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Synthesis of (*trans*-A₂)BC-Type Porphyrins with Acceptor Diethoxyphosphoryl and Various Donor Groups and their Assembling in the Solid State and at Interfaces

Elizaveta V. Ermakova,^[a,b] Yulia Yu. Enakieva,^[a,b] Sergey E. Nefedov,^{*,[c]} Vladimir V. Arslanov,^{*,[b]} Yulia G. Gorbunova,^[b,c] Aslan Yu. Tsivadze,^[b,c] Christine Stern,^[a] Alla Bessmertnykh-Lemeune^{*,[a]}

Abstract: A versatile synthetic approach to accessing unsymmetrically substituted (*trans*-A₂)BC-type porphyrins bearing two heteroatoms at the macrocycle periphery is developed. For this purpose, experimental conditions for the substitution of the bromine atom in zinc 5-bromo-15-(diethoxyphosphoryl)-10,20-diphenylporphyrin (**2**) by S-, O- and N-nucleophiles were explored. S_NAr reactions afford AlkO-, ArO- and AlkS-substituted porphyrins in good to high yields. In contrast, S_NAr reactions of **2** with N-nucleophiles lead to *meso*-amino-substituted porphyrins in preparative yields only with cyclic secondary amines. Primary amines, anilines and azacrowns may also react with bromide **2** but the palladium catalyst is needed to obtain the products in acceptable yields. The interest of the compounds under investigation for biomimetic assembly of tetrapyrroles was demonstrated by the studies of self-assembly of ditopic morpholinyl-substituted porphyrin **5a** in the solid state. Moreover, we have prepared emissive porphyrin monolayers at the air/water interface and revealed that these porphyrin films were suitable for detection of zinc(II) ions in aqueous solutions.

Introduction

Tetrapyrrolic macrocycles are widely used by living systems in many vital processes such as photosynthesis, transport and storage of small molecules and catalytic oxidative

transformations.^[1] To mimic these processes for dealing more effectively with major societal challenges, the complicated natural systems are frequently replaced by simple synthetic compounds such as *meso*-tetraaryl (A₄-type) or *trans*-diaryl (*trans*-A₂-type) porphyrins (Figure 1) as they can be easily prepared in high yielding reactions and on multigram scale.^[2] Several compounds of such type are already produced in industrial scale.

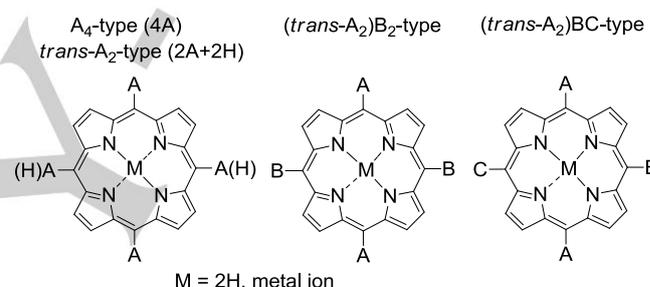


Figure 1. Substitution patterns in porphyrins.

Investigations of porphyrins and their complexes across many fields of chemistry, physics, biology and medicine have demonstrated that they possess rich coordination, photophysical, redox and catalytic properties.^[3] However, most applications such as nonlinear optics (NLO), photodynamic therapy (PDT), development of solar fuel and catalysis call for more sophisticated porphyrin derivatives such as push-pull chromophores ((*trans*-A₂)BC-type porphyrins bearing donor and acceptor groups at the opposite *meso* positions of the macrocycle) for NLO and energy transformation, amphiphilic surrogates for PDT or compounds modified by anchoring groups to prepare functional organic-inorganic materials according to their grafting onto polymer or metal oxide supports.^[2a, 4] Hence, development of synthetic approaches to unsymmetrically functionalized porphyrins has become as a priority in porphyrin synthesis.

In the last decades, the introduction of heteroatom-containing substituents at the periphery of the macrocycle was widely studied to benefit from strong electronic effects of functional groups attached directly to the macrocycle.^[5] Substitution reactions at *meso*- and β -pyrrolic positions of the macrocycle have received much attention.^[6] Both transition-metal-catalysed heterocoupling^[7] and catalyst-free nucleophilic substitution reactions^[8] have been recognized as efficient synthetic approaches to heteroatom-substituted derivatives.

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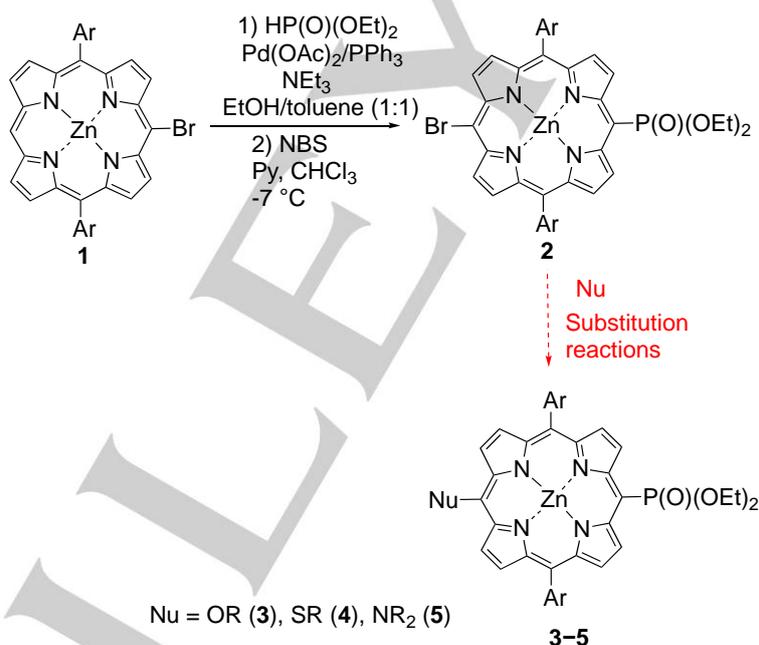
Supporting information for this article (¹H, ¹³C and ³¹P NMR spectra, MALDI-TOF and ESI-HR mass spectra, FT-IR and UV-vis spectra, X-ray crystal data, additional data for monolayers at the air/water interface and LS films) is given via a link at the end of the document.

However, low air stability (particularly under sunlight) of many porphyrins bearing peripheral electron-donating groups is a serious drawback for their practical application. In this context, air stable electron-deficient phosphorylporphyrins are of particular interest.

The first examples of *meso*-phosphorylporphyrins prepared from *meso*-halogenides under palladium- and copper-catalyzed conditions were reported independently by the groups of Arnold and Matano.^[7h, 9] Later palladium catalysts were employed to facilitate the reaction of readily accessible *meso*- and β -bromoporphyrins with dialkyl phosphites, giving a concise and versatile method for the synthesis of porphyrinylphosphonate diesters in reasonably high yield.^[10] In particular, many (*trans*-A₂)B- and (*trans*-A₂)B₂-type porphyrins (A = aryl, B = diethoxyphosphoryl (P(O)(OEt)₂)) were obtained from *meso*-bromoporphyrins **1** (Scheme 1) and 5,15-dibromoporphyrins taking advantage of the relatively simple separation of the target compounds from crude mixtures of the polar porphyrin derivatives.^[11]

In this article, we report a preparation of push-pull porphyrins of this series from *meso*-bromoporphyrinylphosphonate diesters **2** using the substitution reactions (Scheme 1). Both transition metal-catalyzed and catalyst-free conditions were exploited for

the reactions of bromoporphyrins **2** with of S-, O- and N-nucleophiles to develop concise procedures for the synthesis of polar derivatives **3–5**. The electron-deficient character of porphyrinylphosphonate diesters **2** allows to increase the scope of S_NAr reactions compared to that of analogous aryl-substituted porphyrins and perform the synthetic sequence shown in Scheme 1 by using Zn complexes **1** avoiding preparation of more reactive free base porphyrins and their Ni(II) complexes. (*trans*-A₂)BC-type porphyrinylphosphonate diesters bearing electron-donating substituents were found to be more stable in air compared to analogous non-phosphorylated derivatives. These molecules exhibit dipole moments whose strength can be finely tuned by changing the peripheral electron-donating groups. Moreover, these porphyrins have potential application in material science because the phosphonic acids can be grafted on metal oxide supports. They are also useful in supramolecular chemistry as organic linkers to create multiporphyrin systems. Finally, amphiphilic derivatives **3–5** (R = long alkyl chain) are of particular interest for PDT and science at interfaces. Several preliminary results on their self-assembling in the solid state and at interfaces are reported in this work.



Scheme 1. Proposed synthetic route to (*trans*-A₂)BC-type porphyrinylphosphonate diesters **3–5**.

Results and Discussion

Synthesis

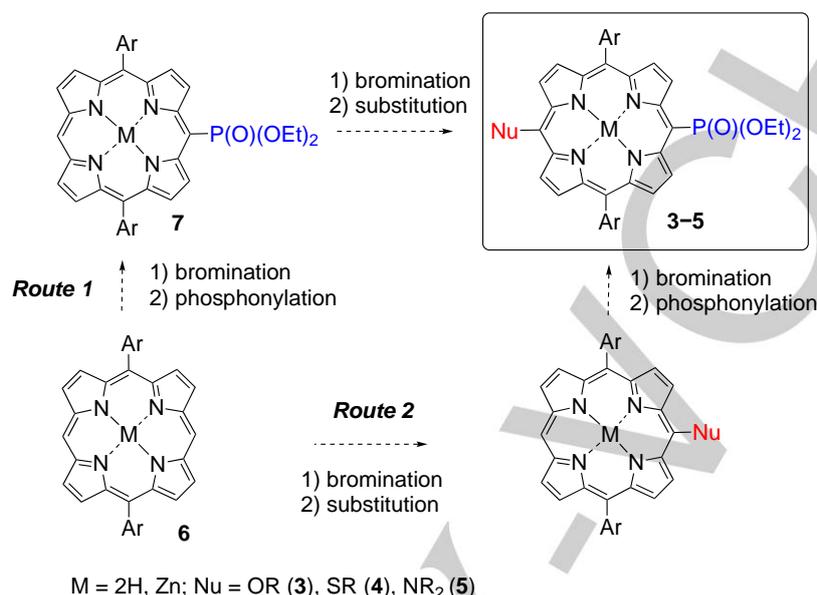
There are ample examples of porphyrins in which donor and acceptor groups are linked to the macrocycle through phenylene or acetylene spacers.^[12] In contrast, compounds with these substituents attached directly to the macrocycle are less studied.

To our knowledge, only (*trans*-A₂)BC-type porphyrins with cyano and amino groups were prepared and scarcely investigated by Balaban's group.^[8g]

The most convenient route to synthesize porphyrinylphosphonate diesters **3–5** is a step-wise functionalization of available *trans*-A₂-type porphyrins **6** which can be performed according to two different pathways as shown on Scheme 2. Taking into account that electron-deficient

aromatic bromides are more reactive in both catalytic and catalyst-free reactions with nucleophiles, we placed the introduction of S-, O- and N-heteroatoms at the end of the

reaction sequence after the phosphonylation of 5,15-diarylporphyrins **6** which led to electron-deficient porphyrins **7** (Route 1, Scheme 2).



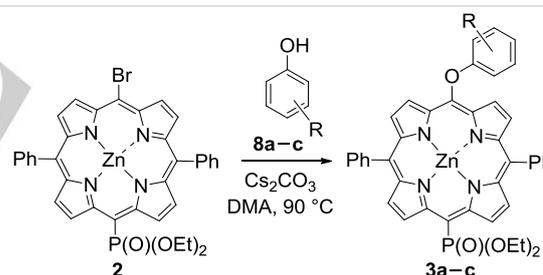
Scheme 2. Synthetic approaches to (*trans*-A₂)BC-type porphyrinylphosphonate diesters **3–5**.

Zinc 5,15-diphenylporphyrin (**6**, Ar = Ph) was chosen as a model compound which was easily obtained by [2+2] condensation of benzaldehyde and dipyrromethane followed by the oxidation with DDQ and the complexation with zinc acetate dihydrate.^[13] Then [10-(diethoxyphosphoryl)-5,15-diphenylporphyrinato]zinc (**7**, Ar = Ph) was synthesized in 72% yield according to a two-step procedure depicted on Scheme 2.^[11] Bromination of **7** with NBS in chloroform at -7°C afforded bromoporphyrin **2** (Ar = Ph) in 85% yield.^[11]

First we investigated the aromatic nucleophilic substitution (S_NAr) of the bromine atom in zinc porphyrin **2** aiming to avoid competing reactions of the dialkyl phosphonate group such as the transesterification in the presence of alcohols under basic conditions^[11] and the dealkylation by amines in polar solvents at reflux.^[14]

Initial screening of experimental conditions was carried out with a series of phenols because these compounds smoothly reacted with free base porphyrins and their nickel(II) complexes being heated in DMF as recently has been shown.^[7c, 8i, 15] The reactions of zinc porphyrins with phenolates were reported to be much more sluggish and afforded the products in very low yields.^[8i, 15] In our case, the removal of zinc atom was not necessary because zinc bromoporphyrin **2** smoothly reacted with an excess of phenol **8a** (15 equiv.) in DMA at 90°C . However, the reaction course should be carefully monitored by MALDI-TOF spectrometry because the target product **3a** is unstable under reaction conditions. It was isolated in 98% yield when heating was stopped just after achieving a complete conversion of the starting bromide **2** (Table 1, entry 1). In

Table 1. S_NAr reaction of **2** with phenols **8a–c**.^[a]



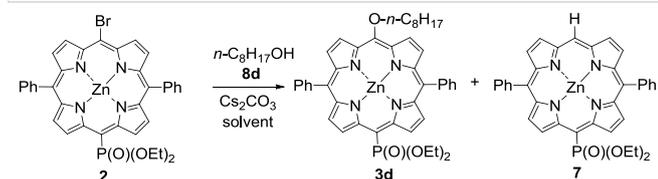
Entry	Phenol	<i>t</i> [h]	Product, yield [%] ^[b]
1		2	3a , 98
2	8a	16	3a , 51
3		8	3b , 95
4		1.5	3c , 54

[a] Reaction conditions: bromide **2**, phenol (15–20 equiv.) and cesium carbonate (5 equiv.) were heated in DMA under N₂ until complete conversion (monitored by MALDI-TOF MS). [b] Isolated yields.

contrast, when the reaction was run overnight, a partial decomposition of product **3a** was occurred decreasing the yield down to 51% (entry 2). 3,5-Dimethylphenol (**8b**) also afforded the product in high yield (95%) but this reaction was complete in 8 h (entry 3). The reaction of **2** with 4-bromophenol (**8c**) proceeded faster but porphyrin **3c** was isolated in only 54% yield presumably due to the side reactions involving highly reactive bromine at the phenol ring. Note that porphyrinylphosphonate diester **3c** is a useful intermediate compound on the pathway to modular porphyrins owing to its expected high reactivity in transition-metal-catalysed coupling reactions.

The reaction of bromide **2** with octanol (**8d**) was complicated due to competing hydrodebromination^[80] of the starting porphyrin and a careful optimization of conditions was needed to prepare the target product **3d** in acceptable yield (Table 2).

Table 2. S_NAr reaction of bromoporphyrin **2** with *n*-octanol.^[a]

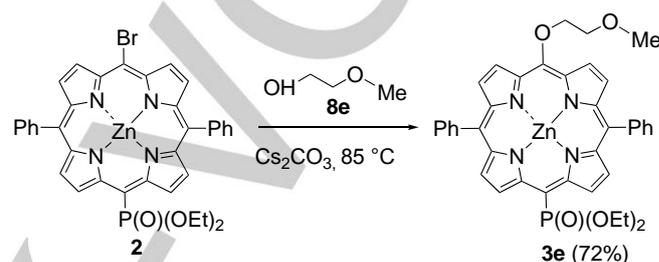


Entry	ROH [equiv.]	Solvent	T [°C]	t [h]	Conv. [%]	Yield [%] ^[b]	
						3d	7
1	15	DMA	90	2	20	10	5
2	15	DMA	120	16	100	(10) ^[c]	(5) ^[c]
3	100	DMA	120	3	100	68	32
4 ^[d]	100	DMA	120	12	14	7	7
5	100	DMA	90	2	100	90	10
6 ^[e]	[f]	<i>n</i> -octanol	85	4	100	(87) ^[g]	-

[a] Reaction conditions: bromide **2**, *n*-octanol, cesium carbonate (3 equiv.) and solvent were heated under N₂ until complete conversion (monitored by MALDI-TOF MS). [b] Determined by ¹H NMR analysis. Isolated yields are given in parentheses. [c] Two products were isolated as a mixture. The yield was determined by ¹H NMR analysis of this mixture. [d] Na₂CO₃ was employed as a base. [e] 10 equiv. of Cs₂CO₃ was used. [f] *n*-Octanol was used as a solvent. [g] The best yield is given. When the reaction was repeated the product was isolated in 65% yield.

