Inorganic Chemistry

Article

UV Photostability of Metal Phthalocyanines in Organic Solvents

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Kinetic studies of photochemical reactions induced by UV radiation in solutions of metal phthalocyanines have been carried out to determine the factors which might have influenced the stability of photosensitized phthalocyanines. Complexes of the molecular type Mpc, M'$_2$pc, and Lnpc$_2$ (where M = Li, Mg, Fe, Co, Zn, Pb; M'= Tl; Ln = rare earth; pc = phthalocyanine ligand, $C_{32}H_{16}N_8{}^{2-}$) were investigated in DMF, DMSO, and pyridine. Progressive decay of the phthalocyanine macrocycle due to absorption of UV light was observed. Phthalimide found in the final photolysis product may indicate some chemically bonded oxygen involved in the solid phthalocyanine material. Fluorescence lifetimes determined for the studied compounds (2.91–5.98 ns) have shown no particular relation to the stability of the excited macrocyclic system. The bonding strength of the photosensitized phthalocyanine moiety appears to rely on typical chemical factors, rather than on the properties of the excited states. Kinetics of the degradation process has proved to depend on the molecular structure of the complex and seems to be controlled by interactions of the macrocycle bridging nitrogen atoms with the solvent molecules. The use of electron acceptor solvents such as DMSO may enhance the molecular stability of phthalocyanines excited by UV radiation. Sandwich-type rare earth diphthalocyanines dissolved in DMSO displayed the highest photostability.

Introduction

Phthalocyanines are regarded as synthetic analogues of the porphyrin family. The very close chemical relationship between these compounds has promised phthalocyanines could be used as a convenient research model which would allow us to mimic the function of natural biochemical species, with practical application in mind. Hence, one of the principal scientific targets was to learn about the photoactivity of these macrocyclic compounds.

Photochemical properties of metal complexes of phthalocyanine have been intensively studied for some decades already. A survey of the basic research in this field has been presented by Simon and André[1] and subsequently expanded in the work of Ferraudi.[2] Experiments have proved that interaction of the macrocyclic phthalocyanine moiety with radiation from the UV and visible range results in population of excited states which may be quenched in different ways, depending on the studied system. Thus, it may be possible to design reactions in which the optical properties of phthalocyanines would be effectively utilized. High absorption of light both in the near UV range and at the red end of the vis spectrum, catalytic properties even when not activated, considerable thermal stability, typical synthesis and purification procedures, as well as relative low cost have become the principal advantages of these compounds. Therefore, phthalocyanines are considered to be very attractive photo- and radiosensitizers thought to find extensive application in chemical technology, ecology, medicine, and electronics.[3−12]

Stability of metal phthalocyanines in solution is generally determined by the complexed metal, type of the solvent used,

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as well as the presence of reducers and/or oxidants. Since illumination by light may generate excited phthalocyanine molecules, these could be expected to react also toward decomposition of the macrocycle, particularly when oxygen or another radical oxidizing species is found in the system. Thus, the application of such compounds may be restricted according to their individual stability limits. However, there is not much literature concerning the strength of a photo-sensitized phthalocyanine macrocycle, and it seems the problem has been only occasionally referred to.[2,13,14] The fact that such an otherwise very stable molecular setup could be broken down by absorption of light has not been clarified enough, and we think that the problem still needs to be given more attention to better understand the nature and the photochemical potential both of phthalocyanines and related compounds.

Photochemical decay of phthalocyanines in solution is considered to be a complex process due to the possible formation of different intermediate radical compounds, which may interact with each other and also with the system components. Because the reactive excited state is believed to be localized at the phthalocyanine ligand rather than at the metal ion, the phthalocyanine macrocycle may therefore be expected to be particularly sensitive to a destructive chemical attack. The quantum yield of the photodestruction process is generally assumed not to be central metal dependent.[2] Nevertheless, it seems that the molecular structure of the complex as well as the nature of the metal−ligand bond should also affect the photostability of these compounds. If so, a definite proof could be derived from kinetic investigations of photolyzed phthalocyanines representing different metal-related structural modifications.

In our work, we report on the stability of a range of metal phthalocyanines when exposed to UV radiation. In order to eliminate additional effects at the macrocycle, only phthalocyanine compounds with no peripheral ring substituents have been used. Thus, the kinetics of the studied photochemical process may be addressed first of all to the complex structure and the medium conditions.

Experimental Section

Phthalocyanine complexes of Li^I (dilithium), Mg^{II}, Fe^{II}, Co^{II}, Zn^{II}, Tl^I, Pb^{II}, and Ln^{III} (rare earth = $Ce^{III}-Lu^{III}$) were synthesized and purified in our laboratory according to commonly applied methods.[15] The rare earth diphthalocyanines were obtained in their blue form, extracted from the crude reaction product by DMF.

