Isomeric porphyrin phenanthrenequinones: synthesis, NMR spectroscopy, electrochemical properties, and *in situ* EPR/ENDOR studies of the *o*-semiquinone anion radicals †

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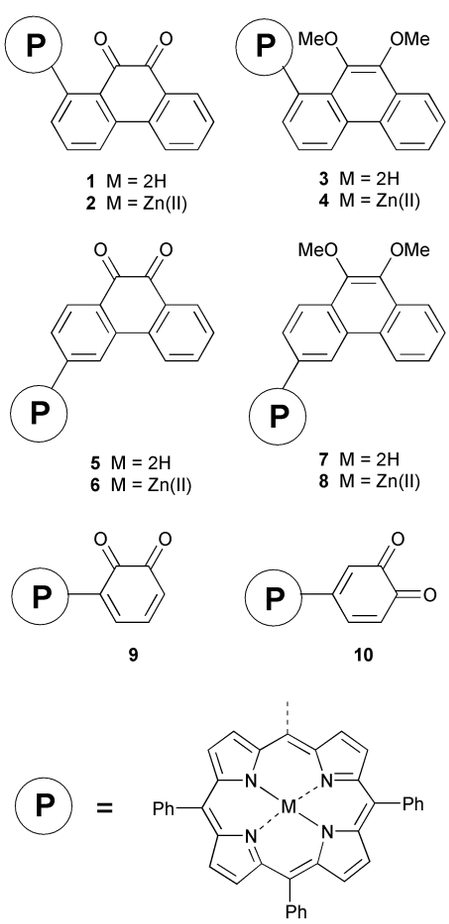
Porphyrin quinones are attractive model compounds for mimicking natural electron transfer processes. While the overwhelming majority of studies have been performed with porphyrin *p*-quinones the isomeric porphyrin *o*-quinones have been mostly neglected. Using phenanthrene-9,10-quinones as the acceptor component we have prepared several porphyrin *o*-quinones (**1**, **2**, **5**, **6**) and show that a facile and simple variation of ΔG_{ET} can be achieved by using the *in situ* formed semiquinones for metal chelatization. Additionally, detailed NMR studies show that for asymmetrically substituted porphyrins a complete assignment of the ^{1}H- and ^{13}C-chemical shifts is possible. Complete NMR assignments were necessary for an unambiguous structure determination.

Introduction

Porphyrin quinones serve as biomimetic models for fundamental studies on photo-induced electron transfer.[1] While most studies in this area have been performed with the well-known porphyrin *p*-quinones, the isomeric, but synthetically less accessible porphyrin *o*-quinones are much better electron acceptors. This results in a higher ΔG_{ET} and thus in a higher efficiency of the electron transfer. In order to achieve a variation of ΔG_{ET} the general strategy in electron transfer studies generally involves the synthesis of different models *via* chemical modification of the porphyrin donor or the quinone acceptor. However, this also leads to changes in a number of other variables such as distance, solvent term, and electronic matrix element resulting in altered electron transfer rates. Here the utilization of porphyrin *o*-quinones as electron transfer systems offers an attractive alternative. *o*-Quinones allow a chelatization of the *o*-semiquinones with metal cations. Thus, a large variety of model systems with different ΔG_{ET} might be prepared with minimal synthetic effort. Such compounds should show a significantly better agreement in other electron transfer relevant parameters then differently substituted porphyrin *p*-quinones. Here we show that utilizing such a strategy, compounds suitable for electron transfer studies can be prepared using the porphyrin phenanthrenequinones **1** and **5** or their metal complexes **2** and **6**.

Due to their higher chemical reactivity, use of porphyrin *o*-quinones in electron transfer studies has lagged behind that of the isomeric *p*-quinones.[2] In earlier studies we showed that the synthesis of stable porphyrin *o*-benzoquinones requires substitution of the neighboring positions 3 and 6, although the "unsubstituted" porphyrin *o*-quinones **9** and **10** have also been characterized.[3] Giangiacomo and Dutton showed in reconstitution experiments, *e.g.* using the phenanthrene-9,10-quinone **12**, that *o*-quinones can serve as electron acceptors in native systems without changes in the functionality of the photosystems.[4] Porphyrin anthraquinones have been prepared and studied by Connolly and co-workers.[5] In order to have material complementary to these studies we have prepared the two constitutionally isomeric phenanthrylporphyrins **3** and **7** and converted them into the corresponding porphyrin phenanthrylquinones **1** and **5** and their zinc(II) complexes **2** and **6**.



Results and discussion

Synthesis

As we had shown earlier the synthesis of the *o*-quinones requires use of the corresponding bis(methyl ether) as starting

† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR data for various phenanthrene derivatives. See http://www.rsc.org./suppdata/p2/b1/b110273g/

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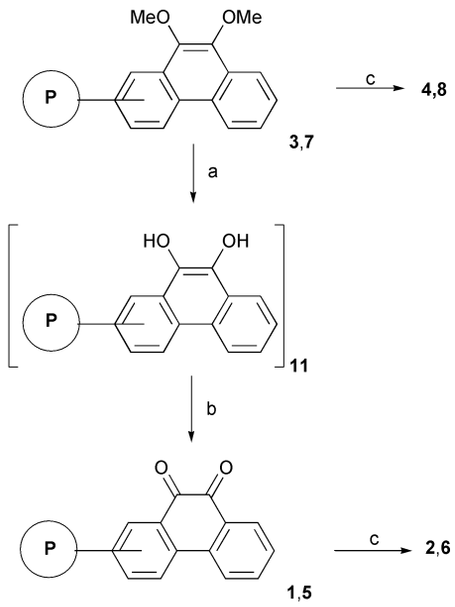
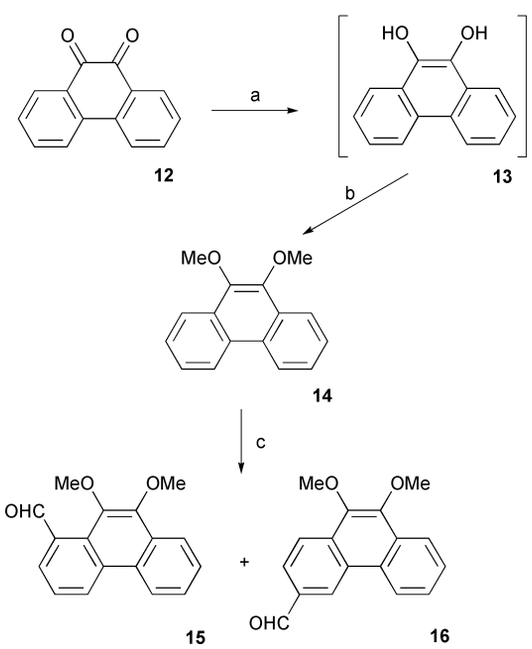
material.[3] Thus, the methyl protected porphyrin *o*-quinones were prepared first, then demethylated to the intermediary dihydroxy derivatives **11** and oxidized with Ag_2O to the desired porphyrin *o*-quinones (Scheme 1).



Scheme 1 a: BBr_3, CH_2Cl_2, −80 °C; b: Ag_2O.

