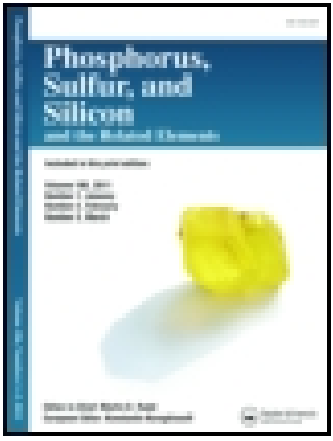

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A Novel and Effective Synthetic Approach to 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) Derivatives

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*DOPO and its derivatives generally exhibit an outstanding performance as flame retardants in various polymers. Starting from trivalent 10-alkoxy-10*H*-9-oxa-10-phosphaphenanthrenes, a broad range of DOPO derivatives was synthesized via transesterification with aliphatic alcohols and subsequent Michaelis-Arbuzov rearrangement using catalytic amounts of* p*-toluenesulfonic acid methylester. Due to the considerable differences in the nature of the alcohols employed, several procedures for processing them are presented.*

Keywords DOPO; flame retardant; Michaelis-Arbuzov rearrangement; transesterification

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INTRODUCTION

Phosphorus is able to form stable compounds with a coordination number ranging from 1 to 6 and an oxidation state of −III to +V. Consequently, organophosphorus compounds are characterized by an unusually large variety of structures and a wide range of uses. They are commonly found in applications for plant protection, pharmaceutics, and flame retardancy.[1,2]

With the increasing use of natural and synthetic polymeric materials and changing legislation regarding their halogen-based alternatives, phosphorus-based flame retardants are gaining increasing attention. In particular, commercially available 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO, Figure 1) and its derivatives were found to exhibit an outstanding performance as flame retardant components in various polymers.[2–4]

Commonly, DOPO derivatives are synthesized by nucleophilic reactions of DOPO on activated double bonds (e.g., acrylics[5]), oxiranes,[6] halides (**1**,[7] **9**[8]), and carbonylic compounds.[9] Besides the increase of applications for DOPO derivatives, limitations of these reactions lead to a high demand for new possibilities of incorporating this compound in larger chemical frameworks.

As recently demonstrated by our group, pentavalent DOPO reacts with trialkyl orthoformates and a large excess of alkyl alcohols under acidic conditions to form trivalent 10-alkoxy-10*H*-9-oxa-10-phosphaphenanthrenes.[10] Alternatively, these compounds can be synthesized via base-catalyzed alcoholysis of trivalent 10-chloro-10*H*-9-oxa-10-phosphaphenanthrene.[11,12]

Generally alkoxy substituted, trivalent phosphorus derivatives (phosphites, phosphinous acid esters, and phosphonous acid diesters) readily undergo transesterification (e.g., trialkylphosphites,[13] methylethylphosphinous acid ethylester,[14] alkylphosphonous acid diethylesters[15]). Transesterification of the phosphonous acid diesters 10-alkoxy-10*H*-9-oxa-10-phosphaphenanthrene with aliphatic alcohols

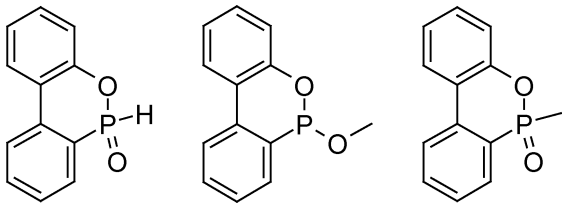


FIGURE 1 DOPO (left), 10-methyl-10*H*-9-oxa-10-phosphaphenanthrene (middle), **1** (right).

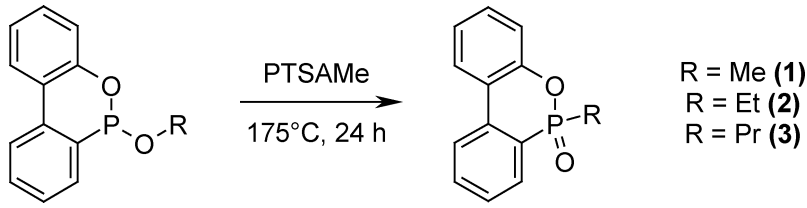
has not been described so far. Combined with a subsequent Michaelis-Arbuzov rearrangement[16] using catalytic amounts of a suitable species (e.g., halides, sulfonates), new opportunities result for the effective synthesis of DOPO-based flame retardants. This rearrangement has already been demonstrated by Chernyshev *et al.* for the conversion of trivalent 10-methoxy-10*H*-9-oxa-10-phosphaphenanthrene into **1** (Figure 1), but only by using an equimolar amount of methyl iodide.[12]

We used these two types of reaction to synthesise a broad range of chemical compounds containing one or more DOPO subunits. Due to the considerable differences in the nature of the alcohols used, several procedures for processing them are presented. Furthermore, in order to prepare an oligomeric DOPO-based flame retardant, a procedure for the synthesis of a 1,3,5-tris-(2-hydroxyethyl) cyanuric acid-based oligomeric compound has been developed.

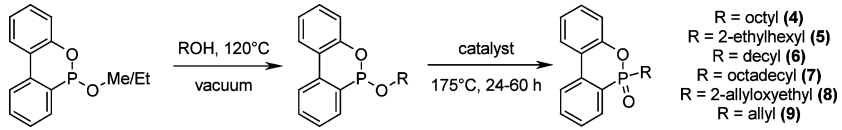
RESULTS AND DISCUSSION

10-Alkyl-9-oxa-10-phosphaphenanthrene-10-oxides **1–3** were synthesised with a purity exceeding 95% starting from the corresponding 10-alkoxy-10*H*-9-oxa-10-phosphaphenanthrenes, which were prepared in a manner recently reported by our group.[10] To obtain absolutely halogen-free products, *p*-toluenesulfonic acid methylester (0.7 mol. %) was used instead of the commonly employed alkylhalides (Scheme 1). The structure of **1** was confirmed by single crystal X-ray diffractometry (Figure 2). The torsion angle between the two aromatic rings in **1** C1-C6-C7-C12 of 13.0° once again reflects the uniqueness of the ring system of unmodified DOPO with a corresponding torsion angle of only 2.7°.[17] This fact and the resulting exceptional chemical properties of DOPO were discussed recently.[10]

For the synthesis of 10-alkyl-9-oxa-10-phosphaphenanthrene-10-oxides **4–9**, a two-step and one-pot procedure (Scheme 2) was adopted using 10-alkoxy-10*H*-9-oxa-10-phosphaphenanthrenes as starting



SCHEME 1 Rearrangement of 10-alkoxy-10*H*-9-oxa-10-phosphaphenanthrenes to form **1**, **2**, and **3**; PTSAMe: *p*-toluenesulfonic acid methylester.



SCHEME 2 Transesterification of 10-ethoxy-10*H*-9-oxa-10-phosphaphenanthrene with various aliphatic monoalcohols and subsequent Michaelis-Arbuzov rearrangement; catalyst for **4**, **6** – **9**: *p*-toluenesulfonic acid methylester, for **5**: 1-bromo-2-ethyl-hexane.

compounds. In the first step, the alkoxy group was replaced by another one via non-catalyzed transesterification with a different aliphatic alcohol, and the released alcohol was removed in situ by vacuum distillation. For this purpose, an excess of the alcohol had to be used with low-boiling alcohols, because otherwise this alcohol would have been removed entirely prior to the completion of the reaction. Furthermore, 10-methoxy-10*H*-9-oxa-10-phosphaphenanthrene was used because of the lower boiling point of methanol compared to that of ethanol and 1-propanol.

