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High-Yielding Synthesis of β-Octaalkyl-*meso*-(bromophenyl)-Substituted Porphyrins and X-ray Study of Axial Complexes of Their Zinc Complexes with THF and 1,4-Dioxane

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Keywords: *meso*-Substituted porphyrins / Metalloporphyrins / Axial coordination / Supramolecular structures / X-ray diffraction / Porphyrinoids / Zinc

New 5-(4-bromophenyl)-3,7,12,13,17,18-hexamethyl-2,8-dipentyl- and 5,15-bis(4-bromophenyl)-2,8,12,18-tetramethyl-2,8,12,18-tetrapentylporphyrins (**H_2P-1** and **H_2P-2**) and their zinc metal complexes (**ZnP-1** and **ZnP-2**, respectively) were synthesized in high yields by condensation of β-tetraalkyl-substituted dipyrromethanes with 2-formyl-3,4-dialkylpyrroles or 4-bromobenzaldehyde and subsequent metallation. X-ray analysis data showed the formation of axial complexes of **ZnP-1** and **ZnP-2** with the solvent molecules of THF and dioxane in the solid state. Coordination of **ZnP-1** with dioxane led to polymer multidecker structures.

Introduction

Among organic chromophores, porphyrins have a special place owing to their unique structural, redox and photochemical/physical properties,[1] the rigidity of their planar aromatic frameworks, their high stabilities over a wide range of temperatures and the significant values of their oxidation and reduction potentials. This is a reason why porphyrins and their metal complexes are of remarkable importance in biological systems in nature, being components of oxygen-carrier heme complexes, cytochrome catalysts and chlorophyll in light-harvesting photosynthesis centres.[2] Synthetic metalloporphyrin complexes are therefore of particular interest in terms of creating analogues of natural systems and molecular devices.

Moreover, porphyrins have also been identified as remarkable building blocks in supramolecular chemistry.[3] Intensive progress in this area of chemistry has led to the discovery of new applications of porphyrin systems in materials science,[4] molecular electronics[5] and nanotechnology.[6] The ability to produce sharp changes in their spectral properties[7] depended on the architectural arrangement of the chromophores, with their environments playing crucial roles in the use of metalloporphyrins as receptors and sensors.[8] Axial coordination of ligands to a metalloporphyrin affords an additional means for assembly and organization of supramolecular materials.

The main objective of this work is the synthesis of new soluble porphyrin building blocks based on the unsymmetrical 5-(4-bromophenyl)-3,7,12,13,17,18-hexamethyl-2,8-dipentylporphyrin (**H_2P-1**, Figure 1) and the symmetrical 5,15-bis(4-bromophenyl)-2,8,12,18-tetramethyl-2,8,12,18-tetrapentylporphyrin (**H_2P-2**), which are suitable for further modification through substitution of their bromine atoms with an assortment of well-developed transition metal catalysis methods[9] to create functionalized porphyrin derivatives and covalently bound porphyrin arrays. We have recently demonstrated that ditopic ligands such as azacrown-ether-appended porphyrins could be formed through Pd-catalysed amination of mono- and bis-*meso*-bromophenyl-substituted porphyrins with aza-crown ethers.[10]

In many cases, poor solubilities of porphyrins in nonpolar solvents cause difficulties in their subsequent application. High solubilities can be achieved through selection of suitable substituents and modification of the periphery of the porphyrin core. For this reason we synthesized new β-octaalkyl-*meso*-(bromophenyl)-substituted porphyrins, containing methyl and pentyl substituents in their pyrrole rings to assist the solubilities of these porphyrins in nonpolar solvents.

The 5-aryl- and 5,15-diaryl-β-octaalkylporphyrins **H_2P-1** and **H_2P-2**, as well as their zinc complexes **ZnP-1** and **ZnP-2**, have been successfully synthesized in high yields and completely characterized by spectral methods and by X-ray structural analysis. Single crystals of free-base porphyrins **H_2P-1** and **H_2P-2** were easily grown from chloroform/hex-

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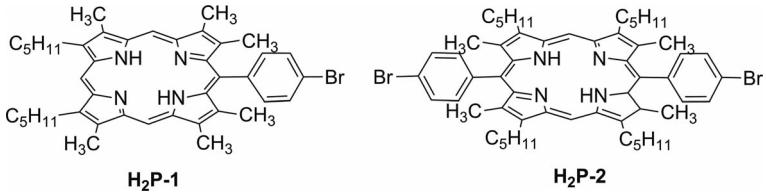
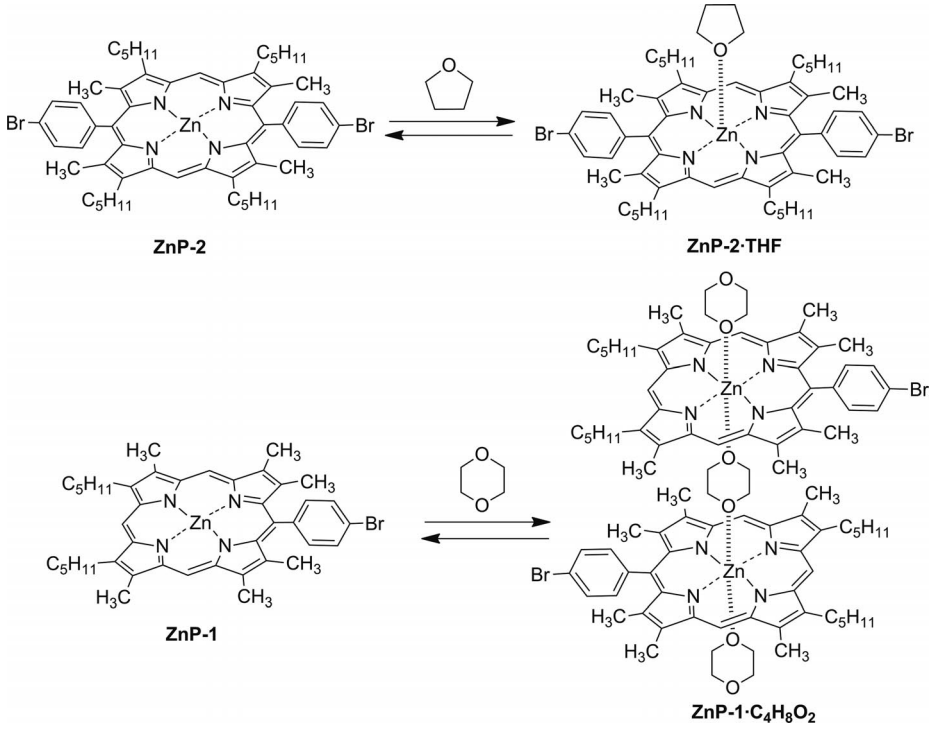


Figure 1. 5-(4-Bromophenyl)-β-octaalkylporphyrin (**H_2P-1**) and 5,15-bis(4-bromophenyl)-β-octaalkylporphyrin (**H_2P-2**).



Scheme 1. Self-assembly of axially coordinated complexes of **ZnP-1** and **ZnP-2** with oxygen-containing ligands.

ane mixtures, whereas their zinc complexes were crystallized from THF or 1,4-dioxane solutions. X-ray studies showed the formation of supramolecular structures of the zinc–porphyrins with the oxygen-containing solvent molecules in the solid state. Coordination of monodentate oxygen ligands such as THF to zinc porphyrins leads to the formation of 1:1 axial complexes (**ZnP-2·THF**, Scheme 1). In this case the zinc dication has a coordination number of 5. In contrast to this, the bidentate oxygen ligands of 1,4-dioxane each coordinate to two zinc–porphyrins to form sandwich stacking columns (**ZnP-1·$C_4H_8O_2$**, Scheme 1) in which the zinc dications have coordination numbers of 6. Equilibria operating in solutions of zinc–porphyrins with ligands are usually shifted to five-coordinate zinc, but in the solid state the packing forces result in the usually less favoured six-coordinate structure.

