1}, 1081 cm^{-1} (δ_{C-H}), 876 cm^{-1}, 740 cm^{-1}, 710 cm^{-1}, 520 cm^{-1}, 494 cm^{-1}, 428 cm^{-1}.

3. Results and discussions

3.1. The synthesis of new phtalocyanine compound 5

The obtaining of the new original compound involves the following steps:
- the synthesis and characterization of zinc phtalocyanine tetracarboxylic acid ;
- the binding of two phtalocyanine chromophore units by a spacer, according to scheme 1.

The synthesis of zinc phtalocyanine tetracarboxylic acid was made according to scheme 2.



Scheme 2. Synthesis of zinc phthalocyanine tetracarboxylic acid 2

The synthesis consists in mixing the trimellitic anhydride with urea and the metallic salt (4:20:1.1 molar ratio) in nitrobenzene, then the catalyst (ammonium phosphomolybdate) is added and the mixture is heated at 180 °C for 8 hours. After the reaction takes place, the mixture is cooled down, it is filtered, and the solid product is washed with methanol for the complete removal of nitrobenzene and it is dried.

As a result of the reaction between the trimellitic anhydride and urea in the presence of $ZnCl_2$ the corresponding amide as the major product due to the large excess of urea is obtained. This fact is confirmed by the IR spectrum of the intermediary product by the band from 3100 cm^{-1} and by the bands in the region 1500-1760 cm^{-1} [9]. In order to obtain zinc phtalocyanine tetracarboxylic acid, hydrolysis is needed, which is made by treating the mixture with 20% KOH solution for 24 hours at reflux, acidulation and filtration. For a more advanced purification, the synthesized product is dissolved in a 10% KOH solution by heating, filtered while hot, and the filtrate is acidulated with HCl 35% when the zinc tetracarboxy phtalocyanine precipitates, which is isolated by filtering and washed with cold water followed by drying. For further purification the dried product is dissolved in H_2SO_4 conc. (1g phtalocyanine compound in 20 ml H_2SO_4 96%), after is poured in water with ice (10 times the H_2SO_4 used volume).

The synthesized compound was characterized by elemental analysis, IR spectra and absorption and emission electronic spectra.

IR analysis reveals the characteristic bands of the phthalocyanine macrocycle (cm^{-1}): - 3103, 3078, 3042 (νC-H), 1654 (υC=N), 1590 (νC-C), 1484 (υC-N), - 1228, 1088 (δC-H).

The carboxyl groups can be highlighted by bands at 1710 cm^{-1} (νC=O), 1173 (δC-O) and 3300 cm^{-1} (νO-H).

According to the data from the literature [9], the characteristic peaks confirm the obtaining of zinc phtalocyanine tetracarboxylic acid.

The second step of the synthesis aimed the binding of two phtalocyanine chromophore units with a spacer. As spacer pentaerythritol was used.

The transformation of zinc phtalocyanine tetracarboxylic acid in acyl chloride was made by heating at reflux with $SOCl_2$ excess for 12 hours. Finally the $SOCl_2$ excess is distilled, benzene is added and the product is filtered. After that is washed with benzene and acetone and is dried in a dessicator.

The reaction with pentaerythritol takes place by the dissolution of the acid chloride in N,N-dimethylformamide, addition of pentaerythritol (zinc phthalocyanine tetracarbonyl tetrachloride : pentaerythritol 2:1.1 molar ratio) and heating at 100 °C for 4 hours. Finally to hydrolyze the unreacted acid chloride groups, water is added and the reactor was kept at 50 °C under stirring for 6 hours. The final product is separated by filtration, followed by washing with water and drying.

The analysis of the purity has been made by thin film chromatography on silicagel using as eluent a mixture of tetrahydrofuran: ethyl acetate 10:1 (v/v). Several spots typical to the resulted reaction products are obtained. For the desired product (being the most polar) the R_f value is 0.4.

The separation was done by column chromatography using as eluent the mixture presented above. Finally we obtain the purified product with a yield of 20% compared to zinc phthalocyanine tetracarbonyl tetrachloride used.

The synthesized compound is moderately soluble in water, DMSO and DMF and highly soluble in alkaline and ammonia solution.

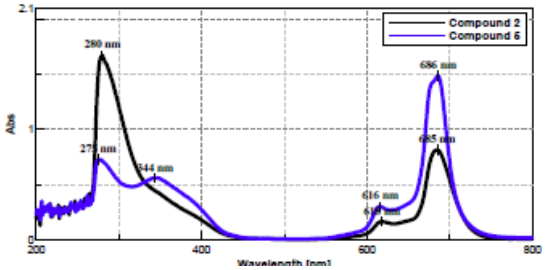
The obtained compound was characterized by IR spectra and absorption and emission spectra.