The studied phthalocyanines include metals of the s, p, d, and f blocks and display versatile molecular structures, i.e., flat, with the central metal fitting the "window" of the macrocycle (complexes of Li, Mg, Fe, Co, and Zn),[1] binuclear, with an almost flat bridging phthalocyanine unit (Tl2pc),[16] concave (Pbpc),[17] and sandwich (Lnpc2),[1] as shown in Figure 1. As far as the lanthanide diphthalocyanines are concerned, we have investigated the complete series

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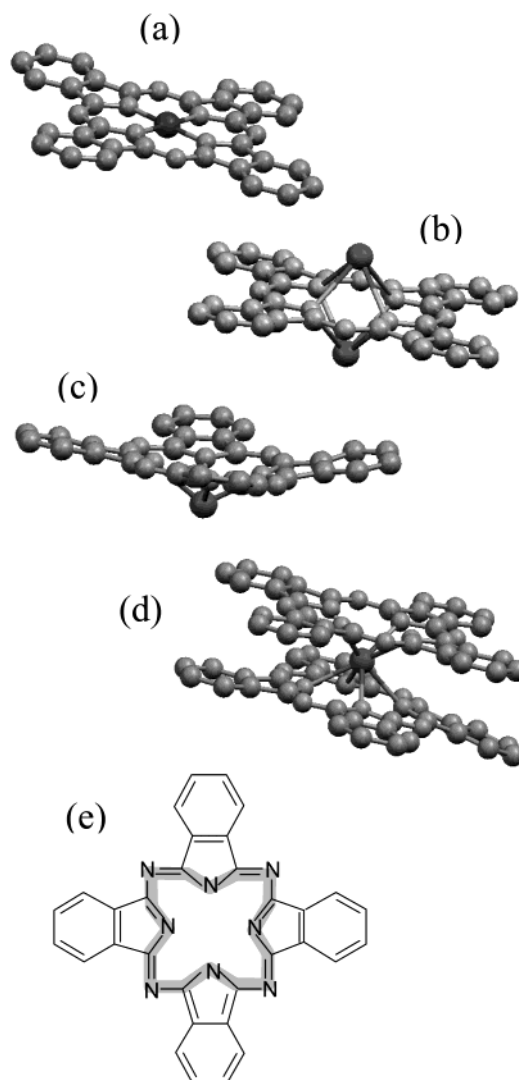(17) Ukei, K. *Acta Crystallogr.* **1973**, *B29*, 2290−2292.

Figure 1. Molecular structures of the investigated metal phthalocyanines: (a) flat (Mpc), (b) binuclear (Tl2pc), (c) concave (Pbpc), (d) sandwich (Lnpc2), and (e) representation of the phthalocyanine ligand, $C_{32}H_{16}N_8^{2-}$. The shaded path in part e shows the conjugated π-electronic bonding system of the macrocycle.

of these compounds. Since there was no peculiar relationship found which would allow one to unequivocally combine the photostability with any individual property of the rare earth elements, only results for the complexes of Ce and Eu have been presented. These illustrate the span between the lowest (Ce) and the highest (Eu) UV photostability determined for the studied Lnpc2 compounds.

Deaeration of solvents used in photochemical experiments is generally carried out either by saturating them with deoxygenated nitrogen or argon only[13] and/or by applying a freeze−thaw vacuum degassing technique.[18] The latter one proved to be more effective, which has been reflected by essentially lower rates of the photolysis. Also, particular care should be taken to keep the solvents absolutely dry since water molecules would eventually hydrolyze the excited phthalocyanines.

Solid phthalocyanine was added to the frozen solvent after three cycles of freezing and thawing under vacuum (77 K, 10 Pa), and after dissolving, the system was once again frozen, evacuated, and thawed. The phthalocyanine concentration (the order of 10^{-5} M,

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depending on the compound) was fixed to achieve initial absorbance values between 1.5 and 2.0. Prior to photolysis, the solutions were saturated for 30 min with dry nitrogen (oxygen-free) and, in some experiments, also with oxygen. This was always carried out directly in a quartz flow-cell (10 mm path length), the same as that next used in the test.

The photochemical reaction was performed at $T = 293$ K (thermostated), under continuous illumination by UV light (UV-lamp EMITA VP-60, $\lambda = 254$ nm, intensity 1.6 mW/cm^2), and electronic absorption spectra were measured in the range $\lambda = 190-1100$ nm (Unicam UV-310, Vision 32 software and Ocean Optics SD 2000, Basic Acquisition software). For comparison only, some tests were performed using a visible light source (100 W tungsten lamp, $\lambda = \sim400-800$ nm, filtered, global intensity 96 mW/cm^2). Radiation intensity was measured at the illuminated spot of the quartz cell.

