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Photochemical Stability of Various Porphyrins in Solution and as Thin Film Electrodes

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The stabilities of various porphin analogue compounds such as unsubstituted and substituted phthalocyanines, tetraphenylporphyrin, naphthalocyanine and tetraazaporphyrin have been investigated. The compounds were dissolved either in organic solvents or water. Electronic spectra in the visible region were recorded after the samples were kept either under inert gas or air in the dark and under illumination. The rate of decay of absorption is explained by a decomposition reaction which is of first-order kinetics with respect to the porphyrin concentration. Illumination, and the presence of oxygen, enhance the rate of decomposition. In general, an increase of the size of the ligand and an increase of the electron donating ability of substituents further enhance the rate of decomposition. Central metal ions with open shell arrangements of electrons favour the photodecomposition of the molecules. Thin solid films of phthalocyanines obtained by vapour deposition were investigated for their stability in contact with either air or an aqueous electrolyte. The influence of a cathodic bias potential was studied in the dark and under illumination. When compared to the dissolved molecules the crystalline solids turned out to be much more stable although, decomposition could be detected in a long-term photoelectrochemical experiment. Decomposition products were determined and appropriate mechanisms are discussed.

Porphin analogue compounds such as phthalocyanines (**1**), 5,10,15,20-tetraphenylporphyrins (**2**), naphthalocyanines (**3**) and their substituted derivatives function as active components in various processes driven by visible light: photoredox reactions and photooxidations in solution,[1–3] activity in the photodynamic therapy of cancer,[2,4,5] photoelectro-chemical cells,[6,7] photovoltaic cells[8,9] and electrophotographic applications.[10,11] For the synthesis, purification and investigation of the above-mentioned properties the stability of the macrocyclic compounds is of fundamental importance. However, to our knowledge, no paper is available that concentrates on this subject.

Several theoretical calculations show the apparent similarity between these macrocyclic systems and correlate predicted energy levels to those actually observed from absorption and emission spectra.[2,12–14] The electronic spectra of the square planar porphyrins and related macrocyclic systems in solution are mainly characterised by an intense absorption band in the near-infrared region (Q band at 600–800 nm) and another intense absorption in the near ultraviolet region (B or Soret band at 300–400 nm). In the solid state the absorptions are preserved although broadened and split owing to weak intermolecular interactions.

In this paper the stabilities of various porphin analogue compounds **1**–**6** were measured in solution (organic solvents or water) and exemplarily for **1** as a thin film in an electrochemical cell or in the dry state. The macrocyclic compounds were employed as used in visible light energy conversion devices: solution of 10^{-5} mol dm^{-3} in a quartz cell or *ca.* 100 nm thin solid films. The samples were kept either under air or inert gas in the dark and under illumination with visible light. The stabilities were determined quantitatively by the decay of absorption in the visible region of the electronic spectra.

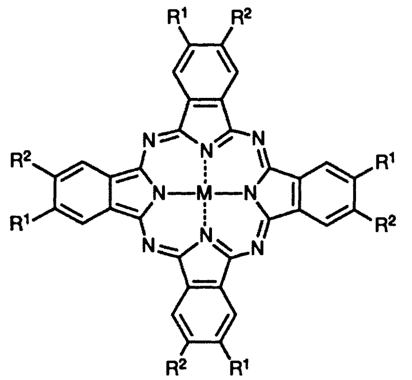
Results and Discussion

Stability in Solution.—Measurements in organic solvents of the zinc and cobalt complexes of phthalocyanine (**1a**), the zinc complex of 2,3,9,10,16,17,22,23-octabutoxyphthalocyanine (**1b**) and the zinc complex of 2,3,9,10,16,17,22,23-octacyanophthalocyanine (**1c**) allowed us to compare the influence of the central metal ion and of substituents on the stability. In addition, the zinc complex of 2,3,7,8,12,13,17,18-octamethylthio-5,10,15,20-tetraazaporphyrin (**4**) was used. As water soluble compounds the zinc complex of the anionic 2,9,16,23-tetrasulfophthalocyanine (**1d**), the metal-free cationic tetramethylpyrido[2,3-*b*:2′,3′-*g*:2″,3″-*l*:2‴,3‴-*q*]-5,10,15,20-tetraazaporphyrin (**5**) and the polymer-bound **6** were employed. The use of the zinc complexes of **1a**, **2** and 2,11,20,29-tetra(1,1-dimethylethyl)naphthalocyanine (**3b**) allowed us to study the influence of the ligands on the stability.

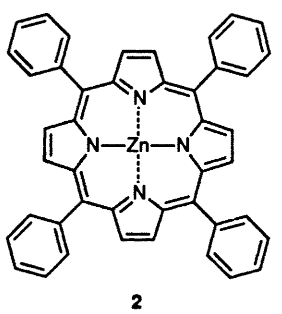
10^{-5} mol dm^{3} solutions of the complexes were employed in a quartz cell. This concentration is comparable with those used for the investigation of sensitizer activities (photoredox or photo energy transfer reactions).[1,215–22] The stability was determined by the decay in the intensity of the main absorption band (Q-band for **1**, **3**, **5** or a Soret-band for **2**, **4**, **6**)[1,2] in the visible region. The measurements were conducted in air or under argon either in the dark or under illumination (λ = 350–850 nm, 20 mW cm^{-2}).

The presentation and discussion of the quantitative measurements and results are started with the unsubstituted phthalocyanine **1a**, before derivatives are referred too. Exemplarily, the change of the absorption spectrum over time is shown in Figs. 1 and 2 for the phthalcyanine zinc complex (**1a**) dissolved in DMF after illumination either under argon or exposed to air. From Fig. 3 it is seen that under air the phthalocyanine is quantitatively decomposed after 3 h of irradiation whereas under argon only about 25% is decomposed after the same time. In both cases the decay obeys first-order kinetics in the concentration of the complex [eqn. (1); $E_{\lambda,0}$ = extinction at $t = 0$, $E_{\lambda,t}$ = at different times, Fig. 4].

$$\ln \frac{E_{\lambda,0}}{E_{\lambda,t}} = k_{\mathrm{D}} t \qquad (1)$$



1a: R^1, R^2 = H; M = Zn, Co
1b: R^1, R^2 = OC_4H_9; M = Zn
1c: R^1, R^2 = CN; M = Zn
1d: R^1 = SO_3H, R^2 = H; M = Zn