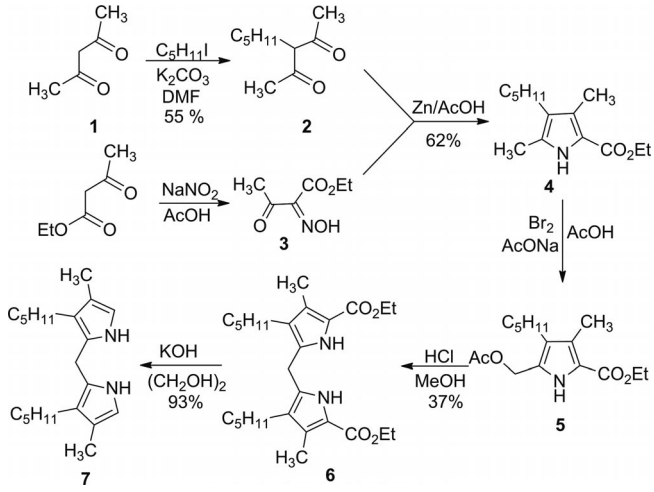
Results and Discussion

The obtained *meso*-(bromophenyl)-substituted β-octaalkylporphyrins efficiently combine features of synthetic and natural porphyrins. The alkyl substituents inherent to natural porphyrins at the β-pyrrole positions on the porphyrin macrocycle promote the required solubility in nonpolar solvents. In turn, the synthetic *meso*-aryl-substituted porphyrins containing active halogen atoms such as bromine on their benzene rings offer the potential for further structural functionalization of the porphyrins. On the other hand, *meso*-aryl-substituted porphyrins can be readily obtained by condensation of pyrrole with the corresponding benzaldehydes in acidic media.[11] It is therefore evident why the synthesis and investigation of the properties of this particular class of porphyrins has attracted great attention. Indeed, many synthetic functionalized porphyrin systems are based on 5,15-diaryl-2,3,7,8,12,13,17,18-octaalkylporphyrins, due to their ease of preparation, high symmetry and thermal stabilities.[12] In some cases, the molecular architecture of a 5,15-diarylporphyrin can be more readily manipulated than that of the corresponding *meso*-tetraarylporphyrin.[13]

A rational approach to a *trans-meso*-substituted porphyrin involves consecutive condensation of acetoxymethylpyrrole with dipyrromethane, followed by its condensation with an aldehyde, in a process known as MacDonald [2+2] condensation. Two molecules of dipyrromethane react with

two molecules of aldehyde to give a *trans*-symmetrical porphyrin.[14] Although the synthesis of symmetrical porphyrins is well developed, the unsymmetrical *meso*-monosubstituted porphyrins are not easily available. Monosubstituted porphyrins could be accessible by condensation of aldehydes with *a*,*c*-biladiene,[15] but unsubstituted biladiene is highly unstable and difficult to obtain, making it an unsuitable component for the synthesis. Senge et al. have recently reported an alternative route based on 2-formylpyrrole as a building block[16] together with dipyrromethane in a condensation reaction.[17] We successfully utilized this method in the synthesis of **H_2P-1.**

The starting material for the syntheses both of **H_2P-1** and of **H_2P-2** was 4,4′-dimethyl-3,3′-dipentyldipyrromethane-2,2′ (**7**, Scheme 2), obtained by a five-step synthesis.[17]



Scheme 2. Synthesis of 4,4′-dimethyl-3,3′-dipentyldipyrromethane-2,2′ (**7**).

Alkylation of acetylacetone (**1**) with 1-iodopentane in the presence of K_2CO_3 in DMF gave 3-pentylpentane-2,4-dione (**2**). Reductive Knorr cyclocondensation of this with ethyl 2-(hydroxyimino)-3-oxobutanoate (**3**) and zinc powder in acetic acid led to the formation of 2-ethoxycarbonyl-3,5-dimethyl-4-pentylpyrrole (**4**). Bromination at the α-methyl unit was then carried out in acetic acid, and simultaneous nucleophilic substitution of bromine by an acetoxy group occurred to give α-acetoxymethylpyrrole **5**.

Self-condensation of **5** in methanol and HCl gave 5,5-diethoxycarbonyldipyrromethane **6** (Scheme 2). Hydrolysis with simultaneous decarboxylation under reflux in ethylene glycol and in the presence of KOH led to the unstable α-unsubstituted dipyrromethane **7**, which was used immediately without purification in the synthesis of porphyrin **H_2P-1**.

The next building block needed for the synthesis of porphyrin **H_2P-1**, 2-formyl-3,4-dimethylpyrrole (**12**, Scheme 3), was obtained by a three-step process from urethane (**8**) and 2,3-dimethylbuta-1,3-diene (**9**) as shown. Urethane was transformed into *N*-(ethoxycarbonyl)sulfinylimine in a one-pot reaction by treatment with SO_2Cl_2 in pyridine. Addition of 2,3-dimethylbuta-1,3-diene (**9**) to the reaction mixture gave the heterocyclic Diels–Alder adduct2-ethoxycarbonyl-4,5-dimethyl-3,6-dihydro-1,2-thiazine-1-oxide (**10**). This was transformed into 3,4-dimethylpyrrole (**11**) with a methanol solution of KOH (excess). Vilsmeier formylation of **11** led to the desired 2-formylpyrrole **12**.

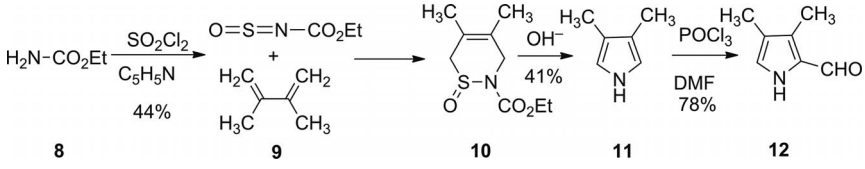
The first stage of the synthesis of the unsymmetrical monosubstituted 5-(4′-bromophenyl)-2,3,7,8,12,18-hexamethyl-13,17-dipentylporphyrin **H_2P-1** involved condensation of 2-formylpyrrole **12** with dipyrromethane **7** (Scheme 4) in methanol containing HBr to afford the intermediate dihydrobromide of 2,3,7,13,17,18-hexamethyl-8,12-dipentylbiladiene-*a*,*c* (**13**). Interaction of dipyrromethanes with 2-formylpyrrole in alcohol solutions has usually led to the formation of byproducts such as corrole **14** and consequently to decreases in the yields of porphyrins. Carrying out this reaction in butanol at reflux allowed this side reaction to be avoided and **H_2P-1** to be obtained in a good yield of 57%. Moreover, the synthesis of **H_2P-1** was carried out as a one-pot reaction without isolation of biladiene **13**.

The obtained porphyrin was purified by column chromatography and crystallized from chloroform/hexane. Single crystals of **H_2P-1** were studied by X-ray diffraction. According to the X-ray data, the nitrogen atoms in **H_2P-1** porphyrin molecules (Figure 2) are situated practically in the same plane (deviations are ±0.0031 Å).

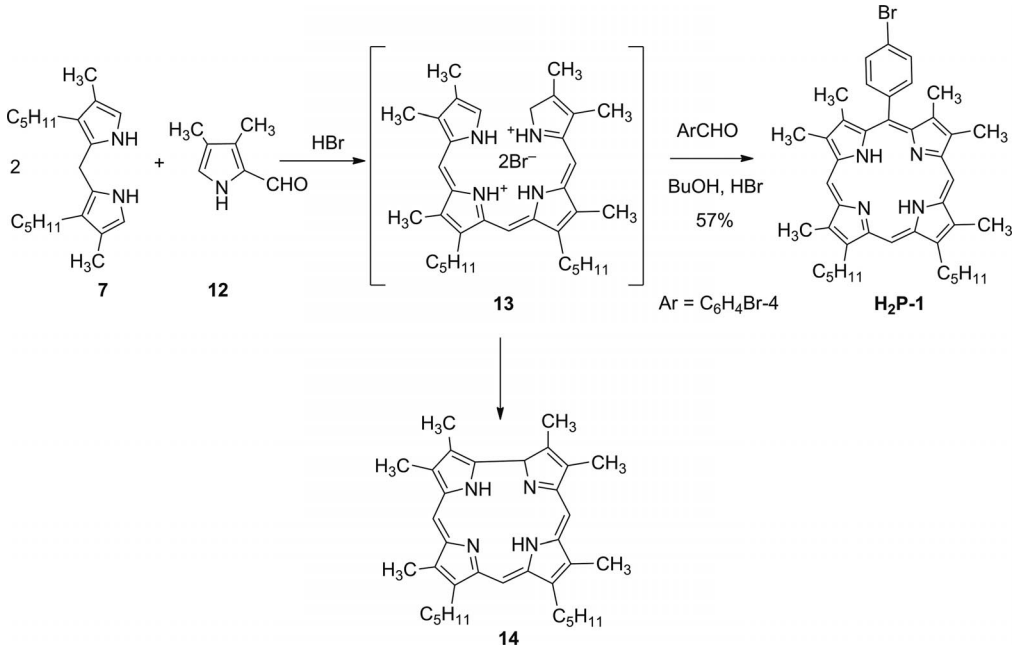
Similar significant distortions of the macrocycle have been observed in other mono-*meso*-aryl-substituted porphyrins[18] with one exception in 2,3,7,8,12,13,17,18-octaethyl-5-phenylporphyrin, which has an unexpectedly planar macrocycle (deviation of atoms from plane N_4 0.010 Å),[19] in spite of the presence of quite weak CH–π contacts (3.926–3.989 Å) and even though its crystal contained molecules of dichloromethane solvent.

