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Electron donor–acceptor compounds: exploiting the triptycene geometry for the synthesis of porphyrin quinone diads, triads, and a tetrad

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Abstract—Rigidly and covalently linked porphyrin quinones are well established as model compounds for studying photo-induced electron transfer (PET) reactions like those occurring during the primary processes of photosynthesis. In this context, the synthesis of a number of porphyrin quinones is reported in which one or two porphyrin electron donors are connected to either one or two quinone electron acceptors, resulting in diad, triad, and tetrad model systems, respectively. The porphyrin(s) and the quinone(s) are linked by triptycene, 1,4-phenylene, and *cis*- or *trans*-1,4-cyclohexylene bridges. The use of the 1,4-phenylene, and *cis*- or *trans*-1,4-cyclohexylene bridges results in donor–acceptor compounds with the same number of bonds between donor and acceptor(s), but differing in distance and orientation. Analysis of the ^{1}H NMR spectra confirmed the chair conformation for the *cis*- and *trans*-cyclohexylene-linked diads and triads. NOE experiments gave information about the spatial arrangement of the target compounds. The key compounds in the syntheses of all these new PET model systems are the triptycene quinones, which are formed via a $[\pi_s^4+\pi_s^2]$-cycloaddition between an anthracene derivative and a suitable quinone. The triptycene system enforces a rigid orientation on the quinone acceptor(s) in the final model system. Evidence is given that the triptycene system has further potential for constructing tailor-made donor–acceptor compounds.

1. Introduction

Photosynthetic reaction centers (RC) consist of the protein matrix and the donor–acceptor redox active pigments. In RC, photo-induced electron transfer (PET) takes place within about 3 ps after singlet excitation and the initial energy conversion act proceeds with a quantum yield of nearly unity.[1] The unpaired electron moves energetically downhill from (bacterio)chlorophylls or their corresponding dimers to bacteriopheophytins and quinone acceptors Q_A and Q_B. Very recently, the first well-resolved X-ray structure of the photosystem I of the thermophilic cyanobacterium *Synechococcus elongatus* has been published.[2]

To gain a better insight into the dependencies of PET rate constants on donor–acceptor distance, relative orientation, free energy of reaction, and electronic coupling, numerous porphyrin quinone (P–Q) models have been prepared and studied by different optical and magnetic resonance techniques. A number of reviews have appeared in recent years, reporting on the synthesis and investigation of these covalently linked donor acceptor systems.[3] Moreover, the study of ET in donor–acceptor compounds is of fundamental importance for current research fields such as photovoltaics,[4] solar energy conversion,[3e,5] and ET processes in DNA.[6] Recently, a porphyrin quinone molecule was shown to exhibit photonuclease activity.[7]

One of the requirements that define a suitable model compound is a fairly rigid structure of the aggregate, as flexible spacers introduce some ambiguity in the geometrical arrangement of donor and acceptor. Well-defined geometrical parameters are a prerequisite for a sound theoretical interpretation of the spectroscopic data. Spacers like cyclohexylene,[8] phenylene[9] or triptycene[10] have proved successful in this context. In the present paper, we take advantage of all of these three spacers for the construction of a variety of donor–acceptor systems differing in distance, orientation and exergonicity of the ET process.

The key step in all porphyrin quinone syntheses reported here is the formation of a triptycene quinone with a suitable substitution pattern. We have developed a general method for such triptycene quinones, which are readily accessible by the reaction between an anthracene derivative and excess quinone in acetic acid.[11] Under these conditions, the primarily formed $[\pi_s^4+\pi_s^2]$-cycloadduct tautomerizes

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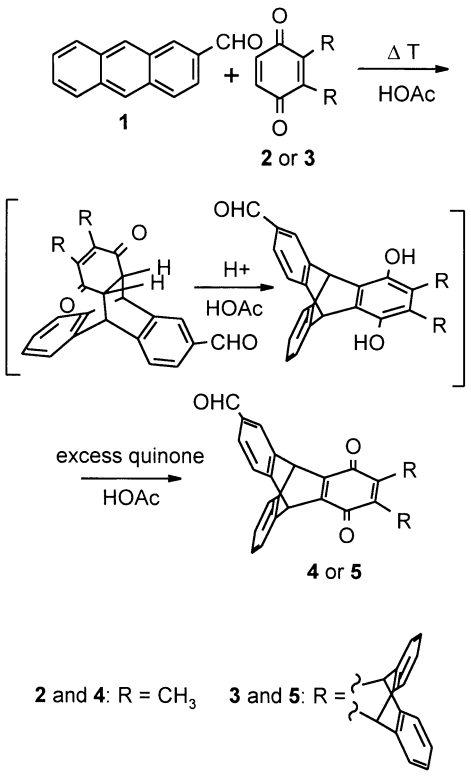


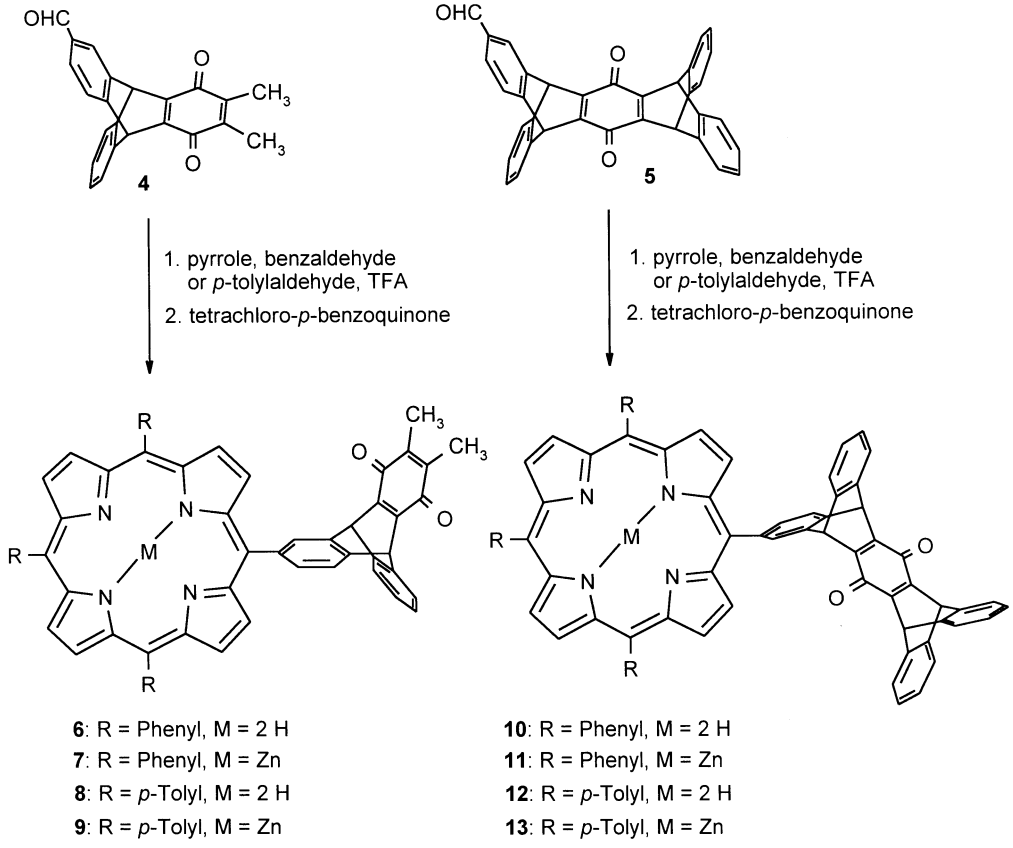
Scheme 1.

in situ to a triptycene hydroquinone that is then oxidized (by the excess quinone) to the corresponding triptycene quinone. This method tolerates a variety of functional groups and is perfectly suited for the construction of building blocks incorporating two quinones in a triptycene system connected with an additional spacer like 1,4-phenylene or *cis*/*trans*-1,4-cyclohexylene. The structural and conformational characteristics of such triptycene quinones are well known from X-ray investigations.[11] We now report on the application of this synthetic strategy for the synthesis of various porphyrin quinone diads, triads, and tetrads.

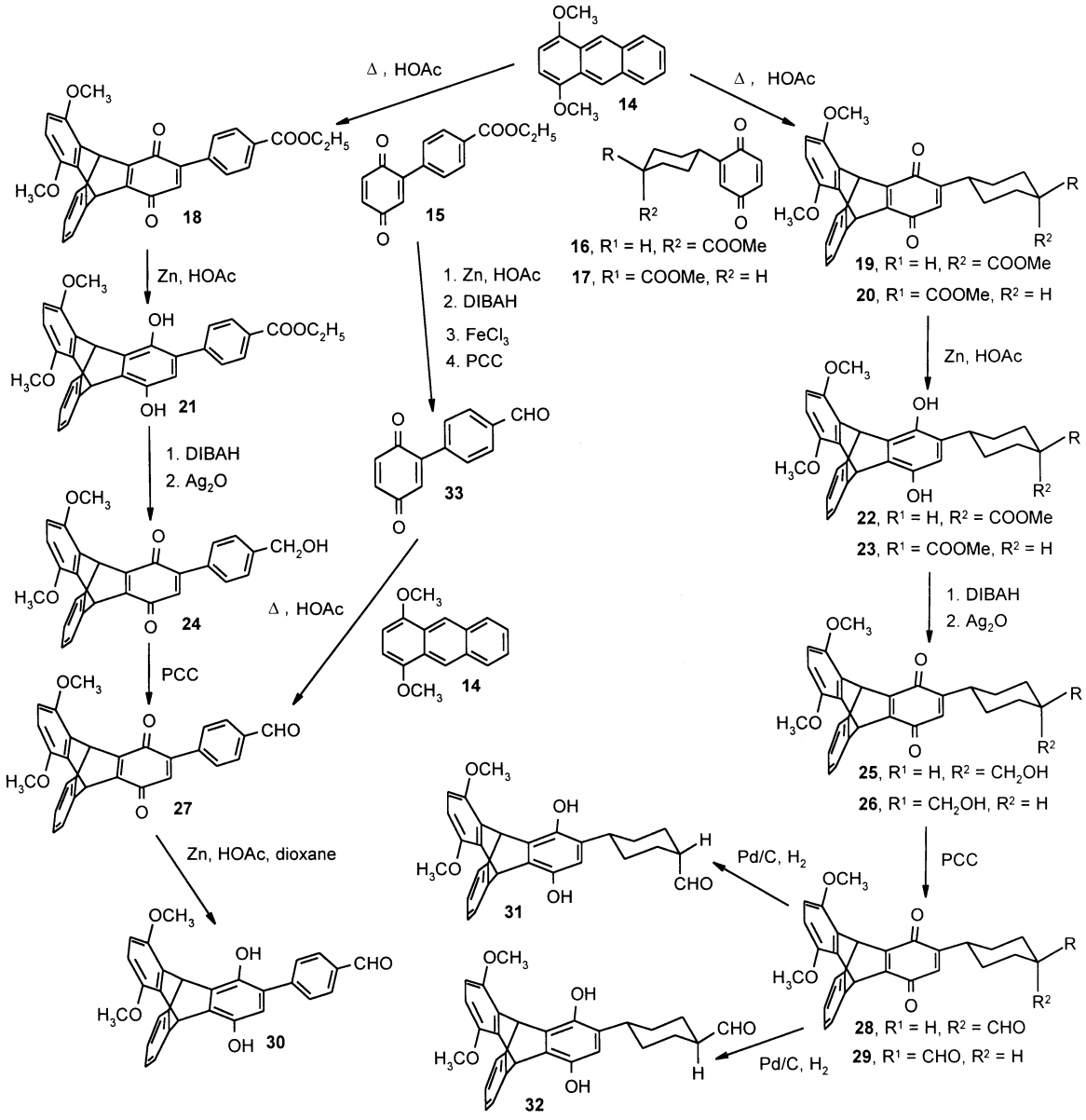
2. Results and discussion

2.1. Synthesis of simple porphyrin quinone diads with the triptycene system

Simple porphyrin quinone diads can be prepared by condensation of a triptycene quinone aldehyde, a second aldehyde, and pyrrole under modified Lindsey conditions. The triptycene aldehyde itself can be synthesized from 2-formyl anthracene and an appropriate quinone via the above-mentioned cycloaddition–tautomerization–oxidation sequence. The aldehyde obtained via this reaction may directly be used for porphyrin quinone synthesis, as long as all positions of the quinonoid system are substituted; otherwise a reduction prior to the porphyrin condensation is necessary to avoid unwanted side reactions between the



Scheme 2.



Scheme 3.

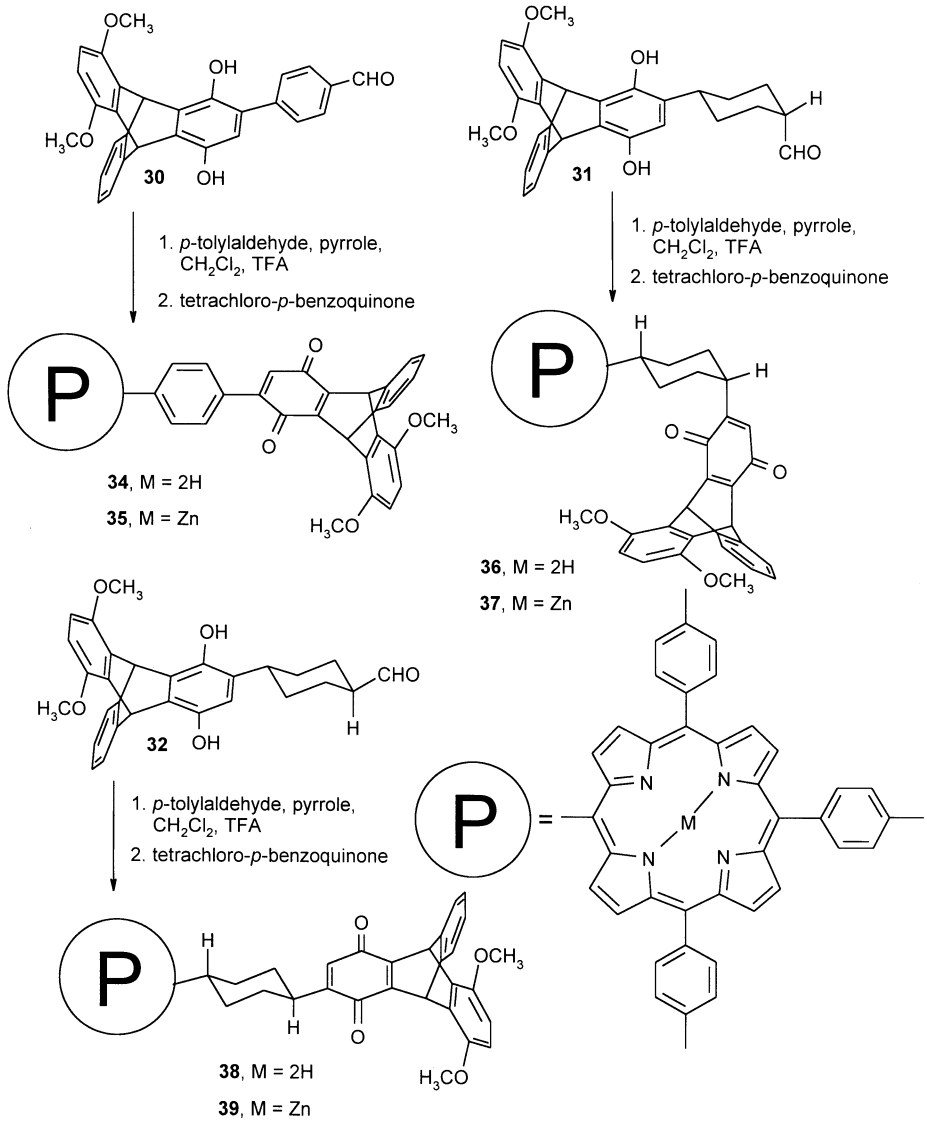
quinonoid system and pyrrole.[12] Thus, the two triptycene quinone aldehydes **4** and **5** were synthesized by reacting anthracene-2-aldehyde **1** with 2,3-dimethyl-*p*-benzoquinone **2** and the simple triptycene quinone **3**, respectively (Scheme 1).[11] The triptycene quinone aldehydes **4** and **5** were then subjected to the condensation with benzaldehyde and *p*-tolylaldehyde to give the porphyrin quinones **6**, **8**, **10**, and **12**, respectively (Scheme 2). Yields of the condensation in the range of 12–14%, obtained after HPLC-purification, illustrate that this method is well-suited for preparing larger quantities of donor–acceptor compounds. A standard metallation procedure yielded the corresponding zinc complexes **7**, **9**, **11**, and **13**. The condensation may also be performed with aliphatic aldehydes, yielding porphyrin quinones with the same acceptor but with a donor of different redox potential.[11]

Porphyrin quinones of this type have been used widely in various investigations of PET.[13] In some cases, the cyclo-addition–tautomerization–oxidation sequence has also been performed after porphyrin synthesis, i.e. an anthracenyl-substituted porphyrin was reacted with a quinone, e.g. benzo- or naphthoquinone.[14]

2.2. Synthesis of porphyrin quinone triads with the triptycene system

PET model compounds that combine not only one electron-donor and one electron-acceptor but several redox-active units, thus enabling a multistep ET such as that occurring in native photosynthesis, are of particular interest. Hence, a cornucopia of various donor–acceptor triads, tetrads, and even pentads have been synthesized. Many of these systems use not only *p*-quinones and porphyrins as donors and acceptors but i.a. carotenes, quinodimethanes, *o*-quinones or fullerenes.[15]

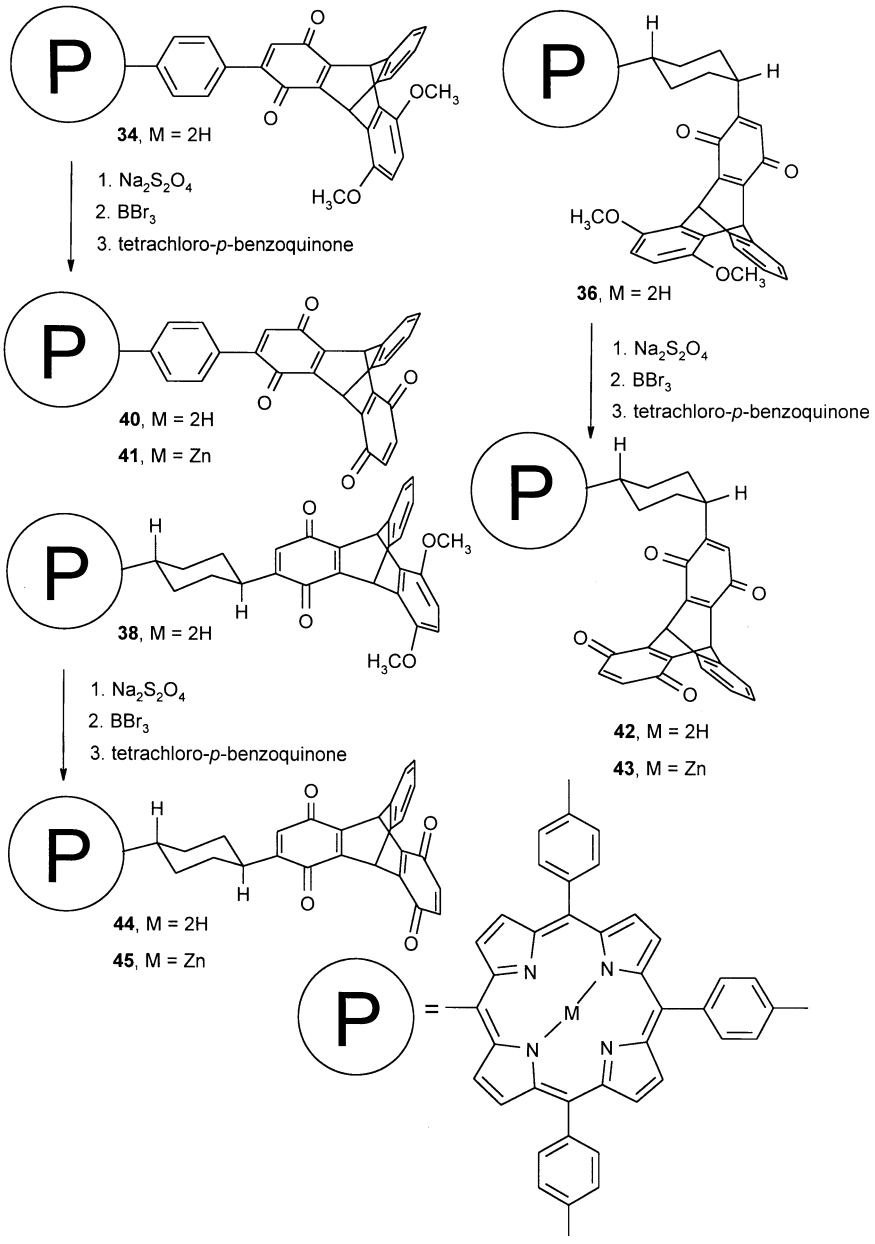
The triptycene system consists of three aromatic rings with a