When this reaction was performed under the conditions developed for phenols **8a-c** (DMA, 90 °C, 2 h), the conversion of **2** was only 20% (entry 1). The bromide **2** was completely consumed only after 16 hours of the reaction run in DMA at 120 °C (entry 2). However, in this case at least three different compounds were obtained and their separation by column chromatography on silica gel was impossible. The increase in alcohol excess up to 100 equiv. accelerated the reaction and only **3d** and **7** were obtained under these conditions according to ¹H NMR data (entry 3). However, the separation of these two

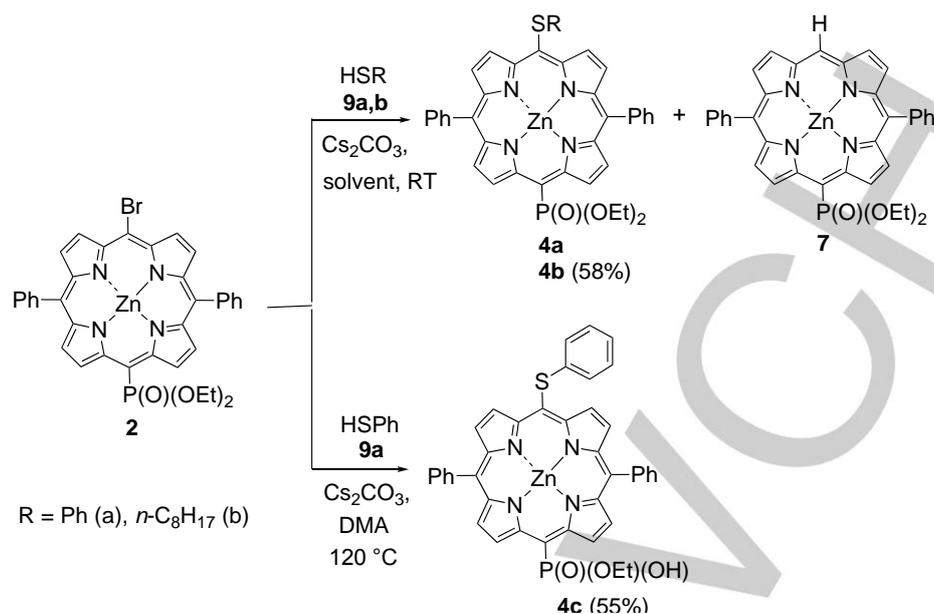
compounds by column chromatography on silica gel also failed. Then sodium carbonate was employed as a base but the reaction was slow and non-selective (entry 4). Lowering temperature to 90 °C was more efficient and alkoxyphyrin **3d** was obtained in 90% yield according NMR analysis of the crude solid but the product was contaminated by **7** (10%) (entry 5). Selective reaction was observed only at 85 °C when octanol was used as a solvent (entry 6). Under these conditions, a complete conversion was achieved in 4 hours affording **3d** in 87% yield (entry 6). 2-Methoxyethanol (**8e**) also smoothly reacted with bromide **2** under the same conditions affording **3e** in 72% yield (Scheme 3).



Scheme 3. S_NAr reaction of bromide **2** with alcohol **8e**.

The aromatic substitution reactions involving S-nucleophiles usually require a high temperature or metal catalysts. As a result, the S_NAr reactions at the *meso* positions of porphyrins are scarce but were briefly reported for the free base porphyrins and their Ni(II) complexes.^[81, 8n, 8q, 8r]

The reactions of zinc porphyrin **2** with thiols **9a,b** under the conditions developed for O-nucleophiles were rapid but non-selective (Scheme 4). Among different competing reactions, extensive hydrodebromination was observed. This unusual process has been recently reported as a competing reaction in S_NAr reactions of nitroporphyrins with S-nucleophiles.^[8q] The optimization of this reaction was performed by varying the temperature when bromoporphyrin **2** and thiophenol (**9a**) were reacted in DMA. Proceeding this reaction at room temperature, a complete conversion of bromide was achieved in 2 hours but a chromatographically inseparable mixture of the target porphyrin **4a** and reduced compound **7** in 2:1 molar ratio was obtained. The reaction was also rapid at 0 °C but the amount of side product **7** increased up to 50%. Only 10 minutes was needed to complete the substitution at 120 °C and a pure product was easily isolated by the column chromatography in 55% yield. Surprisingly, this compound was identified by spectroscopic methods and HR-MS as monoethyl porphyrinylphosphonate **4c**. The ¹H and ³¹P{¹H} NMR spectra of **4c** are typical for *meso*-ethoxyhydroxyphosphoryl porphyrins, the P(O)(OH)(OEt) signals appear at δ_H 3.84 and 1.12 and δ_P 17.34 ppm.^[16] The role of thiophenol in this competing reaction was not investigated but the dealkylation of dialkyl phosphonates in the presence of nucleophiles such as triethylamine or triphenylphosphine was previously reported.^[14]



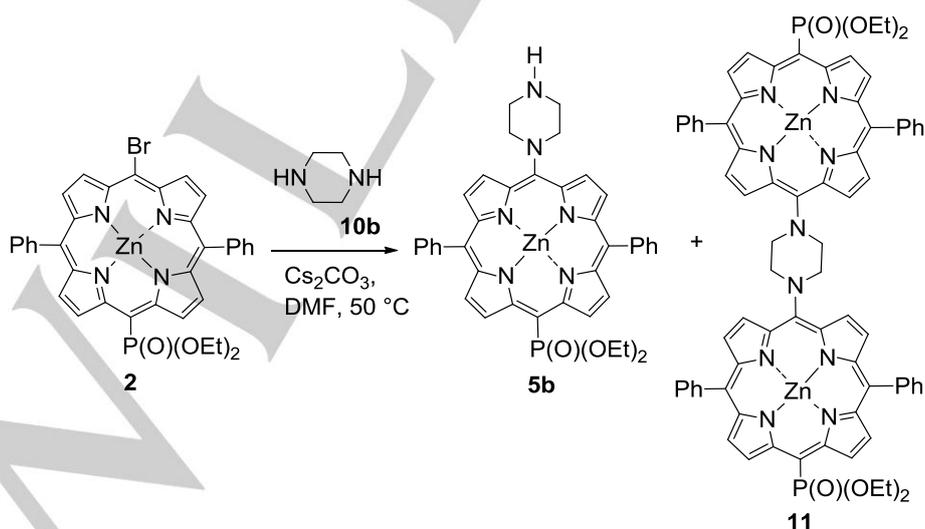
Scheme 4. S_NAr reactions of bromide **2** with thiols **9a,b**.

When the procedure developed for the reaction of **2** with octanol (**8d**) (Table 2, entry 6) was employed for reacting with thiooctanol (**9b**), rapid hydrodebromination of the starting porphyrin was observed according to MALDI-TOF MS analysis. Fortunately, this competing reaction did not occur at room temperature, while the substitution proceeds in 3 hours affording **4b** in 58% yield.

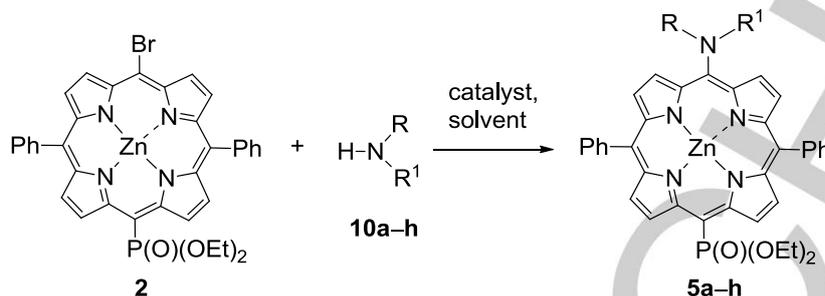
The S_NAr reactions with less nucleophilic amines **10a–h** are summarized in Table 3. They were also complicated in part due to dealkylation of the diethoxyphosphoryl substituent by amines.

The reaction of bromide **2** with an excess of morpholine

(**10a**) proceeded even in a weakly polar chloroform at 50 °C but was more rapid (6 hours) in DMF when cesium carbonate was added as a base (entries 1 and 2). In both reactions, the target product **5a** was isolated in high 87% and 95% yields, respectively. Piperazine (**10b**) reacted with the bromide **2** under the same conditions (entries 3–5), but the reaction was less selective because both amino groups of the cyclic diamine were involved in the substitution reaction as shown in Scheme 5. Fortunately, the second substitution step proceeded slowly and **5b** was obtained in a good yield in all cases but the reaction was faster and more selective in DMF (entry 3).



Scheme 5. S_NAr of bromoporphyrim **2** with piperazine (**10b**) in DMF.

Table 3. Synthesis of amino-substituted porphyrinylphosphonates **5a-h**.^[a]

Entry	Amine	[equiv.]	Catalyst [mol%]	Base [equiv.]	Solvent	T [°C]	t [h]	Product, Yield, [%] ^[b]
1	10a	(5)	-	Cs ₂ CO ₃ (4)	DMF	50	6	5a , 95
2	10a	(200)	-	-	CHCl ₃	50	72	5a , 87
3	10a	(5)	-	Cs ₂ CO ₃ (4)	DMF	50	24	5b , 87 ^[c]
4	10b	(200)	-	-	CHCl ₃	50	100	5b , 79 ^[d]
5	10b	(5)	-	Cs ₂ CO ₃ (4)	CHCl ₃	50	24	5b , 76 ^[d]
6	10c	(5)	-	Cs ₂ CO ₃ (4)	DMF	50	100	5c , 24 ^[e]
7	10c	(5)	-	Cs ₂ CO ₃ (4)	DMF	50	125	5d , 25
8	10d	(10)	Pd(OAc) ₂ /1.5BINAP (5)	Cs ₂ CO ₃ (1.4)	Toluene	reflux	8	5d , 38
9	10d	(5)	-	Cs ₂ CO ₃ (4)	DMF	50	24	5e , 27
10	<i>n</i> -C ₆ H ₁₃ -NH ₂ 10e	(5)	-	Cs ₂ CO ₃ (4)	CHCl ₃	50	24	5e , 0
11	<i>n</i> -C ₆ H ₁₃ -NH ₂ 10e	(10)	Pd(OAc) ₂ /1.5BINAP ^[f] (5)	Cs ₂ CO ₃ (1.4)	Toluene	reflux	2	5e , 76
12	<i>n</i> -C ₈ H ₁₇ -NH ₂ 10f	(10)	Pd(OAc) ₂ /1.5BINAP ^[f] (5)	Cs ₂ CO ₃ (1.4)	Toluene	reflux	2	5f , 78
13	10d	(5)	-	Cs ₂ CO ₃ (4)	DMF	50	100	5g , 0
14	10g	(5)	-	Cs ₂ CO ₃ (4)	CHCl ₃	50	100	5g , 0
15	10g	(10)	Pd(OAc) ₂ /1.5BINAP (5)	Cs ₂ CO ₃ (1.4)	Toluene	reflux	16	5g , 87
16	10g	(10)	Pd(OAc) ₂ /1.5BINAP (5)	Cs ₂ CO ₃ (1.4)	Toluene	reflux	3	5h , 17 ^[g]
17	10h	(10)	Pd(OAc) ₂ /2dppf ^[h] (5)	Cs ₂ CO ₃ (1.4)	Toluene	reflux	24	5h , 0
18	10h	(10)	Pd(OAc) ₂ /3JohnPhos ^[i] (5)	Cs ₂ CO ₃ (1.4)	Toluene	reflux	24	5h , 0
19	10h	(50)	Pd(OAc) ₂ /1.5BINAP (5)	Cs ₂ CO ₃ (1.4)	Toluene	reflux	3	5h , 48

[a] Reaction conditions: bromoporphyrin **2** (0.067 mmol), Cs₂CO₃, amine (0.335 mmol, 5 equiv.) and solvent (17.5 mL) were heated at corresponding temperature under N₂ until the total consumption of the starting porphyrin (MALDI-TOF MS analysis). [b] Isolated yields. [c] Compound **11** was also obtained in 10% yield. [d] The yield was determined by NMR analysis. [e] Conversion of the starting porphyrin was ca. 50%. [f] BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthalene. [g] Conversion of the starting porphyrin was ca. 60%. [h] dppf = Bis(diphenylphosphino)ferrocene. [i] JohnPhos = (2-Biphenyl)di-*tert*-butylphosphine.

The reactions of bromoporphyrin **2** with azacrown ethers **10c** and **10d** in DMF at 50 °C proceed slowly affording **5c** and **5d** in 24 and 25% yield, respectively (entries 6 and 7). Similar product yield (27%) was obtained reacting **2** with hexylamine (**10e**) (entry 9) while no product was detected when these compounds were heated in chloroform (entry 10). Unfortunately, less nucleophilic aniline (**10g**) did not react with bromide **2** in DMF or CHCl_3 at 50 °C (entries 13 and 14).

To increase product yields and the scope of the amination reaction, the catalytic conditions were explored. A relatively cheap and commercially available $\text{Pd}(\text{OAc})_2/\text{BINAP}$ precatalyst was chosen for these experiments based on previous reports on the amination of aryl bromides.^[17] These catalytic reactions were performed in weakly polar toluene but reflux of the reaction mixtures was needed (111 °C). The positive effect of the catalyst was observed for all of studied amines being the largest for the least nucleophilic aniline (**10g**). In this case, the switch to catalytic conditions increased the product yield from 0 up to 87% (entry 15). Hexylamine (**10e**) and octylamine (**10f**) also smoothly reacted under catalytic conditions affording aminoporphyrins **5e** and **5f** in 76 and 78%, respectively (entries 11 and 12). As expected, the heterocoupling reaction with sterically hindered azacrown **10d** was more sluggish and the product was obtained in only 38% yield (entry 8). However, it should be noted, that $\text{S}_{\text{N}}\text{Ar}$ conditions reported above were even less efficient (25%).

When bromide **2** was heated with bulky diphenylamine (**10h**), the 60% conversion was achieved after 3 hours but the target product **5h** was isolated in only 17% yield (entry 16). Our attempts to optimize of the precatalyst by changing BINAP ligand to dppe or JohnPhos failed (entries 17 and 18). In contrast, when the amine loading was increased up to 50 equivalents, the product **5h** was isolated in acceptable yield (48%) (entry 19).

Thus, this comparative study of the palladium-catalysed and catalyst-free amination of (bromoporphyrinato)zinc **2** demonstrates that the catalytic amination reactions are more efficient than less expensive $\text{S}_{\text{N}}\text{Ar}$ reactions. The scope of Pd-catalysed heterocoupling is quite large and anilines, primary and cyclic secondary amines afford the amino-substituted products **5d–g** in acceptable and sometimes high yields. In contrast, most reactive cyclic secondary amines such as piperazine or morpholine should be reacted with bromide **2** under $\text{S}_{\text{N}}\text{Ar}$ conditions.

All of the studied compounds **3–5** were unambiguously characterized by ESI-MS and NMR, IR, and UV-vis spectroscopies (see, SI). The electronic absorption spectra of polar porphyrins **3–5** are of particular interest. The representative examples are shown in Figure 2 and spectroscopic data for all of the studied compounds are summarized in Table S1.

Very strong absorption centered at 420–430 nm (Soret or B bands) and several less intensive bands in the 500–620 nm region (Q bands) were observed in all spectra recorded in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) mixture. Unsymmetrical substitution pattern of the macrocycle imparts some distinctive features to the studied spectra compared to typical spectra of *meso*-tetraaryl-substituted derivatives.

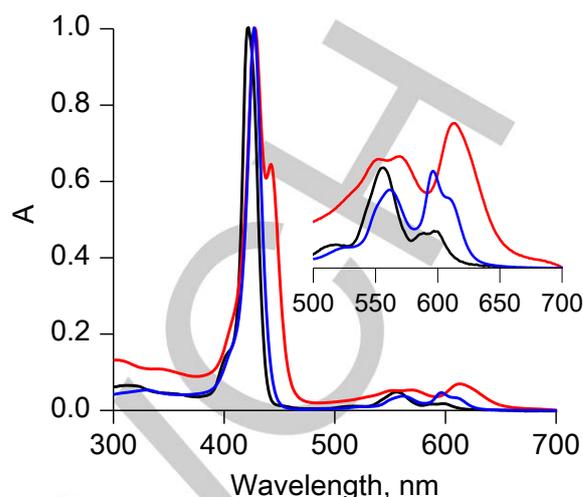


Figure 2. Normalized electronic absorption spectra of **3d** (black line), **4b** (blue line), and **5f** (red line) (Nu = O-*n*-C₈H₁₇, S-*n*-C₈H₁₇, N-*n*-C₈H₁₇) in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solution ($c = 6.25 \mu\text{M}$).

