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Carboxyphenyl Substituted Pyrazinoporphyrazines — Promising Linkers for Metal-Organic Frameworks

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*Starting from the new building-block – dimethyl-4,4'-(5,6-dicyanopyrazine-2,3-diyl)dibenzoate **1**, a new symmetrical porphyrazine annelated with four bis(4-carboxyphenyl)pyrazine rings and its Zn(II) complex **MPyzPz(COOH)$_8$**, M = = 2H and Zn, have been synthesized for the first time. It was shown that template condensation of **1** in the presence of Zn(OAc)$_2$ and DBU, followed by alkaline hydrolysis of the ester groups, failed to yield the target Zn(II) complex due to its degradation in strongly basic media. In contrast, template condensation of **1** in the presence of metal Mg in pentanol followed by demetallation afforded the metal-free ester derivative **H$_2$PyzPz(COOPent)$_8$**, which could be hydrolyzed to **H$_2$PyzPz(COOH)$_8$** without degradation of the macrocycle. Its reaction with Zn(OAc)$_2$ in DMF resulted in the insertion of Zn^{2+} into the tetrapyrrole macrocycle, yielding **ZnPyzPz(COOH)$_8$**. The difference in hydrolytic stability of metal-free porphyrazine and its metal complex was explained by electrostatic potential analysis. Due to their structural similarity with an organic linker 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine **H$_4$TCPP**, it is suggested that the synthesized pyrazinoporphyrazines can be used as linkers of novel metal-organic frameworks.*

Keywords: Porphyrazine, pyrazinoporphyrazine, electrostatic potential, hydrolysis.

Карбоксифенил-замещенные пиразинопорфиразины — потенциальные мостиковые лиганды для создания металл-органических координационных полимеров

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*С использованием нового строительного блока диметил-4,4'-(5,6-дицианопиразин-2,3-диил)дибензоата **1** впервые синтезирован новый симметричный порфиразин, аннелированный четырьмя бис(4-карбоксифенил)-пиразиновыми группами, и его комплекс с цинком **MPyzPz(COOH)$_8$**, M = 2H и Zn. Показано, что темплатная конденсация **1** в присутствии Zn(OAc)$_2$ и DBU с последующим щелочным гидролизом сложноэфирных групп не позволяет получить целевой комплекс Zn(II) из-за его деградации в сильноосновной среде. Напротив, темплатная конденсация **1** в присутствии металлического магния в пентаноле с последующим деметаллированием позволила получить свободное сложноэфирное производное **H$_2$PyzPz(COOPent)$_8$**, которое можно гидролизовать до **H$_2$PyzPz(COOH)$_8$** без деградации макроцикла. Его реакция с Zn(OAc)$_2$ в ДМФА привела к введению катиона Zn^{2+} в тетрапиррольное кольцо с получением **ZnPyzPz(COOH)$_8$**. Разница в гидролитической стабильности порфиразинов в виде свободного основания и металлокомплекса была объяснена с помощью анализа электростатического потенциала. Благодаря структурному сходству с органическим линкером 2,3,5,6-тетракис(4-карбоксифенил)пиразином **H$_4$TCPP**, предполагается, что синтезированные пиразинопорфиразины могут выступать в качестве компонентов новых металл-органических каркасных полимеров.*

Ключевые слова: Порфиразин, пиразинопорфиразин, электростатический потенциал, гидролиз.

Introduction

Porous compounds are considered to be promising components of novel functional materials, which will help to solve urgent tasks of modern science, including separation of mixtures of substances with similar properties, storage of gases, development of selective heterogeneous catalysts, *etc*.[1,2] Among the classes of porous compounds, metal-organic frameworks (MOFs) are of particular interest because of their unique sorption properties due to their high specific surface area and simultaneously free volume.[3,4]

The variation of metal cations as well as organic linkers in MOFs allow to control the size and shape of pores in order to tune their physicochemical properties.[5] Among the known linkers special attention is paid to carboxy-substituted compounds due to their synthetic availability and versatility.[6–8]

It is also possible to use carboxy-substituted tetrapyrrole compounds, such as porphyrins, as components of MOFs[9] due to the possibility of functionalization of four *meso*- and eight β-positions, as well as the introduction of endocyclic metal ions providing broad diversity of linkers. Moreover, porphyrins possess unique photo- and electrochemical properties, porphyrin-based MOFs have proven to be efficient sensors,[10,11] gas storage systems,[12,13] materials for CO_2 photoreduction,[14,15] proton-conducting materials in fuel cells, *etc*.[16,17]

At the same time, much less work has been focused on the preparation of MOFs based on synthetic analogues of porphyrins – phthalocyanines and porphyrazines, while such compounds can afford the expansion of the range of properties and possible applications of MOFs due to higher photo- and chemical stability and intense absorption in the red and near-infrared spectral range.

