Synthesis and Fluorescence Quenching Studies of a Series of Carotenoporphyrins with Carotenoids of Various Lengths

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Foi sintetizada uma série de díades moleculares, consistindo de uma porfirina covalentemente ligada a um carotenóide (carotenoporfirinas). O comprimento da cadeia conjugada do carotenóide foi variado sistematicamente de 5 a 11 duplas ligações (não incluindo a carbonila) e cada carotenóide foi diretamente ligado à 5-(4-aminofenil)-10,15,20-tris(4-metil-fenilporfirina) (TPPA). Foram preparadas também Zn-carotenoporfirinas, pela metalação da base livre de cada carotenoporfirina. A supressão da fluorescência da porfirina pelos carotenóides foi estudada em função do comprimento da cadeia conjugada dos carotenóides. Carotenóides com 5 a 7 duplas ligações não suprimem a fluorescência da porfirina. Carotenóides com 10 e 11 duplas ligações suprimem a fluorescência da porfirina acoplada a 10% do valor da porfirina livre e carotenóides com 8 e 9 duplas ligações exibem um efeito de supressão intermediário que é dependente do solvente. Nos casos intermediários, maior supressão da fluorescência é observada para as zinco-carotenoporfirinas.

A series of molecular dyads, each consisting of a porphyrin covalently linked to a carotenoid, was synthesized. The carotenoid conjugated chain length was systematically varied from 5 to 11 double bonds (not including the carbonyl group) and each carotenoid was linked to 5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (TPPA) by an amide bond. The analogous zinc carotenoporphyrins were prepared by metallation of the free base species. Porphyrin fluorescence quenching by the carotenoids was studied as a function of the length of the carotenoid conjugated system. Carotenoids containing from 5 to 7 double bonds do not quench porphyrin fluorescence. Carotenoids with 10 or 11 double bonds quench the fluorescence of the attached porphyrin to ~10% of the value of the parent porphyrin, and carotenoids with 8 or 9 double bonds exhibit an intermediate quenching effect that is solvent dependent. In the intermediate cases greater fluorescence quenching is observed for the zinc carotenoporphyrins.

Keywords: carotenoporphyrins; carotenoid, photoprotection, porphyrin

Introduction

Carotenoid pigments are found in the photosynthetic membranes of all naturally occurring photosynthetic organisms. These pigments absorb light and transfer excitation energy to chlorophylls where the photochemical reactions of photosynthesis originate. In this way they act as antennas which increase the absorption cross section of

the photosynthetic unit. They are also triplet energy acceptors or traps. Triplets arising on the chlorophyll pigments are rapidly quenched by energy transfer to yield the carotenoid triplet. This energy transfer is much faster than the competing bimolecular process in which chlorophyll triplets sensitize the formation of singlet oxygen. The carotenoid triplet is less energetic than singlet oxygen and therefore sensitization of singlet oxygen by the carotenoid

triplet is thermodynamically forbidden. Additionally, singlet oxygen is efficiently quenched by carotenoids. These two methods of controlling singlet oxygen in photosynthetic membranes are termed "photoprotection"^{1,2}. There is significant evidence for a third photochemical role of carotenoids in plants. The xanthophylls violaxanthin and zeaxanthin participate in the regulation of singlet energy flow in photosynthetic membranes. It has been proposed that zeaxanthin quenches chlorophyll singlet states under conditions where the rate of light absorption exceeds the turnover rate of the photosynthetic reaction center³. A fourth carotenoid function is suggested by the three-dimensional structure of an integral membrane protein responsible for light harvesting in plants. Xanthophylls bound to this protein extend across the thickness of the thylakoid membrane, where they may perform a structural role as molecular rivets by hydrogen bonding to sites near the surface, but on opposite sides of the membrane⁴.

In order to provide the three photochemical functions, three photochemical processes must occur between chlorophylls and carotenoids. Antenna function requires extremely rapid singlet-singlet energy transfer, which is facilitated if the carotenoid donor singlet is at higher energy than the acceptor chlorophyll singlet state⁵. Because the S_1 lifetime of carotenoids found in photosynthetic membranes is a few tens of picoseconds at most, efficient energy transfer from S_1 must occur within a few picoseconds. It is difficult to analyze the thermodynamics of this energy transfer process from S_1 due to the uncertain energy of S_1 . Because of its electric-dipole-forbidden nature, S_1 has not been observed in absorption or emission in most relevant carotenoids¹. The S_2 level gives rise to the characteristic orange color of carotenoids, and is energetically well above the chlorophyll S_1 . In this respect, the S_2 level would make an attractive donor species. However, its lifetime is typically only ~200 femtoseconds, so that efficient energy transfer would require an extremely fast process for which there is little precedent^{6,7}. Because the S_1 energy in the carotenoid is a function of the number of conjugated double bonds, systematically changing its length should alter the energy transfer efficiency from S_1 .

Photoprotection by quenching the chlorophyll triplet requires that triplet energy transfer to a carotenoid occurs much faster than the bimolecular sensitization of singlet oxygen by the chlorophyll triplet. The thermodynamics of the energy transfer process are uncertain, in that the energy of the carotenoid triplet is not precisely known. It is probably around 0.7 eV, which is well below that of singlet oxygen at 1 eV, chlorophyll *a* at ~1.4 eV, and bacteriochlorophyll *a* at ~1.1 eV. The T_1 level of the carotenoid is a function of the number of conjugated double bonds, so that by decreasing the length of the carotenoid, T_1 should move from below to above singlet oxygen, and then to above the T_1 level of chlorophyll. Carotenoids having T_1 energies

between those of singlet oxygen (1 eV) and the porphyrin sensitizer (1.5 eV) could sensitize singlet oxygen formation^{8,9}.

The control of the energy flow into photosynthetic reaction centers by carotenoid quenching of the chlorophyll singlet states can occur by several possible mechanisms. If the relevant carotenoid S_1 level is lower than that of the chlorophyll S_1 , then energy transfer from the chlorophyll to the carotenoid can occur. Even if the S_1 state of the carotenoid is nearly isoenergetic with the chlorophyll S_1 , energy transfer and rapid internal conversion in the carotenoid can drain singlet energy out of the chlorophyll system. In other words, the short S_1 lifetime of the carotenoid would constitute a shunt to divert the energy flow away from the reaction centers. Quenching by energy transfer should be a function of the S_1 level and therefore of the number of conjugated double bonds. If energy transfer is involved, changing the S_1 level should reflect this dependence.

Quenching of chlorophyll fluorescence by electron transfer from the carotenoid to the chlorophyll singlet is also possible. The resulting charge-transfer state would have a characteristic transient absorption spectrum, but could be difficult to detect due to its short lifetime. In a related bichromophoric system, in which a carotenoid was linked to a porphyrin modified to be an unusually good electron acceptor, such a transient species has been reported and electron transfer established as the quenching mechanism¹⁰. It is expected that the thermodynamics of electron transfer from the carotenoid to the tetrapyrrole S_1 would depend on the oxidation potential of the carotenoid, which is a function of the conjugated chain length. Thus, if electron transfer quenching occurs, it should reflect the dependence of the oxidation potential on the chain length.