The unit cell of **H_2P-1** is composed of parallel molecules (angle is 2.9°, Figure 3.) stacked in nominally "head-to-tail" dimer fragments (distance between the centres of two adjacent molecules is 6.410 Å; Figures 3 and 4).

It is likely that two molecules are bound in such a "dimer" by stacking contacts of pyrrole fragments (3.565–3.972 Å) and shifted relative to each other [the angle between bonds of Br(1)–C(33) is 27°] (Figure 4). The same "head-to-tail" packing is observed in the crystal of β-octaethyl-*meso*-phenylporphyrin. Packing effects and observed



Scheme 3. Synthesis of 2-formyl-3,4-dimethylpyrrole (**12**).



Scheme 4. Synthesis of β-octaalkyl-5-(4-bromophenyl)porphyrin **H_2P-1**.

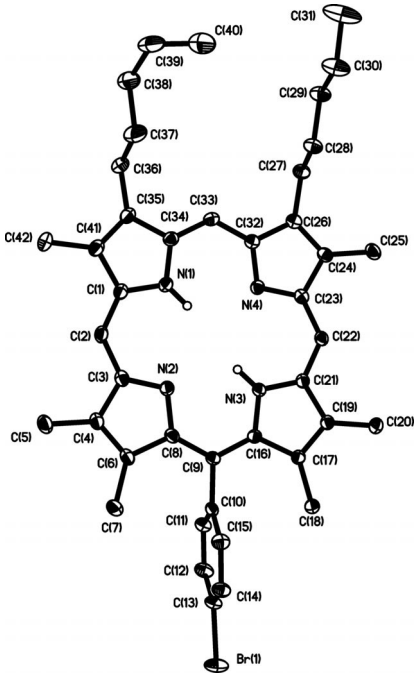


Figure 2. Molecular structure of porphyrin **H_2P-1** with thermal ellipsoids drawn at the 30% probability level.

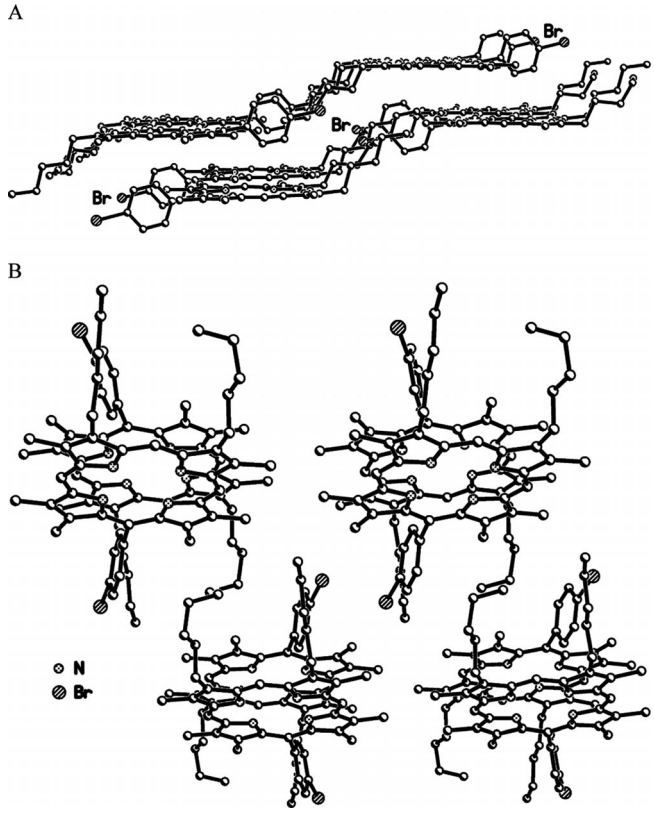


Figure 3. Fragment of packing of molecules of **H_2P-1**: (A) top view, (B) lateral view.

stacking interactions seemingly result in a deviation of the acceptor bromo substituent from the porphyrin plane [an angle between N4 mean plane and C(10)–Br(1) bond vector is 12.5°], whereas the deviation of Br(1) from the porphyrin ring's mean plane at 1.408 Å and corresponding distortion of the sp^2 environment of carbon atom C(9) are related to CH–π interactions of C(14)–H and C(15)–H hydrogen atoms of the aryl substituent with the pyrrole fragment of another molecule and competing steric repulsion at distances of 3.337–3.998 Å (Figure 4).

The bromophenyl substituent, however, is virtually perpendicular to the porphyrin plane [angle of C(8)C(9)C(16)/

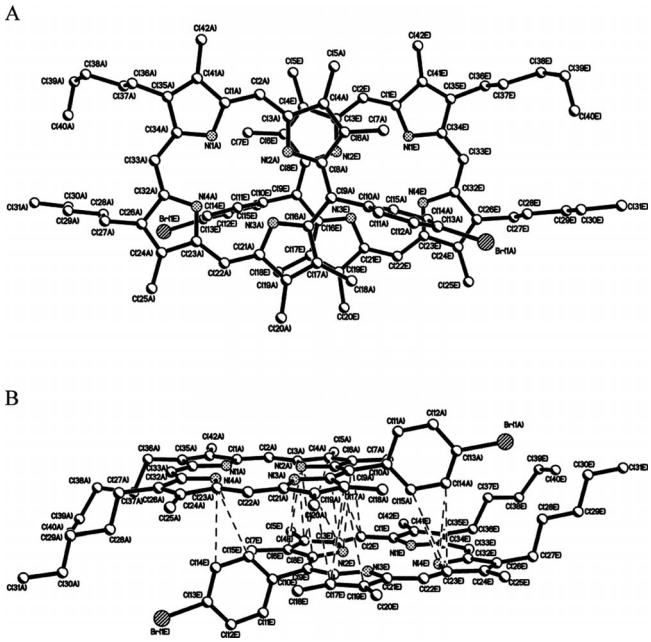


Figure 4. Short contacts of two adjasent molecules of **H_2P-1**: (A) top view, (B) lateral view.

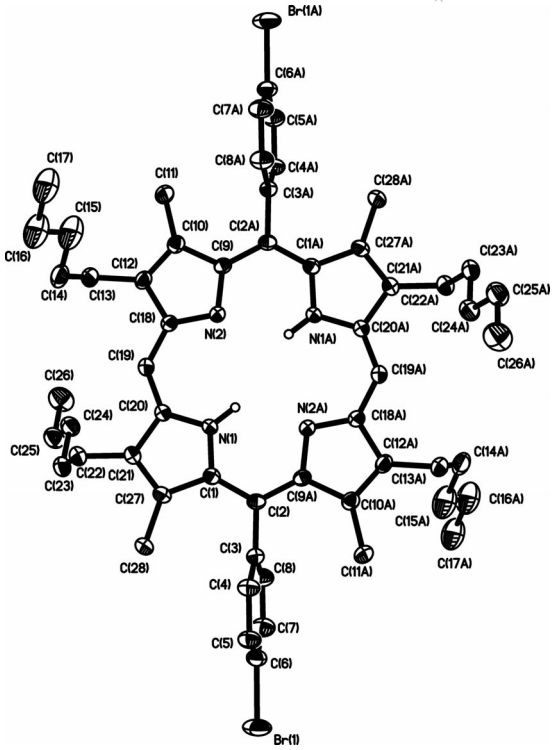


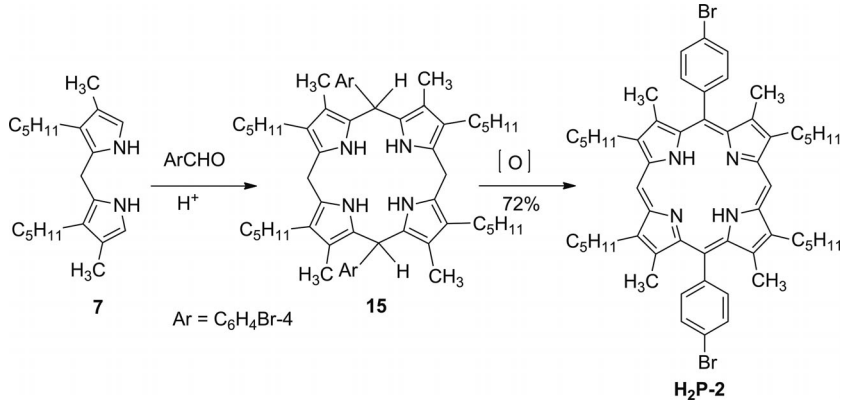
Figure 5. Molecular structure of porphyrin **H_2P-2** with thermal ellipsoids drawn at 30% probability level.

C(11)C(10)C(15) is 86.1°], due to the steric repulsion with the methyl substituents at the pyrrole β-positions (C···Ph is 3.167–3.210 Å).

