Effect of pH on Acid–Base and Photophysicochemical Properties of 2,3,9,10,16,17,23,24-Octacarboxyphthalocyanines in Aqueous Media

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The results of study of pH effect on the aggregation, acid-base and photophysicochemical properties of 2,3,9,10,16,17,23,24-octacarboxy substituted Zn, Al, Co, Pt and Pd phthalocyanines (MPcoc) in aqueous media are presented. The ionization of peripheral carboxyl groups and axial ligation of central metal atom are the principal factors, governing aggregation. The multi-step ionization of MPcoc, induced by change of pH, was considered as pseudo two-step process affecting four carboxyl groups on each step. The photophysicochemical properties of three differently ionized forms of ZnPcoc (unionized, tetra- and octacarboxylated) were studied.

Keywords: Octacarboxyphthalocyanine, ionization, aggregation, fluorescence, singlet oxygen, photostability.

Влияние pH на кислотно–основные, фото– и физико–химические свойства 2,3,9,10,16,17,23,24–октакарбоксифталоцианинов в водной среде

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Исследовано влияние pH на агрегацию, кислотно–основные, фото– и физико–химические свойства 2,3,9,10,16,17,23,24–октакарбоксиглассеоцианинов Zn, Al, Co, Pt и Pd (MPcoc) в водной среде. Ионизация карбоксильных групп на периферии и наличие аксиальных лигандов у центрального атома металла являются ключевыми факторами, определяющими степень агрегации MPcoc. Многоступенчатая ионизация MPcoc при изменении pH была аппроксимирована двухступенчатым процессом с ионизацией четырех карбоксильных групп на каждой ступени. Исследованы фото- и физико-химические свойства трех различно ионизованных форм ZnPcoc (кислотной, тетра- и окта-ионизованной).

Ключевые слова: Октакарбоксифталоцианин, ионизация, агрегация, флуоресценция, синглетный кислород, фотостабильность.
Introduction

Phthalocyanines (Pc) substituted with carboxylic groups are the object of wide investigations. They are interesting as photosensitizers for photodynamic therapy, dye-sensitized solar cells, catalysts of different reactions, including so-called catalytic therapy of cancer, and so on. The most known, to date, in this series are highly symmetric 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines (MPCs). Methods of synthesis and some properties of MPCes were reviewed recently. In form of their alkali salts MPCes are highly soluble in water, that is important for practical applications. The corresponding acids have tendency for self-association (aggregation) in solutions due mainly to the stack π-π interactions of adjacent Pc macrocycles. In the case of MPCes acids the interaction via hydrogen bonding should be also taken into consideration. The aggregation of PCs influences their properties, including photochemical and photocatalytic efficiency, the latter drastically decreases due to an enhancement of radiationless deactivation of excited singlet state. In order to rationalize catalytic, photochemical and photobiological effects it is important to characterize more in detail the aggregation and properties of MPCes differently ionized forms.

The effects of pH on aggregation of zinc, copper, nickel and metal-free 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines in aqueous solutions have been studied in wide pH interval using UV-vis absorption and fluorescence emission spectroscopy. Unlike to pH < 5, where only the aggregates have been observed, at pH > 8.0 exclusive presence of monomers was found. Such strong influence of pH on the aggregation of MPCes is caused by dissociation of carboxyl groups, resulting in accumulation of negative charge on the molecules, electrostatic repulsion of which prevents their aggregation. The pH value of monomer–associate transition depends on the central metal, increasing in the order: Zn ≈ Cu < Ni.[9]

In this paper, we present the effect of nature of central metal atom and, especially, its ability to axial coordination on pH-dependent aggregation of MPCes in aqueous solution. The MPCes (M = Al, Zn, Pt, Pd, Co) were studied, where Zn, Al and Co complexes are capable of axial coordination, unlike to PtPc and PdPce. We also report on pH dependence of spectral-fluorescent properties of ZnPce, monomerized in Cremophor EL solution.

