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New Trends in Photobiology (Invited review)

Photophysical properties of porphycene derivatives (18π porphyrinoids) [1]

Silvia E. Braslavsky *, Martin Müller, Daniel O. Mártire [2], Sigrid Pörting, Sonia G. Bertolotti, Sankar Chakravorti, Gül Koç-Weier, Bernd Knipp, Kurt Schaffner

Max-Planck-Institut für Strahlenchemie, Postfach 10 13 65, D-45413 Mülheim an der Ruhr, Germany

Abstract

Absorption and fluorescence spectral data and triplet energy content, as well as quantum yields of fluorescence, of triplet state formation, and of sensitized generation of singlet molecular oxygen, $O_2(^1\Delta_g)$, of 38 porphycene derivatives are reported. Long-wavelength absorption and the efficiency of fluorescence and $O_2(^1\Delta_g)$ sensitization qualify most of these porphycenes as potential photodynamic therapy agents (so-called second-generation sensitizers), unless steric or electronic effects by substitution perturb the parent aromatic 18π system. © 1997 Elsevier Science S.A.

Keywords: Porphyrins; Photodynamic therapy; Triplet; Singlet oxygen; Sensitization

1. Introduction

In innumerable investigations of the past, sensitizers of molecular singlet oxygen, $O_2(^1\Delta_g)$, applicable in photodynamic therapy (PDT) of malignant tissues, have been employed which constitute either mixtures of diastereoisomers (e.g. benzoporphyrin derivative) or mixtures of components not completely known structurally (e.g. Photofrin®) [1,2]. This practice has often obstructed comparative preclinical evaluations of photophysical and photochemical properties, and of pharmacokinetic and phototherapeutic results. As a consequence, attention has been focused increasingly on structurally well-defined homogeneous substances in the screening for "second-generation" sensitizers applicable in PDT.

Porphycenes [3–6] belong to this group. Some have proven to be very effective as in-vivo antitumor agents

[7–22]. A series of porphycene derivatives has been synthesized in the meantime with the intention to optimize these sensitizers in response to the particular requirements of PDT, notably with regard to in-vivo transport, specificity of localization in tumor tissue, and optical absorption in the long-wavelength region. Based on first experiences concerning structure/activity relations, the porphycene substitution pattern has been systematically modified in order to offer a broad choice of potential PDT sensitizers of this class. We present in this paper photophysical properties of these porphycenes (for the structures see Schemes 1 and 2), such as absorption and fluorescence data, singlet and triplet state yields and energy content, and the efficiency of $O_2(^1\Delta_g)$ sensitization. These data are germane to the proper functioning of a sensitizer in PDT, and their knowledge should facilitate the screening for efficient agents [22,23].
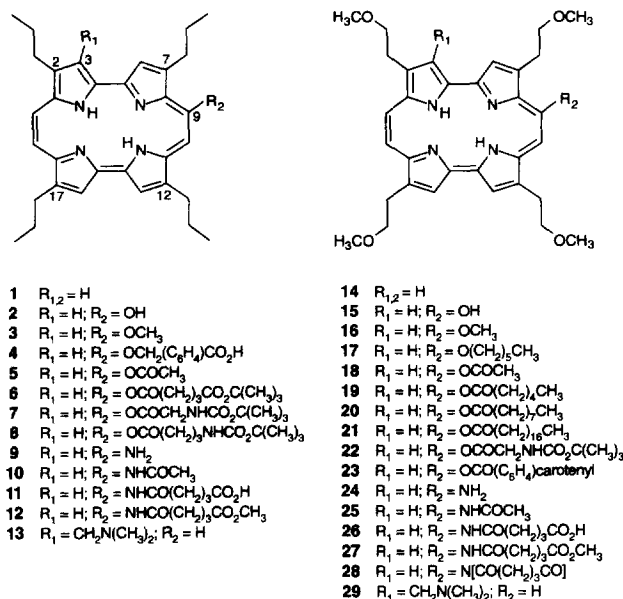
2. Materials and methods

References to the syntheses of the porphycenes are given in Tables 1–3. The solvents used in the measurements are specified in the tables. Degassing of the sample solutions was performed in three freeze-pump-thaw cycles.
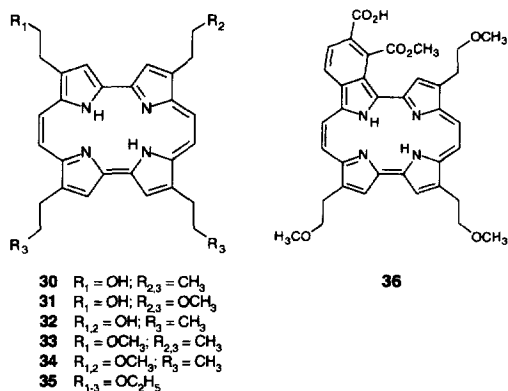
* Corresponding author: Tel.: +49 208 306 36 81; Fax: +49 208 306 39 51; e-mail: braslavskys@mpi-muelheim.mpg.de

[1] Dedicated to Professor Waldemar Adam on the occasion of his 60th birthday.