The symmetrical *trans*-disubstituted 5,15-bis(4-bromophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrapentylporphyrin (**H_2P-2**) was obtained in higher yield than the monosubstituted **H_2P-1**. In the first step, condensation of dipyrromethane **7** with 4-bromobenzaldehyde in the presence of TFA in dichloromethane under argon gave intermediate porphyrinogen **15** (Scheme 5), oxygenation of which (*p*-chloranil) led to the formation of porphyrin **H_2P-2**.

Porphyrin **H_2P-2** was purified and isolated in the same way as porphyrin **H_2P-1**. Single crystals were grown from chloroform/hexane and investigated by X-ray diffraction. According to the X-ray data for symmetrical 5,15-(4-bromophenyl)porphyrin **H_2P-2** (Figure 5), the nitrogen atoms of the porphyrin component of **H_2P-2** are situated in practically the same plane (deviations are 0 Å), the carbon atoms of the "inner" macrocycle (i.e., *meso* and α-pyrrole atoms) are set almost in the same plane as the nitrogen atoms [maximum deviation of atom C(9) is ±0.0755 (centrosymmetrical molecule)], whereas the β-pyrrole atoms, corresponding to methyl and pentyl substitutes, deviate at ±0.139 Å [atom C(10)] and at ±0.129 Å [atom C(21)].

The deviations are apparently the result of steric contacts, arising in the unit cell in "head-to-head" molecule packing, which also determine the conformations of aryl substituents. The "head-to-head" arrangement of the mole-



Scheme 5. Synthesis of β-octaalkyl-5,15-bis(4′-bromophenyl)porphyrin **H_2P-2**.

cules of **H_2P-2**, as opposed to the "head-to-tail" packing of the asymmetric **H_2P-1**, is possibly the result of the symmetric aryl substitution. Molecules of **H_2P-2** arrange themselves parallel to each other in planes in the crystal (Figure 6).

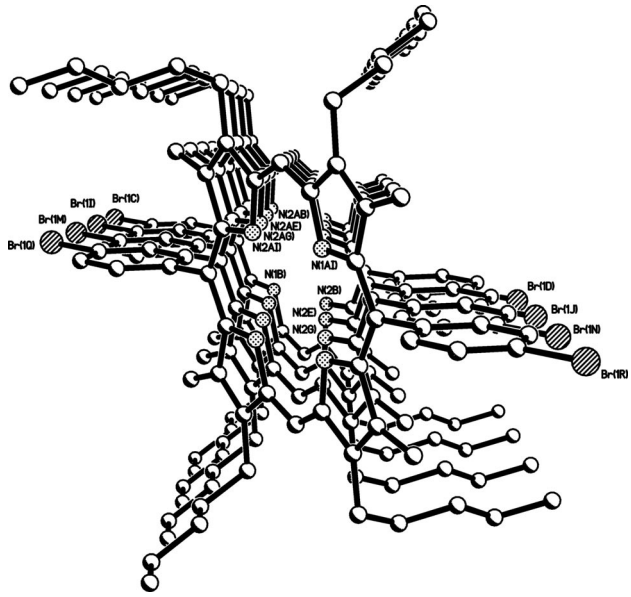


Figure 6. Fragment of packing of molecules of **H_2P-2**.

It should be noted that the arrangement of the molecules in the crystal forms voids that are clearly seen (Figure 7).

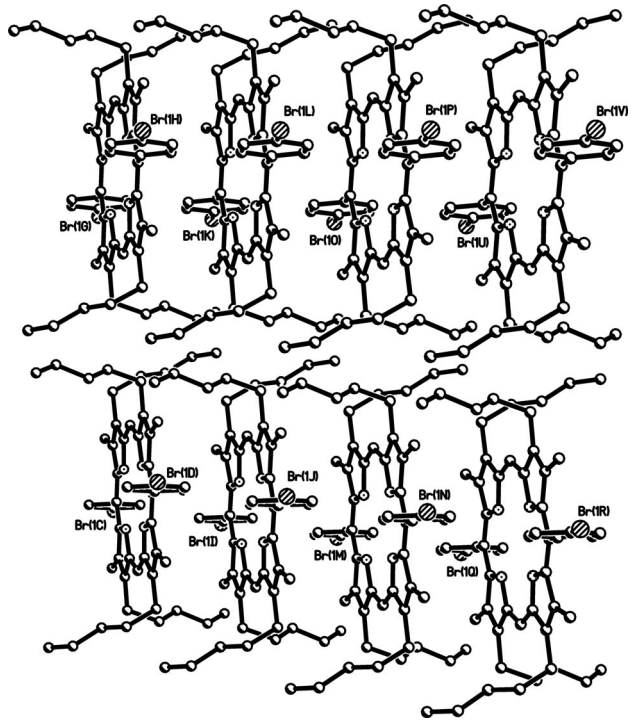


Figure 7. The arrangement of **H_2P-2** molecules in the crystal.

Nominally, molecules of porphyrin **H_2P-2** (Figure 8) can be regarded as dimer associates (the distance between molecule centres is 6.878 Å), just as in the case of **H_2P-1**. However, there appears to be stronger stacking contacts of pyrrole fragments in **H_2P-2** than in **H_2P-1**, which can be concluded from the corresponding interatomic distances in the parallel arrangement of the molecules along the axis perpendicular to the porphyrin plane (Figure 8). There are also competing steric and CH–π contacts of the bromophenyl substituent with nitrogen and carbon atoms of the pyrrolic fragment (C–N and C–C distances are 3.347–3.820 Å) that lead to distortion of the sp^2 reference carbon atom of the bromophenyl fragment [the deviation of C(2) from the plane of N_4 is ±0.129 Å, displacement of atom Br(1) is 1.507 Å, angle of N_4/bond Br(1)–C(2) is 13.1°]. *meso*-Bromophenyl substituents are perpendicular to the porphyrin plane (angle is 87.7°), which is a consequence, as also in the case of **H_2P-1**, of steric contacts with β-methyl substituents, as distinct from the known 5,15-diphenylporphyrin without β-substitution, which has similar molecular packing in the unit cell, but this angle is 54.5°.[20] The same perpendicular arrangement of 5,15-diaryl substituents with respect to the N_4 plane was observed for all porphyrins containing methyl groups in the 3-, 7-, 13- and 17-positions.[20–25]

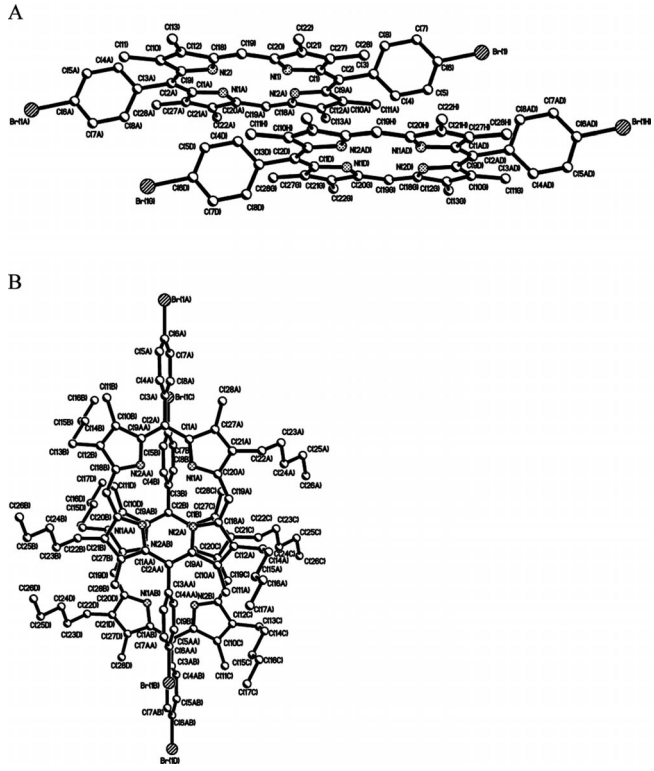


Figure 8. Mutual arrangement of two adjacent molecules of **H_2P-2**: (A) lateral view, pentyl substituents omitted, (B) top view.