As shown in Figure 2, the shape of absorbance curves is more complicated compared to those of conventional metalloporphyrins of A_4 - or *trans*- A_2 -type. Additional broadening or even split of the B absorption bands' envelope was observed in high energy region. The pseudo allowed (Q) transitions also show splitting pattern not presented in the conventional metalloporphyrins. The absorption maxima are very similar in the spectra of alkoxy- and aryloxy-substituted derivatives **3** and red-shifted only slightly in the spectrum of their thio analogue **4b**. In contrast, bathochromic shift of the band maxima is more pronounced for the main absorption bands for spectra of aminoporphyrins **5**. The linear correlation of absorbance and concentration from Beer's law was observed in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) mixture for all studied compounds except **5b**. This deviation from the linearity for porphyrin **5b** can be explained by its self-assembly because this compound possesses two coordinating sites at the periphery of the macrocycle, namely the oxygen atom of the phosphoryl group and the nitrogen atom of piperazine fragment. It was previously shown that the self-assembly of (dialkoxyphosphoryl)porphyrins was achieved through a weak axial coordination bonding the phosphoryl oxygen atom to the zinc atom of partner porphyrin molecule.^[10a,10b,18] Commonly, these supramolecular aggregates are stable only in weakly coordinating solvents such as toluene or chloroform and dissociate into monomers in more strongly coordinating solvents such as alcohols because porphyrin species bearing axially ligated solvent molecules occur in these solutions. In the studied compounds, self-assembly process may be more complicated due to the presence of additional S-, O- or N-coordinating sites at the periphery of the macrocycle. It seems that the piperazine nitrogen atom is axially coordinated to the zinc atom located at the macrocyclic cavity of neighbouring molecule even in $\text{CHCl}_3/\text{MeOH}$ (2:1, v/v) solvent mixture.

To gain a deeper insight into the self-assembly of porphyrins **3–5**, their electronic absorption spectra were studied in chloroform. The aggregation was clearly observed when 10^{-5} M solutions of the compound **3a** was gradually diluted in 16-fold. Dilution leads to a hypsochromic shift (3–5 nm) of all bands in the spectrum of **3a** as shown in Figure S93. Such spectral changes are typical for the formation of supramolecular aggregates of *meso*-(diethoxyphosphoryl)porphyrins.^[10b]

In accordance with these data, signals in ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 10^{-4} M CDCl_3 solutions of porphyrins **3–5** were broadened. In contrast, the signals in the spectra recorded in a mixture of $\text{CDCl}_3/[\text{D}_4]\text{MeOH}$ (2:1, v/v) for the same concentration of porphyrins are sharp and markedly different from those observed in CDCl_3 for all studied compounds except for the porphyrin **5b**. As a representative example, the spectra of

porphyrin **5a** in these two solvents are shown in Figure 3. The chemical shifts and the intensities of proton signals were in the agreement with assigned structures of monomeric species **5a** when the spectrum was recorded in $\text{CDCl}_3/[\text{D}_4]\text{MeOH}$ (2:1, v/v) mixture. The most important feature of the spectrum obtained in CDCl_3 is a strong up-field shift of methylene protons of the OCH_2 groups of morpholine ring and the phosphoryl substituent accompanied by up-field shifts of β -pyrrolic protons adjacent to the phosphorous substituent. The relative shift of these protons respective to their usual position in the monomer might be understood if we assume that these atoms are within the cone of the aromatic ring current of the other porphyrin molecule, what is possible due to competitive coordination of the phosphoryl oxygen atom and the morpholine oxygen atom to the zinc atom of the shielding porphyrin molecule.

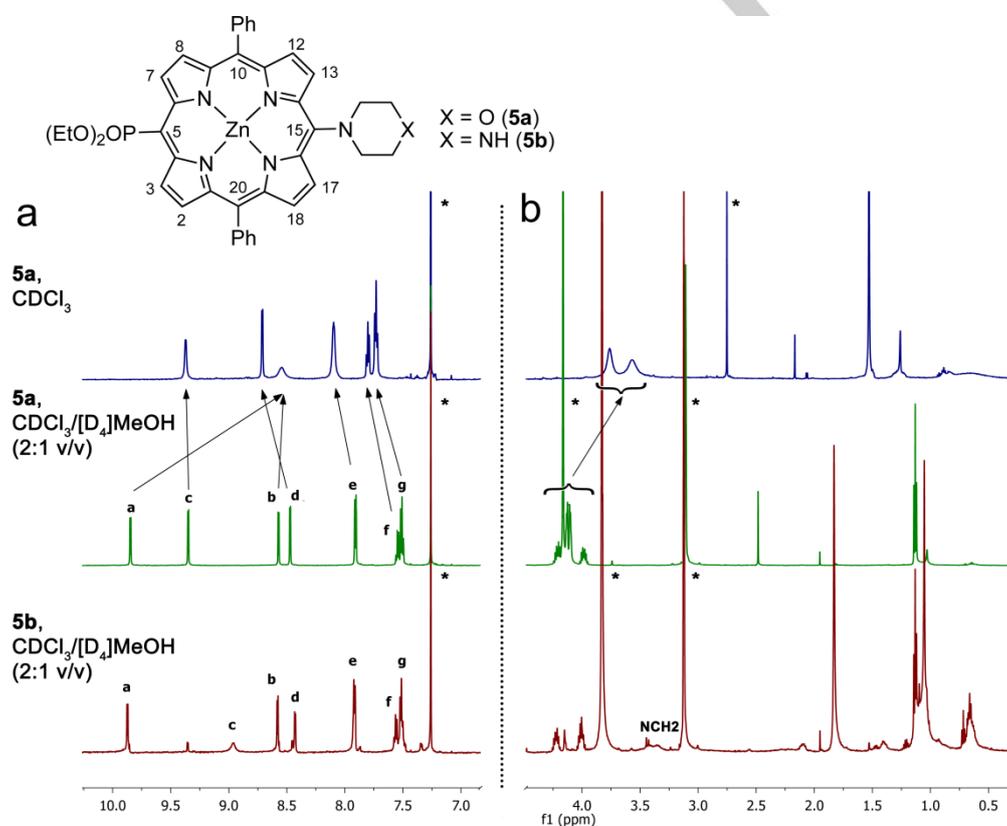


Figure 3. Aromatic (a) and aliphatic (b) regions of ^1H NMR spectra of porphyrins **5a** and **5b** in CDCl_3 and in a $\text{CDCl}_3/[\text{D}_4]\text{MeOH}$ (2:1, v/v) mixture. The labelled peaks are as follows: a = 3,7 - β ; b = 2,8 - β ; c = 13,17 - β ; d = 12,18 - β ; e = α -H_{Ph}; f = p -H_{Ph}; g = m -H_{Ph}.

Additional investigations are still needed to elucidate the structure of these associates. However, at this point it is to be noted that the studied aggregates are quite unstable as are all early reported self-assembled (dialkoxyphosphoryl)porphyrin species.^[10a, 10b] An interesting exception is piperazinylporphyrin **5b** bearing the aliphatic secondary amino group at the cyclic amine fragment. Several proton signals of this compound are broadened even when its ^1H NMR spectrum is recorded in $\text{CDCl}_3/[\text{D}_4]\text{MeOH}$ (2:1, v/v) mixture (Figure 3). In particular, the

signals of β -pyrrolic protons adjacent to piperazinyl substituent are observed as broad singlets shifted up-field while other aromatic protons appeared as sharp multiplets with chemical shifts expected for the monomeric form. It seems that the self-assembly of porphyrin **5b** occurs through the axial Zn-N coordination^[8k] which is stronger compared to Zn-O(P) bonding. The structure of compound **5b** was finally unambiguously established by ESI-MS analysis and ^1H and ^{31}P NMR

spectroscopic investigations in pyridine-*d*5 (see Experimental Section).

To gain a deeper insight into the self-assembly of ditopic self-complementary porphyrins **3–5**, many attempts have been made to grow single crystals of piperazinyl- and morpholinylporphyrins **5a** and **5b** exhibiting different spectral behaviours in CDCl₃/[D₄]MeOH (2:1, v/v). However, the single crystals suitable for X-ray diffraction analysis were obtained only for **5a**.

Crystal structure of porphyrin **5a**

Single crystals of porphyrin **5a** were grown by a slow diffusion of hexane into 10⁻³ M solution of porphyrin in a CHCl₃/MeOH mixture (97:3, v/v). According to single-crystal X-ray diffractational analysis, molecules of zinc porphyrin **5a** are coordinatively bonded forming 1D coordination polymer in the crystals (Figure 4). The *meso*-diarylporphyrin macrocycle exhibits a typical geometry with a small out-of-plane distortion (maximal deviation of carbon atoms from the mean N₄ plane is 0.371 Å). The twist angles of the *meso*-phenyl substituents towards the porphyrin plane are 83.9 and 84.4°. The dihedral angle between the planes of the phosphoryl substituents

(C_{meso}P=O) and the mean N₄ plane equals to 3.2° and adjacent macrocycles of the polymer chain form the angle of 91°.

Zig-zag polymer chains are formed through the axial coordination of the phosphoryl oxygen atom of one porphyrin molecule to the zinc atom located in the centre of another macrocyclic cavity. The Zn–O bond length is quite short and equals to 2.2675(17) Å. The oxygen of morpholinyl substituent also forms contacts with the zinc atom of another porphyrin molecule which is situated in the nearest polymer chain. However, this contact is weak as manifested by the Zn⋯O bond length (2.582(3) Å). These weak interactions determine a spacial organization of 1D polymer chains in 2D layers in which all Zn atoms are located in the same plane (Figure 4). The displacement of zinc atoms from the mean N₄ plane of porphyrin macrocycle to the phosphoryl oxygen atom of the adjacent molecule is 0.159 Å which is typical for square pyramidal stereochemistry of the zinc atom. The four nitrogen atoms of the macrocycle are arranged in the base plane (Zn–N 2.0451(18)–2.0701(19) Å). The oxygen atom of the morpholine ring is located opposite to the phosphoryl oxygen atom but too far to be considered as bonded through full-scale coordinative bond. The distances between the nearest zinc atoms in this polymer structure are equal to 8.267 Å (P=O–Zn) and 9.727 Å (morpholinyl⋯O–Zn).

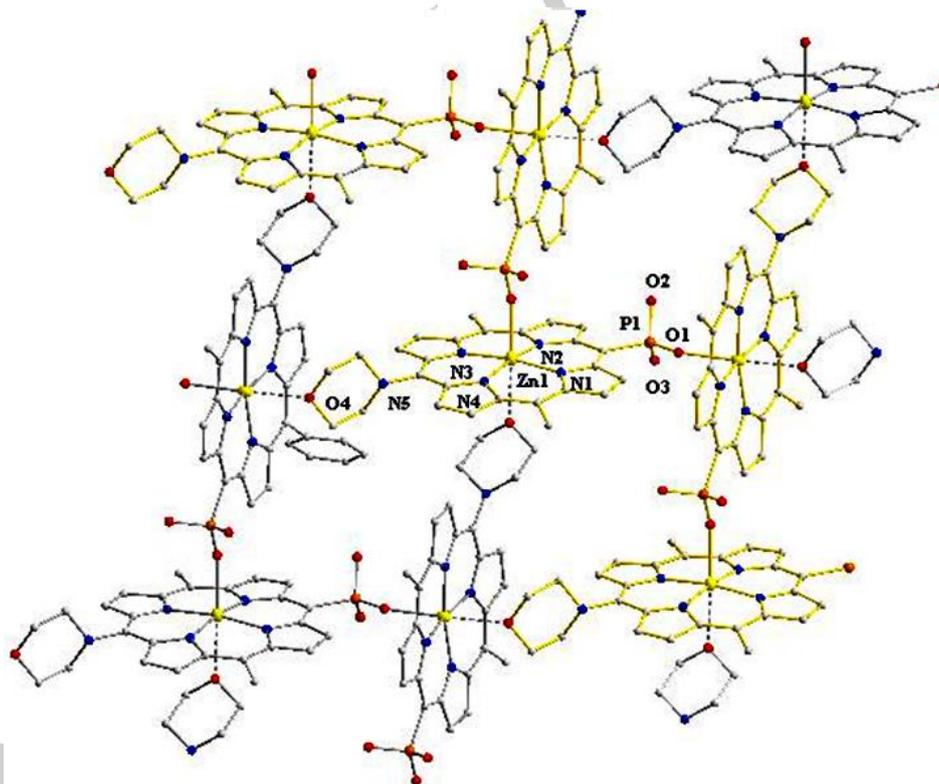


Figure 4. The structure of porphyrin **5a** in crystals. Ethyl substituent of phosphonate groups are omitted and only *ipso*-C atoms of *meso*-phenyl substituents are shown for clarity.

The structure exhibits a low porosity (about 1% of total volume) due to the presence of voids situated between the layers and surrounding by phenyl substituents (Figures S95-97).

The structure of [5,15-di(morpholin-1-yl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrinato]zinc(II) (**12**) was reported by Balabans' group.^[8h] This porphyrin also forms a zig-zag coordination polymer in the crystals in which zinc atoms exhibit a five-coordinated environment as in compound **5a**. The oxygen atom of one morpholinyl group forms coordinative bond with the Zn atom situated in the nearest macrocyclic cavity (Zn–O 2.20 Å). The spacial organization of polymer chains in crystals is totally different from that observed in the crystals **5a** because the oxygen atom of the second morpholine substituent does not have any short contacts with Zn atoms. The crystal packing of compound **12** is much more similar to that of zinc 5,15-bis(diethoxyphosphoryl)-10,20-diphenylporphyrin (**13**)^[10b] which displays 2D coordination polymer structure (Figure 5). In these crystals, Zn(II) atoms located in the mean N₄ plane of the porphyrin macrocycle and exhibit a six-coordinated environment. In CDCl₃/[D₄]MeOH (2:1, v/v) solvent mixture, both porphyrins **5a** and **13** dissociate affording monomeric species.

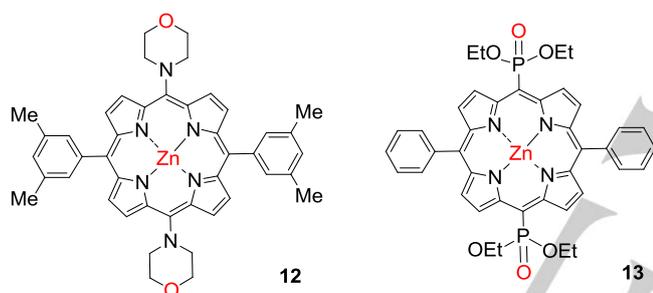


Figure 5. Referenced porphyrins characterized by single-crystal X-ray analysis.

Assembling of porphyrins at the air/water interface

Along with the study of 3D organization of metalloporphyrins in crystals, considerable attention is paid to their 2D assembly at various interfaces because these biomimetic studies are important for better understanding of light-harvesting natural systems and for the development of sensors and catalysts. High values of molar extinction coefficients of porphyrins and their appropriate luminescence quantum yields (about 10%) supply excellent brightness to their films. Therefore, very sensitive sensors can be developed using changes of absorbance or emission of porphyrin films in the presence of metal ions and other small molecules.^[19]

However, due to the low solubility and reactivity of porphyrins in aqueous media, it is necessary to use special approaches that would ensure the binding of metal ions under physiologically and environmentally significant conditions. For this purpose, approaches based on the complexation of metal ions from their aqueous solutions by free porphyrin bases organized in Langmuir monolayers at the air/water interface^[19b],

^{20]} or grafted onto the glass surface^[21] have been proposed. For example, a mixed monolayer composed of porphyrin and long-chain alkyl surfactant molecules was developed to prevent the aggregation of A₄-type porphyrins and facilitate the complexation of metal ions.^[20a] Another approach to achieve a complexation of zinc ions in aqueous media at room temperature was recently developed by us using 5,10,15,20-tetrapyridinylporphyrin (TPyP) as a ligand.^[19b]

Despite these promising examples, the use of porphyrin films in sensing is still limited. One of serious drawbacks of 5,10,15,20-tetraaryl-substituted porphyrin films is a strong π - π stacking in the monolayers which leads to high density of the molecular packing in the films as indicated by low values of limiting molecular areas (55–125 Å² per molecule) observed for these films.^[19a, 19c, 20b, 22] This aggregation reduces the rate of the insertion of metal ions into the macrocyclic cavity and decreases the efficiency of the sensors. Thus, the studies on the influence of peripheral substituents at the tetrapyrrolic macrocycle on the organization of porphyrin molecules in the Langmuir films are of particular importance for the development of porphyrin sensors. The amphiphilic (*trans*-A₂)BC-type porphyrins **3** are of interest from this point of view because the bulky diethoxyphosphoryl group may prevent the aggregation of porphyrin molecules in the monolayers. Moreover, the rather long-chain alkoxy substituent decreases the interlayer coupling in multi-layer films deposited on solid supports.

In this paper, we show that unsymmetrically substituted porphyrins **2H-3a** and **2H-3d** and their zinc complexes **3a** and **3d**, in contrast to tetra-substituted derivatives of A₄-type, provide the formation of rarified films on liquid and solid substrates that can be used for sensing metal cations in aqueous medium.

Monolayers at the air/water interface were formed according to Langmuir technique and the surface pressure–area isotherms for the films of four investigated porphyrins are depicted in Figure 6. Compression isotherms of the zinc porphyrinates **3a** and **3d** which structurally differ one from another only by the presence of a phenylene-type linker between the macrocycle and the medium-chain alkoxy substituent in the compound **3a** are very similar both in the shape and in the values of molecular areas. The rise of surface pressure starts at extremely large surface areas (about 260–300 Å² per molecule) indicating the horizontal orientation of the macrocycle of both discotics at the interface.

