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Photophysical and photochemical properties of non-peripheral butoxy-substituted phthalocyanines with absorption in NIR range

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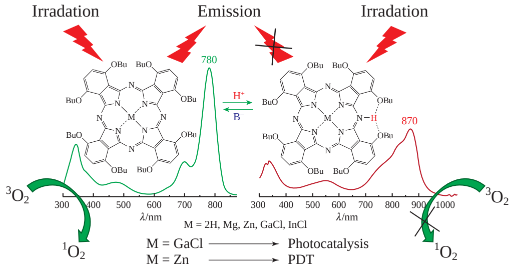
The optical properties of non-peripheral octabutoxyphthalocyanine (PcH_2) and the corresponding complexes PcM (M = Mg^{II}, Zn^{II}, Ga^{III}, In^{III}) in DMSO solutions were examined. Singlet oxygen generation quantum yields increase in the sequence PcH_2 < PcMg < PcInCl < PcGaCl < PcZn and vary from 4 up to 36%; protonation of PcM quenches both fluorescence and singlet oxygen generation. The photocatalytic activity of PcGaCl in the photooxidation of 1,5-dihydroxynaphthalene was revealed.



Phthalocyanines and their analogues with absorption in near-infrared (NIR) range have attracted special attention as photosensitizers for photodynamic therapy (PDT) due to the exceptional ability of red light to penetrate tissues.[1–3] There are several approaches towards the shifting of phthalocyanines absorption to NIR area: expansion of a macrocycle,[4,5] oligomerization of phthalocyanine derivatives,[6] or lowering molecular symmetry.[7] All these methods have serious disadvantages: the strong tendency of extended phthalocyanines to aggregate, synthetic and isolating difficulties in case of unsymmetrical and oligomeric phthalocyanines, *etc*. Another strategy is introducing of non-peripheral substituents into α-positions, which leads to bathochromic shift in absorption spectra and also increases the solubility.[8,9]

The series of α-octabutoxy-substituted phthalocyanines was in focus of interest as potential photosensitizers for different applications.[10–12] Fluorescence properties, singlet oxygen ($^1O_2$) quantum yields and triplet state characteristics were successfully described for free-base α-octabutoxy-substituted phthalocyanine and its Zn^{II}, Ga^{III} and In^{III} complexes.[10–12] However, these measurements were made for different conditions, therefore, these results are not comparable.

Another important characteristic of phthalocyanines is their basicity that was firstly investigated by Lukyanets and Kaliya groups.[13,14] Introduction of electron-donating groups into α-positions of phthalocyanine ring dramatically increases basicity of complexes. Thus, the basicity constants of α-substituted phthalocyanine complexes are one order of magnitude higher than those for β-substituted derivatives.[15] Mechanism of interactions of phthalocyanines with acids was a point of discussion for years.[16,17] Later it was proved by NMR spectroscopy that protonation involves *meso*-N atoms of phthalocyanine ring and O-atoms of non-peripheral groups.[18,19] Also it was reported that such a protonation affects redox activity,[20] quenches fluorescence[19] and singlet oxygen generation.[21]

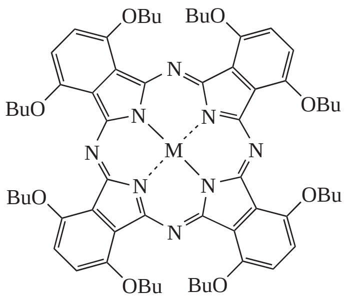
Tetrapyrrolic compounds and materials based on them are also promising candidates for photocatalysis.[22–28]

Herein, we describe systematic investigation of photophysical and photochemical properties of series of non-peripheral α-octabutoxy-substituted phthalocyanines including novel Mg^{II} and Ga^{III} complexes in DMSO known as a non-toxic biocompatible solvent and demonstrate the examples of their photocatalytic behaviour in the photooxidation of 1,5-dihydroxynaphthalene.

α-Octabutoxyphthalocyanine PcH_2 was synthesized following described procedure[11] (see Online Supplementary Materials). Magnesium(II) complex PcMg was obtained for the first time by the direct metallation of PcH_2 with $Mg(OAc)_2$ in DMF (yield 75%). New gallium(III) complex with chloride axial ligand PcGaCl was synthesized from $Ga_2(SO_4)_3$ followed by treatment with HCl in 62% yield. Note that related complex $GaPc(OBu)_8OSiEt_3$ was previously obtained in 53% yield.[11] Zinc(II) complex PcZn was synthesized according to the reported procedure.[11] Indium complex PcInCl was prepared by the modified Lobo's method,[10] however, the product was separated only with application of size-exclusion chromatography (SEC) in 57% yield.

The UV-VIS spectra of the DMSO solutions of PcM demonstrated characteristic absorption in the Q-band region at *ca.* 746–780 nm (Table 1, Figure S1, see Online Supplementary Materials). The B-band was observed at 300–350 nm.