Excited state (fluorescence) lifetimes were determined by a laser-excited time-correlated single-photon-counting (TCSPC) method using a picosecond laser spectrometer, at $\lambda_{exc} = 385$ nm (Centre of Ultrafast Laser Spectroscopy, AMU Poznań, Poland). A detailed description of the measuring technique and the setup applied in this study may be found elsewhere.[19]

To determine the photolysis decomposition products, concentrated solutions of the studied metal phthalocyanines (2.5×10^{-4} M, deaerated) were exposed to UV radiation until the decay of the compound was completed, which was confirmed by absorbance measurements. Afterward, the solvent was vacuum evaporated ($P = 10$ Pa, T = 310 K) to yield a nonsolid yellow-brown residue of a considerable viscosity. This product was studied by a thin-film FT-IR method using KBr plates (Philips FTIR PU 9800 spectrometer). Moreover, electronic absorption spectra of that product were also measured in concentrated sulfuric acid in order to examine the UV absorption bands for the presence of typical aromatic compounds one could expect to result due to the cleavage of the phthalocyanine macrocycle. It is to be mentioned that attempts to obtain a stable solid decomposition product have failed and evaporation of the solvent at higher temperatures produced a carbon-like dark material, probably due to the carbonization of the compounds, as followed from FT-IR investigations.

Results and Discussion

A solution of lead phthalocyanine (Pbpc) in DMF, normally very stable when stored in the dark, features a progressive loss in color intensity after being exposed to daylight. A similar light-sensitive reaction, although less dramatic, could be visually noticed also for the daylight illuminated phthalocyanines of Li, Mg, and Zn, particularly when dissolved in DMF. Preliminary studies proved the observed process was predominantly related to the share and intensity of the ultraviolet portion in the applied radiation (Figure 2). Interestingly, also in DMF the lanthanide diphthalocyanines (Lnpc$_2$) have practically resisted both daylight exposure and irradiation with light from the 400−800 nm range (tungsten lamp) contrary to the other studied species. This fact suggested the photostability should be related to the molecular structure of the phthalocyanine compound. Furthermore, the kind of applied solvent has appeared to be significant, as well.
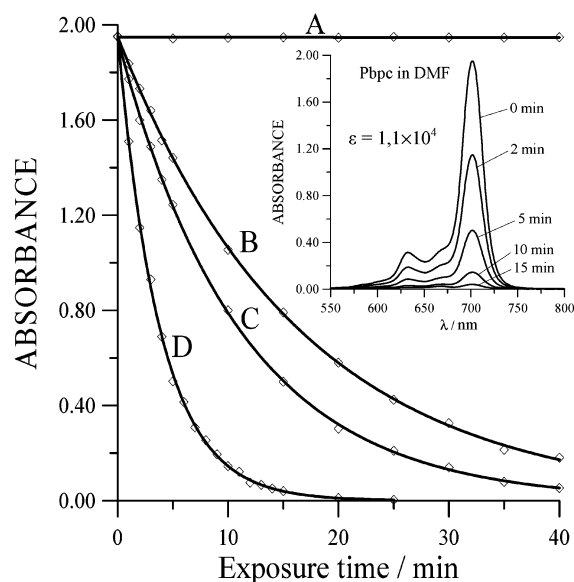
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Figure 2. Kinetic curves of photolyzed Pbpc in DMF: A, dark; B, laboratory scattered daylight (global radiation intensity 30 mW/cm^2, UV portion 0.015 mW/cm^2; $k_e = 0.06$ min^{-1}); C, tungsten lamp (96 mW/cm^2; $k_e = 0.09$ min^{-1}); D, UV lamp (1.6 mW/cm^2; $k_e = 0.26$ min^{-1}). Inset shows spectral changes (Q-band region) induced by UV radiation.

The character of spectral changes observed in UV-photolyzed solutions of the different metal phthalocyanines evidently depends on the electronic structure of the individual molecules. As a rule, three types of spectral changes have been identified, as shown in Figure 3.

Type I, for which λ_{max} of the photolyzed solution remained constant during the irradiation period, was found to be typical for Mpc's, where M = Li, Mg, Fe, Zn, and Pb, irrespective of the solvent used and for Tl$_2$pc in pyridine. Also in the case of Copc in DMF and Lnpc$_2$ in DMF and pyridine, the observed time-related spectral changes have in general followed the same scheme. However, for Copc there was a small bathochromic shift ($\Delta\lambda_{max} = 3$ nm) noticed during the first 20 min of irradiation, and afterward, the λ_{max} value has not altered more. In turn, the Lnpc$_2$ photolyzed in DMF and/or pyridine, during the initial reaction period, developed an additional plain peak ($\lambda_{max} = 670-680$ nm, relative to the complexed rare earth metal) of low intensity, but the position of the most intensive Q-band in the spectrum remained unchanged. The λ_{max} of the both absorption bands did not change while the samples were studied.

Type II was featured by Copc when photolyzed in pyridine and DMSO. During the first period of irradiation, the initial Q-band absorption peak shifted bathochromic for ca. 10 nm, and, after reaching a new peak point, stepwise switched back to the initial λ_{max} position.