In order to systematically change the carotenoid S_1 level, T_1 level and oxidation potential so that the issues described above can be addressed, a series of carotenoporphyrins was synthesized. In this series the porphyrin moiety (P) and the linkage are not changed, while the carotenoid component (C) varies in length from 5 (CP5) to 11 (CP11) conjugated double bonds. The amide linkage was chosen because it provides electronic coupling between the chromophores, which is adequate for rapid triplet energy transfer from the porphyrin to the carotenoid, for measurable singlet energy transfer from the carotenoid to the porphyrin, and for quenching of the porphyrin fluorescence by the attached carotenoid. NMR studies indicate that there are no large changes in the conformation of the carotenoid relative to the porphyrin within this series of dyads. The relatively rigid linkage results in a conformation in which the carotenoid extends away from the porphyrin. The report of the synthesis and preliminary studies of the porphyrin fluorescence quenching in the series of dyads follows.

Results and Discussion

Synthesis

Schemes 1 and 2 illustrate the strategy used in the preparation of the carotenoporphyrin series. The following basic steps were used sequentially in the synthesis:

- 1) Starting with a polyene-aldehyde, a polyene-ester was generated *via* a Wittig reaction.
- 2) Expansion of the conjugated chain was attained by the reduction of the polyene-ester to the corresponding polyene-aldehyde, followed by another Wittig reaction.
- 3) Basic hydrolysis of the esters generated by the Wittig reactions was used to produce the corresponding carboxylic acids.
- 4) Linkage through amide bonds of the polyene-acid (*via* its acid chloride derivative) with an aminoporphyrin resulted in the desired carotenoporphyrin.

For the preparation of **CP5**, retinoic acid (**C5A**) was converted into its acid chloride using thionyl chloride in dry toluene and the acid chloride was used for the coupling with

5-(4-aminophenyl)-10,15,20-tris-(4-methylphenyl) porphyrin (Scheme 1)¹¹. Dyad **CP6** was synthesized by a Wittig reaction with retinal, using methyl (triphenylphosphoranylidene) acetate, (Ph)₃PCHCO₂Me). Basic hydrolysis of the ester obtained from the Wittig reaction using 10% aqueous potassium hydroxide yielded the carotenoid acid which was then converted to the acid chloride and coupled to the aminoporphyrin.

The alternate use of two yields, $(\text{Ph})_3\text{PCHCO}_2\text{Me}$ and $(\text{Ph})_3\text{PC}(\text{CH}_3)\text{CO}_2\text{Et}$, in the Wittig reaction with polyene-aldehydes allowed the assembly of conjugated chains with a methyl group on every fifth carbon atom, as is commonly observed in natural carotenoids¹². The conversion of the ester obtained after a Wittig reaction into an aldehyde was necessary for the preparation of the next compound in the series through another Wittig reaction. This was accomplished by the reduction of the ester to the alcohol with DIBAL-H in THF at 0 °C, followed by oxidation of the alcohol to the aldehyde with activated MnO_2 .

Scheme 1. (a) Toluene, (Ph)₃PCHCO₂CH₃, 100 °C, 24; (b) THF, DIBAL-H, 0 °C; (c) THF, activated MnO₂, 24 h; (d) Toluene, (Ph)₃PC(CH₃)CO₂CH₂CH₃, 100 °C, 24 h; (e) THF, MeOH, 10% aq. KOH, 20 h; (f) CHCl₃, pyridine, SOCl₂; (g) Toluene, pyridine, TTPNH₂, argon, 24 h.

Scheme 2. (a-g) are the same as in Scheme 1; (h) MeOH, NaCN, MnO₂, HOAc, argon, 24 h.

The preparation of **CP9** required the conversion of 8'-apo-β-caroten-8'-al (**VI**), a commercially available compound which features a synthetically versatile aldehyde group, into its acid derivative (Scheme 2). Due to the sensitivity of carotenoids to acidic media it was necessary to carry out the oxidation under neutral or slightly basic conditions. This was achieved using a method described by Corey *et al.*¹³, and successfully applied in the oxidation of retinal¹⁴ and retinol¹⁵ to the respective methyl esters. Thus, **VI** was treated with NaCN and MnO₂ in methanol to give the corresponding methyl ester in a reasonable yield (33%). The methyl ester was hydrolyzed to its acid derivative, which was then coupled with the aminoporphyrin.

Absorption spectra

The spectra of the synthetic carotenoids (Fig. 1), exhibit the predicted red shift as a function of the length of the conjugated system. The absorption spectrum of a toluene solution of the parent porphyrin, 5-(4-acetamidophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (TPPA), shows the Soret band at 420 nm and the typical four Q bands at 517, 552, 593 and 650 nm. The absorption spectra of the

Figure 1. The absorption spectra of toluene solutions of the carotenoid series. C5A, C6A, C7A, C8A', and C8A are carboxylic acids, while C9E, C10E, and C11E are esters.

carotenoporphyrin dyads in toluene are presented in Fig. 2. The spectra are essentially linear combinations of the spectra of TPPA and the corresponding carotenoids. This is consistent with a weak interaction between the chromo-

Figure 2. The absorption spectra of 5-(4-acetamidophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (TTPA) and carotenoporphyrins in toluene solutions.

phores; the porphyrin and the carotenoid moieties preserve their individual identities.

Time-resolved fluorescence studies

The degree of the intramolecular quenching of the porphyrin excited singlet state by the carotenoid component in the carotenoporphyrins was determined by time-resolved emission studies carried out using the single photon timing technique. Excitation of the porphyrin moiety in solutions of **CP5** to **CP11**, in toluene and acetonitrile, with 590-nm laser pulses resulted in the observation of single exponential decays. The quantum yields of fluorescence were calculated using the fluorescence lifetime of tetraphenylporphyrin (TPP) as a reference. Zinc metallated carotenoporphyrins (ZnCP) were analyzed in toluene solutions using zinc-TTPA as a reference. A graphic presentation of the results is shown in Fig. 3.

Negligible fluorescence quenching was observed for **CP5**, **CP6** and **CP7** in either toluene or acetonitrile. The onset of fluorescence quenching was with **CP8'** and **CP8**, in which the fluorescence lifetimes for the model porphyrin and the shorter CPs, were reduced from 11 ns, to 8 and 9 ns in toluene solution, respectively. Both dyads exhibited increased fluorescence quenching in acetonitrile, a more polar solvent with a higher dielectric constant. Increased fluorescence quenching was observed for **CP9** in both toluene and acetonitrile. In contrast to this behavior, the singlet lifetimes of **CP10** and **CP11** were both quenched to the same extent, about 10% of the unquenched lifetime, and the quenching was essentially independent of the solvent. The zinc substituted dyads presented qualitatively similar behavior, in that the maximum quenching was independent of the solvent and occurred with **ZnCP10** and **ZnCP11**. However, the onset of solvent dependent quenching in the metallated CPs was more abrupt.

Figure 3. Φ/Φ_0 : Relative quantum yields of fluorescence of porphyrins and carotenoporphyrins. (◆) Free base porphyrins and CPs in toluene (the reference is TPP). (■) Free base porphyrins and CPs in acetonitrile (the reference is TPP). (▲) Zn metallated porphyrins and Zn-CPs in toluene (the reference is Zn-TTPA).

These results are enigmatic in their bearing on the mechanism of quenching. As mentioned in the introduction, both electron transfer and energy transfer are potential quenching mechanisms. Enhanced quenching in solvents with a high dielectric constant, as observed for **CP8'**, **CP8** and **CP9**, is consistent with electron transfer to yield a charge-separated species. Changing the solvent affects both the thermodynamic driving force for electron transfer and the solvent reorganization energy. The rate enhancement in polar solvents is thought to arise from the solvation of the ion pair state, which increases the driving force for charge separation, and thereby increases the rate. The solvent-independent quenching of fluorescence in **CP10** and **CP11** is, however, unexpected for an electron transfer mechanism. Attempts to correlate the observed quenching with oxidation potentials of the carotenoids await the results of electrochemical measurements.

