

Aluminum Phthalocyanine on Silica Nanoparticles: Aggregation and Excited States

Anton V. Lobanov,^{a,b@} Nataliya B. Sultimova,^c Petr P. Levin,^c Ivan B. Meshkov,^d and Mikhail Ya. Melnikov^e

^aN.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 119334 Moscow, Russia

^bG.V. Plekhanov Russian University of Economics, 117997 Moscow, Russia

^cN.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, 119334 Moscow, Russia

^dN.S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, 117393 Moscow, Russia

^eM.V. Lomonosov Moscow State University, Department of Chemistry, 119991 Moscow, Russia

@Corresponding author E-mail: avlobanov@mail.ru

Aluminum phthalocyanines (AlClPc) adsorbed on the surface of silica nanoparticles with diameter of 60 nm in aqueous solutions have been found to form H-aggregates, which possess characteristic absorption spectra with bands (having maximum at 640 nm) in a shorter wavelength region with respect to the main Q-band of the monomer (having maximum at 670 nm). For AlClPc on the surface, J-aggregates of two types (long-wavelength bands with maxima at 740 and 770 nm) are also observed. Using nanosecond laser photolysis (with the excitation wavelength of 337 nm) in deoxygenated solutions of AlClPc on the surface, the formation of the triplet excited states of J-aggregates has been detected. Triplet excited states of J-aggregates are characterized by a broad absorption spectrum in the region of 600–800 nm and a lifetime of 360 μs.

Keywords: Aluminum phthalocyanine, J-aggregates, triplet state.

Фталоцианин алюминия на наночастицах кремнезема: агрегация и возбужденные состояния

А. В. Лобанов,^{a,b@} Н. Б. Сультимова,^c П. П. Левин,^c И. Б. Мешков,^d М. Я. Мельников^e

^aФГБУН Институт химической физики им. Н.Н. Семенова РАН, 119334 Москва, Россия

^bФГБОУ ВО «Российский экономический университет имени Г.В. Плеханова», 117997 Москва, Россия

^cФГБУН Институт биохимической физики им. Н.М. Эмануэля РАН, 119334 Москва, Россия

^dФГБУН Институт синтетических полимерных материалов им. Н.С. Ениколопова РАН, 117393 Москва, Россия

^eФГБОУ ВО «Московский государственный университет имени М. В. Ломоносова», Химический факультет, 119991 Москва, Россия

@E-mail: avlobanov@mail.ru

Обнаружено, что фталоцианин алюминия (AlClPc), адсорбированный на поверхности наночастиц кремнезема диаметром 60 нм в водных растворах, формирует H-агрегаты, характеризующиеся полосой поглощения в коротковолновой области электронного спектра (при 640 нм) по сравнению с Q-полосой мономера (при 670 нм), а также J-агрегаты двух типов с полосами поглощения в длинноволновой области при 740 и 770 нм. Методом наносекундного лазерного фотоллиза (с длиной волны возбуждения 337 нм) было зарегистрировано образование триплетных состояний J-агрегатов AlClPc на поверхности наночастиц кремнезема в обескислороженных водных растворах. Триплетные состояния J-агрегатов AlClPc характеризуются широким спектром поглощения в интервале 600–800 нм и временем жизни 360 мкс.

Ключевые слова: Фталоцианин алюминия, J-агрегаты, триплетные состояния.

Introduction

Complexes of tetrapyrrole macrocycles (phthalocyanines (Pc) and chlorins) with metals having filled d -orbital shells (*e.g.* Mg, Zn, Al, Sn) are capable of forming long-lived (0.1–1 ms) triplet electronically excited states with high quantum yields and possess intense electronic absorption bands in the long-wavelength region of 640–700 nm. By their properties, these complexes form a group of compounds promising for photocatalysis^[1–3] and photomedicine.^[4–7] Frontier molecular orbitals HOMO and LUMO of the metal complexes are located on the macroheterocyclic ligand only (Figure 1).^[8] So the consideration of the $\pi \rightarrow \pi^*$ electronic transitions in d^0 - and d^{10} -metal complexes provides important information about the aggregation or coordination interaction with the environment and the ability to regulate the physical and chemical tetrapyrrole properties changing environment.