It should be noted that the previously characterized 5,15-diphenyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin has a unit cell packing similar to that of **H_2P-2** and "inner" macrocycle atoms located virtually in one plane (deviation of the *meso* atoms in the 5- and 15-positions bearing phenyl substituents is ±0.047 Å). Only β-pyr-

role carbon atoms with methyl and ethyl substituents deviate from the N_4 plane, by ±0.124 Å and ±0.194 Å, respectively. The phenyl substituents also make contacts (3.517–3.869 Å) with the nitrogen and carbon atoms of the pyrrole fragments, leading to geometry distortion of the reference sp^2 carbon atom [angle between 5,15-atoms axis and the corresponding benzene carbon atoms axis (C1–C4) is 8.3°, displacement of the peripheral carbon atom of the phenyl substituent from the N_4 plane is ±0.664 Å].[26]

It was found out that interaction of $Zn(OAc)_2 \cdot 2H_2O$ (excess) with **H_2P-1** and **H_2P-2** in chloroform at room temperature led to the formation of fine-crystalline red-purple complexes **ZnP-1** and **ZnP-2** in 94% yield. According to the data from X-ray analysis of the 1,4-dioxane complex **ZnP-1·$C_4H_8O_2$** (Figure 9, obtained by slow concentration at room temperature from a heptane/dioxane mixture, the zinc(II) atom has a distorted tetragonal-bipyramidal environment involving four porphyrin nitrogen atoms [Zn–N 2.050(5)–2.059(5) Å] and two dioxane oxygen atoms [Zn–O 2.414(5), 2.499(5) Å]. The axially coordinated bidentate dioxane ligands connect porphyrin molecules, forming a 1-D polymer (Figure 9).

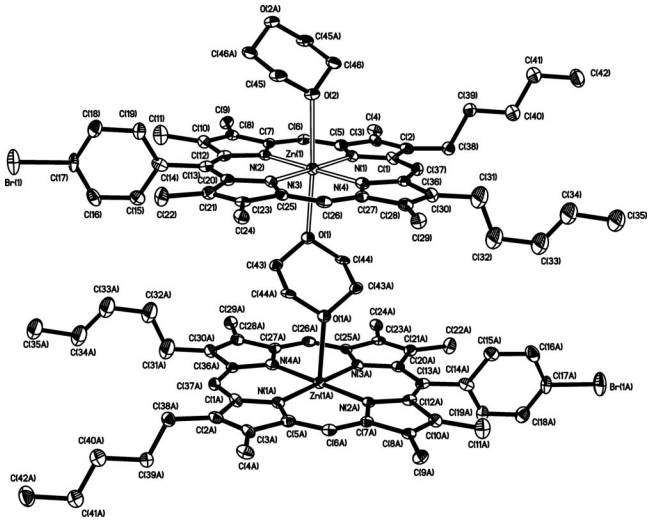


Figure 9. Molecular structure of the axial complex of **ZnP-1** with dioxane (**ZnP-1·$C_4H_8O_2$**) with thermal ellipsoids drawn at 30% probability level..

Molecules of metal–porphyrin complex **ZnP-1**, like those of the ligand **H_2P-1**, are packed in a "head-to-tail" arrangement. However, because of the separation by dioxane molecules in **ZnP-1**, significant steric, stacking and CH–π contacts are absent, leading to a virtually plane geometry of the macrocycle component (deviation of nitrogen atoms from the mean N_4 plane is ±0.007 Å, displacement of zinc atom out of the mean N_4 plane is 0.009 Å, deviation of bromine atom from the plane is –0.112 Å, max/min bromine atom deviation is +0.033 Å/–0.074 Å).

It should be pointed out that the obtained complex **ZnP-1** represents the first example of a 1-D polymer structure formed with a bridging dioxane ligand (Figure 10). There are three known zinc complexes that contain solvating dioxane molecules. The first is a dimer of 2,3,7,8,12,13,17,18-octaethylporphyrinatozinc, bridged by a dioxane molecule (Zn–O 2.240 Å), in which the zinc atoms are in distorted tetragonal-pyramidal environments (Zn–N 2.042–2.055 Å).[27] The second is monomeric 2,3,5,10,12,15,20-tetraphenylporphyrinatozinc (Zn–N 2.015–2.104), in which the oxygen atom occupies the fifth position in the distorted tetragonal-pyramidal environment of zinc [Zn–O 2.274 Å][28] The third complex, a Zn^{II} 4,4′-{[10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin-5,15-diyl]diethyne-2,1-diyl}dibenzoate with diradical bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl), like **ZnP-1** with dioxane, has a distorted tetragonal-bipyramidal environment based on four nitrogen atoms (Zn–N 2.033–2.053 Å) and two oxygen atoms of the coordinated dioxane molecules (Zn–O 2.462, 2.494 Å).[29] A distorted tetragonal-bipyramidal environment is also observed in a Cd^{II} complex of tetraphenylporphyrin containing coordinated dioxane molecules.[30,31] In all the complexes described, the porphyrin macrocycles are virtually planar, independently of the zinc coordination number.

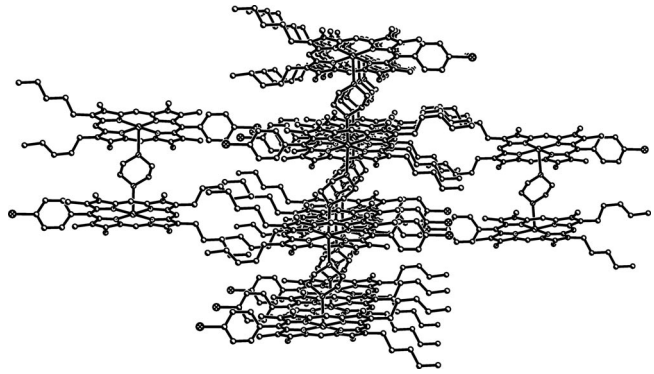


Figure 10. Fragment of packing of **ZnP-1** molecules.

Recrystallization of complex **ZnP-2** from a THF/hexane mixture resulted in the formation of a complex containing coordinated THF molecules. From the X-ray analysis data for the complex **ZnP-2·THF** (Figure 11), the central zinc atom is bound to the four nitrogen atoms of the tetrapyrrole macrocycle [Zn–N 2.046(4)–2.065(4) Å] and the oxygen atom of coordinated THF [Zn–O 2.183(3) Å] and has a distorted tetragonal-pyramidal environment.

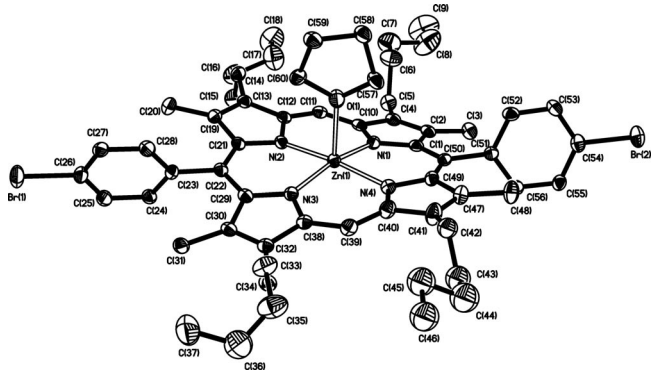


Figure 11. Molecular structure of complex of **ZnP-2·THF**, with thermal ellipsoids drawn at 30% probability level.

The tetrapyrrolic macrocycle is distorted (min/max displacements of nitrogen and zinc atoms from the mean N_4 plane are –0.059/0.06 Å and 0.186 Å, respectively, the deviation of *meso*- and α-pyrrolic carbon atoms is –0.219/0.191 Å, and that of β-pyrrolic atoms is as follows: the displacements of carbon atoms in methyl substituents are –0.498 and 0.416 Å, and those in pentyl substituents are –0.515 and 0.407 Å). This is apparently a consequence of strong CH–π interactions (C···C distances between bromophenyl substituents and pyrrole moieties are 3.447–3.856 Å) observed in two adjacent molecules in the unit cell of the complex (Zn···Zn 6.256 Å; Figures 12 and 13). Despite the presence of these contacts, the bromine atoms in the bromophenyl substituents are much less displaced from the N_4 mean plane (–0.156, 0.698 Å) than in the cases of the distortions observed in **H_2P-1** and **H_2P-2**. The reference sp^2-carbon atoms of the PhBr fragments are also not in the N_4 plane, which is probably related to distortions of the macrocycle, as opposed to the protonated porphyrin components.

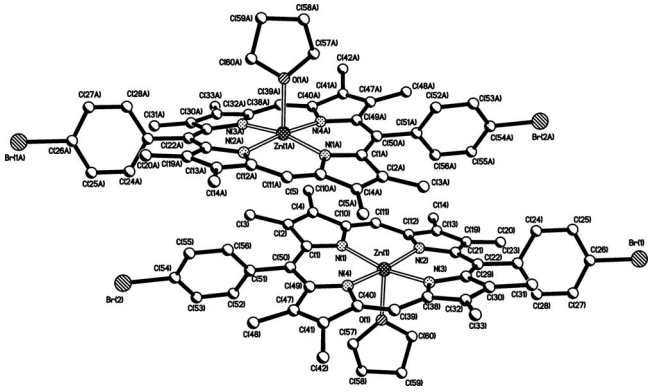


Figure 12. Arrangement of adjacent molecules in the unit cell of the complex **ZnP-2·THF**.