Type III spectral changes were demonstrated exclusively by the Lnpc$_2$ species in DMSO. There was a new sharp absorption band being developed between 670 and 680 nm, whereas the primarily very intense Q-band ($\lambda_{max} = 620-636$ nm) had gradually extinguished. This could mean that a different modification of the Lnpc$_2$ was formed, apparently more stable under the experimental conditions than the initial one. The separation between the initial and the final position of the Q-band ($\Delta\lambda_{max}$) has appeared metal dependent and

TYPE I
$\lambda_{max} = const$

TYPE II
$\Delta\lambda_{max} = 10$ nm

TYPE III
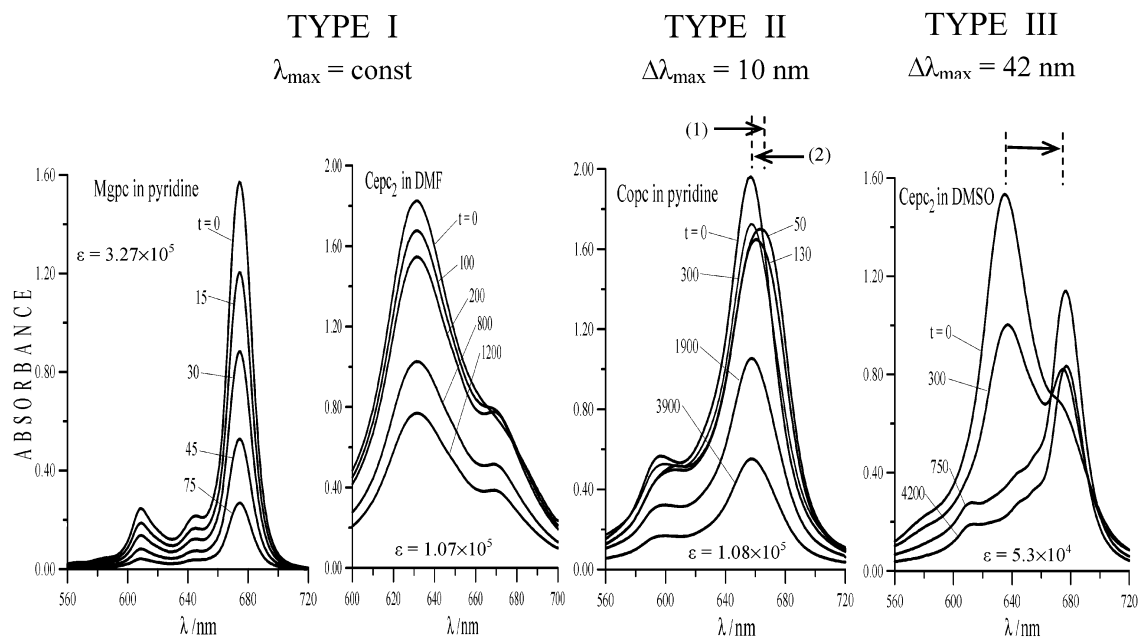$\Delta\lambda_{max} = 42$ nm

Figure 3. Types of spectral changes in the Q-band range revealed by UV-photolyzed phthalocyanines: (1) first stage, bathochromic shift of the Q-band; (2) Q-band peak moving backward, UV irradiation time, t/min, ϵ/dm^3 mol^{-1} cm^{-1} (Cepc$_2$, blue form, $\lambda_{max} = 635$ nm).

Table 1. Effective Reaction Rate Constants, k_e, Determined for the UV-generated Photolysis of the Investigated Metal Phthalocyanines

molecular structure:[a] central metal:	k_e, min^{-1}								
	a					**b**	**c**	**d**	
	Li	Mg	Fe	Co	Zn	Tl	Pb	Ce	Eu
DMF	0.10	9.17×10^{-2}	b	1.40×10^{-2}	3.00×10^{-2}	b	0.26	7.20×10^{-4}	2.30×10^{-4}
pyridine	2.90×10^{-2}	2.24×10^{-2}	3.80×10^{-3}	3.20×10^{-4}	9.85×10^{-3}	7.72×10^{-3}	0.10	3.70×10^{-3}	4.72×10^{-4}
DMSO	4.34×10^{-3}	4.90×10^{-4}	9.70×10^{-4}	1.20×10^{-4}	4.20×10^{-4}	b	1.34×10^{-2}	9.16×10^{-5}	4.14×10^{-5}

[a] The letters **a**, **b**, **c**, and **d** refer to the structures shown in Figure 1. [b] No homogeneous solutions have been obtained.

falls within the 40−50 nm range, as found for Ndpc$_2$ and Eupc$_2$, respectively.

A more detailed discussion of these results has been presented in the subsection describing the effect of the solvent, in the later part of this work.