Quenching by energy transfer requires that the carotenoid S_1 energy level be below or near that of the porphyrin. Due to its optically-forbidden nature, the S_1 level of these carotenoids has not been determined. However, within this series of carotenoids the S_1 level is expected to decrease monotonically with the number of double bonds¹⁶, and thus could shift below the porphyrin level at some point. It is possible to attribute the change in quenching at **CP8** and **CP9** to this crossing of energy levels. Because the free base porphyrin in all dyads has a lower S_1 level than the zinc porphyrin, the zinc carotenoporphyrin should demonstrate more quenching in the transition region from non-quenching to quenching, *e.g.*, **CP9**. This was observed.

Experimental

Solvents and reagents

Reagent grade chloroform and methylene chloride were distilled and stored over anhydrous potassium carbonate.

Dry chloroform was prepared by treating reagent grade chloroform with phosphorus pentoxide, distillation under an argon atmosphere and storage over 4 Å molecular sieves. Chloroform dried by the above procedure was used within 48 h. Dry toluene was prepared by distillation and storage over 4 Å molecular sieves. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride under a nitrogen atmosphere. Absolute ethanol was dried over 3 Å molecular sieves before use. Retinoic Acid (Aldrich), retinal (Sigma), activated MnO_2 (Fluka), methyl (triphenylphosphoranylidene) acetate, $(\text{Ph})_3\text{PCHCO}_2\text{Me}$ (Aldrich), ethyl 2-(triphenylphosphoranylidene) propionate, $(\text{Ph})_3\text{PC}(\text{CH}_3)\text{CO}_2\text{Et}$ (Aldrich), and diisobutylaluminum hydride (DIBAL-H) (1.0 M solution in cyclohexane, Aldrich)

were used as obtained from the commercial sources, unless otherwise noted. 8'-Apo- β -caroten-8'-al (VI) (Hoffmann-La Roche) was purified by flash column chromatography (silica/100% CH_2Cl_2) before use. The 5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl) porphyrin and 5-(4-acetamidophenyl)-10,15,20-tris(4-methylphenyl) porphyrin were prepared as described in the literature¹¹.

General methods

^1H -NMR spectra were obtained at 300 MHz (Varian Gemini spectrometer) or 500 MHz (Varian Unity spectrometer) from <1% solutions in chloroform-*d*. Mass spectra were taken with a Varian Matt 311 operating in EI mode 70 eV and with a Vestec Laser Tec Research Instrument by

laser desorption time of flight mass spectrometry. The UV-Vis spectra were recorded with a Shimadzu UV2100 UV-Vis Spectrometer. Fluorescence decay measurements were performed on $<10^{-5}$ M deaerated solutions in toluene or acetonitrile using the single photon timing method. All samples were purified prior to use by either column chromatography or TLC. The excitation source was a frequency-doubled Coherent Antares 76s Nd:YAG laser routed through a variable beam splitter to pump a cavity-dumped dye laser¹⁷. The instrument response function was measured at the excitation wavelength (590 nm) for each decay experiment with Ludox AS-40 under the same conditions as the sample. Thin layer chromatography was performed on pre-coated silica gel plates (Analtech). Flash column chromatography was done using silica gel (Merck, 43 μ m average particle diameter). Reactions were run under dry nitrogen, unless otherwise noted. Solutions were concentrated under vacuum using a rotatory evaporator.

Methyl 14'-apo- β -caroten-14'-oate (C6E)

Retinal (I) (441 mg, 1.55 mmol) was dissolved in dry toluene (50 mL), and a solution of methyl (triphenylphosphoranylidene) acetate (1.30 g, 3.88 mmol) in dry toluene was added. The mixture was kept under reflux, well stirred, for 24 h. Thin-layer chromatography (silica gel/100% CHCl₃) indicated the quantitative formation of the methyl ester. The solution was concentrated and the product isolated by flash chromatography (silica gel/CH₂Cl₂). ¹H-NMR (300 MHz, CDCl₃) δ 1.00 (6H, s, 16C-CH₃, 17C-CH₃), 1.42-1.53 (2H, m, 2C-CH₂), 1.57-1.61 (2H, m, 3C-CH₂), 1.69 (3H, s, 18C-CH₃), 1.96 (3H, s, 19C-CH₃), 1.96-2.04 (2H, m, 4C-CH₂), 2.04 (3H, s, 20C-CH₃), 3.73 (3H, s, 14'C-CO₂CH₃), 5.86 (1H, d, J = 15.00 Hz, 15'C-H), 6.12 (1H, d, J = 16.11 Hz, 8C-H), 6.13 (1H, d, J = 10.26 Hz, 10C-H), 6.08-6.25 (2H, m, 7C-H, 14C-H), 6.32 (1H, d, J = 15.12 Hz, 12C-H), 6.81 (1H, dd, J = 15.03 and 11.50 Hz, 11C-H), 7.68 (1H, dd, J = 15.06 and 11.91 Hz, 15C-H). MS: m/z 340 (M⁺). UV-Vis $\lambda_{\max}$ (toluene) (nm): 391.

14'-Apo- β -caroten-14'-ol (II)

Methyl 14'-apo- β -caroten-14'-oate (C6E) (610 mg, 1.79 mmol) was dissolved in 50 mL of dry THF, and a solution of diisobutylaluminum hydride (3.60 mL, 3.60 mmol) was added by drops at 0 °C with stirring. Thin-layer chromatography (silica gel/100% CHCl₃) indicated the quantitative formation of the product. One mL of methanol followed by 1 mL of water were added to eliminate the excess of hydride. The crude mixture was passed through a sintered glass filter containing neutral alumina, and washed with CH₂Cl₂ and water, followed by extraction with CH₂Cl₂. The solvent was evaporated and the product dried under high vacuum for 15 h.

14'-Apo- β -caroten-14'-al (III)

14'-Apo- β -caroten-14'-ol (II) was dissolved in THF, and 6 g of activated MnO₂ was added. The reaction was allowed to proceed at room temperature, well stirred, for 24 h. Thin-layer chromatography (silica gel/100% CHCl₃) indicated the quantitative formation of the aldehyde. The mixture was passed through a sintered glass filter containing Celite and washed with CH₂Cl₂. The solution was concentrated and the product was isolated by flash chromatography (silica gel/CH₂Cl₂). ¹H-NMR (300 MHz, CDCl₃) δ 0.99 (6H, s, 16C-CH₃, 17C-CH₃), 1.40-1.44 (2H, m, 2C-CH₂), 1.54-1.60 (2H, m, 3C-CH₂), 1.67 (3H, s, 18C-CH₃), 1.96 (3H, s, 19C-CH₃), 1.93-2.04 (2H, m, 4C-CH₂), 2.06 (3H, s, 20C-CH₃), 6.11 (1H, d, J = 16.41 Hz, 8C-H), 6.13 (1H, d, J = 14.88 Hz, 15'C-H), 6.10-6.15 (1H, m, 10C-H), 6.24 (1H, d, J = 17.22 Hz, 7C-H), 6.29 (1H, d, J = 11.67 Hz, 14C-H), 6.33 (1H, d, J = 14.88 Hz, 12C-H), 6.88 (1H, dd, J = 14.86 and 11.53 Hz, 11C-H), 7.47 (1H, dd, J = 14.88 and 11.97 Hz, 15C-H), 9.56 (1H, d, J = 7.9 Hz, 14'C-CHO). MS: m/z 310 (M⁺).

