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Effect of the Medium on Fluorescence Parameters and Photostability of Porphyrins of Different Structure

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Abstract—Fluorescence and photostability against the action of UV irradiation of different porphyrins in benzene, DMF, and acetic acid media have been studied. The effect of the macroheterocycle structure on the conditions of its thermal decomposition under inert atmosphere has been investigated.

Keywords: porphyrin, photodecomposition, NH-activity, nonplanar macrocycles, thermal stability

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Aromatic tetrapyrrole macroheterocycles (porphyrins H_2P, their structural analogs, and metal complexes) are promising for a wide range of applications including industrial catalysis and medicine [1]. One of important relevant properties of these compounds is their photostability determined by the structure of an H_2P molecule and its intermolecular interactions in the solution. We have earlier shown that the polarization of the macroheterocycle due to the features of the functional substitution or nonplanar conformations of the molecules is the major factor affecting the photostability of porphyrin analogs (porphyrinoids) [2]. Here we have aimed to verify whether the earlier made conclusions are applicable to various structural types of porphyrins as such. To do so, we investigated the fluorescence parameters and stability against UV irradiation of a series of H_2P compounds **1**–**15** (Scheme 1). The experiments were performed as described in [2], in the media of non-coordinating (benzene), coordinating electron-donor (DMF), and weakly coordinating proton-donor (acetic acid) solvents. Furthermore, we elucidated the effect of the macroheterocycles nonplanarity on their thermal stability in inert medium.

The H_2P compounds as such can exist either in planar aromatic or strongly nonplanar conformation [3–5]. The deviation from the planarity of aromatic macrocycles is an important factor affecting the properties of conventional porphyrins [6]. The nonplanar porphyrins in the crystal as well as in the solution exist in the most typical grooved or saddle conformation [4, 6]. The increase in the nonplanarity of H_2P in the solution is marked by the growing Stokes shift {$\Delta\nu_\mathrm{I}^\mathrm{St}$ [Eq. (1)], Table 1} of the boundary bands in the spectra of fluorescence and absorbance [4, 7].

$$\Delta\nu_\mathrm{I}^\mathrm{St} = 10^7(\lambda_\mathrm{I}^\mathrm{fl} - \lambda_\mathrm{I}^\mathrm{a})/\lambda_\mathrm{I}^\mathrm{fl}\lambda_\mathrm{I}^\mathrm{a}, \tag{1}$$

where $\lambda_\mathrm{I}^\mathrm{fl}$ being the wavelength of the first emission band and $\lambda_\mathrm{I}^\mathrm{a}$ being the wavelength of the first absorption band (nm).

The compounds considered in this study can be divided into porphyrins with predominantly planar (**1**, **2**, **4**, **5**, **13**), rigid aromatic (**6**, **8**, **9**), and strongly nonplanar (**3**, **7**, **10**–**12**, **14**, **15**) structure, belonging to different structural groups of the macroheterocycles [6]. The nonplanar structure of the molecules has been confirmed by the data of X-ray diffraction analysis and quantum-chemical simulation [4–5], high Stokes shift (Table 1), and significant (up to 2–3 orders of magnitude) weakening of the fluorescence [7], as, for example, exemplified by the comparison of the predominantly planar compound **2** and strongly nonplanar macroheterocycle **10** (Fig. 1). The fluorescence is generally stronger in nonpolar solvents (benzene) than in the polar media (DMF).

The predominantly planar H_2P compounds represent β- and *meso*-substitute porphyrins, if the substitutes are not bulky and do not significantly

Scheme 1.