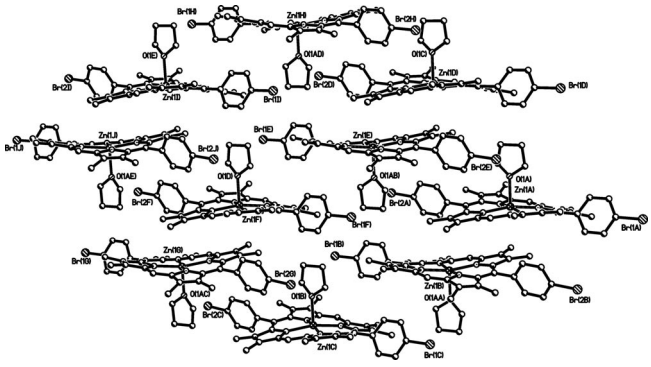


Figure 13. Fragment of molecular packing in a crystal of complex **ZnP-2·THF**.

In the previously reported zinc porphyrinates, the metal atoms were in distorted tetragonal-pyramidal environments in which the lengths of metal–oxygen bonds varied in the 2.132–2.211 Å range. The geometries of the tetrapyrrole fragments are determined by the electronic and steric natures of substituents at the *meso*- and β-positions, and also by the presence of solvent molecules.[32–42] Complexes of porphyrins with only two *meso* substituents have not been studied. In zinc complexes containing two coordinated THF molecules, the metal atoms were in distorted tetragonal-bipyramidal environments. The tetrapyrrolic fragments were always planar regardless of the natures and locations of substituents and also of the presence of solvent molecules. Metal–oxygen distances were noticeably increased (2.371–2.555 Å)[43–49] and close to that observed in complex **ZnP-1**.

The features of the geometries of porphyrins **H_2P-1** and **H_2P-2**, containing acceptor bromophenyl substituents at their *meso* positions, and also those of their zinc(II) complexes are thus mostly determined by the effects of molecular packing in the crystals and the related possibilities of stacking interactions, CH–π contacts of *meso*-aryl substituents with pyrrole fragments and also steric hindrance. The *meso*-(bromophenyl) substituents are situated in the planes perpendicular to the tetrapyrrole macrocycle, due to the steric contacts with the β-methyl substituents.

Crystal data and structure refinement details of **H_2P-1** and **H_2P-2** and their metal complexes are listed in Table 1.

Conclusions

The new porphyrin compounds β-octaalkyl-5-(bromophenyl)- and -5,15-bis(bromophenyl)porphyrins **H_2P-1** and **H_2P-2** and their zinc complexes were successfully synthesized with high yields. We have demonstrated that the coordination structures of zinc–porphyrins **ZnP-1** and **ZnP-2** with oxygen-containing ligand molecules of solvents such as 1,4-dioxane and THF in axial arrangement occur in the crystal state. Although such axial coordination complexes also exist in solutions, the coordination number of the zinc atom is usually 5, and only the crystal environment can give rise to the six-coordinate state. This rare observed coordination was produced as a consequence of the formation of a polymeric structure with a bridging 1,4-dioxane ligand. Note that in the case of the monodentate THF ligand, which is not able to form coordination polymers, the usual 1:1 zinc–porphyrin/ligand complexes with five-coordinate zinc were formed.

Experimental Section

General: UV/Vis spectra were recorded with a Lambda 20 spectrophotometer. ^{1}H (300 MHz, 400 MHz) and ^{13}C (125 MHz) NMR spectra were recorded with Bruker Avance 300 and 400 spectrometers at room temperature and referenced to the residual proton signals of the solvent ($CDCl_3$: δ = 7.28 ppm; [D_4]MeOH: δ = 4.84 ppm, 3.31 ppm). MALDI-ToF mass spectra were recorded with an Ultraflex MALDI ToF Bruker Daltonics spectrometer with a dithranol matrix. High-resolution mass spectra (HRMS) were measured with a Bruker micrOTOF II instrument by electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage –4500 V, end plate offset –500 V); mass range from m/z = 50 to 6000 Da; external or internal calibration was achieved with an electrospray calibrant solution (Fluka). Syringe injection was used for solutions in acetonitrile

(flow rate 3 mL min^{-1}). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C. All reactions were monitored by TLC (Macherey–Nagel Alugram SIL G/UV254 silica gel 60 UV_{254}, CH_2Cl_2). Column chromatography was performed on silica gel (Macherey–Nagel 60 0.04–0.063, 230–400 mesh). The X-ray studies were performed with a SMART APEX II diffractometer. CH_2Cl_2 was distilled from CaH_2; $CHCl_3$ was distilled from P_2O_5 and was freed of acids by stirring in the presence of K_2CO_3. DMF was distilled from CaH_2. Methanol was distilled from magnesium turnings. The starting materials were generally used as received.

Syntheses of Porphyrins and Metalloporphyrins

3-(*n*-Pentyl)pentane-2,4-dione (2): A mixture of acetylacetone (300 mL, 2.91 mol) and 1-iodopentane (380 mL, 2.91 mol) was gradually added to a stirred suspension of K_2CO_3 powder in DMF (500 mL). The reaction mixture was stirred at 100 °C for 8 h; it was then cooled, the precipitate was filtered off and washed with acetone, and the solvent was evaporated in vacuo. The residue was diluted with water, the organic layer was collected, and the water layer was extracted with diethyl ether. The combined organic fractions were concentrated in vacuo to yield the product (272 g, 55%). ^{1}H NMR ($CHCl_3$, 298 K, 400 MHz): δ = 4.00 [t, J = 7.7 Hz, 2 H, CH_2(CH$_2$)$_3$CH$_3$], 2.24 (s, 6 H, CH$_3$) 2.21 (m, 2 H, CH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.74 (m, 2 H, CH$_2$CH$_2$CH_2CH$_2$CH$_3$), 1.54 (m, 2 H, CH$_2$CH$_2$CH$_2$CH_2CH$_3$), 0.98 (t, J = 7.26 Hz, 3 H, CH$_2$CH$_2$CH$_2$CH$_2$CH_3) ppm.

5-(Ethoxycarbonyl)-2,4-dimethyl-3-(*n*-pentyl)pyrrole (4): A solution of $NaNO_2$ (111 g, 1.61 mol) in water (180 mL) was added gradually with stirring and cooling at –35 °C to a mixture of ethyl acetoacetate (203 mL, 1.60 mol) and acetic acid (400 mL). The solution was stirred at room temperature overnight. After that, it was added to a solution of **2** (777 g, 1.60 mol) in acetic acid (700 mL, temperature was about 90 °C) simultaneously with steady addition of zinc powder (420 g, 6.43 mol). This mixture was stirred at 95 °C for 1 h and diluted with water (11 L). The precipitated pyrrole was filtered off, washed with water and dissolved in dichloromethane. The solution was filtered to remove inorganic solids and washed with water, and dichloromethane was evaporated in vacuo. The resulting pyrrole was dried in vacuo to give crude product (357 g, 94%). Purification was performed by recrystallization from aqueous methanol: the crude product (100 g) was dissolved in methanol at reflux (150 mL), water (60 mL) was added to this solution up to turbidity, and the mixture was cooled with stirring. The precipitate was filtered off and dried in vacuo to yield pure **4** (236 g, 62%). M.p. 73 °C. ^{1}H NMR (CCl_4, 298 K, 300 MHz): δ = 9.83 (br. s, 1 H, NH), 4.10 (q, J = 6.97 Hz, 2 H OCH_2CH$_3$), 2.10 [m, 8 H, 3,5-CH$_3$, 4-CH_2(CH$_2$)$_3$CH$_3$], 1.23 (t, J = 6.97 Hz, 3 H, OCH$_2$CH_3), 1.12 [m, 6 H, 4-CH$_2$(CH_2)$_3$CH$_3$], 0.75 [t, J = 8.0 Hz, 3 H, 4-CH$_2$(CH$_2$)$_3$CH_3] ppm.

5,5-Bis(ethoxycarbonyl)-4,4′-dimethyl-3,3′-di(*n*-pentyl)dipyrromethane-2,2′ (6): Bromine (21.6 mL, 0.42 mol) was added gradually with stirring and cooling by water to suspension of **4** (100 g, 0.42 mol) and anhydrous CH_3COONa (69 g, 0.84 mol) in acetic acid (500 mL). This suspension was stirred for 30 min and diluted 3:1 with cooled water. The precipitate was filtered off, washed with water and heated at reflux with stirring in a 1 L flask with methanol (500 mL) and concentrated HCl (10 mL) for 3 h. After cooling of the reaction mixture, the residue was stirred overnight and filtered, washed with methanol and dried, yielding 48 g (50%). The crude product was purified by recrystallization from methanol to give **6** (35.2 g, 37%). M.p. 124 °C. ^{1}H NMR (CCl_4, 298 K, 300 MHz): δ = 9.97 (br. s, 2 H, NH), 4.00 (q, J = 6.97 Hz, 4 H, OCH_2CH$_3$), 3.70 (s, 2 H, CH$_2$), 2.17 [t, J = 6.82 Hz, 4 H, 3,3′-CH_2(CH$_2$)$_3$CH$_3$], 2.07 (s, 6 H, 4,4′-CH$_3$), 1.13 [m, 18 H, OCH$_2$CH_3, 3,3′-CH$_2$-(CH_2)$_3$CH$_3$], 0.75 [t, J = 8.0 Hz, 6 H, CH$_2$(CH$_2$)$_3$CH_3] ppm.

