Макрогетероциклы
http://macroheterocycles.isuct.ru

DOI: 10.6060/mhc2012.120466n

Synthesis and Some Properties of Phosphonomethyl Substituted Phthalocyanines

Alexey N. Komissarov, Dmitry A. Makarov, Olga A. Yuzhakova, Lubov P. Savvina, Nina A. Kuznetsova, Oleg L. Kaliya, Evgeny A. Lukyanets, and Vladimir M. Negrimovsky@

State Research Center “Organic Intermediates and Dyes Institute” (SRC “NIOPIK”), 123995 Moscow, Russia
@Corresponding author E-mail: vnegrimovsky@mail.ru

A new method of synthesis of phthalocyanines with phosphonate moieties by reaction of chloromethyl substituted phthalocyanines with phosphorus trichloride in the presence of aluminum chloride followed by hydrolysis of the intermediately formed phosphonic acid chlorides under mild conditions is developed. A number of phosphonomethyl substituted phthalocyanines with different central metal atoms (aluminum, silicon, titanium, copper, zinc and gallium) and/or with the presence of unreacted chloromethyl groups were obtained. Significant dependence of monomer – aggregate equilibrium and, as consequence, of photochemical and photophysical properties of the synthesized complexes on pH value was found. Quantum yields of singlet oxygen generation and photodegradation of complexes were determined. The photodestruction of the synthesized compounds, except of rather photostable copper phthalocyanine, proceeds with participation of self-sensitized singlet oxygen and is significantly accelerated by the presence of chloromethyl groups in the macrocycle.

Keywords: Phthalocyanines, phosphonic substituents, electronic absorption spectra, fluorescence, photodegradation, singlet oxygen generation.

Introduction

Phthalocyanines possess some unique physical and chemical properties. Many compounds of this class are traditionally used as dyes,[1] catalysts,[2] materials for nonlinear optics,[3] gas sensors,[4] *etc*. Phthalocyanines and porphyrins are considered as effective photosensitizers of titanium dioxide solar cells.[5,6] The introduction of hydroxyl[7] or acid groups[8,9] in the phthalocyanines allows to bind them to metal oxide surface, and phosphonate substituents provide the most effective binding.[8] Phthalocyanines are used also as photosensitizers for photodynamic therapy of cancer (PDT) [10,11] and phthalocyanines with phosphonate groups have the marked advantages here.[12]

The present work is devoted to search an approach for synthesis of phthalocyanines with phosphonate moieties. A new method of phthalocyanines phosphorylation is proposed, a series of phosphonomethyl substituted phthalocyanines have been synthesized and some of their properties have been studied.

Experimental

Chloromethyl substituted aluminum, copper and zinc phthalocyanines were obtained by known methods.[13] Chloromethyl substituted titanyl phthalocyanine was prepared according to the method.[14] Chloromethyl substituted gallium and silicon phthalocyanines were obtained by chloromethylation of unsubstituted chlorogallium and dichlorosilicon phthalocyanines correspondingly according to known method.[13] Tetrasodium salt of α,α’-(anthracene-9,10-diyl)bismethylmalonic acid (ADMA) was obtained by known methods.[15,16] Other chemicals with purity not less than reagent grade were purchased from LLC "Sigma-Aldrich Rus".

Electronic absorption spectra were recorded on spectrophotometers Cary 50 UV-Vis (Varian) and Hewlett Packard 8453. Fluorescence spectra were recorded on a spectrofluorimeter Cary Eclipse (Varian) with a xenon lamp as the excitation source. Elemental analysis of C, H, N were performed on the C, H, N, S-analyzer Vario EL cube (Abacus). Elemental analysis of P and Cl were determined by methods of quantitative microanalysis.[17] ^{1}H NMR spectra were recorded on spectrometer Inova 500 MHz NMR (Varian), internal standard TMS.

Hydroxy[octakis(phosphonomethyl)phthalocyaninato]aluminum (LAlOH). Triethylamine (5 ml, 0.0359 mol) was added to aluminum chloride (19.2 g, 0.144 mol) and phosphorus trichloride (12 ml, 0.137 mol) was added into the mixture at 70 °C. Then chloro[octakis(chloromethyl)phthalocyaninato]aluminum (4 g, 4.15 mmol; chlorine content 34.1 %) was added and reaction mixture was heated with stirring at 70-80 °C for 17 hours. After cooling the mass was discharged on ice, filtered, washed with water and heated at 60-70 °C in 10 % hydrochloric acid for 2 h. The product was washed with water and dried in vacuum over phosphorus pentoxide at 100 °C. Yield of LAlOH 4.8 g (88.4 %). Found: C 36.45, H 3.22, N 8.20, P 18.72 %. Calculated for $C_{40}H_{41}AlN_8O_{25}P_8$: C 36.71, H 3.16, N 8.56, P 18.94 %. ^{1}H NMR (D_2O + NaOD, 293 K) δ_H ppm: 3.39 (8H, m, Ar-CH_2-P), 3.59 (8H, m, Ar-CH_2-P), 8.10 (4H, m, Ar-H), 9.30 (4H, m, Ar-H) (Figure 1).