According to spectral data, the complexes were monomers, which was evidenced from a single narrow Q-bands typical of



PcM, M = 2H, Mg, Zn, GaCl, InCl

Table 1 Absorption and fluorescence data for PcM.

Compound	λ_{Amax}/nm	Φ_F (%)	λ_F/nm	Stokes shift/nm	Φ_F (%) (protonated)
PcH_2	774	2	806	32	–
PcZn	748	4	771	23	1
PcMg	746	3	768	22	–
PcGaCl	780	3	813	33	1
PcInCl	768	<1	781	13	–

Table 2 Concentrations of TFA required for the 1st and 2nd protonation of compounds PcM in DMSO.

Compound	Percentage of TFA	
	1st protonation	2nd protonation
PcH_2	12.7	–
PcZn	0.2	18.6
PcGaCl	37.0	–
PcInCl	1.0	–

metalated phtalocyanines. Surprisingly, only one Q-band was detected in the UV-VIS spectrum of PcH_2 instead of two bands typical of phtalocyanine ligands. Note that the spectrum of non-polar benzene solution of PcH_2 consists of two bands.[8]

In search for appropriate conditions of protonation and deprotonation of *meso*-N atoms of PcH_2 and its complexes in DMSO, the amounts of trifluoroacetic acid (TFA) required for protonation were determined for 1.1×10^{-5} M solutions (Table 2). Moreover, for PcZn we reached the second protonation form in DMSO (Figure 1). It is worth noting that in nonpolar chloroform protonation stages can be reached much easier. Protonation of all four *meso*-N atoms of the nonperipheral-substituted phtalocyanines was described previously.[19,29,30] In the case of PcMg, protonation process was not investigated because of easiness of its demetallation.[19]

Protonation is a reversible process: addition of base causes deprotonation and return to starting UV-VIS spectra for all complexes. Intensity of UV-VIS spectrum of PcH_2H^+ solution decreases in time (Figure S2), while protonated forms of PcZn, PcGaCl and PcInCl are stable (Figures S3 and S4). Protonation rates for PcZn and PcH_2 correlate with the data for similar compounds.[21]

Fluorescence emission peaks of the studied compounds (see Table 1) locate in the range from 768 to 813 nm. Fluorescence quantum yields are low for all complexes and do not exceed 5%. Note that the intensity of PcInCl fluorescence is extremely low. It can be explained by heavy atom effect: the presence of In atom in the molecule increases the quantum yield of triplet state and thus decreases quantum yield of fluorescence. Figure 2 demonstrates absorption and emission spectra of PcZn in DMSO, similar to those of other investigated compounds.

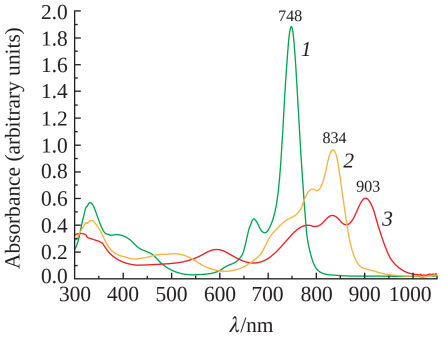


Figure 1 UV-VIS spectra of (*1*) PcZn and its (*2*) 1st and (*3*) 2nd protonated forms in DMSO (1.1×10^{-5} M) in the presence of different amounts of TFA (0, 0.2 and 18.6%, respectively).

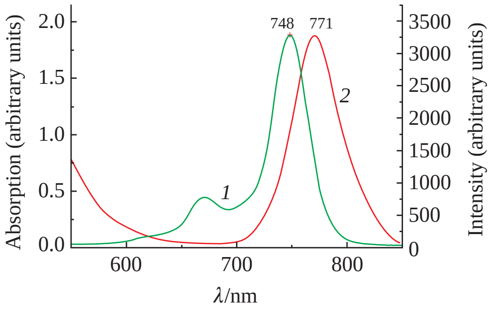


Figure 2 Normalized (*1*) absorption and (*2*) emission spectra of PcZn in DMSO at room temperature (λ_{ex} = 400 nm).

Table 3 Quantum yields of $^1O_2$ generation (Φ_Δ) of PcM and their protonated forms and rates of autophotodestruction of PcM (*V*) in solution in DMSO (~10^{-5} M).

Compound	Φ_Δ (%)	Φ_Δ of protonated forms (%)		V/ 10^{-11} mol s^{-1}
		1st protonation	2nd protonation	
PcH_2	4	–	–	39.0
PcMg	10	–	–	11.0
PcZn	36	3	0	4.5
PcGaCl	30	0	–	0
PcInCl	15	–	–	3.2

On the examples of PcZn, PcGaCl and PcInCl, it was shown that protonation of *meso*-N atoms of the phtalocyanine ring quenches fluorescence (see Table 1). As it was mentioned above, PcH_2 and PcMg are not stable under acidic conditions and their protonation cannot be studied properly.

