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PAPER

Synthesis, characterization and cation-induced dimerization of new aza-crown ether-appended metalloporphyrins†

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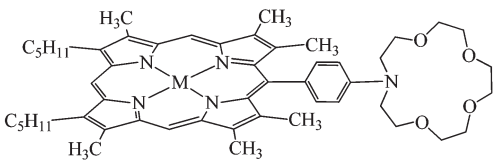
New metalloporphyrins bearing one or two aryl-aza-crown ether moieties at *meso*-positions have been synthesized using a palladium catalyzed amination reaction and fully characterized by spectral techniques. X-Ray structural data have been presented for the zinc and copper complexes of mono-substituted aza-crown ether appended metalloporphyrins. UV-Vis and ^{1}H NMR spectroscopic studies showed that addition of K^+ cations to a solution of monomeric aza-crowned porphyrins in $CHCl_3$/MeOH led to cation-induced dimerization of these porphyrins, whereas addition of Na^+ cations yielded a monomeric complex. Axial coordination of the exobidentate ligand (DABCO) to zinc complexes of aza-crowned porphyrins and following binding metal ions led to formation of sandwich complexes with high stability constants.

Introduction

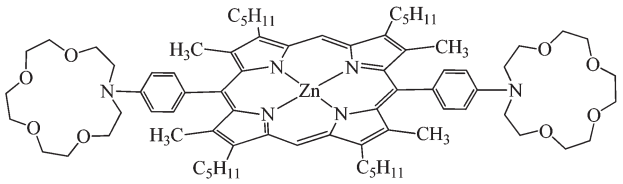
Supramolecular assemblies based on intermolecular interactions have been of wide interest in view of constructing complicated molecular architectures by self-organization.[1] In this regard, porphyrins are qiute attractive components of such systems due to their unique photophysical,[2] electrochemical, catalytic[3] and structural properties.[4] Consequently porphyrin assemblies have been used as model compounds to mimic biological functions such as cytochrome catalytic activity, heme oxygenation, photochemical electron transport[5] and as new materials for electronic and optical devices,[6] light-harvesting complexes,[7] switches and gates.[8] In order to create these systems, porphyrin units have to be modified by multitopic binding centers which facilitate self-assembling into non-covalent supramolecular arrays. Constructing supramolecular non-covalent assemblies by virtue of linking binding centers of porphyrins can be realized by numerous means such as π–π interaction,[9] hydrogen bonding[10] and cation coordination.[11] The dimerization of porphyrins is of interest since sandwiched porphyrin dimers mimic the primary donor entity of the bacterial photosynthetic reaction center and act as electrocatalysts.[12] One of the ways to obtain cofacial bisporphyrins was reported by Thanabal and Krishnan[13] whose crown ether appended porphyrins and their metal derivatives interact with large cations to produce the corresponding dimers.

Phthalocyanines functionalized with crown ether also resulted in supramolecular entities displaying dimerization in presence of alkali metal ions.[14] For three decades after that pioneering work a number of crowned porphyrins have been synthesized,[15–21] nevertheless the scope of the available compounds is narrow and their supramolecular chemistry is quite far from being adequately explored.

In this work we report the synthesis and cation-induced dimerization of new aza-crown ether appended metalloporphyrins: 5-(4′-(aza-15-crown-5)-phenyl) (**MP,3**) and 5,15-bis(4′-(aza-15-crown-5)-phenyl) (**ZnP,5**) β-octaalkyl metalloporphyrins (Fig. 1) in which the aza-crown ether and porphyrin fragments are directly linked *via* a phenyl ring at meso-position of the porphyrin core.



MP,3 M=Zn, Cu



ZnP,5

Fig. 1 5- and 5,15-bis-*N*-aza-crowned β-octaalkyl metalloporphyrins **MP,3** and **ZnP,5**.

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In comparison with benzo-15-crown-5 ether units of earlier reported crown porphyrins[13,17,19] aza-crown ether functionalities are more conformationally flexible. The nearly free rotation around the C_{phenyl}–N bond and the flexibility of aza-crown ether to deviate from coplanarity with a phenyl ring can provide accommodation of cations of different sizes. In addition, an absence of a rigid benzene ring inside the crown macrocycle in aza-15-crown-5 allows to avoid stereo- and atropoisomers inherent in benzo-crown ether appended porphyrins as reported by Notash *et al.*[19c] The porphyrin–crown ether conjugate is a heterotopic ligand capable of coordination of two types of metals at different sites. Zinc (or other proper transition metals) complexes of crowned porphyrins can concurrently coordinate both Lewis acids and bases at crown ether and zinc sites, respectively. For the first time we have studied the dimer formation in the three component system of zinc porphyrin–cation–exobidentate ligand. Interaction with cations and anions facilitates receptor properties of crowned metalloporphyrins with respect to salts of alkali metals.[19d]

Results and discussion

Synthesis of aza-crown ether-appended metalloporphyrins ZnP,3 and ZnP,5

Brominated β-octaalkyl substituted porphyrins 5-(4′-bromophenyl)-3,7,12,13,17,18-hexamethyl-2,8-dipentyl) porphyrin (**H_2P,1**) and 5,15-bis(4′-bromodiphenyl)-2,8,12,18-tetramethyl-2,8,12,18-tetrapentyl porphyrin (**H_2P,2**) were chosen as parent porphyrins and synthesized according to previously reported techniques.[23] 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, satisfactory solubility and thermal stability,[24] in some cases, the molecular architecture of 5,15-diarylporphyrins can be more readily manipulated than that of tetraarylporphyrins.[25] Presence of alkyl substituents in β-positions of **H_2P,1** and **H_2P,2** facilitates their solubility in organic solvents such as $CHCl_3$, CH_2Cl_2 and toluene. The corresponding metalloporphyrins **MP** (**ZnP,1**; **CuP,1 ZnP,2**) were prepared from zinc and copper acetates.

The junction of bromoporphyrin and aza-crown ether units was achieved *via* palladium catalyzed Buchwald–Hartwig amination reaction. This reaction representing a modern cross-coupling methodology has emerged as a powerful tool for the formation of carbon–nitrogen bonds.[26] Application of the transition metal catalysis in porphyrin chemistry started in mid 90s and had a rapid development in 2000s[27,28] but it is still rather limited. There are not examples of catalytic coupling of porphyrins and azacrown macrocycles. *N*-Arylation of aza-15-crown-5 ethers by aryl bromides was accomplished by Buchwald and Zhang[29] using the following catalyst system: 1–2 mol% $Pd_2(dba)_3$, 3–6 mol% of monophosphine ligand DavePhos (Fig. 2) and 1.4 equiv of NaO–*t*-Bu as a base at 100 °C in toluene. A similar method was used by Beletskaya *et al.*[30] to obtain *N*-aryl and *N*-vinyl diaza-18-crown-6 derivatives. On the other hand, Chen and Zhang[31] reported palladium-catalyzed amination of *meso*-halogenated and *meso*-(haloaryl) porphyrin substrates by primary aliphatic and primary and secondary aromatic amines, using 2.5–5 mol% of $Pd(OAc)_2$ and 5–7.5 mol%

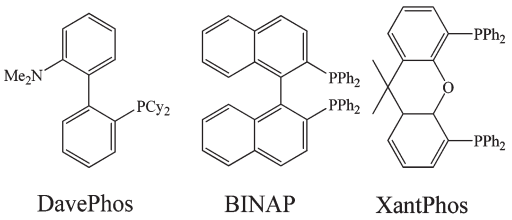
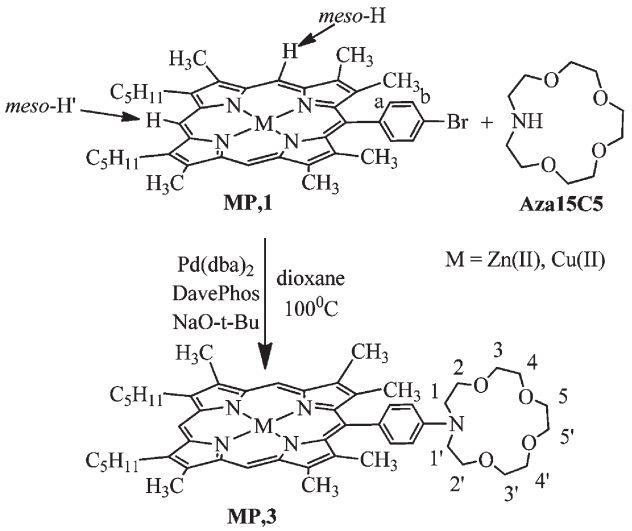


Fig. 2 Structures of electron-rich bulky mono- and chelating diphosphine ligands.



Scheme 1 Synthesis of **MP,3** *via* Pd-catalyzed amination reaction.

of diphosphine ligands DPEphos, BINAP and Xantphos (Fig. 2) with yields up to 98%. Thus amination of haloporphyrins with amines and arylation of azacrown ethers with arylhalides was carried out at different reaction conditions and with different ligands. Use of bulky sterically hindered amines in Pd-catalyzed amination leads to decrease in conversion and reaction yield. Flexible nitrogen substituents in aza-15-crown-5 ether hamper the path of secondary amine to arylbromine. Anilines, primary and less hindered or rigid cyclic secondary amines such as morpholine and piperazine reacted under the same conditions with great conversion.[31]

Amination reactions of **MP,1** were carried out at 100 °C in dioxane under Ar atmosphere with 1 equiv of **MP,1**; 1.14 equiv of aza-15-crown-5 ether (**Aza15C5**) at the presence of NaO–*t*-Bu as a base, $Pd(dba)_2$, varying ligands and catalyst loading (Scheme 1, Table 1).