At present, particular attention is given to studies of the photochemical properties of Pc in nanosystems used in photodynamic therapy of cancer. Nanostructured Pc can have potential applications in modern technology, in particular, in production of artificial light-harvesting antennas, molecular wires, *etc.*^[9] The particular interest is photochemical and photophysical processes occurring in aggregates of Pc in nano-assemblies. In respect to orientation of molecules, the main types of nano-structured Pc can be recognized: *H*-aggregates, in which molecules

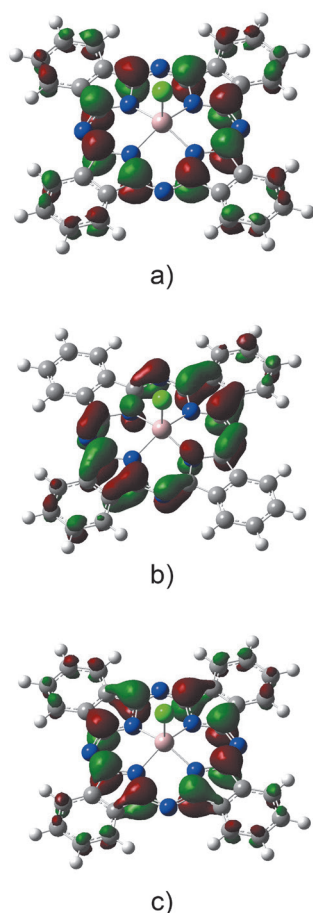


Figure 1. The nature of the frontier orbitals of AlClPc: HOMO (a) and LUMO in the singlet (b) and triplet (c) states.

are aligned following the “sandwich” pattern, *J*-aggregates, which follow the “head-to-head” pattern, and aggregates with intermediate “brickwork” structure, which can form *J*-type species if $\theta < 54.7^\circ$ (Figure 2).^[9] It is supposed that *H*-aggregates of Pc, which are most often formed in many systems, are not photoactive, in contrast to *J*-aggregates, which could be photoactive, but are formed much more rarely.^[10,11]

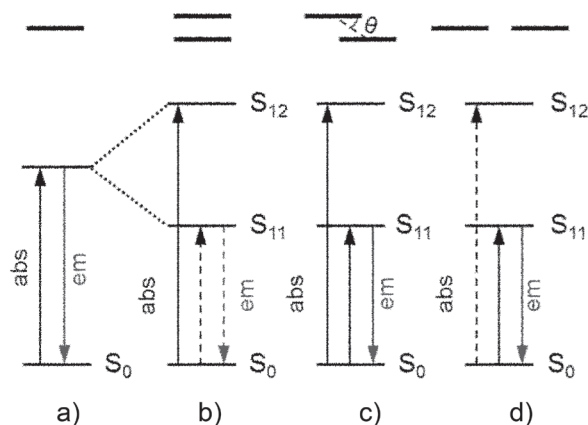


Figure 2. Energy level diagram of AlClPc for its monomer (a), *H*-aggregate (b), aggregate with intermediate structure of *H*-type for $54.7^\circ < \theta < 90^\circ$ or *J*-type for $0^\circ < \theta < 54.7^\circ$ (c), and pure *J*-aggregate (d). Arrows show the allowed (solid line) or forbidden (dash line) electron transitions for light absorption (abs) and fluorescence (em).

First of all the studies of nanostructured Pc are mainly focused on the development of the method of preparation of the aggregate with a necessary structure. However, the study of nanostructured Pc was not concerned with a research of their photochemical features whereas they could be used in photodynamic therapy, fluorescent diagnosis of pathologic states, and as vectors for targeted drug delivery.^[12] It is known that a combination of phthalocyanine with a carrier often promotes improved dye accumulation in actively proliferating cells, especially in pathological states.^[13,14]

In this work, for the first time, we describe the spectral and kinetic characteristics of short-lived intermediate products formed during photolysis of aluminum phthalocyanine (AlClPc) and its aggregates on the surface of silica nanoparticles in aqueous media by nanosecond laser photolysis.