Dichloro[octakis(phosphonomethyl)phthalocyaninato]silicon ($LSiCl_2$). $LSiCl_2$ was prepared from dichloro[octakis(chloromethyl)phthalocyaninato]silicon (chlorine

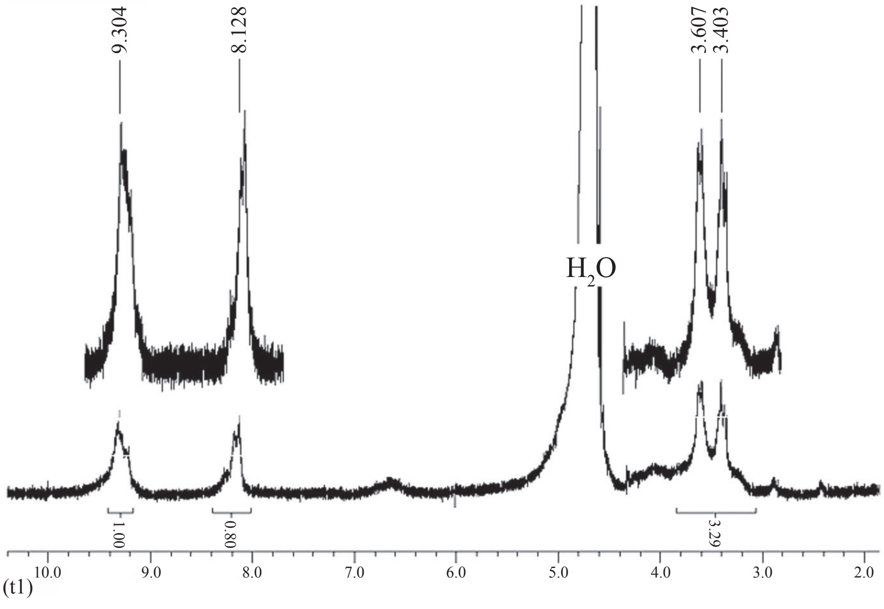


Figure 1. ^1H NMR spectra of hydroxy[octakis(phosphonomethyl)phthalocyaninato]aluminum (LAlOH).

content 35.2 %) analogously to synthesis of LAlOH after 15 h heating with 60.0 % yield. Found: C 34.84, H 3.10, Cl 5.79, N 7.81, P 17.56 %. Calculated for $C_{40}H_{40}Cl_2N_8O_{24}P_8Si$: C 35.23, H 2.95, Cl 5.19, N 8.21, P 18.17 %.

Elemental analysis of a sample, taken from reaction mixture after 3 hours and treated as above, showed the presence of five phosphonomethyl and three chloromethyl groups.

Oxo[octakis(phosphonomethyl)phthalocyaninato]titanium (LTiO). LTiO was prepared from oxo[octakis(chloromethyl) phthalocyaninato]titanium (chlorine content 29.7 %) analogously to synthesis of LAlOH after 20 h heating with yield 71.0 %. Found: C 35.82, H 3.06, N 8.03, P 18.12 %. Calculated for $C_{40}H_{40}N_8O_{25}P_8Ti$: C 36.14, H 3.03, N 8.43, P 18.64 %.

[Octakis(phosphonomethyl)phthalocyaninato]zinc (LZn). LZn was prepared from [octakis(chloromethyl)phthalocyaninato]zinc (chlorine content 28.8 %) analogously to synthesis of LAlOH after 11 h heating. After additional re-precipitation from alkali solution by hydrochloric acid and drying as above the product was obtained with yield 77.6 %. Found: C 35.87, H 3.51, N 7.97, P 17.98 %. Calculated for $C_{40}H_{40}N_8O_{24}P_8Zn$: C 36.12, H 3.20, N 8.42, P 18.60 %.

[Octakis(phosphonomethyl)phthalocyaninato]copper (LCu). LCu was prepared from [octakis(chloromethyl)phthalocyaninato] copper (chlorine content 29.6 %) analogously to synthesis of LAlOH with yield 88.0 %. Found: C 35.74, H 3.34, N 7.98, P 18.09 %. Calculated for $C_{40}H_{40}N_8O_{24}P_8Cu$: C 36.17, H 3.04, N 8.44, P 18.66 %.

Hydroxy[octakis(phosphonomethyl)phthalocyaninato] gallium (LGaOH). LGaOH was prepared from chloro[octakis(chloromethyl)phthalocyaninato]gallium (chlorine content 31.5 %) analogously to synthesis of LAlOH with yield 86.5 %. Found: C 35.17, H 3.31, N 7.64, P 17.86 %. Calculated for $C_{40}H_{41}GaN_8O_{25}P_8$: C 35.55, H 3.06, N 8.29, P 18.14 %.

Hydroxy[chloromethylheptakis(phosphonomethyl) phthalocyaninato]aluminum (L'AlOH). L'AlOH was prepared from chloro[octakis(chloromethyl)phthalocyaninato]aluminum (chlorine content 34.1 %) analogously to synthesis of LAlOH after 4 hours heating with yield 85.4 %. Found: C 37.27, H 3.52, Cl 2.65, N 8.54, P 16.90 %. Calculated for $C_{40}H_{39}AlClN_8O_{22}P_7$: C 38.04, H 3.11, Cl 2.81, N 8.87, P 17.17 %. ^1H NMR (D_2O + NaOD, 293 K) δ_H ppm: 3.37 (8H, m, Ar-CH_2-P), 3.56 (6H, m, Ar-CH_2-P), 4.9 (2H, m, Ar-CH_2-Cl), 8.15 (4H, m, Ar-H), 9.31 (4H, m, Ar-H).