[2] Facultad de Ciencias Exactas, Universidad de la Plata, Argentina.

Scheme 1.

1 $R_{1,2}$ = H
2 R_1 = H; R_2 = OH
3 R_1 = H; R_2 = OCH_3
4 R_1 = H; R_2 = $OCH_2(C_6H_4)CO_2H$
5 R_1 = H; R_2 = $OCOCH_3$
6 R_1 = H; R_2 = $OCO(CH_2)_3CO_2C(CH_3)_3$
7 R_1 = H; R_2 = $OCOCH_2NHCO_2C(CH_3)_3$
8 R_1 = H; R_2 = $OCO(CH_2)_3NHCO_2C(CH_3)_3$
9 R_1 = H; R_2 = NH_2
10 R_1 = H; R_2 = $NHCOCH_3$
11 R_1 = H; R_2 = $NHCO(CH_2)_3CO_2H$
12 R_1 = H; R_2 = $NHCO(CH_2)_3CO_2CH_3$
13 R_1 = $CH_2N(CH_3)_2$; R_2 = H

14 $R_{1,2}$ = H
15 R_1 = H; R_2 = OH
16 R_1 = H; R_2 = OCH_3
17 R_1 = H; R_2 = $O(CH_2)_5CH_3$
18 R_1 = H; R_2 = $OCOCH_3$
19 R_1 = H; R_2 = $OCO(CH_2)_4CH_3$
20 R_1 = H; R_2 = $OCO(CH_2)_7CH_3$
21 R_1 = H; R_2 = $OCO(CH_2)_{16}CH_3$
22 R_1 = H; R_2 = $OCOCH_2NHCO_2C(CH_3)_3$
23 R_1 = H; R_2 = $OCO(C_6H_4)$carotenyl
24 R_1 = H; R_2 = NH_2
25 R_1 = H; R_2 = $NHCOCH_3$
26 R_1 = H; R_2 = $NHCO(CH_2)_3CO_2H$
27 R_1 = H; R_2 = $NHCO(CH_2)_3CO_2CH_3$
28 R_1 = H; R_2 = $N[CO(CH_2)_3CO]$
29 R_1 = $CH_2N(CH_3)_2$; R_2 = H

Scheme 2.

30 R_1 = OH; $R_{2,3}$ = CH_3
31 R_1 = OH; $R_{2,3}$ = OCH_3
32 $R_{1,2}$ = OH; R_3 = CH_3
33 R_1 = OCH_3; $R_{2,3}$ = CH_3
34 $R_{1,2}$ = OCH_3; R_3 = CH_3
35 R_{1-3} = OC_2H_5

36

37   38

Absorption spectra were measured with a UV2102PC Shimadzu spectrophotometer. The molar absorption coefficients (ϵ) were determined at least three times with samples of < 1 mg each dissolved in either 50 or 100 ml solvent.

Fluorescence spectra and fluorescence quantum yields were determined with a computer-controlled Spex Fluorolog spectrofluorometer, as described by Aramendía et al. [24]. The fluorescence quantum yields, Φ_f, were determined from the ratio of the integrated areas under the emission curves of sample and reference by using solutions in the same solvent of matched ($A \pm 0.02$) absorbances (about 0.08) at the excitation wavelength of 370 nm. The Φ_f values for the reference, 2,7,12,17-tetra-n-propyl-porphycene (1) [25], in degassed

and aerated toluene solutions were the same within the experimental error ($\Phi_f = 0.35 \pm 0.06$ and 0.38 ± 0.06, respectively) [24,26]. Unless specified otherwise, aerated solutions were therefore used for all fluorescence measurements and Φ_f determinations.

The determination of the quantum yield of $O_2(^1\Delta_g)$ formation, Φ_Δ, by time-resolved phosphorescence detection (TRPD) of the $O_2(^1\Delta_g)$ emission has been described previously [26–28]. Excitation pulses of 15 ns at 650 nm from a Nd:YAG-pumped dye laser (DCM, Radiant Dyes) were employed. A silicon filter ($\lambda > 1$ μm) and a 1270 nm interference filter (± 12 nm, Schott) were placed in front of the liquid nitrogen-cooled Ge detector (North Coast EO 817FP). In each case a series of solutions of different absorbances ($A_{650} = 0.05 - 0.25$) was measured. Solvent-saturated oxygen was bubbled through the sample solutions. The maximum of the $O_2(^1\Delta_g)$ decay curve, obtained by extrapolating the fitted monoexponential decay curve to zero time, was taken as a measure of the amount of $O_2(^1\Delta_g)$ formed [26,27]. The values were determined for each concentration at various laser fluences in order to ascertain linearity, i.e. the absence of multiphotonic processes. The ratio of the slopes of the linear fluence-dependent plots for sample and reference were used for the Φ_Δ determination, with 1 ($\Phi_\Delta = 0.36$ [26], Tables 1 and 3) and 14 ($\Phi_\Delta = 0.37$, Table 2) as references. The lifetime of $O_2(^1\Delta_g)$ was in all cases $\tau_\Delta = (30 \pm 2)$ μs in toluene (with the exception of 23) and $\tau_\Delta = 70$ μs in CH_2Cl_2, which is in good accord within experimental error with the literature values of $\tau_\Delta = 29$ μs [29,30] and (70–100) μs [29–31], respectively.