With high-boiling alcohols, an equimolar amount of 10-ethoxy-10*H*-9-oxa-10-phosphaphenanthrene was employed (for a short overview of the different procedures applied, see Table I). It is worth mentioning

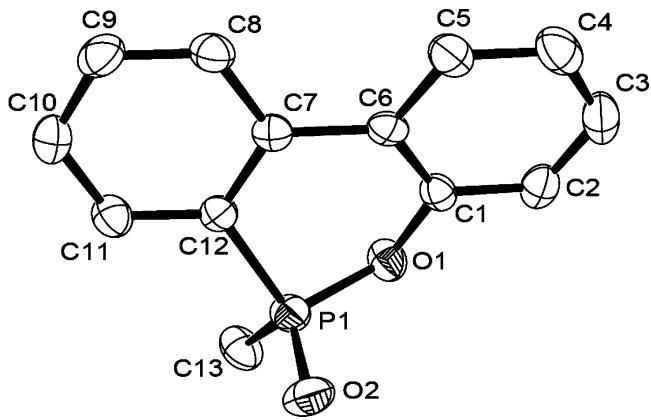


FIGURE 2 Molecular structure of **1** in the crystal; hydrogen atoms are omitted for clarity; selected bond lengths (Å): C13-P1 = 1.753(3), O2-P1 = 1.480(2), P1-C12 = 1.782(2), C7-C12 = 1.404(3), C6-C7 = 1.483(3), C1-C6 = 1.394(3), O1-C1 = 1.400(3), P1-O1 = 1.604(2); selected bond angles (°): O2-P1-C13 = 114.1(1), O2-P1-C12 = 113.1(1), O2-P1-O1 = 114.3(1), O1-P1-C13 = 101.8(1), O1-P1-C12 = 101.8(1), C13-P1-C12 = 110.6(1), C7-C12-P1 = 117.8(2), C12-C7-C6 = 120.9(2), C1-C6-C7 = 121.4(2), C6-C1-O1 = 121.5(2), C1-O1-P1 = 119.7(1).

TABLE I Main Reaction Features Applied for Different Types of Alcohols

Alcohols used	Main reaction features	Synthesised compounds
None	Rearrangement of 10-alkoxy-10*H*-9-oxa-10-Phosphaphenanthrenes[a]	**1–3**
High-boiling monoalcohols	Transesterification with equimolar alcohol	**4-–8**
Low-boiling monoalcohols	Transesterification of 10-methoxy-10*H*-9-oxa-10-Phosphaphenanthrene with excess alcohol	**9**
Well miscible polyalcohols	Longer reaction time for transesterification, Deficit alcohol	**10**–**13**b
Poorly miscible polyalcohols	Higher temperature for transesterification, Deficit alcohol	**14**, **15**

[a]alkoxy = methyl, ethyl, propyl; [b]Michaelis-Arbuzov rearrangement failed for **10** and **11.**

that—as long as the released alcohol could be removed in situ—the specific 10-alkoxy-10*H*-9-oxa-10-phosphaphenanthrene applied for transesterification never appeared to change the reaction progress in a perceivable manner.

In the second step, the resulting intermediates were rearranged in the same way as for the synthesis of **1–3** to yield the products at a purity exceeding 95%. Only when using 2-ethylhexanol to obtain compound **5**, a considerably longer reaction time and larger amounts of catalyst (1-bromo-2-ethylhexane was used to minimise the by-products) were required. The strongly decreased reactivity is attributed to steric hindrance due to the additional alkyl group in β-position.

For the synthesis of compounds **12–15** (Figure 3), procedures similar to those described for the processing of the monoalcohols were adopted. To minimize the by-products arising from the incomplete transesterification of the hydroxy groups within the polyalcohols, the reaction time for this step was extended, and an excess of 10-ethoxy-10*H*-9-oxa-10-phosphaphenanthrene was used and removed after the completion of the reaction by vacuum distillation. Furthermore, the reaction temperature was increased for poorly soluble compounds (e.g., 1,3,5-tris-(2-hydroxyethyl) cyanuric acid and its oligomeric analogue **16**) to achieve a sufficient solubility. The Michaelis-Arbuzov rearrangement was accomplished smoothly and a product purity exceeding 95% was achieved. The

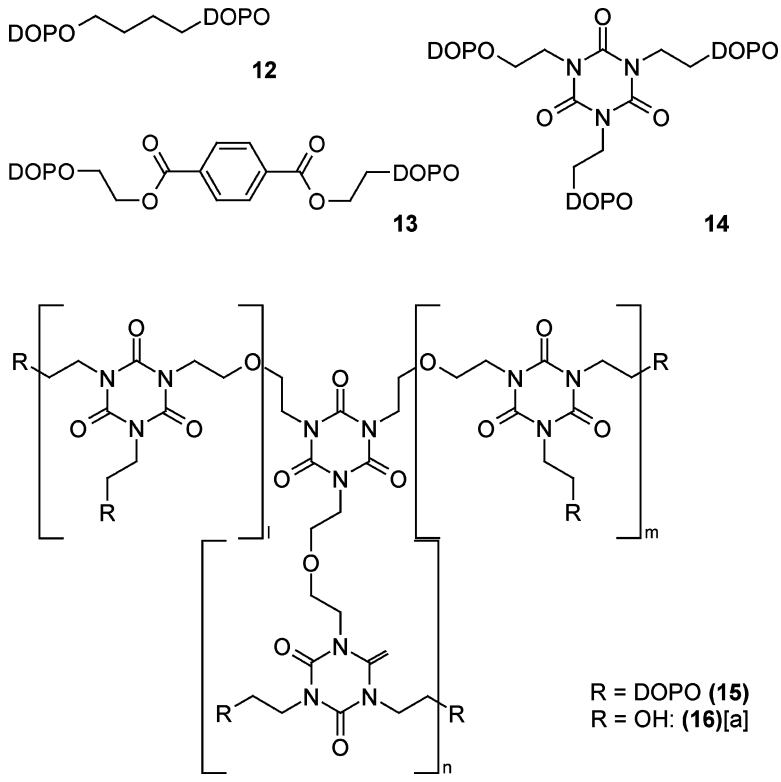
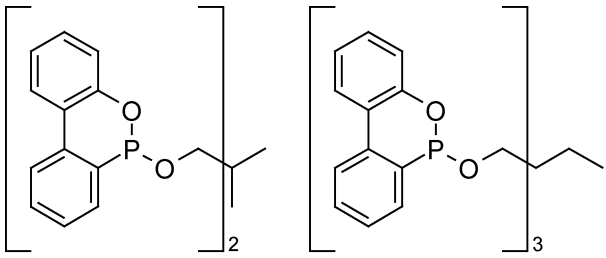


FIGURE 3 Di-, tri-, and oligo-DOPO derivatives **12**–**15**; oligomeric 1,3,5-tris-(2-hydroxyethyl) cyanuric acid **16**; l, m, n = 0, 1, 2. . . ; [a] for reasons of simplicity and relative frequency, secondary branchings are not plotted.

above procedure using *p*-toluenesulfonic acid methylester as a catalyst was applied.

Synthesis of the novel oligomeric 1,3,5-tris-(2-hydroxyethyl) cyanuric acid-based compound **16** (Figure 3) was accomplished with a sulfonate-containing cation exchange resin as a catalyst under heat and vacuum. An immobilised catalyst was chosen, because acidic species strongly interfere with the transesterification reaction and removal can be performed easily in this way. The reaction was monitored by ^{1}H NMR and stopped when the CH/OH ratio reached $\approx$ 7.5 (ratio $_{t=0} = 4$). At this polymerisation level, a maximum chain length of 6 could be detected via ESI. The resulting transesterification and rearrangement product **15** was found to have a maximum chain length of 9 using MALDI.

It was intended to synthesise DOPO-containing flame retardants based on 2,2-dimethyl-1,3-propandiol and trimethylolpropane using



10 **11**

FIGURE 4 Compounds **10** and **11** that could not be rearranged via Michaelis-Arbuzov reaction due to steric hindrance.

the approach presented here. Transesterification was accomplished smoothly when applying the procedures for readily soluble polyols to yield **10** and **11** (Figure 4) at a purity exceeding 95%. Michaelis-Arbuzov rearrangement with these compounds failed; **10** was left completely unaffected and **11** was largely destroyed. This is attributed to steric hindrance, which is even larger than in the precursor of **5** and which is caused by the quaternary carbon atom in β-position.

CONCLUSIONS

A novel and effective synthetic approach to 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide derivatives was presented. A broad range of chemical compounds containing one or more DOPO subunits was synthesized starting from aliphatic alcohols. Their large multitude and diversity, in combination with the method presented herein, result in a large number of alternatives to design such compounds in terms of synthetic effort or chemical, physical, processing, and flame-retardant properties.

In the course of the reaction DOPO subunits were introduced at the hydroxy groups and due to the considerable differences in the nature of the alcohols used, several procedures for processing them were applied and presented. The only limitations encountered concerned the steric hindrance arising from β-branching of the aliphatic alcohols, which makes difficult or completely inhibits the Michaelis-Arbuzov rearrangement of the trivalent 10-alkoxy-10*H*-9-oxa-10-phosphaphenanthrene intermediates. It is assumed that α-branching restricts Michaelis-Arbuzov rearrangement to an even larger extent.