Oxo[chloromethylheptakis(phosphonomethyl)phthalocyaninato]titanium L'TiO. L'TiO was prepared from oxo[octakis(chloromethyl)phthalocyaninato]titanium (chlorine content 29.7 %) analogously to synthesis of L'AlOH with yield 68.0 %. Found: C 37.15, H 3.13, Cl 2.78, N 8.58, P 15.96 %. Calculated for $C_{40}H_{38}ClN_8O_{22}P_7Ti$: C 37.45, H 2.99, Cl 2.76, N 8.73, P 16.90 %.

Methods for Determination of Quantum Yields of Photodegradation and Singlet Oxygen Generation

Photochemical properties were studied in the aqueous solutions at p*H* 8.5, 9.5 and 12. At first, ~$1 \cdot 10^{-6}$ M solution of the examined compound in 0.1 M sodium hydroxide was prepared, which was neutralized with hydrochloric acid to the corresponding p*H*. Fluorescence quantum yields (Φ_{fl}) of phosphonomethyl substituted phthalocyanine solutions were referred to the standard – a solution of unsubstituted zinc phthalocyanine in DMSO (Φ_{fl} = 0.20[18]) with the same excitation intensity on λ_{exc}. Spectra obtained were normalized on the intensity of standard fluorescence.

Quantum yields of the photodecomposition (Φ_d) and singlet oxygen generation (Φ_Δ) were estimated by excitation of phthalocyanine solutions in 1 cm standard cell in the long-wavelength absorption band *Q*. For excitation a xenon lamp (150 W) was used; 520 nm glass filter and water filter were used to cut off ultraviolet and infrared radiation; interference filter of 710 ± 10 nm was placed in the light path. The intensity of the light was measured using a Thorlabs silicon photodiode. The part of absorbed light was calculated by integrating of an overlap of the filters transmission spectra and the sample absorption spectrum.

Φ_Δ values were determined relatively to the sulfonated aluminum phthalocyanine (in water Φ_Δ 0.38[19]). Sulfonated aluminum phthalocyanine was irradiated through an interference filter with transmission 680 ± 25 nm. ADMA[15] was used as an acceptor of singlet oxygen. A solution of phthalocyanine (~$1 \cdot 10^{-5}$ M) containing acceptor ($6 \cdot 10^{-5}$ M) was irradiated in a 1 cm standard cell. Photosensitized oxidation of ADMA was controlled by intensity of band with maximum 401 nm in its electronic absorption spectra. The initial concentration of ADMA in all experiments was constant.

Next equation was used for calculation of Φ_Δ value:

$$\Phi_\Delta = \Phi_\Delta^{ref} \cdot \frac{W \cdot I_{abs}^{ref}}{W^{ref} \cdot I_{abs}}$$

where Φ_Δ^{ref} – quantum yield of singlet oxygen generation by sulfonated aluminum phthalocyanine (standard);

W and W^{ref} – rates of ADMA consuming during sensitization by investigated phthalocyanine and the standard, respectively;
I_{abs} and I_{abs}^{ref} – number of the absorbed photons by the sample and the standard, respectively.
The accuracy of Φ_d and Φ_Δ estimation was 10 %.

Results and Discussion

Earlier we have shown that phosphonomethyl substituted phthalocyanines are promising photosensitizers for PDT.[20] These complexes were synthesized via Michaelis-Arbuzov reaction of chloromethyl substituted phthalocyanines with trialkylphosphites and subsequent hydrolysis of intermediate alkyl phosphonates.[20] Due to stability of alkyl phosphonates to hydrolysis the harsh conditions were used at the last stage: complete hydrolysis was achieved by heating of intermediate esters with concentrated hydrobromic acid, which led to destruction and significant decrease of the yield. For example, the yield of the hydrolysis stage was only 17 % in case of zinc phthalocyanine.

Here we describe the new method of preparation of phosphonomethyl substituted phthalocyanines by the phosphorylation of chloromethyl substituted phthalocyanines with phosphorus trichloride in the presence of aluminum trichloride and consequent hydrolysis of intermediate chloroanhydrides of corresponding phosphonic acids in mild conditions. A series of octakis(phosphonomethyl) substituted phthalocyanines, which differ by central metal atom (LM, where M = hydroxyaluminum, dichlorosilicon, titanyl, copper, zinc and hydroxygallium) as well as complexes with some unreacted chloromethyl groups (L’M) were synthesized (Scheme 1).