Compression isotherms of the free base porphyrins **2H-3a** and **2H-3d** are also similar one to another but rather different from those of corresponding zinc porphyrinates. The observed limiting molecular areas of 150 Å² per molecule are in agreement with inclined orientations of the macrocycles with respect to the surface (Figure 6, Figure S98). Thus, the metal ion located into the macrocyclic cavity plays a key role in the structural organization of the monolayers of **3a** and **3d**. The face-on orientation of the macrocycles **3a** and **3d** is presumably provided by the axial coordination of a water molecule to the zinc atom. In the absence of zinc cations, the surface pressure–area isotherms are shifted to smaller limiting molecular areas by 100 Å² per molecule and the compressibility of monolayers dramatically decreases. The bulky diethyl

phosphonate group seems to prevent the formation of tight porphyrin aggregates because limiting molecular areas observed for the films of **2H-3a** and **2H-3d** are fairly large and the increase in surface pressure for monolayers is quite steep

(Figure 6b). The phenylene-type linker slightly increases the observed limiting molecular areas and gives the monolayers exhibiting a higher rigidity.

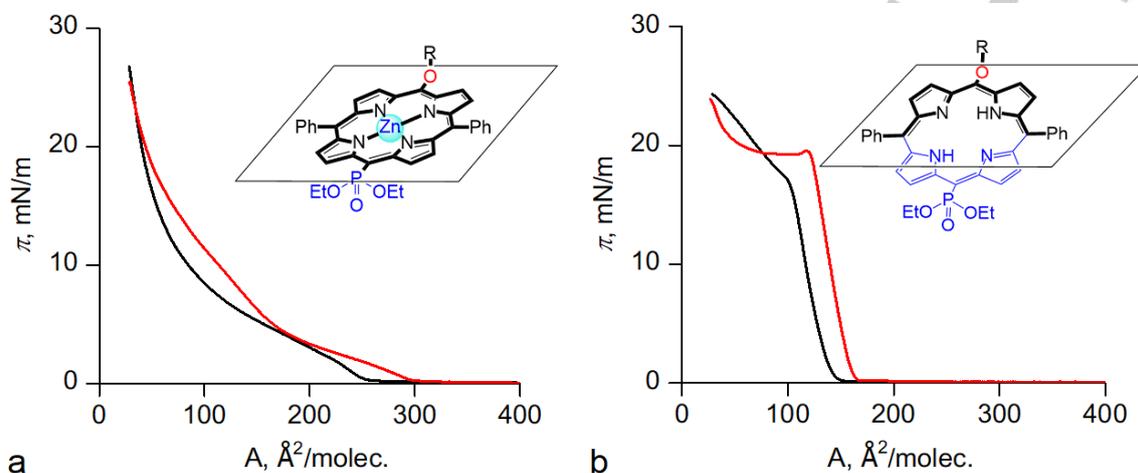


Figure 6. Surface pressure vs area isotherms (π -A curves) for the monolayer of (a) **3a** (red line) and **3d** (black line), (b) **2H-3a** (red line) and **2H-3d** (black line) on the surface of deionized water.

Interestingly, the behavior of 5,10,15,20-tetrapyridinylporphyrin (TPyP) and its zinc complex ZnTPyP which were taken as a representative example of A_4 -type porphyrins is different from that of porphyrinylphosphonate diesters in question (Figure S99). These two compounds being organized in the monolayers exhibit similar surface pressure-area isotherms characterized by the limiting molecular areas of 100 \AA^2 per molecule that is in agreement with an inclined orientation of the aggregated porphyrin molecules and indicates stronger π - π stacking of porphyrin macrocycles in the

monolayers.

The difference in the behavior of zinc complexes **3a**, **3d** and ZnTPyP presumably can be explained by increasing ability of porphyrins **3a** and **3d** bearing electron-deficient porphyrinylphosphonate ligands for axial coordination of water molecules.

UV-vis spectra of **3a**, **3d**, **2H-3a**, and **2H-3d** in chloroform solutions and at the air/water interface are depicted in Figures 7 and S100 and their absorption characteristics are summarized in Tables S3–S5.

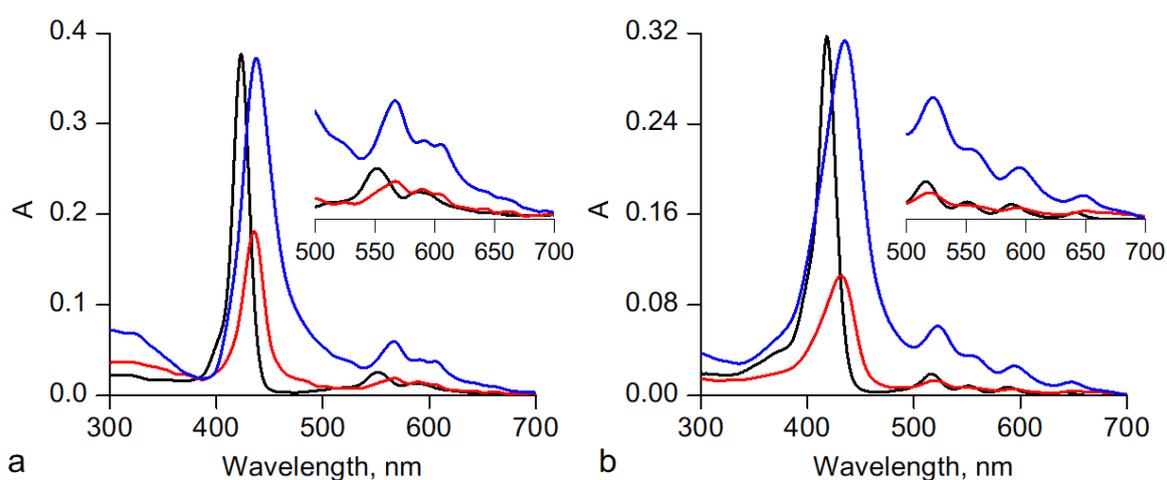


Figure 7. UV-vis spectra of porphyrins in CHCl_3 solution (black line) and *in situ* UV-vis spectra of the monolayer on the surface of deionized water at 0 mN m^{-1} (red line) and 25 mN m^{-1} (blue line) for (a) **3a** and (b) **2H-3a**.

The spectra of free base porphyrins **2H-3a** and **2H-3d** and their Zn complexes **3a** and **3d** in chloroform solutions are typical for porphyrin derivatives. Both B and Q absorbance maxima underwent a significant red shift (9–12 nm) in the monolayers which is likely resulted from the change of the local molecular environment when porphyrin molecules are organized at the interface. It has to be noted, that the shifts of Soret and Q bands were similar for the films formed by free base porphyrins and their complexes despite the different orientation of the macrocycles in these films. The increase of surface pressure induces small red shifts (1–3 nm) of the bands that is typically observed in ordered (quasisolid) A_4 -type porphyrin systems. The absorbance of the monolayers **3a**, **3d**, **2H-3a** and **2H-3d** increases with their compression due to an increase the density of monolayers (Figure S101). It is of interest, that absorption properties of films formed by amphiphilic porphyrins **2H-3a** and **2H-3d** and their zinc complexes are similar to those reported for A_4 -type porphyrins organized in ordered (quasisolid) supramolecular systems at the interfaces and in particular for **TPyP** (Figure S102). However, when the monolayer of **ZnTPyP** is compressed the the second blue-shifted maximum is observed in the Soret-band region indicating strong π - π stacking of porphyrin macrocycles in the monolayers (Figure S102).

To prepare thin solid films of free base porphyrins **2H-3a** and **2H-3d** and their zinc complexes **3a** and **3d**, Langmuir-Schaefer (LS) technique was applied.^[23] The Langmuir monolayers were transferred horizontally onto hydrophobic polyvinyl chloride support at surface pressure of 5 mN m^{-1} . The obtained porphyrin films were examined by electron absorption and fluorescence spectroscopies (Figures S103–S105). The intensity of Soret band increases linearly with the number of transferred layers for all porphyrins, indicating that equal amount of compounds was transferred onto the solid support at each deposition cycle (Figure S103). Moreover, the shape of the spectra resembles those of Langmuir monolayers (Figure S104). The films were

emissive and intensity of fluorescence also gradually increased with the number of layers (Figure S105). This confirms that the bulky diethoxyphosphoryl groups and alkoxy substituents located at opposite *meso* positions of the macrocycle prevent porphyrin aggregation between the layers in the studied multilayer films. It should be noted, that the similar films formed of 10 layers of **TPyP** or **ZnTPyP** exhibit much broader Soret band compared to Langmuir monolayer of porphyrins under investigation (Figure S102) that can be regarded as a signature of stronger intermolecular interactions in the films of tetrapyrrolyl-substituted porphyrins.

Finally, sensing properties of the monolayers formed by a free base porphyrin **2H-3a** at the air/water interface were explored. Detection of zinc ion was chosen as the first goal taking into account the unusual change of the compression isotherm after insertion of metal ions into the macrocyclic cavity discussed above (Figure 6). Porphyrin **2H-3a** was spread on the surface of aqueous solution of $\text{Zn}(\text{ClO}_4)_2$ and the surface pressure-area isotherm was recorded after 60 min (Figure 8a).

The obtained isotherm was very similar to that of monolayer formed from zinc porphyrinate **3a**. The increase in surface pressure starts already at a large limiting molecular area that indicates the formation of zinc complex. A very sharp rise in surface pressure at large areas probably indicates that zinc ions were not only inserted into the macrocyclic cavity but also bonded to diethoxyphosphoryl groups belonging to one or two adjacent porphyrin molecules, because such bonding should increase the rigidity of the monolayer due to the formation of supramolecular complexes and electrostatic interactions. The complexation of $\text{Zn}(\text{II})$ ions was also observed by UV-vis spectroscopy as the change of the number and maxima of Q bands (Figure 8b). Absorbance spectrum of free base **2H-3a** monolayer on the surface of aqueous solution of zinc perchlorate was identical to that of zinc complex **3a** on the surface of pure water.

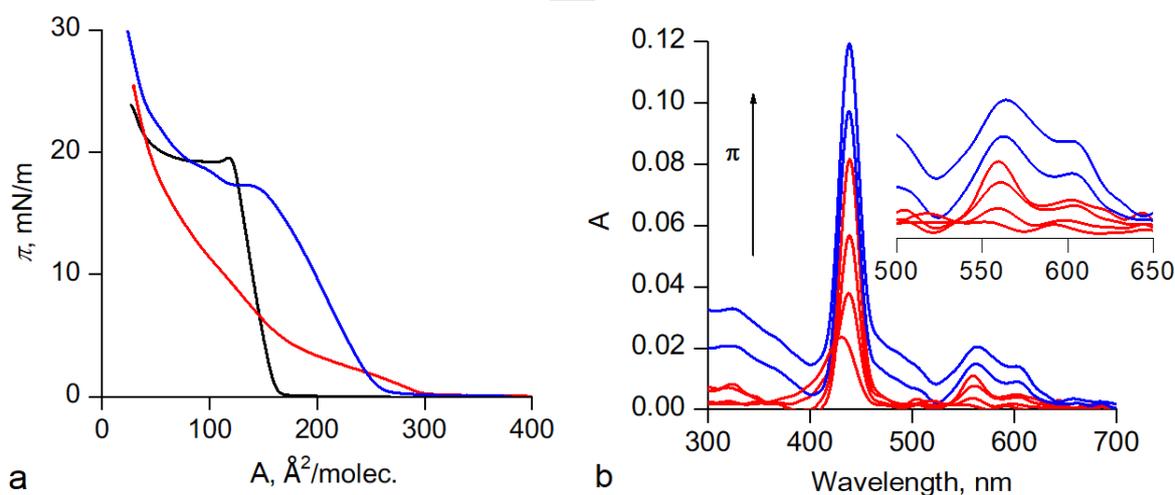


Figure 8. (a) Surface pressure vs area isotherms (π - A curves) for the monolayer of **3a** (red line), **2H-3a** (black line) on the surface of deionized water, and **2H-3a** (blue line) on the surface of $\text{Zn}(\text{ClO}_4)_2$ (0.1 M) aqueous solution. Equilibration time before compression was 15 (red and black lines) and 60 min (blue line), respectively. (b) *In situ* UV-vis spectra for **2H-3a** monolayer on the surface of $\text{Zn}(\text{ClO}_4)_2$ (0.1 M) aqueous solution. The spectra were recorded during the equilibration (red lines) and compression (blue lines) of the monolayer.

Conclusions

Here we report a novel family of (*trans*-A₂)BC-type porphyrins bearing the electron-donating groups (SR, OR, NR₂) and the electron-withdrawing diethoxyphosphoryl substituent at opposite *meso* positions of the macrocycle.

These porphyrins were prepared from *trans*-A₂-type derivatives according to a multi-step procedure involving the phosphorylation and bromination followed by the substitution of bromine atom at the macrocycle. S_NAr reactions with S- and O-nucleophiles are convenient for introduction of these heteroatoms at the macrocyclic periphery. In contrast, S_NAr reactions with N-nucleophiles afford *meso*-aminoporphyrins in good yields only for cyclic secondary amines. Primary amines, anilines and azacrowns could also be reacted with bromide **2** but palladium catalysts are needed to achieve acceptable product yields.

Changes in the electronic and conformational structure induced by heteroatom substituents may result in their unique properties for specific applications ranging from amphiphilic porphyrins for PDT and interface science, push-pull systems for optics and solar-fuel developments to chiral systems for catalysis. In this article, we introduce them as ditopic ligands for supramolecular chemistry by structural characterization of 1D coordination polymer of [5-(diethoxyphosphoryl)-15-(morpholin-1-yl)-10,20-diphenylporphyrinato]zinc (**5a**). Moreover, we demonstrated that (*trans*-A₂)BC-type porphyrins form stable Langmuir monolayers at the air/water interface. The bulky diethoxyphosphoryl group together with medium-chain alkoxy substituent prevents a strong π - π stacking of porphyrin molecules in these monolayers. The comparison of the compression isotherms of four electron-deficient porphyrins reveals the crucial role of the central metal ion in the structural organization of Langmuir films formed by these compounds. The monolayer formed by the free base porphyrin **2H-3a** can be used for the detection of zinc ions in environmentally relevant conditions. Moreover, ten-layers Langmuir-Schaefer films of free base porphyrins formed on the surface of polyvinyl chloride are stable and emissive. Taken together, these data show the interest of these amphiphilic compounds for the development of solid-state sensors for toxic metal ions. This work is now in progress.

Experimental Section

Materials: Unless otherwise noted, all chemicals and starting materials were obtained commercially from Acros® or Aldrich® and used without further purification. Chloroform (analytical grade) was purchased from Merck and was distilled over CaH₂. DMA was dried over molecular sieves. Toluene (HPLC-grade) was dried over alumina cartridges using a solvent purification system PureSolv PS-MD-5 model from Innovative Technology. Cs₂CO₃ was dried under reduced pressure at 120 °C for 48 hours. Methanol (MeOH, Merck, 99.8%) and zinc perchlorate hexahydrate (Aldrich) were used without further purification. *We emphasize that perchlorate salts are potentially explosive when mixed*

with organic ligands and should be therefore used only in very small amount; all manipulations should be done with special care. [5,15-Diphenylporphyrinato]zinc (**6**) were prepared according to published procedures.^[13] [10-(Diethoxyphosphoryl)-5,15-diphenylporphyrinato]zinc was obtained in 72% yield according to a two-steps procedure involving bromination of porphyrin **6** (2 g, 4.31 mmol) followed by Pd-catalysed phosphonilation.^[11] Bromination of this porphyrin with NBS in chloroform at -7 °C afforded bromoporphyrin **2** (Ar = Ph) in 85% yield (Scheme 1).^[11]

Methods: Analytical thin-layer chromatography (TLC) was carried out using Merck silica gel 60 plates (precoated sheets, 0.2 mm thick, with the fluorescence indicator F254). Column chromatography purification was carried out on silica gel (silica 60, 63–200 mm, Aldrich). Catalytic reactions were carried out using Carousel 12 Plus equipment for parallel synthesis (Radleys) unless otherwise noted.

Spectroscopic measurements: ¹H, ³¹P and ¹³C NMR spectra were acquired either on a Bruker Avance II 300 MHz, Bruker Avance III 500 MHz or a Bruker Avance III Nanobay 600 MHz spectrometers. Chemical shifts are expressed in parts per million (ppm), referenced on the δ scale by using residual non-deuterated solvent signals as internal standard for ¹H and ¹³C NMR spectroscopy and external phosphonic acid (H₃PO₄) for ³¹P NMR spectroscopy. The coupling constants are expressed in units of frequency (Hz). FT-IR spectra were registered on FT-IR Nexus (Nicolet) and Bruker Vector 22 spectrophotometers. Micro-ATR accessory (Pike) was used in order to obtain FT-IR spectra of polycrystalline solid complexes. The UV-vis spectra were recorded with a Varian Cary 5000 and SHIMADZU-2450 spectrophotometers by using a rectangular quartz cell (Hellma, 100-QS, 45 × 12.5 × 12.5 mm, light path 10 mm, chamber volume 3.5 mL) or a cylindrical quartz cell (Hellma, 121.000, light path 1 mm, chamber volume 0.28 mL).