Porphyrin synthesis using a mixed condensation and following the Lindsey method[6] necessitates use of the aldehydes **15** and **16**, respectively. Their synthesis started with phenanthrene-9,10-quinone **12** which was transformed into 9,10-dimethoxyphenanthrene **14** (*via* the intermediary hydroquinone **13**) in 84% yield using sodium dithionite and methyl iodide followed by Rieche formylation;[7] the latter method being especially suited for activated aromatic compounds (Scheme 2).



Scheme 2 a: $Na_2S_2O_4$, aq, EtOH; b: KOH, DMSO, MeI; c: Cl_2CH–OMe, $TiCl_4$, CH_2Cl_2, 0 °C.

This reaction yields a regioisomeric mixture of **15** and **16** (1 : 3 in 79% yield) with the sterically more demanding aldehyde **15** being the minor component.

The assignment of the two isomers was performed using complex 1D and 2D NMR experiments. In order to unambiguously characterize the two isomeric porphyrins **3** and **7** the separated aldehydes **15** and **16** were used individually for porphyrin synthesis giving the two porphyrins in 22 and 13% yield, respectively. For larger scale synthesis use of the crude aldehyde mixture **15**–**16** for porphyrin condensation was more advantageous as the porphyrin mixture **3**–**7** is more easily separated *via* HPLC as the aldehyde mixture. The free base porphyrins **1** and **5** were also converted to the zinc(II) complexes **2** and **6** using ZnO in quantitative yield. For comparison, the two zinc(II) complexes **4** and **8** were prepared from the two dimethoxyphenanthrylporphyrins **3** and **7**.

NMR spectroscopy

In order to allow a detailed spectroscopic characterization the ^1H and ^{13}C chemical shifts of all compounds were assigned. Individual positions are labelled as shown in Fig. 1. Normally,

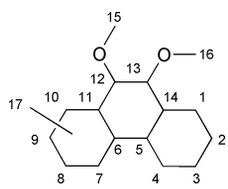


Fig. 1 Numbering scheme for the positions in the phenanthrene ring system used for NMR assignments.

fluorescence quenching is an unambiguous indicator for the presence of a porphyrin quinone. As fluorescence quenching is often not complete for compounds **1**, **2** or **5**, **6**,[8] ^{13}C NMR spectroscopy is a necessary analytical tool to assure the formation of a porphyrin quinone as opposed to the dihydroxy compounds.

Numerical values for the ^1H NMR spectra are compiled in the supplementary material (Table S1†); for comparison data for the symmetric parent compounds phenanthrene-9,10-quinone **12** and 9,10-dimethoxyphenanthrene **14** are also listed.

^1H NMR data especially illustrate the different influence that substituents at position 17 exert on the two phenyl rings of the phenanthrene unit (H1–H4 and H7–H10). For example, a shift difference of 0.17 and 0.06 ppm between the two methoxy groups H15 and H16 is observed in the case of the isomeric aldehydes **15** and **16**. The significantly larger difference in the case of compound **15** is a result of the anisotropy effect of the carbonyl group C17. Even stronger anisotropy effects, this time a result of the diamagnetic shift anisotropy of the porphyrin, were observed for the porphyrins **3** and **7** and the related Zn(II) complexes **4** and **8**. For compound **3** a shift of the two methoxy groups of 1.87 and 3.54 ppm is observed (Fig. 2). The resulting shift difference between the two methoxy groups is 1.67 ppm, quite different from the value of 0.08 ppm found for compound **7**.

Thus, the ^1H chemical shifts of the methoxy groups in compounds **3** and **7** are excellent sensors for a determination of the spatial separation from the porphyrin macrocycle. Accordingly, the methoxy group with the largest high field shift (δ = 1.87 ppm) is closer to the porphyrin core than the other methoxy group (δ = 3.54 ppm). For compounds **7** and **8** no influence of the porphyrin ring current on the chemical shift of the methoxy groups was observed (δ = 4.39, 4.31 ppm and 4.17, 4.11 ppm). For the parent compound **14** this value is δ = 4.11 ppm. These observations are in accordance with results from single crystal X-ray data for the zinc(II) complexes **4** and **8**,[9] the distance between the center of the porphyrin core and the methoxy carbon atoms were determined as 4.588, 7.517 and 11.061, 12.269 Å, respectively.

Furthermore, a significantly smaller influence of the 17-substituent on the distal phenyl ring (H1–H4) can be delineated for the dimethoxy phenanthrylporphyrins **3**, **4** and **7**, **8**. For an assignment of the individual isomers—1- or 3-bridged—, the chemical shifts of the protons H7–H10 and the multiplet

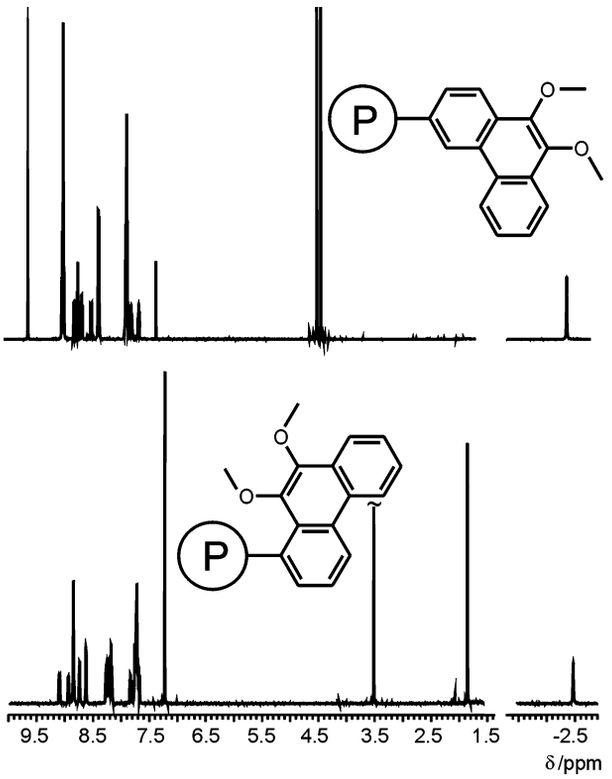


Fig. 2 Proton NMR spectra of the protected dimethoxyphenanthryl-porphyrins.