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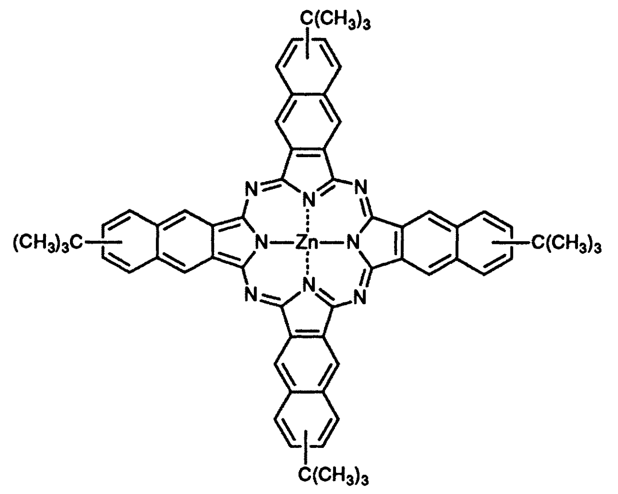

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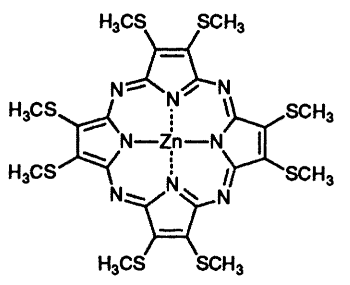

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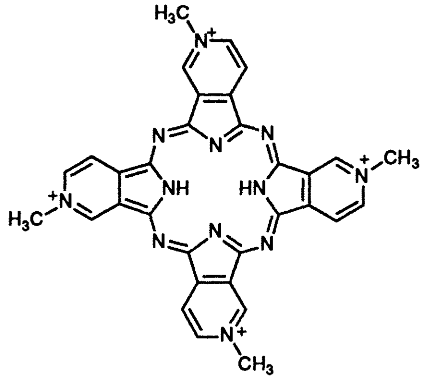

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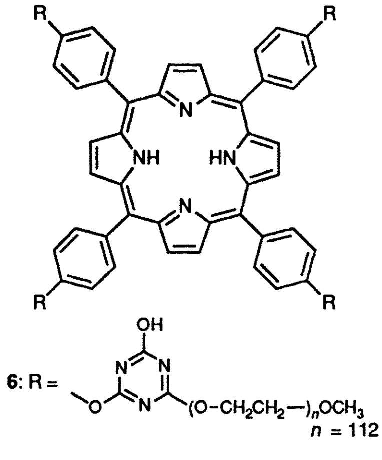


It is assumed that the decomposition consists of reactions of the complex with O_2 and/or the solvent. As the experiments were conducted under an excess of these reactants, the decomposition reaction is classified as being of pseudo-first-order kinetics. Values of k_D and of the time needed to decompose 5%, 10% and 50% of the original compounds **1**–**6** are listed in Tables 1 and 2.

The comparison of **1a** with M = Zn and M = Co shows that under air the cobalt complex exhibits a higher stability. Under argon in the dark the DMF solutions of both complexes are stable for several weeks whereas in the presence of air within one week 2.3% of the cobalt complex and 5.3% of the zinc complex is decomposed. It is seen from the values of Table 1 that under illumination the decompositions occur rapidly, and this is even more pronounced under air. Phthalocyanines have been intensively investigated because of their potential use as sensitisers in electron and energy transfer reactions. From the fact that the decomposition reactions in the presence of dioxygen occur much more rapidly than under argon it is concluded that the macrocycle is oxidized during the reaction.

Two mechanisms with O_2 are possible, either a direct electron transfer reaction or an energy transfer reaction leading to the formation of singlet dioxygen, $^1O_2$ ($^1\Delta_g$), from triplet dioxygen, $^3O_2$ ($^3\Sigma_g^-$).[1,2,15–17] $^1O_2$ could, in a second step, attack the macrocycle and oxidize it. One necessity for efficient sensitising in electron or energy transfer is a high lifetime of the excited triplet state τ_T. Phthalocyanines with central metal ions having a closed shell arrangement of their electrons, like Zn^{II}, exhibit high triplet state life times, whereas phthalocyanines having a paramagnetic metal ion like Co^{II} possess only very short triplet life times (Table 3). If no other quenchers are present, the sensitiser is decomposed by the energy rich $^1O_2$ or reduced dioxygen. For different zinc phthalocyanines under

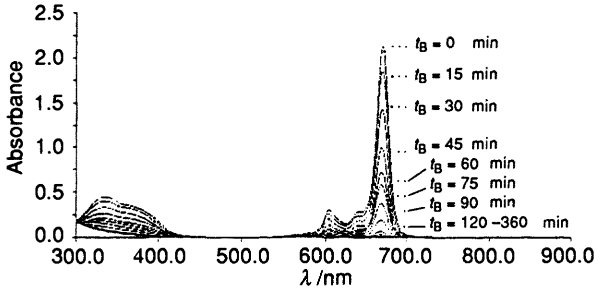


Fig. 1 Visible spectra of **1a** (M = Zn) in DMF under air at different times of illumination

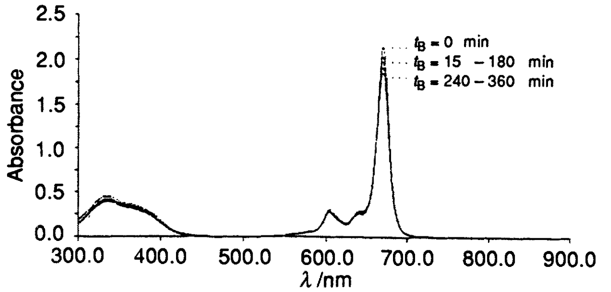


Fig. 2 Visible spectra of **1a** (M = Zn) in DMF under argon at different times of illumination

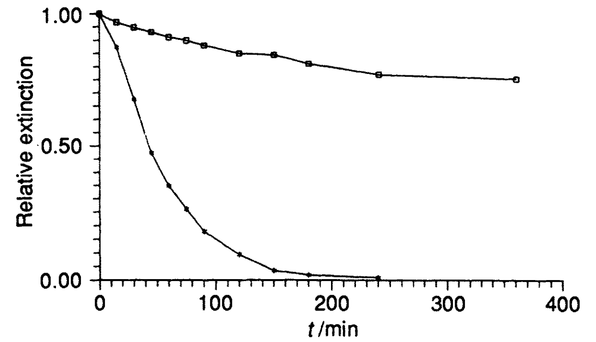


Fig. 3 Decrease of the relative extinction for **1a** (M = Zn) at λ = 668 nm with time under illumination. □: measurements under argon, *: measurements under air.