Ethyl 12'-apo- β -caroten-12'-oate (C7E)

C7E was prepared as described for C6E using 14'-apo- β -caroten-14'-al (III) (250 mg, 0.806 mmol) and ethyl 2-(triphenylphosphoranylidene) propionate (411 mg, 1.13 mmol). Thin-layer chromatography (silica gel/100% CHCl₃) indicated the quantitative formation of the ethyl ester. ¹H-NMR (300 MHz, CDCl₃) δ 1.01 (6H, s, 16C-CH₃, 17C-CH₃), 1.29 (3H, t, J = 7.12 Hz, 12'C-CO₂CH₂CH₃), 1.43-1.47 (2H, m, 2C-CH₂), 1.57-1.62 (2H, m, 3C-CH₂), 1.70 (3H, s, 18C-CH₃), 1.96 (6H, s, 19C-CH₃, 20C-CH₃), 1.98 (3H, s, 20'C-CH₃), 1.95-2.02 (2H, m, 4C-CH₂), 4.19 (2H, q, J = 7.12 Hz, 12'C-CO₂CH₂CH₃), 6.12 (1H, d, J = 16.11 Hz, 8C-H), 6.13 (1H, d, J = 11.55 Hz, 10C-H), 6.18 (1H, d, J = 15.78 Hz, 7C-H), 6.27 (1H, d, J = 11.49 Hz, 14C-H), 6.33 (1H, d, J = 15.00 Hz, 12C-H), 6.50 (1H, dd, J = 14.40 and 11.97 Hz, 15'C-H), 6.72 (1H, dd, J = 14.97 and 11.46 Hz, 11C-H), 6.88 (1H, dd, J = 14.34 and J = 11.67 Hz, 15C-H), 7.29 (1H, d, J = 11.73 Hz, 14'C-H). UV-Vis $\lambda_{\max}$ (toluene) (nm): 415.

12'-Apo- β -caroten-12'-ol(IV)

IV was prepared as described for II, using ethyl 12'-apo- β -caroten-12'-oate (C7E) (200 mg, 0.507 mmol) and diisobutylaluminum hydride (2.00 mL, 2.00 mmol). Thin-layer chromatography (silica gel/100% CHCl₃) indicated the quantitative formation of the product.

12'-Apo- β -caroten-12'-al (V)

V was prepared as described for III using 12'-apo- β -caroten-12'-ol (IV) and 2 g of activated MnO₂. Thin-layer chromatography (silica gel/100% CHCl₃) indicated the

quantitative formation of the product. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.00 (6H, s, 16C- CH_3 , 17C- CH_3), 1.41-1.46 (2H, m, 2C- CH_2), 1.56-1.61 (2H, m, 3C- CH_2), 1.69 (3H, s, 18C- CH_3), 1.85 (3H, s, 20'C- CH_3), 1.95-2.01 (2H, m, 4C- CH_2), 1.96 (3H, s, 19C- CH_3), 2.01 (3H, s, 20C- CH_3), 6.12 (1H, d, J = 16.05 Hz, 8C-H), 6.14 (1H, d, J = 11.10 Hz, 10C-H), 6.22 (1H, d, J = 16.11 Hz, 7C-H), 6.27 (1H, d, J = 11.67 Hz, 14C-H), 6.34 (1H, d, J = 15.00 Hz, 12C-H), 6.65 (1H, dd, J = 14.43 and 11.70 Hz, 15'C-H), 6.77 (1H, dd, J = 14.97 and 11.49 Hz, 11C-H), 6.93 (1H, d, J = 12.66 Hz, 14'C-H), 7.00 (1H, dd, J = 14.40 and 11.97 Hz, 15 C-H), 9.43 (1H, s, 12'C-CHO). MS: m/z 350 (M^+).

Ethyl 11'-methyl-10'-apo- β -caroten-10'-oate (C8E')

C8E' was prepared as described for **C6E** using 12'-apo- β -caroten-12'-al (**V**, 150 mg, 0.428 mmol) and ethyl 2-(triphenylphosphoranylidene) propionate (406 mg, 1.12 mmol). Thin-layer chromatography (silica gel/100% CHCl_3) indicated the quantitative formation of the ethyl ester. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.01 (6H, s, 16C- CH_3 , 17C- CH_3), 1.29 (3H, t, J = 7.17 Hz, 10'C-CO $_2$ CH $_2$ CH $_3$), 1.42-1.46 (2H, m, 2C- CH_2), 1.57-1.63 (2H, m, 3C- CH_2), 1.70 (3H, s, 18C- CH_3), 1.96 (6H, s, 19C- CH_3 , 20C- CH_3), 1.96-2.02 (2H, m, 4C- CH_2), 2.04 (3H, s, 20'C- CH_3), 2.08 (3H, s, 21'C- CH_3), 4.20 (2H, q, J = 7.17 Hz, 10'C-CO $_2$ CH $_2$), 6.11 (1H, d, J = 16.62 Hz, 8C-H), 6.13 (1H, d, J = 11.55 Hz, 10C-H), 6.18 (1H, d, J = 16.50 Hz, 7C-H), 6.23 (1H, d, J = 11.67 Hz, 14C-H), 6.33 (1H, d, J = 14.94 Hz, 12C-H), 6.39 (1H, d, J = 11.52 Hz, 14'C-H), 6.55 (1H, dd, J = 13.96 and 11.47 Hz, 15'C-H), 6.67 (1H, dd, J = 14.85 and 11.52 Hz, 11C-H), 6.69 (1H, dd, J = 13.87 and 11.38 Hz, 15C-H), 7.18 (1H, s, 12'C-H). MS: m/z 434 (M^+). UV-Vis λ_{max} (toluene) (nm): 432.

Methyl 10'-apo- β -caroten-10'-oate (C8E)

C8E was prepared as described for **C6E**, using 12'-apo- β -caroten-12'-al (**V**, 170 mg, 0.485 mmol) and methyl (triphenylphosphoranylidene)acetate (255 mg, 0.726 mmol). Thin-layer chromatography (silica gel/100% CHCl_3) indicated the quantitative formation of the methyl ester. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.00 (6H, s, 16C- CH_3 , 17C- CH_3), 1.42-1.47 (2H, m, 2C- CH_2), 1.55-1.62 (2H, m, 3C- CH_2), 1.69 (3H, s, 18C- CH_3), 1.89 (3H, s, 20'C- CH_3), 1.95 (3H, s, 19C- CH_3), 1.95-2.01 (2H, m, 4C- CH_2), 1.97 (3H, s, 20C- CH_3), 3.73 (3H, s, 10'C-CO $_2$ CH $_3$), 5.85 (1H, d, J = 15.87 Hz, 11'C-H), 6.11 (1H, d, J = 16.11 Hz, 8C-H), 6.13 (1H, d, J = 11.67 Hz, 10C-H), 6.18 (1H, d, J = 16.51 Hz, 7C-H), 6.26 (1H, d, J = 10.56 Hz, 14C-H), 6.32 (1H, d, J = 14.94 Hz, 12C-H), 6.48 (1H, d, J = 11.13 Hz, 14'C-H), 6.52-6.76 (3H, m, 11C-H, 15'C-H, 11'C-H), 7.36 (1H, d, J = 15.48 Hz, 12'C-H). UV-Vis λ_{max} (toluene) (nm): 437.