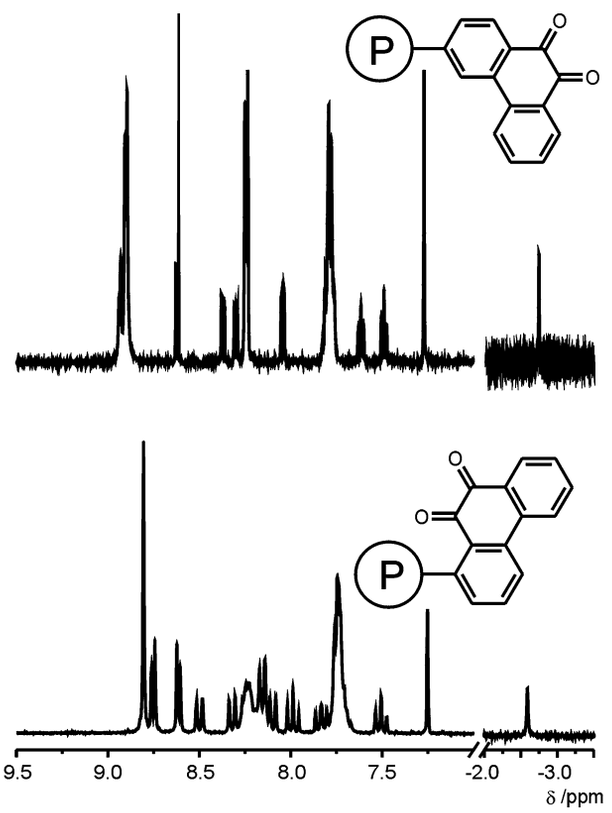


Fig. 3 Proton NMR spectra of the isomeric porphyrin phenanthrene-quinones.

pattern of the phenanthrene skeleton were used. The chemical shift of the carbonyl atoms is especially suited for structural analyses of *o*-quinones.[10] In the case of the phenanthrene-*o*-quinones the values of the C12 and C13 chemical shifts are δ = 180.1–180.8 ppm, an unambiguous indication for a C=O group (see Table S2†). ^{13}C chemical shifts of 135–145 ppm would be expected for the corresponding dihydroxy groups. Together with the ^{1}H chemical shifts the ^{13}C NMR spectra allow an assignment of the phenanthrene skeleton and determination of the different isomeric forms for compounds **1**–**8**, **15** and **16**. Note that assignments given in the literature[11] for the ^{13}C NMR chemical shifts for compound **14** were corrected according to the data given in the supplementary material (Table S2†).

The two isomeric phenanthrenequinones **1** and **5** exhibit quite different spectra. Both the β-pyrrole and the *o*-phenyl proton signals are split significantly as a result of the interaction between porphyrin ring current and the anisotropy resulting from the carbonyl groups.

EPR spectroscopy

During photoexcitation both porphyrin cation radicals and the corresponding semiquinone radicals are formed in native systems according to the general formula (P = porphyrin; Q = quinone):

$$P - Q \xrightarrow{h\nu} P^{+\bullet} - Q^{-\bullet} \quad (1)$$

Thus, we were interested first in the spin density distribution in the phenanthrene ring system in chemically generated semiquinone anion radicals (sq). Initial studies on porphyrin cation radicals were performed by Fajer *et al.*[12] In later investigations by Huber *et al.* additional hyperfine coupling constants (hfcs) were determined, which are relevant for triphenyl-substituted porphyrins of the type used in our study.[13] As the model compounds employed here have the acceptor connected to the donor at a position of small spin density and basic data for porphyrin cation radicals are available.[14] We have concentrated on functional studies. Of special interest was the question of how the large substituent (porphyrin) might influence the spin density distribution in a semiquinone anion radical, and whether the spin density distribution can be varied by chelating the quinone oxygen atoms.

Low resolution EPR spectra gave evidence for three protons being located at positions of high spin density and for four protons at low spin density positions (Fig. 4).

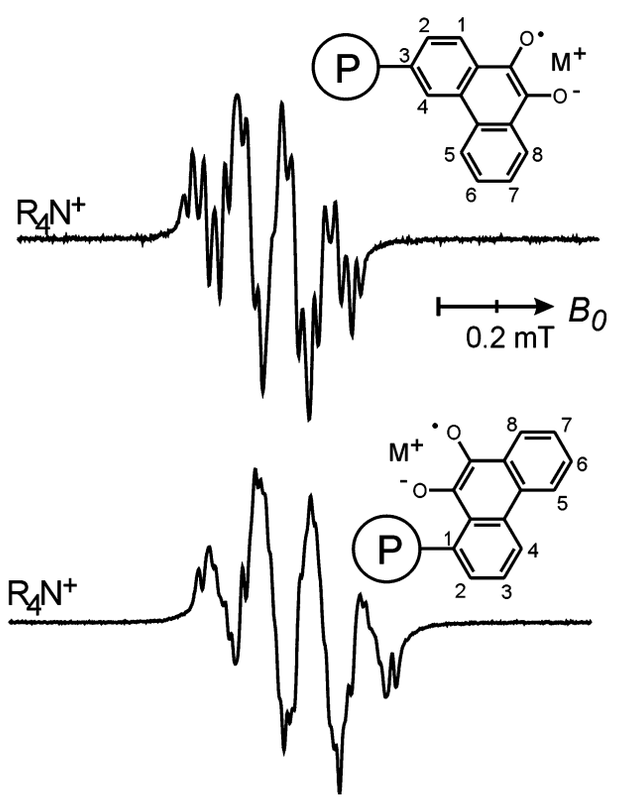


Fig. 4 EPR spectra of the nonchelated semiquinone anion radicals of the porphyrin phenanthrenequinones.

Table 1 Hyperfine coupling constants a_H and a_{M^+} (MHz) for substituted phenanthrene-*o*-semiquinone anion radicals (sq) in isotropic solution (propan-2-ol)

Compound	M^+	T/K	$a_{1,8}$	$a_{2,7}$	$a_{3,6}$	$a_{4,5}$	a_{M^+}
12 sq[15b]	NR_4^{+a}	230	−4.44	+0.96	−4.86	+1.16	—
1 sq	NR_4^+	260	−4.24	+0.92	−5.50	+1.43	—
				+0.58	−4.87	+1.15	
	Li^+	260	−4.64	+0.74	−5.22	+1.28	−1.49
					−4.85	+1.06	
	Na^+	270	−4.62	+0.69	−5.32	+1.32	−1.23
						+1.06	
	K^+	270	−4.65	+0.83	−5.14	+1.26	—
						+1.08	
5 sq	NR_4^+	270	−4.18	+1.23	−4.55	+0.78	—
			−4.05	+1.08			
	Li^+	270	−4.53	+1.15	−4.90	+0.95	−1.32
	Na^+	260	−4.41	+1.12	−4.83	+0.98	−0.62
	K^+	290	−4.33	+1.10	−4.81	+0.86	—

[a] NR_4^+ = benzyltrimethylammonium.

When the semiquinone radicals were treated with metal salts, chelatization with lithium und sodium (nuclear spin $I = \frac{3}{2}$) resulted in further splitting of the pseudo-quadruplet and no unambiguous assignments for the signals can be given on the basis of EPR measurements. Only electron nuclear double resonance (ENDOR) spectroscopy, with its higher resolution, allowed a determination of almost all hfcs at positions of different spin density (Fig. 5).