Experimental

Silica with particles of 60 nm in diameter was synthesized at ISPM RAS.^[15] A transparent aqueous solution of silica (1 wt. %) was used in the experiments. Aluminum phthalocyanine with chloride extraligand of the spectroscopic grade was obtained from Acros Organics, Belgium. Structure and purity of AlClPc was further confirmed by MALDI mass-spectrometry method using device Thermo DSQ II. Content of AlClPc in DMF and silica solution was 1×10^{-5} M. Aqueous solutions of AlClPc supported on silica nanoparticles were prepared by addition of 1 % (by

volume) of the corresponding AlClPc solution in DMF into the starting silica solution stirring. Because AlPc is quite insoluble in water, it should be assumed that AlClPc is present on the surface of nanoparticles only in silica solutions. No precipitation was observed within a few days.

The absorption spectra and the formation and decay kinetics of transients were measured on a nanosecond laser photolysis setup.^[16] A nitrogen laser (PRA LN 1000, with 1 ns pulse duration and 337 nm radiation wavelength), operating in the frequency mode of ≤ 10 Hz was used as an excitation source. Rate curves were averaged (by ≥ 16 laser pulses) with a UF258 high-speed digitizer (Sweden) connected to a Pentium 4 computer. Each rate curve contained 12–14 bits of points with a distance between points of 4–400 ns. The data presented in the work are average values obtained by processing of no less than ten rate curves measured under the mentioned conditions.

Dissolved oxygen was *in vacuo*. All measurements were carried out at 20 °C in a quartz cell with an optical path length of 8 mm. Electronic absorption spectra were measured on a UV-VIS-NIR spectrometry using Shimadzu UV-3101PC spectrophotometer. To allow for light scattering in AlPc absorption measurements in solutions of silica nanoparticles, the corresponding silica solution was used as a reference. Emission spectroscopic measurements were performed with Shimadzu RF-5000 fluorimeter in a 1 cm quartz cell.

Quantum chemical calculations were performed using the procedure 6-31G** in the DFT-approximation with the exchange-correlation functional PBE1PBE in the program Gaussian 03.^[17]

Singlet oxygen quantum yield (Φ_D) was determined using chemical trapping method based on diphenylisobenzofuran (DPBF) bleaching.^[9] Experiments was performed in standard quartz cuvettes (1 cm) under irradiation by halogen lamp (150 W) with lens, condenser and filters for selection of different radiation range. Light power was 10 mW/cm².

Accumulation and photodynamic activity of AlClPc supported on silica nanoparticles were studied in the mesenchymal stromal cells by the method described elsewhere.^[18]

Results and Discussion

Figure 3 shows the electronic absorption spectra of AlClPc in DMF and silica aqueous solution. The absorption spectra of Pc in aqueous silica solutions are significantly broadened with respect to the relevant bands in DMF. The absorption spectrum of AlClPc supported on silica surface

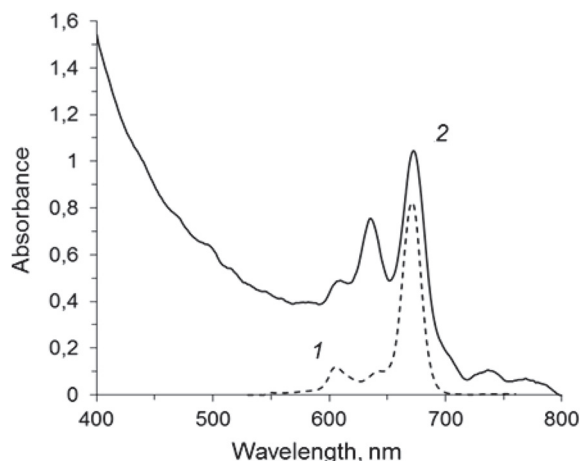


Figure 3. Absorption spectra of AlClPc ($1 \cdot 10^{-5}$ M) in DMF solution (1) and on silica nanoparticles surface in water (2).

is different from AlClPc spectrum in DMF by slight shift (*ca.* 5 nm) of Q-band to longer wavelengths due to changes in the solvation shell of the metal complex. Also there are new absorption bands at both longer and shorter wavelengths with respect to the Q-band. These new absorption bands indicate the formation of *H*-aggregates (in the short-wavelength region) and *J*-aggregates (in the long-wavelength region) on the silica nanoparticles surface (Figure 3).