Our efforts to optimize the synthesis have shown that the nature of phosphine ligand, catalyst loading and reaction time are the key factors of the reaction. We found that bisphosphine ligands BINAP and Xantphos being highly operative for the amination of meso-(bromophenyl)porphyrins with simple amines,[31] were ineffective in reaction with aza-crown ether (Table 1, entries 1, 2). The monophosphine ligand DavePhos used for arylation of azacrown ether previously[29] has also been found to be the most efficient in the reaction under investigation.

The amination of **MP,1** with 2 mol% $Pd(dba)_2$ and 2 mol% DavePhos afforded the desired aza-crown ether appended

metalloporphyrins **ZnP,3** and **CuP,3** in 37 and 36% yields respectively (Table 1, entry 3). With a twofold increase in catalyst loading the yields doubled (Table 1, entry 4). The excellent yield of the products **ZnP,3** and **CuP,3** (90%) was achieved by increasing the ratio ligand–palladium = 2 : 1 (Table 1, entry 5). Thus the arylation of azacrown ether by bromophenylporphyrin required considerably higher palladium and ligand loading compared to arylation with arylbromides. Along with the target product the minor 5-phenylporphyrin was obtained as a result of reduction of the C–Br bond in the course of the competitive side β-hydrogen elimination.

Synthesis of bis-aza-crown ether appended metalloporphyrin **ZnP,5** was carried out from the corresponding bis(bromophenyl)-porphyrin **ZnP,2** (Scheme 2).

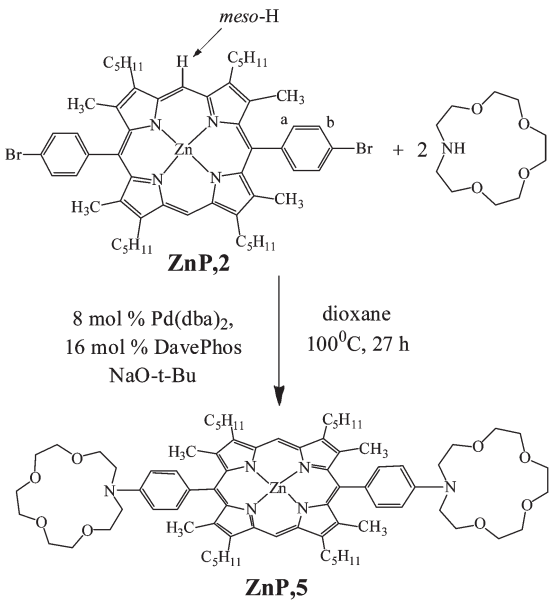
Double amination in porphyrins was observed to proceed with much more difficulty than monosubstitution (Fig. 3). The reaction became complicated by reduction of bromine at one or two positions. With 4 mol% $Pd(dba)_2$ and 4 mol% DavePhos with ratio of reagents **ZnP,2**/**Aza15C5** = 1 : 2.3 the reaction yielded after 32 h only 16% of bisamination product **ZnP,5** together with side products of reduction **ZnP,4** and **ZnP,6** (Table 2, entry 1). **ZnP,4** was formed in 14% yield as a result of the β-hydrogen elimination at one of two substitution steps. The side product of double bromine reduction 5,15-diphenylporphyrin **ZnP,6** was formed in 25% yield.

Doubling of the catalyst loading to 8 mol% led to almost double improvement in the product yield to 28%. Concurrently, the product of monoamination–monoreduction **ZnP,4** was raised too (Table 2, entry 2). Then we found that use of the double excess of the ligand (16 mol% of DavePhos) as well as larger (1.5 equiv.) excess of amine component (**ZnP,2**/**Aza15C5** = 1 : 3) enhanced the bis-aminated product yield to good 64%. It is remarkable that increasing the catalyst loading led to a considerable decrease of the yield of the reduction product **ZnP,6** from 25 down to 5% (Table 2, entry 3). With less both catalyst and amine quantities the yield of reduction products significantly rised (Table 2, entry 4). Surprisingly, no monoamination product was detected meaning all bromine not replaced by amine was

Table 1 Palladium catalyzed amination reactions of bromophenylporphyrins **ZnP,1** and **CuP,1**[a]

Entry	$Pd(dba)_2$ mol%	Ligand	Ligand, mol%	Time, h	Yield[b] % **ZnP,3**	Yield[b] % **CuP,3**
1	2	BINAP	2	32	Traces	Traces
2	2	Xantphos	2	32	—	—
3	2	DavePhos	2	37	37	36
4	4	DavePhos	4	27	73	70
5	4	DavePhos	8	27	90	90

[a] Reactions were carried out at 100 °C in dioxane under Ar atmosphere with 1.0 equiv of **MP,1**; 1.14 equiv of **Aza15C5** and 1.4 equiv of NaO–*t*-Bu. Concentration: 0.57 M **MP,1**. [b] Isolated yields.



Scheme 2 Amination of bis(bromophenyl)porphyrin with **Aza15C5**.

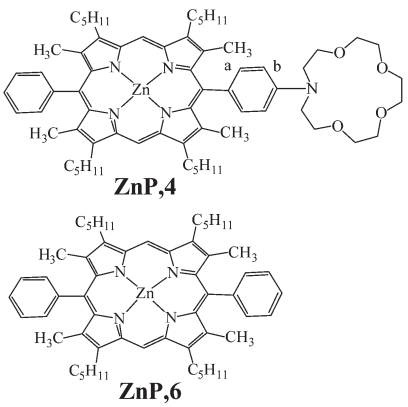


Fig. 3 Side products of the double amination reaction.

Table 2 Palladium catalyzed double amination reactions of dibromophenylporphyrin **ZnP,2**[a]

Entry	$Pd(dba)_2$ mol%	*L*, mol%	**Aza15C5**, equiv	Time, h	Yield **ZnP,5**[b], %	Yield **ZnP,4**[b], %	Yield **ZnP,6**, %
1	4	4	2.3	32[c]	16	14	25
2	8	8	2.3	37	28	25	25
3	8	16	3	27	64	30	5
4	4	8	1.14	40	18	57	25

[a] Reactions were carried out at 100 °C in dioxane under Ar atmosphere with 1.0 equiv of **ZnP,2** and 1.4 equiv of NaO–*t*-Bu. Concentration: 2 mL solvent/1 mmol **ZnP,2**. [b] Isolated yields of **ZnP,4** and **ZnP,5**. [c] In addition to major products of amination in the reaction mixture product of homo coupling when two porphyrin fragments bound to each other was found by MALDI MS.

Table 3 ^{1}H NMR spectra **ZnP,1** and **ZnP,3** in $CDCl_3$

Compounds	*meso*-H, $\delta(\Delta\delta)$ ppm		H_{Ar}, $\delta(\Delta\delta)$ ppm		CH_2crown, δ, ppm			
	H_a	H_b	*a*	*b*	1, 1′	2, 2′	3, 3′	4, 4′
ZnP,1	9.90	9.52	7.90	7.90	—	—	—	—
ZnP,3	9.97 (0.07)	9.63 (0.11)	7.77 (−0.13)	7.00 (−0.9)	3.88	3.84	3.74	3.71
ZnP,2	10.15	—	8.00	7.90	—	—	—	—
ZnP,4	10.17 (0.02)	—	7.83 (−0.17)	7.04 (−0.86)	3.98	3.88	3.80	3.77
ZnP,5	10.16 (0.01)	—	7.83 (−0.17)	7.01 (−0.89)	3.99	3.86	3.76	3.74

reduced even at lack of reducing agent—**Aza15C5**. It was also noted that prolonged reaction time always led to increased formation of side product **ZnP,6**. These results can not be explained within the framework of the accepted mechanism revealing that the particular details of the actual pathway of the amination reaction are still unclear. In addition to Zn porphyrin complexes free base bis-aza-crowned porphyrin (5%) was detected in the reaction mixture by MALDI MS and ^{1}H NMR.

The newly synthesized porphyrins were characterized by NMR, UV-Vis spectroscopy, MALDI ToF MS and X-ray crystallography.

Spectroscopic characterization

The ^{1}H NMR study of aza-crowned porphyrins **ZnP,3** and **ZnP,5** revealed changes of the chemical shifts of *para*-substituted benzene hydrogens to a high field with $\Delta\delta$ = −0.13 ppm and −0.90 ppm, −0.17 ppm and −0.89 ppm, respectively (Table 3).

The spectra of **ZnP,4** have additional hydrogen resonances attributed to the phenyl unit. The upshifting can be attributed to the change of the *p*-substituent from an electron-withdrawing bromine atom in **ZnP,1** to an electron-donating secondary amine group of aza-15-crown-5 ether in **ZnP,3**. The resonances of aza-crowned porphyrin *meso*-protons appeared at a slightly lower field. The UV-Vis absorption spectra of porphyrins in chloroform are presented in Fig. 4 and Table 4.

The spectra displayed the intense Soret bands with a maximum at the range from 403 to 414 nm and the weaker four Q bands of free-base porphyrin and two Q bands of metalloporphyrins. Absorption maxima of aza-crowned metalloporphyrins appeared at 407 nm (**ZnP,3**) and 404 nm (**CuP,3**), which is slightly red-shifted relative to the parent compounds **ZnP,1** (406 nm) and **CuP,1** (403 nm). The absorption maxima of bis(aza-crowned) porphyrins appeared at 414 nm (**ZnP,5**), which is also slightly red-shifted relative to the parent **ZnP,2** (412 nm). The bathochromic character of the Soret band shift can be explained by an increase of electron density of the porphyrin system from an electron-donating secondary amine group of aza-crown ether. And the small magnitude of the effect is resulted from the weak conjugation of the porphyrin system with a phenyl substituent due to its nearly orthogonal position.[32]

The fluorescence quantum yields of aza-crowned porphyrins **ZnP,3** and **ZnP,5** (0.5×10^{-6} M), determined relative to ZnTMsPTMS (zinc 5,10,15-tri-mesityl-20-trimethylsilylacetylene porphyrin),[42] are 0.059 and 0.030 respectively. The decrease of quantum yield of **ZnP,5** can be attributed to the increase of the electron transfer to the porphyrin core from unshared electron pairs of nitrogens from two aza-crown ether units in comparison to the one unit in **ZnP,3**.