Most of known Pc-based MOFs were obtained starting from symmetrical octahydroxyphthalocyanine complexes M[Pc(OH)$_8$] and provide two-dimensional structures.[18–20] Thus, 2-D MOFs based on cobalt and nickel complexes were obtained and applied to the electrochemical reduction of CO_2, which is important in terms of reducing the carbon footprint of modern industry.[21] Another example was based of copper complex forming MOFs with high electrical conductivity values. The obtained complex was tested as a component of cathodes in lithium-ion batteries. It was shown that these MOFs have high stored charge values, which makes these MOFs promising components of modern power sources.[22]

To the contrast, carboxy-substituted phthalocyanines and their analogues had only limited application in this area – for example, coordination polymer with tetracarboxy substituted phthalocyanine linker was synthesized and used as a sensor for vanillin detection.[23] Obviously, the obtained polymer was amorphous because the applied linker was used as a mixture of isomers. It can be envisaged that the development of approaches to symmetrically-substituted monoisomeric linkers with carboxy-groups can give rise to highly ordered crystalline MOFs based on phthalocyanines and their analogues.

Recently, we proposed a pathway towards derivatives of symmetric octacarboxy-substituted tetraquinoxalino-porphyrazine **ZnQPz(COOH)$_8$** bearing eight benzoate groups,[24] which can be potentially used as a linker in new tetrapyrrole-based MOFs. However, because of the extended π-system, this compound had strong tendency to aggregation which hindered its application.

In order to reduce the undesired aggregation, in the present work we proposed to obtain a π-contracted analogue of **ZnQPz** – a monoisomeric porphyrazine derivative annelated with four bis(4-carboxyphenyl)-pyrazine rings – **ZnPyzPz(COOH)$_8$** (Figure 1), which can potentially be used as a linker to form MOFs. This assumption of its applicability is based on the structural relevance of the synthesized complex to another linker – 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine **H$_4$TCPP**, whose frameworks were suggested as sensors, agents for removal of heavy metal ions from wastewater, CO_2 adsorption, *etc*.[25–28]

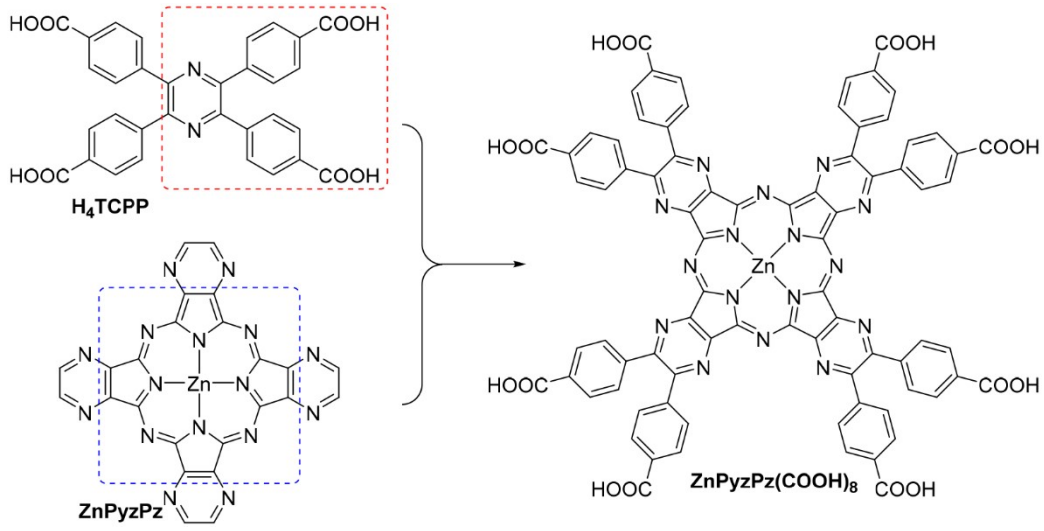


Figure 1. Design of novel octa(carboxyphenyl)pyrazinoporphyrazine **ZnPyzPz(COOH)$_8$** synthesized in the present work.