Scheme 4.

fixed spatial orientation. As triptycenes with two and three quinonoid rings have been described[16] it seemed feasible to connect, e.g. a triptycene bis-quinone via an additional spacer with a porphyrin donor, in this way constructing molecular triads with a rigid arrangement of the chromophores. A retrosynthetic analysis reveals that precursors for such a donor–acceptor system are 1,4-dimethoxyanthracene and a *p*-benzoquinone derivative that contains the additional spacer and a functional group suitable for porphyrin condensation reactions. As additional spacers, we choose 1,4-phenylene and 1,4-cyclohexylene units, which have already been used successfully for the construction of PET models with acceptor groups other than triptycene. In particular, the 1,4-cyclohexylene spacer offers the intriguing possibility to construct donor–acceptor systems with the same number of bonds between donor and acceptor but differing distance and orientation.[8a–c,17]

Reaction of 1,4-dimethoxyanthracene **14** with an excess of the *p*-benzoquinone derivatives **15** or **16/17** afforded the triptycene quinones **18** and **19/20** in excellent yields (82 and 90%, respectively, Scheme 3).[11] In a few steps, these triptycene quinones can be converted to the triptycene quinone aldehydes via reduction of the quinone unit (**21**–**23**) followed by reduction of the ester functionality. The resulting alcohols (**24**–**26**) are converted to the aldehydes (**27**–**29**). The transformations of the 1,4-cyclohexylene-linked triptycene quinones were performed with the diastereomeric mixture; for characterization, analytical amounts of the isomers **19/20** and **25/26**, were separated by HPLC. At the stage of the triptycene quinone aldehyde, the two diastereomers of the 1,4-cyclohexylene-linked compound (**28/29**) were quantitatively separated by HPLC. As the triptycene quinones **27**–**29** possess an unsubstituted position at the quinone moiety, a reduction to the corresponding hydroquinones was necessary prior to porphyrin condensation. In the case of the 1,4-cyclohexylene-substituted triptycene quinone this could easily be achieved by catalytic hydrogenation, yielding compounds **31** and **32**. To circumvent reduction to the benzylic alcohol of **27**, this compound was reduced with zinc dust in an acetic acid/dioxane mixture at 0°C, yielding the desired compound **30**



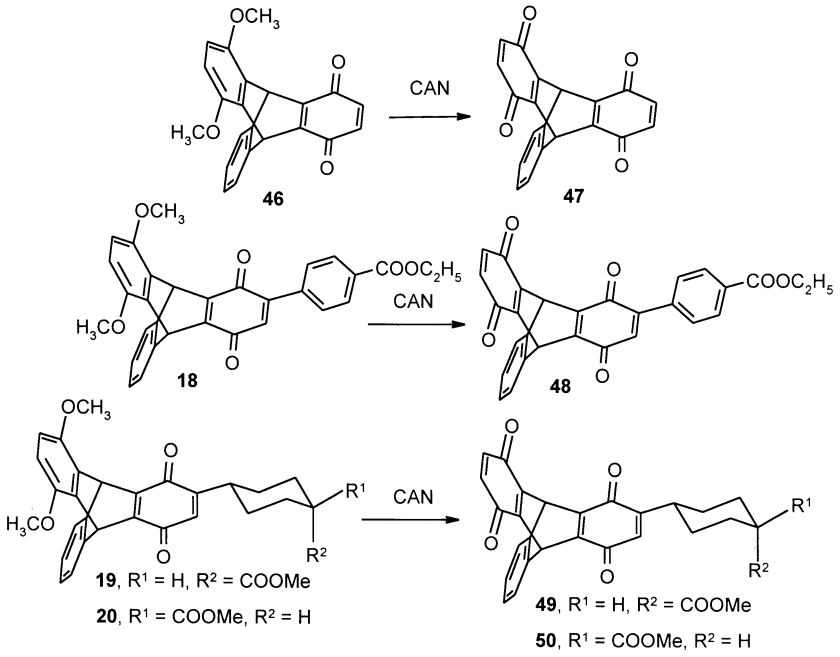
Scheme 5.

in quantitative yield. Note, that in the case of the 1,4-phenylene bridge, aldehyde **27** may also synthesized in 'reverse order', i.e. functionalization of the ester-substituted quinone **15** to the aldehyde **33** followed by the reaction with 1,4-dimethoxyanthracene **14**.[11]

The triptycene hydroquinone aldehydes **30**–**32** were then subjected to a condensation with *p*-tolylaldehyde under modified Lindsey conditions, resulting in the porphyrin quinone diads **34**, **36**, and **38**, respectively, and—after metal insertion—their corresponding zinc complexes **35**, **37**, and **39** (Scheme 4). No *cis–trans* isomerization was observed during the condensation reaction of **31** and **32**, which is consistent with observations for other quinone-substituted cyclohexylene aldehydes.[8e] The condensation yields of 7 and 10%, respectively, for the 1,4-cyclohexylene-linked compounds **36** and **38**, and of 16% for the 1,4-phenylene-linked compound **34** are quite acceptable given the low yields generally obtained in mixed porphyrin condensations. The zinc insertion reactions were quantitative.

The free-base porphyrin quinone diads **34**, **36**, and **38** were then transformed to the corresponding triads with good yields (76–84%). Reduction of the quinone moiety with sodium dithionite and subsequent deprotection of the second hydroquinone with boron tribromide,[18] followed by oxidation gave the final porphyrin–quinone–quinone triads **40**, **42**, and **44** (Scheme 5). After metal insertion, the zinc complexes **41**, **43**, and **45** were obtained.

The investigation of the PET properties of such porphyrin quinones rests on the estimation of the free enthalpy for the PET, which can be obtained i.a. from cyclovoltammetric



Scheme 6.

measurements. Not only the final donor–acceptor model compounds but also the individual donor and acceptor units are needed for this purpose. The synthesis of the simple triptycene bis-quinone **47** from the methoxy-substituted compound **46** by oxidative demethylation with CAN has been described (Scheme 6).[16a] Fortunately, this method also proved to be applicable to the synthesis of the substituted triptycene bis-quinones **48**–**50** using **18**–**20** as starting materials.

As described above, this synthetic pathway generates porphyrin quinone diads in which the second quinone is still blocked in the first step. This strategy proved to be advantageous for the ongoing spectroscopic investigations of the PET properties.[19] The porphyrin quinone diads can serve as reference compounds, which greatly facilitates the interpretation of the complex ET properties of the final donor–acceptor triad systems. In the diads and triads, the free enthalpy for PET ranges from 0.52 to 1.2 eV. Time-resolved fluorescence measurements showed that a very fast and efficient PET occurs in these compounds, with charge separation rates ranging from 5×10^{9} to $>1\times10^{11}$ s^{-1}.[19b] The porphyrin quinone diads and triads were also investigated by time-resolved EPR in isotropic solution and liquid crystalline matrix. After pulsed laser excitation, the occurring ET reactions were elucidated and the transient charge-separated radical pair states were identified. Interestingly, both methods indicate that parallel ET pathways (i.e. from the porphyrin to both quinones) may be prevalent in the triads.[19a,b]

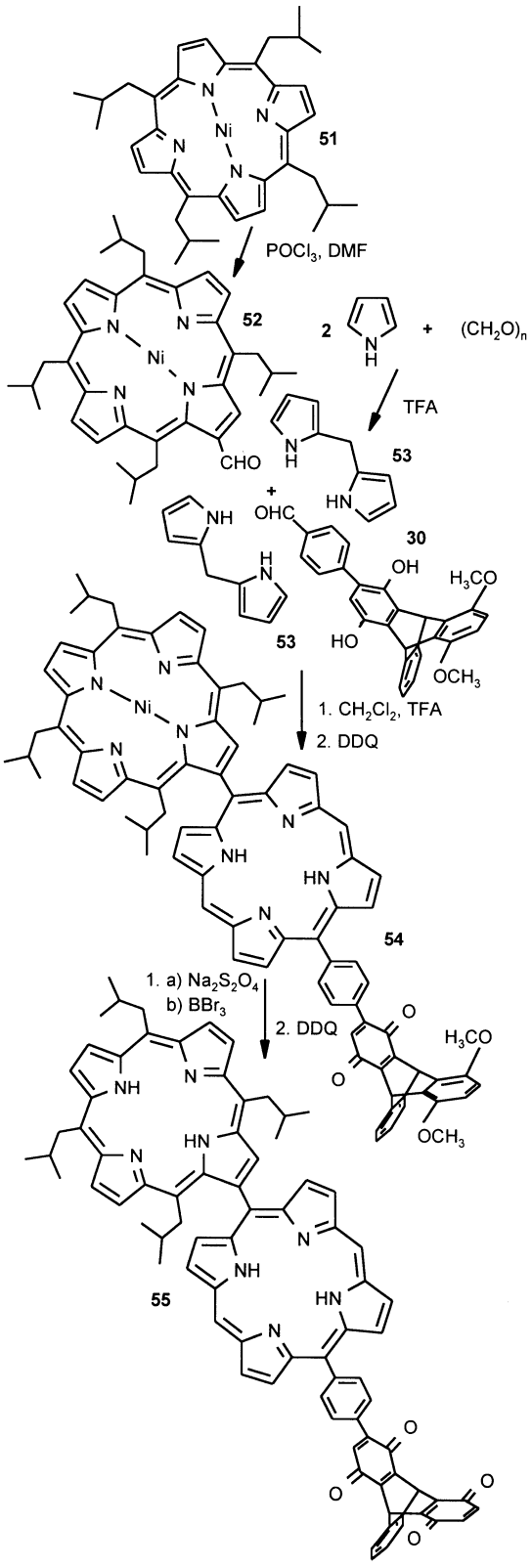
2.3. Synthesis of a porphyrin quinone tetrad employing the triptycene system

In order to model the complex natural photosynthetic system more closely, more elaborate mimicks are necessary. Thus, we extended the synthetic strategy described above by constructing a porphyrin–porphyrin–quinone–quinone tetrad using the triptycene system for the connection of the two quinones. A direct β-*meso* linkage was chosen to ensure a rigid arrangement of the two porphyrin units. Only a limited number of examples are known for such systems.[20]

The tetrad was synthesized in a convergent synthesis utilizing three molecular building blocks (Scheme 7). The first one was a β-formylated 5,10,15,20-tetraisobutylporphyrin **52**, which was prepared by classic Vilsmeier formylation of (5,10,15,20-tetraisobutylporphyrinato)-nickel(II) **51**.[21,22] The isobutyl substituent was chosen: (i) as tetraalkylporphyrins are more easily oxidized than aryl-substituted porphyrins,[13a] thus assuring a downhill ET cascade in the target tetrad and (ii) to increase the solubility of the final target. The other building blocks were the triptycene hydroquinone aldehyde **30** and an unsubstituted dipyrromethane **53**. Compared to many other dipyrromethanes, the latter is not sensitive to 'scrambling' (i.e. formation of reactive monomeric pyrroles) that usually occurs during the condensation of such dipyrromethanes under acidic conditions.[23]

Condensation of these three compounds in dichloromethane under acid catalysis, followed by oxidation and chromatographic workup yielded the triad **54**. For a mixed condensation, the yield of 30% was satisfying. A porphyrin trimer with two terminal 5,10,15,20-tetraisobutylporphyrin units was isolated as a by-product and identified on the basis of mass spectrometric data.

After reduction of the vicinal quinone, the distal hydroquinone was deprotected with boron tribromide in the last step. Subsequent oxidation with DDQ generated the tetrad **55**. Treatment with boron tribromide was also effective in demetalating the (5,10,15,20-tetraisobutylporphyrinato)-nickel(II) substituent. The mild demetalation of porphyrins



Scheme 7.

with boron tribromide developed by us[18] seems to be especially suitable for sensitive systems (such as **54** and **55**) as such compounds are often incompatible with established demetalation techniques using concentrated sulfuric acid.

2.4. ^{1}H NMR structural investigations on the 1,4-cyclohexylene-linked porphyrin quinone diads and triads

The structural arrangement of the diastereomeric 1,4-cyclohexylene-linked porphyrin triptycene quinones and their precursor triptycene quinones is of particular interest. The donor–acceptor diads and triads possess the same number of bonds between donor and acceptor but differ in the spatial arrangement of the redox-active units. The *cis* and *trans* stereochemistry of these compounds was investigated with ^{1}H NMR spectroscopy and the assignments were confirmed by ^{1}H, ^{1}H COSY and NOE experiments. The assignment of the signals and interpretation of the coupling patterns was facilitated by existing studies on simpler 1,4-cyclohexylene-linked porphyrin quinones.[8e,17]

The different magnitudes[24] of vicinal and geminal couplings between two axial (9–13 Hz), an axial and an equatorial (3–5 Hz), two equatorial (2–4 Hz), and two geminally grouped protons (11–15 Hz), respectively, gave rise to characteristic coupling patterns that allowed an unambiguous discrimination between the *cis* and *trans* diastereomers. Of special interest are the coupling patterns for the protons connected to the cyclohexane ring carbons bearing the substituents, i.e. to C-1 and C-4, respectively. For all *trans* isomers, the two protons bound to C-1 and C-4 were in an axial position (1a-H and 4a-H). In this case, a triplet of triplets due to a large coupling constant of about 12 Hz with the axial neighbor protons and a smaller one of about 3.5 Hz with the equatorial protons bound to the neighboring ring carbons was observed in the ^{1}H NMR spectrum of 1a-H and 4a-H (see below). In the corresponding *cis* isomers, the protons at C-1 and C-4 are in different positions: one proton is in the axial position the other in the equatorial position. For the axial proton, a triplet of triplets is observed for the same reason as for the *trans* isomer. On the other hand, for the equatorial proton, a broad multiplet, resulting from vicinal couplings with the axial and equatorial protons at the adjacent cyclohexylene ring carbons, was found.

The observed coupling patterns are consistent with the expected chair conformation of the cyclohexylene spacer. In the *trans* isomers, both quinone substituent and functional group (e.g. in **20**, **26**, and **29**), or quinone substituent and porphyrin unit (e.g. in **38** and **44**) occupy the energetically favored equatorial positions.

In the *cis* isomers, the sterically more demanding substituent is in the equatorial position and forces the sterically less demanding substituent into the axial position. Hence, in the triptycene quinones, the quinone moiety is in the equatorial position and the functional group in the axial position (e.g. **19**, **25**, and **28**), whereas in the porphyrin triptycene quinones, the bulky porphyrin occupies the equatorial position and the quinone moiety the axial position (e.g. **36** and **42**). No evidence was found for a distortion of the cyclohexylene bridge for the *cis* or the *trans* isomer. A distortion of cyclohexylene-bridged porphyrin quinones can be observed only if the 3-position of the quinone adjacent to the cyclohexylene ring is substituted.[8e]

An interesting feature of the triptycene quinones and the

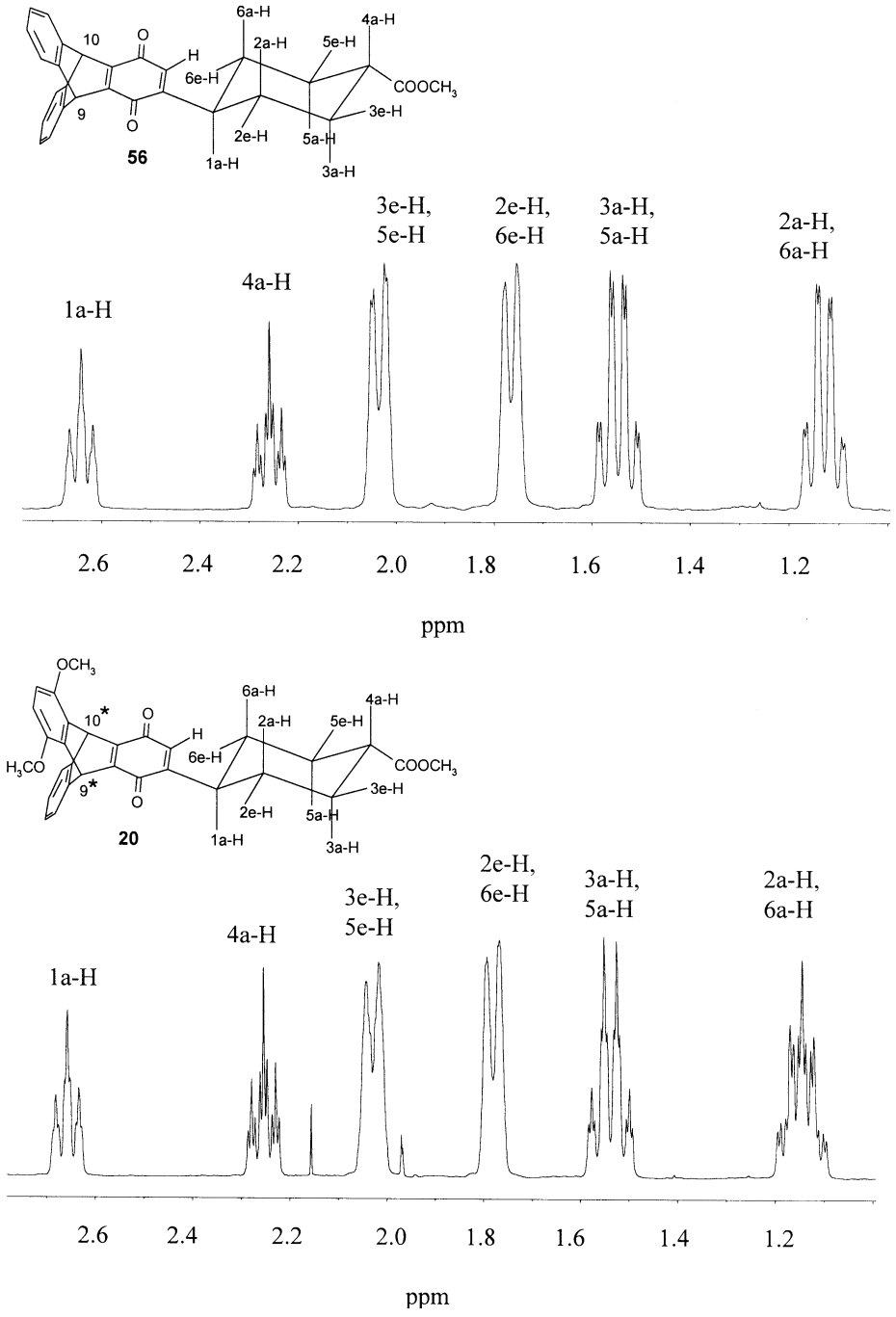


Figure 1. ^{1}H NMR spectra of the achiral triptycene quinone **56** and the chiral triptycene quinone **20** in $CDCl_3$ (cyclohexylene proton range).