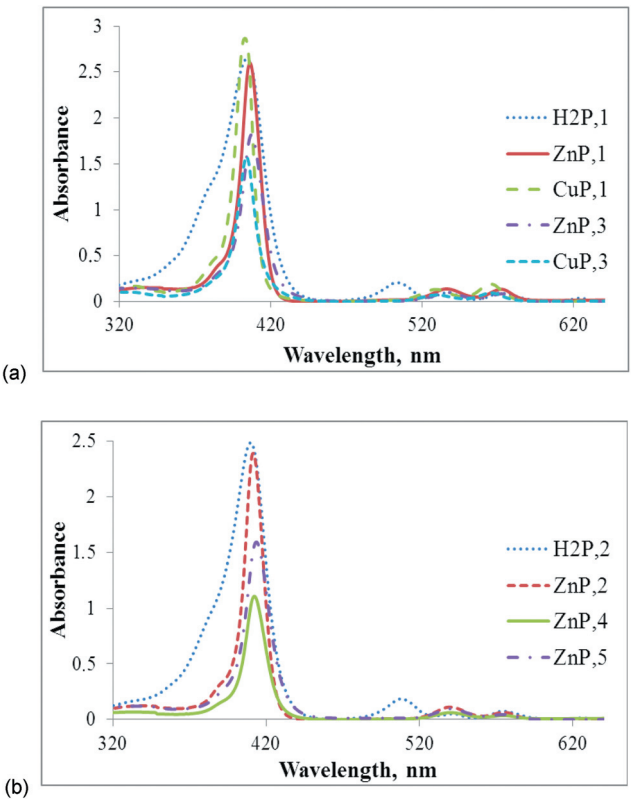


Fig. 4 (a) UV-visible spectra of 16×10^{-6} M **H_2P,1**; 7×10^{-6} M **ZnP,1**; 2×10^{-6} M **CuP,1**; 20×10^{-6} M **ZnP,3**; 15×10^{-6} M **CuP,3**. Fig. 4b. UV-visible spectra of 5×10^{-6} M **H_2P,2**; 5×10^{-6} M **ZnP,2**; 15×10^{-6} M **ZnP,5**; 13×10^{-6} M **ZnP,4** in $CHCl_3$.

Table 4 UV-Vis spectroscopic data of **ZnP,1**, **ZnP,3** **CuP,3**, **ZnP,2**, **ZnP,4**, **ZnP,5** in $CHCl_3$

Compounds	λ_{max}, nm	
	Soret band ($\varepsilon \times 10^{-3}$, $dm^3\ mol^{-1}\ cm^{-1}$)	Q bands ($\varepsilon \times 10^{-3}$, $dm^3\ mol^{-1}\ cm^{-1}$)
ZnP,1	406 (360.9)	572 (8.98), 536 (9.52)
CuP,1	403 (1056.82)	565 (50.95), 529 (28.83)
ZnP,3	407 (104.92)	537 (3.15), 572 (6.14)
CuP,3	404 (104.99)	529 (3.15), 565 (6.14)
ZnP,2	412 (47.93)	540 (2.41), 575 (1.46)
ZnP,4	412 (85.12)	540 (4.8), 574 (2.72)
ZnP,5	414 (107)	541 (7.43), 574 (3.96)

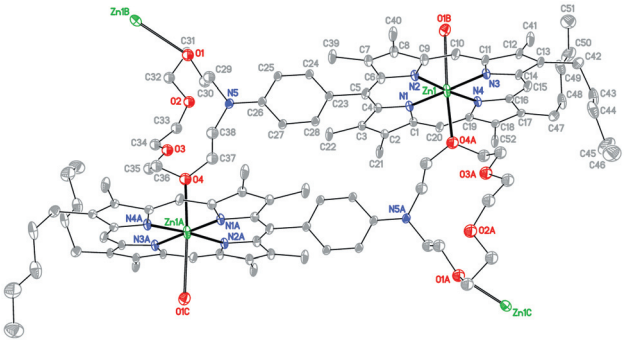


Fig. 5 X-Ray structure of **(ZnP,3)$_2$** (40% probability ellipsoids). The labeling A denotes a symmetrically equivalent atom relative to the inversion center (symmetry code: $1 - x$, $1 - y$, $1 - z$). Hydrogen atoms have been omitted.

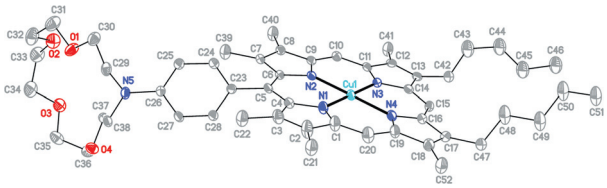


Fig. 6 X-Ray structure of **CuP,3** (30% probability ellipsoids). The statistically disordered solvate chloroform molecule is not shown. Hydrogen atoms have been omitted.

X-Ray study

The structures of **ZnP,3** and **CuP,3** were unambiguously established by a single-crystal X-ray diffraction study and are shown in Fig. 5 and 6 along with the atomic numbering schemes.

Mono-aza-crowned zinc porphyrins **ZnP,3** crystallize as centrosymmetric dimers through the additional intermolecular Zn–O4 coordination bonds of 2.357(7) Å. Further, the dimers are linked into the layers parallel to (100) by the weaker additional intermolecular Zn–O1 coordination bonds of 2.812(7) Å (Fig. 5). Thus, the coordination environment of each zinc atom can be considered as a [5 + 1] distorted octahedron. The porphyrin unit of **ZnP,3** adopts a slightly domed conformation, with the phenyl ring perpendicular to the mean porphyrin core (the interplane angle is 83.8(3)°). Due to the participation of the O1 and O4 oxygen atoms into the intermolecular interactions, the four oxygen atoms of the aza-crown ether unit do not lie within one plane. The interplane angles between the mean aza-crown ether plane and the planes of phenyl and porphyrin fragments are 53.5(3) and 72.0(3)°, respectively. The pentyl "tails" are arranged from the different sides of the porphyrin plane and stretch perpendicular to it.

Contrary to **ZnP,3**, the molecule of **CuP,3** is a monomer with a practically planar porphyrin unit (Fig. 6). The Cu atom has a tetragonal-planar environment without any additional coordinations. The molecules form the centrosymmetric dimeric associates by the π–π stacking interaction between the pyrrole N3-C11-C12-C13-C14 rings of neighbouring porphyrin cores. The distance between the pyrrole planes is 3.41 Å. The phenyl ring is orthogonal to the porphyrin plane (the interplane angle is 89.9(2)°). The four oxygen atoms of the aza-crown ether residue

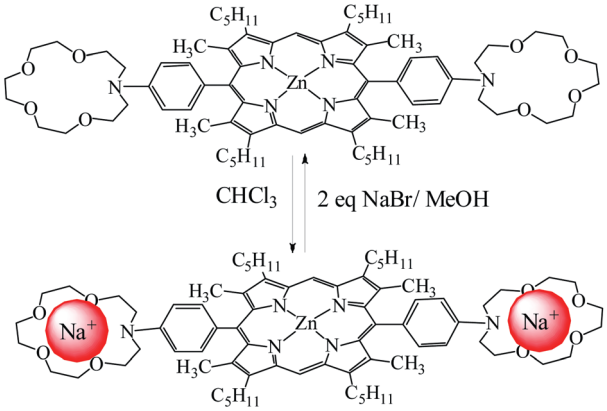


Fig. 7 Structural scheme of the complexation of **ZnP,5** with Na^+ cations.

lie almost within one plane. The interplane angles between the mean crown-ether plane and the planes of phenyl and porphyrin fragments are 68.4(2) and 77.7(2)°, respectively.

The pentyl "tails" are arranged from the one side of the porphyrin plane and stretch parallel to it.

The solvate chloroform molecule is bound to the aza-crown ether unit by the C53-H53A···O2 [C···O 3.033(6) Å, H···O 2.14 Å, C–H···O 147°] hydrogen bonding interaction. This interaction leads to decrease of conformational flexibility of the aza-crown ether unit, facilitating the process of crystallization.

Spectroscopic studies of cation-induced dimerization of aza-crown ether appended porphyrins

The coordination properties of aza-crowned porphyrins **ZnP,3** and **ZnP,5** were investigated by UV-Vis and ^{1}H NMR spectroscopy. Spectrometric titrations were used to estimate the stoichiometry of binding and stability constants of coordination complexes. UV-Vis absorption spectroscopic measurements were taken at a porphyrin concentration of *ca.* 10^{-5} M, and NMR measurements were carried out at *ca.* 10^{-2} M. Obviously this large disparity in concentrations was reflected in the major differences in the corresponding complexes observed.