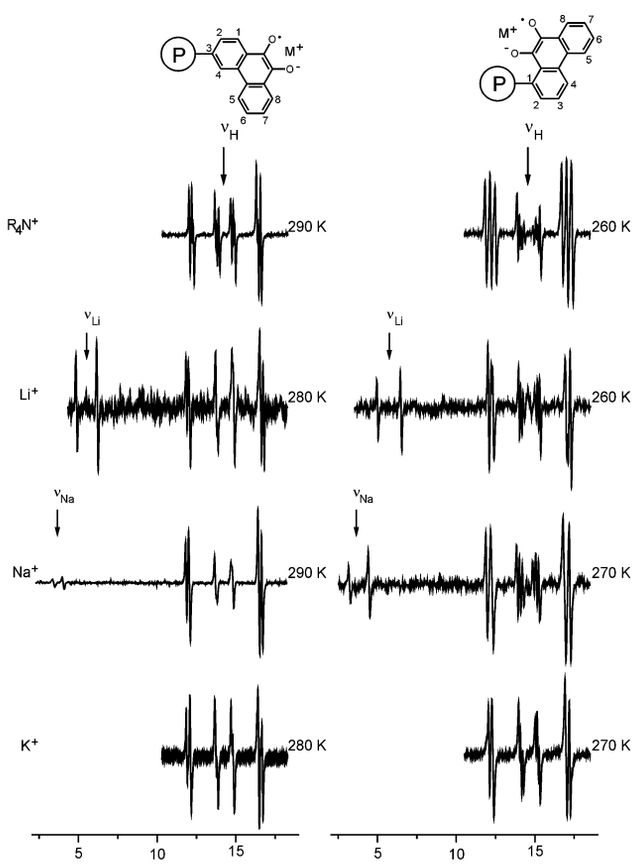


Fig. 5 ENDOR spectra of the semiquinone anion radicals of the phenanthrenequinones with different counter ions.

The signs of the individual hfcs were determined in analogy to the works of Stegman *et al.* and Kirste.[15] No clear assignment was possible for hfcs with two resolved values for the same position in different phenyl rings (Table 1).

The clearly resolved signals of the individual metals used for chelatization (Li^+, Na^+) which were observed in the spectra of the two porphyrin semiquinone anion radicals unambiguously proved that chelatization had taken place (Fig. 3). However, the additional coupling of the semiquinone anion radical with potassium resulted in line broadening. Potassium ENDOR spectroscopy is possible only under "extreme" conditions (high spin density on the potassium) which could not be employed for the compounds studied here.[16] The unusually large sodium coupling of $a_M = -1.23$ MHz in the chelate of **1** has to be the result of steric interactions.

In conclusion, EPR and especially ENDOR spectroscopy allow identification of the semiquinone anion radicals formed. The couplings of the cations (Li^+ and Na^+) as well as the different spectral pattern constituted clear proof for changes in the spin density at different positions of the phenanthrene ring.

Cyclic voltammetry

Determination of redox potentials is mandatory for characterization of electron transfer compounds. Up to now it was only possible to vary the oxidation potential of the porphyrin *via* insertion of different metal cations.[17] Variation of the reduction potential of the quinone was only possible by construction of different acceptor systems *via* multistep syntheses. Exceptions are the crown ether substituted porphyrin quinones from Sun *et al.*, where the reduction potential of the quinone is dependent on the charging of the crown ether.[18] Nevertheless crown ethers are strongly ion selective and thus broader variations of the ions that can be used for complexation require further, complex syntheses. On the basis of the groundbreaking work of Fujinaga *et al.*,[19] Kalinowski *et al.*[20] and Krygowski,[21] who studied the influence of metal ions on the reduction potential of the phenanthrenequinone **12** we could show that the same effect occurs in covalently linked porphyrin phenanthrenequinones. In analogy to phenanthrenequinone itself, this effect is larger for diavalent metal ions than for monovalent ions.[19,20] The cyclovoltammetric measurements showed that the reduction potential of the phenanthrenequinone anions is ion selective. The differences in the reduction potentials of the porphyrin phenanthrenequinones **1** and **6** are an indication of the steric demand of the phenanthrenequinone substituent in compound **1**. The EPR/ENDOR measurements showed the same effect. Depending on the solvent (DCM or DMF) differences in the redox potentials of up to 100 mV were found. Note that Nagaoka *et al.*[19b] and Kalinowski and Tenderende-Guminska[20] described differences in the redox potentials of up to 40 mV when the same compound was measured under identical conditions in different sets of apparatuss.

As shown in Table 2, variation of the metal can be used for fine-tuning in the region of 260 mV. Thus, the reduction potential can be up to 600 mV higher in comparision to the isomeric anthraquinone.[5a] The results indicate that porphyrin phenanthrenequinones possess high potential as model

Table 2 Redox potentials of the model compounds and their metal complexes *vs.* SCE, working electrode Pt, conducting salt 0.1 M TBAP

Compound	E_2^{OX}/V	E_1^{OX}/V	$-E_1^{RED}$/V	$-E_2^{RED}$/V
In DCM				
1		1.04	0.58	
5	1.32	1.12	0.55	
2	1.13	0.82	0.60	
6	1.36	0.86	0.55	1.25
In DMF				
1		1.02	0.57	
1 Li		1.07	0.52	
1 Mg		1.03	0.46	
6		0.92	0.59	
6 Li		0.92	0.52	
6 K		0.92	0.49	
6 Mg	1.14	0.92	0.31	

compounds for light-induced electron transfer. More detailed photophysical studies on these compounds will be published in due course.

Experimental

General

All chemicals used were of analytical grade and purchased from Aldrich Co. The solvents were purified before use by distillation. Melting points are uncorrected and were measured with a Reichert Thermovar apparatus. Silica gel 60 (Merck) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel (neutral, fluorescence indicator F_{254}) precoated plates. ^{1}H NMR spectra were recorded at frequencies of 500 MHz with a Bruker AMX 500 instrument, carbon-13 spectra at 126 MHz. All chemical shifts are given in ppm and have been converted to the δ scale and are referenced against the $CDCl_3$ signal as internal standard. Absorption spectra were recorded with a Specord S10 (Carl Zeiss) spectrophotometer using DCM as solvent. Mass spectra were obtained using a Varian MAT 711 mass spectrometer. HPLC Columns: Nucleosil 50 SiO_2 (5 μm), 300 mm × 5 mm id and 107 mm × 32 mm id; HPLC instrumentation: Knauer HPLC pump 64 high pressure, Knauer MPLC pump and variable-wavelength monitor UV/Vis detector from Knauer; all chromatograms were taken at ambient temperature with the detector wavelength fixed at $\lambda = 420$ nm.

Cyclic voltammetry

Electrochemical experiments were carried out at room temperature (25 °C) under argon using a PGSTAT10 analyzer (Metrohm), a 0.1 M solution of tetra-*n*-butylammonium perchlorate (TBAP) in dry DMF; working electrode: Ag /AgCl electrode; auxiliary electrode: platinum wire, concentration of compounds 4×10^{-4} M, voltage increase rate 100 mV s^{-1}, reference: [E(Fc/Fc$^+$) = +0.5 ± 0.01 V]. The solvent system was calibrated prior to addition of the electroactive agent by determining the CV potential limits, defined by a background current < 20 μA. The synthesis of the metal complexes was performed under argon by addition of aliquots of the corresponding metal perchlorate solution in DMF (4×10^{-4} M).