In the IR spectra for compound number 5 one can see the newly formed bands at 1732 and 1472 cm^{-1} which correspond to the ester bond and some bands characteristic to the OH group at 3200-3260 cm^{-1} (wide band).

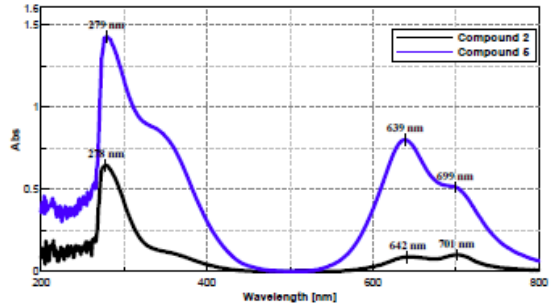
3.2. The study of the photophysical properties of the obtained compounds

The recorded absorption and emission spectra in different solvent (water, N,N-dimethylformamide, water-ethanol mixture) of the newly synthesized

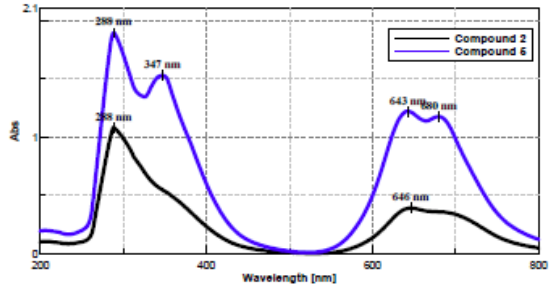
compound have been analyzed in comparison with the ones of zinc phtalocyanine tetracarboxylic acid. The absorption spectra presented in fig. 1, were measured at the same concentration (10^{-5} mol/l) for both compounds, using quartz cells with 1 cm optic way; as reference the corresponding solvent was used.



a. N,N-dimethylformamide



b. Water



c. ethanol-water 1:1 (vol)

Fig. 1. Absorption spectra of Zn tetracarboxy phtalocyanine and compound **5** (conc. 10^{-5} mol/l)

The phtalocyanine compounds have the tendency to aggregate in solution due to the electronic interactions present in the macrocycles. The aggregation is usually illustrated by a coplanar association between the rings, progressively from the monomer to the dimer or supramolecular complexes of higher order and is guided by the increase of the van der Waals forces between the macrocycles. In aggregated state the electronic structure of the phtalocyanine cycle is disturbed, resulting in modifying the properties of the fundamental and excited state. The

aggregation in the phtalocyanine case results in widening the Q band with a shift coresponding to hipsocrom (H type aggregate), or batocrom (J type aggregate) wavelength, or by splitting band Q. The recorded spectral effects depend on the vicinity of the rings, on the type and volume of the substituent, on the slope of the macrocycles, on their overlapping, and on other factors that can influence the overlapping of the π electron cloud from the phtalocyanine cycles.

The electronic absorption spectra of zinc phtalocyanine tetracarboxylic acid in N.N-dimethylformamide shows an intense absorption band (Q band) at 685 nm which corresponds to the electronic transition π-π* in the macrocycle conjugated system. The band position and the shape of the spectral curve corresponding to the maximum of absorption is defined by the nature of the carboxylic substituents present on the macrocycle. Compared with the unsubstituted Zn phtalocyanine, the electron withdrawing carboxyl groups shift the Q band towards red. The presence of a sharp band, corresponding to this absorption maximum shows that at this concentration, the proportion of the monomeric form is very large.

The second band, situated at 618 nm corresponds to the aggregated form, usually to the dimer. The peak intensity is weaker due to the large proportion of monomeric form. The absorption spectra measured in water and in water:ethanol mixture 1:1 (vol) show that in these cases the proportion of the aggregated form increases with the decrease of the intensity of the absorption maximum. In water, compared to the spectrum in DMF, a bathochromic effect is seen, the absorption spectra being present at 642 and 701 nm. In ethanol:water solution (1:1) the same effect is recorded, indicating that the proportion of the aggregated forms is a little bit larger.

The analysis of the spectral data for the two compounds shows the obvious superiority of compound 5 regarding the absorption of light in the UV-VIS range. For the same molar concentrations the absorption has superior values.