Experimental

The Al, Zn, Pt, Pd and Co 2,3,9,10,16,17,23,24-octacarboxyphthalocyanines were synthesized according to papers. Cremophor EL and 1,3-diphenylisobenzofuran (DPBF) were purchased from Fluka. DPBF in Cremophor EL aqueous solution, 4% (v/v), was solubilized according to the methodology described earlier, that is DPBF (50 mg) and Cremophor EL (400 mg) were first dissolved in 20 mL of toluene, then toluene was evaporated, residue was dried at temperature about 40–50 °C and sonicated for 10 min with water (10 mL) in ultrasonic water bath. After sonication, fine solution with insignificant light scattering due to the presence of Cremophor EL micelles was obtained. Solutions were prepared in deionized water, pH was adjusted by addition of HCl or NaOH.

Methods

Electronic absorption spectra were recorded with Hewlett Packard 8453 spectrophotometer, fluorescence spectra – with Cary Eclipse spectrophotofluorimeter. The monochromatic light intensity was measured with a calibrated Si photodiode (Thorlabs).

The fluorescence quantum yields (Φf) were determined by the comparative method according to equation: Φf = Φf(ref) (F/F ref) (Aref/Af) (τref/τf), in which F, A and τ are the measured fluorescence (area under the emission peak), the absorbance at the excitation wavelength and the refractive index of the solvent, respectively. ZnPc octaanion was used as the reference (Φf(ref) = 0.18 at pH 10). The ratio Aref/Af was equal to 1 (the optical densities at a wavelength of excitation were the same in our experiments and equal to 0.1–0.2).

The singlet oxygen quantum yields (Φs) were estimated by the chemical-trapping method in water – Cremophor EL (4 %, v/v) solutions by using ZnPc octaanion as a reference (Φs(ref) = 0.54 in PBS with pH 7.4) and DPBF as the singlet oxygen trap. DPBF is insoluble in water, but it is readily solubilized in aqueous solution of Cremophor EL. The light source for the singlet oxygen measurements was a red light from a 150 W xenon lamp, passed through a water tank for cooling, a yellow glass cut-off filter and an interference filter (684 nm). Eq. (1) was employed for the calculations of Φs:

\[
\Phi_s = \Phi_s^{ref} \frac{W_{fl}^{ref}}{W_{fl}^{abs}} \frac{I_{fl}^{ref}}{I_{fl}^{abs}} \frac{I_{abs}}{I_{abs}^{ref}},
\]

where Φs(ref) is the singlet oxygen quantum yield for reference; Wfl and Wabs are the trap photobleaching rates in the presence of sensitizer and reference, respectively, and Ifl and Iabs are the intensities of their light absorption. The initial trap concentrations are kept the same for reference and the samples. The accuracy of Φs estimation was about 10 %.

The photodegradation of ZnPc and PtPc ionized forms was investigated under emitting diode IS-2-693 (ZAO “Technoelektro”, Russia) irradiation, light flux of 688–698 nm and 1.1–10% photons∙s⁻¹·cm⁻² at the sample surface. For the photodegradation quantum yields (Φp) determination, a 3 mL portion of air-saturated 5 μM ZnPce aqueous solution, containing 4 % (v/v) of Cremophor EL, was adjusted to pH 7.4, 5 or 2.8 and irradiated in the Q band region. The decrease of the ZnPc (area under the emission peak), the absorbance at the excitation wavelength (Table 2) were measured with a calibrated Si photodiode (Thorlabs).

Results and Discussion

Behavior of AlPc, ZnPc, PtPc, PdPc and CoPce in aqueous solutions was studied by UV-vis spectral and fluorescent methods, as a rule at λmax and λmax (Table 1).

Figure 1 represents the influence of pH on absorbance of MPCs aqueous solutions at Q-band maxima. Generally,
Acid-Base and Photophycochemical Properties of Octacarboxyphthalocyanines

Table 1. Spectral-fluorescent data and \( \text{pH} \) of monomer–aggregate transition for MPc\(^{\text{oc}} \).