EXPERIMENTAL

Infrared spectra (IR) were obtained using a Perkin-Elmer system 2000 FT-IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker AC-250 instrument using tetramethylsilane and trimethylphosphate[18] as internal standards. Elemental analysis was performed with a Vario EL III instrument from Elementar Analysensysteme GmbH. Electron impact mass spectrometry (MS) was accomplished with a Finnigan MAT-4000-1 spectrometer. Electron spray ionisation mass spectrometry (ESI) was carried out with a Hewlett-Packard LC-MSD 1100 instrument. Matrix-assisted laser desorption/ionisation mass spectrometry (MALDI) was performed with an Applied Biosystems Voyager DE-STR instrument. Melting points were obtained with a Büchi B-545 apparatus at a heating rate of 3°C/min. Purity of the compounds was determined by ^{1}H and ^{31}P NMR spectroscopy.

X-ray diffractometry (XRD) was performed using a Siemens SMART CCD 1000 diffractometer with an irradiation time of 10 s to 20 s per frame, thus collecting a full sphere of data using an ω-scan technique with $\Delta\omega$ ranging from 0.3 to 0.45°. For searches relating to single-crystal X-ray diffraction data, the Cambridge Structural Database was used.[19] Data were corrected for polarization and Lorentz effects, and an experimental absorption correction was performed with SADABS.[20] SHELX-97[21] was used for the structure refinement, for graphical evaluation and visualisation of the data XPMA[22] and ORTEP-3[23] were used.

Structures with more than one DOPO subunits were considered too complex to be denominated correctly according to IUPAC and just referred to by their numbers.

Synthesis of Compounds 1—3: General Procedure

10-Alkoxy-10*H*-9-oxa-10-phosphaphenanthrene [1 mol; R = Me (230.1 g), Et (244.1 g), Pr (258.1 g)] and *p*-toluenesulfonic acid methylester (7 mmol, 1.06 mL) were stirred under argon for 24 h at 175°C to yield the corresponding clear, glassy 10-alkyl-9-oxa-10-phosphaphenanthrene-10-oxide (**1–3**) in a purity exceeding 95%. Recrystallization from ethanol.

Compound 1

M.p. 131°C (lit: 124–6°C[7]). $\text{Anal}_{\text{found}}$: C, 68.67; H, 4.79%. $\text{Anal}_{\text{calc}}(C_{13}H_{11}O_2P)$: C, 67.83; H, 4.82%. MS (70 eV): m/z = 230, 215, 168. IR (KBr): 3059, 2981, 2919, 1606, 1595, 1581, 1560, 1477, 1446, 1431, 1308, 1272, 1226, 1205, 1171, 1147, 1118 cm^{-1}. ^{1}H NMR ($CDCl_3$):

δ = 1.78 (d, J_{PH} = 14.6 Hz, 3H, CH_3), 7.18 (d, J_{HH} = 8.1 Hz, 1H, O–C–CH), 7.19 (t, J_{HH} = 7.2 Hz, 1H, –O–C–C–CH–C<u>H</u>), 7.32 (t, J_{HH} = 7.6 Hz, 1H, O–C–CH–C<u>H</u>), 7.45 (td, J_{HH} = 7.5 Hz, J_{PH} = 3.0 Hz, 1H, P–C–CH–C<u>H</u>), 7.63 (t, J_{HH} = 7.8 Hz, 1H, P–C–C–CH–C<u>H</u>), 7.81 (dd, J_{HH} = 7.3 Hz, J_{PH} = 13.0 Hz, 1H, P–C–CH), 7.85 (d, J_{HH} = 7.7 Hz, 1H, O–C–C–CH), 7.89 (dd, J_{HH} = 8.9 Hz, J_{PH} = 4.7 Hz, 1H, P–C–C–CH). ^{13}C NMR ($CDCl_3$): δ = 14.6 (J_{PC} = 100.3 Hz, CH_3), 120.3 (J_{PC} = 5.9 Hz, O–C–<u>C</u>H), 122.3 (J_{PC} = 11.3 Hz, O–C–<u>C</u>), 123.7 (J_{PC} = 9.5 Hz, P–C–C–<u>C</u>H), 124.5 (O–C–C–CH–<u>C</u>H), 125.0 (O–C–C–<u>C</u>H), 125.6 (J_{PC} = 123.4 Hz, P–C), 128.3 (J_{PC} = 13.6 Hz, P–C–CH–<u>C</u>H), 129.2 (J_{PC} = 11.5 Hz, P–C–<u>C</u>H), 130.4 (O–C–CH–<u>C</u>H), 132.9 (J_{PC} = 2.3 Hz, P–C–C–CH–<u>C</u>H), 134.9 (J_{PC} = 5.9 Hz, P–C–<u>C</u>), 148.8 (J_{PC} = 8.0 Hz, O-C). ^{31}P NMR ($CDCl_3$): δ = 36.0. XRD: T = 200(2) K, λ(Mo Kα) = 0.71073 Å, crystal system = monoclinic, space group = P2(1)/n (No. 14), a = 8.4590(18) Å, b = 11.807(3) Å, c = 10.853(2) Å, β = 92.150(3)°, volume = 1083.2(4) Å^3, Z = 4, D_{calc} = 1.412 g.cm^{-3}, μ(Mo-K$_\alpha$) = 0.233 mm^{-1}, F(000) = 480, crystal size = 0.15 × 0.05 × 0.05 mm^3, θ range = 2.55° to 28.46°, hkl range = −11/11; −15/14; −14/14, reflections collected = 10488, unique reflections = 2703, R_{int} = 0.1061, reflections observed (I > 2σ) = 1361, parameters refined = 149, goodness-of-fit on F^2 = 0.854, $(\Delta p)_{max,min}$ = 0.235 and −0.285 e.Å^{-3}, final R indices (I > 2σ): R_1 = 0.0455; wR_2 = 0.0911, R indices (all data): R_1 = 0.1196; wR_2 = 0.1092.

Compound 2

M.p. 105°C. $Anal_{found}$: C, 69.80; H, 5.33%. $Anal_{calc}$($C_{14}H_{13}O_2P$): C, 68.85; H, 5.37 %. MS (70 eV): m/z = 244, 216, 215, 168. IR (KBr): 3064, 2979, 2936, 1604, 1595, 1580, 1558, 1479, 1445, 1431, 1379, 1287, 1273, 1239, 1209, 1169, 1145, 1118 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.11 (td, J_{HH} = 7.7 Hz, J_{PH} = 19.5 Hz, 3H, CH_3), 2.04 (qd, J_{HH} = 7.7 Hz, J_{PH} = 15.2 Hz, 2H, CH_2), 7.18 (d, J_{HH} = 8.1 Hz, 1H, O–C–CH), 7.19 (t, J_{HH} = 7.0 Hz, 1H, O–C–C–CH–C<u>H</u>), 7.33 (t, J_{HH} = 7.5 Hz, 1H, O–C–CH–C<u>H</u>), 7.46 (td, J_{HH} = 7.5 Hz, J_{PH} = 2.9 Hz, 1H, P–C–CH–C<u>H</u>), 7.64 (t, J_{HH} = 7.7 Hz, 1H, P–C–C–CH–C<u>H</u>), 7.82 (dd, J_{HH} = 7.5 Hz, J_{PH} = 12.6 Hz, 1H, P–C–CH), 7.87 (d, J_{HH} = 8.8 Hz, 1H, O–C–C–CH), 7.92 (dd, J_{HH} = 8.4 Hz, J_{PH} = 5.0 Hz, 1H, P–C–C–CH). ^{13}C NMR ($CDCl_3$): δ = 5.7 (J_{PC} = 5.7 Hz, CH_3), 21.6 (J_{PC} = 98.6 Hz, CH_2), 120.2 (J_{PC} = 5.9 Hz, O–C–<u>C</u>H), 122.1 (J_{PC} = 10.7 Hz, O–C–<u>C</u>), 123.7 (J_{PC} = 9.3 Hz, P–C–C–<u>C</u>H), 124.1 (J_{PC} = 118.2 Hz, P-C), 124.3 (O–C–C–CH–<u>C</u>H), 125.0 (O–C–C–<u>C</u>H), 128.2 (J_{PC} = 13.2 Hz, P–C–CH–<u>C</u>H), 129.8 (J_{PC} = 11.0 Hz, P–C–<u>C</u>H), 130.4 (O–C–CH–<u>C</u>H), 133.0 (J_{PC} = 2.3 Hz, P–C–C–CH–<u>C</u>H), 135.5 (J_{PC} = 5.8 Hz, P-C-<u>C</u>), 149.1 (J_{PC} = 8.3 Hz, O-C). ^{31}P NMR ($CDCl_3$): δ = 40.6.