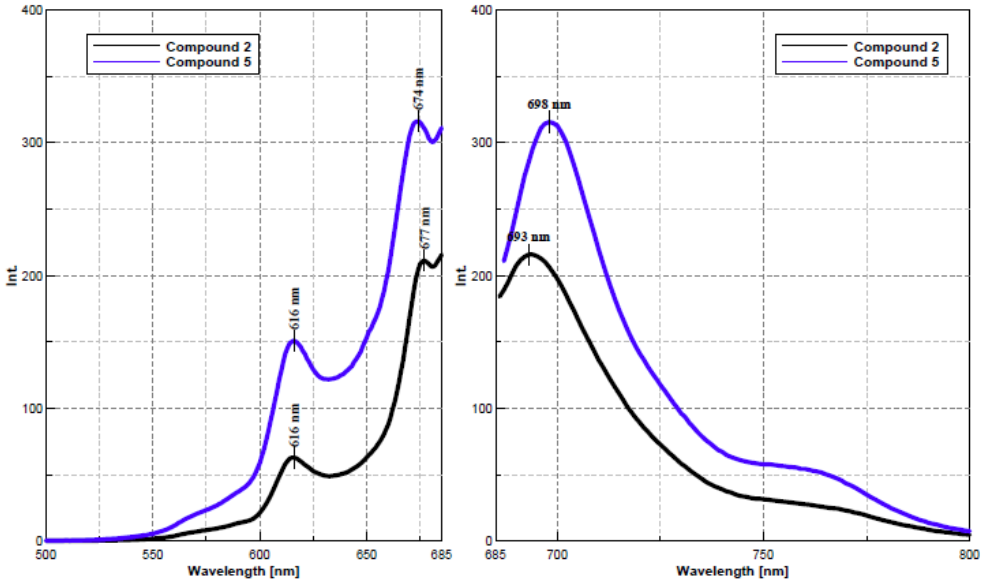
In the case of compound 5, if for the spectrum in DMF is recorded basically the same phenomenon as in the case of compound 2, except that in the UV range the absorption maximum is less intense compared with compound 2 and is also splitted. For the other 2 solvents the differences are more important. The aggregated forms, with an absorption maximum at 640 nm have a larger proportion compared to compound 2. The broadening of the absorption domain and the increase of the intensity leads to a better harvesting of the incident light, thus one of the research objectives has been met.

Also, for the same compound a hypsochromic shift of the lower absorption maximum is seen compared with zinc tetracarboxy phtalocyanine for all the 3 analyzed solvents, in the case of water being more substantial.

The excitation and emission spectra measured in N.N-dimethylformamide at a concentration of 10^{-5} mol/l, using a quartz cell with 1 cm optic way, show a

bathochromic shift for compound 5 in the case of emission. The fluorescence is more intense in the case of compound 5 compared with the one of compound 2.

The emission spectrum presented in figure 2 shows that the Zn phtalocyanine tetracarboxylic acid has an intense fluorescence with an emission maximum at 693 nm, having a Stokes shift of 13 nm. The excitation spectrum shows the existence of a maximum like to the absorption one due to the Soret band in the region 350-390 nm and due to the Q band in the region 600-680 nm respectively. For compound **5** an intense fluorescence is observed at 698 nm, the Stokes shift being of 24 nm.



a. excitation b. emission

Fig. 2. The excitation and emission spectra of Zn tetracarboxy phthalocyanine and compound number 5 (DMF, conc. 10^{-5} mol/l)

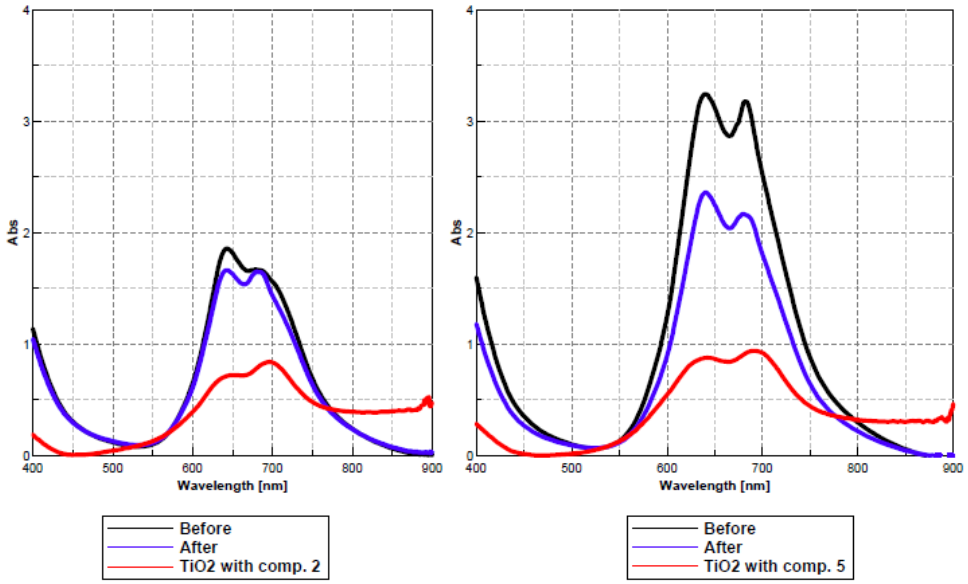
3.3. Tests regarding the adsorption of the obtained dyes on TiO_2 substrates