Mass spectrometry: MALDI-TOF mass-spectra were obtained on a Bruker Ultraflex II LRF 2000 mass-spectrometer in positive ion mode with a dithranol matrix. Accurate mass measurements (HRMS) were recorded on a Thermo LTQ Orbitrap XL apparatus equipped with electrospray ionization (ESI) source. Solutions in CHCl₃/methanol (1:1) were used for the analysis.

All spectroscopic and mass measurements were performed at the "Pôle Chimie Moléculaire", the technological platform for chemical analysis and molecular synthesis (<http://www.wpcm.fr>) which relies on the Institute of Molecular Chemistry of University of Burgundy and Welience™, a Burgundy University private subsidiary and Shared Facility Centers at the Institute of Physical Chemistry and Electrochemistry RAS.

X-ray crystallographic analysis: Crystals suitable for single crystals X-ray analysis were grown in an open glass tube by a slow diffusion of hexane into a solution of **5a** in a CHCl₃/MeOH solvent mixture (97:3, v/v, c = 10⁻³ M). SCXRD experiment and refinement are detailed in Supporting Information. The X-ray measurements were performed using shared experimental facilities supported by IGIC RAS state assignment. Measurements were performed in Shared Facility Center at the Institute of General and Inorganic Chemistry RAS. Data **CCDC**-1893716 contains the supplementary crystallographic information for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis.

{5-(Diethoxyphosphoryl)-15-[4-(octyloxy)phenoxy]-10,20-diphenylporphyrinato}zinc (3a): A 10 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with bromoporphyrin **2** (20 mg, 0.027 mmol), 4-octyloxyphenol **8a** (90 mg, 0.405 mmol) and cesium carbonate (44 mg, 0.135 mmol). The reaction vessel was evacuated and purged by N₂ for 3 times. Subsequently, 4 mL of DMA was added by syringe and the mixture was stirred at 90°C for 2 h. After cooling, the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using CH₂Cl₂ and CH₂Cl₂/MeOH (99.5:0.5, v/v) as eluents. The target compound **3a** was isolated as a red solid in 98% yield (23 mg). ¹H NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25°C): δ_H = 10.10 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 9.24 (d, ³J_{H,H} = 4.6 Hz, 2H, β-H), 8.82 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 8.64 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 8.13 (d, 4H, *o*-Ph), 7.73–7.70 (m, 6H, *m*- and *p*-Ph), 6.96 (d, 2H, OArOR), 6.76 (d, 2H, OArOR), 4.44–4.42 (m, 2H, POCH₂), 4.21–4.19 (m, 2H, POCH₂), 3.85 (t, ³J_{H,H} = 7.0 Hz, 2H, OCH₂C₇H₁₅), 1.35 (t, ³J_{H,H} = 7.1 Hz, 6H, OCH₂Me), 1.27–1.22 (m, 12H, OCH₂(CH₂)₆), 0.84 (t, ³J_{H,H} = 7.1 Hz, 3H, Me) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃/CD₃OD 2:1, v/v, 25°C): δ_C = 160.63 (1C, *i*-C_{Ar}(O)), 154.37 (d, ²J_{C,P} = 20.1 Hz, 2C, α-C(CP)), 153.67 (2C, α-C), 150.63 (1C, *i*-C_{Ar}(O)), 149.33 (2C, α-C), 145.18 (2C, α-C), 142.67 (2C, *i*-C_{Ph}), 137.12 (1C, *meso*-C15), 134.16 (4C, *o*-C_{Ph}), 133.28 (2C, β-C), 132.03 (2C, β-C), 131.15 (2C, β-C), 128.27 (2C, β-C), 127.43 (2C, *p*-C_{Ph}), 126.38 (4C, *m*-C_{Ph}), 122.15 (2C, *meso*-C10, 20), 117.09 (2C, *o*-C_{Ar}), 115.40 (2C, *m*-C_{Ar}), 96.15 (d, ²J_{C,P} = 183 Hz, 1C, *meso*-C5), 68.63 (1C, OCH₂(CH₂)₆Me), 62.62 (d, ²J_{C,P} = 5.0 Hz, 2C, POCH₂), 31.67 (1C, CH₂), 29.19 (1C, CH₂), 29.08 (2C, CH₂), 25.88 (1C, CH₂), 22.48 (1C, CH₂), 16.11 (d, ²J_{C,P} = 7.0 Hz, 2C, OCH₂Me), 13.76 (1C, O(CH₂)₇Me) ppm. ³¹P{¹H} NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v): δ_P = 30.54 ppm. FT-IR (neat): ν_{max} = 3374 (w), 3168 (w), 3125 (w), 3052 (w), 3022 (w), 2925 (m), 2854 (m), 2532 (w), 2343 (w), 2324 (w), 2196 (w), 2178 (w), 2165 (w), 2150 (w), 2109 (w), 2080 (w), 2052 (w), 2043 (w), 2011 (w), 1982 (w), 1968 (w), 1897 (w), 1840 (w), 1808 (w), 1660 (w), 1597 (w), 1571 (w), 1550 (w), 1530 (w), 1497 (w), 1468 (m), 1456 (m), 1440 (m), 1420 (m), 1391 (w), 1359 (w), 1342 (m), 1326 (w), 1289 (w), 1244 (w), 1222 (m, P=O), 1194 (s, P=O), 1148 (m), 1092 (m), 1068 (m), 1044 (m), 1008 (s), 977 (m, P=O), 960 (m, P=O), 891 (m), 874 (m), 847 (w), 823 (m), 795 (m), 784 (m), 760 (m), 747 (m), 729 (m), 714 (m), 701 (m), 660 (m), 624 (w), 580 (m), 563 (m), 549 (w), 534 (w), 515 (m) cm⁻¹. UV/Vis (CHCl₃/MeOH 2:1, v/v): λ_{max} [log ε (M⁻¹ cm⁻¹)] = 403 (5.43), 424 (6.33), 519 (4.26), 557 (4.92), 589 (4.57), 601 nm (4.53). HRMS (ESI): *m/z* calcd. for C₅₀H₄₉N₄O₅PZn [M-e]⁺ 880.27226; found 880.27553; calcd. for C₅₀H₅₀N₄O₅PZn [M+H]⁺ 881.28048; found 881.28019.

Diethyl {15-[4-(octyloxy)phenoxy]-10,20-diphenylporphyrin-5-yl}phosphonate (2H-3a): A 100 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with **3a** (10.0 mg, 0.011 mmol). Subsequently, 25.0 mL of chloroform and 100 μL of HCl were added by syringe and the mixture was stirred at room temperature for 1 h. Then the mixture was washed with distilled water (4x100 mL). The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure. The target compound **2H-3a** was isolated as red solid in 94% yield (8 mg).

[5-(Diethoxyphosphoryl)-15-(3,5-dimethylphenoxy)-10,20-diphenylporphyrinato]zinc (3b): A 10 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with bromoporphyrin **2** (10 mg, 0.014 mmol), 3,5-dimethylphenol (**8b**) (34.0 mg, 0.28 mmol) and cesium carbonate (22 mg, 0.07 mmol). The reaction vessel was evacuated and purged by N₂ for 3 times. Subsequently, 2 mL of DMA was added by syringe and the mixture was stirred at 85°C for 8 h. After cooling, 20 mL of chloroform was added to the mixture, after that, the mixture was washed with Na₂CO₃ (3 x 10 mL) and distilled water (10 mL). The organic phase was dried over MgSO₄, filtered and evaporated

under reduced pressure. The residue was purified by column chromatography on silica gel using CH₂Cl₂ and CH₂Cl₂/MeOH (85:15, v/v) as eluents. The porphyrin was isolated as a red solid in 95% yield (10 mg). ¹H NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25°C): δ_H = 10.10 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 9.25 (d, ³J_{H,H} = 4.6 Hz, 2H, β-H), 8.84 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 8.66 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 8.14 (d, 4H, *o*-Ph), 7.75–7.70 (m, 6H, *m*- and *p*-Ph), 7.46 (s, 1H, *p*-OAr), 6.63 (s, 2H, *o*-OAr), 4.44–4.42 (m, 2H, POCH₂), 4.20–4.18 (m, 2H, POCH₂), 2.11 (s, 6H, OArMe), 1.35 (t, ³J_{H,H} = 7.1 Hz, 3H, OCH₂Me) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃/CD₃OD 2:1, v/v, 25°C): δ_C = 166.08 (1C, *i*-C_{Ar}), 154.38 (d, ²J_{C,P} = 20.1 Hz, 2C, α-C(P)), 150.67 (2C, α-C), 149.33 (2C, α-C), 146.16 (2C, α-C), 142.69 (2C, *i*-C_{Ph}), 139.34 (2C, *m*-C_{Ar}), 136.73 (1C, *meso*-C15), 134.17 (4C, *o*-C_{Ph}), 133.27 (2C, β-C), 132.02 (2C, β-C), 131.17 (2C, β-C), 128.31 (2C, β-C), 127.43 (2C, *p*-C_{Ph}), 126.38 (4C, *m*-C_{Ph}), 123.30 (1C, *p*-C_{Ar}), 122.14 (2C, *meso*-C10, 20), 114.40 (2C, *o*-C_{Ar}), 95.84 (d, ²J_{C,P} = 186 Hz, 1C, *meso*-C5), 62.59 (d, ²J_{C,P} = 5.0 Hz, 2C, OCH₂), 20.93 (2C, ArMe), 16.08 (d, ²J_{C,P} = 7.0 Hz, 2C, OCH₂Me) ppm. ³¹P{¹H} NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v): δ_P = 26.60 ppm. FT-IR (neat): ν_{max} = 3270 (m), 3260 (m), 3226 (m), 3199 (m), 3162 (m), 3114 (w), 3055 (m), 3026 (m), 2956 (m), 2922 (m), 2852 (m), 2568 (m), 2543 (m), 2351 (w), 2324 (w), 2288 (w), 2204 (w), 2165 (w), 2147 (w), 2114 (w), 2079 (w), 2052 (w), 2039 (w), 1980 (w), 1950 (w), 1889 (w), 1844 (w), 1808 (w), 1728 (w), 1683 (m), 1616 (m), 1594 (m), 1574 (m), 1549 (m), 1531 (m), 1464 (m), 1455 (s), 1440 (m), 1416 (m), 1394 (m), 1358 (m), 1341 (m), 1324 (m), 1312 (m), 1291 (m), 1262 (s), 1222 (m, P=O), 1201 (s, P=O), 1187 (m), 1161 (s), 1129 (m), 1088 (m), 1070 (m), 1042 (m), 1007 (s), 978 (s, P=O), 961 (m, P=O), 889 (m), 872 (m), 846 (m), 823 (m), 790 (m), 748 (m), 730 (m), 715 (m), 701 (m), 684 (m), 660 (m), 634 (w), 580 (m), 562 (m), 518 (m), 511 (m) cm⁻¹. UV/Vis (CHCl₃/MeOH 2:1, v/v): λ_{max} [log ε (M⁻¹ cm⁻¹)] = 423 (5.63), 517 (3.65), 557 (4.33), 589 (4.02), 600 nm (3.97). HRMS (ESI): *m/z* calcd. for C₄₄H₃₇N₄O₄PZn [M-e]⁺ 780.18384; found 780.18635; calcd. for C₄₄H₃₈N₄O₄PZn [M+H]⁺ 781.19167; found 781.19107.

[5-(4-bromophenoxy)-15-(Diethoxyphosphoryl)-10,20-diphenylporphyrinato]zinc (3c): A 10 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with bromoporphyrin **2** (20 mg, 0.027 mmol), 4-bromophenol (**8c**) (93 mg, 0.54 mmol) and cesium carbonate (44.0 mg, 0.135 mmol). The reaction vessel was evacuated and purged by N₂ for 3 times. Subsequently, 4 mL of DMA was added by syringe and the mixture was stirred at 85°C for 1.5 h. After cooling, 20 mL of chloroform was added to the mixture, after that, the mixture was washed with Na₂CO₃ (3 x 10 mL) and distilled water (20 mL). The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using CH₂Cl₂ and CH₂Cl₂/MeOH (85:15, v/v) as eluents. The porphyrin **3c** was isolated as a red solid in 54% yield (12 mg). ¹H NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25°C): δ_H = 10.13 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 9.19 (d, ³J_{H,H} = 4.6 Hz, 2H, β-H), 8.84 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 8.67 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 8.11 (d, 4H, *o*-Ph), 7.72–7.70 (m, 6H, *m*- and *p*-Ph), 7.31 (d, 2 H, OArBr), 6.91 (d, 2H, OArBr), 4.45–4.43 (m, 2H, OCH₂), 4.22–4.20 (m, 2H, OCH₂), 1.35 (t, ³J_{H,H} = 7.1 Hz, 6H, Me) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃/CD₃OD 2:1, v/v, 25°C): δ_C = 164.84 (1C, *i*-C_{Ar}), 154.39 (d, ²J_{C,P} = 20.1 Hz, 2C, α-CP), 150.80 (2C, α-C), 149.52 (2C, α-C), 144.58 (2C, α-C), 142.58 (2C, *i*-C_{Ph}), 135.79 (4C, *o*-C_{Ph}), 133.38 (2C, β-C), 132.42 (2C, β-C), 132.24 (2C, *m*-C_{Ar}), 131.52 (2C, β-C), 127.96 (2C, β-C), 127.49 (2C, *p*-C_{Ph}), 126.42 (4C, *m*-C_{Ph}), 122.22 (2C, *meso*-C10,20), 118.18 (2C, *o*-C_{Ar}), 113.92 (1C, *i*-C_{Ar}), 62.67 (d, ²J_{C,P} = 5.0 Hz, 2C, OCH₂), 16.20 (d, ²J_{C,P} = 7.0 Hz, 2C, Me), signals of *meso*-C5 and *meso*-C15 are not observed. ³¹P{¹H} NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v): δ_P = 26.31 ppm. FT-IR (neat): ν_{max} = 2922 (m), 2852 (m), 2676 (w), 2576 (w), 2528 (w), 2502 (w), 2351 (w), 2325 (w), 2288 (w), 2248 (w), 2240 (w), 2219 (w), 2203 (w), 2166 (w), 2149 (w), 2140 (w), 2106 (w), 2082 (w), 2052 (w), 2011 (w), 1981 (w), 1954

(w), 1940 (w), 1909 (w), 1885 (w), 1809 (w), 1790 (w), 1716 (w), 1696 (w), 1682 (w), 1660 (w), 1651 (w), 1645 (w), 1634 (w), 1597 (w), 1576 (w), 1550 (w), 1531 (w), 1479 (m), 1441 (m), 1392 (w), 1359 (w), 1341 (m), 1326 (w), 1288 (m), 1263 (m, P=O), 1202 (s, P=O), 1164 (m), 1148 (m), 1092 (m), 1070 (m), 1044 (m), 1007 (s), 978 (m, P–O), 960 (m, P–O), 891 (m), 874 (m), 847 (w), 823 (m), 794 (m), 749 (m), 730 (m), 715 (m), 702 (m), 684 (w), 660 (m), 636 (w), 582 (w), 565 (m), 537 (m), 518 (m) cm^{-1} . UV/Vis ($\text{CHCl}_3/\text{MeOH}$ 2:1, v/v): λ_{max} [$\log \epsilon$ ($\text{M}^{-1} \text{cm}^{-1}$)] = 320 (4.18), 404 (4.64), 424 (5.31), 518 (3.44), 556 (4.12), 588 (3.83), 600 nm (3.76). HRMS (ESI): m/z calcd. for $\text{C}_{42}\text{H}_{32}\text{BrN}_4\text{O}_4\text{PZn}$ [M-e^+] 830.06305; found 830.06554; calcd. for $\text{C}_{42}\text{H}_{33}\text{BrN}_4\text{O}_4\text{PZn}$ [M+H^+] 831.07088; found 831.07117.