<table>
<thead>
<tr>
<th>MPc(^{\text{oc}} )</th>
<th>( \text{pH} ) of monomer–aggregate transition</th>
<th>Monomer (( \text{pH} ) 8–9)</th>
<th>Aggregate (( \text{pH} ) 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_{\text{max , abs}} ), nm</td>
<td>( \lambda_{\text{max , fl}} ), nm</td>
<td>( \lambda_{\text{max , abs}} ), nm</td>
</tr>
<tr>
<td>AlPc(^{\text{oc}} )</td>
<td>4.05</td>
<td>690</td>
<td>695</td>
</tr>
<tr>
<td>ZnPc(^{\text{oc}} )</td>
<td>6.1</td>
<td>690</td>
<td>700</td>
</tr>
<tr>
<td>PdPc(^{\text{oc}} )</td>
<td>6.6</td>
<td>680</td>
<td>–</td>
</tr>
<tr>
<td>PtPc(^{\text{oc}} )</td>
<td>6.5</td>
<td>669</td>
<td>–</td>
</tr>
<tr>
<td>CoPc(^{\text{oc}} )</td>
<td>5.3</td>
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<td>–</td>
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MPc\(^{\text{oc}} \) within the \( \text{pH} \) range from 7 to 10 at Q band maxima have high absorption, which does not change significantly. Electronic absorption spectra at \( \text{pH} > 7 \) have the intensive Q\(_{0-0}\) bands, typical for monomeric species. Titration of these solutions by HCl, specific for each complex, results in the decrease of absorbance due to replacement of the narrow and intensive Q\(_{0-0}\) bands by the broad bands of aggregates (influence of \( \text{pH} \) on spectra of MPc\(^{\text{oc}} \) are exemplified with PtPc\(^{\text{oc}} \) on Figure 2).

In water, ionized MPc\(^{\text{oc}} \) owing to the electrostatic repulsion between molecules and better solubility of a carboxylate form exist as monomers, whereas unionized MPc\(^{\text{oc}} \) have limited solubility and demonstrate the aggregation behavior. According to literature on the aggregation of Pcs, two main aggregate species have been identified as J- and H-aggregates with J-aggregates marked by a red-shift in the monomer peak due to head-to-tail aggregation, while H-aggregates are characterized by a blue shift caused by face-to-face aggregation.[19,20] All aggregates of MPc\(^{\text{oc}} \) under investigation in the Q region have broadened bands, blue shifted (Figure 2, Table 1) in relation to the Q band of the monomer, hence associated with the H-aggregates. As it was found in paper,[11] ZnPc\(^{\text{oc}} \) at low concentrations in slightly acidic (\( \text{pH} \) 4–5) aqueous solutions forms dimers. At lower \( \text{pH} \) values and higher concentrations the multimeric forms were present almost exclusively. In this paper we did not study the association degree of MPc\(^{\text{oc}} \), however, for CoPc\(^{\text{oc}} \)

Table 1

<table>
<thead>
<tr>
<th>MPc(^{\text{oc}} )</th>
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<td>CoPc(^{\text{oc}} )</td>
<td>5.3</td>
<td>678</td>
<td>–</td>
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</table>

Figure 1. Influence of \( \text{pH} \) on absorbance of MPc\(^{\text{oc}} \) solutions at Q-band maximum, MPc\(^{\text{oc}} \) (\( \lambda_{\text{max \, abs}} \), nm), A: 1 – PtPc\(^{\text{oc}} \) (669), 2 – PdPc\(^{\text{oc}} \) (680); B: 1 – AlPc\(^{\text{oc}} \) (690), 2 – CoPc\(^{\text{oc}} \) (678), 3 – ZnPc\(^{\text{oc}} \) (698).

Figure 2. Absorption spectral changes in the course of titration of PtPc\(^{\text{oc}} \) in water with HCl in \( \text{pH} \) range 5.3 – 10.
two waves on the titration curve, basing on spectral data, may be tentatively associated with dimerization at pH 5.3 and multimerization at pH 3.4. The Pt, Pd and Al MPc\textsuperscript{ex} complexes directly gave aggregates with strongly broadened Q bands, typical for mixture of multimers.