In order to test the adsorption and retention ability of the synthesized dyes on TiO_2 substrates TiO_2 layers were deposited on glass. Nanometric TiO_2 (Degussa P25) was used, which was dispersed in 10% acetic acid solution and then it was deposited by a brush on rectangular glass plates with dimensions of 5x2.5 cm. The plates were sintered at 400 °C for 30 minutes. The coated layers have a thickness of about 20 μm (measured with a micrometer).

The plates were immersed in dye solutions (10^{-4} mol/l) ethanol:water 1:1 (v/v) at pH = 10, made with NH_3 25% solution, for 2 hours. The plates were then

washed 2 times with distilled water and with ethanol for the removal of the unfixed dye, followed by drying in nitrogen flux.

To verify the fixation ability, spectral analysis has been carried out both on the dye solutions and on the thin TiO_2 substrates. The absorption spectra of the solutions belonging to the two dyes before and after deposition on TiO_2 are shown in fig. 3.



a. For compound 2 **b.** For compound 5

Fig. 3. The absorption spectra of the solutions used to transfer the dyes on the TiO_2 substrate

The spectra for the TiO_2 thin films sensitized with dye were made as reflectance spectra and have been converted in absorption spectra using Spectra Manager I software. They are presented in fig. 4.

The data analysis shows that the new obtained compound has much better adsorption and fixation properties on the TiO_2 layer than the Zn phtalocyanine tetracarboxylic acid.

The dye enters very well in the TiO_2 layer, both the absorption spectra for TiO2 layer in direct contact and for glass contact being almost identical. The TiO_2 spectra which was sensitized with the 2 compounds show the existence of some supramolecular aggregation complexes in a much greater proportion for the newly synthesized compound.

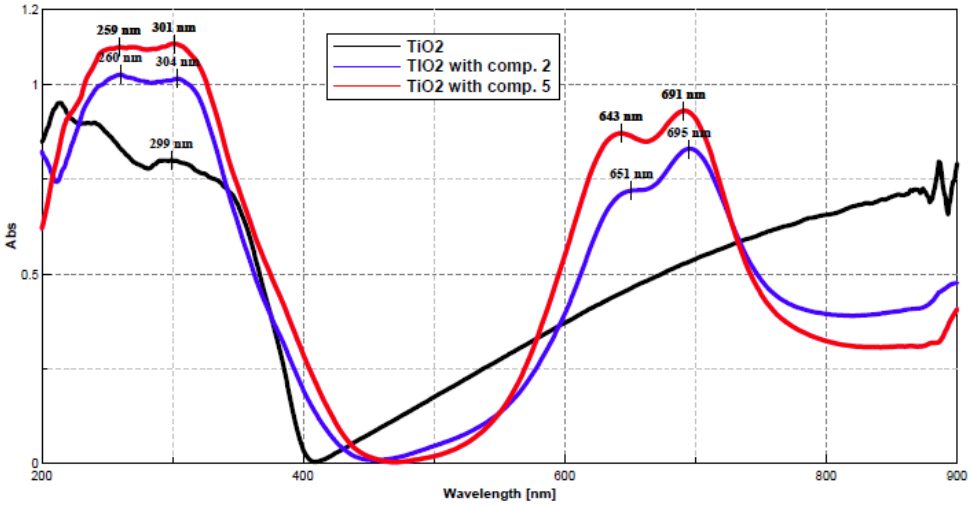


Fig. 4. Absorption spectra of the adsorbed dyes on TiO_2 layer

4. Conclusions

A novel cromophore compound have been synthesized by binding two phtalocyanine by means of a pentaerythritol residue.

The obtained dye was analyzed from the point of view of its spectral behavior and its adsorption fixation ability on the TiO_2 substrate.

The obtained compound, compared with Zn phtalocyanine tetracarboxylic acid show higher performances both in terms of absorption and emission of light as well as on the fixation in the thin TiO_2 layer.

Future research will analyze the behavior of the newly obtained cromophores in view of Gratzel type solar cells applications.

Acknowledgement

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R E F E R E N C E S

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