It is known that phthalocyanines are able to form dimers^[19] and organized *H*- or *J*-type aggregates.^[9] The band in the short-wavelength region (about 640 nm) of the absorption spectra of AlClPc indicates the presence of *H*-aggregates on the surface. The new bands in the absorption spectrum of AlClPc in the regions of 705, 740, and 770 nm indicate the formation of *J*-aggregates on silica nanoparticles, whose molecules are aligned following the “brickwork” pattern, which leads to an appearance of absorption bands in the long-wavelength region with respect to the monomer absorption.^[9–11]

Earlier the formation of *J*-aggregates in a mixture of DMF and water was observed with the appearance of the absorption maximum at 740 nm.^[9] Evidently aluminum phthalocyanine molecules on silica surface, in addition to *J*-aggregates analogous to those formed in solutions, also form previously not described *J*-aggregates of other type with absorption band much stronger shifted to longer wavelengths (maximum at ~ 770 nm). Note that fluorescence of novel aggregates AlClPc on the silica surface is observed at 720 and 750 nm (Figure 4). This emission belongs to the *J*-aggregate with the absorption bands at 705 and 740 nm apparently.

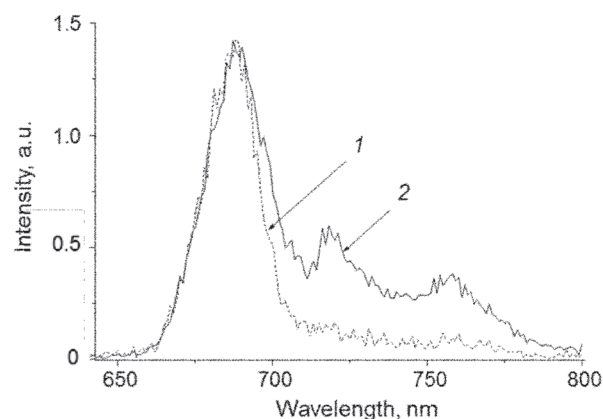


Figure 4. Normalized fluorescence spectra of AlClPc ($1 \cdot 10^{-5}$ M) in DMF solution (1) and on silica nanoparticles surface in water (2).

The formation of *H*-type aggregates of tetrapyrroles occurs spontaneously and is the most common case under the local concentration in multicomponent systems and solubilization. *H*-aggregation leads to the strengthening of non-radiative channels for all excited states. Consequently, *H*-type aggregates of tetrapyrroles possess no photosensitizing activity carried out on the mechanism of triplet-triplet energy transfer to oxygen. Also, tetrapyrrole *H*-aggregates do not fluoresce. *J*-aggregation of tetrapyrroles is rarely observed. It was found that porphyrin ions and zwitter-ions

are capable to form *J*-aggregates followed by the formation of porphyrin nanotubes even.^[20,21] However *J*-type aggregates of phthalocyanines were only reported in a few cases.^[9–11] Quantum chemical calculations show that when two AlClPc molecules are near, they spontaneously assume two configurations of *H*-type aggregate (Figure 5), while attempts to place them on the *J*-type aggregate do not succeed. It can be concluded that to obtain aggregates on the surface in addition to requirements for the structure of the metal complex it requires special conditions favorable for the formation of the structure type. Apparently, it may be defects or specific pores on the surface of nanoparticles. Photophysical properties of *J*-aggregates of phthalocyanines are not studied practically. It is known from a few data in the literature that phthalocyanine *J*-aggregates retain such photophysical properties of monomeric phthalocyanines as the ability to generate fluorescence and triplet states. Important characteristic of *J*-aggregate is the significant bathochromic shift of the absorption band to 740–750 nm and more. Data on the photochemical activity of non-covalent supramolecular complexes of *J*-aggregates of phthalocyanines are absent in the literature.