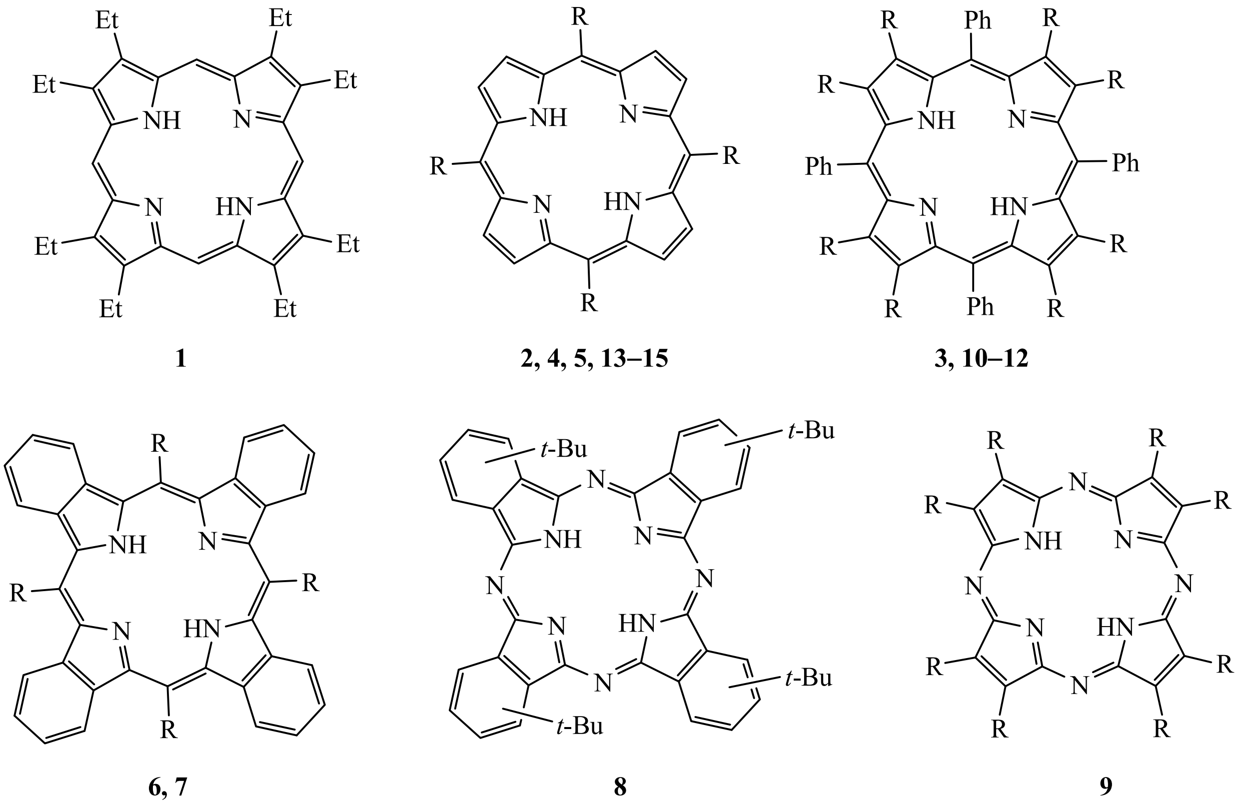


Table 1. Positions and Stokes shifts of the boundary bands in the absorption and emission spectra of porphyrins **1–15** in benzene and DMF media

Comp. no.	Absorption λ_1, nm	Emission λ_I, nm	$\Delta\nu_I^{St}$, cm^{-1} (nm)	Absorption λ_1, nm	Emission λ_I, nm	$\Delta\nu_I^{St}$, cm^{-1} (nm)	$\Delta\Delta\nu_I^{St}$, cm^{-1} (nm)
	DMF			benzene			
1	647	654	142 (6)	650	657	141 (6)	1 (0)
2	620	624	103 (4)	623	626	77(3)	26 (1)
3	749	804	867 (54)	715	767	948 (52)	81 (2)
7	697	710	263(13)	696	705	183 (9)	80 (4)
8	697	703	122 (6)	699	704	81 (4)	41 (2)
9	653	675	499 (22)	670	683	262 (12)	237 (10)
10	697	714	342 (17)	692	749	1100 (56)	758 (39)
11	731	783	909 (52)	713	747	620 (33)	289 (19)
12	725	771	823 (46)	695	730	690 (35)	133 (11)
13	–	–	–	661	663	46 (2)	–
14	658	665	160 (7)	661	668	136 (6)	24 (1)
15	660	667	159 (7)	664	669	113 (5)	46 (2)

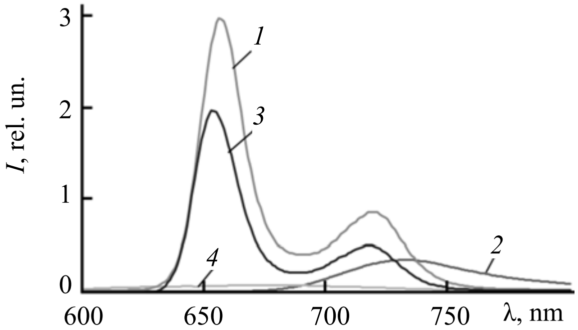


Fig. 1. Fluorescence emission spectra of macroheterocycles **2** (*1*) and **10** (*3*) in benzene; **2** (*2*) and **10** (*4*) in DMF.