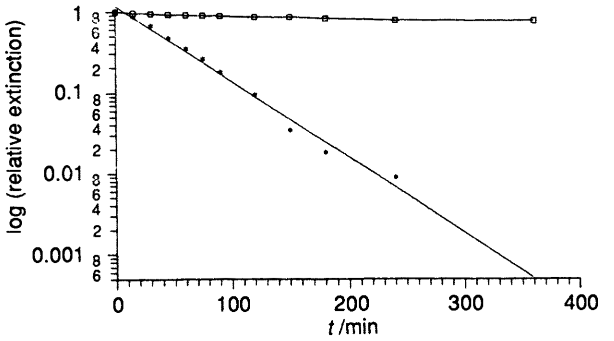


Fig. 4 First-order plot of the decrease of the relative extinction for **1a** (M = Zn) at λ = 668 nm under illumination. □: measurements under argon, *: measurements under air.

Table 1 Stability of compounds **1a–c**, **2**, **3**, **4** in DMF

Compound λ/nm; ε/dm^3 mol^{-1} cm^{-1}	Conditions	k_D/min^{-1}	Decomposition time/min 5%	10%	50%
1a (M = Zn)	argon/dark	stable			
668; 215 000	argon/illum.	8.2 × 10^{-4}	62	128	845
	air/dark	5.6 × 10^{-6}	9 160	—	—
	air/illum.	2.1 × 10^{-2}	2.5	5.0	33
1a (M = Co)	argon/dark	stable			
667; 62 000	argon/illum.	9.6 × 10^{-4}	53	110	720
	air/dark	2.5 × 10^{-6}	20 500	—	—
	air/illum.	6.5 × 10^{-3}	8	16	107
1b (M = Zn)	argon/dark	1.2 × 10^{-5}	4 280	—	—
673; 240 000	argon/illum.	7.8 × 10^{-4}	66	135	890
	air/dark	1.9 × 10^{-5}	2 700	—	—
	air/illum.	4.4 × 10^{-2}	1.2	2.4	16
1c (M = Zn)	argon/dark	stable			
693, 92 000	argon/illum.	5.8 × 10^{-4}	88	181	—
	air/dark	2.2 × 10^{-6}	23 320	—	—
	air/illum.	7.5 × 10^{-3}	6.9	14	92
4 (M = Zn)	argon/dark	stable			
664; 60 000	argon/illum.	5.2 × 10^{-4}	99	202	—
	air/dark	1.7 × 10^{-6}	30 180	—	—
	air/illum.	1.0 × 10^{-3}	51	105	690
2 (M = Zn)	argon/dark	stable			
423; 380 000	argon/illum.	7.7 × 10^{-4}	67	137	900
	air/dark	2.7 × 10^{-6}	19 000	—	—
	air/illum.	2.5 × 10^{-3}	21	42	277
3 (M = Zn)	argon/dark	stable			
760; 124 000	argon/illum.	2.5 × 10^{-3}	21	42	277
	air/dark	7.6 × 10^{-6}	6 730	—	—
	air/illum.	1.5 × 10^{-1}	0.3	0.7	5

Table 2 Stability of **1b** (M = Zn) in various organic solvents and **1d** (M = Zn), **5** and **6** in water

Compound λ/nm; ε/dm³ mol⁻¹ cm⁻¹	Solvent	Conditions	k_D/min⁻¹	Decomposition time/min 5%	10%	50%
1b	pyridine	argon/dark	4.4×10^{-6}	11 660	—	—
678; 142 000		argon/illum.	6.6×10^{-4}	78	160	1 050
		air/dark	5.3×10^{-6}	9 680	—	—
		air/illum.	7.8×10^{-3}	6.6	14	89
1b	DMF	argon/dark	1.2×10^{-5}	4 280	—	—
673; 240 000		argon/illum.	7.8×10^{-4}	66	135	890
		air/dark	1.9×10^{-5}	2 700	—	—
		air/illum.	4.4×10^{-2}	1.2	2.4	16
1b	toluene	argon/dark	5.1×10^{-6}	10 060	—	—
676; 184 000		argon/illum.	1.4×10^{-4}	366	753	—
		air/dark	5.3×10^{-6}	9 680	—	—
		air/illum.	8.6×10^{-3}	6.0	12	81
1b	CH_2Cl_2	argon/dark	9.2×10^{-6}	5 580	—	—
677; 138 000		argon/illum.	3.3×10^{-2}	1.6	3.2	21
		air/dark	2.0×10^{-5}	2 560	—	—
		air/illum.	6.2×10^{-2}	0.8	1.7	11
1d	water	air/dark	3.9×10^{-6}	13 000	—	—
672; 48 000		air/illum.	1.1×10^{-3}	47	96	630
5	water	air/dark	1.3×10^{-5}	4 000	—	—
687; 102 000		air/illum.	3.2×10^{-4}	160	330	2 165
6	water	air/dark	3.7×10^{-7}	140 000	—	—
406; 116 000		air/illum.	2.3×10^{-4}	220	460	3 010

Table 3 Life time τ_T, quantum yield θ_T, and energy E_T of the triplet state, oxidation and reduction potentials E (in V *vs.* NHE) in the ground and triplet state of some compounds **1–3**

Compound	τ_T/μs	θ_T	E_T/eV	$E°(S^+/S)$ $[E(S^+/S_T^*)]$	$E(S/S^-)$ $[E(S_T^*/S^-)]$
1a (M = Zn)	1100[1]	*ca.* 0.5[1]	1.13[1]	+0.92[1] (−0.21)[1]	−0.65[1] (+0.48)[1]
1a (M = Co or Cu)	0.065[1]	< 0.5[1]	1.15[1]	+1.11[1] (−0.05)[1]	−0.49[1] (+0.67)[1]
1b (M = Zn)	—	—	—	+0.72[24] (−0.41)[a]	−0.84[24] (+0.29)[a]
1c (M = Zn)	—	—	—	+1.55[a]	+0.05[24] (+1.14)[a]
1d (M = Zn)	245[1]	0.56[1]	1.12[1]	+0.95[25] (−0.25)[25]	−0.65[25] (+0.53)[25]
2 (M = Zn)	1200[1]	0.88[1]	1.59[1]	+0.95[1] (−0.64)[1]	1.11[1] (+0.48)[1]
3 (M = Zn or SiR_2)	115[22]		0.93[23]	+0.58[12] (−0.45)[a]	−0.71[18] (+0.32)[a]
dioxygen			0.97[b]		−0.33/−0.50[c] +0.34[d]