Flash photoexcitation of solutions of non-aggregated (monomeric) AlClPc in DMF leads within the laser flash time to the appearance of the triplet states $^3\text{AlClPc}$ (T_m), which is characterized by a broad difference spectrum with a maximum at ~ 490 nm and bleaching in the region of the AlClPc ground state absorption bands as well as it was previously observed in solutions of phthalocyanines.^[9]

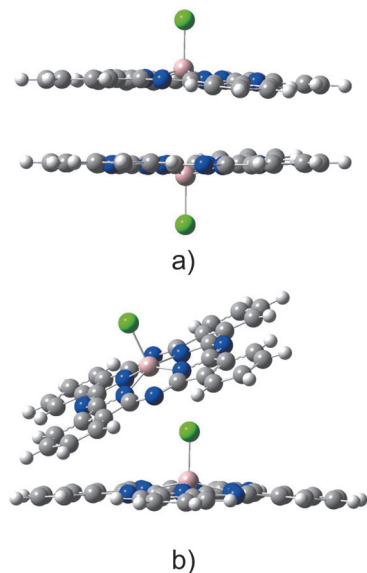


Figure 5. The structure of the AlClPc dimers with outwardly oriented chloride ligands (a) and on one side (b). Al–Al distances are 4.95 and 5.46 Å respectively.

In air-saturated solutions, the decay kinetics of T_m is described by the first order law with rate constants of $1.1 \cdot 10^6 \text{ s}^{-1}$ (Figure 6). Rate constant of T_m quenching in DMF molecular oxygen is $\sim 3 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ (concentration of dissolved oxygen in air-saturated solution of DMF was taken as $1 \cdot 10^{-3} \text{ M}$ ^[22]). This value is typical for the rate constants of

quenching of triplet states of organic molecules by molecular oxygen (usually $(2\text{--}5) \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$) via energy transfer to form singlet oxygen.^[23–25] It is known that the quantum yield of $^1\text{O}_2$ upon photolysis of Pc can be in the range of 0.1–0.7.^[5,6]

In deoxygenated solutions, the kinetics of decay of T_m is described by the first-order rate constant of $7.8 \cdot 10^3 \text{ s}^{-1}$ (Figure 6). The obtained value is in good agreement with the lifetime of the triplet state of phthalocyanines in DMSO.^[26] Flash photoexcitation of deoxygenated aqueous solutions of AlClPc on the silica surface leads to the appearance of difference absorption spectrum with maximum at 465 and 720 nm

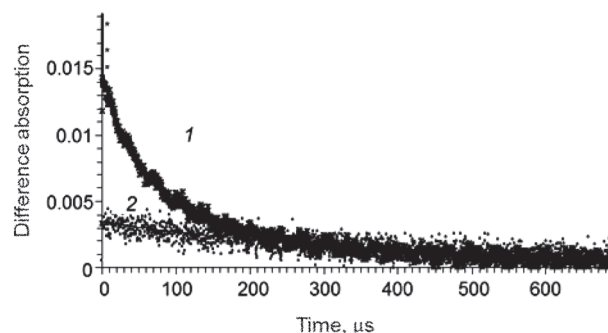


Figure 6. Decay kinetics of the intermediate products absorbing at 520 nm obtained upon laser photolysis of deoxygenated AlClPc solutions ($1 \cdot 10^{-5} \text{ M}$) in DMF (1) and on silica nanoparticles surface (2). The lines represent the results of approximation in terms of the exponential model.