According to the shape of titration curves, compounds under investigation may be divided into two groups: first one consists of PtPc\textsuperscript{ex} and PdPc\textsuperscript{ex} – with sharp change in the absorbance at pH about 6.5 (Figure 1A), and the second one – of AlPc\textsuperscript{ex}, CoPc\textsuperscript{ex} and ZnPc\textsuperscript{ex} – with titration curves mildly sloping at lower values of pH (Figure 1B), evidencing the higher solubility of these MPc\textsuperscript{ex} and their ionized forms. It is noteworthy that the first group consists of complexes with metals, incapable of axial coordination, while complexes of the second group can coordinate axially\textsuperscript{[23]} in aqueous solutions – OH\textsuperscript{−} and H\textsubscript{2}O species particularly. It is generally known also that presence of an axial ligand at the central metal atom hinders the sandwich orientation of phthalocyanine molecules during aggregation. Thus, observed differences of pH-aggregation behavior for two groups of MPc\textsuperscript{ex} may be caused by their different solubility – under stepwise ionization conditions the less number of ionized groups on macrocycle periphery is needed for monomerization of coordinating AlPc\textsuperscript{ex}, CoPc\textsuperscript{ex} and ZnPc\textsuperscript{ex} than in the case of PtPc\textsuperscript{ex} and PdPc\textsuperscript{ex}.

The effect of number of ionized carboxyl groups on macrocycle periphery upon aggregation of MPc\textsuperscript{ex} in water has not been studied. However, it is known that for cationic aluminum and zinc phthalocyanines, correspondingly, about four and six charged groups per molecule are needed for monomerization\textsuperscript{[24]} Increase of pH of MPc\textsuperscript{ex} solutions results in progressive dissociation of carboxyl groups and accumulation of negative charge on the periphery of molecule and, when electrostatic repulsion becomes sufficient, dye monomerization. Since in MPc\textsuperscript{ex} the adjacent carboxyl groups exert the most efficient acceptor impact at each other, and by analogy with o-phthalic acid (pK\textsubscript{a} are 2.95 and 5.41),\textsuperscript{[25]} it is reasonable to simplify multi-step ionization of carboxyl groups in MPc\textsuperscript{ex} to two-step process, with pK\textsubscript{a} of first four carboxyl groups (one on each of four benzene rings of macrocycle) ionization standing far apart from those of other four ones. In this regard the differences in curves on Figure 1 can be tentatively explained as follows. Neutralization of the first four carboxylate groups in MPc\textsuperscript{ex} octaanion evidently occurs at pH about 6. For Pt and Pd complexes this process is accompanied by abrupt aggregation (Figure 1A). Compounds ZnPc\textsuperscript{ex} and CoPc\textsuperscript{ex}, being more soluble, have monomer–aggregate transition more sloping and shifted to lower pH. AlPc\textsuperscript{ex} remains soluble till the other four carboxylates neutralization at pH 3.5–4., the apparent first step is visible as a wave in pH interval from 5 to 6 (Figure 1B). It should be mentioned that for this compound the titration curve may also be affected by deprotonation of the axial hydroxyl group.\textsuperscript{[26]} Thus, it may be concluded that at pH below 3.5, unionized MPc(COOH)\textsubscript{ex} and at pH above 7 octacarboxylated MPc(COONa)\textsubscript{ex} form predominate. Intermediate tetraanion MPc(COOH)\textsubscript{4}(COONa)\textsubscript{4} evidently prevails at pH about 5. In 3.5–4.5 and 5.5–6.5 pH intervals transitions MPc(COOH)\textsubscript{4} → MPc(COOH)\textsubscript{2}(COONa)\textsubscript{2} and MPc(COOH)\textsubscript{2}(COONa)\textsubscript{2} → MPc(COONa)\textsubscript{8} occur, correspondingly (Scheme 1).

To prove this statement, with ZnPc\textsuperscript{ex} as an example we studied the effect of pH on its absorbance and fluorescence in the presence of surfactant (4 % Cremophor EL) for disaggregation. As it follows from solubility and monomerization of all differently ionized forms, the use of Cremophor EL solutions is advantageous. Figure 3 demonstrates changes of the absorbance at Q band maximum and fluorescence intensity during titration of ZnPc\textsuperscript{ex} alkaline solution, containing Cremophor EL, by HCl. Within the pH range of 7–10, the absorption (λ\textsubscript{max} 690 nm) and fluorescence intensity (λ\textsubscript{max} < 700 nm) of octaanion were nearly the same. Reducing