Methyl 8'-apo- β -caroten-8'-oate (C9E)

8'-Apo- β -caroten-8'-al (**VI**) (122 mg, 0.293 mmol) was stirred with a mixture of NaCN (248 mg, 5.06 mmol), MnO_2 (1.540 g) and acetic acid (0.10 mL) in 50 mL of MeOH for 24 h under an argon atmosphere. The solution was filtered through a sintered glass funnel containing neutral alumina and washed with CH_2Cl_2 . Water was added and the product was extracted with CH_2Cl_2 . The solvent was removed and the residue was dried under high vacuum. The product was isolated by flash chromatography (silica gel/ CH_2Cl_2) yielding 43.4 mg (33.4%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 0.99 (6H, s, 16C- CH_3 , 17C- CH_3), 1.41-1.45 (2H, m, 2C- CH_2), 1.55-1.60 (2H, m, 3C- CH_2), 1.68 (3H, s, 18C- CH_3), 1.94 (6H, s, 19C- CH_3 , 20C- CH_3), 1.94-1.99 (2H, m, 4C- CH_2), 1.96 (6H, s, 20'C- CH_3 , 19'C- CH_3), 3.73 (3H, s, 8'C-CO $_2$ CH $_3$), 6.09 (1H, d, J = 16.11 Hz, 8C-H), 6.12 (1H, d, J = 11.13 Hz, 10C-H), 6.17 (1H, d, J = 19.44 Hz, 7C-H), 6.22 (1H, d, J = 11.22, 14C-H), 6.32 (1H, d, J = 15.00 Hz, 12C-H), 6.33 (1H, d, J = 10.02 Hz, 14'C-H), 6.43-6.74 (5H, m, 11'C-H, 15'-C-H, 11C-H, 15C-H, 12'C-H), 7.26 (1H, d, J = 10.9 Hz, 10'C-H). MS: m/z 446 (M^+). UV-Vis λ_{max} (toluene) (nm): 454.

Methyl 6'-apo- β -caroten-6'-oate (C10E)

C10E was prepared as described for **C6E**, using 8'-apo- β -caroten-8'-al (**VI**, 518 mg, 1.25 mmol) and methyl (triphenylphosphoranylidene) acetate (653 mg, 1.95 mmol). Thin-layer chromatography (silica gel/100% CHCl_3) indicated the quantitative formation of the methyl ester. $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 1.01 (6H, s, 16C- CH_3 , 17C- CH_3), 1.42-1.46 (2H, m, 2C- CH_2), 1.55-1.61 (2H, m, 3C- CH_2), 1.69 (3H, s, 18C- CH_3), 1.91 (3H, s, 19'C- CH_3), 1.95 (6H, s, 19C- CH_3 , 20C- CH_3), 1.95-2.01 (2H, m, 4C- CH_2), 1.96 (3H, s, 20'C- CH_3), 3.74 (3H, s, 6'C-CO $_2$ CH $_3$), 5.85 (1H, d, J = 15.57, 7'C-H), 6.11 (1H, d, J = 15.96 Hz, 8C-H), 6.13 (1H, d, J = 11.67 Hz, 10C-H), 6.18 (1H, d, J = 16.17 Hz, 7C-H), 6.23 (1H, d, J = 11.67 Hz, 14C-H), 6.32 (1H, d, J = 10.86 Hz, 14'C-H), 6.33 (1H, d, J = 15.00, 12C-H), 6.43-6.73 (6H, m, 11'C-H, 15'-C-H, 11C-H, 12'C-H, 15C-H, 10'C-H), 7.37 (1H, d, J = 15.5 Hz, 8'C-H). UV-Vis λ_{max} (toluene) (nm): 476.

6'-Apo- β -caroten-6'-ol (VII)

VII was prepared as described for **II** using methyl 6'-apo- β -caroten-6'-oate (**C10E**) (106 mg, 0.224 mmol) and diisobutylaluminum hydride (2.00 mL 2.00 mmol). Thin-layer chromatography (silica gel/100% CHCl_3) indicated the quantitative formation of the product.

6'-Apo- β -caroten-6'-al (VIII)

VIII was prepared as described for (**III**), using 6'-apo- β -caroten-6'-ol (**VII**) and 1 g of activated MnO_2 . Thin-layer

chromatography (silica gel/100% CHCl₃) indicated the quantitative formation of the product. ¹H-NMR (300 MHz, CDCl₃) δ 1.01 (6H, s, 16C-CH₃, 17C-CH₃), 1.42-1.46 (2H, m, 2C-CH₂), 1.55-1.63 (2H, m, 3C-CH₂), 1.69 (3H, s, 18C-CH₃), 1.94-2.01 (2H, m, 4C-CH₂), 1.95 (12H, s, 19C-CH₃, 19'C-CH₃, 20C-CH₃, 20'C-CH₃), 6.11 (1H, d, J = 15.87 Hz, 8C-H), 6.14 (1H, d, J = 10.44 Hz, 10C-H), 6.17 (1H, d, J = 15.24 Hz, 7'C-H), 6.19 (1H, d, J = 15.72 Hz, 7C-H), 6.24 (1H, d, J = 12.00 Hz, 14C-H), 6.33 (1H, d, J = 15.00 Hz, 12C-H), 6.36 (1H, d, J = 10.20 Hz, 14'C-H), 6.56-6.74 (6H, m, 12'C-H, 11'C-H, 15'C-H, 11C-H, 10'C-H, 15C-H), 7.14 (1H, d, J = 15.42 Hz, 8'C-H), 9.56 (1H, d, J = 7.77 Hz, 6'C-CHO).

Ethyl 4'-apo-β,y-caroten-4'-oate (C11E)

C11E was prepared as described for C6E, using 6'-apo-β-caroten-6'-al (VIII) (90 mg, 0.203 mmol) and ethyl 2-(triphenylphosphoranylidene)propionate (128 mg, 0.353 mmol). Thin-layer chromatography (silica gel/100% CHCl₃) indicated the quantitative formation of the ethyl ester. ¹H-NMR (300 MHz, CDCl₃) δ 1.01 (6H, s, 16C-CH₃, 17C-CH₃), 1.29 (3H, t, J = 7.16 Hz, 4'C-CO₂CH₂CH₃), 1.42-1.46 (2H, m, 2C-CH₂), 1.57-1.61 (2H, m, 3C-CH₂), 1.69 (3H, s, 18C-CH₃), 1.95 (6H, s, 19C-CH₃, 20C-CH₃), 1.97 (9H, s, 20'C-CH₃, 19'C-CH₃, 18'C-CH₃), 1.96-2.02 (2H, m, 4C-CH₂), 4.19 (2H, q, J = 7.08 Hz, 4'C-CO₂CH₂), 6.10 (1H, d, J = 16.11 Hz, 8C-H), 6.13 (1H, d, J = 11.56 Hz, 10C-H), 6.17 (1H, d, J = 16.65 Hz, 7C-H), 6.23 (1H, d, J = 10.00 Hz, 14C-H), 6.32 (1H, d, J = 10.02 Hz, 14'C-H), 6.33 (1H, d, J = 15.45 Hz, 12C-H), 6.42 (1H, d, J = 14.79 Hz, 12'C-H), 6.47 (1H, d, J = 11.25 Hz, 10'C-H), 6.50 (1H, d, J = 14.94 Hz, 8'C-H), 6.56-6.88 (5H, m, 7'C-H, 11'C-H, 15'C-H, 11C-H, 15C-H), 7.26 (1H, J = 11.91 Hz, 6'C-H). UV-Vis λ_{max}(toluene) (nm): 486.