4,4′-Dimethyl-3,3′-di(*n*-pentyl)dipyrromethane-2,2′ (7): A solution of **6** (2.0 g, 4.36 mol) and KOH (2.0 g, 35.6 mol) in ethylene glycol (30 mL) was heated at reflux for 1 h. The mixture was diluted with cooled water (200 mL), and the precipitate was filtered off, washed with water and dried at room temperature to give **7** (1.28 g, 93%). The resulting dipyrromethane was further used without purification. ^{1}H NMR ($CHCl_3$, 298 K, 400 MHz): δ = 9.97 (br. s, 2 H, 2NH), 6.31 (s, 2 H, pyrrolic CH), 3.70 (s, 2 H, CH$_2$), 2.17 [t, J = 6.82 Hz, 4 H, 3,3′-CH_2(CH$_2$)$_3$CH$_3$], 2.07 (s, 6 H, 4,4′-CH$_3$), 1.13 [m, 4 H, 3,3′-CH$_2$(CH_2)$_3$CH$_3$], 0.75 [t, J = 8.0 Hz, 6 H, CH$_2$-(CH$_2$)$_3$CH_3] ppm.

2,3-Dimethylbuta-1,3-diene (9): A mixture of pinacone (156 g, 1.32 mol) and concentrated HBr (5 mL) in a 500 mL round-bottomed flask fitted with a dumped packing fractionating column and condenser was heated to reflux and slowly distilled with collection of the fraction boiling up to 95 °C. The distillate was washed twice with water, hydroquinone (0.5 g) was added, and drying was accomplished with $CaCl_2$. The product was distilled, and the fraction with boiling point about 69–72 °C was collected to give **9** (47.5 g, 44%). ^{1}H NMR ($CHCl_3$, 298 K, 300 MHz): δ = 5.06 (s, 2 H, CH$_2$), 4.97 (s, 2 H, CH$_2$), 1.92 (s, 6 H, CH$_3$) ppm.

3,4-Dimethylpyrrole (11): A solution of urethane **8** (39.2 g, 0.44 mol) in dry benzene (220 mL) was mixed simultaneously with dry pyridine (72 mL, 0.89 mol) and freshly distilled SO_2Cl_2 (32 mL, 0.45 mol) in a 1 L round-bottomed flask, with cooling of the mixture to maintain a temperature of below 45 °C. The mixture was stirred for about a further 1 h, and **9** (50 mL, 0.44 mol) was added. After that, the mixture was heated to reflux with stirring for 1 h and left at room temperature overnight. The precipitate of pyridine hydrochloride was filtered off and washed with benzene, and the combined solutions were concentrated in vacuo. The concentrated residue was added with cooling and stirring to a solution of KOH (198 g, 3.53 mol) in methanol (440 mL). The resulting mixture was heated at reflux for 2 h, and the product was steam-distilled. The distillate was extracted twice with dichloromethane, washed with water and dried with Na_2SO_4. The solution was distilled in vacuo, with collection of the fraction with boiling point about 70 °C. The yield of **11** was 34.6 g (41%). M.p. 33–34 °C. ^{1}H NMR (CCl_4, 298 K, 300 MHz): δ = 7.17 (br. s, 1 H, NH), 6.18 (s, 2 H, 2,5-H), 1.88 (s, 6 H, 3,4-CH$_3$) ppm.

2-Formyl-3,4-dimethylpyrrole (12): $POCl_3$ (36.6 mL, 0.4 mol) was added to a solution of **11** (28.5 g, 0.3 mol) in DMF (200 mL) with stirring and maintenance of the temperature below 15 °C. The reaction mixture was stirred at room temperature for 1.5 h and then diluted with water (900 mL), and a solution of KOH (20%, about 2.4 mol) was added. The resulting precipitate was filtered off, washed with water and dried to yield **12** (28.9 g, 78%). M.p. 142–143 °C. ^{1}H NMR (CCl_4, 298 K, 300 MHz): δ = 9.63 (br. s, 1 H, NH), 9.40 (s, 1 H, CHO), 6.75 (s, 1 H, 5-H), 2.18 (s, 3 H, 3-CH$_3$), 1.93 (s, 3 H, 4-CH$_3$) ppm.

5-(4-Bromophenyl)-2,3,7,8,12,18-hexamethyl-13,17-di(*n*-pentyl)-porphyrin (H_2P-1): Initially, concentrated HBr (2 mL, 16.6 mmol) was added at room temperature with stirring to a solution of **7** (1.28 g, 4.07 mmol) and **12** (1.0 g, 8.14 mmol) in butanol (100 mL), after which a precipitate settled. 4-Bromobenzaldehyde (4.0 g, 21.6 mmol) was added after 1 h, and the reaction mixture was heated to reflux. The mixture was kept at reflux for 4 h, iodine (1.0 g, 3.9 mmol) was then added, and the mixture was stirred for 10 min. After that, the reaction mixture was allowed to cool, and concentrated ammonia solution (4 mL) was added gradually. The

precipitate was filtered off, washed with methanol and dried at 70 °C. The crude product was purified by column chromatography on silica gel with dichloromethane as eluent to yield **H_2P-1** (1.6 g, 57%). R_f [benzene/hexane (3:1)] = 0.53. ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz): δ = 10.17 (s, 2 H, 10,20-H), 9.95 (s, 1 H, 15-H), 7.88 (s, 4 H, 2′,3′,5′,6′-H-Ar), 4.03 [t, J = 6.82 Hz, 4 H, 13,17-CH_2(CH$_2$)$_3$-CH$_3$], 3.67 (s, 6 H, 12,18-CH$_3$), 3.55 (s, 6 H, 2,8-CH$_3$), 2.48 (s, 6 H, 3,7-CH$_3$), 2.32 (m, 4 H, 13,17-CH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.76 (m, 4 H, 13,17-CH$_2$CH$_2$CH_2CH$_2$CH$_3$), 1.57 (m, 4 H, 13,17-CH$_2$CH$_2$CH$_2$CH_2CH$_3$), 1.00 (t, J = 7.20 Hz, 6 H, 13,17-CH$_2$CH$_2$CH$_2$CH$_2$CH_3), –3.19 (s, 1 H, NH), –3.32 (s, 1 H, NH) ppm. UV/Vis ($CHCl_3$): λ [log(ε/M^{-1}cm^{-1})] = 624 [3.57], 571 [3.88], 537 [3.92], 503 [4.21], 404 nm [5.29]. HRMS (ESI): calcd. for [$C_{42}H_{49}BrN_4$]$^+$ 688.3141 [M + H]$^+$; found 688.3239.

5,15-Bis(4-bromophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra(*n*-pentyl)porphyrin (H_2P-2): Initially, a solution of trifluoroacetic acid (0.4 mL, 5.38 mmol) in dichloromethane (30 mL) was added with stirring at room temperature under argon to a solution of **12** (1.28 g, 4.07 mmol) and 4-bromobenzaldehyde (0.8 g, 4.32 mmol) in dichloromethane (450 mL). The mixture was stirred for 4 h, *p*-chloranil (1.6 g, 6.51 mmol) was then added, and the reaction mixture was left at room temperature overnight. The solvent was then evaporated in vacuo, and the residue was washed with aqueous KOH and water and dried at 70 °C. The solid was dissolved in dichloromethane and purified by column chromatography on silica gel. The solution after chromatography was concentrated, and the product was precipitated by addition of methanol. The product was filtered off, washed with methanol and dried at 70 °C. R_f [benzene/hexane (3:1)] = 0.76. ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz): δ = 10.27 (s, 2 H, 10,20-H), 7.95 (d, J = 8.08 Hz, 4 H, 2,6-H), 7.90 (d, J = 8.34 Hz, 4 H, 3,5-H), 4.00 [t, J = 7.7 Hz, 8 H, 2,8,12,18-CH_2(CH$_2$)$_3$CH$_3$], 2.63 (s, 12 H, 3,7,13,17-CH$_3$), 2.21 (m, 8 H, 2,8,12,18-CH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.74 (m, 8 H, 2,8,12,18-CH$_2$CH$_2$CH_2CH$_2$CH$_3$), 1.54 (m, 8 H, 2,8,12,18-CH$_2$CH$_2$CH$_2$CH_2CH$_3$), 0.98 (t, J = 7.26 Hz, 12 H, 2,8,12,18-CH$_2$CH$_2$CH$_2$CH$_2$CH_3), –2.43 (br. s, 2 H, NH) ppm. UV/Vis ($CHCl_3$): λ [log(ε/M^{-1}cm^{-1})] = 626 [3.49], 574 [3.96], 542 [3.87], 508 [4.30], 410 nm [5.40]. HRMS (ESI): calcd. for [$C_{56}H_{69}Br_2N_4$]$^+$ 956.3790 [M + H]$^+$; found 956.3913.