The triplet energy level, E_T, was determined with a home-built near-IR steady-state emission spectrometer which has been described previously [26] and has since been improved in some respects: a 2.5 kW Xe lamp was used for excitation and a liquid nitrogen-cooled Ge diode (North Coast EO 817L) for the phosphorescence detection. Excitation wavelengths between 530 and 700 nm were chosen. A water filter absorbed the IR radiation of the lamp. All measurements were performed at room temperature and in degassed iodopropane solution in order to increase intersystem crossing. Our assumption that the heavy atom effect does not affect the triplet energy level is supported by the similarity of the E_T values obtained by this method with those obtained for some comparable compounds, e.g., octaethylporphyrin, by low-temperature phosphorescence [32]. The highest energy band was taken as the 0–0 band (λ_{T-S} in the tables) [26].

Flash photolysis with optical detection was used for the singlet–triplet (S–T) difference absorption measurements. The triplet decay was measured in deoxygenated solutions (either degassed or Ar bubbled) after excitation with the laser specified above. Extrapolation of the absorbance decay curve to zero time after laser excitation gave the S–T difference absorbance, ΔA_0, which was plotted vs. the detection wavelength in order to obtain the S–T difference absorption spectrum.

Table 1

Photophysical data of 9-substituted derivatives of 2,7,12,17-tetra-n-propylporphycene (cf. Schemes 1 and 1)

Compound [C-3 and C-9 substituents]	Absorption λ^{abs}/nm ($\epsilon \times 10^{-3}$/M^{-1} cm^{-1})	Fluorescence λ^{em}/nm	ϕ_f (± 0.05) $\lambda^{exc} = 370$ nm	λ_{T-S}/nm	Φ_T (± 0.1) $\lambda^{exc} = 650$ nm [§] LIOAS [¶] Flash photolysis	Φ_Δ (± 0.05) $\lambda^{exc} = 650$ nm	Solvent
1 [a] [3-H, 9-H]	637 (42.30)	641	0.35 (deg [b]) 0.38 (aer [c])	964	0.3 [§,d]	0.36	toluene
2 [e] [3-H, 9-OH]	677 (23.83)	683	0.15 (aer)	1060	0.44 [§]	0.34	toluene
3 [f] [3-H, 9-OCH₃]	682 (17.45)	688	0.18 (aer)	1080	0.28 [§]	0.3	toluene
4 [g] [3-H, 9-OCH₂(C₆H₄)CO₂H]	677 (16.63)	685	0.21 (aer)	1080	0.3 [§]	0.3	toluene
5 [h] [3-H, 9-OCOCH₃]	636 (28.65) 645 (27.43)	650	0.28 (aer)	960	0.4 [§]	0.36	toluene [i]
6 [j] [3-H, 9-OCO(CH₂)₃CO₂C(CH₃)₃]	645 (44.65)	651	0.21 (aer)	984	0.67 [¶]	0.28	toluene
7 [k] [3-H, 9-OCOCH₂NHCO₂C(CH₃)₃]	635, 644					0.32	toluene
8 [l] [3-H, 9-OCO(CH₂)₃NH-CO₂C(CH₃)₃]	635, 645					0.30	toluene
9 [m] (unstable; see text) [3-H, 9-NH₂]	710 (19.14)	729	0.06 (aer)	1120	0.28 [§]	no signal [n]	toluene
10 [o] [3-H, 9-NHCOCH₃]	639 (40.23)	679	0.1 (aer)	980	0.33 [§]	0.3	toluene
11 [p] [3-H, 9-NHCO(CH₂)₃-CO₂H]	636 (42.20)	680	0.15 (aer)	1060–1100	0.3 [§]	0.25	CH₂Cl₂ [q]
12 [r] [3-H, 9-NHCO(CH₂)₃CO₂-CH₃]	634 634 (44.50)	680	0.2 (aer) 0.16 (deg)	1080	0.4 [¶]	0.36	toluene CH₂Cl₂ [q]
13 [s] [3-CH₂N(CH₃)₂, 9-H]	643					0.33	toluene

[a] 2,7,12,17-Tetra-n-propylporphycene [24,25].