![Figure 3. Influence of pH on the absorbance (at 690 nm, ▴) and fluorescence intensity (at 700 nm, ◦) of ZnPc\textsuperscript{ex} aqueous solutions, containing 4 % Cremophor EL.](image)

**Scheme 1.** Ionization of MPc\textsuperscript{ex}.
the pH from 7 to 5.5 caused the significant changes – decrease in the absorption and fluorescence intensities to minimum at pH 5–5.5 along with a 5 nm red shift in their spectra were observed. Then, with further pH decrease to about 3, the restoration, complete for fluorescence and partial for absorption, took place. In solutions of pH < 3 both absorption and fluorescence were nearly unchanged. These observations are in agreement with apparent two-step ionization of ZnPc\textsuperscript{ac} ranges of pH > 7, 5–5.5 and < 3 may be ascribed to predominant existence of ZnPc\textsuperscript{ac} as octaanion, tetaanion and neutral acid, correspondingly. Spectral changes during transitions ZnPc(COOH)\textsubscript{4} – ZnPc(COOH)\textsubscript{4}(COONa)\textsubscript{4} and ZnPc(COOH)\textsubscript{4}(COONa)\textsubscript{4} – ZnPc(COONa)\textsubscript{4} are presented in Figure 4. Isosbestic points were observed for each process, indicating protonation-deprotonation without the presence of side reactions such as aggregation or decomposition.

We believe that both above-mentioned transitions are also multi-step, but close and overlapping processes, not resolvable spectroscopically.

Dependences of fluorescence intensity for AlPc\textsuperscript{ac} and absorption for non-fluorescing CoPc\textsuperscript{ac} vs. pH in the presence of Cremophor EL were similar to those of ZnPc\textsuperscript{ac} in Figure 3, evidencing minimum at pH 5. Corresponding studies of PtPc\textsuperscript{ac} and PdPc\textsuperscript{ac} were unsuccessful because these complexes failed monomerization by surfactant at acidic conditions. However, for all MPc\textsuperscript{ac} we suppose the similar two-step ionization with predominant existence of octaanion, tetaanion and neutral acid at pH > 7, about 5 and < 4, respectively.

For ZnPc\textsuperscript{ac} we have compared the spectral-fluorescent, photochemical and photosensitizing properties of three differently ionized forms (Table 2). It should be noted that photophysical and photochemical properties of this complex in aqueous medium and in the presence of bovine serum albumin were studied by Nyokong et al.\textsuperscript{[21,27]} We found that presence of Cremophor EL made no difference in their absorption and fluorescence maxima. Unionized acidic and intermediate tetraanionic forms of ZnPc\textsuperscript{ac} were studied for the first time in this paper. It was found that the Q-band absorption maxima of highly symmetric acid and octaanion are almost the same (689 and 690 nm, correspondingly), while that of tetaanion is 5 nm red shifted. The most striking effect ionization exerted upon molar extinction coefficient, which was 1.86 and 1.3 times higher for ZnPc\textsuperscript{ac} octaanion compared to that of tetaanion and acid (Table 2).

Fluorescence emission peaks were observed at: 696 nm for ZnPc(COOH)\textsubscript{4}, 705 nm for ZnPc(COOH)\textsubscript{4}(COONa)\textsubscript{4} and 700 nm for ZnPc(COONa)\textsubscript{4} in water–4% Cremophor EL (Table 2). Quantum yields of fluorescence (Φ\textsubscript{f}) for ZnPc(COOH)\textsubscript{4} and ZnPc(COOH)\textsubscript{4}(COONa)\textsubscript{4} were estimated relatively to that of octaanion (Φ\textsubscript{f}=0.18 at pH 10\textsuperscript{[21]} similar value can be assumed for ZnPc\textsuperscript{ac} octaanion in the presence of Cremophor EL). It was found that Φ\textsubscript{f} for the three differently ionized forms of ZnPc\textsuperscript{ac} were, however, not significantly (within experimental error of 10%), affected by ionization (Table 2). Hence, the distinct minimum on plot of fluorescence intensity vs. pH (Figure 3) is caused not by possibly lower Φ\textsubscript{f} of tetaanion, but by decrease of incident light absorption.