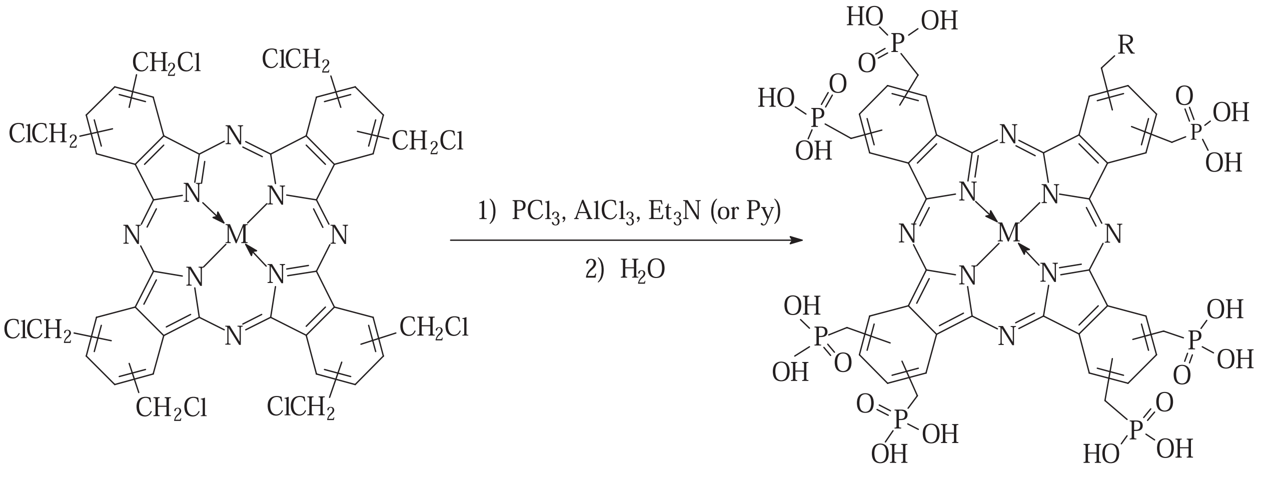
Starting chloromethyl substituted phthalocyanines are poorly soluble in mixture of phosphorus trichloride with aluminum chloride. The use of tertiary amines such as triethylamine or pyridine leads to formation of their complexes with aluminum chloride that increases solubility of starting compounds and allows to phosphorylate poly(chloromethyl)phthalocyanines with acceptable rate and high yield. But even in this case the complete conversion of chloromethyl groups requires a rather significant time – 15-20 hours. Reduction of the reaction time leads to incomplete conversion; for example, in the case of dichlorosilicon octakis(chloromethyl)phthalocyanine only five of the eight chlorine atoms in macrocycle were substituted after 3 hours of reaction proceeding.

The main advantage of this method is the ease of hydrolysis of the intermediate chloroanhydrides under heating with water, aqueous alkaline or acidic media. Under these conditions destruction of phthalocyanine macrocycle was not observed and overall yield of phosphonomethyl substituted phthalocyanines was rather high – 60-88 %.

The obtained phosphonomethyl substituted phthalocyanines in acidic form are insoluble neither in water nor in organic solvents, but their alkaline metal salts are readily soluble in aqueous solutions. At p*H* 12 their electronic absorption spectra are typical for monomer (not aggregated) state – an intense *Q* band is located in the range 700-740 nm, resolved vibration satellite is blue shifted by ~ 50 nm compared to the main peak (Figure 2). Seemingly, the absence of aggregation under these conditions is provided by full ionization of phosphonate groups, and, as a consequence, by a significant electrostatic repulsion of macrocycles carrying a large number of charges. As a result, at p*H* 12 molar extinction coefficients of complexes are rather high (Table 1) except for LTiO and $LSiCl_2$, which at high p*H* can form linear oligomers through oxygen at central atom of type -Si-O-Si-O.[21]

When changing p*H* from 12 to 8.5, electronic absorption spectra of $LSiCl_2$, LAlOH and LGaOH, which contain axial ligand, retain the character typical to the monomeric state. At the same time a noticeable decrease of LAlOH and LGaOH molar extinction coefficients along with 5-9 nm hypsochromic shift of *Q* band were observed. It indicates the presence of intermolecular interactions, most likely caused by intermolecular hydrogen bonding by phosphonate hydroxyl groups. Additional absorption at 650, 654 and 670 nm observed at p*H* 8.5 in the spectra of LCu, LZn and LTiO correspondingly indicates the appearance of aggregates (π-π dimers and oligomers). At p*H* < 8 absorption of aggregates is observed in the spectra of all studied compounds, and for LCu, LZn and LTiO it is characterized by the highest intensity. Lowering the p*H* value to 7 leads to precipitation of phosphonomethyl substituted phthalocyanines.

It is well-known that phthalocyanine complexes with metals used in this work (except copper), have long lifetimes



Scheme 1. Synthesis of phosphonomethyl substituted phthalocyanines LM и L’M. LM: R = $P(O)(OH)_2$, M = AlOH, $SiCl_2$, TiO, Cu, Zn, GaOH; L’M: R = Cl; M = AlOH, TiO.

of the excited states, high quantum yields of triplet state, therefore possess good photochemical activity, particularly, they are efficient sensitizers of singlet oxygen generation.[22,23] We have studied some photochemical properties of phosphonomethyl substituted phthalocyanines, which determine the possibility of practical application of this class of compounds, namely, fluorescence, generation of singlet oxygen and photostability.

Analogous p*H* dependence of absorption and fluorescence spectra was noted for $LSiCl_2$, LZn and LGaOH.