[a] Calculated values after ref. 25. [b] Energy difference between $^3O_2$ and $^1O_2$.[23] [c] Reduction potential for $O_2/O_2^{\bullet -}$ in protic and aprotic solvents.[26] [d] Reduction potential for $O_2/HO_2^{\bullet -}$.[26]

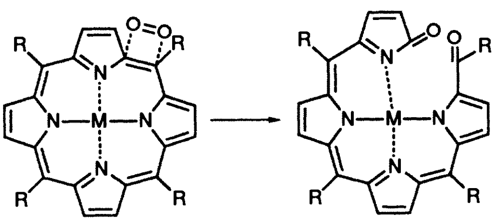
690 nm illumination photogeneration of $^1O_2$ in quantum yields of 0.4–0.7 were described, whereas a substituted copper phthalocyanine shows a quantum yield of only 0.16.[15–17] The higher concentration of $^1O_2$ obtained by the zinc complex under irradiation results in an enhanced decomposition compared to the cobalt complex. The photophysical and photochemical properties of some complexes are listed in Table 3. Because the oxidation potentials of the phthalocyanines $E(S^+/S^*)$ are only slightly more negative than $E(O_2/O_2^{\bullet -})$ an electron transfer to dioxygen as the second possibility cannot be excluded. It has been reported that the yield of $^1O_2$ is at least one order of magnitude higher than that of $O_2^{\bullet -}$.[27]

In order to determine the decomposition products, a solution of 10 mg **1a** (M = Zn) in DMF was illuminated in the presence of O_2. As main oxidation product phthalimide was identified by IR and mass spectra. Therefore $^1O_2$ may react mainly with the unsaturated carbon–nitrogen double bonds of the interior ligand. The mechanism of the photooxidation of zinc tetraphenylporphyrin (**2**) and other porphyrins by $^1O_2$ obtained from $^3O_2$ by porphyrin sensitisation [eqns. (2) and (3)] had been studied in detail.[28] The process involves singlet dioxygen addition to the macrocyclic ring followed by cleavage at the *meso*-positions [eqns. (4) and (5)]. Similar initial oxidation reactions of $^1O_2$ with **1a** can be considered. For this reason the mechanism of energy transfer from the excited macrocycle **1a** to form singlet dioxygen appears to be more probable when compared to the electron transfer leading to the formation of $O_2^{\bullet -}$.

From Table 1 it is seen that an increase in the size of the resonant structure from **2** to **1a** and to **3** (M = Zn) results in a reduced stability under the different conditions used. In the presence of air under illumination 50% decomposition occurs after 277 min for **2**, after 33 min for **1a** and after 0.3 min for **3**. Stability over a longer period was observed only under argon in the dark. Under air in the dark slow oxidation occurs (*e.g.* 5% decomposition of **3** after *ca.* 5 days). A bathochromic shift of the long-wavelength transition is observed in going from **2** to **1** and to **3** (Table 1). This shift is a result of narrowing of the HOMO–

$$\text{Sens} + h\nu \longrightarrow {}^1\text{Sens}^* \longrightarrow {}^3\text{Sens}^* \quad (2)$$

$$^3\text{Sens}^* + {}^3\text{O}_2 \longrightarrow \text{Sens} + {}^1\text{O}_2 \quad (3)$$



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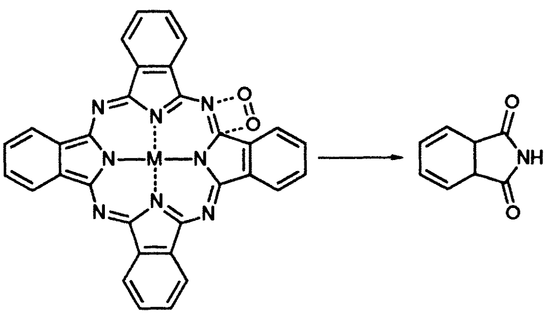

(5)

LUMO energy gap.[12] Theoretical VEH calculations indicate that the extension of the conjugated system by annelation of benzene rings produces a continuous destabilization of the HOMO and consequently a lower reducing power of the macrocycle. Photophysical measurements with a substituted naphthalocyanine in benzene in the presence of dioxygen led to the result that the naphthalocyanine T_1, obtained in a quantum yield of 0.20, can convert $^3O_2$ to $^1O_2$ in a quantum yield of 0.19.[23] A similar quantum yield was found for **3** dissolved in DMSO in the presence of 1,3-diphenylisobenzofuran as quencher.[29] In measurements with sulfonated phthalocyanines and naphthalocyanines in methanol/water the photodecomposition occurs in quantum yields of 1.1×10^{-6} and 3×10^{-3}, respectively.[22] The lower aromatic character of the naphthalocyanine, shown by the destabilization of the HOMO,[12] seems to result in a fast addition of $^1O_2$ at the C=N bonds of the interior ligand resulting in easier photodecomposition.

The influence of substituents on the stability of phthalocyanines is seen by comparing the measurements for the zinc complexes **1a–c**. In the dark under argon only the octabutoxy-substituted phthalocyanine **1b** shows slow decomposition. The presence of air in the dark results in a decrease of stability. On illumination photodecomposition occurs rapidly: 10% decomposition under argon within 2–3 h and under air within a few minutes. The stability decreases in the order **1c** (containing electron withdrawing substituents) > **1a** (unsubstituted) > **1b** (containing electron donating substituents). The increasing electron withdrawing effect at the phthalocyanine ring causes both the occupied and the unoccupied levels to shift to lower energy.[30] This can be seen in the shift of the oxidation and reduction potentials to more positive values (Table 3). Therefore it is concluded that the reactivity of the electron acceptor dioxygen toward the phthalocyanine is reduced with decreasing electron density within the ligand.