Singlet oxygen quantum yields (Φ\textsubscript{D}) of differently ionized ZnPc\textsuperscript{ac} forms are given in Table 2. The selective excitation of differently ionized ZnPc\textsuperscript{ac} in the Q absorption band resulted in disappearance of DPBF (example for ZnPc\textsuperscript{ac} acid is given in Figure 5). The DPBF absorption at 416 nm was monitored and the decrease in absorbance was

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**Figure 4.** Spectral changes during transitions ZnPc(COOH)\textsubscript{4}(COONa)\textsubscript{4} – ZnPc(COOH)\textsubscript{4} (a) and ZnPc(COOH)\textsubscript{4} – ZnPc(COOH)\textsubscript{4}(COONa)\textsubscript{4} (b).

**Table 2.** Photophysicochemical properties of ZnPc\textsuperscript{ac} differently ionized forms.

<table>
<thead>
<tr>
<th>ZnPc\textsuperscript{ac}</th>
<th>λ\textsubscript{abs, nm}</th>
<th>ε</th>
<th>λ\textsubscript{em, nm}</th>
<th>Φ\textsubscript{f}</th>
<th>Φ\textsubscript{D} = Φ\textsubscript{D}/Φ\textsubscript{f}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid (pH 2.8)</td>
<td>689</td>
<td>175000</td>
<td>696</td>
<td>0.20</td>
<td>0.55</td>
</tr>
<tr>
<td>Tetraanion (pH 5)</td>
<td>695</td>
<td>120000</td>
<td>705</td>
<td>0.19</td>
<td>0.59</td>
</tr>
<tr>
<td>Octaanion (pH 7.4)</td>
<td>690</td>
<td>224000</td>
<td>700</td>
<td>0.18 (pH 10\textsuperscript{[21]})</td>
<td>0.57 (PBS, pH 7.4\textsuperscript{[24]})</td>
</tr>
</tbody>
</table>
Conclusions

Effect of \( \mathrm{pH} \) upon aggregation of MPc\(^{n-}\) (where \( \text{M} = \text{Al, Zn, Pt, Pd, Co} \)) in aqueous media has been studied using absorption and fluorescence spectroscopy. The results show that the solubility and aggregation of MPc\(^{n-}\) in aqueous solutions are affected by ionization of peripheral carboxyl groups but also by axial ligation of central metal atom. For Pt and Pd complexes \( \mathrm{pH} \) decrease results in abrupt aggregation at \( \mathrm{pH} \) about 6, while for capable to axial ligation ZnPc\(^{n-}\), AlPc\(^{n-}\) and CoPc\(^{n-}\) it is more sloping.

For the first time the evidence for the multi-step, notably pseudo two-step, process for MPc\(^{n-}\) ionization, induced by change of \( \mathrm{pH} \), was provided by study of ZnPc\(^{n-}\) and AlPc\(^{n-}\) in aqueous Cremophor EL solution. One from two carboxyl groups of each benzene ring of macrocycle is protonated–deprotonated within 5–6, and another – within 3.5–4 pH ranges. It was established that at \( \mathrm{pH} \) below 3 insoluble unionized MPc(COOH)\(_n\), and at \( \mathrm{pH} \) above 6.5 fully deprotonated MPc(COONa)\(_n\), forms predominate while intermediate tetraanion form MPc(COOH)\(_2\)(COONa)\(_2\) prevails at \( \mathrm{pH} \) about 5.

The photophysicochemical properties of three differently ionized forms of ZnPc\(^{n-}\) were compared in Cremophor EL solution. The Q-band absorption maxima of highly symmetric acid and octaanion are almost the same (689 and 690 nm) while that of tetraanion is 5 nm red shifted. The most striking effect ionization exerted upon molar extinction coefficient, which was 1.85 and 1.3 times higher for ZnPc\(^{n-}\) octaanion than those of tetraanion and acid. It was found that all differently ionized forms of ZnPc\(^{n-}\) have nearly the same quantum yields of fluorescence (0.18–0.20) and singlet oxygen generation (0.55–0.59), while hundred-fold difference in photobleaching quantum yields was observed accordingly with electrophilic singlet oxygen contribution to its photodecomposition.

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