Generally, the photolysis induced by UV radiation has followed a first-order reaction scheme

$$\text{Mpc} \xrightarrow{k_e} \text{products} \quad A(t) = A_0 \exp(-k_e \cdot t)$$
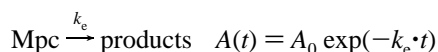
where A and A_0 are absorbances measured for the Q-band of the Mpc complex at time t and $t = 0$, respectively, and k_e is the effective reaction rate constant. The determined values of k_e have been collected in Table 1. The k_e parameter was used to evaluate and compare the photostability of the phthalocyanines explored in our experiments.

The kinetic curves $A = f(t)$ in each studied case have been determined for the finally established form of the complex, i.e., this one, which exhibited no shifts of λ_{max} versus time. Thus, for Copc in pyridine and DMSO (type II, Figure 3), only the $A(t)$ values have been used which referred to the spectra collected after the peak of the Q-band has switched back to its starting position. Similarly, for Lnpc$_2$ in DMSO (type III, Figure 3) only the new developed spectrum for the so-called green Lnpc$_2$ form[7] has been considered for the kinetic calculations. Since the transformation from the

initially blue form to the final green was found much faster than the rate of the photochemical degradation, we have estimated the k_e parameter from the portion of the kinetic curve featuring the decay of the green form. However, for the photolysis performed in DMF and/or pyridine the k_e values given in Table 1 correspond to the blue form of Lnpc$_2$.

The chemistry of photodegradation of the studied compounds involves excited molecular states of the phthalocyanine macrocycle, first of all resulting from the S0 → S1 excitation.[2] Electrons used in these transitions are those of the π-electronic bonding system. Thus, one may have expected the stability of photosensitized phthalocyanines to be related to the kinetic properties of the excited state. We have determined the lifetimes, τ, of the S1 state by the means of a picosecond laser spectrometer,[19] and the results are shown in Table 2. The measured lifetimes are on the nanosecond scale and match the respective data presented elsewhere,[20,21] although our values are somewhat lower.

Evidently, the lifetimes of the excited state depend both on the complexed metal and the applied solvent. From the results collected in Table 2, one may conclude, however, that it is the electronic structure of the metal phthalocyanine

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Table 2. Excited State Lifetimes, τ's, of the Investigated Metal Phthalocyanines ($\lambda_{exc} = 385$ nm)

molecular structure:[a] central metal:	τ, ns								
	a					b	c	d	
	Li	Mg	Fe	Co	Zn	Tl	Pb	Ce	Eu
DMF	3.43	5.98	b	b	2.91	b	3.46	5.32	4.00
pyridine	3.05	5.36	4.00	3.35	3.00	4.26	3.00	4.08	4.39
DMSO	4.75	5.87	4.64	4.70	3.04	b	3.25	4.21	3.98

[a] The letters **a**, **b**, **c**, and **d** refer to the structures shown in Figure 1. [b] No data available.

molecule that determines both the value of τ as well as the effect of interaction with the solvent. Thus, it must not be found surprising that the fluorescence lifetimes generally do not correlate with the photostability revealed by the studied phthalocyanines (Table 1). Apparently the kinetics of the photolytic degradation of the pc macrocycle depends predominantly on the conjugated bonding system strength which is controlled by the distribution of the π-electrons, in particular at the outer C−N bonds coupling the four benzopyrole units of the phthalocyanine moiety. Due to excitation, the electronic density of these bonds is supposed to decrease, and the resulting excited molecule would become less stable than in its ground state. Thus, the data collected in Tables 1 and 2 indicate the photostability to be determined by the extent of fluctuations in electronic density inside the macrocycle. This, however, is not reflected by the values of τ. Therefore, we have assumed that, for the differences in stability of photosensitized phthalocyanines, as observed in our experiments, one should rather relate to the metal-dependent molecular and electronic structure of the Mpc's and interactions with the solvent.

These suggestions are going to be discussed in the following subsections: effect of the molecular structure, effect of the solvent, and product of photodegradation and the oxygen problem.

Effect of the Molecular Structure. There are a variety of excited phthalocyanine particles that are possibly produced by UV illumination,[2−8] and these display different molecular stabilities closely related to the individual properties of the original compound. As mentioned before, durability of the phthalocyanine macrocycle is determined by the distribution of the π-electrons engaged in the bonding system. One may then expect the strength of the C−N bonds coupling the four benzopyrole rings of the pc unit to depend on the degree of polarization of the π-electronic cloud (see Figure 1e) inside the macrocycle by the complexed metal. This was proved by small but distinct differences in length of the considered C−N bonds found in different phthalocyanines and was related to the metal's electronegativity and its electronic configuration.[22]

Moreover, solid phthalocyanines proved capable to accommodate guest molecules such as O_2 or N_2,[23,24] whereas in solution they often tend to bind additional axial ligands.[25]