porphyrin triptycene quinones results from the stereochemistry of the triptycene moiety. If the three rings of the triptycene system possess a different substitution pattern, the bridgehead carbons are asymmetric. Therefore, all triptycene quinones and the porphyrin triptycene quinones are chiral compounds. Thus, in case of the cyclohexylene spacer, the adjacent protons on both sides of the cyclohexylene ring are no longer enantiotopic but diastereotopic. This is illustrated in Fig. 1 by a comparison between the achiral triptycene quinone **56**[11] and the chiral compound **20**, which differ only in the substitution of one of the benzenoid rings of the triptycene. The effect of diastereotopicity is most pronounced for the axial protons 3a-H and 5a-H, and 2a-H and 6a-H, respectively. In the triptycene quinone **56**, a signal resembling a 'quartet of doublets' is observed for both pairs of protons, resulting from three large coupling constants of nearly the same magnitude, ~13 Hz, (to the neighboring axial and the geminal protons) and a smaller coupling constant of about 3 Hz (to the neighboring equatorial protons). In the chiral compound **20**, where the two protons of each pair are diastereotopic, a signal resembling a 'quartet of *triplets*' is obtained for 3a-H and 5a-H, and a complicated multiplet for 2a-H and 6a-H. This observation can be rationalized by

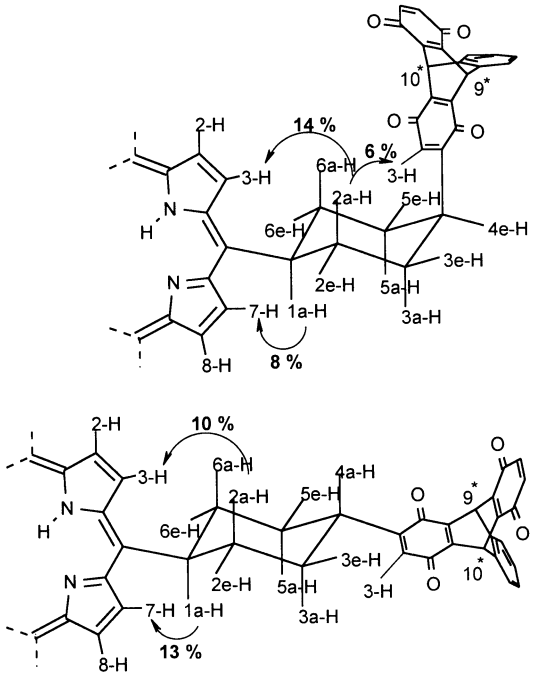


Figure 2. NOE experiments with the 1,4-cyclohexylene-linked triads **42** (top) and **44** (bottom).

combining three nearly large coupling constants and a small coupling constant (as indicated above) and the assumption that the chemical shift of the two diastereotopic protons in each pair is different. Depending on the difference in chemical shift, various multiplet patterns can arise, some of which are observed in the cyclohexylene-linked triptycene quinones and porphyrin triptycene quinones presented here.

Thus, if the difference in chemical shift is small (i.e. in the order of the small coupling constant), a 'quartet of triplets' as for 3a-H and 5a-H (in compound **20**) is observed. If the difference in chemical shift lies between the two coupling constants, a multiplet as for 2a-H and 6a-H (in compound **20**) is observed. If the difference in chemical shift approximates the large coupling constant, a 'quintet' is observed. This can be seen, e.g. for 2a-H and 6a-H in the spectra of quinone **26** and triad **44**. Finally, with large differences in chemical shift between the two protons, two separated quartets of doublets are found, as for 2a-H and 6a-H in the spectrum of the triad **42**.

The arrangement of the chromophores in the final triads was also investigated using NOE-experiments (Fig. 2). For both isomers, a significant NOE was observed between the porphyrin protons 3-H and 7-H and the axial protons (2a-H, 6a-H, and 1a-H) of the cyclohexylene ring, suggesting a perpendicular orientation of the cyclohexylene ring relative to the porphyrin plane. This perpendicular orientation of porphyrin plane and cyclohexylene ring was also observed for other 1,4-cyclohexylene-linked porphyrin quinones.[8e] For the triptycene quinone substituent, no preferred orientation could be deduced from the NOE experiments, though small NOEs between the quinone 3-H and 3a-H and 5a-H were detected for the *trans* isomer. For the *cis* isomer, a NOE of 6% for the quinonoid proton 3-H was observed upon irradiation of 2a-H and 6a-H, again confirming the axial position of the quinone substituent.

Molecular modeling calculations[19b,c,25] on the final triads support the orthogonal orientation of porphyrin and cyclohexylene ring. For the *trans* isomer, the calculations yielded center-to-center distances between the porphyrin and the two quinones of 10.6 and 13.4 Å, respectively, both values being in a remarkably good agreement with the center-to-center distances deduced from the zero-field splitting parameter of time-resolved EPR measurements (10.2 and 13.2 Å, respectively).[25] The calculated distance between the porphyrin and the first (proximal) quinone, 10.6 Å, is nearly the same as in the 1,4-phenylene-linked diad **35**, the structure of which was determined by X-ray crystallography, and in which the distance between porphyrin and proximal quinone is 10.7 Å.[26] Donor–acceptor systems of this type—having the same distance between the chromophores but differing in the nature of the bridge between them—are utilized to elucidate the bridge dependence of PET properties. In agreement, the PET results of the 1,4-phenylene- and the 1,4-cyclohexylene-linked diads and triads differ significantly.[19b,d]

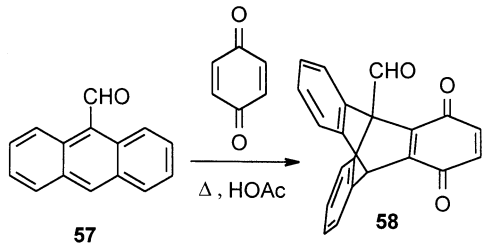
Molecular modeling calculations[19b] on the *cis* isomer **42** resulted in two structures of nearly equal energy, differing in the orientation of the second (distal) quinone, which can be either turned towards the porphyrin plane or away from it. The calculated center-to-center distances between porphyrin and the proximal and distal quinone are 8.3 and 9.7 Å for the first, and 9.0 and 13.4 Å for the second structure.

2.5. Outlook and conclusions

The synthesis of 22 new porphyrin quinones comprising diads, triads, and a tetrad model system illustrates the versatility of triptycene quinones for constructing donor–acceptor systems. All of these model systems use triptycene quinones as building blocks, which are easily accessible from the reaction of a suitably substituted quinone with an anthracene derivative. The triptycene system ensures a rigid orientation of donor and acceptor in the final donor–acceptor compound and may easily be combined with other spacers, such as 1,4-phenylene or 1,4-cyclohexylene, to construct more sophisticated molecular architectures. In combination with these other spacers, systems with adjusted distance and orientation can be synthesized. NOE experiments were performed especially on the *cis*- and *trans*-1,4-cyclohexylene-linked porphyrin quinone diads and triads to elucidate their conformation and the orientation of donor and acceptor units in these compounds. Optical and electron paramagnetic resonance spectroscopic studies on these systems have been or will be published elsewhere.

Nevertheless, additional possibilities to use triptycene quinones as building blocks for donor–acceptor systems exist. For example, triptycene tris-quinones have been described[16b] and thus systems possessing one proximal and two identical distal acceptors should be accessible.

Another important topic in current research on donor–acceptor models is the synthesis of systems that possess



Scheme 8.

quinone acceptors in a close rigid orientation, perpendicular to, or above the porphyrin plane.[27] Such systems are also relevant as building blocks for supramolecular systems useful for molecular recognition studies. Having this in mind, we tried to extend triptycene quinone synthesis to such building blocks. And indeed, simply by heating the commercially available anthracene-9-aldehyde **57** with an excess of benzoquinone, the triptycene quinone aldehyde **58**, which is a promising precursor for the above-mentioned model systems, is available in 48% yield (Scheme 8).

3. Experimental

3.1. General methods

All chemicals used were of analytical grade and were purchased from Aldrich Co. unless stated otherwise. Melting points were measured on a Reichert Thermovar apparatus and are uncorrected. Silica gel 60 (Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates (precoated sheets, 0.2 mm thick, with and without fluorescence indicator F254). Proton NMR spectra were recorded at a frequency of 250 MHz (AC 250) or 500 MHz (Bruker, AMX 500), ^{13}C NMR spectra at a frequency of 125 MHz. All chemical shifts are given in ppm, referenced on the δ scale downfield from the TMS signal as internal standard. Electronic absorption spectra were recorded on a Specord S10 (Carl Zeiss) spectrophotometer using dichloromethane as solvent. Mass spectra were recorded using a Varian MAT 711 mass spectrometer using the EI technique with a direct insertion probe and an excitation energy of 80 eV, the same spectrometer was used for the HRMS spectra of the simple diads **6**–**13**. The HRMS spectra of the porphyrin quinones **34**–**45** were recorded with a AutoSpecEQ mass spectrometer using the FAB technique. Elemental analyses were performed with a Perkin–Elmer 240 analyzer. Preparative HPLC was performed with columns (23×15 and 23×30 mm, respectively) filled with silica gel [Merck, Nucleosil 50 (5 μ)] using a Knauer-pump (Knauer MPLC Pump and Knauer HPLC Pump 64, respectively). The solvent flow rate was 64 ml/min (P=23 bar=23×10^5 Pa). UV detection (Knauer Variable Wavelength Monitor) was performed at 280 nm for the triptycene quinones and at 420 nm for the porphyrins. Analytical HPLC was performed using a Spectra Physics pump (SP 8810) and an analytical column (4×250 mm) filled with silica gel (Merck, Nucleosil 50 (5 μ)). The solvent flow rate was 1 ml/min, with UV detection at 280 nm for the triptycene quinones and at 280 *and* 420 nm for the porphyrins.

3.2. Starting materials

{2-Formyl-5,10,15,20-tetrakis(2-methylpropyl)-porphyrinato}-nickel(II) **52** and dipyrromethane **53** were synthesized according to known literature procedures.[18,22a] 4-Ethoxycarbonylphenyl-*p*-benzoquinone **15** and *cis*/*trans*-2-(4-methoxycarbonylcyclohexyl)-*p*-benzoquinone **16/17** were prepared from *p*-benzoquinone by arylation and alkylation, respectively.[28] 1,4-Dimethoxyanthracene **14** was synthesized in three steps starting from 1,4-dihydroxy-9,10-anthraquinone (Aldrich). Alkylation led to 1,4-dimethoxy-9,10-anthraquinone,[29] reduction of the carbonyl groups gave 9,10-dihydro-1,4-dimethoxyanthracene-9,10-diol[30] and finally, reduction of the diol with phenylhydrazine afforded **14**.[31] The syntheses of 6-formyl-1,4,9,10-tetrahydro-2,3-dimethyl-9,10-(*o*-benzeno)anthracene-1,4-dione **4**, 2-formyl-5,6,7,12,13,14-hexahydro-5,14:7,12-bis-(*o*-benzeno)pentacene-6,13-dione **5**, 1,4,9,10-tetrahydro-2-[4(e)-methoxycarbonylcyclohex-(e)-yl]-9,10-(*o*-benzeno)anthracene-1,4-dione **56**, 2-(4-formylphenyl)-1,4-benzoquinone **33**, (*R*,*S*)-2-(4-ethoxycarbonylphenyl)-1,4,9,10-tetrahydro-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-dione **18**, (*R*,*S*)-1,4,9,10-tetrahydro-5,8-dimethoxy-2-[4(a)-methoxycarbonylcyclohex-(e)-yl]-9,10-(*o*-benzeno)anthracene-1,4-dione **19**, and (*R*,*S*)-1,4,9,10-tetrahydro-5,8-dimethoxy-2-[4(e)-methoxycarbonylcyclohex-(e)-yl]-9,10-(*o*-benzeno)anthracene-1,4-dione **20** have been described previously.[11] Anthracene-9-aldehyde **57** was purchased from Aldrich.

3.3. Triptycene quinones

3.3.1. (*R*,*S*)-2-(4-Ethoxycarbonylphenyl)-9,10-dihydro-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-diol (21). 3.0 g (6.1 mmol) of **18** were dissolved under gentle warming in 50 ml glacial acetic acid. Zinc dust (5.0 g, 76 mmol) was added carefully in several portions. The resulting mixture was stirred until the color of the solution had changed from red to light yellow. The suspension was then suction filtered through a glass frit into 500 ml of water. This mixture was set aside for 5–10 min and the precipitated diol **21** was isolated by suction filtration and dried in vacuo, yield: 2.8 g (5.7 mmol, 93%). Mp 256–257°C (dec.); ^1H NMR (250 MHz, $CDCl_3$, TMS): δ=1.32 (t, 3H, J=7 Hz, CH_2–CH_3), 3.78 (s, 6H, OCH_3), 4.32 (q, 2H, J=7 Hz, CH_2–CH_3), 6.20 (s, 1H, triptycene 3-H), 6.40, 6.46 (each s, 1H, triptycene 9-H, 10-H), 6.62 (s, 2H, triptycene 6-H, 7-H), 6.95–7.02 (m, 2H, arom. H), 7.37–7.45 (m, 2H, arom. H), 7.54–7.58 (m, 2H, arom. H), 7.94–7.97 (m, 2H, arom. H), 8.46, 9.15 (each s, 1H, O*H*, determined by D_2O-exchange); ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ= 14.15 (CH_2–CH_3), ~41 (triptycene bridgehead C, superimposed with DMSO-d_6 signal), 56.07 and 56.15 (OCH_3), 60.54 (CH_2), 108.99, 109.13, 113.87, 123.54, 123.82, 124.57, 126.64, 127.71, 128.77, 129.33, 132.54, 134.92, 135.18, 141.35, 143.93, 145.56, 145.85, 145.94, 148.49, 148.58, 165.66 ($COOC_2H_5$); MS (EI, 80 eV); *m*/*z* (%): 494 (100) [M^+], 477 (13) [M^+-OH], 463 (20) [M^+-CH_3O], 449 (6) [$M^+-C_2H_5O$], 446 (5) [$M^+-OH-CH_3O$], 431 (3) [$M^+-OH-H_2O-C_2H_4$], 421 (3) [$M^+-COOC_2H_5$], 390 (4)

[$M^+-COOC_2H_5-CH_3O$]; [$C_{31}H_{26}O_6$, 494.54 g mol^{-1}]: anal. calcd C 75.29, H 5.30, found C 75.18, H 5.10.

3.3.2. (*R,S*)-9,10-Dihydro-5,8-dimethoxy-2-[4(a)-methoxycarbonylcyclohex-(e)-yl]-9,10-(*o*-benzeno)anthracene-1,4-diol (22) and (*R,S*)-9,10-dihydro-5,8-dimethoxy-2-[4(e)-methoxycarbonylcyclohex-(e)-yl]-9,10-(*o*-benzeno)-anthracene-1,4-diol (23). 4.0 g (8.3 mmol) of the isomeric mixture **19/20** were reduced with zinc dust (6.5 g, 100 mmol) in glacial acetic acid as described for **21**. Workup as described for **21** yielded 3.8 g (7.8 mmol, 95%) of the isomeric mixture **22/23**. ^{1}H NMR (250 MHz, DMSO-d$_6$, TMS): δ=1.15–1.65 (m, 10H, cyclohexylene H, *cis*- and *trans*-isomer), 1.69 (d, 2H, cyclohexylene H, *trans*-isomer), 1.94 (d, 2H, cyclohexylene H, *trans*-isomer), 2.07 (d, 2H, cyclohexylene H, *cis*-isomer), 3.31 (tt, 1H, cyclohexylene H, *trans*-isomer), 2.65–2.85 (m, 2H, cyclohexylene H, *cis*- and *trans*-isomer), 3.59 (s, COOC*H*$_3$, cyclohexylene H, *trans*-isomer), 3.62 (s, COOC*H*$_3$, *cis*-isomer), 3.75 (s, OC*H*$_3$, *cis*- and *trans*-isomer), 6.06, 6.20 (each s, triptycene 9-H, 10-H, *cis*-isomer), 6.08, 6.25 (each s, triptycene 9-H, 10-H *trans*-isomer), 6.28 (s, triptycene 3-H, *cis*- and *trans*-isomer), 6.59 (s, 2H, triptycene 6-H, 7-H, *cis*- and *trans*-isomer), 6.90–6.98 [m, 2H, arom. H, *cis*- and *trans*-isomer), 7.29–7.41 [m, 2H, arom. H, *cis*- and *trans*-isomer), 8.07, 8.75 (each s, O*H*, *cis*- and *trans*-isomer); MS (EI, 80 eV); *m/z* (%): 486 (100) [M^+], 469 (2) [M^+-OH], 455 (7) [M^+-CH_3O], 454 (7) [M^+-CH_4O], 426 (7) [M^+-CH_3O-CHO], 425 (6) [$M^+-CH_3O-CH_2O$]; [$C_{30}H_{30}O_6$, 486.56 g mol^{-1}]: anal. calcd C 74.06, H 6.21, found C 74.22, H 6.06.

3.3.3. (*R,S*)-9,10-Tetrahydro-2-(4-hydroxymethylphenyl)-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-dione (24). 2.5 g (5.1 mmol) **21** were dissolved in 20 ml of dry THF under argon and 25 ml (25 mmol) of a 1 M DIBAH solution were added dropwise. After stirring the mixture for 2 h at room temperature, 150 ml of dry diethyl ether were added. Subsequently, the reaction mixture was cooled to −30°C, hydrolyzed by dropwise addition of water (20 ml), and warmed to room temperature. Residual aluminum hydroxide was dissolved by adding 30 ml of 10% hydrochloric acid solution. The phases were separated and the aqueous phase extracted with three 50-ml portions of diethyl ether. The combined organic phases were washed once with water and dried over anhydrous sodium sulfate. After removal of the drying agent, the filtrate was treated with 1.76 g (7.6 mmol) silver(I)oxide and 2 g of anhydrous sodium sulfate and stirred for 1 h. The mixture was then filtered through silica gel and the filtrate evaporated to dryness. The crude product was purified by column chromatography on silica gel (eluent: dichloromethane/diethyl ether, 15:1, v/v). The product fractions were evaporated to dryness and recrystallization from acetic acid ester/*n*-hexane yielded 2.1 g (4.7 mmol, 92%) of the alcohol **24** as red crystals, mp 253–254°C; ^{1}H NMR (250 MHz, CDCl$_3$, TMS): δ=1.63 (s (br.), 1H, O*H*, determined by D$_2$O-exchange), 3.81 (s, 3H, OC*H*$_3$), 3.82 (s, 3H, OC*H*$_3$), 4.72 (s, 2H, C*H*$_2$), 6.28, 6.32 (each s, 1H, triptycene 9-H, 10-H), 6.55 (s, 2H, triptycene 6-H, 7-H), 6.65 (s, 1H, triptycene 3-H), 7.00–7.05 (m, 2H, arom. H), 7.37–7.39 (m, 4H, arom. H), 7.44–7.49 (m, 2H, arom. H); ^{13}C NMR (125 MHz, CDCl$_3$, TMS): δ=41.29 and 41.69 (C-9, C-10, triptycene bridgehead C), 56.41 (O*C*H$_3$), 64.77 (*C*H$_2$), 109.51, 109.55, 124.53, 124.57, 125.29, 125.32, 126.72, 129.53, 131.44, 132.28, 133.58, 133.73, 142.62, 144.21, 144.35, 144.73, 149.57, 149.62, 152.73, 153.01, 182.97 and 183.58 (triptycene C-1, C-4, *C*=O); MS (EI, 80 eV); *m/z* (%): 450 (26) [M^+], 435 (2) [M^+-CH_3], 419 (3) [M^+-CH_3O], 262 (8) [$C_{18}H_{14}O_2^+$], 247 (12) [$C_{18}H_{14}O_2^+$], 43 (100) [$C_2H_3O^+$]; [$C_{29}H_{22}O_5$, 450.49 g mol^{-1}]: anal. calcd C 77.32, H 4.92, found C 77.28, H 5.06.