Quantum yields of fluorescence (Φ_{fl}) of phosphonomethyl substituted phthalocyanines at p*H* 12 are generally much higher than Φ_{fl} at p*H* 8.5 (Table 1), but lower than for other substituted phthalocyanines of corresponding metals in molecular solution. For example, LAlOH has Φ_{fl} 0.14 and 0.04 at p*H* 12 and 8.5, respectively, and these values are lower

Table 1. The maxima of the *Q* band absorption (λ_{max}) and fluorescence ($\lambda_{max}{}^{fl}$), molar extinction coefficients (ε_{max}), quantum yields of fluorescence (Φ_{fl}), photodegradation (Φ_d) and generation of singlet oxygen (Φ_Δ) of phosphonomethyl substituted phthalocyanines in aqueous solutions at different p*H*.

Compound	p*H* = 12				p*H* = 8.5				p*H* = 9.5		p*H* = 8.5	
	λ_{max}, nm	ε_{max}, $l \cdot mol^{-1} \cdot cm^{-1}$	$\lambda_{max}{}^{fl}$, nm	Φ_{fl}	λ_{max}, nm	ε_{max}, $l \cdot mol^{-1} \cdot cm^{-1}$	$\lambda_{max}{}^{fl}$, nm	Φ_{fl}	Φ_d,×10^2	Φ_Δ	Φ_d,×10^2	Φ_Δ
LAlOH (L'AlOH)	716	115 000	722	0,14	711	90 000	720	0,04	0.40 (1.00)	0.28 (0.40)	0.13 (0.40)	0.15 (0.20)
$LSiCl_2$	721	55 000	730	0,11	712	60 000	717	0,06	—	—	0.015	0.13
LTiO (L'TiO)	742	60 000	—	—	738	40 000	—	—	0.60 (4.0)	0.52 (~0.5)	—	—
LCu	704	110 000	—	—	697	50 000	—	—	≤ 0.005	< 0.01	—	—
LZn	703	110 000	716	0,12	697	60 000	710	0,03	3.40	~0.4	0.08	0.15
LGaOH	727	130 000	741	0,06	715	100 000	728	0.05	0.50	0.49	0.36	0.29

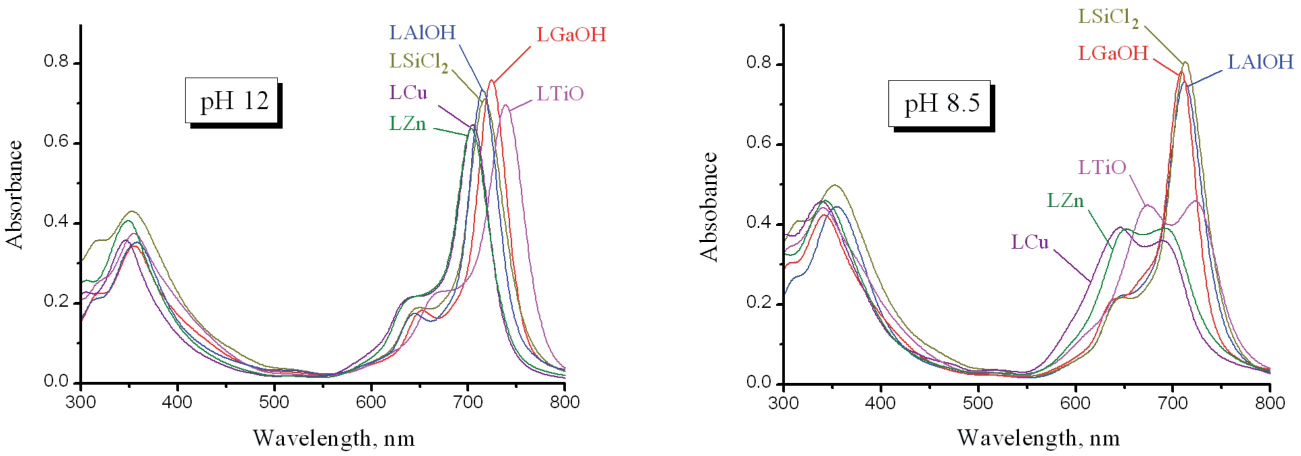


Figure 2. The electronic absorption spectra of phosphonomethyl substituted phthalocyanines in aqueous solutions at p*H*~12 and ~ 8.5.

Fluorescence in aqueous solution was found for $LSiCl_2$, LZn, LAlOH and LGaOH, unlike for LCu and LTiO where fluorescence was not detected. As an example, the normalized absorption and fluorescence spectra of LAlOH in aqueous solution at p*H* 12 and 8.5 are shown on Figure 3.

It could be seen that in absorption spectrum *Q* band is significantly broadened at p*H* 8.5 compared with that at p*H* 12. At the same time fluorescence spectra are the same at both p*H* values and represent a mirror image of the absorption *Q* band at p*H* 12 (Figure 3), and it means that specular reflection of the absorption and fluorescence spectra at p*H* 8.5 is not observed. This behavior clearly indicates that, unlike the highly alkaline solution, LAlOH aggregates occur in weakly alkaline solution. The latter ones do not possess fluorescence (only monomer fraction of LAlOH in solution is fluorescent) and lead to a broadening of the *Q* band in absorption spectra.