EPR and ENDOR measurements

Instrumentation. EPR and ENDOR spectra were recorded on a Bruker ER 220D EPR spectrometer equipped with a Bruker ENDOR cavity (ER200ENB); laboratory built NMR facilities are described elsewhere.[22] The spectra were accumulated *via* a D/A-interface (MetraByte DAS-16) with an AT486 PC. For EPR measurements typical experimental conditions were: 2 mW microwave power level and 0.01 mT field modulation. For ENDOR a microwave power level of 10 mW was used; the RF power was 220 W, FM modulation amplitude was ±25 kHz (modulation frequency 10 kHz). The solvents for spectroscopy were purified by distillation over Na (propan-2-ol). The chemicals for the radical generation were purchased from Merck and used without further purification. The temperatures of measurement are given in the respective spectra.

Sample preparation. All anion radicals were prepared immediately prior to measurement in solution in a sample tube of quartz (3 mm external diameter) under an argon atmosphere. Specifically, the base was added directly as a solid (lithium *tert*-butylate, sodium *tert*-butylate, potassium *tert*-butylate) or in solution (20 μl of a 40% solution of benzyltrimethylammonium hydroxide in methanol) to a solution of the porphyrin quinones in propan-2-ol. Metal chelates were prepared immediately thereafter and quantitatively using the corresponding counterions (NR_4^+, Li^+, Na^+, K^+).

Synthesis of 9,10-dimethoxyphenanthrene 14

In variation of a known procedure[23] 0.1 mol (20.8 g) of freshly sublimated phenanthrene-9,10-quinone **12** was reduced with sodium dithionite under an argon atmosphere in a water–ethanol solution. After the reaction mixture became colorless, the product was extracted with diethyl ether (4 × 150 mL). After desiccation with anhydrous sodium sulfate, the solvent was removed under reduced pressure and the product dissolved in 350 mL of anhydrous DMSO. After addition of 0.4 mol (22.4 g) pulverized potassium hydroxide, 31.1 mL of methyl iodide were added dropwise under ice cooling in the course of 1 hour. Work up of the mixture after a reaction time of 12 hours yielded a crude product, which was purified using column chromatography (dichloromethane–*n*-hexane = 5 : 1, v/v). Sublimation of this product completed the work up and yielded the product **14** as colorless crystals, mp: 58–60 °C. In contrast to earlier reports[11,23] this method yields highly crystalline material and facilitated a revision of the analytical data. Yield 20.0 g (84%); δ_H(500 MHz, $CDCl_3$) 4.11 (s, 6H, OMe), 7.64 (ddd, *J* 8.0, 7.2, 1.5, 2H, ArH), 7.66 (dd, *J* 7.3, 7.3, 2H, ArH), 8.30 (dd, *J* 7.3, 1.5, 2H, ArH), 8.66 ppm (ddd, *J* 8.0, 2H, ArH); δ_C(126 MHz, $CDCl_3$) 60.93, 122.09, 122.59, 126.45, 125.77, 126.78, 128.61, 129.05, 143.88 ppm; Found: C, 80.52; H, 6.01. Calc. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92%; *m/z* (EI, 80 eV) 239 (17.4%, $[M + 1]^{\bullet+}$), 238 (100%, $[M]^{\bullet+}$), 223 (58.6%, $[M - CH_3]^{\bullet+}$).

Formylation of 9,10-dimethoxyphenanthrene 14

To a stirred solution of 4.76 g (20 mmol) 9,10-dimethoxyphenanthrene **14** in 100 mL of dichloromethane, 4.76 g (25 mmol) of titanium(IV) chloride was added at 0 °C, followed by dropwise addition of 3.45 g (30 mmol) freshly distilled dichloromethyl methyl ether. The reaction mixture was warmed up to room temperature, stirred for 1 h and poured into ice water. The mixture was extracted with dichloromethane. The combined organic layers were washed with 5% aqueous $NaHCO_3$ and dried over sodium sulfate. After evaporation of the solvent 4.2 g (79%) of a crude mixture of the regioisomeric aldehydes (1 : 3) was obtained. After a crude purification with column chromatography (silica gel, *n*-hexane–dichloromethane = 1 : 1, v/v) the aldehydes were separated *via* HPLC (eluent: *n*-hexane–ethyl acetate = 90 : 10, v/v).

1-Formyl-9,10-dimethoxyphenanthrene 15. Yield 1.1 g (4.1 mmol, 21%) of colorless crystals, HPLC: elution time: 7 min, mp 112–114 °C; δ_H(500 MHz, $CDCl_3$) 3.93 (s, 3H, OMe), 4.10 (s, 3H, OMe), 7.58 (ddd, *J* 8.4, 7.3, 0.7, 1H, ArH), 7.61 (ddd, *J* 8.2, 7.1, 1.7, 1H, ArH), 7.64 (ddd, *J* 8.0, 7.1, 1.3, 1H, ArH), 7.88 (dd, *J* 7.3, 1.3, 1H, ArH), 8.24 (dd, *J* 8.0, 1.7, 1H, ArH), 8.56 (dm, *J* 8.2, 1H, ArH), 8.72 (ddd, *J* 8.4, 1.3, 0.6, 1H, ArH), 10.99 ppm (s, 1H, CHO); δ_C(126 MHz, $CDCl_3$) 60.27,

61.05, 122.10, 122.80, 125.29, 126.45, 126.80, 127.38, 127.46, 127.58, 128.43, 128.84, 129.11, 135.07, 144.39, 146.31, 195.22 ppm; Found: C, 76.39; H, 5.30. Calc. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%; *m/z* (EI, 80 eV) 267 (19.2%, $[M + 1]^{\bullet +}$), 266 (100%, $[M]^{\bullet +}$), 251 (26.3%, $[M - CH_3]^{\bullet +}$), 236 (66.1%, $[M - 2CH_3]^{\bullet +}$), 180 (77.9%, $[C_{13}H_8O]^{+\bullet}$), 152 (61.1%, $[C_{12}H_8]^{+\bullet}$).

3-Formyl-9,10-dimethoxyphenanthrene 16. Yield 3.1 g (11.6 mmol, 58%) of colorless crystals, HPLC: elution time: 8 min, mp 92–94 °C; δ_H(500 MHz, $CDCl_3$) 4.09 (s, 3H, OMe), 4.15 (s, 3H, OMe), 7.69 (dd, 1H, ArH), 7.71 (dd, 1H, ArH), 8.10 (dd, *J* 8.5, 1.3, 1H, ArH), 8.29 (dd, 1H, ArH), 8.35 (d, *J* 8.5, 1H, ArH), 8.73 (dd, 1H, ArH), 9.12 (d, *J* 1.3, 1H, ArH), 10.25 ppm (s, 1H, CHO); δ_C(126 MHz, $CDCl_3$) 60.83, 122.36, 122.47, 122.76, 125.17, 126.53, 126.74, 127.38, 127.91, 128.63, 129.15, 133.17, 133.26, 143.12, 146.64, 192.03 ppm; Found: C, 76.15; H, 5.23. Calc. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30%; *m/z* (EI, 80 eV) 267 (18.8%, $[M + 1]^{\bullet +}$), 266 (100%, $[M]^{\bullet +}$), 251 (41.1%, $[M - CH_3]^{\bullet +}$), 223 (24.2%, $[M - CO - CH_3]^{\bullet +}$), 208 (5.9%, $[C_{14}H_8O_2]^{+\bullet}$).