[b] Degassed.

[c] Aerated.

[d] Value from Refs. [24,26].

[e] 2,7,12,17-Tetra-n-propyl-9-hydroxyporphycene [41].

[f] 2,7,12,17-Tetra-n-propyl-9-methoxyporphycene [42].

[g] 2,7,12,17-Tetra-n-propyl-9-p-benzoylcarboxyporphycene [42].

[h] 2,7,12,17-Tetra-n-propyl-9-acetoxyporphycene [41].

[i] Similar values in EtOH.

[j] 2,7,12,17-Tetra-n-propyl-9-(t-butylglutaroxy)porphycene [42].

[k] 2,7,12,17- Tetra-n-propyl-9-(N-t-butoxycarbonylglycinoxy)porphycene [42].

[l] 2,7,12,17- Tetra-n-propyl-9-(4-N-t-butoxycarbonylbutyroxy)porphycene [42].

[m] 2,7,12,17-Tetra-n-propyl-9-aminoporphycene [41].

[n] Insufficient signal accumulation due to sample instability.

[o] 2,7,12,17-Tetra-n-propyl-9-acetamidoporphycene [41,42].

[p] 2,7,12,17-Tetra-n-propyl-9-glutaramidoporphycene [42].

[q] Measurements in CH₂Cl₂ for solubility reasons.

[r] 2,7,12,17-Tetra-n-propyl-9-(methyl glutaramido)porphycene [42].

[s] 2,7,12,17-Tetra-n-propyl-3-(N,N-dimethylaminomethyl)porphycene [39].

The comparative flash photolysis method [33] was used in several cases (Tables 1 and 2) in order to determine the triplet quantum yield, Φ_T, with **1** as a reference ($\Phi_T = 0.3$) [26]. The monitoring wavelength was $\lambda_{obs} = 395$ nm for **1** and $\lambda_{obs} = 410$ nm for the other samples. The ratios of the laser fluence-dependent linear plots for sample and reference gave the corresponding ratios of the product $\Phi_T \Delta \epsilon_{T-T}$. As discussed previously [26], this method has the problem of a proper estimation of $\Delta \epsilon_{T-T}$ for each compound.

In order to avoid this difficulty, laser-induced optoacoustic spectroscopy (LIOAS) was used instead in most Φ_T determinations [26,34]. The amplitudes of the LIOAS signal, recorded at various fluences and concentrations of degassed solutions of sample and of either **1** or I₂ as calorimetric references ($\alpha = 1$, vide infra), were plotted vs. the fractions of fluence absorbed, E_a. The ratio of the slopes for sample and reference afforded α, which is the fraction of absorbed energy dissipated promptly as heat to the medium. Since the triplet

Table 2
Photophysical data for 9-substituted derivatives of 2,7,12,17-tetrakis(2-methoxyethyl)porphycene (cf. Scheme I)

Compound {C-3 and C-9 substituents}	Absorption λ^{abs}/nm ($\epsilon \times 10^{-3}$/M^{-1} mol^{-1})	Fluorescence λ^{em}/nm	ϕ_f (±0.05) λ^{exc} = 370 nm	λ_{T-S}/nm	Φ_T (±0.1) λ^{exc} = 650 nm [§] LIOAS [¶] Flash photolysis	Φ_Δ (±0.05) λ^{exc} = 650 nm	Solvent
14 [a] {3-H, 9-H}	638 (48.25)	642	0.47 (deg [b]) 0.38 (aer [c])	980	0.11 [§] 0.27 [¶]	0.37 0.5	toluene MeOH
15 [d] (unstable; see text) {3-H, 9-OH}	680 (27.54)	688	0.18 (aer)	1080	0.45 [§]	0.36 0.68	toluene MeOH
16 [e] {3-H, 9-OCH$_3$}	684 (19.15)	690	0.18 (aer)	1080	0.36 [§]	0.35	toluene
17 [f] {3-H, 9-O(CH$_2$)$_5$CH$_3$}	684					0.36	toluene
18 [g] {3-H, 9-OCOCH$_3$}	638 (36.98) 647 (35.68)	652	0.30 (deg) 0.27 (aer)	988	0.43 [§]	0.37	toluene
19 [h] {3-H, 9-OCO(CH$_2$)$_4$CH$_3$}	636, 646					0.27	toluene
20 [i] {3-H, 9-OCO(CH$_2$)$_7$CH$_3$}	637, 647					0.29	toluene
21 [j] {3-H, 9-OCO(CH$_2$)$_{16}$CH$_3$}	636, 646					0.28	toluene
22 [k] {3-H, 9-OCOCH$_2$NHCO$_2$C(CH$_3$)$_3$}	637, 644					0.32	toluene
23 [l] {3-H, 9-OCO(C$_6$H$_4$)-carotenyl}	641 (35.20)	652	0.1 (aer)		6×10^{-3} [¶]	ca. 10^{-2}	toluene
24 [m] (unstable; see text) {3-H, 9-NH$_2$}	716 (13.16)	748	0.04 (aer)	1080		0.3	toluene
25 [n] {3-H, 9-NHCOCH$_3$}	643, 670 (shoulder)					0.39	toluene
26 [o] {3-H, 9-NHCO(CH$_2$)$_3$CO$_2$H}	645 (38.63)	680	0.15 (aer)	1060	0.5 [§]	0.48	toluene
27 [p] {3-H, 9-NHCO(CH$_2$)$_3$CO$_2$CH$_3$}	642, 670 (shoulder)					0.36	toluene
28 [q] {3-H, 9-N[CO(CH$_2$)$_3$CO]}	640 (50.28)	646	0.39 (deg) 0.36 (aer)	980	0.13 [§] 0.22 [¶]	0.32	toluene
29 [r] {3-CH$_2$N(CH$_3$)$_2$, 9-H}	643					0.26 [s]	toluene
29·HCl [t] {3-CH$_2$N(CH$_3$)$_2$·HCl, 9-H}	620 (61.00)	645	0.02 (aer)		$< 10^{-3}$	$< 10^{-4}$	H$_2$O D$_2$O