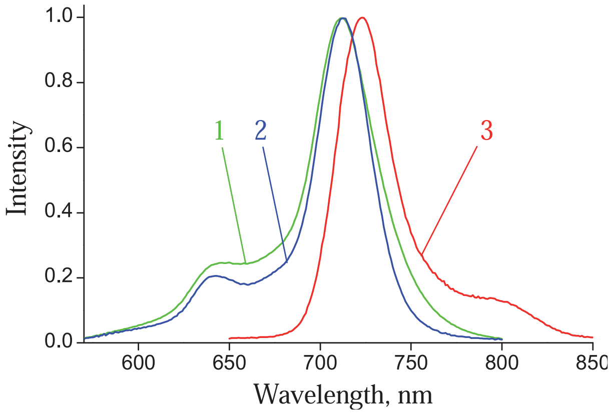


Figure 3. Normalized absorption (1, 2) and luminescence spectra (3) for LAlOH in aqueous solution with p*H* = 8.5 (1) and 12 (2). Normalized luminescence spectra at p*H* 8.5 and 12 are identical.

than typical for aluminum phthalocyanines (Φ_{fl} 0.3-0.4).[22] This fact shows the great role of competitive nonradiative degradation of excitation energy in phthalocyanines with phosphonomethyl groups. Stokes shifts (3-10 nm) are typical for phthalocyanines. Similarly to absorption, fluorescence maximum is shifted to longer wavelengths if p*H* increases.

Investigation of photostability showed that irradiation of air-saturated dye solutions with light corresponding to the *Q* band leads to the dye photobleaching (decrease of *Q* and *B* bands intensity without the appearance of new bands). Such character of process points on the chromophore destruction and formation of photoproducts not absorbing in visible range. According to literature data these photoproducts are most likely the corresponding phthalimides.[24]

Values of quantum yields of photodegradation (Φ_d, Table 1) show that most of the investigated phosphonomethyl substituted phthalocyanines have low, p*H* dependent photostability. Slight change of p*H* from 8.5 to 9.5 causes significant increase of quantum yield of photodegradation: for aluminum and zinc complexes Φ_d values raise up to 3-4 times. LGaOH is less sensitive to p*H* change in this range. Aggregation of compounds in weak alkaline medium can be one of the reasons of such behaviour since aggregates are not photochemically active due to rapid nonradiative degradation of the excited states.

Presence of chloromethyl groups in L'AlOH and L'TiO considerably decreases their photostability, presumably by either photoinitiation of radical reactions in solutions with involvement of chlorine atoms or increase of triplet state yields due to heavy atom effect. These complexes as well as LZn turned out to be the least photostable among studied compounds.

On the contrary LCu is exceptionally photostable. It does not undergo photobleaching during prolonged irradiation even in alkaline solutions with p*H* 12, that could be explained, by analogy with other copper phthalocyanines,[25] with low lifetime of its excited states.

We studied also the possibility of self-sensitized photo-oxidation of our complexes in aerated solutions by singlet oxygen ($^1O_2$). Analysis of solvent deuterium isotope effect is one of the principal test for $^1O_2$ involvement in the process. It is known that lifetime of $^1O_2$ in H_2O is 3.1 ms[26] and this value increases by 20 times in D_2O (68 ms)[27] leading up to 20-fold acceleration of reactions with $^1O_2$ in D_2O comparatively with H_2O. We compared the kinetics of the photobleaching of LGaOH, $LSiCl_2$, LAlOH and LZn solutions at p*H* 9.5 in H_2O and D_2O (Figure 4). In all cases the acceleration of photodegradation was observed – by 11.7, 3.4, 3.0 and 1.7 times, respectively, showing noticeable (in the case of LGaOH – dominant) contribution of $^1O_2$ in photodegradation process.

So, phosphonomethyl substituted phthalocyanines have low photostability in air-saturated aqueous solutions, and self-sensitized oxidation by $^1O_2$ is one of the reasons.

On the other hand, as can be seen from Table 1, phthalocyanines studied (except LCu) have high quantum yield of generation of $^1O_2$ (Φ_Δ), which determines their efficacy in PDT. Together with low photostability compared to other phthalocyanines this can be a significant advantage in using of these dyes as photosensitizers in photodynamic