Compound 3

M.p. 108°C. $Anal_{found}$: C, 70.48; H, 5.80%. $Anal_{calc}(C_{15}H_{15}O_2P)$: C, 69.76; H, 5.85 %. MS (70 eV): m/z = 258, 230, 216, 215, 168. IR (KBr): 3051, 2966, 2929, 2876, 1606, 1595, 1583, 1558, 1479, 1445, 1429, 1381, 1345, 1302, 1273, 1252, 1225, 1203, 1164, 1138 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0.95$ (t, $J_{HH} = 7.3$ Hz, 3H, CH_3), 1.49–1.71 (m, 2H, CH_3-C$\underline{H}_2$), 1.90–2.07 (m, 2H, P-CH_2), 7.17 (d, $J_{HH} = 7.7$ Hz, 1H, O–C–CH), 7.18 (t, $J_{HH} = 7.6$ Hz, 1H, O–C–C–CH–C$\underline{H}$), 7.32 (t, $J_{HH} = 7.6$ Hz, 1H, O–C–CH–C$\underline{H}$), 7.45 (td, $J_{HH} = 7.5$ Hz, $J_{PH} = 2.9$ Hz, 1H, P–C–CH–C$\underline{H}$), 7.63 (t, $J_{HH} = 7.7$ Hz, 1H, P–C–C–CH–C$\underline{H}$), 7.81 (dd, $J_{HH} = 7.2$ Hz, $J_{PH} = 12.3$ Hz, 1H, P–C–CH), 7.85 (d, $J_{HH} = 8.1$ Hz, 1H, O–C–C–CH), 7.90 (dd, $J_{HH} = 8.3$ Hz, $J_{PH} = 4.8$ Hz, 1H, P–C–C–CH). ^{13}C NMR ($CDCl_3$): $\delta = 15.1$ ($J_{PC} = 16.3$ Hz, CH_3), 15.3 ($J_{PC} = 4.4$ Hz, CH_3-$\underline{C}H_2$), 30.4 ($J_{PC} = 96.5$ Hz, P-CH_2), 120.2 ($J_{PC} = 6.0$ Hz, O-C-$\underline{C}$H), 122.1 ($J_{PC} = 10.9$ Hz, O–C–$\underline{C}$), 123.7 ($J_{PC} = 9.3$ Hz, P–C–C–$\underline{C}$H), 124.3 (O–C–C–CH–$\underline{C}$H), 124.6 ($J_{PC} = 118.0$ Hz, P–C), 125.0 (O–C–C–$\underline{C}$H), 128.2 ($J_{PC} = 13.1$ Hz, P–C–CH–$\underline{C}$H), 129.8 ($J_{PC} = 10.9$ Hz, P–C–$\underline{C}$H), 130.3 (O–C–CH–$\underline{C}$H), 132.9 ($J_{PC} = 2.3$ Hz, P–C–C–CH–$\underline{C}$H), 135.4 ($J_{PC} = 5.9$ Hz, P–C–$\underline{C}$), 149.1 ($J_{PC} = 8.2$ Hz, O–C). ^{31}P NMR ($CDCl_3$): $\delta = 39.1$.

Synthesis of Compounds 4–8—General Procedure

10-Ethoxy-10*H*-9-oxa-10-phosphaphenanthrene (1 mol, 230.1 g) and the respective alcohol [1 mol, 1-octanol (157.5 mL), 2-ethyl-1-hexanol (156.3 mL), 1-decanol (190.9 mL), 1-octadecanol (270.5 g), 2-allyloxyethanol (106.9 mL)] were stirred intensely at 120°C. Pressure was slowly decreased down to ≈10 mbar—keeping the reaction mixture boiling gently. When boiling was not noticed any longer, temperature and pressure were kept at 120°C and ≈10 mbar, respectively, for another 3 h. The reaction vessel was charged with argon, *p*-toluenesulfonic acid methylester [precursor of **4**, **6**–**8**, 7 mmol, 1.06 mL] or 1-bromo-2-ethylhexane (precursor of **5**, 50 mmol, 8.89 mL) was added, the temperature was increased to 175°C, and kept for another 24 h (precursor of **4**, **6**–**8**) or 60 h (precursor of **5**), respectively, to yield the corresponding clear 10-alkyl-9-oxa-10-phosphaphenanthrene-10-oxide (**4** oily liquid, **5** oily liquid, **6** oily liquid, **7** glassy substance, **8** oily liquid) in a purity exceeding 95%. Recrystallization of **7** from hexane.

Compound 4

$Anal_{found}$: C, 74.65; H, 7.90%. $Anal_{calc}(C_{20}H_{25}O_2P)$: C, 73.15; H, 7.67%. MS (70 eV): m/z = 328, 243, 230, 216, 215, 168. IR (film): 3064,

2953, 2927, 2855, 1606, 1595, 1582, 1560, 1477, 1448, 1432, 1296, 1275, 1252, 1235, 1207, 1147, 1119 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 0.81$ (t, $J_{HH} =$ 6.5 Hz, 3H, CH_3), 1.04–1.41 (m, 10H, CH_3-($C\underline{H}_2$)$_5$), 1.47–1.68 (m, 2H, P-CH_2-$C\underline{H}_2$), 1.91–2.14 (m, 2H, P-CH_2), 7.18 (d, $J_{HH} = 7.7$ Hz, 1H, O–C–CH), 7.19 (t, $J_{HH} = 7.4$ Hz, 1H, O–C–C–CH–C$\underline{H}$), 7.33 (t, $J_{HH} =$ 7.6 Hz, 1H, O–C–CH–C$\underline{H}$), 7.46 (td, $J_{HH} = 7.4$ Hz, $J_{PH} = 2.8$ Hz, 1H, P–C–CH–C$\underline{H}$), 7.64 (t, $J_{HH} = 7.7$ Hz, 1H, P–C–C–CH–C$\underline{H}$), 7.82 (dd, $J_{HH} = 7.2$ Hz, $J_{PH} = 12.4$ Hz, 1H, P–C–CH), 7.86 (d, $J_{HH} = 7.9$ Hz, 1H, O–C–C–CH), 7.91 (dd, $J_{HH} = 8.2$ Hz, $J_{PH} = 4.9$Hz, 1H, P-C-C-CH). ^{13}C NMR ($CDCl_3$): $\delta = 13.8$ (CH_3), 21.3 ($J_{PC} = 4.6$ Hz, P-CH_2-$\underline{C}H_2$), 22.3 (CH_2), 28.2 ($J_{PC} = 96.6$ Hz, P-CH_2), 28.59 (CH_2), 28.62 (CH_2), 30.2 ($J_{PC} =$ 15.4 Hz, P-CH_2-CH_2-$\underline{C}H_2$), 31.4 (CH_2), 120.0 ($J_{PC} = 5.9$Hz, O-C-$\underline{C}$H), 122.0 ($J_{PC} = 10.7$Hz, O-C-$\underline{C}$), 123.6 ($J_{PC} = 9.3$ Hz, P–C–C–$\underline{C}$H), 124.2 (O–C–C–CH-$\underline{C}$H), 124.5 ($J_{PC} = 118.0$ Hz, P-C), 124.8 (O-C-C-$\underline{C}$H), 128.0 ($J_{PC} = 13.1$ Hz, P–C–CH-$\underline{C}$H), 129.6 ($J_{PC} = 10.9$ Hz, P–C–$\underline{C}$H), 130.2 (O–C–CH–$\underline{C}$H), 132.8 ($J_{PC} = 2.3$ Hz, P–C–C–CH–$\underline{C}$H), 135.2 ($J_{PC} = 6.0$ Hz, P–C–$\underline{C}$), 148.9 ($J_{PC} = 8.3$ Hz, O–C). ^{31}P NMR ($CDCl_3$): $\delta = 39.2$.