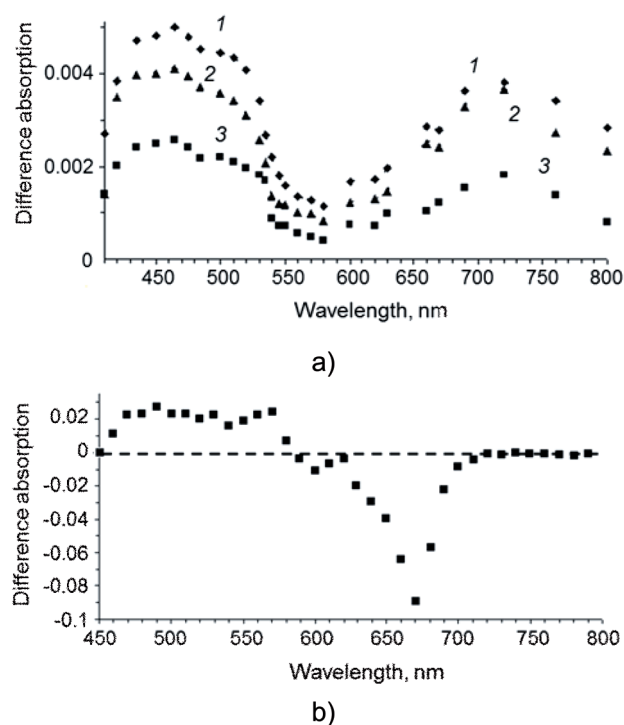


Figure 7. Difference absorption spectra of the intermediate products obtained upon laser photolysis of AlClPc ($1 \cdot 10^{-5} \text{ M}$) on the silica nanoparticles surface in deoxygenated water within 0.1 (1), 50 (2), and 200 μs (3) after the laser flash (a) and in deoxygenated DMF solution (b).

(Figure 7a). This absorption spectrum is markedly different from the absorption spectrum of T_m in solution (Figure 7b) in the absence of bleaching of the absorption bands of the ground state of the monomer AlClPc and the presence of intense absorption in the longer wavelengths. Apparently, this spectrum belongs to the triplet states of J -aggregates on the surface of silica (T_J).

The decay kinetics of this intermediate obeys the first order law with a rate constant in deoxygenated solutions of about $2.5 \cdot 10^3 \text{ s}^{-1}$, which noticeably less than the decay rate constant of $^3\text{AlClPc}$ in DMF. It should be noted that the T_J formation is not observed in air-saturated solutions of silica due to static quenching of T_J by molecular oxygen adsorbed in close proximity to the aggregates. Aggregation of organic molecules to silica surfaces generally proceeds in defects in which oxygen molecules appears to be concentrated also.

Comparing T_m quantum yields and T_J shows that the yield of triplet state of J -aggregates on the surface of silica is less than that of the triplet state of monomer in DMF. A similar regularity was found in solutions and attributed the appearance of charge transfer processes in the singlet electronic excited states of phthalocyanine J -aggregates, competing with intersystem crossing.^[27]

Singlet oxygen quantum yield was determined for monomer and J -aggregate of AlClPc ($1 \cdot 10^{-5} \text{ M}$) on the silica nanoparticles surface in DMF-water (50/50, v/v). The Φ_Δ values are 0.24 and 0.10 respectively. For comparison, calculated values of Φ_Δ for AlClPc in the same DMF-water mixture is 0.17. Thus AlClPc ($1 \cdot 10^{-5} \text{ M}$) on the silica nanoparticles surface is effective photosensitizer with broad spectral range of excitation.

Experiments with mesenchymal stromal cells^[18] have shown that the immobilization of AlClPc on silica nanoparticles leads to increase of AlClPc accumulation in the cells by 8 times. Thus a risk of toxic effects was reduced. At accumulation of 40–50 ng per 1 ml of culture medium the efficiency of photodynamic activity was higher by one order of magnitude than that of water-soluble sulfonated aluminum phthalocyanine with an absorption maximum 678 nm.

Conclusions

In summary, the laser photolysis study of AlPc aggregates on the nanosized silica surface permitted us to reveal the presence of two intermediate products, presumably triplet states of J -aggregated AlPc, which absorb in the long-wavelength region at $\lambda \geq 700 \text{ nm}$ and are efficiently quenched by molecular oxygen. Yield of the triplet states of the aggregated AlPc is significantly below the value for the monomer AlPc, which could be explained by the appearance of the competing process of charge transfer in the singlet excited state. The presence of absorption of photoactive aggregates in the 740–770 nm allows the use of medical lasers with larger light penetration. Knowledge of the kinetic characteristics of the intermediates produced during the photolysis of Pc makes it possible to regulate mechanisms of photodynamic processes.

Acknowledgements. The reported study was supported by RFBR, research project No. 15-03-03591.