Undoubtedly, this must also influence the stability of the whole molecular system. It has been shown[22] that in such cases the distribution of electronic density within the macrocycle may be noticeably affected. Particularly, one could expect this to occur at the bridging N atoms. In fact, this has been proved by structural changes reflected by a slight increase in length of the C−N (bridging) bonds.[26,27] Also the electronic density was found to be raised at the N bridges as confirmed by X-ray investigations.[27]

In a solution exposed to UV radiation, these bonds become weaker, and the photolysis rate is subject to the electron density at the bridging nitrogen atoms. Hence, it is first of all supposed to be strongly related to the molecular structure of the phthalocyanine compound. Thus, the UV photostability as observed in DMF, low for Pbpc and very high for Lnpc$_2$ (Table 1), may be considered to reflect a better "organized" and therefore stronger π-electronic bonding system in the case of sandwich-type Lnpc$_2$ molecules than in the case of Pbpc with a concave strained pc ligand (Figure 1). Also, the "flat" phthalocyanine complexes of Li, Mg, Co, and Zn appeared evidently more stable than Pbpc but much less than Cepc$_2$ (found to be the least durable one in the whole Lnpc$_2$ series). It can be expected that in Lnpc$_2$ molecules the ligands are more weakly polarized by the metal than in the case of a monophthalocyanine complex, and this fact should allow some higher electronic density of the C−N bonds at the N bridges in the macrocycles of Lnpc$_2$. This might have elucidated the considerable photostability of lanthanide diphthalocyanines.

A similar structure-linked explanation could be proposed in the case of the binuclear thalium compound, Tl$_2$pc (Figure 1b), which has proved more UV-resistant than those of Li, Mg, Zn, and Pb. Note that this particular molecular structure with the Tl atoms placed *trans* in relation to the macrocycle plane should also favor higher electronic density at the outer N bridges of the C−N bonding system.

The fact that some molecular modifications appear particular stable has been revealed also in oxygen-saturated solutions illuminated by UV radiation (as discussed farther on). Again, the rare earth diphthalocyanines proved to be the most stable ones.

It seems, then, that to a certain extent the photostability of phthalocyanines may be a measure of the molecular stress within the phthalocyanine macrocycle.

Effect of the Solvent. The rate of the photochemical reaction proved to depend on the solvent used. Each of the studied Mpc compounds showed increasing stability in the order DMF < pyridine < DMSO. A somewhat different sequence, namely pyridine < DMF < DMSO, was featured by the lanthanide complexes (Lnpc$_2$'s). In particular, DMSO appeared to produce a substantial stabilizing effect upon the macrocycle, very pronounced also in the case of the least stable compounds (see Table 1).

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The influence of the solvent one may attribute either to different solvation effects or a possible chemical interaction between the phthalocyanine complex and the solvent molecules. Any of the investigated solvents have been reported to give [MpcL$_2$] complexes including two axially coordinated solvent ligands (L = solvent), *trans* positioned in relation to the phthalocyanine plane.[25,28-30] Effective σ-donating ligands were found to reduce the polarization of the π-electronic cloud inside of the macrocycle and raise the electronic density of the conjugated C−N bonding system (see marked area in Figure 1e).[22,27] This may enhance the chemical stability of the phthalocyanine moiety.

In our study, only pyridine could be expected to reveal a strong axial coordination potential. In contrary, DMF and DMSO used to be placed among the weakly coordinating solvent ligands. As shown in Table 1, the magnitude of the observed stabilizing effect has been found to be markedly influenced by the complexed metal. The half-lives of the photolyzed phthalocyanines of Li, Mg, Zn, and even Pb determined in pyridine proved to be only about 3−4 times greater than those in DMF; however, in the case of Copc (the most stable compound in pyridine), that value was over 40. Perhaps it is so, because the other metals, opposite to cobalt, are not that prone to form effective axial bonds with pyridine, as suggested also by other workers.[22,31] As one may notice, the considerably lower stabilized phthalocyanines of Li, Mg, Zn, Tl, and Pb include closed-shell metal ions, which probably do not that accommodate additional axial ligands as effectively as the open-shell Co(II) ion does. This is also featured in the absorption spectra registered during photolysis (Figure 3). The different behavior of Copc in pyridine and DMSO, opposite to that of the other monophthalocyanines, is most probably generated by a multistep process of axial ligand bonding, involving both mono- and disubstituted species, as described elsewhere.[27,31]

In all of the studied cases, the phthalocyanines displayed evidently higher UV photostability in DMSO than in both pyridine and/or DMF. That fact does not conform to the generally accepted σ-donor strength sequence of the considered solvent ligands.[25] Note that in the case of sandwich phthalocyanines any effective axial ligation by either of these ligands must be excluded. Therefore, one should rather relate the much higher photostability generated in DMSO environment to other reasons, e.g., the well-known soft oxidizing properties of dimethyl sulfoxide.