Compound 5

$Anal_{found}$: C, 74.07; H, 7.73%. $Anal_{calc}(C_{20}H_{25}O_2P)$: C, 73.15; H, 7.67%. MS (70 eV): m/z = 328, 299, 271, 230, 216, 215, 168. IR (film): 3067, 3065, 2959, 2931, 2872, 1607, 1595, 1583, 1559, 1476, 1457, 1448, 1432, 1399, 1380, 1275, 1255, 1236, 1205, 1147, 1118 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta =$ 0.66–0.90 (m, 8H), 1.02–1.26 (m, 4H), 1.26–1.50 (m, 4H), 1.74–2.00 (m, 3H, P-CH_2, CH_2-C$\underline{H}$), 7.10–7.25 (m, 2H, O-C-CH, O–C–C–CH–C$\underline{H}$), 7.33 (t, $J_{HH} = 7.5$ Hz, 1H, O–C–CH–C$\underline{H}$), 7.46 (td, $J_{HH} = 7.5$ Hz, $J_{PH} = 2.5$ Hz, 1H, P–C–CH–C$\underline{H}$), 7.64 (t, $J_{HH} = 7.5$ Hz, 1H, P–C–C–CH–C$\underline{H}$), 7.78–7.96 (m, 3H, P–C–CH, O–C–C–CH, P-C-C-CH). ^{13}C NMR ($CDCl_3$): $\delta =$ 10.2, 10.3 (CH-CH_2-$\underline{C}H_3$), 13.9 (CH_2-CH_2-$\underline{C}H_3$), 22.60, 22.65 (CH_2-$\underline{C}H_2$-CH_3), 26.8, 27.0 ($J_{CP} = 24.4$ Hz, CH-$\underline{C}H_2$-CH_3), 28.1, 28.2 ($\underline{C}H_2$-CH_2-CH_3), 32.4, 32.5 ($J_{CP} = 95.0$ Hz, P–CH_2), 33.4–33.8 (m, CH-$\underline{C}H_2$-CH_2, CH_2-C$\underline{H}$), 120.3 ($J_{PC} = 5.7$ Hz, O–C–$\underline{C}$H), 122.3 ($J_{PC} = 10.7$ Hz, O–C–$\underline{C}$), 123.6 ($J_{PC} = 9.5$ Hz, P–C–C–$\underline{C}$H), 124.3 (O–C–C–CH–$\underline{C}$H), 125.0 (O–C–C–$\underline{C}$H), 125.5, 125.6 ($J_{PC} = 116.7$ Hz, P–C), 128.2 ($J_{PC} = 12.8$ Hz, P–C–CH–$\underline{C}$H), 123.0 ($J_{PC} = 10.3$ Hz, P–C–$\underline{C}$H), 130.4 (O–C–CH–$\underline{C}$H), 132.9 ($J_{PC} =$ 2.3 Hz, P–C–C–CH–$\underline{C}$H), 135.4 ($J_{PC} = 6.3$ Hz, P–C–$\underline{C}$), 149.3 ($J_{PC} =$ 8.2 Hz, O–C). ^{31}P NMR ($CDCl_3$): $\delta = 39.4$, 39.6.

Compound 6

$Anal_{found}$: C, 74.50; H, 8.34%. $Anal_{calc}(C_{22}H_{29}O_2P)$: C, 74.13; H, 8.20%. MS (70 eV): m/z = 356, 243, 230, 216, 215, 168. IR (film):

3065, 2925, 2854, 1607, 1595, 1583, 1560, 1477, 1448, 1432, 1255, 1235, 1208, 1148, 1119 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.87 (t, J_{HH} = 6.6Hz, 3H, CH_3), 1.07–1.43 (m, 14H, CH_3-($C\underline{H}_2$)$_7$), 1.49–1.72 (m, 2H, P-CH_2-$C\underline{H}_2$), 1.92–2.12 (m, 2H, P-CH_2), 7.13-7.24 (m, 2H, O–C–CH, O–C–C–CH–C<u>H</u>), 7.32 (t, J_{HH} = 7.6 Hz, 1H, O–C–CH–C<u>H</u>), 7.46 (td, J_{HH} = 7.4 Hz, J_{PH} =2.6 Hz, 1H, P–C–CH–C<u>H</u>), 7.62 (t, J_{HH} = 7.7 Hz, 1H, P–C–C–CH–C<u>H</u>), 7.81-7.94 (m, 3H, P–C–CH, O–C–C–CH, P–C–C–CH). ^{13}C NMR ($CDCl_3$): δ = 13.5 (CH_3), 21.0 (J_{PC} = 4.6 Hz, P–CH_2-$\underline{C}H_2$), 22.0 (CH_2), 27.9 (J_{PC} = 97.1 Hz, P-CH_2), 28.4 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 28.9 (CH_2), 29.9 (J_{PC} = 15.4 Hz, P-CH_2-CH_2-$\underline{C}H_2$), 31.2 (CH_2), 119.7 (J_{PC} = 5.9 Hz, O–C–<u>C</u>H), 121.7 (J_{PC} = 10.8 Hz, O–C–<u>C</u>), 123.3 (J_{PC} = 9.3 Hz, P–C–C–<u>C</u>H), 123.9 (O–C–C–CH–<u>C</u>H), 124.2 (J_{PC} = 118.1 Hz, P-C), 124.6 (O–C–C–<u>C</u>H), 127.7 (J_{PC} = 13.1 Hz, P–C–CH–<u>C</u>H), 129.3 (J_{PC} = 10.9 Hz, P–C–<u>C</u>H), 129.9 (O–C–CH–<u>C</u>H), 132.5 (J_{PC} = 2.2 Hz, P–C–C–CH–<u>C</u>H), 134.9 (J_{PC} = 5.9 Hz, P–C–<u>C</u>), 148.6 (J_{PC} = 8.2 Hz, O–C). ^{31}P NMR ($CDCl_3$): δ = 39.2.

Compound 7

M.p. 59—61°C. $Anal_{found}$: C, 77.17; H, 9.96%. $Anal_{calc}$($C_{30}H_{45}O_2P$): C, 76.88; H, 9.68%. MS (70 eV): m/z = 468, 243, 230, 216, 215, 168. IR (KBr): 2953, 2918, 2850, 1606, 1594, 1581, 1560, 1477, 1467, 1445, 1432, 1401, 1378, 1275, 1259, 1249, 1231, 1203, 1146, 1120 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.85 (t, J_{HH} = 6.5 Hz, 3H, CH_3), 1.07–1.42 (m, 30H, CH_3-($C\underline{H}_2$)$_{15}$), 1.47–1.69 (m, 2H, P-CH_2-$C\underline{H}_2$), 1.93–2.12 (m, 2H, P-CH_2), 7.19 (d, J_{HH} = 7.8 Hz, 1H, O-C-CH), 7.21 (t, J_{HH} = 7.4 Hz, 1H, O–C–C–CH–C<u>H</u>), 7.34 (t, J_{HH} = 7.5 Hz, 1H, O–C–CH–C<u>H</u>), 7.47 (td, J_{HH} = 7.4 Hz, J_{PH} = 2.8 Hz, 1H, P–C–CH–C<u>H</u>), 7.65 (t, J_{HH} = 7.7 Hz, 1H, P–C–C–CH–C<u>H</u>), 7.84 (dd, J_{HH} = 6.8 Hz, J_{PH} = 11.0 Hz, 1H, P–C–CH), 7.88 (d, J_{HH} = 7.0 Hz, 1H, O–C–C–CH), 7.92 (dd, J_{HH} = 8.4 Hz, J_{PH} = 4.9 Hz, 1H, P–C–C–CH). ^{13}C NMR ($CDCl_3$): δ = 14.0 (CH_3), 21.5 (J_{PC} = 4.7 Hz, P–CH_2–$\underline{C}H_2$), 22.6 (CH_2), 28.4 (J_{PC} = 96.8 Hz, P-CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 29.5-29.7 (m, CH_2), 30.4 (J_{PC} = 15.6 Hz, P–CH_2–CH_2–$\underline{C}H_2$), 31.8 (CH_2), 120.3 (J_{PC} = 6.0 Hz, O–C–<u>C</u>H), 122.2 (J_{PC} = 10.8 Hz, O–C–<u>C</u>), 123.7 (J_{PC} = 9.2 Hz, P–C–C–<u>C</u>H), 124.4 (O–C–C–CH–<u>C</u>H), 124.7 (J_{PC} = 118.0 Hz, P-C), 125.0 (O-C-C-<u>C</u>H), 128.2 (J_{PC} = 13.1 Hz, P–C–CH–<u>C</u>H), 129.8 (J_{PC} = 10.9 Hz, P–C–<u>C</u>H), 130.4 (O–C–CH–<u>C</u>H), 133.0 (J_{PC} = 2.3 Hz, P–C–C–CH–<u>C</u>H), 135.5 (J_{PC} = 5.9 Hz, P–C–<u>C</u>), 149.2 (J_{PC} = 8.2 Hz, O–C). ^{31}P NMR ($CDCl_3$): δ = 39.2.