It is known that the relative size of the cation and the diameter of the crown ether cavity determines the stoichiometry of the resulting complex.[33] It is known that 15-crown-5 ether forms 1 : 1 and 2 : 1 complexes with Na^+ and K^+, respectively.[34,35] Formation of 1 : 1 complexes of crowned porphyrins with metal cations was usually accompanied by a large red shift of the Soret band.[36] In our case addition of solution of NaBr to **ZnP,3** and **ZnP,5** in chloroform–methanol (v/v = 20 : 1) led to a slight red shift of Soret and Q bands for 5 nm. Soret bands of **ZnP,3** (ESI S.1†) and **ZnP,5** (Fig. 7 and 8) were shifted from 407 to 412 nm and from 414 to 419 nm, respectively. Spectrophotometric titration of **ZnP,3** and **ZnP,5** with 0 to 4 equivalents of NaBr revealed the appearance of distinct isobestic points on the absorption spectra at 410 and 416 nm, respectively. The stoichiometry of (**ZnP,3**)Na^+ and (**ZnP,5**)Na_2^{2+} cation complexes was confirmed by spectrophotometric titration curves which were plotted as an optical density change of the Soret band *vs.* the molar ratio of sodium bromide to the porphyrin. **ZnP,3** and

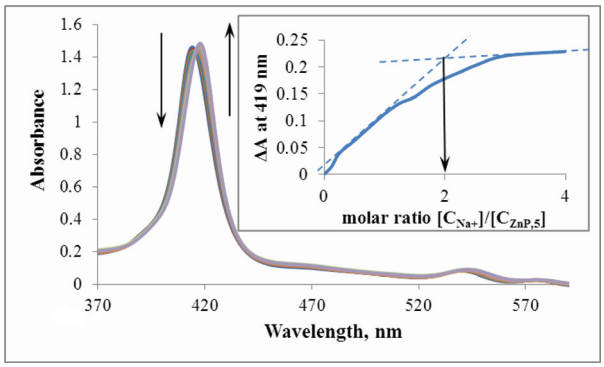


Fig. 8 Spectral changes of **ZnP,5** ([**ZnP,5**] = 2 × 10^{-5} M) at addition of 0–4 equiv of NaBr in $CHCl_3$–MeOH (20 : 1) (A). Spectrophotometric titration curve at λ = 419 nm (B).

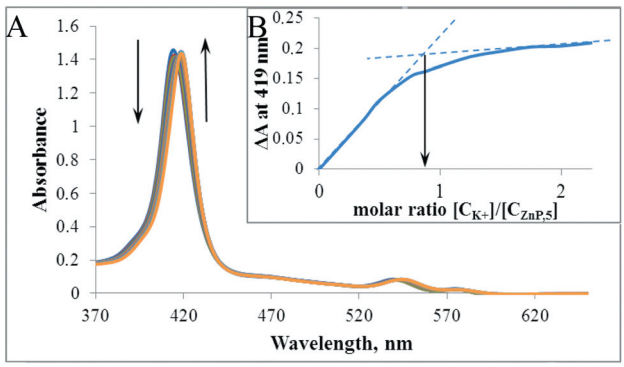


Fig. 10 Spectral changes of **ZnP,5** ([**ZnP,5**] = 2 × 10^{-5} M) on addition of 0–4 equiv of K^+ cation in $CHCl_3$–MeOH (20 : 1) (A). Spectrophotometric titration curve at λ = 419 nm (B).

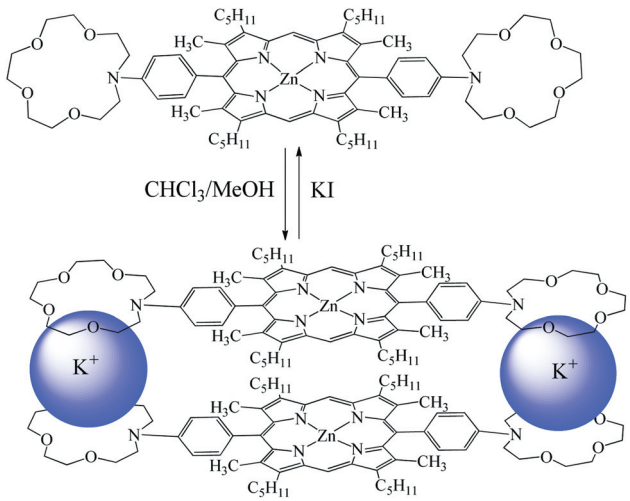


Fig. 9 Structural scheme of the cation-induced dimerization of **ZnP,5** by K^+ cations.

ZnP,5 titration plots gave distinct culminating points at 1 : 1 and 1 : 2 ratio of porphyrin/NaBr, respectively (insertions of Fig. 7 and 8).

Previously zinc 5,10,15,20-tetrakis[(benzo-15-crown-5)-4′-yl]-porphyrin (**ZnTCP**)[13] and zinc 5,15-bis-(benzo-15-crown-5)porphyrin (**ZnBCP**)[19a] were shown to exhibit high selectivity for K^+ cations forming sandwiched dimers. The stability constants of the complex of two molecules of **ZnTCP** with four K^+ cations and those of two molecules of **ZnBCP** with two K^+ cations were determined to amount to 10^{23} M^{-5} and 10^{18} M^{-3}, respectively. Cation-induced dimerization of **ZnTCP** and **ZnBCP** was accompanied by blue shifts of Soret bands *ca.* 20 nm and slight red shifts of Q-bands with lowered intensity, which was explained by parallel transition dipoles in a composite sandwiched molecules in accordance with excitons model of McRae and Kasha.[37]

In our case, the addition of K^+ cations to **ZnP,3** and **ZnP,5** in $CHCl_3$–MeOH (20 : 1) produced slight red shifts of Soret and Q absorption bands with lowered intensity (for 5 nm) from 407 to 412 nm and 414 to 419 nm, respectively (ESI S.2,† Fig. 9 and 10). The opposite sign of the Soret band shift as compared to the previously reported benzocrownporphyrins points out to a different structure of complexes. The main geometric difference is that benzocrown ether units are turned to ~30° angle relative to the porphyrin plane whereas aza-crown units can adopt almost coplanar conformation with the porphyrin macrocycle (Fig. 9). Another difference is the weaker electronic interaction between tetrapyrrolic and crown macrocycles resulting from the different nature and length of the link between them. Spectrophotometric titration of **ZnP,3** and **ZnP,5** with KI revealed distinct isobestic points at 410 and 417 nm respectively. The stoichiometry of the porphyrin complexes with potassium cations was determined by titration curves which gave culminating points at 2 : 1 and 1 : 1 (2 + 2 complex) ratio of the corresponding **ZnP,3** – KI and **ZnP,5** – KI components.

Spectroscopic studies of DABCO coordination to porphyrins

Zinc porphyrin complexes can axially coordinate extra ligands to the central zinc atom due to its coordinative unsaturation. We chose to focus on 1,4-diazabicyclo[2.2.2]octane (DABCO) ligand, because its exobidentate nature allows to coordinate two molecules of porphyrin, thus constructing coplanar bisporphyrin dimers. Moreover, the high basicity of DABCO is expected to lead to particularly stable complexes. The coordination of DABCO to zinc porphyrin proceeds through two steps: reaction of DABCO with one porphyrin molecule leading to 1 : 1 complex with constant K_{11} and coordination of the second porphyrin molecule leading to 1 : 2 complex with a stepwise constant $K_{11<=>12}$ and the overall binding constant K_{12} (Fig. 11). The presence of two binding sites at the DABCO molecule gives a statistical factor of two of the stepwise constant K_{11} as compared to the microscopic constant K_m of the interaction of zinc porphyrin with one binding site. The second binding step is influenced by the negative cooperativity effect: the microscopic binding at the second site is weaker by the interaction factor α. Together with the statistical multiplier $\frac{1}{2}$ the second stepwise constant $K_{11<=>12}$ equals $(\alpha/2)K_m$. The overall binding constant K_{12} is a product of stepwise constants $K_{11}K_{11<=>12}$ and equals αK_m^2. First we studied how DABCO binds to zinc aza-crowned porphyrins, using UV-Vis spectrophotometric titration which elucidated the stoichiometry of binding and the stability constants of

monomeric and dimeric complexes. The addition of DABCO to **ZnP,3** and **ZnP,5** led to red shifts of Soret bands for 10–11 nm and Q bands for 6–9 nm. Absorption changes data showed distinct isobestic points at 414 and 419 nm, respectively (Fig. 11). Analysis of the titration curve plotted as ΔA (absorbance change) against the molar ratio of DABCO to porphyrin (insertion at Fig. 11) showed that a simple 1 : 1 complex was formed with a

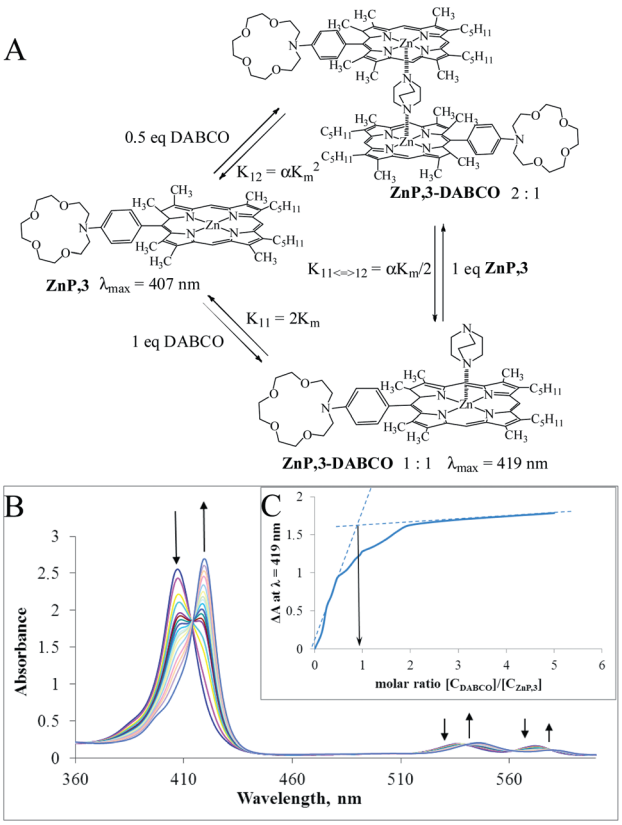


Fig. 11 Structural scheme of axial ligand coordination DABCO to **ZnP,3** (A). Spectral change of **ZnP,3** ([**ZnP,3**] = 2 × 10^{-5} M) on addition of 0–5 equiv of DABCO in $CHCl_3$ (B). Spectrophotometric titration curve at λ = 419 nm (C).