[5-(Diethoxyphosphoryl)-15-(octyloxy)-10,20-

diphenylporphyrinato]zinc (3d): A 10 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with bromoporphyrin **2** (17.0 mg, 0.023 mmol) and cesium carbonate (75 mg, 0.229 mmol). The reaction vessel was evacuated and purged by N_2 for 3 times. Subsequently, 2.5 mL of 1-octanol (**8d**) was added by syringe and the mixture was stirred at 85°C for 4 h. After cooling, the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 and $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99.4:0.6, v/v) as eluents. The porphyrin **3d** was isolated as a red solid in 87% yield (25 mg). ^1H NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25°C): δ_{H} = 10.05 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 9.42 (d, $^3J_{\text{H,H}} = 4.6$ Hz, 2H, β -H), 8.79 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 8.69 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 8.13 (d, 4H, α -Ph), 7.78–7.72 (m, 6H, m - and p -Ph), 5.06 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 2H, $\text{OCH}_2\text{C}_7\text{H}_{15}$), 4.48–4.46 (m, 2H, POCH_2), 4.20–4.18 (m, 2H, POCH_2), 2.38–2.36 (m, 2H, $\text{OCH}_2\text{CH}_2\text{C}_6\text{H}_{13}$), 1.90–1.88 (m, 2H, $\text{OC}_2\text{H}_4\text{CH}_2\text{C}_5\text{H}_{11}$), 1.58–1.56 (m, 2H, $\text{OC}_3\text{H}_6\text{CH}_2\text{C}_4\text{H}_9$), 1.47–1.45 (m, 2H, $\text{OC}_4\text{H}_8\text{CH}_2\text{C}_3\text{H}_7$), 1.37–1.38 (m, 4H, $\text{OC}_5\text{H}_{10}(\text{CH}_2)_2\text{Me}$), 1.34 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 6H, Me), 0.92 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 3H, OCH_2Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25°C): δ_{C} = 154.52 (d, $^2J_{\text{C,P}} = 20.1$ Hz, 2C, α -C(P)), 150.48 (1C, *meso*-C15), 148.93 (2C, α -C), 145.27 (2C, α -C), 143.23 (2C, α -C), 142.82 (2C, i -C_{Ph}), 134.14 (4C, o -C_{Ph}), 133.24 (2C, β -C), 131.77 (2C, β -C), 130.63 (2C, β -C), 127.48 (2C, β -C), 127.40 (2C, p -C_{Ph}), 126.38 (4C, m -C_{Ph}), 122.12 (2C, *meso*-C10,20), 95.84 (d, $^2J_{\text{C,P}} = 186$ Hz, 1C, *meso*-C5), 85.09 (1C, $\text{OCH}_2(\text{CH}_2)_6\text{Me}$), 62.53 (d, $^2J_{\text{C,P}} = 5.0$ Hz, 2C, OCH_2), 31.79 (1C, CH_2), 31.06 (1C, CH_2), 29.54 (1C, CH_2), 29.28 (1C, CH_2), 26.41 (1C, CH_2), 22.57 (1C, CH_2), 16.08 (d, $^2J_{\text{C,P}} = 7.0$ Hz, 2C, OCH_2Me), 13.79 (1C, $\text{O}(\text{CH}_2)_7\text{Me}$) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25°C): δ_{P} = 26.97 ppm. FT-IR (neat): ν_{max} = 3374 (w), 3315 (w), 3291 (w), 3237 (w), 3197 (w), 3170 (w), 3119 (w), 3058 (w), 2955 (m), 2924 (m), 2854 (m), 2396 (w), 2325 (w), 2164 (w), 2150 (w), 2114 (w), 2079 (w), 1982 (w), 1845 (w), 1808 (w), 1733 (m), 1636 (w), 1598 (m), 1563 (w), 1550 (m), 1531 (w), 1519 (w), 1498 (w), 1465 (m), 1440 (m), 1418 (m), 1397 (m), 1378 (m), 1356 (m), 1343 (w), 1325 (m), 1288 (m), 1261 (w), 1223 (m, P=O), 1203 (m, P=O), 1190 (m), 1160 (m), 1152 (m), 1122 (m), 1092 (m), 1064 (m), 1046 (m), 1012 (s), 985 (m, P–O), 977 (m, P–O), 927 (w), 891 (m), 874 (m), 846 (w), 824 (m), 798 (m), 750 (m), 730 (m), 715 (w), 702 (m), 661 (m), 633 (m), 594 (m), 579 (m), 539 (m), 505 (m) cm^{-1} . UV/Vis ($\text{CHCl}_3/\text{MeOH}$ 2:1, v/v): λ_{max} [$\log \epsilon$ ($\text{M}^{-1} \text{cm}^{-1}$)] = 400 (5.09), 422 (5.98), 518 (3.99), 556 (4.65), 587 (4.1), 598 nm (4.20). HRMS (ESI): m/z calcd. for $\text{C}_{44}\text{H}_{45}\text{N}_4\text{O}_4\text{PZn}$ [M-e^+] 788.24644; found 788.24783; calcd. for $\text{C}_{44}\text{H}_{46}\text{N}_4\text{O}_4\text{PZn}$ [M+H^+] 789.25427; found 789.25294.

Diethyl [15-4-(octyloxy)-10,20-diphenylporphyrin-5-yl]phosphonate (2H-3d). A 100 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with **3a** (10 mg, 0.013 mmol). Subsequently, 25.0 mL of chloroform and 100 μL of HCl were added by syringe and the mixture was stirred at room temperature for 1 h. Then the mixture was washed with distilled water (4x100 mL). The organic phase was dried over MgSO_4 , filtered and evaporated under reduced pressure.

The target compound **2H-3a** was isolated as red solid in 94% yield (9 mg).

[5-(Diethoxyphosphoryl)-15-(2-methoxyethoxy)-10,20-

diphenylporphyrinato]zinc (3e): A 10 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with bromoporphyrin **2** (10.0 mg, 0.014 mmol) and cesium carbonate (44.0 mg, 0.14 mmol). The reaction vessel was evacuated and purged by N_2 for 3 times. Subsequently, 1.5 mL of 2-methoxyethanol (**8e**) was added by syringe and the mixture was stirred at 85°C for 2.5 h. After cooling, the reaction mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 and $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99:1, v/v) as eluents. The porphyrin **3e** was isolated as a red solid in 72% yield (7.5 mg). ^1H NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25°C): δ_{H} = 10.07 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 9.51 (d, $^3J_{\text{H,H}} = 4.6$ Hz, 2H, β -H), 8.80 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 8.70 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 8.13 (d, 4H, α -Ph), 7.74–7.70 (m, 6H, m - and p -Ph), 5.52 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 2H, OCH_2R), 4.48–4.46 (m, 2H, POCH_2), 4.20–4.18 (m, 2H, $\text{POCH}_2 + 2\text{H}$, OCH_2R), 3.71 (s, 3H, OMe), 1.34 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 6H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25°C): δ_{C} = 154.50 (d, $^2J_{\text{C,P}} = 20.1$ Hz, 2C, α -C(P)), 150.60 (2C, α -C), 149.03 (2C, α -C), 145.18 (2C, α -C), 142.80 (2C, i -C_{Ph}), 142.84 (1C, *meso*-C15), 134.13 (4C, o -C_{Ph}), 133.22 (2C, β -C), 131.83 (2C, β -C), 130.76 (2C, β -C), 127.48 (2C, p -C_{Ph}), 127.39 (2C, β -C), 126.36 (4C, m -C_{Ph}), 122.12 (2C, *meso*-C10,20), 96.09 (d, $^2J_{\text{C,P}} = 186$ Hz, 1C, *meso*-C5), 82.74 (1C, $\text{OCH}_2\text{CH}_2\text{OMe}$), 72.08 (1C, $\text{OCH}_2\text{CH}_2\text{OMe}$), 62.53 (d, $^2J_{\text{C,P}} = 6.0$ Hz, 2C, POCH_2), 59.00 (1C, $\text{OCH}_2\text{CH}_2\text{OMe}$), 16.04 (d, $^2J_{\text{C,P}} = 7.0$ Hz, 2C, OCH_2Me) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25°C): δ_{P} = 26.87 ppm. FT-IR (neat): ν_{max} = 2921 (m), 2851 (m), 2817 (m), 2567 (w), 2528 (w), 2397 (w), 2355 (w), 2338 (w), 2325 (w), 2240 (w), 2218 (w), 2203 (w), 2194 (w), 2171 (w), 2149 (w), 2107 (w), 2079 (w), 2052 (w), 2035 (w), 2023 (w), 2011 (w), 1979 (w), 1950 (w), 1941 (w), 1888 (w), 1810 (w), 1770 (w), 1714 (w), 1681 (w), 1661 (w), 1652 (w), 1634 (w), 1597 (w), 1565 (m), 1550 (m), 1532 (m), 1505 (w), 1465 (m), 1455 (m), 1440 (m), 1417 (w), 1394 (w), 1369 (w), 1354 (m), 1325 (m), 1289 (m), 1261 (m), 1223 (m, P=O), 1202 (m, P=O), 1158 (m), 1123 (m), 1092 (m), 1067 (m), 1039 (m), 1008 (s), 976 (s, P–O), 961 (s, P–O), 890 (w), 873 (m), 846 (m), 823 (w), 798 (m), 784 (m), 750 (m), 730 (w), 714 (m), 701 (m), 681 (w), 660 (m), 623 (w), 584 (m), 538 (m), 511 (m) cm^{-1} . UV/Vis ($\text{CHCl}_3/\text{MeOH}$ 2:1, v/v): λ_{max} [$\log \epsilon$ ($\text{M}^{-1} \text{cm}^{-1}$)] = 402 (4.71), 422 (5.51), 517 (3.61), 554 (4.23), 586 (3.77), 599 nm (3.78). HRMS (ESI): m/z calcd. for $\text{C}_{39}\text{H}_{35}\text{N}_4\text{O}_5\text{PZn}$ [M-e^+] 734.16310; found 734.16427; calcd. for $\text{C}_{39}\text{H}_{36}\text{N}_4\text{O}_5\text{PZn}$ [M+H^+] 735.17093; found 735.17051.

[5-(Diethoxyphosphoryl)-15-(octylsulfanyl)-10,20-

diphenylporphyrinato]zinc (4b): A 10 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with bromoporphyrin **2** (30 mg, 0.04 mmol) and cesium carbonate (132 mg, 0.405 mmol). The reaction vessel was evacuated and purged by N_2 for 3 times. Subsequently, 5 mL of 1-octanethiol (**9b**) was added by syringe and the mixture was stirred at room temperature for 3 h. After that, the mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using CH_2Cl_2 and $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99.4:0.6, v/v) as eluents. The porphyrin **4b** was isolated as a red solid in 58% yield (19 mg). ^1H NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25°C): δ_{H} = 10.16 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 9.99 (d, $^3J_{\text{H,H}} = 4.6$ Hz, 2H, β -H), 8.86 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 8.82 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 8.16 (d, 4 H, α -Ph), 7.75–7.77 (m, 6H, m - and p -Ph), 4.44–4.42 (m, 2H, OCH_2), 4.21–4.19 (m, 2H, OCH_2), 3.47 (t, $^3J_{\text{H,H}} = 7.0$ Hz, 2H, SCH_2), 1.60–1.58 (m, 2H, SCH_2CH_2), 1.42–1.38 (m, 2H, $\text{S}(\text{CH}_2)_2\text{CH}_2$), 1.35 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 6H, OCH_2Me), 1.11–1.09 (m, 8H, $\text{S}(\text{CH}_2)_3(\text{CH}_2)_4$), 0.75 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 3H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25°C): δ_{C} = 153.52 (2C, α -C), 153.18 (d, $^2J_{\text{C,P}} = 20.1$ Hz, 2C, α -C(P)), 151.61 (2C, α -C), 149.64 (2C, α -C), 142.87 (2C, i -C_{Ph}), 134.27

(4C, *o*-C_{Ph}), 132.91 (2C, β -C), 132.72 (2C, β -C), 132.31 (2C, β -C), 131.88 (2C, β -C), 127.46 (2C, *p*-C_{Ph}), 126.33 (4C, *m*-C_{Ph}), 122.09 (2C, *meso*-C10,20), 117.38 (1C, *meso*-C15), 98.60 (d, $^2J_{C,P}$ = 186 Hz, 1C, *meso*-C5), 62.68 (d, $^2J_{C,P}$ = 5.0 Hz, 2C, OCH₂), 43.78 (1C, SCH₂), 31.56 (1C, CH₂), 29.88 (1C, CH₂), 28.95 (2C, CH₂), 28.65 (1C, CH₂), 22.37 (1C, CH₂), 16.09 (d, $^2J_{C,P}$ = 7.0 Hz, 2C, OCH₂Me), 13.65 (1C, S(CH₂)₂Me) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v): δ_{P} = 26.12 ppm. FT-IR (neat): ν_{max} = 3394 (m), 3367 (m), 3354 (m), 3337 (m), 3237 (m), 3026 (w), 2955 (m), 2920 (m), 2851 (m), 2325 (w), 2204 (w), 2195 (w), 2164 (w), 2139 (w), 2106 (w), 2078 (w), 2051 (w), 2039 (w), 2011 (w), 1981 (w), 1965 (w), 1952 (w), 1890 (w), 1811 (w), 1733 (m), 1646 (m), 1634 (m), 1614 (m), 1599 (m), 1550 (w), 1514 (w), 1495 (w), 1465 (m), 1455 (m), 1414 (w), 1394 (w), 1377 (w), 1335 (w), 1321 (w), 1260 (m), 1219 (m, P=O), 1198 (m, P=O), 1090 (s), 1069 (s), 1047 (s), 1015 (s), 984 (m, P=O), 964 (m, P=O), 893 (w), 883 (w), 831 (w), 797 (m), 750 (m), 731 (m), 701 (m), 659 (m), 639 (m), 615 (m), 585 (m), 556 (m), 525 (m), 509 (m) cm⁻¹. UV/Vis (CHCl₃/MeOH 2:1, v/v): λ_{max} [log ϵ (M⁻¹ cm⁻¹)] = 427 (5.45), 523 (3.42), 561 (4.03), 596 (4.12), 609 nm (4.18). HRMS (ESI): *m/z* calcd. for C₄₄H₄₆N₄O₃PSZn [M-e]⁺ 804.22360; found 804.22416; calcd. for C₄₄H₄₆N₄O₃PSZn [M+H]⁺ 805.23142; found 805.22952.

[5-[Etoxy(hydroxy)phosphoryl]-10,20-diphenyl-15-

(phenylsulfanyl)porphyrinato]zinc (4c): A 10 mL two-necked flask equipped with a magnetic stirrer and a back-flow condenser was charged with bromoporphyrin **2** (10 mg, 0.014 mmol) and cesium carbonate (22 mg, 0.07 mmol). The reaction vessel was evacuated and purged by N₂ for 3 times. Subsequently, 4 mL of DMA was added by syringe and the mixture was heated to 120 °C. Then thiophenol (**9a**) (28.0 μ L, 0.28 mmol) was added by syringe and the mixture was stirred at 120 °C for 10 min. After cooling, the mixture was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using CH₂Cl₂ and CH₂Cl₂/MeOH (60:40, v/v) as eluents. The porphyrin was isolated as red solid in 55% yield (6.0 mg). ^1H NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_{H} = 10.43 (d, $^3J_{\text{H,H}}$ = 5.0 Hz, 2H, β -H), 9.82 (d, $^3J_{\text{H,H}}$ = 4.6 Hz, 2H, β -H), 8.75 (d, $^3J_{\text{H,H}}$ = 5.0 Hz, 2H, β -H), 8.73 (d, $^3J_{\text{H,H}}$ = 5.0 Hz, 2H, β -H), 8.06 (d, 4H, *o*-Ph), 7.64–7.60 (m, 6H, *m*- and *p*-Ph), 6.94 (d, 2H, *o*-PhS), 6.90 (t, $^3J_{\text{H,H}}$ = 7.3 Hz, 2H, *m*-PhS), 6.84 (t, $^3J_{\text{H,H}}$ = 7.3 Hz, 1H, *p*-PhS), 3.85–3.83 (m, 2H, OCH₂), 1.12 (t, $^3J_{\text{H,H}}$ = 7.1 Hz, 3H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_{C} = 153.79 (1C, α -CS), 153.05 (d, $^2J_{C,P}$ = 20.1 Hz, 2C, α -C(P)), 151.07 (2C, α -C), 150.01 (2C, α -C), 144.03 (1C, *i*-C_{Ar}), 143.09 (2C, *i*-C_{Ph}), 134.24 (4C, *o*-C_{Ph}), 133.99 (2C, β -C), 132.23 (2C, β -C), 132.19 (2C, β -C), 132.19 (2C, β -C), 128.48 (2C, *m*-C_{Ar}), 127.25 (2C, *p*-C_{Ph}), 126.45 (2C, *o*-C_{Ar}), 126.19 (4C, *m*-C_{Ph}), 124.48 (1C, *p*-C_{Ar}), 121.18 (2C, *meso*-C10, 20), 109.08 (2C, *meso*-C15), 60.86 (d, $^2J_{C,P}$ = 5.0 Hz, 1C, OCH₂), 15.92 (d, $^2J_{C,P}$ = 7.0 Hz, 1C, OCH₂Me). $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v) δ_{P} = 17.34 ppm. FT-IR (neat): ν_{max} = 3395 (s), 3377 (s), 3361 (s), 3351 (s), 3340 (s), 3318 (s), 3292 (s), 3261 (s), 3239 (s), 3215 (s), 3205 (s), 3172 (s), 3164 (s), 3056 (m), 2972 (m), 2925 (m), 2854 (m), 2562 (m), 2356 (m), 2325 (m), 2238 (w), 2219 (w), 2205 (w), 2169 (w), 2148 (w), 2106 (w), 2080 (w), 2052 (w), 2039 (w), 2011 (w), 1982 (w), 1950 (w), 1889 (w), 1809 (w), 1770 (w), 1615 (m), 1598 (m), 1581 (m), 1557 (m), 1548 (m), 1520 (m), 1495 (m), 1475 (m), 1455 (m), 1439 (m), 1414 (m), 1387 (m), 1324 (m), 1297 (m), 1261 (m, P=O), 1177 (m, P=O), 1082 (m), 1070 (m), 1037 (s), 1000 (s), 988 (s, P=O), 946 (m, P=O), 846 (m), 793 (w), 752 (s), 735 (m), 700 (s), 689 (s), 658 (m), 573 (m), 566 (m), 555 (m), 520 (m), 509 (m) cm⁻¹. UV/Vis (CHCl₃/MeOH 2:1, v/v): λ_{max} [log ϵ (M⁻¹ cm⁻¹)] = 423 (5.46), 461 (4.21), 517 (3.72), 555 (4.19), 597 nm (3.91).