Compound 8

$Anal_{found}$: C, 67.39; H, 5.60%. $Anal_{calc}$($C_{17}H_{17}O_3P$): C, 68.00; H, 5.71%. MS (70 eV): m/z = 300, 216, 215, 168. IR (film): 3066, 2867,

1606, 1595, 1583, 1559, 1477, 1448, 1432, 1254, 1236, 1208, 1147, 1119 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.39$ (td, $J_{HH} = 7.0$ Hz, $J_{PH} = 14.3$ Hz, 2H, P–CH_2), 3.59–3.77 (m, 2H, P–CH_2–$C\underline{H}_2$), 3.80 (d, $J_{HH} = 5.6$ Hz, 2H, C$\underline{H}$–CH=CH_2), 5.01–5.18 (m, 2H, CH=C$\underline{H}_2$), 5.61–5.81 (m, 1H, C$\underline{H}$=CH_2), 7.17 (d, J_{HH} =7.8 Hz, 1H, O–C–CH), 7.18 (t, $J_{HH} = 7.7$ Hz, 1H, O–C–C–CH–C$\underline{H}$), 7.31 (t, $J_{HH} = 7.6$ Hz, 1H, O–C–CH–C$\underline{H}$), 7.45 (td, $J_{HH} = 7.5$ Hz, $J_{PH} = 3.0$ Hz, 1H, P–C–CH–C$\underline{H}$), 7.63 (t, $J_{HH} = 7.7$ Hz, 1H, P–C–C–CH–C$\underline{H}$), 7.82-7.95 (m, 3H, P–C–CH, O–C–C–CH, P–C–C–CH). ^{13}C NMR ($CDCl_3$): $\delta = 29.8$ ($J_{PC} = 96.4$ Hz, P-CH_2), 63.0 ($J_{PC} = 1.9$ Hz, P-CH_2-$\underline{C}H_2$), 71.6 ($\underline{C}H_2$-CH=CH_2), 117.0 (CH=$\underline{C}H_2$), 120.1 ($J_{PC} = 6.1$ Hz, O–C–$\underline{C}$H), 121.9 ($J_{PC} = 11.0$ Hz, O–C–$\underline{C}$), 123.5 ($J_{PC} = 9.7$ Hz, P–C–C–$\underline{C}$H), 124.4 (O–C–C–CH-$\underline{C}$H), 124.4 ($J_{PC} = 121.6$ Hz, P-C), 124.9 (O–C–C–$\underline{C}$H), 128.2 ($J_{PC} = 13.6$ Hz, P–C–CH–$\underline{C}$H), 130.1 ($J_{PC} = 11.3$ Hz, P–C–$\underline{C}$H), 130.3 (O–C–CH–$\underline{C}$H), 133.0 ($J_{PC} = 2.4$ Hz, P-C-C-CH-$\underline{C}$H), 133.8 ($\underline{C}$H=CH_2), 135.2 ($J_{PC} = 6.3$ Hz, P–C–$\underline{C}$), 148.8 ($J_{PC} = 8.3$ Hz, O-C). ^{31}P NMR ($CDCl_3$): $\delta = 36.6$.

10-Allyl-9-oxa-10-phosphaphenanthrene-10-oxide (9)

10-Methoxy-10*H*-9-oxa-10-phosphaphenanthrene (0.175 mol, 40.3 g) and allyl alcohol (0.175 mol, 12.0 mL) were stirred for 6 h under argon at 120°C in a 100 mL flask equipped with a Vigreux column (200 mm height, 14 mm diameter) and a Liebig chiller. Every hour, the removed distillate was replaced by the same volume of allyl alcohol. Subsequently, ≈10 mbar were applied for 5 min to remove volatile compounds and the apparatus was filled with argon again. Another 1.2 mL of allyl alcohol were added, the reaction mixture stirred for another 3 h, ≈10 mbar were applied for 5 min to remove volatile compounds, and the apparatus filled with argon again; this procedure was repeated once. *p*-Toluenesulfonic acid methylester [1 mmol, 0.15 mL] was added and the reaction mixture stirred for 16 h at 160°C. Recrystallisation from toluene/cyclohexane = 1:1 gave white crystals of **9** with a purity exceeding 95%. Yield: 33.2 g (74%). Mp: 106°C (lit: 102 - 3°C[8]). $Anal_{found}$: C, 70.59; H, 5.20 %. $Anal_{calc}(C_{15}H_{13}O_2P)$: C, 70.31; H, 5.11 %. MS (70 eV): m/z = 256, 216, 215, 168. IR (KBr): 3083, 3054, 3008, 2959, 2887, 1635, 1608, 1595, 1582, 1559, 1479, 1443, 1421, 1394, 1303, 1296, 1273, 1249, 1219, 1199, 1162, 1137 cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 2.88$ (dd, $J_{HH} = 7.5$ Hz, $J_{PH} = 17.8$ Hz, 2H, P-CH_2), 4.97–5.16 (m, 2H, CH=C$\underline{H}_2$), 5.59–5.81 (m, 1H, C$\underline{H}$=CH_2), 7.18 (d, $J_{HH} = 8.4$ Hz, 1H, O–C–CH), 7.20 (t, $J_{HH} = 8.2$ Hz, 1H, O–C–C–CH–C$\underline{H}$), 7.33 (t, $J_{HH} = 7.6$ Hz, 1H, O–C–CH–C$\underline{H}$), 7.46 (td, $J_{HH} = 7.5$ Hz, $J_{PH} = 3.0$ Hz, 1H, P–C–CH–C$\underline{H}$), 7.65 (t, $J_{HH} = 7.8$ Hz, 1H, P–C–C–CH–C$\underline{H}$), 7.84 (dd, $J_{HH} = 7.6$ Hz, $J_{PH} = 12.7$ Hz, 1H, P–C–CH), 7.87 (d, J_{HH} =

7.3 Hz, 1H, O–C–C–CH), 7.91 (dd, J_{HH} = 8.1 Hz, J_{PH} = 4.9 Hz, 1H, P–C–C–CH). ^{13}C NMR ($CDCl_3$): δ = 34.6 (J_{PC} = 94.3 Hz, P-CH_2), 120.2 (J_{PC} = 6.2 Hz, O–C–CH), 121.0 (J_{PC} = 13.2 Hz, CH=CH_2), 122.0 (J_{PC} = 10.9 Hz, O-C-C), 123.6 (J_{PC} = 9.7 Hz, P–C–C–CH), 123.9 (J_{PC} = 120.1 Hz, P-C), 124.4 (O–C–C–CH–CH), 125.0 (O–C–C–CH), 125.9 (J_{PC} = 10.2 Hz, CH=CH_2), 128.2 (J_{PC} = 13.2 Hz, P–C–CH–CH), 130.2 (J_{PC} = 10.5 Hz, P–C–CH), 130.4 (O–C–CH–CH), 133.2 (J_{PC} = 2.4 Hz, P–C–C–CH–CH), 135.6 (J_{PC} = 6.1 Hz, P-C-C), 149.2 (J_{PC} = 8.6 Hz, O-C). ^{31}P NMR ($CDCl_3$): δ = 34.4.

Synthesis of Compounds 10—13—General Procedure

10-Ethoxy-10*H*-9-oxa-10-phosphaphenanthrene (0.36 mol, 82.8 g) and the respective alcohol [2,2-dimethyl-1,3-propanediol (0.15 mol, 15.6 g), trimethylolpropane (0.10 mol, 13.4 g), 1,4-butandiol (0.15 mol, 13.3 mL), terephthalic acid diglycolester (0.15 mol, 38.1 g)] were stirred intensely at 120°C. Over a period of 6 h, pressure was slowly decreased down to ≈10 mbar, keeping the reaction mixture boiling gently, and subsequently kept there for another 12 h. Excess of 10-ethoxy-10*H*-9-oxa-10-phosphaphenanthrene was distilled off (10^{-3} bar, T < 150°C). At this point, clear glassy compounds **10** and **11** were obtained in a purity exceeding 95%.

Afterwards, the reaction vessel was charged with argon, *p*-toluenesulfonic acid methylester (2 mmol, 0.3 mL) was added, temperature was increased to 175°C, and kept for another 24 h to yield clear glassy **12** and **13** in a purity exceeding 95%. Hot **12** was poured into 200 mL intensely stirred, boiling toluene. The resulting suspension was cooled to RT and the formed precipitate filtered off and dried in vacuo.