3.3.4. (*R,S*)-1,4,9,10-Tetrahydro-2-[4(a)-hydroxymethylcyclohex-(e)-yl]-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-dione (25) and (*R,S*)-1,4,9,10-tetrahydro-2-[4(e)-hydroxymethylcyclohex-(e)-yl]-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-dione (26). 2.00 g (4 mmol) **22/23** were reacted with 20 ml (20 mmol) of a 1 M DIBAH solution in 20 ml of dry THF under argon as described for **24**. After workup and oxidation with 1.19 g (5 mmol) silver(I)-oxide in the presence of 3 g of anhydrous sodium sulfate, the crude product was purified by column chromatography on silica gel (eluent: dichloromethane/diethyl ether, 15:1, v/v). The product fractions were evaporated to dryness and recrystallization from dichloromethane/*n*-hexane yielded 1.80 g (39 mmol, 96%) of the isomeric mixture **25/26** as red crystals; [$C_{29}H_{28}O_5$, 456.54 g mol^{-1}]: anal. calcd C 76.30, H 6.18, found C 76.20, H 6.12. 1 g of the isomeric mixture **25/26** was separated by HPLC for analytical purposes (Nucleosil 50, 5 μ, dichloromethane/ethyl acetate, 97:3, v/v).

25: mp 181–182°C; ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ=1.27–1.38 (m, 2H, cyclohexylene 2a-H, 6a-H), 1.51–1.68 (m, 5H, cyclohexylene 2e-H, 6e-H, 3a-H, 5a-H, CH$_2$O*H*), 1.72 (d, 2H, $^2J_{ea}$=13 Hz, cyclohexylene 3e-H, 5e-H), 1.87 (mc, 1H, cyclohexylene 4e-H), 2.73 (tt, 1H, J_{aa}=12 Hz, J_{ae}=3 Hz, cyclohexylene 1a-H), 3.62 (d, 2H, J=8 Hz, C*H*$_2$OH), 3.796, 3.803 (each s, 3H, OC*H*$_3$), 6.21, 6.25 (each s, 1H, triptycene 9-H, 10-H), 6.33 (d, 1H, $J\approx$ 1 Hz, triptycene 3-H), 6.54 (s, 2H, triptycene 6-H, 7-H), 6.96–7.04 (m, 2H, arom. H), 7.42–7.47 (m, 2H, arom. H); MS (EI, 80 eV); *m/z* (%): 456 (100) [M^+], 441 (2) [M^+-CH_3], 425 (4) [M^+-CH_3O], 262 (12) [$C_{18}H_{14}O_2^+$], 247 (7) [$C_{18}H_{14}O_2^+-CH_3$]; HRMS [$C_{29}H_{28}O_5$]: calcd 456.19368, found 456.19330; [$C_{29}H_{28}O_5$, 456.54 g mol^{-1}]: anal. calcd C 76.30, H 6.18, found: C 75.87, H 6.29.

26: mp 204–205°C; ^{1}H NMR (500 MHz, CDCl$_3$, TMS): δ=1.05–1.23 (m, 4H, cyclohexylene 2a-H, 6a-H, 3a-H, 5a-H), 1.49 (mc, 1H, cyclohexylene 4a-H), 1.79 (d, 3H, $^2J_{ea}$=12 Hz, cyclohexylene 2e-H, 6e-H, CH$_2$O*H*), 1.88 (d, 2H, $^2J_{ea}$=12 Hz, cyclohexylene 3e-H, 5e-H), 2.66 (tt, 1H, J_{aa}=12 Hz, J_{ae}=3 Hz, cyclohexylene 1a-H), 3.48 (d, 2H, J=7 Hz, C*H*$_2$OH), 3.809, 3.814 (each s, 3H, OC*H*$_3$), 6.24, 6.27 (each s, 1H, triptycene 9-H, 10-H), 6.34 (d, 1H, $J\approx$ 1 Hz, triptycene 3-H), 6.54 (s, 2H, triptycene 6-H, 7-H), 7.01–7.05 (m, 2H, arom. H), 7.43–7.49 (m, 2H, arom. H); MS (EI, 80 eV); *m/z* (%): 456 (100) [M^+], 441 (2) [M^+-CH_3], 425 (3) [M^+-CH_3O], 262 (14) [$C_{18}H_{14}O_2^+$], 247 (8) [$C_{18}H_{14}O_2^+-CH_3$]; HRMS [$C_{29}H_{28}O_5$]: calcd 456.19368, found 456.19312; [$C_{29}H_{28}O_5$, 456.54 g mol^{-1}]: anal. calcd C 76.30, H 6.18, [$C_{29}H_{28}O_5\times0.5$ H_2O, 465.55 g mol^{-1}]: anal. calcd C 74.82, H 6.28, found C 74.68, H 6.18.

3.3.5. (*R*,*S*)-2-(4-Formylphenyl)-1,4,9,10-tetrahydro-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-dione (27). The triptycene quinone **24** (1.0 g, 2.2 mmol) was dissolved in 50 ml of dry dichloromethane and treated with a suspension of 1 g (4.6 mmol) of pyridinium chlorochromate in 20 ml of the same solvent. The mixture was stirred for 3 h at room temperature, diluted with dry diethyl ether and filtered through silica gel. The product was purified by column chromatography on silica gel (eluent: dichloromethane/diethyl ether, 15:1, v/v). Recrystallization from dichloromethane/*n*-hexane yielded 0.9 g (2.1 mmol, 93%) of aldehyde **27** as red crystals, mp 222–223°C. Analytical data were identical to those reported by us before for the material obtained from a reaction of **14** with **33** (71% yield).[11]

3.3.6. (*R*,*S*)-2-[4(a)-Formylcyclohex-(e)-yl]-1,4,9,10-tetrahydro-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-dione (28) and (*R*,*S*)-2-[4(e)-formylcyclohex-(e)-yl]-1,4,9,10-tetrahydro-5,8-dimethoxy-9,10-(*o*-benzeno)-anthracene-1,4-dione (29). The isomeric mixture **25/26** (2.00 g, 4.4 mmol) was oxidized with 2.00 g (9 mmol) pyridinium chlorochromate as described for **27**. The crude product was purified by column chromatography on silica gel (eluent: dichloromethane/diethyl ether, 15:1, v/v) and recrystallized from dichloromethane/*n*-hexane. Yield 1.73 g (3.8 mmol, 87%) of red crystals. Separation of the isomers was accomplished by HPLC using a Nucleosil 50 column (5 μ) eluting with *n*-hexane/ethyl acetate (17:3, v/v); [$C_{29}H_{26}O_5$, 454.52 g mol^{-1}]: anal. calcd C 76.63, H 5.77, found C 76.40, H 5.89.

28: mp 217–218°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=1.06–1.17 (m, 2H, cyclohexylene 2a-H, 6a-H), 1.59–1.73 (m, 4H, cyclohexylene 3a-H, 5a-H, 2e-H, 6e-H), 2.28 (d, 2H, $^2J_{ea}$=13 Hz, cyclohexylene 3e-H, 5e-H), 2.50 (mc, 1H, cyclohexylene 4e-H), 2.68 (tt, 1H, J_{aa}=12 Hz, J_{ae}= 2.5 Hz, line-broadening due to long-range coupling to triptycene 3-H, cyclohexylene 1a-H), 3.79, 3.80 (each s, 3H, OCH_3), 6.20 (s, 1H, triptycene 9-H or 10-H), 6.24 (m, 2H, triptycene 9-H or 10-H, triptycene 3-H), 6.53 (s, 2H, triptycene 6-H, 7-H), 6.92–7.04 (m, 2H, arom. H), 7.41–7.46 (m, 2H, arom. H), 9.69 (s, 1H, C*H*O); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=24.44, 28.46, 28.58, 35.48, 41.15 and 41.50 (C-9, C-10, triptycene bridgehead C), 45.94, 56.34 (O*C*H$_3$), 109.36, 124.43, 124.50, 125.18, 125.23, 129.69, 133.62, 144.27, 144.35, 149.53, 151.64, 152.30, 152.90, 183.22 and 183.82 (triptycene C-1, C-4, *C*=O), 204.72 (*C*HO); MS (EI, 80 eV); *m*/*z* (%): 454 (100) [M^+], 439 (7) [M^+-CH_3], 426 (3) [M^+-CO], 423 (5) [M^+-CH_3O], 411 (2) [M^+-CH_3-CO], 262 (13) [$C_{18}H_{14}O_2{}^+$], 247 (9) [$C_{18}H_{14}O_2{}^+-CH_3$]; [$C_{29}H_{26}O_5$, 454.52 g mol^{-1}]: anal. calcd C 76.63, H 5.77, found C 76.53, H 5.82.

29: mp 200–202°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=1.19 (m, 2H, cyclohexylene 2a-H, 6a-H), 1.37 (qt, 2H, cyclohexylene 3a-H, 5a-H), 1.84 (d, 2H, $^2J_{ea}$=12 Hz, cyclohexylene 2e-H, 6e-H), 2.05 (d, 2H, $^2J_{ea}$=12 Hz, cyclohexylene 3e-H, 5e-H), 2.19 (ttd, 1H, J_{aa}=12 Hz, J_{ae}= 3.5 Hz, $J_{4a\text{-}CHO}\approx$1.5 Hz, cyclohexylene 4a-H), 2.64 (tt, 1H, J_{aa}=12 Hz, J_{ae}=3 Hz, coupling to triptycene 3-H not resolved, cyclohexylene 1a-H), 3.78, 3.79 (each s, 3H, OCH_3), 6.22, 6.26 (each s, 1H, triptycene 9-H, 10-H), 6.31 (d, 1H, $J\approx$1 Hz, triptycene 3-H), 6.52 (s, 2H, triptycene 6-H, 7-H), 6.98–7.02 (m, 2H, arom. H), 7.42–7.46 (m, 2H, arom. H), 9.60 (d, 1H, $J_{CHO\text{-}4a}\approx$1.5 Hz, C*H*O); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=25.68, 30.63, 30.72, 35.65, 41.05 and 41.40 (C-9, C-10, triptycene bridgehead C), 49.54, 56.18 (O*C*H$_3$), 109.14, 109.17, 124.41, 124.42, 125.15, 125.18, 129.49, 133.43, 133.50, 144.16, 144.24, 149.34, 149.37, 151.49, 152.22, 152.94, 183.05 and 183.83 (triptycene C-1, C-4, *C*=O), 203.80 (*C*HO); MS (EI, 80 eV); *m*/*z* (%): 454 (100) [M^+], 439 (5) [M^+-CH_3], 426 (3) [M^+-CO], 423 (4) [M^+-CH_3O], 411 (2) [M^+-CH_3-CO], 262 (6) [$C_{18}H_{14}O_2{}^+$], 247 (5) [$C_{18}H_{14}O_2{}^+-CH_3$]; [$C_{29}H_{26}O_5$, 454.52 g mol^{-1}]: anal. calcd C 76.63, H 5.77, found C 76.27, H 5.69.

3.3.7. (*R*,*S*)-2-(4-Formylphenyl)-9,10-dihydro-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-diol (30). The triptycene quinone **27** (1.00 g, 2.2 mmol) was dissolved in 20 ml of a dioxane/acetic acid mixture (1:1, v/v) and cooled to 0°C with an ice bath. Then, 2.00 g (31 mmol) of zinc dust were poured into the solution all at once, and the mixture shaken vigorously in the ice bath for 2 min. At this time the color of the solution had changed from red to light yellow.[32] The reaction mixture was filtered through silica gel over a glass frit and the residue in the frit washed with 30 ml of 50% acetic acid. The filtrate was poured into water and cooled for 15 min. The precipitated diol was isolated by suction filtration and dried in vacuo, yielding 0.95 g (2.1 mmol, 96%) of **30** as a white solid, mp 182–184°C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=3.77 (s (br.), 6H, OCH_3), 6.19 (s, 1H, triptycene 3-H), 6.39, 6.45 (each s, 1H, triptycene 9-H, 10-H), 6.63 (s, 2H, triptycene 6-H, 7-H), 6.95–7.01 (m, 2H, arom. H), 7.37–7.45 (m, 2H, arom. H), 7.60–7.63 (m, 2H, arom. H), 7.88–7.91 (m, 2H, arom. H), 8.51 (s (br.), 1H, O*H*, determined by D_2O-exchange), 9.16 (s (br.), 1H, O*H*, determined by D_2O-exchange), 10.00 (s, 1H, C*H*O); ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ=~41 (bridgehead C, superimposed with DMSO-d_6 signal), 56.08 and 56.14 (O*C*H$_3$), 109.01, 113.92, 123.55, 123.82, 124.60, 126.61, 129.18, 129.77, 132.78, 134.26, 134.89, 135.24, 141.42, 145.37, 145.60, 145.82, 145.91, 148.50, 148.57, 150.32, 192.57 (*C*HO); MS (EI, 80 eV); *m*/*z* (%): 450 (100) [M^+], 433 (16) [M^+-OH], 419 (26) [M^+-CH_3O], 402 (7) [M^+-CH_3O-OH], 387 (5) [$M^+-CH_3O-OH-CH_3$], 359 (5) [$M^+-CH_3O-OH-CH_3-CO$]; [$C_{29}H_{22}O_5$, 450.49 g mol^{-1}]: anal. calcd C 77.32, H 4.92, found C 77.02, H 4.96.

3.3.8. (*R*,*S*)-2-[4(a)-Formylcyclohex-(e)-yl]-9,10-dihydro-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-diol (31) and (*R*,*S*)-2-[4(e)-formylcyclohex-(e)-yl]-9,10-dihydro-5,8-dimethoxy-9,10-(*o*-benzeno)anthracene-1,4-diol (32). The reduction of **28** and **29** was performed separately for each isomer by catalytic hydrogenation. The triptycene quinone was dissolved in THF, 10 wt% of the catalyst (palladium on active carbon, 10% oxidic state) were added and the hydrogenation was carried out using a standard hydrogenation apparatus. After 15 min, reduction of the quinone was complete and the reaction mixture was suction filtered through celite to remove the catalyst. After the filtrate was evaporated to dryness the residue was dried in vacuo and the hydroquinone obtained in quantitative yield.

31: mp 174–176°C; ^{1}H NMR (250 MHz, DMSO-d_6, TMS): δ=1.05–1.25 (m, 2H, cyclohexylene 2a-H, 6a-H), 1.45–1.65 (m, 4H, cyclohexylene 3a-H, 5a-H, 2e-H, 6e-H), 2.15 (d, 2H, $^2J_{ea}$=13 Hz, cyclohexylene 3e-H, 5e-H), 2.50 (m, 1H, cyclohexylene 4e-H), 2.77 (t, 1H, J_{aa}=13 Hz, cyclohexylene 1a-H), 3.74, 3.75 (each s, 3H, OCH_3), 6.06, 6.14, 6.27 (each s, 1H, triptycene 9-H, 10-H, 3-H), 6.59 (s, 2H, triptycene 6-H, 7-H), 6.89–6.98 (m, 2H, arom. H), 7.30–7.40 (m, 2H, arom. H), 8.06 (s, 1H, O*H*), 8.75 (s, 1H, O*H*), 9.66 (s, 1H, C*H*O); ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ=24.62, 29.67, 35.56, 40.43 and 40.64 (C-9, C-10, triptycene bridgehead C), 45.33, 56.05 and 56.14 (O*C*H$_3$), 108.95, 109.14, 110.12, 123.44, 123.62, 124.46, 129.08, 132.64, 133.73, 135.20, 135.39, 141.32, 145.24, 146.25, 148.44, 148.54, 206.36 (*C*HO); MS (EI, 80 eV); *m/z* (%): 456 (100) [M^+], 439 (4) [M^+-OH], 428 (8) [M^+-CO], 345 (4) [M^+-CO–C_6H_{11}], 315 (9) [M^+-CO–C_6H_{11}–CH_2O]; HRMS [$C_{29}H_{28}O_5$]: calcd 456.19368, found 456.19357; [$C_{29}H_{28}O_5$, 456.54 g mol^{-1}]: anal. calcd C 76.30, H 6.18, [$C_{29}H_{28}O_5$×1 H_2O, 474.55 g mol^{-1}]: anal. calcd C 73.40, H 6.37, found C 73.25, H 6.68.

32: mp 277°C (decomp.); ^{1}H NMR (250 MHz, DMSO-d_6, TMS): δ=1.10–1.35 (m, 4H, cyclohexylene 2a-H, 6a-H, 3a-H, 5a-H), 1.75 (mc, 2H, cyclohexylene 2e-H, 6e-H), 1.96 (mc, 2H, cyclohexylene 3e-H, 5e-H), 2.27 (t, 1H, J_{aa}=13 Hz, cyclohexylene 4a-H), 2.73 (t, 1H, J_{aa}=13 Hz, cyclohexylene 1a-H), 3.75 (s, 6H, OCH_3), 6.08, 6.26, 6.28 (each s, 1H, triptycene 9-H, 10-H, 3-H), 6.59 (s, 2H, triptycene 6-H, 7-H), 6.90–9.98 (m, 2H, arom. H), 7.28–7.40 (m, 2H, arom. H), 8.08 (s, 1H, O*H*), 8.78 (s, 1H, O*H*), 9.57 (s, 1H, C*H*O); ^{13}C NMR (125 MHz, DMSO-d_6, TMS): δ= 26.04, 31.74, 35.86, 40.43 and 40.64 (C-9, C-10, triptycene bridgehead C), 49.07, 56.05 and 56.13 (O*C*H$_3$), 108.77, 108.95, 110.21, 123.73, 123.92, 124.42, 129.21, 132.37, 133.74, 135.20, 135.39, 141.46, 145.22, 146.28, 148.44, 148.53, 205.09 (*C*HO); MS (EI, 80 eV); *m/z* (%): 456 (100) [M^+], 439 (4) [M^+-OH], 428 (27) [M^+-CO], 345 (5) [M^+-CO–C_6H_{11}], 315 (13) [M^+-CO–C_6H_{11}–CH_2O]; HRMS [$C_{29}H_{28}O_5$]: calcd 456.19368, found 456.19358; [$C_{29}H_{28}O_5$, 456.54 g mol^{-1}]: anal. calcd C 76.30, H 6.18, [$C_{29}H_{28}O_5$×1 H_2O, 474.55 g mol^{-1}]: anal. calcd C 73.40, H 6.37, found C 73.39, H 6.48; after drying at 130°C for several days: found C 75.73, H 6.24.