Carotenoporphyrin CP5

Retinoic acid (C5A) (35 mg, 0.12 mmol) was dissolved in 4 mL of dry chloroform and 1 mL of pyridine. One drop of thionyl chloride was added, and after 15 min a small aliquot of the mixture was mixed with one drop of methanol. Detection of the methyl ester by thin-layer chromatography (silica gel/1% MeOH/CHCl₃) indicated the quantitative formation of the acid chloride. The solvents were evaporated at reduced pressure and the residue kept under high vacuum for 30 min. The residue was re-dissolved in 3 mL of dry toluene and 1 mL of pyridine. 5-(4-Amino-phenyl)-10,15,20-tris(4-methylphenyl) porphyrin (116 mg, 0.173 mmol) was dissolved in 3 mL of dry toluene and 1 mL of pyridine and added to the acid chloride solution. The mixture was stirred under an argon atmosphere for 24 h. Thin-layer chromatography (silica gel/1% MeOH/CHCl₃) indicated the quantitative formation of the carotenoporphyrin. The solvent was evaporated and the

crude product was purified by flash chromatography (silica gel/CH₂Cl₂). ¹H-NMR (500 MHz, CDCl₃) δ -2.78 (2H, s, pyrrole-NH), 1.04 (6H, s, 16C-CH₃, 17C-CH₃), 1.46-1.49 (2H, m, 2C-CH₂), 1.57-1.61 (2H, m, 3C-CH₂), 1.73 (3H, s, 18C-CH₃), 2.04 (3H, s, 19C-CH₃), 1.98-2.04 (2H, m, 4C-CH₂), 2.54 (3H, s, 20C-CH₃), 2.68 (9H, s, 10,15,20Ar-CH₃), 5.95 (1H, s, 14C-H), 6.17 (1H, d, J = 16.00 Hz, 8C-H), 6.20 (1H, d, J = 12.50 Hz, 10C-H), 6.30 (1H, d, J = 16.00 Hz, 7C-H), 6.38 (1H, d, J = 15.00 Hz, 12C-H), 7.07 (1H, dd, J = 15.25 and 11.75 Hz, 11C-H), 7.44 (1H, s, 5Ar-NHCO), 7.53 (6H, d, J = 8.00 Hz, 10,15,20Ar3-H, Ar5-H), 7.90 (2H, d, J = 7.50 Hz, 5Ar3-H, Ar5-H), 8.07 (6H, d, J = 7.50 Hz, 10,15,20Ar2-H, Ar6-H), 8.14 (2H, d, J = 8.5 Hz, 5Ar2-H, Ar6-H), 8.84 (8H, d, J = 4.00 Hz, 2,3,7,8,12,13,17,18pyrrole-H). MS: m/z 953 (M⁺). UV-Vis λ_{max}(toluene) (nm): 372, 420, 517, 553, 594, 650.

Carotenoporphyrin CP6

C6E (200 mg, 0.588 mmol) was dissolved in 10 mL of THF. Ten mL of MeOH and 2 mL of 10% aqueous KOH were added and the mixture was stirred for 20 h under N₂ atmosphere. Thin-layer chromatography (silica gel/10% MeOH/CHCl₃) indicated the quantitative formation of the acid. The workup involved dilution with chloroform, extraction (x 3) with an aqueous solution of acetic acid (3:100), and extraction with water. The solvent was evaporated and the product was dried under high vacuum for 24 h. 14'-Apo-β-caroten-14'-oic acid (C6A, 53 mg, 0.16 mmol) was dissolved in 4 mL of dry chloroform and 1 mL of pyridine. One drop of thionyl chloride was added, and after 15 min a small aliquot of the mixture was mixed with one drop of methanol. Thin-layer chromatography (silica gel/1% MeOH/CHCl₃) indicated the quantitative formation of the acid chloride. The solvents were evaporated at reduced pressure and the residue was kept under high vacuum for 30 min. The residue was redissolved in 3 mL of dry toluene and 1 mL of pyridine. 5-(4-Amino-phenyl)-10,15,20-tris(4-methylphenyl) porphyrin (143 mg 0.213 mmol) was dissolved in 3 mL of dry toluene and 1 mL of pyridine and added to the acid chloride solution. The mixture was stirred under an argon atmosphere for 24 h. Thin-layer chromatography (silica gel/1% MeOH/CHCl₃) indicated the quantitative formation of the carotenoporphyrin. The solvent was evaporated and the crude product was purified by flash chromatography (silica gel/CH₂Cl₂). ¹H-NMR (500 MHz, CDCl₃) δ -2.78 (2H, s, pyrrole-NH), 1.03 (6H, s, 16C-CH₃, 17C-CH₃), 1.46-1.49 (2H, m, 2C-CH₂), 1.57-1.61 (2H, m, 3C-CH₂), 1.72 (3H, s, 18C-CH₃), 2.00 (3H, s, 19C-CH₃), 1.97-2.03 (2H, m, 4C-CH₂), 2.10 (3H, s, 20C-CH₃), 2.68 (9H, s, 10,15,20Ar-CH₃), 6.05 (1H, d, J = 14.00 Hz, 15'C-H), 6.16 (1H, d, J = 16.50 Hz, 8C-H), 6.17 (1H, d, J = 11.00 Hz, 10C-H), 6.24 (1H, J = 10.00 Hz, 14C-H), 6.25 (1H, d, J = 17.50 Hz, 7C-H), 6.33 (1H, d, J =

15.50 Hz, 12C-H), 6.83 (1H, dd, $J = 14.75$ and 11.75 Hz, 11C-H), 7.05 (1H, t, $J = 14.25$ Hz, 15C-H), 7.43 (1H, s, 5Ar-NHCO), 7.53 (6H, d, $J = 7.50$ Hz, 10,15,20Ar3-H, Ar5-H), 7.94 (2H, d, $J = 6.00$ Hz, 5Ar3-H, Ar5-H), 8.07 (6H, d, $J = 7.50$ Hz, 10,15,20Ar2-H, Ar6-H), 8.15 (2H, d, $J = 8.5$ Hz, 5Ar2-H, Ar6-H), 8.84 (8H, d, $J = 3.50$ Hz, 2,3,7,8,12,13,17,18pyrrole-H). MS: m/z 979 (M^+). UV-Vis $\lambda_{\max}$ (toluene) (nm): 424, 517, 553, 593, 650.

Carotenoporphyrin CP7

CP7 was prepared as described for CP6. Hydrolysis of C7E (100 mg, 0.254 mmol) gave 12'-apo- β -caroten-12'-oic acid (C7A, 77 mg, 0.21 mmol). The preparation of the acid chloride and coupling with 5-(4-amino-phenyl)-10,15,20-tris(4-methylphenyl) porphyrin (185 mg, 0.276 mmol) were performed as above. $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ -2.75 (2H, s, pyrrole-NH), 1.04 (6H, s, 16C-CH₃, 17C-CH₃), 1.46-1.49 (2H, m, 2C-CH₂), 1.58-1.63 (2H, m, 3C-CH₂), 1.73 (3H, s, 18C-CH₃), 1.97-2.03 (2H, m, 4C-CH₂), 2.00 (3H, s, 19C-CH₃), 2.05 (3H, s, 20C-CH₃), 2.23 (3H, s, 20'C-CH₃), 2.69 (9H, s, 10,15,20Ar-CH₃), 6.16 (1H, d, $J = 15.50$ Hz, 8C-H), 6.20 (1H, d, $J = 11.00$ Hz, 10C-H), 6.23 (1H, d, $J = 16.50$ Hz, 7C-H), 6.32 (1H, $J = 12.00$ Hz, 14C-H), 6.39 (1H, d, $J = 15.00$, 12C-H), 6.62 (1H, dd, $J = 14.00$ and 12.00 Hz, 15'C-H), 6.77 (1H, dd, $J = 14.75$ and 11.75 Hz, 11C-H), 7.00 (1H, t, $J = 13.00$ Hz, 15C-H), 7.31 (1H, d, $J = 11.5$ Hz, 14'C-H), 7.54 (6H, d, $J = 8.00$ Hz, 10,15,20Ar3-H, Ar5-H), 7.82 (1H, s, 5Ar-NHCO), 7.96 (2H, d, $J = 9.00$ Hz, 5Ar3-H, Ar5-H), 8.08 (6H, d, $J = 7.50$ Hz, 10,15,20Ar2-H, Ar6-H), 8.18 (2H, d, $J = 8.00$ Hz, 5Ar2-H, Ar6-H), 8.86 (8H, d, $J = 5.00$ Hz, 2,3,7,8,12,13,17,18pyrrole-H). MS: m/z 1019 (M^+). UV-Vis $\lambda_{\max}$ (toluene) (nm): 420, 517, 553, 594, 650.