Synthesis of the porphyrins

General procedure according to Lindsey conditions. Pyrrole (0.8 mL, 10 mmol), benzaldehyde (0.9 mL, 8.75 mmol) and 2.5 mmol of the corresponding phenanthrene aldehyde were dissolved in 1 L of CH_2Cl_2 (+7.5 mL of anhydrous ethanol) under argon. The condensation reaction was initiated by addition of 4 mmol of a 25% BF_3–diethyl etherate solution in the dark. After stirring for 1 h, the porphyrinogen formed was oxidized with 1.1 fold excess DDQ, followed by stirring for about 12 h. The reaction mixture was neutralized with triethylamine and the product extracted with dichloromethane. Purification was achieved by repeated column chromatography with *n*-hexane–dichloromethane mixtures (1 : 10, v/v) on silica gel followed by preparative HPLC. As separation of the different porphyrin phenanthrenes proved to be easier than separation of the aldehydes only one condensation of each pure phenanthrene aldehyde was performed. For large scale synthesis the mixture of aldehydes **15** and **16** was used for condensation.

5-(9,10-Dimethoxyphenanthren-1-yl)-10,15,20-triphenylporphyrin 3. According to the general procedure 0.67 g (2.5 mmol) of phenanthrene aldehyde **15** were condensed with the porphyrin. After purification with HPLC (*n*-hexane–ethyl acetate = 95 : 5, v/v, elution time: 2.8 min) and recrystallization from methanol–dichloromethane, 425 mg of purple crystals (0.55 mmol, 22%) were obtained, mp > 330 °C; δ_H(500 MHz, $CDCl_3$) −2.46 (s, 2H, NH), 1.87 (s, 3H, OMe), 3.54 (s, 3H, OMe), 7.73 (dd, H, ArH), 7.76 (dd, 1H, ArH), 7.83–7.71 (m, 9H, *m*- and *p*-phenyl), 7.88 (dd, *J* 8.4, 7.6, 1H, ArH), 8.23–8.19 (m, 2H, *o*-phenyl), 8.24 (dd, 1H, ArH), 8.26 (dd, 1H, ArH), 8.34–8.27 (m, 4H, *o*-phenyl), 8.67 (d, *J* 4.6, 2H, β-pyrrole), 8.79 (d, *J* 4.6, 2H, β-pyrrole), 8.90 (s, 4H, β-pyrrole), 8.99 (d, *J* 8.3, 1H, ArH), 9.15 ppm (dd, *J* 8.4, 0.8, 1H, ArH); δ_C(126 MHz, $CDCl_3$) 59.00, 60.27, 119.36, 119.96, 121.88, 123.18, 123.21, 123.41, 123.77, 126.14, 126.66, 127.15, 127.58, 127.61, 128.51, 128.86, 129.54, *ca.* 130.8, 131.21, 134.45, 134.49, 134.55, 134.70, 135.33, 137.35, 142.18, 142.35, 146.05, 146.03 ppm; Found: C, 83.77; H, 5.19; N, 6.82. Calc. for $C_{54}H_{38}O_2N_4$: C, 83.70; H, 4.94; N, 7.23%; *m/z* (EI, 80 eV) 775 (57.0%, $[M + 1]^{\bullet +}$), 774 (100%, $[M]^{\bullet +}$), 744 (12.4%, $[M - 2CH_3]^{\bullet +}$), 728 (22.6%, $[M - C_2H_6O]^{\bullet +}$); HRMS: $C_{54}H_{38}O_2N_4$ Calc. 774.29948, Found 774.29966; UV/Vis (CH_2Cl_2): λ_{max} [lg (ε/dm^3 mol^{-1} cm^{-1})] 420 (5.67), 516 (4.27), 552 (4.00), 592 (3.76), 648 nm (3.72).

5-(9,10-Dimethoxyphenanthren-3-yl)-10,15,20-triphenylporphyrin 7. As described above, 0.67 g of the phenanthrene aldehyde **16** was condensed with the porphyrin **7**. After HPLC separation (*n* hexane–ethyl acetate = 95 : 5, v/v, elution time: 3.4 min) and recrystallization from methanol–dichloromethane 250 mg of purple crystals (0.32 mmol, 13%) were obtained, mp > 330 °C; δ_H(500 MHz, $CDCl_3$) −2.56 (s, 2H, NH), 4.31 (s, 3H, OMe), 4.39 (s, 3H, OMe), 7.58 (ddd, *J* 8.4, 7.0, 1.2, 1H, ArH), 7.72 (ddd, *J* 8.3, 7.0, 0.8, 1H, ArH), 7.85–7.76 (m, 9H, *m*- and *p*-phenyl), 8.33–8.28 (m, 6H, *o*-phenyl), 8.43 (dd, *J* 8.3, 1.2, 1H, ArH), 8.59 (dd, *J* 8.3, 1.5, 1H, ArH), 8.68 (d, *J* 8.3, 1H, ArH), 8.74 (d, *J* 8.4, 1H, ArH), 8.92 (AB, 2H, β-pyrrole), 8.94 (AB, 4H, β-pyrrole), 8.96 (AB, *J* 4.6, 2H, β-pyrrole), 9.57 ppm (d, *J* 1.5, 1H, ArH); δ_C(126 MHz, $CDCl_3$) 61.14, 61.26, 120.18, 120.27, 122.30, 122.95, 126.06, 126.69, 127.15, 127.71, 128.48, 128.77, 128.96, 129.78, *ca.* 131.1, 133.40, 134.54, 139.68, 142.10, 144.10, 144.51 ppm; Found: C, 83.68; H, 5.17; N, 6.59. Calc. for $C_{54}H_{38}O_2N_4$: C, 83.70; H, 4.94; N, 7.23%; *m/z* (EI, 80 eV) 775 (61.0%, $[M + 1]^{\bullet +}$), 774 (100%, $[M]^{\bullet +}$), 744 (63.1%, $[M - 2CH_3]^{\bullet +}$); HRMS: $C_{54}H_{38}O_2N_4$ Calc. 774.29948, Found 774.29911; UV/Vis (CH_2Cl_2): λ_{max} [lg (ε/dm^3 mol^{-1} cm^{-1})] 420 (5.60), 515 (4.25), 551 (3.95), 591 (3.73), 646 nm (3.64).

Demethylation of the dimethoxyporphyrins

General procedure. For demethylation 0.1 mmol of the porphyrin was dissolved in 50 mL of dichloromethane and under Ar at −80 °C, 15 mL of BBr_3 was added dropwise (1 h) under vigorous stirring. The reaction mixture was warmed to room temperature, poured onto ice and adjusted to pH 7.0 with $NaHCO_3$. After extraction with dichloromethane the combined extracts were dried over anhydrous sodium sulfate and purified as described below. The oxidation proceeded during the work up on the column.