Zinc 5-(4-Bromophenyl)-2,3,7,8,12,18-hexamethyl-13,17-di(*n*-pentyl)porphyrinate (ZnP-1): Zinc acetate (0.438 g, 2 mmol, excess) was added to a solution of porphyrin **H_2P-1** (69 mg, 0.1 mmol) in $CHCl_3$ (30 mL). The mixture was stirred at room temperature overnight, and the solvent was removed in vacuo. The resulting powder was dissolved in $CHCl_3$, and the solution was filtered and directly loaded onto a silica gel chromatography column. The expected compound (eluted with $CHCl_3$) was obtained as a crimson solid. It was precipitated from chloroform solution by addition of methanol and washed with methanol to yield **ZnP-1** (0.8 mg, 94%). ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz): δ = 9.90 (s, 2 H, 10,20-H), 9.52 (s, 1 H, 15-H), 7.90 (s, 4 H, 2′,3′,5′,6′-H-Ar), 3.79 [t, J = 6.82 Hz, 4 H, CH_2(CH$_2$)$_3$CH$_3$], 3.48 (s, 12 H, 12,18-CH$_3$, 2,8-CH$_3$), 2.44 (s, 6 H, 3,7-CH$_3$), 2.18 (m, 4 H, 13,17-CH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.71 (m, 4 H, 13,17-CH$_2$CH$_2$CH_2CH$_2$CH$_3$), 1.55 (m, 4 H, 13,17-CH$_2$CH$_2$CH$_2$CH_2CH$_3$), 1.01 (t, J = 7.20 Hz, 6 H, 13,17-CH$_2$CH$_2$CH$_2$CH$_2$CH_3) ppm. UV/Vis ($CHCl_3$): λ [log(ε/M^{-1}cm^{-1})] = 536 [3.98], 572 [3.95], 406 [5.56]. HRMS (ESI): calcd. for [$C_{42}H_{49}BrN_4Zn$]$^+$ 751.2354 [M + H]$^+$; found 751.2256.

Table 1. Crystal data and structure refinement for porphyrin compounds.

	H_2P-1	**H_2P-2**	**ZnP-1·$C_4H_8O_2$**	**ZnP-2·THF**
Empirical formula	$C_{42}H_{49}BrN_4$	$C_{56}H_{68}Br_2N_4$	$C_{46}H_{55}BrN_4O_2Zn$	$C_{60}H_{74}Br_2N_4OZn$
Formula mass	689.76	956.96	841.22	1092.42
Colour	red	red	red	red
T [K]	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	14.9705(11)	6.8777(9)	8.675(5)	10.300(3)
b [Å]	13.0783(10)	12.8756(18)	14.398(9)	16.247(4)
c [Å]	18.5991(14)	15.354(2)	18.172(11)	16.690(5)
α [°]	90	67.982(2)	68.026(10)	83.775(4)
β [°]	96.3170(10)	77.252(2)	78.351(10)	89.870(4)
γ [°]	90	87.795(2)	79.909(10)	73.886(4)
V [Å^3]	3619.4(5)	1227.9(3)	2049(2)	2666.1(13)
Z	4	1	2	2
d(calcd.) [Mg m^{-3}]	1.266	1.493	1.363	1.361
μ [mm^{-1}]	1.171	1.691	1.617	2.003
F(000)	1456	502	880	1140
Crystal size [mm]	0.14×0.12×0.10	0.16×0.14×0.12	0.14×0.12×0.10	0.14×0.12×0.10
θ range for data collection [°]	2.28–28.00	2.79–28.00	2.27–26.00	2.40–27.00
Index ranges	$-19 \le h \le 19$ $-17 \le k \le 17$ $-24 \le l \le 24$	$-9 \le h \le 9$ $-16 \le k \le 16$ $-20 \le l \le 20$	$-10 \le h \le 10$ $-17 \le k \le 17$ $-22 \le l \le 22$	$-13 \le h \le 13$ $-20 \le k \le 20$ $-21 \le l \le 21$
Reflections collected	30890	12490	17303	25191
Independent reflections	8636 [R(int) = 0.0414]	5815 [R(int) = 0.0272]	7912 [R(int) = 0.0994]	11514 [R(int) = 0.0628]
Data/restraints/parameters	8636/0/449	5815/0/272	7912/1/459	11514/1/609
Goodness-of-fit on F^2	1.005	1.040	1.023	0.993
Final R indices [$I > 2\sigma(I)$][a]	R_1 = 0.0482, wR_2 = 0.1127	R_1 = 0.0473, wR_2 = 0.1155	R_1 = 0.0821, wR_2 = 0.1838	R_1 = 0.0633, wR_2 = 0.1518
R indices (all data)[a]	R_1 = 0.0847, wR_2 = 0.1308	R_1 = 0.0650, wR_2 = 0.1243	R_1 = 0.1650, wR_2 = 0.2252	R_1 = 0.1303, wR_2 = 0.1864
Largest difference peak/hole [e Å^{-3}][b]	1.313/–0.795	1.125/–1.336	1.530/–1.224	1.337/–1.445

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$. [b] In all structures the largest difference peak is observed in the vicinity of the heavy atom.

Zinc 5,15-Bis(4-bromophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetra(*n*-pentyl)porphyrinate (ZnP-2): The synthesis of **ZnP-2** is similar to that of **ZnP-1**. A solution of **H_2P-2** (95.7 mg, 0.1 mmol) in $CHCl_3$ (30 mL) was mixed with zinc acetate (0.438 g, 2 mmol, excess). The yield of **ZnP-2** was 95.7 mg (94%). ^{1}H NMR ($CDCl_3$, 298 K, 400 MHz): δ = 10.15 (s, 2 H, 10,20-H), 8.00 (d, J = 8.08 Hz, 4 H, 2,6-H), 7.90 (d, J = 8.34 Hz, 4 H, 3,5-H), 3.98 [t, J = 7.71 Hz, 8 H, 2,8,12,18-CH_2(CH$_2$)$_3$CH$_3$], 2.50 (s, 12 H, 3,7,13,17-CH$_3$), 2.18 (m, 8 H, 2,8,12,18-CH$_2$CH_2CH$_2$CH$_2$CH$_3$), 1.73 (qv, 8 H, CH$_2$CH$_2$CH_2CH$_2$CH$_3$), 1.55 (sc, 8 H, 13,17-H$_2$CH$_2$CH$_2$CH_2CH$_3$), 0.99 (t, J = 7.26 Hz, 12 H, 13,17-CH$_2$CH$_2$CH$_2$CH$_2$CH_3) ppm. UV/Vis ($CHCl_3$): λ [log(ε/M^{-1}cm^{-1})] = 575 [3.16], 540 [3.38], 412 nm [4.68]. HRMS (ESI): calcd. for [$C_{56}H_{69}Br_2N_4Zn$]$^+$ 1021.3160 [M + H]$^+$; found 1021.3280.

X-ray Diffraction Analysis: The data collection and structure-refinement data for compounds **H_2P-1**, **H_2P-2**, **ZnP-1**, **ZnP-2** are presented in Table 1. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer and a CCD area detector (graphite monochromator, Mo-K_α radiation, λ = 0.71073 Å, ω-scans). The semiempirical method SADABS[50] was applied for the absorption correction. The structures were solved by direct methods and refined by the full-matrix, least-squares technique against F^2 with anisotropic displacement parameters for all non-hydrogen atoms. In compounds **H_2P-1** and **ZnP-2**, carbon atoms C(38)–C(40) and C(42)–C(46) of the pentyl substituents are disordered over two sites with occupancies of 0.7:0.3 and 0.6:0.4, respectively. All the hydrogen atoms in the complexes were placed geometrically and included in the structure-factor calculations in the riding-motion approximation. All the data reduction and further calculations were performed with the aid of the SAINT[51] and SHELXTL-97[52] program packages. CCDC-867054 (for **H_2P-1**), -867055 (for **H_2P-2**), -867056 (for **ZnP-1**) and -867057 (for **ZnP-2**) contain the supplementary crystallographic data 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.

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