Experimental

General

The starting dimethyl 4,4'-oxalyldibenzoate was synthesized according to previously reported procedures.[29] Chloroform was distilled over K_2CO_3. Pentanol (Aldrich) was distilled over Mg and stored under argon. Zinc acetate was dried at 90 °C in vacuum. All other reagents were used without purification as received from commercial suppliers. Column chromatography was performed on silica.

MALDI-TOF mass spectral data were acquired on Bruker Daltonics Ultraflex spectrometer with 2,4-dihydroxybenzoic acid or 2,4,6-trihydroxyacetophenone as matrices. NMR spectra were recorded with Bruker Avance 600 spectrometer. NMR spectra were referenced against the residual solvent signal. Deuterated chloroform was filtered through the layer of dry neutral alumina prior the preparation of samples.

UV–vis spectra were recorded with a Jasco V-770 spectrophotometer in the 250–900 nm range in rectangular quartz cuvettes with optical pathways of 10 mm at room temperature.

DFT calculations were performed in ORCA 5.0.3 package.[30] Geometry optimization was performed at BP86/def2-SVP level. Single point calculations were performed at CAM-B3LYP/6-31G(d) level, electrostatic potential maps were calculated using Multiwfn 3.8(dev) package.[31] Visualization was performed in VMD 1.9.4.[32]

X-Ray diffraction study

Single crystals of **1** were obtained by slow evaporation of the solution of dinitrile in the mixture of CH_2Cl_2 and MeOH. Single-crystal X-ray diffraction experiment was carried out on a Bruker APEX-II CCD diffractometer. The crystal was kept at 150(2) K during data collection. The structure was solved with the SHELXT[33] structure solution program using Intrinsic Phasing and refined with the SHELXL [34] refinement package using the full-matrix least-squares technique against F^2 with anisotropic thermal parameters for all non-hydrogen atoms. Crystals ($C_{22}H_{14}N_4O_4$, M =398.37 g×mol^{-1}) are monoclinic, space group P21/c (no. 14), a = 9.5089(8) Å, b = 7.2974(7) Å, c = 27.982(2) Å, β = 95.370(3)°, V = 1933.1(3) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 0.097 mm^{-1}, d_{calc} = 1.369 g/cm^3, 25022 reflections measured (2.15° ≤ 2Θ ≤ 27°), 4220 unique (R_{int} = 0.0402) which were used in all calculations. The refinement converged to wR_2 = 0.1462 and GOF = 1.103 for all independent reflections (R_1 = 0.0628 was calculated against F for 3465 observed reflections with I > 2σ(I)).

CCDC-2260045 contains the supplementary crystallographic data for compound **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via *www.ccdc.cam. ac.uk/data_request/cif.*

Synthesis

*Dimethyl-4,4'-(5,6-dicyanopyrazine-2,3-diyl)dibenzoate **1***. Dimethyl-4,4'-oxalyldibenzoate (292 mg; 0.89 mmol) and diaminomaleonitrile (97 mg; 0.89 mmol) were suspended in 30 mL of EtOH + 0.5 mL CH_3COOH and the mixture was brought to reflux. The reaction was monitored by TLC on Silufol (30 vol.% ethylacetate-hexane mixture). After completion of the reaction, the formed brown precipitate was washed with EtOH, washed off the filter with $CHCl_3$ and the filtrate was evaporated. Target dicyanopyra-zine was obtained as golden crystals (290 mg; 81%). M.p. 210 °C. ^{1}H NMR (600 MHz, chloroform-*d*) δ_H ppm: 8.05 (d, J = 8.2 Hz, o-H_{Ph}, 4H), 7.61 (d, J = 8.2 Hz, m-H_{Ph}, 4H), 3.96 (s, CH_3, 6H). ^{13}C NMR (151 MHz, chloroform-*d*) δ_C ppm: 165.92, 154.52, 138.81, 132.61, 130.10, 129.95, 112.82, 52.53.