The investigation of the electrochemically well-characterized complex **1c** led us towards the detection of approximate energy levels of species taking part in the photochemical reactions. If a solution of **1c** in DMF is flushed with argon and illuminated (Fig. 5) the absorptions of the Q-band at 693 nm and the Soret-bands at 340 nm and 400 nm decrease while new absorptions occur at 470 nm, 590 nm and 770 nm with isosbestic points present, typical of a transition to a new chromophore. The developing spectrum is characteristic of the reduced **1c**.[31] An electron transfer reaction occurs that reduces the macrocycle [$E(S/S^-) = 0.05$ V *vs.* NHE][24] and oxidizes suitable donors which seem to be present, most probably as decomposition products of DMF (alkylated amines). As the reduction reaction was not observed with any of the other complexes the oxidation potential of these donors must be positioned between 0.05 V *vs.* NHE and −0.49 V *vs.* NHE, the nearest other $E(S/S^-)$ [Table 3, eqn. (6)].

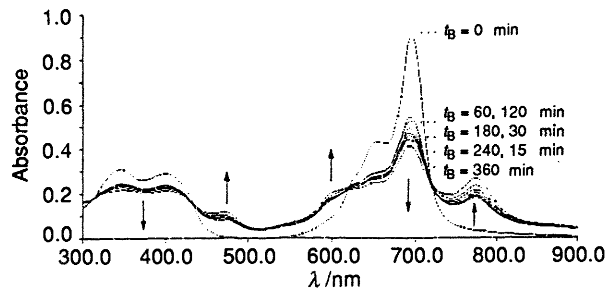

Fig. 5 Visible spectra of **1c** (M = Zn) in DMF under argon at different times of illumination

$$\mathbf{1c} + \text{`DMF'} \longrightarrow \mathbf{1c}^{\bullet -} + \text{`DMF'}_{\text{ox}} \quad (6)$$

By bubbling air through this solution the absorption at 770 nm vanishes and the original spectrum characterized by the absorption at 693 nm, is obtained indicating the re-oxidation of the macrocycle. Although the potential for the first reduction step of oxygen lies far away in the cathodic region [$E°(O_2/O_2^{\bullet -})$] = −0.50 V *vs.* NHE][26] its reduction under the present conditions is possible at potentials more anodic than 0.05 V *vs.* NHE. A potential matching these results would be $E°(O_2/HO_2^{\bullet -}) = 0.34$ V *vs.* NHE [Table 3, eqn. (7)].

$$\mathbf{1c}^{\bullet -} + \tfrac{1}{2}O_2 + H^+ \longrightarrow \mathbf{1c} + \tfrac{1}{2}HO_2^{\bullet -} \quad (7)$$

In the investigation of octamethylthiotetraazaporphyrin **4** it turned out, that this complex is more stable against air than all other investigated compounds. On the one hand this is surprising, as **4** has an intermediate HOMO level (Table 3).[32] But on the other hand this is another example of the trend, that the larger the peripheral but conjugated aromatic system is, the lower the stability toward oxygen (**4** > **1** > **3**). The good stability of **2** (Table 1) gives further proof for this trend, as its phenyl groups are not conjugated with the macrocycle. The importance of the conjugated systems for an efficient decomposition may be seen from eqns. (4) and (5) as more stable transition states, intermediates and products are formed.

Owing to the high solubility of the substituted phthalocyanine **1b** (M = Zn) in various solvents, it was possible to compare the stability of this compound in DMF, pyridine, toluene and dichloromethane (Table 2). In every solvent the stability decreases in the following order: argon/dark > air/dark ≫ argon/illumination > air/illumination. Only in the dark is a good stability over a few days observed. Under illumination, especially in the presence of O_2, photodecomposition occurs within a few minutes and the stability decreases as follows: toluene, pyridine > DMF > dichloromethane. In the case of dichloromethane under illumination cleavage of the C–Cl bond might occur, and the resulting radicals could be the reason for the rapid photodecomposition.

To get a deeper insight into their usefulness in photodynamic cancer therapy and as sensitisers with the aim of water photolysis, complexes were also investigated in aqueous

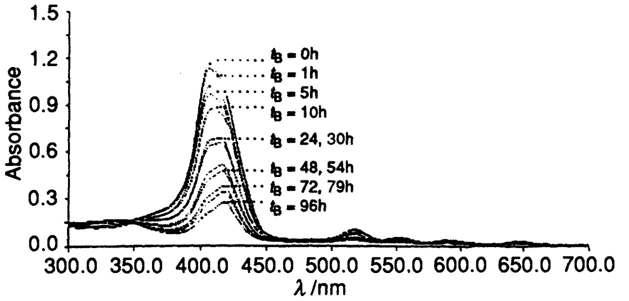

Fig. 6 Visible spectra of **6** in water under air at different times of illumination

Table 4 Stability of **1a** as thin film (thickness 100 nm) under illumination in air

Sample	k_D/min^{-1}	Decomposition time/min	
		5%	10%
1a (M = Co)[a]	—	stable	
1a (M = Zn)[a]	4.3 × 10^{-7}	120 000	
1a (M = Zn)[b]	4.6 × 10^{-6}	11 000	
1a (M = Zn)[c]	1.4 × 10^{-5}	3 700	7 500

[a] Film in contact with air. [b] Film in 0.5 mol dm^{-3} aqueous KNO_3 saturated by air. [c] Film in aqueous KNO_3 at −60 mV *vs.* NHE.

solution as far as their solubility allowed. The stability of the zinc complex of the anionic tetrasulfophthalocyanine **1d** and the metal-free cationic tetramethylpyridinotetraazaporphyrin **5** were investigated at pH 7 in the presence of air in the dark and under illumination (Table 2). The rates of photodecomposition of **1d** and **5** containing electron withdrawing substituents are lower than the rate for octacyanophthalocyanine **1c** (Tables 1, 2). As is well known, charged phthalocyanines form molecular aggregates such as dimers and oligomers even in dilute solution.[15,33–35] This is seen by a bathochromic shift of the Q-band absorption to shorter wavelength for **1d** and **5**. Carboxylated phthalocyanine zinc complexes exhibit a quantum yield of $^1O_2$ formation for monomeric species of 0.7 and for the dimeric species of only 0.1 owing to bimolecular processes of triplet–triplet annihilation.[15] The lower amount of $^1O_2$ formation by **1d** and **5** in water in comparison to the other phthalocyanines in organic solvents existing in a non-aggregated state is therefore responsible for a higher stability. But the photodecomposition of **1d** and **5** under illumination in the presence of O_2 shows that the use of these sensitisers for water splitting by photoredox processes seems not to be promising. In addition, tetrahydroxyphenylporphyrin bonded to methoxypoly(ethylene glycol) (compound **6**) was tested for stability in water (Table 2). This compound is important for use in the photodynamic therapy of cancer and shows a high accumulation in tumours and a good photoactivity.[5,36] The hydrophilic polymer is non-toxic. It was shown that necrosis of tumour cells is mainly induced by photooxidation through $^1O_2$.[2,4] A suitable sensitiser should exhibit a high stability in the dark (for storage and after intravenous injection) and slow photobleaching during laser illumination. For **6** in the dark in the presence of air only 5% decomposition is observed after *ca.* 40 days whereas under illumination 50% decomposition occurs after *ca.* one day (Table 2, Fig. 6). The stability of the polymer porphyrin **6** in water is higher than the low molecular weight **2** in DMF. Compound **6** exhibits suitable stability for the use as an anti-tumour agent.