stability constant $K_{11} = 1.0 \pm 0.7 \times 10^4$ M^{-1} for **ZnP,3–DABCO** complex and $K_{11} = 5.4 \pm 1.4 \times 10^4$ M^{-1} for the **ZnP,5–DABCO** complex, respectively. The stability constants were calculated by means of the Rose–Drago method.[38] Under these dilute conditions there was no significant concentration of the 2 : 1 complex, so the binding isotherm was analyzed to yield the stoichiometric association constant K_{11}. To probe this equilibrium at higher porphyrin concentrations, *ca.* 10^{-3}–10^{-2} M, we used ^{1}H NMR spectroscopy (Table 5). An axially coordinated sandwich complex with 2 : 1 stoichiometry was observed in fast exchange with the reagents when up to 0.5 equiv. of DABCO ligand was added to **ZnP,3** and **ZnP,5** in $CDCl_3$. Methylene hydrogens of DABCO were upshifted with $\Delta\delta \sim -7$ ppm. With more than 0.5 equiv of DABCO a fast-exchange equilibrium between 2 : 1 and 1 : 1 complexes has been established, which gradually shifted towards 1 : 1 complex in increasing DABCO concentration.

The aromatic and *meso*-hydrogens of **ZnP,3** and **ZnP,5** in 2 : 1 sandwich complex were slightly upshifted with $\Delta\delta = -0.14$ ppm and −0.17 ppm, respectively, and returned to their roughly initial values in 1 : 1 complex.

Addition of alkali cations of Na^+ and K^+ to sandwich bis-aza-crowned porphyrin complexes with DABCO **(ZnP,5)$_2$DABCO** led to red shifts for 4 nm and enhanced intensity of Soret and Q absorption bands. Note that in absence of DABCO the addition of alkali cations lowered the absorption bands.[39] **(ZnP,5)$_2$DABCO** sandwich complex can coordinate 4 sodium or 2 potassium cations. Spectrophotometric titration curves of **(ZnP,5)$_2$DABCO** in chloroform–methanol solution (v/v = 20 : 1), plotted as absorbance change ΔA at λ_{max} against the molar ratio of K^+ to the porphyrin complex revealed distinct culmination points at addition of 4 mol Na or 2 mol K cations which indicated the formation of complexes of 1 : 4 and 1 : 2 stoichiometry, respectively (ESI S.3,† Fig. 12 and 13).

The stability constants of the complexes of aza-crowned porphyrins with alkali cations were calculated as follows.

The corresponding equilibrium can be expressed by eqn (1)

$$2\mathrm{ZnP} + n\mathrm{M}^+ = ((\mathrm{ZnP})_2\mathrm{M}_n)^{n+}, n = 1 \text{ or } 2 \qquad (1)$$

where ZnP, M^+ and n are zinc aza-crowned porphyrin, alkali metal cation and number of coordinated cations in complex

Table 5 Chemical shifts (δ) and chemical shift changes ($\Delta\delta$) of proton resonances of aza-crowned porphyrin complexes with alkali cations and DABCO in $CDCl_3$

			H_{Ar} δ ($\Delta\delta$)		CH_2 crown δ ($\Delta\delta$)		
	Complexes	H-*meso* δ ($\Delta\delta$)	*a*	*b*	1, 1′	2, 2′	DABCO[a] δ ($\Delta\delta$)
I	**(ZnP,5)$_2$K$_2^{2+}$**	10.00 (−0.05)	7.78 (−0.05)	7.00 (0.12)	3.92 (−0.05)	3.83 (−0.15)	—
II	**[(ZnP,5)$_2$DABCO]K$_2^{2+}$**	9.89 (−0.27)	—	7.01 (−0.12)	3.88 (−0.11)	3.83 (−0.03)	−4.90 (−7.2)
III	**(ZnP,3)$_2$K$^+$**	10.03 (−0.19) 9.74 (−0.44)	7.82 (0.04)	7.05 (0.05)	3.93 (0.1)	3.89 (0.16)	—
IV	**(ZnP,3)$_2$DABCO**	9.87 (0.03) 9.78 (0.48)	7.63 (−0.15)	6.99 (0)	4.01 (0.18)	3.90 (0.17)	1.75 (0.55) −4.62 (−6.92)
V	**[(ZnP,3)$_2$DABCO] K$^+$**	9.65 (−0.22) 9.56 (−0.22)	7.46 (−0.17)	6.93 (−0.06)	3.84 (−0.17)	3.84 (−0.06)	−4.62 (−6.92)
VI	**(ZnP,5)Na$_2^{2+}$**	10.30 (0.14)	8.01 (0.20)	7.31 (0.28)	4.03 (0.05)	3.84 (−0.05)	—
VII	**(ZnP,3)Na$^+$**	10.10 (−0.24) 9.91 (−0.57)	8.07 (0.29)	7.57 (0.57)	3.84 (0.01)	3.82 (0.09)	—

[a] Chemical shift of free DABCO protons in $CDCl_3$ δ = 2.30 ppm.

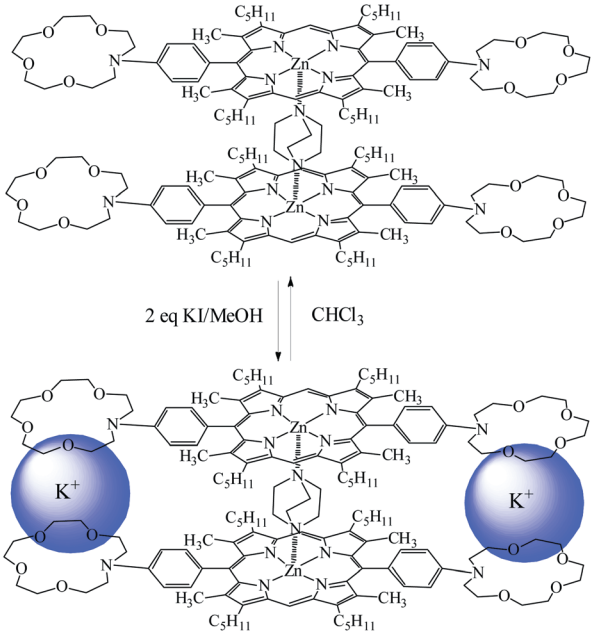


Fig. 12 Structural scheme of complexation of **(ZnP,5)$_2$DABCO** with potassium cations.

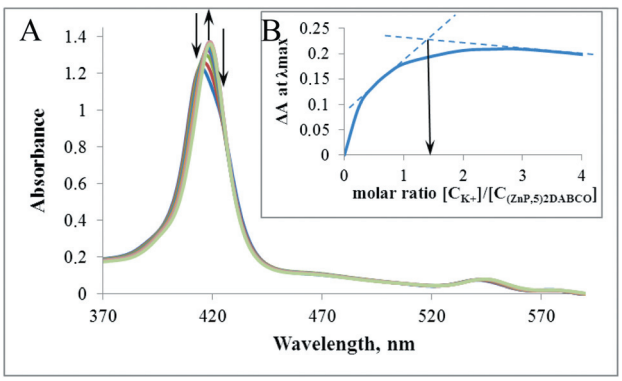


Fig. 13 Spectral change at formation of 1 : 2 complexes of **(ZnP,5)$_2$DABCO** with K^+ in $CDCl_3$–MeOH (20 : 1 v/v) (A). Spectrophotometric titration curve of **(ZnP,5)$_2$DABCO** at λ_{max} (B).

$(ZnP_2M_n)^{n+}$, respectively. The overall formation constant of (1) is given as expression (2).

$$K = [((ZnP)_2M_n)^{n+}]/[ZnP]^2[M]^n \quad (2)$$

If it is assumed that x mol of the dimer was formed then it can be shown that

$$K = x/([ZnP]_0 - 2x)^2([M^+]_0 - nx]^n \quad (3)$$

where $[ZnP]_0$ and $[M^+]_0$ denote the total concentrations of aza-crowned porphyrin and cation, respectively. Theoretical plots of the optical density change ΔA *vs.* the concentration of cation salts $[M^+]_0$ for various values of the stability constants (K) were constructed. The experimental points were then mapped into this plot, and the best fit was chosen for the value of the overall formation constant of the dimer. For example, a representative plot for the cation-induced dimerization of **(ZnP,3)$_2$**DABCO is given in ESI S.4.† The values of K thus computed are given in Table 6.