[a] 2,7,12,17-Tetrakis(2-methoxyethyl)porphycene [15].
[b] Degassed.
[c] Aerated.
[d] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-hydroxyporphycene [42].
[e] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-methoxyporphycene [42].
[f] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-n-hexyloxyporphycene [43].
[g] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-acetoxyporphycene [42].
[h] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-caproyloxyporphycene [44].
[i] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-pelargonyloxyporphycene [44].
[j] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-stearoyloxyporphycene [44].
[k] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-(N-t-butoxycarbonylglycinoxy)porphycene [42].
[l] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-[4-(β-apo-7-carotenyl)benzoyloxy]porphycene [42].
[m] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-aminoporphycene [42].
[n] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-acetamidoporphycene [42].
[o] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-glutaramidoporphycene [42].
[p] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-(methylglutaramido)porphycene [42].
[q] 2,7,12,17-Tetrakis(2-methoxyethyl)-9-(glutarimido)porphycene [42].
[r] 2,7,12,17-Tetrakis(2-methoxyethyl)-3-(N,N-dimethylaminomethyl)porphycene [42].
[s] In preliminary experiments, addition of acetic acid did not decrease this value significantly
[t] 2,7,12,17-Tetrakis(2-methoxyethyl)-3-(N,N-dimethylaminomethyl)porphycene hydrochloride [42].

states, functioning as energy-storing species, are long-lived (ca. 400 μs, i.e. longer than the heat integration time of ca. 1.5 μs [33]) the LIOAS amplitudes could be used directly rather than having to resort to a more complex data analysis [35].

For the determination of Φ_T from LIOAS data, the regular energy balance Eq. (1) was used, in which the first term (αE_a) represents the prompt heat, $\Phi_f E_f$ is the energy dissipated by fluorescence, and $\Phi_T E_T$ is the energy stored by the triplet state. The fluorescence maximum was equated with E_f.

Table 3

Photophysical properties of various porphycene derivatives (cf. Scheme 2)

Compound	Absorption λ^{abs}/nm ($\epsilon \times 10^{-3}$/M^{-1} cm^{-1})	Fluorescence λ^{em}/nm	ϕ_f (±0.05) λ^{exc} = 370 nm	λ_{T-S}/nm	Φ_T (±0.1) λ^{exc} = 650 nm § LIOAS ¶ Flash photolysis	Φ_Δ (±0.05) λ^{exc} = 650 nm	Solvent
30 [a]	637					0.41	toluene
31 [b]	637 (52.20)	643	0.32 (deg [c]) 0.37 (aer [d])	980	0.2	0.34	toluene
32 [e]	638 (31.00)	642	0.4 (aer)	976	0.3 § 0.25 ¶	0.29	toluene
33 [f]	637					0.38	toluene
34 [g]	638 (50.00)	642	0.54 (deg) 0.44 (aer)	980	0.3 §	0.36	toluene
35 [h]	638					0.33	toluene
36 [i]	636 (36.00)					0.55	CH$_2$Cl$_2$/MeOH (9:1)
						0.1	DMPC liposomes
37 [j]	762 (23.10)		<10^{-4} (deg)			<10^{-3}	toluene
38 [k]	764 (ca. 22)		<10^{-4} (deg)		ca. 0.2	<10^{-4}	toluene

[a] 2-(2-Hydroxyethyl)-7,12,17-tri-n-propylporphycene [42].

[b] 2-(2-Hydroxyethyl)-7,12,17-tris(2-methoxyethyl)porphycene [15].