Compound 10

$Anal_{found}$: C, 70.12; H, 5.09 %. $Anal_{calc}$($C_{29}H_{26}O_4P_2$): C, 69.60; H, 5.24%. MS (70 eV): m/z = 500, 415, 301, 233, 217, 216, 215, 200, 199, 168, 152. IR (KBr): 3061, 2960, 2872, 1604, 1593, 1583, 1476, 1445, 1429, 1398, 1364, 1277, 1236, 1202, 1116 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.43–0.57 (m, 6H, CH_3), 3.20–3.46 (m, 4H, CH_2), 7.12–7.23 (m, 4H, O–C–C–CH–CH, O–C–CH), 7.32 (t, J_{HH} = 7.6 Hz, 2H, O–C–CH–CH), 7.44 (t, J_{HH} = 7.8 Hz, 2H, P–C–CH–CH), 7.54–7.71 (m, 4H, P–C–C–CH–CH, P-C-CH), 7.88–8.04 (m, 4H, O–C–C–CH, P-C-C-CH). ^{13}C NMR ($CDCl_3$): δ = 20.68–20.97 (CH_3), 36.57-36.90 (CH_3-C), 73.12–73.54 (CH_2), 120.4 (O-C-CH), 122.5 (J_{PC} = 6.0 Hz, O-C-C), 123.0 (O–C–C–CH-CH), 123.2 (P-C-C-CH), 124.6 (O–C–C–CH), 127.3 (J_{PC} = 13.4 Hz, P–C–CH–CH), 129.4 (O–C–CH–CH), 131.20, 131.24

(J_{PC} = 47.3 Hz, P–C–<u>C</u>H), 131.4 (P–C–C–CH–<u>C</u>H), 131.82–131.93 (P–C ∧ P–C–<u>C</u>), 132.3 (J_{PC} = 17.0 Hz, P–C ∧ P–C–<u>C</u>), 149.6 (J_{PC} = 9.2 Hz, O-C). ^{31}P NMR ($CDCl_3$): δ = 128.7.

Compound 11

$Anal_{found}$: C, 70.13; H, 4.80%. $Anal_{calc}(C_{42}H_{35}O_6P_3)$: C, 69.22; H, 4.84%. MS (70 eV): m/z = 728, 529, 513, 415, 414, 413, 313, 297, 217, 216, 215, 200, 199, 168, 152. IR (KBr): 3060, 2935, 2878, 1603, 1592, 1582, 1475, 1444, 1429, 1277, 1236, 1201, 1116 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.28 (t, J_{HH} = 7.5 Hz, 3H, CH_3), 0.75 (q, J_{HH} = 7.5 Hz, 2H, C<u>H</u>$_2$-CH_3), 3.15–3.39 (m, 6H, O-CH_2), 7.10–7.24 (m, 6H, O–C–C–CH–C<u>H</u>, O-C-C<u>H</u>), 7.33 (t, J_{HH} = 7.3 Hz, 3H, O–C–CH–C<u>H</u>), 7.43 (t, J_{HH} = 7.1 Hz, 3H, P–C–CH–C<u>H</u>), 7.50–7.66 (m, 6H, P–C–C–CH–C<u>H</u>, P-C-C<u>H</u>), 7.86–8.03 (m, 6H, O–C–C–C<u>H</u>, P-C-C-C<u>H</u>). ^{13}C NMR ($CDCl_3$): δ = 6.6 (CH_3), 20.9 (<u>C</u>H_2-CH_3), 43.43–43.94 (CH_2-<u>C</u>), 66.78–67.69 (O-CH_2), 120.3 (O-C-<u>C</u>H), 122.4 (J_{PC} = 5.8 Hz, O-C-<u>C</u>), 123.0 (O–C–C–CH-<u>C</u>H), 123.1 (P-C-C-<u>C</u>H), 124.5 (O–C–C–<u>C</u>H), 127.2 (J_{PC} = 13.0 Hz, P–C–CH–<u>C</u>H), 129.4 (O-C-CH-<u>C</u>H), 131.2 (J_{PC} = 48.6 Hz, P–C–<u>C</u>H), 131.4 (P–C–C–CH–<u>C</u>H), 131.8 (P-C ∧ P–C–<u>C</u>), 132.2 (J_{PC} = 16.9 Hz, P–C ∧ P–C–<u>C</u>), 149.5 (J_{PC} = 8.9 Hz, O–C). ^{31}P NMR ($CDCl_3$): δ = 129.1.

Compound 12

$Anal_{found}$: C, 69.31; H, 4.92%. $Anal_{calc}(C_{28}H_{24}O_4P_2)$: C, 69.14; H, 4.97%. MS (70 eV): m/z = 486, 271, 243, 216, 215, 168. IR (KBr): 3059, 2929, 1607, 1592, 1582, 1560, 1474, 1449, 1430, 1402, 1321, 1299, 1277, 1246, 1233, 1205, 1182, 1148 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.53–1.77 (m, 4H, P-CH_2-C<u>H</u>$_2$), 1.86–2.07 (m, 4H, P-CH_2), 7.11 (d, J_{HH} = 8.0Hz, 2H, O–C–CH), 7.19 (t, J_{HH} = 7.4 Hz, 2H, O–C–C–CH–C<u>H</u>), 7.31 (t, J_{HH} = 7.6 Hz, 2H, O–C–CH–C<u>H</u>), 7.44 (td, J_{HH} = 7.4 Hz, J_{PH} = 2.9 Hz, 2H, P–C–CH–C<u>H</u>), 7.63 (t, J_{HH} = 7.7 Hz, 2H, P–C–C–CH–C<u>H</u>), 7.77 (dd, J_{HH} = 7.6 Hz, J_{PH} = 12.7 Hz, 2H, P–C–CH), 7.85 (d, J_{HH} = 8.7 Hz, 2H, O–C–C–CH), 7.89 (dd, J_{HH} = 8.1 Hz, J_{PH} = 4.8 Hz, 2H, P–C–C–CH). ^{13}C NMR ($CDCl_3$): δ = 22.5 (dd, J_{PC} = 16.7, 4.5 Hz, P-CH_2-<u>C</u>H_2), 27.0 (J_{PC} = 97.0 Hz, P–CH_2), 120.2 (J_{PC} = 6.1 Hz, O–C–<u>C</u>H), 122.0 (J_{PC} = 11.0 Hz, O–C–<u>C</u>), 123.8 (J_{PC} = 9.6 Hz, P-C-C-<u>C</u>H), 124.1 (J_{PC} = 119.4 Hz, P-C), 124.5 (O–C–C–CH–<u>C</u>H), 125.0 (O–C–C–<u>C</u>H), 128.3 (J_{PC} = 13.2 Hz, P–C–CH–<u>C</u>H), 129.8 (J_{PC} = 11.0 Hz, P–C–<u>C</u>H), 130.5 (O–C–CH–<u>C</u>H), 133.2 (J_{PC} = 2.4 Hz, P–C–C–CH–<u>C</u>H), 135.4 (J_{PC} = 6.2 Hz, P–C–<u>C</u>), 148.9 (J_{PC} = 8.4 Hz, O-C). ^{31}P NMR ($CDCl_3$): δ = 38.3.

Compound 13

$Anal_{found}$: C, 66.86; H, 4.43 %. $Anal_{calc}(C_{36}H_{28}O_8P_2)$: C, 66.45; H, 4.34%. ESI (10eV): m/z = 668 ($M + NH_4^+$), 489, 459, 430, 326,

245, 198, 186. IR (KBr): 3064, 3006, 2960, 2908, 1717, 1607, 1597, 1583, 1560, 1478, 1459, 1448, 1432, 1413, 1384, 1282, 1270, 1248, 1230, 1213, 1174, 1146 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.47-2.75 (m, 4H, P-CH_2), 4.48–4.70 (m, 4H, O-CH_2), 7.12 (d, J_{HH} = 8.0 Hz, 2H, O–C–CH), 7.19 (t, J_{HH} = 7.5 Hz, 2H, O–C–C–CH–C<u>H</u>), 7.30 (t, J_{HH} = 7.6 Hz, 2H, O–C–CH–C<u>H</u>), 7.42 (td, J_{HH} = 7.4 Hz, J_{PH} = 3.0 Hz, 2H, P–C–CH–C<u>H</u>), 7.62 (t, J_{HH} = 7.8 Hz, 2H, P–C–C–CH–C<u>H</u>), 7.75-7.93 (m, 10H, P–C–CH, O–C–C–CH, P–C–C–CH, O=C-C-CH). ^{13}C NMR ($CDCl_3$): δ = 28.7 (J_{PC} = 97.1 Hz, P-CH_2), 58.8 (J_{PC} = 2.5 Hz, P–CH_2-<u>C</u>H_2), 120.1 (J_{PC} = 6.2 Hz, O–C–<u>C</u>H), 121.7 (J_{PC} = 11.2 Hz, O–C–<u>C</u>), 123.8 (J_{PC} = 9.6 Hz, P–C–C–<u>C</u>H), 123.9 (J_{PC} = 122.4 Hz, P-C), 124.7 (O–C–C–CH–<u>C</u>H), 125.0 (O–C–C–<u>C</u>H), 128.5 (J_{PC} = 13.5 Hz, P–C–CH–<u>C</u>H), 129.3 (O=C–C–<u>C</u>H), 129.9 (J_{PC} = 11.2 Hz, P–C–<u>C</u>H), 130.6 (O–C–CH–<u>C</u>H), 133.2 (O=C–<u>C</u>), 133.4 (J_{PC} = 2.3 Hz, P–C–C–CH–<u>C</u>H), 135.4 (J_{PC} = 6.3 Hz, P–C–<u>C</u>), 148.7 (J_{PC} = 8.3 Hz, O–C), 164.9 (O=C). ^{31}P NMR ($CDCl_3$): δ = 34.0.