hinder the structure sterically. The second group includes tetraaryl-fused (in particular, benzoannelated) and(or) tetra-*meso*-aza-substituted macroheterocycles. The planar structure is strongly distorted by the tetra-*meso* substitution of the macrocycle with bulky groups (compounds **14** and **15**), multiple simultaneous β- and *meso* substitution (up to the maximum of 12 substituents) (compounds **3**, **7**, and **10–12**), or protonation of the tertiary nitrogen atoms of the coordination cavity of the H_2P molecule in the acid medium resulting in the formation of dications H_4P^{2+}, where the localization of the protons is similar in the considered compounds, except for macroheterocycles **8** and **9** [4].

Hence, functionalization at the peripheral or central part of the porphyrin macrocycle can efficiently tune the molecule conformation to be typical of certain structural group. For example, substitution of tetrabenzoporphyrin **6** (belonging to the second group of the macroheterocycles) at four *meso*-positions with alkyl or aryl groups imparts the properties of strongly nonplanar dodecasubstituted H_2P [8, 9]. The three considered groups of porphyrins are significantly different in the physicochemical parameters and reactivity [6].

Analysis of the obtained photophysical data (Table 1) revealed the lowest Stokes shift (practically insensitive to the solvent nature, the difference between those in benzene and DMF not exceeding 1–3 nm) for compounds **1**, **2**, **7**, **8**, and **13–15**. This fact evidenced the same conformation of the macrocycle irrespective of the medium. At the same time, the H_2P compounds **1**, **2**, and **13** were planar macroheterocycles of the first group, whereas other listed compounds belonged to the macrocycles of rigid (**8**) or strongly nonplanar (**7**, **14**, and **15**) structure. These macroheterocycles possess weak reactivity of the NH bonds and either do not form the H-associates of the acid-base type (2) with electron-donor molecules (**14**, **15**) [10] or exhibit very weak interactions not manifested in the electron absorption spectra (**7**, **8**) [4].

$$H_2P\ (\mathbf{3}, \mathbf{9}\text{–}\mathbf{12}) + \mathrm{Solv} \rightleftarrows \mathrm{Solv}\cdots H\text{–}P\text{–}H\cdots \mathrm{Solv}. \qquad (2)$$

The formation and properties of the H-associates of NH-active H_2P compounds and their analogs with electron donors have been earlier studied in detail by means of electronic and NMR spectroscopy [6, 10, 11], chemical kinetics and spectrophotometric titration [9, 12, 13], calorimetry [14, 15], thermal analysis [16, 17], and quantum chemistry methods [18, 19].

Porphyrins of the second and third groups can form the H-associates with electron-donor solvents Solv (2) like DMF, as manifestation of the polarization component of the macrocyclic effect [4]. Analysis of their electron absorption spectra and the changes in the Stokes shift depending on the solvent nature should account for the stability of the formed H-associates. For example, benzo- and azabenzo-substituted macroheterocycles exhibited quite low NH-activity and form weak H-associates which were not reflected in the electron absorption spectra (Table 1). This was further evidenced by practically constant (irrespectively of the solvent nature) Stokes shifts (1) of these compounds, as, for example, in the case of macroheterocycle **8**. At the same time, the low $\Delta\nu_{\mathrm{I}}^{\mathrm{St}}$ value suggested planarity of macroheterocycle **8**. Activation of the NH bonds in those compounds (for example, via the introduction of electron-acceptor substituents) led to the strengthening of the H-associates and their manifestation in the electron absorption spectra (compare the spectra of compound **9** recorded in weakly coordinating benzene and in electron-donor DMF).