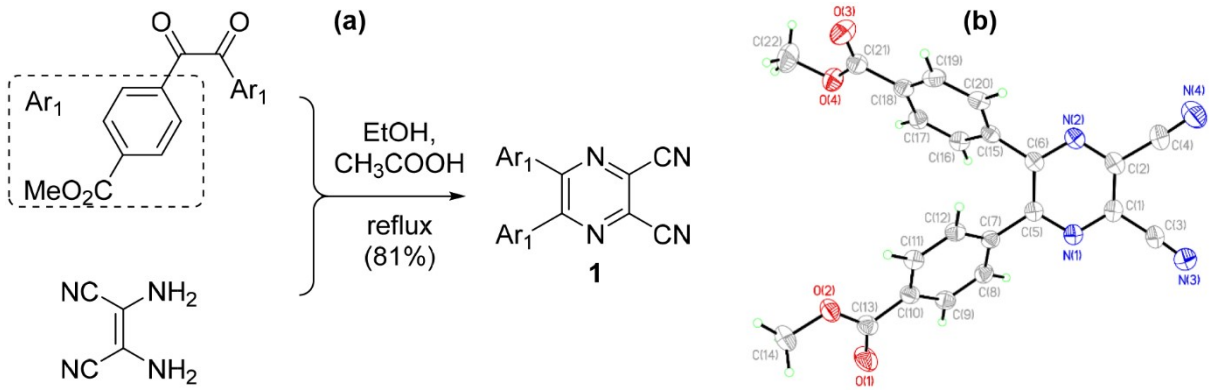
H_2PyzPz(COOPent)$_8$. A mixture of dibenzoate **1** (751 mg; 0.75 mmol) and Mg (9 mg; 0.37 mmol) were suspended in 5 mL of 1-pentanol and brought to reflux. After 16 h the resulting reaction mixture was evaporated, sonicated with the mixture of water and 40 vol% EtOH. The precipitate was filtered, washed with 3×20 mL aqueous EtOH, washed off the filter with 20 mL $CHCl_3$ + 10 vol.% MeOH mixture and the filtrate was evaporated. Obtained dark-blue solid was dissolved in 10 mL of $CHCl_3$, 1 mL of mixture CF_3COOH:H_2O (1:1) was added, and reaction mixture was refluxed following the progress of demetallation by UV-Vis. After 5 min, reaction was complete. The excess of acid was neutralized with an aqueous $NaHCO_3$ solution, target compound was isolated by extraction by $CHCl_3$ and evaporated. Target **H_2PyzPz(COOPent)$_8$** was obtained as a dark-green solid (650 mg; 67%). MALDI TOF MS *m/z*: $[M]^+$ calcd for $C_{120}H_{122}N_{16}O_{16}$ – 2044.4, found 2045.8. UV–Vis ($CHCl_3$) λ_{max} nm (log ε): 672 (4.83), 642 (4.72), 612 (4.19), 589 (4.04), 362 (4.72). ^{1}H NMR (600 MHz, chloroform-*d*) δ_H ppm: 8.46 – 7.92 (m, o-H_{Ph}, 16H), 7.94 – 7.63 (m, m-H_{Ph} 16H), 4.45 (s, α-CH_2, 16H), 2.07 – 1.50 (m, β- γ- δ-CH_2, 48H), 1.01 (s, CH_3, 24H), 0.07 (s, NH, 2H).

H_2PyzPz(COOH)$_8$. Pyrazinoporphyrazine **H_2PyzPz(COOPent)$_8$** (100 mg; 0.048 mmol) was dissolved in 5 mL of THF and 30 mL of saturated solution of NaOH in MeOH/H_2O (5:1 v/v) was added, mixture was heated to 40°C for 1 h. The precipitate of **H_2PyzPz(COONa)$_8$** formed upon the hydrolysis was filtered, washed with 3×20 mL of $CHCl_3$ and hexane, washed off the filter with 20 mL of water. After that, 1 mL of 1M HCl was added. The formed precipitate was filtered, washed with 3×20 mL of water and $CHCl_3$. Target **H_2PyzPz(COOH)$_8$** was obtained as a dark green solid (60 mg; 88%). MALDI TOF MS *m/z*: calcd for $C_{80}H_{42}N_{16}O_{16}$ – 1483.3, found 1483.3. UV–Vis (DMSO) λ_{max} nm (log ε): 667 (5.04), 614 sh (4.51), 360 (4.94).