References

1. Kiwi J., Kalyanasundaram K., Grätzel M. *Structure and Bonding* **1981**, 49, 37–125.
2. Darwent J.R., Douglas P., Harriman A., Porter G., Richoux M.-C. *Coord. Chem. Rev.* **1982**, 44, 83–126.
3. Wöhrle D. *Chimia* **1991**, 45, 307–310.
4. Rosenthal I. *Photochem. Photobiol.* **1991**, 53, 859–870.
5. Henderson B.W., Dougherty T.J. *Photochem. Photobiol.* **1992**, 55, 145–157.
6. Krasnovsky A.A., Jr., Rodgers M.A., Galpern M.G., Rihter B., Kenney M.E., Lukjanetz E.A. *Photochem. Photobiol.* **1992**, 55, 691–696.
7. de la Torre G., Claessens C.G., Torres T. *Chem. Commun.* **2007**, 2000–2015.
8. Lobanov A.V., Kobzev G.I., Sinko G.V. Molecular and Associated Tetrapyrroles: Excited States and Photochemical Reactions. In: *Highly Reactive Intermediates* (Egorov M.P., Mel'nikov M.Ya., Eds.), Moscow: Krasand, **2014**, pp. 203–230 (in Russ.) [Лобанов А.В., Кобзев Г.И., Синько Г.В. Молекулярные и ассоциированные тетрапирролы: возбужденные состояния и фотохимические реакции. В кн.: *Высокоакционные интермедиаты* (Егоров М.П., Мельников М.Я., ред.), М.: Красанд, **2014**, с. 203–230].
9. Zhang X.F., Xi Q., Zhao J.J. *Mater. Chem.* **2010**, 20, 6726–6733.
10. FitzGerald S., Farren C., Stanley C.F., Beeby A., Bryce M.R. *Photochem. Photobiol. Sci.* **2002**, 1, 581–587.
11. Kameyama K., Morisue M., Satake A., Kobuke Y. *Angew. Chem., Int. Ed.* **2005**, 44, 4763–4766.
12. Li W.-S., Aida T. *Chem. Rev.* **2009**, 109, 6047–6076.
13. Chatterjee S.R., Srivastava T.S. *J. Porphyrins Phthalocyanines* **2000**, 4, 147–157.
14. Hamblin M.R., Newman E.L. *J. Photochem. Photobiol., B* **1994**, 23, 3–8.
15. Stöber W., Fink A., Bohn E. *J. Colloid Interface Sci.* **1968**, 26, 62–69.
16. Levin P.P., Tatikolov A.S., Panova I.G., Sul'timova N.B. *High Energy Chem.* **2010**, 44, 216–219.
17. Frisch M.J., Trucks G.W., Schlegel H.B., *et al.* *Gaussian 03* (ReVision A.1); Gaussian Inc., Pittsburgh, PA, **2003**.
18. Udartseva O.O., Lobanov A.V., Andreeva E.R., Dmitrieva G.S., Mel'nikov M.Ya., Buravkova L.B. *Biophysics* **2014**, 59, 856–862.
19. Palewska K., Sujka M., Urańska-Wójcik B., Sworakowski J., Lipiński J., Nešpůrek S., Rakušan J., Karásková M. *J. Photochem. Photobiol., A* **2008**, 197, 1–12.
20. Sheinin V.B., Bobritskaya E.V., Shabunin S.A., Koifman O.I. *Macroheterocycles* **2014**, 7, 209–217.
21. Martin K.E., Tian Y., Busani T., Medforth C.J., Franco R., van Swol F., Shelnutt J.A. *Chem. Mater.* **2013**, 25, 441–447.
22. Achord J.M., Hussey C.L. *Anal. Chem.* **1980**, 52, 601–602.
23. Das P.K., Encinas M.V., Scaiano J.C. *J. Am. Chem. Soc.* **1981**, 103, 4154–4162.
24. Scaiano J.C. *J. Photochem.* **1973**, 2, 81–118.
25. Encinas M.V., Scaiano J.C. *J. Am. Chem. Soc.* **1981**, 103, 6393–6397.
26. Li Y., Pritchett T. M., Huang J., Ke M., Shao P., Sun W. *J. Phys. Chem., A* **2008**, 112, 7200–7207.
27. Würthner F., Kaiser T.E., Saha-Möller C.R. *Angew. Chem., Int. Ed.* **2011**, 50, 3376–3410.

Received 25.04.2015

Accepted 17.08.2015