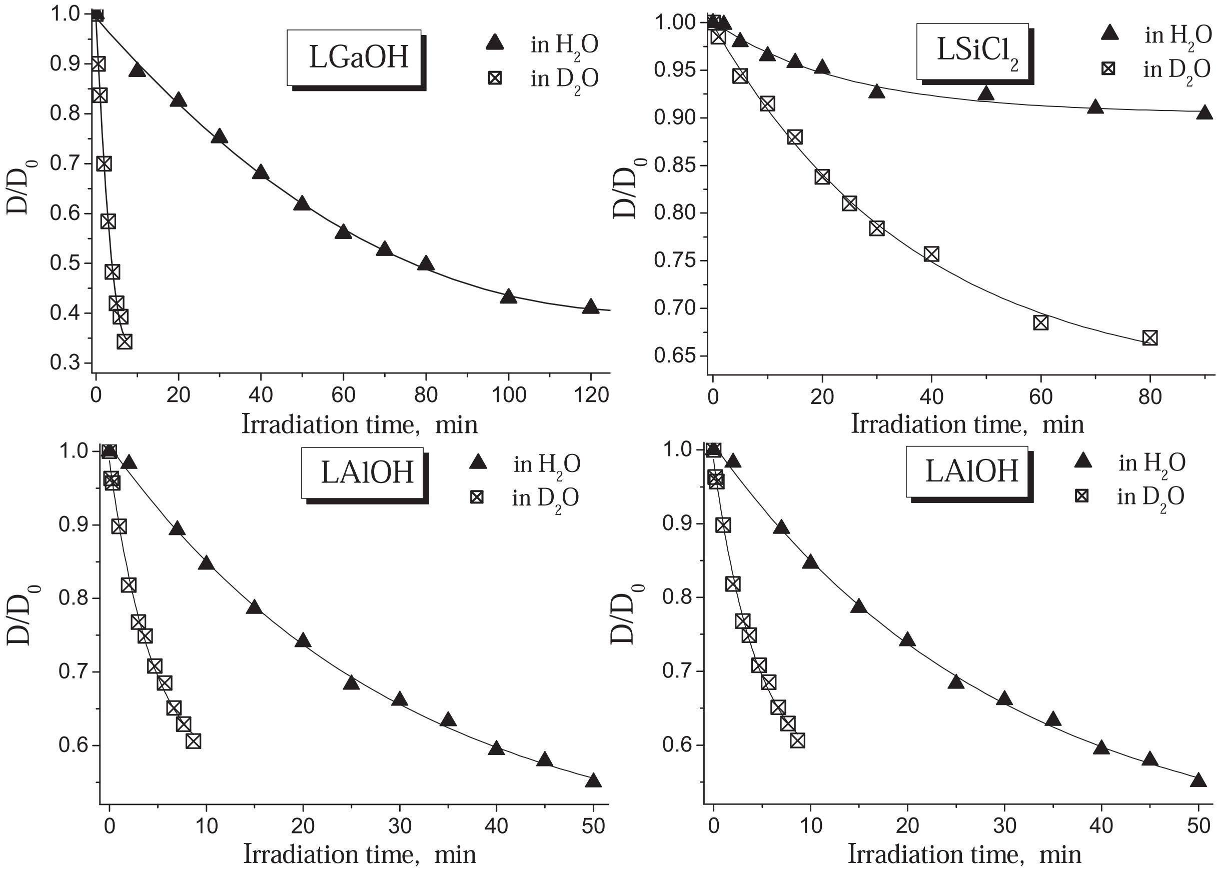


Figure 4. Photodegradation kinetic curves of LM in H_2O and D_2O at p*H* 9.5 and 710 ± 10 nm excitation light.

therapy since it allows to avoid an undesirable prolonged skin sensitivity of patients after treatment.

LSiCl$_2$ and LAlOH also showed satisfactory efficacy of $^1O_2$ generation at p*H* 8.5 (Φ_Δ 0.15 and 0.13, respectively). Previously,[28] Φ_Δ for LAlOH was found to be 0.11 at p*H* 7.4 (phosphate buffer), which was close to found in the present work. p*H* change from 8.5 to 9.5 led to almost twofold increase of Φ_Δ for these complex. L'AlOH generates $^1O_2$ even more effectively than LAlOH due to heavy atom effect (Φ_Δ 0.2 and 0.4 at p*H* 8.5 and 9.5, respectively). LCu is not active in the generation of $^1O_2$ as well as in other photochemical and photophysical processes studied.

Low photostability of LZn and L'TiO complexes at p*H* 9.5 did not permit the determination of Φ_Δ values with sufficient accuracy, so corresponding values given in Table 1 have an estimating character. Nevertheless, these values evidently show the efficient generation of $^1O_2$, particularly for titanyl phthalocyanines with $\Phi_\Delta \sim 0.5$. For LZn efficacy of $^1O_2$ generation (Φ_Δ 0.4) was slightly lower than typical values for zinc phthalocyanines in monomer form (Φ_Δ 0.6–0.7)[21] because of partial aggregation at p*H* 9.5. Lowering p*H* value to 8.5 increases the degree of LZn aggregation, leading to the decrease of Φ_Δ to 0.15.

Conclusions

A new method of synthesis of phthalocyanines with phosphonate moieties by reaction of chloromethyl substituted phthalocyanines with phosphorus trichloride in the presence of aluminum chloride followed by hydrolysis of the intermediately formed phosphonic acid chlorides at mild conditions is developed. A number of phosphonomethyl substituted phthalocyanines with different central metal atoms (aluminum, silicon, titanium, copper, zinc and gallium) and/or with the presence of unreacted chloromethyl groups were obtained. Significant dependence of monomer – aggregate equilibrium and, as consequence, of photochemical and photophysical properties of synthesized complexes on the p*H* value was found. Quantum yields of singlet oxygen generation and photodegradation of complexes were determined. The photodestruction of the synthesized compounds, except of rather photostable copper phthalocyanine, proceeds with participation of self-sensitized singlet oxygen and is significantly accelerated by the presence of chloromethyl groups in the macrocycle.