Carotenoporphyrin CP8

CP8 was prepared as described for CP6. Hydrolysis of C8E' (150 mg, 0.345 mmol) yielded 130 mg (0.320 mmol) of 11'-methyl-10'-apo- β -caroten-10'-oic acid (C8A'). This carotenoid acid was then used for the synthesis of the acid chloride, which was coupled with 5-(4-amino-phenyl)-10,15,20-tris(4-methylphenyl) porphyrin (288 mg, 0.429 mmol). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ -2.76 (2H, s, pyrrole-NH), 1.03 (6H, s, 16C-CH₃, 17C-CH₃), 1.45-1.48 (2H, m, 2C-CH₂), 1.58-1.63 (2H, m, 3C-CH₂), 1.72 (3H, s, 18C-CH₃), 1.99 (3H, s, 19C-CH₃), 1.97-2.03 (2H, m, 4C-CH₂), 2.01 (3H, s, 20C-CH₃), 2.14 (3H, s, 20'C-CH₃), 2.34 (3H, s, 21'C-CH₃), 2.69 (9H, s, 10,15,20Ar-CH₃), 6.14 (1H, d, $J = 16.00$ Hz, 8C-H), 6.17 (1H, d, $J = 12.50$ Hz, 10C-H), 6.20 (1H, d, $J = 17.00$ Hz, 7C-H), 6.27 (1H, $J = 12.50$ Hz, 14C-H), 6.37 (1H, d, $J = 15.00$ Hz, 12C-H), 6.47 (1H, d, $J = 11.00$ Hz, 14'C-H), 6.60-6.78 (3H, m, 11C-H, 15C-H, 15'C-H), 7.10 (1H, s, 12'C-H), 7.54 (6H, d, $J = 7.50$ Hz, 10,15,20Ar3-H, Ar5-H), 7.81 (1H, s, 5Ar-NHCO), 7.95

(2H, d, $J = 8.50$ Hz, 5Ar3-H, Ar5-H), 8.08 (6H, d, $J = 7.50$ Hz, 10, 15, 20Ar2-H, Ar6-H), 8.18 (2H, d, $J = 8.50$ Hz, 5Ar2-H, Ar6-H), 8.85 (8H, d, $J = 5.50$ Hz, 2,3,7,8,12,13,17,18pyrrole-H). MS: m/z 1059 (M^+). UV-Vis $\lambda_{\max}$ (toluene) (nm): 420, 516, 553, 594, 650.

Carotenoporphyrin CP8

CP8 was prepared as described for CP6. Hydrolysis of C8E (90 mg, 0.22 mmol) yielded 80 mg (0.20 mmol) of 10'-apo- β -caroten-10'-oic acid (C8A). This carotenoid acid was then used for the synthesis of the acid chloride, which was coupled with 5-(4-amino-phenyl)-10,15,20-tris(4-methylphenyl) porphyrin (183 mg, 0.273 mmol). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ -2.75 (2H, s, pyrrole-NH), 1.04 (6H, s, 16C-CH₃, 17C-CH₃), 1.45-1.49 (2H, m, 2C-CH₂), 1.58-1.64 (2H, m, 3C-CH₂), 1.73 (3H, s, 18C-CH₃), 1.97-2.03 (2H, m, 4C-CH₂), 1.98 (3H, s, 19C-CH₃), 2.01 (3H, s, 20C-CH₃), 2.03 (3H, s, 20'C-CH₃), 2.68 (6H, s, 10,15,20Ar-CH₃), 6.12 (1H, d, $J = 14.00$ Hz, 11'C-H), 6.14 (1H, d, $J = 16.50$ Hz, 8C-H), 6.17 (1H, d, $J = 13.00$ Hz, 10C-H), 6.19 (1H, d, $J = 17.50$ Hz, 7C-H), 6.27 (1H, $J = 13.00$ Hz, 14C-H), 6.37 (1H, d, $J = 14.50$, 12C-H), 7.44 (1H, s, 5Ar-NHCO), 6.45 (1H, d, $J = 12.00$, 14'C-H), 6.60-6.76 (3H, m, 11C-H, 15C-H, 15'C-H), 6.82 (1H, d, $J = 13.00$ Hz, 12'C-H), 7.51 (6H, d, $J = 8.50$ Hz, 10,15,20Ar3-H, Ar5-H), 7.89 (2H, d, $J = 8.00$ Hz, 5Ar3-H, Ar5-H), 8.05-8.14 (8H, m, 5, 10,15,20Ar2-H, Ar6-H), 8.85 (8H, d, $J = 5.00$ Hz, 2,3,7,8,12,13,17,18pyrrole-H). MS: m/z 1045 (M^+). UV-Vis $\lambda_{\max}$ (toluene) (nm): 420, 516, 553, 593, 650.

Carotenoporphyrin CP9

CP9 was prepared as described for CP6. Hydrolysis of C9E (40 mg, 0.089 mmol) yielded 35 mg (0.081 mmol) of 8'-apo- β -caroten-8'-oic acid (C9A). This carotenoid acid was used for the synthesis of the acid chloride, which was coupled with 5-(4-amino-phenyl)-10,15,20-tris(4-methylphenyl) porphyrin (80 mg, 0.119 mmol). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ -2.78 (2H, s, pyrrole-NH), 1.02 (6H, s, 16C-CH₃, 17C-CH₃), 1.45-1.48 (2H, m, 2C-CH₂), 1.58-1.63 (2H, m, 3C-CH₂), 1.71 (3H, s, 18C-CH₃), 1.97 (3H, s, 19C-CH₃), 1.99 (3H, s, 20C-CH₃), 1.97-2.03 (2H, m, 4C-CH₂), 2.03 (3H, s, 20'C-CH₃), 2.25 (3H, s, 19'C-CH₃), 2.69 (9H, s, 10,15,20Ar-CH₃), 6.13 (1H, d, $J = 16.00$ Hz, 8C-H), 6.15 (1H, d, $J = 9.00$ Hz, 10C-H), 6.19 (1H, d, $J = 17.50$ Hz, 7C-H), 6.27 (1H, $J = 11.00$ Hz, 14C-H), 6.35 (1H, d, $J = 15.00$ Hz, 12C-H), 6.41 (1H, d, $J = 11.50$ Hz, 14'C-H), 6.60-6.78 (4H, m, 11C-H, 15C-H, 15'C-H, 11'C-H), 7.19 (1H, d, $J = 15.50$ Hz, 12'C-H), 7.29 (1H, d, $J = 11.00$ Hz, 10'C-H), 7.53 (6H, d, $J = 7.50$ Hz, m 10,15,20Ar3-H, Ar5-H), 7.81 (1H, s, 5Ar-NHCO), 7.96 (2H, d, $J = 8.50$ Hz, 5Ar3-H, Ar5-H), 8.07 (6H, d, $J = 8.00$ Hz, 10,15,20Ar2-H, Ar6-H), 8.17 (2H, d, $J = 8.50$ Hz, 5Ar2-H, Ar6-H), 8.86 (8H, d, $J = 6.50$ Hz, 2,3,7,8,12,13,17,18 pyrrole-H). MS:

m/z 1085 (M^+). UV-Vis $\lambda_{\max}$ (toluene) (nm): 420, 457, 552, 593, 650.