3.3.9. (*R*,*S*)-2-(4-Ethoxycarbonylphenyl)-9,10-dihydro-9,10-(*o*-benzeno)anthracen-1,4,5,8-tetrone (48). 100 mg (0.2 mmol) **18** were dissolved in 10 ml of 1,4-dioxane under argon. A solution of 0.5 g (0.9 mmol) of CAN in 10 ml of 1,4-dioxane/water (1:1, v/v) was added dropwise to this solution. The reaction mixture was stirred for 3 h. Then, 20 ml water and 30 ml diethyl ether were added and the phases were separated. The water phase was extracted with 20 ml of diethyl ether (3×). The organic phase was dried (Na_2SO_4), the drying agent filtered off, and the organic phase evaporated to dryness. The residue was chromatographed on silica gel (eluent: toluene/ethyl acetate, 9:1, v/v). The product was recrystallized from dichloromethane/*n*-hexane yielding 59 mg (0.13 mmol, 63%). Mp>150°C (decomp.); ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=1.40 (t, 3H, *J*=7.5 Hz, CH_2–CH_3), 4.40 (q, 2H, *J*=7.5 Hz, CH_2–CH_3), 6.23 and 6.27 (each s, 1H, triptycene 9-H and 10-H), 6.67 (s, 2H, triptycene 6-H and 7-H), 6.75 (s, 1H, triptycene 3-H), 7.06–7.14 (m, 2H, arom. H), 7.46–7.53 (m, 4H, arom. H), 8.06–8.09 (m, 2H, arom. H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=14.28 (CH_2–*C*H$_3$), 42.17 and 42.55 (C-9 and C-10, triptycene bridgehead C), 61.26 (*C*H$_2$–CH_3), 125.53, 126.9, 129.29, 129.54, 132.37, 135.48, 136.66, 144.72, 151.57, 165.89 (*C*OOC$_2$H$_5$), 181.37, 181.97 and 182.24 (C-1, C-4, C-5, C-8, triptycene carbonyl C); MS (EI, 80 eV); *m/z* (%): 464 (84) [M+2H]$^+$, 462 (100) [M^+], 447 (16) [M^+-CH_3], 434 [M^+-28 (CO or C_2H_4], 418 (17) [[M+2H]$^+-H_2O-C_2H_4$], 417 (19) [$M^+-C_2H_5O$], 390 (38) [$M^+-C_2H_4O$–CO], 389 (47) [$M^+-COOC_2H_5$], 362 (12) [$M^+-COOC_2H_5$–CO], 232 (13) [$C_{16}H_8O_2^+$]; HRMS [$C_{29}H_{18}O_6$]: calcd 462.1103, found 462.1109.

3.3.10. (*R*,*S*)-9,10-Dihydro-2-(4(a)-methoxycarbonylcyclohex-(e)-yl)-9,10-(*o*-benzeno)anthracene-1,4,5,8-tetrone (49) and (*R*,*S*)-9,10-dihydro-2-(4(e)-methoxycarbonylcyclohex-(e)-yl)-9,10-(*o*-benzeno)anthracene-1,4,5,8-tetrone (50). The isomeric mixture **19/20** (500 mg, 1 mmol) was dissolved in 20 ml 1,4-dioxane and reacted with 1.64 g (3 mmol) CAN dissolved in 20 ml of dioxane/water (1:1, v/v) as described for **48**. Workup as described for **48** yielded 260 mg (0.58 mmol, 56%) of the isomeric mixture **49/50**. An attempt to separate the diastereomers by column chromatography was only partly successful and resulted in the isolation of pure *cis* isomer **49** (50 mg); **49/50**: ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=1.10–1.42 [m, 2H (*cis*) and 2H (*trans*), cyclohexylene H], 1.50–1.73 [m, 4H (*cis*) and 2H (*trans*), cyclohexylene H], 1.83 [mc, 2H (*trans*), cyclohexylene H], 2.08 [d, 2H (*trans*), cyclohexylene H], 2.13–2.35 [m, 2H (*cis*) and 1H (*trans*), cyclohexylene H], 2.60–2.78 [m, 2H (*cis*) and 1H (*trans*), cyclohexylene H], 3.64 [s, CH_3 (*trans*)], 3.68 [s, CH_3 (*cis*)], 6.15 and 6.19 [each s, triptycene 9-H and 10-H (*cis* and *trans*)], 6.36 [s, triptycene 3-H (*cis* and *trans*)], 6.64 [s, triptycene 6-H and 7-H (*cis* and *trans*)], 7.04–7.11 [m, 2H, arom. H (*cis* and *trans*)], 7.43–7.52 [m, 2H, arom. H (*cis* and *trans*)]; ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=27.02, 28.23, 28.47, 28.65, 30.99, 31.16, 35.55, 35.70, 38.48, 42.02, 42.37, 42.63, 51.58 (COO*C*H$_3$), 125.39, 125.81, 129.63, 129.86, 135.39, 142.23, 151.02, 151.70, 152.24, 152.42, 175.07 and 175.79 [*C*OOCH$_3$ (*cis* and *trans*)], 181.95, 182.21, 182.58 (triptycene carbonyl C); MS (EI, 80 eV); *m/z* (%): 454 (100) [M^+], 436 (8) [M^+-H_2O], 426 (4) [M^+-CO], 423 (6) [M^+-CH_3O], 395 (16) [$M^+-C_2H_3O_2$], 394 (24) [M^+-CH_4O–CO], 366 (8) [M^+-CH_4O–2×CO]; HRMS [$C_{28}H_{22}O_6$]: calcd 454.14164, found 454.14111; [$C_{28}H_{22}O_6$, 454.48 g mol^{-1}]: anal. calcd C 74.00, H 4.88, found C 73.62, H 4.99.

49: mp>250°C (decomp.); ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=1.34 (q, 2H, *J*=13 Hz, cyclohexylene H), 1.54–1.74 (mc, 4H, cyclohexylene H), 2.20 (d, 2H, *J*=13 Hz, cyclohexylene H), 2.62–2.82 (m, 2H, cyclohexylene H), 3.68 (s, 3H, COOCH_3), 6.15 and 6.19 (each s, 1H, triptycene 9-H and 10-H), 6.36 (s, 1H, triptycene 3-H), 6.64 (s, 2H, triptycene 6-H and 7-H), 7.00–7.11 (m, 2H, arom. H), 7.43–7.52 (m, 2H, arom. H).

3.3.11. 9-Formyl-1,4,9,10-tetrahydro-9,10-(*o*-benzeno)-anthracene-1,4-dione (58). A solution of 0.10 g (1.00 mmol) anthracene-9-aldehyde (**57**) and 1.00 g

(9.25 mmol) *p*-benzoquinone in 10 ml acetic acid were heated to reflux for 6 h. The cooled reaction mixture was diluted with dichloromethane (150 ml) and acetic acid was extracted with water. The organic phase was then washed with saturated sodium bicarbonate solution, twice with water, dried over anhydrous Na_2SO_4, filtered and the filtrate evaporated to dryness. Chromatography of the brown residue with dichloromethane/*n*-hexane (3:1, v/v) followed by crystallization from dichloromethane/*n*-hexane yielded 0.15 g (0.48 mmol, 48%) of yellow crystals. Mp 250–251°C; ^{1}H NMR (250 MHz, $CDCl_3$, TMS): δ=5.76 (s, 1H, triptycene 10-H), 6.62 (m, 2H, quinone H), 7.03–7.11 (m, 4H, arom. H), 7.40–7.47 (m, 2H, arom. H), 7.87–7.95 (m, 2H, arom. H), 10.99 (s, 1H, C*H*O); MS (EI, 80 eV); *m/z* (%): 312 (100) [M^+], 284 (65) [M^+-CO], 283 (16) [M^+-CHO], 257 (34) [$M^+-CHO-CO$], 256 (36) [$M^+-2\times CO$], 226 (38) [$C_{15}H_{10}O^+$], 202 (45) [$C_{16}H_{10}^+$]; HRMS [$C_{21}H_{12}O_3$]: calcd 312.0786, found 312.0755.

3.4. Porphyrin triptycene quinines: general procedure for porphyrin triptycene quinone synthesis

In a 2 l three-necked flask, 1.5 l dry dichloromethane was heated to reflux for 15 min while passing a stream of dry argon through the solution. After cooling to room temperature, 3.75 mmol triptycene (hydro)quinone aldehyde, 15.00 mmol pyrrole and 11.25 mmol of the second aldehyde (benzaldehyde or *p*-tolylaldehyde, respectively) were added. The reaction flask was shielded from ambient light and the mixture was stirred for 10 min. Then, 15 mmol of trifluoroacetic acid was added as a catalyst. After stirring for 3 h, 11.25 mmol (in case of the triptycene *quinone* aldehydes) or 15.00 mmol (in case of the triptycene *hydroquinone* aldehydes) *p*-chloranil (tetrachloro-*p*-benzoquinone), suspended in dry dichloromethane was added, the reaction mixture heated for 1 h to reflux and then stirred at room temperature overnight. The solution was subsequently concentrated to a volume of about 50 ml, 1.5 g sodium bicarbonate and 3 ml of water were added, and the mixture was stirred for about 5 min until a color change from green (porphyrin dication) to red-brown (free-base porphyrin) was observed. The mixture was then poured onto a short silica column and the purple porphyrin fractions were eluted with dichloromethane and concentrated to dryness. Further purification was achieved by repeated column chromatography (see individual compounds for details).

In order to remove any traces of the respective chlorins, the porphyrin was dissolved in dichloromethane and a solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in the same solvent (molar ratio porphyrin/DDQ: 10:1, concentration of the DDQ solution: 1 mg/ml) was added. The mixture was stirred at room temperature until no further chlorin absorption bands could be detected by UV/vis spectroscopy. Once this was the case, the organic solution was extracted with an equal volume of a dilute aqueous sodium bicarbonate solution. After separation of the layers, the organic phase was filtered through silica gel and the filtrate was concentrated to dryness. Final purification was achieved by HPLC (see individual substances for details). The zinc porphyrins were prepared using the acetate method, yields were quantitative.[33]

3.4.1. (*R*,*S*)-5-[2-(5,8,9,10-Tetrahydro-6,7-dimethyl-5,8-dioxo-9,10-(*o*-benzeno)anthracenyl)]-10,15,20-triphenylporphyrin (6). Compound **4** (1.28 g, 3.75 mmol), 1.04 ml (1.01 g, 15 mmol) of pyrrole and 1.14 ml (1.19 g, 11.25 mmol) benzaldehyde, together with 1.16 ml (1.71 g, 15 mmol) of trifluoroacetic acid were reacted according to the general procedure. The reaction was quenched oxidatively by addition of 2.77 g (11.25 mmol) *p*-chloranil. Purification of the crude product was achieved by repeated column chromatography using dichloromethane/*n*-hexane (3:1, v/v) followed by elution with dichloromethane/*n*-hexane (2:1, v/v). After final purification by HPLC (Nucleosil 50 column, 5 μ, eluting with dichloromethane/ethyl acetate, 99:1, v/v) 380 mg (0.45 mmol, 12%) of the porphyrin quinone **6** were obtained. Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.83 (s (br.), 2H, N*H*), 2.05 and 2.09 (each s, 3H, CH_3), 6.01 and 6.14 (each s, 1H, triptycene 9-H and 10-H), 7.13–7.21 (m, 2H, triptycene-H), 7.54 (d, 1H, *J*=7 Hz, triptycene-H) 7.63 (d, 1H, *J*=7 Hz, triptycene-H), 7.70–7.80 (m, 10H, 1 triptycene-H and 9 phenyl-H), 7.89 (dd, 1H, *J*=7, 1.5 Hz, triptycene 3-H), 8.16–8.24 (m, 6H, phenyl-H), 8.26 (d, 1H, *J*=1.5 Hz, triptycene 1-H), 8.70–8.86 (m, 8H, β-pyrrole-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=12.40 (*C*H_3), 47.52 and 47.59 (triptycene C-9 and C-10), 119.50, 120.14, 122.50, 124.57, 124.63, 125.63, 126.67, 127.69, 130.65, 131.88, 134.54, 139.42, 139.64, 139.68, 142.07, 142.44, 143.36, 144.22, 151.75, 151.79, 183.73 and 183.88 (C-5 and C-8, *C*=O); MS (EI, 80 eV); *m/z* (%): 848 (2) [M^+], 714 (1) [$M^+-C_8H_6O_2$], 246 (100) [M^+-602]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=291 nm (4.30), 374 (4.37), 418 (5.67), 483 (3.54), 515 (4.26), 550 (3.92), 590 (3.73), 645 (3.63); HRMS [$C_{60}H_{40}N_4O_2$]: calcd 848.31513, found 848.31573; [$C_{60}H_{40}N_4O_2$, 849.00 g mol^{-1}]: anal. calcd C 84.88, H 4.75, N 6.60, found C 84.67, H 4.99, N 6.42.

3.4.2. (*R*,*S*)-{5-[2-(5,8,9,10-Tetrahydro-6,7-dimethyl-5,8-dioxo-9,10-(*o*-benzeno)-anthracenyl)]-10,15,20-triphenylporphyrinato}zinc(II) (7). Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=1.99 and 2.03 (each s, 3H, CH_3), 5.92 and 6.07 (each s, 1H, triptycene 9-H and 10-H), 7.11–7.20 (m, 2H, triptycene-H), 7.50 (d, 1H, *J*=7 Hz, triptycene-H), 7.61 (d, 1H, *J*=7 Hz, triptycene-H), 7.69–7.79 (m, 10H, 1 triptycene-H, 9 phenyl-H), 7.89 (dd, 1H, *J*=7.5, 1.7 Hz, triptycene 3-H), 8.16–8.25 (m, 7H, 1 triptycene-H and 6 phenyl-H), 8.81 (d, 1H, *J*=5 Hz, β-pyrrole 3-H or 7-H), 8.84–8.88 (m, 2H, β-pyrrole 2-H and 8-H), 8.89 (d, 1H, *J*=5 Hz, β-pyrrole 3-H or 7-H), 8.92–8.95 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=12.33 (*C*H_3), 47.57 and 47.67 (triptycene bridgehead C-9 and C-10), 120.51, 121.15, 122.34, 124.54, 125.61, 126.51, 127.48, 130.55, 131.65, 131.98, 134.41, 139.63, 140.13, 142.29, 142.79, 143.16, 144.29, 150.21, 151.80, 151.84, 183.65 and 183.82 (C-5 and C-8, *C*=O); MS (EI, 80 eV); *m/z* (%): 910 (26) [M^+], 776 (12) [$M^+-C_8H_6O_2$], 698 (5) [$M^+-C_8H_6O_2-C_6H_6$], 57 (100) [$C_4H_9^+$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=308 nm (4.29), 345 (4.12), 401 (4.65), 419 (5.77), 511 (3.63), 548 (4.37), 586 (3.72); HRMS [$C_{60}H_{38}N_4O_2Zn$]: calcd 910.22862, found 910.22856; [$C_{60}H_{38}N_4O_2Zn$, 912.37 g mol^{-1}]: anal. calcd C 78.99, H 4.20, N 6.14, [$C_{60}H_{38}N_4O_2Zn\times 0.5\ H_2O$, 921.38 g mol^{-1}]: anal. calcd C 78.33, H 4.28, N 6.09, found C 78.43, H 4.24, N 5.77.

3.4.3. (*R*,*S*)-5-[2-(5,8,9,10-Tetrahydro-6,7-dimethyl-5,8-dioxo-9,10-(*o*-benzeno)anthracenyl)]-10,15,20-tri-*p*-tolylporphyrin (8). 1.28 g (3.75 mmol) of **4**, 1.04 ml (1.01 g, 15 mmol) of pyrrole and 1.33 ml (1.35 g, 11.25 mmol) *p*-tolylaldehyde together with 1.16 ml (1.71 g, 15 mmol) of trifluoroacetic acid, were reacted according to the general procedure. The reaction was quenched oxidatively by addition of 2.77 g (11.25 mmol) *p*-chloranil. Purification of the crude product as described for **6** yielded 400 mg (0.45 mmol, 12%) of the porphyrin quinone **8**. Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.82 (s (br.), 2H, N*H*), 2.03 and 2.07 (each s, 3H, CH_3), 2.67 (s, 3H, tolyl-CH_3), 2.69 (s, 6H, tolyl-CH_3), 6.01 and 6.13 (each s, 1H, triptycene 9-H and 10-H), 7.12–7.20 (m, 2H, triptycene-H), 7.48–7.57 (m, 7H, 1 triptycene-H and 6 tolyl-H), 7.63 (d, 1H, *J*=7 Hz, triptycene-H), 7.77 (d, 1H, *J*=7 Hz, triptycene 4-H), 7.89 (dd, 1H, *J*=7, 1.5 Hz, triptycene 3-H), 8.03–8.12 (m, 6H, tolyl-H), 8.25 (d, 1H, *J*=1.5 Hz, triptycene 1-H), 8.67–8.87 (m, 8H, β-pyrrole-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=12.38 (*C*H_3 quinone), 21.50 (*C*H_3 tolyl), 47.51 and 47.59 (triptycene bridgehead C-9 and C-10), 119.20, 120.14, 120.24, 122.47, 124.55, 124.63, 125.61, 127.38, 130.66, 131.86, 134.49, 137.30, 139.19, 139.53, 139.61, 139.65, 142.39, 143.28, 144.25, 151.79, 183.71 and 183.88 (C-5 and C-8, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 890 (80) [M^+], 756 (86) [$M^+-C_8H_6O_2$], 445 (12) [M^{2+}], 44 (100) [CO_2^+]; UV/vis (CH_2Cl_2): λ_{max} (log ε)= 298 nm (4.19), 371 (4.35), 419 (5.67), 485 (3.59), 516 (4.24), 552 (3.99), 591 (3.74), 647 (3.71); HRMS [$C_{63}H_{46}N_4O_2$]: calcd 890.36208, found 890.36231; [$C_{63}H_{46}N_4O_2$, 891.08 g mol^{-1}]: anal. calcd C 84.92, H 5.20, N 6.29, found C 84.57, H 5.31, N 6.11.

3.4.4. (*R*,*S*)-{5-[2-(5,8,9,10-Tetrahydro-6,7-dimethyl-5,8-dioxo-9,10-(*o*-benzeno)-anthracenyl)]-10,15,20-tri-*p*-tolylporphyrinato}zinc(II) (9). Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=2.01 and 2.05 (each s, 3H, CH_3), 2.67 (s, 3H, CH_3-tolyl), 2.68 (s, 6H, tolyl-CH_3), 5.93 and 6.09 (each s, 1H, triptycene 9-H and 10-H), 7.10–7.19 (m, 2H, triptycene-H), 7.48–7.55 (m, 7H, 1 triptycene-H and 6 tolyl-H), 7.61 (d, 1H, *J*=7 Hz, triptycene-H), 7.75 (d, 1H, *J*=7 Hz, triptycene 4-H), 7.87 (dd, 1H, *J*=7, 1.5 Hz, triptycene 3-H), 8.02–8.10 (m, 6H, tolyl-H), 8.22 (d, 1H, *J*=1.5 Hz, triptycene-H-1), 8.78 (d, 1H, *J*=5 Hz, β-pyrrole 3-H or 7-H), 8.83 and 8.86 (each d, 1H, *J*=5 Hz, β-pyrrole 2-H and 8-H), 8.90 (d, 1H, *J*=5 Hz, β-pyrrole 3-H or 7-H), 8.92–8.95 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=12.37 and 12.39 (*C*H_3 quinone), 21.52 (*C*H_3 tolyl), 47.50 and 47.58 (triptycene bridgehead C-9 and C-10), 119.96, 121.15, 122.34, 124.52, 124.59, 125.58, 127.25, 130.56, 131.62, 131.77, 131.93, 134.34, 134.40, 137.05, 139.59, 139.63, 139.76, 139.80, 140.15, 142.18, 144.26, 144.28, 150.06, 150.21, 150.23, 150.26, 150.29, 151.81, 183.67 and 183.87 (C-5 and C-8, *C*=O); In the EI mass spectrum of **9** depending on time and temperature either the M^+ or the $[M+2H]^+$ ion signal exhibits a higher intensity: MS (EI, 80 eV); *m*/*z* (%): 952 (35) [M^+], 818 (8) [$M^+-C_8H_6O_2$], 43 (100) [$C_3H_7^+$]; when holding the temperature at 300°C a different spectrum is observed: MS (EI, 80 eV); *m*/*z* (%): 954 (84) $[M+2H]^+$, 952 (77) [M^+], 818 (61) $[[M+2H]^+-C_8H_8O_2]$, 727 (21) $[[M+2H]^+-C_8H_8O_2-C_7H_7]$, 43 [$C_3H_7^+$]; UV/vis ($CH_2Cl_2$): λ_{max} (log ε)=301 nm (4.25), 344 (4.08), 401 (4.62), 421 (5.73), 512 (3.59), 549 (4.33), 588 (3.76); HRMS [$C_{63}H_{44}N_4O_2Zn$]: calcd 952.27557, found 952.27576; [$C_{63}H_{44}N_4O_2Zn$, 954.45 g mol^{-1}]: anal. calcd C 79.28, H 4.65, N 5.87, found C 79.22, H 4.89, N 5.22.