Nonplanar *meso*-substituted H_2P, for example, compounds **14** and **15**, take grooved conformations exhibiting zero dipole moment (Fig. 2) and low reactivity of the NH bonds [4, 11]. The changes in the values of Stokes shift of *meso*-substituted H_2P revealed that the degree of the nonplanarity was enhanced in the $\mathbf{13} < \mathbf{2} \leq \mathbf{14} \approx \mathbf{15}$ series. The saddle-type nonplanar structures (Fig. 2), for example, dodecasubstituted compounds **3**, **7**, and **10–12**, exhibited prominent NH-reactivity, as evidenced by the difference in the λ_{I} values (electron absorption spectra) depending on the electron-donor properties and polarity of the solvent as well as by the change in the $\Delta\nu_{\mathrm{I}}^{\mathrm{St}}$ values depending on the solvent nature (Table 1). The formation of the H-associate between H_2P and an electron donor can either enhance the nonplanarity or make the π-system

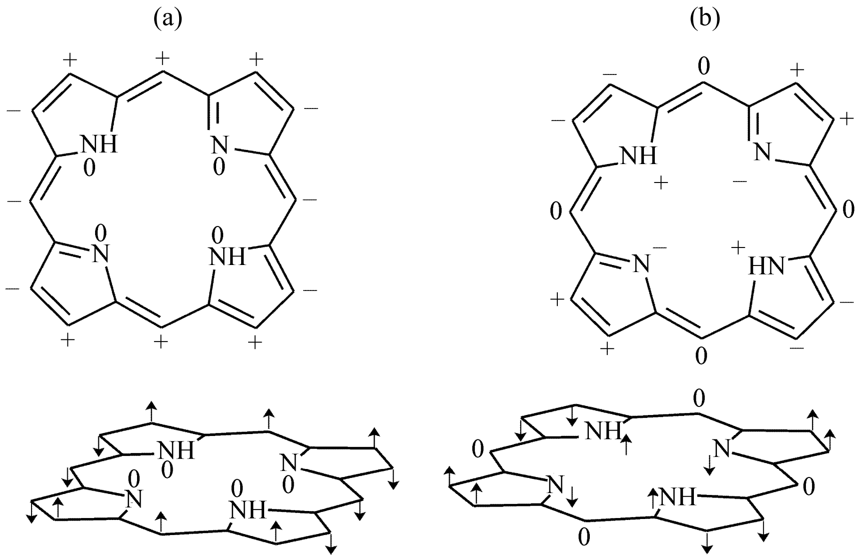


Fig. 2. Grooved (a) and saddle (b) nonplanar conformations of the porphyrin ligands. “+,” “–,” and “0” marks denote the location of the atoms above, under, and in the macrocycle plane, respectively.

more planar, as reflected in the changes in the Stokes shift of compounds **3**, **9**–**12** in different solvents (Table 1). For example, the Stokes shift was increased by 10–20 nm upon formation of the H-associate of compounds **9**, **11**, and **12** with DMF, being almost constant in the case of compound **3** and significantly decreasing in the case of compound **10** due to the molecule flattening.

We studied the photostability of a series of the macroheterocycles (Table 2) under the action of UV irradiation to elucidate the related effects of the molecule structure and the medium. The obtained data on the degree of the macrocycles photodecomposition (η_t) after 50 min of UV-irradiation revealed that the most planar compounds **1** and **2** revealing low NH-activity were also the most stable against irradiation (Table 2). The highest stability was observed for the more planar molecule **1** containing eight β-alkyl substituents (the degree of photodecomposition 5 to 11% depending on the medium), and *meso*-tetraphenylporphyrin **2** was somewhat less stable (degree of photodecomposition 16 to 32%).

The introduction of phenyl substituents at the β-positions of tetraphenylporphyrin molecule (compound **3,** Table 2) enhanced the substrate photostability in aprotic benzene and proton-donor acetic acid (the degree of photodecomposition being below 2%), whereas the degree of the pigment photodecomposition in DMF was as high as 79%, much higher then for less

Table 2. Photostability of porphyrins **1**–**8** upon 50 min UV irradiation

Comp. no.	DMF		Benzene		AcOH	
	λ, nm	η_{50}, %	λ, nm	η_{50}, %	λ, nm	η_{50}, %
1	620	11	622	9	547	5
2	647	32	650	22	656	16
3	742	79	739–727	2	708	0
4	647	< 1	647	12	647	0
5	649	7	649	12	657	0
6	662	38	664	54	662	86
7	642	55	642	57	643	73
8	696	80	699	63	735	100