The pyramidal DMSO molecule with the positive charge localized at the top S atom is an electron acceptor. Thus, it may not be considered a good axial ligand for the metal phthalocyanines. However, it is possible via the S atom that the DMSO molecules would interact with the nitrogen bridges of the pc moiety which would result in a partial back-polarization of the π-electrons inside the macrocycle. One
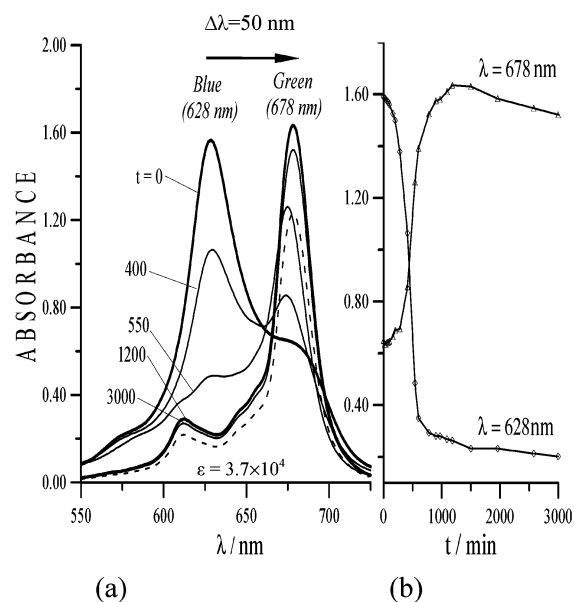

Figure 4. Photolysis of Eupc$_2$ in DMSO generated by UV radiation: (a) spectral changes in the Q-band region, UV irradiation time, t/min; ϵ/dm^3 mol^{-1} cm^{-1} (blue form); (b) raw kinetic curves measured at 628 nm (blue form) and 678 nm (green form).

could expect this to reinforce the C−N bonds linking the benzopyrole units of the macrocycle. This might have explained the higher UV photostability revealed by the studied phthalocyanines in DMSO in contrast to the other solvents. A similar stabilizing effect was observed for radical phthalocyanine species containing electron-withdrawing peripheral ring substituents, such as fluorines.[32]

The principle of the stabilization mechanism suggested in DMSO is very like that proposed for pyridine; however, the DMSO molecules proved to act more efficiently. To some extent, the DMSO molecules attracted by the N-bridges may additionally protect this weakest point of the phthalocyanine macrocycle from other reactive species present in the system. From the other perspective, both the molecular structure of DMF and the negative charge at the pyridine nitrogen atom do not allow these solvents to yield such an effect like DMSO does. That is probably why the sensitized Lnpc$_2$ complexes were found even somewhat less stable in pyridine than in DMF.

The described interaction between DMSO molecules and the bridging nitrogen atoms one may consider in terms of a "soft oxidizing effect" induced within a photosensitized phthalocyanine macrocycle. It is best reflected by spectral changes shown in Figure 4, which are considered typical for Lnpc$_2$.[25,33] At the first stage of UV irradiation, the initially blue Lnpc$_2$ has been irreversibly converted into its green modification, and hence, only the decay of the green compound could be followed from the spectra. The profile of the $A = f(t)$ curves measured for the Q-band (see Figure 4b) would suggest that for this class of phthalocyanines the studied process must include parallel and/or successive

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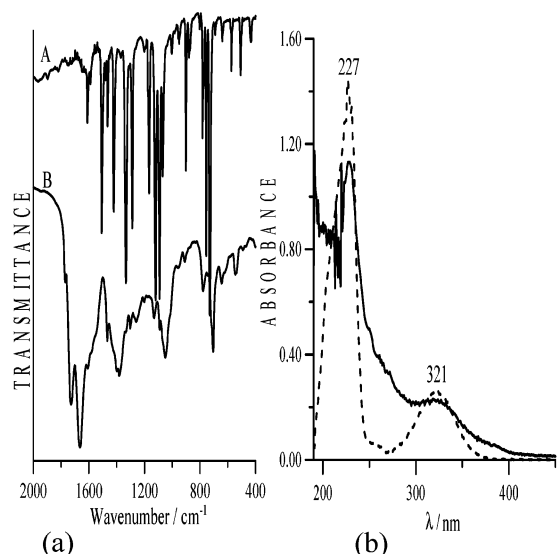(33) Nicholson, M. M.; Weismuller, T. P. *J. Electrochem. Soc.* **1984**, *131*, 2311−2313.

Figure 5. Final product of UV photodegradation of Pbpc in DMF: (a) FTIR spectra of pure Pbpc (A) and of the degradation product (B); (b) UV−vis spectra (in concentrated H_2SO_4), the degradation product (—) and phthalimide for comparison (- - -).

reactions. The very stable green form is believed to represent an "oxidiized molecular state" of Lnpc$_2$ as compared with the blue one.[33]

Due to the specific in-solution chemistry of rare earth diphthalocyanines, this behavior could not have been observed for the other studied compounds. However, also in the case of monophthalocyanines, the reason for a considerably better UV photostabilization produced by DMSO is supposed to be the same.