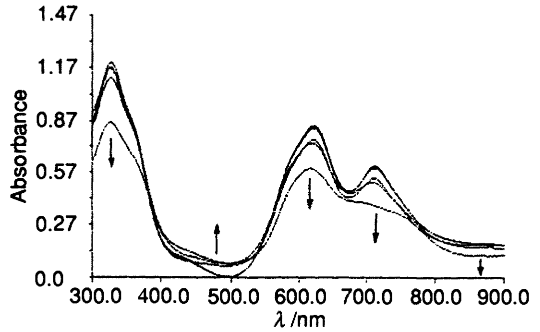

Fig. 7 Visible spectra of film of **1a** (M = Zn) (thickness 100 nm) on ITO at different times. Spectra of the film on ITO in 0.5 mol dm^{-3} aqueous KNO_3 at −60 mV *vs.* NHE under illumination in the presence of air.

Stability as Films.—Aside from general comparison purposes with the results obtained in solution, the stability of thin solid films prepared from compounds structurally similar to porphin is of interest in view of their photovoltaic and photoelectrochemical properties. Films were therefore prepared and investigated under conditions similar to those under which these effects are studied. Porphin analogue compounds, especially phthalocyanines, have been intensively investigated as thin film electrodes in photoelectrochemical cells in contact with various redox couples in aqueous solution.[6,7] The interface between the porphyrin as molecular organic semiconductor and the electrolyte forms a junction which is active in photoconversion. Unsubstituted phthalocyanines behave as p-type materials and show cathodic photocurrents under illumination with visible light in the presence of acceptor in solution. The behaviour of the thin film electrodes in the presence of dioxygen is of special interest because this acceptor is incorporated as dopant in the solid, and, if it is used as oxidant in aqueous solution, high cathodic currents are measured.[7]

In order to obtain information about the stability of phthalocyanines in contact with an O_2-containing electrolyte and, in addition, under the condition of a current flowing through the film and its surface, thin films (thickness 100 nm) of **1a** (M = Zn) were prepared by vapour deposition at 10^{-5} Torr on conducting indium tin oxide ITO coated glass. The electronic spectrum in transmission shows absorptions of the Q-band transition at 620 and 690 nm with the 620 nm band being of higher intensity, characteristic of the α-modification (Fig. 7).[7,35] In the dark and presence of air, **1a** (M = Zn) on ITO dipped into aqueous KNO_3 exhibits no decomposition. On illumination 5% photodecomposition occurs after *ca.* 8 days (Table 4; Fig. 8, upper part). Cyclic voltammetry with the electrode of **1a** (M = Zn) was performed in the electrolyte. When the electrode potential was scanned negatively in the dark only a small cathodic current corresponding to the reduction of dioxygen was observed.[7] A significant cathodic current due to photoreduction of O_2 from air could be obtained only under illumination (Fig. 8, lower part).[7] 5% Photodecomposition occurs now after *ca.* 60 h (Table 4; Fig. 8, upper part). The density of the photocurrent seems to be constant after an initial decay during the first five hours; no significant change is observed in the dark current. It has been shown that in this reaction and under these conditions O_2 is reduced at the interfacial contact between the bulk phase and the electrolyte, and that only the electrode surface is active.[7] The obtained results are therefore explained by a nearly constant surface area in spite of an overall decomposition. The decomposition reaction is therefore characterized as an etching of surface molecules leading to new molecules being exposed to the electrolyte. As the surface texture is strongly influenced by such a reaction the initial decay at nearly no decomposition proceeds

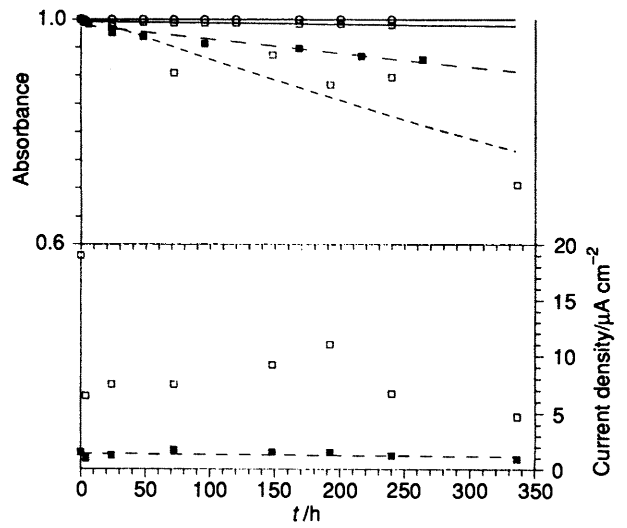

Fig. 8 Upper part: first-order plot of the decrease of the relative extinction for thin films of **1a** (thickness 100 nm) on ITO at different times under illumination in the presence of air. ○, **1a** (M = Co) film; ☐, **1a** (M = Zn) film, in 0.5 mol dm^{-3} aqueous KNO_3; ■, **1a** (M = Zn) film in 0.5 mol dm^{-3} aqueous KNO_3; ☐, **1a** (M = Zn) in aqueous KNO_3 at −60 mV *vs.* NHE. Lower part: Current density of **1a** (Zn) film in aqueous KNO_3 at −60 mV *vs.* NHE; ■, in the dark; ☐, under illumination.

are understood. The photoreduction of O_2 consists of an electron transfer, and H_2O_2 has been characterized as a reaction product.[7] We have no experimental evidence, that an energy transfer step leading to $^1O_2$ is involved. It is therefore concluded, that reduced dioxygen, like $HO_2^{\bullet}$ and H_2O_2, is responsible for a higher decomposition at a cathodic potential under illumination.