Carotenoporphyrin CP10

CP10 was prepared as described for **CP6**. Hydrolysis of **C10E** (49 mg, 0.10 mmol) yielded 46 mg (0.10 mmol) of 6'-apo- β -caroten-6'-oic acid (**C10A**). This carotenoic acid was then used for the synthesis of the acid chloride, which was coupled with 5-(4-amino-phenyl)-10,15,20-tris(4-methylphenyl) porphyrin (90 mg, 0.13 mmol). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ -2.78 (2H, s, pyrrole-NH), 1.01 (6H, s, 16C-CH₃, 17C-CH₃), 1.44-1.47 (2H, m, 2C-CH₂), 1.58-1.62 (2H, m, 3C-CH₂), 1.71 (3H, s, 18C-CH₃), 1.96-2.02 (11H, m, 19C-CH₃, 20C-CH₃, 20'C-CH₃, 4C-CH₂), 2.06 (3H, s, 19'C-CH₃), 2.68 (9H, s, 10,15,20Ar-CH₃), 6.12 (1H, d, J = 15.50 Hz, 8C-H), 6.15 (1H, d, J = 10.50 Hz, 10C-H), 6.17 (1H, d, J = 16.00 Hz, 7C-H), 6.23 (1H, d, J = 15.50 Hz, 7'C-H), 6.26 (1H, J = 11.50 Hz, 14C-H), 6.35 (1H, d, J = 14.00 Hz, 12C-H), 6.43 (1H, d, J = 11.50 Hz, 14'C-H), 6.44 (1H, d, J = 15.00 Hz, 12'C-H), 6.54-6.97 (5H, m, 11C-H, 15C-H, 15'C-H, 11'C-H, 10'C-H), 7.19 (1H, d, J = 15.50 Hz, 8'C-H), 7.53 (6H, d, J = 8.00 Hz, 10,15,20Ar3-H, Ar5-H), 7.44 (1H, s, 5Ar-NHCO), 7.96 (2H, d, J = 8.50 Hz, 5Ar3-H, Ar5-H), 8.07 (6H, d, J = 7.50 Hz, 10, 15, 20Ar2-H, Ar6-H), 8.17 (2H, d, J = 8.50 Hz, 5Ar2-H, Ar6-H), 8.84 (8H, d, J = 5.00 Hz, 2,3,7,8,12,13,17,18pyrrole-H). MS: m/z 1111 (M^+). UV-Vis $\lambda_{\max}$ (toluene) (nm): 420, 474, 508, 550, 594, 650.

Carotenoporphyrin CP11

CP11 was prepared as described for **CP6**. Hydrolysis of **C11E** (68 mg, 0.13 mmol) yielded 62 mg (0.12 mmol) of 4'-apo- β , γ -caroten-4'-oic acid (**C11A**). This carotenoic acid was then used for the synthesis of the acid chloride, which was coupled with 5-(4-amino-phenyl)-10,15,20-tris(4-methylphenyl) porphyrin (155 mg, 0.231 mmol). $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ -2.77 (2H, s, pyrrole-NH), 1.01 (6H, s, 16C-CH₃, 17C-CH₃), 1.44-1.48 (2H, m, 2C-CH₂), 1.58-1.63 (2H, m, 3C-CH₂), 1.71 (3H, s, 18C-CH₃), 1.96-2.02 (11H, m, 19C-CH₃, 20C-CH₃, 20'C-CH₃, 4C-CH₂), 2.05 (3H, s, 19'C-CH₃), 2.26 (3H, s, 18'C-CH₃), 2.68 (9H, s, 10,15,20Ar-CH₃), 6.13 (1H, d, J = 16.50 Hz, 8C-H), 6.15 (1H, d, J = 10.00 Hz, 10C-H), 6.17 (1H, d, J = 15.50 Hz, 7C-H), 6.26 (1H, J = 11.50 Hz, 14C-H), 6.28 (1H, d, J = 12.00 Hz, 14'C-H), 6.32 (1H, d, J = 10.50 Hz, 10'C-H), 6.39 (1H, d, J = 14.00 Hz, 12C-H), 6.47 (1H, d, J = 15.00 Hz, 12'C-H), 6.57-6.86 (5H, m, 11C-H, 15C-H, 15'C-H, 11'C-H, 7'C-H), 7.29 (1H, d, J = 15.50 Hz, 8'C-H), 7.35 (1H, d, J = 10.50 Hz, 6'C-H), 7.54 (6H, d, J = 8.00 Hz, 10,15,20Ar3-H, Ar5-H), 7.82 (1H, s, 5Ar-NHCO), 7.97 (2H, d, J = 8.25 Hz, 5Ar3-H, Ar5-H), 8.08 (6H, d, J = 8.00 Hz, 10,15,20Ar2-H, Ar6-H), 8.19 (2H, d, J = 8.25 Hz, 5Ar2-H, Ar6-H), 8.85 (8H, d, J = 6.50 Hz,

2,3,7,8,12,13,17,18pyrrole-H). MS: m/z 1151 (M^+). UV-Vis $\lambda_{\max}$ (toluene) (nm): 420, 484, 513, 593, 650.

Zinc-carotenoporphyrins. General method

The metallated carotenoporphyrins were prepared by dissolving a small amount of the free base carotenoporphyrins (**CP5** to **CP11**) in CH_2Cl_2 , and adding a saturated solution of zinc acetate in methanol. The mixture was magnetically stirred for 30 min, and quantitative metallation was confirmed by thin-layer chromatography and UV-Vis absorption. The four Q-bands at 650, 593, 552 and 515 nm characteristic of free base compounds changed to two bands at 590 and 550 nm, which is typical of zinc-metallated porphyrins. The product was isolated from a small flash column (silica/ CH_2Cl_2) and dried under high vacuum for 6 h.

Conclusions

In the series of carotenoporphyrins presented in this study porphyrin fluorescence quenching is observed for those dyads in which the carotenoid moiety has 8 or more double bonds in the conjugated system. Carotenoids having 10 or 11 double bonds provide the greatest quenching, with the quantum yield of fluorescence reduced to ~10% relative to TPP.

As mentioned above, the chlorophyll fluorescence quenching observed in natural systems at high levels of light has been interpreted as a mechanism of energy dissipation, and has been correlated with the increased concentration of zeaxanthin in the photosynthetic membranes³. Violaxanthin (9 double bonds) is transformed into zeaxanthin (11 double bonds) at high levels of light. Likewise, in the dyads described in this study, the change of two double bonds transforms a carotenoid from a non-quencher to an effective quencher of porphyrin fluorescence. In this respect, the CP series mimics *in vivo* behavior.

In terms of the mechanism, the quenching of the porphyrin singlet state by carotenoids is an intriguing process. The data presented above are in some ways consistent with an electron transfer mechanism and in other ways with an energy transfer process. It is even possible that the mechanism switches, depending on the carotenoid and the solvent.

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