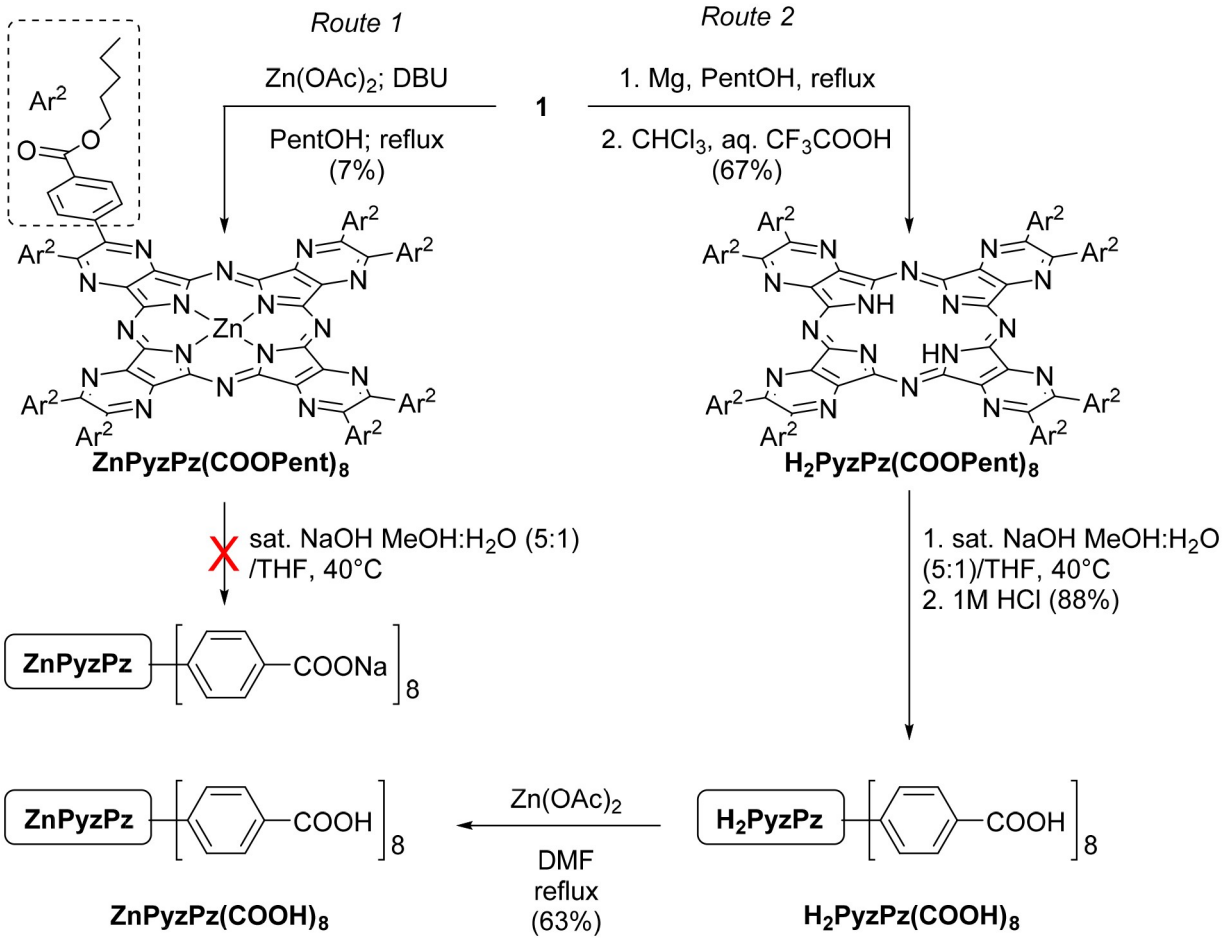
ZnPyzPz(COOH)$_8$. Pyrazinoporphyrazine **H_2PyzPz(COOH)$_8$** (50 mg; 0.033 mmol) and $Zn(OAc)_2$ (12 mg; 0.065 mmol) was suspended in 3 mL of DMF and brought to reflux. After 12 h CH_3COOH (3 mL) was added to the resulting reaction mixture and sonicated for 30 min. After that, H_2O (30 mL) was added and the resulting precipitate was filtered, washed with 3×20 mL of water and $CHCl_3$. Target **ZnPyzPz(COOH)$_8$** was obtained as a dark-green solid (33 mg; 63%). MALDI TOF MS *m/z*: calcd for $C_{80}H_{40}N_{16}O_{16}Zn$ – 1546.7, found 1547.5. UV–Vis (DMSO) λ_{max} nm (log ε): 656 (5.17), 595 (4.36), 375 (4.96). ^{1}H NMR (600 MHz, DMSO-d_6, 90 °C) δ_H ppm: 13.2 – 12.6 (s, 8H, -OH), 7.97 (s, o-H_{Ph}, 16H), 7.88 (s, m-H_{Ph}, 16H).