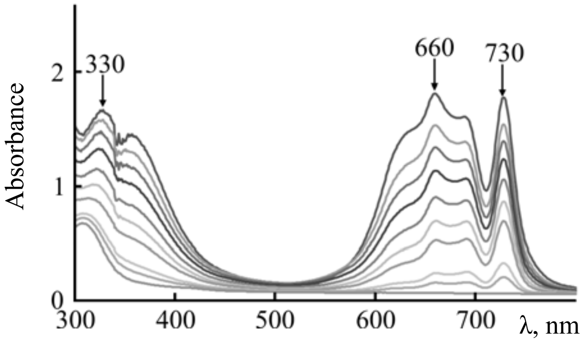


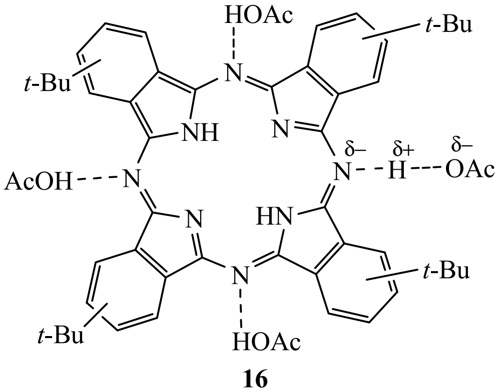
Fig. 3. Evolution of the electron absorption spectrum during photodecomposition (UV) of compound **8** in acetic acid (Δτ = 60 s).

substituted compound **2**. That was likely to some extent due to the strong nonplanarity of molecule **3** evidenced by the Stokes shift (Table 1) but was mainly related to the formation of the acid-base H-associates between the macroheterocycle and DMF [Eq. (2)].

Unexpectedly, the introduction of *para*-substituents to the phenyl rings of macroheterocycle **2** (compounds **4** and **5**, Table 2) did not reduce the chromophore photostability, irrespective of the electronic nature of the substituents. The introduction of the acceptor nitro and donor *tert*-butyl groups resulted in the degree of photodecomposition of the substrates 0 to 12%, depending on the solvent nature.

Compounds **6**, **7**, and **8**, tetrabenzoannulated molecular systems, were the least photostable of the studied macroheterocycles (Table 2). Even though *tert*-butylphthalocyanine **8** was conformationally rigid, the degree of its photodegradation (63 to 100% depending on the solvent) was higher than that of compounds **6** and **7**; the degradation in the proton-donor solvent was complete within 10 min (Fig. 3). This was likely due to the formation of asymmetric associate **16** of the macroheterocycle with the acid at the exocyclic *meso*-nitrogen, leading to the chromophore polarization. Thus, the UV photostability of tetrabenzo- and tetraaza-substituted porphyrins was low (Scheme 2).

Scheme 2.



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We suggested that thermal stability of the considered H_2P compounds should follow the same trends. The relevant experimental data are shown in Table 3. Thermogravimetric analysis of solid samples of predominantly planar macroheterocycle **2** and strongly nonplanar compounds **3** and **7** revealed that the temperature of onset of their thermal decomposition under inert atmosphere decreased in the **2** (470) ≥ **3** (401) >> **7** (159) series, i.e. the benzo-annulated macroheterocycle **7** was significantly less stable than another dodecasubstituted compound. Thermal decomposition of compound **7** was complete at the lowest temperature (437°C) as compared with compounds **2** and **3**.

Moreover, thermogravimetry data confirmed the difference in the formation of acid-base H-associates of compounds **3** and **7** with DMF. In partyicular, the formation of the associates was not manifested in the thermogram of macroheterocycle **7**, whereas porphyrin **3** gave the 1 : 1 H-associate exhibiting the solvent evaporation enthalpy $\Delta_{vap}H$ 19 kJ/mol [16].

Returning to the photostability of the studied compounds, that of macroheterocycles **6** and **7** was close in the noncoordinating (benzene) medium (Table 2), even though the introduction of *meso*-phenyl groups in compound **6** imparted significant nonplanarity of the molecule. In the electron-donor coordinating medium (DMF) the change in the degree of photodecomposition of compounds **6** (38%), **7** (55%), and **8** (80%) coincided with the increase in the NH-activity of the compounds and strengthening of the H-associates with the solvent [Eq. (2)].

The degree of decomposition of the macroheterocycles in DMF increased with the increase in the ability to form the acid-base H-associates with electron donors [6] in the **2** < **6** < **7** < **3** ~ **8** series. The studied compounds formed the following series of the decreasing photostability against UV irradiation in benzene: **3** > **1** > **4** ~ **5** > **2** > **6** > **7** > **8**. The NH-activity effect was ruled out; however, the analysis of the photophysical properties (Table 2) showed that the enhancement of photostability of the compounds in benzene was not directly related to the nonplanarity of the ligands in H_2P: for example, the η_τ values were close for planar and nonplanar compounds **6** and **7**.