S_NAr Amination of [5-bromo-15-(diethoxyphosphoryl)-10,20-diphenylporphyrinato]zinc (**2**). *General Procedure*: A two-necked round-bottomed flask equipped with a condenser and a magnetic stirrer bar was charged with a porphyrin **2** (50 mg, 0.067 mmol), cesium carbonate (87

mg, 0.268 mmol) and an amine (0.335 mmol), if this compound was a solid. The reaction vessel was evacuated and purged with N₂ three times. Anhydrous DMF (17.5 ml) and an amine, if this compound was a liquid, were added by a syringe. The reaction mixture was heated at 50 °C, monitored by MALDI-TOF. After complete conversion of starting compound, water was added and a precipitate was filtered. This solid was dissolved in dichloromethane and subjected to column chromatography on silica gel using a CH₂Cl₂/MeOH mixture as an eluent. The combined fractions containing the product were evaporated under reduced pressure to afford **5a-c** as a green-violet solid. The experimental conditions of these reactions are detailed in Table 3 (entries 1-7, 9,10, 13 and 14).

[5-(Diethoxyphosphoryl)-15-(morpholin-4-yl)-10,20-diphenylporphyrinato]zinc (5a):

The compound was prepared from **2** and morpholine (**10a**) (0.029 mL, 0.335 mmol) by heating of the reaction mixture for 6 h. The crude product was chromatographed with a CH₂Cl₂/MeOH mixture (99.5:0.5, v/v) as an eluent to afford porphyrin **5a** in 95% yield (48 mg). ^1H NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_{H} = 9.85 (d, $^3J_{\text{H,H}}$ = 4.8 Hz, 2H, β -H), 9.35 (d, $^3J_{\text{H,H}}$ = 4.5 Hz, 2H, β -H), 8.57 (d, $^3J_{\text{H,H}}$ = 4.8 Hz, 2H, β -H), 8.47 (d, $^3J_{\text{H,H}}$ = 4.5 Hz, 2H, β -H), 7.91 (d, $^3J_{\text{H,H}}$ = 6.7 Hz, 4H, *o*-Ph), 7.56–7.50 (m, 6H, *m*- and *p*-Ph), 4.24–4.19 (m, 2H, POCH₂), 4.13 (d, $^3J_{\text{H,H}}$ = 4.5 Hz, 4H, NCH₂), 4.10 (d, $^3J_{\text{H,H}}$ = 4.1 Hz, 4H, OCH₂), 4.02–3.95 (m, 2H, POCH₂), 1.13 (t, $^3J_{\text{H,H}}$ = 7.0 Hz, 6H, Me) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl₃/MeOD 2:1, v/v, 25 °C) δ_{C} = 153.86 (d, $^2J_{C,P}$ = 18.2 Hz, 2C, α -C(P)), 150.21 (2C, α -C), 150.03 (2C, α -C), 148.86 (2C, α -C), 142.74 (2C, *i*-C_{Ph}), 134.63 (1C, *meso*-C15), 134.00 (4C, *o*-C_{Ph}), 132.83 (2C, β -C), 131.68 (2C, β -C), 130.56 (2C, β -C), 129.11 (2C, β -C), 127.20 (2C, *p*-C_{Ph}), 126.14 (4C, *m*-C_{Ph}), 121.79 (2C, *meso*-C10, 20), 96.22 (d, $^2J_{C,P}$ = 188.2 Hz, 1C, *meso*-C5), 68.59 (2C, OCH₂), 57.83 (2C, NCH₂), 62.34 (d, $^2J_{C,P}$ = 5.0 Hz, 2C, OCH₂), 15.84 (d, $^2J_{C,P}$ = 6.9 Hz, 2C, OCH₂CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_{P} = 26.76 ppm. FT-IR (neat): ν_{max} = 2981 (w), 2953 (w), 2884 (w), 2846 (w), 1771 (w), 1696 (w), 1596 (w), 1549 (w), 1530 (w), 1466 (m), 1438 (m), 1415 (w), 1390 (w), 1368 (m), 1339 (m), 1320 (m), 1288 (m), 1257 (m, P=O), 1217 (m), 1198 (s, P=O), 1167 (m), 1154 (m), 1112 (m), 1094 (m), 1066 (m), 1033 (m), 1006 (s, P=O), 982 (s, P=O), 964 (s, P=O), 954 (s), 888 (s), 871 (s), 844 (m), 821 (m), 791 (s), 768 (s), 752 (s), 738 (s), 726 (s), 711 (s), 700 (s), 659 (s), 620 (m), 579 (s), 568 (s) cm⁻¹. UV/Vis (CHCl₃/MeOH 2:1, v/v): λ_{max} [log ϵ (M⁻¹ cm⁻¹)] = 320 (4.26), 400 (4.59), 425 (5.45), 519 (3.47), 559 (4.14), 590 (3.97), 601 (3.89), 616 nm (3.69). HRMS (ESI): *m/z* calcd. for C₄₀H₃₆N₅O₄PZnNa [M+Na]⁺ 768.16886; found 768.16632.

[5-(Diethoxyphosphoryl)-15-(piperazin-1-yl)-10,20-diphenylporphyrinato]zinc (5b):

The compound was prepared from porphyrin **2** and piperazine (**10b**) (29 mg, 0.335 mmol) after heating of the reaction mixture for 24 h. The crude product was chromatographed with a mixture of CH₂Cl₂/MeOH (90:10, v/v) as an eluent to afford the porphyrin **5b** (purity ~ 95%) in 87% yield (44 mg). ^1H NMR (600 MHz, py-*d*₅, 25 °C): δ_{H} = 10.82 (d, $^3J_{\text{H,H}}$ = 4.8 Hz, 2H, β -H), 9.79 (d, $^3J_{\text{H,H}}$ = 4.4 Hz, 2H, β -H), 9.06 (d, $^3J_{\text{H,H}}$ = 4.8 Hz, 2H, β -H), 8.89 (d, $^3J_{\text{H,H}}$ = 4.2 Hz, 2H, β -H), 8.31 (d, $^3J_{\text{H,H}}$ = 6.9 Hz, 4H, *o*-Ph), 7.77–7.83 (m, 6H, *m*- and *p*-Ph), 4.58–4.65 (m, 2H, POCH₂), 4.43–4.34 (m, 2H, POCH₂), 4.39 (br s, 4H, NCH₂), 3.49 (br s, 4H, NCH₂), 1.28 (t, $^3J_{\text{H,H}}$ = 7.1 Hz, 6H, Me) ppm, the signal of NH was not observed. $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, Py-*d*₅, 25 °C): δ_{P} = 26.89 ppm. FT-IR (neat): ν_{max} = 2958 (m), 2920 (m), 2852 (m), 1722 (w), 1593 (s), 1563 (s), 1549 (s), 1438 (s), 1414 (s), 1360 (m), 1341 (m), 1322 (m), 1288 (m), 1260 (m, P=O), 1215 (m), 1200 (m, P=O), 1159 (w), 1116 (m), 1088 (m), 1072 (m), 1044 (s), 1008 (s, P=O), 984 (s, P=O), 962 (s, P=O), 890 (s), 873 (s), 844 (w), 821 (m), 796 (s), 753 (s), 728 (m), 714 (m), 701 (s), 669 (s), 632 (w), 616 (s), 578 (s), 563 (s), 552 (s) cm⁻¹. UV/Vis (CHCl₃/MeOH 2:1, v/v): λ_{max} = 423, 521, 559, 590, 603 nm. The self-assembly of compound **5b** in CHCl₃, CH₂Cl₂ and a CHCl₃/MeOH

mixture (2:1, v/v) was observed by ^1H NMR spectroscopy. This aggregation also impedes the accurate determination of molar extinction coefficients (ϵ) of the dye. HRMS (ESI): m/z calcd. for $\text{C}_{40}\text{H}_{38}\text{N}_6\text{O}_3\text{PZn} [\text{M} + \text{H}]^+$ 745.20290; found 745.20158.

μ -[5,5'-(Piperazine-1,4-diyl)bis[15-(diethoxyphosphoryl)-10,20-diphenylporphyrinato]dizinc (11): was isolated as a side product by column chromatography using of a mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (98:2, v/v) as an eluent. Yield 10% (4.6 mg). ^1H NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{H}} = 9.88$ (d, $^3J_{\text{H,H}} = 4.9$ Hz, 4H, β -H), 9.84 (d, $^3J_{\text{H,H}} = 4.6$ Hz, 4H, β -H), 8.64 (t, $^3J_{\text{H,H}} = 4.5$ Hz, 4H, β -H), 8.63 (t, $^3J_{\text{H,H}} = 4.5$ Hz, 4H, β -H), 8.00 (dd, $^3J_{\text{H,H}} = 7.5$ Hz, 1.8 Hz, 8H, α -Ph), 7.61–7.54 (m, 12H, m - and p -Ph), 4.80 (s, 8H, NCH_2), 4.33–4.21 (m, 4H, POCH_2), 4.08–3.97 (m, 4H, POCH_2), 1.18 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 12H, CH_3) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{P}} = 26.93$ ppm. HRMS (ESI): m/z calcd. for $\text{C}_{76}\text{H}_{64}\text{N}_{10}\text{O}_6\text{P}_2\text{Zn}_2\text{Na} [\text{M} + \text{Na}]^+$ 1425.29607; found 1425.29823.

[15-(Diethoxyphosphoryl)-10,20-diphenyl-15-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)porphyrinato]zinc (5c): The compound was prepared from **2** and 1,4,7,10-tetraoxa-13-azacyclopentadecane (**10c**) (74 mg) by heating of the reaction mixture for 100 h. The crude solid was chromatographed using a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99:1, v/v) mixture as an eluent to afford the porphyrin **5c** in 24% yield (14 mg). ^1H NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{H}} = 9.91$ (d, $^3J_{\text{H,H}} = 4.9$ Hz, 2H, β -H), 9.40 (d, $^3J_{\text{H,H}} = 4.6$ Hz, 2H, β -H), 8.62 (d, $^3J_{\text{H,H}} = 4.9$ Hz, 2H, β -H), 8.52 (d, $^3J_{\text{H,H}} = 4.6$ Hz, 2H, β -H), 7.95 (d, $^3J_{\text{H,H}} = 8.2$ Hz, 4H, α -Ph), 7.60–7.51 (m, 6H, m - and p -Ph), 4.28–4.24 (m, 4H, OCH_2), 4.24–4.19 (m, 2H, POCH_2), 4.07–3.96 (m, 2H, POCH_2), 3.82 (t, $^3J_{\text{H,H}} = 5.7$ Hz, 4H, OCH_2), 3.69–3.67 (m, 8H, OCH_2), 3.56–3.53 (m, 4H, OCH_2), 1.15 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 6 H, Me) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{P}} = 25.82$ ppm. FT-IR (neat): $\nu_{\text{max}} = 2917$ (m), 2850 (m), 1731 (w), 1716 (w), 1697 (w), 1682 (w), 1670 (w), 1652 (w), 1635 (w), 1597 (w), 1547 (w), 1506 (w), 1468 (m), 1438 (m), 1389 (w), 1354 (m), 1322 (m), 1288 (m), 1260 (m, P=O), 1217 (m), 1199 (s, P=O), 1089 (s), 1070 (s), 1042 (s), 1009 (s, P=O), 983 (s, P=O), 962 (s, P=O), 889 (s), 872 (s), 844 (m), 797 (s), 748 (s), 729 (s), 715 (m), 700 (s), 660 (m), 578 (s), 562 (s), 552 (m) cm^{-1} . UV/Vis ($\text{CHCl}_3/\text{MeOH}$ 2:1, v/v): $\lambda_{\text{max}} [\log \epsilon (\text{M}^{-1} \text{cm}^{-1})] = 320$ (4.28), 403 (4.72), 424 (5.45), 520 (3.56), 558 (4.18), 590 (4.02), 601 nm (3.95). HRMS (ESI): m/z calcd. for $\text{C}_{46}\text{H}_{48}\text{N}_5\text{O}_7\text{PZnNa} [\text{M} + \text{Na}]^+$ 900.24548; found 900.24750.

Palladium-catalyzed amination of [5-bromo-15-(diethoxyphosphoryl)-10,20-diphenylporphyrinato]zinc (2). *General Procedure*: A two-necked round-bottomed flask, equipped with a condenser, a magnetic stirrer bar and a gas outlet, was charged with bromoporphyrin **2** (1 equiv.), Cs_2CO_3 (1.4 equiv.), $\text{Pd}(\text{OAc})_2/1.5$ BINAP precatalyst (5 mol-%) and amine, if this compound was a solid. In the case of diphenylamine the reaction was carried out with 50 equiv. of amine. The reaction vessel was evacuated and purged with nitrogen three times. Subsequently, anhydrous toluene (0.01 mol/L) and amine, when it was a liquid, were added by syringes. The reaction mixture stirred at reflux and monitored by MALDI-TOF. After complete conversion of porphyrin **2**, the reaction mixture was allowed to cool to room temperature and concentrated under reduced pressure. The solid residue was taken up in dichloromethane and subjected to column chromatography on silica gel using a $\text{CH}_2\text{Cl}_2/\text{MeOH}$ mixture as an eluent. The combined fractions containing the product were evaporated under reduced pressure to afford **5d-h**. All compounds were obtained as green-violet solids. The experimental conditions of these reactions are detailed in Table 3 (entries 8, 11, 12 and 15-19).

[5-(Diethoxyphosphoryl)-10,20-diphenyl-15-(1,4,10,13-tetraoxa-7,16-diazacyclooctadecan-7-yl)porphyrinato]zinc (5d): The compound was prepared from **2** (100 mg, 0.135 mmol) and 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**10d**) (354 mg, 1.35 mmol, 10 equiv.) after

refluxing of the reaction mixture for 8 h. The resulting crude solid was chromatographed with a mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (92.5:7.5, v/v) as an eluent to afford **5d** as a green-violet solid in 38% yield (47 mg). ^1H NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{H}} = 9.86$ (d, $^3J_{\text{H,H}} = 4.9$ Hz, 2H, β -H), 9.32 (d, $^3J_{\text{H,H}} = 4.5$ Hz, 2H, β -H), 8.58 (d, $^3J_{\text{H,H}} = 4.8$ Hz, 2H, β -H), 8.46 (d, $^3J_{\text{H,H}} = 4.5$ Hz, 2H, β -H), 7.91 (d, $^3J_{\text{H,H}} = 6.8$ Hz, 4H, α -Ph), 7.56–7.49 (m, 6H, m - and p -Ph), 4.35 (t, $^3J_{\text{H,H}} = 5.5$ Hz, 4H, OCH_2), 4.23–4.20 (m, 2H, POCH_2), 4.00–3.94 (m, 2H, POCH_2), 3.61–3.57 (m, 8H, OCH_2), 3.46–3.45 (m, 4 H, OCH_2), 3.36–3.34 (m, 4 H, OCH_2), 2.97 (bs, 4 H, OCH_2), 1.12 (t, $^3J_{\text{H,H}} = 7.0$ Hz, 6 H, Me) ppm, signal of NH was not observed. $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{C}} = 153.76$ (d, $^2J_{\text{C,P}} = 18.3$ Hz, 2C, α -C(P)), 151.33 (2C, α -C), 150.30 (2C, α -C), 148.96 (2C, α -C), 142.78 (2C, i -C_{Ph}), 133.98 (4C, o -C_{Ph}), 133.69 (1C, $meso$ -C15), 132.77 (2C, β -C), 131.74 (2C, β -C), 130.65 (2C, β -C), 130.01 (2C, β -C), 127.22 (2C, p -C_{Ph}), 126.14 (4C, m -C_{Ph}), 121.63 (2C, $meso$ -C10, 20), 70.99 (2C, OCH_2), 70.25 (2C, OCH_2), 69.59 (2C, OCH_2), 66.43 (2C, OCH_2), 62.37 (d, $^2J_{\text{C,P}} = 5.0$ Hz, 2C, POCH_2), 61.11 (2C, NCH_2), 47.65 (2C, NCH_2), 15.84 (d, $^2J_{\text{C,P}} = 6.8$ Hz, 2C, OCH_2Me) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{P}} = 26.59$ ppm. FT-IR (neat): $\nu_{\text{max}} = 2951$ (m), 2920 (m), 2850 (m), 1723 (m), 1639 (w), 1598 (w), 1576 (w), 1538 (m), 1491 (w), 1458 (m), 1408 (w), 1384 (w), 1343 (m), 1318 (m), 1259 (s, P=O), 1200 (m, P=O), 1169 (m), 1133 (m), 1094 (s), 1040 (s), 1013 (s, P=O), 965 (s, P=O), 889 (m), 873 (m), 844 (m), 794 (s), 754 (m), 725 (s), 700 (s), 660 (m), 621 (m), 576 (s), 554 (m) cm^{-1} . UV/Vis ($\text{CHCl}_3/\text{MeOH}$ 2:1, v/v): $\lambda_{\text{max}} [\log \epsilon (\text{M}^{-1} \text{cm}^{-1})] = 320$ (4.23), 401 (4.88), 424 (5.77), 520 (3.47), 559 (4.10), 590 (3.94), 601 (3.86), 616 nm (3.67). HRMS (ESI): m/z calcd. for $\text{C}_{48}\text{H}_{54}\text{N}_6\text{O}_7\text{PZn} [\text{M} + \text{H}]^+$ 921.30776; found 921.30733, calcd. for $\text{C}_{48}\text{H}_{53}\text{N}_6\text{O}_7\text{PZnNa} [\text{M} + \text{Na}]^+$ 943.28970; found 943.28624.