Table 6 Stability constants of the complexes of KI with aza-crowned porphyrins and with sandwiched aza-crowned porphyrins/DABCO aggregates in chloroform–methanol (20 : 1)

Complex	Constant	lg K
(ZnP,3)$_2$K$^+$	$K_{12} = (9.19 \pm 0.16) \times 10^8$ M^{-2}	8.96
[(ZnP,3)$_2$DABCO]K$^+$	$K_{11} = (2.29 \pm 0.2) \times 10^4$ M^{-1}	4.35
(ZnP,5)$_2$K$_2^{2+}$	$K_{22} = (2.4 \pm 1.02) \times 10^{13}$ M^{-3}	13.38
[(ZnP,5)$_2$DABCO]K$_2^{2+}$	$K_{21} = (7.8 \pm 1.9) \times 10^{11}$ M^{-2}	11.8

The stability constant value of sandwich dimers of tetra-15-crown-5-phthalocyanine series with potassium cations were about lg K = 8.[14f] If we compare the stability constants of the complexes of **ZnP,3** containing one aza-crown ether unit and phthalocyanines substituted with four crown-ethers with potassium iodide it becomes clear that these values are quite similar (Table 6). It should be noted that the stability constant of crowned phthalocyanine calculated per one crown ether unit is about lg K = 2. Thus the sandwich complexes of aza-crowned porphyrins are more stable than these of phthalocyanines. Moreover, certain crowned phthalocyanines require more than 2000 equivalents of sodium cations and *ca.* 10 equivalents of potassium cations in order to saturate this system[14l] while aza-crowned porphyrins were completely coordinated with much less amounts of cations. This difference in the complexing ability can in part be explained by the conformational analysis.

The stability constants of the complexes of KI with aza-crowned porphyrins and with sandwiched aza-crowned porphyrins/DABCO aggregates (Table 6) are of several orders of magnitude less than those observed reported for complexes of K^+ with **ZnTCP**[13] and **ZnBCP**.[19a] The high values of the latter (~10^{23} M^{-5} and ~10^{18} M^{-3} correspondingly) were ascribed to the cooperative interaction of four and two crown ether binding sites together with π–π interactions between porphyrin electronic systems. It has been demonstrated that π–π interactions between aza-crowned porphyrins are lower than between benzo-crowned porphyrins which can result from the larger interplane distance between two porphyrin molecules in the aza-crowned porphyrin dimers (about 5.35 Å) as compared to the benzo-crowned porphyrin dimers (3.4–3.6 Å).[19a] Another reason for the lower values of the stability constants for aza-crowned porphyrins in comparison to benzo-crown ether porphyrins consists in that the aza-crown ethers coordinate alkaline cations weaker than crown ethers.[40,41] Thus for 1 : 1 complex of K^+ with 15-crown-5 lg K_{11} = 3.9 whereas for unsubstituted aza-15-crown-5 and for N-phenyl-aza-15-crown-5 ethers lg K_{11} = 1.6 and 1.7, respectively.

The interaction of aza-crown ether appended porphyrins with alkali cations was further investigated by ^{1}H NMR spectroscopy (Table 5). Upon addition of NaBr solution in methanol-d_4 to **ZnP,5** in $CDCl_3$ *meso*-porphyrin hydrogens and methylene aza-crown ether hydrogens were shifted downfield with $\Delta\delta$ ~ 0.14 ppm and $\Delta\delta$ = 0.2–0.05 ppm, respectively, which is explained by the deshielding effect of the sodium cation positive charge. Addition of methanol-d_4 solution of KI to **ZnP,5** in $CDCl_3$ led to upfield shifts of resonances of *meso*- and phenyl hydrogens of porphyrin and methylene hydrogens of aza-crown

ether with $\Delta\delta$ from −0.05 to −0.15 ppm. This can be attributed to the shielding effect of the cofacial porphyrin ring arrangement indicating that K^+ caused dimerization of aza-crown porphyrins by coordination of two crown ethers by one K^+ cation.

The addition of solution of DABCO in chloroform-d_1 to **(ZnP,5)$_2$K$_2^{2+}$** led to the formation of corresponding complexes **[(ZnP,5)$_2$K$_2^{2+}$]DABCO**. The resonances of phenyl protons in the complexes were broad and moved to a high field with $\Delta\delta \sim -0.12$ ppm. The resonances of aza-crown ether units were shifted with $\Delta\delta \sim -0.1$ ppm. Large upfield shifts of DABCO protons were observed at $\delta = -4.62$ ppm. That corresponds to the axially coordinated DABCO located between two porphyrin units according to similar reported structures.[22]

Addition of methanol solution of KI to chloroform solution of **ZnP,3** in 1 : 2 ratio led to the following changes: *meso*-hydrogens were shifted with $\Delta\delta \sim 0.19$ and 0.4 ppm, aza-crown ether methylene hydrogens were shifted with $\Delta\delta \sim 0.1$–0.16 ppm. Downfield shifts of resonances of the porphyrin dimers argue for their edge-to-edge association (ESI S.2†). Addition of DABCO to **(ZnP,3)$_2$K$^+$** led to upshifts of porphyrin *meso*-proton resonances with $\Delta\delta \sim -0.11$ ppm, phenyl hydrogens with $\Delta\delta \sim -0.14$ ppm and aza-crown ether hydrogens with $\Delta\delta \sim 0.17$. Addition of potassium cations to 2 : 1 complexes of **ZnP,3** with DABCO led to upfield shifting of porphyrin *meso*-hydrogens with $\Delta\delta \sim -0.22$ ppm, *orto*-phenyl hydrogens with $\Delta\delta \sim -0.17$ ppm, methylene crown ether hydrogens with $\Delta\delta \sim -0.17$ ppm and methylene hydrogen of DABCO with $\Delta\delta \sim -6.92$ ppm. The large upfield shift of DABCO protons clearly demonstrated that a cofacial porphyrin dimer was formed. The observed chemical shift changes, $\Delta\delta$, of the *meso*- and phenyl hydrogens in **(ZnP,3)$_2$K$^+$**, **[(ZnP,3)$_2$DABCO]K$^+$**, **(ZnP,5)$_2$K^{2+}** and **[(ZnP,5)$_2$DABCO]K^{2+}** were lower (Table 5) than $\Delta\delta = -3.29$ ppm of *meso*-hydrogens in **ZnBCP**. These results suggested that the interporphyrin distance was larger in the aza-crowned dimeric complexes than in the dimers of **ZnTCP** and **ZnBCP**.

^{1}H NMR titration of mono- and bis-aza-crowned porphyrins and their DABCO sandwich complexes with KI in$CHCl_3$/MeOD-d_4 (v/v = 1 : 1) showed distinct culmination points confirming the stoichiometry calculated previously by means of UV-Vis spectrophotometric titration. ^{1}H NMR of complexes of **ZnP,3**, **ZnP,5**, **(ZnP,3)$_2$DABCO** and **(ZnP,5)$_2$DABCO** with a potassium cation revealed slight downfield shifts of *meso*- and phenyl hydrogens with $\Delta\delta \sim 0.01$ and 0.09 ppm, respectively. Methylene hydrogens of aza-crown ether units of **ZnP,3** and **ZnP,5** and their sandwich complexes with DABCO (ESI S.5,† Fig. 14) are upfield shifted with $\Delta\delta \sim -0.30$ ppm and −0.39 ppm, respectively, and methylene hydrogens of DABCO with $\Delta\delta$ −1.75 ppm. To exclude the influence of solvent change, we added methanol-d_4 to aza-crowned porphyrins in $CDCl_3$ and observed no change of the chemical shifts of porphyrin and aza-crown ether hydrogens while DABCO methylene hydrogens were shifted downfield with $\Delta\delta$ 1.2 ppm which is of the opposite sign to that observed at titration.

Experimental

(i) General considerations

^{1}H (400 MHz, 600 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance 600 spectrometers at room temperature and referenced to the residual protons of the solvent ($CDCl_3$ – δ 7.28 ppm, methanol-d_6 – δ 4.84 ppm, 3.31 ppm). MALDI-TOF mass spectra were recorded on an Ultraflex MALDI TOF Bruker Daltonics spectrometer with a dithranol matrix. High resolution mass spectra (HR MS) were measured on a Bruker micrOTOF II instrument using electrospray ionization (ESI). The measurements were done in a positive ion mode (interface capillary voltage −4500 V, end plate offset −500 V); mass range from *m*/*z* 50 to *m*/*z* 3000 Da; external or internal calibration was done with electrospray calibrant solution (Fluka). A syringe injection was used for solutions in acetonitrile or MeOH

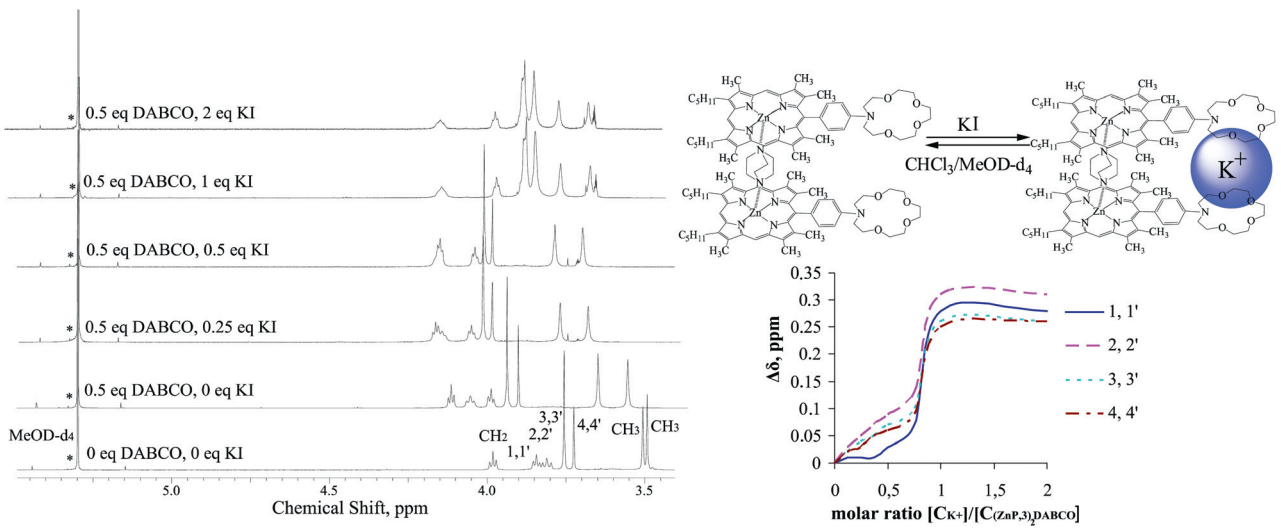


Fig. 14 1H NMR titration (600 MHz) at 298 K of **(ZnP,3)$_2$DABCO** in $CDCl_3$–MeOD-d_4 (v/v = 1 : 1) on addition of KI in $CDCl_3$–MeOD-d_4 at 30 °C; **[(ZnP,3)$_2$DABCO]** = 3×10^{-2} M. The solvent peak is marked. Insert: ^{1}H NMR titration curve of **(ZnP,3)$_2$DABCO** with K^+ (change of the chemical shifts of methylene hydrogens of aza-crown ether units).