The stabilities of 100 nm films of the Co^{II} and Zn^{II} chelates of **1a** on quartz glass were also determined in the presence of air without any solvent or electrolyte present. Organic photovoltaic cells using phthalocyanines as p-conductors in Schottky- or p/n-devices have been mainly investigated under these conditions.[9] In the dark both films are stable. Under illumination slow photodecomposition of **1a** (M = Zn) (5% after *ca.* 80 days; Table 4; Fig. 8, upper part) occurs whereas the Co^{II} chelate is stable within the time of investigation. In the presence of air, dioxygen is incorporated in the bulk of the p-conducting phthalocyanine having a band gap of *ca.* 2.0 eV.[1,7] Illumination of the molecular semiconductor results for **1*** in S_1 and T_1 states with energies of 1.8 and 1.2 eV.[1] Therefore formation of $^1O_2$ from $^3O_2$ is possible, and this may decompose phthalocyanine molecules in the film. The shorter lifetime of the excited state of **1a** (M = Co) in the bulk may be, as discussed before, the reason for the higher stability.

In order to compare the stability of the complexes in solution to that of the solids it is necessary to compare the absolute numbers of illuminated and decomposed molecules. 1 cm^3 of a 10^{-5} mol dm^{-3} solution of **1a** contains *ca.* 6×10^{15} molecules. For a 100 nm thick film of 1 cm^2 area the number of phthalocyanine molecules is around 1.6×10^{16} molecules, taking the density of 1.61 g cm^{-3} into account. Therefore the number of molecules in the film is only about twice as high as the number of molecules in solution. But by comparing the results of measurements in Tables 1, 2 and 4, the stability of the films under illumination and in presence of air is much higher than the stability of dissolved phthalocyanine molecules. As the absorption coefficient is nearly constant, this means that the quantum efficiency of the decomposition reaction is much smaller in the solid than in solution. As pointed out earlier, the lifetimes of the excited states are significantly shorter in aggregates than in perfectly solvated molecules. This tendency stretches into the solid state, where the lifetimes are extremely short. A further reason may be the hindered interaction of O_2 with phthalocyanine molecules within the solid of a highly ordered material (α-modification).[37]

Experimental

Materials.—Organic solvents were distilled and dried in the usual manner and distilled before use. Twice distilled water, dried argon (99.998%) and synthetic air were used.

Compounds **1a** (M = Zn, Co) and **2** (M = Zn) were purchased commercially and sublimed. Synthesis of the zinc complexes of octabutoxyphthalocyanine **1b**, octacyanophthalocyanine **1c**, tetrasulfophthalocyanine **1d**, naphthalocyanine **3** and octamethylthiotetraazaporphyrin **4** were carried out as described.[24,32,38–40]

Tetramethylpyridotetraazaporphyrin **5** was prepared by the reaction of 3,4-dicyanopyridine in pentan-1-ol in the presence of DBU to the tetrapyridotetraazaporphyrin followed by methylation with dimethyl sulfate.[41,42] For the preparation of **6**, the 5,10,15,20-tetra(4-hydroxyphenyl)porphyrin was covalently bound to methoxypoly(ethyleneglycol) (M_w *ca.* 5000) in the presence of 1,3,5-trichlorotriazine.[5,36]

Stability Measurements in Solution.—Measurements were carried out in a quartz cell (1 × 1 cm) with 2 cm^3 of solution containing 10^{-5} mol dm^{-3} porphyrin compound. The visible spectra were recorded with a Perkin-Elmer Lambda 9, and registered by PECSS. The decomposition was followed by the decay in the intensity of the absorption of highest extinction (Q-band for **1**, **3–5** and Soret-band for **2**, **6**). The measurements were conducted under air in the dark and under illumination. For measurements under argon the solution in the quartz cell was flushed with argon through a syringe for 10 min and then protected against air with a rubber septum. For experiments under irradiation, visible light of 350–850 nm from a 24 V 250-halogen lamp with UV cut-off filter and water filter was used. The light intensity was calibrated with a bolometer (Kipp and Zonen, CA1-754399) and adjusted to 20 mW cm^{-2}.

Stability Measurements of Thin Films in a Photoelectrochemical Cell under Air.—ITO of high electrical conductivity (20 ohm/square) was obtained from Matuszaki Shinku Co. Ltd., cut into plates of 2.5 × 1 cm^2, and cleaned with distilled water and methanol. Vapour-deposited films of **1a** (M = Zn, Co) were prepared by using a VEECO VE-7700 vacuum system at 10^{-5} Torr. Films of 100 nm thickness were deposited, and the thickness was determined *in situ* using a Kronos QM-311 thickness monitor. The stability of the films were determined either by dipping the plates into 0.5 mol dm^{-3} aqueous KNO_3 saturated with air or by an additional applied potential of −60 mV *vs.* NHE. Details for the photoelectrochemical measurements are described elsewhere.[7] Illumination was carried out with 20 mW cm^{-2} as described before. The visible spectra were obtained by transmission measurements.

Stability Measurements of Thin Films in Air.—As described before films of 100 nm thickness were deposited on quartz plates of 2 × 2 cm. The films were irradiated with visible light of 20 mW cm^{-2} under air, and the absorption spectra were measured in transmission.

Investigation of Decomposition Products of **1a** (M = Zn).—10 mg of **1a** (M = Zn) were dissolved in 100 cm^3 dry distilled DMF. The dark blue solution was illuminated (20 mW cm^{-2}) in a 500 cm^3 vessel. Dry O_2 was bubbled into the solution. After 48 h DMF was distilled from the yellow coloured solution *in* *vacuo*. The residue was treated by freeze drying and in a dry box over P_4O_{10}.; ν_{max}(KBr)/cm^{-1} 2224 (very weak, C≡N), 1770(w) and 1670s (imide). *m*/*z* (70 eV, 175 °C) 147 ($M^{\cdot+}$ for phthalimide, 100%), 130 (M − 43, 82%). By thin layer chromatography several other products in a lower amount, which could not be identified by mass spectra, were seen.