[15-(Diethoxyphosphoryl)-15-(hexylamino)-10,20-diphenylporphyrinato]zinc (5e): The compound was prepared from **2** (40 mg, 0.054 mmol) and hexylamine (**10e**) (0.071 mL, 0.54 mmol, 10 equiv.) after refluxing of the reaction mixture for 2 h. The resulting crude solid was chromatographed with a mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (99.5:0.5, v/v) as an eluent to afford **5e** as a green-violet solid in 76% yield (31 mg). ^1H NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{H}} = 9.35$ (d, $^3J_{\text{H,H}} = 4.9$ Hz, 2H, β -H), 8.73 (d, $^3J_{\text{H,H}} = 4.4$ Hz, 2H, β -H), 8.21 (d, $^3J_{\text{H,H}} = 4.9$ Hz, 2H, β -H), 8.02 (d, $^3J_{\text{H,H}} = 4.4$ Hz, 2H, β -H), 7.84 (d, $^3J_{\text{H,H}} = 6.4$ Hz, 4H, α -Ph), 7.55–7.49 (m, 6H, m - and p -Ph), 4.23–4.17 (m, 2H, POCH_2), 4.03–3.99 (m, 2H, POCH_2), 1.90–1.88 (m, 2H, CH_2), 1.44–1.39 (m, 2H, CH_2), 1.23–1.15 (m, 4H, $\text{CH}_2 + 6\text{H}$, OCH_2Me), 0.71 (t, 3H, $^3J_{\text{H,H}} = 7.1$ Hz, Me) ppm, the signal NCH_2 group is overlapped with the the signal of water (traces in the solvents), the signal of NH was not observed. ^{31}P NMR(^1H) (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{P}} = 28.15$ ppm. FT-IR (neat): $\nu_{\text{max}} = 2954$ (m), 2919 (m), 2850 (m), 1724 (m), 1597 (w), 1539 (m), 1502 (w), 1461 (m), 1380 (m), 1342 (m), 1319 (m), 1259 (s, P=O), 1200 (s, P=O), 1162 (m), 1082 (s), 1047 (s), 1012 (s, P=O), 963 (s, P=O), 890 (s), 872 (s), 844 (s), 794 (s), 752 (s), 726 (s), 714 (s), 699 (s), 659 (m), 576 (s), 552 (m) cm^{-1} . UV/Vis ($\text{CHCl}_3/\text{MeOH}$ 2:1, v/v): $\lambda_{\text{max}} [\log \epsilon (\text{M}^{-1} \text{cm}^{-1})] = 347$ (4.29), 428 (5.27), 442 (5.09), 514 (3.71), 550 (4.13), 570 (4.03), 613 nm (4.14). HRMS (ESI): m/z calcd. for $\text{C}_{42}\text{H}_{42}\text{N}_5\text{O}_3\text{PZnNa} [\text{M} + \text{Na}]^+$ 782.22089; found 782.21847.

[5-(Diethoxyphosphoryl)-15-(octylamino)-10,20-diphenylporphyrinato]zinc (5f): The compound was prepared according to the general procedure from bromoporphyrin **2** (17 mg, 0.022 mmol) and *n*-octylamine (**10f**) (36 μL , 0.22 mmol, 10 equiv.). The crude product was purified by column chromatography on silica gel using a $\text{CHCl}_3/\text{pentane}$ (2:3, v/v) mixture as an eluent. The porphyrin **5f** was isolated as a red solid in 78% yield (14 mg). ^1H NMR (600 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$ 2:1, v/v, 25 °C): $\delta_{\text{H}} = 9.40$ (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 8.79 (d, $^3J_{\text{H,H}} = 4.6$ Hz, 2H, β -H), 8.26 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 8.07 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 2H, β -H), 7.91 (d, 4H, α -Ph), 7.62–7.55 (m, 6H, m - and p -

Ph), 4.30–4.25 (m, 2H, OCH₂), 4.22 (t, ³J_{H,H} = 7.1 Hz, 2H, NHCH₂), 4.10–4.02 (m, 2H, OCH₂), 3.96 (s, 1H, NH), 1.89–1.95 (m, 2 H, NHCH₂CH₂), 1.42–1.48 (m, 2 H, NHCH₂CH₂CH₂), 1.25 (t, ³J_{H,H} = 7.1 Hz, 6 H, Me), 1.13–1.20 (m, 8 H, NH(CH₂)₃(CH₂)₄), 0.75 (t, ³J_{H,H} = 7.1 Hz, 3 H, Me) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_C = 157.10 (d, ²J_{C,P} = 20.1 Hz, 2C, α-C(P)), 148.41 (2C, α-C), 147.54 (2C, α-C), 142.79 (2C, α-C), 142.15 (2C, *i*-C_{Ph}), 133.60 (4C, *o*-C_{Ph}), 133.33 (2C, β-C), 130.52 (2C, β-C), 127.97 (2C, β-C), 127.21 (2C, *p*-C_{Ph}), 126.41 (4C, *m*-C_{Ph}), 124.38 (2C, β-C), 123.37 (2C, *meso*-C10, 20), 62.18 (d, ²J_{C,P} = 5.0 Hz, 2C, OCH₂), 55.36 (1C, NHCH₂), 31.62 (1C, CH₂), 31.28 (1C, CH₂), 29.24 (1C, CH₂), 29.07 (1C, CH₂), 27.06 (1C, CH₂), 22.43 (1C, CH₂), 16.01 (d, ²J_{C,P} = 7.0 Hz, 2C, OCH₂Me), 13.66 (1C, NH(CH₂)₇Me) ppm, signals of *meso*-C5 and *meso*-C15 are not observed. ³¹P{¹H} NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_P = 28.34 ppm. FT-IR (neat): ν_{max} = 2925 (m), 2855 (m), 2817 (m), 2424 (w), 2402 (w), 2361 (w), 2342 (w), 2324 (w), 2289 (w), 2260 (w), 2247 (w), 2233 (w), 2226 (w), 2197 (w), 2185 (w), 2177 (w), 2165 (w), 2150 (w), 2140 (w), 2111 (w), 2099 (w), 2078 (w), 2052 (w), 2045 (w), 2036 (w), 2022 (w), 2012 (w), 1997 (w), 1982 (w), 1964 (w), 1953 (w), 1938 (w), 1899 (w), 1882 (w), 1846 (w), 1834 (w), 1804 (w), 1794 (w), 1719 (w), 1687 (w), 1656 (w), 1648 (w), 1638 (w), 1598 (w), 1552 (m), 1501 (w), 1465 (s), 1441 (m), 1385 (w), 1365 (w), 1343 (m), 1320 (w), 1308 (w), 1263 (m, P=O), 1203 (s, P=O), 1178 (w), 1165 (w), 1085 (w), 1049 (m), 984 (s, P=O), 966 (w, P=O), 891 (m), 874 (m), 846 (w), 787 (s), 757 (s), 728 (m), 714 (m), 701 (m), 667 (w), 662 (w), 632 (m), 576 (m), 562 (m), 575 (m) cm⁻¹. UV/Vis (CHCl₃/MeOH 2:1, v/v): λ_{max} [log ε (M⁻¹ cm⁻¹)] = 428 (5.97), 551 (4.76), 570 (4.78), 613 (4.89), 690 nm (4.01). HRMS (ESI): *m/z* calcd. for C₄₄H₄₆N₅O₃PZn [M-e]⁺ 787.26242; found 787.26447; calcd. for C₄₄H₄₇N₅O₃PZn [M+H]⁺ 788.27025; found 788.27961.

[5-Anilino-15-(diethoxyphosphoryl)-10,20-diphenylporphyrinato]zinc (5g):

The compound was prepared from **2** (50 mg, 0.067 mmol) and aniline (**10g**) (0.061 mL, 0.67 mmol, 10 equiv.) by refluxing of the reaction mixture for 16 h. The resulting crude solid was chromatographed using a CH₂Cl₂/MeOH (99:1, v/v) mixture as an eluent to afford **5g** as a green-violet solid (purity ~ 95%) in 87% yield (44 mg). ¹H NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_H = 9.81 (d, ³J_{H,H} = 4.9 Hz, 2H, β-H), 9.07 (d, ³J_{H,H} = 4.6 Hz, 2H, β-H), 8.54 (d, ³J_{H,H} = 5.0 Hz, 2H, β-H), 8.34 (d, ³J_{H,H} = 4.6 Hz, 2H, β-H), 7.90 (d, ³J_{H,H} = 7.6 Hz, 4H, α-Ph), 7.46–7.56 (m, 6H, *m*- and *p*-Ph), 6.95 (t, ³J_{H,H} = 7.7 Hz, 2H, α-PhNH), 6.85 (t, ³J_{H,H} = 7.7 Hz, 2H, *m*-PhNH), 6.61 (t, ³J_{H,H} = 7.0 Hz, 1H, *p*-PhNH), 4.24–4.19 (m, 2 H, POCH₂), 4.04–3.96 (m, 2 H, POCH₂), 1.15 (t, ³J_{H,H} = 7.1 Hz, 6 H, Me) ppm, signal of NH was not observed. ³¹P{¹H} NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_P = 25.93 ppm. FT-IR (neat): ν_{max} = 3386 (w), 3167 (w), 3055 (w), 2920 (w), 2850 (w), 1726 (w), 1650 (w), 1627 (w), 1598 (m), 1562 (w), 1548 (m), 1529 (w), 1492 (m), 1467 (m), 1442 (m), 1416 (w), 1394 (w), 1361 (m), 1341 (w), 1324 (w), 1307 (m), 1286 (w), 1259 (w, P=O), 1244 (m, P=O), 1219 (s), 1200 (s, P=O), 1158 (m), 1092 (s, P=O), 1071 (s), 1038 (s), 1011 (s, P=O), 978 (s, P=O), 959 (s, P=O), 887 (s), 872 (s), 846 (w), 832 (w), 805 (m), 787 (s), 755 (m), 737 (s), 729 (s), 714 (s), 695 (s), 658 (s), 620 (m), 594 (m), 578 (s), 561 (m), 551 (s) cm⁻¹. HRMS (ESI): *m/z* calcd. for C₄₂H₃₄N₅O₃PZnNa [M+Na]⁺ 774.15829; found 774.15532.

[5-(Diethoxyphosphoryl)-10,20-diphenyl-15-

(diphenylamino)porphyrinato]zinc (5h): The compound was prepared from **2** (65 mg, 0.088 mmol) and diphenylamine (**10h**) (745 mg, 4.4 mmol, 50 equiv.) after refluxing of the reaction mixture for 3 h. A crude solid was chromatographed using a CH₂Cl₂/MeOH (99.75:0.25, v/v) mixture as an eluent to afford **5h** as a green-violet solid in 48% yield (35 mg). ¹H NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_H = 9.92 (d, ³J_{H,H} = 4.8 Hz, 2H, β-H), 8.98 (d, ³J_{H,H} = 4.5 Hz, 2H, β-H), 8.60 (d, ³J_{H,H} = 4.8 Hz, 2H, β-H), 8.39 (d, ³J_{H,H} = 4.5 Hz, 2H, β-H), 7.90 (d, ³J_{H,H} = 6.9 Hz, 4H, α-Ph), 7.52–7.46 (m, 6H, *m*- and *p*-Ph), 7.08 (d, ³J_{H,H} = 8.2 Hz, 4H, *o*-PhN), 6.93

(t, ³J_{H,H} = 8.0 Hz, 4H, *m*-PhN), 6.64 (t, ³J_{H,H} = 7.3 Hz, 2H, *p*-PhN), 4.27–4.20 (m, 2H, POCH₂), 4.04–3.97 (m, 2H, POCH₂), 1.14 (t, ³J_{H,H} = 7.0 Hz, 6H, Me) ppm. ³¹P{¹H} NMR (600 MHz, CDCl₃/CD₃OD 2:1, v/v, 25 °C): δ_P = 26.37 ppm. FT-IR (neat): ν_{max} = 2925 (m), 2851 (w), 1722 (m), 1688 (w), 1598 (m), 1587 (m), 1562 (w), 1549 (w), 1529 (w), 1491 (s), 1469 (m), 1441 (m), 1412 (w), 1392 (w), 1357 (m), 1337 (w), 1325 (m), 1289 (m), 1273 (m), 1262 (m, P=O), 1219 (s), 1200 (s, P=O), 1177 (m), 1157 (m), 1090 (s), 1070 (s), 1042 (s), 1012 (s, P=O), 983 (s, P=O), 968 (s, P=O), 890 (s), 872 (s), 844 (m), 831 (m), 820 (m), 791 (s), 749 (s), 727 (s), 714 (m), 699 (s), 660 (s), 649 (s), 628 (m), 618 (m), 604 (m), 581 (s), 562 (s), 553 (s) cm⁻¹. UV/Vis (CHCl₃/MeOH 2:1, v/v): λ_{max} [log ε (M⁻¹ cm⁻¹)] = 309 (4.22), 420 (5.02), 445 (4.64), 564 (3.92), 598 (3.85), 625 nm (3.81). HRMS (ESI): *m/z* calcd. for C₄₈H₃₈N₅O₃PZnNa [M+H]⁺ 850.18959; found 850.18690.

Studies of porphyrins at the water/air interface

Apparatus for UV-vis absorption and fluorescent measurements of solutions and films deposited on solid substrates. The UV-vis absorption spectra of solutions and films deposited on solid substrates were recorded on a SHIMADZU-2450 spectrometer (Japan) in a wavelength range of 200–900 nm. The fluorescent spectra of films deposited on solid substrates were recorded on a «SHIMADZU RF-5301» spectrofluorometer (Japan) in a wavelength range of 220–900 nm. The measurements were performed in a quartz cuvette with an optical path length of 1 cm at 20±1 °C. Excitation wavelength was 420 nm.

Deposition and study of porphyrin monolayers. The monolayer experiments were performed on 1000-2 KSV Minitrough (*l* × *w* = 36.4 × 7.5 cm) model (KSV Instrument Ltd., Helsinki, Finland) equipped with two moving hydrophobic barriers allowing for symmetric and asymmetric compressions as well as with a platinum Wilhelmy plate. The monolayers were formed on the surface of deionized water (18.2 MΩ cm) or aqueous solution of zinc perchlorate (0.01 M) by spreading of 0.08 mM solution of the porphyrin in chloroform. The solution was delivered in 2.5 μL portions by using an automatic micropipette (Gilson). The total amount of spread solution was 200 μL. The spread monolayers were compressed with a rate of 5 mm/min after equilibration at the interface for 15 or 60 min. All measurements were performed at a constant temperature of the subphase (20±1 °C). Each measurement was repeated at least three times to demonstrate a satisfactory reproducibility of obtained data.

Fiber optic spectrophotometer AvaSpec-2048 (Avantes, Netherlands) with a wavelength range of 200–750 nm was used for recording UV-vis spectra of monolayers at the air/water interface. Deuterium and halogen lamps were used as irradiation sources. The reflectometric probe with a fiber-optic diameter of 400 μm, combined with a 6-fiber irradiating bundle, was placed perpendicular to the studied surface at a distance of 2–3 mm. The UV-vis spectra were recorded in a mode, which allows for minor modifications of the spectra.

Preparation of Langmuir-Schaefer (LS) films. LS films deposition was accomplished by using a computer controlled 1000-2 KSV Minitrough. The porphyrin monolayers were transferred onto polyvinyl chloride (PVC) substrate by the horizontal LS method at a surface pressure of 5 mN m⁻¹. The transfer ratios for the LS films were no less than 0.95 for all substrates.

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