Generation of $^1O_2$ was investigated for PcH_2, PcZn and PcInCl previously, however in toxic solvents like THF[10] or benzene-d_6/pyridine mixture.[11] Importantly, $^1O_2$ lifetime in deuterated solvents is dramatically higher,[31] which leads to increase of quantum yields. In this work DMSO was chosen as biologically compatible solvent. It is worth noting that all experiments were carried out under the same conditions (Table 3). For all test compounds, $^1O_2$ generation quantum yields are in the range of 4–36% growing in the sequence PcH_2 < PcMg < PcInCl < PcGaCl < PcZn. In the series of PcH_2, PcZn and PcGaCl, the obtained results correlate with the Rihter's data,[11] who studied Ga^{III} phtalocyanine complex with different axial ligand.

Previously, for Zn α-octahexyloxyphthalocyanine it was shown that protonation can quench $^1O_2$ generation.[21] Here for the complexes with the highest $^1O_2$ generation quantum yields (PcZn, PcGaCl), influence of protonation was also studied. It was revealed that the first protonation quenches $^1O_2$ generation of PcZn by 92% and PcGaCl by 100%. For full quenching of PcZn the second step of protonation is necessary. This can be explained by smaller amounts of acid needed to obtain first protonated form of PcZn as compared with PcGaCl.

The investigated phtalocyanine complexes displayed appropriate photosensitizing efficiency that is promising for photocatalysis. We have chosen a model reaction of 1,5-dihydroxynaphthalene (DHN) oxidation into 5-hydroxynaphthoquinone (juglone) in

Scheme 1

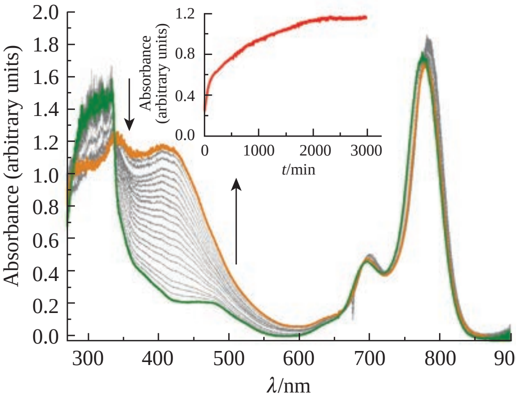


Figure 3 PcGaCl catalyzed oxidation of DHN monitored by UV-VIS spectroscopy; [PcGaCl] ≈ 10^{-5} and [DHN] = 10^{-4} mol dm^{-3}. Inset is a plot of juglone band intensity (410 nm) *vs.* time.

DMSO to estimate catalytic activity[22,23] (Scheme 1). The experiments were carried out under the same conditions as in case of singlet oxygen quantum yield determination. All test compounds demonstrated photocatalytic activity in the DHN oxidation. However, only PcGaCl was found to be stable under these conditions (670 nm red laser, Figure 3). Decrease in the intensity of absorption band at *ca.* 320 nm indicates lowering the DHN concentration. Simultaneously, absorbance band at *ca.* 450 nm increases, that means appearance of juglone (Figure 3).

Other four complexes (PcH_2, PcMg, PcZn and PcInCl) reveal the photobleaching of their UV-VIS spectra (Figures S5–S8), which prevents their use as photocatalysts. However, for the purpose of PDT this property is an advantage, since after the PDT procedure the photosensitizer decomposes. Moreover, PcZn has appropriate $^1O_2$ generation quantum yield (see Table 3), that makes it a promising compound for further biological investigations.[32] Meantime, first of all, it is necessary to evaluate photostability of the series of test phthalocyanines.

The photostability was estimated under the same conditions as those used for $^1O_2$ experiments and reaction with DHN. As we expected, only PcGaCl does not undergo autophotodestruction. Compounds PcH_2, PcMg, PcZn and PcInCl are not stable under red laser irradiation (Figures S9–S12), however the rates of their decomposition are significantly different (see Table 3). The photostability of studied compounds decreases in the line PcGaCl(stable) > > PcInCl > PcZn > PcMg > PcH_2. Based on obtained data we consider that PcGaCl and PcZn are promising for further investigations in the field of photocatalysis and PDT, respectively.

In summary, photophysical and photochemical properties of series of α-octabutoxyphthalocyanines were systematically studied. Their protonation quenches both fluorescence and singlet oxygen generation, but the required amounts of the acid are individual for each complex. Complex PcGaCl is a promising photocatalyst for photooxidation reactions, while PcZn is more appropriate as a photosensitizer for PDT or antimicrobial therapy, which requires further investigations.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.05.015.

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