References

1 J. R. Darwent, P. Douglas, A. Harriman, G. Porter and M. C. Richoux, *Coord. Chem. Rev.*, 1982, **44**, 83.

2 C. C. Leznoff and A. B. P. Lever, *Phthalocyanines: Properties and Applications*, VCH Publishers, New York, 1989.

3 D. Wöhrle, J. Gitzel, G. Krawczyk, E. Tsuchida, H. Ohno and T. Nishisaka, *J. Macromol. Sci., Chem. A*, 1988, **25**, 1227.

4 B. A. Henderson and T. J. Dougherty, *Photochem. Photobiol.*, 1992, **55**, 145.

5 D. Wöhrle, A. Ardeschirpur, A. Heuermann, S. Müller, G. Graschew, H. Rinneberg, M. Kohl and J. Neukammer, *Makromol. Chem., Macromol. Symp.*, 1992, **59**, 17.

6 T. J. Klofta, J. Danzinger, P. Lee, J. Pankow, K. W. Nebesny and N. R. Armstrong, *J. Phys. Chem.*, 1987, **91**, 5646, and refs. cited therein.

7 D. Schlettwein, M. Kaneko, A. Yamada, D. Wöhrle and N. I. Jaeger, *J. Phys. Chem.*, 1991, **95**, 1748 and refs. cited therein.

8 J. J. Simon and H. J. Andre, *Molecular Semiconductors*, Springer-Verlag, Berlin, 1985.

9 D. Wöhrle and D. Meissner, *Adv. Mater.*, 1991, **3**, 129.

10 R. O. Loutfy, C. K. Hsiao, A. M. Hor and G. J. DiPaola-Baranyl, *J. Imaging Sci.*, 1985, **29**, 148.

11 S. Takano, T. Enokida and A. Kabata, *Chem. Lett.*, 1984, 2037.

12 E. Orti, M. C. Piqueras, R. Crespo and J. L. Bredas, *Chem. Mater.*, 1990, **2**, 110.

13 C. Fierro, A. B. Anderson and D. A. Scherson, *J. Phys. Chem.*, 1988, **92**, 6902.

14 L. K. Lee, N. H. Sabelli and P. R. LeBreton, *J. Phys. Chem.*, 1982, **86**, 3926.

15 M. E. Daraio, P. F. Aramendia, E. A. San Roman and S. E. Braslavsky, *Photochem. Photobiol.*, 1991, **54**, 367.

16 G. Valduga, S. Nonell, E. Reddi, G. Jori and S. E. Braslavsky, *Photochem. Photobiol.*, 1988, **48**, 1.

17 M. G. Lagorio, L. E. Dicello, E. A. San Roman and S. E. Braslavsky, *J. Photochem. Photobiol. B*, 1989, **3**, 615.

18 S. Tai, S. Hayashida and N. Hayashi, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1637.

19 D. Wöhrle and G. Krawczyk, *Makromol. Chem.*, 1986, **187**, 2535.

20 D. Wöhrle, M. Paliuras and I. Okura, *Makromol. Chem.*, 1991, **192**, 819.

21 D. Wöhrle, J. Gitzel, I. Okura and S. Aono, *J. Chem. Soc., Perkin Trans. 2*, 1985, 1171.

22 I. McCubbin and D. Phillips, *J. Photochem.*, 1986, **34**, 187.

23 P. A. Firey, W. E. Ford, J. R. Sounik, M. E. Kenney and M. A. J. Rodgers, *J. Am. Chem. Soc.*, 1988, **110**, 7626.

24 D. Wöhrle and V. Schmidt, *J. Chem. Soc., Dalton Trans.*, 1988, 549.

25 A. B. P. Lever, S. Licoccia, B. S. Ramaswamy, S. A. Kandil and D. V. Stynes, *Inorg. Chim. Acta*, 1981, **51**, 169.

26 J. Wilshire and D. T. Sawyer, *Acc. Chem. Res.*, 1979, **12**, 105.

27 R. J. Wagner, H. Ali, R. Langlois, N. Brasseur and J. E. van Lier, *Photochem. Photobiol.*, 1987, **45**, 587.

28 J. A. S. Cavaleiro, M. G. P. S. Neves, M. J. E. Hewlis and A. H. Jackson, *J. Chem. Soc., Perkin Trans.*, 1990, 1937.

29 D. Wöhrle, M. Shopova, S. Müller, A. D. Milev, V. N. Mantareva and K. K. Kraster, *Photochem. Photobiol.*, submitted.

30 P. D. Hale, W. J. Pietro, M. A. Ratner, D. E. Ellis and T. J. Marks, *J. Am. Chem. Soc.*, 1987, **109**, 5943.

31 A. Louati, M. ElMeray, J. Andre, J. Simon, K. Kadish, M. Gross and A. Giraudeau, *Inorg. Chem.*, 1985, **24**, 1175.

32 L. A. Bottomley and W. J. H. Chiou, *J. Electroanal. Chem.*, 1986, **198**, 331.

33 Y.-C. Yang, J. R. Ward and R. P. Seiders, *Inorg. Chem.*, 1985, **24**, 1765.

34 E. W. Abel, J. M. Pratt and R. Whelan, *J. Chem. Soc., Dalton Trans.*, 1976, 509.

35 D. Wöhrle, N. Iskandar, G. Graschew, H. Sinn, E. A. Friedrich, W. Maier-Borst, J. Stern and P. Schlag, *Photochem. Photobiol.*, 1990, **51**, 351.

36 H. J. Sinn, H.-H. Schrenk, W. Maier-Borst, E. A. Friedrich, G. Graschew, D. Wöhrle and T. Klenner, *Polyether-substituted Anti-Tumour Agents*, European Patent PCT/EP91/00992.

37 E. A. Lucia and F. D. Verdrame, *J. Chem. Phys.*, 1968, **48**, 2674.

38 D. Wöhrle, G. Meyer and B. Wahl, *Makromol. Chem.*, 1980, **181**, 2127.

39 J. H. Weber and D. H. Busch, *Inorg. Chem.*, 1965, **4**, 469.

40 E. I. Koshev and E. A. Luk'yanets, *Zh. Obshch. Khim.*, 1972, **42**, 1593.

41 S. Palacin, A. Ruaudel-Teixier and A. Barroud, *J. Phys. Chem.*, 1989, **93**, 7195.

42 D. Wöhrle, G. Schnurpfeil and G. Knothe, *Dyes and Pigments*, 1992, **18**, 91.

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