3.4.5. (*R*,*S*)-5-[2-(5,6,7,12,13,14-Hexahydro-6,13-dioxo-5,14:7,12-bis(*o*-benzeno)-pentacenyl)]-10,15,20-triphenylporphyrin (10). 1.83 g (3.75 mmol) of **5**, 1.04 ml (1.01 g, 15 mmol) of pyrrole and 1.14 ml (1.19 g, 11.25 mmol) benzaldehyde together with 1.16 ml (1.71 g, 15 mmol) of trifluoroacetic acid, were reacted according to the general procedure. The reaction was quenched oxidatively by addition of 2.77 g (11.25 mmol) *p*-chloranil. Purification of the crude product was achieved by repeated column chromatography using dichloromethane/*n*-hexane (first 3:1, v/v, then 2:1, v/v). 520 mg (0.52 mmol, 14%) of the porphyrin quinone **10** were obtained. Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.84 (s (br.), 2H, N*H*), 5.84, 5.90, 5.96, 6.08 (each s, 1H, triptycene 5-H, 7-H, 12-H, 14-H), 6.98–7.16 (m, 6H, arom. H), 7.38–7.53 (m, 5H, arom. H), 7.58 (d, 1H, *J*=7 Hz, triptycene H), 7.68–7.78 (m, 10H, arom. H), 7.86 (dd, 1H, *J*=7, 1.5 Hz, triptycene 3-H), 8.15–8.24 (m, 7H, arom. H), 8.67–8.87 (m, 8H, β-pyrrole H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=47.50 (triptycene bridgehead C-5, C-7, C-12 C-14), 119.42, 120.14, 122.43, 124.35, 124.52, 124.59, 125.56, 125.69, 126.63, 127.66, 130.58, 131.07, 131.85, 134.53, 139.57, 142.14, 143.11, 143.70, 143.94, 147.04, 151.09, 151.15, 151.24, 151.31, 180.02 and 180.16 (C-6 and C-13, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 996 (100) [M^+], 714 (1) [$M^+-C_{20}H_{10}O_2$], 498 (4) [M^{2+}], 178 (1) [$C_{14}H_{10}^+$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=306 nm (4.16), 374 (4.39), 417 (5.67), 481 (3.61), 514 (4.28), 549 (3.94), 590 (3.79); HRMS [$C_{72}H_{44}N_4O_2$]: calcd 996.34643, found 996.34620; [$C_{72}H_{44}N_4O_2$, 997.17 g mol^{-1}]: anal. calcd C 86.72, H 4.45, N 5.62, found C 86.42, H 4.66, N 5.26.

3.4.6. (*R*,*S*)-{5-[2-(5,6,7,12,13,14-Hexahydro-6,13-dioxo-5,14:7,12-bis(*o*-benzeno)-pentacenyl)]-10,15,20-triphenylporphyrinato}zinc(II) (11). Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=5.80, 5.86, 5.89, 6.03 (each s, 1H, triptycene: 5-H, 7-H, 12-H, 14-H), 6.95–7.15 (m, 6H, arom. H), 7.35–7.53 (m, 5H, arom. H), 7.56 (d, 1H, *J*=7 Hz, triptycene H), 7.66–7.77 (m, 10H, arom. H), 7.84 (d, 1H, *J*=7 Hz, triptycene H), 8.12–8.21 (m, 7H, arom. H), 8.76 (d, 1H, *J*=4 Hz, β-pyrrole H), 8.82 (mc, 2H, β-pyrrole H), 8.86 (d, 1H, *J*=4 Hz, β-pyrrole H), 8.88–8.92 (m, 4H, β-pyrrole H); ^{13}C NMR (125 MHz, CD_2Cl_2, TMS): δ= 47.72 and 47.80 (triptycene bridgehead C-5, C-7, C-12 and C-14), 120.45, 121.37, 122.60, 124.56, 124.70, 124.81, 125.74, 125.80, 125.87, 126.86, 127.77, 130.67, 131.94, 132.20, 132.40, 134.75, 140.38, 142.46, 143.07, 143.41, 144.19, 144.39, 144.48, 150.45, 150.52, 151.26, 151.35, 151.66, 180.26 and 180.37 (C-6 and C-13, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 1058 (4) [M^+], 776 (5) [$M^+-C_{20}H_{10}O_2$], 698 (4) [$M^+-C_{20}H_{10}O_2-C_6H_6$], 286 (20) [$C_{20}H_{14}O_2^+$], 178 (100) [$C_{14}H_{10}^+$]; UV/vis ($CH_2Cl_2$): λ_{max} (log ε)=308 nm (4.22), 347 (4.06), 419 (5.78), 399 (4.65), 510 (3.53), 547 (4.36), 586 (3.62); HRMS [$C_{72}H_{42}N_4O_2Zn$]: calcd 1058.25990, found 1058.25910; [$C_{72}H_{42}N_4O_2Zn$, 1060.53 g mol^{-1}]: anal. calcd C 81.54, H 3.99, N 5.28, [$C_{72}H_{42}N_4O_2Zn\times0.5\ H_2O$, 1069.54 g mol^{-1}]:

anal. calcd C 80.86, H 4.05, N 5.24, found C 80.85, H 4.43, N 4.64.

3.4.7. (*R*,*S*)-5-[2-(5,6,7,12,13,14-Hexahydro-6,13-dioxo-5,14:7,12-bis(*o*-benzeno)-pentacenyl)]-10,15,20-tri-*p*-tolylporphyrin (12). 1.83 g (3.75 mmol) of **5**, 1.04 ml (1.01 g, 15 mmol) of pyrrole and 1.33 ml (1.35 g, 11.25 mmol) *p*-tolylaldehyde together with 1.16 ml (1.71 g, 15 mmol) of trifluoroacetic acid, were reacted according to the general procedure. The reaction was quenched oxidatively by addition of 2.77 g (11.25 mmol) *p*-chloranil. Purification of the crude product as described for **6** yielded 470 mg (0.45 mmol, 12%) of the porphyrin quinone **12**. Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=-2.86 (s (br.), 2H, N*H*), 2.67 (s, 3H, CH_3), 2.679 (s, 3H, CH_3), 2.683 (s, 3H, CH_3), 5.84, 5.89, 5.94 and 6.07 (each s, 1H, triptycene 5-H, 7-H, 12-H, 14-H), 6.97–7.15 (m, 6H, arom. H), 7.37–7.58 (m, 12H, arom. H), 7.72 (d, 1H, *J*=7 Hz, triptycene 4-H), 7.85 (dd, 1H, *J*=7, 1.5 Hz, triptycene 3-H), 8.01–8.10 (m, 6H, arom. H), 8.20 (d, 1H, *J*=1.5 Hz, triptycene 1-H), 8.64 (d, 1H, *J*=5 Hz, β-pyrrole 3-H or 7-H), 8.72–8.76 (m, 3H, β-pyrrole 3-H or 7-H and 2-H, 8-H), 8.80–8.85 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.52 (*C*H_3), 47.37 and 47.43 (triptycene bridgehead C-5, C-7, C-12, C-14), 120.15, 120.20, 122.41, 124.35, 124.52, 124.60, 125.55, 125.67, 127.36, 130.60, 131.84, 134.49, 137.27, 139.17, 139.21, 139.63, 142.04, 142.96, 143.65, 143.89, 143.94, 151.11, 151.22, 180.03 and 180.18 (C-6 and C-13, *C*=O); MS (EI, 80 eV); *m/z* (%): 1038 (22) [M^+], 756 (3) [$M^+-C_{20}H_{10}O_2$], 520 (3) [[M+2H]$^{2+}$], 178 (100) [$C_{14}H_{10}^+$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=300 nm (4.34), 373 (4.39), 419 (5.71), 485 (3.61), 516 (4.28), 552 (4.01), 591 (3.76), 647 (3.71); HRMS [$C_{75}H_{50}N_4O_2$]: calcd 1038.3934, found 1038.3930; [$C_{75}H_{50}N_4O_2$, 1039.25 g mol^{-1}]: anal. calcd C 86.68, H 4.85, N 5.39, [$C_{75}H_{50}N_4O_2$×1 H_2O, 1057.26 g mol^{-1}]: anal. calcd C 85.19, H 4.96, N 5.30, found C 84.98, H 4.93, N 4.93.

3.4.8. (*R*,*S*)-{5-[2-(5,6,7,12,13,14-Hexahydro-6,13-dioxo-5,14:7,12-bis(*o*-benzeno)-pentacenyl)]-10,15,20-tri-*p*-tolylporphyrinato}zinc(II) (13). Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=2.66 (s, 3H, CH_3), 2.67 (s, 6H, CH_3), 5.79, 5.85, 5.88 and 6.02 (each s, 1H, triptycene 5-H, 7-H, 12-H, 14-H), 6.95–7.15 (m, 6H, arom. H), 7.34–7.57 (m, 12H, arom. H), 7.69 (d, 1H, *J*=7.25 Hz, triptycene 4-H), 7.83 (d, 1H, *J*=7.25 Hz, triptycene 3-H), 7.99–8.09 (m, 6H, arom. H), 8.18 (s (br.), 1H, triptycene 1-H), 8.74 (d, *J*=4.5 Hz, 1H, β-pyrrole 3-H or 7-H), 8.82–8.88 (m, 3H, β-pyrrole 3-H or 7-H and 2-H, 8-H), 8.92–8.95 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H); MS (EI, 80 eV); *m/z* (%): 1102 (23) [[M+2H]$^+$], 1100 (14) [M^+], 218 (7) [[M+2H]$^+-C_{20}H_{12}O_2$], 286 (16) [$C_{20}H_{14}O_2^+$], 178 (100) [$C_{14}H_{10}^+$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=301 nm (4.20), 345 (4.00), 401 (4.64), 421 (5.78), 512 (3.40), 549 (4.34), 588 (3.70); HRMS [$C_{75}H_{48}N_4O_2Zn$]: calcd 1100.30687, found 1100.30724; [$C_{75}H_{48}N_4O_2Zn$, 1102.61 g mol^{-1}]: anal. calcd C 81.70, H 4.39, N 5.08, [$C_{75}H_{48}N_4O_2Zn$×2 H_2O, 1138.64 g mol^{-1}]: anal. calcd C 79.11, H 4.60, N 4.92, found C 79.08, H 4.59, N 4.22.

3.4.9. (*R*,*S*)-5-[4-(2-(1,4,9,10-Tetrahydro-5,8-dimethoxy-1,4-dioxo-9,10-(*o*-benzeno)anthracenyl)-phenyl)]-10,15,20-tri-*p*-tolylporphyrin (34). 1.69 g (3.75 mmol) of **30**, 1.04 ml (1.01 g, 15 mmol) of pyrrole, and 1.33 ml (1.35 g, 11.25 mmol) *p*-tolylaldehyde, together with 1.16 ml (1.71 g, 15 mmol) of trifluoroacetic acid, were reacted according to the general procedure. The reaction was quenched oxidatively by addition of 3.69 g (15 mmol) *p*-chloranil. Purification of the crude product was achieved by repeated column chromatography [column 1: elution with dichloromethane, column 2: elution with dichloromethane/*n*-hexane (4:1, v/v)]. After final purification by HPLC (Nucleosil 50, 5 μ, elution with *n*-hexane/ethyl acetate (83:17, v/v) 600 mg (0.6 mmol, 16%) of the porphyrin quinone **34** were obtained. Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.81 (s (br.), 2H, N*H*), 2.69 (s, 9H, tolyl CH_3), 3.85 (s, 6H, OCH_3), 6.37, 6.45 (each s, 1H, triptycene 9-H, 10-H), 6.59 (s, 2H, triptycene 6-H, 7-H), 7.01 (s, 1H, triptycene 3-H), 7.06–7.11 (m, 2H, triptycene H), 7.52–7.56 (m, 8H, 2 triptycene H, 6 tolyl H), 7.78–7.82 (m, 2H, phenylene bridge H), 8.06–8.10 (m, 6H, tolyl H), 8.22–8.26 (m, 2H, phenylene bridge H), 8.81–8.88 (m, 8H, β-pyrrole H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.53 (*C*H_3 tolyl substituents), 41.37 and 41.77 (C-9, C-10, triptycene bridgehead C), 56.36, 56.39 (O*C*H_3), 109.39, 118.62, 120.29, 120.46, 124.64, 124.69, 125.38, 125.40, 127.42, 127.68, 131.12, 131.96, 132.28, 133.57, 133.71, 134.50, 134.60, 137.24, 137.36, 139.14, 143.95, 144.26, 144.41, 144.85, 149.57, 149.61, 152.94, 153.04, 153.22, 183.34 and 183.71 (C-1, C-4, *C*=O); MS (EI, 80 eV); *m/z* (%): 998 (6) [M^+], 967 (1) [M^+-CH_3O], 499 (1) [M^{2+}], 238 (100) [$C_{16}H_{14}O_2^+$]; MS (FAB+, DMSO/*m*-NO_2-Bzl-OH/Xe) *m/z* (%): 1001 (4) [M+3H]$^+$, 1000 (2) [M+2H]$^+$, 999 (1) [M+H]$^+$; UV/vis (CH_2Cl_2): λ_{max} (log ε)=299 nm (4.33), 378 (4.42), 418 (5.65), 485 (3.83), 515 (4.27), 552 (4.03), 591 (3.86), 648 (3.83); HRMS [$C_{69}H_{50}N_4O_4$]: calcd 998.38321, found 998.38363; [$C_{69}H_{50}N_4O_4$, 999.18 g mol^{-1}]: anal. calcd C 82.94, H 5.04, N 5.61, found C 82.89, H 5.29, N 5.44.

3.4.10. (*R*,*S*)-{5-[4-(2-(1,4,9,10-Tetrahydro-5,8-dimethoxy-1,4-dioxo-9,10-(*o*-benzeno)anthracenyl)-phenyl)]-10,15,20-tri-*p*-tolylporphyrinato}zinc(II) (35). Mp 300–301°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=2.70 (s, 9H, tolyl CH_3), 3.829, 3.832 (each s, 3H, OCH_3), 6.32, 6.44 (each s, 1H, triptycene 9-H, 10-H), 6.54 (s (br.), 2H, triptycene 6-H, 7-H), 6.93 (s, 1H, triptycene 3-H), 7.06–7.11 (m, 2H, triptycene H), 7.52–7.57 (m, 8H, 2 triptycene H, 6 tolyl H), 7.78–7.82 (m, 2H, phenylene bridge H), 8.07–8.12 (m, 6H, tolyl H), 8.24–8.27 (m, 2H, phenylene bridge H), 8.93–8.99 (m, 8H, β-pyrrole H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.52 (*C*H_3 tolyl substituents), 41.42 and 41.85 (C-9, C-10,triptycene bridgehead C), 56.47 (O*C*H_3), 109.56, 119.72, 121.33, 121.48, 124.63, 124.68, 125.4, 127.31, 127.58, 131.64, 131.86, 132.00, 132.14, 132.22, 133.69, 133.83, 134.37, 134.48, 137.12, 139.83, 144.32, 144.46, 144.68, 144.95, 149.4, 149.65, 149.69, 149.81, 150.36, 150.48, 152.93, 153.25, 183.36 and 183.65 (C-1, C-4, *C*=O); MS (EI, 80 eV); *m/z* (%): 1062 (1) [M+2H]$^+$, 238 (100) [$C_{16}H_{14}O_2^+$]; MS (FAB+, DMSO/*m*-NO_2-Bzl-OH/Xe) *m/z* (%): 1063 (10) [M+3H]$^+$, 1061 (2) [M+H]$^+$; UV/vis (CH_2Cl_2): λ_{max} (log ε)=302 nm (4.38), 348 (4.16), 401 (4.66), 419 (5.73), 511 (3.83), 548 (4.36), 588 (3.93); HRMS (FAB+) [$C_{69}H_{49}N_4O_4Zn$ [M+H]]: calcd

1061.304527, found 1061.302734, [$C_{69}H_{51}N_4O_4Zn$ [M+3H]]: calcd 1063.320177, found 1063.313232; [$C_{69}H_{48}N_4O_4Zn$, 1062.54 g mol^{-1}]: anal. calcd C 78.00, H 4.55, N 5.27, found C 78.28, H 4.77, N 4.94.

3.4.11. (*R*,*S*)-5-[4(a)-(2-(1,4,9,10-Tetrahydro-5,8-dimethoxy-1,4-dioxo-9,10-(*o*-benzeno)anthracenyl)-cyclohex-(e)-yl)]-10,15,20-tri-*p*-tolylporphyrin (36). 1.71 g (3.75 mmol) of **31**, 1.04 ml (1.01 g, 15 mmol) of pyrrole, and 1.33 ml (1.35 g, 11.25 mmol) of *p*-tolylaldehyde, together with 1.16 ml (1.71 g, 15 mmol) of trifluoroacetic acid were reacted according to the general procedure. The reaction was quenched oxidatively by addition of 3.69 g (15 mmol) *p*-chloranil. Purification of the crude product was achieved by repeated column chromatography [column 1: elution with neat dichloromethane, column 2: elution with dichloromethane/*n*-hexane (4:1, v/v)]. After final purification by HPLC (Nucleosil 50, 5 μ, elution with *n*-hexane/ethyl acetate (17:3, v/v) 260 mg (0.26 mmol, 7%) of the porphyrin quinone **36** were obtained, mp 282–283°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.70 (s (br.), 2H, N*H*), 2.38–2.52 (m, 4H, cyclohexylene 3a-H, 5a-H, 3e-H, 5e-H), 2.61 (d, 2H, $^2J_{ea}$=12 Hz, cyclohexylene 2e-H, 6e-H), 2.68 (s, 3H, tolyl CH_3), 2.72 (s, 6H, tolyl CH_3), 3.16–3.29 (m, 2H, cyclohexylene 2a-H, 6a-H), 3.57 (mc, 1H, cyclohexylene 4e-H), 3.84, 3.90 (each s, 3H, OCH_3), 5.27 (tt, 1H, J_{aa}=12 Hz, J_{ae}≈4 Hz, cyclohexylene 1a-H), 6.37, 6.38 (each s, 1H, triptycene 9-H, 10-H), 6.60 (m, 2H, triptycene 6-H, 7-H, AB), 7.04–7.12 (m, 2H, triptycene H), 7.22 (d, 1H, *J*≈1 Hz, triptycene 3-H), 7.51–7.59 (m, 8H, 2 triptycene H, 6 tolyl H), 8.02–8.08 (m, 6H, tolyl H), 8.78 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H, AB), 8.85 (d, 2H, *J*=5 Hz, β-pyrrole 2-H, 8-H), 9.48 (d, 2H, *J*=5 Hz, β-pyrrole 3-H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.49, 21.54, 30.71, 30.81, 31.79, 33.97, 41.32 and 41.70 (C-9, C-10, triptycene bridgehead C), 46.43, 56.41 and 56.47 (O*C*H$_3$), 109.41, 119.62, 123.97, 124.64, 124.68, 125.32, 127.29, 127.50, 132.00, 133.76, 133.84, 134.40, 134.51, 137.24, 137.28, 138.84, 139.67, 144.44, 144.53, 149.61, 149.64, 151.98, 152.42, 153.59, 183.83 and 183.93 (C-1, C-4, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 1006 (0.7) [M+2H]$^+$, 1004 (0.3) [M$^+$], 580 (100) [M$^+$−$C_{28}H_{24}O_4$], 428 (97) [$C_{28}H_{28}O_4^+$], 238 (40) [$C_{16}H_{14}O_2^+$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=298 nm (4.24), 372 (4.33), 419 (5.61), 485 (3.57), 517 (4.21), 552 (3.94), 593 (3.68), 649 (3.71); HRMS [$C_{69}H_{56}N_4O_4$]: calcd 1004.4302, found 1004.4309; [$C_{69}H_{56}N_4O_4$, 1005.23 g mol^{-1}]: anal. calcd C 82.44, H 5.62, N 5.57, found C 82.09, H 5.73, N 5.22.