Acknowledgments. This work was supported by the Moscow City Government. The authors appreciate A.P. Perepuhov, the research assistant of Moscow Institute of Physics and Technology, for registration of NMR spectra.

References

1. Erk P., Hengelsberg H. Phthalocyanine Dyes and Pigments. In: *The Porphyrin Handbook* (Kadish K.M., Smith K.M., Eds.), Vol. 19, Academic Press. **2002**, p. 105.
2. Kaliya O.L., Lukyanets E.A., Vorozhtsov G.N. *J. Porphyrins Phthalocyanines* **1999**, *3*, 592.
3. Torre G., Vazquez P., Agullo-Lopez F., Torres T. *Chem. Rev.* **2004**, *104*, 3723.
4. Vilakazi S., Nyokong T. *Polyhedron* **2000**, *19*, 229.
5. Walter M., Rudine A., Wamser. C. *J. Porphyrins Phthalocyanines* **2010**, *14*, 759.
6. Imahori H., Umeyama T., Ito S. *Acc. Chem. Res.* **2009**, *42*, 1809.
7. Werner F., Gnichwitz J., Marczak R., Palomares E., Peukert W., Hirsch A., Guldi D. *J. Phys. Chem., B* **2010**, *114*, 14671.
8. Pechy P., Rotzinger F.P., Nazeeruddin M.K., Kohle O., Zakeeruddin S.M., Humpry-Baker R., Gratzel M. *J. Chem. Soc., Chem. Commun.* **1995**, 65.
9. Ardo S., Meyer G. *Chem. Soc. Rev.* **2009**, *38*, 115.
10. Lukyanets E.A. *J. Porphyrins Phthalocyanines* **1999**, *3*, 424.
11. Nyman E.S., Hynninen P.H. *J. Photochem. Photobiol., B* **2004**, *73*, 1.
12. Meerovich G.A., Lukyanets E.A., Yuzhakova O.A., Torshina N.L., Loschenov V.B., Stratonnikov A.A., Kogan E.A., Vorozhtsov G.N., Kunets A.V., Kuvshinov Y.P., Poddubny B.K., Volkova A.I., Posypanova A.M. *Proc. SPIE* **1997**, *2924*, 86.
13. Yuzhakova O.A., Kuznetsova N.A., Lukyanets E.A., Negrimovsky V.M. Patent RU 2405785, **2009**.
14. Lukyanets E.A., Negrimovsky V.M., Yuzhakova O.A., *et al.* Patent RU 2164136, **1998**.
15. Kuznetsova N., Gretsova N., Yuzhakova O., Negrimovsky V., Kaliya O., Lukyanets E. *Rus. J. Gen. Chem.* **2001**, *71*, 36.
16. Postovsky I.Ya., Bednyagina N.P. *Zh. Obshch. Khim.* **1937**, *7*, 2919.
17. Gelman N.E., Terent'eva E.A., Shanina T.M., Kiparenko L.M. *Metody kolichestvennogo organichesogo elementnogo mikroanaliza* [*Methods of Quantitative Organic Elemental Microanalysis*]. 1987. Moskva: "Khimiya", 296 p. (in Russ.).
18. Ogunsipe A., Chen Ji Y., Nyokong T. *New J. Chem.* **2004**, *28*, 822.
19. Kuznetsova N.A., Gretsova N.S., Derkacheva V.M., *et al. J. Porphyrins Phthalocyanines* **2003**, *7*, 147.
20. Vorozhtsov G.N., Kogan E.A., Loshchenov V.B., *et al.* Patent RU 2146144, **1997**.
21. Ciliberto E., Doris K.A., Pietro W.J., Reisner G.M., Ellis D.E. *J. Am. Chem. Soc.* **1984**, *106*, 7748.
22. Nyokong T. *Coord. Chem. Rev.* **2007**, *251*, 1707.
23. Kuznetsova N., Makarov D., Yuzhakova O., Strizhakov A., Roumbal Y., Ulanova L., Krasnovsky A., Kaliya O. *Photochem. Photobiol. Sci.* **2009**, *8*, 1724.
24. Slota R., Dyrda G. *Inorg. Chem.* **2003**, *42*, 5743.
25. Ferraudi G. Photochemical Properties of Metallophthalocyanines in Homogeneous Solution. In: *Phthalocyanines: Properties and Applications* (Leznoff C.C., Lever A.B.P., Eds.), Vol. 1, New York: VCH. **1989,** p. 291-340.
26. Egorov S.Y., Kamalov V.F., Koroteev N.I., Krasnovsky A.A., Toleutaev B.N., Zinukov S.V. *Chem. Phys. Lett.* **1989**, *163*, 421.
27. Ogilby P.R., Foote C.S. *J. Am. Chem. Soc.* **1982**, *104*, 2069.
28. Kuznetsova N., Gretsova N., Derkacheva V., Mikhalenko S., Solov'eva L., Yuzhakova O., Kaliya O., Lukyanets E. *Rus. J. Gen. Chem.* **2002**, *72*, 300 [*Zh. Obsch. Khim.* **2002**, *72*, 325 (in Russ.)].

Received 06.04.2012
Accepted 20.04.2012