Results and Discussion

In order to obtain compound structurally similar to **H_4TCPP**, a novel building block – *o*-dicyanopyrazine **1** functionalized with 4-carbomethoxyphenyl groups was synthesized by condensation of oxalyl dibenzoate with diaminomaleonitrile in refluxing ethanol (Scheme 1a). The structure of the dinitrile **1** was determined by single crystal X-ray diffraction analysis (Scheme 1b). The angles between the planes of the pyrazine heterocycle and aromatic substituents of 42.6 and 49.8° evidence of partial conjugation between them.



Scheme 1. (a) - Synthesis of the dimethyl 4,4'-(5,6-dicyanopyrazine-2,3-diyl)dibenzoate 1, **(b)** – X-ray structure of the dinitrile 1; thermal ellipsoids are shown with 50% probability.



Scheme 2. Synthesis of pyrazinoporphyrazines.

We attempted to perform template condensation of *o*-dicyanopyrazine **1** in the presence of zinc acetate and DBU in refluxing 1-pentanol (Scheme 2, route 1). During the reaction, transesterification took place with replacement of methyl groups by pentyl groups in the ester substituents, which was confirmed by MALDI TOF mass-spectrometry yielding **ZnPyzPz(COOPent)$_8$**. Importantly, prolonged refluxing of the reaction mixture resulted in a gradual decay of the initially formed complex, as evidenced by a decrease in Q-band intensity at 661 nm and an increase in absorbance in the UV region. Thus, after overnight refluxing, the yield of crude porphyrazine after precipitation from the reaction mixture was less than 10%.

Moreover, the complex was unstable under the conditions of alkaline hydrolysis of the ester groups which was performed in the attempt to obtain **ZnPyzPz(COONa)$_8$**. Thus, the Q-band of the porphyrazine completely vanished upon refluxing its solution with NaOH in the mixture of THF and aqueous methanol.

Possibly, due to the electron-deficient nature of the synthesized complex, ring degradation occurred during the hydrolysis reaction – similar behavior was also observed previously upon alkaline hydrolysis of ester groups in zinc octa(3,5-dicarbethoxyphenyl)porphyrazine.[35] This process might start from the nucleophilic attack of the hydroxide anion on the tetrapyrrole ring. The possibility of such a nucleophilic attack is evidenced by the results obtained previously in our research group on the example of the cationic P^V phthalocyaninate, which undergoes reversible nucleophilic addition under the action of OH^- and OMe^- anions.[36]

To verify the susceptibility of zinc complex to nucleophilic attack, we have analyzed the electrostatic potential (ESP) maps of the model macrocycle **ZnPyzPz(COOMe)$_8$** (Figure 2a) and indeed positive ESP values were observed for the areas of tetrapyrrolic ring. This observation explains both degradation of zinc complex in course of its synthesis in the presence of DBU in PentOH, and decomposition of the complex upon the alkaline hydrolysis of ester groups.

However, we found that the value of ESP in this ring decreases in the case of the metal-free compound **H$_2$PyzPz(COOMe)$_8$**, (Figure 2b) thus we decided to synthesize the free base of the carboxyphenyl-substituted porphyrazine and study its hydrolysis.