3.4.12. (*R*,*S*)-{5-[4(a)-(2-(1,4,9,10-Tetrahydro-5,8-dimethoxy-1,4-dioxo-9,10-(*o*-benzeno)anthracenyl)-cyclohex-(e)-yl)]-10,15,20-tri-*p*-tolylporphyrinato}zinc(II) (37). Mp 308–309°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ= 2.38–2.52 (m, 4H, cyclohexylene 3a-H, 5a-H, 3e-H, 5e-H), 2.60 (d, 2H, $^2J_{ea}$=12 Hz, cyclohexylene 2e-H, 6e-H), 2.67 (s, 3H, tolyl CH_3), 2.71 (s, 6H, tolyl CH_3), 3.20–3.33 (m, 2H, cyclohexylene 2a-H, 6a-H), 3.56 (mc, 1H, cyclohexylene 4e-H), 3.82, 3.88 (each s, 3H, OCH_3), 5.38 (t, 1H, J_{aa}=12 Hz, cyclohexylene 1a-H), 6.35, 6.37 (each s, 1H, triptycene 9-H, 10-H), 6.58 (m, 2H, triptycene 6-H, 7-H, AB), 7.03–7.10 (m, 2H, triptycene H), 7.22 (d, 1H, *J*≈1 Hz, triptycene 3-H), 7.49–7.57 (m, 8H, 2 triptycene H, 6 tolyl H), 8.01–8.08 (m, 6H, tolyl H), 8.87 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H, AB), 8.96 (d, 2H, *J*= 5 Hz, β-pyrrole 2-H, 8-H), 9.61 (d, 2H, *J*=5 Hz, β-pyrrole 3-H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.52, 21.56, 29.70, 30.81, 31.83, 34.08, 41.66 (C-9, C-10, triptycene bridgehead C), 46.75, 56.34 and 56.42 (O*C*H$_3$), 109.28, 120.61, 124.62, 125.20, 125.28, 125.31, 127.24, 131.79, 132.00, 133.65, 134.27, 136.98, 137.02, 138.02, 139.93, 144.41, 144.50, 149.51, 149.87, 150.29, 152.39, 153.01, 153.54, 183.85 (C-1, C-4, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 1068 (24) [M+2H]$^+$, 1066 (10) [M$^+$], 642 (51) [[M+2H]$^+$−$C_{28}H_{26}O_4$], 428 (100) [$C_{28}H_{28}O_4^+$], 238 (37) [$C_{16}H_{14}O_2^+$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=301 nm (4.30), 346 (4.03), 401 (4.65), 420 (5.76), 513 (3.45), 550 (4.33), 588 (3.71); HRMS [$C_{69}H_{54}N_4O_4Zn$]: calcd 1066.3437, found 1066.3430; [$C_{69}H_{54}N_4O_4Zn$, 1068.59 g mol^{-1}]: anal. calcd C 77.56, H 5.09, N 5.24, found C 77.31, H 5.37, N 4.78.

3.4.13. (*R*,*S*)-5-[4(e)-(2-(1,4,9,10-Tetrahydro-5,8-dimethoxy-1,4-dioxo-9,10-(*o*-benzeno)anthracenyl)-cyclohex-(e)-yl)]-10,15,20-tri-*p*-tolylporphyrin (38). 1.71 g (3.75 mmol) of **32**, 1.04 ml (1.01 g, 15 mmol) of pyrrole, and 1.33 ml (1.35 g, 11.25 mmol) of *p*-tolylaldehyde, together with 1.16 ml (1.71 g, 15 mmol) of trifluoroacetic acid were reacted according to the general procedure. The reaction was quenched oxidatively by addition of 3.69 g (15 mmol) *p*-chloranil. Purification of the crude product as described for **36** yielded 377 mg (0.37 mmol, 10%) of the porphyrin quinone **38**, mp 291–292°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.67 (s (br.), 2H, N*H*), 1.89 (qt, 2H, cyclohexylene 3a-H, 5a-H), 2.27 (d, 2H, $^2J_{ea}$=13 Hz, cyclohexylene 3e-H, 5e-H), 2.67 (s, 3H, tolyl CH_3), 2.71 (s, 6H, tolyl CH_3), 2.83 (d, 2H, $^2J_{ea}$=13 Hz, cyclohexylene 2e-H, 6e-H), 3.30 (qt, 2H, cyclohexylene 2a-H, 6a-H), 3.40 (tt, 1H, J_{aa}=13 Hz, J_{ae}=4 Hz, cyclohexylene 4a-H), 3.82, 3.84 (each s, 3H, OCH_3), 5.25 (tt, 1H, J_{aa}=13 Hz, J_{ae}=4 Hz, cyclohexylene 1a-H), 6.30, 6.37 (each s, 1H, triptycene 9-H, 10-H), 6.55 (s (br.), 2H, triptycene 6-H, 7-H), 6.64 (s (br.), 1H, triptycene 3-H), 7.04–7.09 (m, 2H, triptycene H), 7.49–7.56 (m, 8H, 2 triptycene H, 6 tolyl H), 8.04–8.08 (m, 6H, tolyl H), 8.78 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H, AB), 8.90 (d, 2H, *J*=5 Hz, β-pyrrole 2-H, 8-H), 9.62 (s (br.), 2H, β-pyrrole 3-H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.55, 34.14, 36.47, 38.12, 41.23 and 41.60 (C-9, C-10, triptycene bridgehead C), 46.23, 56.35 and 56.39 (O*C*H$_3$), 109.32, 119.60, 123.66, 124.59, 125.31, 127.28, 127.50, 129.78, 131.44, 133.67, 133.76, 134.40, 134.51, 137.28, 138.79, 139.66, 144.34, 144.44, 149.53, 152.46, 153.18, 183.58 and 184.20 (C-1, C-4, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 1006 (12) [M+2H]$^+$, 1004 (9) [M$^+$], 580 (72) [M$^+$−$C_{28}H_{24}O_4$], 428 (100) [$C_{28}H_{28}O_4^+$], 238 (84) [$C_{16}H_{14}O_2^+$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=298 nm (4.27), 374 (4.36), 418 (5.63), 485 (3.58), 517 (4.24), 552 (3.98), 593 (3.70), 649 (3.74); HRMS [$C_{69}H_{56}N_4O_4$]: calcd 1004.4302, found 1004.4305; [$C_{69}H_{56}N_4O_4$, 1005.23 g mol^{-1}]: anal. calcd C 82.44, H 5.62, N 5.57, [$C_{69}H_{56}N_4O_4$×0.5 H_2O, 1014.24 g mol^{-1}]: anal. calcd C 81.71, H 5.66, N 5.52, found C 81.63, H 5.78, N 5.21.

3.4.14. (*R*,*S*)-{5-[4(e)-(2-(1,4,9,10-Tetrahydro-5,8-dimethoxy-1,4-dioxo-9,10-(*o*-benzeno)anthracenyl)-cyclohex-(e)-yl)]-10,15,20-tri-*p*-tolylporphyrinato}zinc(II) (39).

Mp 294–295°C; ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=1.91 (qt, 2H, cyclohexylene 3a-H, 5a-H), 2.27 (d, 2H, $^2J_{ea}$=13 Hz, cyclohexylene 3e-H, 5e-H), 2.68 (s, 3H, tolyl CH_3), 2.71 (s, 6H, tolyl CH_3), 2.85 (d, 2H, $^2J_{ea}$=13 Hz, cyclohexylene 2e-H, 6e-H), 3.31–3.46 (m, 3H, cyclohexylene 2a-H, 6a-H, 4a-H), 3.82, 3.84 (each s, 3H, OCH_3), 5.38 (tt, 1H, J_{aa}=13 Hz, J_{ae}=4 Hz, cyclohexylene 1a-H), 6.29, 6.36 (each s, 1H, triptycene 9-H, 10-H), 6.56 (s (br.), 2H, triptycene 6-H, 7-H), 6.64 (d, 1H, $J\approx$1 Hz, triptycene 3-H), 7.03–7.08 (m, 2H, triptycene H), 7.48–7.57 (m, 8H, 2 triptycene H, 6 tolyl H), 8.04–8.08 (m, 6H, tolyl H), 8.89 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H, AB), 9.02 (d, 2H, J=5 Hz, β-pyrrole 2-H, 8-H), 9.78 (s (br.), 2H, β-pyrrole 3-H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.52, 21.56, 34.22, 34.28, 36.51, 38.23, 41.24 and 41.61 (C-9, C-10, triptycene bridgehead C), 46.60, 56.35 and 56.39 (OCH_3), 109.32, 120.62, 120.65, 124.60, 124.91, 125.28, 125.31, 127.24, 127.28, 129.78, 131.82, 131.88, 133.68, 133.78, 134.30, 137.00, 137.05, 139.74, 139.98, 144.36, 144.46, 149.52, 149.54, 149.95, 150.33, 152.44, 152.55, 153.18, 183.61 and 184.20 (C-1, C-4, C=O); MS (EI, 80 eV); m/z (%): 1068 (3) $[M+2H]^+$, 1066 (2) $[M^+]$, 642 (10) $[[M+2H]^+-C_{28}H_{26}O_4]$, 428 (100) $[C_{28}H_{28}O_4{}^+]$, 238 (89) $[C_{16}H_{14}O_2{}^+]$; UV/vis (CH_2Cl_2): λ_{max} (log ε)=300 nm (4.19), 347 (3.99), 402 (4.62), 420 (5.73), 514 (3.48), 550 (4.31), 588 (3.69); HRMS $[C_{69}H_{54}N_4O_4Zn]$: calcd 1066.3437, found 1066.3435; $[C_{69}H_{54}N_4O_4Zn$, 1068.59 g mol^{-1}]: anal. calcd C 77.56, H 5.09, N 5.24, $[C_{69}H_{54}N_4O_4Zn\times0.5\ H_2O$, 1077.60 g mol^{-1}]: anal. calcd C 76.91, H 5.14, N 5.20, found C 76.62, H 5.20, N 4.88.

3.4.15. (*R,S*)-5-[4-(2-(1,4,5,8,9,10-Hexahydro-1,4,5,8-tetraoxo-9,10-(*o*-benzeno)anthracenyl)-phenyl)]-10,15,20-tri-*p*-tolylporphyrin (40). *(a) Reduction of the porphyrin quinone to porphyrin hydroquinone*. The diad **34** (100 mg, 0.100 mmol) was dissolved in 100 ml dichloromethane and agitated with a freshly prepared 1 M aqueous solution of sodium dithionite until all porphyrin quinone had been reduced to the corresponding porphyrin hydroquinone (TLC control on silica gel, eluent dichloromethane/*n*-hexane, 5:1, v/v, the porphyrin hydroquinone can be identified by its intensive red fluorescence under 366 nm UV light illumination, R_f P-Q: 0.8, R_f P-HQ: 0.1). The phases were separated; the organic phase was washed with water (2×), brine (1×), dried over anhydrous sodium sulfate, evaporated to dryness, and dried in vacuo. *(b) Cleavage of the methoxy groups*. The porphyrin hydroquinone was dissolved in 50 ml of dry dichloromethane under argon and cooled to −78°C (acetone/solid carbon dioxide). Within 5 min, 7 ml (0.70 mmol) of a 1 M boron tribromide solution in dichloromethane were added dropwise. The reaction mixture was stirred for 6 h at −78°C, and then stirred overnight under subsequent warming to ambient temperature. For workup, the reaction mixture was cooled again to −30°C, and 20 ml of water were added dropwise. After warming to ambient temperature the phases were separated and the organic phase was washed once with dilute sodium bicarbonate solution and with water [during this washing, the organic phase changed its color from green (porphyrin dication) to violet (free base porphyrin)]. The organic phase was separated, dried over anhydrous sodium sulfate, and evaporated to dryness. *(c) Oxidation and final purification*. The remaining solid was dissolved in 30 ml dichloromethane, 50 mg (0.220 mmol) of DDQ dissolved in 50 ml dichloromethane were added, and the mixture was stirred for 15 min. The reaction mixture was then filtered through a short silica column, the filtrate was evaporated to dryness and chromatographed on silica gel (eluent: dichloromethane). Final purification was achieved by HPLC (Nucleosil 50, 5 μ, eluting with *n*-hexane/ethyl acetate, 4:1, v/v). Recrystallization from dichloromethane/*n*-hexane afforded 81 mg (0.084 mmol, 84%) of **40** as purple crystals. Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=-2.78 (s (br.), 2H, NH), 2.69 (s, 9H, tolyl CH_3), 6.32, 6.40 (each s, 1H, triptycene 9-H, 10-H), 6.66 (s, 2H, triptycene 6-H, 7-H), 7.05 (s, 1H, triptycene 3-H), 7.12–7.17 (m, 2H, triptycene H), 7.52–7.56 (m, 6H, tolyl H), 7.56–7.62 (m, 2H, triptycene H), 7.78–7.82 (m, 2H, phenylene bridge H), 8.07–8.10 (m, 6H, tolyl H), 8.24–8.27 (m, 2H, phenylene bridge H), 8.79–8.89 (m, 8H, β-pyrrole H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.42 (CH_3 tolyl substituents), 42.12 and 42.54 (C-9, C-10, triptycene bridgehead C), 118.27, 120.23, 120.45, 125.47, 125.52, 125.89, 125.91, 127.33, 127.58, 131.66, 131.81, 134.40, 134.59, 135.37, 137.27, 139.00, 139.03, 142.12, 142.26, 144.24, 145.05, 151.57, 151.72, 151.83, 182.04 and 182.23, 182.25, 182.27 (C-1, C-4, C-5, C-8, C=O); MS (EI, 80 eV); m/z (%): 208 (71) $[C_{14}H_8O_2{}^+]$, 180 (40) $[C_{14}H_8O_2{}^+-CO]$, 152 (100) $[C_{14}H_8O_2{}^+-2\times CO]$; MS (FAB+, DMSO/*m*-$NO_2$-Bzl-OH/Xe) m/z (%): 971 (36) $[M+3H]^+$, 970 (36) $[M+2H]^+$, 969 (17) $[M+H]^+$, 863 (6) $[[M+H]^+-C_6H_2O_2]$, 681 (9) $[[M+H]^+-C_{18}H_8O_4]$; UV/vis (CH_2Cl_2): λ_{max} (log ε)=300 nm (4.15), 374 (4.39), 418 (5.63), 484 (3.81), 515 (4.25), 552 (4.00), 591 (3.86), 648 (3.79); HRMS (FAB+) $[C_{67}H_{47}N_4O_4$ $[M+3H]]$: calcd 971.359731, found 971.358917, $[C_{67}H_{49}N_4O_4$ $[M+5H]]$: calcd 973.375382, found 973.373611; $[C_{67}H_{44}N_4O_4$, 969.11 g mol^{-1}]: anal. calcd C 83.04, H 4.58, N 5.78, found C 82.96, H 4.80, N 5.22.

3.4.16. (*R,S*)-{5-[4-(2-(1,4,5,8,9,10-Hexahydro-1,4,5,8-tetraoxo-9,10-(*o*-benzeno)anthracenyl)-phenyl)]-10,15,20-tri-*p*-tolylporphyrinato}zinc(II) (41). Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=2.69 (s, 9H, tolyl CH_3), 6.29, 6.38 (each s, 1H, triptycene 9-H, 10-H), 6.69 (s (br.), 2H, triptycene 6-H, 7-H), 7.03 (s, 1H, triptycene 3-H), 7.11–7.16 (m, 2H, triptycene H), 7.52–7.55 (m, 6H, tolyl H), 7.55–7.59 (m, 2H, triptycene H), 7.78–7.82 (m, 2H, phenylene bridge H), 8.06–8.10 (m, 6H, tolyl H), 8.24–8.28 (m, 2H, phenylene bridge H), 8.89–8.97 (m, 8H, β-pyrrole H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.41 (CH_3 tolyl substituents), 42.09, 42.51 (C-9, C-10, triptycene bridgehead C), 119.32, 121.20, 121.40, 125.47, 125.56, 125.89, 127.17, 127.44, 131.44, 131.88, 131.95, 132.11, 134.21, 135.37, 137.01, 139.60, 139.63, 142.24, 144.92, 149.52, 150.13, 150.20, 150.30, 151.51, 151.57, 151.71, 182.07 and 182.21, 182.24, 182.27 (C-1, C-4, C-5, C-8, C=O); MS (EI, 80 eV); m/z (%): 1034 (1) $[M+4H]^+$, 208 (100) $[C_{14}H_8O_2{}^+]$; MS (FAB+, DMSO/*m*-NO_2-Bzl-OH/Xe); m/z (%): 1035 (7) $[M+5H]^+$, 1033 (1) $[M+3H]^+$; UV/vis (CH_2Cl_2): λ_{max} (log ε)=303 nm (4.26), 348 (4.11), 401 (4.64), 420 (5.73), 512 (3.68), 548 (4.33), 589 (3.79); HRMS (FAB+) $[C_{69}H_{45}N_4O_4Zn$ $[M+3H]]$: calcd 1033.273227, found 1033.270508, $[C_{67}H_{47}N_4O_4Zn$

[M+5H]]: calcd 1035.288877, found 1035.285339; [$C_{67}H_{42}N_4O_4Zn$, 1032.47 g mol^{-1}]: anal. calcd C 77.94, H 4.10, N 5.43, found C 77.74, H 4.80, N 4.75.

3.4.17. (*R*,*S*)-5-[4(a)-(2-(1,4,5,8,9,10-Hexahydro-1,4,5,8-tetraoxo-9,10-(*o*-benzeno)anthracenyl)-cyclohex-(e)-yl)]-10,15,20-tri-*p*-tolylporphyrin (42). The porphyrin quinone diad **36** (100 mg, 0.100 mmol) was converted to the corresponding triad by reduction with sodium dithionite, reaction with 1 M boron tribromide solution (7 ml, 0.700 mmol), and oxidation with 50 mg (0.220 mmol) DDQ, followed by chromatography on silica gel (eluent dichloromethane), as described for **40**. Final purification was achieved by HPLC (Nucleosil 50, 5 μ, eluting with *n*-hexane/ethyl acetate, 4:1, v/v). Recrystallization from dichloromethane/*n*-hexane afforded 74 mg (0.076 mmol, 76%) of **42** as purple crystals. Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.70 (s (br.), 2H, N*H*), 2.35–2.53 (m, 4H, cyclohexylene 3a-H, 5a-H, 3e-H, 5e-H), 2.55–2.66 (m, 2H, cyclohexylene 2e-H, 6e-H), 2.67 (s, 3H, tolyl CH_3), 2.71 (s, 6H, tolyl CH_3), 3.15 (qd, 1H, $^2J_{ae}\approx J_{aa}\approx$13 Hz, J_{ae}=4 Hz, cyclohexylene 2a-H or 6a-H), 3.25 (qd, 1H, $^2J_{ae}\approx J_{aa}\approx$13 Hz, J_{ae}=4 Hz, cyclohexylene 2a-H or 6a-H), 3.56 (mc, 1H, cyclohexylene 4e-H), 5.27 (tt, 1H, J_{aa}=13 Hz, J_{ae}=4 Hz, cyclohexylene 1a-H), 6.29, 6.31 (s, 1H, triptycene 9-H, 10-H), 6.62 (s (br.), 2H, triptycene 6-H, 7-H), 7.08–7.15 (m, 2H, triptycene H), 7.26 (s (br.), 1H, triptycene 3-H), 7.50–7.60 (m, 8H, 2 triptycene H, 6 tolyl H), 8.00–8.06 (m, 6H, tolyl H), 8.77 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H, AB), 8.85 (d, 2H, *J*=5 Hz, β-pyrrole n 2-H, 8-H), 9.45 (d, 2H, *J*=5 Hz, β-pyrrole 3-H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.46, 21.52, 30.36, 31.05, 31.93, 33.95, 42.16 and 42.55 (C-9, C-10, triptycene bridgehead C), 46.44, 119.68, 123.79, 125.49, 125.87, 127.31, 127.50, 130.62, 131.42, 131.61, 132.04, 134.31, 134.49, 135.17, 137.26, 137.32, 138.76, 139.61, 142.34, 142.44, 146.30, 151.20, 151.57, 152.25, 152.48, 182.13 and 182.23, 182.56, 182.62 (C-1, C-4, C-5, C-8, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 972 (0.5) [M−2H]$^+$, 580 (100) [$C_{41}H_{32}N_4^+$], 400 (13) [$C_{26}H_{24}O_4^+$]; MS (FAB+, DMSO/*m*-NO_2-Bzl-OH/Xe); *m*/*z* (%): 980 (100) [M+6H]$^+$, 979 (69) [M+5H]$^+$, 978 (23) [M+4H]$^+$, 977 (11) [M+3H]$^+$, 976 (8) [M+2H]$^+$, 581 (56) [$C_{41}H_{33}N_4$]$^+$; UV/vis (CH_2Cl_2): λ_{max} (log ε)=299 nm (4.19), 375 (4.32), 418 (5.60), 485 (3.58), 517 (4.20), 552 (3.95), 593 (3.72), 649 (3.72); HRMS (FAB+) [$C_{67}H_{50}N_4O_4$ [M$^+$]]: calcd 974.383207, found 974.382202; [$C_{67}H_{51}N_4O_4$ [M+H]]: calcd 975.391032, found 975.387695.