[c] Degassed.

[d] Aerated.

[e] 2,7-Bis(2-hydroxyethyl)-12,17-di-n-propylporphycene [42].

[f] 2-(2-Methoxyethyl)-7,12,17-tri-n-propylporphycene [42].

[g] 2,7-Bis(2-methoxyethyl)-12,17-di-n-propylporphycene [42].

[h] 2,7,12,17-Tetrakis(2-ethoxyethyl)porphycene [42].

[i] 2,3-(2^3-Carboxy-2^4-methoxycarbonylbenzo)-7,12,17-tris(2-methoxyethyl)porphycene [15].

[j] 2,7,12,17-Tetra-n-propyl-9,10-benzoporphycene [45].

[k] 2,7,12,17-Tetra-t-butyl-3,6; 13,16-dibenzoporphycene [46].

$$E_a = \alpha E_a + \Phi_f E_f + \Phi_T E_T \qquad (1)$$

The solutions of 9, 15 and 24 proved too unstable to survive the degassing procedure and thus permit the determination of λ_{T-S}, Φ_T and Φ_f under the exclusion of oxygen. Furthermore, the measurements were restricted to absorption and Φ_Δ values in a number of other cases (not explicitly referred to in the discussion) with far-reaching structural analogies to the compounds thoroughly analysed.

3. Results and discussion

The data are compiled in Table 1 for the tetrapropylporphycenes and in Table 2 for the tetrakis(methoxyethyl) derivatives. Table 3 lists miscellaneous other derivatives, inter alia amphiphilic compounds which had been prepared to screen for possible pharmacokinetic advantages of amphiphilic vs. less polar sensitizers.

All porphycenes exhibit appreciable absorptions at wavelengths longer than 630 nm, which is to the red of the heme absorption in tissues and therefore of critical importance for the purpose of sensitizer applications in PDT. Substitution of the aromatic system by strongly electron-donating (hydroxy, methoxy, amino) groups resulted in substantial red shifts (about 40–80 nm; cf. Fig. 1).

The emission spectra of all compounds were independent of the excitation wavelength. With the exception of 23, they were also reasonably good mirror images of the S_0-S_1 excitation spectra. The full excitation spectra were, in turn, identical with the corresponding absorption spectra (Fig. 1). This establishes also that in each case only a single species was emitting in the dilute solution.

The T–T absorption spectra were very similar in all cases, with a maximum at around 400 nm, i.e. red-shifted from the Soret band in analogy to the porphyrins (e.g., cf. Fig. 2). A spectral bleaching mirroring the absorption appeared immediately after excitation, with identical time constants for the bleaching recovery and the triplet decay. This indicates that several nanoseconds after excitation of the porphycenes in degassed toluene solutions only ground and triplet states of the starting material are present, and that the triplet states are exclusively deactivated by radiationless decay to the ground state.

All porphycene triplet energies, E_T, are ca. 110 kJ mol^{-1}, i.e. higher than the energy content of singlet oxygen, $O_2(^1\Delta_g)$, [36] by about 20 kJ mol^{-1}, which permits an exothermic and diffusion-controlled energy transfer in the process of triplet quenching by ground-state oxygen, $O_2(^3\Sigma_g)$. In most compounds the physical quenching was not accompanied by any noticeable chemical competition between triplet-excited porphycenes and $O_2(^3\Sigma_g)$, since no porphycene
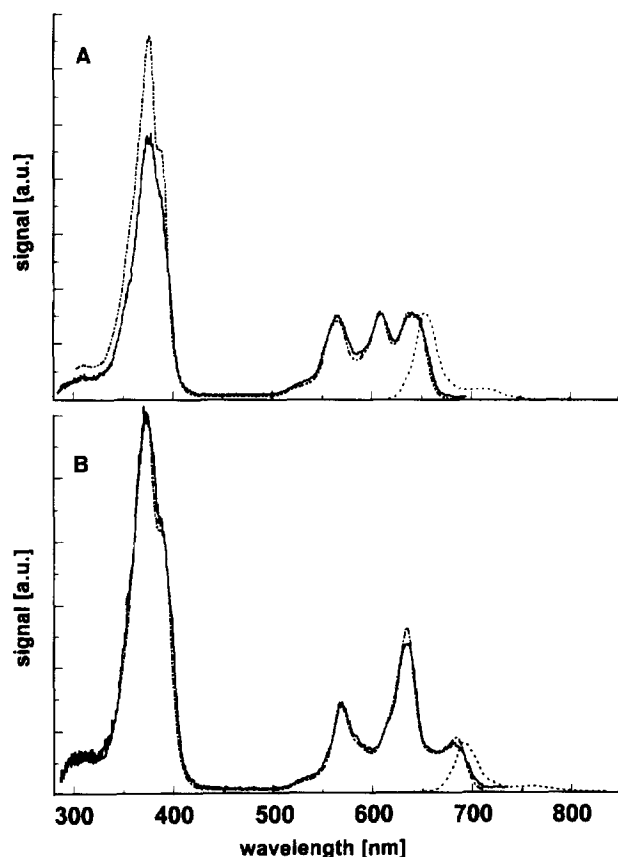
Fig. 1. (a) Absorption ($\cdot$ · — · ·), fluorescence (- - -; $\lambda_{exc} = 370$ nm), and fluorescence excitation (———; $\lambda_{em} = 712$ nm) spectra of 12 in toluene. (b) Absorption (- · -), fluorescence (- - -; $\lambda_{exc} = 370$ nm), and fluorescence excitation (———; $\lambda_{em} = 760$ nm) spectra of 14 in toluene.
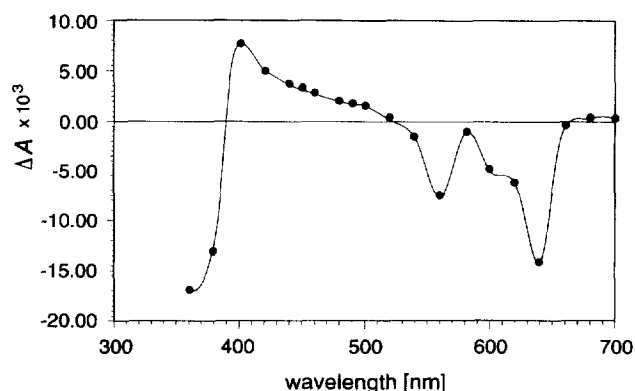