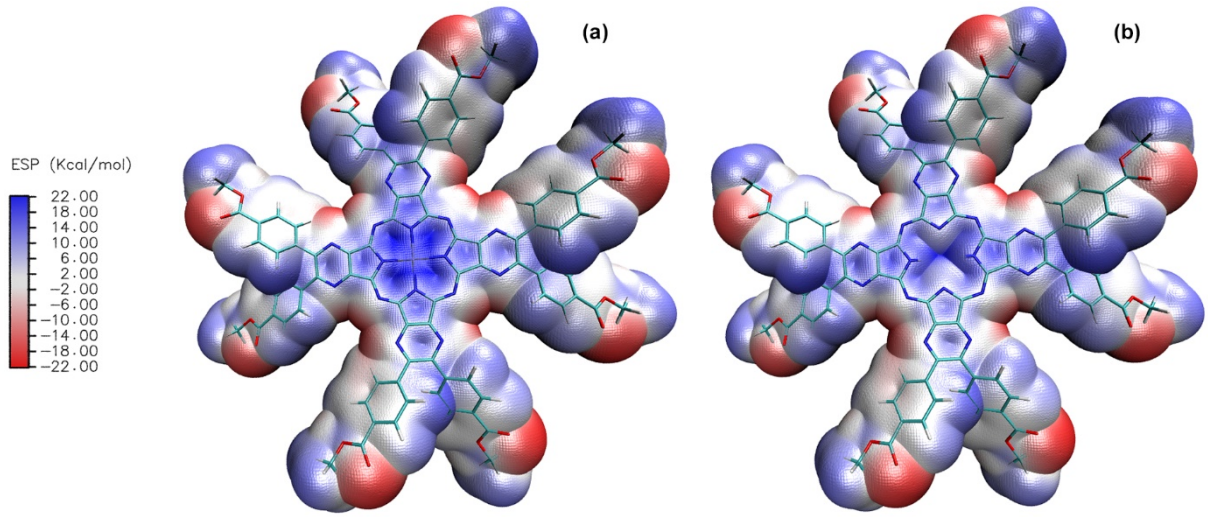


Figure 2. Distribution of electrostatic potential ESP in model porphyrazines **ZnPyzPz(COOMe)$_8$** (a) and **H$_2$PyzPz(COOMe)$_8$** (b) according to DFT calculations at CAM-B3LYP/6-31G(d) level.

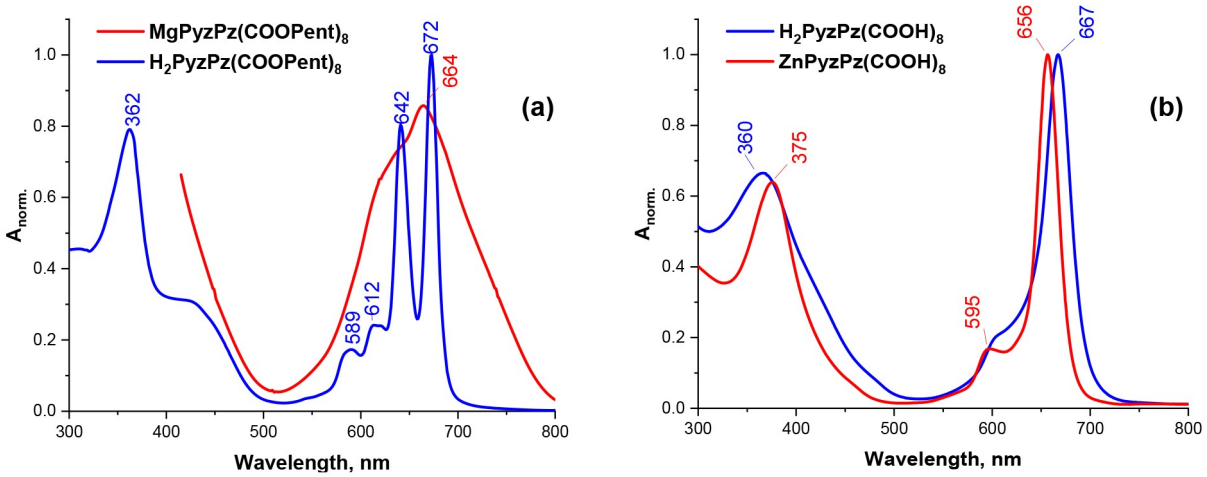


Figure 3. (a) – UV-Vis spectra of magnesium complex **MgPyzPz(COOPent)$_8$** (sample from reaction mixture) and free ligand **H$_2$PyzPz(COOPent)$_8$** in $CHCl_3$; (b) – UV-Vis spectra of **ZnPyzPz(COOH)$_8$** and **H$_2$PyzPz(COOH)$_8$** in DMSO.