3.4.18. (*R*,*S*)-{5-[4(a)-(2-(1,4,5,8,9,10-Hexahydro-1,4,5,8-tetraoxo-9,10-(*o*-benzeno)anthracenyl)-cyclohex-(e)-yl)]-10,15,20-tri-*p*-tolylporphyrinato}zinc(II) (43). Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=2.43–2.61 (m, 4H, cyclohexylene 3a-H, 5a-H, 3e-H, 5e-H), 2.63–2.74 (t, 2H, cyclohexylene 2e-H, 6e-H), 2.73 (s, 3H, tolyl CH_3), 2.77 (s, 6H, tolyl CH_3), 3.27 (qd, 1H, $^2J_{ae}\approx J_{aa}\approx$13 Hz, J_{ae}=4 Hz, cyclohexylene 2a-H or 6a-H), 3.37 (qd, 1H, $^2J_{ae}\approx J_{aa}\approx$13 Hz, J_{ae}=4 Hz, cyclohexylene 2a-H or 6a-H), 3.63 (mc, 1H, cyclohexylene 4e-H), 5.46 (tt, 1H, J_{aa}=13 Hz, J_{ae}=4 Hz, cyclohexylene 1a-H), 6.36, 6.37 (s, 1H, triptycene 9-H, 10-H), 6.74 (m, 2H, triptycene 6-H, 7-H, AB), 7.15–7.21 (m, 2H, triptycene H), 7.32 (d, 1H, *J*=1.5 Hz, triptycene 3-H), 7.55–7.66 (m, 8H, 2 triptycene H, 6 tolyl H), 8.7–8.11 (m, 6H, tolyl H), 8.94 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H, AB), 9.03 (d, 2H, *J*=5 Hz, β-pyrrole 2-H, 8-H), 9.67 (d, 2H, *J*=5 Hz, β-pyrrole 3-H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.53, 30.54, 31.20, 32.05, 34.07, 42.28 and 42.64 (C-9, C-10, triptycene bridgehead C), 46.72, 120.69, 124.96, 125.55, 125.63, 125.95, 127.28, 128.84, 131.90, 132.13, 134.26, 135.52, 135.57, 137.04, 137.13, 139.77, 139.98, 142.39, 142.49, 149.65, 150.02, 150.44, 151.27, 151.84, 152.34, 152.64, 182.41 and 182.64 (C-1, C-4, C-5, C-8, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 642 (100) [$C_{41}H_{30}N_4Zn^+$], 400 (52) [$C_{26}H_{24}O_4^+$], 210 (99) [$C_{14}H_{10}O_2^+$]; MS (FAB+, DMSO/*m*-NO_2-Bzl-OH/Xe); *m*/*z* (%): 1042 (4) [M+6H]$^+$, 1040 (3) [M+4H]$^+$, 643 (5) [[M+6H]$^+$−$C_{26}H_{23}O_4$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)= 301 nm (4.21), 346 (4.03), 401 (4.63), 420 (5.73), 513 (3.49), 550 (4.31), 588 (3.71); HRMS (FAB+) $C_{67}H_{49}N_4O_4Zn$ [M+H]: calcd 1037.304527, found 1037.335754, [$C_{67}H_{53}N_4O_4Zn$ [M+5H]]: calcd 1041.335827, found 1041.344238.

3.4.19. (*R*,*S*)-5-[4(e)-(2-(1,4,5,8,9,10-Hexahydro-1,4,5,8-tetraoxo-9,10-(*o*-benzeno)anthracenyl)-cyclohex-(e)-yl)]-10,15,20-tri-*p*-tolylporphyrin (44). 100 mg (0.100 mmol) of the porphyrin quinone diad **38** were converted to the corresponding triad by reduction with sodium dithionite, reaction with 1 M boron tribromide solution (7 ml, 0.700 mmol), and oxidation with 50 mg (0.220 mmol) DDQ, followed by chromatography on silica gel (eluent dichloromethane), as described for **40**. Final purification was achieved by HPLC (Nucleosil 50, 5 μ, eluting with *n*-hexane/ethyl acetate, 4:1, v/v). Recrystallization from dichloromethane/*n*-hexane afforded 79 mg (0.081 mmol, 81%) of **44** as purple crystals. Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.67 (s (br.), 2H, N*H*), 1.88 (qt, 2H, cyclohexylene 3a-H, 5a-H), 2.22 (d, 1H, $^2J_{ea}$=13 Hz, cyclohexylene 3e-H or 5e-H), 2.28 (d, 1H, $^2J_{ea}$=13 Hz, cyclohexylene 3e-H or 5e-H), 2.67 (s, 3H, tolyl CH_3), 2.71 (s, 6H, tolyl CH_3), 2.79–2.89 (m, 2H, cyclohexylene 2e-H, 6e-H), 3.31 (quin, 2H, cyclohexylene 2a-H, 6a-H), 3.39 (tt, 1H, J_{aa}=13 Hz, J_{ae}=3 Hz, cyclohexylene 4a-H), 5.24 (tt, 1H, J_{aa}=13 Hz, J_{ae}=3 Hz, cyclohexylene 1a-H), 6.25, 6.33 (each s, 1H, triptycene 9-H, 10-H), 6.63 (s, 2H, triptycene 6-H, 7-H), 6.68 (s (br.), 1H, triptycene 3-H), 7.10–7.15 (m, 2H, triptycene H), 7.51–7.59 (m, 8H, 2 triptycene H, 6 tolyl H), 8.04–8.08 (m, 6H, tolyl H), 8.79 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H, AB), 8.91 (d, 2H, *J*=5 Hz, β-pyrrole 2-H, 8-H), 9.61 (s (br.), 2H, β-pyrrole 3-H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.53, 34.08, 34.25, 36.63, 38.08, 42.21 and 42.57 (C-9, C-10, triptycene bridgehead C), 46.24, 119.68, 123.44, 125.53, 125.93, 127.30, 127.52, 127.96, 129.93, 130.61, 131.39, 134.42, 134.52, 135.47, 137.32, 138.85, 139.72, 142.38, 142.48, 151.28, 151.77, 151.86, 151.96, 152.99, 182.30 and 182.37, 182.79 (C-1, C-4, C-5, C-8, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 978 (0.3) [M+4H]$^+$, 976 (0.2) [M+2H]$^+$, 974 (0.1) [M$^+$], 580 (100) [$C_{41}H_{32}N_4^+$], 400 (75) [$C_{26}H_{24}O_4^+$]; MS (FAB+, DMSO/*m*-NO_2-Bzl-OH/Xe); *m*/*z* (%): 980 (100) [M+6H]$^+$, 979 (74) [M+5H]$^+$, 978 (29) [M+4H]$^+$, 977 (9) [M+3H]$^+$, 976 (5) [M+2H]$^+$, 581 (78) [$C_{41}H_{33}N_4$]$^+$; UV/vis (CH_2Cl_2): λ_{max} (log ε)=296 nm (4.23), 372 (4.36),

418 (5.65), 485 (3.53), 517 (4.24), 552 (3.97), 593 (3.69), 648 (3.71); HRMS [$C_{67}H_{54}N_4O_4$ [M+4H]]: calcd 978.414510, found 978.414440; HRMS (FAB+) [$C_{67}H_{50}N_4O_4$]: calcd 974.383207, found 974.385666, [$C_{67}H_{51}N_4O_4$ [M+H]]: calcd 975.391032, found 975.388626.

3.4.20. (*R*,*S*)-{5-[4(e)-(2-(1,4,5,8,9,10-Hexahydro-1,4,5,8-tetraoxo-9,10-(*o*-benzeno)anthracenyl)-cyclohex-(e)-yl)]-10,15,20-tri-*p*-tolylporphyrinato}zinc(II) (45). Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=1.93 (qd, 2H, $^2J_{ae}\approx J_{aa}\approx$13 Hz, J_{ae}=3 Hz, cyclohexylene 3a-H, 5a-H), 2.23–2.34 (m, 2H, cyclohexylene 3e-H, 5e-H), 2.69 (s, 3H, tolyl C*H*$_3$), 2.72 (s, 6H, tolyl C*H*$_3$), 2.87 (d, 2H, $^2J_{ea}$=13 Hz, cyclohexylene 2e-H, 6e-H), 3.34–3.49 (m, 3H, 2a-H, cyclohexylene 6a-H, 4a-H), 5.40 (tt, 1H, J_{aa}=13 Hz, J_{ae}=3 Hz, cyclohexylene 1a-H), 6.22, 6.32 (each s, 1H, triptycene 9-H, 10-H), 6.63 (s (br.), 2H, triptycene 6-H, 7-H), 6.66 (s (br.), 1H, triptycene 3-H), 7.10–7.15 (m, 2H, triptycene H), 7.51–7.59 (m, 8H, 2 triptycene H, 6 tolyl H), 8.05–8.10 (m, 6H, tolyl H), 8.91 (m, 4H, β-pyrrole 12-H, 13-H, 17-H, 18-H, AB), 9.05 (d, 2H, *J*=5 Hz, β-pyrrole 2-H, 8-H), 9.79 (s (br.), 2H, β-pyrrole 3-H, 7-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.52, 34.19, 34.35, 36.63, 38.17, 42.16 and 42.53 (C-9, C-10, triptycene bridgehead C), 46.59, 120.66, 120.72 124.66, 125.50, 125.90, 127.24, 128.77, 129.85, 131.90, 134.31, 135.41, 137.05, 139.77, 140.02, 142.34, 142.44, 150.02, 150.40, 151.22, 151.73, 151.82, 151.92, 153.06, 182.26 and 182.35, 182.75 (C-1, C-4, C-5, C-8, *C*=O); MS (EI, 80 eV); *m*/*z* (%): 1040 (1) [M+4H]$^+$, 1038 (1) [M+2H]$^+$, 1036 (1) [M$^+$], 642 (100) [M$^+$−$C_{26}H_{18}O_4$], 400 (84) [$C_{26}H_{24}O_4^+$]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=300 nm (4.26), 345 (4.10), 400 (4.63), 420 (5.71), 512 (3.72), 550 (4.34), 587 (3.91); HRMS [$C_{67}H_{52}N_4O_4Zn$ [M+4H]]: calcd 1040.3280, found 1040.3282; HRMS (FAB+) [$C_{67}H_{49}N_4O_4Zn$ [M+H]]: calcd 1037.304527, found 1037.304291.

3.4.21. (*R*,*S*)-(2-{10-[4-(1,4,9,10-Tetrahydro-5,8-dimethoxy-1,4-dioxo-9,10-(*o*-benzeno)anthracen-2-yl)-phenyl]-porphyrinyl}-5,10,15,20-tetrakis(2-methylpropyl)-porphyrinato)nickel(II) (54). The porphyrin aldehyde **52** (50 mg, 0.08 mmol), 38 mg (0.084 mmol) of the triptycene hydroquinone aldehyde **30**, and 25 mg (0.17 mmol) of dipyrromethane **53** were dissolved in 30 ml of dry dichloromethane under an argon atmosphere. Trifluoroacetic acid (12 μl, 0.16 mmol) was added and the reaction mixture was stirred for 18 h in the dark. Subsequently, 77 mg (0.34 mmol) of DDQ dissolved in dry dichloromethane (30 ml) were added and the reaction mixture was stirred for 1 h followed by addition of 1 g of wet sodium bicarbonate. The mixture was filtered through silica gel and washed with dichloromethane. All high R_f-value fractions were collected, evaporated to dryness and then chromatographed on silica using dichloromethane as eluent. The first fraction was a porphyrin trimer, the second fraction is the porphyrin quinone **54**. Reddish brown crystals, yield: 32 mg (0.024 mmol, 30%). Mp>300°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.84 (s, 1H, N*H*), −2.65 (s, 1H, N*H*), −0.90 (d, 6H, *J*=5.6 Hz, CH_2CHMe_2), 0.82 (d, 6H, *J*=6.7 Hz, CH_2CHMe_2), 0.91 (m, 12H, CH_2CHMe_2), 1.08 (m, 1H, CH_2CHMe_2), 2.28 (m, 3H, CH_2CHMe_2), 2.97 (d, 2H, *J*=7.2 Hz, CH_2CHMe_2), 3.88 (s, 3H, O*Me*), 3.89 (s, 3H, O*Me*), 4.50 (d, 2H, *J*=7.2 Hz, CH_2CHMe_2), 4.57 (m, 4H, CH_2CHMe_2), 6.41 (s, 1H, triptycene), 6.50 (s, 1H, triptycene), 6.62 (s, 2H, arom. H), 7.04 (s, 1H, triptycene 3-H), 7.12 (m, 2H, arom. H), 7.59 (m, 2H, arom. H), 7.88 (d, 2H, *J*=8.3 Hz, arom. H), 8.35 (AB system, 2H, arom. H), 8.93 (d, 1H, *J*=5.0 Hz, β-pyrrole H), 9.09 (d, 2H, *J*=4.6 Hz, β-pyrrole H), 9.14 (d, 2H, *J*=4.6 Hz, β-pyrrole H), 9.16 (d, 1H, *J*=5.0 Hz, β-pyrrole H), 9.41 (m, 4H, β-pyrrole H), 9.38 (s, 2H, β-pyrrole H), 9.45 (d, 2H, *J*=4.6 Hz, β-pyrrole H), 9.94 (s, 1H, β-pyrrole H), 10.38 (s, 2H, *meso*-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.76, 23.40, 29.51, 35.44, 36.05, 36.68, 36.88, 42.36, 42.79, 43.69, 44.23, 57.15, 58.02, 95.04, 105.85, 117.21, 117.46, 117.87, 118.20, 125.64, 126.09, 128.04, 130.83, 131.05, 131.50, 131.55, 131.84, 131.93, 131.97, 132.02, 134.92, 135.52, 142.51, 143.56, 145.29, 145.43, 145.47, 145.72, 146.91, 148.39, 151.34, 151.79, 151.90, 182.36, 182.43; MS (FAB+, DMSO/*m*-NO_2-Bzl-OH/Xe); *m*/*z* (%): 1319 (100) [[M+2H]$^+$], 1318 (62) [[M+H]$^+$], 1317 (43) [M$^+$], 1261 (49) [M$^+$−C_4H_8]; UV/vis (CH_2Cl_2): λ_{max} (log ε)= 409 nm (5.19) 435 (5.32), 505 (4.37), 549 (4.42), 582 (4.13), 635 (3.68).

3.4.22. (*R*,*S*)-5-{4-[1,4,5,8,9,10-Hexahydro-1,4,5,8-tetraoxo-9,10-(*o*-benzeno)anthracen-2-yl]-phenyl}-10-[5,10,15,20-tetrakis(2-methylpropyl)-porphyrin-2-yl]-porphyrin (55). 30 mg (0.023 mmol) of the porphyrin quinone triad **54** were converted to the corresponding nickel-free tetrad by reduction with sodium dithionite, reaction with 1 M boron tribromide solution (3.4 ml, 0.340 mmol), and oxidation with 15 mg (0.060 mmol) *p*-chloranil, followed by chromatography on silica gel (eluent dichloromethane/acetone, 10:1, v/v), as described for **40**. Reddish brown crystals, yield: 22 mg (0.018 mmol, 80%), mp>250°C (decomp.); ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ=−2.75 (s, 1H, N*H*), −2.52 (s, 1H, N*H*), −2.08 (s (br.), 2H, N*H*), −0.52 (s (br.), 6H, CH_2CHMe_2), 1.26 (m, 18H, CH_2CHMe_2), 1.87 (m, 1H, CH_2CHMe_2), 2.81 (m, 2H, CH_2CHMe_2), 2.94 (m, 1H, CH_2CHMe_2), 3.60 (d, 2H, *J*=7.1 Hz, CH_2CHMe_2), 4.86 (d, 2H, *J*=7.1 Hz, CH_2CHMe_2), 4.90 (d, 2H, *J*=7.1 Hz, CH_2CHMe_2), 4.97 (d, 2H, *J*=7.1 Hz, CH_2CHMe_2), 6.40 (s, 1H, triptycene), 6.47 (s, 1H, triptycene), 6.64 (s, 2H, triptycene 6-H, 7-H), 7.10 (s, 1H, triptycene 3-H), 7.18 (m, 2H, arom. H), 7.64 (m, 2H, arom. H), 7.87 (m, 2H, arom. H), 8.35 (m, 2H, arom. H), 9.01 (s (br.), 1H, β-pyrrole H), 9.12 (d, 3H, *J*=4.5 Hz, β-pyrrole H), 9.19 (d, 1H, *J*=4.7 Hz, β-pyrrole H), 9.28 (s (br.), 2H, β-pyrrole H), 9.41 (d, 1H, *J*=4.7 Hz, β-pyrrole H), 9.43 (d, 2H, *J*= 4.6 Hz, β-pyrrole H), 9.52 (s, 2H, β-pyrrole H), 9.57 (d, 1H, *J*=4.7 Hz, β-pyrrole H), 9.61 (d, 1H, *J*=4.7 Hz, β-pyrrole H), 10.15 (s, 1H, β-pyrrole H), 10.35 (s, 2H, *meso*-H); ^{13}C NMR (125 MHz, $CDCl_3$, TMS): δ=21.78, 23.39, 23.42, 23.45, 36.11, 36.67, 36.72, 36.92, 42.21, 42.24, 42.27, 42.69, 43.65, 43.81, 44.19, 44.21, 105.86, 117.20, 117.44, 118.19, 119.75, 125.64, 125.68, 126.05, 126.06, 128.03, 130.85, 131.87, 131.89, 131.95, 131.96, 131.98, 134.89, 135.02, 135.47, 142.30, 142.44, 143.48, 145.22, 145.81, 151.70, 151.72, 151.84, 151.97, 182.15, 182.36, 182.39, 182.41. MS (FAB+, DMSO/*m*-NO_2-Bzl-OH/Xe); *m*/*z* (%): 1233 (8) [[M+3H]$^+$], 1232 (5) [[M+2H]$^+$], 1177 (5) [[M+3H]$^+$−C_4H_8]; UV/vis (CH_2Cl_2): λ_{max} (log ε)=420 nm (5.32), 435 (5.41), 510 (4.44), 549 (4.34), 638 (3.95), 664 (3.91).

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