Fig. 2. Singlet–triplet difference absorption spectrum immediately after pulse excitation of a toluene solution of 12; $A_{650} = 0.193$, $\lambda_{exc} = 650$ nm.

bleaching was observed even after several flashes. Moreover, in general no chemical reaction occurred between ground-state porphycene and $O_2(^1\Delta_g)$ since in all cases, with the exception of 23 (vide infra), the decay kinetics of the $O_2(^1\Delta_g)$ formed by energy transfer was monoexponential throughout and the $O_2(^1\Delta_g)$ lifetime was identical with that in neat toluene, i.e., $\tau_\Delta = (30 \pm 2)$ μs (see Figs. 3–5 for examples of E_T, Φ_T and Φ_Δ measurements).
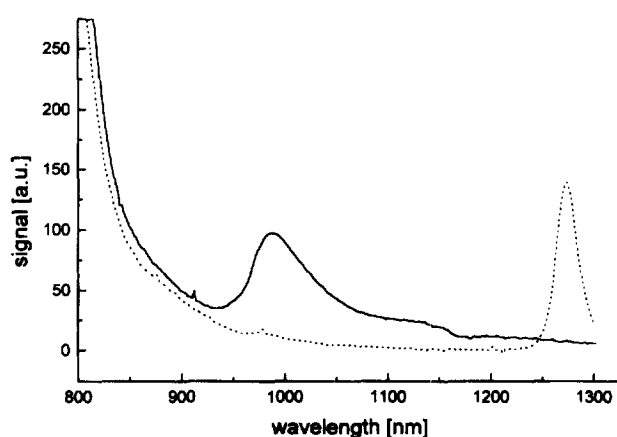
Fig. 3. Near-IR emission spectra of a (———) degassed and an (- - -) aerated solution of 12 in iodopropane.
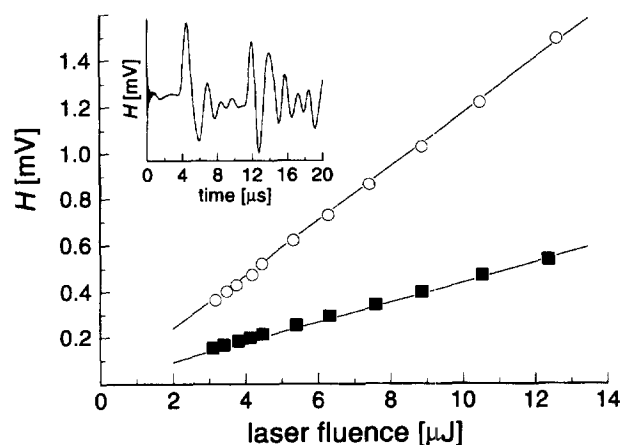