Table 3. Thermal decomposition of macrocycles H_2P and their H-associates in DMF under argon[a]

Comp. no.	H-associates				Macrocycle				
	t_o, °C	t_{max}, °C	t_f, °C	composition	$\Delta_{vap}H$, kJ/mol	t_o, °C	t_{max}, °C		t_f, °C
2 [19]	–	–	–	–	–	470	486	–	498
3 [16]	107	155	184	1 : 1	19	401	410	718	≈920
7	–	–	–	–	–	159	219	398	437

[a] t_o, t_{max}, and t_f are temperatures of the onset, fastest mass loss, and finish of the decomposition of the sample, respectively.

The most nonplanar macrocycle **3** was the most stable since it existed in the monoprotonated form H_3P^+ in the benzene solution, due to strong basicity [4].

Photostability of the studied compounds in acetic acid decreased in the **4** ~ **5** ~ **3** < **1** < **2** << **7** < **6** < **8** series. In AcOH medium, the studied macroheterocycles (except for weakly basic tetrabenzoporphine **6** and the derivative of *meso*-tetraphenylporphine **4** containing electron-acceptor substituents) were protonated at the tertiary nitrogen atoms. The lowest photostability of phthalocyanine **8** was likely due to the polarization of the molecule owing to the unsymmetrical structure of the acid-base H-associate formed via one of the exocyclic nitrogen atoms [20]. Symmetrical doubly protonated (at the transannular atoms) H_4P^{2+} species formed by the porphyrins proper in acidic media [21], for example, compounds **1**–**3**, **5**, and **7** were generally more photostable.

Hence, the UV photostability and thermal stability of the porphyrins was determined by the modification of the macroheterocyclic scaffold of the molecule, for example, benzoannulation or aza-substitution, but were less sensitive to the nonplanarity of the macroheterocycles or the nature of the functional groups in the *meso*-phenyl fragments.

The formation of acid-base H-associates between H_2P and electron-donor solvent or appearance of asymmetric protonated forms leading to the molecule polarization reduced the compounds photostability. Vice versa, the formation of the symmetrical cationic forms (compound **3**) could stabilize the molecule due to the decrease in the electron density in the π-system.

As in the case of porphyrinoids [2], the Stokes shift value [Eq. (1)] characterized the degree on nonplanarity of the macrocycle, and significant change in this parameter depending on the medium (non-coordinating or electron-donor one) evidenced the compound NH-activity, including the formation of acid-base H-associates [Eq. (2)].

EXPERIMENTAL

Compounds **1**–**15** were synthesized as described elsewhere: **1**, **2**, **4**–**6**, **13** [22]; **3**, **12** [23]; **7** [24]; **8** [25]; **9** [26]; **11** [27]; **14** [28]; **15** [29]. The solvents were purified and dried via conventional methods [30].

Electron absorption and emission spectra were measured using an SM2203 spectrofluorimeter (450–800 nm). Emission spectra were registered at 90° angle with respect to the excitation source (high-pressure xenon lamp, λ_{ex} = 450 nm). The measurements were performed in a 10×10 mm cell, the solutions absorbance at the long-wave band being about 0.1. The Stokes shift ($\Delta\nu_I^{St}$) was calculated using Eq. (1).

Photostability of the compounds was studied by irradiating the dilute solutions of the macroheterocycles (about 10^{-6} mol/L) with a mercury-quartz lamp DRT 125 (230–400 nm, 30 μW cm^{-2} s^{-1}, irradiation duration 50 min). A quartz cell was placed at 70 mm from the lamp, and the absorption spectra were measured at regular time intervals using a UV-1800 Shimadzu spectrophotometer. The degree of photodecomposition (η) was estimated from the decrease in the absorbance of the long-wave band in the electron absorption spectra of macroheterocycles.

Thermogravimetric studies were performed using a DSC 204 F1 differential scanning calorimeter equipped with a TG 209 F1 Iris balance (NETZSCH). About 5 mg specimen was put in a platinum crucible and heated under static argon atmosphere at 10 K/min rate (298–1223 K range).

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CONFLICT OF INTERESTS

No conflict of interests was declared by the authors.

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