Product of Photodegradation and the Oxygen Problem. Attempts to identify the products of the photochemical process have included FT-IR and UV−vis spectral studies of the postreaction system. As indicated by the results shown in Figure 5, the phthalocyanine macrocycle has been split into predominantly aromatic compounds, characterized by the bands at 710 and 1610 cm^{-1} in the IR spectrum as well as in the UV range at $\lambda \sim 227$ and 321 nm. The set of bands at 1381−1665 cm^{-1} together with two characteristic bands at 1745 and 1753 cm^{-1} has allowed us to assume the principal reaction product to be phthalimide.[34] Moreover, the UV absorption bands show features corresponding to phthalimide, as well. As it may be learned from the spectra, there is enough evidence for some other species included in the postreaction product. Unfortunately, we were not in position either to isolate or identify other components of the UV-decomposed system, which would perhaps help to better understand the chemistry of sensitized phthalocyanines. Other authors have also reported only phthalimide to be identified in the photolysis product resulting from the cleavage of the pc ring.[2,14]

Formation of phthalimide must be related to a reaction localized at the macrocycle bridging nitrogen atoms with oxygen or eventually water molecules. It has to be emphasized that there is a general problem to get rid of oxygen

from solvents commonly used in photochemical experiments, particularly when the dissolved compounds tend to combine the O_2 molecules, as phthalocyanines do. Thus, there is always a question of limits at which the investigated system could be considered clean. Although investigation of the oxygen effect was not the main scope of this study, we felt it interesting to report some results obtained for solutions in oxygen-saturated DMF. For the monophthalocyanines listed in Table 1, the k_e parameter has increased by a factor from ca. 6 (Znpc) to 16 (Pbpc) and only about 3 times for Eupc$_2$. This would also indicate some compound-dependent reactivity of the phthalocyanines toward oxygen and is in good agreement with the results discussed in the preceding subsections. Additionally, we have also found the effect of water may be neglected at least up to 0.1% vol H_2O.

In our principal experiments, phthalimide was detected despite the phthalocyanine solutions having been thoroughly deaerated and prevented from contacting moisture. Hence, according to the published data we suppose it is possible that prior to preparation of the solutions some molecular oxygen could already have been chemically combined with the phthalocyanine complex (in the solids) and therefore might not have been entirely removed from the system by the applied degassing technique. As reported,[35] about 30% of the oxygen primarily adsorbed from air by solid Znpc appeared quite firmly fixed to the phthalocyanine material and could be removed only after thermal treatment at 150 °C. This "fixed oxygen" content was estimated to 1 O_2 molecule per 10 units of Znpc. The fact that oxygen molecules have got the potential to form more or less effective chemical bonds with the phthalocyanine unit, as proved by other workers,[18,23,24,33] may considerably influence the photochemistry of metal phthalocyanines, both in the solid state and in solution. Although we have failed to find oxygen in the photolyzed solutions, in our opinion it is the most likely reason for the reaction observed in the studied UV-sensitized phthalocyanine systems. Therefore, we suggest the possible route of the photochemical decay of the pc macrocycle should include the reaction with oxygen molecules, chemically involved in the phthalocyanine compound.

The conjugated π-electronic bonding system of the pc ligand has proved to be very sensitive to molecules, which may combine with the bridging nitrogen atoms of the macrocycle.[36] Molecular oxygen in its triplet ground state ($^3O_2$) will not oxidize a phthalocyanine molecule while in its singlet ground state (^{1}Mpc). Hence, even oxygen-saturated phthalocyanine solutions remain stable unless exposed to light. Due to absorption of UV radiation, the presumable Mpc−O$_2$ bond is supposed to be weakened enough to give off the oxygen molecule.

In a photochemical process, the ^{1}Mpc is been excited first of all to the ^{1}Mpc* (singlet) state which could be converted into the triplet state, ^{3}Mpc*, of sufficient energy to be quenched by the oxygen molecules being present in the

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system. Such a reaction may eventually produce molecular oxygen in its singlet excited state ($^1O_2^*$, $^1\Delta_g$).[8] At this stage, the reactivity of the excited system components seems to be high enough to be able to react toward oxidation of the macrocycle. This may account for the formation of phthalimide identified in the product of UV-decomposed phthalocyanines.

Summarizing our work, we would like to emphasize the importance of stabilizing effects, which may expand the lifetime of photoexcited macrocycles such as phthalocyanines. As it has been proved, properly balanced distribution of the π-electrons involved in the conjugated bonding system produced higher strength of the phthalocyanine moiety. In our opinion, the chemistry of the studied photodegradation process is determined by the nature of interactions between the bridging nitrogen atoms of the macrocycle and the solvent molecules, which we suppose most likely control the kinetics of the decay of photosensitized phthalocyanines. Thus, by combining structural features of the phthalocyanine compound and chemical properties of the applied solvent, it is possible to design the most optimized conditions for a photochemical reaction.