(flow rate 3 mL min^{-1}). Nitrogen was applied as a dry gas; the interface temperature was set at 180 °C. UV-Visible spectra were recorded on a Cary-100 Varian spectrometer. Fluorescence spectra were recorded on fluorescence spectrometer PerkinElmer LS-55. Dioxane was distilled and dried over sodium under an atmosphere of Ar. CH_2Cl_2 was distilled over CaH_2, $CHCl_3$ was distilled over P_2O_5 and was freed of acids by stirring over K_2CO_3. Methanol was distilled over magnesium turnings. The starting materials were generally used as received (Aldrich). 5-(4′-Bromophenyl)-3,7,12,13,17,18-hexamethyl-2,8-dipentyl) porphyrin (**H_2P,1**) and 5,15-(4′-bromodiphenyl)-2,8,12,18-tetramethyl-2,8,12,18-tetrapentyl porphyrin (**H_2P,2**) were synthesized as previously described[23] and purified by column chromatography on silica gel. All reactions were performed under argon atmosphere and monitored by TLC Macherey-Nagel Alugram SIL G/UV_{254} silica gel 60 UV_{254} (CH_2Cl_2–MeOH). Column chromatography was performed on silica gel Macherey-Nagel 60 0.04–0.063 (230–400 mesh).

(ii) Porphyrin metal complexes

Zn 5-(4′-Bromophenyl)-3,7,12,13,17,18-hexamethyl-2,8-dipenthyl) porphyrinate (ZnP,1). The preparation conditions of **ZnP,1** are similar to those for **ZnP,2**. Solution **H_2P,1** (0.1 mmol, 69 mg) in 30 mL $CHCl_3$ mixed with zinc acetate excess (2 mmol, 0.438 g). ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz): δ = 9.90 (2H, s, *meso*-H), 9.52 (1H, s, *meso*-H), 7.90 (4H, s, H_{Ar}), 3.79 (4H, t, $J_1 = J_2$ = 6.82 Hz, CH_2), 3.48 (6H, s, CH_3), 2.44 (6H, s, CH_3), 2.21–2.14 (4H, m, CH_2), 1.75–1.67 (4H, m, CH_2), 1.59–1.50 (4H, m, CH_2), 1.01 (6H, t, $J_1 = J_2$ = 7.20 Hz, CH_3). UV-Vis ($CHCl_3$): λ, nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 406 (360.9), 572 (8.98), 536 (9.52). HRESI MS: calcd *m/z* = 751.2354 $[M + H^+]$ for $[C_{42}H_{48}BrN_4Zn]^+$, found 751.2256.

Cu 5-(4′-Bromophenyl)-3,7,12,13,17,18-hexamethyl-2,8-dipenthyl) porphyrinate (CuP,1). The procedure is similar to that used for **ZnP,1**. Solution **H_2P,1** (0.1 mmol, 69 mg) in 30 mL $CHCl_3$ mixed with an excess of copper acetate (2 mmol, 0.436 g). UV-Vis ($CHCl_3$): λ, nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 403 (1056.82), 565 (50.95), 529 (28.83). HRESI MS: calcd *m/z* = 750.2358 $[M + H]^+$ for $[C_{42}H_{48}BrN_4Cu]^+$, found 750.2335.

Zn 5,15-di(4′-bromophenyl)-2,8,12,18-tetramethyl-2,8,12,18-tetrapenthyl porphyrinate (ZnP,2). Excess of zinc acetate (2 mmol, 0.438 g) was added to a solution of porphyrin **H_2P,2** (0.1 mmol, 95.7 mg) in $CHCl_3$ (30 mL). The mixture was stirred overnight at room temperature, then solvent was removed under vacuum. The resulting powder was dissolved in $CHCl_3$, the solution was filtered and directly loaded onto a silica gel chromatography column. The expected compound eluted with $CHCl_3$ was obtained as red powder in 94% yield (95.9 mg). ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz): δ = 10.15 (2H, s, *meso*-H), 8.00 (4H, d, J = 8.08 Hz, H_{Ar}), 7.90 (4H, d, J = 8.34 Hz, H_{Ar}), 3.98 (8H, t, $J_1 = J_2$ = 7.83 Hz, CH_2), 2.50 (12H, s, CH_3), 2.22–2.14 (8H, m, CH_2), 1.77–1.69 (8H, m, CH_2), 1.59–1.51 (8H, m, CH_2), 0.99 (12H, t, $J_1 = J_2$ = 7.26 Hz, CH_3). UV-Vis ($CHCl_3$): λ, nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 412 (47.93), 540 (2.41), 575 (1.46). HRESI MS: calcd *m/z* = 1021.3160 [M + H^+] for $[C_{56}H_{69}Br_2N_4Zn]^+$, found 1021.3280.

(iii) Aza-crown ether-appended metalloporphyrin synthesis

Zn 5,15-bis[4′-(1,4,7,10-tetraoxa-13-aza-cyclopentadec-13-yl)-phenyl]-3,7,13,17-tetramethyl-2,8,12,18-tetrapenthyl porphyrinate (ZnP,5). 2-(Dicyclohexylphosphino)-2′-(*N*,*N*-dimethylamino)biphenyl (DavePhos) 16 mol% (3.6 mg, 9.2 × 10^{-3} mmol), 8 mol% $Pd(dba)_2$ (2.6 mg, 4.6 × 10^{-3} mmol), and sodium *tert*-butoxide (7.8 mg, 0.16 mmol) were placed in a dried, resealable round-bottom flask, which was backfilled with argon. A stock solution of 3 equiv of aza-15-crown-5 ether in dioxane (0.4 mL, 0.33 M, 0.13 mmol) was added *via* a syringe. Then **ZnP,2** (59 mg, 58 μmol) was added in the Ar flow. The flask was purged with argon for 3 min. The flask was sealed, and its contents were heated at 100 °C with stirring for 27 h. The reaction path was monitored by TLC. The reaction mixture was then cooled to room temperature, taken up in dichloromethane (10 mL), filtered, and concentrated in a vacuum. The crude product was purified by column chromatography on silica gel using gradient elution by 0–2% mixture of CH_2Cl_2–MeOH as an eluting solvent. The major compound **ZnP,5** was isolated as a dark red solid (36 mg, 64%). ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz): δ = 10.16 (2H, s, *meso*-H), 7.83 (4H, d, J = 8,44 Hz, H_{Ar}), 7.01 (4H, d, J_1 = 8,44 Hz, H_{Ar}), 4.03 (8H, t, $J_1 = J_2$ = 6.75 Hz, CH_2), 3.98 (8H, m, NCH_2), 3.89 (8H, m, CH_2O), 3.81 (16H, s, $C_2H_4O(CH_2O)_2$), 3.78 (8H, s, CH_2O), 2.59 (12H, s, CH_3), 2.19–2.13 (8H, m, CH_2), 1.73–1.68 (8H, m, CH_2), 1.54–1.49 (8H, m, CH_2), 1.01 (12H, t, $J_1 = J_2$ = 7.26 Hz, CH_3).^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.57, 147.57, 146.27, 142.84, 139.30, 138.33, 133.84, 114.08, 110.66, 97.19, 71.41, 70.24, 68.83, 52.71, 33.85, 33.08, 32.55, 31.94, 31.52, 30.14, 29.71, 29.53, 29.38, 29.18, 28.96, 26.76, 22.84, 22.71, 15.55, 14.21, 14.15. UV-Vis ($CHCl_3$): λ, nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 414 (107), 541 (7.43), 574 (3.96). HRESI MS: calcd *m/z* = 1295.7436 $[M]^+$ for $[C_{76}H_{106}N_6O_8Zn]^+$, found 1295.7384.