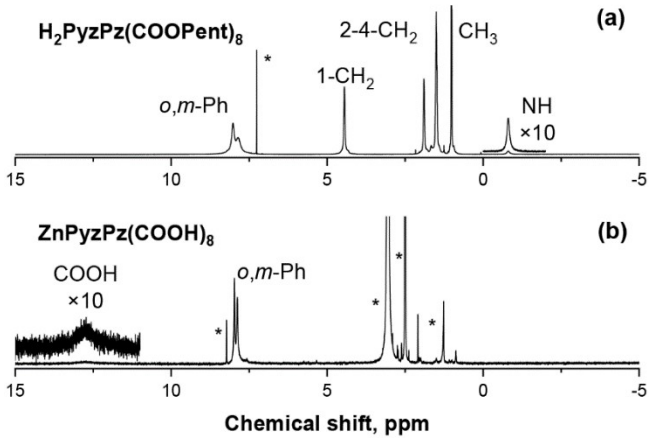


Figure 4. ^{1}H NMR spectra of **H_2PyzPz(COOPent)$_8$** in $CDCl_3$ (a) and **ZnPyzPz(COOH)$_8$** in DMSO-d_6 at 80°C (b). Asterisks mark solvent impurities.

Template condensation of the dinitrile **1** with magnesium acetate and DBU in PentOH again resulted in low yield of the target magnesium complex because of its degradation in alkaline media. Thus, we performed condensation of **1** with metal magnesium in PentOH which allowed us to avoid the presence of strong bases in reaction media. The obtained **MgPyzPz(COOPent)$_8$** was demetalated with trifluoroacetic acid without isolation yielding the target ligand **H_2PyzPz(COOPent)$_8$** (67%). It is noteworthy that the free ligand is less aggregated in chloroform than the metal complex, which is evidenced by the well-resolved split Q-band in UV-Vis of the ligand in contrast to the broad Q-band of the metal complex (Figure 3a). The isolated **H_2PyzPz(COOPent)$_8$** was characterized by MALDI-TOF MS and ^{1}H NMR (Figure 4a).

Alkaline hydrolysis of **H_2PyzPz(COOPent)$_8$** was then performed, and on the contrary to **ZnPyzPz(COOPent)$_8$**, this compound did not decompose during the reaction in accordance with expectations based on quantum-chemical modelling, thus providing a water-soluble form **H_2PyzPz(COONa)$_8$** in a high yield. By acidifying its aqueous solution using HCl, the **H_2PyzPz(COOH)$_8$** complex with free carboxy-groups was obtained and characterized by UV-Vis, MALDI TOF MS and ^{1}H NMR (Figure 4b). Remarkably, the UV-Vis spectrum of the synthesized porphyrazine in DMSO contains single Q-band (Figure 3b), which may be related to the deprotonation of NH-groups in this solvent with formation of the dianionic form, existing very likely in the form of an H-associate with the protonated DMSO molecules [2DMSOH$^+$…PyzPz^{2-}].[37–40] Analogous behavior was reported previously for other electron-deficient pyrazinoporphyrazines and these results were summarized in a comprehensive review.[41]

Then we attempted to synthesize **ZnPyzPz(COOH)$_8$** starting from the metal-free carboxylic acid **H_2PyzPz(COOH)$_8$**. We performed its reaction with zinc acetate in boiling DMF. After 12 h of reaction we observed the appearance of a green precipitate, insoluble in a wide range of organic solvents. Presumably, the precipitate was a coordination polymer formed due to the interaction of carboxyl substituents and zinc cations. We developed an approach to isolate the target complex from the resulting polymer by adding acetic acid to the precipitate followed by dilution with water. After filtration, we obtained a green precipitate which was the new target pyrazinoporphyrazine complex **ZnPyzPz(COOH)$_8$**. It was successfully isolated that was confirmed by MALDI-TOF, ^{1}H NMR and UV-Vis (Figure 3b and 4b). The observed UV-vis spectrum is similar to that of previously reported octacarboxy substituted porphyrazines.[42]

Also, the absence of aliphatic signals in NMR spectrum of **ZnPyzPz(COOH)$_8$** in DMSO-d_6 evidenced of complete hydrolysis of ester groups at the previous stage of the synthesis (Figure 4).

Conclusions

Herein we proposed method for the synthesis of derivatives of the new carboxyphenyl substituted pyrazinoporphyrazine as well as its Zn^{II} complex. We have shown that the sequence of synthetic stages of complex formation and hydrolysis strongly affects the yields of target compounds, which was explained by analysis of electrostatic potentials in series of the studied porphyrazines. Due to the structural similarity of the synthesized macrocycles to the organic ligand 2,3,5,6-tetrakis(4-carboxyphenyl)pyrazine **H_4TCPP**, our results are expected to pave paths to new tetrapyrrole-based MOFs.

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