1-(10,15,20-Triphenylporphyrin-5-yl)phenanthrene-9,10-quinone 1. According to the general procedure 77 mg (0.1 mmol) of the porphyrin **3** were subjected to demethylation. After purification (HPLC, *n*-hexane–ethyl acetate = 85 : 15, v/v, elution time: 6.1 min), followed by recrystallization from methanol–dichloromethane the quinone **1** was obtained as red-brown crystals, 38 mg (51%), mp > 330 °C; δ_H(500 MHz, $CDCl_3$) −2.55 (s, 2H, NH), 7.38 (ddd, *J* 8.1, 7.4, 0.9, 1H, ArH), 7.65 (ddd, *J* 8.1, 7.4, 1.5, 1H, ArH), 7.79–7.69 (m, 9H, *m*- and *p*-phenyl), 7.82 (dd, *J* 8.2, 7.6, 1H, ArH), 8.03 (dd, 1H, ArH), 8.10 (d, *J* 7.6, 1.2, 1H, ArH), 8.12 (d, *J* 8.1, 1H, ArH), 8.20–8.16 (m, 2H, *o*-phenyl), 8.29–8.20 (m, 4H, *o*-phenyl), 8.31 (dd, *J* 8.2, 1.2, 1H, ArH), 8.62 (d, *J* 4.7, 2H, β-pyrrole), 8.78 (d, *J* 4.7, 2H, β-pyrrole), 8.84 ppm (s, 4H, β-pyrrole); δ_C(126 MHz, $CDCl_3$) 118.49, 120.08, 120.15, 124.86, 124.89, 126.53, 126.58, 126.70, 127.59, 127.62, 129.63, 130.07, *ca.* 131.1, 131.19, 131.96, 132.75, 134.52, 136.04, 136.25, 136.46, 136.79, 142.10, 142.22, 146.04, 180.64, 180.74 ppm; *m/z* (EI, 80 eV) 745 (56.7%, $[M + 1]^{\bullet +}$), 744 (100%, $[M]^{\bullet +}$), 728 (8.1%, $[M - O]^{\bullet +}$), 716 (3.0%, $[M - CO]^{\bullet +}$), 149 (11.1%); HRMS: $C_{52}H_{32}O_2N_4$ Calc. 744.25253, Found 744.25279; UV/Vis (CH_2Cl_2): λ_{max} [lg (ε/dm^3 mol^{-1} cm^{-1})] 419 (5.55), 515 (4.19), 550 (3.83), 593 (3.72), 650 nm (3.61).

3-(10,15,20-Triphenylporphyrin-5-yl)phenanthrene-9,10-quinone 5. For synthesis of the quinone **5** 77 mg of the bis-(methyl ether) **7** were demethylated to yield 43 mg (0.06 mmol, 58%) of red-brown crystals after recrystallization from methanol–dichloromethane. HPLC: *n*-hexane–ethyl acetate = 85 : 15, v/v, elution time: 5.0 min; mp > 330 °C, δ_H(500 MHz, $CDCl_3$) −2.77 ppm (s, 2H, NH), 7.46 (ddd, *J* 7.8, 7.0, 1.2, 1H, ArH), 7.59 (ddd, *J* 8.0, 7.0, 1.2, 1H, ArH), 7.81–7.72 (m, 9H, *m*- and *p*-phenyl), 8.01 (d, *J* 8.0, 1H, ArH), 8.21–8.19 (m, 3H, *o*-phenyl), 8.24–8.21 (m, 3H, *o*-phenyl), 8.25 (dd, *J* 7.8, 1.4, 1H, ArH), 8.34 (dd, *J* 7.7, 1.5, 1H, ArH), 8.59 (d, *J* 7.7, 1H, ArH), 8.88 (s, 1H, ArH), 8.93–8.83 ppm (AB, 8H, β-pyrrole); δ_C(126 MHz, $CDCl_3$) 117.32, 120.70, 121.09, 124.26, 126.74, 127.88, 128.89, 129.80, 130.06, 130.25, 130.69, 130.7, 131.56, 134.06, 134.54, 135.45, 135.83, 136.04, 141.85, 141.89, 150.46,

180.36, 180.54 ppm; *m*/*z* (EI, 80 eV) 745 (57.0%, $[M + 1]^{\bullet+}$), 744 (100%, $[M]^{\bullet+}$), 716 (2.2%, $[M - CO]^{\bullet+}$), 358 (12.4%); HRMS: $C_{52}H_{32}O_2N_4$ Calc. 744.25253, Found 744.25243; UV/Vis (CH_2Cl_2): λ_{max} [lg (ε/dm^3 mol^{-1} cm^{-1})] 416 (5.54), 515 (4.24), 555 (3.94), 590 (3.87), 648 nm (3.68).

Preparation of the zinc(II) porphyrins

General procedure. In all cases 0.05 mmol of the free base porphyrin were dissolved in 20 mL of dried dichloromethane and treated with 200 mg of zinc oxide. After the addition of four drops of TFA the reaction mixture turned green. A color change back to red indicated the completion of the reaction. The product was separated from ZnO and most of the TFA by filtration through a short silica column. Remaining traces of TFA were removed by washing with water. After drying with sodium sulfate, the solvent was removed *in vacuo* and the product purified by column chromatography (silica gel, dichloromethane) and HPLC. The reaction was quantitative.

[5-(9,10-Dimethoxyphenanthren-1-yl)-10,15,20-triphenylporphyrinato]zinc(II) 4. HPLC: *n*-hexane–dichloromethane = 1 : 1, v/v; elution time: 6.5 min; mp 255–258 °C; δ_H(500 MHz, $CDCl_3$) 1.72 (s, 3H, OMe), 3.42 (s, 3H, OMe), 7.64 (ddd, H, ArH), 7.68 (dd, 1H, ArH), 7.67–7.77 (m, 9H, *m*- and *p*-phenyl), 7.82 (dd, *J* 8.3, 7.7, 1H, ArH), 8.12 (dd, 1H, ArH), 8.15–8.18 (m, 2H, *o*-phenyl), 8.21–8.18 (m, 1H, *o*-phenyl), 8.24 (dd, 1H, ArH), 8.25–8.29 (m, 3H, *o*-phenyl), 8.71 (d, *J* 4.6, 2H, β-pyrrole), 8.84 (d, *J* 4.6, 2H, β-pyrrole), 8.91 (d, 1H, ArH), 8.95 (AB, 4H, β-pyrrole), 9.08 ppm (dd, *J* 8.3, 1H, ArH); δ_C(126 MHz, $CDCl_3$) 59.04, 60.30, 120.50, 121.02, 121.80, 123.01, 123.10, 123.37, 124.68, 126.06, 126.51, 126.52, 127.06, 127.38, 127.42, 128.54, 128.82, 129.43, 131.17, 131.62, 131.72, 131.89, 134.36, 134.45, 134.58, 135.17, 137.99, 142.85, 142.95, 145.96, 146.19, 149.92, 149.95, 150.14, 150.15 ppm; *m*/*z* (EI, 80 eV) 838 (79.3%, $[M + 2]^{\bullet+}$), 837 (64.9%, $[M + 1]^{\bullet+}$), 836 (100%, $[M]^{\bullet+}$), 806 (26.8%, $[M - 2CH_3]^{\bullet+}$), 790 (26.6%, $[M - 2CH_3 - O]^{\bullet+}$); HRMS: $C_{54}H_{36}O_2N_4Zn$ Calc. 836.2129, Found 836.21258; UV/Vis (CH_2Cl_2): λ_{max} [lg (ε/dm^3 mol^{-1} cm^{-1})] = 422 (5.82), 513 (3.54), 550 (4.26), 589 nm (3.69).