Synthesis of Compounds 14 and 15—General Procedure

10-Ethoxy-10*H*-9-oxa-10-phosphaphenanthrene (0.36 mol; 82.8 g) and the respective alcohol [1,3,5-tris-(2-hydroxyethyl) cyanuric acid (0.1 mol, 26.1 g); **16** made of 0.15 mol of 1,3,5-tris-(2-hydroxyethyl) cyanuric acid (dissolved in ≈25 mL of dioxane remaining from preparation of **16**)] were unified under vigorous stirring. In the case of **16**, dioxane was primarily removed by vacuum distillation while simultaneously heating the reaction mixture up to 135°C.

Starting from 135°C, the temperature was constantly increased up to 160°C over 9 h applying a vacuum of 10 mbar. After another 6 h of stirring at 160°C and 10 mbar, excess 10-ethoxy-10*H*-9-oxa-10-phosphaphenanthrene was distilled off (10^{-3} bar, T < 160°C). Following this procedure, the reaction vessel was charged with argon, *p*-toluenesulfonic acid methylester (2 mmol, 0.3 mL) was added, the temperature was increased to 175°C, and the mixture was kept for another 24 h at the same temperature to yield clear glassy **14** and **15** in a purity exceeding 95%.

Compound 14

$Anal_{found}$: C, 63.81; H, 4.30; N, 4.54%. $Anal_{calc}(C_{45}H_{36}N_3O_9P_3)$: C, 63.16; H, 4.24; N, 4.91%. ESI (10 eV): m/z = 873 ($M + NH_4^+$), 856 ($M + H^+$), 511, 489, 430, 245, 186. IR (KBr): 3060, 2962, 2931, 2873, 1689, 1609, 1595, 1583, 1561, 1475, 1431, 1402, 1376, 1338, 1260, 1245, 1204, 1146, 1120 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.26–2.61 (m, 6H, P-CH_2), 3.88–4.15 (m, 6H, N-CH_2), 7.10–7.25 (m, 6H, O–C–CH,

O–C–C–CH–C<u>H</u>), 7.32 (t, J_{HH} = 7.6 Hz, 3H, O–C–CH–C<u>H</u>), 7.46 (td, J_{HH} = 7.4 Hz, J_{PH} = 2.9 Hz, 3H, P–C–CH–C<u>H</u>), 7.64 (t, J_{HH} = 7.7 Hz, 3H, P–C–C–CH–C<u>H</u>), 7.73–7.96 (m, 9H, P–C–CH, O–C–C–CH, P–C–C–CH). ^{13}C NMR ($CDCl_3$): δ = 26.1 (J_{PC} = 96.4 Hz, P–CH_2), 36.5 (N–CH_2), 120.3 (J_{PC} = 5.9 Hz, O–C–<u>C</u>H), 121.7 (J_{PC} = 11.1 Hz, O–C–<u>C</u>), 123.6 (J_{PC} = 122.3 Hz, P–C), 123.8 (J_{PC} = 9.6 Hz, P–C–C–<u>C</u>H), 124.7 (O–C–C–CH–<u>C</u>H), 125.0 (O–C–C–<u>C</u>H), 128.3 (J_{PC} = 13.6 Hz, P–C–CH–<u>C</u>H), 129.8 (J_{PC} = 11.7 Hz, P–C–<u>C</u>H), 130.5 (O–C–CH–<u>C</u>H), 133.3 (J_{PC} = 2.2 Hz, P–C–C–CH–<u>C</u>H), 135.3 (J_{PC} = 6.0 Hz, P–C–<u>C</u>), 147.7 (C=O), 148.6 (J_{PC} = 8.3 Hz, O–C). ^{31}P NMR ($CDCl_3$): δ = 33.54, 33.59, 33.63.

Compound 15

MALDI: m/z = 4287 (nonamer), 3946 (octamer), 3504, 3063, 2622, 2181, 1738, 1297 (dimer), 856 (monomer). IR (KBr): 3066, 2968, 2913, 2876, 1692, 1607, 1595, 1582, 1562, 1463, 1431, 1367, 1325, 1260, 1233, 1201, 1147, 1118 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.25–2.70 (m, P–CH_2), 3.38–3.66 (m, O–CH_2), 3.74–4.14 (m, N–CH_2), 7.08–7.21 (m, O–C–CH, O–C–C–CH–C<u>H</u>), 7.23–7.34 (m, O–C–CH–C<u>H</u>), 7.35–7.48 (m, P–C–CH–C<u>H</u>), 7.52–7.66 (m, P–C–C–CH–C<u>H</u>), 7.71–7.91 (m, P–C–CH, O–C–C–CH, P–C–C–CH). ^{13}C NMR ($CDCl_3$): δ = 25.6 (bd, J_{PC} = 96.3 Hz, P-CH_2), 35.9 (bs, P–CH_2-<u>C</u>H_2), 41.1 (bs, O–CH_2–<u>C</u>H_2), 66.2 (bs, O–CH_2), 119.4–119.9 (m, O–C–<u>C</u>H), 121.1 (bd, J_{PC} = 11.1 Hz, O–C–<u>C</u>), 123.0 (bd, J_{PC} = 121.1 Hz, P–C), 123.3 (bd, J_{PC} = 8.9 Hz, P–C–C–<u>C</u>H), 124.1 (bs, O–C–C–CH–<u>C</u>H), 124.5 (bs, O–C–C–<u>C</u>H), 127.5–128.1 (m, P–C–CH–<u>C</u>H), 129.1 (bd, J_{PC} = 11.1 Hz, P–C–<u>C</u>H), 129.9 (bs, O–C–CH–<u>C</u>H), 132.8 (bs, P–C–C–CH–<u>C</u>H), 134.5 (bd, J_{PC} = 5.8 Hz, P–C–<u>C</u>), 146.9–148.3 (m, C=O, O–C). ^{31}P NMR ($CDCl_3$): δ = 33.8–34.2 (m).

Oligomeric 1,3,5-Tris-(2-hydroxyethyl) Cyanuric Acid (16)

1,3,5-Tris-(2-hydroxyethyl) cyanuric acid (0.15 mol, 39.2 g) and 4.5 g Amberlite IR-120 (plus) were stirred at 170°C under a gentle stream of argon. Every hour, a pressure of ≈10 mbar was applied for 5 min to remove formed water. The reaction was traced by ^{1}H NMR and when the CH/OH-ratio reached 7.0 (≈10–15 h; $ratio_{t=0}$ = 4), vacuum was applied a last time for 5 min. The oligomer was cooled to 80°C and dissolved in 150 mL of boiling dioxane. The solution was cooled to RT and filtered through kieselguhr. 40 mL of toluene were added and the solvents were removed by vacuum distillation to remove the remaining water azeotropically. The residue was dissolved in another 80 mL of dioxane and a few drops of triethanolamine and 2 g of triethyl orthofor-

mate were added to neutralise the remaining traces of acid and water. The solution was reduced to half of its volume by vacuum distillation and used without further treatment. ESI (50 eV): m/z = 1494 (hexamer + NH_4^+), 1251 (pentamer + NH_4^+), 1008 (tetramer + NH_4^+), 765 (trimer + NH_4^+), 748 (trimer + H^+), 522 (dimer + NH_4^+), 505 (dimer + H^+), 262 (monomer + H^+), 244 (monomer-OH^-). ^{1}H NMR (d_6-DMSO): δ = 3.40-3.62 (m, 3.5H, O—CH_2), 3.65-3.96 (m, 3.5H, N—CH_2), 4.73 (s, 1H, OH). ^{13}C NMR (d_6-DMSO): δ = 41.5 ($\underline{C}H_2$-CH_2-O-CH_2), 44.6 ($\underline{C}H_2$-CH_2-OH), 57.8 ($\underline{C}H_2$-OH), 66.7 ($\underline{C}H_2$—O—$\underline{C}H_2$), 149.1 (C=O), 149.2 (C=O), 149.3 (C=O), 149.4 (C=O).

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