Fig. 4. Laser fluence-dependent amplitude of the LIOAS signal for solutions of ($\bigcirc$) I_2 as a calorimetric reference and ($\blacksquare$) 12. Inset: LIOAS signal of a N_2-saturated toluene solution of 12; $A_{650} = 0.219$, $\lambda_{exc} = 650$ nm.
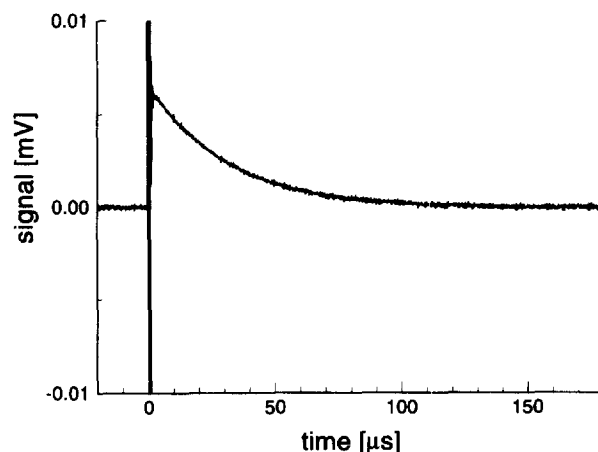

Fig. 5. Time-resolved near-IR emission of a toluene solution of 12: $A_{650} = 0.203$, $\lambda_{exc} = 650$ nm, $\tau_\Delta = 31$ μs. The strong instrumental overshooting immediately after pulse excitation is due to intense fluorescence.

4. General conclusions

With the exception of **23**, the photophysical properties of all porphycenes possessing unperturbed 18π aromaticity are qualitatively similar when measured in an organic solvent.

In the cases, in which considerable red shifts in absorption are associated with the introduction of certain structural changes and substituents, the fluorescence and triplet yields are drastically reduced. Such is the case with **37** and **38**, in which steric strain introduced by (bis)benzo annellation and crowding with adjacent alkyl substituents force the conjugated ring system out of plane and thus perturb the aromatic properties [6,37]. It is also encountered with the porphycenes substituted with electron-donating groups (-OH, -OCH$_2$R, and -NH$_2$) at C-9. In these examples, the red shift in absorption is accompanied by a decrease in Φ_f by 30 to 80% with respect to **1**. No similar decrease in Φ_T (and consequently in Φ_Δ) is observed. Evidently, the fluorescence channel does not compete noticeably with the intersystem crossing, but rather with radiationless internal conversion. The reduction in Φ_f is greatest for 9-amino substituted porphycenes. It is to be noted, however, that the presence of a non-substituted amino group at C-9 renders the compounds in both series, the tetra-n-propyl and tetrakis(2-methoxyethyl) derivatives, quite unstable. In fact, **9** was too labile to permit detection of any sensitized $O_2(^1\Delta_g)$ formation.

Apart from the compounds, in which the aromaticity is impaired conformationally, the Φ_f values are between 6 and 40% in organic solvents, and Φ_Δ is between 15 and 40%. The values of Φ_T, which are subject to a larger error inherent to the methods of determination, are close to Φ_Δ within this experimental error, similar to the case of the porphyrins and some other non-polarizable triplet sensitizers [38].

Compound **23** deserves special mention as an interesting case. The ground state absorption spectrum is essentially the sum of the spectra of the non-linked porphycene and carotenoid molecules [39]. The low Φ_f value points to intramolecular quenching of the excited singlet state by the carotenyl moiety. Fluorescence arises only from the lowest excited singlet state of the porphycene system as indicated by the long-wavelength emission band. The ratio of carotene to porphycene bands is smaller in the fluorescence excitation spectrum than in the absorption, which reflects the fact that the carotene-to-porphycene singlet energy transfer is only 50% efficient (calculated from the ratio of absorption and fluorescence excitation at 22000 cm^{-1} [40]). Triplet formation was seen only indirectly, by the measurement of sensitized $O_2(^1\Delta_g)$ generation, albeit in quite low quantum yield (Φ_Δ). Furthermore, the short lifetime of $\tau_\Delta = 7$ µs in toluene indicates quenching of $O_2(^1\Delta_g)$, probably by energy transfer to the carotenoid moiety. The findings with **23** are reminiscent of the properties of a porphyrin-carotene dyad system in which the carotenoid moiety quenches the fluorescence of the attached porphyrin, presumably by a through-bond mechanism which increases internal conversion of the excited sin-

glet to the electronic ground state (at the expense of intersystem crossing to triplet) [40].

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Corrigendum

Corrigendum to "Photophysical properties of porphycene derivatives (18 π porphyrinoids)" [Journal of Photochemistry and Photobiology B: Biology 40 (1997) 191–198] [1]

Silvia E. Braslavsky*, Martin Müller, Daniel O. Mártire, Sigrid Pörting, Sonia G. Bertolotti, Sankar Chakravorti, Gül Koç-Weier, Bernd Knipp, Kurt Schaffner

Max-Planck-Institut für Strahlenchemie, Postfach 10 13 65, D-45413 Mülheim an der Ruhr, Germany

In the above article the following correction should be made:

On p. 195, Table 3, the value of triplet formation quantum yield for compound **38** should read $< 5 \times 10^{-2}$.