Zn 5-[(4′-(1,4,7,10-Tetraoxa-13-aza-cyclopentadec-13-yl)-phenyl)-15-phenyl]-3,7,13,17 - tetramethyl-2,8,12,18-tetrapenthyl porphyrinate (ZnP,4). The preparation procedure as above for **ZnP,5** was applied to couple 1.13 equivalents of 1-aza-15-crown-5 (5.78 mg, 26 μmol) with **ZnP,2** (23.7 mg, 23 μmol). The reaction was conducted at 100 °C with 4 mol% Pd $(dba)_2$ and 8 mol % DavePhos for 40 hours in dioxane. Compound **ZnP,4** was isolated as a dark red solid (18.5 mg, 57%). Moreover, the bis-aminated product **ZnP,5** (5.5 mg, 18%) and by-product of β-H elimination **ZnP,6** (4.9 mg, 25%) were obtained and isolated. ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz): δ = 10.17 (2H, s, *meso*-H), 8.10 (2H, d, J = 8.07 Hz, H_{Ar}), 7.83 (2H, d, C_6H_4, J_1 = 8.25 Hz), 7.81 (2H, t, $J_1 = J_2$ = 7.43 Hz, H_{Ar}), 7.76 (1H, t, $J_1 = J_2$ = 7.70 Hz, H_{Ar}), 7,04 (2H, d, J_1 = 8.25 Hz, C_6H_4), 3.99 (8H, d, J = 6.75 Hz, CH_2), 3.96 (4H, m, NCH_2), 3.85 (8H, m, CH_2O), 3.75 (8H, s, $C_2H_4O(CH_2O)_2$), 3.72 (4H, s, CH_2O), 2.57 (6H, s, CH_3), 2.43 (6H, s, CH_3), 2.19–2.15 (8H, m, CH_2), 1.75–1.68 (8H, m, CH_2), 1.56–1.50 (8H, m, CH_2), 1.01 (12H, t, CH_3, $J_1 = J_2$ = 7.33 Hz). UV-Vis ($CHCl_3$): λ, nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 412 (85.12), 540 (4.8), 574 (2.72). HRESI MS: calcd *m/z* = 1079.6161 for $[M + H]^+$ $[C_{66}H_{88}N_5O_4Zn]^+$, found 1079.6153.

Zn 5-(4′-(1,4,7,10-Tetraoxa-13-aza-cyclopentadec-13-yl)-phenyl)-3,7,12,13,17,18-hexamethyl-2,8-dipenthylporphyrinate (ZnP,3). Preparation procedure as above for **ZnP,5** was applied to couple

N-aza-15-crown-5 (16.8 mg, 77 μmol) with **ZnP,1** (55.9 mg, 75 μmol). The reaction was conducted at 100 °C in dioxane with 4 mol% Pd $(dba)_2$ and 8 mol% DavePhos for 27 h. The major compound **ZnP,3** was isolated as a dark red solid (60 mg, 90%). ^{1}H NMR ($CDCl_3$, 298 K, 300 MHz): $\delta = \delta$ 9.84 (2H, s, *meso*-H), 9.31 (1H, s, *meso*-H), 7.78 (2H, d, J = 7.96 Hz, H_{Ar}), 7.00 (2H, d, J = 8.46 Hz, H_{Ar}), 3.96 (4H, t, $J_1 = J_2$ = 4.29 Hz, CH_2), 3.83 (4H, t, $J_1 = J_2$ = 3.54 Hz, NCH_2), 3.73–3.68 (16H, m, $C_2H_4O(CH_2O)_4$), 3.52 (6H, s, CH_3), 3.43 (6H, s, CH_3), 2.56 (12H, s, CH_3) 2.14–2.09 (4H, m, CH_2), 1.73–1.66 (4H, m, CH_2), 1.58–1.49 (4H, m, CH_2), 1.02 (6H, m, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.03, 147.88, 147.66, 147.02, 140.95, 138.58, 137.64, 135.69, 133.73, 110.67, 96.82, 95.90, 71.31, 70.28, 70.20, 68.80, 66.19, 52.70, 32.97, 32.35, 26.43, 22.79, 15.67, 14.20, 12.18. UV-Vis ($CHCl_3$): λ, nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 404 (104.92), 529 (3.15), 565 (6.14). HRESI MS: calcd m/z = 890.4557 $[M]^+$ for $[C_{52}H_{67}N_5O_4Zn]^+$, found 890.4547.

Cu 5-(4′-(1,4,7,10-Tetraoxa-13-aza-cyclopentadec-13-yl)-phenyl)-3,7,12,13,17,18-hexamethyl-2,8-dipenthylporphyrinate (CuP,3). Preparation conditions of **CuP,3** are similar to **ZnP,3**. UV-Vis ($CHCl_3$): λ, nm (10^{-3} ε, dm^3 mol^{-1} cm^{-1}): 404 (104.99), 529 (3.15), 565 (6.14). HRESI MS: calcd m/z = 889.4567 $[M + H]^+$ for $[C_{52}H_{68}N_5O_4Cu]^+$, found 889.4805.

Complexes of aza-crown ether-appended metalloporphyrins with potassium and sodium cations (I–VII). Complex **I**. Methanol solution of KI (3.6×10^{-3} M, 1.04 mL) was added to a solution of **ZnP,5** in chloroform (3.8×10^{-6} mol). After 30 min of stirring the solution was concentrated in vacuum and redissolved in $CDCl_3$. Complex **II**. DABCO (0.015 M, 0.178 mL) was added to a solution of **I** in $CDCl_3$ (10.7×10^{-3} M). Complexes **III–VII** were obtained similarly.

(iv) UV-Vis spectrophotometric titration

Solutions of **ZnP,3** and **ZnP,5** porphyrins in chloroform were titrated directly in 1 cm absorption cells by DABCO chloroform solution, potassium iodide and sodium bromide methanol solution while monitoring the UV-Vis spectra between 390 and 460 nm. An increasingly concentrated DABCO (2.9×10^{-6}–2.0×10^{-5} M), KI and NaBr (4.98×10^{-6}–7.44×10^{-5} M) solution was added to 5 in 200 μL aliquots using a microliter syringe. The original porphyrin solution was 0.2 μM in a total volume of 3.0 mL.

(v) Typical procedure for NMR titration experiments

NMR titrations were carried out directly in NMR tubes. To a solution of **ZnP,3** and **ZnP,5** (12.3×10^{-3} M) (1 eq.) and their axial face-to-face complexes with DABCO in a mixture 1 : 1 of chloroform-d_1 and methanol-d_4 (0.7 mL), chloroform-d_1/methanol-d_4 solutions of KI (74×10^{-3} M) (v/v = 1 : 1) were added directly into the tube in small portions from 25 μL (0.25 eq.) up to 200 μL–300 μL (2–3 eq.) by micropipette, until there was no further shift in the resonances of the compounds. The NMR sample was thoroughly mixed after each addition and the ^{1}H NMR spectrum was recorded within 10 min.

Table 7 Detailes of data collection, structure solution and refinement for zinc and copper mono-aza-crowned porphyrins

Compound	**$(ZnP,3)_2$**	**CuP,3**·0.75 ($CHCl_3$)
Empirical formula	$C_{104}H_{134}N_{10}O_8Zn_2$	$C_{52.75}H_{67.75}N_5O_4Cl_{2.25}Cu$
M_r	1782.99	979.17
T/K	100	173
Crystal size/mm	0.18 × 0.15 × 0.02	0.24 × 0.22 × 0.20
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a/Å	20.044(15)	12.769(2)
b/Å	13.779(10)	13.437(3)
c/Å	17.745(15)	17.341(3)
α/°	90.00	100.068(3)
β/°	111.71(2)	91.765(3)
γ/°	90.00	115.554(3)
V/Å^3	4553(6)	2624.0(9)
Z	2	2
D_c/g cm^{-3}	1.300	1.239
μ/cm^{-1}	0.591	0.578
F(000)	1904	1037
θ range/°	1.93–24.00	2.97–25.00
Index range, *hkl*	−22–22; −15–15; −20–20	−15–15; −15÷15; −20–20
No. of rflns collected	35 389	20 935
No. of unique rflns	7093	9114
No. of rflns observed	1585	5257
Restraints/ parameters	16/285	19/519
R_1 ($I > 2\sigma(I)$)	0.106	0.085
wR_2 (all data)	0.149	0.226
GOF on F^2	0.868	1.000
Completeness/%	99.1	98.6
$T_{min,max}$	0.901; 0.988	0.874; 0.893
$\Delta\rho_{max,min}$/e Å^{-3}	0.460/−0.604	0.938/−1.043

(vi) Crystallographic method

Data were collected on a Bruker SMART APEX II CCD diffractometer (λ(Mo Kα)-radiation, graphite monochromator, ω and φ scan mode) and corrected for absorption using the SADABS program.[42] For details, see Table 7. The structures were solved by direct methods and refined by the full-matrix least squares technique on F^2 with anisotropic thermal parameters for non-hydrogen atoms. The independent part of the unit cell of **CuP,3** contains a statistically disordered chloroform solvate molecule. The hydrogen atoms were placed in calculated positions and refined within the riding model with fixed thermal parameters (U_{iso}(H) = 1.5U_{eq}(C) for the CH_3-groups and U_{iso}(H) = 1.2U_{eq}(C) for the other groups). All calculations were carried out using the SHELXTL program.[43,44] Crystallographic data for **ZnP,3** and **CuP,3**·$\frac{3}{4}$**$CHCl_3$** have been deposited with the Cambridge Crystallographic Data Center. CCDC 855624 and 855625 contain the supplementary crystallographic data for this paper.†

Conclusions

The new supramolecular structures based on the novel aza-crowned metalloporphyrins were obtained and investigated. Coordination of aza-crowned metalloporphyrins with potassium cations led to the formation of sandwich face-to-face dimers.

Adding DABCO led to the axial coordination of the ligand inside the cavity between two zinc porphyrins. Thus investigated aza-crowned porphyrins can be used as heterotopic ligands for binding different metal cations and ligands and constructing complex supramolecular coordination systems. We compared the complexing ability and selectivity to those of alkali cations of mono- and bis-aza-crown substituted porphyrins and tetra-crown substituted phthalocyanines. The several differences in conformation, flexibility and manner of bonding of aza-crown and crown-ether moieties gave rise to a different coordination style and cation behavior in the two series. We would like to highlight that the stability constants of aza-crowned porphyrins with potassium cations are several orders of magnitude higher in comparison with analogous complexes of crowned phthalocyanine series.

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