[5-(9,10-Dimethoxyphenanthren-3-yl)-10,15,20-triphenylporphyrinato]zinc(II) 8. HPLC: *n*-hexane–ethyl acetate = 92 : 8, v/v; elution time: 7.6 min; mp 241 °C; δ_H(500 MHz, $CDCl_3$) 4.11 (s, 3H, OMe), 4.17 (s, 3H, OMe), 7.39 (ddd, *J* 8.4, 7.3, 1.2, 1H, ArH), 7.54 (ddd, *J* 8.4, 7.3. 0.8, 1H, ArH), 7.77–7.68 (m, 9H, *m*- and *p*-phenyl), 8.25–8.18 (m, 6H, *o*-phenyl), 8.21 (dd, *J* 8.4, 1.2, 1H, ArH), 8.46 (d, 1H, ArH), 8.50 (dd, 1H, ArH), 8.57 (d, *J* 8.4, 1H, ArH), 8.94 (AB, 2H, β-pyrrole), 8.96 (AB, 6H, β-pyrrole), 9.45 ppm (d, 1H, ArH); δ_C(126 MHz, $CDCl_3$) 61.04, 61.15, 120.02, 121.12, 121.24, 122.17, 122.84, 125.85, 126.54, 126.97, 127.47, 128.21, 128.71, 129.62, 132.03, 132.12, 133.28, 134.40, 140.30, 142.75, 142.77, 143.96, 144.23, 150.21, 150.24, 150.26, 150.40 ppm; *m*/*z* (EI, 80 eV) 838 (8.2%, $[M + 2]^{\bullet+}$), 837 (5.2%, $[M + 1]^{\bullet+}$), 836 (11.5%, $[M]^{\bullet+}$), 806 (16.5%, $[M - 2CH_3]^{\bullet+}$), 792 (100%, $[M - CH_3 - CO]^{\bullet+}$); HRMS: $C_{54}H_{36}O_2N_4Zn$ Calc. 836.2129, Found 836.21299; UV/Vis (CH_2Cl_2): λ_{max} [lg (ε/dm^3 mol^{-1} cm^{-1})] 421 (5.71), 511 (3.48), 548 (4.31), 587 nm (3.64).

[5-(9,10-Dihydro-9,10-dioxophenanthren-1-yl)-10,15,20-triphenylporphyrinato]zinc(II) 2. HPLC: neat dichloromethane; elution time: 11.1 min; mp 283–285 °C; δ_H(500 MHz, $CDCl_3$) 7.38 (dd, *J* 7.6, 7.4, 1H, ArH), 7.77–7.65 (m, 9H, *m*- and *p*-phenyl), 7.78 (ddd, *J* 8.2, 7.4, 1.2, 1H, ArH), 8.00 (dd, 1H, ArH), 8.03 (dd, *J* 7.6, 1.2, 1H, ArH), 8.19–8.11 (m, 2H, *o*-phenyl), 8.26–8.19 (m, 4H, *o*-phenyl), 8.23 (1H, ArH), 8.28 (d, *J* 8.2, 1H, ArH), 8.47 (d, *J* 8.1, 1H, ArH), 8.70 (AB, *J* 4.5, 2H, β-pyrrole), 8.84 (AB, *J* 4.5, 2H, β-pyrrole), 8.90 ppm (AB, 4H, β-pyrrole); δ_C(126 MHz, $CDCl_3$) 119.24, 121.06, 121.15, 124.81, 124.91, 126.35, 126.46, 126.54, 127.37, 129.65, 129.85, 130.11, 131.18, 131.90, 131.96, 132.03, 132.34, 132.83, 134.31, 134.36, 134.49, 136.09, 136.42, 136.47, 142.71, 142.82, 146.94, 148.57, 149.98, 150.20, 180.67, 180.85 ppm; *m*/*z* (EI, 80 eV) 808 (12.2%, $[M + 2]^{\bullet+}$), 807 (8.1%, $[M + 1]^{\bullet+}$), 806 (14.3%, $[M]^{\bullet+}$), 790 (2.9%, $[M - O]^{\bullet+}$), 57 (100%); HRMS: $C_{52}H_{30}O_2N_4Zn$ Calc. 806.16602, Found 806.16603; UV/Vis (CH_2Cl_2): λ_{max} [lg (ε/dm^3 mol^{-1} cm^{-1})] 421 (5.60), 550 (4.32), 590 nm (3.89).

[5-(9,10-Dihydro-9,10-dioxophenanthren-3-yl)-10,15,20-triphenylporphyrinato]zinc(II) 6. HPLC: neat dichloromethane; elution time: 9.3 min; mp > 330 °C; δ_H(500 MHz, $CDCl_3$) 7.44 ppm (ddd, *J* 7.8, 7.0, 1.1, 1H, ArH), 7.55 (ddd, *J* 8.0, 7.0, 1.6, 1H, ArH), 7.80–7.70 (m, 9H, *m*- and *p*-phenyl), 7.99 (d, *J* 8.0, 1H, ArH), 8.23–8.18 (m, 6H, *o*-phenyl), 8.24 (dd, *J* 7.8, 1.6, 1H, ArH), 8.34 (dd, *J* 7.9, 1.5, 1H, ArH), 8.57 (d, *J* 7.9, 1H, ArH), 8.87 (d, *J* 1.5, 1H, ArH), 8.96 (AB, 4H, β-pyrrole), 8.96 (AB, 2H, β-pyrrole), 8.99 ppm (AB, 2H, β-pyrrole); δ_C(126 MHz, $CDCl_3$) 117.85, 121.13, 121.50, 124.14, 126.36, 127.33, 128.39, 129.48, 129.65, 130.18, 130.39, 130.66, 131.48, 131.83, 131.96, 132.31, 133.61, 134.45, 135.61, 135.75, 135.94, 143.03, 148.83, 150.05, 150.17, 150.34, 151.76, 180.37, 180.50; *m*/*z* (EI, 80 eV) 808 (79.0%, $[M + 2]^{\bullet+}$), 807 (62.8%, $[M + 1]^{\bullet+}$), 806 (100%, $[M]^{\bullet+}$), 778 (19.9%, $[M - CO]^{\bullet+}$), 44 (50.2%); HRMS: $C_{52}H_{30}O_2N_4Zn$ Calc. 806.16602, Found 806.16603; UV/Vis (CH_2Cl_2): λ_{max} [lg (ε/dm^3 mol^{-1} cm^{-1})] 418 (5.66), 507 (3.86), 550 (4.31), 594 nm (3.76).

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